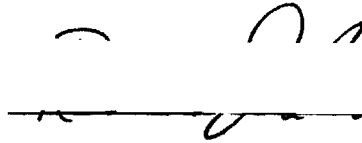


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b

THE KINETICS AND MECHANISM OF THE IODINATION
OF ANISOLE, PHENOL, p-NITROPHENOL, AND 2,4-DINITROPHENOL

A THESIS

Presented to

The Faculty of the Graduate Division

by

Robert John Sullivan

In Partial Fulfillment

of the Requirements for the Degree


Doctor of Philosophy

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May, 1968

THE KINETICS AND MECHANISM OF THE IODINATION
OF ANISOLE, PHENOL, p-NITROPHENOL, AND 2,4-DINITROPHENOL

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Chairman




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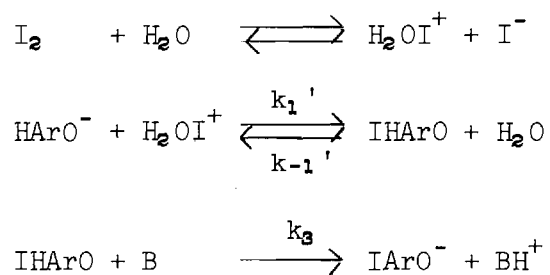
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SUMMARY

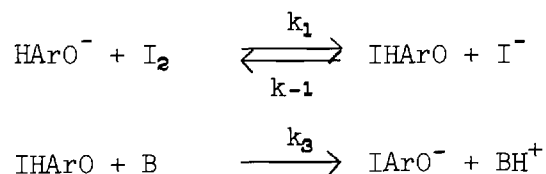
The kinetics of the iodination of phenol, p-nitrophenol, 2,4-dinitrophenol, and anisole and their deuterated derivatives in aqueous solution have been studied as a function of iodide ion concentration. In addition, the effect of pH upon the iodination of phenol and 2,4-dinitrophenol has been examined, as well as the effect of acetate ion catalysis upon the iodination of phenol and of phosphate ion catalysis upon the iodination of 2,4-dinitrophenol.

The purpose of this work was to elucidate the mechanism of the iodination of aromatic compounds in aqueous solution. The results of some previous kinetic studies upon iodination of aromatic compounds were consistent with either of two mechanisms, which can be summarized as follows for the iodination of phenoxide ion.

Mechanism I:



Mechanism II:



The kinetic data from this previous work requires that the proton-removal step be rate-determining under the experimental conditions if molecular iodine is the iodinating agent (mechanism II), while the mechanism involving hypiodous acidium ion as the iodinating agent (mechanism I) is consistent with the data regardless of whether or not this is the slow step.

The basic piece of evidence in this previous work which indicates that either one of the above mechanisms is operating is that the reaction rates, which are first order in aromatic compound, show inverse first order dependence upon iodide ion concentration after correction has been made for the formation of triiodide ion and hypiodous acid. In principle, the two mechanisms can be distinguished at sufficiently low iodide ion concentrations. In mechanism II, the ratio $k_{-1}[I^-]/k_3[B]$ will decrease as iodide ion concentration decreases, until the proton-removal step ceases to be rate-determining; when the iodide ion concentration is low enough for this phenomenon to be observable, the order of inverse iodide dependence will decrease to zero and any hydrogen isotope effect will decrease to near unity ($k_H/k_D \approx 1$). In the case of mechanism I, both the iodide dependence and the isotope effect will be unaffected by the decrease in iodide ion concentration.

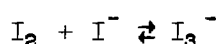
The fact that the iodide dependence was not observed to vary with iodide ion concentration in much of the earlier work can be interpreted as support for hypiodous acidium ion as the iodinating agent, or it may be that the iodide ion concentrations studied were too high to permit observation of the phenomena predicted when molecular iodine is the iodinating agent.

The work reported here was conducted over a range of iodide concentrations including concentrations considerably lower than those employed previously, and the effect of varying the iodide ion concentration has been used to distinguish between mechanisms I and II for phenol, 2,4-dinitrophenol, and anisole. p-Nitrophenol had already been shown to iodinate by mechanism II under conditions where the phenoxide anion was the species attacked, over the iodide range 1.22×10^{-2} M to 2.34×10^{-5} M. This work was extended here to still lower iodide ion concentrations in order to gain more quantitative kinetic information.

All of the reactions studied were found or were previously known to be first order in iodine and first order in aromatic compound. The effect of varying hydrogen ion concentration demonstrated that phenoxide was the principal subject of iodination in the case of phenol at 0.0052 M hydrogen ion. The iodination of p-nitrophenol was conducted at 200×10^{-6} M hydrogen ion, at which acidity previous work had shown essentially all of the reaction to occur via p-nitrophenoxide. The iodination of 2,4-dinitrophenol was conducted at 70×10^{-6} M hydrogen ion concentration, at which acidity previous work had shown all of the iodination to occur via 2,4-dinitrophenoxide.

The iodination reactions were carried out in low actinic, 50 ml volumetric flasks with specially ground glass stoppers. The flasks were immersed in a constant temperature bath controlled to $\pm 0.1^\circ\text{C}$. Reactions were quenched by the addition of a large excess of sodium iodide, which converted essentially all of the iodine to triiodide ion. In the experiments in which the pH was so low that a measurable amount of the quenching iodide was oxidized to iodine during the time required to make the

analytical measurement, the quenched solutions were buffered with a bicarbonate-carbonic acid buffer. Iodine concentrations in the quenched solutions were determined from the spectrophotometrically measured absorbances due to triiodide ion, coupled with the measured extinction coefficient of the triiodide and the known constant for the triiodide equilibrium

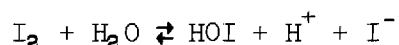


In the experiments in which the aromatic compound and its iodinated derivatives absorbed at the wavelength used to measure triiodide, the pertinent extinction coefficients were determined under the conditions of the quenched reactions, and the corrections were included in the kinetic equation.

Variation of iodide dependence and of isotope effect with iodide ion concentration demonstrated that phenoxide was iodinated by molecular iodine over the iodide range studied in this and previous work, $4.65 \times 10^{-1} \text{ M}$ to $3.2 \times 10^{-7} \text{ M}$. Over this iodide range, the isotope effect dropped from 6.6 to 3.1. At low iodide ion concentrations, acetate ion was found to catalyze the iodination of phenol beyond what would be the limiting rate on the basis of mechanism II, assuming the only function of acetate to be the catalysis of step k_3 . Also, the isotope effect did not decrease upon catalysis to the extent expected in light of the decreasing kinetic significance of the proton-removal step. The conclusion was drawn that acetyl hypoiodite was an effective iodinating agent under the conditions of the catalyzed reactions, $0.33 \times 10^{-6} \text{ M}$ iodide and 0.36 M

acetate, in either a two-step or a concerted reaction.

The iodination of 2,4-dinitrophenoxide was studied over the iodide range 3.89×10^{-3} M to 2.59×10^{-6} M. The iodide dependence decreased with decreasing iodide ion concentration, and the isotope effect decreased from 4.3 to 2.4. However, both iodide dependence and isotope effect became constant in the lower part of the iodide range, indicating that iodine was the effective iodinating agent at the higher iodide ion concentrations and that hypiodous acidium ion became the predominant iodinating agent at the lower iodide concentrations. At low iodide (93×10^{-6} M to 4×10^{-6} M), the second order rate constant (first order in iodine and first order in 2,4-dinitrophenoxide) was found, at constant iodide ion concentration, to increase as $[H^+]$ was decreased. The isotope effect increased from 2.4 to 3.0 as the acidity was decreased from 70×10^{-6} M to 1.7×10^{-6} M hydrogen ion. This information was interpreted as indicating hypiodous acid, formed from the equilibrium



to be a significant iodinating agent under these conditions.

Phosphate catalysis of the iodination of 2,4-dinitrophenoxide at low iodide ion concentration (93×10^{-6} M to 4×10^{-6} M) increased the reaction rate but did not lower the isotope effect as expected on the basis of catalysis of the proton-removal step, and this suggests monohydrogen phosphoryl hypiodite (HPO_4I^-) as an iodinating agent in either a two-step or a concerted mechanism.

When the iodination of p-nitrophenoxide was carried to lower iodide

ion concentrations than covered in earlier work, it was found that, as the iodide ion concentration decreased below about 1×10^{-6} M, the predominant iodinating agent changed from molecular iodine to hypiodous acidium ion. The evidence for this conclusion was similar to that obtained in the study of the iodination of 2,4-dinitrophenoxide.

For anisole, the iodide dependence and the isotope effect remained constant within experimental error over the entire iodide range included in this and previous work, 4.8×10^{-4} M to 2.9×10^{-6} M. (The isotope effect was 3.0.) In addition, an experiment performed by another worker at 3.4×10^{-11} M iodide (in the presence of silver ions) showed the same isotope effect. While the possibility that molecular iodine was the iodinating agent over the entire iodide range 4.8×10^{-4} M to 3.4×10^{-11} M could not be rigorously excluded (i.e., that iodide dependence and isotope effect would decrease at still lower iodide ion concentrations), quantitative consideration of the data showed that this was unlikely and that hypiodous acidium ion was probably the effective iodinating agent over at least the low part of this iodide range.

All of the data were treated mathematically on the basis of the steady-state approximation. This treatment yielded values for the rate constants of some of the individual rate constants.

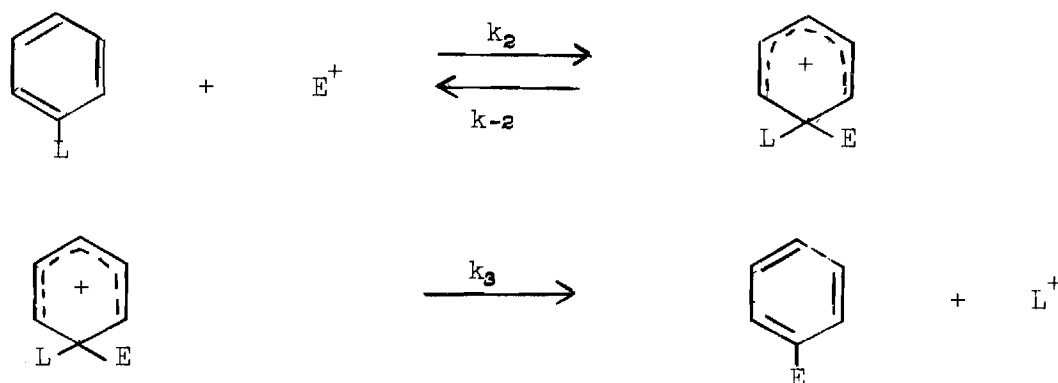
The relative importance of molecular iodine and hypiodous acidium ion in the iodinations of the various aromatic compounds studied can be explained on the basis that the less reactive compounds exercise greater selectivity for the much more reactive but much less plentiful iodinating agent, hypiodous acidium ion.

CHAPTER I

INTRODUCTION

Mechanism of Electrophilic Aromatic Substitution

The development of the general mechanism of electrophilic aromatic substitution has been reviewed by Berliner.⁽¹⁾ The two-step mechanism, in which departure of the leaving group occurs in a distinct step subsequent to introduction of the electrophile is now generally accepted



as opposed to the concerted mechanism, in which the leaving group departs simultaneously with the attack of the electrophile. The electrophile, of course, need not be positively charged. The intermediate shown is a sigma-complex, but this would not necessarily be the first

1. E. Berliner in Progress in Physical Organic Chemistry, Vol. 3 S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Eds., Interscience Publishers, New York, 1964, pp. 253-321.

intermediate formed; it might be preceded by a pi-complex.

The acceptance of the two-step mechanism resulted largely from the work of Melander,^(2,3) who established the absence of a hydrogen isotope effect of the magnitude ordinarily attributed to the breaking of a carbon-to-hydrogen bond in the rate-determining step in several electrophilic aromatic substitution reactions. These were nitration and bromination reactions, and the conclusion was that the attack of the electrophile was rate-determining and was followed by a fast proton-removal step. Since that time, a considerable number of substitution reactions have been found which are ordinarily devoid of an isotope effect, notably nitrations,^(4,5,6,7,8) chlorinations,^(9,10,11) and bromi-

2. L. Melander, Arkiv Kemi, 2, 211 (1950).
3. U. Berglund-Larson and L. Melander, Arkiv Kemi, 6, 219 (1953).
4. P. C. Myhre, Acta Chem. Scand., 14, 219 (1960).
5. W. M. Lauer and W. E. Noland, J. Am. Chem. Soc., 75, 3689 (1953).
6. T. G. Bonner, F. Bowyer, and G. Williams, J. Chem. Soc., 2650 (1953).
7. K. Halvarson and L. Melander, Arkiv Kemi, 11, 77 (1957).
8. J. F. Eastham, J. L. Bloomer, and F. M. Hudson, Tetrahedron, 18, 653 (1962).
9. E. Baciocchi, G. Illuminati, and G. Sleiter, Tetrahedron Letters, 30 (1960).
10. P. B. D. de la Mare, I. C. Hilton, and S. Varma, J. Chem. Soc., 4044 (1960).
11. G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardie, J. Am. Chem. Soc., 86, 1039 (1964).

nations. (2, 12,13,14,15,16) On the other hand, several reactions have been found which do exhibit large isotope effects, including sulfonations, (17) brominations, (4, 16, 18,19,20,21,22) diazo couplings, (23,24) mercurations, (25) and iodinations, which will be discussed. Very recently, a primary isotope effect was observed in the nitration of anthracene with nitronium tetrafluoroborate. (26) It is generally considered that the

12. P. B. D. de la Mare, T. M. Dunn, and J. T. Harvey, J. Chem. Soc., 923 (1957).

13. F. M. Vainshtein, E. A. Shilov, and O. M. Grishin, Zh. Vses. Khim. Obshchestva im. D. I. Mendeleeva, 5, 119 (1960); Chem. Abstr., 54, 24492 (1960).

14. E. Berliner, Chem. Ind. (London), 177 (1960).

15. R. Josephson, R. M. Keefer, and L. J. Andrews, J. Am. Chem. Soc., 83, 3562 (1961).

16. F. M. Vainshtein and E. A. Shilov, Dokl. Akad. Nauk. SSSR, 133, 581 (1960).

17. J. C. D. Brand, A. W. P. Jarvic, and W. C. Horning, J. Chem. Soc., 3844 (1959).

18. M. Christen and H. Zollinger, Helv. Chim. Acta, 45, 2057, 2066 (1962).

19. M. Christen, W. Koch, W. Simon, and H. Zollinger, Ibid., 2077.

20. P. G. Farrell and S. F. Mason, Nature, 183, 250 (1959); 590 (1963).

21. J. E. Dubois and R. Uzan, Tetrahedron Letters, 309 (1965).

22. G. Illuminati and F. Stegel, Ric. Sci., 34, 460 (1964).

23. H. Zollinger, Helv. Chim. Acta, 38, 1597, 1617, 1623 (1955).

24. R. Ernst, O. A. Stamm, H. Zollinger, Helv. Chim. Acta, 41, 2274 (1958).

25. A. J. Kresge and J. F. Brennan, Proc. Chem. Soc., 215 (1963).

26. H. Cerfontain and A. Telder, Rec. Trav. Chim. Pays-Bas, 86, 371 (1967).

two-step mechanism holds in these cases as well, but that the proton-removal step is rate-determining. However, except for the improbability of termolecular collisions, there is no inherent reason why a given electrophilic aromatic substitution might not occur by a concerted mechanism.

Hydrogen Isotope Effects

Hydrogen isotope effects arise because the vibrational zero-point energies for the bonds of hydrogen to a given atom differ for the three isotopes of hydrogen: protium, deuterium, and tritium.⁽²⁷⁾ Heavier isotopes give bonds of lower zero-point vibrational energy than lighter isotopes. While there is a zero-point energy contribution in the transition state, the differences in zero-point energy for the different isotopic species is smaller in the transition state than in the ground state, and therefore the activation energies will differ for the isotopic species; i.e., the zero-point energies for the ground state and transition state do not cancel out.⁽²⁷⁾

From the Arrhenius equation

$$\ln k = - E_a/RT + \text{const.}$$

the rates of reaction are different for the different isotopically labelled molecules. Since the zero-point energy is higher for the ground state carbon-to-protium bond than for the carbon-to-deuterium bond, and since the zero-point energy of the carbon-to-deuterium bond is higher

27. R. P. Bell, The Proton in Chemistry, Cornell University Press, Ithaca, N. Y., 1959, Chapt. 11.

than for the carbon-to-tritium bond, the k_H/k_D and k_D/k_T isotope effects are greater than unity when there is a net bond-breaking in the transition state relative to the reactants.

In the absence of special effects, the maximum k_H/k_D isotope effect for the breaking of a C-H bond is approximately seven at 25°. ⁽²⁷⁾ It can be, and often is, less than this maximum value, either because the reactant C-H bond is not very completely broken in the transition state, or because a bond is partly formed between the hydrogen and some other atom, e.g., oxygen in a basic catalyst. (The maximum isotope effect is expected when the proton is most loosely bound both to the initial reactant and to the basic catalyst in the transition state.) Therefore, as Hammond ⁽²⁸⁾ has pointed out, the absence of an appreciable isotope effect does not unambiguously establish that proton-removal is not rate-determining.

Special effects which can give rise to isotope effects much higher than seven are quantum mechanical tunnelling ⁽²⁷⁾ and related steric effects. ⁽²⁹⁾

A reaction can have an isotope effect smaller than the isotope effect of a proton-removal step which forms part of the reaction when this step is not completely rate-determining. In the extreme case, the rate of removal of the proton is so great that it has no measurable effect on the kinetics; this situation will be referred to as the kinetic

28. G. S. Hammond, J. Am. Chem. Soc., 77, 334 (1955).

29. E. S. Lewis and L. Funderbunk, J. Am. Chem. Soc., 89, 2322 (1967).

insignificance of the proton-removal step. Small isotope effects can also arise from changes in carbon-to-hydrogen bonds other than the reacting bond. The only such "secondary" isotope effect of importance in aromatic substitution is that resulting from the change in the bond between hydrogen and the carbon atom which is undergoing the attack in the formation of the intermediate in the two-step mechanism. Streitwieser⁽³⁰⁾ has shown that the secondary isotope effect is determined by the relative contributions of competing phenomena. The increased out-of-plane bending frequency for the carbon-to-hydrogen bond in the transition state, possessing more sp^3 and less sp^2 character than the same bond in the reactant, tends to produce a secondary isotope effect smaller than unity (i.e., the compound containing the heavier isotope reacts faster), but the increase in hyperconjugation due to the greater p-character of the carbon-to-hydrogen bond in the transition state tends to raise the secondary isotope effect above unity. Secondary isotope effects in electrophilic aromatic substitution reactions of more and less than one have been recorded, and in some of the latter cases the authors have invoked the possibility that, for those cases, the hyperconjugation factor outweighs the rehybridization factor.^(31,32)

The catalysis of the proton-removal step with different bases is often employed in kinetic studies of electrophilic aromatic substitution,

30. A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, J. Am. Chem. Soc., **80**, 2326 (1958).

31. E. Berliner and K. E. Schueller, Chem. Ind. (London), 1444 (1960).

32. A. N. Bourns, Trans. Roy. Soc. Canada, **2**, 277 (1964).

and it must be borne in mind that, since varying the basic catalyst is likely to change the net extent to which hydrogen is bound in the transition state, the kinetic isotope effect may change as the base is changed. Bell, et al.^(33,34) have found, in the ionization of aliphatic carbon-to-hydrogen bonds by different bases, that the isotope effect increased as the pKa values of the ionizing acid and the attacking base became more similar.

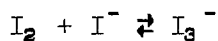
Iodination

Soper and Smith⁽³⁵⁾ studied the iodination of phenol in aqueous solution with phosphate buffers. (Unless otherwise specified, kinetic studies discussed in this chapter were made in aqueous solution.) They found that the rate of iodination was directly proportional to the first power of stoichiometric iodine and phenol concentrations, and inversely proportional to the square of the iodide ion concentration and to the hydrogen ion concentration raised to a power between one and two. They considered this to be consistent with iodination of undissociated phenol and phenoxide anion with hypiodous acid, HOI. The proton-removal step was assumed to be kinetically insignificant; i.e., fast. The inverse squared iodide dependence was considered to arise from the preequilibria

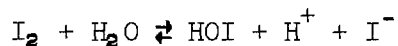
33. R. P. Bell and D. M. Goodall, Proc. Roy. Soc. (London), A294, 273 (1966).

34. R. P. Bell and J. E. Crooks, Ibid., A286, 285 (1965).

35. F. G. Soper and G. F. Smith, J. Chem. Soc., 1582 (1926).



and



The first of these equilibria introduced an inverse dependence of the rate upon the iodide ion concentration because the iodide ion concentration was so great that essentially all of the iodine was converted to triiodide, so that there was an inverse dependence of true iodine concentration upon the iodide ion concentration. This contribution to the dependence of rate upon iodide can be eliminated by considering the rate to vary linearly with the true iodine concentration (the hypiodous acid equilibrium consumed a negligible portion of the iodine in Soper and Smith's case because of the high iodide ion concentration) instead of stoichiometric iodine concentration. This will be done henceforth in this thesis, since some of the work reported here will not involve a large excess of iodide over iodine. The rate constant in terms of true iodine concentration will be denoted by k^* .

One inverse order of hydrogen ion concentration was considered to arise from the hypiodous acid equilibrium, and an additional inverse hydrogen ion dependence from the dissociation of phenol, the phenoxide anion accounting for only part of the total reaction.

Li,⁽³⁶⁾ in studying the diiodination of tyrosine in acetate buffers, reported the rate expression

36. C. H. Li, J. Am. Chem. Soc., 64, 1147 (1942).

$$k^* = \frac{A}{[I^-]} + B \quad \dagger$$

with a similar hydrogen ion dependence to that of Soper and Smith.⁽³⁵⁾

He concluded that both tyrosine and the corresponding phenoxide were iodinated by two iodinating agents; viz., hypoiodous acid, corresponding to the $\frac{A}{[I^-]}$ term, and molecular iodine, corresponding to the B term.

The proton-removal step was assumed to be kinetically insignificant.

The results, however, appear to be invalidated by the fact that the introduction of the second iodine into the tyrosine molecule, which was assumed by Li in his kinetic treatment to be a fast step compared to the introduction of the first iodine, has been shown by Roche, et al.⁽³⁷⁾ to be the slow step, and this has been confirmed by Mayberry, Rall, and Bertoli.⁽³⁸⁾

Li⁽³⁹⁾ obtained a similar rate expression for the iodination of histidine. Here again, however, the reaction was considered as a diiodi-

[†]This is an example of converting the kinetics from stoichiometric iodine to actual iodine. The original paper used the expression

$$k = \frac{A}{[I^-]^2} + \frac{B}{[I^-]}$$

37. J. Roche, S. Lissitzky, O. Michel, and R. Michel, Compt. Rend., 232, 357 (1951); Ann. Pharm. franc., 9, 163 (1951).

38. W. E. Mayberry, J. E. Rall, and D. Bertoli, J. Am. Chem. Soc., 86, 5302 (1964).

39. C. H. Li, J. Am. Chem. Soc., 66, 225 (1944).

nation; it has since been shown that monoiodohistidine iodates less rapidly than histidine. (40)

Li⁽⁴¹⁾ also studied the iodination of glycyl tyrosine, p-chlorophenol, and p-hydroxyphenylethylamine (tyramine), this time finding the rate expression

$$k^* = \frac{A}{[I^-]}$$

He concluded that iodination proceeded via hypiodous acid. This reaction was also considered as a diiodination, and the proton-removal was again considered to be kinetically insignificant.

Shilov and Kurakin⁽⁴²⁾ studied the kinetics of iodination of amino sulfonic acids, and they found that the results fit a formula of the type

$$\text{rate} = k_1^*[S^-]^2[I_2] + \frac{k_2^*[S^-]^2[I_2]}{[I^-]} + k_3^*[S^-][HPO_4^-][I_2] + \frac{k_4^*[S^-][HPO_4^-][I_2]}{[I^-]}$$

They proposed iodination by a complex formed between the substrate and I_2 or I^+ which then rapidly attacks a second molecule of the substrate, followed by a slow base-catalyzed removal of proton.

The iodination of some pyrroles in aqueous dioxane was studied by

40. L. Schutte, P. Provo Kluit, and E. Havinga, Tetrahedron, Suppl. no. 7, 295 (1966).

41. C. H. Li, J. Am. Chem. Soc., 70, 1716 (1948).

42. A. N. Kurakin and E. A. Shilov, Ukrain. Khim. Zhur., 23, 31 (1957).

Doak and Corwin,⁽⁴³⁾ who found the reactions (k^*) to be first order in actual iodine concentration and pyrrole concentration, and essentially independent of iodide ion concentration. From this they concluded that molecular iodine was the iodinating agent and that the proton-removal step was kinetically insignificant. An upward drift of the rate constant at low iodide concentrations led the authors to suggest the possibility that hypiodous acid was also an iodinating agent.

Upon reexamining the work of Soper and Smith⁽³⁵⁾ on the iodination of phenol, Painter and Soper⁽⁴⁴⁾ found that catalysis by the phosphate buffer had been overlooked in the earlier work. It became clear that part of the effect of hydrogen ion described in the earlier study reflected different extents of catalysis resulting from changes in the buffer composition. It was now seen that the rate of the uncatalyzed reaction (k^*) varied inversely with the first power of the hydrogen ion concentration and the first power of the iodide ion concentration. It was also determined that the rate varied linearly with the concentration of the buffer acid (acetic or phosphoric) and that this catalytic effect varied inversely as the square of the hydrogen ion concentration. The kinetics therefore conformed to either of the equations

$$\text{rate} = k_0'[\text{HOI}][\text{PhOH}] + k'[\text{AcOI}][\text{PhO}^-]$$

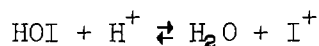
or

43. K. W. Doak and A. H. Corwin, J. Am. Chem. Soc., 71, 159 (1949).

44. B. S. Painter and F. G. Soper, J. Chem. Soc., 342 (1947).

$$k_0''[I^+][PhO^-] + k''[AcOI][PhO^-]$$

the equilibrium between HOI and I^+ being



The authors preferred the second alternative; i.e., that phenoxide anion was iodinated by both iodonium cation and acetyl hypiodite.

Berliner⁽⁴⁵⁾ studied the iodination of aniline in phosphate buffers. The kinetic form of the reaction was identical with that found by Painter and Soper⁽⁴⁴⁾ for the iodination of phenol, with anilinium ion replacing phenol and aniline replacing the phenoxide anion. Therefore, it was not possible from the kinetics to determine whether the uncatalyzed reaction involved iodination of the anilinium ion by hypiodous acid or the iodination of aniline by I^+ (or H_2OI^+). However, product analysis showed that substitution was occurring at the para-position, whereas anilinium ion is a strong meta-director. It was therefore concluded that the uncatalyzed reaction was via I^+ or H_2OI^+ attack on aniline. (Hypiodous acidium ion, H_2OI^+ , will be used henceforth when a compound is considered to undergo iodination by either I^+ or H_2OI^+ , since there is no basis for distinguishing between the two in any of the data presented.) It was noted that the catalyzed term could be written

$$k'[AcO^-][I^+][C_6H_5NH_2]$$

45. E. Berliner, J. Am. Chem. Soc., 72, 4003 (1950).

involving base-catalyzed iodination by iodonium ion rather than iodination by the acetyl hypoiodite. The function of the basic catalyst was not clear, since it was not known whether the proton-removal was kinetically significant.

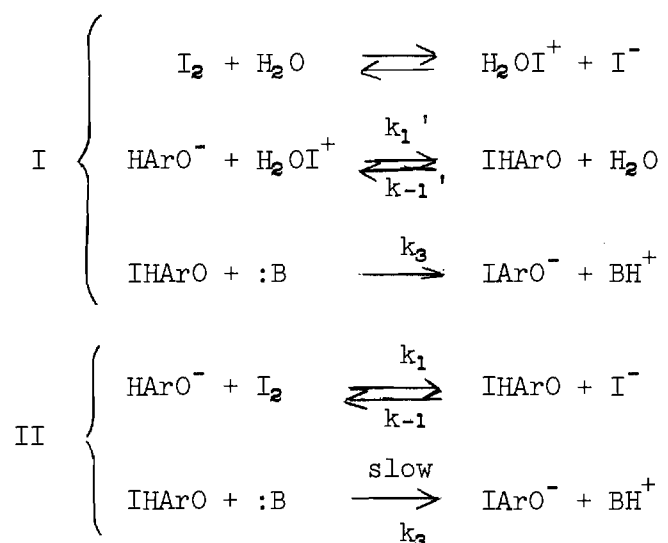
Berliner⁽⁴⁶⁾ next studied the iodination of phenol, using phosphate and acetate buffers. The kinetic form was again the same as that found by Painter and Soper,⁽⁴⁴⁾ but Berliner reinterpreted the data analogously to the iodination of aniline. Calculations based upon the assumption that the phenoxide anion rather than phenol was being iodinated gave an uncatalyzed rate constant 25,000 times greater than the corresponding rate constant for the iodination of aniline, and a lower activation energy. These findings are chemically reasonable, and it was concluded that the iodination proceeded by the attack of H_2OI^+ on phenoxide. Catalysis by acetate, monohydrogen phosphate and dihydrogen phosphate was observed.

In the work discussed above, inverse dependence of rate of iodination of an aromatic compound upon iodide ion concentration has been interpreted as evidence for hypoiodous acid, at first, and later hypoiodous acidium ion as the iodinating agent. However, it was pointed out by Grovenstein and Henderson⁽⁴⁷⁾ that such iodide dependence is equally consistent with iodination by molecular iodine, with the proton-removal step rate-determining. For the iodination of phenol, the alternative

46. E. Berliner, J. Am. Chem. Soc., 73, 4307 (1951).

47. E. Grovenstein, Jr. and U. V. Henderson, Jr., J. Am. Chem. Soc., 78, 569 (1956).

mechanisms involving H_2OI^+ and I_2 , respectively, can be written



Since the iodination step may have been at or near equilibrium in the work done up to this time, the nature of the iodinating agent could not be specified. Molecular iodine had already been shown to be the iodinating agent in the iodinolysis of *p*-methylbenzene boronic acid,⁽⁴⁸⁾ in which case there was no iodide dependence, the boronic acid group apparently leaving in a fast step. Therefore, molecular iodine would appear to be a reasonable agent to attack phenol.

Grovenstein and Kilby⁽⁴⁹⁾ reported an isotope effect of 4.0, too large to be a secondary isotope effect, in the iodination of phenol. This clearly demonstrated that proton-removal was kinetically signifi-

48. H. G. Kuivila and R. M. Williams, J. Am. Chem. Soc., 76, 2679 (1954).

49. E. Grovenstein, Jr. and D. C. Kilby, J. Am. Chem. Soc., 79, 2972 (1957).

cant, and therefore that the previously reported inverse iodide dependence of the rate of iodination could be interpreted on the basis of molecular iodine as the iodinating agent.

Primary isotope effects have since been discovered in the iodination of other aromatic compounds, including aniline derivatives, ^(50,51) 3-phenol sulfonic acid, ⁽¹³⁾ and imidazole. ⁽⁵²⁾

Ridd ^(52,53) investigated the iodination of glyoxaline and found that the effects could be expressed

$$\text{rate} = \frac{k_0^* [G^-] [I_2]}{[I^-]} + \frac{k^* [G^-]^2 [I_2]}{[I^-]}$$

An isotope effect of 4.4 was observed. The iodinating agents were considered $H_2O I^+$, corresponding to the first term on the right-hand side of the equation, and probably an iodinating agent formed from the glyoxaline anion and iodine, corresponding to the second term. However, the second term can also be explained as base catalysis of the proton-removal step.

Similar inverse iodide dependencies have been observed for a series of aniline derivatives, ^(50,51) for acetyl tyrosine, ⁽⁵⁴⁾ for 2,4-

50. E. A. Shilov and F. Weinstein, Nature, 182, 1300 (1958).

51. F. M. Vainshtein and E. A. Shilov, Dokl. Akad. Nauk. SSSR, 123, 93 (1958).

52. J. H. Ridd, J. Chem. Soc., 1238 (1955).

53. A. Grimison and J. H. Ridd, J. Chem. Soc., 3019 (1959).

54. W. E. Mayberry and D. A. Bertoli, J. Org. Chem., 30, 2029 (1965).

dichlorophenol,⁽⁵⁵⁾ and for pyrazole derivatives.^(56,57)

Choguill and Ridd⁽⁵⁸⁾ found no iodide dependence in the proto-deiodination of iodoaniline, indicating that iodide was not included in the transition state of the slow step. They concluded that the transition state for deiodination was similar to that for iodination, which they considered to occur via a positive iodinating agent, in light of the results of Berliner.⁽⁴³⁾ However, the finding of Choguill and Ridd is equally consistent with a slow proton transfer being the rate-determining step in both the forward and reverse reaction, in which case either I_2 or H_2OI^+ might be the iodinating agent in the iodination reaction.

Although the inverse iodide dependence is consistent with either hypiodous acidium ion or molecular iodine as the iodinating agent, provided that the proton-removal step is rate-determining (no case with this iodide dependence has been shown not to have a primary isotope effect), it is possible in principle to distinguish between the iodinating agents. This is what Grovenstein and Aprahamian⁽⁵⁹⁾ set out to do in their kinetic study of the iodination of p-nitrophenol. They found a large

55. W. C. Buss and J. E. Taylor, J. Am. Chem. Soc., 82, 5991 (1960).

56. J. D. Vaughan, D. G. Lambert, and V. L. Vaughan, J. Am. Chem. Soc., 86, 2857 (1964).

57. J. D. Vaughan, G. L. Jewett, and V. L. Vaughan, J. Am. Chem. Soc., 89, 6218 (1967).

58. H. S. Choguill and J. H. Ridd, J. Chem. Soc., 822 (1961).

59. E. Grovenstein, Jr. and N. S. Aprahamian, J. Am. Chem. Soc., 84, 212 (1962).

primary isotope effect (5.6). If hypiodous acidium ion were the iodinating agent, the inverse iodide dependence would arise from the rapid preequilibrium in which this agent is formed from iodine in the mechanism I, and the iodide dependence would be invariant with respect to iodide concentration, assuming that the formation of H_2OI^+ never becomes rate-determining. On the other hand, if molecular iodine were the iodinating agent, the inverse iodide dependence would arise from the iodination preequilibrium in mechanism II; as the iodide ion concentration was decreased, the iodination of phenoxide would attain increasing kinetic significance because of the suppression of the reversal step, until finally this step would become rate-determining. The result would be that the power of the inverse iodide dependence would shrink with the lowering of the iodide ion concentration. These alternative possibilities can be restated in another way: if H_2OI^+ were the iodinating agent, the rate constant multiplied by the iodide concentration would be a constant with respect to the iodide ion concentration; if molecular iodine were the iodinating agent, this product would decrease as the iodide ion concentration decreased. In cases where such a decrease has not been observed, it is possible that H_2OI^+ was the iodinating agent, or else that molecular iodine was the iodinating agent but that the experiments had not been conducted at sufficiently low iodide ion concentrations for the proton-removal step to lose any of its rate-determining character.

Since the primary isotope effect must reside in the proton-removal step, it follows that any decrease in the kinetic significance of that step ought to be accompanied by a decrease in isotope effect. Therefore, while the isotope effect ought to be independent of iodide

ion concentration when H_2OI^+ is the iodinating agent, the isotope effect should decrease with decreasing iodide ion concentration when molecular iodine is the iodinating agent.

In studying the kinetics of iodination of p-nitrophenol, Grovenstein and Aprahamian found that the product of the rate-constant and the iodide ion concentration decreased by a factor of 2.5 in going from $1216 \times 10^{-6} \text{ M}$ to $2.34 \times 10^{-6} \text{ M}$ iodide ion concentration, and that the isotope effect dropped from 5.5 at $222 \times 10^{-6} \text{ M}$ iodide to 3.1 at $2.34 \times 10^{-6} \text{ M}$ iodide.

Considered more quantitatively, the mechanism involving H_2OI^+ as the iodinating agent, with the proton-removal step rate-determining, can be solved by assuming a steady state low concentration of intermediate to yield an equation of the form

$$\frac{1}{k^*} = A[\text{I}^-]$$

whereas the mechanism involving molecular iodine as the iodinating agent yields the equation

$$\frac{1}{k^*} = A[\text{I}^-] + B$$

When the reciprocal of the rate constant was plotted against the iodide ion concentration, Grovenstein and Aprahamian found a straight line with a positive intercept, in accordance with molecular iodine as the iodinating agent.

Other aromatic compounds have since been found to display kinetics

of this type: a series of imidazole derivatives,⁽⁴⁰⁾ nickel-coordinated imidazole,⁽⁶⁰⁾ and adrenochromes.⁽⁶¹⁾ In the latter case, the authors claimed that the rate showed no iodide dependence and concluded that the iodinating agent was molecular iodine, while the proton-removal step was rate-determining, on the basis of observed general base catalysis. This analysis is incorrect, since in such a case an inverse iodide dependence should be observed. However, examination of the experimental data shows that the rate is not independent of iodide, but fits very well to an equation of the same form as observed by Grovenstein and Aprahamian for the iodination of p-nitrophenol.

Vainshtein, Tomilenko, and Shilov⁽⁶²⁾ have observed a decrease in isotope effect with decreasing iodide ion concentration in the iodination of aniline, indicating iodination via molecular iodine with the proton-removal step rate-determining at high iodide ion concentrations.

It has been suggested^(52, 47, 63) that the relative importance of iodinating agents H_2OI^+ and I_2 might vary with the reactivity of the substrate and the concentration of the iodide ion.

It can be seen from much of the kinetic data discussed up to this point that general base catalysis has been observed in a great many of the iodination reactions of aromatic compounds. The question has been

60. D. G. Lambert and M. M. Jones, J. Am. Chem. Soc., 88, 5573 (1966).

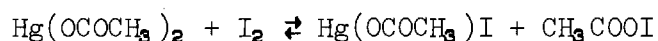
61. G. L. Mattok and D. L. Wilson, Can. J. Chem., 45, 1721 (1967).

62. F. M. Vainshtein, E. I. Tomilenko, and E. A. Shilov, Kinetika i Kataliz, 4, 357 (1963); Chem. Abstr., 59, 7338 (1963).

63. B. D. Batts and V. J. Gold, J. Chem. Soc., Supplement no. 1, 5753 (1964).

raised whether the increase of the rate of the proton-removal step is the only source of this catalysis. For instance, Grimison and Ridd⁽⁵³⁾ noted that the catalyzed and uncatalyzed isotope effects in the iodination of glyoxaline were almost identical and suggested that this fact, plus the observations of general base catalysis even in the absence of isotope effects^(50,51,16) might indicate that the base catalysis arose from the formation of an alternative iodinating agent. More recently it was found that in the iodination of azulene⁽⁶⁴⁾ the isotope effect was essentially identical for some of the bases studied despite their widely differing basicities. This was attributed to steric effects (possibly proton-tunnelling).

Chen, Keefer, and Andrews⁽⁶⁵⁾ generated acetyl hypiodite from mercuric acetate and iodine in acetic acid as solvent and they spectrophotometrically determined the equilibrium constant for the equilibrium



They studied the kinetics of pentamethylbenzene at various concentrations of iodine and mercuric acetate, and the results were consistent with the assumption of acetyl hypiodite as the iodinating agent; i.e., the rate constant calculated by considering the reaction to be first order in pentamethylbenzene and first order in acetyl hypiodite did not vary with changes in mercuric acetate or iodine concentration. However, the results

64. E. Grovenstein, Jr. and F. C. Schmalsteig, J. Am. Chem. Soc., 89, 5084 (1967).

65. E. M. Chen, R. M. Keefer, and L. J. Andrews, J. Am. Chem. Soc., 89, 428 (1967).

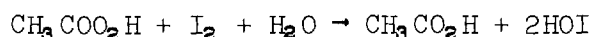
do not rule out I_2 as an iodinating agent.

A specific function has been suggested for monohydrogen phosphate in the catalyzed iodination of pyrazole, ⁽⁵⁶⁾ on the basis of a distinctly higher experimental activation energy and experimental frequency factor for the HPO_4^- catalyzed reaction as compared with the reactions catalyzed by water and ammonia for pyrazole substrate and with imidazole catalysis of imidazole. In addition, HPO_4^- was found to be a more effective catalyst for the iodination of pyrazole than ammonia, even though ammonia is more basic than HPO_4^- .

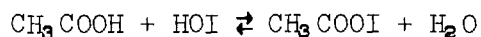
Ogata and Nakajima ^(66,67) studied the iodination of benzene by peroxyacetic acid in aqueous acetic acid solution. The rate data were independent of benzene concentration and could be expressed

$$\text{rate} = k[I_2][CH_3COOH]$$

suggesting a rate-determining formation of the iodinating agent, which might be hypoiodous acid



or acetyl hypoiodite



66. Y. Ogata and K. Nakajima, Tetrahedron, 20, 43 (1964).

67. Y. Ogata and K. Nakajima, Tetrahedron, 20, 2751 (1964).

However, the authors pointed out that H_2OI^+ , I^+ , and I_2O were possible iodinating agents and were indistinguishable from hypiodous acid or acetyl hypiodite on the basis of the available evidence.

Purpose of This Thesis

The purpose of the work reported in this thesis is the determination of the iodinating agent(s) in the aqueous iodination of phenol, 2,4-dinitrophenol, and anisole by studying the iodide dependence and isotope effect at very low iodide ion concentrations. The iodination of p-nitrophenol has also been studied, at iodide ion concentrations considerably lower than those used by Grovenstein and Aprahamian. (59)

It was also desired to study the kinetics as a function of acidity in order to determine the relative extents of iodination of the phenols and the corresponding phenoxide anions.

Basic catalysis has been employed in an attempt to decrease the kinetic significance of the proton-removal step.

CHAPTER II

PREPARATION AND PURIFICATION OF MATERIALS

Anisole

The anisole was purified by E. Grovenstein, Jr. and N. S. Gnanapragasam as follows.

One kg of Eastman White Label anisole was washed with 400 ml of ten percent sodium hydroxide and then with four portions of 400 ml of water. The anisole was next stored overnight over Drierite, then distilled through a four and one-half foot fractionating column (packed with glass helices) at atmospheric pressure (734.5 mm). The 700 ml fraction boiling at 152° was collected after discarding the first 60 ml and was observed to be slightly cloudy. About 18 g of freshly cut sodium metal was added, and the anisole was refluxed for three hours and then distilled at atmospheric pressure (733 mm), the boiling point being 152°. The anisole distillate was distilled at 11 mm pressure, and the 400 ml fraction boiling at 47.0° was collected after discarding the first 25 ml.

Forty ml of this anisole was shaken with 71.8 g of 41.6 percent sulfuric acid[†] for 38 hours. The anisole was extracted twice with aque-

[†]The aqueous sulfuric acid solution had been pretreated by shaking for 48 hours with 30 ml of mesitylene. This was done because the deuterated sulfuric acid used to deuterate the anisole had been first shaken with mesitylene.

ous potassium hydroxide and twice with aqueous sodium chloride, dried over anhydrous magnesium sulfate, filtered, and distilled through a one foot spinning band column. A three ml forerun was discarded, and 22 ml was collected, b.p. 152.3°. This fraction was then redistilled through a two foot spinning band column. A two ml forerun was discarded and 13 ml was collected, b.p. 152.0°. This was the anisole used in the kinetic experiments described in this thesis.

Anisole-2,4,6-d₃

The starting material for the preparation of anisole-2,4,6-d₃ was the anisole described in the preceding preparation of protio anisole after distillation at 11 mm (b.p. 47.0°). (This material was not treated with sulfuric acid.) Forty ml of this material was equilibrated six times with 42 ml of 39 mole percent deuterium sulfate in deuterium oxide, each equilibration consisting of mechanical shaking for about six hours. The isotopic purity of the deuterium sulfate-deuterium oxide solution used in the deuteration was as follows: first equilibration, 86.8 mole percent[†]; second, 96.0 mole percent[†]; third, 98.9 mole percent[†]; fourth, fifth, and sixth, 99.8 mole percent. The anisole-2,4,6-d₃ was washed twice with an aqueous solution of potassium hydroxide plus sodium chloride, and twice with a solution of sodium chloride. After this it was

[†]These deuterium sulfate-deuterium oxide solutions had been used previously for the deuteration of mesitylene; the isotopic purity figures are based upon the assumption that equilibrium was achieved in these deuteration.

dried over anhydrous magnesium sulfate, filtered, and about 18 ml was distilled through a one foot spinning band column. A 14 ml fraction was collected, b.p. 152°. This fraction was combined with about four ml of anisole-2,4,6-d₃ which was prepared similarly, but in which case longer shaking times resulted in a high percentage loss of anisole, presumably due to sulfonation. The combined fractions were distilled through a two foot spinning band column. A 13 ml fraction was collected, b.p. 152°. This was the material used in the kinetic experiments described in this thesis. This deuteration procedure is similar to one described by Berliner.⁽⁶⁸⁾

Benzene

Freshly distilled commercial benzene was used.

Calcium Sulfate

"Drierite," anhydrous calcium sulfate produced by the Hamond Drierite Company, Xenia, Ohio, was used without purification.

Carbon Tetrachloride

The carbon tetrachloride was purified by N. S. Gnanapragasam and J. M. McKelvey in the following way. About 1.3 l of technical grade carbon tetrachloride was filtered through glass wool into a two l bottle, to which was added 500 ml of an aqueous solution containing 50 g of sodium hydroxide and 20 g of potassium permanganate. The mixture was mechanically shaken for three hours and the water layer removed. The

68. E. Berliner, J. Am. Chem. Soc., 82, 5435 (1960).

carbon tetrachloride layer was washed with 2 N sulfuric acid and then with water, and dried over Drierite. The dry carbon tetrachloride was distilled through a four and one-half foot silver-jacketed vacuum fractionating column packed with glass helices, and a constant boiling fraction (75.7°) was collected.

Deuterium Oxide

Samples used were from Liquid Carbonic Company, 767 Industrial Road, San Carlos, California, and from Isotopes Specialties Inc.

The deuterium oxide had been standing in screw cap bottles for some time prior to use. The Liquid Carbonic material was found to be 99.0 mole percent isotopically pure and the Isotopes Specialties material to be 99.8 mole percent isotopically pure by nmr.

The determination of the isotopic purity of deuterium oxide was made by comparison of the nmr spectrum of the deuterium oxide sample with the spectrum of the deuterium oxide containing a measured percentage of added protium oxide. The difference between the areas of proton peaks in the two spectra corresponded with the percentage of added protium oxide. From this measure of sensitivity and from the area of the proton peak in the spectrum of the original deuterium oxide, the isotopic purities of deuterium oxide samples were calculated.

Deuterium oxide samples of lower purity were also used; these had been recovered by Aprahamian from the deuteration of p-nitrophenol.

Deuteriosulfuric Acid

This was prepared by E. Grovenstein, Jr. and J. M. McKelvey as

follows.

Into a round-bottomed flask containing 227 g (11.3 moles) of 99.8 mole percent deuterium oxide, 925 g (11.6 moles) of liquid sulfur trioxide ("Sulfan B") was added from a dropping funnel--dropwise at first, then, after delivery of about 300 ml, in a slow stream. The apparatus was cooled in an ice bath and was kept under nitrogen atmosphere. The solution was permitted to stand overnight, after which time 4.2 g more (0.2 mole) deuterium oxide was added, making 100 percent deuteriosulfuric acid. The deuteriosulfuric acid was sealed in 50 ml ampoules immediately after preparation and the ampoules were not opened until the time of use. This method of preparation is essentially that of Berliner.⁽⁶⁸⁾

The isotopic purity of one batch, which was prepared on February 14, 1964, was determined by J. M. McKelvey to be greater than 99.5 percent, on the basis of the absence of any detectable protium peak in the nmr spectrum. Another batch, made according to the same procedure on October 25, 1965, was checked by the author for isotopic purity on July 19, 1966. Nmr spectra were obtained on the deuterium sulfate sample and on the deuterium sulfate sample plus a measured percentage of protium oxide. Isotopic purity was determined analogously to the previously described determination on deuterium oxide and found to be 99.4 mole percent. Both deuterium sulfate batches were used in syntheses and are so labelled in the descriptions of the syntheses.

2,6-Diiodo-4-nitrophenol

The 2.4 g of undissolved solid from the preparation of 2-iodo-4-nitrophenol (cf. below) was recrystallized from diethyl ether, yielding

1.3 g of pale yellow crystals, which was then sublimed in vacuo. The sublimate, which was used to determine the spectral properties of 2,6-diiodo-4-nitrophenol, melted at 156-159°, uncor. (recorded m.p., 156.5°, decomposes at a somewhat higher temperature⁽⁶⁹⁾).

2,4-Dinitrophenol

Commercial 2,4-dinitrophenol was purified by T. C. Berethein according to the method of Bird, Panciera, and Shafer⁽⁷⁰⁾ as follows.

One hundred grams of dinitrophenol was stirred with 567 ml water, and 94 ml of 20 percent sodium hydroxide was added. The mixture was heated to 70-80° on a water bath, and 15 g of Norite activated carbon was added. The mixture was filtered while hot. A mixture of 42.5 g of glacial acetic acid plus 42.5 g of water was added to the filtrate, and when cold, this mixture was filtered and the dinitrophenol washed with a little water. The compound was further purified by two recrystallizations from water; m.p. 112.5°-113.0°.

This dinitrophenol was recrystallized two additional times from water and sublimed in vacuo by A. Fort; m.p. 113-114°, with prior softening. (Literature melting points vary; e.g., 110-111°,⁽⁷¹⁾ 112-113°,⁽⁷²⁾

69. W. Körner, Comptes Rend., 166 (1868).

70. J. C. Bird, Z. Panciera, and E. G. E. Shafer, Amer. J. Pharm., 106, 462 (1934).

71. F. H. Westheimer, E. Segal, and R. Schramm, J. Am. Chem. Soc., 69, 773 (1947).

72. W. E. Bachmann, J. M. Chemerda, N. C. Deno, and E. C. Horning, J. Org. Chem., 13, 390 (1948).

112-114°. (73) This is the material used in experiment no. 23 (Table 31) of this thesis.

For experiments no. 29, 31, 33, 35, 36, and 37 (Tables 37, 41, 33, 42, and 43) some of Berethein's purified dinitrophenol was further purified by recrystallization once from water and twice from ethanol and sublimation; m.p. 112-114°.

For experiments no. 98, 100, 102, 104, 106, 110, 112, and 114 (Tables 62, 64, 66, 60, 58, 56, 54, and 52) some of Berethein's purified dinitrophenol was recrystallized once from ethanol and twice from water, then sublimed; m.p. 112-114°.

2,4-Dinitrophenol-6-d

A sample of 2,4-dinitrophenol-6-d prepared by A. Fort was resublimed before use. Fort had prepared the material as follows. Commercial phenol was equilibrated four times with deuteriosulfuric acid in deuterium oxide. The first equilibration mixture consisted of 22.5 g (0.24 mole) phenol, 1.0 ml carbon tetrachloride, and 35 g of 25 mole percent deuteriosulfuric acid in deuterium oxide,[†] and was shaken for seven hours; for the second equilibration, the carbon tetrachloride layer plus one additional ml of carbon tetrachloride was shaken for eight hours with 58.5 g of 25 mole percent deuteriosulfuric acid; the carbon tetrachloride layer was next shaken with 81.8 g of the 25 mole percent deuteriosulfuric acid

[†]The isotopic purity of these deuteriosulfuric acid solutions was 99.5 mole percent.

73. The Merck Index of Chemicals and Drugs, 47th ed., Merck and Co., Inc., Rahway, N. J., 1960, p. 376.

for 12 hours; finally, the carbon tetrachloride layer was shaken for eight hours with 131.5 g of the 25 mole percent deuteriosulfuric acid.

The carbon tetrachloride layer was added to a 500 ml round-bottomed flask containing 46.5 g of 94.8 weight percent of deuteriosulfuric acid in deuterium oxide. The mixture was cooled with an ice water bath and stirred magnetically while 51 g (0.60 mole) of sodium nitrate in 60 g of deuterium oxide (99.5 percent isotopic purity) was added dropwise. During the addition of the sodium nitrate solution, an additional 15 g of deuterium oxide was added in order to dilute the reaction mixture, since the formation of tars and the evolution of nitrogen dioxide was proceeding very rapidly. When the addition of sodium nitrate was complete, the ice water bath was removed, and the temperature rose gradually to 40°, evolution of nitrogen dioxide continuing steadily. The mixture was stirred overnight and then heated on a steam bath for 90 minutes. The reaction mixture was treated with a liter of ice and water; the water was decanted from the dark solids, and the solids were washed with more cold water, then recrystallized from ethanol-water. The crystals were doubly sublimed in vacuo and the sublimate was recrystallized from water.

Fort used this material in his kinetic experiments. He then recovered it from the reaction solutions as follows. The combined reaction solutions from several experiments on the iodination of 2,4-dinitrophenol-6-d were treated with an excess of sodium bicarbonate and concentrated by evaporation on a rotary evaporator. The concentrated mixtures, with much solid present, were acidified with cold dilute hydrochloric acid and the precipitated phenol was collected by filtration and recrystallized

from water. (In the experiments using the reaction solutions of 2,4-dinitrophenol-6-d, conditions were such that less than one percent of the phenol was iodinated.)

The recovered deuterated phenol was sublimed in vacuo just prior to the work reported in this thesis; m.p. 112-114°.

Isotopic purity was determined by comparing the nmr spectra of the deuterated 2,4-dinitrophenol with that of protium 2,4-dinitrophenol (40 percent wt/wt in acetone). The high field doublet (ca. 2.67) was absent in the spectrum of the deuterated compound, corresponding to deuteration at the 6-position. Since a peak area one percent as large as the area corresponding to either of the remaining two protons would have been measurable, it was concluded that isotopic purity of the 2,4-dinitrophenol-6-d exceeded 99.0 percent.

2,4-Dinitro-6-iodophenol

This compound was prepared according to the method outlined by W. Körner. (69)

To a mixture of 4.0 g (22 mmoles) of Eastman White Label 2,4-dinitrophenol in 125 ml of concentrated sodium hydroxide solution was added 0.86 g (4.3 mmoles) of sodium iodate and 2.19 g (17.5 mmoles) of iodine. The mixture was stirred magnetically and alternately made acid and alkaline with concentrated hydrochloric acid and sodium hydroxide until the absence of violet color in the acid solution indicated that all of the iodine had reacted. A light yellow solid was filtered out of the acid reaction mixture and sublimed in vacuo. The sublimate was recrystallized twice from ethanol-water and resublimed. The 0.56 g of

sublimate melted at 105.5-107.0°, uncor. (recorded m.p., 106-107°⁽⁷⁴⁾).

Ethanol

Freshly distilled commercial 95 percent grain alcohol was used.

Hydrochloric Acid

Baker Reagent Grade concentrated hydrochloric acid was used.

Iodine

Baker Analyzed Reagent grade iodine was used without purification.

2-Iodo-4-nitrophenol

This compound was prepared according to the method outlined by Körner.⁽⁶⁹⁾

To a mixture of 3.5 g (28.5 mmoles) of Eastman White Label p-nitrophenol in concentrated sodium hydroxide was added 1.0 g (5.05 mmoles) of sodium iodate in 15 ml of water and 2.6 g (20.5 mmoles) of iodine. The solution was stirred magnetically and alternately made acidic and basic with concentrated hydrochloric acid and sodium hydroxide until the absence of violet color from the acidic solution indicated the complete consumption of iodine. The precipitate from the acid solution was filtered and washed with water. The 4.8 g of moist yellow solid was treated with one liter of boiling water; 2.4 g of solid did not dissolve. (This was the 2,6-diiodo-4-nitrophenol. See above for the purification of this compound.)

74. D. B. Murphy, F. R. Schwartz, J. P. Picard, and J. V. R. Kaufman, J. Am. Chem. Soc., 75, 4289 (1953).

The mother liquor was evaporated to 40 ml, from which a fine precipitate recrystallized. The crystals were sublimed in vacuo, recrystallized from water, and resublimed. The 2-iodo-4-nitrophenol sublimate melted at 92-94° uncor. (recorded m.p., 93°⁽⁶⁹⁾).

p-Nitrophenol

Eastman Kodak p-nitrophenol was recrystallized six times from water by Aprahamian and was used without additional purification; m.p. 116-117° uncor. (recorded m.p., 114°⁽⁷⁵⁾).

p-Nitrophenol-2,6-d

A sample of partially deuterated phenol prepared by Fort by the equilibration of commercial phenol with deuteriosulfuric acid was found by nmr analysis to be 94.0 mole percent isotopically pure phenol-2,4,6-d₃. The isotopic purity was determined by obtaining the nmr spectra of phenol and of the phenol-2,4,6-d₃ (25 percent solution in acetone). The spectrum of the protio phenol is complex but can be considered to be composed of three slightly overlapping band envelopes, the area of the farthest upfield envelope being one-half that of each of the other two. Therefore, the upfield envelope must correspond to the para proton. The spectrum of the deutero phenol consisted of a single principal peak, corresponding to the approximate center of gravity of the envelope farthest downfield in the spectrum of the protio phenol. This single peak must represent the protons at the undeuterated meta positions, which are

75. R. L. Shriner, R. C. Fuson, and D. Y. Curtin, Systematic Identification of Organic Compounds, 4th ed., John Wiley and Sons, Inc., New York, 1956, p. 326.

not expected to split with the other positions deuterated. There was also a small peak at the center of gravity of the middle envelope in the spectrum of protio phenol, indicating a slight degree of residual proton at the ortho positions. The percentage isotopic purity was obtained from the ratio of the two peak areas. (This is actually isotopic purity at the ortho positions, which are of primary interest in this work. The peak in the spectrum of phenol-2,4,6- d_3 corresponding to the para position indicated a similar isotopic purity at that position.)

Sixteen g (165 mmoles) of this material in a few ml of carbon tetrachloride was extracted four times with deuterium oxide: with 8.0 g (355 mmoles), then with 13.0 g (580 mmoles), then with 7.5 g (333 mmoles) of deuterium oxide of 88.9 mole percent isotopic purity, and finally with 9.3 g (477 mmoles) of 97.5 mole percent deuterium oxide. This was done to replace any acidic proton which might have been picked up during storage. The solvent was then stripped off the carbon tetrachloride phase in a rotary evaporator.

Ten g (103 mmoles) of this phenol in about two ml of carbon tetrachloride was then mechanically shaken three times, for several hours each time, with deuteriosulfuric acid. In the first two equilibrations, 26.3 g of deuteriosulfuric acid (99.4 mole percent isotopic purity) plus 13.1 g of deuterium oxide (99.0 mole percent isotopic purity) were used. About 75 percent of the phenol was lost into the water phase, presumably as the sulfonate in the second of these equilibrations when the room temperature rose to about 35°. The final equilibration with the carbon tetrachloride layer of the remaining phenol was with 18.2 g of deuteriosulfuric

acid (99.8 mole percent isotopic purity) and 9.7 g of deuterium oxide (99.8 mole percent isotopic purity). The deuterated phenol was 99.5 percent isotopically pure, by nmr. This deuterated phenol was now used for the preparation of p-nitrophenol-2,6-d.

A 100 ml round-bottomed, three-necked flask was fitted with a reflux condenser, which in turn was fitted with a calcium sulfate drying tube. The second neck was fitted with a glass stopper and the third with a dropping funnel. The entire apparatus was flame-dried and the reaction flask was set in an ice water bath. A solution of 9.0 g of deuteriosulfuric acid (99.4 mole percent isotopic purity) in 15.0 g of deuterium oxide (99.8 mole percent isotopic purity) was introduced followed by 2.2 g (29 mmoles) sodium nitrate plus 3.5 g (59 mmoles) sodium nitrite in 7.5 ml of the deuterium oxide. The carbon tetrachloride solution of phenol from the above deuteration equilibration was added slowly into the magnetically stirred reaction mixture. The reaction was continued for eight hours, during which time nitrogen dioxide was generated. The temperature was maintained at or below 25° by the ice bath.

The reaction mixture was extracted three times with sodium-dried diethyl ether. The combined ether phase was extracted twice with small quantities of deuterium oxide. Some sodium-dried benzene was added to the ether solution (to reduce the solubility of deuteriosulfuric acid) and the solution was extracted several more times with deuterium oxide. The solvent was stripped off, leaving a tar, which was sublimed in vacuo. The sublimate was recrystallized twice from benzene to give 0.3 g of p-nitrophenol-2,6-d, which was found to be more than 99 mole percent isotopically pure by nmr; m.p. 115-117°. The nmr analysis was made in the

same way as for phenol-2,4,6-d₃, except that in the case of p-nitrophenol only two bands were present in the spectrum of the protio compound.

Perchloric Acid

Baker Analyzed Reagent Grade perchloric acid (70-72 percent) was used. Solutions were standardized against potassium biphthalate.

Phenol

The phenol was purified by Aprahamian as follows.

Baker Analyzed Reagent Grade phenol was distilled through a three foot column packed with three-sixteenths inch glass helices under atmospheric pressure. The phenol which distilled at 180-181° was collected. The distillate was then heated overnight at 80° over anhydrous calcium sulfate. The phenol was decanted and then dried over anhydrous calcium chloride for 30 minutes at 50°. The phenol was filtered while warm and distilled in vacuum through the same column. The portion boiling at 75-81° under 15-20 millimicrons was collected and sealed under nitrogen in glass vials.

The phenol was sublimed in vacuo prior to use in the work described in this thesis.

Phenol-2,4,6-d₃

The phenol-2,4,6-d₃ prepared by Aprahamian⁽⁷⁶⁾ according to the

76. N. S. Aprahamian, The Kinetics and Mechanism of Iodination of Phenol, p-Nitrophenol, Anisole and Their Deuterated Derivatives, Ph.D. Thesis, Georgia Institute of Technology, 1960, p. 51.

general procedure of Ingold, et al.⁽⁷⁷⁾ was sublimed in vacuo prior to use. The isotopic purity was determined to be 99.3 mole percent by nmr.

Potassium Biphthalate

Baker Analyzed Primary Standard potassium biphthalate was used without further purification.

Potassium Dichromate

Baker Analyzed Reagent Grade potassium dichromate was used without further purification.

Potassium Permanganate

Baker Analyzed Reagent Grade potassium permanganate was used without further purification.

Sodium Acetate

For experiments no. 60-63 (Tables 128-131), Baker Analyzed Reagent Grade sodium acetate trihydrate was used without further purification. For experiments no. 68, 69, 70, 71, 74, and 75 (Tables 132-137), this sodium acetate was purified in the following way.

Fourteen ml of sodium hypochlorite solution was added to a solution of 1638 g of the sodium acetate trihydrate in 65 ml of 11.66 M perchloric acid in a tightly stoppered bottle. The solution was kept overnight at room temperature, then heated at 60-80° for 90 minutes. The salt was crystallized by evaporating some of this solution and then was

77. C. K. Ingold, C. G. Raisin, and C. L. Wilson, J. Chem. Soc., 915 (1936).

recrystallized from water. The doubly recrystallized salt was dried to constant weight at 200° to give anhydrous sodium acetate. Stock buffer solutions were filtered prior to use in order to remove traces of insoluble material.

Sodium Bicarbonate

Baker Analyzed Reagent grade sodium bicarbonate was used without purification.

Sodium Chloride

Baker Analyzed Reagent grade sodium chloride was used without purification.

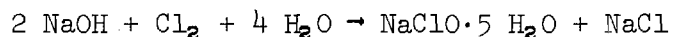
Sodium Dihydrogen Phosphate

Fifty ml of sodium hypochlorite solution was added to a solution of 1775 g of Baker Analyzed Reagent grade sodium dihydrogen phosphate in 1000 ml of water in a tightly stoppered bottle. The solution was heated at 50° for five days, after which time salt was crystallized by evaporating some of the solution. The salt was recrystallized twice from water and dried to constant weight at 150°. Stock buffer solutions, which also contained purified sodium monohydrogen phosphate (cf below) were filtered prior to use in order to remove traces of insoluble material.

Sodium Hypochlorite Solution

Clorox, a commercial bleach manufactured by The Clorox Company, Oakland, California, was used. This product is labelled as containing

5.25 percent sodium hypochlorite. The Merck Index⁽⁷⁸⁾ lists Clorox as an aqueous solution of sodium hypochlorite prepared according to the equation



A heavy precipitate was produced by the application of a drop of approximately one molar silver nitrate solution, indicating considerable chloride concentration.

Sodium Iodide

Fisher Certified Reagent Grade sodium iodide was used without purification.

Sodium Hydroxide

Baker Analyzed Reagent Grade sodium hydroxide was used without further purification.

Sodium Metal

Baker Purified sodium metal was used.

Sodium Monohydrogen Phosphate

Twenty ml of sodium hypochlorite solution was added to a solution of 500 g of Baker Analyzed Reagent Grade sodium monohydrogen phosphate heptahydrate in 500 ml of water in a tightly stoppered bottle. The solution was heated at 50° for two weeks. The salt was crystallized by eva-

78. The Merck Index of Chemicals and Drugs, 47th ed., Merck and Co., Inc., Rahway, N. J., 1960, p. 954.

porating some of the solution and recrystallized twice from water. It was then dried to constant weight at 150°. Stock buffer solutions, which also contained purified sodium dihydrogen phosphate (cf. above) were filtered prior to use in order to remove traces of insoluble material.

Sodium Nitrate

Baker Analyzed Reagent Grade sodium nitrate was used without further purification.

Sodium Perchlorate

For the experiments at ionic strength 0.0030, sodium perchlorate monohydrate from the G. Frederick Smith Co. was recrystallized from water. This material was also found satisfactory for the phenol experiments which, although at a higher ionic strength (0.30), were at lower temperatures than the other experiments (25.0° and 10.0°).

For the high ionic strength experiments (0.30 M and higher) with 2,4-dinitrophenol at 50.0°, special treatment of the sodium perchlorate was found necessary to reduce the blank drop to an acceptable level. The treatment was as follows.

A solution of 2000 g of the sodium perchlorate monohydrate in 1000 ml of water plus several ml of sodium hypochlorite solution was heated for several days at 50.0° in a tightly stoppered bottle. Some of the water was then evaporated, and sodium perchlorate recovered by crystallization. This salt was then recrystallized from water and dried to constant weight at 150°. The solutions of sodium perchlorate were filtered prior to use in order to remove traces of insoluble material.

Sulfuric Acid

Fisher Reagent grade sulfuric acid was used.

Water

A 12 ℓ glass still containing 235 g of potassium dichromate and 44.4 ml of sulfuric acid was charged with distilled water from a Barnstead still and distilled through a five foot Vigreux column (20 mm O.D.) after an initial reflux of approximately 20 minutes. The distillate was introduced into another 12 ℓ still, containing 110 g of potassium permanganate and 28 g of sodium hydroxide, from which it was distilled through a five foot packed column (20 mm O.D.), after an initial reflux of approximately 20 minutes. Distillation from either still was not allowed to continue when less than about four liters of solution was left in the pot.

Approximately the first liter of distillate from the permanganate still was discarded, and the remainder of the distillate was used in the kinetic experiments, the syntheses and purifications of compounds, and for the cleaning of glass vessels. The acid dichromate and alkaline permanganate solutions were periodically replaced.

This is similar to the method described by A. O. Allen.⁽⁷⁹⁾

79. A. O. Allen, Radiation Chemistry of Water and Aqueous Solutions, D. Van Nostrand Co., Inc., Princeton, N. J., 1961, p. 18.

CHAPTER III

GENERAL EXPERIMENTAL PROCEDURE

In all experiments, a multiple flask method was employed, and the consumption of iodine was followed spectrophotometrically by modifications of a method developed by N. S. Gnanapragasam.⁽⁸⁰⁾ The initial concentrations of aromatic compound, salt (for ionic strength), and other desired ingredients were duplicated in several red low-actinic 50 ml volumetric flasks with hand-ground stoppers; these concentrations were obtained by means of aliquots of stock solutions of individual ingredients. The flasks had previously been soaked in concentrated iodine solutions to destroy any iodine-consuming impurities. The flasks were immersed in a constant temperature bath. A stock solution of known concentrations of iodine and iodide in a 250 ml red low-actinic flask was also in the bath. Reaction was begun by pipetting the iodine-iodide solution from a pipette calibrated to deliver 5.00 ml (and checked by weight of delivered water) into the individual reaction flasks.[†] The stoppers in the flasks containing stock solution were replaced as soon as each aliquot was withdrawn, and the stoppers on the reaction solutions were replaced immediately upon introduction of the aliquot, and this solution was

[†]In a few cases, it was found more convenient to add a stock solution of aromatic compound to reaction flasks containing all of the other ingredients.

80. N. S. Gnanapragasam, laboratory notes, 1964-1965, Georgia Institute of Technology; work done in Dr. Grovenstein's laboratories.

rapidly shaken to ensure proper mixing. Both reaction solutions and stock solutions were equilibrated to reaction temperature at the start of the reaction. The starting time of the reaction was read off the electrical timer when approximately one-half of the liquid was delivered from the pipette.

After measured times, the reaction flasks were quenched by the addition of a known amount of sodium iodide, thereby converting most of the iodine to triiodide. The addition of sodium iodide was in some cases preceded or accompanied by the addition of a buffer to maintain a certain pH in the quenched solution, as will be described in the appropriate chapters. For those reactions which were run at 50.0°, the reaction flask was cooled in an ice bath to room temperature before introduction of the quenching solutions. The method of delivery of quenching solutions varied and will be discussed in the chapters dealing with the individual compounds.

The triiodide concentrations of the quenched solutions were determined by use of the Cary 14 spectrophotometer and from these concentrations the stoichiometric concentration[†] of iodine in the reaction solution was determined. This calculation was made according to equation (1).

[†]In this thesis, the term "stoichiometric concentration" will be used to indicate the concentration of a chemical entity which would exist if all reversible equilibria that consume it were completely reversed. Specifically, (I_2) is the concentration of iodine that would be determined by thiosulfate titration, and $(ArOH)$ is the concentration of a phenol at sufficiently high acidity to completely suppress dissociation. Round brackets () will be used to denote stoichiometric concentrations and square brackets [] to denote true concentrations.

$$(I_2) = \frac{\text{Abs}}{\epsilon_{I_3^-} \cdot l} \left\{ \frac{1 + K[I^-]_q}{K[I^-]_q} \right\} \cdot \frac{\text{vol } q}{\text{vol } r} = \text{Abs} \cdot E \quad (1)$$

where

$$E = \left\{ \frac{1 + K[I^-]_q}{K[I^-]_q} \right\} \cdot \frac{\text{vol } q}{\text{vol } r} \cdot \frac{1}{\epsilon_{I_3^-} \cdot l}$$

$[I^-]_q$ = true concentration (mole/liter) of iodide ion in quenched solution

(I_2) = stoichiometric concentration of iodine in reaction solution

l = path length of cell

$$K = \frac{[I_3^-]}{[I_2][I^-]}$$

vol q = volume of quenched solution

vol r = volume of reaction solution

$\epsilon_{I_3^-}$ = extinction coefficient of triiodide at the wavelength used

Equation (1) is derived as follows.

$$K = \frac{[I_3^-]_q}{\{(I_2)_q - [I_3^-]_q\} \{(I^-)_q - [I_3^-]_q\}} \quad (2)$$

where $(I_2)_q$ and $(I^-)_q$ refer to the concentrations of these species in the quenched solution, uncorrected for triiodide formation, and $[I_3^-]_q$ denotes true concentration in the quenched solution. K is 768 at 25.0° and 490 at 50.0°. (81)

81. M. Davies and E. Gwynne, J. Am. Chem. Soc., 74, 2748 (1952).

But,

$$[I^-]_q = (I^-)_q - [I_3^-]_q \approx (I^-)_q \quad (3)$$

because in all cases $(I^-)_q \gg (I_2)_q$

Therefore

$$[I_3^-]_q = K \{ [I^-]_q (I_2)_q - [I^-]_q [I_3^-]_q \} \quad (4)$$

$$(I_2)_q = [I_3^-]_q \left\{ \frac{1 + K[I^-]_q}{K[I^-]_q} \right\} \quad (5)$$

$$\text{Abs}_{\text{due to } I_3^-} = \epsilon_{I_3^-} \cdot (I_2)_q \frac{K[I^-]_q}{1 + K[I^-]_q} \ell \quad (6)$$

$$\text{Abs}_{\text{due to } I_2} = \epsilon_{I_2} \{ (I_2)_q - [I_3^-]_q \} \ell \quad (7)$$

However, the values of $\epsilon_{I_3^-}$ and ϵ_{I_2} at the wavelengths used are such that

absorbance due to iodine is in all cases negligible compared with absorbance due to triiodide[†]; therefore, the total absorbance is given by (6).

