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THE KINETICS AND MECHANISM OF IODINATION OF PHENOL, p-NITROPHENOL, ANISOLE AND THEIR DEUTERATED DERIVATIVES

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SUMMARY

The kinetics of iodination of *p*-nitrophenol, anisole, phenol, and their deuterated derivatives were studied at different iodide, iodine, and hydrogen ion concentrations but at constant ionic strength and temperature in order to add to the general fund of information regarding the nature of the electrophile, reacting species and the presence of intermediates, if any. Specifically, the study was directed toward the elucidation of the mechanism of iodination, since it was felt that such an investigation would probably throw light on the general mechanism of iodination of aromatic compounds and broaden the knowledge of electrophilic aromatic substitutions.

It was demonstrated that at constant hydrogen ion and iodide ion concentrations the rate of the reaction of iodine with *p*-nitrophenol is first order in stoichiometric iodine and first order in substrate. The kinetics of the reaction were next studied at constant hydrogen ion and substrate concentrations but at different iodide ion concentrations. The ionic strength of the reaction mixture was maintained at 0.300 and the temperature at 50.0°. The reaction was run in 50 ml. or 100 ml. red, low-actinic flasks and the rate was measured by stopping the reaction with a saturated solution of sodium iodide at measured time intervals. The concentration of unreacted iodine was determined by titration with standard sodium thiosulfate solution to the starch-iodine end point.

Biomolecular rate constants were calculated at each per cent reaction by the integrated rate equation

$$k_{app} = \frac{2.303}{(a-b)t} \log \frac{b(a-x)}{a(b-x)}$$

in which a and b designate the initial stoichiometric substrate and iodine concentrations respectively, t is the time elapsed in seconds between the mixing of reactants and the stopping of the reaction, and x is the concentration of iodine consumed throughout the reaction.

These apparent rate constants generally showed a downward drift as the reaction proceeded. Such a drift was more pronounced at low iodide ion concentrations. Therefore, such apparent rate constants were plotted versus per cent reaction and were extrapolated to zero per cent reaction to give the initial apparent rate constant. However, at relatively high iodide ion concentrations, the apparent rate constants remained essentially constant throughout a run and therefore they were averaged.

One reason for the variation of apparent rate constants with the concentration of iodide is in the conversion of iodine into unreactive triiodide ion by the reaction

$$I_2 + I^- \overset{K}{\rightleftharpoons} I_3^- ; \quad K = \frac{[I_3^-]}{[I_2][I^-]}$$

The apparent rate constantw were therefore corrected for triiodide formation through the equation

$$k^* = k_{app} \frac{(I_2)}{[I_2]}$$

in which I_2 refers to the actual concentration of iodine and (I_2) refers to the stoichiometric concentration of iodine. The values of k^* were calculated for each run at zero per cent reaction. Similarly the rate constant k'

$$k' = \frac{k_{app}(I_2)\left[I^-\right]^2 K}{\left[I_3^-\right]}$$

which should remain constant according to Berliner's mechanism of iodination, was calculated for each run at different iodide ion concentrations.

The rate of iodination of *p*-nitrophenol was found to be inversely dependent on the iodide ion concentration raised to a non-integral and variable power somewhere between zero and two. The reaction showed also an inverse hydrogen ion dependence, at least at low hydrogen ion concentration. The data are consistent with a mechanism in which molecular iodine reacts eith *p*-nitrophenoxide ion in a reversible step to yield an intermediate having a cyclohexadienone structure (ArHOI) followed by the abstraction of a protone by a Bronsted base such as the solvent.

$$ArHOH \rightleftharpoons ArHO^- + H^+$$

$$ArHO^- + I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArHOI + I^-$$

$$ArHOH + I_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ArHOI + I^- + H^+$$

$$ArHOI \xrightarrow[k_3]{} \text{product}$$

Such a mechanism demands that a plot of $1/k^*\left[H^+\right]$ versus $\left[I^-\right]$ at varying hydrogen ion concentrations, give a straight line. The experimental results were in agreement with the postulated mechanism since a straight line was obtained with an intercept at zero iodide ion concentration of 500 sec^{-1} and a slope of 2059 x 10^4 l./mole sec. Furthermore, such a mechanism demands the presence of a maximum deuterium isotope effect at high iodide ion concentrations which diminishes with decreasing iodide ion concentration. As predicted by the mechanism proposed, the isotope effect was observed to attain a maximum of 5.2 at high iodide ion concentration and to drop to 2 at very low iodide ion concentration.

Other mechanisms, such as Berliner's mechanism and its modifications were considered. According to Berliner, the reaction proceeds via hypoiodous acidium ion (H_2OI^+) or (I^+) and substrate in a slow step followed by fast proton abstraction.

$$I_2 + H_2O \rightleftharpoons H_2OI^+ + I^-$$

$$H_2OI^+ + ArO^- \longrightarrow \text{products.}$$

Such a mechanism was discarded since the values of k' diminished with decreasing iodide ion concentration, which fact is contrary to the requirements of this mechanism.

The possibility of iodination by both I_2 and H_2OI^+ was also considered. However, due to the fact that the plot of k* versus $1/[I^-]$ did not give a straight line, this "mixed" mechanism was also disproven.

Iodination at extremely low but constant iodide ion concentration was studied by the use of thallium perchlorate, which acts as iodide ion regulator by precipitating iodide ion formed throughout the reaction as TlI. Such an experiment was thought to be useful since it allows the measurement of deuterium isotope effect $k^{H}_{(app)} / k^{D}_{(app)}$ at very low iodide ion concentration.

The iodination of anisole and its deuterated derivative was studied under the same conditions as for p-nitrophenol. The experimental results were analogous to the one found in the case of p-nitrophenol, except that no hydrogen ion dependence was expected or found since in the case of anisole no ionization is possible. A plot of $1/k^*$ versus $[I^-]$ gave a straight line with intercept at zero iodide ion concentration of 30 l./mole sec. and slope of 296×10^4 sec.$^{-1}$.

The maximum deuterium isotope effect observed in this case was 3.2, remaining essentially constant except at extremely low iodide ion concentrations, where it dropped to approximately 1.3. Such a medium with low iodide ion concentration was achieved by the use of high thallium perchlorate concentration (0.5 M).

It was therefore concluded that the iodination of anisole proceeds via molecular iodine in a reversible step to yield an intermediate with structure of p-quinoid type which then loses a proton, generally in a slow step.

The possibility of iodination via Berliner's mechanism, i.e., H_2OI^+ or I^+ being the iodinating species was disproven on the grounds of the inconstancy of the values of k'. The "mixed" mechanism was also disproven since a plot of k^* versus $1/[I^-]$ was not linear.

The iodination of phenol was studied at 25.0° at an ionic strength 0.300. The acidity of all the runs except those with thallium perchlorate was maintained at 0.0174 M. In this case a first order dependence of rate on both the iodine and phenol concentration was assumed on the basis of previous work. When the reaction was studied at varying iodide ion concentrations, the values of k' remained essentially constant. The magnitude of deuterium isotope effect remained essentially constant at 6.6 at several iodide ion concentrations. Due to the rapid rate of the reaction, it was not possible to study the reaction at very low iodide ion concentrations. Therefore, it is not possible to exclude, on the basis of the present experiments, any of the possible mechanisms mentioned previously.