[†]The most severe interference from I_2 absorption occurs in experiments no. 110-117, which were read at 2875 Å and in which about six percent of the stoichiometric iodine existed as free iodine in the quenched solution. The extinction coefficients of iodine and triiodide at 2875 Å are 95 and 40,000, respectively, (82) so that an error of slightly more than 0.01 percent was introduced into the calculated iodine concentrations in samples and blanks in these reactions.

82. A. D. Awtrey and R. E. Connick, J. Am. Chem. Soc., 73, 1842 (1951).

In order to express equation (6) in terms of the stoichiometric concentration of iodine in the reaction solution, (I_2) , instead of the concentration in quenched solution, $(I_2)_q$

$$\text{Abs}_{\text{due to } I_3^-} = \epsilon_{I_3^-} \cdot (I_2) \frac{K[I^-]_q}{1 + K[I^-]_q} \ell \frac{\text{vol } r}{\text{vol } q} \quad (8)$$

Equation (8) rearranges to (1).

The triiodide extinction coefficient at 3530 Å at 25.0°, the approximate temperature of the quenched solutions at the time of spectral measurement (it is estimated that the actual temperature might have varied ± 3 degrees), was taken as 26,400. This value is given by Awtrey and Connick⁽⁸²⁾ and Keefer and Andrews⁽⁸³⁾; it was checked quite closely by Gnanapragasam⁽⁸⁰⁾ and by Aprahamian.⁽⁸⁴⁾

Since kinetic measurements were also made using 2875 Å and 3475 Å, extinction coefficients were determined at these wavelengths. This was done by measuring absorbance at each wavelength on a triiodide solution which was also measured at 3530 Å, taking the 3530 Å extinction coefficient as 26,400. The results were 26,195 at 3475 Å and 39,830 at 2875 Å. Since the literature value at 2875 Å is 40,000,^(82,83) this value was adopted in the present work.

83. T. L. Allen and R. M. Keefer, J. Am. Chem. Soc., 77, 2957 (1955).

84. N. S. Aprahamian, The Kinetics and Mechanism of Iodination of Phenol, p-Nitrophenol, Anisole and Their Deuterated Derivatives, Ph.D. Thesis, Georgia Institute of Technology, 1960, p. 274.

Background absorbance due to species other than triiodide must be taken into account. In some cases, this becomes more complicated than a single arithmetic operation, and these corrections will be discussed in the sections dealing with the individual compounds.

Samples were quenched at different times, the time of quenching minus the starting time equalling the reaction time. Reaction times were chosen so that the interval from about 20 percent to about 60 percent iodine consumption was covered.

Concentrations of the various ingredients other than iodine were determined by the weight of the amount introduced. For phenol and 2,4-dinitrophenol, concentrations of aromatic compound were determined spectrally as well as by weight. These spectral determinations of concentration will be discussed in the individual chapters.

The order of reaction was determined by measuring the effect of varying concentrations of aromatic compound, iodine, iodide, and general base. In all cases reported here, the reactions were first order in iodine and first order in aromatic compound in the concentration ranges studied. Therefore, the second order rate expression was employed

$$k_{\text{app}} = \frac{2.303}{\{(ArH)_0 - (I_2)_0\}t} \log \frac{(I_2)_0 \{(ArH)_0 - x\}}{(ArH)_0 \{(I_2)_0 - x\}} \quad (9)$$

where $(ArH)_0$ and $(I_2)_0$ refer to initial (zero percent reaction) stoichiometric concentrations

x is stoichiometric concentration of iodine consumed
and t equals reaction time.

It turned out that in all cases there was some inverse iodide ion dependence; this is not included in the k_{app} defined in equation (9).

A series of blank reactions, containing the same concentrations of the same ingredients as the sample flasks (including acidity) except for aromatic compound were run along with the samples and were quenched at similar time intervals, but included one blank quenched soon after the start of the reaction. This made possible a plot of iodine concentration versus time, from which could be obtained an initial iodine concentration and a rate of blank drop (slope), which is the consumption or loss of iodine due to experimental variables other than aromatic compound. A given set of blanks usually measured blank drop for two experiments (one protio and one deutero) which were run simultaneously and under the same conditions. A blank drop was, in fact, observed in most cases, and the rate constants had to be corrected accordingly. In every such case, it was noted that when blank absorbance was plotted against reaction time a reasonably good straight line could be drawn through the points. The value x for equation (9) was taken as the iodine concentration in sample solution at time t subtracted from the iodine concentration in the blank at the same time, and $(I_2)_0$ as the iodine concentration in the blank at one-half time. This is shown in Figure 1.

From Figure 1

$$(I_2)_0 = (F_1 - F_2 t/2)E \quad (10)$$

and
$$x = (F_1 - F_2 t - Abs_t)E \quad (11)$$

where F_2 = negative of the slope of the blank line.

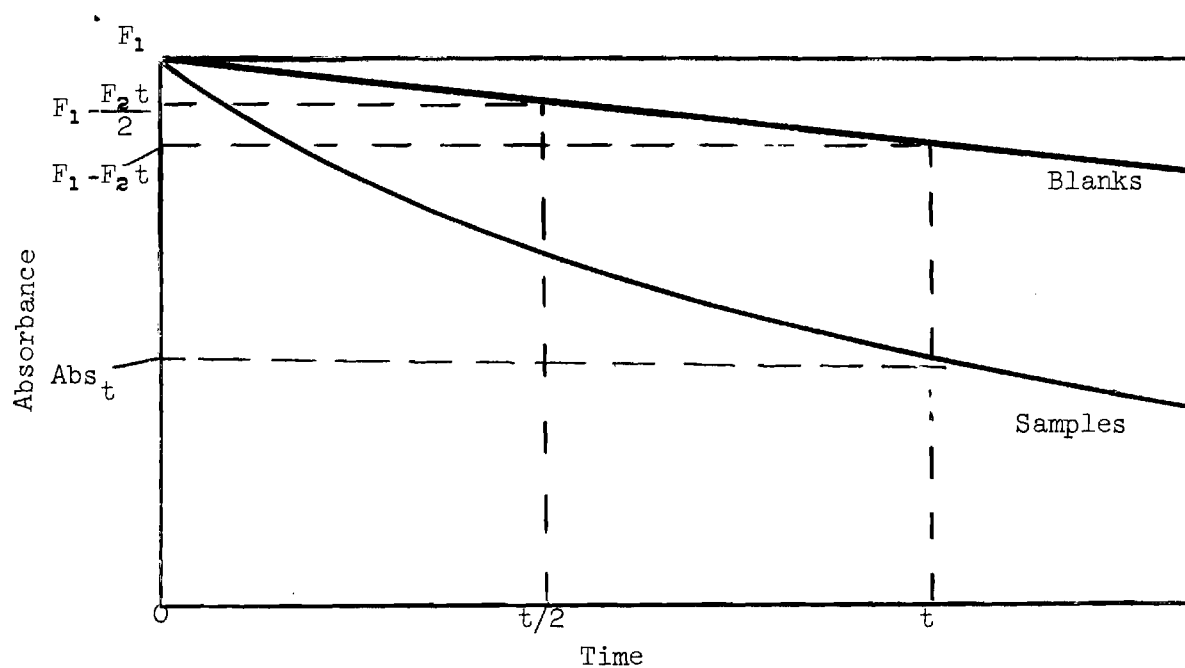


Figure 1. Blank Drop Correction Diagram

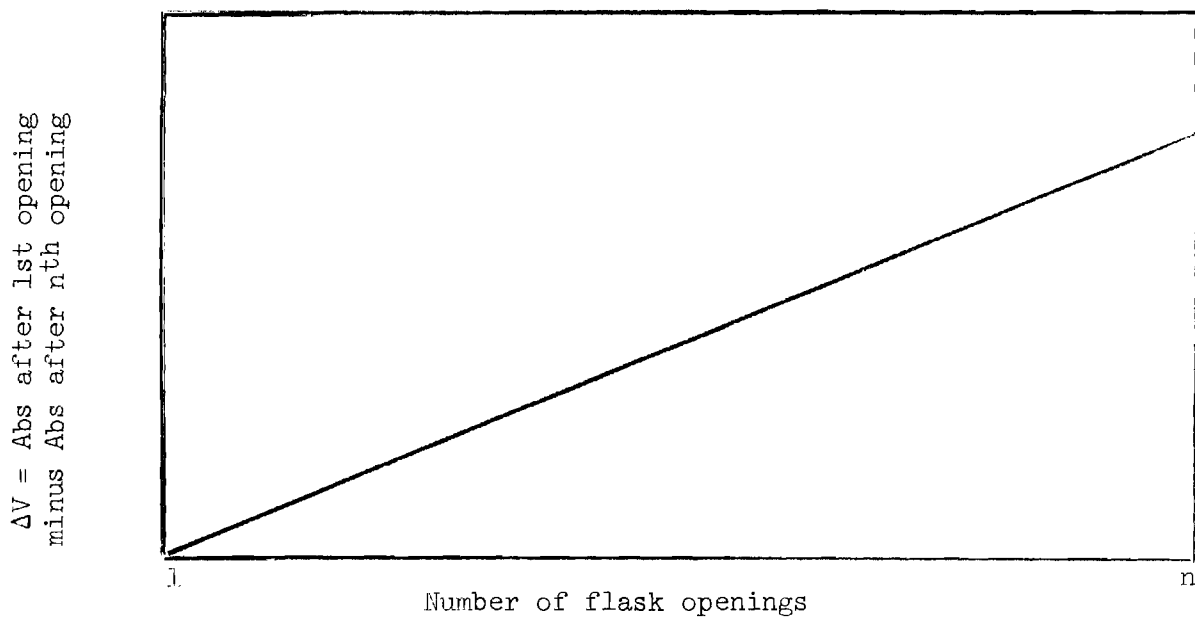


Figure 2. Diagram for Correcting for Iodine Loss by Volatilization from the Stock Solution

A more sophisticated treatment of blank drop correction, but still involving assumptions, has been developed by Berliner.⁽⁸⁵⁾ However, Gnanapragasam⁽⁸⁰⁾ found that for small blank drops (10 percent after 50 percent reaction), the correction described above gives very similar results. The blank drops to be treated in this thesis were limited to this magnitude, so the use of Gnanapragasam's method was justified.

In a few experiments, a small correction had to be applied for volatilization of iodine during the process of introducing iodine stock solution (at 50.0°C) into the reaction flask. Two blanks, which were started near the beginning and end of the reaction starting sequence, so that a maximum amount of volatilization from the stock solution would have occurred, but the reaction times of which were similar, so that there was little blank drop between them, were plotted on coordinates of absorbance difference versus number of openings of the iodine stock solution flask, as shown in Figure 2.

The equation for this straight line in Figure 2 is

$$\frac{\Delta V}{(\text{no. of openings} - 1)} = S \quad (12)$$

where S is the slope. Next, the volatilization loss corresponding with each blank and each reaction flask was obtained from

$$\Delta V = S (\text{no. of openings} - 1) \quad (13)$$

85. E. Berliner, J. Am. Chem. Soc., 83, 905 (1961).

This ΔV was then added to the observed absorbance for that flask.[†]

Since iodide ion is produced in the iodination reactions and since there is some inverse dependence of reaction rate upon iodide ion concentration, the k_{app} values had to be extrapolated to zero percent reaction when the predicted effect of the change in iodide ion concentration was sufficient to require this refinement. The first step in the procedure was to obtain average k_{app} values for a given experiment (corresponding to a given initial iodide concentration, $[I^-]_0$), and from these data to calculate the approximate order of iodide dependence of k_{app} at this $[I^-]_0$.

Now the true instantaneous rate constants can be written

$$\text{rate}_0 = \frac{k[I_2]_0 [ArH]_0}{[I^-]_0^n}; \quad k = \frac{\text{rate}_0 [I^-]_0^n}{[ArH]_0 [I_2]_0} \quad (14)$$

and

$$\text{rate}_t = \frac{k\{[I_2]_0 - x\}\{[ArH]_0 - x\}}{\{[I^-]_0 + x\}^n}; \quad k = \frac{\text{rate}_t \{[I^-]_0 + x\}^n}{\{[I_2]_0 - x\}\{[ArH]_0 - x\}} \quad (15)$$

where the subscript zero places the variables at zero time and subscript t places them at time t. The term x refers to the concentration of iodine (or of aromatic compound) consumed in the reaction. The square brackets indicate true concentrations in the reaction solution, and the k in these equations is the true rate constant.

[†]The ΔV correction is added to the measured absorbance instead of subtracted from F_1 for convenience of tabulation. Strictly speaking, the ΔV correction should be subtracted from F_1 , and a different value of F_1 used for each kinetic point. The ΔV values are so small that the method used gives a result that varies from the result obtained by the more rigorous method of correction by about one percent in each experiment involved, which is clearly insignificant within experimental error.

But, what was actually measured was, according to equation (9)

$$k_{app_0} = \frac{\text{rate}_0}{[I_2]_0 [ArH]_0} = \frac{k}{[I^-]_0^n} \quad (16)$$

and

$$k_{app_t} = \frac{\text{rate}_t}{\{[I_2]_0 - x\} \{[ArH]_0 - x\}} = \frac{k}{\{[I^-]_0 + \frac{x}{2}\}^n} \quad (17)$$

(The $\frac{x}{2}$ in equation (17) is an approximation; the increase in effective iodide concentration over the time t need not be exactly one half of the iodide produced, but unless the reaction is carried to the point of nearly complete consumption of iodine, this is a reasonable approximation.) These equations assume that the true iodine concentrations were used in the calculations of k_{app} values. Actually, stoichiometric iodine concentrations were used, but the error thereby introduced was approximately the same for k_{app_0} and k_{app_t} . The k_{app} values were subsequently corrected to true iodine concentration, as will be described. Now, since k_{app_0} was the rate constant of interest, corresponding to $[I^-]_0$, k_{app_t} had to be multiplied by a factor.

$$k_{app_t} \times \frac{\{[I^-]_0 + \frac{x}{2}\}^n}{[I^-]_0^n} = k_{app_0} \quad (18)$$

In order to be able to make this correction, a value for n was necessary. This was found to vary directly as a function of iodide concentration; therefore, it was determined, for any $[I^-]_0$, in the following manner.

The average k_{app} for the experiment of interest was obtained, as well as average k_{app} values for the experiments at the next higher and the next lower iodide ion concentrations.

$$\text{at } [I^-]_I, k_{app_{avI}} = \frac{k}{[I^-]_{\circ I}^n} \quad (19)$$

and

$$\text{at } [I^-]_{II}, k_{app_{avII}} = \frac{k}{[I^-]_{\circ II}^n} \quad (20)$$

Therefore,

$$\frac{k_{app_{avI}}}{k_{app_{avII}}} = \left(\frac{[I^-]_{\circ II}}{[I^-]_{\circ I}} \right)^n \quad (21)$$

and

$$n = \frac{\log \left\{ \frac{k_{app_{avI}}}{k_{app_{avII}}} \right\}}{\log \left\{ \frac{[I^-]_{\circ II}}{[I^-]_{\circ I}} \right\}} \quad (22)$$

In this way, a value of \underline{n} was determined between the reaction at the iodide of interest and the next higher iodide concentration; another value of \underline{n} was determined between the iodide concentration of interest and the next lower iodide concentration. These two values of \underline{n} were averaged, and the extrapolation k_{app} to zero percent reaction was made using this latter \underline{n} .

The measured (uncorrected) values of k_{app} were plotted against percent reaction, from which plot the k_{app} corresponding with 50 percent reaction was visually determined. Next, a value of k_{app} at zero percent reaction was calculated from the k_{app} at 50 percent reaction and the

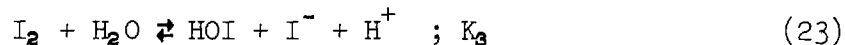
value of \underline{n} , using equation (18). A straight line was drawn on the plot between these values of k_{app} at 50 percent reaction and k_{app0} , and the vertical position of this line was shifted so as to give the best visual fit with the data, the slope being maintained.

Of course, for the highest iodide concentration studied, there was no higher iodide from which to determine one of the \underline{n} values. However, since in all such cases the \underline{n} between the iodide concentration of interest and the next lower iodide ion concentration was unity, for both protio and deutero compounds, and since it was known from other work that iodide ion dependence did not exceed first order even at much higher iodide concentrations, $\underline{n} = 1$ was used in these extrapolations of k_{app} .

The problem was more serious for the lowest iodide concentration studied. The \underline{n} between this experiment and the one at next higher iodide was used as a first approximation, and the k_{app0} obtained using this \underline{n} was included on a plot of k_{app0} versus $[I^-]_0$. A k_{app} corresponding to a still lower (three-fold lower) iodide concentration was picked off this plot, an \underline{n} was determined between this iodide concentration and the one of interest. This new \underline{n} was then averaged with that previously obtained. From this result, the k_{app} versus percent reaction data was again extrapolated to zero percent, and this k_{app0} value was considered the correct one.

The k_{app0} values are in terms of stoichiometric iodine, and they had to be corrected to rate constants in terms of true iodine concentrations. Iodine concentrations in reaction solution were corrected for two equilibria. Firstly, the triiodide equilibrium, the constant for which is 768 for reactions run at 25.0° and 490 for reactions run at

50.0°. (81) This correction is unimportant in low-iodide experiments, but it becomes important at high iodide concentrations. Secondly, the hydrolysis equilibrium



the equilibrium constant of which has been measured as 5.4×10^{-13} at 25.0°. (83) Their data extrapolate to 4.78×10^{-12} at 50.0°. This correction, while unimportant at the higher iodide concentrations, becomes significant in the experiments at lowest iodide concentrations that were run at low acidity and at 50.0°. This equilibrium constant was corrected for ionic strength by dividing by the square of the activity coefficient of the species comprising the bulk of the ionic strength.

The $k_{\text{app}0}$ values were converted to k^* values, as defined by equation (24).

$$k^* = k_{\text{app}0} \frac{(\text{I}_2)_0}{[\text{I}_2]_0} \quad (24)$$

The solutions for equation (9), $(\text{I}_2)_0$ and \underline{x} being defined by equations (10) and (11), were accomplished with the use of a computer. The ALGOL programs were written by Mr. J. M. McKelvey.

An example of the extraction of a k^* value from an experiment is given in Appendix I, incorporating the operations discussed in this chapter.

Once the appropriate rate constants were extracted from the data, they had to be treated in combination with the iodide concentrations for purposes of interpretation. These treatments will be described in the interpretive parts of the thesis. The iodide concentrations were corrected for triiodide and hydrolysis equilibria, just as were the iodine concentrations. For every iodide concentration used, runs were made on both protio and deutero compounds, because the effect of iodide concentration upon isotope effect is important. In almost all cases, this was done by running protio and deutero experiments together, employing the same set of blanks, so as to minimize the effect of any systematic errors upon isotope effect results.

The constant temperature baths which were used to maintain the reaction temperatures at 25.0° and 50.0° were calibrated using a platinum resistance thermometer, and they were found to be accurate within 0.1° over this temperature range.

In some cases, semiquantitative considerations had to be made on the basis of differences in ionic strength and, therefore, differences in activity coefficients, between experiments. When this was done, the activity coefficients chosen were the average activity coefficients for its principal source of ions; viz, sodium perchlorate.

All absorbances given in this thesis are on the basis of a 10 cm cell path length; where a different path length has been used in the actual spectral measurement, the appropriate correction has been used. Consequently, all extinction coefficients and effective extinction coefficients, such as E , refer to a 10 cm path length.

CHAPTER IV

IODINATION OF PHENOL

Introduction

Aprahamian⁽⁸⁶⁾ and Kilby⁽⁸⁷⁾ have measured the rates of iodination of phenol and of phenol-2,4,6-d₃ as a function of iodide concentration, using thiosulfate titration to follow iodine concentration. They found that for both compounds there was an inverse first-order relationship between k^* and $[I^-]$, at a given pH, over the $[I^-]$ range of 8×10^{-2} M to 9×10^{-6} M. Aprahamian found, over the $[I^-]$ range of 3.8×10^{-4} M to 9×10^{-6} M, a reasonably constant isotope effect of 6.6. (The value of about 4.0 measured by Kilby may reflect incomplete deuteration in synthesizing his phenol-2,4,6-d₃.[†]) At an iodide concentration of 0.0043 M, Kilby showed the kinetics of iodination of phenol to be first-order in phenol and first-order in iodine, since k^* was essentially constant between phenol concentrations of 0.008 M and 0.002 M, and between iodine concentrations of 0.0019 M and 0.0043 M.

[†]For this reason, the phenol-2,4,6-d₃ results of Kilby will not be used for comparisons with the data to be reported in this thesis.

86. N. S. Aprahamian, The Kinetics and Mechanism of Iodination of Phenol, p-Nitrophenol, Anisole and Their Deuterated Derivatives, Ph.D. Thesis, Georgia Institute of Technology, 1960, pp. 172-191, 241-253.

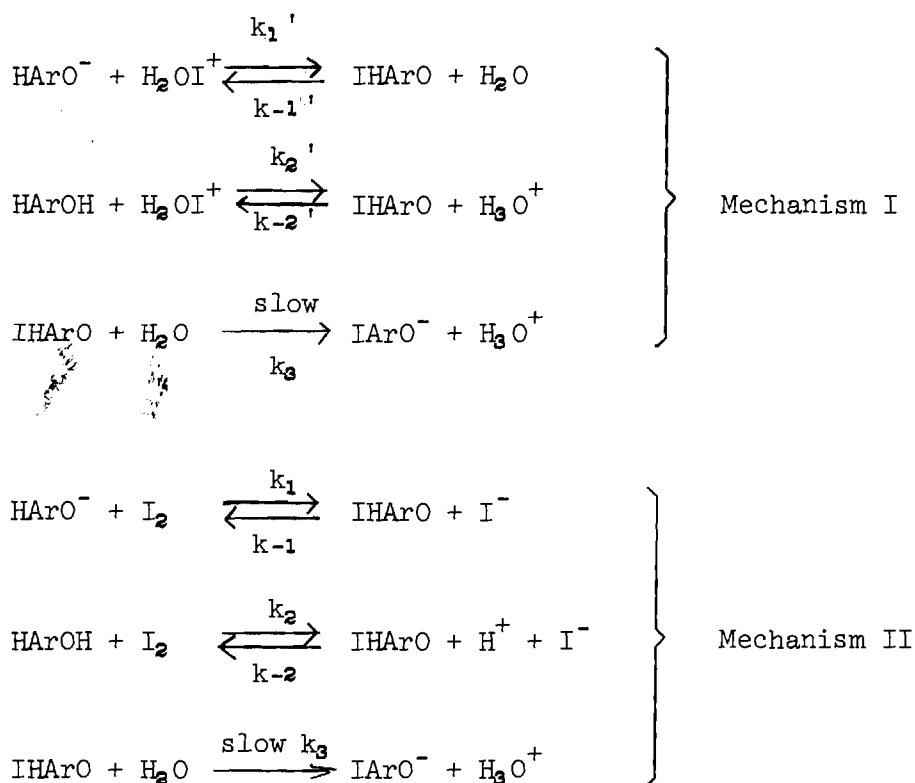
87. D. C. Kilby, Kinetic Study of the Mechanism of the Iodination of Phenol, M.S. Thesis, Georgia Institute of Technology, 1958.

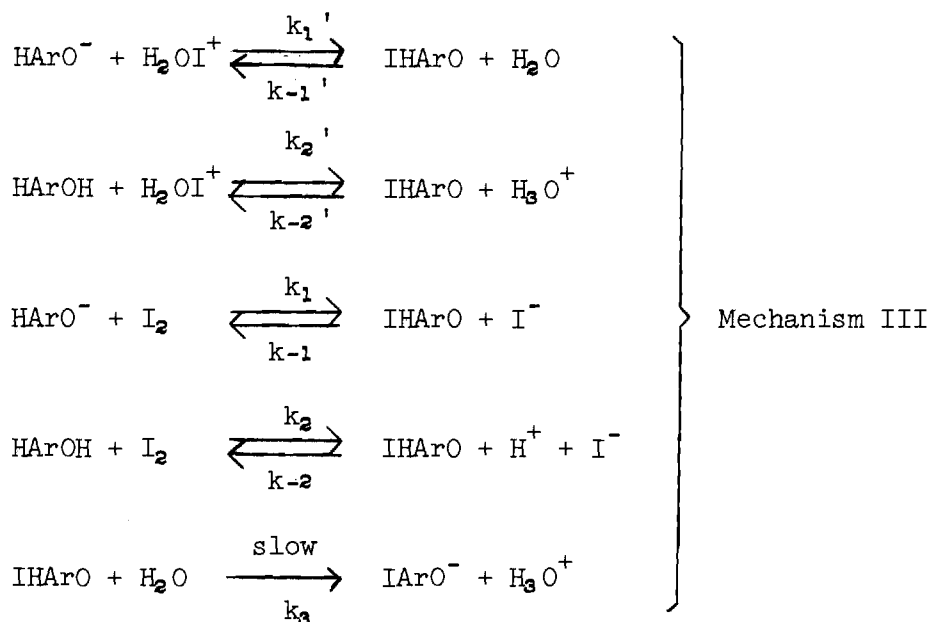
The effect of pH upon rate constants for the iodination of phenol can also be calculated from Kilby's work. Experiments were performed in perchloric acid with $[H^+] = 1.74 \times 10^{-2} \text{ M}$ and $[I^-]$ between $399 \times 10^{-6} \text{ M}$ and $18.7 \times 10^{-6} \text{ M}$, and in acetate-acetic acid buffers with $[H^+] = 3.17 \times 10^{-4} \text{ M}$ and $[I^-]$ between $7.8 \times 10^{-2} \text{ M}$ and $386 \times 10^{-6} \text{ M}$. All of these experiments were run at ionic strength = 0.30μ .[†] Since it appears that $k^*[I^-]$ (which is k' in Kilby's terminology) is independent of $[I^-]$ over the range of $[I^-]$ covered, values for $k^*[H^+][I^-]$ can be obtained for each set by multiplying the $[H^+]$ value by the average $k^*[I^-]$ (a value for $k^*[I^-]$ at $[H^+] = 1.74 \times 10^{-2} \text{ M}$ and $[I^-] = 2 \times 10^{-6} \text{ M}$ is not included because of apparent unreliability due to an excessive extrapolation of k_{app} to k_{app0}). The results are $k^*[I^-][H^+] = 7.5 \times 10^{-8} \frac{\text{mole}}{\ell \text{ sec}}$ at $[H^+] = 1.74 \times 10^{-2} \text{ M}$ and $11.0 \times 10^{-8} \frac{\text{mole}}{\ell \text{ sec}}$ at $[H^+] = 3.17 \times 10^{-4} \text{ M}$. However, Berliner⁽⁴⁶⁾ has investigated the catalysis of the iodination of phenol by acetate, finding the ratio of the water-catalyzed to acetate-catalyzed second order rate constants to be $0.083 \frac{\text{mole}}{\ell}$ at $[I^-] = 0.12 \text{ M}$, ionic strength = 0.3μ and at 25° . (The concentration of water is included in the water-catalyzed rate constant, while the concentration of acetate is not included in the acetate-catalyzed rate constant.) Extend-

[†]The ionic strength, μ , is defined by $\mu = \frac{1}{2} \sum C_i Z_i^2$, where C_i is the concentration of the i 'th ionic species, and Z_i is its numerical charge coefficient (Z_e being the charge of one electron). Therefore, the proper unit for ionic strength is a concentration unit, and in this thesis that is mole/ ℓ . The common practice, however, is to omit the unit when recording ionic strength, possibly because of the confusion that might arise when dealing with polyvalent ions; in such a case, the ionic strength, expressed in a concentration unit, is not equal to the concentration of ions. Accordingly, ionic strength will be recorded in this thesis without units.

ing this finding to Kilby's work, then, from the acetate concentration in Kilby's work of 0.05 M, the $k^*[H^+][I^-]$ for the water-catalyzed reaction can be shown to be $6.9 \times 10^{-8} \frac{\text{mole}}{\text{l sec}}$ for the reactions at $[H^+] = 3.17 \times 10^{-4} \text{ M}$. From the comparison of $k^*[I^-][H^+]$ values of $7.5 \times 10^{-8} \frac{\text{mole}}{\text{l sec}}$ and $6.9 \times 10^{-8} \frac{\text{mole}}{\text{l sec}}$ at $[H^+] = 1.74 \times 10^{-2} \text{ M}$ and $3.17 \times 10^{-4} \text{ M}$, respectively, Kilby's k^* data can be said to show approximately inverse first-order dependence upon $[H^+]$, as was found earlier by Berliner⁽⁴⁶⁾ and also by Painter and Soper.⁽⁴⁴⁾

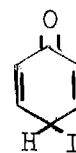
The results are consistent with three mechanistic possibilities: I, involving hypiodous acidium ion (H_2OI^+); II, involving molecular iodine; or III, involving both, as iodinating agents.





where

HArOH and HArO⁻ refer to phenol and undissociated phenol, respectively, IHarO refers to an intermediate, possibly



and IArO⁻ refers to iodinated phenoxide anion.

Considering the most general case, III, by steady state approximation

$$\begin{aligned}
 \frac{d[\text{IHarO}]}{dt} &= k_1[\text{HArO}^-][\text{I}_2] + k_2[\text{HArOH}][\text{I}_2] + k_1'[\text{HArO}^-][\text{H}_2\text{OI}^+] \quad (1) \\
 &+ k_2'[\text{HArOH}][\text{H}_2\text{OI}^+] - k_{-1}[\text{IHarO}][\text{I}^-] - k_{-2}[\text{IHarO}][\text{H}^+][\text{I}^-] \\
 &- k_{-1}'[\text{IHarO}] - k_{-2}'[\text{IHarO}][\text{H}^+] - k_3[\text{IHarO}] = 0
 \end{aligned}$$

$$[\text{IHAro}] \quad (2)$$

$$= \frac{k_1 [\text{HAro}^-][\text{I}_2] + k_2 [\text{HAroH}][\text{I}_2] + k_1' [\text{HAro}^-][\text{H}_2\text{OI}^+] + k_2' [\text{HAroH}][\text{H}_2\text{OI}^+]}{k_{-1}[\text{I}^-] + k_{-2}[\text{H}^+][\text{I}^-] + k_{-1}' + k_3 + k_{-2}'[\text{H}^+]}$$

But



$$K_1 = \frac{[\text{H}_2\text{OI}^+][\text{I}^-]}{[\text{I}_2]} \quad (4)$$

$$[\text{H}_2\text{OI}^+] = \frac{K_1 [\text{I}_2]}{[\text{I}^-]} \quad (5)$$

and



$$K_2 = \frac{[\text{HAro}^-][\text{H}^+]}{[\text{HAroH}]} \quad (7)$$

$$[\text{HAro}^-] = \frac{K_2 [\text{HAroH}]}{[\text{H}^+]} \quad (8)$$

Therefore

$$[\text{IHAro}] \quad (9)$$

$$= \frac{\frac{k_1 K_2 [\text{HAroH}][\text{I}_2]}{[\text{H}^+]} + k_2 [\text{HAroH}][\text{I}_2] + \frac{k_1' K_1 K_2 [\text{HAroH}][\text{I}_2]}{[\text{H}^+][\text{I}^-]} + \frac{k_2' K_1 [\text{HAroH}][\text{I}_2]}{[\text{I}^-]}}{k_{-1}[\text{I}^-] + k_{-2}[\text{H}^+][\text{I}^-] + k_{-1}' + k_3 + k_{-2}'[\text{H}^+]}$$

But

$$\text{rate} = k_3 [\text{IHAro}] \quad (10)$$

Substituting into equation (9)

rate (11)

$$= \frac{\frac{k_1 k_3 K_2 [\text{HArOH}][\text{I}_2]}{[\text{H}^+]} + k_2 k_3 [\text{HArOH}][\text{I}_2] + \frac{k_1' k_3 K_1 K_2 [\text{HArOH}][\text{I}_2]}{[\text{H}^+][\text{I}^-]} + \frac{k_2' k_3 K_1 [\text{HArOH}][\text{I}_2]}{[\text{I}^-]}}{k_{-1}[\text{I}^-] + k_{-2}[\text{H}^+][\text{I}^-] + k_{-2}'[\text{H}^+] + k_{-1}' + k_3}$$

However, by definition

$$\text{rate} = k^* [\text{HArOH}][\text{I}_2] \quad (12)$$

Therefore

$$k^* = \frac{\frac{k_1 k_3 K_2}{[\text{H}^+]} + k_2 k_3 + \frac{k_1' k_3 K_1 K_2}{[\text{H}^+][\text{I}^-]} + \frac{k_2' k_3 K_1}{[\text{I}^-]}}{k_{-1}[\text{I}^-] + k_{-2}[\text{H}^+][\text{I}^-] + k_{-2}'[\text{H}^+] + k_{-1}' + k_3} \quad (13)$$

and

$$\frac{1}{k^*[\text{H}^+]} = \frac{k_{-1}[\text{I}^-] + k_{-2}[\text{H}^+][\text{I}^-] + k_{-2}'[\text{H}^+] + k_{-1}' + k_3}{k_1 k_3 K_2 + k_2 k_3 [\text{H}^+] + \frac{k_1' k_3 K_1 K_2}{[\text{I}^-]} + \frac{k_2' k_3 K_1 [\text{H}^+]}{[\text{I}^-]}} \quad (14)$$

Using the microscopic reversibility relationships and multiplying numerators and denominators by identical terms

$$\frac{k_{-1}}{k_1 K_2} = \frac{k_{-2}}{k_2} = \frac{k_{-2}'}{k_2' K_1} = \frac{k_{-1}'}{k_1' K_1 K_2} \quad (15)$$

Equation (14) can then be rewritten

$$\frac{1}{k^*[\text{H}^+]} = \left(\frac{k_{-1}}{k_1 k_3 K_2} \right) [\text{I}^-] + \frac{1}{k_1 K_2 + k_2 [\text{H}^+] + \frac{k_1' K_1 K_2}{[\text{I}^-]} + \frac{k_2' K_1 [\text{H}^+]}{[\text{I}^-]}} \quad (16)$$

Equations (14) and (16) are descriptive statements of mechanism III. Mechanisms I and II are limiting cases of the general mechanism III, and the descriptive equations for mechanisms I and II can be derived from equation (14) or (16). In mechanism II, the primed terms are equal to zero, and

$$\frac{1}{k^*[H^+]} = \left(\frac{k-1}{k_1 k_3 K_2} \right) [I^-] + \frac{1}{k_1 K_2 + k_2 [H^+]} \quad (17)$$

is a useful descriptive equation for mechanism II. This is the equation derived by Aprahamian⁽⁸⁸⁾ for this mechanism. On the other hand, for mechanism I, the unprimed terms except k_3 in equation (14) or the first term of equation (16) are equal to zero.

$$\frac{1}{k^*[H^+]} = \left(\frac{k-1}{k_1 k_3 K_2} + \frac{1}{k_1 'K_1 K_2 + k_2 'K_1 [H^+]} \right) [I^-] \quad (18)$$

Utilizing the microscopic reversibility relationships shown in equation (15), equation (18) can be rearranged to another useful form

$$\frac{1}{k^*[H^+]} = \left(\frac{k-2 '[H^+] + k-1 ' + k_3}{k_1 'k_3 K_1 K_2 + k_2 'k_3 K_1 [H^+]} \right) [I^-] \quad (19)$$

Equations (18) and (19) are useful descriptive statements of mechanism I.

88. N. S. Aprahamian, The Kinetics and Mechanism of Iodination of Phenol, p-Nitrophenol, Anisole and Their Deuterated Derivatives, Ph.D. Thesis, Georgia Institute of Technology, 1960, p. 246.

Equations (17) and (19) are limiting cases of equation (14) or (16) as mechanisms I and II are limiting cases of mechanism III.

From equation (19), it is seen that mechanism I requires that a plot of $\frac{1}{k^*[\text{H}^+]}$ versus $[\text{I}^-]$ be a straight line through the origin for phenol and for phenol-2,4,6-d₃. Corollaries of this are that the isotope effect and $k^*[\text{H}^+][\text{I}^-]$ must be independent of iodide ion concentration. As far as can be determined from Aprahamian's and Kilby's data, these conditions are met in the iodination of phenol and phenol-2,4,6-d₃.

Equation (17), for mechanism II, shows that a plot of $\frac{1}{k^*[\text{H}^+]}$ versus $[\text{I}^-]$ is a straight line with a positive intercept, from which it follows that the isotope effect and $k^*[\text{H}^+][\text{I}^-]$ at a given acidity must decrease with decreasing iodide ion concentrations (as steps k_1 and/or k_2 become kinetically rate-determining).

While both Aprahamian's and Kilby's $\frac{1}{k^*[\text{H}^+]}$ versus $[\text{I}^-]$ data can be plotted through the origin without requiring unreasonable error in any point, it is, however, not possible to distinguish between a zero intercept and a small positive intercept. By the same token, the constancy of $k^*[\text{H}^+][\text{I}^-]$ and of the isotope effect are inconclusive, since they might or might not remain constant at still lower iodide concentrations. Aprahamian pointed out the necessity to extend his work to lower iodide ion concentrations in order to distinguish between these mechanisms. (89) While it is conceivable that data such as obtained by Apraha-

89. N. S. Aprahamian, The Kinetics and Mechanism of Iodination of Phenol, p-Nitrophenol, Anisole and Their Deuterated Derivatives, Ph.D. Thesis, Georgia Institute of Technology, 1960, p. 250.

mian might set a maximum upon possible intercepts such that any non-zero intercept consistent with the data would require impossibly high (beyond diffusion control) values for k_1 and for k_2 , thereby disproving mechanism II, this is not the case here--the matter will be discussed later.

Finally, equations (14) and (16) for mechanism III demonstrate that $\frac{1}{k^*[\text{H}^+]}$ versus $[\text{I}^-]$ would not be a straight line, but rather a curve approaching two different straight lines at extreme iodide concentrations. The two limiting straight lines are given by equation (17), representing limiting mechanism II in which iodine is the iodinating agent, at high iodide concentrations, and by equation (19), representing limiting mechanism I, in which H_2OI^+ is the iodinating agent, at low iodide concentrations. This requires that the isotope effect and $k^*[\text{H}^+][\text{I}^-]$ will approach different constant values at low and high iodide concentrations. It is not possible to say whether Kilby's or Aprahamian's data, or any other data through which a straight line can be drawn, lie on a true straight line or upon a slightly curved line. Also, while $k^*[\text{H}^+][\text{I}^-]$ and the isotope effect are constant within experimental error, the possibility remains that the limiting values at high and at low iodide concentrations are so similar; i.e., that the slopes of the high and low iodide lines are so similar, that the variations in $k^*[\text{H}^+][\text{I}^-]$ and isotope effect are too small to distinguish. The restriction that the similarity of high and low iodide slopes places upon certain individual rate constants will be discussed later, in the section on anisole.

The situation at this point is ambiguous; the data do not distinguish between the mechanistic possibilities. What is needed, as was

pointed out by Aprahamian, is an extension of the kinetic study of the iodination of phenol and phenol-2,4,6-d₃ to lower iodide concentrations. By thus magnifying the low-iodide portion of the $\frac{1}{k^* [H^+]}$ versus $[I^-]$ plots, a small positive intercept might be more clearly discerned. On the other hand, if the intercept is zero, the experiments might be carried to such low iodide concentrations that a better-defined maximum value might be placed upon the intercept, which would require impossibly high individual rate constants. Therefore, experiments were performed on the iodination of protio and deuterio phenol at lower iodide concentrations, this being rendered possible by the spectrophotometric method of Gnana-pragasam.

Specific Experimental Details

In order to study the kinetics of iodination of phenol, it was desired to run the experiments at 25.0° and at $\mu = 0.30$, so that these data might be comparable with those obtained by Aprahamian. It was also desired to employ acidities such that the reactions would proceed at a reasonable rate, and to vary the pH sufficiently to determine to what extent phenol and to what extent phenoxide anion were being iodinated.

The acidities chosen were $[H^+] = 1.74 \times 10^{-2}$ M, 5.21×10^{-3} M, and 1.30×10^{-3} M. Reaction solutions of such high acidities could not be quenched by simple introduction of sodium iodide, since the oxidation of iodide to iodine is rapid at these acidities. This problem is exemplified in Tables 1 and 2,^{† ‡} which show it to be serious in the range

[†]The volume of all blank and reaction solutions in Tables 1-10 is approximately 47 ml, and all are quenched to 50 ml, using additional water when necessary.

[‡]The method of delivery of quenching solutions in the experiments outlined in Tables 1-10 was by blowing in through wide-bore pipettes.

of acidity proposed for the phenol experiments, even though the quenched solution is neutralized with sodium bicarbonate immediately after addition of sodium iodide.

An alternative possibility is to add sodium bicarbonate before the sodium iodide. However, this was found to completely eliminate the triiodide absorbance in the quenched solution. This is undoubtedly because raising the pH increased the concentration of phenoxide anion sufficiently to react with all of the iodine in the few seconds between introduction of sodium bicarbonate and sodium iodide.

Since experiments showed that the sodium iodide and sodium bicarbonate could not be introduced separately, it was decided to attempt a quenching procedure which involved adding them simultaneously. Such attempts, described in Tables 3 and 4, showed that absorbances of quenched solutions were similar for cases in which reaction solutions were $1.74 \times 10^{-2} \text{ M } [H^+]$, $5.2 \times 10^{-3} \text{ M } [H^+]$, and $1.4 \times 10^{-5} \text{ M } [H^+]$, with the possibility of slightly more oxidation of iodide to iodine occurring when the more acidic solutions were quenched. The precision of this quenching technique was checked on solutions of composition given in Table 5, and it was found to be good. In order to determine the degree of iodide to iodine oxidation in this quenching procedure at $[H^+] = 5.2 \times 10^{-3} \text{ M}$, quenching experiments were run with zero acid present in the controls. Compositions of the acidified blanks are given in Tables 6 and 7. It was established that the addition of sodium iodide to solutions containing only sodium perchlorate gave rise to no measurable absorbance. The greater absorbance in the $5.2 \times 10^{-3} \text{ M } [H^+]$ quenched blanks

relative to the zero acid quenched blanks must result from interaction of quenching iodide with blank acid and ought to be independent of iodine and iodide concentrations in the reaction solution, so long as the iodide concentration of the reaction solution is much smaller than the iodide concentration of the quenched solution. (It is known from the absence of any rise in absorbance, upon quenching, of blank solutions as a function of time, and from Gnanapragasam's measurements on the rate of oxidation of iodide to iodine as a function of acidity⁽⁸⁰⁾ that the increase in absorbance observed here does not result from oxidation of iodide to iodine prior to quenching.)

Since experiments were planned at acidities other than 5.2×10^{-3} $\underline{M} [H^+]$, the quenching procedure was checked at the other acidities. Table 8 describes an experiment at 1.3×10^{-3} $\underline{M} [H^+]$ and Table 9 describes an experiment at 1.7×10^{-2} $\underline{M} [H^+]$.

The conclusion from the experiments outlined in Tables 6, 7, 8, and 9 is that corrections for oxidation of iodide to iodine must be made; 0.008 absorbance units for reactions at 5.2×10^{-3} $\underline{M} [H^+]$, 0.005 absorbance units for reactions at 1.3×10^{-3} $\underline{M} [H^+]$, and 0.011 absorbance units for reactions at 1.7×10^{-2} $\underline{M} [H^+]$. This correction amounted, in the most severe cases, to about ten percent of the initial absorbance reading and 20 percent of the final absorbance reading. These corrections have already been applied to the absorbance readings in Tables 11-26. Judging from all of the experiments until now, the relationship between the acidity of the reaction solution and the iodide-to-iodine oxidation during quenching with a solution of sodium iodide and sodium bicarbonate is a complicated one. This may reflect the fact that several variables are

involved here, such as relative rates of diffusion of iodide and bicarbonate anions, relative rates of acid oxidation of iodide and neutralization of acid by bicarbonate, lower concentrations of sodium bicarbonate used in quenching solutions of lower acidity, etc.

On the basis of these experiments, the quenching procedure adopted for the phenol work was to rapidly blow by mouth 3.0 ml of a sodium bicarbonate solution containing 0.38 g of sodium iodide from a wide bore pipette into the 47.0 ml reaction solution. For reactions at $1.74 \times 10^{-3} \text{ M } [\text{H}^+]$, the quenching solution was 0.33 M in NaHCO_3 ; for reactions at $5.2 \times 10^{-3} \text{ M } [\text{H}^+]$, the quenching solution was 0.10 M in NaHCO_3 ; and for reactions at $1.3 \times 10^{-3} \text{ M } [\text{H}^+]$, the quenching solution was 0.025 M in NaHCO_3 .

Additional possible contributions to background absorbance at 3530 Å had to be checked. Several experiments were performed in which two sets of solutions were at the same acidity, one set containing phenol at a concentration appropriate to a kinetic experiment, the other with no phenol. The purpose was to check for consumption of iodine by phenoxide anion produced instantaneously during the simultaneous sodium bicarbonate-sodium iodide quench. The observed absorbances of quenched solutions with and without phenol differed by less than 0.001 absorbance units, which is less than experimental error. Therefore, no correction was made for this hypothetical phenomenon.

Background absorbance corrections were found necessary for the sodium bicarbonate-perchloric acid buffer in the quenched solutions. These were determined by making up some solutions of this buffer at the same concentrations as in the actual quenched solutions. The buffer com-

position differed according to the acidity of the reaction, and corrections were applied accordingly. For instance, the buffer in the quenched $1.74 \times 10^{-2} \text{ M } [\text{H}^+]$ reaction absorbed .010 in a 10 cm cell at 3530 Å; other buffer absorbances were smaller, proportional to the buffer concentration in the quenched solution, and hence to the acidity of the reaction solution. These corrections have already been applied to the absorbances in Tables 11-26.

A background correction was also necessary for sodium perchlorate. Different sodium perchlorate stock solutions were found to give different background absorbances. The correction which was applied to any particular reaction, therefore, was determined by the sodium perchlorate stock solution employed; corrections ranged from .002 to .008 absorbance units in a 10 cm cell. During the course of the phenol work, it was found that absorbance due to sodium perchlorate could be significantly reduced by double filtration through a medium porosity fritted glass Büchner funnel, and this technique was employed in the subsequent high-ionic strength work on 2,4-dinitrophenol.

A very small background correction was necessary for the phenol used in some of the experiments, depending upon the concentration of phenol in the reaction solution. This was experimentally determined and applied. The correction was never greater than .002 absorbance units for 3530 Å, 10 cm cell, which was the case in experiments no. 38, 39, 44, and 45 (Tables 11, 12, 19, and 20). In contrast to all other background absorbance corrections, this one was applied only to the reaction solutions and not to the blanks.

It was determined that no measurable background absorbance was produced by the iodophenol generated in the reaction. A solution described in Table 10 was quenched first with sodium bicarbonate and then with sodium iodide, thereby consuming all of the iodine. The absorbance of the quenched solution equalled the sum of the separately measured background absorbances, with no contribution from iodophenol.

After the background absorbance corrections were applied to blanks and samples in the phenol experiments, k_{app} values were calculated by extrapolation and these were converted to k^* values, as described in Chapter III.

Each phenol concentration was determined both by weight and from the absorbance of the phenol stock solution at 2695 Å, which wavelength was experimentally found to be the wavelength of maximum absorbance, with a molar extinction coefficient of 1497. The use of absorbance as a measure of concentration was justified because in any experiment on phenol, both in this chapter and in Chapter IX, the acidity and the stoichiometric concentration of phenol are such that the extent of dissociation of phenol is negligible (far less than one percent) relative to the stoichiometric concentration of phenol. The reaction acidity of choice was obtained simply by including the requisite amount of perchloric acid in the reaction solution prior to introduction of the phenol stock solution.

Results and Discussion

The kinetic results are given in Tables 11-26. Absorbances which are recorded have already been corrected for all background contributions to absorbance (oxidation of iodide to iodine during

quenching, absorbance of buffer, absorbance due to sodium perchlorate, absorbance of phenol). The absorbance at zero percent reaction is F_1 , as described in Chapter III; F_2 and E are also defined in Chapter III.

The k_{app} values can be calculated from the data given in Tables 11-26, using equations (1) and (9) in Chapter III.

All absorbances and constants F_1 , F_2 , and E are on the basis of a spectrophotometric cell path length of 10 cm and a wavelength of measurement of 3530 Å.

The kinetic data are summarized in Tables 27 and 28. The first-order dependence of rate upon phenol concentration, which was demonstrated by Kilby at higher iodide concentrations, is seen here in Table references no. 13, 14, and 15 in Table 27, in which a threefold change in phenol concentration at $14.8 \times 10^{-6} \text{ M } [I^-]$ does not materially affect $k^*[H^+]$. Acidity also varies in these experiments; however, Table references no. 13 and 15, in which acidity varies thirteen-fold while phenol concentration remains constant demonstrate that at this iodide concentration $k^*[H^+]$ is independent of $[H^+]$. The first-order dependence of rate upon iodine concentration, which was also demonstrated by Kilby at higher $[I^-]$, is shown here by the fact that calculated rate constants at different percent reactions generally decrease to only about the extent anticipated from increasing iodide concentration.

When the data from Tables 27 and 28 are plotted at $1/k^*[H^+]$ versus $[I^-]$, it is clear that the plot for the protio compound is a straight line with a definite positive intercept (Figure 3). The plot for the deuterio compound (Figure 4) does not readily distinguish between a small positive intercept and the origin, because of the greater slope.

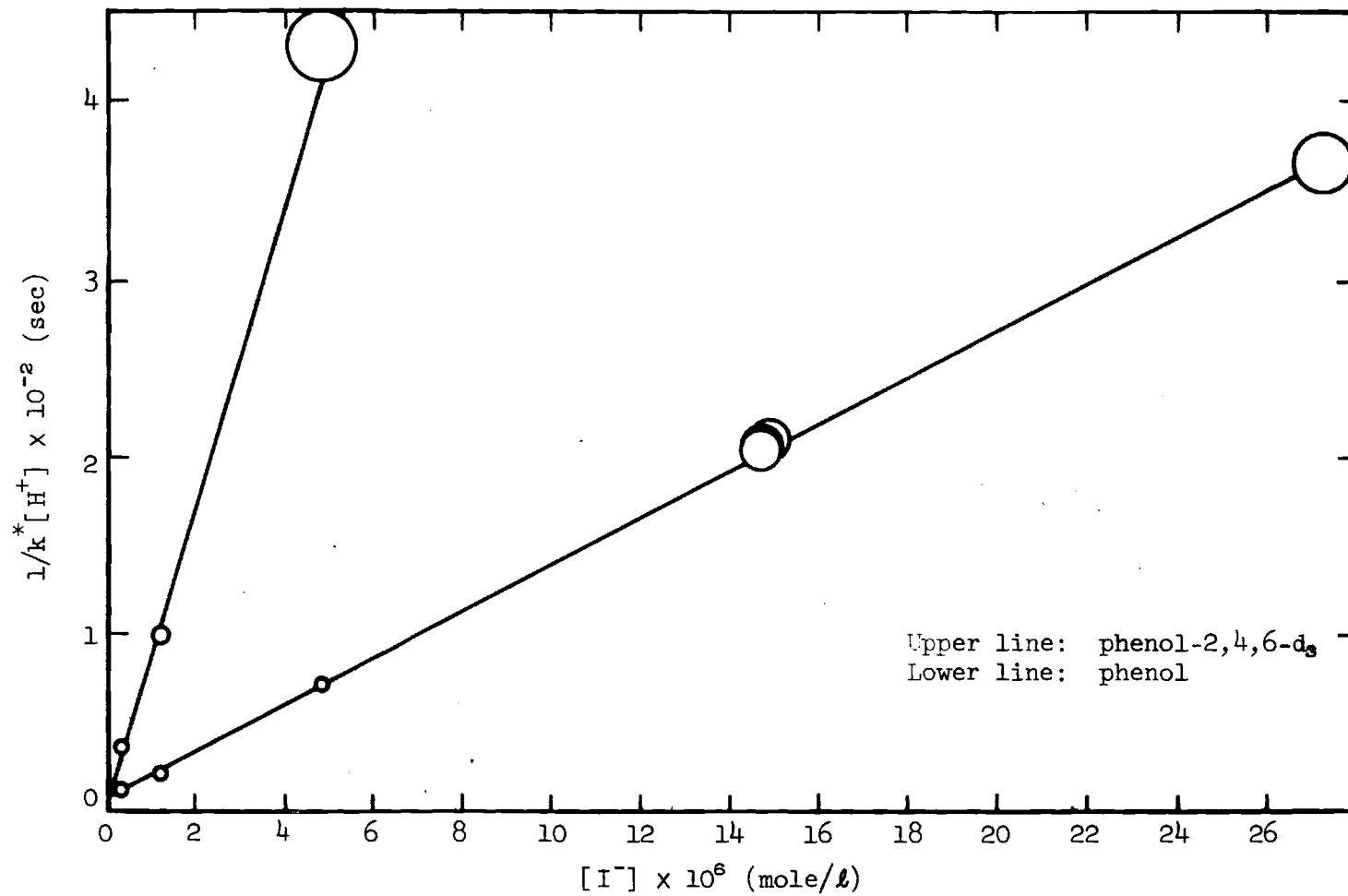


Figure 3. Phenol and Phenol-2,4,6-d₃ at Temperature, 25.0°; Ionic Strength, 0.30; [H⁺], 5.212 × 10⁻³ M

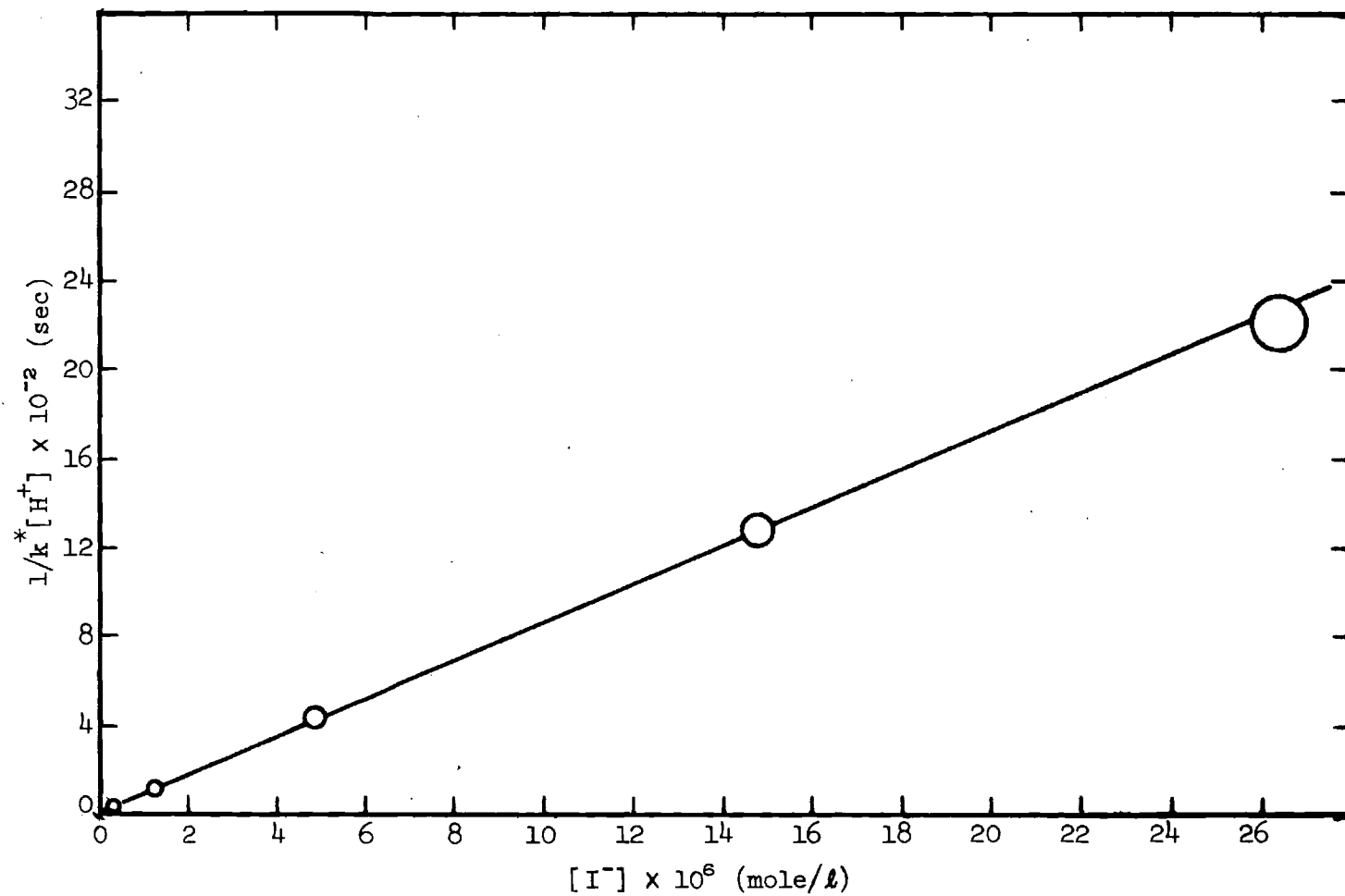


Figure 4. Phenol-2,4,6- d_3 at Temperature, 25.0°; Ionic Strength, 0.30;
 $[H^+]$, 5.212×10^{-3} M

However, the magnification of this line at lower $[I^-]$, which is included in Figure 3, shows that the intercept of protio line falls on a good straight line with the data for phenol-2,4,6- d_3 . If mechanism II or III is operative, i.e., if iodine is the iodinating agent at the higher iodide concentrations investigated, this intercept is equal to $\frac{1}{k_1 K_2 + k_2 [H^+]}$ (cf. equation (17)). Therefore, the isotope effect on the intercept should be small; accordingly, the protio and deutero $\frac{1}{k^* [H^+]}$ versus $[I^-]$ plots are drawn to the same intercept. This intercept is too small to have been clearly differentiable from zero in Aprahamian's or Kilby's work at higher iodide concentrations.

As drawn, the intercept of the curves at $[H^+] = 5.212 \times 10^{-8} \text{ M}$ in Figures 3 and 4 is 8.0 sec, the slope for the protio phenol is $13.6 \times 10^6 \frac{\text{l sec}}{\text{mole}}$, and the slope for the deutero phenol is $86. \times 10^6 \frac{\text{l sec}}{\text{mole}}$. By comparison, the slopes calculated from Aprahamian's data are $12.0 \times 10^6 \frac{\text{l sec}}{\text{mole}}$ for phenol and $79 \times 10^6 \frac{\text{l sec}}{\text{mole}}$ for phenol-2,4,6- d_3 , while a plot of $\frac{1}{k^* [H^+]}$ versus $[I^-]$ on Kilby's results for phenol gives a slope of $12.4 \times 10^6 \frac{\text{l sec}}{\text{mole}}$. (This is a plot of Kilby's data which were obtained in the absence of acetate; the data from the acetate-catalyzed experiments have not been plotted because of the impossibility of accurately separating the water-catalyzed reaction from the acetate-catalyzed reaction.)

The difference in slopes between the $\frac{1}{k^* [H^+]}$ versus $[I^-]$ plots of Kilby's and Aprahamian's results, on the one hand, and the slopes for the results reported in this thesis on the other, may result from different methods of extrapolating the k_{app} values to zero percent reaction. Kilby and Aprahamian extrapolated k_{app} to k_{app0} by simple visual curve fitting,

while the results reported here were extrapolated considering both the theoretical extrapolation and the visual fit, as discussed in Chapter III. Therefore, it was decided to apply this latter method to Aprahamian's data. Since this method assumes that a straight line adequately describes the extrapolation of k_{app} as a function of percent reaction, it becomes less satisfactory as the necessary extrapolation increases, in which case the theoretical extrapolations are described by lines of increasing curvature; for this reason only Aprahamian's phenol and phenol-2,4,6- d_3 data at $380 \times 10^{-6} \text{ M } [I^-]$ and $46 \times 10^{-6} \text{ M } [I^-]$ and Kilby's phenol data at $400 \times 10^{-6} \text{ M } [I^-]$ were reevaluated by the second extrapolation method. The $\frac{1}{k^*[H^+]}$ values calculated by Kilby and Aprahamian and those calculated from the same data by the alternative extrapolation method are compared in Table 29 with the values obtained by extension to the higher iodide ion concentrations of the $\frac{1}{k^*[H^+]}$ versus $[I^-]$ lines in Figure 3. It appears that the kinetic results on the iodination of phenol which are reported in this thesis are quite consistent with Kilby's and Aprahamian's results when the extrapolations of k_{app} to k_{app_0} are made in the same manner.

The nature of the variation of rate constants with iodide ion concentration is evident in the $k^*[H^+][I^-]$ values included in Tables 27 and 28. The observed decrease in $k^*[H^+][I^-]$ with decreasing $[I^-]$ reflects the straight lines with positive intercepts. The effect is less evident for the deuterio compound because of the greater ratio of slope-to-intercept. Another consequence of $\frac{1}{k^*[H^+]}$ versus $[I^-]$ plots like those in Figures 3 and 4 is that the isotope effect ought to decrease with decreasing iodide ion concentration, as the curve approaches the intercept. This

effect is observed and is summarized in Table 30.

These trends were not clearly evident in either Kilby's or Aprahamian's results because of the higher iodide ion concentrations used by them.

All of the results are consistent with a mechanism whereby molecular iodine is the sole iodinating agent, as discussed in the introduction to this chapter. Since neither the entire curve nor the lower portion of it is a straight line through the origin, there is no evidence that H_2OI^+ , or any other iodinating agent of the same iodide dependence, is involved to any extent.

The question does arise, however, to what extent an iodinating agent such as H_2OI^+ could be participating in the reaction without that participation being determinable from the results. It is clear that such an agent cannot be solely operable over the entire iodide concentration range, because the drawing of the best straight line through the origin on a $\frac{1}{k^*[\text{H}^+]}$ versus $[\text{I}^-]$ plot for the protio data would require that the measured k^* at lowest $[\text{I}^-]$ be in error by about 100 percent. Therefore, mechanism I does not apply. The alternative that species such as H_2OI^+ become predominant only at the lower iodide part of the curve (mechanism III) also requires unreasonably large errors in one or more measured values of k^* , although the infinite number of possibilities for relative importance of the two iodinating agents at any given iodide ion concentration makes it impossible to specify any particular error requirements. A more rigorous reason for excluding mechanism III over the iodide range studied here will be developed later in this chapter. Since there is no apparent reason why H_2OI^+ should be a better iodinating

agent relative to I_2 for phenol-2,4,6- d_3 than for phenol, the above considerations should apply to the deuterio compound as well. (Because of the higher slope of the $\frac{1}{k^*[H^+]}$ versus $[I^-]$ plot for phenol-2,4,6- d_3 , a line could be drawn through the data and the origin without requiring such large errors in measured values of k^* .)

It is necessary to know to what extent the reaction proceeds through the undissociated phenol and to what extent through the phenoxide anion. Since a preliminary examination of the pH-dependence data indicates that at $[H^+] = 5.2 \times 10^{-8}$ M most of the reaction is via phenoxide,[†] the conclusion of predominance of I_2 over H_2OI^+ as an iodinating agent is considered to apply to phenoxide. That is, the reaction of phenoxide with iodine is more important than the reaction of phenoxide with hypiodous acidium ion. On the other hand, any iodination of undissociated phenol, being less important than iodination of phenoxide, might, subject to further considerations, be by way of either molecular iodine or hypiodous acidium ion, since in either case the overall iodination of stoichiometric phenol would proceed principally by I_2 as required by the experimental results.

[†]The data for references no. 21, 22, 23, 24, and 25 in Table 27 show that even at $[I^-]$ of 0.315×10^{-6} M, the $1/k^*[H^+]$ value can be seen from Figure 3 to be similar to the intercept value on the $1/k^*[H^+]$ versus $[I^-]$ plot, a thirteen-fold change in $[H^+]$ producing only a 25 percent change in $1/k^*[H^+]$; moreover, it will be seen later that even this 25 percent variation is possibly exaggerated by the method of extrapolation of k_{app} to k_{app0} . Equation (16) shows that if the kinetic terms for iodination of undissociated phenol were important, that fact would be reflected in a large hydrogen-ion concentration dependence of $k^*[H^+]$ at iodide ion concentrations which are sufficiently low that the slope term $\frac{k-i}{k_1 k_2 K_1} [I^-]$ ceases to be dominant.

The general equation for iodination of both phenol and phenoxide by both iodine and hypiodous acidium ion is

$$\frac{1}{k^*[H^+]} = \left(\frac{k-1}{k_1 k_3 K_2} \right) [I^-] + \frac{1}{k_1 K_2 + k_2 [H^+] + \frac{k_1 'K_1 K_2}{[I^-]} + \frac{k_2 'K_1 [H^+]}{[I^-]}} \quad (16)$$

Considering the reaction between phenoxide and H_2OI^+ to be unimportant

$$\frac{1}{k^*[H^+]} = \left(\frac{k-1}{k_1 k_3 K_2} \right) [I^-] + \frac{1}{k_1 K_2 + k_2 [H^+] + \frac{k_2 'K_1 [H^+]}{[I^-]}} \quad (20)$$

Now, taking the case in which any iodination of phenol goes via I_2 (mechanism II)

$$\frac{1}{k^*[H^+]} = \left(\frac{k-1}{k_1 k_3 K_2} \right) [I^-] + \frac{1}{k_1 K_2 + k_2 [H^+]} \quad (17)$$

Iodination of undissociated phenol will show up as dependence of the $\frac{1}{k^*[H^+]}$ versus $[I^-]$ intercept upon $[H^+]$. The reciprocal of the intercept is $k_2 [H^+] + k_1 K_2$, so that if the reciprocal of the intercept is plotted against $[H^+]$, the slope of such a plot will be k_2 in $\frac{l}{\text{mole sec}}$ and the intercept will be $k_1 K_2$ in sec^{-1} . From combination of the forward steps signified by k_1 and k_2 in mechanism II, and the dissociation equation for phenol (equation (7)), the ratio $\frac{k_2 [H^+]}{k_1 K_2}$ can be shown to measure the importance of phenol relative to phenoxide as an object of iodination.

From the $\frac{1}{k^*[H^+]}$ versus $[I^-]$ curves, the $\frac{1}{k_2 [H^+] + k_1 K_2}$ inter-

cept values are seen to depend very heavily upon the $\frac{1}{k^*[H^+]}$ values at lowest iodide ion concentration. But the extrapolations to be applied to the k_{app} values in these lowest iodide experiments depend upon the intercepts. The extrapolation of k_{app} values for $[H^+]$ of $5.212 \times 10^{-3} \text{ M}$ was determined from a first approximation plot of $\frac{1}{k^*[H^+]}$ versus $[I^-]$, and then refined, as described earlier in Chapter III. Since, due to a possible contribution by $k_2[H^+]$, a greater intercept than determined for the $5.212 \times 10^{-3} \text{ M}$ $[H^+]$ data might correspond with $[H^+] = 1.303 \times 10^{-3} \text{ M}$ and a smaller one with $[H^+] = 1.740 \times 10^{-2} \text{ M}$, a smaller and a greater extrapolation, respectively, might be appropriate for the k_{app} values at lowest $[I^-]$ experiments at these acidities, relative to that extrapolation applied to the k_{app} values for the lowest $[I^-]$ run at $5.212 \times 10^{-3} \text{ M}$ $[H^+]$.[†]

There is not a sufficient number of points at $1.303 \times 10^{-3} \text{ M}$ $[H^+]$ or at $1.740 \times 10^{-2} \text{ M}$ $[H^+]$ to get good intercept values by first approximation plotting; therefore, the appropriate extrapolations of k_{app} to zero percent reaction were not known. Instead, the extrapolations were simply made to fit the k_{app} data. The resulting differences between extrapolations at different hydrogen ion concentrations were in the same direction as noted above from consideration of the possible intercept differences. (At $1.740 \times 10^{-2} \text{ M}$ $[H^+]$, a greater extrapolation was neces-

[†]The slope of a $\frac{1}{k^*[H^+]}$ versus $[I^-]$ should be independent of $[H^+]$, while for the case in which there is some contribution of iodination of undissociated phenol, the intercept is dependent upon $[H^+]$. The order of inverse iodide dependence of k^* decreases as the intercept increases; therefore, the extent of required extrapolation of k_{app} to k_{app0} decreases as the intercept increases.

sary than was made at $5.212 \times 10^{-3} \text{ M } [\text{H}^+]$; at $1.303 \times 10^{-3} \text{ M } [\text{H}^+]$, a smaller extrapolation was necessary than was made at $5.212 \times 10^{-3} \text{ M } [\text{H}^+]$.) A second approximation would lower the $k_{\text{app}0}$ for $1.740 \times 10^{-2} \text{ M } [\text{H}^+]$ and increase it for $1.303 \times 10^{-2} \text{ M } [\text{H}^+]$; i.e., bring $1/k^*[\text{H}^+]$ closer for the two acidities, thereby reducing the apparent contribution of iodination of undissociated phenol. However, this would lessen the fit with experimental k_{app} values, and so the first set of values is used here.

The $1/k^*[\text{H}^+]$ values at zero $[\text{I}^-]$, equal to $\frac{1}{k_2[\text{H}^+] + k_1K_2}$, for the different acidities are found from the $\frac{1}{k^*[\text{H}^+]}$ versus $[\text{I}^-]$ plots in Figure 5 to be 10.0 sec at $1.303 \times 10^{-3} \text{ M } [\text{H}^+]$, 8.0 sec at $5.212 \times 10^{-3} \text{ M } [\text{H}^+]$, and 6.0 sec at $1.740 \times 10^{-2} \text{ M } [\text{H}^+]$. Plotting the reciprocals of these quantities against $[\text{H}^+]$ gives an intercept of 0.093 sec^{-1} , equal to k_1K_2 , and a slope of 5.1 l/mole sec , equal to k_2 (Figure 6). From this, at $5.212 \times 10^{-3} \text{ M } [\text{H}^+]$, $k_2[\text{H}^+]$ equals 0.027 sec^{-1} , and the ratio $\frac{k_2[\text{H}^+]}{k_1K_2}$ equals 0.29; in other words, assuming that iodination of undissociated phenol is by molecular iodine, at the acidity of most of the experiments ($5.212 \times 10^{-3} \text{ M } [\text{H}^+]$) about 23 percent of iodination is via the undissociated phenol. If the extrapolations to $k_{\text{app}0}$ on the $1.740 \times 10^{-2} \text{ M } [\text{H}^+]$ and the $1.303 \times 10^{-3} \text{ M } [\text{H}^+]$ data at lowest iodide ion concentration were subjected to a second approximation, this contribution would be less than 23 percent, again assuming iodination of undissociated phenol by molecular iodine.

On the other hand, a contribution of iodination of undissociated phenol by hypiodous acidium ion would show up as a curve of the $\frac{1}{k^*[\text{H}^+]}$ versus $[\text{I}^-]$ plot toward the origin at low iodide ion concentrations. At sufficiently low $[\text{I}^-]$ for this reaction to have become predominant,

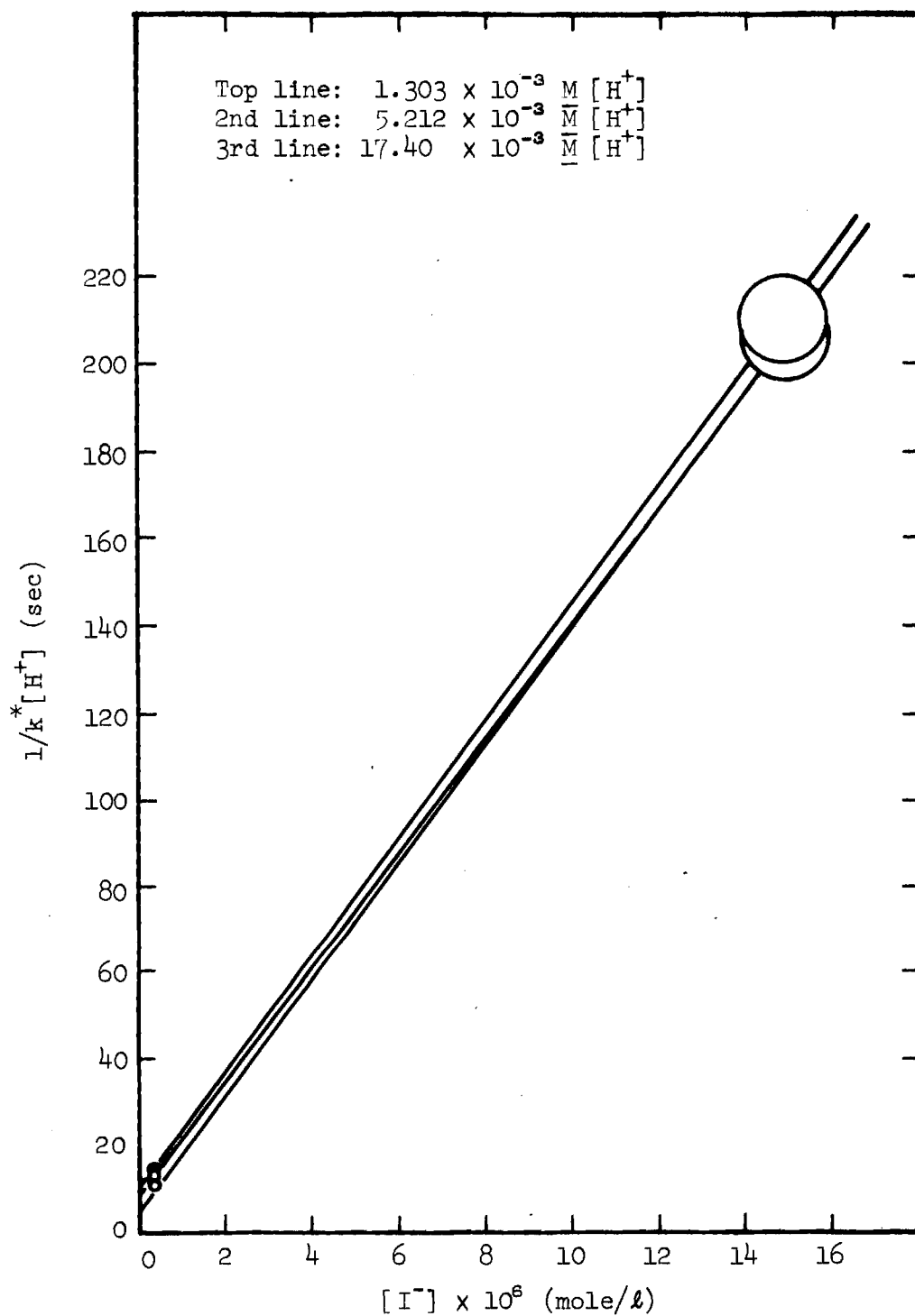


Figure 5. Phenol at Temperature, 25.0° ; Ionic Strength, 0.30. Effect of $[\text{H}^+]$ Variation on Intercept of Plot of $1/k^*[\text{H}^+] \text{ vs } [\text{I}^-]$

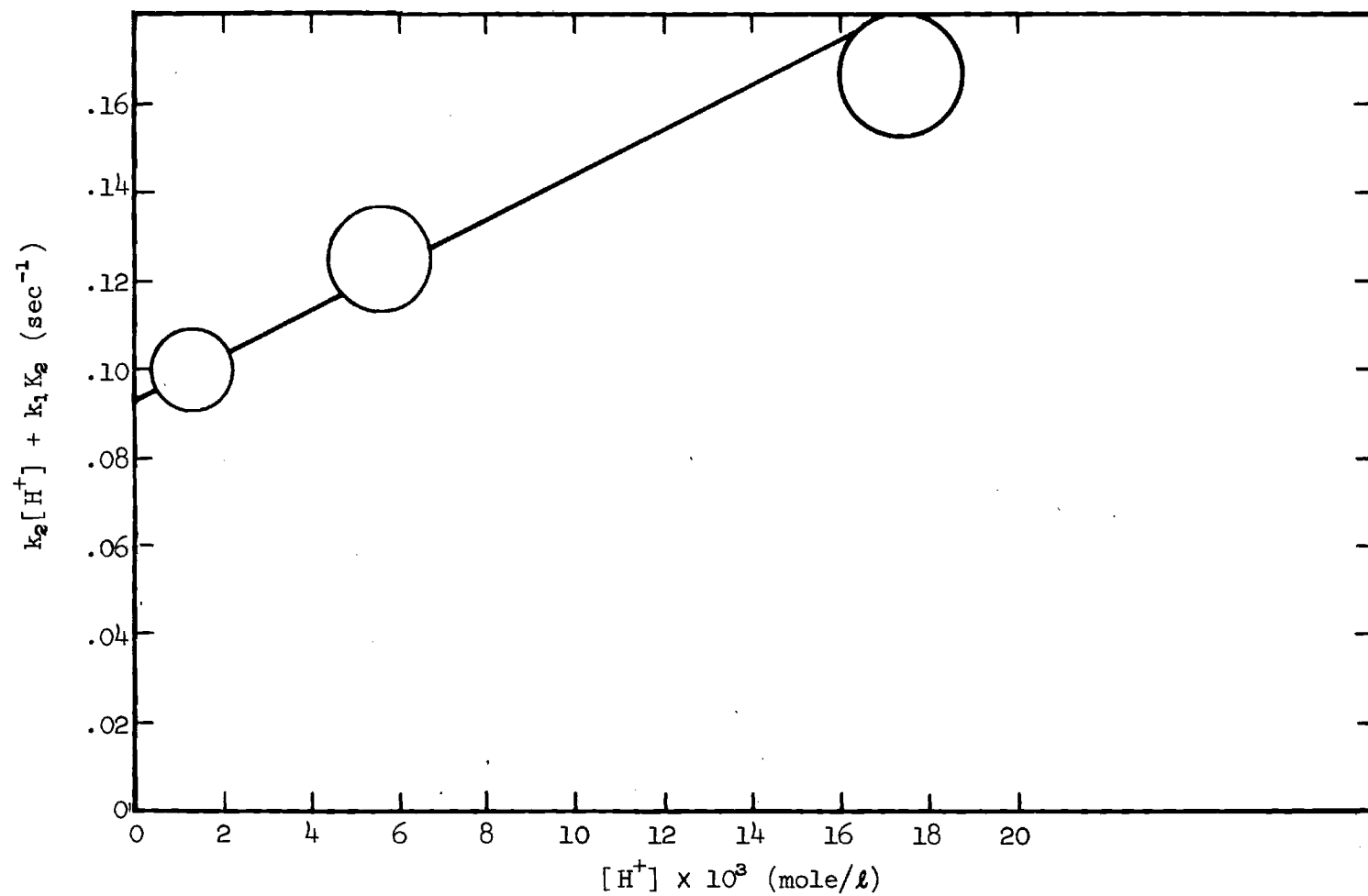


Figure 6. Phenol at Temperature, 25.0°; Ionic Strength, 0.30

the equation for $\frac{1}{k^*[H^+]}$ versus $[I^-]$ would be

$$\frac{1}{k^*[H^+]} = \left(\frac{k-1}{k_1 k_3 K_2} + \frac{1}{k_2 'K_1 [H^+]} \right) [I^-] \quad (21)$$

The fact that drawing a straight line through the origin and through any of the points on the $\frac{1}{k^*[H^+]}$ versus $[I^-]$ curve requires unreasonably large experimental errors shows that at $5.212 \times 10^{-3} \text{ M } [H^+]$, the reaction of undissociated phenol with H_2OI^+ is not very important over the iodide ion concentration range studied, in comparison with the iodination of phenoxide by molecular iodine. However, the variation of $1/k^*[H^+]$ with $[H^+]$ at lowest $[I^-]$ might reflect a slight contribution from the iodination of phenol by H_2OI^+ at $5.212 \times 10^{-3} \text{ M } [H^+]$.

While the nature of the data makes it impossible to know the relative values of $k_1 K_2$ and $k_2 [H^+]$ or $k_2 'K_1 [H^+]$ with great accuracy, it is clear that at $5.212 \times 10^{-3} \text{ M } [H^+]$, most of the reaction is by phenoxide anion.

There is no strong evidence regarding possible iodination of undissociated phenol in either Kilby's or Aprahamian's work. The finding that Kilby's water- and acetate-catalyzed k^* data show approximate inverse first order dependence upon $[H^+]$ applies at such high $[I^-]$ that differences in intercept would not show up strongly. Aprahamian performed an experiment at $2.11 \times 10^{-6} \text{ M } [I^-]$ and $0.0870 \text{ M } [H^+]$, in contrast to his other phenol experiments, which were at $0.0174 \text{ M } [H^+]$. The k_{app} values dropped so rapidly with increasing percentage of reaction, because of the approximately fifty-fold excess of $(I_2)_0$ over $[I^-]_0$, that

Aprahamian felt that no accurate extrapolation was possible. However, an approximate extrapolation of the k_{app} values in this experiment suggests that $\frac{1}{k^*[H^+]}$ at $0.0870 \text{ M } [H^+]$ and $2.11 \times 10^{-6} \text{ M } [I^-]$ is about 23, as compared with a value of about 35 obtained by extrapolation to $2.11 \times 10^{-6} \text{ M } [I^-]$ of Aprahamian's $\frac{1}{k^*[H^+]}$ versus $[I^-]$ plot of his $0.0174 \text{ M } [H^+]$ data. This appears to reflect considerable contribution of iodination of undissociated phenol at $0.0870 \text{ M } [H^+]$.

Using the k_1K_2 value of 0.093 sec^{-1} , calculated considering the iodination of phenol to proceed by molecular iodine, and from the literature value of K_2 at 25.0° (1.28×10^{-10}),⁽⁹⁰⁾ a value of k_1 can be calculated. Since all data in this chapter have been given in terms of concentrations, the thermodynamic value 1.28×10^{-10} for K_2 must be corrected for ionic strength (0.30) by division by the square of the activity coefficient of sodium perchlorate ($0.70^2 = 0.49$),⁽⁹¹⁾ which comprises the bulk of the ionic strength. This gives a K_2 of $2.6 \times 10^{-10} \frac{\text{mole}}{l}$, and a k_1 value of $3.6 \times 10^8 \frac{l}{\text{mole sec}}$, which may indicate diffusion control.⁽⁹²⁾

Now the more rigorous argument against H_2OI^+ as an iodinating agent for phenoxide will be made, using the approximation that all iodination goes via phenoxide anion. Considering equation (18), the descriptive equation for mechanism I, the $k_2'[H^+]$ term is set equal to zero be-

90. CRC Handbook of Chemistry and Physics, 47th ed., The Chemical Rubber Co., Cleveland, Ohio, 1964, -5, -6, p. D-87.

91. Ibid., p. D-89.

92. A. A. Frost and R. G. Pearson, Kinetics and Mechanism, 2nd ed., John Wiley and Sons, Inc., New York, 1961, pp. 268-274.

cause of the insignificance of iodination of undissociated phenol, giving

$$\frac{1}{k^*[H^+]} = \left(\frac{k_{-1}}{k_1 k_3 K_1 K_2} + \frac{1}{k_1 K_1 K_2} \right) [I^-] \quad (22)$$

From microscopic reversibility (cf. equation (15)), equation (22) can be rewritten

$$\frac{1}{k^*[H^+]} = \left(\frac{k_{-1}}{k_1 k_3 K_2} + \frac{1}{k_1 K_1 K_2} \right) [I^-] \quad (23)$$

The descriptive equation for mechanism II, neglecting iodination of undissociated phenol, is

$$\frac{1}{k^*[H^+]} = \left(\frac{k_{-1}}{k_1 k_3 K_2} \right) [I^-] + \frac{1}{k_1 K_2} \quad (24)$$

If H_2OI^+ were one of the iodinating agents over the iodide range studied, i.e., if mechanism III applied, equations (23) and (24) would describe the low- and high-iodide portions of that curve, respectively, and the difference between the two slopes would be $\frac{1}{k_1 K_1 K_2}$.

The value of K_1 at 25.0° has been determined as 1.2×10^{-11} mole/l. (93) There is considerable disagreement with this result; e.g., Hine (94) considers a value of 10^{-20} mole/l to be at least as reliable as

93. R. P. Bell and E. Gelles, J. Chem. Soc., 2734 (1951).

94. J. Hine, Physical Organic Chemistry, 2nd ed., McGraw-Hill Company, Inc., New York, 1962, pp. 362-363.

the value of Bell and Gelles. At any rate, Allen and Keefer⁽⁸³⁾ have experimentally set an upper limit of 1×10^{-10} mole/l for K_1 .

Using $K_1 = 1 \times 10^{-10}$ mole/l as the most favorable possibility for iodination by H_2OI^+ and using the value of K_2 of 2.6×10^{-10} mole/l calculated above, the difference between high- and low-iodide slopes that is consistent with a reasonable value of k_1' can be calculated. Setting an upper (diffusion control) limit of 1×10^{10} mole/l on k_1' , then $\frac{1}{k_1' K_1 K_2}$, the difference between high- and low-iodide slopes, would be about 1×10^{10} l sec/mole. Therefore, the slope of the $1/k^*[H^+]$ versus $[I^-]$ curve at sufficiently low iodide that H_2OI^+ could be the sole iodinating agent would be at least one thousand times larger than the high-iodide slope (13.6×10^6 l sec/mole). From the straightness of the $1/k^*[H^+]$ versus $[I^-]$ line in Figure 3, it is obvious that no appreciable part is played at low iodide ion concentrations by a line whose slope is one-thousand times as large as the slope of the high iodide line. In other words, iodine is the principal iodinating agent for the phenoxide anion over the range of iodide ion concentrations studied (mechanism II).

For mechanism II, the slope of the $1/k^*[H^+]$ versus $[I^-]$ curve is equal to $\frac{k-1}{k_1 k_3 K_2}$. For the protio compound, this slope has been determined as 13.6×10^6 l sec/mole. Since $k_1 K_2$ is approximately 0.093 sec^{-1} , $k-1/k_3$, the reversibility ratio, is 1.46×10^6 l/mole. For the deuterio compound, the slope is 86 l sec/mole and, assuming the same value of $k_1 K_2$, the reversibility ratio is 9.25×10^6 l/mole. The ratio $9.25/1.46 = 6.34$ is the isotope effect of the k_3 step (assuming that the secondary isotope effect on $k-1$ is negligible).

Table 1. Quenching of Blank with Sodium Iodide Followed by Sodium Bicarbonate; $1.7 \times 10^{-2} \text{ M } [\text{H}^+]$ vs $2.9 \times 10^{-6} \text{ M } [\text{H}^+]$; Temperature, 25.0°

	$1.7 \times 10^{-2} \text{ M } [\text{H}^+]$ Solutions		$2.9 \times 10^{-6} \text{ M } [\text{H}^+]$ Solutions	
Composition	(I ₂)	$5.0 \times 10^{-7} \text{ M}$	(I ₂)	$5.0 \times 10^{-7} \text{ M}$
	(NaI)	$7.1 \times 10^{-7} \text{ M}$	(NaI)	$7.1 \times 10^{-7} \text{ M}$
	(NaClO ₄)	$2.8 \times 10^{-3} \text{ M}$	(NaClO ₄)	$2.8 \times 10^{-3} \text{ M}$
	(HClO ₄)	$1.7 \times 10^{-2} \text{ M}$	(HClO ₄)	$2.9 \times 10^{-6} \text{ M}$
Quenching Procedure	0.38 g NaI in 1.0 ml water, followed immediately by 1.0 ml of 1.0 M NaHCO_3		0.38 g NaI in 1.0 ml water	
Absorbance 10cm 3530 Å (corrected for buffer absorbance)	0.206, 0.205 ^{a,b}		0.190, 0.188 ^{a,b}	

^aIf the NaHCO_3 was not added, the absorbance continued rising rapidly.

^bIn Tables 1-10, the absorbance reading is given for each sample quenched; in this case, two samples at each acidity were quenched.

Table 2. Quenching of Blank with Sodium Iodide Followed by Sodium Bicarbonate; $1.8 \times 10^{-3} \text{ M } [\text{H}^+]$ vs $1.4 \times 10^{-5} \text{ M } [\text{H}^+]$; Temperature, 25.0°

	$1.8 \times 10^{-3} \text{ M } [\text{H}^+]$ Solutions		$1.4 \times 10^{-5} \text{ M } [\text{H}^+]$ Solutions	
Composition	(I_2)	$5.0 \times 10^{-7} \text{ M}$	(I_2)	$5.0 \times 10^{-7} \text{ M}$
	(NaI)	$3.5 \times 10^{-7} \text{ M}$	(NaI)	$3.5 \times 10^{-7} \text{ M}$
	(NaClO_4)	$1.4 \times 10^{-3} \text{ M}$	(NaClO_4)	$1.4 \times 10^{-3} \text{ M}$
	(HClO_4)	$1.8 \times 10^{-3} \text{ M}$	(HClO_4)	$1.4 \times 10^{-5} \text{ M}$
Quenching Procedure	0.38 g of NaI in 1.0 ml water followed quickly ^a by 0.10 ml of 1.0 M NaHCO_3		0.38 g NaI in 1.0 ml water	
Absorbance 10cm 3530 Å (corrected for buffer absorbance)	0.191, 0.186, 0.188		0.175, 0.178, 0.176	

^aThere was a longer time between sodium iodide addition and sodium bicarbonate addition (a few seconds) than was the case in the experiments summarized in Table 1; this is probably the reason for similar iodide-to-iodine absorbance at $1.7 \times 10^{-2} \text{ M}$ and at $1.8 \times 10^{-3} \text{ M } [\text{H}^+]$.

Table 3. Quenching of Blank by Simultaneous Addition of Sodium Iodide and Sodium Bicarbonate; $1.7 \times 10^{-2} \text{ M} [\text{H}^+]$ vs $1.4 \times 10^{-5} \text{ M} [\text{H}^+]$; Temperature, 25.0°

	$1.7 \times 10^{-2} \text{ M} [\text{H}^+]$ Solutions		$1.4 \times 10^{-5} \text{ M} [\text{H}^+]$ Solutions	
Composition	(I ₂)	$5.0 \times 10^{-7} \text{ M}$	(I ₂)	$5.0 \times 10^{-7} \text{ M}$
	(NaI)	$3.5 \times 10^{-7} \text{ M}$	(NaI)	$3.5 \times 10^{-7} \text{ M}$
	(NaClO ₄)	$1.4 \times 10^{-3} \text{ M}$	(NaClO ₄)	$1.4 \times 10^{-3} \text{ M}$
	(HClO ₄)	$1.7 \times 10^{-2} \text{ M}$	(HClO ₄)	$1.4 \times 10^{-5} \text{ M}$
	(Phenol)	$3.2 \times 10^{-6} \text{ M}^a$		
Quenching Procedure	0.38 g NaI in 1.0 ml of 1.0 M NaHCO ₃ solution		0.38 g NaI in 3.0 ml water	
Absorbance (corrected for buffer absorbance)	10cm 3530 Å 0.182, 0.173, 0.180		0.175, 0.178, 0.176	

^aHowever, the quenching solution was added within a few seconds of the start of the reaction, so that no measurable reaction of phenol with iodine ought to have occurred; *cf.*, for example, Table 25, experiment no. 55.

Table 4. Quenching of Blank by Simultaneous Addition of Sodium Iodide and Sodium Bicarbonate; $5.2 \times 10^{-3} \text{ M} [\text{H}^+]$ vs $1.4 \times 10^{-5} \text{ M} [\text{H}^+]$; Temperature, 25.0°

	$5.2 \times 10^{-3} \text{ M} [\text{H}^+]$ Solutions		$1.4 \times 10^{-5} \text{ M} [\text{H}^+]$ Solutions	
Composition	(I ₂)	$5.0 \times 10^{-7} \text{ M}$	(I ₂)	$5.0 \times 10^{-7} \text{ M}$
	(NaI)	$3.5 \times 10^{-7} \text{ M}$	(NaI)	$3.5 \times 10^{-7} \text{ M}$
	(NaClO ₄)	$1.4 \times 10^{-3} \text{ M}$	(NaClO ₄)	$1.4 \times 10^{-3} \text{ M}$
	(HClO ₄)	$5.2 \times 10^{-3} \text{ M}$	(HClO ₄)	$1.4 \times 10^{-5} \text{ M}$
Quenching Procedure	0.38 g NaI in 3.0 ml 0.10 M NaHCO ₃		0.38 g NaI in 3.0 ml water	
Absorbance 10cm 3530 Å (corrected for buffer absorbance)	0.278, 0.276, 0.276		0.279, 0.280, 0.269	

Table 5. Quenching of Blank by Simultaneous Addition of Sodium Iodide and Sodium Bicarbonate; Precision Check; Temperature, 25.0°

	(I ₂)	6.1 × 10 ⁻⁷ <u>M</u>
	(NaI)	1.21 × 10 ⁻⁶ <u>M</u>
Composition	(NaClO ₄)	0.27 <u>M</u>
	(HClO ₄)	5.2 × 10 ⁻³ <u>M</u>
Quenching Procedure	0.38 g NaI in 3.0 ml 0.10 <u>M</u> NaHCO ₃	
Absorbance 10cm 3530 Å (uncorrected)	0.157, 0.155, 0.161, 0.155, 0.156, 0.158	
Average	0.157 ± 0.002	

Table 6. Quenching of Blank by Simultaneous Addition of Sodium Iodide and Sodium Bicarbonate; $5.2 \times 10^{-3} \text{ M} [\text{H}^+]$ vs $10^{-7} \text{ M} [\text{H}^+]$; Temperature, 25.0°

	$5.2 \times 10^{-3} \text{ M} [\text{H}^+]$ Solutions		$10^{-7} \text{ M} [\text{H}^+]$ Solutions	
Composition	(I ₂)	$0.71 \times 10^{-6} \text{ M}$	(I ₂)	$0.71 \times 10^{-6} \text{ M}$
	(NaI)	$0.31 \times 10^{-6} \text{ M}$	(NaI)	$0.31 \times 10^{-6} \text{ M}$
	(NaClO ₄)	0.30 <u>M</u>	(NaClO ₄)	0.30 <u>M</u>
	(HClO ₄)	$5.2 \times 10^{-3} \text{ M}$	(HClO ₄)	0.0 <u>M</u>
Quenching Procedure	0.38 g NaI in 3.0 ml 0.10 <u>M</u> NaHCO ₃		0.38 g NaI in 3.0 ml water	
Absorbance 10cm 3530 Å (corrected for buffer absorbance)	0.134, 0.135, 0.135		0.128, 0.129, 0.123	

Table 7. Quenching of Blank by Simultaneous Addition of Sodium Iodide and Sodium Bicarbonate; $5.2 \times 10^{-3} \text{ M} [\text{H}^+]$ vs $10^{-7} \text{ M} [\text{H}^+]$ ^a; Temperature, 25.0°

	$5.2 \times 10^{-3} \text{ M} [\text{H}^+]$ Solutions		$10^{-7} \text{ M} [\text{H}^+]$ Solutions	
Composition	(I ₂)	$7.2 \times 10^{-7} \text{ M}$	(I ₂)	$7.2 \times 10^{-7} \text{ M}$
	(NaI)	$10.0 \times 10^{-7} \text{ M}$	(NaI)	$10.0 \times 10^{-7} \text{ M}$
	(NaClO ₄)	0.30 <u>M</u>	(NaClO ₄)	0.30 <u>M</u>
	(HClO ₄)	$5.2 \times 10^{-3} \text{ M}$	(HClO ₄)	0.0 <u>M</u>
Quenching Procedure	0.38 g NaI in 3.0 ml 0.10 <u>M</u> NaHCO ₃		0.38 g NaI in 3.0 ml water	
Absorbance 10cm 3530 Å (corrected for buffer absorbance)	0.194, 0.196, 0.196		0.187, 0.187	

^aThis is a repeat of the experiment summarized in Table 6 except for different NaI concentrations.

Table 8. Quenching of Blank by Simultaneous Addition of Sodium Iodide and Sodium Bicarbonate; $1.30 \times 10^{-3} \text{ M} [\text{H}^+]$ vs $10^{-7} \text{ M} [\text{H}^+]$; Temperature, 25.0°

	$1.30 \times 10^{-3} \text{ M} [\text{H}^+]$ Solutions	$10^{-7} \text{ M} [\text{H}^+]$ Solutions
Composition	(I ₂) $6.4 \times 10^{-7} \text{ M}$	(I ₂) $6.4 \times 10^{-7} \text{ M}$
	(NaI) $3.2 \times 10^{-7} \text{ M}$	(NaI) $3.2 \times 10^{-7} \text{ M}$
	(NaClO ₄) 0.30 M	(NaClO ₄) 0.30 M
	(HClO ₄) $1.30 \times 10^{-3} \text{ M}$	(HClO ₄) $1.30 \times 10^{-3} \text{ M}$
Quenching Procedure	0.38 g NaI in 3.0 ml 0.025 M NaHCO ₃	0.38 g NaI in 3.0 ml water
Absorbance ^{10cm} 3530 Å (corrected for buffer absorbance)	0.174, 0.175	0.168, 0.172

Table 9. Quenching of Blank by Simultaneous Addition of Sodium Iodide and Sodium Bicarbonate; $1.70 \times 10^{-2} \text{ M} [\text{H}^+]$ vs $10^{-7} \text{ M} [\text{H}^+]$; Temperature, 25.0°

	$1.70 \times 10^{-2} \text{ M} [\text{H}^+]$ Solutions	$10^{-7} \text{ M} [\text{H}^+]$ Solutions
Composition	(I ₂) $6.4 \times 10^{-7} \text{ M}$	(I ₂) $6.4 \times 10^{-7} \text{ M}$
	(NaI) $3.2 \times 10^{-7} \text{ M}$	(NaI) $3.2 \times 10^{-7} \text{ M}$
	(NaClO ₄) 0.30 M	(NaClO ₄) 0.30 M
	(HClO ₄) $1.70 \times 10^{-2} \text{ M}$	(HClO ₄) 0.0 M
Quenching Procedure	0.38 g NaI in 3.0 ml 0.333 M NaHCO ₃	0.38 g NaI in 3.0 ml water
Absorbance 10cm 3530 Å (corrected for buffer absorbance)	0.170, 0.168	0.158

Table 10. Quenching of Reaction Solutions with Sodium Bicarbonate Followed by Sodium Iodide; Temperature, 25.0°

	(I ₂)	$2.2 \times 10^{-6} \text{ M}$
	(NaI)	$1.1 \times 10^{-6} \text{ M}$
Composition	(NaClO ₄)	$9.2 \times 10^{-4} \text{ M}$
	(HClO ₄)	$5.2 \times 10^{-3} \text{ M}$
	(Phenol)	$32.0 \times 10^{-6} \text{ M}$
Quenching Procedure	1 ml 0.3 M NaHCO ₃ followed, after several seconds, by 0.38 g NaI in 1 ml water	
Absorbance 10cm 3530 Å (uncorrected)	0.010	
Absorbance Corrections	buffer = 0.003; I ⁻ → I ₂ = 0.007	
Absorbance due to 2-Iodo-4-nitrophenol	0.000	

Table 11. Run 38, Phenol in 27.30×10^{-6} M Sodium Iodide Solution at 25.0°

$(I_2)_o$	5.148×10^{-6} M	$(HClO_4)_o$	5.212×10^{-3} M
$[I_2]_o$	5.040×10^{-6} M	$[NaClO_4]$	0.295 M
$(I^-)_o$	27.30×10^{-6} M	$(Phenol)_o$	221.6×10^{-6} M
$[I^-]_o$	27.19×10^{-6} M	μ	0.30
$[HOI]_o$	0.000×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
1402	1.065	14.2	0.492
3685	0.843	32.0	.474
5205	.716	42.2	.478
6067	.658	46.9	.473
7143	.602	51.4	.458
8171	.541	56.3	.460
8609	.517	58.2	.461

$$F_1 = 1.241 \quad F_2 = 0.37 \times 10^{-6} \text{ sec}^{-1} \quad E = 4.148 \times 10^{-6} \text{ mole cm/l}^a$$

$$k_{appo} = 0.492 \text{ l/mole sec} \quad k^* = 0.502 \text{ l/mole sec}$$

$$k^*[H^+] = 2.62 \times 10^{-3} \text{ sec}^{-1}$$

^aThe effective extinction coefficients in this thesis, such as the reciprocal of E, refer to a cell path length of 10 cm. Strictly speaking, the units are

$$\frac{\text{l}}{\text{mole cm}} \times 10 \text{ cm} = \frac{\text{l}}{\text{mole}}$$

However, the usual extinction coefficient units,

$$\frac{\text{l}}{\text{mole cm}} \text{ (or } \frac{\text{mole cm}}{\text{l}} \text{ for E),}$$

are used in the tables.

Table 12. Run 39, Phenol-2,4,6-d in 27.30×10^{-6} M Sodium Iodide Solution at 25.0°

$(I_2)_0$	5.148×10^{-6} M	$(HClO_4)_0$	5.212×10^{-3} M
$[I_2]_0$	5.040×10^{-6} M	$[NaClO_4]$	0.295 M
$(I^-)_0$	27.30×10^{-6} M	$(Phenol-2,4,6-d_3)_0$	207.1×10^{-6} M
$[I^-]_0$	27.19×10^{-6} M	μ	0.30
$[HOI]_0$	0.000×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
7144	1.101	11.1	0.080
10610	1.042	15.8	.078
15865	0.960	22.2	.077
24660	.807	34.4	.083
30301	.752	38.7	.078
36319	.681	44.3	.078
40682	.629	48.4	.079

$$F_1 = 1.241$$

$$F_2 = 0.37 \times 10^{-6} \text{ sec}^{-1}$$

$$E = 4.148 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 0.0820 \text{ l/mole sec}$$

$$k^* = 0.0837 \text{ l/mole sec}$$

$$k^*[H^+] = 4.36 \times 10^{-4} \text{ sec}^{-1}$$

Table 13. Run 56, Phenol in 14.93×10^{-6} M Sodium Iodide Solution at 25.0°

$(I_2)_0$	3.941×10^{-6} M	$(HClO_4)_0$	1.303×10^{-3} M
$[I_2]_0$	3.896×10^{-6} M	$[NaClO_4]$	0.299 M
$(I^-)_0$	14.93×10^{-6} M	$(Phenol)_0$	63.22×10^{-6} M
$[I^-]_0$	14.88×10^{-6} M	μ	0.30
$[HOI]_0$	0.000×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
760	0.798	15.8	3.60
1140	.737	22.1	3.49
1515	.682	27.8	3.42
2215	.590	37.3	3.37
2760	.525	44.0	3.36
3360	.461	50.6	3.37
3800	.426	54.1	3.30

$$F_1 = 0.950$$

$$F_2 = 3.26 \times 10^{-6} \text{ sec}^{-1}$$

$$E = 4.148 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 3.60 \text{ l/mole sec}$$

$$k^* = 3.64 \text{ l/mole sec}$$

$$k^*[H^+] = 4.74 \times 10^{-3} \text{ sec}^{-1}$$

Table 14. Run 48, Phenol in 14.80×10^{-6} M Sodium Iodide Solution at 25.0°

$(I_2)_0$	3.791×10^{-6} M	$(HClO_4)_0$	5.212×10^{-3} M
$[I_2]_0$	3.748×10^{-6} M	$[NaClO_4]$	0.295 M
$(I^-)_0$	14.80×10^{-6} M	$(Phenol)_0$	211.7×10^{-6} M
$[I^-]_0$	14.76×10^{-6} M	μ	0.30
$[HOI]_0$	0.000×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
1105	0.738	19.2	0.91
2395	.583	36.1	.89
2500	.579	36.6	.86
3850	.458	49.7	.85
3995	.446	51.1	.85
5165	.364	60.0	.84
5765	.332	63.5	.83

$$F_1 = 0.914$$

$$F_2 = 0.52 \times 10^{-6} \text{ sec}^{-1}$$

$$E = 4.148 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 0.92 \text{ l/mole sec}$$

$$k^* = 0.93 \text{ l/mole sec}$$

$$k^*[H^+] = 4.85 \times 10^{-3} \text{ sec}^{-1}$$

Table 15. Run 57, Phenol in 14.93×10^{-6} M Sodium Iodide Solution at 25.0°

$(I_2)_0$	3.941×10^{-6} M	$(HClO_4)_0$	1.740×10^{-2} M
$[I_2]_0$	3.896×10^{-6} M	$[NaClO_4]$	0.299 M
$(I^-)_0$	14.93×10^{-6} M	$(Phenol)_0$	63.32×10^{-6} M
$[I^-]_0$	14.88×10^{-6} M	μ	0.30
$[HOI]_0$	0.000×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
6885	0.854	10.1	0.245
12315	.765	19.5	.280
21850	.635	33.2	.295
23420	.642	32.4	.267
28970	.587	38.2	.266
34545	.547	42.4	.256

$$F_1 = 0.950$$

$$F_2 = 0.0 \text{ sec}^{-1}$$

$$E = 4.148 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 0.278 \text{ l/mole sec}$$

$$k^* = 0.281 \text{ l/mole sec}$$

$$k^*[H^+] = 4.89 \times 10^{-3} \text{ sec}^{-1}$$

Table 16. Run 49, Phenol-2,4,6-d in 14.80×10^{-6} M Sodium Iodide Solution at 25.0°

$(I_2)_0$	3.791×10^{-6} M	$(HClO_4)_0$	5.212×10^{-3} M
$[I_2]_0$	3.748×10^{-6} M	$[NaClO_4]$	0.295 M
$(I^-)_0$	14.80×10^{-6} M	$(Phenol-2,4,6-d_3)_0$	255.3×10^{-6} M
$[I^-]_0$	14.76×10^{-6} M	μ	0.30
$[HOI]_0$	0.000×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} ($l/mole\ sec$)
4715	0.769	15.6	0.141
7615	.689	24.2	.143
11085	.599	34.0	.147
15230	.521	42.3	.142
17465	.482	46.5	.141
23315	.399	55.4	.136
27255	.351	60.5	.134

$$F_1 = 0.914$$

$$F_2 = 0.52 \times 10^{-6} \text{ sec}^{-1}$$

$$E = 4.148 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 0.148 \text{ l/mole sec}$$

$$k^* = 0.150 \text{ l/mole sec}$$

$$k^*[H^+] = 7.82 \times 10^{-4} \text{ sec}^{-1}$$

Table 17. Run 46, Phenol in 4.826×10^{-6} M Sodium Iodide Solution at 25.0°

$(I_2)_0$	2.447×10^{-6} M	$(HClO_4)_0$	5.212×10^{-3} M
$[I_2]_0$	2.438×10^{-6} M	$[NaClO_4]$	0.295 M
$(I^-)_0$	4.826×10^{-6} M	$(Phenol)_0$	112.3×10^{-6} M
$[I^-]_0$	4.817×10^{-6} M	μ	0.30
$[HOI]_0$	0.000×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
1130	0.435	26.2	2.41
1525	.390	33.9	2.42
2025	.343	41.8	2.39
2720	.290	50.8	2.34
2925	.276	53.2	2.32
3865	.220	62.6	2.29
3985	.212	64.0	2.30

$$F_1 = .590$$

$$F_2 = .25 \times 10^{-6} \text{ sec}^{-1}$$

$$E = 4.148 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 2.63 \text{ l/mole sec}$$

$$k^* = 2.64 \text{ l/mole sec}$$

$$k^*[H^+] = 1.38 \times 10^{-2} \text{ sec}^{-1}$$

Table 18. Run 47, Phenol-2,4,6-d in 4.826×10^{-6} M Sodium Iodide Solution at 25.0°

$(I_2)_0$	2.447×10^{-6} M	$(HClO_4)_0$	5.212×10^{-3} M
$[I_2]_0$	2.438×10^{-6} M	$[NaClO_4]$	0.295 M
$(I^-)_0$	4.826×10^{-6} M	$(Phenol-2,4,6-d_3)_0$	128.9×10^{-6} M
$[I^-]_0$	4.817×10^{-6} M	μ	0.30
$[HOI]_0$	0.000×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
4605	0.454	22.9	0.439
7520	.396	32.6	.409
9820	.357	39.2	.394
12790	.316	46.0	.376
16815	.255	56.3	.384
19485	.235	59.6	.363
21760	.206	64.5	.372

$$F_1 = 0.590$$

$$F_2 = 0.25 \times 10^{-6} \text{ sec}^{-1}$$

$$E = 4.148 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 0.439 \text{ l/mole sec}$$

$$k^* = 0.441 \text{ l/mole sec}$$

$$k^*[H^+] = 2.30 \times 10^{-9} \text{ sec}^{-1}$$

Table 19. Run 44, Phenol in 1.206×10^{-6} M Sodium Iodide Solution at 25.0°

$(I_2)_0$	0.6056×10^{-6} M	$(HClO_4)_0$	5.212×10^{-3} M
$[I_2]_0$	0.6050×10^{-6} M	$[NaClO_4]$	0.295 M
$(I^-)_0$	1.206×10^{-6} M	$(Phenol)_0$	19.78×10^{-6} M
$[I^-]_0$	1.205×10^{-6} M	μ	0.30
$[HOI]_0$	0.0000×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
1150	0.123	15.5	7.4
1950	.110	24.2	7.2
2275	.102	29.6	7.8
3410	.091	36.9	6.9
3505	.082	43.1	8.2
4145	.073	49.2	8.3
5625	.060	57.8	7.8

$$F_1 = 0.146$$

$$F_2 = 0.40 \times 10^{-6} \text{ sec}^{-1}$$

$$E = 4.148 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 8.5 \text{ l/mole sec}$$

$$k^* = 8.5 \text{ l/mole sec}$$

$$k^*[H^+] = 4.45 \times 10^{-2} \text{ sec}^{-1}$$

Table 20. Run 45, Phenol-2,4,6-d in 1.206×10^{-6} M Sodium Iodide Solution at 25.0°

$(I_2)_0$	0.6056×10^{-6} M	$(HClO_4)_0$	5.212×10^{-3} M
$[I_2]_0$	0.6050×10^{-6} M	$[NaClO_4]$	0.295 M
$(I^-)_0$	1.206×10^{-6} M	$(Phenol-2,4,6-d_3)_0$	24.02×10^{-6} M
$[I^-]_0$	1.205×10^{-6} M	μ	0.30
$[HOI]_0$	0.0000×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
4915	0.117	18.7	1.75
8150	.108	24.1	1.41
11275	.088	37.2	1.73
11475	.088	37.2	1.70
13745	.083	40.2	1.56
17565	.069	49.1	1.61
20820	.062	53.4	1.54

$$F_1 = 0.146$$

$$F_2 = 0.40 \times 10^{-7} \text{ sec}^{-1}$$

$$E = 4.148 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 1.92 \text{ l/mole sec}$$

$$k^* = 1.92 \text{ l/mole sec}$$

$$k^*[H^+] = 1.00 \times 10^{-2} \text{ sec}^{-1}$$

Table 21. Run 53, Phenol in 0.3145×10^{-6} M Sodium Iodide Solution at 25.0°

$(I_2)_0$	0.6471×10^{-6} M	$(HClO_4)_0$	1.303×10^{-3} M
$[I_2]_0$	0.6457×10^{-6} M	$[NaClO_4]$	0.298 M
$(I^-)_0$	0.3145×10^{-6} M	$(Phenol)_0$	4.889×10^{-6} M
$[I^-]_0$	0.3155×10^{-6} M	μ	0.30
$[HOI]_0$	0.0012×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
780	0.130	16.8	48.8
850	.126	19.3	52.3
1825	.092	38.7	55.9
1840	.095	40.6	60.1
2625	.077	49.9	55.9
3135	.067	56.1	56.0
4720	.047	68.3	52.7

$$F_1 = 0.157$$

$$F_2 = 0.89 \times 10^{-6} \text{ sec}^{-1}$$

$$E = 4.148 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 64.0 \text{ l/mole sec}$$

$$k^* = 64.1 \text{ l/mole sec}$$

$$k^*[H^+] = 8.35 \times 10^{-2} \text{ sec}^{-1}$$

Table 22. Run 54, Phenol in 0.3145×10^{-6} M Sodium Iodide Solution at 25.0°

$(I_2)_0$	0.7010×10^{-6} M	$(HClO_4)_0$	5.212×10^{-3} M
$[I_2]_0$	0.7002×10^{-6} M	$[NaClO_4]$	0.285 M
$(I^-)_0$	0.3145×10^{-6} M	$(Phenol)_0$	14.39×10^{-6} M
$[I^-]_0$	0.3149×10^{-6} M	μ	0.30
$[HOI]_0$	0.0006×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
870	0.132	20.8	18.8
1090	.129	22.2	16.1
1970	.113	30.3	12.8
2630	.094	40.6	13.9
3375	.081	47.3	13.4
4265	.077	48.4	10.9

$$F_1 = 0.170$$

$$F_2 = 3.33 \times 10^{-6} \text{ sec}^{-1}$$

$$E = 4.148 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 15.9 \text{ l/mole sec}$$

$$k^* = 15.9 \text{ l/mole sec}$$

$$k^*[H^+] = 8.29 \times 10^{-2} \text{ sec}^{-1}$$

Table 23. Run 50, Phenol in 0.3145×10^{-6} M Sodium Iodide Solution at 25.0°

$(I_2)_0$	0.5289×10^{-6} M	$(HClO_4)_0$	5.212×10^{-3} M
$[I_2]_0$	0.5282×10^{-6} M	$[NaClO_4]$	0.295 M
$(I^-)_0$	0.3145×10^{-6} M	$(Phenol)_0$	14.30×10^{-6} M
$[I^-]_0$	0.3150×10^{-6} M	μ	0.30
$[HOI]_0$	0.0006×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
980	0.102	19.9	15.9
2160	.074	41.4	17.4
2510	.073	42.1	15.3
2810	.066	47.5	16.2
3040	.063	49.7	16.0
4920	.046	62.5	14.1
6145	.040	66.9	12.8

$$F_1 = 0.128$$

$$F_2 = 0.60 \times 10^{-8} \text{ sec}^{-1}$$

$$E = 4.148 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 17.7 \text{ l/mole sec}$$

$$k^* = 17.7 \text{ l/mole sec}$$

$$k^*[H^+] = 9.23 \times 10^{-2} \text{ sec}^{-1}$$

Table 24. Run 52, Phenol in 0.3415×10^{-6} M Sodium Iodide Solution at 25.0°

$(I_2)_0$	0.6471×10^{-6} M	$(HClO_4)_0$	5.212×10^{-3} M
$[I_2]_0$	0.6462×10^{-6} M	$[NaClO_4]$	0.298 M
$(I^-)_0$	0.3145×10^{-6} M	$(Phenol)_0$	4.889×10^{-6} M
$[I^-]_0$	0.3148×10^{-6} M	μ	0.30
$[HOI]_0$	0.0005×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
3755 ^a	0.119	22.3	14.0
4605	.109	28.3	15.1
5805	.104	31.0	13.4
8155	.098	33.7	10.6
12885	.063	54.6	13.0

$$F_1 = 0.157$$

$$F_2 = 0.89 \times 10^{-6} \text{ sec}^{-1}$$

$$E = 4.148 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 15.1 \text{ l/mole sec}$$

$$k^* = 15.1 \text{ l/mole sec}$$

$$k^*[H^+] = 7.87 \times 10^{-2} \text{ sec}^{-1}$$

^aA point taken at 1745 seconds, corresponding to only eight per-cent reaction, was disregarded as unreliable.

Table 25. Run 55, Phenol in 0.3145×10^{-6} M Sodium Iodide Solution at 25.0°

$(I_2)_0$	0.7010×10^{-6} M	$(HClO_4)_0$	1.740×10^{-2} M
$[I_2]_0$	0.7008×10^{-6} M	$[NaClO_4]$	0.285 M
$(I^-)_0$	0.3145×10^{-6} M	$(Phenol)_0$	14.39×10^{-6} M
$[I^-]_0$	0.3143×10^{-6} M	μ	0.30
$[HOI]_0$	0.0000×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
3695	0.128	23.7	5.12
6365	.110	33.7	4.52
6390	.116	30.1	3.92
8210	.098	40.3	4.42
11910	.085	47.2	3.77
14085	.078	50.9	3.55
17305	.069	55.5	3.30

$$F_1 = 0.170$$

$$F_2 = 0.529 \times 10^{-6} \text{ sec}^{-1}$$

$$E = 4.148 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 4.70 \text{ l/mole sec}$$

$$k^* = 4.70 \text{ l/mole sec}$$

$$k^*[H^+] = 8.18 \times 10^{-2} \text{ sec}^{-1}$$

Table 26. Run 51, Phenol-2,4,6-d in 0.3145×10^{-6} M Sodium Iodide Solution at 25.0°

$(I_2)_0$	0.5289×10^{-6} M	$(HClO_4)_0$	5.212×10^{-3} M
$[I_2]_0$	0.5282×10^{-6} M	$[NaClO_4]$	0.295 M
$(I^-)_0$	0.3145×10^{-6} M	$(Phenol-2,4,6-d_3)_0$	13.67×10^{-6} M
$[I^-]_0$	0.3150×10^{-6} M	μ	0.30
$[HOI]_0$	0.0006×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
2350	0.109	13.8	4.64
3575	.099	21.2	4.87
5760	.086	30.5	4.66
7150	.079	35.5	4.53
9275	.070	41.9	4.32
12795	.060	48.6	3.84
15730	.051	54.8	3.74

$$F_1 = 0.128$$

$$F_2 = 0.60 \times 10^{-6} \text{ sec}^{-1}$$

$$E = 4.148 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 5.23 \text{ l/mole sec}$$

$$k^* = 5.23 \text{ l/mole sec}$$

$$k^*[H^+] = 2.73 \times 10^{-2} \text{ sec}^{-1}$$

Table 27. Data on the Iodination of Phenol at Temperature, 25.0°; μ , 0.30

Table Ref.	$[I_2]_0$ $\times 10^2$ (mole/l)	$[I^-]_0$ $\times 10^2$ (mole/l)	$[H^+]$ $\times 10^3$ (mole/l)	$(ArOH)_0$ $\times 10^2$ (mole/l)	k_{app} (l/mole sec)	k^* (l/mole sec)	$k^*[H^+]$ $\times 10^2$ (sec ⁻¹)	$k^*[H^+][I^-]$ $\times 10^8$ (mole/l sec)	$1/k^*[H^+]$ (sec)
11	5.04	27.2	5.212	222	0.492	0.502	0.262	7.12	382
13	3.90	14.9	1.303	63.3	3.60	3.64	0.474	7.05	211
14	3.75	14.8	5.212	212	0.920	0.930	0.485	7.16	206
15	3.90	14.9	17.40	63.3	0.278	0.281	0.489	7.28	206
17	2.44	4.82	5.212	112	2.63	2.64	1.38	6.65	72.5
19	0.605	1.21	5.212	19.8	8.52	8.53	4.45	5.36	22.4
21	.646	0.315	1.303	4.89	56.5	56.6	7.37	2.32	13.6
22	.701	.315	5.212	14.4	15.9	15.9	8.29	2.61	12.1
23	.528	.315	5.212	14.3	17.7	17.7	9.23	2.91	10.8
24	.647	.315	5.212	4.89	15.1	15.1	7.87	2.48	12.7
25	.701	.315	17.40	14.4	5.25	5.25	9.14	2.88	10.9

Table 28. Data on the Iodination of Phenol-2,4,6-d at Temperature 25.0°; μ , 0.30

Table Ref.	$[I_2]_0$ $\times 10^5$ (mole/l)	$[I^-]_0$ $\times 10^5$ (mole/l)	$[H^+]$ $\times 10^3$ (mole/l)	$(ArOH)_0$ $\times 10^5$ (mole/l)	k_{app} (l/mole sec)	k^* (l/mole sec)	$k^*[H^+]$ $\times 10^3$ (sec ⁻¹)	$k^*[H^+][I^-]$ $\times 10^8$ (mole/l sec)	$1/k^*[H^+]$ (sec)
12	5.04	27.2	5.212	207	0.082	0.084	0.0436	1.19	2290
16	3.75	14.8	5.212	255	0.148	0.150	0.0782	1.15	1280
18	2.44	4.82	5.212	129	0.439	0.441	0.230	1.11	435
20	0.605	1.21	5.212	24.0	1.92	1.917	1.00	1.21	100
26	0.528	0.315	5.212	13.7	5.23	5.23	2.73	0.85	36.6

Table 29. Values of $1/k^*[H^+]$ for Iodination of Phenol from Work of Aprahamian⁽⁸⁶⁾ and Kilby,⁽⁸⁷⁾ Calculated by Two Different Methods of Extrapolation of k_{app} ; Temperature, 25.0°; μ , 0.30; $[H^+]$, 0.0174 M

Reference ^a	$[I^-] \times 10^8$ (mole/l)	Compound	$1/k^*[H^+]^b$ (sec)	$1/k^*[H^+]^c$ (sec)	$1/k^*[H^+]^d$ (sec)
87, 95	403	protio	5130	5438	5500
87, 94	399	protio	4950	5297	5448
86, 177	380	protio	4690	5040	5176
86, 178	46	protio	541	594	634
86, 183	387	deutero	31200	31400	33290
86, 184	387	deutero	30900	33063	33290
86, 185	46	deutero	3510	4000	3956

^aThe first number refers to the literature reference, the second number to the page number in that reference.

^bBy extrapolation method of Kilby and Aprahamian.

^cBy extrapolation method of this thesis.

^dValue obtained from extrapolation of Figure 3 in this thesis.

Table 30. Isotope Effects in the Iodination of Phenol at
 Temperature, 25.0°; μ , 0.30; $[H^+]$, 5.212×10^{-3} M

Table Ref.	$[I^-] \times 10^6$ (mole/l)	$k_H^*[H^+] \times 10^2$ (sec ⁻¹)	$k_D^*[H^+] \times 10^2$ (sec ⁻¹)	$\frac{k_H^*[H^+]}{k_D^*[H^+]}$
11, 12	27.2	0.262	0.0436	6.01
14, 16, 13, 15	14.8	0.483 ^a	0.0782	6.18
17, 18	4.82	1.38	0.230	6.00
19, 20	1.21	4.45	1.00	4.45
23, 26, 24, 21, 22, 25	0.315	8.38 ^b	2.73	3.07

^aAverage of three experimental values.

^bAverage of five experimental values.

CHAPTER V

IODINATION OF 2,4-DINITROPHENOL

Introduction

A. Fort studied the iodination of 2,4-dinitrophenoxide anion as a function of iodide ion concentration.⁽⁹⁵⁾ The conditions were temperature, 50.0°; $[H^+]$, $70 \times 10^{-8} \text{ M}^\dagger$; and μ , 0.30. The iodide range was $8460 \times 10^{-6} \text{ M}$ to $98.1 \times 10^{-6} \text{ M}$ and iodine concentrations were measured by thiosulfate titration. The rate constants were calculated in terms of the phenoxide anion and are designated in this thesis by k^∇ ; i.e., $\text{rate} = k^\nabla [I_2][ArO^-]$.

A nonlinear inverse dependence of rate constant upon iodide ion concentration was found, together with a decrease in $k^\nabla [I^-]$ with decreasing iodide ion concentration. In addition, the isotope effect decreased from about 4.0 to about 2.8 over the iodide ion concentration range studied.

These data suggest that neither H_2OI^+ nor I_2 is the sole iodinating agent over the entire iodide range. However, the measured isotope

[†]This is obtained from Fort's data in light of the dissociation constant of 2,4-dinitrophenol at 50.0° in terms of concentrations, at ionic strength 0.30. The determination of this dissociation constant is described in this chapter.

95. A. Fort, laboratory notes, 1962-1963, Georgia Institute of Technology; work done in Dr. Grovenstein's laboratories.

effect change was fairly small, as well as somewhat erratic, and a $1/k^{\nabla}$ versus $[I^-]$ plot of Fort's data left some doubt as to the best curves to fit the data (Figures 7 and 8). It appears possible that at low iodide ion concentrations, the curve is bending toward the origin.

In one protio experiment, at 2940×10^{-6} M iodide, Fort worked at 194×10^{-6} M $[H^+]$ and at a phenoxide concentration of about one-third of that employed in most of the experiments. This point fit the $1/k^{\nabla}$ versus $[I^-]$ curve within experimental error and affords probable evidence that the reaction is first order in phenoxide anion and, at this iodide ion concentration, independent of pH.

Extension of the 2,4-dinitrophenol work to lower iodide ion concentrations was undertaken to obtain a more clear-cut mechanistic interpretation of the reaction.

Specific Experimental Details

Data were collected at ionic strengths of 0.0030 and 0.30 and at various acidities. The data at 0.30 μ were obtained after the data at 0.0030 μ indicated mechanistic complexities that prevented their direct quantitative comparison with Fort's results (obtained at 0.30 μ). Most of the work at 0.30 μ was done at 70×10^{-6} M hydrogen ion, the acidity employed by Fort, but experiments were performed at other acidities as well.

A serious problem in the 2,4-dinitrophenol work, which was minor and easily corrected in the case of phenol, was the background absorbance of the aromatic compound at any wavelength at which triiodide could be spectrophotometrically measured. The two triiodide absorption maxima

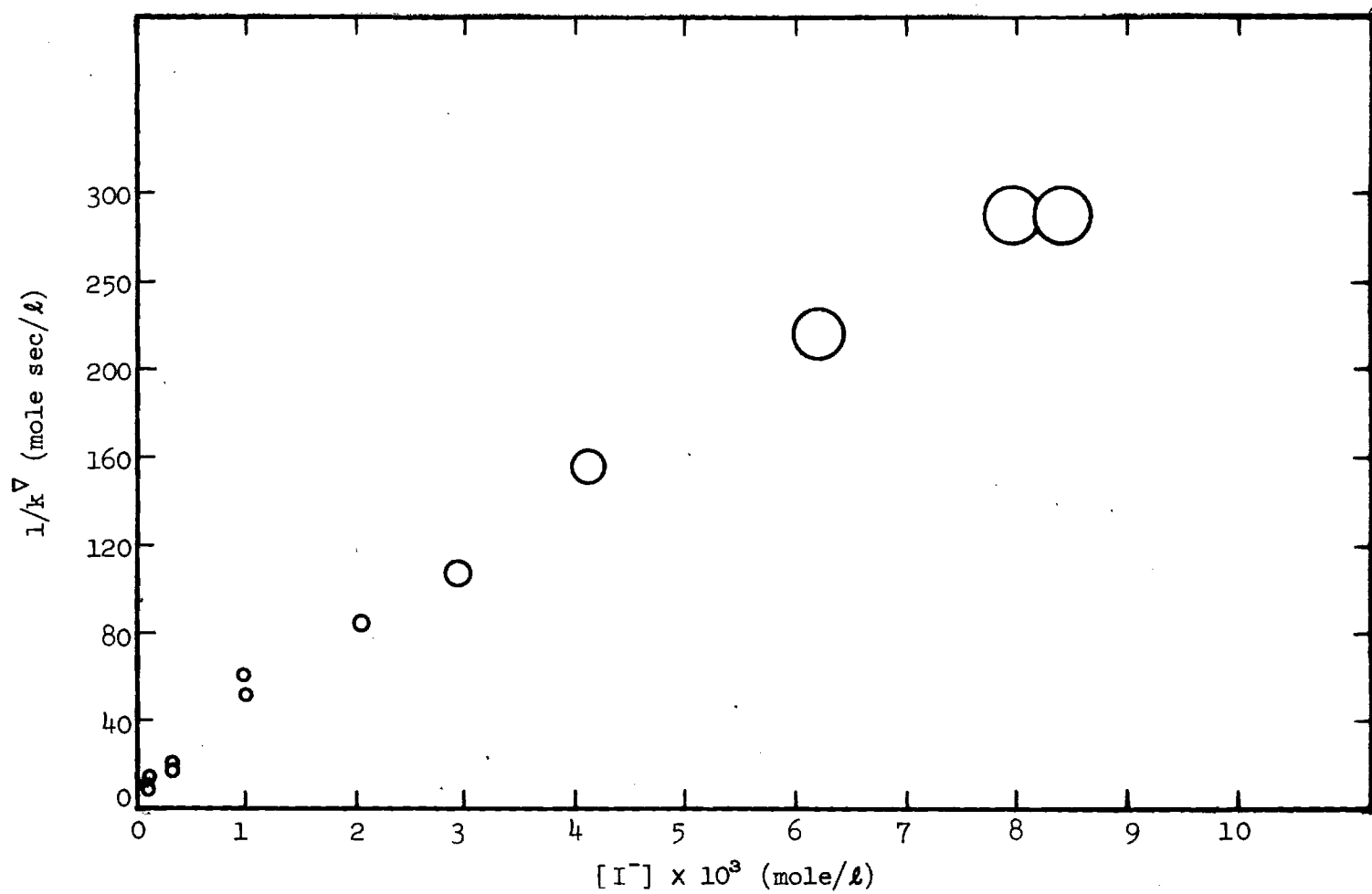


Figure 7. 2,4-Dinitrophenol at Temperature, 50.0°; Ionic Strength, 0.30; $[H^+]$, 70×10^{-6} M; Data of A. Fort

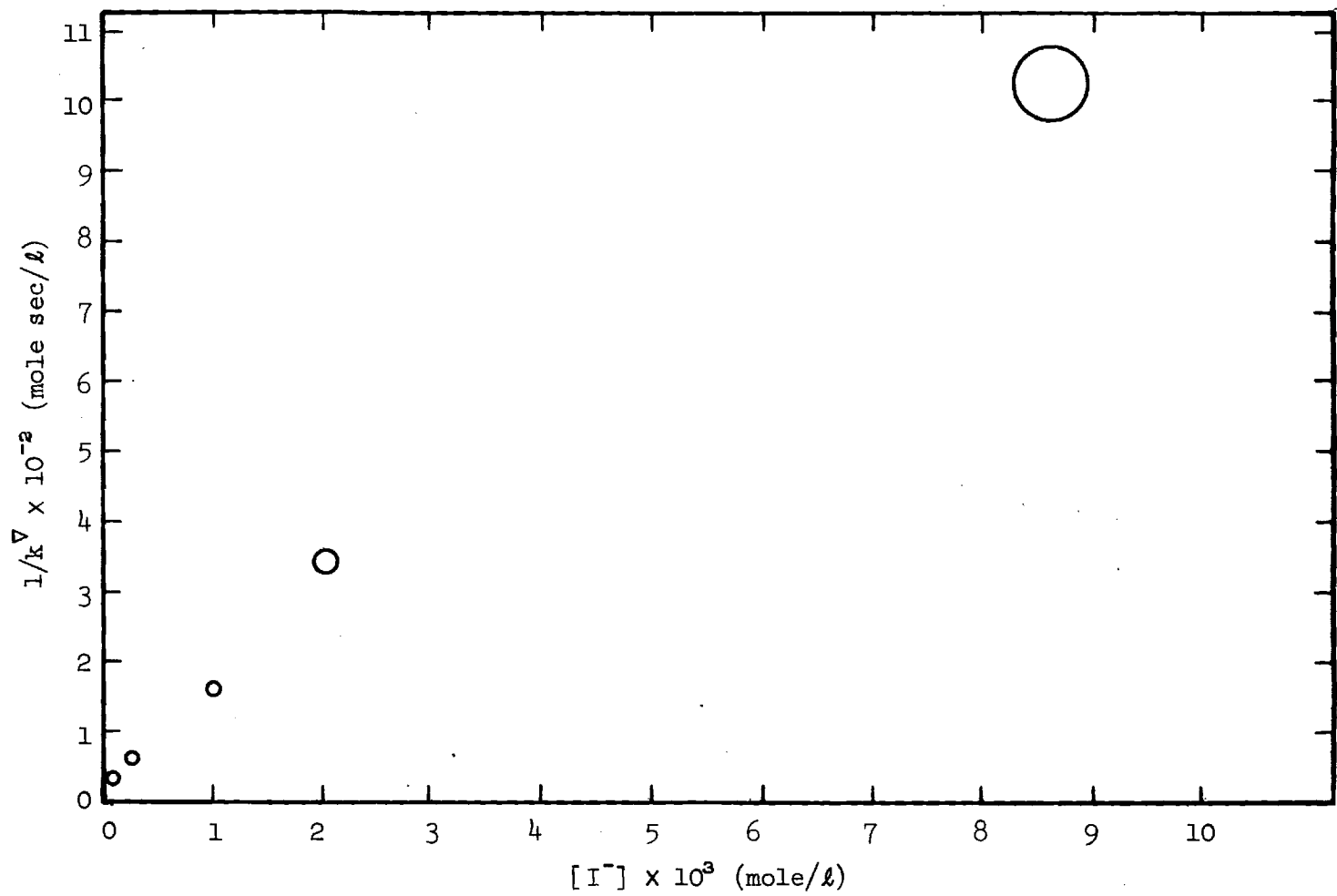


Figure 8. 2,4-Dinitrophenol-6-d at Temperature, 50.0°; Ionic Strength, 0.30; $[H^+]$, 70×10^{-6} M; Data of A. Fort

were found to occur at 3530 Å and 2875 Å. The extinction coefficients corresponding to these wavelengths are 26,400 and 40,000, ^(82,83) as discussed in Chapter III. Absorption data on 2,4-dinitrophenol and 2,4-dinitrophenoxide anion were obtained by measuring spectra of 2,4-dinitrophenol dissolved in 0.098 M HClO₄ and in 0.0098 M NaOH, respectively, these conditions having been calculated from the acidity constant of 2,4-dinitrophenol ⁽⁹⁶⁾ to give 100 percent of the unionized or ionized phenol, respectively. Measurements of absorption under the same conditions were made for 2-iodo-4,6-dinitrophenol and 2-iodo-4,6-dinitrophenoxide anion. Because of the rapid oxidation of iodide to iodine at lower pH values, ⁽⁸⁰⁾ it was necessary that the pH of the quenched solutions be such that most of the 2,4-dinitrophenol would be in the phenoxide form. The extinction coefficient of the phenoxide at 3530 Å was found to be 13,800, which was too high to permit the triiodide concentration to be measured at 3530 Å at the concentrations of the phenol and iodine required to afford reasonable reaction rates. At 2875 Å, the extinction coefficients for the various species were 9003 for 2,4-dinitrophenol, 2737 for 2,4-dinitrophenoxide, 10,474 for 2-iodo-4,6-dinitrophenol, and 5233 for 2-iodo-4,6-dinitrophenoxide. On the basis of these figures, iodine concentration was followed by measurement of the intense triiodide absorbance at 2875 Å.

It was experimentally determined that a buffer consisting of 1250×10^{-6} M H₂CO₃ and 1250×10^{-6} M HCO₃⁻ yielded reproducible effec-

⁹⁶. R. G. Bates and G. Schwarzenbach, Helv. Chim. Acta, 37, 1069 (1954).

tive extinction coefficients for the phenol-phenoxide pair for both 2,4-dinitrophenol and 2-iodo-4,6-dinitrophenol under the conditions of the quenched solution. (Slight variations were found between experiments and seemed to be related to the ionic strength of the quenched solution. For each experiment, the pertinent value was determined and used.) Further, no change in triiodide absorbance occurred over the time period required between quenching and spectral measurement. The buffer composition was achieved by adding enough sodium bicarbonate in 1.0 ml of solution to yield 2500×10^{-6} M in the 50.0 ml of quenched solution and then enough perchloric acid in 1.0 ml of solution so that the total hydrogen ion concentration from it and from the 2,4-dinitrophenol in solution would equal 1250×10^{-6} M in the quenched solution.

Experiments showed that variations in delivered amounts of sodium bicarbonate and perchloric acid solutions, exceeding the variations reasonably expected in the reaction experiments, had no measurable effect upon effective extinction coefficients. Further, since the instrument slit width showed some variation from day to day, experiments were performed which showed that variations in slit width in excess of those ordinarily encountered had no measurable effect upon effective extinction coefficients.

The observed absorbance measurements had to be translated into rate constant data, taking into account changes in concentrations of all of the absorbing species. The usual second order expression was used

$$k_{\text{app}} = \frac{2.303}{t\{(\text{ArOH})_0 - (\text{I}_2)_0\}} \log \frac{(\text{I}_2)_0 \{(\text{ArOH})_0 - x\}}{(\text{ArOH})_0 \{(\text{I}_2)_0 - x\}} \quad (1)$$

as described in Chapter III. At constant hydrogen ion concentration, this implies first order kinetics in stoichiometric concentration of the phenol, a result which is consistent with Fort's data, and first order in stoichiometric iodine, a result which is consistent with the observed behavior of the k_{app} values at various percentages of iodine consumption, provided that the iodide ion concentration is approximately constant.

An expression for \underline{x} was obtained by utilizing the following relationships.

$$\text{Abs (ArOH)} = P_1 \{(\text{ArOH})_0 - x\} \quad (2)$$

$$\text{Abs (IArOH)} = P_2 \{x\} \quad (3)$$

$$\text{Abs (I}_2) = P_3 \{(\text{I}_2)_0 - x\} \quad (4)$$

where Abs (ArOH), Abs (IArOH), and Abs (I₂) are the absorbance contributions from the stoichiometric concentrations of 2,4-dinitrophenol, 2-iodo-4,6-dinitrophenol, and iodine (which contributes absorbance through its conversion to triiodide) in the quenched solution, \underline{P}_1 and \underline{P}_2 are the effective extinction coefficients in the quenched solution for 2,4-dinitrophenol and 2-iodo-4,6-dinitrophenol, respectively; \underline{P}_3 is equal to $1/E$ (cf. Chapter III, equation (1)); and $(\text{ArOH})_0$ and $(\text{I}_2)_0$ are the initial stoichiometric concentrations of 2,4-dinitrophenol and iodine, respectively. The extinction coefficients \underline{P}_1 , \underline{P}_2 , and \underline{P}_3 were corrected for the volume change from reaction to quenched solution as follows.

$$P = \frac{\text{vol reaction solution}}{\text{vol quenched solution}} \cdot \epsilon \quad \dagger \quad (5)$$

[†]As noted earlier, slight variations occur in \underline{P}_1 and \underline{P}_2 between experiments; these differences seem to reflect differences in ionic strength (in the high concentration runs, quenched solutions (continued))

Now

$$\text{Abs}_{(\text{total})} = P_1(\text{ArOH})_0 - P_1x + P_3(\text{I}_2)_0 - P_3x + P_2x \quad (6)$$

and

$$x = \frac{P_1(\text{ArOH})_0 + P_3(\text{I}_2)_0 - \text{Abs}_{(\text{total})}}{P_1 + P_3 - P_2} \quad (7)$$

This is the x used in the second order rate equation (1).

The iodine concentrations and blank drops, as well as volatilization losses, were determined in the usual manner. The initial 2,4-dinitrophenol concentrations were determined spectrally--either as phenoxide in .0030 M NaOH at 3600 Å, for which the extinction coefficient was determined to be 14,329; or by the absorbance at 2875 Å in quenched solution minus iodine and iodide, using the effective extinction coefficient. As usual, background absorbance due to the quenched solution without iodine and 2,4-dinitrophenol was determined and subtracted from the observed absorbance.

The method of quenching was to cool the reaction solution or blank in an ice bath to about room temperature, then add by pipette in rapid succession 1.0 ml of the NaHCO₃ solution; 1.0 ml of the HClO₄ solution, and 1.0 ml of the sodium iodide solution, containing 0.38 g of sodium iodide. Experiments showed that when sample solutions were quenched at such an early time that essentially zero percent reaction should have occurred, the absorbance equalled that of a quenched blank plus the ab-

had to be diluted), and also small variations in the ratio of volume of reaction solution to volume of quenched solution.

sorbance due to the 2,4-dinitrophenol; therefore, no reaction between the aromatic and iodine was induced by the quenching procedure. In some of the higher concentration experiments, the absorbance of the quenched solutions was too great for spectral measurement. In such cases, an aliquot of the quenched solution was pipetted into a volume of a solution the composition of which was such that the final H_2CO_3 and HCO_3^- concentrations of the diluted quenched solutions were the same ($1250 \times 10^{-6} \text{ M}$) as in the undiluted quenched solutions, although the ionic strength was lower by the dilution factor. Additional sodium iodide solution was added to the diluted quenched solution, and the E and P_a factors calculated on the basis of the iodide ion concentration of this solution.

The $k_{\text{app}0}$ values were converted to k^* in the same way as for phenol. Then, since all of the reaction was considered to proceed via the phenoxide anion, $^\dagger k^*$ was converted to a rate constant in terms of this moiety, called k^∇ .

$$k^\nabla = k^* \frac{(\text{ArOH})_0}{[\text{ArO}^-]_0} = k^* \frac{[\text{H}^+]}{K_a} \quad (8)$$

The concentration dissociation constant for 2,4-dinitrophenol was necessary in order to make this calculation. It was also necessary for another reason. In order to achieve reasonably fast reactions, it was necessary to set reaction acidity low enough that a large percentage of

[†]Justification for this will be considered later in this chapter.

2,4-dinitrophenol would be dissociated. This requirement, plus the concentrations of aromatic compound desired, meant that the 2,4-dinitrophenol itself would play a role in determining pH. Therefore, the dissociation constant had to be determined under the conditions of reaction, so that the correct amount of 2,4-dinitrophenol and of 2,4-dinitrophenoxide could be added to the reaction solutions to adjust the pH to the desired value. (In some experiments, this required the addition of sodium hydroxide to the 2,4-dinitrophenol stock solution.)

The dissociation constant in terms of concentrations was measured at the experimental ionic strengths of 0.30 and 0.0030. A solution of 2,4-dinitrophenol was acidified with perchloric acid to a pH of approximately four, so that roughly equal concentrations of the phenol and phenoxide would exist. The actual concentrations of phenol and phenoxide were determined spectrophotometrically at 3600 \AA in a cell equilibrated in the Cary at 50.0° , using independently measured extinction coefficients for both species, according to the equation

$$\text{Abs} = l [\epsilon_1 x + \epsilon_2 (c - x)] \quad (9)$$

where

l = path

c = stoichiometric concentration of ArOH

x = concentration of ArO^- generated

ϵ_1 = extinction coefficient of ArO^-

ϵ_2 = extinction coefficient of ArOH

The concentrations of 2,4-dinitrophenol and of the phenoxide were then substituted into the equation

$$\frac{[\text{ArO}^-]}{[\text{ArOH}]} \{(\text{H}^+)_0 + [\text{ArO}^-]\} = K_a \quad (10)$$

where $[\text{ArO}^-]$ and $[\text{ArOH}]$ are the spectrally determined concentrations from equation (9) and $(\text{H}^+)_0$ is the concentration of HClO_4 put into the solution.

Knowledge of the K_a and of the stoichiometric concentration of 2,4-dinitrophenol permitted calculation of the concentration of NaOH and/or HClO_4 to be added to a given set of reaction solutions in order to obtain the desired pH. These calculations were made according to the equation

$$\frac{\{(\text{ArO}^-)_0 + x\}\{(\text{H}^+)_0 + x\}}{\{(\text{ArOH})_0 - x\}} = K_a \quad (11)$$

where the subscript zero indicates initially introduced concentrations. The blank solutions, which contained no aromatic compound, were brought to the same acidity by the introduction of HClO_4 . A sample calculation is given in Appendix I.

The K_a values determined in this way were 1.22×10^{-4} at 0.0030μ and 1.94×10^{-4} at 0.30μ . These values compare with a thermodynamic dissociation constant of 7.8×10^{-5} at 25° measured by Bates and Schwarzenbach.⁽⁹⁶⁾ In making the presently reported measurements at 50.0° , it was noted that K_a increased with temperature, and it appeared (no accurate determination was made at 25.0°) to be about 1.6×10^{-4} at 25° and 0.30μ . Division by the square of the activity coefficient in sodium perchlorate at 0.30μ ($\mu = 0.70$ ⁽⁹¹⁾) gives 8×10^{-5} , which is

very close to the reported value.

Extrapolations of k_{app} data back to zero percent reaction were performed using the principle described in Chapter III, except that in the 2,4-dinitrophenol experiments n was approximately unity at all iodide concentrations and was considered as such. In addition, a complication existed in the high iodide 2,4-dinitrophenol experiments (which also contained higher concentrations of aromatic and iodine) in that sufficient HI was produced to affect the pH of the solution after some reaction had occurred. This increased the $\frac{(\text{ArOH})}{[\text{ArO}^-]}$ factor by which k^* had to be multiplied to give k^∇ . This correction was made in the following way.

Initial true concentrations of 2,4-dinitrophenol, 2,4-dinitrophenoxide, and hydrogen ion are represented by $[\text{ArOH}]_0$, $[\text{ArO}^-]_0$, and $[\text{H}^+]_0$, respectively. The initial stoichiometric concentration of iodine is $(\text{I}_2)_0$. After consumption of 50 percent of the iodine, an amount of $[\text{ArO}^-]$ equivalent to $(\text{I}_2)_0/2$ has been consumed and the same quantity of $[\text{H}^+]$ has been produced.[†] Concentrations at 50 percent reaction can be obtained from

$$\frac{([\text{ArO}^-]_0 - (\text{I}_2)_0/2 - x)([\text{H}^+]_0 + (\text{I}_2)_0/2 - x)}{([\text{ArOH}]_0 + x)} = K_a \quad (12)$$

[†]The assumption is made here that 2-iodo-4,6-dinitrophenol is completely dissociated. This certainly appears reasonable, since the 2,4-dinitrophenol is largely dissociated, and the iodo-derivative is undoubtedly more acidic. Also, cf. Chapter VI for comparison of acidities of p-nitrophenol and 2-iodo-4-nitrophenol.

where x is the amount of $[\text{ArO}^-]$ lost by protonation.