CHAPTER I

INTRODUCTION

Electrophilic aromatic substitution involves the attack of a Lewis acid on an aromatic molecule to replace, most commonly, a hydrogen atom; however, if a compound is suitably activated, groups other than hydrogen may be displaced. Thus in the reaction of dibromohydroxybenzoic acid with bromine in aqueous acetic acid[1], carbon dioxide is eliminated and tribromophenol is formed.

$$ArBr_2(OH)(COOH) + Br_2 \longrightarrow ArBr_3(OH) + CO_2 + HBr$$

Substitutions involving hydrogen displacement could conceivably proceed by a one step termolecular mechanism which involves an activated complex such as (X---ArH---B) wherein X is the attacking electrophile, ArH is the substrate and B is a base. Such a mechanism has been discarded[2] and yet it has not bee disproven[3]. The second, a generally more acceptable mechanism, is the two stage process which involves the attack of the electrophile on the aromatic nucleus in the first step followed by the removal of hydrogen in the subsequent step.

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

(2) C. K. Ingold, Structure and Mechanism in Organic Chemistry, Ithaca, N. Y., Cornell University Press, 1953, p. 207-212.

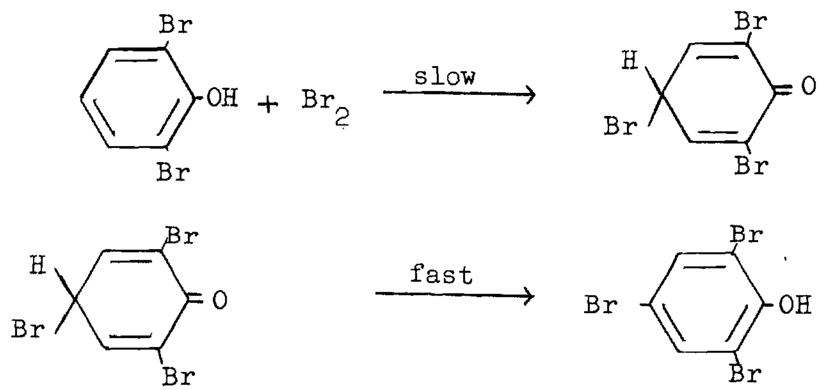
(3) G. S. Hammond, J. Am. Chem. Soc., 77, 334 (1955).

In such a process, the rate determining step can be either the attack of the electrophile, or the removal of the proton. In a few cases, however, the rate determining step may be the formation of the attacking species. An example of the latter type is the chlorination of phenol in a mixture of hypochlorous and perchloric acid solution[78].

$$HOCl + H_3O^+ \rightleftharpoons H_2OCl^+ + H_2O$$

$$H_2OCl^+ \xrightarrow{\text{slow}} Cl^+ + H_2O$$

An example of a reaction involving a slow attack by the Lewis acid on the aromatic nucleus, followed by a fast loss of a proton, is the bromination of 2,6-dibromophenol[1].



For reactions in which the C-H bond is broken in the slow step, it is expected that a C-D or a C-T bond will be broken at a slower rate than a C-H bond, although the difference in rate may be small. The major factor which contributes to the generally lower reactivity of bonds to deuterium or tritium is the difference in zero-point energy between a bond to deuterium or tritium and the corresponding bond to a protium.

The magnitude of the isotope effect is temperature dependent. In many cases the observed effect is less than that calculated. The extent of bond breaking and bond making in the transition state determines the magnitude of the isotope effect. A maximum isotope effect corresponds to practically no bonding between the hydrogen or deuterium in the activated complex. On the other hand, the opposite is true for a minimum or for no isotope effect. A complete discussion of the theory of the isotope effect is given by Melander[4,5,6,7].

It has been argued quite recently[3] that the absence of an isotope effect in a substitution reaction does not necessarily exclude the possibility of a slow, rate determining proton removal. Conceivably in such cases the isotope effect may merely be too small to be detectable.

In halogenation of aromatic compounds, a considerable confusion exists as to whether substitution takes place through a preformed halogen cation (X^+ or H_2OX^+) or whether halogen is always conveyed to the aromatic nucleus by a carrier such as, for iodination, I_2, CH_3COOI or even more complex agents. Unfortunately the kinetic distinction between some of these iodinating agents is rather difficult. Painter and Soper[8] concluded that the species which iodinates phenol in aqueous medium

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(4) L. Melander, Arkiv Kemi., 7, 287 (1954).

(5) L. Melander, Acta. Chem. Scand., 3, 95 (1949).

(6) L. Melander, Arkiv. Kemi., 2, 211 (1950).

(7) L. Melander, Nature., 163, 599 (1949).

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

is the hypoiodous acidium ion. Similarly, Berliner[9] concluded that the hypoidous acidium ion or iodine cation is the active iodinating agent for aniline.

Shilov and co-workers[10] upon studying the iodination of amino-sulfonic acids in aqueous medium, concluded that the iodinating species is a molecular complex such a (^{-}SO $-Ar-NR_2-I^{+}$). Ingold[11] has stated that there is no evidence as yet that any iodine carrier other than the cationic species is effective for aromatic iodination in aqueous solutions. He has further stated that the mode of attack of electrophilic halogenating agents on the benzene ring is probably similar to that of nitrating agents, which leads one to believe that the loss of the aromatic proton is kinetically insignificant[12].

Molecular iodine has been found to be effective iodinating species in a few aromatic molecules. Kuivila and Williams[13] concluded that the iodinolysis of p-methoxybenzeneboronic acid in aqueous solution proceeds via molecular iodine, which is also apparently responsible for the exchange reaction between radioactive iodine and diiodotyrosine[14].

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

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

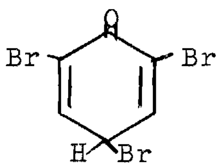
(11) C. K. Ingold, Structure and Mechanism in Organic Chemistry, Ithaca, N. Y., Cornell University Press, 1953, p. 291

(12) Ibid., p. 295

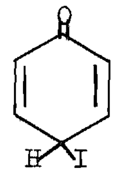
(13) H. G. Kuivila and R. M. Williams, J. Am. Chem. Soc., 76, 2679 (1954).

(14) A. H. Zeltman and M. Kahn, ibid., 76, 1554 (1954).

Grovenstein and co-workers[1,15] have proposed a mechanism for the iodination of phenol. In the bromination of 2,6-dibromophenol they found that under their experimental conditions[1] the intermediate (a) showed little if any tendency to react with a bromide ion. However, they reasoned that intermediate (b) should show greater tendency to react with iodide ion. This argument is supported by the greater



(a)



(b)

nucleophilic character of iodide ion than bromide ion[16] and the greater ease of nucleophilic displacement upon iodine than bromine[17]. The mechanism proposed by Grovenstein and co-workers involves the rapid, reversible attack of molecular iodine on the aromatic nucleus to give an intermediate such as (b) which in the subsequent slow step loses a proton to a base.

The purpose of this research is to attempt to elucidate the mechanism of iodination of aromatic molecules with special regard to the nature of the iodinating agent, the presence of intermediates, if any, and finally the discovery of the rate-determining step. For this

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

(16) C. G. Swain and C. B. Scott, ibid., 75, 141 (1953).

(17) J. Hine and W. H. Brader, Jr., ibid., 75, 3964 (1953)

purpose a rather extensive study has been made of the iodination of phenol, p-nitrophenol, anisole, and their deuterated derivatives under a variety of experimental conditions. It is hoped that knowledge of the mechanism for the iodination of these compounds will contribute appreciably toward understanding the mechanism of the iodination of related compounds.