This gives a value of $\frac{(\text{ArOH})}{[\text{ArO}^-]}$ at 50 percent reaction. The average value of this ratio from zero to 50 percent reaction is

$$\frac{\left\{ \frac{(\text{ArOH})}{[\text{ArOH}]} \right\}_{0\%} + \left\{ \frac{(\text{ArOH})}{[\text{ArOH}]} \right\}_{50\%}}{2}$$

The factor

$$A = 1 + \frac{\left\{ \frac{(\text{ArOH})}{[\text{ArOH}]} \right\}_{0\%} + \left\{ \frac{(\text{ArOH})}{[\text{ArOH}]} \right\}_{50\%}}{2} - \left\{ \frac{(\text{ArOH})}{[\text{ArOH}]} \right\}_{0\%} \quad (13)$$

was used to multiply k_{app} at 50 percent reaction. The equation for extrapolation of $k_{\text{app}t}$ to $k_{\text{app}o}$ (equation (18), Chapter III) was therefore enlarged to

$$k_{\text{app}o} = k_{\text{app}t} \times \frac{\left\{ [I^-]_o + \frac{x}{2} \right\}^n}{[I^-]_o^n} \times A \quad (14)$$

Calculations of standard deviations are made as described in the text. The propagation of standard deviations in computed results is calculated according to the standard procedure. (97)

Results and Discussion

The first series of experiments was run at ionic strength of 0.0030. The iodide ion concentration range was from the lower iodide

97. cf., for example, H. A. Laitinen, Chemical Analysis, McGraw-Hill Company, Inc., New York, 1960, p. 545.

region of Fort's work ($108 \times 10^{-6} \text{ M}$) to $0.30 \times 10^{-6} \text{ M}$. The acidity was $30 \times 10^{-6} \text{ M} [\text{H}^+]$, except for one protio run at $3.88 \times 10^{-6} \text{ M} [\text{H}^+]$ and one at $302 \times 10^{-6} \text{ M} [\text{H}^+]$.

The data are compiled in Tables 68, 69, and 70, and for $30 \times 10^{-6} \text{ M} [\text{H}^+]$, $1/k^{\nabla}$ is plotted against $[\text{I}^-]$ in Figures 9 and 10. (Figure 10 is an enlargement of the low iodide portion of Figure 9.) The curves can be interpreted as a straight line through the origin, with the highest iodide points curving off the line. Since subsequent data on 2,4-dinitrophenol made it clear that this line did indeed pass through the origin, it was desirable to obtain the best such straight line, as well as an estimate of the error range. This was accomplished in the following manner.

For each point thought to lie on the straight line, a line was drawn between it and the origin, and the slope of this line was calculated. This was done for five points for 2,4-dinitrophenol and four points for 2,4-dinitrophenol-6-d in the series of experiments at $30 \times 10^{-6} \text{ M} [\text{H}^+]$ and 0.0030μ . These slopes were then averaged, and standard deviations

$$S = \sqrt{\frac{\sum_i (x_i - \bar{x})^2}{n - 1}}$$

where

$x_i = i^{\text{th}}$ measurement

$\bar{x} =$ average of i measurements

$n =$ number of measurements

were obtained, for 2,4-dinitrophenol and 2,4-dinitrophenol-6-d. The slopes obtained in this way are $1.24 \pm 0.14 \times 10^5 \text{ sec}$ and 2.98 ± 0.40

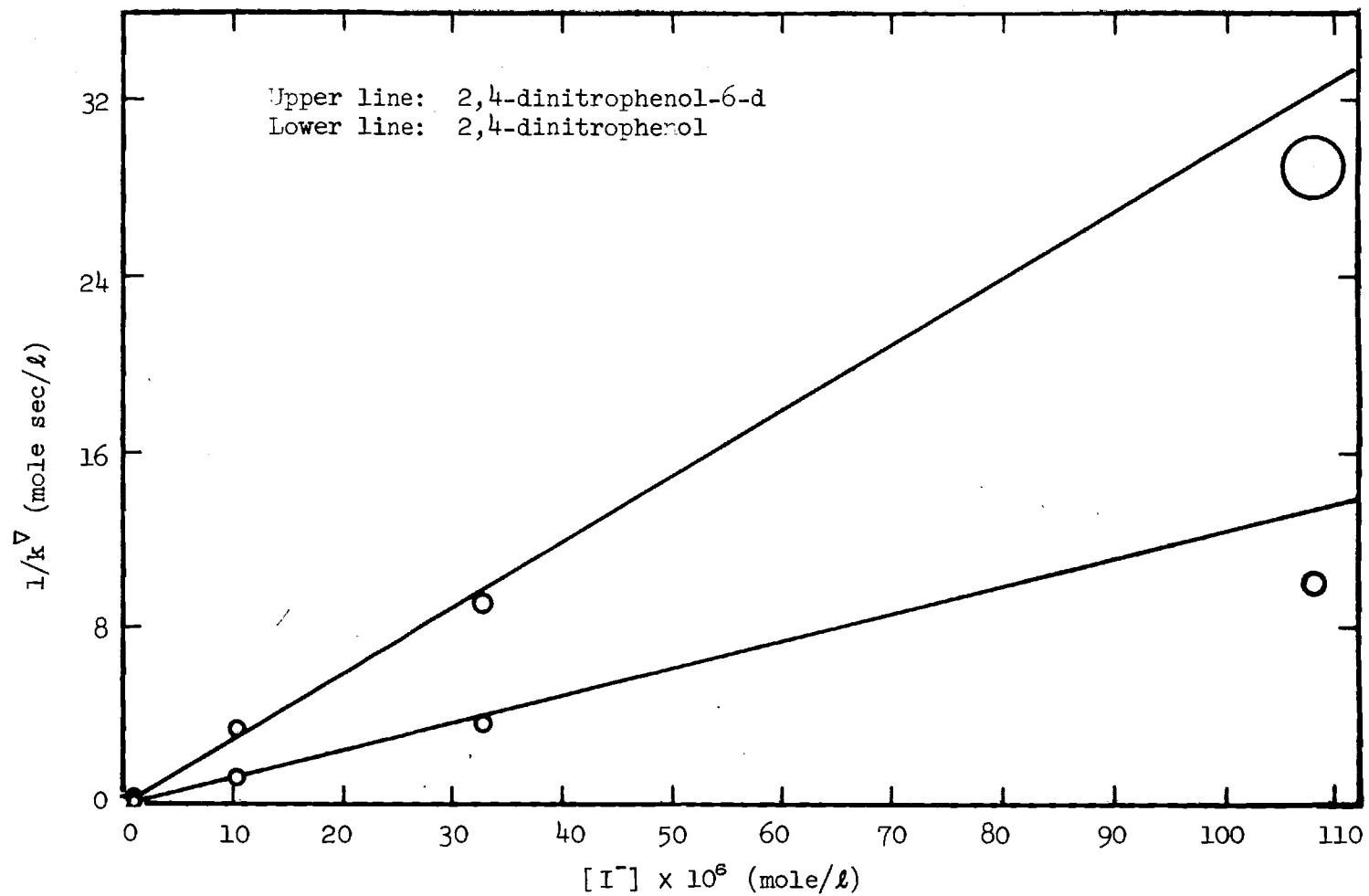


Figure 9. 2,4-Dinitrophenol and 2,4-Dinitrophenol-6-d at Temperature, 50.0°; Ionic Strength, 0.0030; [H⁺], 30 × 10⁻⁶ M

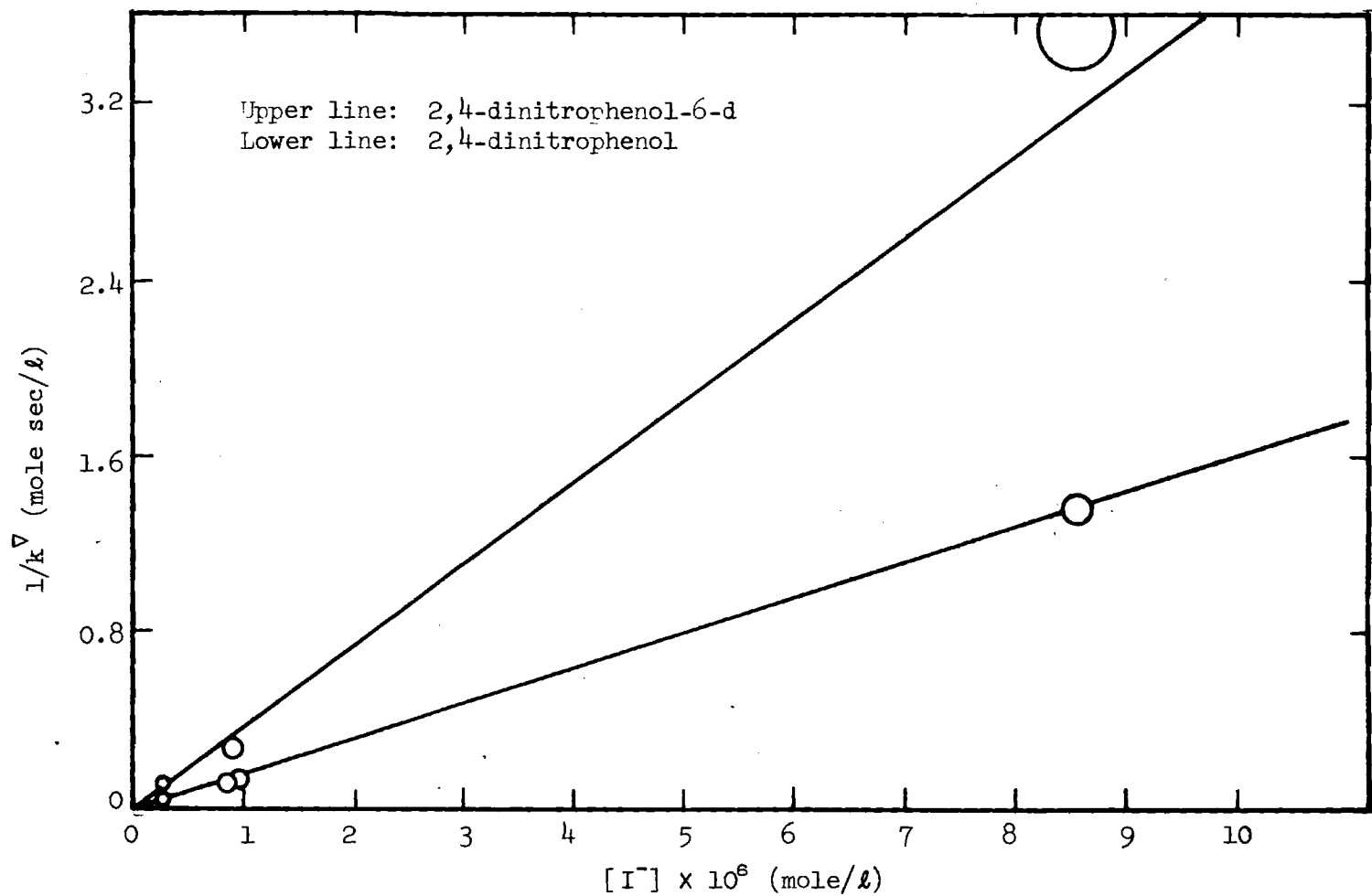


Figure 10. 2,4-Dinitrophenol and 2,4-Dinitrophenol-6-d at Temperature, 50.0°; Ionic Strength, 0.0030; [H⁺], 30 × 10⁻⁶ M

$\times 10^5$ sec for the protio and deutero compounds, respectively. These and all other slope and intercept data are tabulated in Table 71. The straight lines are reflected in the reasonably constant values of $k^{\nabla}[\text{I}^-]$ (Tables 68 and 69) and of the isotope effect (Table 70).

Considered in light of Fort's data at higher iodide ion concentrations, this is qualitatively consistent with mechanism III, Chapter IV; i.e., both I_2 and H_2OI^+ are significant iodinating agents over the range of iodide ion concentrations studied. However, because the data reported here are at much different ionic strength than those of Fort, quantitative interpretation is not yet possible.

Experiments no. 36 and 37 (Tables 42 and 43) suggest that $k^{\nabla}[\text{I}^-]$ is inversely dependent upon $[\text{H}^+]$ in the low-iodide straight line region, although at the time of the 0.0030μ experiments this was considered tentative because of the large experimental scatter in experiments no. 36 and 37. A possible interpretation of such a phenomenon is that another iodinating agent, with the same iodide dependence, but with an inverse hydrogen-ion dependence, is operating to a significant degree; in this connection the possibility of HOI as an iodinating agent will be considered after presentation of the 0.30μ data.

Experiments were run at 0.30μ , the ionic strength employed by Fort. The acidities were $70 \times 10^{-6} \text{ M } [\text{H}^+]$ (the same as Fort's work), $1.80 \times 10^{-6} \text{ M } [\text{H}^+]$,[†] and approximately $200 \times 10^{-6} \text{ M } [\text{H}^+]$. Data are

[†]These low-acidity solutions contained some $\text{H}_2\text{PO}_4^- - \text{HPO}_4^{=}$ buffer, which was used, at higher concentrations to catalyze the iodination of 2,4-dinitrophenol and 2,4-dinitrophenol-6-d, in experiments which will be described in Chapter VIII. As described in that chapter, the k^{∇} values were corrected to zero catalyst concentration and $1.70 \times 10^{-6} \text{ M } [\text{H}^+]$. The corrected values are the ones given in Tables 44-47, 72, and 73.

tabulated in Tables 72, 73, and 74. Low-iodide straight lines were calculated in the same way as described for the experiments at 0.0030 μ . (No standard deviations could be calculated for the experiments at approximately $200 \times 10^{-6} \text{ M } [\text{H}^+]$, since there was only one protio and one deuterio point.) The results are shown graphically in Figures 11, 12, and 14. (Figure 13 is an enlargement of the low-iodide portion of Figures 11 and 12.) The slopes at low-iodide ion concentration are compiled in Table 71. The low-iodide straight lines are reflected in the reasonably constant $k^{\nabla}[\text{I}^-]$ values and isotope effects (Tables 72, 73, and 74). It was found that straight lines could be drawn through the high-iodide points in the $70 \times 10^{-6} \text{ M } [\text{H}^+]$ work, a result which was expected in light of Fort's data. The protio line, shown in Figure 11, results from a least squares treatment, giving an intercept of 10 mole sec/ ℓ^{\dagger} and a slope of $4.15 \pm 0.01 \times 10^4 \text{ sec.}$ (99)

[†]It is not possible to calculate a simple standard deviation for the intercept of a line except in certain special cases.⁽⁹⁸⁾ Therefore, no such value is given for this intercept, nor for any later term which contains it.

98. cf., for example, H. A. Laitinen, Chemical Analysis, McGraw-Hill Company, Inc., New York, 1960, p. 567.

99. The standard deviation of the slope is calculated according to C. A. Bennett and N. L. Franklin, Statistical Analysis in Chemistry and the Chemical Industry, John Wiley and Sons, Inc., New York, 1954, p. 228.

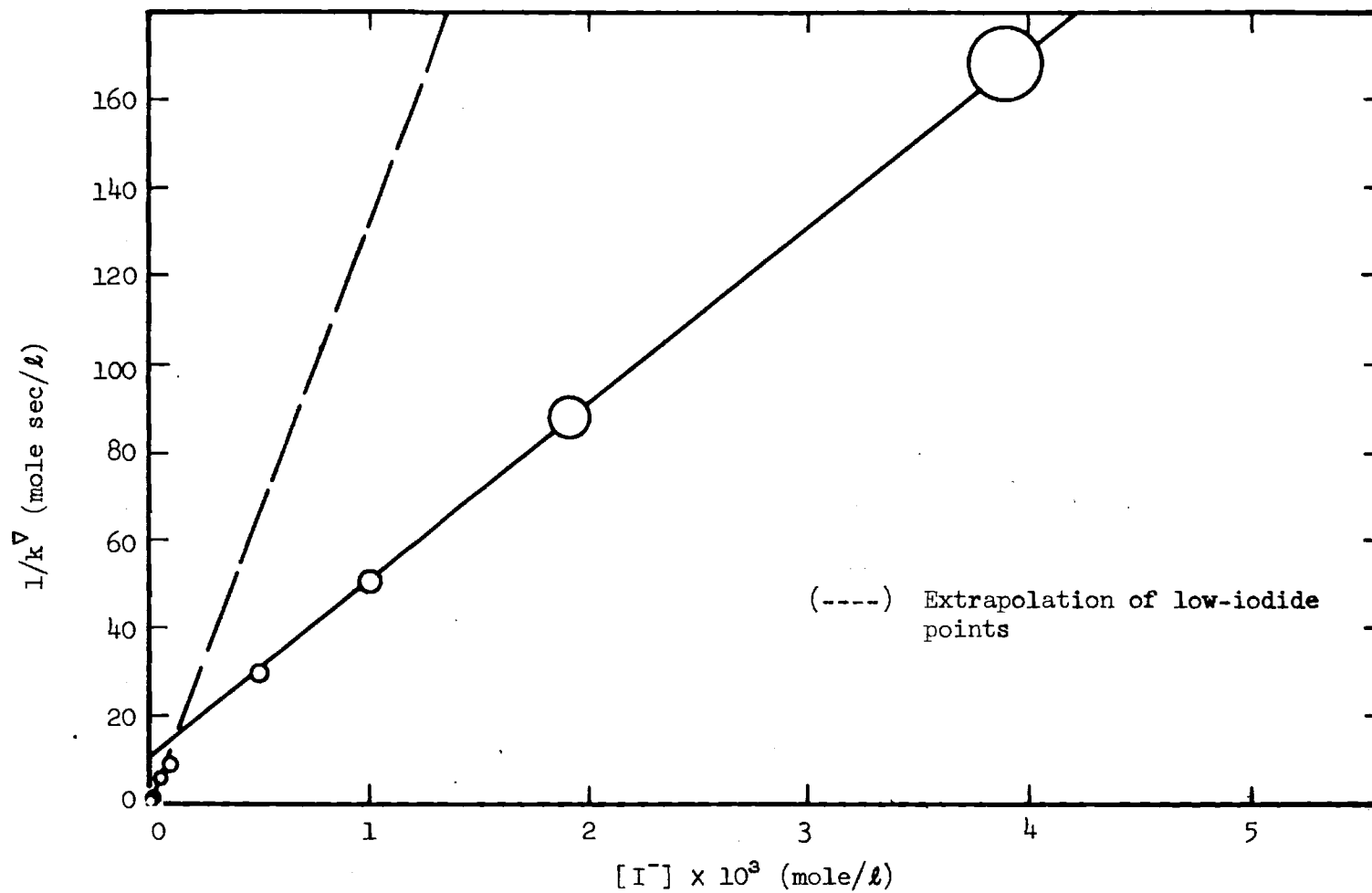


Figure 11. 2,4-Dinitrophenol at Temperature, 50.0° ; Ionic Strength, 0.30; $[H^+]$, $70 \times 10^{-6} \text{ M}$

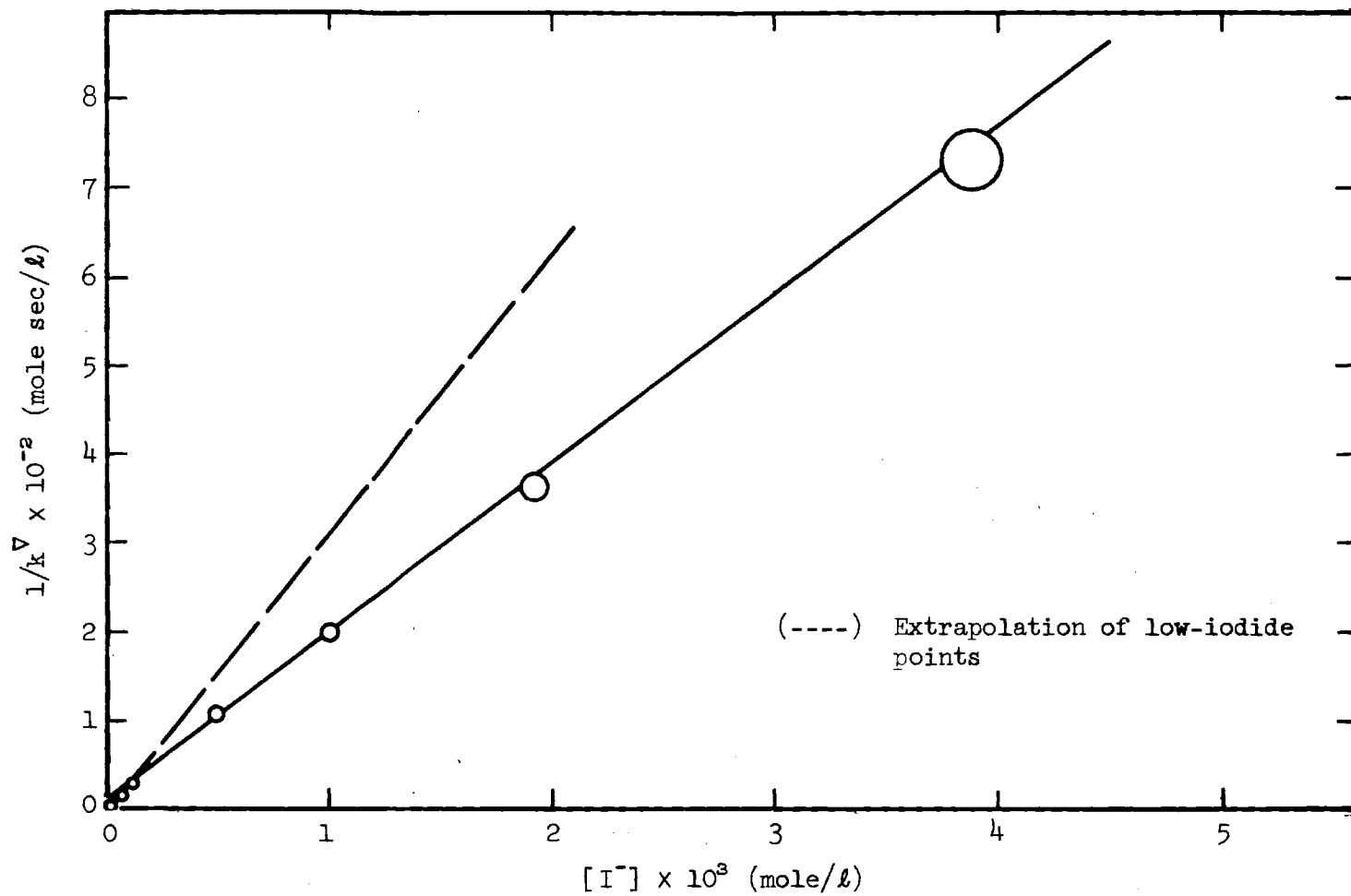


Figure 12. 2,4-Dinitrophenol-6-d at Temperature, 50.0°; Ionic Strength, 0.30;
 $[H^+]$, 70×10^{-6} M

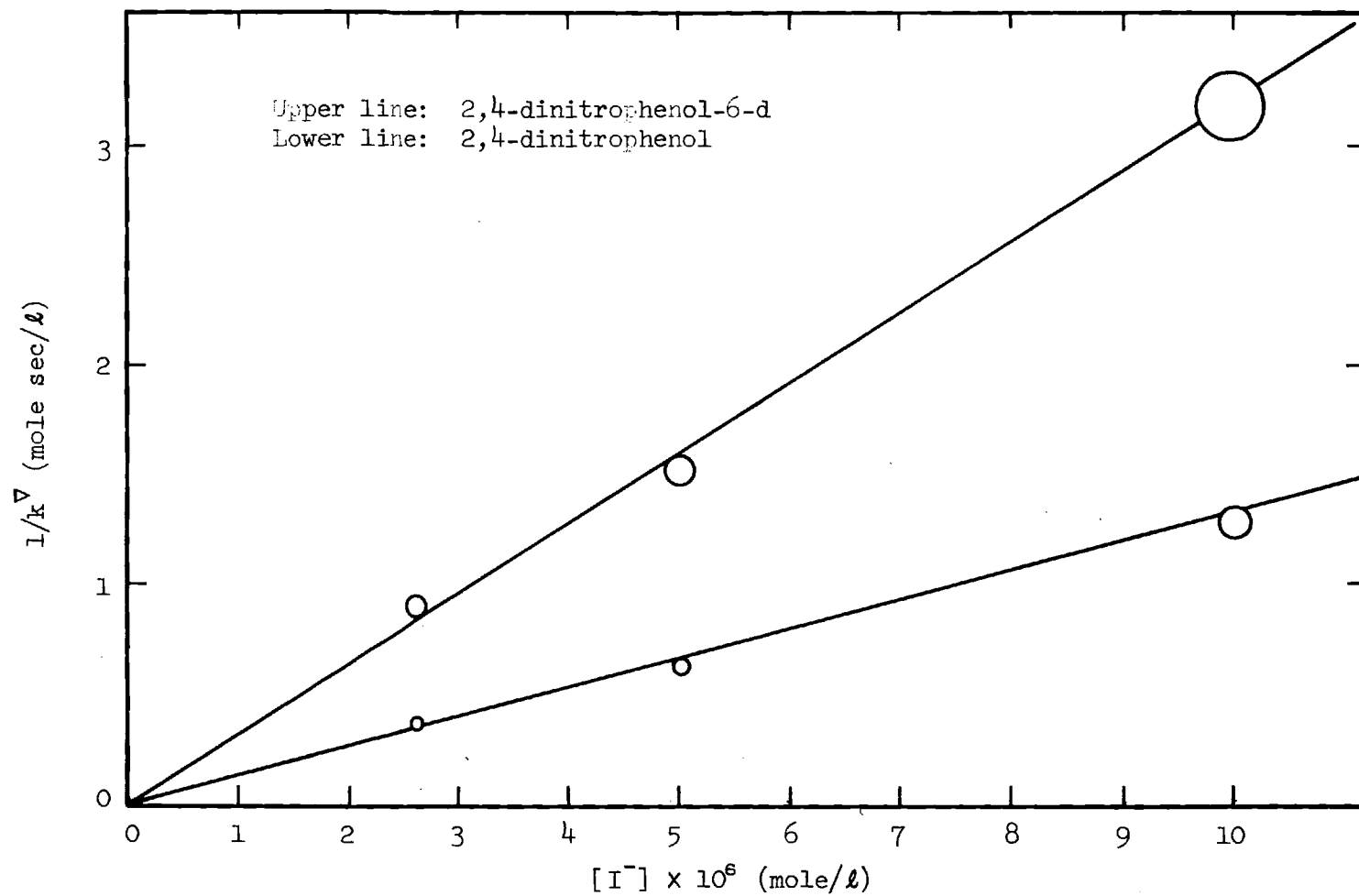


Figure 13. 2,4-Dinitrophenol and 2,4-Dinitrophenol-6-d at Temperature, 50.0°;
Ionic Strength, 0.30; [H⁺], 70 × 10⁻⁶ M

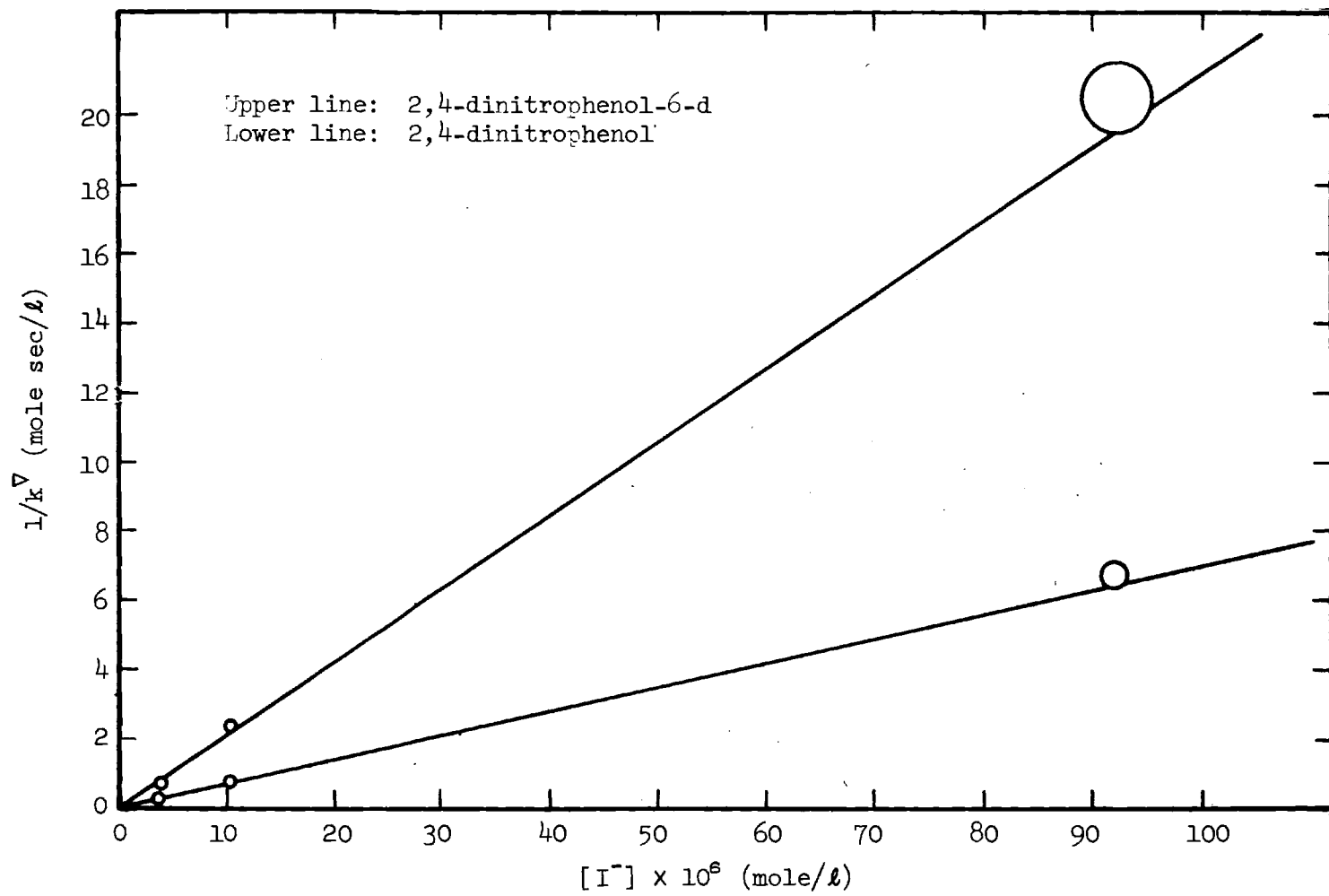


Figure 14. 2,4-Dinitrophenol and 2,4-Dinitrophenol-6-d at Temperature, 50.0°; Ionic Strength, 0.30; [H⁺], 1.8 × 10⁻⁶ M

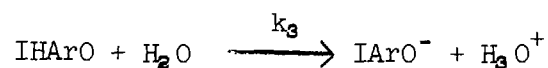
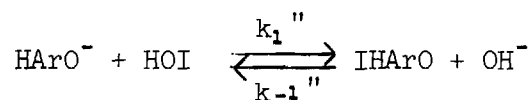
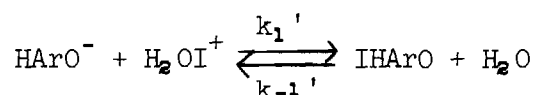
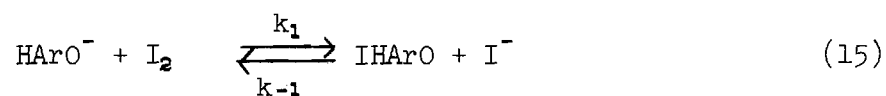
Since the much greater slope of the deuterio line introduces a larger experimental error into the choice of an intercept and since subsequent considerations will indicate that the intercept of the high-iodide line is $1/k_1$, which is not expected to possess a significant isotope effect, an intercept of 10 mole sec/l was adopted for the deuterio high-iodide line as well. Then, assuming this intercept, the high iodide slope for the deuterio compound was calculated in analogous fashion to the previously discussed low iodide slopes, the result being $1.90 \pm 0.03 \times 10^5$ sec.

The qualitative interpretation of the data at 0.30μ is the same as that tentatively made to explain the results at 0.0030μ and Fort's data; viz., I_2 is the iodinating agent at higher iodide ion concentrations, and iodinating species with inverse iodide dependence predominate at lower iodide ion concentrations. At $70 \times 10^{-6} M [H^+]$ the data show curvature from a limiting straight line with a positive intercept at higher iodide ion concentrations to a limiting straight line through the origin at lower iodide ion concentrations. The curvature is quite distinct in the $1/k^\nabla$ versus $[I^-]$ plots for both 2,4-dinitrophenol and 2,4-dinitrophenol-6-d.

The iodination of 2,4-dinitrophenol is considered to go entirely via the phenoxide anion, even though experiments with varying acidity do not unambiguously lead to this conclusion (these experiments are complicated by the pH effect in the opposite direction, discussed above). The facts that p-nitrophenoxide and phenoxide anions iodinate some orders of magnitude more rapidly than the corresponding undissociated phenols, as seen in the paper of Grovenstein and Aprahamian⁽⁵⁹⁾ and in Chapter IV

of this thesis, make it appear unreasonable that undissociated 2,4-dinitrophenol should compete significantly with a considerable excess of 2,4-dinitrophenoxide anions, as is the case in the experiments being discussed here.

The variation of k^{∇} with $[H^+]$ at low iodide, which was suspected from the data at $\mu = 0.0030$, is confirmed by the 0.30μ data. Therefore, equations for a mechanism involving iodination by H_2OI^+ , HOI, and I_2 are derived.



$$\text{rate} = \frac{-d[IHAro]}{dt} = k_3[IHAro]$$

It is seen that in this mechanism the rate of proton removal by hydroxide ion is considered negligible in comparison with proton removal by water. In Fort's protio data, which are plotted in Figure 7, the point at $2940 \times 10^{-6} M [I^-]$ was obtained at $194 \times 10^{-6} M [H^+]$, while all of the other points were obtained at $70 \times 10^{-6} M [H^+]$. From the good fit of this point on the curve generated by the other points, it appears that in this acidity range the concentration of hydroxide does not materially

affect the slope of the line through the high iodide points. Since this slope can be written $\frac{k_{-1}}{k_1(k_3 + k_x[\text{OH}^-])}$, where k_x is the rate constant for proton removal, it is clear that between $70 \times 10^{-6} \text{ M } [\text{H}^+]$ and $194 \times 10^{-6} \text{ M } [\text{H}^+]$, $k_x[\text{OH}^-]$ is small relative to k_3 . The equilibrium constant for water in terms of concentrations can be obtained from data compiled by Bell⁽¹⁰⁰⁾ to be 8.4×10^{-14} at 50° and 0.30μ sodium perchlorate; from this and from the above observation on Fort's data, it can be concluded that $k_3/k_x > 10^{-9}$.

Furthermore, a Brönsted plot of catalysis data on phenol based upon work by Berliner⁽⁴⁶⁾ and Painter and Soper⁽⁴⁴⁾ indicates that for the iodination of phenoxide the ratio k_3/k_x would be approximately 3×10^5 even if hydroxide fell on the plot, and hydroxide ion is usually a less effective catalyst than would be predicted by a Brönsted plot.⁽¹⁰¹⁾ Such a k_3/k_x ratio is sufficiently large to exclude significant hydroxide-catalyzed proton removal at any of the acidities used in the present work.

By the steady state approximation

$$[\text{IHAro}] = \frac{[\text{HArO}^-] \{k_1[\text{I}_2] + k_1'[\text{H}_2\text{OI}^+] + k_1''[\text{HOI}]\}}{k_{-1}[\text{I}^-] + k_{-1}' + k_{-1}''[\text{OH}^-] + k_3} \quad (16)$$

$$\text{rate} = k^\nabla[\text{ArO}^-][\text{I}_2] = \frac{[\text{HArO}^-] k_3 \{k_1[\text{I}_2] + k_1'[\text{H}_2\text{OI}^+] + k_1''[\text{HOI}]\}}{k_{-1}[\text{I}^-] + k_{-1}'[\text{OH}^-] + k_{-1}'' + k_3} \quad (17)$$

but

100. R. P. Bell, Acids and Bases, Methuen and Company, Ltd., London, 1952, p. 15.

101. J. Hine, Physical Organic Chemistry, 2nd ed., McGraw-Hill Company, Inc., New York, 1962, p. 119.

$$[\text{HOI}] = \frac{K_3[\text{I}_2]}{[\text{H}^+][\text{I}^-]} = \frac{K_3}{K_w} \frac{[\text{I}_2][\text{OH}^-]}{[\text{I}^-]} \quad (18)$$

and

$$[\text{H}_2\text{OI}^+] = \frac{K_1[\text{I}_2]}{[\text{I}^-]} \quad (3 - \text{Chapter IV})$$

By substitution

$$k^\nabla[\text{ArO}^-][\text{I}_2] = \frac{k_3[\text{ArO}^-] \left\{ k_1[\text{I}_2] + \frac{k_1'K_1[\text{I}_2]}{[\text{I}^-]} + \frac{k_1''K_3[\text{I}_2][\text{OH}^-]}{K_w[\text{I}^-]} \right\}}{k_{-1}[\text{I}^-] + k_{-1}''[\text{OH}^-] + k_{-1}' + k_3} \quad (19)$$

$$k^\nabla = \frac{k_1k_3 + \frac{k_1'k_3K_1}{[\text{I}^-]} + \frac{k_1''k_3K_3[\text{OH}^-]}{K_w[\text{I}^-]}}{k_{-1}[\text{I}^-] + k_{-1}''[\text{OH}^-] + k_{-1}' + k_3} \quad (20)$$

Inverting, and invoking the principle of microscopic reversibility

$$\frac{1}{k^\nabla} = \left(\frac{k_{-1}}{k_1k_3} \right) [\text{I}^-] + \frac{1}{k_1 + k_1'K_1/[\text{I}^-] + \frac{k_1''K_3[\text{OH}^-]}{[\text{I}^-]}} \quad (21)$$

At high-iodide ion concentrations, I_2 is the only important iodinating agent, and the primed terms drop out.

$$\frac{1}{k^\nabla} = \left(\frac{k_{-1}}{k_1k_3} \right) [\text{I}^-] + \frac{1}{k_1} \quad (22)$$

This is the equation for the iodination of the 2,4-dinitrophenoxide anion by I_2 alone. The reciprocal of the intercept, therefore, equals

k_1 .[†] This is 0.10 l/m sec, and there is nothing unreasonable about such a rate constant. (The fact that both protio and deuterio curves were drawn to the same intercept gives a k_1 isotope effect of unity. This is somewhat arbitrary, since there is some error inherent in the measurement of such an intercept.)

At sufficiently low iodide, the k_1 and k_{-1} terms drop out of equation (21), which can then be written, using microscopic reversibility

$$\frac{1}{k^{\nabla}} = \left(\frac{1}{k_1' K_1 + k_1'' K_3 [\text{OH}^-]/K_w} + \frac{k_{-1}' + k_{-1}'' [\text{OH}^-]}{k_1' k_3 K_1 + \frac{k_1'' k_3 K_3 [\text{OH}^-]}{K_w}} \right) [\text{I}^-] \quad (23)$$

Employing the principle of microscopic reversibility, it can be shown that the second term of the right-hand side of equation (23) is equivalent to $\frac{k_{-1}'}{k_1' K_1 k_3}$.

$$\frac{1}{k^{\nabla}} = \left(\frac{1}{k_1' K_1 + k_1'' K_3 [\text{OH}^-]/K_w} + \frac{k_{-1}'}{k_1' K_1 k_3} \right) [\text{I}^-] \quad (24)$$

This is also the second term in the equation for iodination by H_2OI^+ alone, obtained by dropping k_1'' and k_{-1}'' terms from (23)

[†]This is the intercept of the high-iodide tangent to the $1/k^{\nabla}$ versus $[\text{I}^-]$ curve. Whether such a tangent can be accurately plotted at sufficiently low $[\text{I}^-]$ to yield a reasonably accurate intercept depends upon the ratio between low- and high-iodide slopes. It is clear from the plotted curves (Figures 11 and 12) that in cases of 2,4-dinitrophenol and 2,4-dinitrophenol-6-d, reasonably accurate intercepts can indeed be found.

$$\frac{1}{kV} = \left(\frac{1}{k_1'K_1} + \frac{k_{-1}'}{k_1'k_3K_1} \right) [I^-] \quad (25)$$

Comparing equations (24) and (25), it can be shown that the introduction of HOI as an iodinating agent has two effects on the low-iodide lines: the slopes (protio and deutero) are lowered, and the isotope effect is increased (since the term including k_3 , wherein presumably resides most of the isotope effect, becomes relatively larger). Both of these effects are observed in the low-iodide slopes at the different acidities, as summarized in Table 71.[†] (Isotope effects are measured as the ratio of slopes of the low-iodide lines.) The similarities of the first two isotope effects may simply reflect a small HOI contribution at these higher acidities; this explanation will be seen to be consistent with the considerations developed later.

Since it appears that HOI and H_2OI^+ are involved in low-iodide iodination of the anions of 2,4-dinitrophenol and 2,4-dinitrophenol-6-d and since from microscopic reversibility the second term of the right-hand side of equation (24) is identical with the first term of equation (22), the difference between the low- and high-iodide slopes equals

[†]The measured isotope effects are 3.04 ± 0.18 and 2.42 ± 0.27 , respectively, at $1.70 \times 10^{-6} M [H^+]$ and at $70 \times 10^{-6} M [H^+]$. The ratio of these isotope effects is 1.26 ± 0.13 , and therefore the difference between the isotope effect at the two acidities is significant.

$\frac{1}{k_1'K_1 + \frac{k_1''K_3[OH^-]}{K_w}}$. The terms $k_1'K_1$ and $\frac{k_1''K_3[OH^-]}{K_w}$ can, in principle,

be separated by plotting the reciprocal of the difference between the slopes at low and at high iodide concentrations against $[OH^-]$. (This requires that, over the pH range involved, the high-iodide slope is not measurably affected by pH. This point has been discussed above, and the assumption that $k_x[OH^-]$ is negligible relative to k_3 is equivalent to assuming that the high-iodide slope is independent of $[H^+]$.)

The data on $k_1'K_1 + \frac{k_1''K_3[OH^-]}{K_w}$ are displayed in Table 75, and the plot of the quantity against $[OH^-]$ is shown in Figure 15. The value of $k_1'K_1$ (intercept) is $1.03 \pm 0.10^\dagger \times 10^{-5} \text{ sec}^{-1}$ and the value of $\frac{k_1''K_3}{K_w}$ is $0.53 \pm 0.02 \times 10^8 \text{ l/mole sec}$.

The value of $k_1'K_1$ permits approximate limits to be placed upon possible values of k_1' . It has been determined⁽⁸³⁾ that the maximum possible value of K_1 at 25° is 1×10^{-10} , and this is probably an order of magnitude estimate of the maximum possible K_1 at 50° . There is vast disagreement over the likely true values for K_1 ; for example, Bell and Gelles⁽⁹³⁾ report 1.2×10^{-11} at 25° , whereas Hine⁽⁹⁴⁾ argues that a figure of 10^{-20} is at least an equally reliable estimate. Accepting 1×10^{-10} as an approximate upper limit for K_1 at 50° , the lower limit on k_1' is about 10^5 l/mole sec . Since the true K_1 is probably smaller than 1×10^{-10} , the true k_1' is probably larger and may, in fact, be a

[†]In this case the points at low $[OH^-]$ are so close to zero $[OH^-]$ that they essentially determine the intercept, and the standard deviation is calculated on the basis of the point at $12 \times 10^{-10} \text{ M } [OH^-]$.

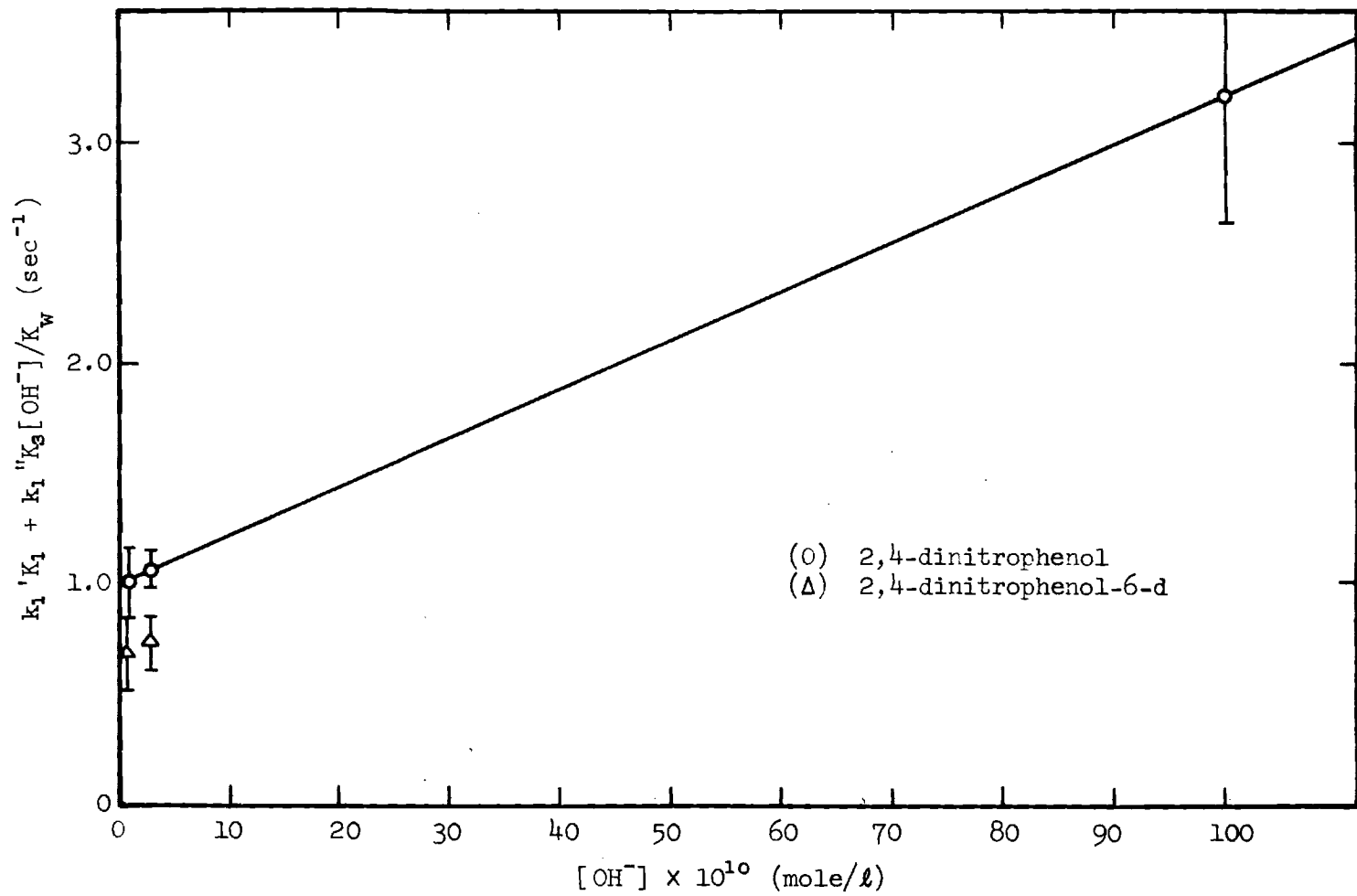


Figure 15. 2,4-Dinitrophenol and 2,4-Dinitrophenol-6-d at Temperature, 50.0°; Ionic Strength, 0.30

diffusion-controlled rate constant. In this case, the reaction of oppositely charged species, the diffusion-controlled rate constant might be as high as 10^{11} l/mole sec.⁽⁹²⁾ As a matter of fact, this can be considered to set a lower limit of approximately 10^{-16} on K_1 .

It is evident from Figure 15 that, for $k_1'K_1$ of 1.03×10^{-5} sec⁻¹ and $\frac{k_1''K_3}{K_w}$ of 0.53×10^3 l/mole sec, approximately 95 percent of the iodination is by way of H_2OI^+ at low iodide ion concentrations at 70×10^{-6} M $[H^+]$ (12×10^{-10} M $[OH^-]$), but only about 30 percent at 1.70×10^{-6} M $[H^+]$ (500×10^{-10} M $[OH^-]$). Using known values of K_2 and K_w , an approximate value of k_1'' can be extracted. At 0.30 μ sodium perchlorate and 50.0°, K_w is 8.4×10^{-14} (cf. above), and K_3 is 9.5×10^{-12} , by extrapolation of the data of Allen and Keefer,⁽⁸³⁾ for 0.30 μ sodium perchlorate solutions (cf. introduction to this chapter). A value of k_1'' equal to 4.7 l/mole sec is obtained, as compared with a value of 0.10 l/mole sec for k_1 (the reciprocal of the intercept of the $1/k^{\nabla}$ versus $[I^-]$ line at high iodide ion concentrations). This means that, for the substrate 2,4-dinitrophenoxide, HOI is about 47 times the better iodinating agent than I_2 . It is expected that a more reactive compound, such as phenoxide, would be less selective, and that for such a compound the ratio of reactivity of HOI and I_2 would be smaller. By comparison, the ratio of reactivity of HOBr to Br_2 was found by Shilov and Kaniaev⁽¹⁰²⁾ to be 0.0015 for the bromination of sodium m-anisole sulfonate.

102. E. A. Shilov and N. P. Kaniaev, N. P., C. R. Acad. Sci. U.R.S.S., 24, 890 (1939).

Although it is impossible to evaluate the reasonableness of the quantitative values for relative reactivities of the two halogens and the corresponding hypohalous acids, one would expect HOI to be a better halogenating agent relative to I_2 than HOBr is relative to Br_2 . The fact that bromine is more electronegative than iodine would be a factor enhancing Br_2 reactivity relative to I_2 , since electronegativity of the halogen carrier is considered to increase reactivity in electrophilic aromatic substitution.⁽¹⁰³⁾ No such factor is involved, however, with respect to the relative reactivities of HOBr and HOI, since the halogen carrier, hydroxyl, is the same in each case. It follows that the reactivity ratio HOI/HOBr should exceed I_2/Br_2 , and therefore that the reactivity ratio HOI/ I_2 should exceed HOBr/ Br_2 .

The above considerations have been based upon data for the protio compound. The magnitude of the standard deviation about the $k_1'K_1 + \frac{k_1''K_3}{K_w}$ value for 2,4-dinitrophenol-6-d ($5.0 \pm 2.3 \times 10^{-6} \text{sec}^{-1}$) at $500 \times 10^{-6} \text{ M } [OH^-]$ makes it impossible to obtain a reliable value for $\frac{k_1''K_3}{K_w}$. This point, therefore, is not included in Figure 15.

However, an isotope effect for $k_1'K_1 + \frac{k_1''K_3[OH^-]}{K_w}$ can be obtained at $70 \times 10^{-6} \text{ M } [H^+]$ and $222 \times 10^{-6} \text{ M } [H^+]$, from data in Table 75. (The value of $k_1'K_1 + \frac{k_1''K_3[OH^-]}{K_w}$ at $222 \times 10^{-6} \text{ M } [H^+]$ for the protio compound is obtained from the plot in Figure 15.) The isotope effect at $70 \times 10^{-6} \text{ M } [H^+]$ is 1.45 ± 0.32 and at $222 \times 10^{-6} \text{ M } [H^+]$ is 1.53. According to the graph in Figure 15, at both of these acidities, almost all of the iodination is by way of H_2OI^+ (assuming that the slopes are similar for

103. E. Berliner, J. Chem. Educ., 43, 124 (1966).

the protio and deutero compounds, which seems reasonable, since no term in the expression for the slope involves a proton transfer), and essentially all of any isotope effect can be considered to be the isotope effect of k_1' . The $70 \times 10^{-6} \text{ M} [\text{H}^+]$ figure is more reliable, being based upon a larger number of experiments, and therefore it appears that k_1' has an isotope effect of 1.45 ± 0.32 . This gives a value of $k_1'K_1$ of 2,4-dinitrophenol-6-d of $7.1 \pm 2.4 \times 10^{-6} \text{ sec}^{-1}$.

Since the slope for the high iodide line can be expressed as $\frac{k_{-1}'}{k_1'k_3K_1}$, the reversibility ratio $\frac{k_{-1}'}{k_3}$ can be determined from the values of $k_1'K_1$ and the high iodide slope. The results are 0.43 ± 0.04 for the protio compound and 1.35 ± 0.26 for the deutero compound. Since the same slope can be expressed as $\frac{k_{-1}}{k_1k_3}$, the reversibility ratio $\frac{k_{-1}}{k_3}$ can be obtained from the values of the slope and $1/k_1$. The results are 4150 mole/l for the protio and 19,000 mole/l for the deutero compound.

Assuming equal intercepts for the high iodide lines for the protio and deutero compounds (equal values of k_1), the k_3 isotope effect is the ratio of the slopes of the high-iodide lines in the $1/k^{\nabla}$ versus $[\text{I}^-]$ plots; this is 4.5 ± 0.1 .

Having obtained these kinetic data for the iodination of 2,4-dinitrophenoxide and 2,4-dinitrophenoxide-6-d, it is now possible to substitute the values back into the general equation to see how well the data describe the experimental results. The case of greatest interest is that of $\mu = 0.30$, $[\text{H}^+] = 70 \times 10^{-6} \text{ M}$; the largest number of points is available under these conditions, and Figure 15 shows that iodination by HOI is of such little importance here as to be negligible to a first approxi-

mation. This latter point is important because of the lack of accurate HOI rate constants for 2,4-dinitrophenol-6-d. Equation (21) can be rearranged, dropping the HOI terms

$$\frac{1}{k^{\nabla}} = \frac{k_{-1}/k_2[I^-] + k_{-1}'/k_2 + 1}{k_1 + k_1'K_1/[I^-]} \quad (26)$$

From the kinetic data discussed above, numerical values can be substituted for all of the constants in equation (26), for both the protio and deutero compounds. From the resulting equation, values of $1/k^{\nabla}$ can be calculated for various $[I^-]$ values and compared with experiment. The results are given in Table 76 and show a good fit between calculated and observed values.

It can be said, therefore, that the kinetics of iodination of 2,4-dinitrophenoxide and 2,4-dinitrophenoxide-6-d are consistent with the mechanism invoking I_2 , H_2OI^+ , and HOI as iodinating agents. The numerical values of individual rate constants have been calculated, and the restrictions imposed upon them as conditions of the proposed mechanism are not such as to require these values to be impossibly high. The measured effect for k_1' of 1.43 is higher than might be expected; however, in light of the error limits inherent in this measurement, such an apparent discrepancy is not surprising.

It is noteworthy that the change in ionic strength from 0.0030 to 0.30, at $70 \times 10^{-6} M [H^+]$, had little effect upon $1/k^{\nabla}$ at the low-iodide ion concentrations involved. (The slopes of the $1/k^{\nabla}$ versus $[I^-]$ lines at 0.0030 μ are 1.24×10^5 sec and 2.98×10^5 sec for the protio

and deuterio compounds, respectively; at 0.30μ , the slopes are 1.34×10^5 sec and 3.23×10^5 sec.) Since at this acidity, HOI is not an important iodinating agent, the low-iodide data are described by equation (25). On the basis of relative charge separation in reactants and products, an increase in ionic strength would be expected to enhance rate constants k_2 and k_{-1}' , to decrease rate constant k_1' and equilibrium constant K_1 , as well as to decrease the activity of the iodide ion at a given concentration. As a result, there are competing ionic strength effects on $1/k^\nabla$, and qualitatively, it is not surprising that the net effect is small.

By contrast, the effect of an increase in ionic strength at high iodide ion concentrations, described by equation (22), would be to decrease $1/k^\nabla$.

Table 31. Run 23, 2,4-Dinitrophenol in 109.9×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	28.0×10^{-6} M	(NaClO ₄)	2770×10^{-6} M
$[I_2]_0$	26.5×10^{-6} M	(2,4-Dinitrophenol) ₀	201.5×10^{-6} M
$(I^-)_0$	109.9×10^{-6} M	μ	0.0030
$[I^-]_0$	108.4×10^{-6} M	$[H^+]_0$	31.0×10^{-6} M
$[HOI]_0$	0.00×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
12981	13.86	17.4	0.074
20238	13.18	24.4	.070
27431	12.37	32.8	.074
35010	11.85	38.1	.070
38640	11.51	41.6	.071
65348	9.98	57.4	.068

$$F_1 = 10.31$$

$$P_1 = 25950 \text{ l/mole cm}$$

$$F_2 = 0.80 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50320 \text{ l/mole cm}$$

$$E = 2.715 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368300 \text{ l/mole cm}$$

$$k_{app0} = 0.074 \text{ l/mole sec}$$

$$k^\nabla = 0.098 \text{ l/mole sec}$$

$$k^* = 0.078 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 10.6 \times 10^{-6} \text{ sec}^{-1}$$

Table 32. Run 24, 2,4-Dinitrophenol-6-d in $109.9 \times 10^{-6} \text{ M}$
Sodium Iodide Solution at 50.0°

$(\text{I}_2)_0$	$28.0 \times 10^{-6} \text{ M}$	(NaClO_4)	$2770 \times 10^{-6} \text{ M}$
$[\text{I}_2]_0$	$26.5 \times 10^{-6} \text{ M}$	(2,4-Dinitrophenol- 6-d) ₀	$201.7 \times 10^{-6} \text{ M}$
$(\text{I}^-)_0$	$109.9 \times 10^{-6} \text{ M}$	μ	0.0030
$[\text{I}^-]_0$	$108.4 \times 10^{-6} \text{ M}$	$[\text{H}^+]_0$	$31.0 \times 10^{-6} \text{ M}$
$[\text{HOI}]_0$	$0.00 \times 10^{-6} \text{ M}$		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
20407	14.56	10.1	0.0260
39398	13.74	18.5	.0261
66127	12.72	28.9	.0262
79017	12.44	31.7	.0245
106803	11.66	39.7	.0242
113376	11.43	42.0	.0246

$$F_1 = 10.31$$

$$P_1 = 25950 \text{ l/mole cm}$$

$$F_2 = 0.80 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50320 \text{ l/mole cm}$$

$$E = 2.715 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368300 \text{ l/mole cm}$$

$$k_{\text{app}0} = 0.0260 \text{ l/mole sec}$$

$$k^\nabla = 0.0345 \text{ l/mole sec}$$

$$k^* = 0.0275 \text{ l/mole sec}$$

$$k^\nabla[\text{I}^-] = 3.74 \times 10^{-6} \text{ sec}^{-1}$$

Table 33. Run 33, 2,4-Dinitrophenol in 33.12×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	9.88×10^{-6} M	(NaClO ₄)	2900	$\times 10^{-6}$ M
$[I_2]_0$	9.76×10^{-6} M	(2,4-Dinitrophenol) ₀	59.59	$\times 10^{-6}$ M
$(I^-)_0$	33.12×10^{-6} M	μ	0.0030	
$[I^-]_0$	32.99×10^{-6} M	$[H^+]_0$	30.0	$\times 10^{-6}$ M
$[HOI]_0$	0.05×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
9502	4.797	11.1	0.210
19652	4.427	21.7	.213
26835	4.197	28.3	.213
33134	4.077	31.6	.198
41803	3.887	37.0	.192
70892	3.327	52.7	.187
73357	3.307	53.3	.183
83794	3.187	56.6	.176

$$F_1 = 3.640$$

$$P_1 = 25950 \text{ l/mole cm}$$

$$F_2 = 1.25 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50320 \text{ l/mole cm}$$

$$E = 2.715 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368300 \text{ l/mole cm}$$

$$k_{app0} = 0.211 \text{ l/mole sec}$$

$$k^\nabla = 0.267 \text{ l/mole sec}$$

$$k^* = 0.214 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 8.8 \times 10^{-6} \text{ sec}^{-1}$$

Table 34. Run 34, 2,4-Dinitrophenol-6-d in 33.12×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	9.88×10^{-6} M	(NaClO ₄)	2900×10^{-6} M
$[I_2]_0$	9.76×10^{-6} M	(2,4-Dinitrophenol-6-d) ₀	59.14×10^{-6} M
$(I^-)_0$	33.12×10^{-6} M	μ	0.0030
$[I^-]_0$	32.99×10^{-6} M	$[H^+]_0$	30.0×10^{-6} M
$[HOI]_0$	0.05×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
33304	4.627	15.0	0.083
41904	4.477	19.1	.087
69900	4.167	27.4	.079
73720	4.157	27.6	.076
84287	4.057	30.2	.074
100400	3.897	34.5	.073
114770	3.727	39.1	.076

$$F_1 = 3.640$$

$$P_1 = 25950 \text{ l/mole cm}$$

$$F_2 = 1.25 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50320 \text{ l/mole cm}$$

$$E = 2.715 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368300 \text{ l/mole cm}$$

$$k_{app0} = 0.086 \text{ l/mole sec}$$

$$k^\nabla = 0.108 \text{ l/mole sec}$$

$$k^* = 0.087 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 3.56 \times 10^{-6} \text{ sec}^{-1}$$

Table 35. Run 25, 2,4-Dinitrophenol in 10.52×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	6.00×10^{-6} M	(NaClO ₄)	2940	$\times 10^{-6}$ M
$[I_2]_0$	5.90×10^{-6} M	(2,4-Dinitrophenol) ₀	40.51	$\times 10^{-6}$ M
$(I^-)_0$	10.52×10^{-6} M	μ	0.0030	
$[I^-]_0$	10.62×10^{-6} M	$[H^+]_0$	30.0	$\times 10^{-6}$ M
$[HOI]_0$	0.10×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
11058	2.817	21.3	0.543
14759	2.719	26.0	.513
21707	2.497	36.6	.534
26760	2.387	41.9	.518
33811	2.247	48.6	.506
38678	2.171	52.2	.493
66185	1.837	68.1	.453

$$F_1 = 2.209$$

$$P_1 = 25950 \text{ l/mole cm}$$

$$F_2 = 0.43 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50320 \text{ l/mole cm}$$

$$E = 2.715 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368300 \text{ l/mole cm}$$

$$k_{app0} = 0.577 \text{ l/mole sec}$$

$$k^\nabla = 0.733 \text{ l/mole sec}$$

$$k^* = 0.587 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 7.78 \times 10^{-6} \text{ sec}^{-1}$$

Table 36. Run 26, 2,4-Dinitrophenol-6-d in 10.52×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	6.00×10^{-6} M	(NaClO ₄)	2940 $\times 10^{-6}$ M
$[I_2]_0$	5.90×10^{-6} M	(2,4-Dinitrophenol-6-d) ₀	40.00×10^{-6} M
$(I^-)_0$	10.52×10^{-6} M	μ	0.0030
$[I^-]_0$	10.62×10^{-6} M	$[H^+]_0$	30.0×10^{-6} M
$[HOI]_0$	0.10×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
13618	3.029	10.3	0.201
27205	2.773	22.5	.238
39384	2.693	26.1	.196
66803	2.397	40.1	.198
73717	2.319	43.8	.203
89001	2.187	50.0	.203
100030	2.117	53.2	.199

$$F_1 = 2.209$$

$$P_1 = 25950 \text{ l/mole cm}$$

$$F_2 = 0.43 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50320 \text{ l/mole cm}$$

$$E = 2.715 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368300 \text{ l/mole cm}$$

$$k_{app0} = 0.225 \text{ l/mole sec}$$

$$k^\nabla = 0.285 \text{ l/mole sec}$$

$$k^* = 0.229 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 3.03 \times 10^{-6} \text{ sec}^{-1}$$

Table 37. Run 29, 2,4-Dinitrophenol in 1.080×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	0.576×10^{-6} M	(NaClO ₄)	2970	$\times 10^{-6}$ M
$[I_2]_0$	0.497×10^{-6} M	(2,4-Dinitrophenol) ₀	4.097×10^{-6} M	
$(I^-)_0$	1.080×10^{-6} M	μ	0.0030	
$[I^-]_0$	1.158×10^{-6} M	$[H^+]_0$	30.1	$\times 10^{-6}$ M
$[HOI]_0$	0.078×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
9281	0.282	18.4	5.40
17327	.250	34.5	6.12
25643	.241	39.1	4.86
27582	.239	40.1	4.67
35211	.226	46.6	4.52
43391	.213	53.2	4.46
72878	.189	65.3	3.75

$$F_1 = 0.212$$

$$P_1 = 25950 \text{ l/mole cm}$$

$$F_2 = 0.0$$

$$P_2 = 50320 \text{ l/mole cm}$$

$$E = 2.715 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368300 \text{ l/mole cm}$$

$$k_{app0} = 5.50 \text{ l/mole sec}$$

$$k^\nabla = 7.93 \text{ l/mole sec}$$

$$k^* = 6.36 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 9.18 \times 10^{-6} \text{ sec}^{-1}$$

Table 38. Run 30, 2,4-Dinitrophenol-6-d in 1.080×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	0.576×10^{-6} M	(NaClO ₄)	2970	$\times 10^{-6}$ M
$[I_2]_0$	0.497×10^{-6} M	(2,4-Dinitrophenol-6-d) ₀	4.076	$\times 10^{-6}$ M
$(I^-)_0$	1.080×10^{-6} M	μ	0.0030	
$[I^-]_0$	1.158×10^{-6} M	$[H^+]_0$	30.1	$\times 10^{-6}$ M
$[HOI]_0$	0.078×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
18593	0.285	16.6	2.42
27474	.276	21.1	2.15
43741	.255	31.7	2.19
73240	.229	44.8	2.07
89648	.214	52.4	2.12
100890	.201	59.0	2.28
101050	.195	62.0	2.48

$$F_1 = 0.212$$

$$P_1 = 25950 \text{ l/mole cm}$$

$$F_2 = 0.0$$

$$P_2 = 50320 \text{ l/mole cm}$$

$$E = 2.715 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368300 \text{ l/mole cm}$$

$$k_{app0} = 2.40 \text{ l/mole sec}$$

$$k^\nabla = 3.45 \text{ l/mole sec}$$

$$k^* = 2.77 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 4.00 \times 10^{-6} \text{ sec}^{-1}$$

Table 39. Run 35, 2,4-Dinitrophenol in 1.000×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	0.682×10^{-6} M	(NaClO ₄)	2970	$\times 10^{-6}$ M
$[I_2]_0$	0.584×10^{-6} M	(2,4-Dinitrophenol) ₀	4.164	$\times 10^{-6}$ M
$(I^-)_0$	1.000×10^{-6} M	μ	0.0030	
$[I^-]_0$	1.097×10^{-6} M	$[H^+]_0$	30.1	$\times 10^{-6}$ M
$[HOI]_0$	0.097×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
9678	0.289	20.9	5.91
17006	.275	26.9	4.53
27345	.257	34.7	3.84
38455	.234	44.8	3.85
40696	.222	50.4	4.32
57124	.200	59.8	4.04
62657	.190	64.3	4.18

$$F_1 = 0.227$$

$$P_1 = 25950 \text{ l/mole cm}$$

$$F_2 = 0.20 \times 10^{-8} \text{ sec}^{-1}$$

$$P_2 = 50320 \text{ l/mole cm}$$

$$E = 2.715 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368300 \text{ l/mole cm}$$

$$k_{app0} = 5.00 \text{ l/mole sec}$$

$$k^\nabla = 7.29 \text{ l/mole sec}$$

$$k^* = 5.85 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 8.00 \times 10^{-6} \text{ sec}^{-1}$$

Table 40. Run 32, 2,4-Dinitrophenol-6-d in $0.108 \times 10^{-6} \text{ M}$
Sodium Iodide Solution at 50.0°

$(\text{I}_2)_0$	$0.603 \times 10^{-6} \text{ M}$	(NaClO_4)	2970	$\times 10^{-6} \text{ M}$
$[\text{I}_2]_0$	$0.386 \times 10^{-6} \text{ M}$	(2,4-Dinitro- phenol-6-d) ₀	4.098	$\times 10^{-6} \text{ M}$
$(\text{I}^-)_0$	$0.1081 \times 10^{-6} \text{ M}$	μ	0.0030	
$[\text{I}^-]_0$	$0.325 \times 10^{-6} \text{ M}$	$[\text{H}^+]_0$	30.0	$\times 10^{-6} \text{ M}$
$[\text{HOI}]_0$	$0.217 \times 10^{-6} \text{ M}$			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
11436	0.287	18.7	4.49
20149	.264	29.0	4.24
29580	.246	36.8	3.90
38254	.220	48.8	4.45
43793	.215	50.7	4.12
81964	.175	67.4	3.53
91748	.175	66.5	3.08

$$F_1 = 0.222$$

$$P_1 = 25950 \text{ l/mole cm}$$

$$F_2 = 0.24 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50320 \text{ l/mole cm}$$

$$E = 2.715 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368300 \text{ l/mole cm}$$

$$k_{\text{app}0} = 4.82 \text{ l/mole sec}$$

$$k^\nabla = 9.38 \text{ l/mole sec}$$

$$k^* = 7.52 \text{ l/mole sec}$$

$$k^\nabla[\text{I}^-] = 3.05 \times 10^{-6} \text{ sec}^{-1}$$

Table 41. Run 31, 2,4-Dinitrophenol in 0.1081×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	0.603×10^{-6} M	(NaClO ₄)	2970	$\times 10^{-6}$ M
$[I_2]_0$	0.386×10^{-6} M	(2,4-Dinitrophenol) ₀	3.935	$\times 10^{-6}$ M
$(I^-)_0$	0.1081×10^{-6} M	μ	0.0030	
$[I^-]_0$	0.325×10^{-6} M	$[H^+]_0$	30.0	$\times 10^{-6}$ M
$[HOI]_0$	0.217×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
9907	0.256	31.9	10.1
10129	.258	30.9	9.5
14396	.235	41.6	9.8
19307	.221	42.0	9.0
29315	.190	62.3	8.9
38714	.172	70.3	8.5
44386	.168	71.8	7.8

$$F_1 = 0.222$$

$$P_1 = 25950 \text{ l/mole cm}$$

$$F_2 = 0.24 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50320 \text{ l/mole cm}$$

$$E = 2.715 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368300 \text{ l/mole cm}$$

$$k_{app0} = 11.0 \text{ l/mole sec}$$

$$k^\nabla = 21.4 \text{ l/mole sec}$$

$$k^* = 17.2 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 6.94 \times 10^{-6} \text{ sec}^{-1}$$

Table 42. Run 36, 2,4-Dinitrophenol in 1.000×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	0.682×10^{-6} M	(NaClO ₄)	2700	$\times 10^{-6}$ M
$[I_2]_0$	0.670×10^{-6} M	(2,4-Dinitrophenol) ₀	4.164	$\times 10^{-6}$ M
$(I^-)_0$	1.000×10^{-6} M	μ	0.0030	
$[I^-]_0$	1.012×10^{-6} M	$[H^+]_0$	302.4	$\times 10^{-6}$ M
$[HOI]_0$	0.012×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
17084	0.310	10.3	1.54
27443	.292	17.9	1.75
38542	.284	20.8	1.48
57506	.265	28.3	1.42
66220	.258	31.1	1.38
90615	.221	47.1	1.76
101060	.220	46.8	1.56

$$F_1 = 0.227$$

$$P_1 = 25950 \text{ l/mole cm}$$

$$F_2 = 0.20 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50320 \text{ l/mole cm}$$

$$E = 2.715 \times 10^{-8} \text{ mole cm/l}$$

$$P_3 = 368300 \text{ l/mole cm}$$

$$k_{app0} = 1.74 \text{ l/mole sec}$$

$$k^\nabla = 6.16 \text{ l/mole sec}$$

$$k^* = 1.77 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 6.23 \times 10^{-6} \text{ sec}^{-1}$$

Table 43. Run 37, 2,4-Dinitrophenol at 0.722×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	0.377×10^{-6} M	(NaClO ₄)	3000	$\times 10^{-6}$ M
$[I_2]_0$	0.147×10^{-6} M	(2,4-Dinitrophenol) ₀	3.638	$\times 10^{-6}$ M
$(I^-)_0$	0.722×10^{-6} M	μ	0.0030	
$[I^-]_0$	0.951×10^{-6} M	$[H^+]_0$	3.88	$\times 10^{-6}$ M
$[HOI]_0$	0.230×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
23576	0.187	35.8	5.26
32554	.178	42.7	4.82
32399	.172	47.3	5.59
41186	.167	51.2	4.93
65122	.144	68.9	5.15
74670	.146	67.3	4.30
74823	.143	69.7	4.58

$$F_1 = 0.139$$

$$P_1 = 25950 \text{ l/mole cm}$$

$$F_2 = 0.0$$

$$P_2 = 50320 \text{ l/mole cm}$$

$$E = 2.715 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368300 \text{ l/mole cm}$$

$$k_{app0} = 4.95 \text{ l/mole sec}$$

$$k^\nabla = 13.0 \text{ l/mole sec}$$

$$k^* = 12.7 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 12.4 \times 10^{-6} \text{ sec}^{-1}$$

Table 44. Run 88, 2,4-Dinitrophenol in 8.81×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	5.26×10^{-6} M	(NaH_2PO_4)	0.0050	M
$[I_2]_0$	3.43×10^{-6} M	(Na_2HPO_4)	0.0010	M
$(I^-)_0$	8.81×10^{-6} M	($NaClO_4$)	0.29	M
$[I^-]_0$	10.64×10^{-6} M	(2,4-Dinitrophenol) $_0$	48.1×10^{-6} M	M
$[HOI]_0$	1.83×10^{-6} M	μ	0.30	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
7316	2.805	24.7	0.817
9244	2.723	28.9	.780
12323	2.571	36.9	.795
16211	2.407	45.4	.798
20168	2.285	51.7	.774
23107	2.193	56.4	.774
25286	2.081	62.4	.837

$$F_1 = 1.938$$

$$P_1 = 27800 \text{ l/mole cm}$$

$$F_2 = 3.3 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50332 \text{ l/mole cm}$$

$$E = 2.713 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368300 \text{ l/mole cm}$$

$$k_{app0} = 0.84 \text{ l/mole sec}$$

$$k^\nabla = 1.29 \text{ l/mole sec}$$

$$k^* = 1.28 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 13.7 \times 10^{-6} \text{ sec}^{-1}$$

Table 45. Run, 89, 2,4-Dinitrophenol-6-d in 8.81×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	5.26×10^{-6} M	(NaH_2PO_4)	0.0050	M
$[I_2]_0$	3.43×10^{-6} M	(Na_2HPO_4)	0.0010	M
$(I^-)_0$	8.81×10^{-6} M	($NaClO_4$)	0.29	M
$[I^-]_0$	10.64×10^{-6} M	(2,4-Dinitrophenol-6-d) ₀	90.7×10^{-6} M	M
$[HOI]_0$	1.83×10^{-6} M	μ	0.30	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
8469	4.100	18.3	0.265
12414	3.947	26.2	.272
18318	3.743	36.6	.278
20252	3.713	38.0	.264
26637	3.580	45.1	.252
29818	3.529	46.9	.238

$$F_1 = 1.938$$

$$P_1 = 27800 \text{ l/mole cm}$$

$$F_2 = 3.3 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50332 \text{ l/mole cm}$$

$$E = 2.713 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368600 \text{ l/mole cm}$$

$$k_{app0} = 0.275 \text{ l/mole sec}$$

$$k^\nabla = 0.425 \text{ l/mole sec}$$

$$k^* = 0.421 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 4.53 \times 10^{-6} \text{ sec}^{-1}$$

Table 46. Run 84, 2,4-Dinitrophenol in 2.38×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	2.03×10^{-6} M	(NaH_2PO_4)	0.0050	M
$[I_2]_0$	0.79×10^{-6} M	(Na_2HPO_4)	0.0010	M
$(I^-)_0$	2.38×10^{-6} M	($NaClO_4$)	0.29	M
$[I^-]_0$	3.62×10^{-6} M	(2,4-Dinitrophenol) $_0$	26.3×10^{-6}	M
$[HOI]_0$	1.24×10^{-6} M	μ	0.30	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
5328	1.334	19.4	1.55
7378	1.286	25.8	1.55
10799	1.206	36.5	1.62
13252	1.176	40.2	1.50
16575	1.118	47.9	1.52
18624	1.096	50.9	1.48

$$F_1 = 0.748$$

$$P_1 = 27800 \text{ l/mole cm}$$

$$F_2 = 2.0 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50332 \text{ l/mole cm}$$

$$E = 2.713 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368600 \text{ l/mole cm}$$

$$k_{app0} = 1.56 \text{ l/mole sec}$$

$$k^\nabla = 4.04 \text{ l/mole sec}$$

$$k^* = 4.00 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 14.7 \times 10^{-6} \text{ sec}^{-1}$$

Table 47. Run 85, 2,4-Dinitrophenol-6-d in 2.38×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	2.03×10^{-6} M	(NaH_2PO_4)	0.0050	M
$[I_2]_0$	0.79×10^{-6} M	(Na_2HPO_4)	0.0010	M
$(I^-)_0$	2.38×10^{-6} M	($NaClO_4$)	0.29	M
$[I^-]_0$	3.62×10^{-6} M	(2,4-Dinitrophenol-6-d) ₀	33.4×10^{-6} M	M
$[HOI]_0$	1.24×10^{-6} M	μ	0.30	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
10849	1.527	18.4	0.564
13304	1.510	20.2	.511
16664	1.460	26.6	.561
18714	1.450	27.5	.520
23198	1.406	32.9	.520
26302	1.376	36.5	.523

$$F_1 = 0.748$$

$$P_1 = 27800 \text{ l/mole cm}$$

$$F_2 = 2.0 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50332 \text{ l/mole cm}$$

$$E = 2.713 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368600 \text{ l/mole cm}$$

$$k_{app0} = 0.538 \text{ l/mole sec}$$

$$k^\nabla = 1.40 \text{ l/mole sec}$$

$$k^* = 1.39 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 5.1 \times 10^{-6} \text{ sec}^{-1}$$

Table 48. Run 92, 2,4-Dinitrophenol in 9.52×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_o$	11.53×10^{-6} M	(NaClO ₄)	0.294	M
$[I_2]_o$	11.48×10^{-6} M	(2,4-Dinitrophenol) _o	77.88×10^{-6}	M
$(I^-)_o$	9.52×10^{-6} M	μ	0.30	
$[I^-]_o$	9.57×10^{-6} M	$[H^+]_o$	192	$\times 10^{-6}$ M
$[HOI]_o$	0.046×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
5932	5.679	16.0	0.381
9023	5.478	20.9	.338
12749	5.211	27.4	.329
19560	4.823	36.8	.311
19988	4.808	37.2	.308
24201	4.564	43.2	.311
30089	4.344	48.4	.294

$$F_1 = 4.251$$

$$P_1 = 26660 \text{ l/mole cm}$$

$$F_2 = 2.42 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50332 \text{ l/mole cm}$$

$$E = 2.713 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368600 \text{ l/mole cm}$$

$$k_{appo} = 0.382 \text{ l/mole sec}$$

$$k^\nabla = 0.73 \text{ l/mole sec}$$

$$k^* = 0.384 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 7.0 \times 10^{-6} \text{ sec}^{-1}$$

Table 49. Run 93, 2,4-Dinitrophenol-6-d in 9.52×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	11.53×10^{-6} M	(NaClO ₄)	0.294×10^{-6} M
$[I_2]_0$	11.49×10^{-6} M	(2,4-Dinitrophenol-6-d) ₀	147.0×10^{-6} M
$(I^-)_0$	9.52×10^{-6} M	μ	0.30
$[I^-]_0$	9.56×10^{-6} M	$[H^+]_0$	222×10^{-6} M
$[HOI]_0$	0.042×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
7048	7.619	13.5	0.140
9834	7.450	17.6	.135
13250	7.261	22.1	.130
20077	6.919	30.4	.124
25068	6.725	35.1	.119
31197	6.521	39.9	.113
35367	6.365	43.7	.113

$$F_1 = 4.251$$

$$P_1 = 26660 \text{ l/mole cm}$$

$$F_2 = 2.4 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50332 \text{ l/mole cm}$$

$$E = 2.713 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368600 \text{ l/mole cm}$$

$$k_{app0} = 0.146 \text{ l/mole sec}$$

$$k^\nabla = 0.286 \text{ l/mole sec}$$

$$k^* = 0.146 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 2.73 \times 10^{-6} \text{ sec}^{-1}$$

Table 50. Run 116, 2,4-Dinitrophenol in 4037×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	219.0×10^{-6} M	(NaClO ₄)	0.294	M
$[I_2]_0$	75.0×10^{-6} M	(2,4-Dinitrophenol) ₀	796.8	$\times 10^{-6}$ M
$(I^-)_0$	4037 $\times 10^{-6}$ M	μ	0.30	
$[I^-]_0$	3893 $\times 10^{-6}$ M	$[H^+]_0$	70.0	$\times 10^{-6}$ M
$[HOI]_0$	0.0×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
294700	78.91	27.5	0.00143
339540	76.77	30.5	.00141
389360	75.02	32.9	.00135
467800	71.72	37.4	.00133
552300	68.41	41.9	.00132
647240	65.11	46.4	.00130
738160	62.00	50.7	.00131

$$F_1 = 78.49$$

$$P_1 = 25790 \text{ l/mole cm}$$

$$F_2 = 0.0 \text{ sec}^{-1}$$

$$P_2 = 50340 \text{ l/mole cm}$$

$$E = 2.790 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 358400 \text{ l/mole cm}$$

$$k_{app0} = 1.50 \times 10^{-3} \text{ l/mole sec}$$

$$k^\nabla = 6.00 \times 10^{-3} \text{ l/mole sec}$$

$$k^* = 4.38 \times 10^{-3} \text{ l/mole sec}$$

$$k^\nabla[I^-] = 23.4 \times 10^{-6} \text{ sec}^{-1}$$

Table 51. Run 117, 2,4-Dinitrophenol-6-d in $4037 \times 10^{-6} \text{ M}$
Sodium Iodide Solution at 50.0°

$(\text{I}_2)_0$	$219.0 \times 10^{-6} \text{ M}$	(NaClO_4)	0.294	M
$[\text{I}_2]_0$	$75.0 \times 10^{-6} \text{ M}$	(2,4-Dinitro- phenol-6-d) $_0$	2049	$\times 10^{-6} \text{ M}$
$(\text{I}^-)_0$	$4037 \times 10^{-6} \text{ M}$	μ	0.30	
$[\text{I}^-]_0$	$3893 \times 10^{-6} \text{ M}$	$[\text{H}^+]_0$	70.0	$\times 10^{-6} \text{ M}$
$[\text{HOI}]_0$	$0.0 \times 10^{-6} \text{ M}$			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} ($\ell/\text{mole sec}$)
517500	109.8	29.4	0.000334
555090	108.8	30.8	.000329
646910	105.0	36.1	.000345
649700	104.8	36.4	.000347
736480	102.6	39.3	.000338
769460	98.5	44.9	.000388
940990	96.8	47.3	.000341

$$F_1 = 78.49$$

$$P_1 = 25790 \ell/\text{mole cm}$$

$$F_2 = 0.0 \text{ sec}^{-1}$$

$$P_2 = 50340 \ell/\text{mole cm}$$

$$E = 2.790 \times 10^{-6} \text{ mole cm}/\ell$$

$$P_3 = 358400 \ell/\text{mole cm}$$

$$k_{\text{app}0} = 3.39 \times 10^{-4} \ell/\text{mole sec}$$

$$k^\nabla = 13.6 \times 10^{-4} \ell/\text{mole sec}$$

$$k^* = 9.90 \times 10^{-4} \ell/\text{mole sec}$$

$$k^\nabla[\text{I}^-] = 5.29 \times 10^{-6} \text{ sec}^{-1}$$

Table 52 a. Run 114 (a), 2,4-Dinitrophenol in $2035 \times 10^{-6} \text{ M}$
Sodium Iodide Solution at 50.0°

$(\text{I}_2)_0$	$202.5 \times 10^{-6} \text{ M}$	(NaClO_4)	0.294	M
$[\text{I}_2]_0$	$103.9 \times 10^{-6} \text{ M}$	(2,4-Dinitro-phenol) $_0$	1633	$\times 10^{-6} \text{ M}$
$(\text{I}^-)_0$	$2035 \times 10^{-6} \text{ M}$	μ	0.30	
$[\text{I}^-]_0$	$1936 \times 10^{-6} \text{ M}$	$[\text{H}^+]_0$	70.0	$\times 10^{-6} \text{ M}$
$[\text{HOI}]_0$	$0.0 \times 10^{-6} \text{ M}$			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} ($\text{l}/\text{mole sec}$)
52251	94.26	30.2	0.00431
68445	90.96	35.1	.00396
79405	87.85	39.7	.00401
106934	82.22	48.1	.00388
138257	76.58	56.4	.00383

$$F_1 = 72.59$$

$$P_1 = 25790 \text{ l/mole cm}$$

$$F_2 = 0.0 \text{ sec}^{-1}$$

$$P_2 = 50340 \text{ l/mole cm}$$

$$E = 2.790 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 358400 \text{ l/mole cm}$$

For rate constants, see run no. 114 (b), Table 52 b. Run 114 (b) is comprised of two experimental points, in the measurement of which a small dilution error gave rise to slightly different concentrations and factors. The rate data for runs 114 (a) and 114 (b) are evaluated together.

Table 52 b. Run 114 (b), 2,4-Dinitrophenol in $2126 \times 10^{-6} \text{ M}$
Sodium Iodide Solution at 50.0°

$(\text{I}_2)_0$	$211.5 \times 10^{-6} \text{ M}$	(NaClO_4)	0.294	M
$[\text{I}_2]_0$	$106.3 \times 10^{-6} \text{ M}$	(2,4-Dinitro-phenol) ₀	1706	$\times 10^{-6} \text{ M}$
$(\text{I}^-)_0$	$2126 \times 10^{-6} \text{ M}$	μ	0.30	
$[\text{I}^-]_0$	$2021 \times 10^{-6} \text{ M}$	$[\text{H}^+]_0$	70.0	$\times 10^{-6} \text{ M}$
$[\text{HOI}]_0$	$0.0 \times 10^{-6} \text{ M}$			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} ($\text{l}/\text{mole sec}$)
56266	93.10	32.2	0.00413
96894	84.16	45.5	0.00379

$$F_1 = 72.59$$

$$P_1 = 24690 \text{ l/mole cm}$$

$$F_2 = 0.0 \text{ sec}^{-1}$$

$$P_2 = 48196 \text{ l/mole cm}$$

$$E = 2.914 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 341300 \text{ l/mole cm}$$

$$k_{\text{app}0} = 0.00410 \text{ l/mole sec}$$

$$k^\nabla = 0.0109 \text{ l/mole sec}$$

$$k^* = 0.00798 \text{ l/mole sec}$$

$$k^\nabla[\text{I}^-] = 21.2 \times 10^{-6} \text{ sec}^{-1}$$

The rate constants are calculated from runs no. 114 (a) and 114 (b) together.

Table 53. Run 115, 2,4-Dinitrophenol-6-d in 2035×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_o$	202.5×10^{-6} M	(NaClO ₄)	0.294	M
$[I_2]_o$	103.9×10^{-6} M	(2,4-Dinitro-phenol-6-d) _o	1891	$\times 10^{-6}$ M
$(I^-)_o$	2035×10^{-6} M	μ	0.30	
$[I^-]_o$	1936×10^{-6} M	$[H^+]_o$	70.0	$\times 10^{-6}$ M
$[HOI]_o$	0.0×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
139814	105.5	23.4	0.001022
161206	103.8	26.0	.001002
193034	100.7	30.6	.001018
229776	97.6	35.2	.001019
248165	96.6	36.6	.00099
270506	94.5	39.8	.00102
319256	91.7	43.8	.00098

$$F_1 = 72.59$$

$$P_1 = 25790 \text{ l/mole cm}$$

$$F_2 = 0.0 \text{ sec}^{-1}$$

$$P_2 = 50340 \text{ l/mole cm}$$

$$E = 2.790 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 358400 \text{ l/mole cm}$$

$$k_{appo} = 0.00102 \text{ l/mole sec}$$

$$k^\nabla = 0.00272 \text{ l/mole sec}$$

$$k^* = 0.00198 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 5.26 \times 10^{-6} \text{ sec}^{-1}$$

Table 54. Run 112, 2,4-Dinitrophenol in 1057×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	188.4×10^{-6} M	(NaClO ₄)	0.294	M
$[I_2]_0$	126.6×10^{-6} M	(2,4-Dinitrophenol) ₀	1650	$\times 10^{-6}$ M
$(I^-)_0$	1057×10^{-6} M	μ	0.30	
$[I^-]_0$	995×10^{-6} M	$[H^+]_0$	70.0	$\times 10^{-6}$ M
$[HOI]_0$	0.0×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
14178	97.96	19.3	0.0094
20428	93.29	26.8	.0094
30756	86.88	36.9	.0093
37168	85.52	39.1	.0083
43271	81.63	45.3	.0087
64690	73.08	58.9	.0087

$$F_1 = 67.58$$

$$P_1 = 25790 \text{ l/mole cm}$$

$$F_2 = 0.0 \text{ sec}^{-1}$$

$$P_2 = 50340 \text{ l/mole cm}$$

$$E = 2.790 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 358400 \text{ l/mole cm}$$

$$k_{app0} = 0.0091 \text{ l/mole sec}$$

$$k^\nabla = 0.0185 \text{ l/mole sec}$$

$$k^* = 0.0149 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 18.4 \times 10^{-6} \text{ sec}^{-1}$$

Table 55. Run 113, 2,4-Dinitrophenol-6-d in 1057×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	188.4×10^{-6} M	(NaClO ₄)	0.294	M
$[I_2]_0$	126.6×10^{-6} M	(2,4-Dinitrophenol-6-d) ₀	2038	$\times 10^{-6}$ M
$(I^-)_0$	1057×10^{-6} M	μ	0.30	
$[I^-]_0$	995×10^{-6} M	$[H^+]_0$	70.0	$\times 10^{-6}$ M
$[HOI]_0$	0.0×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
35086	110.4	15.5	0.00237
45200	108.3	18.9	.00229
65078	103.2	26.9	.00239
81347	99.7	32.5	.00241
89823	98.5	34.3	.00233
108614	94.5	40.8	.00242
117636	93.1	43.0	.00239

$$F_1 = 67.6$$

$$P_1 = 25790 \text{ l/mole cm}$$

$$F_2 = 0.0 \text{ sec}^{-1}$$

$$P_2 = 50340 \text{ l/mole cm}$$

$$E = 2.790 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 358400 \text{ l/mole cm}$$

$$k_{app0} = 0.00242 \text{ l/mole sec}$$

$$k^\nabla = 0.00493 \text{ l/mole sec}$$

$$k^* = 0.00360 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 4.91 \times 10^{-6} \text{ sec}^{-1}$$

Table 56. Run 110, 2,4-Dinitrophenol in 528×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	217	$\times 10^{-6}$	<u>M</u>	(NaClO ₄)	0.294	<u>M</u>
$[I_2]_0$	175	$\times 10^{-6}$	<u>M</u>	(2,4-Dinitrophenol) ₀	1199	$\times 10^{-6}$ <u>M</u>
$(I^-)_0$	528	$\times 10^{-6}$	<u>M</u>	μ	0.30	
$[I^-]_0$	486	$\times 10^{-6}$	<u>M</u>	$[H^+]_0$	70.0	$\times 10^{-6}$ <u>M</u>
$[HOI]_0$	0.0	$\times 10^{-6}$	<u>M</u>			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
9629	94.07	19.9	0.0196
11879	92.32	22.3	.0181
16305	87.85	28.3	.0175
20567	83.96	33.6	.0171
26973	78.52	40.9	.0170
33240	74.05	46.9	.0167
40748	68.22	54.8	.0172

$$F_1 = 77.82$$

$$P_1 = 25790 \text{ l/mole cm}$$

$$F_2 = 26.2 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50340 \text{ l/mole cm}$$

$$E = 2.790 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 358400 \text{ l/mole cm}$$

$$k_{app0} = 0.0187 \text{ l/mole sec}$$

$$k^\nabla = 0.0318 \text{ l/mole sec}$$

$$k^* = 0.0232 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 15.5 \times 10^{-6} \text{ sec}^{-1}$$

Table 57. Run 111, 2,4-Dinitrophenol-6-d in 528×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	217	$\times 10^{-6}$ M	(NaClO ₄)	0.294	M
$[I_2]_0$	175	$\times 10^{-6}$ M	(2,4-Dinitro-phenol-6-d) ₀	2148	$\times 10^{-6}$ M
$(I^-)_0$	528	$\times 10^{-6}$ M	μ	0.30	
$[I^-]_0$	486	$\times 10^{-6}$ M	$[H^+]_0$	70.0	$\times 10^{-6}$ M
$[HOI]_0$	0.0	$\times 10^{-6}$ M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
10171	125.0	11.0	0.0054
18642	118.6	19.6	.0055
27896	113.1	26.9	.0053
35611	109.0	32.3	.0052
41085	105.5	37.0	.0054
46366	103.6	39.5	.0052
51505	102.2	41.2	.0049

$$F_1 = 77.8$$

$$P_1 = 25790 \text{ l/mole cm}$$

$$F_2 = 26.2 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50340 \text{ l/mole cm}$$

$$E = 2.790 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 358400 \text{ l/mole cm}$$

$$k_{app0} = 0.00553 \text{ l/mole sec}$$

$$k^\nabla = 0.0094 \text{ l/mole sec}$$

$$k^* = 0.00686 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 4.56 \times 10^{-6} \text{ sec}^{-1}$$

Table 58. Run 106, 2,4-Dinitrophenol in 99.3×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	46.28×10^{-6} M	(NaClO ₄)	0.294	M
$[I_2]_0$	44.17×10^{-6} M	(2,4-Dinitrophenol) ₀	542.0×10^{-6}	M
$(I^-)_0$	99.3×10^{-6} M	μ	0.30	
$[I^-]_0$	97.2×10^{-6} M	$[H^+]_0$	70.0×10^{-6}	M
$[HOI]_0$	0.0×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
7138	26.92	25.6	0.077
9104	26.04	30.9	.076
10773	25.27	35.7	.077
12465	24.78	38.6	.073
15355	24.05	43.0	.069
15494	23.91	43.9	.070
20090	22.64	51.5	.068

$F_1 = 17.06$	$P_1 = 25890$ l/mole cm
$F_2 = 16.0 \times 10^{-6}$ sec ⁻¹	$P_2 = 50360$ l/mole cm
$E = 2.713 \times 10^{-6}$ mole cm/l	$P_3 = 368800$ l/mole cm
$k_{app0} = 0.080$ l/mole sec	$k^\nabla = 0.115$ l/mole sec
$k^* = 0.084$ l/mole sec	$k^\nabla[I^-] = 11.18 \times 10^{-6}$ sec ⁻¹

Table 59. Run 107, 2,4-Dinitrophenol-6-d in $99.3 \times 10^{-6} \text{ M}$
Sodium Iodide Solution at 50.0°

$(\text{I}_2)_0$	$46.28 \times 10^{-6} \text{ M}$	(NaClO ₄)	0.294	<u>M</u>
$[\text{I}_2]_0$	$44.17 \times 10^{-6} \text{ M}$	(2,4-Dinitro- phenol-6-d) ₀	$530.6 \times 10^{-6} \text{ M}$	<u>M</u>
$(\text{I}^-)_0$	$99.3 \times 10^{-6} \text{ M}$	μ	0.30	
$[\text{I}^-]_0$	$97.2 \times 10^{-6} \text{ M}$	$[\text{H}^+]_0$	$70.0 \times 10^{-6} \text{ M}$	<u>M</u>
$[\text{HOI}]_0$	$0.0 \times 10^{-6} \text{ M}$			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} ($\ell/\text{mole sec}$)
12076	27.89	17.1	0.0296
14959	27.45	19.6	.0278
20791	26.53	24.9	.0263
30172	25.12	33.1	.0255
38710	24.10	38.8	.0244
43673	23.47	42.5	.0244
48348	23.03	44.9	.0237

$$F_1 = 17.06$$

$$P_1 = 25890 \ell/\text{mole cm}$$

$$F_2 = 16.0 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50360 \ell/\text{mole cm}$$

$$E = 2.713 \times 10^{-6} \text{ mole cm}/\ell$$

$$P_3 = 368800 \ell/\text{mole cm}$$

$$k_{\text{app}0} = 0.0280 \ell/\text{mole sec}$$

$$k^\nabla = 0.040 \ell/\text{mole sec}$$

$$k^* = 0.0293 \ell/\text{mole sec}$$

$$k^\nabla[\text{I}^-] = 3.89 \times 10^{-6} \text{ sec}^{-1}$$

Table 60. Run 104, 2,4-Dinitrophenol in 49.64×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	23.90×10^{-6} M	(NaClO ₄)	0.294	M
$[I_2]_0$	23.33×10^{-6} M	(2,4-Dinitrophenol) ₀	241.7×10^{-6}	M
$(I^-)_0$	49.64×10^{-6} M	μ	0.30	
$[I^-]_0$	49.07×10^{-6} M	$[H^+]_0$	70.0×10^{-6}	M
$[HOI]_0$	0.057×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
6359	13.73	16.4	0.118
9719	12.98	25.5	.127
13805	12.32	33.3	.124
16722	11.90	38.4	.123
20359	11.41	44.3	.122
22056	11.18	47.0	.122
25469	10.83	51.3	.120

$$F_1 = 8.810$$

$$P_1 = 25970 \text{ l/mole cm}$$

$$F_2 = 1.90 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50360 \text{ l/mole cm}$$

$$E = 2.713 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368600 \text{ l/mole cm}$$

$$k_{app0} = 0.135 \text{ l/mole sec}$$

$$k^\nabla = 0.189 \text{ l/mole sec}$$

$$k^* = 0.138 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 9.3 \times 10^{-6} \text{ sec}^{-1}$$

Table 61. Run 105, 2,4-Dinitrophenol-6-d in 49.64×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_o$	23.90×10^{-6} M	(NaClO ₄)	0.294	M
$[I_2]_o$	23.33×10^{-6} M	(2,4-Dinitrophenol-6-d) _o	292.1×10^{-6}	M
$(I^-)_o$	49.64×10^{-6} M	μ	0.30	
$[I^-]_o$	49.07×10^{-6} M	$[H^+]$	70.0×10^{-6}	M
$[HOI]_o$	0.057×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
14891	14.75	20.4	0.0524
19061	14.42	24.3	.0502
25677	13.54	34.9	.0577
34240	13.19	39.1	.0500
39784	12.88	42.8	.0486
46555	12.30	49.8	.0514
52934	12.15	51.4	.0474

$$F_1 = 8.81$$

$$P_1 = 25970 \text{ l/mole cm}$$

$$F_2 = 1.9 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50360 \text{ l/mole cm}$$

$$E = 2.713 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368600 \text{ l/mole cm}$$

$$k_{appo} = 0.0545 \text{ l/mole sec}$$

$$k^\nabla = 0.080 \text{ l/mole sec}$$

$$k^* = 0.0558 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 3.90 \times 10^{-6} \text{ sec}^{-1}$$

Table 62. Run 98, 2,4-Dinitrophenol in 9.93×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	8.76×10^{-6} M	(NaClO ₄)	0.294	M
$[I_2]_0$	8.67×10^{-6} M	(2,4-Dinitrophenol) ₀	155.1×10^{-6}	M
$(I^-)_0$	9.93×10^{-6} M	μ	0.30	
$[I^-]_0$	10.02×10^{-6} M	$[H^+]_0$	70.0×10^{-6}	M
$[HOI]_0$	0.089×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
3936	6.490	26.4	0.513
3995	6.519	25.4	.483
5135	6.315	32.2	.499
6051	6.189	36.3	.493
7911	5.965	43.8	.482
10194	5.733	51.4	.471
11468	5.683	53.1	.439

$$F_1 = 3.229$$

$$P_1 = 26520 \text{ l/mole cm}$$

$$F_2 = 0.0 \text{ sec}^{-1}$$

$$P_2 = 50360 \text{ l/mole cm}$$

$$E = 2.713 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368600 \text{ l/mole cm}$$

$$k_{app0} = 0.563 \text{ l/mole sec}$$

$$k^\nabla = 0.780 \text{ l/mole sec}$$

$$k^* = 0.569 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 7.82 \times 10^{-6} \text{ sec}^{-1}$$

Table 63. Run 99, 2,4-Dinitrophenol-6-d in 9.93×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	8.76×10^{-6} M	(NaClO ₄)	0.294	M
$[I_2]_0$	8.67×10^{-6} M	(2,4-Dinitrophenol-6-d) ₀	173.9×10^{-6}	M
$(I^-)_0$	9.93×10^{-6} M	μ	0.30	
$[I^-]_0$	10.02×10^{-6} M	$[H^+]_0$	70.0×10^{-6}	M
$[HOI]_0$	0.089×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
5394	7.258	16.9	0.202
6934	7.102	22.1	.212
8583	6.966	26.6	.212
10844	6.830	31.1	.202
15430	6.558	40.1	.196
20158	6.315	48.2	.193
23614	6.150	53.6	.193

$$F_1 = 3.229$$

$$P_1 = 26520 \text{ l/mole cm}$$

$$F_2 = 0.0 \text{ sec}^{-1}$$

$$P_2 = 50360 \text{ l/mole cm}$$

$$E = 2.713 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368600 \text{ l/mole cm}$$

$$k_{app0} = 0.230 \text{ l/mole sec}$$

$$k^\nabla = 0.317 \text{ l/mole sec}$$

$$k^* = 0.232 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 3.18 \times 10^{-6} \text{ sec}^{-1}$$

Table 64. Run 100, 2,4-Dinitrophenol in 4.964×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	5.97×10^{-6} M	(NaClO ₄)	0.294	M
$[I_2]_0$	5.85×10^{-6} M	(2,4-Dinitrophenol) ₀	104.4×10^{-6}	M
$(I^-)_0$	4.964×10^{-6} M	μ	0.30	
$[I^-]_0$	5.08×10^{-6} M	$[H^+]_0$	70.0×10^{-6}	M
$[HOI]_0$	0.119×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
2002	4.537	19.0	1.03
2836	4.421	24.7	0.98
3894	4.275	31.7	0.96
5722	4.071	41.7	0.93
7280	3.954	47.4	0.87
9176	3.828	53.5	0.82
10594	3.740	57.8	0.81

$$F_1 = 2.199$$

$$P_1 = 26520 \text{ l/mole cm}$$

$$F_2 = 0.0 \text{ sec}^{-1}$$

$$P_2 = 50360 \text{ l/mole cm}$$

$$E = 2.713 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368600 \text{ l/mole cm}$$

$$k_{app0} = 1.11 \text{ l/mole sec}$$

$$k^\nabla = 1.55 \text{ l/mole sec}$$

$$k^* = 1.13 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 7.9 \times 10^{-6} \text{ sec}^{-1}$$

Table 65. Run 101, 2,4-Dinitrophenol-6-d in 4.964×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	5.97×10^{-6} M	(NaClO ₄)	0.294	M
$[I_2]_0$	5.85×10^{-6} M	(2,4-Dinitro-phenol-6-d) ₀	95.5×10^{-6}	M
$(I^-)_0$	4.964×10^{-6} M	μ	0.30	
$[I^-]_0$	5.08×10^{-6} M	$[H^+]_0$	70.0×10^{-6}	M
$[HOI]_0$	0.119×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
6830	4.227	22.7	0.404
9416	4.081	29.8	.404
11173	3.964	35.5	.423
12693	3.925	37.4	.398
14183	3.886	39.3	.379
17367	3.780	44.5	.366
21582	3.653	50.6	.354

$$F_1 = 2.199$$

$$P_1 = 26520 \text{ l/mole cm}$$

$$F_2 = 0.0 \text{ sec}^{-1}$$

$$P_2 = 50360 \text{ l/mole cm}$$

$$E = 2.713 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368600 \text{ l/mole cm}$$

$$k_{app0} = 0.470 \text{ l/mole sec}$$

$$k^\nabla = 0.658 \text{ l/mole sec}$$

$$k^* = 0.480 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 3.34 \times 10^{-6} \text{ sec}^{-1}$$

Table 66. Run 102, 2,4-Dinitrophenol in 2.473×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	2.998×10^{-6} M	(NaClO ₄)	0.294 M
$[I_2]_0$	2.882×10^{-6} M	(2,4-Dinitrophenol) ₀	60.60×10^{-6} M
$(I^-)_0$	2.473×10^{-6} M	μ	0.30
$[I^-]_0$	2.589×10^{-6} M	$[H^+]_0$	70.0×10^{-6} M
$[HOI]_0$	0.116×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
2017	2.496	17.8	1.64
2868	2.438	23.5	1.57
4293	2.341	33.0	1.57
5420	2.273	39.6	1.57
6533	2.224	44.4	1.52
8200	2.185	48.2	1.36
9625	2.108	55.7	1.44

$$F_1 = 1.095$$

$$P_1 = 26520 \text{ l/mole cm}$$

$$F_2 = 0.0 \text{ sec}^{-1}$$

$$P_2 = 50360 \text{ l/mole cm}$$

$$E = 2.713 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368600 \text{ l/mole cm}$$

$$k_{app0} = 1.85 \text{ l/mole sec}$$

$$k^\nabla = 2.63 \text{ l/mole sec}$$

$$k^* = 1.93 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 6.8 \times 10^{-6} \text{ sec}^{-1}$$

Table 67. Run 103, 2,4-Dinitrophenol-6-d in 2.473×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	2.998×10^{-6} M	(NaClO ₄)	0.294	M
$[I_2]_0$	2.882×10^{-6} M	(2,4-Dinitro-phenol-6-d) ₀	63.23×10^{-6}	M
$(I^-)_0$	2.473×10^{-6} M	μ	0.30	
$[I^-]_0$	2.589×10^{-6} M	$[H^+]_0$	70.0×10^{-6}	M
$[HOI]_0$	0.116×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
5097	2.545	19.7	0.70
7652	2.477	26.4	.65
9652	2.390	34.9	.72
11961	2.351	38.7	.66
14437	2.292	44.4	.66
16480	2.263	47.3	.63
20544	2.195	53.9	.61

$$F_1 = 1.095$$

$$P_1 = 26520 \text{ l/mole cm}$$

$$F_2 = 0.0 \text{ sec}^{-1}$$

$$P_2 = 50360 \text{ l/mole cm}$$

$$E = 2.713 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368600 \text{ l/mole cm}$$

$$k_{app0} = 0.78 \text{ l/mole sec}$$

$$k^\nabla = 1.11 \text{ l/mole sec}$$

$$k^* = 0.81 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 2.87 \times 10^{-6} \text{ sec}^{-1}$$

Table 68. Data on Iodination of 2,4-Dinitrophenol at Temperature, 50.0°; μ , 0.0030

Table Ref.	$[I^-] \times 10^6$ (mole/l)	$[ArO^-] \times 10^6$ (mole/l)	$[I_2] \times 10^6$ (mole/l)	$[H^+] \times 10^6$ (mole/l)	k^∇ (l/mole sec)	$k^\nabla [I^-] \times 10^6$ (sec ⁻¹)	$1/k^\nabla$ (mole sec/l)
31	108.4	162	26.5	30.0	0.098	10.6	10.2
33	33.0	47.9	9.8	30.0	0.267	8.8	3.75
35	10.6	32.5	5.9	30.0	0.73	7.8	1.36
37	1.16	3.29	0.50	30.0	7.9	9.2	0.126
39	1.10	3.34	0.58	30.0	7.3	8.0	0.137
41	0.325	3.16	0.386	30.0	21.4	6.9	0.047
42	1.01	1.32	0.67	302.	6.2	6.2	0.162
43	0.95	3.52	0.147	3.88	13.0	12.4	0.077

Table 69. Data on Iodination of 2,4-Dinitrophenol-6-d at Temperature, 50.0°; μ , 0.0030

Table Ref.	$[I^-] \times 10^6$ (mole/l)	$[ArO^-] \times 10^6$ (mole/l)	$[I_2] \times 10^6$ (mole/l)	$[H^+] \times 10^6$ (mole/l)	k^∇ (l/mole sec)	$k^\nabla [I^-] \times 10^6$ (sec ⁻¹)	$1/k^\nabla$ (mole sec/l)
32	108.4	162	26.5	30.0	0.0345	3.74	29.0
34	33.0	47.5	9.8	30.0	0.108	3.56	9.3
36	10.6	32.1	5.9	30.0	0.285	3.03	3.51
38	1.16	3.27	0.50	30.0	3.45	4.00	0.290
40	0.325	3.29	0.386	30.0	9.4	3.05	0.107

Table 70. 2,4-Dinitrophenol Isotope Effect at Temperature,
 50.0°; μ , 0.0030; $[H^+]$, 30×10^{-6} M

Table Ref.	$[I^-] \times 10^6$ (mole/l)	k_H^∇ (l/mole sec)	k_D^∇ (l/mole sec)	k_H^∇/k_D^∇
31, 32	108.4	0.098	0.0345	2.84
33, 34	33.0	0.267	0.108	2.47
35, 36	10.6	0.733	0.285	2.57
37, 38	1.16	7.93	3.45	2.30
40, 41	0.325	21.4	9.4	2.28

Table 71. Data on Straight Line Portions of $1/k^{\nabla}$ vs $[I^-]$
Plots for 2,4-Dinitrophenol and 2,4-Dinitro-
phenol-6-d at 50.0°

$[H^+] \times 10^5$ (mole/l)	μ	Iodide Concentration Range	Slope $\times 10^{-5}$ (sec)	Intercept (l/mole sec)	$k_H^{\nabla}/k_D^{\nabla}$
2,4-Dinitrophenol					
30.0	0.0030	low	1.24 ± 0.14		
192	0.30	low	1.36		
70	0.30	low	1.34 ± 0.12		
70	0.30	high	0.42 ± 0.01	10	
1.70	0.30	low	0.69 ± 0.03		
2,4-Dinitrophenol-6-d					
30.0	0.0030	low	2.98 ± 0.40		2.40 ± 0.32
192	0.30	low	3.36		2.47
70	0.30	low	3.23 ± 0.25		2.42 ± 0.27
70	0.30	high	1.90 ± 0.03	10	4.7 ± 0.1
1.70	0.30	low	2.10 ± 0.08		3.04 ± 0.18

Table 72. Data on Iodination of 2,4-Dinitrophenol at Temperature, 50.0°; μ , 0.30

Table Ref.	$[I^-] \times 10^6$ (mole/l)	$[ArO^-] \times 10^6$ (mole/l)	$[I_2] \times 10^6$ (mole/l)	$[H^+] \times 10^6$ (mole/l)	k^∇ (l/mole sec)	$k^\nabla [I^-] \times 10^6$ (sec ⁻¹)	$1/k^\nabla$ (mole sec/l)
50	3890	586	75	70	0.0059	22.8	169
52	1940	1100	104	70	0.0113	21.9	89
54	995	1213	127	70	0.0196	19.5	51
56	486	881	175	70	0.0330	16.0	30.3
58	97.2	398	44.2	70	0.114	11.1	8.8
60	49.1	178	23.3	70	0.188	9.2	5.3
62	10.0	114	8.7	70	0.78	7.8	1.29
64	5.08	76.7	5.9	70	1.54	7.8	0.65
66	2.59	44.5	2.88	70	2.61	6.8	0.383
44	10.6	47.7	3.43	1.81	1.29	13.7	0.78
46	3.62	26.0	0.79	1.71	4.04	14.6	0.248
48	9.57	41.0	11.5	192	0.77	7.4	1.30

Table 73. Data on Iodination of 2,4-Dinitrophenol-6-d at Temperature, 50.0°; μ , 0.0030

Table Ref.	$[I^-] \times 10^6$ (mole/l)	$[ArO^-] \times 10^6$ (mole/l)	$[I_2] \times 10^6$ (mole/l)	$[H^+] \times 10^6$ (mole/l)	k^∇ (l/mole sec)	$k^\nabla [I^-] \times 10^6$ (sec ⁻¹)	$1/k^\nabla$ (mole sec/l)
51	3890	1506	75.0	70.0	0.00137	5.33	730
53	1940	1390	104	70.0	0.00276	5.34	362
55	995	1498	127	70.0	0.00500	4.97	200
57	486	1579	175	70.0	0.00963	4.69	104
59	97.2	390	44.2	70.0	0.0400	3.86	25.0
61	49.1	215	23.3	70.0	0.0789	3.87	12.7
63	10.0	128	8.67	70.0	0.315	3.16	3.17
65	5.08	70.2	5.85	70.0	0.653	3.32	1.53
67	2.59	44.5	2.88	70.0	1.10	2.85	0.91
45	10.6	89.8	3.43	1.91	0.425	4.53	2.35
47	3.62	33.1	0.79	1.77	1.40	5.07	0.72
49	222	71.9	11.5	222	0.312	2.98	3.21

Table 74. 2,4-Dinitrophenol Isotope Effect at Temperature,
 50.0°; μ , 0.30; $[H^+]$, 70×10^{-6} M

Table Ref.	$[I^-] \times 10^6$ (mole/l)	k_H^∇ (l/mole sec)	k_D^∇ (l/mole ^D sec)	k_H^∇/k_D^∇
50, 51	3890	0.0059	0.00137	4.31
52, 53	1940	0.0113	0.00276	4.09
54, 55	995	0.0196	0.0050	3.92
56, 57	486	0.0330	0.0096	3.43
58, 59	97.2	0.114	0.0400	2.85
60, 61	49.1	0.188	0.079	2.38
62, 63	10.0	0.78	0.315	2.46
64, 65	5.08	1.54	0.65	2.36
66, 67	2.59	2.61	1.10	2.37

Table 75. Values of $k_1'K_1 + \frac{k_1''K_2[OH^-]}{K_w}$ for 2,4-Dinitrophenol and 2,4-Dinitrophenol-6-d at Temperature, 50.0°; μ , 0.30

$[H^+] \times 10^6$ (mole/l)	$[OH^-] \times 10^{10}$ (mole/l)	$\left(k_1'K_1 + \frac{k_1''K_2[OH^-]}{K_w}\right) \times 10^{-5}$ (sec ⁻¹)
2,4-Dinitrophenol		
1.70	500	3.70 ± 0.12
70	12	1.09 ± 0.11
192	4.4	1.06
2,4-Dinitrophenol-6-d		
1.70	500	5.0 ± 2.3
70	12	0.75 ± 0.14
222	3.8	0.68

Table 76. Calculated vs Observed Values of $1/k^{\nabla}$ for 2,4-Dinitrophenol and 2,4-Dinitrophenol 6-d at Temperature, 50.0°; $[H^+]$, 70×10^{-8} M; μ , 0.30

Table Ref.	$[I^-] \times 10^8$ (mole/l)	$1/k^{\nabla}$ (obs.) (mole sec/l)	$1/k^{\nabla}$ (calc.) (mole sec/l)
2,4-Dinitrophenol			
50	3890	169	171
52	1940	89	90
54	995	51	51
56	486	30.3	28.5
58	97.2	8.8	8.9
60	49.1	5.3	5.3
62	10.0	1.29	1.30
64	5.08	0.65	0.68
66	2.59	0.383	0.354
2,4-Dinitrophenol-6-d			
51	3890	730	748
53	1940	362	377
55	995	200	197
57	486	104	101
59	97.2	25.0	24.3
61	49.1	12.7	13.4
63	10.0	3.17	3.14
65	5.08	1.53	1.63
67	2.59	0.91	0.85

CHAPTER VI

IODINATION OF p-NITROPHENOLIntroduction

Grovenstein and Aprahamian investigated the iodination of p-nitrophenol and p-nitrophenol-2,6-d over the iodide ion concentration range $12200 \times 10^{-6} \text{ M}$ to $9.5 \times 10^{-6} \text{ M}$.^(59, 104) The experiments were performed at a temperature of 50.0° and ionic strength of 0.30; hydrogen ion concentration was varied between 0.00109 M and 0.0491 M .

At $0.00982 \text{ M} [\text{H}^+]$, the acidity at which most of the data were collected, a $1/k^*[\text{H}^+]$ versus $[\text{I}^-]$ plot gave a straight line with a positive intercept for both the protio and the deuterio compounds. The isotope effect decreased with decreasing iodide ion concentration (from 5.6 at $6000 \times 10^{-6} \text{ M} [\text{I}^-]$ to 2.1 at $9.5 \times 10^{-6} \text{ M} [\text{I}^-]$), as did $k^*[\text{I}^-]$ (from $52.2 \times 10^{-7} \text{ sec}^{-1}$ at $12200 \times 10^{-6} \text{ M} [\text{I}^-]$ to $14.6 \times 10^{-7} \text{ sec}^{-1}$ at $9.5 \times 10^{-6} \text{ M} [\text{I}^-]$). The value of $k^*[\text{I}^-]$ was unaffected, at similar iodide ion concentrations, by changes in the concentrations of iodine and of the phenol.

While $k^*[\text{H}^+]$ appeared to be independent of hydrogen ion concentration at high iodide ion concentrations, $k^*[\text{H}^+]$ increased with increasing hydrogen ion concentration at low iodide ion concentrations,

104. N. S. Aprahamian, The Kinetics and Mechanism of Iodination of Phenol, p-Nitrophenol, Anisole and Their Deuterated Derivatives, Ph.D. Thesis, Georgia Institute of Technology, 1960, pp. 63-126, 192-220.

as can be seen in Table 85. (The term $k^*[\text{H}^+][\text{I}^-]$ is a better basis for evaluating the effect of hydrogen ion concentration upon k^* , since the effect of slight differences in iodide ion concentration is partially eliminated in the $k^*[\text{H}^+][\text{I}^-]$ value.)

From these results, it appeared that the iodination of p-nitrophenoxide anion was correctly described by mechanism II (molecular iodine) over the iodide ion concentration range of $12200 \times 10^{-6} \text{ M}$ to $9.5 \times 10^{-6} \text{ M}$, and that at $0.00982 \text{ M} [\text{H}^+]$, the iodination of undissociated p-nitrophenol contributed significantly to the value of k^* . Grovenstein and Aprahamian assumed that both p-nitrophenol and p-nitrophenoxide were iodinated by molecular iodine. The equation for such a mechanism, obtained by eliminating from equation (16), Chapter IV, the terms representing iodination by hypiodous acidium ion, is

$$\frac{1}{k^*[\text{H}^+]} = \frac{k-1}{k_1 k_3 K_2} [\text{I}^-] + \frac{1}{k_1 K_2 + k_2 [\text{H}^+]} \quad (1)$$

From this equation and the experimental data, Grovenstein and Aprahamian calculated values of $\frac{k-1}{k_1 k_3 K_2} = 205 \pm 9 \times 10^5 \frac{\text{sec } l}{\text{mole}}$, $k_2 \approx 0.051 \frac{l}{\text{mole sec}}$, and $k_1 K_2 \approx 0.0010 \text{ sec}^{-1}$.

In the work to be reported here, it was undertaken to extend the p-nitrophenoxide kinetic study to lower iodide ion concentrations. Such an extension should increase the probability of hypiodous acidium ion becoming significantly involved in the iodination of p-nitrophenoxide,

although this was not actually the reason for doing the work.[†]

Specific Experimental Details

The kinetics were studied at a temperature of 50.0° and at ionic strength 0.0030. The acidity of the reaction mixtures was $200 \times 10^{-8} \text{ M}$ $[\text{H}^+]$. The dissociation constant of p-nitrophenol is low enough, 12.7×10^{-8} mole/l at 50°, ⁽¹⁰⁵⁾ that acidity could be controlled simply by introducing the requisite concentration of perchloric acid into the reaction solution.

As was true in the 2,4-dinitrophenol work, the aromatic species present in the quenched solutions exhibited considerable absorption in the spectral regions available for triiodide measurement. In this case also, it was necessary to buffer the quenched solutions so as to achieve reproducible relative concentrations of p-nitrophenol and p-nitrophenoxide, and of 2-iodo-4-nitrophenol and 2-iodo-4-nitrophenoxide. A wavelength setting of 3475 Å was experimentally determined to be optimum for the spectral measurements, at which wavelength the extinction coefficient of triiodide was determined, as described in Chapter III, to be 26,200. The extinction coefficient of undissociated p-nitrophenol was measured,

[†]This work was done prior to the 2,4-dinitrophenol experiments, which provided the first evidence for the operation of the combined mechanism III. The original purpose was to determine whether the p-nitrophenol and p-nitrophenol-2,6-d had the same intercept on a $\frac{1}{k^*[\text{H}^+]}$ versus $[\text{I}^-]$ plot; i.e., whether there was any isotope effect in k_1 .

105. A. R. Olson, E. F. Orlemann, and C. W. Koch, Introductory Quantitative Analysis, W. H. Freeman & Co., San Francisco, 1948, p. 176.

in solution of hydrogen ion concentration 20×10^{-6} M and ionic strength 0.0030, to be 5208, and the extinction coefficient of p-nitrophenoxide was measured, in a solution of hydroxide ion concentration 0.030 M and ionic strength 0.0030, to be 5349.

The chosen buffer composition of the quenched solutions was 192×10^{-6} M [HCO_3^-] and 192×10^{-8} M [H_2CO_3]. This was achieved in the following way. The reaction solution was first cooled down to about 25°C in an ice bath. At this temperature, the volume of the reaction solution was 47.6 ml and the hydrogen ion concentration was 202×10^{-6} M. One ml of a water solution of 0.38 g sodium iodide was then delivered with a 1.0 ml pipette, followed by one ml of 1.92×10^{-2} M sodium bicarbonate. The final volume of the quenched solution, therefore, was 49.6 ml, and it contained the above noted concentrations of bicarbonate and carbonic acid.

It was then necessary to determine the effective extinction coefficients, as defined in Chapter V, in the quenched and buffered solution of the p-nitrophenol--p-nitrophenoxide couple and of the 2-iodo-4-nitrophenol--2-iodo-4-nitrophenoxide couple. The effective p-nitrophenol was measured as 5389,[†] and the effective extinction coefficient of 2-iodo-4-

[†]Since the ratio $[\text{ArO}^-]/[\text{ArOH}]$ in the quenched and buffered solution should be $\frac{1}{3}$, on the basis of a dissociation constant for carbonic acid of 4.3×10^{-7} mole/l⁽¹⁰⁵⁾ and a dissociation constant for p-nitrophenol of 1.3×10^{-7} mole/l⁽¹⁰⁶⁾ the effective extinction coefficient might be predicted to be 5243, in light of the extinction coefficients for the phenol and the phenoxide. This three percent difference may be due to experimental error, although it must also be pointed out that the three spectral measurements were made in the environment of different species; the extinction coefficient of the undissociated phenol was determined in 2.0×10^{-5} M perchloric acid and 0.0030 μ sodium perchlorate, the extinction coefficient of the phenoxide ion was measured (continued)

nitrophenol as 4228.[‡] The temperature of the quenched solution, the slit width of the spectrophotometer, and the amount of delivered sodium bicarbonate solution were all varied to an extent greater than the possible variations in the actual kinetic measurements, and they were found to have no discernable effect upon effective extinction coefficients.

Since it was desired to make a kinetic measurement on the iodination of 2-iodo-4-nitrophenol, an effective extinction coefficient was also necessary on 2,6-diiodo-4-nitrophenol, the expected product of such a reaction. This was determined to be 3023.

The background absorbance in the quenched solutions, including oxidation of iodide to iodine during quenching, was experimentally measured as 0.007. This correction was applied to all samples and blanks.

The k_{app} values were obtained from the experimental results using equations (1) and (7) of Chapter V. In the case of p-nitrophenol, the values of P_1 , P_2 , and P_3 are, of course, different from those for the 2,4-dinitrophenol experiments, reflecting the different effective extinction coefficients and the different ratio of volume of reaction solution

in 0.0030 μ sodium hydroxide, and the effective extinction coefficient was measured in a solution containing 0.0029 M sodium perchlorate, 192×10^{-6} M carbonic acid, 192×10^{-6} M sodium bicarbonate, and 0.050 M sodium iodide.

[‡]All absorbance measurements encountered in the determination of extinction coefficients were corrected for absorbance by species other than the phenol-phenoxide couple of interest.

to quenched solution. The P_1 , P_2 , and P_3 values are included in the tabulated results on the p-nitrophenol work, in Tables 77-84.

Extrapolations of k_{app} to k_{app0} were made according to the scheme described in Chapter III. The first approximation $1/k^*$ versus $[I^-]$ plots, using average k_{app} values, had to be drawn through only three points each for p-nitrophenol and p-nitrophenol-2,6-d. For reasons described later, a straight line was drawn between the $27 \times 10^{-6} \text{ M } [I^-]$ point and the $1 \times 10^{-6} \text{ M } [I^-]$ point; another straight line was drawn between the $1 \times 10^{-6} \text{ M } [I^-]$ point and the $2 \times 10^{-7} \text{ M } [I^-]$ point. The k_{app} values for use in estimating values of \underline{n} were taken from these plots, and the \underline{n} values were used to obtain the values of k_{app0} from the experimental data.

In the case of the iodination of 2-iodo-4-nitrophenol, only one kinetic experiment was performed, at $1 \times 10^{-6} \text{ M } [I^-]$. Since there was therefore no basis for a choice of an \underline{n} value, the average k_{app} value was called k_{app0} .

The k_{app0} values were translated into k^* values in the usual way, taking into account the hydrolysis of iodine and triiodide formation.

Experiments no. 15 and 16 (Tables 80 and 84), which were the first runs in the series, were apparently made when the reaction flasks were not sufficiently free of iodine-consuming impurities, giving rise to large blank drops. This reduces the reliability of these results. Experiment no. 16 is on a 2-iodo-4-nitrophenol, for which only an approximate value of k^* was necessary in order to estimate the possible complication of diiodination. Experiment no. 15, the iodination of p-nitrophenol at $1 \times 10^{-6} \text{ M } [I^-]$, was later repeated (experiment no. 19, Table

79).

Tables 79, 80, and 84 show that k^* for p-nitrophenol and 2-iodo-4-nitrophenol are similar at $200 \times 10^{-6} \text{ M } [H^+]$ and $1 \times 10^{-6} \text{ M } [I^-]$. (This probably reflects a smaller rate constant for 2-iodo-4-nitrophenoxide anion than for p-nitrophenoxide anion and a larger dissociation constant for 2-iodo-4-nitrophenol than for p-nitrophenol.) The similarity of these rate constants, plus the approximately four-fold excess of p-nitrophenol over iodine employed in all of these runs, predicts that the effect of diiodination upon the kinetic results will be about five percent.[†]

However, since the p-nitrophenol data are insufficient for the evaluation of individual rate constants and are used only for qualitative comparison with Aprahamian's results (which are, in any case, at a grossly different ionic strength), no attempt was made to correct k^* for diiodination.

In several experiments, reaction flasks were quenched after less than 15 percent reaction; the rate constants from such kinetic points depend upon very small differences in absorbance readings, and they are

[†]This approximation is based on the following considerations. Since the ratio $(I_2)_0 / (ArOH)_0$ equals four, six percent of $(ArOH)_0$ will have been consumed after 25 percent consumption of $(I_2)_0$. During the course of this amount of reaction, the average $(IArOH)$ will be about three percent of $(ArOH)_0$, and therefore about three percent of the consumed iodine will be consumed by $IArOH$ and 97 percent by $ArOH$, because the rates of iodination of $IArOH$ and $ArOH$ are similar. This causes k_{app} to be three percent too high. Similar considerations predict about six percent error at 50 percent iodine consumption. The k_{app} measurements have been made over a range of about 25 percent to 50 percent iodine consumption, predicting an approximate average error of five percent.

inherently inaccurate. Such kinetic points have not been included in the tables.

Results and Discussion

The data on p-nitrophenol and p-nitrophenol-2,6-d are displayed in Tables 86, 87, and 88 and in Figures 16 and 17. The small amount of work done, consisting of only three protio and three deuterio points (one of the protio points being represented by approximately duplicate runs), is not, by itself, sufficient for any mechanistic conclusions. However, in this discussion, these results are considered in light of the results of Grovenstein and Aprahamian.⁽⁵⁹⁾ The low-iodide extrapolations of the $\frac{1}{k^*[\text{H}^+]}$ versus $[\text{I}^-]$ lines reported in that paper[†] are included in Figure 17 and are extended to the zero iodide intercept.

The results being reported here for p-nitrophenol and p-nitrophenol-2,6-d were obtained at a different acidity and a different ionic strength than the work of Grovenstein and Aprahamian; therefore, they would not be expected to fall on the same plots. However, if mechanism II holds, then $\frac{1}{k^*[\text{H}^+]}$ versus $[\text{I}^-]$ plots of the present data should also be straight lines with positive intercepts.

It can be seen from Figure 17 that, if a straight line is drawn between the $27 \times 10^{-6} \text{ M } [\text{I}^-]$ and $1 \times 10^{-6} \text{ M } [\text{I}^-]$ points on $\frac{1}{k^*[\text{H}^+]}$ versus

[†]The protio line is drawn from the value of slope ($205 \pm 9 \times 10^5 \text{ sec } \ell/\text{mole}$) and intercept ($660 \pm 60 \text{ sec}^{-1}$) given in the paper; the deuterio line is reconstructed from the protio line and the calculated isotope effect values at different iodide ion concentrations given in Table V of the paper.

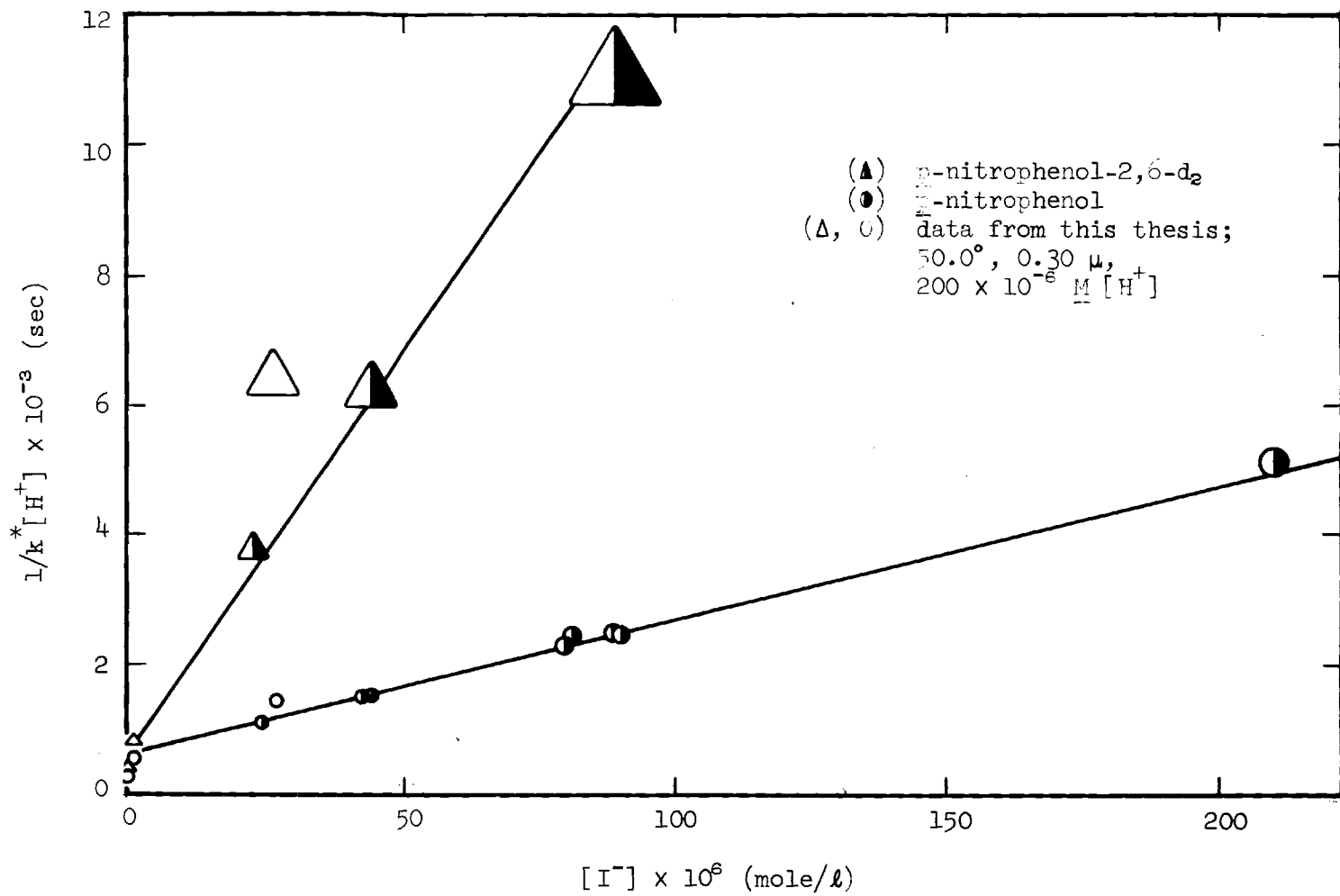


Figure 16. p-Nitrophenol and p-Nitrophenol-4,6-d at Temperature, 50.0°; Ionic Strength, 0.30; [H⁺], 0.00982 M; Data of N. S. Aprahamian

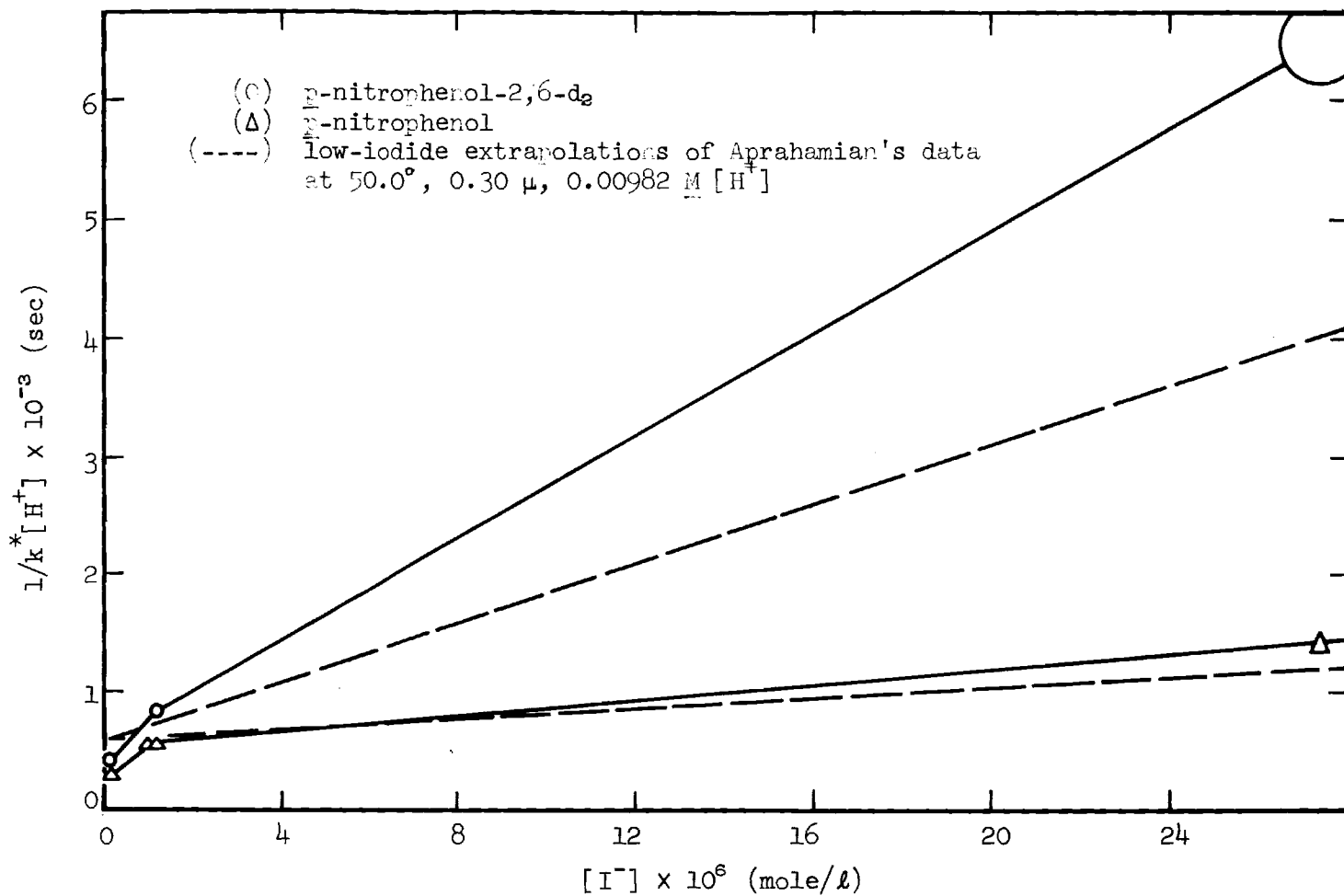


Figure 17. p -Nitrophenol and p -Nitrophenol-4,6-d at Temperature, 50.0°;
 Ionic Strength, 0.0030; [H⁺], 200 × 10⁻⁸ M; Data of N. S.
 Aprahamian

$[I^-]$ plots for the protio and deuterio p-nitrophenol, then curvature toward the origin must be invoked in order to join this line to the $2 \times 10^{-7} \text{ M } [I^-]$ point. It is, of course, conceivable that the curvature is due to experimental error. However, this seems unlikely because there are approximately duplicate points for $1 \times 10^{-6} \text{ M } [I^-]$ (although one is of questionable value, as has been noted), and because the apparent curvature shows up in both the protio and deuterio compounds. Also, the measured isotope effect at $2 \times 10^{-7} \text{ M } [I^-]$ is 1.24 (Table 88), whereas extension of Aprahamian's data to this iodide ion concentration predicts an isotope effect of 1.05, and extension of the lines between the $27 \times 10^{-6} \text{ M } [I^-]$ and $1 \times 10^{-6} \text{ M } [I^-]$ points for the present data predicts an isotope effect of 1.10; if curvature toward the origin were in fact occurring by reason of the introduction of hypiodous acidium ion as a significant iodinating agent, as occurs in the case of 2,4-dinitrophenoxide, such a positive deviation from the predicted isotope effect might be expected.[†]

For these reasons, the data reported here on the iodination of p-nitrophenol and p-nitrophenol-2,6-d are considered to indicate iodination by molecular iodine and hypiodous acidium ion. The question arises, then, of which species (phenol or phenoxide) is iodinated by which iodinating agent (molecular iodine or hypiodous acidium ion).

[†]If the curvature toward the origin were not observed, the isotope effect of 1.24 might have been interpreted as a secondary isotope effect; i.e., the isotope effect of the intercept, representing

$$\frac{1}{k_1 K_2 + k_2 [H^+]}$$

Consideration of Aprahamian's results at varying pH is instructive on this point. Table 85 shows an increase of $k^*[\text{H}^+]$ with increasing hydrogen ion concentration at low iodide ion concentrations. These data demonstrate a significant contribution to k^* from the iodination of undissociated p-nitrophenol, at $0.00982 \text{ M} [\text{H}^+]$ and $44 \times 10^{-6} \text{ M} [\text{I}^-]$. The assumption was made⁽⁵⁹⁾ that the iodination of the undissociated phenol was via molecular iodine; actually, the data are insufficient to distinguish between iodination of the phenol by molecular iodine and iodination of the phenol by hypiodous acidium ion.

Assuming that the undissociated phenol is iodinated by molecular iodine, then from equation (1) and Aprahamian's calculated values of k_1K_2 and k_2 (0.001 sec^{-1} and 0.051 l/mole sec , respectively), it can be calculated that k^* is approximately 17 percent greater for the protio compound at $0.00982 \text{ M} [\text{H}^+]$ and $44 \times 10^{-6} \text{ M} [\text{I}^-]$ than it would be if only phenoxide anion were being iodinated by molecular iodine.

The same approximation of 17 percent enhancement of k^* at $0.00982 \text{ M} [\text{H}^+]$, $44 \times 10^{-6} \text{ M} [\text{I}^-]$ holds if undissociated p-nitrophenol is being iodinated by hypiodous acidium ion, as shown by the following reasoning. The pH variation data of Aprahamian, summarized in Table 85, indicate that at $44 \times 10^{-6} \text{ M} [\text{I}^-]$, $k^*[\text{H}^+]$ is about 17 percent greater at $0.00982 \text{ M} [\text{H}^+]$ than at $0.00327 \text{ M} [\text{H}^+]$. While there are no data at this iodide ion concentration to show whether iodination of undissociated phenol is appreciable at $0.00327 \text{ M} [\text{H}^+]$, there is such information at about $90 \times 10^{-6} \text{ M} [\text{I}^-]$, which shows that there is no measurable contribution of iodination of the undissociated phenol at $0.00327 \text{ M} [\text{H}^+]$. It follows from the equation for iodination of p-nitrophenoxide by molecular

iodine and of p-nitrophenol by hypiodous acidium ion, obtained by eliminating the appropriate terms from equation (16), Chapter IV,

$$\frac{1}{k^*[H^+]} = \frac{k-1}{k_1 k_3 K_2} [I^-] + \frac{1}{k_1 K_2 + \frac{k_2 'K_1 [H^+]}{[I^-]}} \quad (2)$$

that if the contribution of the $\frac{k_2 'K_1 [H^+]}{[I^-]}$ term is negligible at $90 \times 10^{-6} \text{ M } [I^-]$, it cannot be large at $44 \times 10^{-6} \text{ M } [I^-]$. Therefore, at $44 \times 10^{-6} \text{ M } [I^-]$, the 17 percent increase in $k^*[H^+]$ at $0.00982 \text{ M } [H^+]$ over $k^*[H^+]$ at $0.00327 \text{ M } [H^+]$ represents approximately the entire contribution from iodination of undissociated phenol at $0.00982 \text{ M } [H^+]$ by H_2OI^+ .

On the basis of this rate-enhancement information, it is possible to consider the alternative explanations of the curvature of the $\frac{1}{k^*[H^+]}$ versus $[I^-]$ plots of the data being reported here; viz., that either p-nitrophenol or p-nitrophenoxide reacts to a significant extent with hypiodous acidium ion.

If the iodination of the undissociated phenol observed by Aprahamian at $44 \times 10^{-6} \text{ M } [I^-]$, $0.00982 \text{ M } [H^+]$ was by molecular iodine, then in the present work, at $200 \times 10^{-6} \text{ M } [H^+]$, it can be seen from equation (1) and the values for $\frac{k-1}{k_1 k_3 K_2}$, $k_1 K_2$, and k_2 calculated by Aprahamian ($205 \times 10^5 \text{ sec } l/\text{mole}$, 0.001 sec^{-1} and $0.051 \text{ } l \text{ mole}/\text{sec}$, respectively) that there should be no measurable contribution to k^* by the iodination of undissociated p-nitrophenol at $2 \times 10^{-7} \text{ M } [I^-]$, $200 \times 10^{-6} \text{ M } [H^+]$. (This assumes that any iodination of p-nitrophenol continues to be by

molecular iodine down to $2 \times 10^{-7} \text{ M } [I^-]$.) In this case, the curvature of the $\frac{1}{k^*[H^+]}$ versus $[I^-]$ plot toward the origin at $2 \times 10^{-7} \text{ M } [I^-]$, $200 \times 10^{-6} \text{ M } [H^+]$ which is observed in the $30 \times 10^{-6} \mu$ work is due to the iodination of phenoxide by hypiodous acidium ion.

The reasonableness of this possibility; viz., that the curvature toward the origin of the $\frac{1}{k^*[H^+]}$ versus $[I^-]$ plot observed in this work is due to the iodination of phenoxide by hypiodous acidium ion while the pH effect observed by Aprahamian was due to iodination of the phenol by molecular iodine, may now be considered in light of the restrictions that it places upon physical constants. From the equation for this mechanism at the low acidity ($200 \times 10^{-6} \text{ M } [H^+]$)

$$\frac{1}{k^*[H^+]} = \frac{k-1}{k_1 k_3 K_2} [I^-] + \frac{1}{k_1 K_2 + k_1' K_1 K_2 / [I^-]} \quad (3)$$

and from Aprahamian's measured values of $\frac{k-1}{k_1 k_3 K_2}$ and $k_1 K_2$, it can be calculated that in order to give the observed departure of the $2 \times 10^{-7} \text{ M}$ iodide point from the $1/k^*[H^+]$ versus $[I^-]$ line observed in the present work, $k_1' K_1 K_2$ must be about 4×10^{-10} mole l /sec. The literature value of K_2 is 1.3×10^{-7} mole/ l ,⁽¹⁰⁵⁾ so that $k_1' K_1$ must be about 3×10^{-3} sec⁻¹. Setting an approximate diffusion control limit of 1×10^{10} l /mole sec on k_1' , K_1 is greater than about 3×10^{-13} mole/ l . This value of K_1 is below the upper limit determined by Allen and Keefer,⁽⁸³⁾ and hence the mechanism under consideration cannot be ruled out.

If, on the other hand, the iodination of the undissociated phenol observed by Aprahamian at $0.00982 \text{ M } [H^+]$ and $44 \times 10^{-6} \text{ M } [I^-]$ was by way of the hypiodous acidium ion, then from equation (2) and from the mea-

sured value of k^* at $2 \times 10^{-7} \text{ M } [I^-]$, the value of k^* at $2 \times 10^{-7} \text{ M } [I^-]$ extrapolated from the higher iodide line at $30 \times 10^{-6} \mu$, and from the slope of this higher iodide line (Figure 17), it is possible to calculate that at $200 \times 10^{-6} \text{ M } [H^+]$ and $2 \times 10^{-7} \text{ M } [I^-]$, k^* will be about three times as high as it would be with no iodination of the undissociated phenol; i.e., $\frac{1}{k^*[H^+]}$ will be about 33 percent of the value extrapolated from higher iodide in concentrations. This calculation must be considered very approximate, because it depends upon a small number of results--the data reported here and the pH variation data of Aprahamian. Also, the contribution of iodination of the undissociated phenol at 0.30μ is assumed to be the same as at 0.0030μ .