CHAPTER II

SURVEY OF RELATED WORK

The Iodination of Phenol and Related Compounds.--A literature survey reveals that a considerable amount of mechanistic investigation has been carried out on the halogenation of phenols and related compounds. Earlier studies were conducted by Cofman[18], who concluded that molecular iodine is incapable of iodinating aromatic compounds. This conclusion was primarily based on the fact that in acid solution molecular iodine did not iodinate phenol, while in alkaline solution, where iodine is converted to hypoidous acid, iodination proceeded rather smoothly.

Soper and Smith[19,20] studied the halogenation of phenols in an effort to determine the nature of halogenating species. The iodination[20] of phenol was studied in nearly neutral, phosphate-buffered solution with iodide ion concentrations such that essentially all the iodine was converted to triiodide ion. The authors found that the rate of the reaction is directly proportional to the phenol and stoichiometric iodine concentration but inversely proportional to the square of the iodide ion concentration. The rate of the same reaction, when carried out at different hydrogen ion concentrations, was found to vary inversely with less than the square and more than the first power of the actual hydrogen ion concentration. The authors concluded that both phenol and phenoxide

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(18) V. Cofman, J. Chem. Soc., 115, 1040 (1919).

(19) F. G. Soper and G. F. Smith, ibid., 1582 (1926).

(20) F. G. Soper and G. F. Smith, ibid., 2757 (1927)

ion are iodinated by hypoiodous acid.

$$\text{rate} = k_1 \left[\text{PhOH}\right]\left[\text{HOI}\right] + k_2 \left[\text{PhO}^-\right]\left[\text{HOI}\right]$$

Mauger and Soper[21], upon studying the kinetics of the N-chlorination of amides by hypochlorous acid, found that the reaction was catalyzed by the acid component of the buffer. This led Painter and Soper[8] to re-investigate the iodination of phenol. They found that the rate of iodination of phenol when carried out in acetate buffer varied inversely with the hydrogen ion concentration and with the square of the iodide ion concentration. They concluded that the reaction may involve the interaction of hypoiodous acid with unionized phenol or, alternatively, iodine cation with phenoxide ions. In addition, they found that the rate of iodination at constant pH increases linearly with the concentration of the buffer acid and this catalytic effect varied inversely as the square of the hydrogen ion concentration. Such a catalytic effect was interpreted in terms of an interaction of acetyl hypoiodite with phenoxide ions.

$$\frac{dx}{dt} = k_o\,(\text{PhOH})\;(\text{HOI}) + k_{cat}\,(\text{PhO}^-)(\text{AcOI})$$

$$\frac{dx}{dt} = k_o\,(\text{PhO}^-)\;(\text{I}^+) + k_{cat}\,(\text{PhO}^-)(\text{AcOI})$$

Berliner has also studied the kinetics of the iodination of phenol[22] and aniline[9] and has attempted to compare the two reactions theoretically. The reactions were performed at high iodide ion concentration (0.12 M) in

(21) R. P. Mauger anf F. G. Soper, ibid., 71 (1946).

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

phosphate buffers in which both secondary and primary phosphate are catalytically active. The phenol to iodine ratio was 4 to 1 and the total ionic strength was brought to 0.300 by NaCl. His experimental data agreed with the following expression

$$\frac{k_1 [PhOH] [I_2]}{[H^+] [I^-]} + \frac{k_2 [PhOH] [I_2] [HA]}{[H^+]^2 [I^-]}$$

where HA is a buffer acid such as acetic acid or phosphoric acid. It seems probable from his results that the phenoxide ion is the reactive species and the kinetics are compatible with a general acid catalyzed iodination by H_2OI^+. Without direct experimental evidence, the author has stated that the proton loss in the iodination of phenol is probably kinetically insignificant and takes place after the rate determining step. His observed rate constants can be expressed as

$$\frac{k_o}{[H^+]} + \frac{k'_{cat} (base')}{[H^+]} + \frac{k''_{cat} (base'')}{[H^+]}$$

where k_{obs} refers to the observed rate constant, and k_o refers to the uncatalyzed rate constant. The rate constants k'_{cat} and k''_{cat} refer to the catalytic rate constants of the primary phosphate and the secondary phosphate respectively. Thus the rate constants were obtained by plotting $k_{obs} [H^+]$ versus primary phosphate ion concentration using five different buffer ratios (pH 5.71-6.61). A comparison with the aniline reaction showed that the uncatalyzed reaction of phenoxide ion is 25,000 times faster than the corresponding uncatalyzed reaction of aniline. The same conclusion was reached through calculating activation energies of the uncatalyzed reaction of aniline. By analogy to the iodination of aniline Berliner thus concluded that the halogenation of phenol involves phenoxide ion as an active substrate.

$$\text{velocity} = k_o [PhO^-][HOI][H^+] + k_{cat} [PhO^-][HOI][Acid]$$

Few other halogenations in aqueous solution have shown the same kinetic form. Wilson and Soper[23] have observed acid catalysis in the bromination of o-nitroanisole and benzene by hypobromous acid. Derbyshire and Waters[24] have also observed the same kinetic form in the bromination of ω-toluene-sulfonic acid.

Li has studied the iodination of tyrosine[25], histidine[26], p-chlorophenol, tyramine and glycyltyrosine[27] at 25° in acetate buffer. The iodination of tyrosine was studied in different buffers and different concentrations of iodide ion. He concluded that iodination of tyrosine and tyrosinate anion proceeds via molecular iodine and hypoiodous acid.

$$\frac{dx}{dt} = k_1 (TOH)(I_2) + k_3 (TO^-)(I_2) + k_2 (TOH)(HOI) + k_4 (TO^-)(HOI)$$

Where (TOH) and (TO^-) refer to the concentration of tyrosine and tyrosinate anion respectively. The values of k_1, k_3, k_2 and k_4 were found to be

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(23) W. J. Wilson and F. G. Soper, J. Chem. Soc., 3376 (1949).

(24) D. H. Derbyshire and W. A. Waters, ibid., 564 (1950).

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

(26) Ibid., 66, 225 (1944).

(27) Ibid., 70, 1716 (1948).

1.5×10^{-2}; 1.37×10^{4}; 7.7×10^{6}; and 1×10^{10} respectively. Li has furthermore stated that in the polyiodination of tyrosine, the slow step is interaction of the tyrosine molecule with iodine, followed by the introduction of the second iodine atom in a subsequent fast step. This interpretation has been confuted by Roche and co-workers[28,29], who reported that the slow step is the introduction of the second iodine molecule.

In the iodination of p-chlorophenol at varying iodide ion concentrations, Li concluded that the active halogenating species is hypoiodous acid.

$$\text{rate} = k_1 \text{(PhOH)(HOI)} + k_2 \text{(PhO}^-\text{)(HOI)}$$

Doak and Corwin[30] have studied the iodination of substituted pyrroles in the presence of high iodide ion concentration. They found that the reaction rate is inversely proportioal to the iodide ion concentration, and the observed second order rate constant when multiplied by iodide ion concentration was found to be constant especially at high iodide concentrations. However, this product of observed rate constant and iodide ion concentration showed an upward drift as the

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(28) J. Roche, S. Lissitzky, O. Michel and R. Michel, Compt. Rend., 232, 357 (1951).

(29) J. Roche, S. Lissitzky, O. Michel and R. Michel, Ann. pharm. franc., 9, 163 (1951).

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

iodide ion concentration increased which led the authors to the belief that the active iodinating species is both molecular iodine and hypoiodous acid.