From Figure 17, it is seen that the measured value of $\frac{1}{k^*[H^+]}$ at $2 \times 10^{-7} \text{ M } [I^-]$, $200 \times 10^{-6} \text{ M } [H^+]$ is about one-half of the value obtained by extrapolation of the high-iodide line. It is possible that some curvature of the $\frac{1}{k^*[H^+]}$ versus $[I^-]$ plot toward the origin has already set in at $1 \times 10^{-6} \text{ M } [I^-]$, in which case the extrapolated value of $\frac{1}{k^*[H^+]}$ at $2 \times 10^{-7} \text{ M } [I^-]$ is too low, meaning that the measured value of $\frac{1}{k^*[H^+]}$ at this iodide ion concentration actually lies below the true extrapolated high-iodide line by more than one half.

The reasonableness of this possibility; viz., that the curvature toward the origin of the $\frac{1}{k^*[H^+]}$ versus $[I^-]$ plot observed in this work and the pH effect observed by Aprahamian were both due to the iodination of the undissociated phenol by hypiodous acidium ion, is therefore consistent with the data and can now be considered in light of the restrictions that it places upon physical constants. In this case, the value

of $k_2'K_1$ is approximately 2.2×10^{-6} l/mole sec, calculated from equation (2), Aprahamian's values of $\frac{k-1}{k_1k_3K_2}$ and k_1K_2 , and the departure of the 2×10^{-7} M $[I^-]$, 30×10^{-6} μ point from the extrapolated high-iodide line. Then, using the maximum possible value of K_1 (1×10^{-10} mole/l, k_2' would be equal to or greater than 2.2×10^4 l/mole sec. On the other hand, if k_2' is set at 1×10^{10} l/mole sec for diffusion control, the value for K_1 is $\geq 2 \times 10^{-16}$. Therefore, this mechanism is also consistent with the quantitative requirements, in so far as they are known.

(The values of $k_2'K_1$ for p-nitrophenol (2.2×10^{-6} l/mole sec) and $k_1'K_1$ for 2,4-dinitrophenoxide (1×10^{-5} l/mole sec) may be sufficiently close for both to represent diffusion control of the rate constant.)

In summary, the small amount of data collect in the present work on the iodination of p-nitrophenol confirms Aprahamian's conclusion that at iodide ion concentrations down to 23×10^{-6} M, p-nitrophenoxide reacts principally by molecular iodine. The data suggest that at still lower iodide ion concentrations (about 2×10^{-7} M), a reaction with hypoidous acidium ion becomes important, at least at 200×10^{-6} M $[H^+]$, but the data do not distinguish between iodination of p-nitrophenol by hypiodous acidium ion and the iodination of p-nitrophenoxide by the same iodinating agent.

Table 77. Run 21, p-Nitrophenol in 27.4×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	6.09×10^{-6} M	$(HClO_4)_0$	200×10^{-6} M
$[I_2]_0$	6.00×10^{-6} M	$[NaClO_4]$	2750×10^{-6} M
$(I^-)_0$	27.4×10^{-6} M	$(\underline{p}\text{-Nitrophenol})_0$	22.2×10^{-6} M
$[I^-]_0$	27.3×10^{-6} M	μ	0.0030
$[HOI]$	0.01×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} ($l/mole^{-1} sec$)
5151	0.220	28.2	3.02
8257	.200	39.9	2.95
9105	.193	44.4	3.11
10968	.184	49.4	3.03
13303	.173	55.6	3.01
15321	.164	61.2	3.08
17412	.153	67.6	3.27

$$F_1 = 1.511 \quad P_1 = 52170 \text{ l/mole cm} \quad P_3 = 248300 \text{ l/mole cm}$$

$$F_2 = 6.1 \times 10^{-6} \text{ sec}^{-1} \quad P_2 = 40910 \text{ l/mole cm} \quad E = 4.028 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 3.13 \text{ l/mole sec} \quad k^* = 3.17 \text{ l/mole sec}$$

$$k^*[H^+] = 0.00063 \text{ sec}^{-1}$$

Table 78. Run 22, p-Nitrophenol-2,6-d in 27.4×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	6.09×10^{-6} M	$(HClO_4)_0$	200×10^{-6} M
$[I_2]_0$	6.00×10^{-6} M	$[NaClO_4]$	2750×10^{-6} M
$(I^-)_0$	27.4×10^{-6} M	$(p\text{-Nitrophenol-2,6-d})_0$	19.5×10^{-6} M
$[I^-]_0$	27.3×10^{-6} M	μ	0.0030
$[HOI]_0$	0.01×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
16021	0.211	21.1	0.79
19362	.204	24.0	.76
29076	.187	31.9	.72
31948	.183	33.9	.70
35812	.174	38.5	.74

$$F_1 = 1.511$$

$$P_1 = 52170 \text{ l/mole cm} \quad P_3 = 248300 \text{ l/mole cm}$$

$$F_2 = 6.1 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 40910 \text{ l/mole cm} \quad E = 4.028 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 0.76 \text{ l/mole sec}$$

$$k^* = 0.77 \text{ l/mole sec}$$

$$k^*[H^+] = 0.000154 \text{ sec}^{-1}$$

Table 79. Run 19, p-Nitrophenol in 1.15×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	0.64×10^{-6} M	$(HClO_4)_0$	200	$\times 10^{-6}$ M
$[I_2]_0$	0.63×10^{-6} M	$[NaClO_4]$	2800	$\times 10^{-6}$ M
$(I^-)_0$	1.15×10^{-6} M	$(\underline{p}\text{-Nitrophenol})_0$	2.22	$\times 10^{-6}$ M
$[I^-]_0$	1.16×10^{-6} M	μ	0.0030	
$[HOI]$	0.01×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
22384	0.215	33.1	8.52
27661	.207	37.3	8.07
34987	.194	44.4	8.12
39157	.187	48.3	8.20

$$F_1 = 0/159 \quad P_1 = 52170 \text{ l/mole cm} \quad P_3 = 248300 \text{ l/mole cm}$$

$$F_2 = 2.6 \times 10^{-7} \text{ sec}^{-1} \quad P_2 = 40910 \text{ l/mole cm} \quad E = 4.028 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 8.4 \text{ l/mole sec} \quad k^* = 8.6 \text{ l/mole sec}$$

$$k^*[H^+] = 0.00172 \text{ sec}^{-1}$$

Table 80. Run 15, p-Nitrophenol in 1.00×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	0.51×10^{-6} M	$(HClO_4)_0$	200	$\times 10^{-6}$ M
$[I_2]_0$	0.50×10^{-6} M	$[NaClO_4]$	2790	$\times 10^{-6}$ M
$(I^-)_0$	1.00×10^{-6} M	$(\underline{p}\text{-Nitrophenol})_0$	2.22×10^{-6}	M
$[I^-]_0$	1.01×10^{-6} M	μ	0.0030	
$[HOI]_0$	0.01×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
9420	0.211	18.4	9.9
15240	.204	20.7	7.0
26032	.178	36.0	8.1
33348	.167	41.4	7.6
33503	.170	38.8	6.9

$$F_1 = 0.126 \quad P_1 = 52170 \text{ l/mole cm} \quad P_3 = 248300 \text{ l/mole cm}$$

$$F_2 = 7.8 \times 10^{-7} \text{ sec}^{-1} \quad P_2 = 40910 \text{ l/mole cm} \quad E = 4.028 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 8.1 \text{ l/mole sec} \quad k^* = 8.3 \text{ l/mole sec} \quad k^*[H^+] = 16.6 \times 10^{-4} \text{ sec}^{-1}$$

Table 81. Run 20, p-Nitrophenol-2,6-d in 1.15×10^{-6} M
Sodium Iodide Solution at 50.0°

$(I_2)_o$	0.64×10^{-6} <u>M</u>	$(HClO_4)_o$	200	$\times 10^{-6}$ <u>M</u>
$[I_2]_o$	0.63×10^{-6} <u>M</u>	$[NaClO_4]$	2800	$\times 10^{-6}$ <u>M</u>
$(I^-)_o$	1.15×10^{-6} <u>M</u>	$(\underline{p}\text{-Nitrophenol-2-6-d})_o$	1.95×10^{-6}	<u>M</u>
$[I^-]_o$	1.16×10^{-6} <u>M</u>	μ	0.0030	
$[HOI]_o$	0.01×10^{-6} <u>M</u>			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} ($l/mole\ sec$)
24203	0.216	22.0	5.47
32042	.202	29.6	5.94
38011	.200	30.1	5.09
43106	.187	37.6	6.01
46711	.183	39.7	5.97

$$F_1 = 0.156 \quad P_1 = 52170 \text{ } l/mole \text{ cm} \quad P_3 = 248300 \text{ } l/mole \text{ cm}$$

$$F_2 = 2.6 \times 10^{-7} \text{ sec}^{-1} \quad P_2 = 40910 \text{ } l/mole \text{ cm} \quad E = 4.028 \times 10^{-6} \text{ mole cm}/l$$

$$k_{appo} = 5.9 \text{ } l/mole \text{ sec} \quad k^* = 6.0 \text{ } l/mole \text{ sec}$$

$$k^*[H^+] = 0.00120 \text{ sec}^{-1}$$

Table 82. Run 17, p-Nitrophenol in 0.096×10^{-6} M Sodium Solution at 50.0°

$(I_2)_o$	0.552×10^{-6} <u>M</u>	$(HClO_4)_o$	200	$\times 10^{-6}$ <u>M</u>
$[I_2]_o$	0.453×10^{-6} <u>M</u>	$[NaClO_4]$	2800	$\times 10^{-6}$ <u>M</u>
$(I^-)_o$	0.096×10^{-6} <u>M</u>	$(\underline{p}\text{-Nitrophenol})_o$	2.22	$\times 10^{-6}$ <u>M</u>
$[I^-]_o$	0.195×10^{-6} <u>M</u>	μ	0.0030	
$[HOI]_o$	0.099×10^{-6} <u>M</u>			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
9653	0.218	22.5	12.2
13190	.214	24.6	10.0
19654	.190	40.5	12.6
24685	.186	42.5	10.7
30214	.179	46.5	10.0

$$F_1 = 0.137 \quad P_1 = 52170 \text{ l/mole cm} \quad P_3 = 248300 \text{ l/mole cm}$$

$$F_2 = 3.1 \times 10^{-7} \text{ sec}^{-1} \quad P_2 = 40910 \text{ l/mole cm} \quad E = 4.028 \times 10^{-6} \text{ mole cm/l}$$

$$k_{appo} = 13.0 \text{ l/mole sec}$$

$$k^* = 15.9 \text{ l/mole sec}$$

$$k^*[H^+] = 0.00318 \text{ sec}^{-1}$$

Table 83. Run 18, p-Nitrophenol-2,-6d in 0.096×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_o$	0.552×10^{-6} M	$(HClO_4)_o$	200	$\times 10^{-6}$ M
$[I_2]_o$	0.453×10^{-6} M	$[NaClO_4]$	2800	$\times 10^{-6}$ M
$(I^-)_o$	0.096×10^{-6} M	$(\underline{p}\text{-Nitrophenol-2,6-d})_o$	2.23×10^{-6}	M
$[I^-]_o$	0.195×10^{-6} M	μ	0.0030	
$[HOI]_o$	0.099×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
8277	0.228	15.9	9.61
16729	.216	22.7	7.13
22801	.200	33.0	8.25
32739	.180	45.7	8.91
35870	.178	46.6	8.37
39405	.174	48.9	8.18

$$F_1 = 0.137 \quad P_1 = 52170 \text{ l/mole cm} \quad P_3 = 248300 \text{ l/mole cm}$$

$$F_2 = 3.1 \times 10^{-7} \text{ sec}^{-1} \quad P_2 = 40910 \text{ l/mole cm} \quad E = 4.028 \times 10^{-6} \text{ mole cm/l}$$

$$k_{appo} = 10.5 \text{ l/mole sec}$$

$$k^* = 12.8 \text{ l/mole sec}$$

$$k^*[H^+] = 0.00256 \text{ sec}^{-1}$$

Table 84. Run 16, 2-Iodo-4-nitrophenol in 1.00×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	0.62×10^{-6} M	$(HClO_4)_0$	200	$\times 10^{-6}$ M
$[I_2]_0$	0.61×10^{-6} M	$[NaClO_4]$	2790	$\times 10^{-6}$ M
$(I^-)_0$	1.00×10^{-6} M	(2-Iodo-4-nitro-phenol) ₀	2.06	$\times 10^{-6}$ M
$[I^-]_0$	1.01×10^{-6} M	μ	0.0030	
$[HOI]$	0.01×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
10179	0.200	20.1	11.0
20223	.179	30.0	9.0
20277	.176	31.9	9.7
24997	.162	39.4	10.4
25045	.162	39.4	10.4
27944	.157	41.7	10.1

$$F_1 = 0.154 \quad P_1 = 40910 \text{ l/mole cm} \quad P_3 = 248300 \text{ l/mole cm}$$

$$F_2 = 6.3 \times 10^{-7} \text{ sec}^{-1} \quad P_2 = 29250 \text{ l/mole cm} \quad E = 4.028 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 10.1 \text{ l/mole sec} \quad k^* = 10.4 \text{ l/mole sec}$$

$$k^*[H^+] = 20.8 \times 10^{-4} \text{ sec}^{-1}$$

Table 85. Effect of Acidity upon Rate Constant for Iodination of p-Nitrophenol^a

$[I^-] \times 10^4$ (moles/l)	$[H^+]$ (moles/l)	$k^*[H^+] \times 10^4$ (sec ⁻¹)	$k^*[H^+][I^-] \times 10^8$ (moles/l sec)
0.444	0.0491	7.97	3.54
.445	.00982	6.53	2.90
.437	.00327	5.63	2.46
.890	.0491	4.95	4.41
.914	.00982	4.11	3.76
.872	.00327	3.99	3.48
.918	.001091	3.97	3.64

^aThis is the data of Grovenstein and Aprahamian. (59)

Table 86. Data on the Iodination of p-Nitrophenol at Temperature, 50.0°; μ , 0.0030;
 $[H^+]$, 200×10^{-6} M

Table Ref.	$[I_2]_0 \times 10^3$ (mole/l)	$[I^-]_0 \times 10^3$ (mole/l)	$(ArOH)_0$ $\times 10^3$ (mole/l)	k^* (l/mole sec)	$k^*[H^+] \times 10^5$ (sec ⁻¹)	$k^*[H^+][I^-]$ $\times 10^{10}$ (mole/l sec)	$1/k^*[H^+] \times 10^{-2}$ (sec)
77	6.00	27.3	22.2	3.17	63.	172	15.9
79	0.630	1.16	2.22	8.6	172	19.9	5.8
80	0.500	1.01	2.22	8.3	166	16.7	6.0
82	0.453	0.195	2.22	15.9	318	6.2	3.14

Table 87. Data on the Iodination of p-Nitrophenol-2,6-d at Temperature, 50.0°; μ , 0.0030; $[H^+]$, 200×10^{-8} M

Table Ref.	$[I_2]_0 \times 10^6$ (mole/l)	$[I^-]_0 \times 10^6$ (mole/l)	$(ArOH)_0 \times 10^6$ (mole/l)	k^* (l/mole sec)	$k^*[H^+] \times 10^5$ (sec ⁻¹)	$k^*[H^+][I^-] \times 10^{10}$ (mole/l sec)	$1/k^*[H^+] \times 10^{-2}$ (sec)
78	6.00	27.3	19.5	0.77	15.4	42.0	65
81	0.630	1.16	1.95	6.0	120	13.9	8.8
83	0.453	0.195	2.23	12.8	256	4.96	3.92

Table 88. Isotope Effects in the Iodination of p-Nitrophenol
 at Temperature, 50.0°; μ , 0.0030; $[H^+]$, 200×10^{-6} M

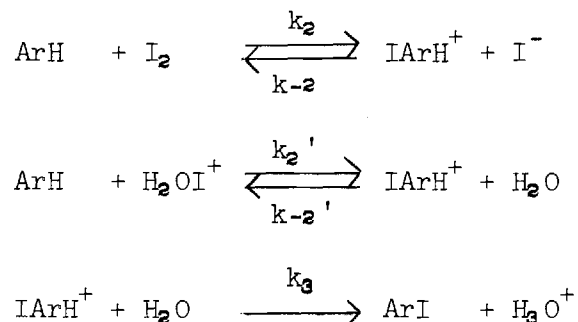
Table Ref.	$[I^-]_0 \times 10^6$ (mole/l)	$k_H^* [H^+] \times 10^6$ (sec ⁻¹)	$k_D^* [H^+] \times 10^6$ (sec ⁻¹)	$\frac{k_H^* [H^+]}{k_D^* [H^+]}$
77, 78	27.3	63.0	15.4	4.12
79, 81	1.16	318	120	1.43
82, 83	0.195	172	256	1.28

CHAPTER VII

IODINATION OF ANISOLE

Introduction

The generalized mechanism, analagous to mechanism III, Chapter IV, for the iodination of anisole differs from that for phenol, p-nitrophenol, and 2,4-dinitrophenol in that there is no entity corresponding to the phenoxide anions. This simplifies the mechanism and its mathematical description, as will be seen. The generalized mechanism may now be written



Aprahamian⁽¹⁰⁷⁾ studied the iodination of anisole over the iodide ion concentration range 9.2×10^{-4} M to 9.4×10^{-8} . The conditions were hydrogen ion concentration, 0.009783 M; temperature, 50°; ionic strength, 0.30. The rate constants were assumed to be independent of pH. The constancy of k^* , at a given iodide ion concentration, with variations in

107. N. S. Aprahamian, The Kinetics and Mechanism of Iodination of Phenol, p-Nitrophenol, Anisole and Their Deuterated Derivatives, Ph.D. Thesis, Georgia Institute of Technology, 1960, pp. 127-172, 221-240.

iodine concentration showed the reaction to be first order in iodine concentration.

The value of $k^* [I^-]$ was observed to decrease from about 30×10^{-8} l/mole sec at 9.2×10^{-4} M $[I^-]$ to about 16×10^{-8} l/mole sec at 9.4×10^{-6} M $[I^-]$ for anisole, and from about 9.0×10^{-8} l/mole sec at 4.8×10^{-4} M $[I^-]$ to about 5.6 l/mole sec at 9.5×10^{-4} M $[I^-]$ for anisole-2,4,6-d₃. The isotope effect averaged about 3.0 over the iodide ion concentration covered, with considerable scatter but no clear trend.

The $1/k^*$ versus $[I^-]$ plots are somewhat puzzling--it is not possible to draw a straight line through the data for either the protio or the deutero compound without requiring very large errors for several points; on the other hand, if a curve is fitted to the data, it curves away from the origin toward a positive intercept at low iodide ion concentrations. Such a plot does not correspond to any of the proposed mechanisms.

As will be seen, $1/k^*$ versus $[I^-]$ plots of the data on anisole and anisole-2,4,6-d₃ to be reported in this thesis give good straight lines through the origin over the iodide ion concentration range 1.0×10^{-4} M to 0.3×10^{-6} M. The discrepancy between these data and data of Aprahamian led to a re-examination of the extrapolations of k_{app} values to k_{app0} employed by Aprahamian, which indicated that the departure from the origin of the $1/k^*$ versus $[I^-]$ plot of Aprahamian's data might be due to the manner of extrapolating k_{app} values to k_{app0} , which was done visually. In light of this, the k_{app} data were extrapolated according to the method described in Chapter II, with n taken as unity.

A complication here was that the iodide ion concentration produced during the reaction in some cases far exceeded the initial iodide ion concentration. In such a case, the experimental k_{app} values will not approximate a straight line between 50 percent and zero percent reaction. Instead, each k_{app} value was corrected to k_{app_0} according to equation (18), Chapter III, and the k_{app_0} values were averaged.

Plots of $1/k^*$ versus $[I^-]$ give reasonably good straight lines passing through the origin for both anisole and anisole-2,4,6- d_3 ; the lowest iodide points still depart somewhat from such a line, but this may reflect the greater uncertainty of these points. (The individual k_{app_0} values within a given kinetic run, obtained as described above, varied widely for these lowest iodide experiments.) The results of this treatment of Aprahamian's data are tabulated in Tables 100 and 101, and the $1/k^*$ versus $[I^-]$ plots are given in Figures 18 and 19. As has been noted before, such results do not distinguish between mechanisms I, II, and III.

If hypiodous acidium ion is the sole iodinating agent (mechanism I), a straight line through the origin is predicted by equation (18), Chapter IV, modified by removal of the k_2' term, the constant K_2 , and the hydrogen ion dependence, since a dissociable phenol is not involved here.

$$\frac{1}{k^*} = \left\{ \frac{k_{-2}}{k_2 k_3} + \frac{1}{k_2' K_1} \right\} [I^-] \quad (1)$$

Within experimental error, such a straight line is observed.

If molecular iodine is the sole iodinating agent over the iodide

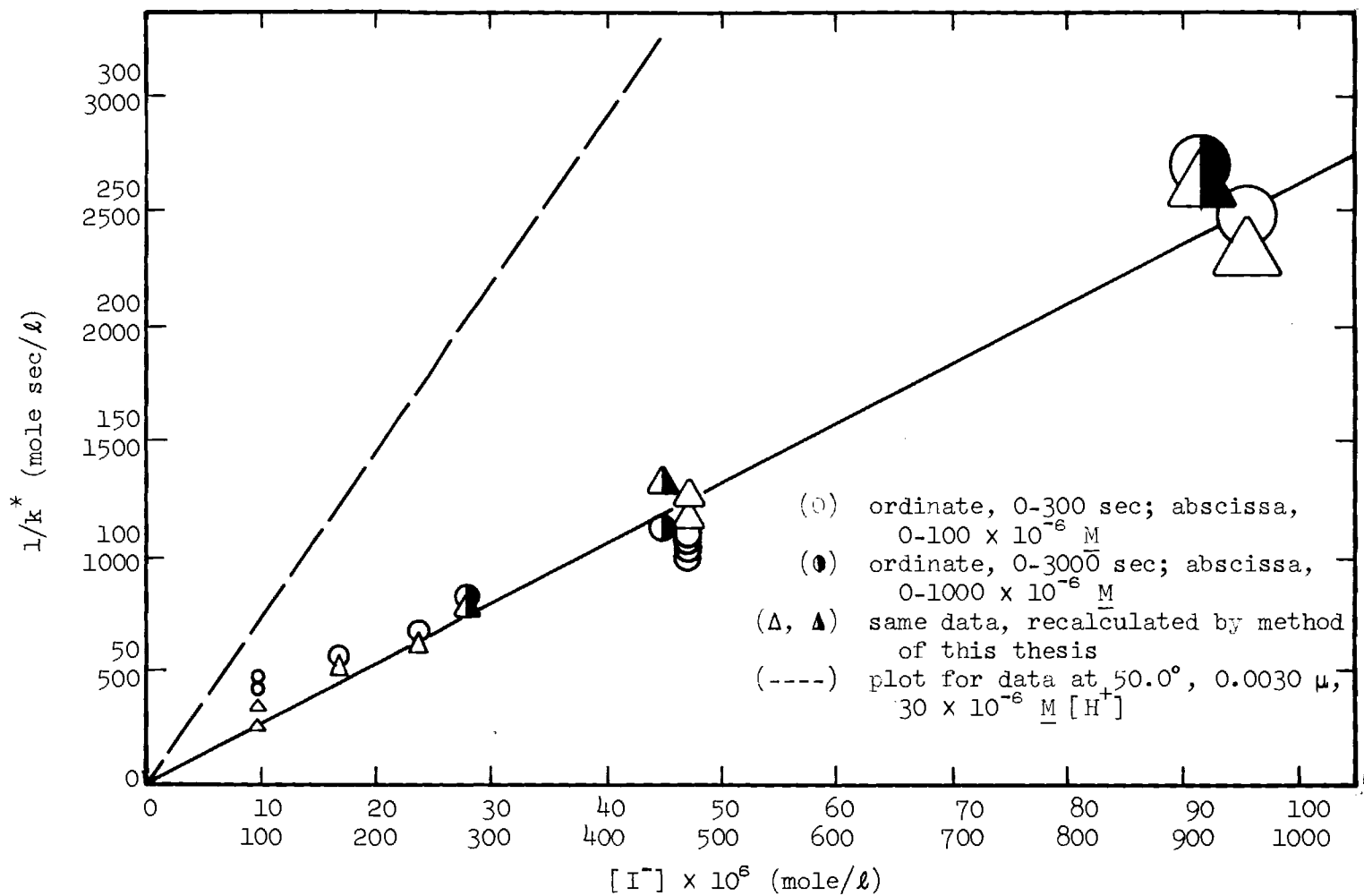


Figure 18. Anisole at Temperature, 50.0°; Ionic Strength, 0.30; [H⁺], 0.009783 M; Data of N. S. Aprahamian

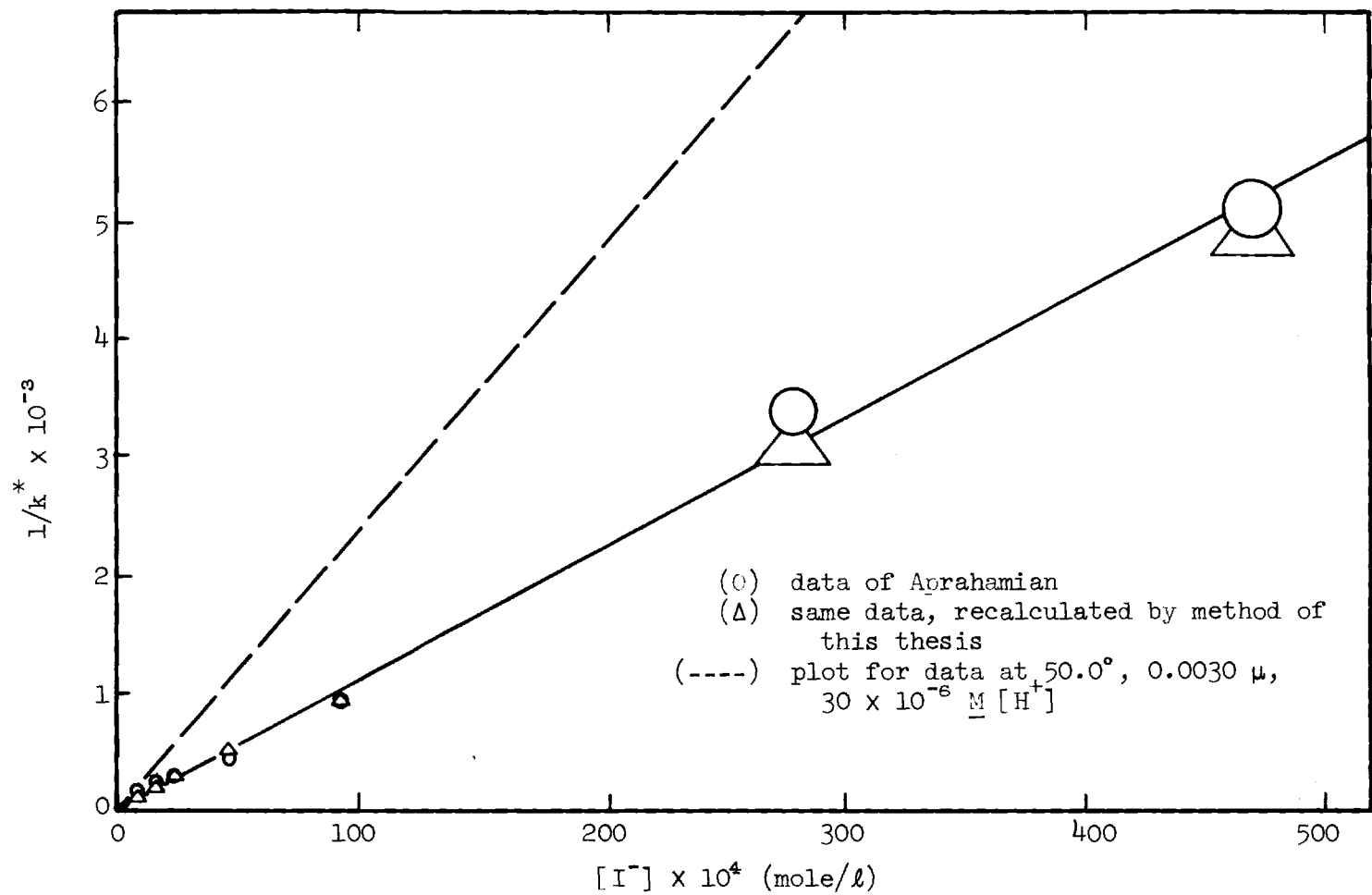


Figure 19. Anisole-2,4,6-d at Temperature, 50.0°; Ionic Strength, 0.30; [H⁺], 0.009783 M; Data of N. S. Aprahamian

ion concentration range studied (mechanism II), then the appropriately modified form of equation (17), Chapter IV, applies.

$$\frac{1}{k^*} = \frac{k-2}{k_2 k_3} [I^-] + \frac{1}{k_2} \quad (2)$$

On the basis of Aprahamian's data, treated by the more rigorous extrapolation method, it is not possible to distinguish between a zero intercept and a positive intercept corresponding with a reasonable value of k_2 .

If both hypiodous acidium ion and molecular iodine are important iodinating agents over the iodide ion concentration range covered (mechanism III), the descriptive equation is a modification of equation (16), Chapter IV.

$$\frac{1}{k^*} = \left(\frac{k-2}{k_2 k_3} \right) [I^-] + \frac{1}{k_2 + \frac{k_2' K_1}{[I^-]}} \quad (3)$$

In this case, the limiting straight lines at high and low iodide ion concentrations are given by equations (2) and (1), respectively.

In the work to be reported here, the kinetics of the iodination of anisole were studied at still lower iodide ion concentrations in an attempt to distinguish between the above mechanistic possibilities.

Specific Experimental Details

The experimental conditions were $\mu = 0.0030$; $[H^+] = 30.0 \times 10^{-8} M$; and temperature = 50.0° . The iodide ion range covered was from 100×10^{-6}

M to 0.30×10^{-6} M.

The concentration of anisole and anisole-2,4,6- d_3 in the stock solutions, and hence in the reaction solutions, was determined by weight. This was accomplished by introducing the hydrocarbon into the 250 ml stock solution flask, which was partially filled with water, from a dropper bottle which was weighed before and after sampling. The stock solution flask, containing water and anisole, was then shaken on a mechanical shaker. Complete solution was observed to occur within a matter of minutes, but the solution was shaken for some additional time in each case. The stock solution was then made up to volume with water.

The absorption maximum of the anisole solutions was experimentally determined to be 2690 Å, the extinction coefficient being 1383. It was determined spectrophotometrically that an anisole stock solution lost approximately two percent of anisole in two weeks, which loss was assumed to be due to volatilization. Stock solutions were kept for less time than this.

It was experimentally determined that anisole, at the concentrations employed in these experiments, did not absorb to any measurable extent at 3530 Å, the wavelength at which the spectral measurements were made on the quenched solutions. Therefore, the k_{app} values were determined using equations (1) and (9), Chapter III, the same procedure as used for the phenol kinetics.

The acidity of these experiments was sufficiently low that quenching could be achieved by pipetting in 1.0 ml of aqueous solution containing 0.38 g of sodium iodide. The rate of oxidation of iodide to iodine

at that acidity was experimentally determined to be much too slow to interfere with the measured absorbance.

Background absorbance was determined by adding the quenching iodide solution to a water solution containing the concentrations of perchloric acid and sodium perchlorate found in the reaction solutions. This absorbance was 0.007 in a 10 cm cell.

The extrapolation of k_{app} values to k_{app0} was made as described in Chapter III. The first approximation $1/k^*$ versus $[I^-]$ plot of the average k_{app} values indicated an n value of unity throughout the entire range of iodide ion concentration range, and the extrapolations were made accordingly.

Results and Discussion

The results of this work are tabulated in Tables 102 and 103, and the $1/k^*$ versus $[I^-]$ plots are shown in Figures 20 and 21.

The reasonably constant value of $k^*[I^-]$ of approximately $0.135 \times 10^{-6} \text{ sec}^{-1}$ for anisole and approximately $0.044 \times 10^{-6} \text{ sec}^{-1}$ for anisole-2,4,6- d_3 and the reasonably constant isotope effect of approximately 3.0 coincide with the reasonably good fit to a straight line $1/k^*$ versus $[I^-]$ plot through the origin. Therefore, the kinetic situation observable from the re-extrapolated results of Aprahamian continues to hold down to iodide ion concentration $3 \times 10^{-7} \text{ M}$.

The slopes of $7.25 \times 10^6 \text{ sec}$ for the anisole line and $23.4 \times 10^6 \text{ sec}$ for the anisole-2,4,6- d_3 line differ from those obtained from the re-extrapolated data of Aprahamian, which are $3.5 \times 10^6 \text{ sec}$ for anisole and $10.9 \times 10^6 \text{ sec}$ for anisole-2,4,6- d_3 . These differences are in the

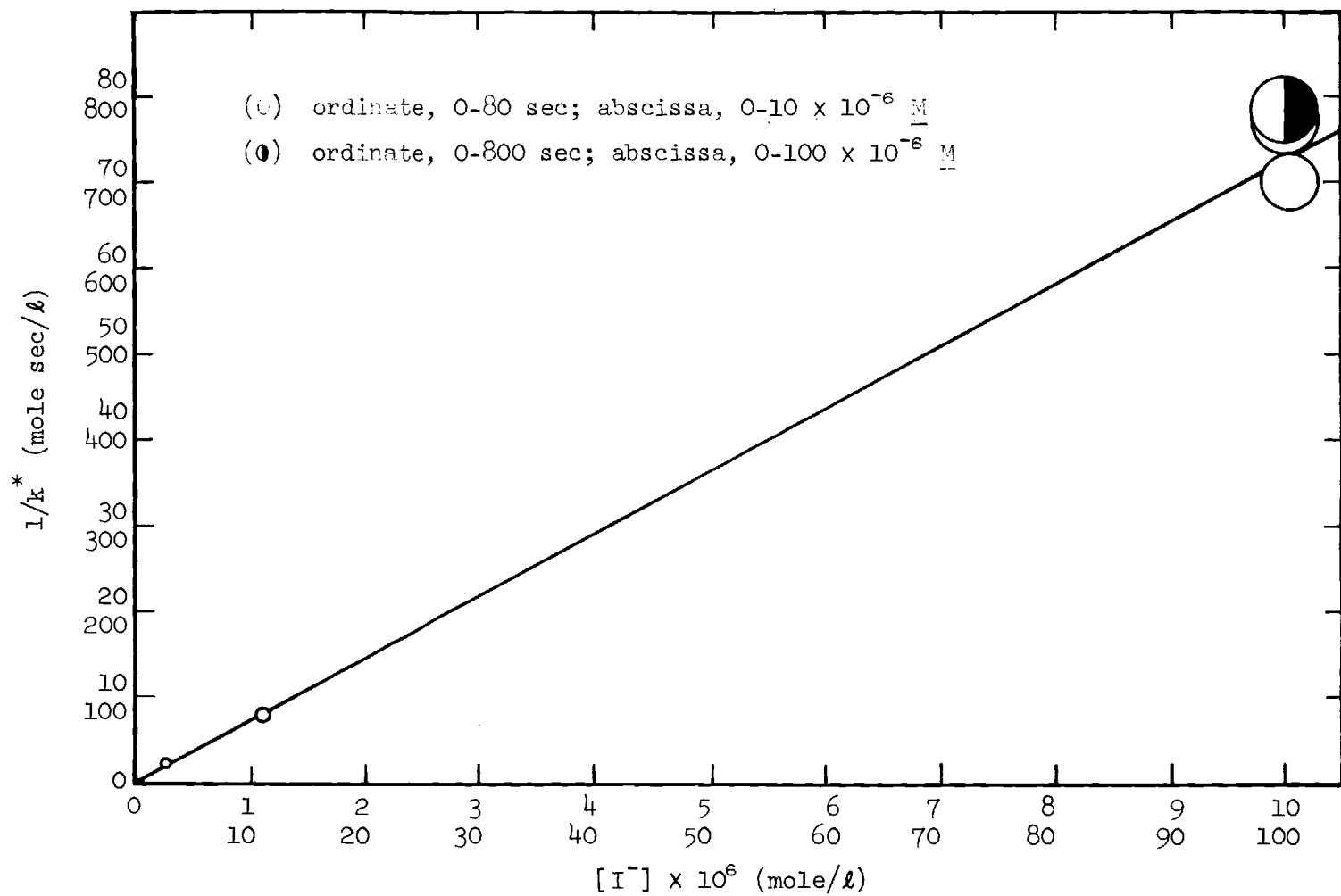


Figure 20. Anisole at Temperature, 50.0°; Ionic Strength, 0.0030; [H⁺], 30 x 10⁻⁶ M

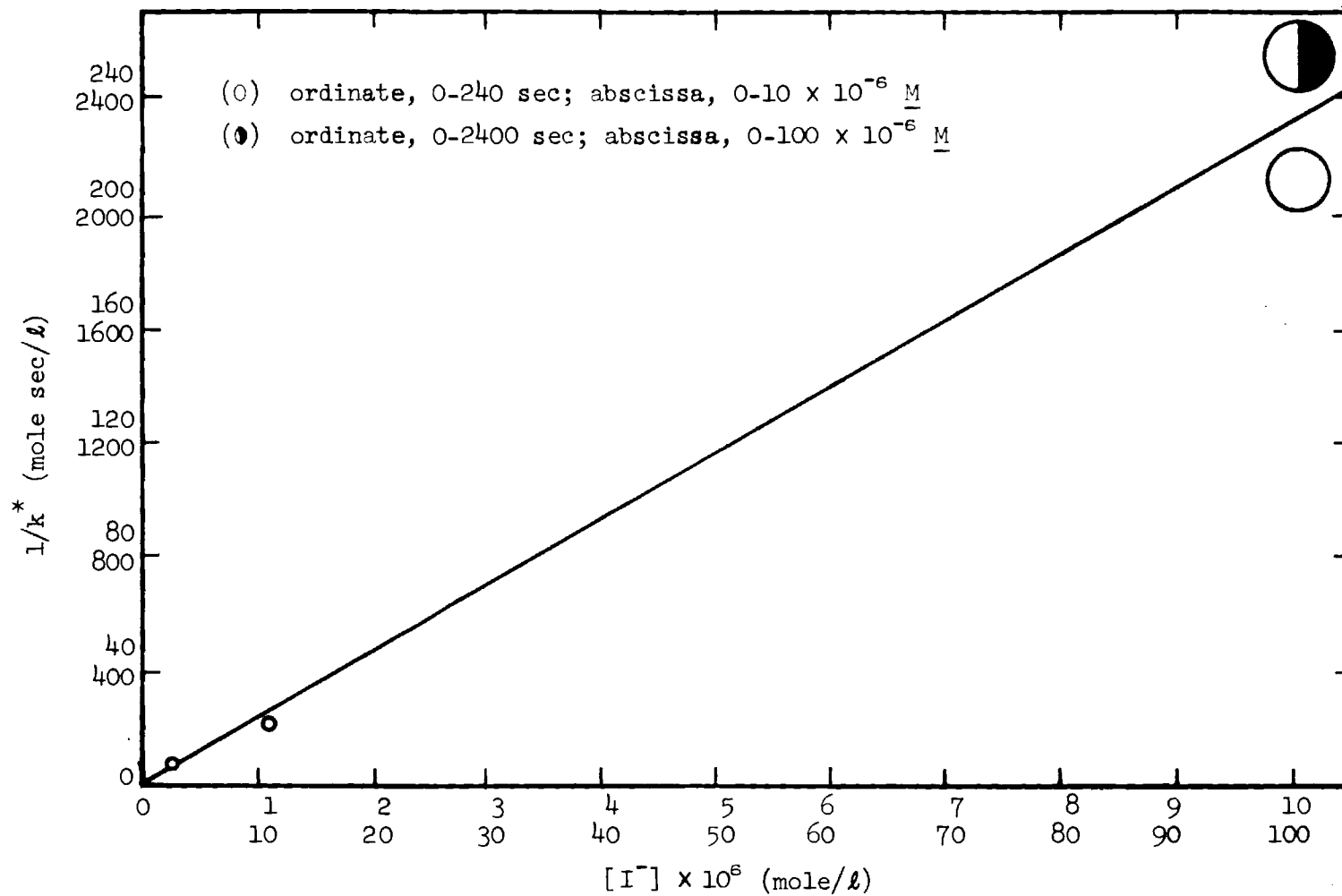


Figure 21. Anisole-2,4,6-d at Temperature, 50.0°; Ionic Strength, 0.0030; [H⁺], 30 × 10⁻⁶ M

direction that would be predicted from the differences in ionic strength (0.0030 in this work and 0.30 in Aprahamian's work), in light of the discussion in Chapter V. The differences in $k^* [I^-]$ values reflect these differences, while, as expected, the isotope effect of 3.0 is similar to that obtained from Aprahamian's data.

From equation (2), it is clear that the question of whether mechanism II can be eliminated as a possibility depends upon whether an intercept corresponding to any reasonable value of k_2 might be indistinguishable from the origin in the $1/k^*$ versus $[I^-]$ plots. Setting the maximum conceivable value of k_2 as 4×10^9 l/mole sec, which is the "typical" upper limit for the rate constant of a bimolecular reaction between neutral molecules in aqueous solution,⁽¹⁰⁸⁾ the minimum conceivable intercept of the $1/k^*$ versus $[I^-]$ plot for anisole would be 2.5×10^{-10} mole sec/l, corresponding to $1/k_2$, which would not be distinguishable from zero.

However, the fact that the slope $\frac{k_{-2}}{k_2 k_3}$ of the $1/k^*$ versus $[I^-]$ plot for anisole is greater than the high iodide slope $\frac{k_{-1}}{k_1 k_3}$ for 2,4-dinitrophenoxide (3.5×10^6 sec and 4.0×10^4 sec, respectively, for the data at $\mu = 0.30$) suggests that k_2 for anisole is not greater than k_2 for 2,4-dinitrophenoxide; i.e., that anisole is not more reactive than 2,4-dinitrophenoxide to molecular iodine. This requires that the reversibility ratio k_{-2}/k_3 for anisole be not more than about two orders of magnitude greater than the reversibility ratio k_{-1}/k_3 for 2,4-dini-

108. I. Amdur and G. G. Hammes, Chemical Kinetics: Principles and Selected Topics, McGraw-Hill Co., Inc., New York, 1966, p. 62.

trophenoxyde. By comparison, the reversibility ratio for phenoxide, 1.46×10^6 (cf., Chapter IV) is about four hundred times greater than the reversibility ratio for 2,4-dinitrophenoxide, 3.64×10^3 (cf., Chapter V).

If 0.103 l/mole sec, the value of k_2 for 2,4-dinitrophenoxide (cf., Chapter VI), can be taken as the upper limit for k_2 for the iodination of anisole by molecular iodine, then the assumption that molecular iodine is the only significant iodinating agent over the iodide ion concentration range 9.2×10^{-4} M to 3×10^{-7} M requires an intercept at zero iodide of 10 mole sec/l. The data at 0.0030 μ plotted in Tables 102 and 103 are inconsistent with an intercept greater than about 1.5 mole sec/l. Since k_2 is the rate constant for a reaction involving uncharged reactants and charged products, the value of k_2 will be greater at 0.30 μ than at 0.0030 μ ; i.e., the intercept would be still smaller.

Therefore, on the basis of the assumption that anisole is not more reactive than 2,4-dinitrophenoxide toward molecular iodine, the experimental data indicate that molecular iodine is not the sole iodinating agent for anisole over the iodide ion concentration range 9.2×10^{-4} M to 3×10^{-7} M.

This tentative conclusion that hypiodous acidium ion is a significant iodinating agent over this iodide range leaves the possibilities of mechanism I, in which it is the sole iodinating agent, and mechanism III, in which both the hypiodous acidium ion and molecular iodine are important over the iodide ion concentration range studied.

Mechanism I is obviously consistent with the experimental results,

since this requires a straight $1/k^*$ versus $[I^-]$ plot through the origin, as observed (within experimental error).

The alternate possibility is that mechanism III applies, with the high-iodide slope k_{-2}/k_2k_3 and the low-iodide slope $k_{-2}/k_2k_3 + 1/k_2'K_1$ being too similar to be experimentally differentiated (cf., equation (3)). This requires that $1/k_2'K_1$ be less than k_{-2}/k_2k_3 ; i.e., less than 3.5×10^6 sec. The maximum possible value of k_2' is about 10^{10} l/mole sec, ⁽⁹²⁾ representing diffusion control. This would set a minimum value of K_1 of 3×10^{-17} mole/l, which is far below the maximum value of 1×10^{-10} determined by Allen and Keefer. ⁽⁸³⁾ Therefore, mechanism III is also consistent with the data.

To summarize, unambiguous differentiation cannot be made between any of the previously discussed mechanistic possibilities for the iodination of anisole over the iodide ion concentration range 9.2×10^{-4} M to 2.9×10^{-7} M. However, it seems likely that hypiodous acidium ion is a significant iodinating agent over the whole or part of this iodide ion concentration range.

N. S. Gnanapragasam ⁽⁸⁰⁾ measured the isotope effect upon the iodination of anisole at 3.4×10^{-11} M iodide ion concentration at 25.0° , using silver ion to maintain the low iodide ion concentration. The aromatic concentration in these experiments upon which the isotope effect is based was 2.87×10^{-6} M. Gnanapragasam's finding of an isotope effect of 3.0 is close to the isotope effect found in Aprahamian's work ⁽¹⁰⁷⁾ (3.1) and in the work reported in this thesis (3.2), at 50.0° . Making the reasonable assumption that there is no large temperature effect on

isotope effect, it appears that the isotope effect remains constant from 9.2×10^{-4} M to 3.4×10^{-11} M iodide.

Now, an approximate upper limit can be placed upon k_2 , the reciprocal of the intercept of the plot of $1/k^*$ versus $[I^-]$, for the case of molecular iodine as iodinating agent. From the first preequilibrium proposed at the beginning of this chapter for the iodination of anisole

$$\frac{k_2}{k^{-2}} = \frac{[I\text{ArH}^+][I^-]}{[\text{ArH}][I_2]} \quad (4)$$

The values of $[I_2]$ and $[I^-]$ in Gnanapragasam's experiments are 2.1×10^{-6} M and 3.4×10^{-11} M, respectively, and the ratio $[I\text{ArH}^+]/[\text{ArH}]$ was much less than 0.04.[†] Substitution of these numbers in equation (4) gives a

[†]This ratio is obtained from Gnanapragasam's results on the iodination of protio anisole at different concentrations of the anisole. Since

$$k^* = \frac{\text{rate}}{[\text{ArH}][I_2]}$$

any error in $[\text{ArH}]$ and/or $[I_2]$ will give rise to an error in k^* . If $I\text{ArH}^+$ is present in considerable concentrations, $[\text{ArH}]$ and $[I_2]$ will be reduced by virtue of being bound up in the intermediate, and values of k^* calculated without taking the $I\text{ArH}^+$ into account will be too low. Since, other things being equal, a larger percentage of the iodine will be tied up as $I\text{ArH}^+$ if the concentration of ArH is higher, such complex storage is expected to be manifested in a decrease in k^* as the anisole concentration is increased. Gnanapragasam did in fact observe a decrease in k^* from 99.9 l/mole sec to 56.2 l/mole sec as the anisole concentration was increased from 2.87×10^{-6} M to 45.9×10^{-6} M. Calculations show that this effect would be consistent with a $[I\text{ArH}^+]/[\text{ArH}]$ ratio of 0.04 in the 2.87×10^{-6} M anisole experiments, which are used in the above calculations. (The consideration of the kinetic importance of I_2 and ArH tied up as intermediate presupposes the steady state; i.e., that k_3 is still completely rate-determining. This must be approximately true in Gnanapragasam's work, since his isotope is essentially unchanged from that at much higher iodide ion concentrations.)

The ratio of 0.04 now seems to be much too high, for J. M. McKelvey, also working at Georgia Institute of Technology, in Dr. (continued)

k_2/k_{-2} ratio of 0.65×10^{-6} . The maximum possible value for k_{-2} is about 5×10^{10} l/mole sec.⁽⁹²⁾ This defines the maximum value of k_2 as about 3.3×10^4 l/mole sec. The smallest possible value, then, for the intercept of the $1/k^*$ versus $[I^-]$ plot for the case of molecular iodine as the sole iodinating agent, corresponding to $1/k_2$, is 3.0×10^{-5} mole sec/l.

From this value of the intercept (it is assumed that the protio and deuterio anisole plots have the same intercept; i.e., that k_2 has no isotope effect) and from the experimental values of the slopes-- 7.25×10^6 sec for the protio and 23.4×10^6 sec for the deuterio anisole--it can be calculated that, assuming molecular iodine to be the sole iodinating agent over the entire iodide range the isotope effect at 3.4×10^{-11} M iodide ought to be 3.0, and therefore that Gnanapragasam's observation of constant isotope effect down to 3.4×10^{-11} M iodide ion concentration does not rule out molecular iodine as the sole iodinating agent over the entire iodide concentration range studied. However, if the ratio $[I\text{ArH}^+]/[\text{ArH}]$ is no larger than 0.004, which seems likely, or if k_{-2} is no higher than 5×10^9 l/mole sec, the maximum value of the isotope effect at 3.4×10^{-11} M $[I^-]$ is 2.0. If such were the case, then Gnanapragasam's finding would prove that molecular iodine could not

laboratories, has recently determined that all or most of the effect of aromatic concentration upon experimental values of k^* , in reactions run in the presence of silver ion, is due to a kinetic competition between the production of iodide in step k_2 and the precipitation of iodide by silver ions, and therefore not to storage of intermediate.

be the sole iodinating agent at iodide ion concentrations as low as 3.4×10^{-11} M.

The fact, then, is that the data indicate that it is just barely possible for molecular iodine to be the sole iodinating agent at 3.4×10^{-11} M iodide ion concentration. This is tantamount to stating that it is unlikely, and that H_2OI^+ is probably involved, at least at that low iodide ion concentration.

Table 89. Run 5, Anisole in 101×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_o$	23.6	$\times 10^{-6}$ M	$(HClO_4)_o$	200	$\times 10^{-6}$ M
$[I_2]_o$	22.4	$\times 10^{-6}$ M	$[NaClO_4]$	2866	$\times 10^{-6}$ M
$(I^-)_o$	101	$\times 10^{-6}$ M	$[Anisole]_o$	1959	$\times 10^{-6}$ M
$[I^-]_o$	99.8	$\times 10^{-6}$ M	μ	0.0030	
$[HOI]_o$	0.040	$\times 10^{-6}$ M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	$k_{app} \times 10^2$ (l/mole sec)
81595	4.933	18.2	0.126
140835	4.253	29.4	0.126
223825	3.503	41.7	0.123
251104	3.293	45.1	0.122
335047	2.713	54.7	0.121
415507	2.303	61.5	0.118

$$F_1 = 6.045$$

$$F_2 = 3.36 \times 10^{-7} \text{ sec}^{-1}$$

$$E = 3.92 \times 10^{-6} \text{ mole cm/l}$$

$$k_{appo} = 1.29 \times 10^{-3} \text{ l/mole sec}$$

$$k^* = 1.36 \times 10^{-3} \text{ l/mole sec}$$

Table 90. Run 6, Anisole-2,4,6-d in 101×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	23.6	$\times 10^{-6}$	<u>M</u>	$(HClO_4)_0$	200	$\times 10^{-6}$	<u>M</u>
$[I_2]_0$	22.4	$\times 10^{-6}$	<u>M</u>	$[NaClO_4]$	2866	$\times 10^{-6}$	<u>M</u>
$(I^-)_0$	101	$\times 10^{-6}$	<u>M</u>	$[Anisole-2,4,6-d]_0$	1900	$\times 10^{-6}$	<u>M</u>
$[I^-]_0$	99.8	$\times 10^{-6}$	<u>M</u>	μ	0.0030		
$[HOI]_0$	0.040	$\times 10^{-6}$	<u>M</u>				

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	$k_{app} \times 10^2$ (l/mole sec)
414185	4.533	24.1	0.0352
565995	3.993	32.9	.0372
740197	3.573	39.7	.0360
849272	3.363	43.0	.0350

$$F_1 = 6.045$$

$$F_2 = 3.4 \times 10^{-7} \text{ sec}^{-1}$$

$$E = 3.92 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 0.372 \times 10^{-3} \text{ l/mole sec}$$

$$k^* = 0.390 \times 10^{-3} \text{ l/mole sec}$$

Table 91. Run 4, Anisole in 10.1×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	2.36×10^{-6} M	$(HClO_4)_0$	200×10^{-6} M
$[I_2]_0$	2.30×10^{-6} M	$[NaClO_4]$	2955×10^{-6} M
$(I^-)_0$	10.1×10^{-6} M	$[Anisole]_0$	978×10^{-6} M
$[I^-]_0$	10.1×10^{-6} M	μ	0.0030
$[HOI]_0$	0.050×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	$k_{app} \times 10^3$ (l/mole sec)
72832	0.254	57.2	1.19
89022	.203	65.7	1.23
90702	.201	66.0	1.22
105890	.171	71.0	1.20

$$F_1 = 0.603$$

$$F_2 = 2.56 \times 10^{-7} \text{ sec}^{-1}$$

$$E = 3.92 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 13.0 \times 10^{-3} \text{ l/mole sec}$$

$$k^* = 13.0 \times 10^{-3} \text{ l/mole sec}$$

Table 92. Run 11, Anisole in 10.1×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	2.21×10^{-6} M	$(HClO_4)_0$	200×10^{-6} M
$[I_2]_0$	2.15×10^{-6} M	$[NaClO_4]$	2955×10^{-6} M
$(I^-)_0$	10.1×10^{-6} M	$[Anisole]_0$	968×10^{-6} M
$[I^-]_0$	10.1×10^{-6} M	μ	0.0030
$[HOI]_0$	0.048×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	$k_{app} \times 10^2$ (l/mole sec)
15419	0.462	17.9	1.33
28965	.386	31.3	1.34
67192	.239	57.3	1.31
67322	.233	58.4	1.35
79205	.205	63.3	1.31
79313	.202	63.9	1.33
100803	.162	71.0	1.27

$$F_1 = 0.564$$

$$F_2 = 1.31 \times 10^{-7} \text{ sec}^{-1}$$

$$E = 3.92 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 14.1 \times 10^{-3} \text{ l/mole sec}$$

$$k^* = 14.4 \times 10^{-3} \text{ l/mole sec}$$

Table 93. Run 12, Anisole-2,4,6-d in 10.1×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	2.21×10^{-6} M	$(HClO_4)_0$	200×10^{-6} M
$[I_2]_0$	2.15×10^{-6} M	$[NaClO_4]$	2955×10^{-6} M
$(I^-)_0$	10.1×10^{-6} M	$[Anisole-2,4,6-d_3]_0$	972×10^{-6} M
$[I^-]_0$	10.1×10^{-6} M	μ	0.0030
$[HOI]_0$	0.048×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	$k_{app} \times 10^3$ (l/mole sec)
78743	0.402	28.1	0.431
99152	.365	34.5	.440
111997	.340	38.9	.453
154125	.288	48.0	.437
165644	.276	50.1	.432

$$F_1 = 0.564$$

$$F_2 = 1.3 \times 10^{-7} \text{ sec}^{-1}$$

$$E = 3.92 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 4.59 \times 10^{-3} \text{ l/mole sec}$$

$$k^* = 4.67 \times 10^{-3} \text{ l/mole sec}$$

Table 94. Run 2, Anisole in 1.01×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	0.561×10^{-6} M	$(HClO_4)_0$	200×10^{-6} M
$[I_2]_0$	0.483×10^{-6} M	$[NaClO_4]$	2999×10^{-6} M
$(I^-)_0$	1.01×10^{-6} M	$[Anisole]_0$	496×10^{-6} M
$[I^-]_0$	1.09×10^{-6} M	μ	0.0030
$[HOI]_0$	0.078×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	$k_{app} \times 10^3$ (l/mole sec)
7738	0.096	32.0	10.0
10090	0.084	40.2	10.3
13189	0.075	46.3	9.5
15548	.061	56.2	10.7
17646	.055	60.3	10.6
20263	.053	61.6	9.5

$$F_1 = 0.143$$

$$F_2 = 5.00 \times 10^{-7} \text{ sec}^{-1}$$

$$E = 3.92 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 112 \times 10^{-3} \text{ l/mole sec}$$

$$k^* = 129 \times 10^{-3} \text{ l/mole sec}$$

Table 95. Run 13, Anisole in 1.01×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	0.584×10^{-6} M	$(HClO_4)_0$	200×10^{-6} M
$[I_2]_0$	0.500×10^{-6} M	$[NaClO_4]$	2967×10^{-6} M
$(I^-)_0$	1.01×10^{-6} M	$[Anisole]_0$	263×10^{-6} M
$[I^-]_0$	1.09×10^{-6} M	μ	0.0030
$[HOI]_0$	0.084×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	$k_{app} \times 10^2$ (l/mole sec)
6599	0.123	17.3	10.9
11239	.107	27.9	11.1
13327	.104	29.9	10.1
15418	.096	35.2	10.7
20666	.082	44.6	10.9
22724	.082	44.5	9.9
24924	.076	48.6	10.1

$$F_1 = 0.149$$

$$F_2 = 1.0 \times 10^{-7} \text{ sec}^{-1}$$

$$E = 3.92 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 111 \times 10^{-3} \text{ l/mole sec}$$

$$k^* = 130 \times 10^{-3} \text{ l/mole sec}$$

Table 96. Run 14, Anisole-2,4,6-d in 1.01×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	0.584×10^{-6} M	$(HClO_4)_0$	200×10^{-6} M
$[I_2]_0$	0.500×10^{-6} M	$[NaClO_4]$	2967×10^{-6} M
$(I^-)_0$	1.01×10^{-6} M	$[Anisole-2,4,6-d]_0$	255×10^{-6} M
$[I^-]_0$	1.09×10^{-6} M	μ	0.0030
$[HOI]_0$	0.084×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	$k_{app} \times 10^2$ (l/mole sec)
22541	0.121	18.2	3.49
54484	.092	37.1	3.34
67411	.083	43.0	3.27
85494	.072	50.3	3.20
85594	.072	50.3	3.20
94229	.063	56.3	3.45
94329	.063	56.3	3.44

$$F_1 = 0.149$$

$$F_2 = 1.0 \times 10^{-7} \text{ sec}^{-1}$$

$$E = 3.92 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 37.0 \times 10^{-3} \text{ l/mole sec}$$

$$k^* = 43.2 \times 10^{-3} \text{ l/mole sec}$$

Table 97. Run 7, Anisole in 0.101×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_o$	0.502×10^{-6} M	$(HClO_4)_o$	200×10^{-6} M
$[I_2]_o$	0.312×10^{-6} M	$[NaClO_4]$	2967×10^{-6} M
$(I^-)_o$	0.101×10^{-6} M	$[Anisole]_o$	95.3×10^{-6} M
$[I^-]_o$	0.291×10^{-6} M	μ	0.0030
$[HOI]_o$	0.190×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	$k_{app} \times 10^2$ (l/mole sec)
9381	0.104	19.1	23.7
13839	0.095	26.0	22.8
29550	.063	50.6	25.1
31009	.072	43.5	19.4
31320	.070	43.1	20.1
35707	.056	56.0	24.2
35814	.057	55.2	23.6

$$F_1 = 0.129$$

$$F_2 = 1.0 \times 10^{-7} \text{ sec}^{-1}$$

$$E = 3.92 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 261 \times 10^{-3} \text{ l/mole sec}$$

$$k^* = 420 \times 10^{-3} \text{ l/mole sec}$$

Table 98. Run 3, Anisole in 0.101×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_o$	0.537×10^{-6} M	$(HClO_4)_o$	200	$\times 10^{-6}$ M
$[I_2]_o$	0.337×10^{-6} M	$[NaClO_4]$	2998	$\times 10^{-6}$ M
$(I^-)_o$	0.101×10^{-6} M	$[Anisole]_o$	98.1	$\times 10^{-6}$ M
$[I^-]_o$	0.301×10^{-6} M	μ	0.0030	M
$[HOI]_o$	0.200×10^{-6} M			

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	$k_{app} \times 10^2$ (l/mole sec)
8063	0.108	19.7	27.7
11317	.101	24.3	25.1
14861	.094	29.0	23.5
21059	.083	36.4	21.9
26147	.080	37.9	18.6

$$F_1 = 0.137$$

$$F_2 = 6.2 \times 10^{-7} \text{ sec}^{-1}$$

$$E = 3.92 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 268 \times 10^{-3} \text{ l/mole sec}$$

$$k^* = 428 \times 10^{-3} \text{ l/mole sec}$$

Table 99. Run 8, Anisole-2,4,6-d in 0.101×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	0.502×10^{-6} M	$(HClO_4)_0$	200 $\times 10^{-6}$ M
$[I_2]_0$	0.312×10^{-6} M	$[NaClO_4]$	2967 $\times 10^{-6}$ M
$(I^-)_0$	0.101×10^{-6} M	$[Anisole-2,4,6-d]_0$	97.8×10^{-6} M
$[I^-]_0$	0.291×10^{-6} M	μ	0.0030
$[HOI]_0$	0.190×10^{-6} M		

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	$k_{app} \times 10^2$ (l/mole sec)
36133	0.095	25.3	8.27
74816	.071	43.3	7.77
88543	.063	51.8	8.43
88762	.060	49.4	7.89
103060	.058	53.2	7.54
102845	.057	54.0	7.73

$$F_1 = 0.129$$

$$F_2 = 1.0 \times 10^{-7} \text{ sec}^{-1}$$

$$E = 3.92 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 94 \times 10^{-3} \text{ l/mole sec}$$

$$k^* = 151 \times 10^{-3} \text{ l/mole sec}$$

Table 100. Iodination of Anisole at $\mu = 0.30$; $[H^+] = 0.009783 \text{ M}$; Temperature = 50.0°
 (from Data of Aprahamian⁽⁵⁹⁾)

$[I^-]_0 \times 10^6$ (mole/l)	$[ArH]_0 \times 10^6$ (mole/l)	$[I_2]_0 \times 10^6$ (mole/l)	$k_{app} \times 10^4$ (l/mole sec)	$k^* \times 10^4$ (l/mole sec)	$k^* [I^-] \times 10^8$ (sec ⁻¹)	$1/k^*$ (mole sec/l)
920	4000	183	1.94	2.81	25.8	3560
477	2000	100	5.35	6.56	31.3	1525
452	4000	217	4.72	5.76	26.0	1780
286	2000	107	8.62	9.74	27.8	1027
95	2000	112	30.2	31.5	29.9	317
47.4	1000	113	65.0	66	31.2	152
47.4	2000	113	65.0	66	31.2	152
47.3	500	115	58.3	59	27.9	170
47.2	3000	118	64.0	66	31.1	152
47.2	4000	118	67.0	68	32.1	147
23.7	2000	116	120	121	28.8	82.5
16.5	2000	130	140	140	23.1	71.5
9.5	4000	101	210	210	20.0	48.0
9.4	2000	124	260	260	24.4	38.5

Table 101. Iodination of Anisole-2,4,6-d at $\mu = 0.30$; $[H^+] = 0.009783 \text{ M}$; Temperature = 50.0°
 (from Data of Aprahamian⁽⁵⁹⁾)

$[I^-]_0 \times 10^3$ (mole/l)	$[ArH]_0 \times 10^3$ (mole/l)	$[I_2]_0 \times 10^3$ (mole/l)	$k_{app0} \times 10^4$ (l/mole sec)	$k^* \times 10^4$ (l/mole sec)	$k^*[I^-] \times 10^3$ (sec ⁻¹)	$1/k^*$ (mole sec/l)	k_H^*/k_D^* ^a
477	2000	99.2	1.64	2.02	9.6	4960	3.25
285	2000	105	2.77	3.15	9.0	3150	3.09
95	2000	117	10.1	10.5	9.6	953	3.06
47.0	2010	134	17.9	18.3	8.6	541	3.58
25.0	2000	120	33.9	34.3	8.6	292	2.99
16.5	2000	119	45.4	46.1	7.6	217	3.04
9.8	1990	112	75.0	74.0	7.3	135	2.76
9.5	2000	117	92.5	92.8	8.8	108	2.76

^aWhere more than one experiment was run at identical, or almost identical, iodide ion concentration for either anisole or anisole-2,4,6-d₃, the isotope effect was calculated using the average values of $k^*[I^-]$.

Table 102. Data on Iodination of Anisole at $\mu = 0.0030$; $[H^+] = 200 \times 10^{-6} M$; Temperature = 50.0°

Table Ref.	$[I^-]_0 \times 10^6$ (mole/l)	$[ArH]_0 \times 10^6$ (mole/l)	$[I_2]_0 \times 10^6$ (mole/l)	$k_{app0} \times 10^3$ (l/mole sec)	$k^* \times 10^3$ (l/mole sec)	$k^*[I^-] \times 10^6$ (sec ⁻¹)	$1/k^*$ (mole sec/l)
89	99.8	1960	22.4	1.29	1.36	0.136	785
91	10.1	978	2.30	13.0	13.0	.131	77.0
92	10.1	968	2.15	14.1	14.4	.145	69.5
94	1.09	496	0.483	112	129	.141	7.75
95	1.09	263	0.500	111	130	.142	7.70
97	0.291	95.3	0.312	261	420	.122	2.38
98	0.301	98.1	0.337	268	428	.129	2.34

Table 103. Data on Iodination of Anisole-2,4,6-d at $\mu = 0.0030$; $[H^+] = 200 \times 10^{-6} M$;
 Temperature = 50.0°

Table Ref.	$[I^-]_0$ $\times 10^6$ (mole/l)	$[ArH]_0$ $\times 10^6$ (mole/l)	$[I_2]_0$ $\times 10^6$ (mole/l)	k_{app} $\times 10^3$ (l/mole sec)	$k^* \times 10^3$ (l/mole sec)	$k^*[I^-]$ $\times 10^6$ (sec ⁻¹)	$1/k^*$ (mole sec/l)	k^*_H/k^*_D
90	99.8	1900	22.4	0.372	0.390	0.0390	2560	3.26
93	10.1	972	2.15	4.58	4.67	.0472	214	3.08
96	1.09	255	0.500	37.0	43.2	.0471	23.2	3.02
99	0.291	97.8	0.312	94.0	151.0	.0439	6.63	2.84

CHAPTER VIII

THE IODINATION OF 2,4-DINITROPHENOL CATALYZED BY MONOHYDROGEN
PHOSPHATE ANIONIntroduction

Monohydrogen phosphate has been found to be an effective catalyst for the iodination of phenol⁽⁴⁶⁾ and for aniline.⁽⁴⁵⁾ It was used here in the hope of sufficiently increasing the rate of proton removal from the iodination intermediate (cf., reaction mechanism in Chapter V) to cause significant reduction of the isotope effect. The requirement that sufficient catalysis should have this effect is inherent in the proposed mechanism, since most of the isotope effect must reside in the proton removal step (k_3).

Specific Experimental Details

The experimental data are summarized in Tables 123 and 124.

All experiments were performed at 50.0°. Most were at ionic strength 0.38, which was necessary in order to increase catalyst concentration without altering the buffer ratio. This buffer ratio, $[\text{H}_2\text{PO}_4^-]/[\text{HPO}_4^{=}]$, was maintained at 5.0 (with the exceptions noted below), the $\text{HPO}_4^{=}$ concentrations being 0.0010 M, 0.025 M, 0.037 M, and 0.047 M. At 0.0010 M and 0.025 M $\text{HPO}_4^{=}$, the ionic strength was brought to 0.30 with sodium perchlorate. The iodide ion concentration range was from 3.50×10^{-6} M to 91.7×10^{-6} M. The hydrogen ion concentration for most of

the reactions was 1.70×10^{-6} M, with a few slightly higher, and with one at 2.74×10^{-6} M. The experiments in which hydrogen ion concentration was higher than 1.70×10^{-6} M were those at 0.0010 M HPO_4^- in which large concentrations of 2,4-dinitrophenol were required, the additional acidity being contributed by the dissociation of the phenol. This in turn slightly reduced the concentration of HPO_4^- , but these were precisely the experiments in which the degree of catalysis was small so the error was not serious.

The hydrogen ion concentration in a given experiment was calculated as follows. Hydrogen ion activity corresponding to a 5/1 ratio of $[\text{H}_2\text{PO}_4^-]/[\text{HPO}_4^-]$ at ionic strength 0.30 was determined by pH meter to be 1.20×10^{-6} . The solution used in this determination was 0.0050 M in sodium dihydrogen phosphate, 0.0010 M in sodium monohydrogen phosphate and 0.291 M in sodium perchlorate. Using 0.70 as the mean activity coefficient in an 0.30 μ sodium perchlorate solution, ⁽⁹¹⁾ the hydrogen ion concentration was calculated to be 1.70×10^{-6} M. Deviations from this acidity occur when the concentration of 2,4-dinitrophenol is significant relative to the buffer concentration. In these cases, the acidity was calculated by successive approximations, using 194×10^{-6} for the dissociation constant of 2,4-dinitrophenol (cf., Chapter V) and the acidic dissociation constant of H_2PO_4^- , which was calculated as 3.42×10^{-7} from the hydrogen ion concentration and buffer ratio of the solution checked by pH meter.

Reactions were quenched by adding 0.38 g of sodium iodide dissolved in 3.0 ml of water to the 47.0 ml reaction solution at $25 \pm 3^\circ$, which had been quickly cooled in an ice bath from the 50.0° temperature

at which the reaction was run (at which temperature the volume was 47.38 ml). No buffering agent was necessary, since the pH was already buffered to a sufficiently high value that oxidation of iodide to iodine was not an experimental problem--the absorbance of the quenched solutions was constant over the period of time required for measurement.

The extinction coefficients at 2875 Å, and hence the values of P_1 and P_2 , for the 2,4-dinitrophenol-2,4-dinitrophenoxide couple and the 2-iodo-4,6-dinitrophenol-2-iodo-4,6-dinitrophenoxide couple were determined in solutions of the same concentrations of sodium perchlorate, sodium dihydrogen phosphate, sodium monohydrogen phosphate, and 2,4-dinitrophenol concentrations as the quenched reaction solutions. The P_1 value in these solutions can be seen from Tables 104-121 to be slightly greater than that in the non-catalyzed solutions (tables 31-67), at the same ionic strength. This undoubtedly reflects the higher concentration of undissociated phenol in the more acidic catalyzed reaction solutions.

The small absorbance corrections for sodium iodide, buffer and sodium perchlorate background (averaging about one percent of total absorbance, three percent in the worst case) were made in the usual way, by measuring the absorbance at 2875 Å of solutions identical to the quenched reaction solutions, but containing neither aromatic compound nor iodine. These corrections have already been made in Tables 104-121. The buffer and sodium perchlorate absorbances were, of course, corrected for in the above-discussed determination of extinction coefficients.

In experiments no. 94, 95, 96, and 97 (Tables 108, 109, 114, and 115), it was necessary to make slight (ca. one percent) corrections for volatilization of iodine during sampling, as described in Chapter III.

Blank drop was determined, as usual, by running a series of blanks (samples minus aromatic compound) simultaneously with the samples. The hypochlorite treatment of the buffer salts as described in Chapter II was necessary to prevent such a large blank drop as to make experiments impossible. Even with this treatment, the consumption of iodine by the buffer salts (or by impurities therein) prevented the extension of the work to higher iodide ion concentrations.

The determination of k_{app0} from k_{app} data was generally obtained as described in Chapter III, according to equation (18) of that chapter. In a few cases, however, due to the extent of iodine hydrolysis at the low acidity of these experiments, the iodide ion concentration at 50 percent iodine consumption could not be accurately obtained by simply adding to $[I^-]$ one-half the value of $(I_2)_0$. In these cases, true iodine and iodide ion concentrations had to be calculated at both zero and 50 percent consumption of iodine by considering the hydrolysis and triiodide equilibria.

The extent of hydrolysis required an additional factor. The $\frac{(I_2)}{[I_2]}$ ratio at any percent reaction was high in these experiments (as high as 2.58). This ratio decreased as more iodine was consumed, due to the lesser importance of iodine hydrolysis as iodine concentration decreased and iodide ion concentration increased. The $\frac{(I_2)}{[I_2]}$ ratio at zero percent iodine consumption and at 50 percent reaction were determined from hydrolysis and triiodide equilibria; the ratios at zero and at 50 percent iodine consumption were averaged and divided by the ratio at zero percent iodine consumption to give this second factor for the extrapolation of k_{app} at 50 percent reaction to k_{app0} . The total equation for the correc-

tion was

$$k_{app0} = k_{app50\%} \left(\frac{[I^-]_{50\%}}{[I^-]_0} \right)^n \frac{\left\{ \frac{(I_2)_{50\%}}{[I_2]_{50\%}} + \frac{(I_2)_0}{[I_2]_0} \right\}}{2 \frac{(I_2)_0}{[I_2]_0}} \quad (1)$$

This extrapolation from 50 percent reaction to k_{app0} was applied in the same way as the extrapolation from 50 percent reaction to k_{app0} described in Chapter III.

In contrast to the uncatalyzed iodination of 2,4-dinitrophenol (cf., Chapter V), it was not necessary here to correct for any change in $[ArO^-]/(ArOH)$ during the course of reaction, since in these catalyzed experiments the solutions were buffered at such high pH that this ratio never departed significantly from unity.