Berliner[9] has studied the kinetics of iodination of aniline with iodine in aqueous solution. At pH's greater than 5.4, he has found that the reaction rate is independent of the hydrogen ion concentration and is inversely proportional to the square of the iodide ion concentration, and the reaction shows general base catalysis. The kinetics of the reaction is in agreement with a mechanism which involves iodination by iodine cation. The same kinetics is also in agreement with iodination of anilinium ion by hypoiodous acid. The two mechanisms, however, are kinetically indistinguishable but it seems logical to eliminate the second mechanism since it is known that anilinium ion is a _meta_ directing group while the main isolated product in this case was _p_-iodoaniline.

The iodination of 2,4-dichlorophenol was studied by Taylor and Evans[31]. An inverse hydrogen ion dependence was observed and it was concluded that the phenolate ion and molecular iodine are the active species.

Tronov and Kolesnikova[32] studied the iodination of phenol in the presence of pyridine. The rate of iodination increased by the addition of pyridine and the authors assumed the formation of a highly reactive molecular species $[C_6H_5NI^+]$ $[I^-]$ which was believed to be the halogenating agent.

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(31) J. Taylor and M. Evans, _Ohio Journal of Science_, _53_, 507 (1954)

(32) B. Tronov and S. Kolesnikova, _Soobshcheniya Mauch Rabot. Vsesoyuz Khim. Obshchestva im. Mendeleeva_, _1_, 46 (1953).

Berliner, Berliner and Nelidow[33] studied the relative rates of iodination of para-alkyl phenols in different aqueous solutions of acetic acid, methyl alcohol and dioxane. In each case the relative rates indicated the predominant operation of inductive effect in the order $Me_3C > Me_2CH > Et > Me$. No mechanism was given by the authors but it was assumed that either I^+ of H_2OI^+ is the real iodinating species.

A literature survey reveals that the iodination of other aromatic compounds has been studied rather extensively. Thus glyoxaline was found to undergo iodination[34] and bromination at the 4(5)-position while diazo coupling[35] led to substitution at the 2-position. This difference was atrributed to the fact that the glyoxaline anion reacts initially at the 2-position, while the neutral molecule reacts at the 4(5)-position[37,38].

Ridd[39] studied the kinetics of iodination of glyoxaline in aqueous solution at pH 7 at rather high iodide ion concentration. His

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(33) E. Berliner, F. Berliner and I. Nelidow, J. Am. Chem. Soc., 76, 507 (1954)

(34) H. Pauly and E. Arauner, J. prakt. Chem., 33, 118 (1928).

(35) R. G. Fargher and F. L. Pyman, J. Chem. Soc., 115 217 (1919).

(36) I. E. Balaban and F. L. Pyman, ibid., 121, 947 (1922).

(37) R. D. Brown, H. C. Duffin, J. C. Maynard, and J. H. Ridd, ibid., 3937 (1953).

(38) I. M. Bassett and R. D. Brown, ibid., 2701 (1954).

(39) J. H. Ridd, ibid., 1238 (1955).

experimental data agreed with the following rate expression.

$$\frac{k\,[GH]\,[I_3^-]}{[H^+]\,[I^-]} + \frac{k'\,[GH]^2\,[I_3^-]}{[H^+]\,[I^-]}$$

According to the author, the first (uncatalyzed) term involves iodination by I^+, while the (self catalyzed) term involves iodination via N-iodo-cation. Grimison and Ridd[40] have reported an isotope effect of 4.47 upon the iodination of 2,4,5-trideuteroglyoxaline. The isotope effect was almost absent in the iodination of 2-deutero glyoxaline. The authors thus concluded that the C-H bond at 4(5) position is weakened in the rate-determining step and under their conditions the initial substitution is mainly at 4(5) position. The diazo coupling of glyoxaline and 2,4,6-trideutero glyoxaline was also studied and no deuterium isotope effect was obtained. Thus the authors concluded that the rate-determining step for the latter is not the proton abstraction. Furthermore, while iodination proceeded mainly at 4(5) position, it was found that the diazo coupling was effected at the 2 position. This was attributed to the fact that in diazo coupling, the active substrate is the conjugate base of glyoxaline in which the charge density is greatest at the 2-position.[41].

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(40) A. Grimison and J. H. Ridd, <u>ibid</u>., 3019 (1959).

(41) A. Grimison and J. H. Ridd, <u>Proc</u>. <u>Chem</u>. <u>Soc</u>., 256 (1958).

The kinetics of iodination of aromatic aminosulfonic acids in aqueous solution has been studied by Shilov and Kurakin[42]. These workers have studied the iodination of m-dimethyaminobenzenesulfonic acid (II), m-diethylaminobenzenesulfonic acid (III) and p-(N-ethylanilino)-phenylsulfonic acid (IV), and found that the overall rates of iodination (in the dark) of I-IV are in the ratio of 1:13:0.7:30 respectively. Their rate of iodination in the dark can be fitted to a formula of the type

$$\frac{-d(I)}{dt} = \frac{k_o[S^-]^2\,(I)}{[I^-]} + \frac{k_p[S^-]^2\,(I)}{[I^-]^2} + \frac{k_o'\,[S^-]\,[HPO_4^{=}]\,(I)}{[I^-]} + \frac{k_p\,[S^-]\,[HPO_4]\,(I)}{[I^-]^2}$$

where S^- and I^- are the actual concentrations of aminosulfonate and iodide ions respectively. k_o refers to the rate constant in which iodination proceeds via molecular iodine and k_p refers to rate constant for iodination by iodine cation and (I) is the analytical concentration of iodine. For compound (IV), the terms involving $HPO_4^{=}$ are not present. According to these authors, hypoiodous acid and iodine cation are not entirely the active halogenating species but rather a complex formed between the substrate and I_2 or I^+ which then rapidly attacks a second molecule of the substrate. This is followed by a subsequent slow step in which a portion is removed by a base. Such a mechanism could account

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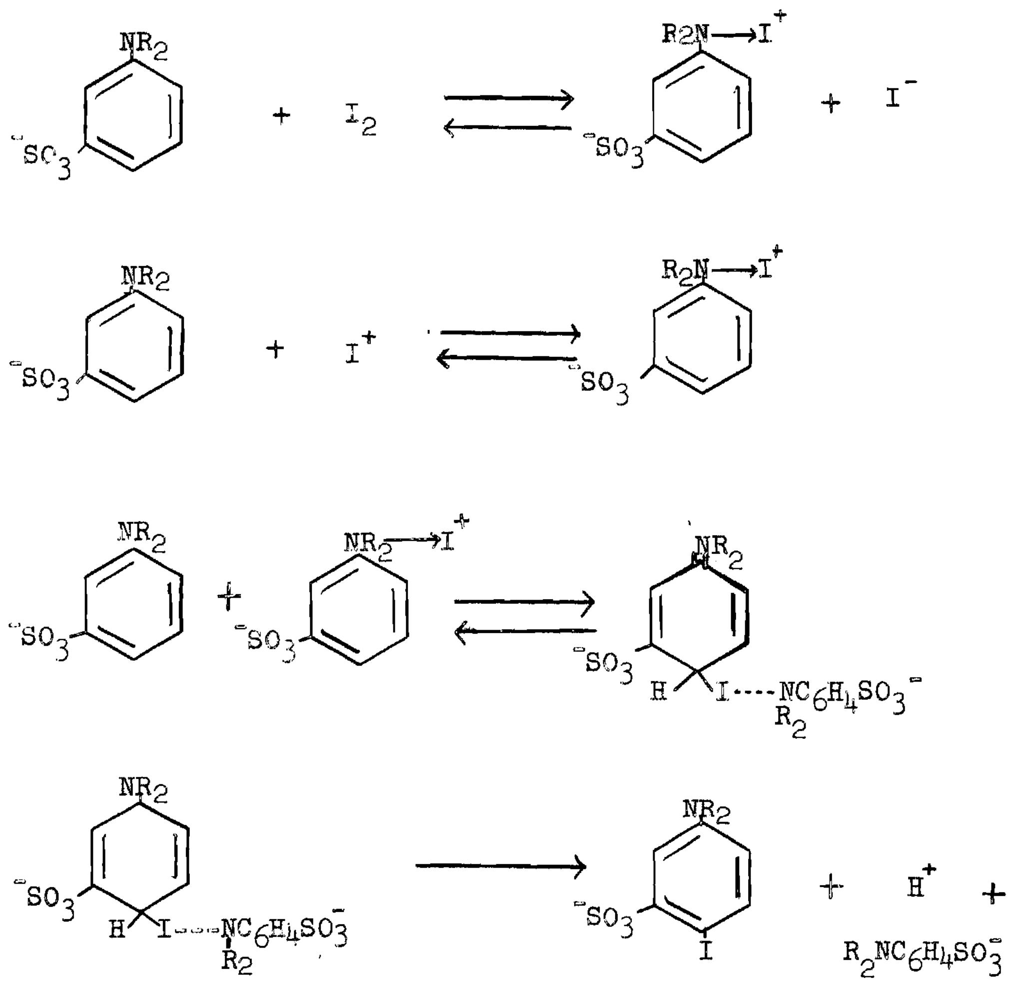
(42) A. N. Kurakin and E. A. Shilov, Ukrain. Khim. Zhur., 23, 31 (1957).

for the second-order dependence of $\left[S^{=}\right]$ and the dependence on phosphate ion. A detailed mechanism can be written as



A second possible mechanism compatible with the same kinetic expression involves the rapid attack of iodine cation followed by the slow abstraction of the proton by a base which in this case could be either phosphate or the amine itself.

A third mechanism presented by the same author involved halogenation by molecular iodine with the proton removal being the slow step. However, without any experimental evidence Shilov and Kurakin prefer the first mechanism.

Survey of the Mechanism of Related Halogenating Agents.--Although iodine monochloride has been used as an iodinating agent for over a hundred years[43-50], relatively little work has been done in the kinetic study of ICl substitution. Chattaway and Constable[51] showed that in acetic acid solution 90 per cent yield of the p-iodo derivative is obtained from acetanilide. The first kinetic study of iodine monochloride substitution is that of Lambourne and Robertson[52], who used glacial acetic acid and chlorobenzene as solvents for the iodination of some aromatic compounds. The authors found that iodination

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(43) J. F. Brown, Ann., 92, 321 (1854).

(44) J. F. Brown, Phil. Mag., [4]8, 201 (1854).

(45) P. Schuatzenberger, Jahresber., 349 (1861).

(46) Ibid., 251, 413 (1862).

(47) J. Stenhouse, J. Chem. Soc., 17, 327 (1864).

(48) C. Willgerodt and E. Arnold, Ber., 34, 3343 (1901).

(49) A. E. Bradfield, K. J. Orton and I. C. Roberts, J. Chem. Soc., 782 (1928).

(50) B. Jones and E. N. Richardson, ibid., 713 (1953).

(51) F. D. Chattaway and A. B. Constable, ibid., 105, 124 (1914).

(52) L. J. Lambourne and P. W. Robertson, ibid., 1167 (1947).

by iodine monochloride in these solvents is inhibited by the liberated hydrogen chloride which combines with ICl to form $HICl_2$. They found that the reaction is first order with respect to the substrate and second order in ICl. At higher temperatures, however, the second order dependence on ICl is reduced. The authors furthermore found that in the presence of sterically hindering groups on the aromatic molecule, as with pentamethylbenzene and p-tolylmethyl ether, there is a competing iodine chloride catalyzed chlorination by ICl. This reaction was attributed to the large "iodine atom" which is hindered by the ortho-methyl groups. Less chlorination was observed in the reaction of iodine-monochloride with anisole in acetic acid solution. On using chlorobenzene as a solvent, the tendency for iodine monochloride halogenation to proceed by the chlorination route becomes more pronounced, even when there is no steric hinderance. No explanation has been given, however, it is believed that the extent of dissociation of the reagent may have some effect on the route of substitution.

$$ArH + ICl \rightleftharpoons ArH \cdot ICl$$
$$ArH \cdot ICl + ICl \xrightarrow{slow} ArHI^+ + ICl_2^-$$
$$ArHI^+ + ICl_2^- \xrightarrow{rapid} ArI + HICl_2$$

Berliner[53] has studied the kinetics of iodination of p-chloroaniline with iodine monochloride in aqueous perchloric acid solution at

(53) E. Berliner, J. Am. Chem. Soc., 78, 3632 (1956).

constant ionic strength in the presence of high chloride ion concentration. The reaction was found to be strictly second order overall and the rate of the reaction was found to be inversely proportional to both the hydrogen ion and chloride ion concentration. The rate of the reaction was furthermore found to decrease with increasing ionic strength. The inverse dependance of the rate on the first power of hydrogen ion concentration was justified by assuming that the species which is iodinated is the free amine. This assumption was based on chemical evidence, since the amine was exclusively substituted ortho to the amino group, whereas meta-substitution would have resulted if the p-chloroanilinium ion were involved. According to Berliner, the mechanism which accounts for the inverse proportionality of both hydrogen ion and chloride ion, must therefore involve the rapid hydrolysis of iodine monochloride to give hypoiodous acidium ion which then attacks the aromatic molecule in the slow step followed by rapid removal of the aromatic proton by base.

$$ICl + H_2O \rightleftharpoons HOI + H^+ + Cl^-$$

$$HOI + H^+ \rightleftharpoons H_2OI^+$$

$$ArH + H_2OI^+ \longrightarrow ArHI^+ + H_2O$$

$$ArHI^+ \longrightarrow ArI + H^+$$

An alternative mechanism may involve the ionization of ICl to give iodine cation which attacks the aromatic molecule in the rapid step.

Berliner[54] has also studied the kinetics of the iodination of 2,4-dichlorophenol and anisole with iodine monochloride in aqueous perchloric acid solution at high chloride and hydrogen ion concentrations. As in the case of p-chloroaniline[53], the reaction was found to be first order in the aromatic compound and first order in iodine monochloride. While the reaction of 2,4-dichlorophenol with the halogenating agent was inversely proportional to the hydrogen ion concentration, it was found that the reaction with anisole was independent of the pH over a wide range of acid concentration except at very high hydrogen ion concentration, where the rate decreased somewhat. This was attributed by Berliner to probable hydrogen bonding of the ether-oxygen of anisole, and the formation of a hydrogen-bonded complex which is less susceptible to electrophilic attack. In 2,4-dichlorophenol, the inverse dependence of the rate on the hydrogen ion concentration was interpreted by the author to mean that the species undergoing iodination was not the phenol but the 2,4-dichlorophenoxide ion which was attacked by hypoiodous acidium ion. Berliner found that the reaction rate is inversely proportional to the chloride ion concentration, and that a plot of observed rate constant versus $K_1/(K_1 + Cl^-)(Cl^-)$ where K_1 is the dissociation constant of ICl_2^-, to give ICl and Cl^-, at various acid concentrations and at constant ionic strength gives a straight line with a definite positive intercept. According to him, this intercept is either kinetically insignificant, or indicates a small amount of iodination by ICl_2^-. Berliner furthermore reported that while the