The activity coefficient of 0.70 (cf., above) was used in iodine hydrolysis calculations.

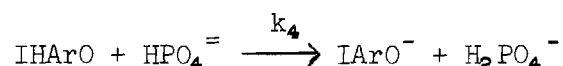
Discussion of Results

The results are summarized in Tables 123 and 124 and reflect rate-enhancement by phosphate,[†] the rate constants k^{∇} increasing with increas-

[†]By analogy with Berliner's results on phenol⁽⁴⁶⁾ and aniline,⁽⁴⁵⁾ where the ratios of catalytic constants for $HPO_4^{=}/H_2PO_4^-$ were 35 and 98, respectively, the importance of $H_2PO_4^-$ catalysis in these experiments is probably small. However, since the buffer ratio is maintained constant in all of these experiments, any $H_2PO_4^-$ catalysis would simply be included in the " $HPO_4^{=}$ catalysis" in a constant percentage, and it would therefore have no effect upon the general arguments.

ing concentration of that species. These results are plotted in Figures 22 and 23, in which the best straight lines at each concentration of phosphate are drawn through the origin and the two lowest iodide points; it is seen that the highest iodide points, at iodide ion concentration $91.7 \times 10^{-6} \text{ M}$, tend to fall below these straight lines, as will be discussed. It is also seen that the isotope effect remained approximately constant with changes in phosphate concentration, rather than the inverse relationship between isotope effect and phosphate concentration predicted in the beginning of this chapter.

The results are considered in light of the mechanism proposed in Chapter V for the iodination of 2,4-dinitrophenoxide. Assuming that the sole effect of phosphate is enhancement of the rate of proton removal, an additional term must be added to general equation (21), Chapter V, corresponding to the catalyzed proton removal



The equation now becomes

$$\frac{1}{k^{\nabla}} = \left\{ \frac{k_{-1}}{k_1 (k_3 + k_4 [\text{HPO}_4^{=}])} \right\} [\text{I}^-] + \frac{1}{k_1 + \frac{k_1' K_1}{[\text{I}^-]} + \frac{k_1'' K_3 [\text{OH}^-]}{K_w [\text{I}^-]}} \quad (2)$$

The corresponding limiting equation at low iodide ion concentrations is

$$\frac{1}{k^{\nabla}} = \left\{ \frac{k_{-1}}{k_1 (k_3 + k_4 [\text{HPO}_4^{=}])} + \frac{1}{k_1' K_1 + \frac{k_1'' K_3 [\text{OH}^-]}{K_w}} \right\} [\text{I}^-] \quad (3)$$

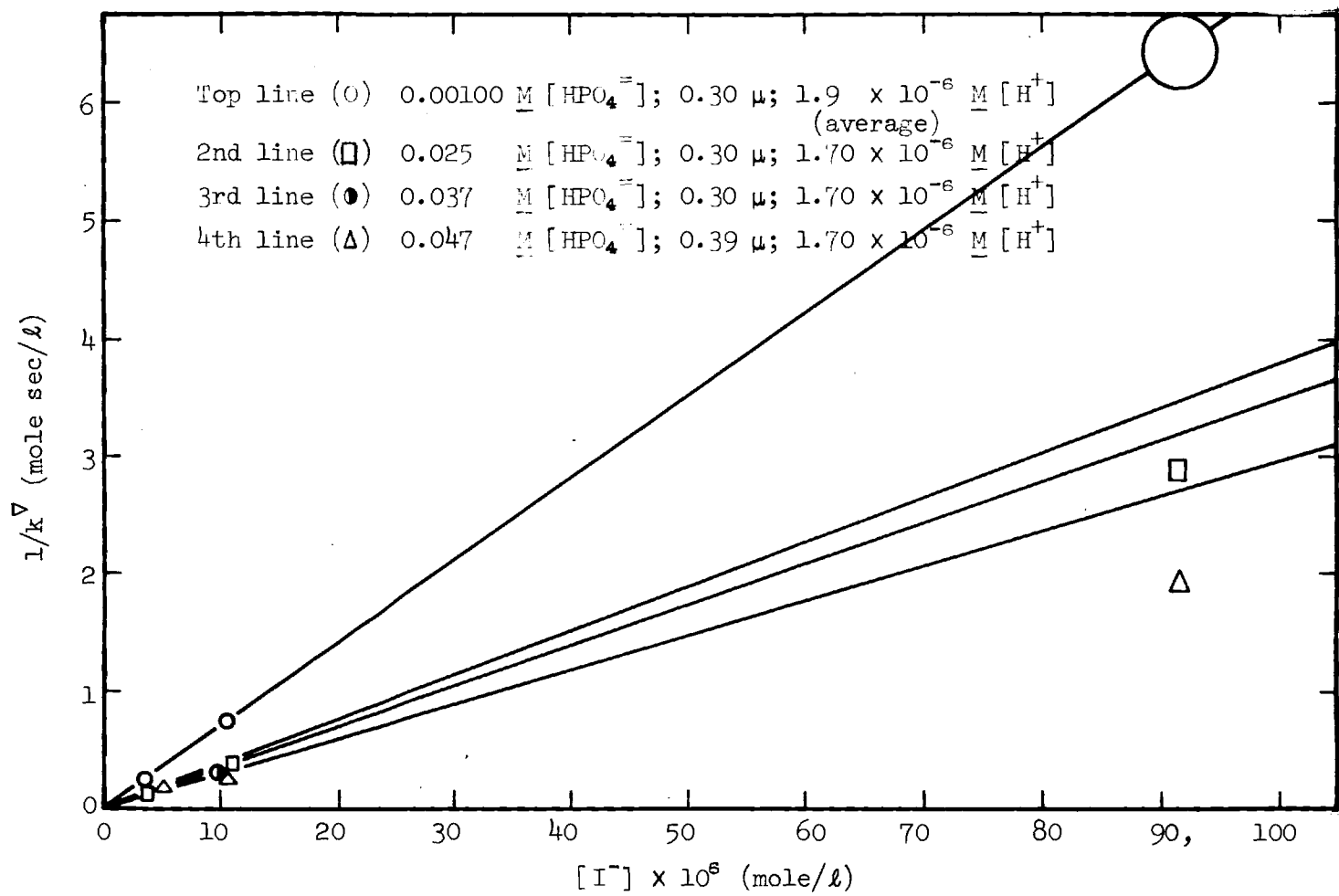


Figure 22. Iodination of 2,4-Dinitrophenol Catalyzed by Phosphate at 50.0°

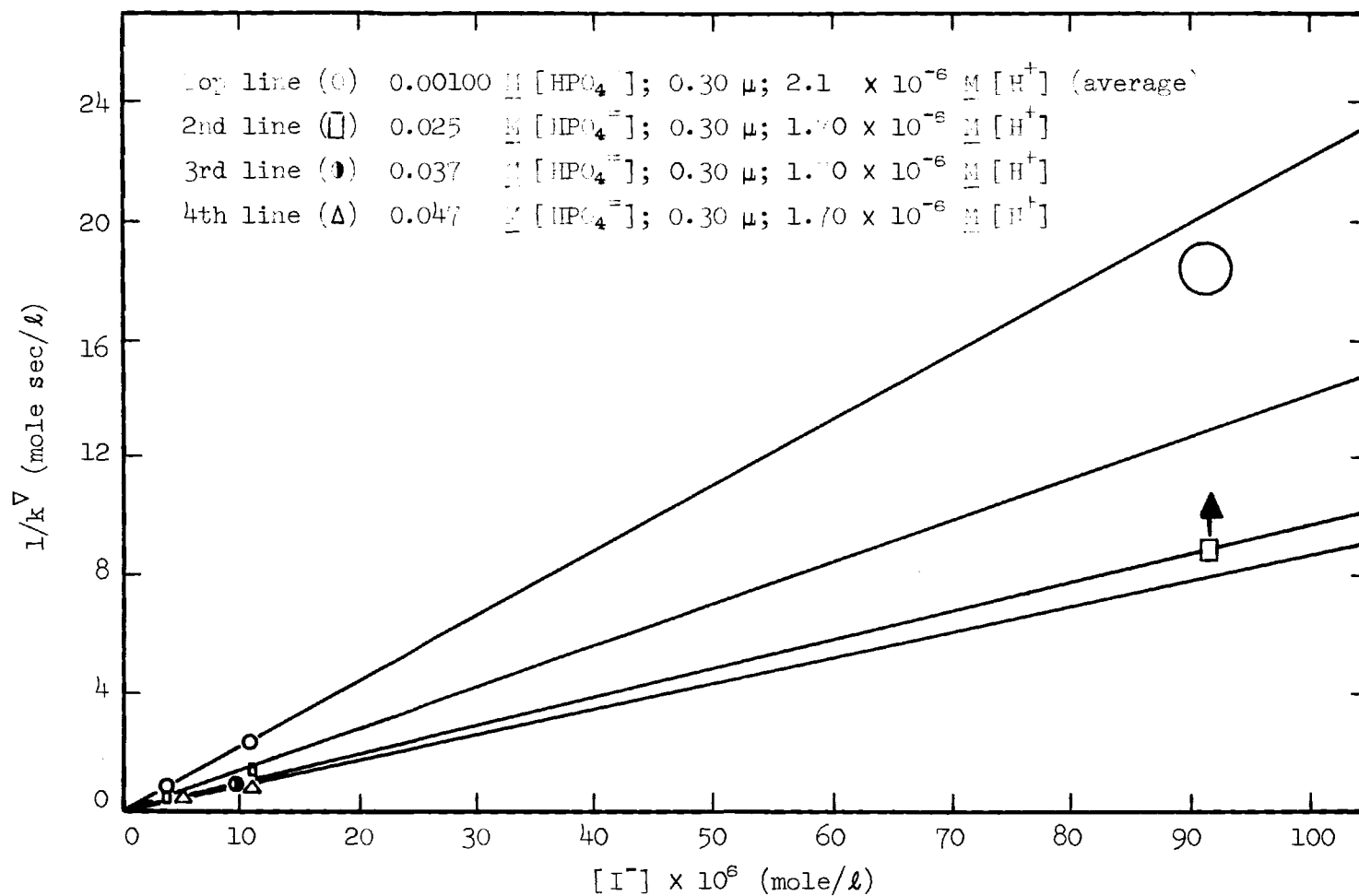


Figure 23. Iodination of 2,4-Dinitrophenol-6-d Catalyzed by Phosphate at 50.0°

The values of $k_1 'K_1$ and $k_1 ''K_3/K_w$ for the protio compound were determined in Chapter V to be $1.03 \pm 0.10 \times 10^{-5} \text{ sec}^{-1}$ and $0.53 \pm 0.02 \times 10^3 \text{ l/mole sec}$, respectively. (It was not possible to obtain reliable figures for the deutero compound.) For the experiments at $1.70 \times 10^{-6} \text{ M}$, and from a value of 8.4×10^{-14} for K_w in terms of concentrations at ionic strength 0.30⁽⁹¹⁾ (cf., Chapter V), hydroxyl ion concentration was calculated to be $5.0 \times 10^{-8} \text{ M}$. From these data, a value of $2.7 \pm 0.1 \times 10^4 \text{ sec}$ can be obtained for $1/k_1 'K_1 + \frac{k_1 ''K_3 [\text{OH}^-]}{K_w}$. At infinite catalysis, therefore, the slope of the low iodide line ought to be $2.7 \pm 0.1 \times 10^4 \text{ sec}$. (This standard deviation refers to the degree of confidence in the calculated theoretical slope; the experimental error in measuring such a slope would be an additional source of error.) Figures 22 and 23 show that the approximate value of the slope for the protio compound at $0.037 \text{ M HPO}_4^{=}$ is $3.5 \times 10^4 \text{ sec}$ and at $0.047 \text{ M HPO}_4^{=}$ is $3.0 \times 10^4 \text{ sec}$.[†] According to the mechanism, $\text{HPO}_4^{=}$ concentrations of this magnitude catalyze proton removal sufficiently that $k_4 [\text{HPO}_4^{=}]$ is greater than k_3 for the protio compound.

The ratios k_4/k_3 can be calculated for the protio and deutero compounds. (In the latter case, however, a value for the limiting slope must be assumed. The assumption is made that it is $2.7 \times 10^4 \text{ sec}$, the same as for the protio compound.) The ratio is calculated as follows.

[†]It should be borne in mind that the $0.047 \text{ M HPO}_4^{=}$ data are at 0.38μ , while the ionic strength is 0.30 for the other data. The same activity coefficient (0.70) was used throughout for the calculation of hydrolysis of iodine, and rate and equilibrium constants were assumed to be unaffected by the difference in ionic strength. This is a possible source of error in the results at 0.38μ .

The value of 2.7×10^4 sec is subtracted from the slope at zero catalyst[†] and also from the slope at the catalyst concentration of interest. This gives the corresponding values of $\frac{k-1}{k_1(k_3 + k_4[\text{HPO}_4^{=}])}$. The ratio of the value at zero $\text{HPO}_4^{=}$ to that at a given concentration $[\text{HPO}_4^{=}]$ is equal to $\frac{k_3 + k_4[\text{HPO}_4^{=}] }{k_3}$; this equation can then be solved for k_4/k_3 .

The calculation was made for the protio and deutero compounds at

[†]The experimental slopes at $0.0010 \text{ M HPO}_4^{=}$, as obtained from Figures 22 and 23, must be subjected to two minor corrections so that they will correspond to zero catalyst at the same acidity as the other experimental lines.

The catalytic effect of the $0.0010 \text{ M HPO}_4^{=}$ is estimated. From Figures 22 and 23, it is seen that the addition of 0.024 M more $\text{HPO}_4^{=}$ decreased the slopes by 3.3×10^4 sec and by 8.0×10^4 sec for the protio and deutero compounds, respectively. (The values of these slopes are given in Table 125. The standard deviations are obtained as in Chapter V.) The small catalytic effect of $0.00100 \text{ M HPO}_4^{=}$ was approximated by multiplying each of these figures by $1/24$, and adding the result to each $0.00100 \text{ M HPO}_4^{=}$ slope to correct to zero catalyst.

Also, correction was made for the fact that the average hydrogen ion concentrations for the $0.0010 \text{ M HPO}_4^{=}$ lines are $1.79 \times 10^{-6} \text{ M}$ and $1.84 \times 10^{-6} \text{ M}$ for the protio and deutero compounds, respectively. (These figures are for the two lowest iodide points only, which are the points involved in the present considerations.) The $1 \div k_1'K_1 + \frac{k_1''K_2[\text{OH}^-]}{K_w}$ terms were calculated at $1.70 \times 10^{-6} \text{ M}$ hydrogen ion and at

these higher acidities. The difference between the values at $1.70 \times 10^{-6} \text{ M}$ and $1.79 \times 10^{-6} \text{ M}$ hydrogen ion was subtracted from the slope of the protio line and the difference between the values for $1.70 \times 10^{-6} \text{ M}$ and $1.84 \times 10^{-6} \text{ M}$ hydrogen ion was subtracted from the slope of the deutero line. This corrected each line to $1.70 \times 10^{-6} \text{ M}$ hydrogen ion.

The net effect of these corrections was to change the protio slope from 0.71×10^5 sec to 0.69×10^5 sec, and the deutero slope (2.1×10^5 sec) not at all.

0.025 M, 0.037 M, and 0.047 M $\text{HPO}_4^{=}$. For the deuterio compound, k_4/k_3 comes to 32[†] at 0.025 M $\text{HPO}_4^{=}$, 45 at 0.037 M $\text{HPO}_4^{=}$, and 45 at 0.047 M $\text{HPO}_4^{=}$. For the protio compound, the calculated value of k_4/k_3 is 112 ± 50 at 0.025 M $\text{HPO}_4^{=}$, 115 at 0.037 M $\text{HPO}_4^{=}$, and 280 ± 380 at 0.047 M $\text{HPO}_4^{=}$.

It is impossible to obtain standard deviations for the k_4/k_3 ratio for the deuterio compound because the calculation required the assumption of a value for $\frac{1}{k_1 K_1 + \frac{k_1 K_3 [\text{OH}^-]}{K_w}}$. The principal source of the large standard deviations in the k_4/k_3 data for the protio compound is the genesis of the $\frac{k-1}{k_1 (k_3 + k_4 [\text{HPO}_4^{=}])}$ value for the different $\text{HPO}_4^{=}$ concentrations, representing as it does a relatively small difference between large numbers, the difference becoming smaller with increasing catalyst concentration. No standard deviation can be calculated for 0.037 M $\text{HPO}_4^{=}$ because there is only one such experimental point.

It appears that the best use can be made of these imprecise data by determining whether a combination of values falling within the range of likely experimental error is consistent with the proposed mechanism.

By accepting the measured values as correct, despite the large standard deviations, a reverse of the k_4/k_3 calculation above can be used to predict the $1/k^\nabla$ versus $[\text{I}^-]$ slopes for the protio and deuterio compounds at the various catalyst concentrations. The values employed,

[†]The k_4/k_3 ratios in this and the following chapter have the units l/mole . The units will be omitted for convenience.

therefore, are 2.7×10^4 sec for $\frac{1}{k_1 K_1 + \frac{k_1 K_2 [\text{OH}^-]}{K_w}}$ for both the protio and deuterio compounds; 115^\dagger for k_4/k_3 for the protio compound; 41^\ddagger for k_4/k_3 for the deuterio compound; $6.9 \times 10^4 \text{ sec}^{-1}$ for the protio $1/k^\nabla$ versus $[\text{I}^-]$ slope at zero $\text{HPO}_4^{=}$; and $21.0 \times 10^4 \text{ sec}^{-1}$ for the deuterio slope at zero $\text{HPO}_4^{=}$. It was calculated that the slopes for the protio compound ought to be $3.8 \times 10^4 \text{ sec}^{-1}$ at $0.025 \text{ M HPO}_4^{=}$ ($3.8 \pm 0.5 \times 10^4 \text{ sec}^{-1}$ observed); $3.5 \times 10^4 \text{ sec}^{-1}$ at $0.037 \text{ M HPO}_4^{=}$ ($3.5 \times 10^4 \text{ sec}^{-1}$ observed); $3.4 \times 10^4 \text{ sec}^{-1}$ at $0.047 \text{ M HPO}_4^{=}$ ($3.0 \pm 0.5 \times 10^4 \text{ sec}^{-1}$ observed). The slopes for the deuterio compound ought to be $11.7 \times 10^4 \text{ sec}^{-1}$ at $0.025 \text{ M HPO}_4^{=}$ ($12.9 \times 10^4 \text{ sec}^{-1}$ observed); $10.4 \times 10^4 \text{ sec}^{-1}$ at $0.037 \text{ M HPO}_4^{=}$ ($9.5 \times 10^4 \text{ sec}^{-1}$ observed); and $8.9 \times 10^4 \text{ sec}^{-1}$ at $0.047 \text{ M HPO}_4^{=}$ ($8.6 \times 10^4 \text{ sec}^{-1}$ observed).

It can be seen that, using the experimental results, the observed slopes are predicted reasonably well by the proposed mechanistic model. However, the ratios of k_4/k_3 for the protio and deuterio compounds, in light of the $k_{3\text{H}}/k_{3\text{D}}$ isotope effect of 4.5 found in the non-catalyzed iodination of 2,4-dinitrophenol, require a $k_{4\text{H}}/k_{4\text{D}}$ isotope effect of 12.6. Since the observed slopes for the protio and deuterio compounds determine the $k_{\text{H}}^\nabla/k_{\text{D}}^\nabla$ isotope effect, this amounts to saying that a $k_{4\text{H}}/k_{4\text{D}}$ isotope effect of 12.6 is necessary to explain the observed constant isotope ef-

[†]This value was determined from the data at $0.025 \text{ M HPO}_4^{=}$ and $0.037 \text{ M HPO}_4^{=}$. Because of the enormous standard deviation, the value of k_4/k_3 (280 ± 380) calculated for $0.047 \text{ M HPO}_4^{=}$ was not included in the averaging process.

[‡]This value represents an average of k_4/k_3 values at the three different concentrations of $\text{HPO}_4^{=}$.

fect with increasing phosphate concentration. This approximately three-fold increase in the isotope effect between water- and phosphate-catalyzed proton removal {4.5 for water-catalyzed (cf., Chapter V), 12.6 for phosphate-catalyzed} is difficult to accept and casts considerable doubt on the validity of a high k_{4H}/k_{4D} isotope effect as an explanation of the constant net isotope effect as phosphate concentration is increased. For instance, it has recently been shown that the isotope effect is the same for the water- and phosphate-catalyzed proton removal from iodoazulenium cation. (64)

It has been noted that the highest iodide points ($91.7 \times 10^{-6} \text{ M}$) tend to fall below the $1/k^\nabla$ versus $[I^-]$ lines drawn through the origin and the lower iodide points. It is possible that this results from the contribution, at this high iodide ion concentration, of molecular iodine as an iodinating agent, whereas at the lower iodide ion concentrations, H_2OI^+ and HOI are the predominant iodinating agents. This proposal can be checked mathematically. Again, the calculation must be regarded as very approximate, because of the large standard deviations involved. As was done for the calculation of theoretical $1/k^\nabla$ versus $[I^-]$ slopes at the various iodide ion concentrations, the nominal experimental values of k_4/k_3 , limiting slopes and measured slopes are used.

$$\frac{1}{k^\nabla} = \left(\frac{1}{k_1} \cdot \frac{k_{-1}}{k_3 + k_4[HPO_4^{=}]}\right) [I^-] \quad (2)$$

$$+ \frac{1}{k_1 + \frac{k_1'K_1}{[I^-]} + \frac{k_1''K_3[OH^-]}{K_w[I^-]}}$$

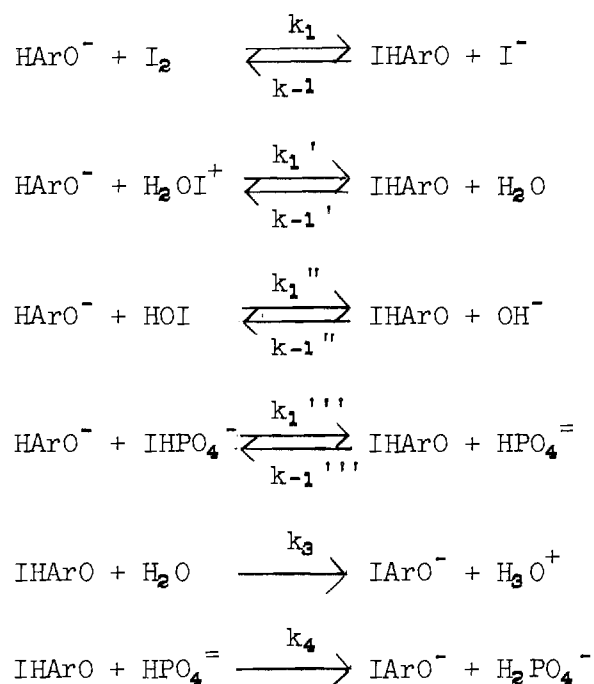
All terms in equation (2) have been evaluated, although the values of k_4 have been evaluated relative to those of k_3 only tentatively, on the basis of the possible explanation that has been put forward to explain the constancy of k_H^∇/k_D^∇ at various phosphate concentrations. Therefore, k^∇ can be calculated for any given $\text{HPO}_4^{=}$ and iodide concentrations.

The calculations show that for all experiments which were performed at iodide ion concentrations of $10.6 \times 10^{-6} \text{ M}$ or lower, the points on the $1/k^\nabla$ versus $[\text{I}^-]$ plots ought to fall on the theoretical straight lines through the origin within two percent; however, there were negative deviations predicted for the $91.7 \times 10^{-6} \text{ M}$ iodide points. It is predicted that at zero $\text{HPO}_4^{=}$, the $91.7 \times 10^{-6} \text{ M}$ iodide point should be seven percent below the line for the protio and ten percent for the deutero compounds (in Figures 22 and 23, the protio point is on the line and the deutero point is six percent below the line); at 0.025 M the $91.7 \times 10^{-6} \text{ M}$ point should be 14 percent below the line for the protio compound and 11 percent below the line for the deutero compound (in Figures 22 and 23, the protio point is 17 percent below the line and the deutero point is 27 percent below the line); at 0.047 M $\text{HPO}_4^{=}$ the $91.7 \times 10^{-6} \text{ M}$ iodide point should be 14 percent below the line in the case of the protio compound (in Figure 22, the protio point is 28 percent below the line). No deutero point was measured at 0.047 M $\text{HPO}_4^{=}$ and $91.7 \times 10^{-6} \text{ M}$ iodide because of blank drop difficulties, and it should be pointed out that the corresponding protio point suffered to some extent from this difficulty and is, therefore, less reliable than the other points.

It is evident that the observed departure from the straight line $1/k^{\nabla}$ versus $[I^-]$ plots at the highest iodide ion concentration is expected when the iodination of 2,4-dinitrophenoxide is catalyzed by a general base.

From the fact that HOI has been invoked as an iodinating agent in the iodination of 2,4-dinitrophenol, it seems logical to consider the possibility of $I\text{HPO}_4^-$ as an iodinating agent in the case of $\text{HPO}_4^{=}$ catalysis of the same reaction. This can be done only qualitatively.

One possibility is that the reaction mechanism is now represented by the scheme



Application of the steady state approximation and the principle of microscopic reversibility leads to the equation

$$\frac{1}{k^{\nabla}} = \left(\frac{k_{-1}}{k_1 (k_3 + k_4 [\text{HPO}_4^{\equiv}])} \right) [\text{I}^-] \quad (4)$$

$$+ \frac{1}{k_1 + \frac{k_1 'K_1}{[\text{I}^-]} + \frac{k_1 ''K_3 [\text{OH}^-]}{K_w [\text{I}^-]} + \frac{k_1 '''K_4 [\text{HPO}_4^{\equiv}]}{[\text{I}^-]}}$$

where $K_4 = \frac{[\text{IHPO}_4^{\equiv}][\text{I}^-]}{[\text{HPO}_4^{\equiv}][\text{I}_2]}$

While the $1/k^{\nabla}$ versus $[\text{I}^-]$ slope at high iodide ion concentration would be the same as if IHPO_4^{\equiv} were not involved; *viz.*, $\frac{k_{-1}}{k_1 (k_3 + k_4 [\text{HPO}_4^{\equiv}])}$, at low iodide ion concentrations the equation will be

$$\frac{1}{k^{\nabla}} = \left(\frac{k_{-1}}{k_1 (k_3 + k_4 [\text{HPO}_4^{\equiv}])} + \frac{1}{k_1 'K_1 + \frac{k_1 ''K_3 [\text{OH}^-]}{K_w} + k_1 '''K_4 [\text{HPO}_4^{\equiv}]} \right) [\text{I}^-] \quad (5)$$

The slope differs from the low-iodide slope when IHPO_4^{\equiv} is not considered (*cf.*, equation (3)) by the term $k_1 '''K_4 [\text{HPO}_4^{\equiv}]$.

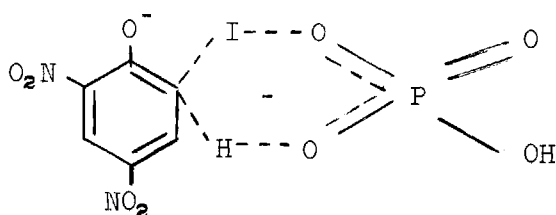
It follows that, at a given HPO_4^{\equiv} concentration, the first term in equation (5) will represent a greater percentage of the slope of the $1/k^{\nabla}$ versus $[\text{I}^-]$ line as a result of iodination by IHPO_4^{\equiv} than had this iodinating agent not been active. Since this first term contains the only constant with a primary isotope effect (k_3), this means that any iodinating activity by IHPO_4^{\equiv} will cause the isotope effect to be higher than otherwise anticipated, at a given HPO_4^{\equiv} concentration. In other words, the $k_{4\text{H}}/k_{4\text{D}}$ isotope effect of 12.6 calculated previously would have been too high. In addition, the k_4/k_3 ratios calculated previously

would have been too high, some of the rate enhancement due to iodination by IHPO_4^- having been erroneously attributed to $\text{HPO}_4^{=}$ catalyzed proton removal.

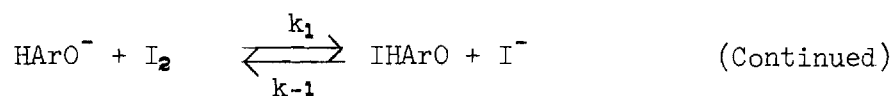
It also follows from this mechanism that the previously calculated limiting slope at infinite catalyst concentration, 2.7×10^4 sec, would not actually be the limiting slope. The slope would decrease below this "limiting" value at sufficiently high catalyst concentration. However, if the value of k_4 were small relative to $k_1'K_1 + \frac{k_1''K_3[\text{OH}^-]}{K_W}$, the $1/k^\nabla$ versus $[\text{I}^-]$ slopes would converge toward 2.7×10^4 sec as catalyst concentration was increased, but with further increase in catalyst concentration the slopes would fall below this value.

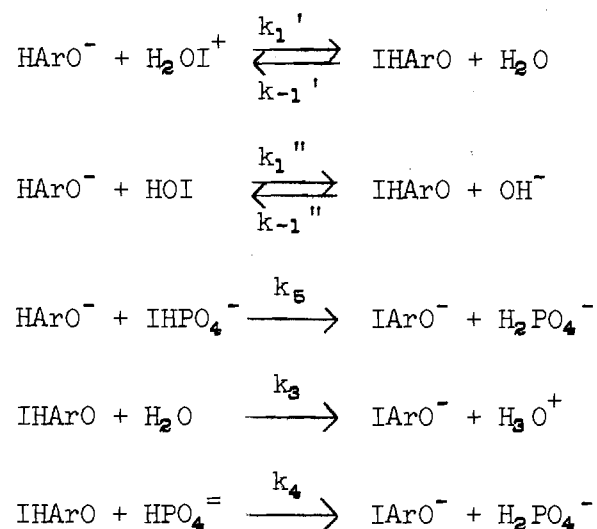
Qualitatively then, the consideration of IHPO_4^- as an iodinating agent in the scheme outlined would be consistent with the data and might account for the large apparent $k_{4\text{H}}/k_{4\text{D}}$ isotope effect.

There is another possible way in which IHPO_4^- might be involved as an iodinating agent. If the iodination of the phenoxide by IHPO_4^- were concerted; i.e., if a transition state such as



were involved, the scheme could be written





This can be considered as two parallel reaction sequences, each producing IArO^- as the end product: one sequence composed of all steps except the k_2 step, the other sequence composed of the k_2 step alone.

By use of the steady state approximation, the following equation can be obtained

$$\begin{aligned}
 1/k^\nabla &= (k_3' + k_{-1}''[\text{OH}^-] + k_{-1}[\text{I}^-] + k_{-1}') \div \left(k_1 k_3' + \frac{k_1' k_3' K_1}{[\text{I}^-]} \right) \quad (6) \\
 &+ \frac{k_1'' k_3' K_3 [\text{OH}^-]}{K_w [\text{I}^-]} + \frac{k_5 K_4 [\text{HPO}_4^{=}] \{k_3' + k_{-1}''[\text{OH}^-] + k_{-1}[\text{I}^-] + k_{-1}'\}}{[\text{I}^-]}
 \end{aligned}$$

where $k_3' = k_3 + k_4[\text{HPO}_4^{=}]$.

At low iodide concentrations, this equation becomes

$$\frac{1}{k^\nabla} = \frac{\{k_{-1}''[\text{OH}^-] + k_{-1}' + k_3'\}[\text{I}^-]}{k_1' k_3' K_1 + \frac{k_1'' k_3' K_3 [\text{OH}^-]}{K_w} + k_5 K_4 [\text{HPO}_4^{=}] \{k_{-1}''[\text{OH}^-] + k_{-1}' + k_3'\}} \quad (7)$$

Since equation (3), representing the low-iodide case where IHPO_4^- is not a significant iodinating agent, can be rewritten (rearranging and making use of the principle of microscopic reversibility)

$$\frac{1}{k^{\nabla}} = \frac{\{k_{-1}''[\text{OH}^-] + k_{-1}' + k_3'\}[\text{I}^-]}{k_1'k_3'K_1 + \frac{k_1''k_3'K_3[\text{OH}^-]}{K_w}} \quad (8)$$

the effect of IHPO_4^- in equation (7) is seen to be the lowering of the slope at a given catalyst concentration. Therefore, the previously calculated ratios of k_4/k_3 would have been too high.

It is not possible to predict, a priori, the isotope effect at a given catalyst concentration, because presumably an isotope effect would reside in the k_2 term. The direction of the effect upon the isotope effect of IHPO_4^- as an iodinating agent in this scheme would depend upon the relative isotope effects of k_2 on the one hand and k_3 and k_4 on the other.

Qualitatively, this mechanism is also consistent with the experimental results and could possibly explain the apparent high k_4 isotope effect.

In summary, the results of the experiments on the phosphate-catalyzed iodination of 2,4-dinitrophenoxide, while not amenable to rigorously quantitative interpretation, are consistent with the mechanistic scheme described in Chapter V, with proton removal catalyzed by both water and by HPO_4^- , provided that the k_4 isotope effect is greater than the k_3 isotope effect. The data are also consistent with the

involvement of IHPO_4^- as an iodinating agent, via either a preequilibrium between phenoxide and intermediate or a concerted iodine introduction and proton removal.

Table 104. Run 84, 2,4-Dinitrophenol in 2.38×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	2.03×10^{-6} M	(NaH_2PO_4)	0.0050	M
$[I_2]_0$	0.79×10^{-6} M	(Na_2HPO_4)	0.00100	M
$(I^-)_0$	2.38×10^{-6} M	$(NaClO_4)$	0.29	M
$[I^-]_0$	3.62×10^{-6} M	$(2,4\text{-Dinitrophenol})_0$	26.3×10^{-6}	M
$[HOI]_0$	1.24×10^{-6} M	μ	0.30	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
5328	1.334	19.4	1.55
7378	1.286	25.8	1.55
10799	1.206	36.5	1.62
13252	1.176	40.2	1.50
16575	1.118	47.9	1.52
18624	1.096	50.9	1.48

$$F_1 = 0.748$$

$$P_1 = 27800 \text{ l/mole cm}$$

$$F_2 = 2.0 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50332 \text{ l/mole cm}$$

$$E = 2.713 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368300 \text{ l/mole cm}$$

$$k_{app0} = 1.56 \text{ l/mole sec}$$

$$k^\nabla = 4.04 \text{ l/mole sec}$$

$$k^* = 4.00 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 14.7 \times 10^{-6} \text{ sec}^{-1}$$

Table 105. Run 85, 2,4-Dinitrophenol-6-d in 2.38×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	2.03×10^{-6} M	(NaH_2PO_4)	0.0050	M
$[I_2]_0$	0.79×10^{-6} M	(Na_2HPO_4)	0.00100	M
$(I^-)_0$	2.38×10^{-6} M	($NaClO_4$)	0.29	M
$[I^-]_0$	3.62×10^{-6} M	(2,4-Dinitro-phenol-6-d) ₀	33.4×10^{-6}	M
$[HOI]_0$	1.24×10^{-6} M	μ	0.30	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
10849	1.527	18.4	0.564
13304	1.510	20.2	.511
16664	1.460	26.6	.561
18714	1.450	27.5	.520
23198	1.406	32.9	.520
26302	1.376	36.5	.523

$F_1 = 0.748$	$P_1 = 27800$ l/mole cm
$F_2 = 2.0 \times 10^{-6}$ sec ⁻¹	$P_2 = 50332$ l/mole cm
$E = 2.713 \times 10^{-6}$ mole cm/l	$P_3 = 368600$ l/mole cm
$k_{app0} = 0.538$ l/mole sec	$k^\nabla = 1.40$ l/mole sec
$k^* = 1.39$ l/mole sec	$k^\nabla[I^-] = 5.1 \times 10^{-6}$ sec ⁻¹

Table 106. Run 88, 2,4-Dinitrophenol in 8.81×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	5.26×10^{-6} M	(NaH_2PO_4)	0.0050	M
$[I_2]_0$	3.43×10^{-6} M	(Na_2HPO_4)	0.00100	M
$(I^-)_0$	8.81×10^{-6} M	($NaClO_4$)	0.29	M
$[I^-]_0$	10.64×10^{-6} M	(2,4-Dinitrophenol) ₀	48.1×10^{-6}	M
$[HOI]_0$	1.83×10^{-6} M	μ	0.30	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
7316	2.805	24.7	0.82
9244	2.723	28.9	.78
12323	2.571	36.9	0.80
16211	2.407	45.4	0.80
20168	2.285	51.7	.77
23107	2.193	56.4	.77
25286	2.081	62.4	0.84

$$F_1 = 1.938$$

$$P_1 = 27800 \text{ l/mole cm}$$

$$F_2 = 3.3 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50332 \text{ l/mole cm}$$

$$E = 2.713 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368600 \text{ l/mole cm}$$

$$k_{app0} = 0.84 \text{ l/mole sec}$$

$$k^\nabla = 1.29 \text{ l/mole sec}$$

$$k^* = 1.28 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 13.7 \times 10^{-6} \text{ sec}^{-1}$$

Table 107. Run 89, 2,4-Dinitrophenol-6-d in 8.81×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	5.26×10^{-6} M	(NaH_2PO_4)	0.0050	M
$[I_2]_0$	3.43×10^{-6} M	(Na_2HPO_4)	0.0010	M
$(I^-)_0$	8.81×10^{-6} M	$(NaClO_4)$	0.29	M
$[I^-]_0$	10.64×10^{-6} M	(2,4-Dinitro-phenol-6-d) ₀	90.7×10^{-6}	M
$[HOI]_0$	1.83×10^{-6} M	μ	0.30	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
8469	4.100	18.3	0.265
12414	3.947	26.2	.272
18318	3.743	36.6	.278
20252	3.713	38.0	.264
26637	3.580	45.1	.252
29818	3.529	46.9	.238

$$F_1 = 1.938$$

$$P_1 = 27800 \text{ l/mole cm}$$

$$F_2 = 3.3 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50332 \text{ l/mole cm}$$

$$E = 2.713 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368600 \text{ l/mole cm}$$

$$k_{app0} = 0.275 \text{ l/mole sec}$$

$$k^\nabla = 0.425 \text{ l/mole sec}$$

$$k^* = 0.421 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 4.53 \times 10^{-6} \text{ sec}^{-1}$$

Table 108. Run 94, 2,4-Dinitrophenol in 91.4×10^{-6} M
Sodium Iodide Solution at 50.0°

$(I_2)_0$	20.13×10^{-6} M	(NaH_2PO_4)	0.0050	M
$[I_2]_0$	18.10×10^{-6} M	(Na_2HPO_4)	0.00100	M
$(I^-)_0$	91.4×10^{-6} M	($NaClO_4$)	0.29	M
$[I^-]_0$	91.7×10^{-6} M	(2,4-Dinitrophenol) ₀	151.6×10^{-6}	M
$[HOI]_0$	1.17×10^{-6} M	μ	0.30	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} ($l/mole\ sec$)
11828	10.067	21.2	0.135
17860	9.445	30.2	.136
22663	9.047	36.0	.133
29074	8.527	43.5	.134
32446	8.251	47.6	.136
36931	7.996	51.3	.134
40131	7.803	54.2	.134

$$F_1 = 7.419$$

$$P_1 = 27800\ l/mole\ cm$$

$$F_2 = 1.6 \times 10^{-6}\ sec^{-1}$$

$$P_2 = 50332\ l/mole\ cm$$

$$E = 2.713 \times 10^{-6}\ mole\ cm/l$$

$$P_3 = 368600\ l/mole\ cm$$

$$k_{app0} = 0.139\ l/mole\ sec$$

$$k^\nabla = 0.156\ l/mole\ sec$$

$$k^* = 0.154\ l/mole\ sec$$

$$k^\nabla[I^-] = 14.3 \times 10^{-6}\ sec^{-1}$$

Table 109. Run 95, 2,4-Dinitrophenol-6-d in 91.4×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	20.13×10^{-6} M	(NaH_2PO_4)	0.0050	M
$[I_2]_0$	18.10×10^{-6} M	(Na_2HPO_4)	0.00100	M
$(I^-)_0$	91.4×10^{-6} M	($NaClO_4$)	0.29	M
$[I^-]_0$	91.7×10^{-6} M	(2,4-Dinitrophenol-6-d) ₀	334.1×10^{-6} M	M
$[HOI]_0$	1.17×10^{-6} M	μ	0.30	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
18315	14.994	23.3	0.0436
22637	14.667	28.1	.0440
32315	14.004	37.6	.0442
39861	13.566	43.9	.0441
42710	13.402	46.4	.0443
45945	13.260	48.5	.0440

$F_1 = 7.419$	$P_1 = 27800$ l/mole cm
$F_2 = 1.6 \times 10^{-6}$ sec ⁻¹	$P_2 = 50332$ l/mole cm
$E = 2.713 \times 10^{-6}$ mole cm/l	$P_3 = 368600$ l/mole cm
$k_{app0} = 0.0454$ l/mole sec	$k^\nabla = 0.0509$ l/mole sec
$k^* = 0.0504$ l/mole sec	$k^\nabla[I^-] = 4.67 \times 10^{-6}$ sec ⁻¹

Table 110. Run 86, 2,4-Dinitrophenol in 0.952×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	4.12×10^{-6} M	(NaH_2PO_4)	0.124	M
$[I_2]_0$	1.57×10^{-6} M	(Na_2HPO_4)	0.025	M
$(I^-)_0$	0.952×10^{-6} M	($NaClO_4$)	0.101	M
$[I^-]_0$	3.50×10^{-6} M	(2,4-Dinitrophenol) ₀	48.1×10^{-6} M	M
$[HOI]_0$	2.55×10^{-6} M	μ	0.30	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} ($l/mole\ sec$)
1890	2.48	21.1	2.63
3014	2.33	28.8	2.37
3884	2.17	38.2	2.62
4040	2.16	38.5	2.54
4913	2.08	42.1	2.36
5899	1.99	46.3	2.24

$$F_1 = 1.52$$

$$P_1 = 27800\ l/mole\ cm$$

$$F_2 = 4.5 \times 10^{-6}\ sec^{-1}$$

$$P_2 = 50332\ l/mole\ cm$$

$$E = 2.713 \times 10^{-6}\ mole\ cm/l$$

$$P_3 = 368600\ l/mole\ cm$$

$$k_{app0} = 2.57\ l/mole\ sec$$

$$k^\nabla = 6.8\ l/mole\ sec$$

$$k^* = 6.74\ l/mole\ sec$$

$$k^\nabla[I^-] = 23.9 \times 10^{-6}\ sec^{-1}$$

Table 111. Run 87, 2,4-Dinitrophenol-6-d in 0.952×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	4.12×10^{-6} M	(NaH_2PO_4)	0.124	M
$[I_2]_0$	1.57×10^{-6} M	(Na_2HPO_4)	0.025	M
$(I^-)_0$	0.952×10^{-6} M	($NaClO_4$)	0.101	M
$[I^-]_0$	3.50×10^{-6} M	(2,4-Dinitro-phenol-6-d) ₀	90.7×10^{-6} M	M
$[HOI]_0$	2.55×10^{-6} M	μ	0.30	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
2869	3.65	19.2	0.82
3727	3.56	23.3	0.79
4535	3.47	27.6	.79
5438	3.37	32.6	.81
6542	3.31	34.0	.71
6341	3.30	35.4	.76

$$F_1 = 1.52$$

$$P_1 = 27800 \text{ l/mole cm}$$

$$F_2 = 4.5 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50332 \text{ l/mole cm}$$

$$E = 2.713 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368600 \text{ l/mole cm}$$

$$k_{app0} = 0.80 \text{ l/mole sec}$$

$$k^\nabla = 2.12 \text{ l/mole sec}$$

$$k^* = 2.10 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 7.5 \times 10^{-6} \text{ sec}^{-1}$$

Table 112. Run 80, 2,4-Dinitrophenol in 8.81×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	5.47×10^{-6} M	(NaH_2PO_4)	0.124	M
$[I_2]_0$	3.57×10^{-6} M	(Na_2HPO_4)	0.025	M
$(I^-)_0$	8.81×10^{-6} M	($NaClO_4$)	0.100	M
$[I^-]_0$	10.71×10^{-6} M	(2,4-Dinitrophenol) ₀	73.2×10^{-6}	M
$[HOI]_0$	1.90×10^{-6} M	μ	0.30	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
2849	3.462	29.2	1.67
4502	3.218	41.1	1.63
5656	3.074	48.1	1.61
5559	3.072	48.3	1.65
6914	2.946	54.2	1.58
7681	2.858	58.5	1.60
8802	2.778	62.2	1.55

$$F_1 = 2.016$$

$$P_1 = 27800 \text{ l/mole cm}$$

$$F_2 = 1.6 \times 10^{-8} \text{ sec}^{-1}$$

$$P_2 = 50332 \text{ l/mole cm}$$

$$E = 2.713 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368600 \text{ l/mole cm}$$

$$k_{app0} = 1.76 \text{ l/mole sec}$$

$$k^\nabla = 2.72 \text{ l/mole sec}$$

$$k^* = 2.69 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 29.2 \times 10^{-6} \text{ sec}^{-1}$$

Table 113. Run 81, 2,4-Dinitrophenol-6-d in 8.81×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	5.47×10^{-8} M	(NaH_2PO_4)	0.124	M
$[I_2]_0$	3.57×10^{-8} M	(Na_2HPO_4)	0.025	M
$(I^-)_0$	8.81×10^{-6} M	($NaClO_4$)	0.100	M
$[I^-]_0$	10.71×10^{-6} M	(2,4-Dinitro-phenol-6-d) ₀	80.5×10^{-6} M	
$[HOI]_0$	1.90×10^{-8} M	μ	0.30	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
6040	3.812	18.8	0.432
6715	3.772	20.5	.427
8416	3.648	26.0	.448
11278	3.472	33.5	.455
14936	3.268	42.3	.464

$F_1 = 2.016$	$F_1 = 27800$ l/mole cm
$F_2 = 1.6 \times 10^{-6}$ sec ⁻¹	$F_2 = 50332$ l/mole cm
$E = 2.713 \times 10^{-6}$ mole cm/l	$F_3 = 368600$ l/mole cm
$k_{app0} = 0.494$ l/mole sec	$k^\nabla = 0.763$ l/mole sec
$k^* = 0.755$ l/mole sec	$k^\nabla[I^-] = 8.1 \times 10^{-6}$ sec ⁻¹

Table 114. Run 96, 2,4-Dinitrophenol in 91.4×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	19.12×10^{-6} M	(NaH_2PO_4)	0.124	M
$[I_2]_0$	17.17×10^{-6} M	(Na_2HPO_4)	0.024	M
$(I^-)_0$	91.4×10^{-6} M	$(NaClO_4)$	0.101	M
$[I^-]_0$	91.7×10^{-6} M	$(2,4\text{-Dinitrophenol})_0$	150.9×10^{-6} M	M
$[HOI]_0$	1.13×10^{-6} M	μ	0.30	
Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)	
5958	9.394	24.2	0.313	
8276	8.925	31.4	.309	
11233	8.425	38.9	.299	
13718	8.007	45.1	.299	
15212	7.813	48.2	.298	
19566	7.232	56.8	.296	
18002	7.415	54.6	.302	
$F_1 = 7.049$		$P_1 = 27800$ l/mole cm		
$F_2 = 15.6 \times 10^{-6}$ sec ⁻¹		$P_2 = 50332$ l/mole cm		
$E = 2.713 \times 10^{-6}$ mole cm/l		$P_3 = 368600$ l/mole cm		
$k_{app0} = 0.311$ l/mole sec		$k^\nabla = 0.347$ l/mole sec		
$k^* = 0.344$ l/mole sec		$k^\nabla[I^-] = 31.8 \times 10^{-6}$ sec ⁻¹		

Table 115. Run 97, 2,4-Dinitrophenoxide-6-d in 91.4×10^{-6} Sodium Iodide Solution at 50.0°

$(I_2)_0$	$19.12 \times 10^{-6} \underline{M}$	(NaH_2PO_4)	0.124	\underline{M}
$[I_2]_0$	$17.17 \times 10^{-6} \underline{M}$	(Na_2HPO_4)	0.024	\underline{M}
$(I^-)_0$	$91.4 \times 10^{-6} \underline{M}$	$(NaClO_4)$	0.101	\underline{M}
$[I^-]_0$	$91.7 \times 10^{-6} \underline{M}$	(2,4-Dinitro-phenol-6-d) ₀	334.8×10^{-6}	\underline{M}
$[HOI]_0$	$1.13 \times 10^{-6} \underline{M}$	μ	0.30	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
7546	14.606	22.5	0.102
11074	14.015	31.1	.101
13587	13.637	36.8	.102
15742	13.362	40.9	.101
19390	12.944	47.0	.099
22783	12.648	51.4	.096
26761	12.240	57.3	.097

$$F_1 = 7.049$$

$$P_1 = 27800 \text{ l/mole cm}$$

$$F_2 = 15.6 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50332 \text{ l/mole cm}$$

$$E = 2.713 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368600 \text{ l/mole cm}$$

$$k_{app0} = 0.103 \text{ l/mole sec}$$

$$k^\nabla = 0.115 \text{ l/mole sec}$$

$$k^* = 0.114 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 10.5 \times 10^{-6} \text{ sec}^{-1}$$

Table 116. Run 108, 2,4-Dinitrophenol in 6.45×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	8.60×10^{-6} M	(NaH_2PO_4)	0.183	M
$[I_2]_0$	5.44×10^{-6} M	(Na_2HPO_4)	0.037	M
$(I^-)_0$	6.45×10^{-6} M	($NaClO_4$)	0.00	M
$[I^-]_0$	9.61×10^{-6} M	(2,4-Dinitrophenol) ₀	55.8×10^{-6}	M
$[HOI]_0$	3.16×10^{-6} M	μ	0.30	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
2599	3.816	25.2	2.04
3521	3.651	29.1	1.79
3639	3.583	31.2	1.89
4438	3.456	34.1	1.73
5938	3.174	41.1	1.65
7456	2.851	46.3	1.55

$F_1 = 3.170$	$P_1 = 27800$ l/mole cm
$F_2 = 67.0 \times 10^{-6}$ sec ⁻¹	$P_2 = 50360$ l/mole cm
$E = 2.713 \times 10^{-6}$ mole cm/l	$P_3 = 368800$ l/mole cm
$k_{app0} = 2.00$ l/mole sec	$k^\nabla = 3.19$ l/mole sec
$k^* = 3.16$ l/mole sec	$k^\nabla[I^-] = 30.7 \times 10^{-6}$ sec ⁻¹

Table 117. Run 109, 2,4-Dinitrophenol-6-d in 6.45×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	8.60×10^{-6} M	(NaH_2PO_4)	0.183	M
$[I_2]_0$	5.44×10^{-6} M	(Na_2HPO_4)	0.037	M
$(I^-)_0$	6.45×10^{-6} M	($NaClO_4$)	0.00	M
$[I^-]_0$	9.61×10^{-6} M	(2,4-Dinitro-phenol-6-d) ₀	128.3×10^{-6}	M
$[HOI]_0$	3.16×10^{-6} M	μ	0.30	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
2543	5.982	20.1	0.694
3465	5.769	25.6	.672
3578	5.730	26.8	.685
4389	5.633	28.5	.602
5842	5.342	35.9	.601
7380	5.118	41.0	.564

$F_1 = 3.170$	$P_1 = 27800$ l/mole cm
$F_2 = 67.0 \times 10^{-6}$ sec ⁻¹	$P_2 = 50360$ l/mole cm
$E = 2.713 \times 10^{-6}$ mole cm/l	$P_3 = 368800$ l/mole cm
$k_{app0} = 0.69$ l/mole sec	$k^\nabla = 1.10$ l/mole sec
$k^* = 1.09$ l/mole sec	$k^\nabla[I^-] = 10.6 \times 10^{-6}$ sec ⁻¹

Table 118. Run 90, 2,4-Dinitrophenol in 0.00 M Sodium Iodide Solution at 50.0°

$(I_2)_0$	$9.57 \times 10^{-6} \text{ M}$	(NaH_2PO_4)	0.249	<u>M</u>
$[I_2]_0$	$4.50 \times 10^{-6} \text{ M}$	(Na_2HPO_4)	0.047	<u>M</u>
$(I^-)_0$	$0.00 \times 10^{-6} \text{ M}$	$(NaClO_4)$	0.00	<u>M</u>
$[I^-]_0$	$5.07 \times 10^{-6} \text{ M}$	$(2,4\text{-Dinitrophenol})_0$	131.1×10^{-6}	<u>M</u>
$[HOI]_0$	$5.07 \times 10^{-6} \text{ M}$	μ	0.39	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
658	6.405	20.4	2.67
1116	6.058	29.2	2.39
1426	5.712	38.7	2.66
1594	4.691	38.7	2.38
1653	5.579	42.0	2.55
2275	5.273	49.3	2.32
2641	5.120	52.8	2.21

$$F_1 = 3.529$$

$$P_1 = 27800 \text{ l/mole cm}$$

$$F_2 = 1.54 \times 10^{-4} \text{ sec}^{-1}$$

$$P_2 = 50332 \text{ l/mole cm}$$

$$E = 2.713 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368600 \text{ l/mole cm}$$

$$k_{app0} = 2.76 \text{ l/mole sec}$$

$$k^{\nabla} = 5.96 \text{ l/mole sec}$$

$$k^* = 5.90 \text{ l/mole sec}$$

$$k^{\nabla}[I^-] = 30.2 \times 10^{-6} \text{ sec}^{-1}$$

Table 119. Run 91, 2,4-Dinitrophenol-6-d in 0.00 M Sodium Iodide Solution at 50.0°

$(I_2)_0$	9.57×10^{-6} M	(NaH_2PO_4)	0.249	M
$[I_2]_0$	4.50×10^{-6} M	(Na_2HPO_4)	0.047	M
$(I^-)_0$	0.00×10^{-6} M	($NaClO_4$)	0.00	M
$[I^-]_0$	5.07×10^{-6} M	(2,4-Dinitro-phenol-6-d) ₀	250.4×10^{-6} M	M
$[HOI]_0$	5.07×10^{-6} M	μ	0.39	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
1407	9.353	28.7	.965
1580	9.322	28.9	.868
1646	9.261	30.6	.890
2169	9.006	36.5	.841
2631	8.792	41.4	.819

$$F_1 = 3.529$$

$$P_1 = 27800 \text{ l/mole cm}$$

$$F_2 = 1.54 \times 10^{-4} \text{ sec}^{-1}$$

$$P_2 = 50332 \text{ l/mole cm}$$

$$E = 2.713 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368600 \text{ l/mole cm}$$

$$k_{app0} = 0.96 \text{ l/mole sec}$$

$$k^\nabla = 2.07 \text{ l/mole sec}$$

$$k^* = 2.05 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 10.5 \times 10^{-6} \text{ sec}^{-1}$$

Table 120. Run 82, 2,4-Dinitrophenol in 8.81×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	5.07×10^{-6} M	(NaH_2PO_4)	0.238	M
$[I_2]_0$	3.29×10^{-6} M	(Na_2HPO_4)	0.047	M
$(I^-)_0$	8.81×10^{-6} M	($NaClO_4$)	0.00	M
$[I^-]_0$	10.59×10^{-6} M	(2,4-Dinitrophenol) ₀	73.4×10^{-6} M	M
$[HOI]_0$	1.78×10^{-6} M	μ	0.38	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} ($l/mole\ sec$)
2073	3.437	25.0	1.91
2857	3.233	36.0	2.16
3609	3.080	44.2	2.24
4856	2.896	53.9	2.22
6190	2.764	60.5	2.09
7241	2.662	65.7	2.07

$$F_1 = 1.869$$

$$P_1 = 27800\ l/mole\ cm$$

$$F_2 = 1.9 \times 10^{-5}\ sec^{-1}$$

$$P_2 = 50332\ l/mole\ cm$$

$$E = 2.713 \times 10^{-6}\ mole\ cm/l$$

$$P_3 = 368600\ l/mole\ cm$$

$$k_{app0} = 2.30\ l/mole\ sec$$

$$k^\nabla = 3.58\ l/mole\ sec$$

$$k^* = 3.54\ l/mole\ sec$$

$$k^\nabla[I^-] = 37.9 \times 10^{-6}\ sec^{-1}$$

Table 121. Run 83, 2,4-Dinitrophenol-6-d in 8.81×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	5.07×10^{-6} M	(NaH_2PO_4)	0.238	M
$[I_2]_0$	3.29×10^{-6} M	(Na_2HPO_4)	0.047	M
$(I^-)_0$	8.81×10^{-6} M	$(NaClO_4)$	0.00	M
$[I^-]_0$	10.59×10^{-6} M	(2,4-Dinitro-phenol-6-d) ₀	81.1×10^{-6}	M
$[HOI]_0$	1.78×10^{-6} M	μ	0.38	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
3452	3.743	18.3	.727
4334	3.621	24.5	.807
5740	3.508	29.8	.766
6839	3.447	32.3	.711
8090	3.315	39.0	.762
9888	3.182	45.3	0.763

$F_1 = 1.869$	$P_1 = 27800$ l/mole cm
$F_2 = 1.9 \times 10^{-6}$ sec ⁻¹	$P_2 = 50332$ l/mole cm
$E = 2.713 \times 10^{-6}$ mole cm/l	$P_3 = 368600$ l/mole cm
$k_{app0} = 0.79$ l/mole sec	$k^\nabla = 1.23$ l/mole sec
$k^* = 1.22$ l/mole sec	$k^\nabla[I^-] = 13.0 \times 10^{-6}$ sec ⁻¹

Table 122. Run 76, 2,4-Dinitrophenol in 91.4×10^{-6} M Sodium Iodide Solution at 50.0°

$(I_2)_0$	5.85×10^{-6} M	(NaH_2PO_4)	0.238	M
$[I_2]_0$	5.27×10^{-6} M	(Na_2HPO_4)	0.050	M
$(I^-)_0$	91.4×10^{-6} M	($NaClO_4$)	0.00	M
$[I^-]_0$	91.4×10^{-6} M	(2,4-Dinitrophenol) ₀	73.3×10^{-6} M	M
$[HOI]_0$	0.33×10^{-6} M	μ	0.38	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
6707	3.732	19.9	0.454
8892	3.572	26.9	.486
11055	3.480	30.6	.457
13548	3.350	36.2	.459

$$F_1 = 2.156$$

$$P_1 = 27800 \text{ l/mole cm}$$

$$F_2 = 1.0 \times 10^{-6} \text{ sec}^{-1}$$

$$P_2 = 50332 \text{ l/mole cm}$$

$$E = 2.713 \times 10^{-6} \text{ mole cm/l}$$

$$P_3 = 368600 \text{ l/mole cm}$$

$$k_{app0} = 0.464 \text{ l/mole sec}$$

$$k^\nabla = 0.520 \text{ l/mole sec}$$

$$k^* = 0.515 \text{ l/mole sec}$$

$$k^\nabla[I^-] = 47.0 \times 10^{-6} \text{ sec}^{-1}$$

Table 123. Data on the Phosphate-Catalyzed Iodination of 2,4-Dinitrophenol at 50.0°

Table Ref.	$[I^-]$ $\times 10^6$ (mole/l)	$[H^+]$ $\times 10^6$ (mole/l)	$[ArO^-]$ $\times 10^6$ (mole/l)	$[I_2]_0$ $\times 10^6$ (mole/l)	k^∇ (l/mole sec)	$k^\nabla[I^-]$ $\times 10^6$ (sec ⁻¹)	$1/k^\nabla$ (mole sec/l)	μ	$[HPO_4^{=}]$ (mole/l)
104	3.62	1.77	26.0	0.79	4.04	14.7	0.248	0.30	0.00100
106	10.64	1.81	47.7	3.43	1.29	13.7	0.78	0.30	0.00100
108	91.7	2.09	150.1	18.1	0.156	14.3	6.4	0.30	0.00100
110	3.50	1.70	47.6	1.57	6.8	23.9	0.147	0.30	0.025
112	10.71	1.70	72.5	3.57	2.72	29.2	0.368	0.30	0.025
114	91.7	1.70	149.4	17.2	0.347	31.8	2.88	0.30	0.024
116	9.61	1.70	55.2	5.44	3.19	30.7	0.314	0.30	0.037
118	5.07	1.70	129.8	4.50	5.96	30.2	0.168	0.39	0.047
120	10.59	1.70	72.7	3.29	3.58	37.9	0.280	0.38	0.047
122	91.4	1.70	72.6	5.27	0.52	47.0	1.95	0.39	0.050

Table 124. Data on the Phosphate-Catalyzed Iodination of 2,4-Dinitrophenol-6-d at 50.0°

Table Ref.	$[I^-]$ $\times 10^6$ (mole/l)	$[H^+]$ $\times 10^6$ (mole/l)	$[ArO^-]$ $\times 10^6$ (mole/l)	$[I_2]_0$ $\times 10^6$ (mole/l)	k^∇ (l/mole sec)	$k^\nabla[I^-]$ $\times 10^6$ (sec ⁻¹)	$1/k^\nabla$ (mole sec/l)	μ	$[HPO_4^{=}]$ (mole/l)	k_H/k_D
105	3.62	1.77	33.1	0.79	1.40	5.1	0.72	0.30	0.00100	2.9
107	10.64	1.91	89.8	3.43	0.425	4.53	2.35	0.30	0.00100	3.0
109	91.7	2.74	331	18.1	0.0509	4.67	19.6	0.30	0.00100	3.1
111	3.50	1.70	89.8	1.57	2.12	7.5	0.472	0.30	0.025	3.2
113	10.71	1.70	79.7	3.57	0.76	8.1	1.32	0.30	0.025	3.6
115	91.7	1.70	332	17.2	0.115	10.5	8.7	0.30	0.024	3.0
117	9.61	1.70	127	5.44	1.10	10.6	0.91	0.30	0.037	2.9
119	5.07	1.70	248	4.50	2.07	10.5	0.483	0.39	0.047	2.9
121	10.59	1.70	80.3	3.29	1.23	13.0	0.81	0.38	0.047	2.9

Table 125. Slopes of the Plots of $1/k^{\nabla}$ vs $[I^-]$ for the Phosphate-Catalyzed Iodination of 2,4-Dinitrophenol and 2,4-Dinitrophenol-6-d at 50.0°

$[HPO_4^-]$ (mole/l)	μ	$[H^+] \times 10^6$ (mole/l)	Slope $\times 10^{-4}$ (sec)
2,4-Dinitrophenol			
0.001	0.30	1.79	7.1 ± 0.3
.025	0.30	1.70	3.8 ± 0.5
.037	0.30	1.70	3.5 (based on single point)
.047	0.38	1.70	3.0 ± 0.5
2,4-Dinitrophenol-6-d			
0.001	0.30	1.84	21.0 ± 1.6
.025	0.30	1.70	12.9 ± 0.8
.037	0.30	1.70	9.5 (based on single point)
.047	0.38	1.70	8.6 ± 1.3

CHAPTER IX

IODINATION OF PHENOL CATALYZED BY ACETATE ANION

Introduction

The attempt to study the acetate-catalyzed iodination of phenol and phenol-2,4,6- d_3 was made for the same reason as the investigation of the phosphate-catalyzed iodination of 2,4-dinitrophenol and 2,4-dinitrophenol-6- d ; viz., to determine whether catalysis at a low iodide ion concentration would reduce the isotope effect. Such a result would be expected, in light of the mechanism proposed in Chapter IV for the iodination of phenol, unless offset by a higher isotope effect for acetate-catalyzed proton removal than for water-catalyzed proton removal.

Acetate catalysis of the iodination of phenol at 25° was studied by Berliner,⁽⁴⁶⁾ who found that the catalytic constant for acetate was approximately 11.7 times as large as k_3 .[†] The iodide ion concentration was 0.12 M.

Kilby⁽⁸⁷⁾ followed the iodination of phenol and phenol-2,4,6- d_3 in aqueous acetate-acetic acid buffer as a function of iodide ion concentration over the iodide concentration range from about 2×10^{-2} M to about 4×10^{-4} M. A comparison of the rate constants observed by Kilby

[†]Berliner notes that this figure may not be very accurate because it is based upon a small number of measurements in which difficulty was encountered in reproducing pH.

in the acetate-acetic acid buffer solution and in 0.0174 M perchloric acid solution indicates that the catalytic constant for acetate was approximately 7.9 times as large as k_3 . In making this calculation, the hydrogen ion concentration for the buffered solution is obtained by using 1.75×10^{-5} mole/l for the thermodynamic acidity constant for acetic acid⁽⁹⁰⁾ and 0.70 for the activity coefficient in 0.30 μ solution, most of the ionic strength being supplied by sodium perchlorate.⁽⁹¹⁾

It is also noted from Kilby's thesis that the isotope effect is the same in the uncatalyzed and acetate-catalyzed experiments, even though in the latter case about 25 percent of the reaction proceeds via acetate catalysis. Since in Kilby's work the iodide ion concentrations are sufficiently high that the proton-removal step is completely rate-determining, this means that the acetate-catalyzed proton removal has an isotope effect similar to that of the water-catalyzed proton removal.

Specific Experimental Details

The effect of acetate ion upon rate constants and isotope effect was studied at the lowest iodide concentration involved in the non-catalyzed work (cf., Chapter IV). This was done since, from equation (17), Chapter IV, the isotope effect is most susceptible to change at the lowest iodide concentration. The acetate ion concentrations and the acetic acid-acetate ratios were chosen on the basis of the approximate catalytic efficiency of acetate, judging from the work of Berliner and of Kilby, the necessity of maintaining the hydrogen ion concentration at a sufficiently high level in order to keep the reaction slow enough to follow kinetically and the requirement of ionic strength. It turned

out to be necessary to exceed the ionic strength of the non-catalyzed reactions and to run experiments at 10° in order to slow down the reaction.

Tables 140 and 141 show that the catalysis study was made at iodide ion concentration of approximately 0.33×10^{-6} M, at hydrogen ion concentrations from 6.5×10^{-5} M to 29.4×10^{-5} M,[†] at ionic strengths from 0.30 to 1.20, at temperatures 10.0° and 25.0° , and at acetate concentrations from zero to 0.36 M.

Since it was found that the use of acetic acid at the concentrations required caused unacceptably rapid blank drops, even after the acetic acid had been distilled over chromium trioxide, the buffers were generated by the mixing of sodium acetate and perchloric acid. This had the disadvantage of increasing ionic strength by virtue of the accumulation of sodium perchlorate. For experiments no. 58, 59, 60, 61, 62, and 63 (Tables 126-130), the sodium acetate and sodium perchlorate were simply recrystallized from water. However, the blank drop problem was too serious to permit higher salt concentrations, and so the salts were treated with hypochlorite, as described in Chapter III. Experiments no. 68-75 (Tables 132-135, 138, 139, 136, and 137) were performed using the treated salts.

[†]These acidities were computed on the basis of the dissociation constants for acetic acid at the temperatures involved (1.75×10^{-5} mole/l at 25.0° and 1.73×10^{-5} at 10.0° (90)), the activity coefficients for the ionic strengths involved, (91) and the buffer ratios employed.

The rapidity of the catalyzed reactions at 25.0° caused the kinetic results to be erratic, as can be seen from Tables 126-131. Since it was desired to increase catalyst concentration still further, it became necessary to run the remaining experiments at 10.0°. This temperature was maintained, plus or minus about 0.2°, by circulating ice water through coils immersed in the constant temperature bath holding the reaction flasks.

The acidities employed in these reactions were such that if quenched to the usual iodide ion concentration of 0.05 M, measurable oxidation of iodide to iodine occurred during the time between quenching and spectral measurement. Moreover, considerable experimental difficulty was found in the use of sodium bicarbonate as a buffer for the quenched solution, because the high concentrations of buffer required the use of large amounts of sodium bicarbonate, with the resultant evolution of carbon dioxide. The reduction of the concentration of iodide in the quenched solution was found to be a practical alternative. At the lower iodide ion concentrations, no bicarbonate was required, and no measurable oxidation of iodide to iodine occurred during the time between quenching and spectral measurement (as judged by the constancy of absorbance over a similar period of time after the spectral measurement). The use of 0.005 M iodide quench for experiments no. 60, 61, 62, and 63 (Tables 128-131) and the use of 0.02 M iodide quench for experiments no. 68-75 (Tables 132-139) required the calculation of new values of E, according to the definition in Chapter IV, and these values are employed in Tables 128-137. (The usual 0.05 M iodide quench was used for experiments no. 58 and 59 (Tables 126 and 127), which does not involve the use of any

buffer.) From equation (2), Chapter II, it was determined that approximately eight percent of the iodine used in the experiments which were quenched with 0.005 M iodide was free iodine in the quenched solution. The spectral measurements were made at 3530 Å, and the extinction coefficient data at this wavelength⁽⁸²⁾ for iodine and triiodide show that the absorbance due to the free iodine would be less than one ten-thousandth of the absorbance due to triiodide. Therefore, equation (1), Chapter III, which is an approximation to the extent that it neglects the contribution of iodine to total absorbance, is valid for the determination of iodine in the reaction solution from the absorbance of the quenched solution.

The concentrations of phenol and phenol-2,4,6-d₃ were determined in the manner described in Chapter IV.

Extrapolation of k_{app} values to k_{app_0} presented a problem. The experiments no. 58, 59, 68, 69, 74, and 75 (Tables 126, 127, 132, 133, 138, and 139) contained approximately zero catalyst concentration,[†] and the extrapolation was made according to equation (18), Chapter III, employing the values of \underline{n} derived in Chapter IV for the iodide ion concentration involved. However, the reactions are considerably accelerated in the catalyzed experiments no. 60, 61, 62, 63, 70, 71, 72, and 73

[†]Experiments no. 68, 69, 74, and 75 contain 0.018 M acetate ion, used as part of a buffer to maintain pH. Judging from the effect of 0.06 M acetate upon values of $k^*[H^+]$ (cf., experiments no. 58 versus 60 (Tables 126 versus 128) and experiments 59 versus 61 (Tables 127 versus 129)), the catalysis due to 0.018 M acetate would be approximately ten percent. Assuming the same intercept for the $1/k^*[H^+]$ versus $[I^-]$ line as in the completely uncatalyzed work, this much catalysis does not seriously alter the proper value of \underline{n} .

(Tables 128, 129, 130, 131, 134, 135, 138, and 139). If the intercept of the $1/k^*[H^+]$ versus $[I^-]$ plot is the same under conditions of catalysis as for the non-catalyzed experiments, then the slope would be smaller, and consequently \underline{n} would be smaller in the catalyzed experiments. On the other hand, if IOAc were to become a significant iodinating agent, it can be seen by analogy with equation (5), Chapter VIII, that the $1/k^*[H^+]$ versus $[I^-]$ plot would tend away from the intercept toward the origin; this would bring about an increase in \underline{n} . The point is that in the absence of knowledge of the reaction mechanism and in the absence of catalyzed experiments at a number of different iodide ion concentrations which would define $1/k^*[H^+]$ as a function of $[I^-]$, it is impossible to choose the correct values for \underline{n} .

The approach taken here was to resolve the question of extrapolation in two ways; average k_{app} values (without extrapolation) were determined and isotope effect values calculated therefrom, and k_{app0} values were determined from the best visual extrapolations of the k_{app} versus percent reaction data (the results of the catalyzed experiments generally indicated that extrapolation should be applied) and the isotope effects also calculated from these values. Both the average k_{app} and the k_{app0} values are included in Tables 140 and 141.

Background absorbance is corrected for in the usual manner, as was blank drop. The appropriate adjustments have already been made in Tables 126-137.

In experiments no. 58, 59, 62, and 63 (Tables 126, 127, 130, and 131), rather large apparent volatilization losses of iodine were noted

upon withdrawing sample from stock solution for introduction into the reaction flasks. That is, the amount of iodine delivered into the reaction flask seemed to decrease significantly with the number of times that the iodine stock solution was opened for sampling. In previous experiments, this phenomenon generally occurred in high iodine experiments and was of considerably smaller magnitude. The correction has been made previously, as described in Chapter III, by adding the appropriate ΔV values to the individual absorbance readings. As was pointed out, this was an approximation, justified by the small magnitude of the volatilization drops.

The apparent volatilization drops in experiments no. 58, 59, 62, and 63, however, are sufficiently great that average k_{app} errors on the order of five percent are caused by the approximate treatment. Therefore, the appropriate value of ΔV was subtracted from F_1 for each experimental point, and the individual values of F_1 are listed in Tables 126, 127, 130, and 131.

Results and Discussion

The results are summarized in Tables 140, 141, and 142. Values for k^* based upon both average k_{app} and upon k_{app_0} are given for the catalyzed experiments; as discussed above, average k_{app} is not pertinent in the uncatalyzed and very slightly catalyzed experiments.