(54) E. Berliner, J. Am. Chem. Soc., 80, 856 (1958).

rates of iodination of phenol decreases with rising salt concentration, the rates of iodination of anisole increase almost linearly with salt concentration except at very high ionic strength in which the rates become irregular. This irregularity has been attributed to a salting-out phenomena. According to Berliner, a mechanism consistent with the kinetic expressions and experimental evidence is the slow attack of hypoiodous acidium ion on the aromatic nucleus followed by the rapid abstraction of the proton. The possibility of a one-step concerted mechanism has also been considered as well as iodination by molecular iodine monochloride with proton abstraction being the slow step. However, it seems that Berliner prefers the first mechanism. Berliner has recently reinvestigated the mechanism of iodination of anisole and anisole-2,4,6-d_3 by ICl in acetic acid[55,56] containing perchloric acid and chloride ions. He has reported that the reaction is independent of the hydrogen ion (0.1 to 0.0001 M) and the chloride ion (0.3 to 0.9 M) concentrations. The maximum isotope effect in each solvent was about 3.8. Berliner has proposed that iodination of anisole by ICl may proceed by either of two routes. The first route may involve iodination by molecular ICl to form an intermediate similar to the one proposed by Grovenstein and co-workers[1,15], which loses a proton in the slow step. The second scheme involves the hydrolysis of ICl to give hypoiodous acidium ion which

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(55) E. Berliner, Chemistry and Industry, 177 (1960).

(56) E. Berliner, private communication, (1960).

attacks anisole to give the same intermediate followed by abstraction of a proton in the slow step.

$$ArH + ICl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArHI^+ + Cl^- \qquad \text{Scheme A}$$

$$k_{-1} \gg k_2$$

$$ArHI^+ \xrightarrow{k_2} ArI + H^+ \qquad \text{or } k_2 \gg k_{-1}$$

or

$$ICl + H_2O \overset{fast}{\rightleftharpoons} H_2OI^+ + Cl^- \qquad \text{Scheme B}$$

$$k_{-1} \gg k_2$$

$$ArH + H_2OI^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArHI^+ + H_2O \qquad \text{or } k_2 \gg k_{-1}$$

$$ArHI^+ \xrightarrow{k_2} ArI + H^+$$

In order to arrive at a possible distinction between the two mechanisms, the author has measured the magnitude of the deuterium isotope effect at varying chloride ion concentrations. Scheme A demands that the isotope effect should be dependent on chloride ion concentrations and at very low chloride ion concentrations it should lead to a situation where the reverse reaction in the first step becomes negligible. The first step should become rate-determining, in which case the isotope effect would disappear. In Scheme B, however, the isotope effect should be independent of the chloride ion concentration, because the chloride ion is formed in a pre-equilibrium, which has nothing to do with the substitution step. Within the range of chloride ion concentrations of 0.3 to 0.9 (also no added Cl^-) no such decrease in the magnitude of deuterium isotope effect was observed, thus Berliner concluded that iodination most probably proceeds via Scheme B. When the same reaction was carried out in D_2O, a 30 per cent decrease in rate was observed. The author attributed this effect to the relatively lower base strength of D_2O as compared to H_2O.

Survey of the Mechanism of Other Halogenation Reactions.--The mechanism and rate of bromination of anilines, phenols, and nitro compounds was first studied by Francis and co-workers[57]. His primary interest was the estimation of the amount of *meta* isomer present in mixtures of mono-substituted aromatic compounds. He noticed that bromine was capable of replacing groups such as -COOH, -CHO, and $-SO_3H$ when present on activated aromatic molecules. The reaction, when carried out in aqueous solution with enough alcohol added to prevent the precipitation of the dibromo compound, was found to go to completion at 20°C with the displacement of the group. However, at 0°C or below such a displacement was halted.

Francis[58,59] studied the relative rates of bromination of certain *ortho*, *meta*, and *para*-isomers of mono-substituted phenols and anilines and found that bromination by free bromine in aqueous solution was difficult to study especially in the case of aniline and phenol due

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(57) A. W. Francis and A. J. Hill, *J. Am. Chem. Soc.*, *46*, 2498 (1924).

(58) A. W. Francis, A. J. Hill, and J. Johnson, *ibid.*, *47*, 2211 (1925).

(59) A. W. Francis, *ibid.*, *48*, 1631 (1926).

to the rapid rate of the reaction. By means of competition experiments using a mixture of two different compounds in the presence of a limited amount of halogen he was able to measure the relative rates of mono-, di-, and tri-halogenation of different compounds at constant temperature and concentration of reactants. Phenols and anilines connot be compared due to the different effect by acid. Francis[60] studied the bromination of m-nitrophenol by free bromine in water. He found that the compound was brominated by free bromine 1000 times as rapidly as by an equivalent concentration of HOBr in which the concentration of free bromine had been reduced to an extremely small value by the addition of silver sulfate. The ratio is approximately that of the equilibrium concentration of free bromine in the solution as calculated from the hydrolysis constant of bromine and the solubilities of silver bromide and silver sulfate. Francis concluded that the active halogenating species is probably a positively charged bromine atom.

The kinetics of chlorination of phenols in alkaline media was first investigated by Soper and Smith[19]. By using HOCl as the halogenating agent, the kinetic data were consistent with a mechanism which involves the reaction of either phenol and hypochlorite ion or phenoxide ion and hypochlorous acid. By studying the same reaction with salicylic acid at different hydroxide ion concentrations, Soper and Smith found that the rate constant was independent of the hydroxide ion concentration. The authors became interested in discovering which of the species actually constituted the active agent in the chlorination

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(60) A. W. Francis, J. Am. Chem. Soc., 47, 2340 (1925).

of phenols. They have shown that if Cl^+ is the active halogenating agent, Cl_2 would be expected to chlorinate 4.5×10^{10} faster than HOCl since the ratios of the ionization constant of Cl_2 to that of HOCl is equal to 4.5×10^{10} to one. Based on a similar argument, it is expected that the values for bromination and iodination by the free halogens and their hypohalous acids ought to be in the ratio of 5×10^5: 1 and 30:1 respectively. Soper and Smith found that in the chlorination of phenols and phenolic ethers by HOCl, the rate of the reaction increased in the presence of a small amount of hydrochloric acid. They found that the reaction rate is independent of the concentration of the phenol but is dependent on the concentration of HOCl and the square of the concentration of HCl. These data indicate that the slow step is the formation of chlorine from HCl and HOCl followed by immediate reaction of chlorine with the phenoxide ion and probably the unionized phenol. Based on a similar argument the authors believe that a similar interaction may be involved in the bromination and iodination by HOBr and HOI respectively. However, because of the instability of both HOBr and HOI relative to HOCl a sharp distinction between the mechanisms of substitution of phenols was not possible. They found, for example, that the rate of iodination by HOI is decreased in strong alkaline solution; this result was attributed to the formation of iodate.