It can be seen from Tables 140 and 141 that measurable catalysis of the iodination occurs. The series of experiments denoted by reference numbers 126, 128, and 130 in Table 140 (phenol) and 127, 129, and 131 in Table 141 (phenol-2,4,6- d_3) demonstrate catalysis at 25.0°,

although some change in ionic strength is involved. At 10.0°, catalysis is observed at approximately 0.60 μ in references no. 132 and 134 in Table 140 and 133 and 135 in Table 141, and at 1.20 μ in references no. 136 and 138 in Table 140 and 137 and 139 in Table 141.

The $k^*[\text{H}^+]$ values of $7.4 \times 10^{-2} \text{ sec}^{-1}$ for experiment no. 58 (reference 126, Table 140) is the same as that observed for experiment no. 53 (Table 21, Chapter IV). This is as expected, since it was calculated in Chapter IV that at the $1.303 \times 10^{-3} \text{ M}$ hydrogen ion concentration of experiment no. 53, 100 percent of the reaction would be via phenoxide anion and, therefore, that $k^*[\text{H}^+]$ at the same iodide concentration should remain constant as the hydrogen ion concentration was decreased.

From equation (17), Chapter IV, and from the fact that $k_2[\text{H}^+]$ is negligible relative to k_1K_2 at the acidities of the reactions under discussion in this chapter, the reactions studied here should conform to the equation

$$\frac{1}{k^*[\text{H}^+]} = \left(\frac{k_{-1}}{k_1 k_3 K_2} \right) [\text{I}^-] + \frac{1}{k_1 K_2} \quad (1)$$

If, now, a catalysis term k_6 is introduced, analagous to the term k_4 for phosphate catalysis of 2,4-dinitrophenoxide in Chapter VIII, this equation becomes

$$\frac{1}{k^*[\text{H}^+]} = \left\{ \frac{k_{-1}}{k_1 K_2 (k_3 + k_6 [\text{CH}_3\text{COO}^-])} \right\} [\text{I}^-] + \frac{1}{k_1 K_2} \quad (2)$$

where it is assumed that the only effect of the acetate is the catalysis

of the removal of the proton from the intermediate iodination product.

The value of $1/k_1 K_2$ was determined as 10.8 sec in Chapter IV, at 25.0° and 0.30 μ . According to equation (2), this is the limiting value of $1/k^*[H^+]$ at infinite catalysis. It can be seen, however, from references no. 128 and 130 in Table 140, that for the iodination of the protio phenol at 25.0°, $1/k^*[H^+]$ is 8.5 sec at 0.060 M acetate and 5.5 sec or 4.5 sec at 0.180 M acetate, depending upon which value of $k^*[H^+]$ is used.

A complicating factor in this comparison is that the uncatalyzed experiment at 25.0° was run at ionic strength 0.30, while the catalyzed experiments were run at about 0.60 μ .

The anticipated effect of ionic strength upon the intercept $1/k_1 K_2$ (K_2 expressed in units of concentration) can be estimated from the following considerations. The rate constant k_1 should be relatively insensitive to changes in ionic strength, since the net change on reactants and products is the same for this step. The concentration equilibrium constant should show an inverse second order dependence upon activity coefficient. The term $[H^+]$ would cause $1/k^*[H^+]$ to vary inversely with first order activity coefficient. This factor must also operate on the intercept $1/k_1 K_2$, being one of the terms comprising $1/k^*[H^+]$. The net effect of ionic strength upon the intercept, then, is direct first order dependence upon the activity coefficient. The activity coefficients for 0.30 μ and 0.60 μ sodium perchlorate solutions are 0.70 and 0.66, respectively.⁽⁹¹⁾ It follows that the intercept at 0.60 μ should be 0.66/0.70 times that of the intercept at 0.3 μ , or 10.3

sec. This value still exceeds the values of $1/k^*[H^+]$ observed at 0.060 M and 0.180 M acetate.

For phenol-2,4,6- d_3 ,[†] $1/k^*[H^+]$ is seen from numbers 129 and 131 in Table 141 to decrease from 44 sec for zero acetate to 30 sec at 0.060 M acetate and 15 sec or 21 sec at 0.180 M acetate, depending upon which value of $k^*[H^+]$ is used.

Table 142 shows that there is no detectable decrease in isotope effect between zero and 0.180 M acetate at 25.0°. This reflects the fact that the protio compound has been catalyzed beyond the predicted limiting value of $1/k^*[H^+]$, since, had the protio compound been catalyzed only toward a limiting value of 10.3 sec for $1/k^*[H^+]$, the isotope effect at 0.060 M acetate would have been less than 2.9 and at 0.180 M acetate would have been less than either 1.5 or 2.0, depending again upon which value of $k^*[H^+]$ is used.

The other experiments related to acetate catalysis (references no. 132, 134, 136, 138, 133, 135, 137, and 139 in Tables 140 and 141) were performed at 10.0°, with acetate concentration extending to 0.360 M. A problem here is that all of the experiments at this temperature have been performed at the same iodide ion concentration; and, therefore, there is no estimate of the intercept $1/k_1K_2$ under these conditions based upon extrapolation of a $1/k^*[H^+]$ versus $[I^-]$ plot.

The definitive equation, in the absence of acetate catalysis, is

[†]As in Chapter IV, the $1/k_1K_2$ intercept is taken to be exactly the same for phenol-2,4,6- d_3 as for phenol.

equation (1). If $\frac{k-1}{k_1 k_3 K_2}$ can be evaluated at 10.0°, then from the value of $1/k^* [H^+]$ at a known iodide ion concentration, $1/k_1 K_2$ can be obtained. Since a value for $\frac{k-1}{k_1 k_3 K_2}$ at 25.0° is known, what is needed is an overall activation energy for this expression.

Berliner⁽⁴⁶⁾ calculated an activation energy for $k_{app_0} \cdot a_{H^+}$ for the iodination of phenol at 0.12 M iodide ion and 0.3 μ, based upon experiments at sufficiently low acidities that only phenoxide anion would be iodinated. The measurements were made at 25.0° and 35.0°. By correcting Berliner's k_{app_0} values to k^* , using values for the triiodide equilibrium constant at 25.0° and 35.0° obtained from the data of Davies and Gwynne,⁽⁸¹⁾ the activation energy for $k^* a_{H^+}$ is found to be 22.6 kcal/mole (as compared with 25.2 kcal/mole calculated by Berliner for $k_{app_0} a_{H^+}$). Berliner's work was done at such high iodide ion concentration that equation (1) reduces to

$$\frac{1}{k^* [H^+]} = \frac{k-1}{k_1 k_3 K_2} [I^-] \quad (3)$$

Therefore, the activation energy of 22.6 kcal/mole for $k^* a_{H^+}$ is approximately the activation energy for $\frac{k_1 k_3 K_2}{k-1}$. On the basis of this activation energy, it is predicted that a temperature change from 25° to 10° will increase the value of $\frac{k-1}{k_1 k_3 K_2}$ by a factor of 7.7 at 0.30 μ. The value of $\frac{k-1}{k_1 k_3 K_2}$ at 25.0°, 0.30 μ, was found in Chapter V to be 13.6×10^6 l sec/mole and is predicted to be 105×10^6 l sec/mole at 10.0°, 0.30 μ. Therefore, in the reaction at 10.0° and 0.32×10^{-6} M iodide ion concentration, $\frac{k-1}{k_1 k_3 K_2} [I^-]$ should be 33.6 sec at 0.30 μ.

Reference no. 132, Table 140, shows that the value of $k^*[\text{H}^+]$ at 10.0° , 0.56μ , is $18.4 \times 10^{-3} \text{ sec}^{-1}$ with acetate ion concentration 0.0180 M . It is necessary to adjust this $k^*[\text{H}^+]$ figure to what it would be at 0.30μ and zero acetate. The correction to zero acetate can be estimated as about ten percent on the basis of references no. 132 and 134, Table 140, in the same manner as for analagous corrections for low concentrations of phosphate in Chapter VIII. The correction to 0.30μ is based upon the following considerations. References no. 132 and 136, Table 140, indicate a rate enhancement of 36 percent upon increasing the ionic strength from 0.60 to 1.20. Since the ratio of activity coefficients in 0.30μ and 0.60μ sodium perchlorate solutions is about the same as the ratio of activity coefficients in 0.60μ and 1.20μ sodium perchlorate solutions, ⁽⁹¹⁾ the same percentage correction is applied to make the adjustment from 0.60μ to 0.30μ . The result is a value of $12.0 \times 10^{-3} \text{ sec}^{-1}$ for $k^*[\text{H}^+]$ at 10.0° , 0.30μ and zero acetate, or a $1/k^*[\text{H}^+]$ value of 83 sec. Subtracting the calculated value of $\frac{k-1}{k_1 k_3 K_2} [\text{I}^-]$ of 33.6 sec from the $1/k^*[\text{H}^+]$ value of 85 sec, a value of 49 sec is obtained for $1/k_1 K_2$ at 10.0° , 0.30μ .

It is now necessary to correct this value of $1/k_1 K_2$ back to 0.60μ . This is done according to the previous calculation of the effect of ionic strength upon $1/k_1 K_2$, resulting in a value of 46 sec for 10.0° , 0.60μ .

If the only effect of acetate ion is to catalyze the proton-removal step, the appropriate equation is (2), which requires that the limiting value of $1/k^*[\text{H}^+]$ at infinite catalysis be $1/k_1 K_2$; i.e., 46 sec at 10.0°

and 0.60 μ .

The values of $1/k^*[H^+]$ for the experiments at 10.0° and 0.60 μ , obtained from the $k^*[H^+]$ data in Table 140, are 54 sec for 0.018 M acetate, which can be corrected, as described above, to 61 sec for zero acetate, and 27 sec or 36 sec for 0.180 M acetate, depending upon which $k^*[H^+]$ value is used. Either of the $1/k^*[H^+]$ values for 0.180 M acetate violates the limiting value imposed by the mechanistic model.

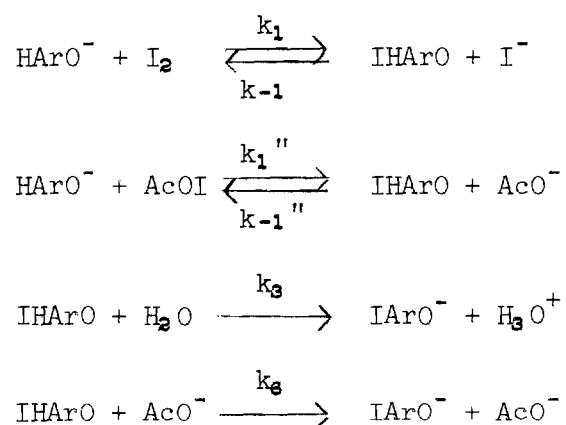
Going now to references no. 136 and 138 in Table 140, a similar consideration of the effect of ionic strength predicts an intercept ($1/k_1K_2$) value of 43 sec. The value of $1/k^*[H^+]$ for 0.0190 M acetate is 40 sec, which can be corrected to 43 sec for zero catalysis; for 0.360 M acetate, $1/k^*[H^+]$ is 12.5 sec or 21 sec, again depending upon which value of $k^*[H^+]$ is used. Both of the $1/k^*[H^+]$ values for 0.360 M acetate seriously violate the lower limit.

For the phenol-2,4,6- d_3 , values of $1/k^*[H^+]$ can be calculated from Table 141 for the 10.0° work. At 0.60 μ , $1/k^*[H^+]$ is 240 sec for 0.0180 M acetate, which can be corrected to 280 sec for zero acetate and 120 sec or 139 sec for 0.180 M acetate. For the experiments at 10.0°, 0.120 μ , $1/k^*[H^+]$ is 192 sec for 0.0190 M acetate, which can be corrected to 232 sec for zero acetate and 43 sec or 77 sec for 0.360 M acetate.

Had the protio compound not exceeded the limiting value of $1/k^*[H^+]$, the isotope effect based upon the results for the phenol-2,4,6- d_3 would have been 2.6 or 3.0 at 0.180 M acetate, 0.60 μ , instead of the observed value of 3.9 or 4.5; the isotope effect would have been 1.0 or 1.8 at 0.360 M acetate, 0.60 μ , instead of 3.7 or 3.5 as observed.

The fact that acetate ion consistently catalyzes phenol beyond the limited extent predicted by the mechanism in which acetate acts solely as a catalyst for proton removal and the fact that the isotope effect is consistently higher than predicted for such a mechanism suggest that this mechanism is inadequate to describe the iodination of phenol in the presence of acetate ion. This situation is similar to that encountered in the study of the phosphate-catalyzed iodination of 2,4-dinitrophenoxide, and a similar explanation is possible.

If AcOI were a significant iodinating agent in a scheme such as



the definitive rate equation could be written

$$\begin{aligned} \frac{1}{k^*[\text{H}^+]} &= \left\{ \frac{k_{-1}}{k_1 K_2 (k_3 + k_3[\text{AcO}^-])} \right\} [\text{I}^-] \\ &+ \frac{1}{k_1 K_2 + \frac{k_1'' K_2 K_4 [\text{AcO}^-]}{[\text{I}^-]}} \end{aligned} \quad (4)$$

$$\text{where } K_4 = \frac{[H^+][AcO^-]}{[AcOH]}$$

The result would be that as the acetate concentration increased, $k_1 K_2$ would become less and less significant relative to $\frac{k_1'' K_2 K_4 [AcO^-]}{[I^-]}$, and at a sufficiently high concentration of acetate and at sufficiently low concentrations of iodide, the $1/k^*[H^+]$ versus $[I^-]$ plot would reduce to a straight line through the origin, and the limiting value of $1/k_1 K_2$ for $1/k^*[H^+]$ at infinite catalysis would not apply. The isotope effect would still be expected to decrease with increasing acetate concentration; but the decrease at any given degree of catalysis would be less than predicted by the mechanism in which acetate acts only as a catalyst for proton removal. Such a mechanism as described by equation (4) would also have the effect of increasing the values of \underline{n} for the extrapolation of k_{app} data; it was observed that the k_{app} data of the catalyzed experiments generally required considerable extrapolation when little or none was anticipated on the basis of the mechanism which did not consider AcOI.

Finally, a concerted iodination and proton removal by AcOI is possible, analogous to that described in Chapter VIII for the iodination of 2,4-dinitrophenol by $IHPO_4^-$. Since the isotope effect of any such concerted reaction is not known, it is not possible to evaluate how well such a mechanism fits with the experimental data.

In summary, while the interpretation of the data on the iodination of phenol and phenol-2,4,6- d_3 catalyzed by acetate requires reliance upon

experimental results obtained under difficult conditions (brief reaction times) and calculated values based upon approximations, the experimental findings seem to require that AcOI be invoked as a significant iodinating agent.

Table 126. Run 58, Iodination of Phenol in 0.31×10^{-6} M Sodium Iodide Solution at 25.0°

$(I_2)_0$	0.60×10^{-6} M	$[CH_3COO^-]$	0.000	M
$[I_2]_0$	0.58×10^{-6} M	$[CH_3COOH]$	0.000	M
$(I^-)_0$	0.31×10^{-6} M	$[NaClO_4]$	0.301	M
$[I^-]_0$	0.33×10^{-6} M	$(Phenol)_0$	2.70×10^{-6}	M
$[HOI]_0$	0.020×10^{-6} M	$[H^+]$	100×10^{-6}	M
		μ	0.30	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	F_1	k_{app} (l/mole sec)
167	.106	25.3	0.144	670
231	.096	31.3	.140	620
301	.082	38.6	.138	630
350	.070	45.0	.135	690
400	.067	48.6	.137	650

$$F_2 = 11.3 \times 10^{-6} \text{ sec}^{-1}$$

$$E = 4.15 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 720 \text{ l/mole sec}$$

$$k^* = 740 \text{ l/mole sec}$$

Table 127. Run 59, Iodination of Phenol-2,4,6-d in 0.31×10^{-6} M Sodium Iodide Solution at 25.0°

$(I_2)_0$	0.60×10^{-6} M	$[CH_3COO^-]$	0.000	M
$[I_2]_0$	0.58×10^{-6} M	$[CH_3COOH]$	0.000	M
$(I^-)_0$	0.31×10^{-6} M	$[NaClO_4]$	0.301	M
$[I^-]_0$	0.33×10^{-6} M	(Phenol-2,4,6-d) ₀	7.97×10^{-6}	M
$[HOI]_0$	0.020×10^{-6} M	$[H^+]$	100	$\times 10^{-6}$ M
		μ	0.30	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	F_1	k_{app} (l/mole sec)
186	0.106	23.5	0.141	182
228	.103	24.3	.139	154
221	.097	28.2	.138	190
300	.082	38.2	.137	204
410	.077	40.7	.136	162

$$F_2 = 11.3 \times 10^{-6} \text{ sec}^{-1}$$

$$E = 4.15 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app0} = 219 \text{ l/mole sec}$$

$$k^* = 226 \text{ l/mole sec}$$

Table 128. Run 60, Iodination of Phenol in 0.32×10^{-6} M Sodium Iodide Solution at 25.0°

$(I_2)_o$	0.52×10^{-6} M	$[CH_3COO^-]$	0.063	M
$[I_2]_o$	0.51×10^{-6} M	$[CH_3COOH]$	0.463	M
$(I^-)_o$	0.32×10^{-6} M	$[NaClO_4]$	0.463	M
$[I^-]_o$	0.32×10^{-6} M	$(Phenol)_o$	5.81×10^{-6}	M
$[HOI]_o$	0.007×10^{-6} M	$[H^+]$	294	$\times 10^{-6}$ M
		μ	0.53	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
213	0.066	36.4	370
214	.062	40.2	420
303	.052	49.2	390
396	.041	59.2	400

$$F_1 = 0.106$$

$$E = 4.90 \times 10^{-6} \text{ mole cm/l}$$

$$F_2 = 8.1 \times 10^{-6} \text{ sec}^{-1}$$

$$\text{average } k_{app} = 398 \text{ l/mole sec}$$

$$k^* \text{ (based on average } k_{app}) = 400 \text{ l/mole sec}$$

$$k_{appo} = 398 \text{ l/mole sec}$$

$$k^* \text{ (based on } k_{appo}) = 400 \text{ l/mole sec}$$

Table 129. Run 61, Iodination of Phenol-2,4,6-d in 0.32×10^{-6} M Sodium Iodide Solution at 25.0°

$(I_2)_0$	0.52×10^{-6} M	$[CH_3COO^-]$	0.063	M
$[I_2]_0$	0.51×10^{-6} M	$[CH_3COOH]$	0.463	M
$(I^-)_0$	0.32×10^{-6} M	$[NaClO_4]$	0.463	M
$[I^-]_0$	0.32×10^{-6} M	$(Phenol-2,4,6-d)_0$	17.8×10^{-6}	M
$[HOI]_0$	0.007×10^{-6} M	$[H^+]$	294×10^{-6}	M
		μ	0.53	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
140	0.080	23.6	109
190	.072	30.8	110
213	.069	33.6	109
309	.055	46.3	114
407	.044	56.3	115

$$F_1 = 0.106$$

$$E = 4.90 \times 10^{-6} \text{ mole cm/l}$$

$$F_2 = 8.1 \times 10^{-6} \text{ sec}^{-1}$$

$$\text{average } k_{app} = 111 \text{ l/mole sec}$$

$$k^* \text{ (based upon average } k_{app}) = 112 \text{ l/mole sec}$$

$$k_{app0} = 111 \text{ l/mole sec}$$

$$k^* \text{ (based upon } k_{app0}) = 112 \text{ l/mole sec}$$

Table 130. Run 62, Iodination of Phenol in 0.32×10^{-6} M Sodium Iodide Solution at 25.0°

$(I_2)_0$	0.48×10^{-6} M	$[CH_3COO^-]$	0.176	M
$[I_2]_0$	0.46×10^{-6} M	$[CH_3COOH]$	0.490	M
$(I^-)_0$	0.32×10^{-6} M	$[NaClO_4]$	0.490	M
$[I^-]_0$	0.33×10^{-6} M	$(Phenol)_0$	2.12×10^{-6}	M
$[HOI]_0$	0.016×10^{-6} M	$[H^+]$	116×10^{-6}	M
		μ	0.67	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	F_1	k_{app} (l/mole sec)
106	0.067	28.3	0.095	1540
131	.062	32.7	.094	1480
151	.056	40.2	.096	1690
177	.052	43.0	.094	1580
200	.050	46.0	.096	1540
247	.043	51.5	.093	1470

$$F_2 = 12.0 \times 10^{-6} \text{ sec}^{-1}$$

$$E = 4.90 \times 10^{-6} \text{ mole cm/l}$$

$$\text{average } k_{app} = 1533 \text{ l/mole sec}$$

$$k^* \text{ (based upon average } k_{app}) = 1580 \text{ l/mole sec}$$

$$k_{app0} = 1850 \text{ l/mole sec}$$

$$k^* \text{ (based upon } k_{app0}) = 1910 \text{ l/mole sec}$$

Table 131. Run 63, Iodination of Phenol-2,4,6-d in 0.32×10^{-6} M Sodium Iodide Solution at 25.0°

$(I_2)_0$	0.48×10^{-6} M	$[CH_3COO^-]$	0.176	M
$[I_2]_0$	0.46×10^{-6} M	$[CH_3COOH]$	0.490	M
$(I^-)_0$	0.32×10^{-6} M	$[NaClO_4]$	0.490	M
$[I^-]_0$	0.33×10^{-6} M	$(Phenol-2,4,6-d)_0$	2.05×10^{-6}	M
$[HOI]_0$	0.016×10^{-6} M	$[H^+]$	116×10^{-6}	M
		μ	0.67	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	F_1	k_{app} (l/mole sec)
241	0.074	19.4	0.095	450
300	.071	21.1	.094	400
390	.064	29.2	.096	450
462	.061	31.6	.096	420
613	.056	34.7	.095	350
700	.052	37.6	.094	340

$$F_2 = 12.0 \times 10^{-6} \text{ sec}^{-1}$$

$$E = 4.90 \times 10^{-6} \text{ mole cm/l}$$

$$\text{average } k_{app} = 400 \text{ l/mole sec}$$

$$k^* \text{ (based upon average } k_{app}) = 410 \text{ l/mole sec}$$

$$k_{app0} = 550 \text{ l/mole sec}$$

$$k^* \text{ (based upon } k_{app0}) = 570 \text{ l/mole sec}$$

Table 132. Run 68, Iodination of Phenol in 0.32×10^{-6} M Sodium Iodide Solution at 10.0°

$(I_2)_0$	0.55×10^{-6} M	$[CH_3COO^-]$	0.0184	M
$[I_2]_0$	0.55×10^{-6} M	$[CH_3COOH]$	0.0426	M
$(I^-)_0$	0.32×10^{-6} M	$[NaClO_4]$	0.540	M
$[I^-]_0$	0.32×10^{-6} M	$(Phenol)_0$	2.51×10^{-6}	M
$[HOI]_0$	0.005×10^{-6} M	$[H^+]$	93×10^{-6}	M
		μ	0.56	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
740	0.092	27.8	181
820	.087	32.3	197
939	.083	33.7	181
1068	.078	36.5	177
1270	.074	39.3	164
1402	.067	43.7	173
1505	.065	47.5	181

$$F_1 = 0.131$$

$$E = 4.21 \times 10^{-6} \text{ mole cm/l}$$

$$F_2 = 2.5 \times 10^{-6} \text{ sec}^{-1}$$

$$k_{app0} = 197 \text{ l/mole sec}$$

$$k^* = 198 \text{ l/mole sec}$$

Table 133. Run 69, Iodination of Phenol-2,4,6-d in 0.32×10^{-6} M Sodium Iodide Solution at 10.0°

$(I_2)_o$	0.55×10^{-6} M	$[CH_3COO^-]$	0.0184	M
$[I_2]_o$	0.55×10^{-6} M	$[CH_3COOH]$	0.0426	M
$(I^-)_o$	0.32×10^{-6} M	$[NaClO_4]$	0.540	M
$[I^-]_o$	0.32×10^{-6} M	(Phenol-2,4,6-d) _o	7.49×10^{-6}	M
$[HOI]_o$	0.005×10^{-6} M	$[H^+]$	93	$\times 10^{-6}$ M
		μ	0.56	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
760	0.103	19.3	38
866	.096	23.8	42
1067	.093	25.7	38
1240	.086	30.9	40
1344	.084	31.5	38
1686	.081	34.8	34
1807	.076	36.9	35

$$F_1 = 0.131$$

$$E = 4.21 \times 10^{-6} \text{ mole cm/l}$$

$$F_2 = 2.5 \times 10^{-6} \text{ sec}^{-1}$$

$$k_{appo} = 44 \text{ l/mole sec}$$

$$k^* = 44 \text{ l/mole sec}$$

Table 134. Run 70, Iodination of Phenol in 0.32×10^{-6} M Sodium Iodide Solution at 10.0°

$(I_2)_0$	0.56×10^{-6} M	$[CH_3COO^-]$	0.181	M
$[I_2]_0$	0.55×10^{-6} M	$[CH_3COOH]$	0.420	M
$(I^-)_0$	0.32×10^{-6} M	$[NaClO_4]$	0.420	M
$[I^-]_0$	0.32×10^{-6} M	$(Phenol)_0$	2.72×10^{-6}	M
$[HOI]_0$	0.005×10^{-6} M	$[H^+]$	93	$\times 10^{-6}$ M
		μ	0.60	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
290	0.099	23.0	340
405	.090	28.7	316
486	.086	32.9	313
551	.083	33.4	282
625	.078	37.7	291
730	.075	38.9	259
820	.068	44.7	279

$$F_1 = 0.132$$

$$E = 4.21 \times 10^{-6} \text{ mole cm/l}$$

$$F_2 = 6.3 \times 10^{-6} \text{ sec}^{-1}$$

$$\text{average } k_{app} = 297 \text{ l/mole sec}$$

$$k^* \text{ (based upon average } k_{app}) = 300 \text{ l/mole sec}$$

$$k_{app0} = 390 \text{ l/mole sec}$$

$$k^* \text{ (based upon } k_{app0}) = 394 \text{ l/mole sec}$$

Table 135. Run 71, Iodination of Phenol-2,4,6-d in 0.32×10^{-6} M Sodium Iodide Solution at 10.0°

$(I_2)_0$	0.56×10^{-6} M	$[CH_3COO^-]$	0.181	M
$[I_2]_0$	0.55×10^{-6} M	$[CH_3COOH]$	0.420	M
$(I^-)_0$	0.32×10^{-6} M	$[NaClO_4]$	0.420	M
$[I^-]_0$	0.32×10^{-6} M	$(Phenol-2,4,6-d)_0$	7.53×10^{-6}	M
$[HOI]_0$	0.005×10^{-6} M	$[H^+]$	93	$\times 10^{-6}$ M
		μ	0.60	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
494	0.093	26.7	85
530	.092	27.4	81
643	.086	30.0	74
724	.083	32.7	74
842	.079	35.3	70
909	.075	38.2	71
1126	.067	44.3	70

$$F_1 = 0.132$$

$$E = 4.21 \times 10^{-6} \text{ mole cm/l}$$

$$F_2 = 6.3 \times 10^{-6} \text{ sec}^{-1}$$

$$\text{average } k_{app} = 75 \text{ l/mole sec}$$

$$k^* \text{ (based upon average } k_{app}) = 76 \text{ l/mole sec}$$

$$k_{app0} = 92 \text{ l/mole sec}$$

$$k^* \text{ (based upon } k_{app0}) = 93 \text{ l/mole sec}$$

Table 136. Run 74, Iodination of Phenol in 0.32×10^{-6} M Sodium Iodide Solution at 10.0°

$(I_2)_0$	0.56×10^{-6} M	$[CH_3COO^-]$	0.0187	M
$[I_2]_0$	0.56×10^{-6} M	$[CH_3COOH]$	0.0427	M
$(I^-)_0$	0.32×10^{-6} M	$[NaClO_4]$	1.182	M
$[I^-]_0$	0.33×10^{-6} M	(Phenol) ₀	2.55×10^{-6}	M
$[HOI]_0$	0.009×10^{-6} M	$[H^+]$	107×10^{-6}	M
		μ	1.20	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
553	0.098	25.3	213
656	.089	31.0	230
756	.084	34.5	229
839	.081	35.8	216
1007	.077	39.1	203
1193	.072	41.7	186
1445	.061	49.4	197

$$F_1 = 0.134$$

$$E = 4.21 \times 10^{-6} \text{ mole cm/l}$$

$$F_2 = 4.4 \times 10^{-6} \text{ sec}^{-1}$$

$$k_{app0} = 231 \text{ l/mole sec}$$

$$k^* = 236 \text{ l/mole sec}$$

Table 137. Run 75, Iodination of Phenol-2,4,6-d in 0.32×10^{-6} M Sodium Iodide Solution at 10.0°

$(I_2)_0$	0.56×10^{-6} M	$[CH_3COO^-]$	0.0187	M
$[I_2]_0$	0.56×10^{-6} M	$[CH_3COOH]$	0.0427	M
$(I^-)_0$	0.32×10^{-6} M	$[NaClO_4]$	1.182	M
$[I^-]_0$	0.33×10^{-6} M	(Phenol-2,4,6-d) ₀	7.51×10^{-6}	M
$[HOI]_0$	0.009×10^{-6} M	$[H^+]$	107×10^{-6}	M
		μ	1.20	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	k_{app} (l/mole sec)
767	0.101	22.4	44
954	.096	24.8	40
1108	.090	29.0	42
1211	.084	32.5	44
1442	.081	34.1	39
1477	.081	34.8	39
1774	.072	40.1	39

$$F_1 = 0.134$$

$$E = 4.21 \times 10^{-6} \text{ mole cm/l}$$

$$F_2 = 4.4 \times 10^{-6} \text{ sec}^{-1}$$

$$k_{app0} = 48 \text{ l/mole sec}$$

$$k^* = 49 \text{ l/mole sec}$$

Table 138. Run 72, Iodination of Phenol in 0.32×10^{-6} M Sodium Iodide Solution at 10.0°

$(I_2)_0$	0.53×10^{-6} M	$[CH_3COO^-]$	0.362	M
$[I_2]_0$	0.52×10^{-6} M	$[CH_3COOH]$	0.839	M
$(I^-)_0$	0.32×10^{-6} M	$[NaClO_4]$	0.839	M
$[I^-]_0$	0.32×10^{-6} M	$(Phenol)_0$	2.52×10^{-6}	M
$[HOI]_0$	0.008×10^{-6} M	$[H^+]$	107×10^{-6}	M
		μ	1.20	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	F_1^a	k_{app} (l/mole sec)
271	0.086	28.5	0.125	510
298	.083	30.7	.125	510
380	.075	33.3	.119	440
414	.075	36.1	.125	450
529	.067	38.4	.119	380
605	.059	41.2	.119	410
682	.052	43.2	.119	430

$$F_2 = 14.5 \times 10^{-6} \text{ sec}^{-1}$$

$$E = 4.21 \times 10^{-6} \text{ mole cm/l}$$

$$k_{app} = 447 \text{ l/mole sec}$$

$$k^* \text{ (based upon average } k_{app}) = 450 \text{ l/mole sec}$$

$$k_{app0} = 740 \text{ l/mole sec}$$

$$k^* \text{ (based upon } k_{app0}) = 750 \text{ l/mole sec}$$

^aTwo values of F_1 are necessary in this experiment because the original iodine stock solution was contaminated and had to be replaced by a second iodine solution.

Table 139. Run 73, Iodination of Phenol-2,4,6-d in 0.32×10^{-6} M Sodium Iodide Solution at 10.0°

$(I_2)_0$	0.53×10^{-6} M	$[CH_3COO^-]$	0.362	M
$[I_2]_0$	0.52×10^{-6} M	$[CH_3COOH]$	0.839	M
$(I^-)_0$	0.32×10^{-6} M	$[NaClO_4]$	0.839	M
$[I^-]_0$	0.32×10^{-6} M	(Phenol-2,4,6-d) ₀	8.10×10^{-6}	M
$[HOI]_0$	0.008×10^{-6} M	$[H^+]$	107	$\times 10^{-6}$ M
		μ	1.20	

Reaction Time (sec)	Absorbance	Iodine Reacted (%)	F_1^a	k_{app} (l/mole sec)
245	0.090	25.5	0.125	150
318	.083	30.5	.125	143
349	.079	30.2	.119	128
416	.078	33.6	.125	123
589	.065	39.9	.119	108
673	.061	42.6	.119	103
771	.059	43.4	.119	93

$$F_2 = 14.5 \times 10^{-6} \text{ sec}^{-1}$$

$$E = 4.21 \times 10^{-6} \text{ mole cm/l}$$

$$\text{average } k_{app} = 121 \text{ l/mole sec}$$

$$k^* (\text{based upon average } k_{app}) = 122 \text{ l/mole sec}$$

$$k_{app0} = 216 \text{ l/mole sec}$$

$$k^* (\text{based upon } k_{app0}) = 218 \text{ l/mole sec}$$

^aTwo values of F_1 are necessary in this experiment because the original iodine stock solution was contaminated and had to be replaced by a second iodine solution.

Table 140. Acetate-Catalyzed Iodination of Phenol

Table Ref.	$[I^-]_0 \times 10^6$ (mole/l)	$[H^+] \times 10^6$ (mole/l)	$[AcO^-]$ (mole/l)	μ	$k^*[H^+] \times 10^3$ (sec ⁻¹) based upon k_{app} average	$k^*[H^+] \times 10^3$ (sec ⁻¹) based upon k_{app0}	T (°C)
126	0.34	100	0.000	0.30	67	74	25.0
128	.32	294	.060	0.53	118	118	25.0
130	.33	116	.180	0.67	183	221	25.0
132	.32	93	.018	0.56	16.7	18.4	10.0
134	.32	93	.180	0.60	28	37	10.0
136	.33	107	.019	1.20	23	25	10.0
138	.33	107	.360	1.20	48	80	10.0

Table 141. Acetate-Catalyzed Iodination of Phenol-2,4,6-d

Table Ref.	$[I^-]_0 \times 10^6$ (mole/l)	$[H^+] \times 10^6$ (mole/l)	$[AcO^-]$ (mole/l)	μ	$k^*[H^+] \times 10^3$ (sec ⁻¹) based upon k_{app} average	$k^*[H^+] \times 10^3$ (sec ⁻¹) based upon k_{app0}	T (°C)
127	0.34	100	.000	0.30	18.4	23	25.0
129	.32	294	.060	0.53	33	33	25.0
131	.33	116	.180	0.67	48	66	25.0
133	.32	93	.018	0.56	3.5	4.1	10.0
135	.32	93	.180	0.60	7.2	8.3	10.0
137	.33	107	.019	1.20	4.5	5.2	10.0
139	.33	107	.360	1.20	13.0	23	10.0

Table 142. Isotope Effect in the Acetate-Catalyzed Iodination of Phenol
 at Iodide Ion Concentration Approximately 0.33×10^{-6} M

Table Ref.	$[H^+] \times 10^6$ (mole/l)	μ	$[AcO^-]$ (mole/l)	(°C)	k_H^*/k_D^* based upon k_{app} average	k_H^*/k_D^* based upon k_{app0}
1, 2	100	0.30	0.000	25.0	3.6	3.2
3, 4	294	0.53	.060	25.0	3.6	3.6
5, 6	116	0.67	.180	25.0	3.8	3.3
7, 8	93	0.56	.018	10.0	4.8	4.5
9, 10	93	0.60	.180	10.0	3.9	4.5
13, 14	107	1.20	.019	10.0	5.1	4.8
11, 12	107	1.20	.360	10.0	3.7	3.5

CHAPTER X

GENERAL DISCUSSION OF KINETIC RESULTS

The iodination of phenol has been found by previous workers to be first order in phenol and in iodine at a given acidity and iodide ion concentration. (35, 44, 86,87) The first order dependence upon phenol has been confirmed in this work.

p-Nitrophenol was similarly found to be first order in the phenol and first order in iodine by Grovenstein and Aprahamian. (59)

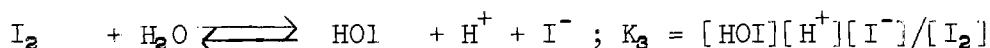
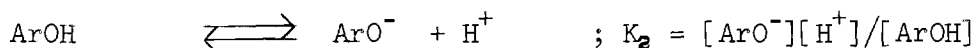
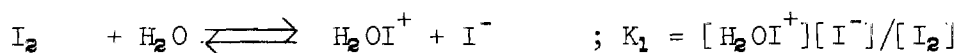
First order dependence upon the concentration of the phenoxide ion in the case of 2,4-dinitrophenol was found by Fort. (95) This iodination is also seen to be first order in iodine concentration from the fact that rate constants, which are calculated on the basis of first order in phenol and first order in iodine, vary, as large percentages of iodine are consumed, only to the extent predicted by the increase in the concentration of iodide ion.

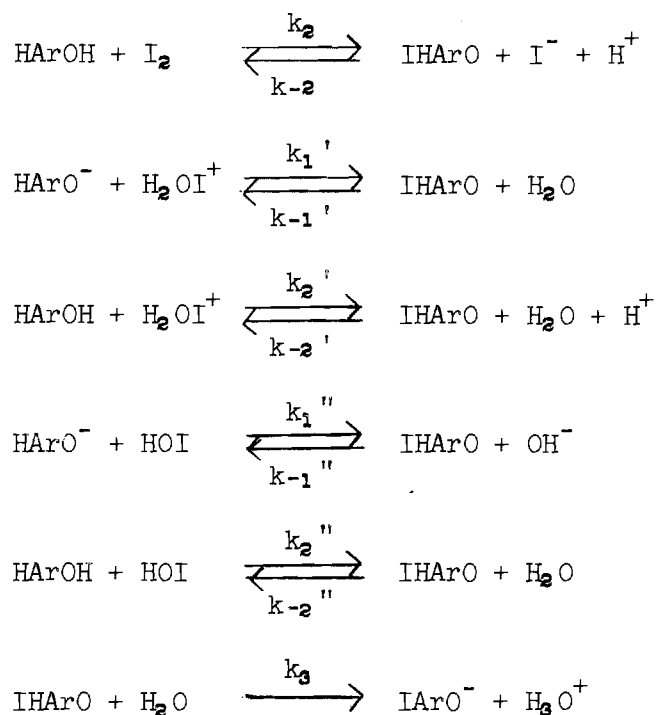
The fact that the iodination of anisole was first order in aromatic and first order in iodine was established by Aprahamian. (107)

The aromatic species undergoing iodination has been established by measuring the effect on rates of varying the acidity. In the case of phenol, work reported in this thesis establishes phenoxide as the principal subject of iodination, with a smaller amount (about 20 percent) of iodination of undissociated phenol at the acidity of most of the experiments, $0.0052 \text{ M } [\text{H}^+]$. On the basis of the study of variation of

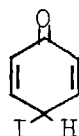
rate with pH by Aprahamian,⁽¹⁰⁴⁾ most iodination of p-nitrophenol proceeds via the phenoxide in the work reported here. In the case of the iodination of 2,4-dinitrophenol, Fort found that at $70 \times 10^{-6} \text{ M } [\text{H}^+]$, the acidity of most of the solutions studied here, iodination proceeded by way of 2,4-dinitrophenoxide. In the iodination of anisole, large variations in acidity between the work of Aprahamian⁽¹⁰⁷⁾ and the work reported here did not measurably affect the rate of reaction; it is concluded that anisole as such is the species iodinated.

In the experiments described in Chapters IV, V, VI, and VII, no basic catalyst was employed. The purpose of this part of the work was to discriminate between molecular iodine (I_2) and hypiodous acidium ion (H_2OI^+) as the iodinating agent in the two-step iodination reaction, since a large part of the reported results on iodination of aromatic compounds is consistent with either of these possibilities. The general mechanism involving these two iodinating agents is described by the following equations, with the additional inclusion of hypiodous acid (HOI) as an iodinating agent, since this latter was invoked to explain some of the results, as will be seen.





Employing the steady-state approximation with respect to the intermediate IHArO (which is assumed to have a quinoid structure; e.g.,



in the iodination of phenol, and to have the structure



in the iodination of anisole), a descriptive equation can be generated for this general mechanism, analogously to the development of the less general equations derived to describe the kinetics of iodination of specific compounds in the body of this thesis.

$$\frac{1}{k^* [H^+]} = \frac{k_{-1}}{k_1 k_3 K_2} [I^-] \quad (1)$$

$$+ \frac{1}{k_1 K_2 + k_2 [H^+] + \frac{k_1 'K_1 K_2}{[I^-]} + \frac{k_2 'K_1 [H^+]}{[I^-]} + \frac{k_1 ''K_2 K_3 [OH^-]}{[I^-]} + \frac{k_2 ''K_3 K_W}{[I^-]}}$$

where k^* is the observed rate constant in terms of stoichiometric concentration of the phenol and the true concentration of iodine (stoichiometric iodine concentration corrected for depletion of iodine by the equilibria involving triiodide and hypoiodous acid; the equilibrium between iodine and hypoiodous acid does not significantly alter the iodine concentration under the experimental conditions. This equation is general for the iodination of phenols. In the case of anisole, there is no phenoxide analogue, and the general mechanism can be described by the equation

$$\frac{1}{k^*} = \frac{k_{-2} [I^-]}{k_2 k_3} + \frac{1}{k_2 + \frac{k_2 'K_1}{[I^-]} + \frac{k_2 ''K_3 [OH^-]}{[I^-]}} \quad (2)$$

It can be seen from these equations that, when the iodide ion concentration is sufficiently high, molecular iodine will be the only significant iodinating agent, and a plot of $1/k^*$ versus $[I^-]$ will be a straight line with a positive $1/k^*$ intercept equal to $1/k_2$. As the iodide ion concentration is lowered, the slope will increase, due to the increasingly important contributions from iodination by H_2OI^+ , at higher acidities, and by HOI, at lower acidities. When the iodide ion concentration is so low that either of these latter is the sole iodinating agent, or both of them are significant iodinating agents to the exclu-

sion of molecular iodine, the plot of $1/k^*$ versus $[I^-]$ will be a straight line through the origin. The slope of this low-iodide line will be smaller at low acidity, where HOI is the iodinating agent, than at high acidity, where H_2OI^+ is the iodinating agent.

From the assumption that all or most of the isotope effect of k^* resides in the proton-removal step k_3 , it follows that the isotope effect will decrease with decreasing iodide ion concentration so long as molecular iodine continues to be essentially the sole iodinating agent, due to the decreasing kinetic significance of the proton-removal step; i.e., due to the increasing contribution of the intercept $k_1K_2 + k_2[H^+]$ to k^* . In the iodide ion concentration range where H_2OI^+ or HOI is sole iodinating agent, however, the isotope effect will show no dependence on iodide ion concentration because the iodide ion concentration no longer affects the kinetic significance of the proton-removal step; i.e., the $1/k^*$ versus $[I^-]$ plot has zero intercept.

Of course, it is possible that the kinetic data that one obtains may not enable one to distinguish between a positive intercept and a zero intercept, and this appears to have been the case with much of the earlier work done at high iodide ion concentrations. This is equivalent to saying that the failure to observe any decrease in isotope effect with decreasing iodide ion concentration can be due either to H_2OI^+ or HOI being the iodinating agent, or to the fact that, although molecular iodine is the iodinating agent, the iodide ion concentration range studied is not to low enough values for the intercept to make any measurable contribution to k^* ; i.e., proton-removal remains completely rate-determining over the iodide ion concentration range studied.

In the noncatalyzed work, the kinetic data yielded information about the relative importance of the various possible iodinating agents. The effect of iodide ion concentration upon the rate constant k^* at a given pH and a given ionic strength was studied. This effect of iodide had already been studied at higher iodide ion concentration for phenol and anisole by Aprahamian, (86, 107) and for 2,4-dinitrophenol by Fort, in which cases the data were insufficient to clearly distinguish between possible iodinating agents, and for p-nitrophenol by Aprahamian, (104) in which case molecular iodine was found to be the iodinating agent in the iodide ion concentration range $1250 \times 10^{-5} \text{ M}$ to $2.5 \times 10^{-5} \text{ M}$ at 25.0° and ionic strength 0.30.

When the kinetic study of the iodination of phenol was extended to lower iodide ion concentrations, at 0.0174 M hydrogen ion and 0.30μ , a plot of $1/k^*$ versus $[I^-]$ was found to be a straight line with a positive $1/k^*$ intercept over the iodide ion concentration range $4.65 \times 10^{-1} \text{ M}$ to $3.2 \times 10^{-7} \text{ M}$. The isotope effect decreased from 6.6 to 3.1 over the same range of iodide ion concentration. This demonstrated that, over this iodide range, the iodinating agent was molecular iodine. Kinetic experiments in which the pH was varied indicated that some iodination of undissociated phenol occurred also at $[H^+] = 0.0052 \text{ M}$, but it was not possible to determine from the results which iodinating agent attacked undissociated phenol.

The plot of $1/k^*$ versus $[I^-]$ for 2,4-dinitrophenol, at $[H^+] = 70 \times 10^{-6} \text{ M}$ and 0.30μ , was a curve which could be considered to be the composite of two straight-line plots: at higher iodide ion concentra-

tions, a straight line with a positive $1/k^*$ intercept; and at low iodide ion concentrations, a straight line through the origin. The isotope effect dropped from 4.3 at 3.89×10^{-3} M iodide to 2.4 at about 10×10^{-6} M iodide and then remained constant within experimental error to 2.6×10^{-6} M $[I^-]$. The isotope effect became constant at about the same iodide ion concentration at which the plot curved toward the origin. The interpretation of the data is that at higher iodide ion concentrations, the less reactive but more plentiful molecular iodine is the iodinating agent, whereas at lower iodide ion concentrations, beginning at 10×10^{-6} M, the more reactive H_2OI^+ becomes the predominant iodinating agent by virtue of its increased concentration.

Evidence was also found for the activity of hypiodous acid as an iodinating agent in the increase in k^* with decrease in hydrogen ion concentration at low iodide ion concentrations, over the range 93×10^{-6} M to 4×10^{-6} M. The fact that the isotope effect increased as the acidity decreased, from 2.42 ± 0.27 at 70×10^{-6} M $[H^+]$ to 3.04 ± 0.18 at 1.70×10^{-6} M $[H^+]$, is consistent with HOI as a significant iodinating agent at 1.70×10^{-6} M $[H^+]$. (At this acidity, approximately twice as much iodination proceeds by HOI as by H_2OI^+ .)

The kinetic data for the iodination of p-nitrophenol, combined with those previously obtained by Aprahamian,⁽¹⁰⁴⁾ indicate that the iodination of p-nitrophenoxide occurs via molecular iodine over the iodide range from 1.25×10^{-2} M to about 1×10^{-6} M, over which range the isotope effect decreases from 5.3 to 1.4. At lower iodide ion concentrations, curvature was found in the plot of $1/k^*$ versus $[I^-]$ similar to that observed in the case of 2,4-dinitrophenol. This indicated that

at the low iodide ion concentration (about 1×10^{-6} M), H_2OI^+ was a significant iodinating agent for either p-nitrophenol or p-nitrophenoxide.

From the kinetic results described thus far and from equation (1), some individual rate constants and ratios of rate constants were evaluated for the individual compounds and these are summarized in Table 143.

The plot of $1/k^*$ versus $[\text{I}^-]$ for anisole was found, after taking into account differences in ionic strength between the higher iodide work of Aprahamian⁽¹⁰⁷⁾ (0.30μ) and the lower iodide work reported here (0.0030μ), to be a straight line which, within experimental error, intersected the origin. The isotope effect was approximately constant at 3.0 over the iodide range 4.8×10^{-4} M to 0.29×10^{-6} M. It was not possible to determine whether the plot of $1/k^*$ versus $[\text{I}^-]$ over this iodide range should be considered to go exactly through the origin, or whether it had a positive $1/k^*$ intercept too small to distinguish from zero. Therefore, it was not possible to distinguish between alternative iodinating agents. However, when the data were considered together with a finding by Gnanaprasam⁽⁸⁰⁾ that the isotope effect is essentially unchanged even at 3.4×10^{-11} M iodide, it was determined to be unlikely that molecular iodine was the iodinating agent at this very low iodide ion concentration, in light of the magnitude that this would require of the rate constant k_2 . Therefore, H_2OI^+ is probably the predominant iodinating agent over at least part of the iodide ion concentration range from 4.8×10^{-4} M to 3.4×10^{-11} M. (The low iodide reactions were run at an acidity much higher than that at which HOI acquired significance relative to H_2OI^+ in the iodination of 2,4-dinitrophenol.) It was also

shown to be impossible to determine from the data whether molecular iodine was an important iodinating agent over any part of the iodide range studied. Because of this lack of knowledge of the iodide range within which molecular iodine is the principal iodinating agent, it was not possible to assign individual rate constants in the case of anisole.

The relative importance of I_2 and H_2OI^+ as iodinating agents for the different compounds can be explained on the basis of the relative reactivities of these compounds. As iodide ion concentration decreases and consequently the ratio $[H_2OI^+]/[I_2]$ increases, H_2OI^+ becomes a more important iodinating agent. Since selectivity for the more reactive electrophile is expected to increase as the reactivity of the aromatic compound decreases,⁽¹⁰⁹⁾ the ratio $[H_2OI^+]/[I_2]$ at which H_2OI^+ will achieve any given degree of importance as an iodinating agent will be smaller for the less reactive compounds. This means that the change over from I_2 to H_2OI^+ as the predominant iodinating agent will occur at higher iodide ion concentrations for the less reactive compounds. Assuming that in the case of p-nitrophenol it is the p-nitrophenoxide that undergoes iodination by H_2OI^+ , this reasoning accounts for the observation that the iodinating agent changes from I_2 to H_2OI^+ at about 20×10^{-6} M iodide for 2,4-dinitrophenoxide and at about 1×10^{-6} M iodide for p-nitrophenoxide, and that molecular iodine is the sole significant iodinating agent for phenoxide as low as 3×10^{-7} M iodide.

109. J. Hine, Physical Organic Chemistry, 2nd ed., McGraw-Hill Company, Inc., New York, 1962, p. 372.

It is difficult to estimate, from the kinetic data, the reactivity toward attack by an iodinating agent of anisole relative to the phenoxides studied. Since the iodination of phenol was studied at $0.0052 \text{ M } [\text{H}^+]$ and since it was determined that at this acidity phenoxide was the predominant subject of iodination (about 80 percent), it can be calculated from the dissociation constant for phenol of 1×10^{-10} at 25° (90) that the substituent $-\text{O}^-$ activated the ring by a factor of about 10^7 relative to the undissociated phenol.[†] Since the methoxy substituent is less strongly electron-donating in aromatic systems than the hydroxy substituent to the extent that anisole has been found to brominate about 100 times less rapidly than phenol,⁽¹¹⁰⁾ anisole should be less reactive than phenoxide toward iodination by a factor of perhaps 10^9 .

But, from Table 143, *p*-nitrophenoxide is less reactive than phenoxide toward molecular iodine by a factor of 4.6×10^4 and 2,4-dinitrophenoxide is less reactive than phenoxide toward molecular iodine by a factor of 3.6×10^9 . However, the *p*-nitrophenol and 2,4-dinitrophenol reactions were run at 50.0° , whereas the phenol reaction was run at 25.0° . Berliner⁽⁴⁶⁾ calculated an activation energy of 19.4 kcal for the iodination of phenoxide. Berliner's work was done at 0.12 M iodide ion con-

[†]The ratio of $[\text{ArO}^-]/[\text{ArOH}]$ at $0.0174 \text{ M } [\text{H}^+]$ comes to 6×10^{-7} using the dissociation constant of 1×10^{-10} . (The stoichiometric phenol concentration was always sufficiently high that it was negligibly depleted by dissociation.) The ratio of phenoxide iodinated to phenol iodinated is about four, and when this is weighted for relative concentrations of phenol and phenoxide by dividing it by 6×10^{-7} , the factor by which phenoxide is more reactive than phenol is determined to be about 0.7×10^7 .

110. P. W. Robertson, P. B. D. de la Mare, and B. E. Sweland, *J. Chem. Soc.*, 782 (1953).

centration, and it is clear from the data obtained in this thesis that the activation energy measured was that of the term $k_1 k_3 / k_{-1}$. If it is assumed that the rate constant k_1 has a similar activation energy, this rate constant should increase from 3.6×10^9 l/mole sec at 25.0° to 4.6×10^9 l/mole sec at 50.0° . When compared at 50.0° , therefore, p-nitrophenoxide is less reactive than phenoxide toward molecular iodine by a factor of about 5.8×10^5 , and 2,4-dinitrophenoxide is less reactive than phenoxide toward molecular iodine by a factor of about 4.6×10^{10} . On this basis, the reactivity of anisole toward iodine is probably fairly close to that of 2,4-dinitrophenoxide, and the iodide ion concentration at which the primary iodinating agent changes from molecular iodine to hypiodous acidium ion ought to be somewhere near 20×10^{-5} M, which is the change over point for 2,4-dinitrophenoxide.

As has been noted, the kinetic data on the iodination of anisole indicate that H_2OI^+ is probably the iodinating agent at 3.4×10^{-11} M iodide, and iodine might or might not become an important iodinating agent between 48×10^{-5} M and 3.4×10^{-11} M iodide. Therefore, as far as can be determined, the experimental results on the iodination are consistent with the proposed explanation for the relative importance of the different iodinating agents for different compounds.

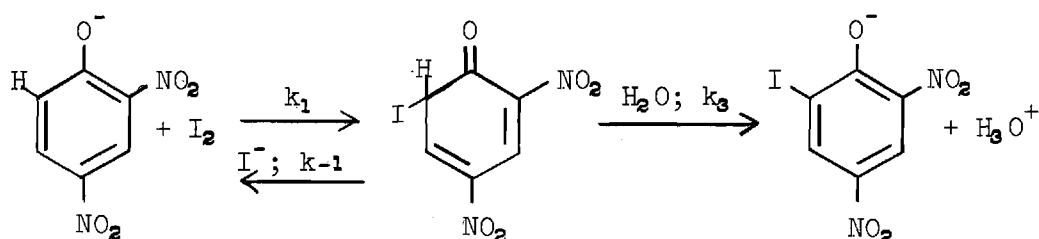
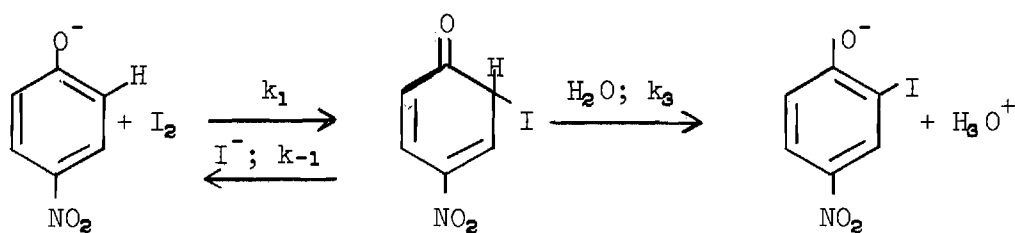
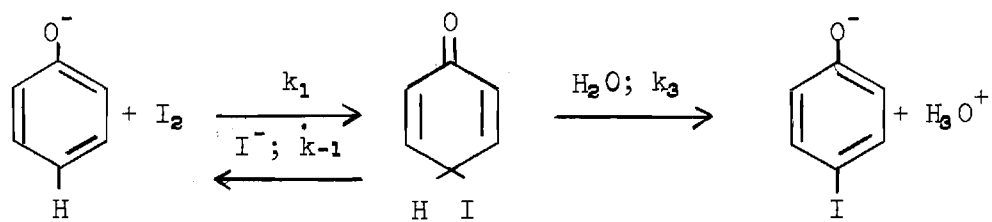
The phosphate catalysis of the iodination of 2,4-dinitrophenol and the acetate catalysis of the iodination of phenoxide were studied at low iodide ion concentrations. In the case of phenoxide, the reaction was catalyzed beyond what would be the limiting value of k^* ($k^* = k_1$), in light of the proposed mechanism of iodination by molecular iodine if

the only effect of the acetate ion were catalysis of the proton-removal step. In addition, the isotope effect did not drop as predicted on the basis of the expected decreased kinetic significance of the proton-removal step. In the case of 2,4-dinitrophenoxide, catalysis does not quite increase the reaction rate to the limiting value predicted by the mechanism of iodination by H_2OI^+ . (The catalysis of the iodination of 2,4-dinitrophenoxide was conducted in the hydrogen ion and iodide ion concentration range where, in the absence of catalyst, H_2OI^+ had been found to be the sole significant iodinating agent.) It is impossible from the data to determine whether the limit would have been surpassed with higher concentrations of catalyst. However, the isotope effect does not decrease as predicted on the basis of H_2OI^+ as the sole iodinating agent. The most probable explanation for the catalysis results is the involvement of iodinating agents such as CH_3COOI and HPO_4I^- , either in two-step or concerted iodination reactions.

Comparisons can be made between the individual rate constants for the various compounds studied, on the basis of the data in Table 143.

The large decreases in k_1 in the order phenol > p-nitrophenol > 2,4-dinitrophenol reflect the order of reactivity of these phenols toward electrophilic attack, caused by the deactivating effect of the nitro substituents.

The reversibility ratio k_{-1}/k_3 decreases in the same order as does k_1 but the range of variation is much smaller. The reaction steps corresponding to each of these rate constants can be illustrated for the three compounds as follows.



It can be argued that the reason why the k_{-1}/k_3 ratio decreases with increasing nitro substitution is that the electron-withdrawing effect of the substituent increases the acidity of the sp^3 hydrogen more than it enhances the ease of removal of I^+ by I^- . This seems reasonable in light of the principle of soft and hard acids and bases.⁽¹¹¹⁾ Polar substituents on the ring ought to make the phenoxide a harder acid and

111. R. G. Pearson and J. Songstad, *J. Am. Chem. Soc.*, **89**, 1827 (1967).

increase the reactivity toward H_2O , a hard base, by a greater factor than toward I^- , a soft base.

The differences in k_{-1}/k_3 between the protio and deutero compounds are due primarily to the differences in k_3 , since the k_{-1} step should be relatively insensitive to isotopic substitution. Therefore, the ratio k_{-1}/k_3 for the deutero compound divided by the ratio k_{-1}/k_3 for the protio compound should give an approximate k_3 isotope effect; these values are 6.3 for phenol, 5.5 for p-nitrophenol, and 4.5 ± 0.1 for 2,4-dinitrophenol.

The question next arises of why the isotope effects vary in the observed direction. Bell's (33,34) postulate that isotope effect is a maximum when the pKa values of the acid and the base are equal would indicate that the pKa of the quinoid intermediate in the iodination of phenol has an acidity not very different from that of water, since the isotope effect is not much smaller than the usual maximum of about seven. It follows that the introduction of each nitro group makes the intermediate progressively more acidic than water, thereby lowering the isotope effect. This analysis is equivalent to saying that in the proton-removal step in the iodination of phenol, the proton is approximately halfway between the phenol moiety and the water in the transition state, thereby minimizing bonding to the proton; whereas the position of the proton in the transition state is rendered closer to the phenol moiety by the introduction of nitro substituents, thereby increasing carbon-to-hydrogen bonding in the transition state and consequently decreasing the isotope effect.

It is seen from Table 143 that the ratios k_{-1}'/k_3 are much smaller than the ratios k_{-1}/k_3 for protio and deuterio 2,4-dinitrophenol; when the k_{-1}'/k_3 ratios are corrected to the same units as k_{-1}/k_3 by including the concentration of water, the values of k_{-1}'/k_3 are lower than the values of k_{-1}/k_3 by factors of 5.4×10^5 for 2,4-dinitrophenol and 7.6×10^5 for 2,4-dinitrophenol. This shows that iodide ion is more effective at removing the iodo substituent than is water, in accordance with the fact that the equilibrium constant K_1 is very small. (83)

The k_1' isotope effect for 2,4-dinitrophenol (1.45 ± 0.32) as observed from the values of $k_1'K_1$ is higher than expected for an α -secondary isotope effect. However, there is considerable uncertainty in this figure because it arises as a ratio of small differences between large numbers. α -Secondary isotope effects have been reported in electrophilic aromatic substitution, as noted in the introduction to this thesis and are explainable on the basis of a contribution from hyperconjugation of the sp^3 proton in the intermediate.

For the iodination of 2,4-dinitrophenol, k_1'' is 47 times greater than k_1 , indicating that HOI is a better iodinating agent than I_2 by that factor; however, there is considerable uncertainty in the value of k_1'' .

Table 143. Summary of Kinetic Data

	k_1 (l/mole sec)	$k_1'K_1$ (l/mole sec)	k_1'' (l/mole sec)	k_{-1}/k_3 (l/mole)	k_{-1}'/k_3
phenol (25.0°)	3.6×10^8			1.46×10^6	
phenol-2,4,6-d ₃ (25.0°)	ca. 3.6×10^8 ^b			9.25×10^6	
p-nitrophenol ^a (50.0°)	7.9×10^3			2.0×10^4	
p-nitrophenol-2,6-d ₂ ^a (50.0°)	ca. 7.9×10^3 ^b			1.1×10^5	
2,4-dinitrophenol (50.0°)	0.10	$1.03 \pm 0.10 \times 10^{-5}$	4.7	4.2×10^3	0.43 ± 0.04
2,4-dinitrophenol- 6-d (50.0°)	ca. 0.10 ^b	$7.1 \pm 2.4 \times 10^{-6}$		1.90×10^4	1.35 ± 0.26

^aThese data are taken from the paper by Grovenstein and Aprahamian. (59)

^bThese values arise from drawing the $1/k^*$ versus $[I^-]$ lines for the deuterio compounds to the same intercept as the protio compounds.

CHAPTER XI

SUGGESTIONS FOR FUTURE EXPERIMENTAL WORK

The conclusion that the iodinating agent for p-nitrophenoxide or p-nitrophenol changes from molecular iodine to hypiodous acidium ion at about 1×10^{-6} M iodide ion rests on a small amount of kinetic data. It is suggested that a more extensive study be made of the iodination of p-nitrophenol at low iodide ion concentrations. The effects of varying iodide and pH should yield more quantitative data on the relative iodinating power of molecular iodine and hypiodous acidium ion and whether p-nitrophenol or p-nitrophenoxide is iodinated by the hypiodous acidium ion.

In the iodination of 2,4-dinitrophenol, the conclusion that hypiodous acid is a significant iodinating agent is based upon the effect of pH upon the rate constant and the isotope effect. The conclusion is legitimate only if pH has no such effects at high iodide ion concentration, where molecular iodine is the iodinating agent. The evidence that this condition holds true consists of a single experiment by Fort, and it would be well to more conclusively demonstrate whether pH does not affect the rate constant (first order in true iodine concentration and first order in 2,4-dinitrophenoxide concentration) or the isotope effect at high iodide ion concentrations.

Part of the evidence for acyl hypiodites as iodinating agents

for phenoxide and 2,4-dinitrophenoxide is the failure to observe a large decrease in isotope effect when the reactions are considerably accelerated by base at low iodide ion concentration. This information could be interpreted more rigorously if the isotope effects were known for the catalyzed proton-removal step. Such data can be obtained by determining the isotope effects at various catalyst concentrations, provided that the iodide ion concentration is sufficiently high that the proton-removal step is completely rate-determining and remains so even when catalyzed.

APPENDIX I

SAMPLE CALCULATIONS

A Sample Calculation of a Rate Constant k_{app}

$$k_{app} = \frac{2.303}{t\{(ArOH)_0 - (I_2)_0\}} \log \frac{(I_2)_0\{(ArOH)_0 - x\}}{(ArOH)_0\{(I_2)_0 - x\}} \quad \begin{array}{l} \text{(Eq. (9),} \\ \text{Chap. III)} \end{array}$$

$$\text{where } x = \frac{P_3(I_2)_0 + P_1(ArOH)_0 - \text{Abs}(\text{total})}{P_1 + P_3 - P_2} \quad \begin{array}{l} \text{(Eq. (7),} \\ \text{Chap. V)} \end{array}$$

$$\text{and } (I_2)_0 = (F_1 - F_2/2) \cdot E \quad \begin{array}{l} \text{(Eq. (10),} \\ \text{Chap. III)} \end{array}$$

This sample calculation is for the kinetic point at $t = 9907$ seconds, experiment no. 31, Table 41.

The measured absorbance in the ten cm cell after this reaction time was 0.279, the background absorbance due to components of the quenched solution other than the triiodide and the aromatic species was determined as 0.023, and the volatilization correction V was zero.

Therefore, $\text{Abs}(\text{total}) = 0.279 - 0.023 + 0.000 = 0.256$.

The values of P_1 , P_2 , and P_3 were determined to be 25,950 ℓ/mole ,[†]

[†]The terms P_1 , P_2 , and P_3 are effective extinction coefficients, referred to a cell path length of ten cm. As such, they equal the effective extinction coefficients for one cm path length, multiplied by 10 cm; i.e., $\epsilon^{1\text{cm}} \ell/\text{mole cm} \times 10 \text{ cm}$. Therefore, P_1 , P_2 , and P_3 are numerically equal to ten times the effective extinction coefficients for one cm path length and can be expressed in the units ℓ/mole .

50,320 ℓ /mole, and 368,300 ℓ /mole, respectively, by independent determinations of the extinction coefficients for 2,4-dinitrophenol, 2-iodo-4,6-dinitrophenol, and triiodide under the conditions of the quenched solution.

The stoichiometric concentration of 2,4-dinitrophenol $(\text{ArOH})_0$, used in this experiment, was 3.935×10^{-6} M.

The term $P_3(I_2)_0$ equals the absorbance in a ten cm cell due to triiodide after 9907 seconds reaction in a blank reaction solution; i.e., one containing all of the ingredients of a reaction solution except the aromatic compound. This can be expressed as $F_1 - F_2 t$, where F_1 is the absorbance in a ten cm cell due to triiodide in a blank reaction solution at zero time and F_2 is the slope of the plot of absorbance versus time, as described in Chapter III. These data are obtained from the blank kinetic run, which yielded the following results:

Reaction Time (sec)	Absorbance (corrected for background)
1405	0.219
20626	.226
33413	.206
44649	.215
81536	.197
92336	.205

Plotting absorbance versus reaction time and extrapolating to zero time gives $F_1 = 0.222$. The slope, equal to F_2 , is $0.24 \times 10^{-6} \text{ sec}^{-1}$.

$$x = \frac{0.22 - 0.24 \times 10^{-6} \times 9907 + 25950 \times 3.935 \times 10^{-6} - 0.256}{25950 + 368300 - 50320}$$

$$x = 0.192 \times 10^{-6} \text{ mole}/\ell$$

Values are now known for $(\text{ArOH})_0$ and x . In order to calculate k_{app} , a value is still necessary for $(\text{I}_2)_0$, and can be obtained from equation (10), Chapter III. The value of E to be used in this equation is the reciprocal of P_3 , the units being mole/l.

$$(\text{I}_2)_0 = (0.222 - \frac{0.24 \times 10^{-6} \times 9907}{2}) \times 2.715 \times 10^{-6}$$

$$(\text{I}_2)_0 = 0.600 \times 10^{-6} \text{ mole/l}$$

Then, solving for k_{app}

$$k_{\text{app}} = \frac{2.303}{9907(3.935 \times 10^{-6} - 0.600 \times 10^{-6})} \log \frac{0.600(3.935 - 0.192)}{3.935(0.600 - 0.192)}$$

$$k_{\text{app}} = 10.1 \text{ l/mole sec.}$$

A Sample Calculation of How Much Sodium Hydroxide
or Perchloric Acid to Add to a 2,4-Dinitrophenol Reaction
Solution in Order to Achieve the Desired Acidity in a
Given Kinetic Run

$$\frac{\{(\text{ArO}^-)_0 + x\}\{(\text{H}^+)_0 + x\}}{\{(\text{ArOH})_0 - x\}} = K_a \quad \begin{array}{l} \text{(Eq. (11),} \\ \text{Chap. V)} \end{array}$$

This sample calculation is for experiment no. 31, Table 41.

$$(\text{ArOH})_0 = 3.935 \times 10^{-6} \text{ mole/l}$$

$$K_a = 1.22 \times 10^{-4} \text{ mole/l}$$

The desired final acidity in this experiment was 30.0×10^{-6} M hydrogen ion. Therefore

$$(\text{H}^+) + x = 30.0 \times 10^{-6} \text{ mole/l}$$

$$x = \{30.0 \times 10^{-6} - (\text{H}^+)_{\circ}\} \text{ mole/l}$$

The calculation is made on the basis of the assumption that perchloric acid rather than sodium hydroxide will have to be added; i.e., $(\text{H}^+)_{\circ} > 0$, $(\text{ArO}^-)_{\circ} = 0$.

$$\frac{\{(\text{ArO}^-)_{\circ} - 30.0 \times 10^{-6} + (\text{H}^+)_{\circ}\}\{30.0 \times 10^{-6}\}}{(\text{ArOH})_{\circ} + (\text{H}^+)_{\circ} - 30.0 \times 10^{-6}} = 1.22 \times 10^{-4}$$

$$\frac{\{3.935 \times 10^{-6} - 30.0 \times 10^{-6} - (\text{H}^+)_{\circ}\}\{30.0 \times 10^{-6}\}}{3.935 \times 10^{-6} - (\text{H}^+)_{\circ} - 30.0 \times 10^{-6}} = 1.22 \times 10^{-4}$$

$$(\text{H}^+)_{\circ} = 26.8 \times 10^{-6} \text{ mole/l}$$

Therefore, each reaction flask was made 26.8×10^{-6} M in perchloric acid, yielding a total hydrogen ion concentration of 30.0×10^{-6} M.

To check the correctness of this concentration of perchloric acid, the values of $(\text{H}^+)_{\circ}$ and $(\text{ArOH}^-)_{\circ}$ are next substituted back into equation (11), Chapter V.

$$\frac{(0 + x)(26.8 \times 10^{-6} + x)}{3.935 \times 10^{-6} - x} = 1.22 \times 10^{-4}$$

$$x = 3.2 \times 10^{-6} \text{ mole/l}$$

But, $x + (\text{H}^+)_{\circ} = 3.2 \times 10^{-6} \text{ mole/l} + 26.8 \times 10^{-6} \text{ mole/l} = 30.0 \times 10^{-6}$ M, which was the required acidity.

APPENDIX II

EVIDENCE FOR ACYL HYPOIODITES AS IODINATING AGENTS
IN THE IODINATION OF ADRENOCHROME

It was pointed out in the introduction to this thesis that the work on the iodination of adrenochrome by Mattok and Wilson,⁽⁶¹⁾ which was misinterpreted by the authors, gives, when properly calculated, a straight line plot of $1/k^*$ versus $[I^-]$ with a positive $1/k^*$ intercept. This indicates that, over the iodide ion range studied ($0.82 \times 10^{-3} \text{ M}$ to $5.04 \times 10^{-3} \text{ M}$), molecular iodine is the sole iodinating agent. The corrected data, calculated in the manner used throughout this thesis, are summarized in Table 144.

The $1/k^*$ intercept is 1.62×10^{-2} mole sec/l, which equals $1/k_2$, giving a value for k_2 of 61.7 l/mole sec. This latter figure is the limiting value of k^* at infinite catalysis, so long as the only effect of the catalyst is to enhance the rate of the proton-removal step, since it represents complete kinetic insignificance of the proton-removal step.

However, in base catalysis work,⁽¹¹²⁾ the same authors obtained data which, when corrected to k^* , gives values far exceeding 61.7 l/mole sec. Using a total acetate concentration (acetic acid plus acetate) of 0.7 M at pH 4.20 (the reaction was found to be independent of pH and ionic strength), k^* was 210 l/mole sec; at a total phosphate concentra-

112. G. L. Mattok and D. L. Wilson, Can. J. Chem., 45, 2473 (1967).

tion (H_2PO_4^- plus $\text{HPO}_4^{=}$) of 0.067 M and pH 6.00, k^* was 350 l/mole sec; and at total phthalate concentration (phthalic acid plus phthalate) of 0.33 M and pH 5.00 k^* was 280 l/mole sec. The iodide ion concentration in each case was 1.7×10^{-3} M. This is evidence, in the same sense as in Chapters VIII and IX, for acyl hypoidites as iodinating agents.

Table 144. Iodination of Adrenochrome at 35.0°,
pH 4.00, Total Acetate Concentration
0.10 M^a

$[I^-] \times 10^3$ (mole/l)	k^* (l/mole sec)	$1/k^* \times 10^3$ (mole sec/l)
0.82	45	2.22
1.32	41	2.42
1.66	36	2.78
2.50	32	3.14
3.36	25	4.00
5.04	20	5.00

Note: The triiodide equilibrium constant used in these calculations is
625 mole/l. (82)

^aThese data are calculated from the results of G. L. Mattok
and D. L. Wilson. (61)

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VITA

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During high school and college, he held part-time jobs, and upon receiving his degree he joined Ungerer and Company, Totowa, New Jersey, as a quality control chemist. He remained there until he entered military service in October, 1956. As an enlisted man in the U. S. Army, he served as an infrared spectroscopist at Army Chemical Center, Maryland, until his separation from active duty in October, 1958; he was subsequently honorably discharged after fulfilling his reserve obligation. In October, 1958, he joined The Coca-Cola Company as a chemist and is presently employed by that company.

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