The kinetics of bromination of phenolic ethers by bromine in 50 per cent aqueous acetic acid (by volume) was studied by Bradfield, Jones and Orton[61]. They found that in the presence of initially introduced HBr or NaBr the bimolecular rate constants decreased as the reaction proceeded. The downward drift in the rate constants was more pronounced in the presence of very small concentrations of bromide ions. This marked decrease in velocity constants was attributed to the formation of Br_3^- which is a very poor brominating agent. In a separate paper, Bradfield and Jones[62] found that the reaction between p-chloroanisole and chlorine in 99 per cent acetic acid is very sensitive to the amount of the water in the medium. Thus the speed of chlorination increased by approximately 66 per cent as the amount of water was increased from one per cent to two per cent. Furthermore, they found that the amount of hydrochloric acid had little effect on the bimolecular rates which may indicate that the trichloride ion in this medium has no effect on the course of the reaction. Mechamisms other than the direct interaction between chlorine and the substrate may, of course, take place in this case. The same authors reported that the chlorination of several ethers of p-hydroxybenzoic acid is accompanied by a small amount of chlorodecarboxylation which disappears in the presence of excess of substrate. A small but significant amount of halodecarboxylation was observed. This is not unusual since numerous cases

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(61) A. E. Bradfield, B. Jones, and K. J. Orton, J. Chem. Soc., 2810 (1929).

(62) A. E. Bradfield and B. Jones, ibid., 1006 (1928).

of halodecarboxylation are reported in the literature[63-72].

Alexander[73], while studying the kinetics of bromination of a monomolecular film of p-hexadecylphenol on water, found that the reaction rate increased in the presence of potassium bromide. He concluded that Br_3^- was the active brominating species. Based on the bromination rates via bromine water in the presence of varying quantities of bromide ion, and with HOBr, he showed that the reactivity of Br_3^- as compared to HOBr is in the ratio of 4:1 respectively. By similar calculations it was shown that the Cl_3^- is one thousand times more reactive than HOCl. These conclusions are subject to considerable doubt because of the heterogeneous nature of the system.

The bromination of anisole m-sulfonic acid by HOBr was studied

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(63) N. A. Cahours, Ann. chim. phys., (3), 13, 87 (1845).

(64) R. Peltzer, Ann., 146, 284 (1868).

(65) H. Hubner and C. Heinzerling, Zeitschrift für chemie, 7, 709 (1871).

(66) P. Weselsky, Ann., 174, 99 (1874).

(67) H. Hubner and O. Benken, Ber., 6, 170 (1873).

(68) E. Lellmann and R. Grothmann, ibid., 17, 2724 (1884).

(69) R. Benedikt, Ann., 199, 127 (1879).

(70) E. Schunck and L. Marchlewski, ibid., 278, 349 (1894).

(71) R. B. Earle and H. L. Jackson, J. Am. Chem. Soc., 28, 104 (1906).

(72) P. Brenans and C. Girod, Compt. rend., 186, 1128 (1928).

(73) A. E. Alexander, J. Chem. Soc., 729 (1938).

by Shilov and co-workers[74], who found that the reaction rate can best be expressed as follows:

$$\text{rate} = (HOBr)(\bar{S}O_3\text{-Ar-OMe})(H^+)$$

According to the authors, the active brominating species in this case is Br^+ or H_2OBr^+. The following relative rate constants were assigned for the various brominating species. HOBr, 0.12; Br_2, 80; BrCl, 43,000; and Br^+, 110,000.

Robertson and co-workers[75] have extensively studied the kinetics of aromatic halogenation in acetic acid. At relatively high bromine concentrations (0.025 M) and at room temperature it was found that, in general, the reactions are of higher than first order in halogen and that the rates are accelerated by addition of salts and acids. Addition of water to the solvents favored a second order overall rate whereas addition of chloroform or carbon tetrachloride to the reaction mixture gave kinetics of greater order than two. The authors believe that the formation of $(Br_2)_2$ in pure acetic acid is responsible for the third order of kinetics.

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(74) E. Shilov and N. Kanyaev, Compt. rend. acad. sci., U. R. S. S., 24, 890 (1939); Chemical Abstracts, 34 4062 (1940).

(75) (a) P. W. Robertson, P. B. D. de la Mare and W. T. G. Johnston, J. Chem. Soc., 276 (1943); (b) P. B. D. de la Mare and P. W. Robertson, ibid., 279, (1943); (c) L. J. Lambourne and P. W. Robertson, ibid., 1167 (1947); (d) P. B. D. de la Mare P. W. Robertson, ibid., 100 (1948); (e) P. W. Robertson, R. M. Dixon, W. G. M. Goodwin, I. R. McDonald and J. F. Scaife, ibid., 294 (1949); (f) P. W. Robertson, ibid., 1267 (1954).

Wilson and Soper[76] studied the bromination of o-nitroanisole and benzene by bromine water at varying concentrations of bromide ion and hydrogen ion. They found that the reaction rate was independent of the hydrogen ion concentration but was slowed by the introduction of bromide ion. The specific rate constants, after correction for the inactive Br_3^-, were found to be unaffected by a one hundred fold change in the bromide ion concentration. A thirty fold change in the hydrogen ion concentration had no effect on the specific rate of bromination by bromine water. The authors concluded that the active brominating species is molecular bromine and not Br^+, which is formed by the ionization of Br_2. This ionization would be greatly affected by the increase in bromide ion concentration. Bromination by HOBr was also studied. The disproportionations of hypobromous acid to $HBrO_3$ and HBr which in turn react to give Br_2, handicapped the exact measurement of reaction rates of some desired compounds The bromination by HOBr was found to be strongly acid dependent, thus a six fold increase in acid concentration raised specific rates of bromination of o-nitroanisole and benzene six fold. This effect was attributed by the authors to the ionization of HOBr to give Br^+ or more likely, H_2OBr^+. Wilson and Soper also observed that weak acid buffers catalyze the bromination of o nitroanisole and benzene by HOBr, while the same acids exhibt no effect on the bromination of the same compounds by molecular bromine.

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(76) W. J. Wilson and F. G. Soper, J. Chem. Soc., 3376 (1949).

Bradfield, Davies and Long[77] have studied the bromination of phenolic ethers by HOBr in 75 per cent acetic acid and have found that the rate expression can be represented by the sum of two terms.

$$\text{rate} = k_1(E)(Br_2) + k_2(E)(Br_2)^2$$

where (E) refers to the concentration of the ether. Since bromination by HOBr cannot account for the termolecular term, the authors feel that bromination in this case may proceed via $(Br_2)_2$. The same halogenating species has been previously observed by Robertson and co-workers[75].

De la Mare, Ketley and Vernon[78] have recently investigated the kinetics of chlorination of phenol, mesitylene, methyl *m*-tolyl ether, methyl *p*-tolyl ether, and anisole. They found that in the presence of perchloric acid and silver perchlorate, the chlorination of anisole by .001 *M* hypochlorous acid in aqueous solution, the reaction assumes a kinetic form

$$\frac{-d(HOCl)}{dt} = k' \left[HOCl\right] + k'' \left[HOCl\right]\left[H^+\right] + k \left[HOCl\right]\left[H^+\right]\left[ArH\right]$$

They found that the third term of the expression is negligible, especially at low concentrations of the substrate. Under these conditions it was concluded that the rate determining step is the heterolytic fission of HOCl and H_2OCl^+ respectively to yield Cl^+.

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(77) A. E. Bradfield, G. I Davies, and E. Long, *J. Chem. Soc.*, 1389 (1949).

(78) P. B. D. de la Mare, A. D. Ketley and C. A. Vernon, *ibid.*, 1290 (1954).

Tsuruta, Sasaki and Furukawa[79,80] have studied the kinetics of iodine catalyzed bromination of benzene and toluene in the dark at 25°. According to the authors, the rate determining step is the loss of hydrogen bromide from a 1:1 aromatic-bromine complex. They found that the rate can be fitted in the following expression

$$v = k\left[C_6H_5Me\right] \cdot \left[Br_2\right]\left[BrI\right]^3$$

An induction period was observed which increased at low concentrations of the reactants, and less polar solvents. This induction period was found to be very pronounced when the reaction was carried out in carbon tetrachloride with the reactants in low concentration. The addition of benzoyl peroxide or molecular oxygen, however, had no effect on the induction period. The authors concluded that this induction period was not caused by free radical reaction. It seems that the nature of the reaction is still obscure to the authors.

The kinetics of bromination of mesitylene in carbon tetrachloride solution have been studied by Keefer, Blake and Andrews[81]. They found that the reaction of mesitylene with bromine at 25° in the dark was subject to catalysis by both water and hydrogen bromide and the rate of consumption of bromine in carbon tetrachloride solutions containing water

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(79) T. Tsuruta, K. Sasaki and J. Furukowa, J. Am. Chem. Soc., 74, 5995 (1952).

(80) Ibid., 76, 994 (1954).

(81) (a) R. M. Keefer, J. H. Blake, and L. J. Andrews, J. Am. Chem. Soc., 76, 3062 (1954); (b) J. H. Blake and R. M. Keefer, ibid., 77, 3707 (1955).

was first order in the concentration of bromine and varied as the square root of the concentration of hydrogen bromide. The reaction, at low concentrations of mesitylene, was found to be first order with respect to the substrate but at higher concentrations of mesitylene, the order with respect to mesitylene decreased. The mechanism proposed by the authors involves the attack of a hydronium ion on a 1:1 mesitylene-bromine addition complex in the rate determining step.

Keefer and co-workers[82,83] have recently investigated the kinetics of bromination of mesitylene, isodurene and pentamethylbenzene in 90 volume per cent aqueous acetic acid solution. They found that the reactions are first order in aromatic hydrocarbon concentration and showed mixed first and second-order dependence on free bromine concentration.

$$\text{Rate} = k_1(M)(Br_2) + k_2(M)(Br_2)^2$$

where (M) refers to the concentration of mesitylene. The reaction rates increased upon the addition of both water and salts to the medium. The salt effect was found to be more pronounced for the first order term in bromine than for the second order reaction. This enhancement of reaction rate was attributed by the authors to the influence of the salt on the capacity of the medium to accommodate the transition state. Based on the observed rate law, the authors have excluded the

(82) R. M. Keefer, A. Ottenberg and L. J. Andrews, J. Am. Chem. Soc., 78 255 (1956).

(83) R. M. Keefer and L. J. Andrews, ibid., 78, 3637 (1956).

possibility of bromination by Br^+ or acetyl hypobromite. They concluded that bromination may proceed by either of two processes. The first involves the transformation of the 1:1 hydrocarbon-bromine complex to the products with the rupture of Br-Br bond being the rate determing step. A second mechanism probably involves the bimolecular reaction of molecular bromine with the hydrocarbon. The second order (in bromine) term is accounted for by bromination by $(Br_2)_2$.

De la Mare, Dunn and Harvey[84] have recently measured the rates of bromination by HOBr of benzene and hexadeuterobenzene in 50 per cent aqueous dioxane and perchloric acid solution. Their kinetic expression is consistent with a mechanism which involves bromination by Br^+ or probably H_2OBr^+. Since no deuterium isotope effect was observed, they concluded that breaking of the C-H or C-D bond is, as in nitration, not rate determining. De la Mare and co-workers[85] have also investigated the acid catalyzed bromination of <u>tert</u>-butylbenzene by HOBr in 50 per cent aqueous-dioxane medium. By using the isotopic dilution technique, they found that the products of the reaction constituted a mixture of 37.7% <u>ortho</u>-, 7.2% <u>meta</u>- and 53.2% <u>para</u>-isomer with 1.9% bromobenzene. Upon bromination of biphenyl by the same halogenating species in the same medium, it was found[86] that biphenyl reacts 12.6 times faster than benzene and substitution was effected <u>o</u>- or <u>p</u> to the phenyl group.

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(84) P. B. D. de la Mare, T. M. Dunn, and J. T. Harvey, <u>J. Chem. Soc.</u>, 923 (1953).

(85) P. B. D. de la Mare and J. T. Harvey, <u>ibid</u>., 131 (1957).

(86) P. B. D. de la Mare and M. Hassan, <u>ibid</u>., 3004 (1957).

Swain and co-workers[87] have reported the presence of secondary kinetic isotope effects in the nitration, mercuration and bromination of toluene-α,α,α-d_3 and toluene-α-t_1. It is of interest to note that the magnitude of his secondary isotope effect is 3% per deuterium atom or less as contrasted to larger (4-30% per deuterium) secondary isotope effects reported in solvolysis reactions[88,89].

Berliner[90] has studied the bromination of naphthalene in 50 volume per cent aqueous acetic acid. Unlike that in glacial acetic acid, the reaction under these conditions was found to be second order overall, first order in each reactant. His kinetic expressions are in agreement with a mechanism involving bromination by molecular bromine. A small amount of bromination by Br_3^- was also observed.

The kinetics of bromination of aromatic compounds in nitromethane has been studied[91]. It was found that bromination in nitromethane is 1000 fold more rapid than in acetic acid, and the data are in agreement with a path in which Br_2 is the active brominating species. It was furthermore found[92] that molecular bromine is more selective than Br^+.

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(87) C. G. Swain, E. C. Knee and A. J. Kresge, J. Am. Chem. Soc., 79, 505 (1957).

(88) E. S. Lewis and C. E. Boozer, ibid., 74, 6306 (1952).

(89) V. J. Shiner, Jr., ibid., 75, 2925 (1953).

(90) E. Berliner and M. C. Beckett, J. Am. Chem. Soc., 79, 1425 (1957).

(91) G. Illuminati and Gianlorenzo Marino, Gazz. chim. ital., 84, 1127-34 (1959).

(92) G. Illuminati, Ricerca. sci., 26, 2752 (1956).

<u>The Kinetics of Hydrogen Isotope Exchange Reactions</u>.--Various investigations have established that hydrogen isotope exchange between aromatic compounds and mineral acids is an electrophilic substitution reaction[93-96]. Such exchange follows the known rules of electrophilic aromatic substitution with respect to the dependence of orientation and reaction velocity on the nature of substituent groups already present in the aromatic compound.

The rate of loss of deuterium from 4-nitrophenol-2,6-d_2, 4-chlorophenol-2,6-d_2, 4-methylphenol-2,6-d_2[97] benzene-d_1,[98] anisole-2-d_1,[99] anisole-4-d_1[100] and toluene-2-, -3-, or -4-d_1[100] in various sulfuric acid-water mixtures have been found to vary linearly with Hammett's acidity function[101,102] H_o, except for a few cases, at the highest acidities (Ho $<$ -8) where the rate increase is less steep[97,103]. A few

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(93) C. K. Ingold, C. G. Raisin and C. L. Wilson, <u>J. Chem. Soc.</u>, 915 (1936).

(94) A. P. Best and C. L. Wilson, <u>ibid.</u>, 28 (1938).

(95) S. Olsson and L. Melander, <u>Acta. Chem. Scand.</u>, <u>8</u>, 523 (1954).

(96) W. M. Lauer and J. T. Day, <u>J. Am. Chem. Soc.</u>, <u>77</u>, 1904 (1955).

(97) V. Gold and D. P. N. Satchell, <u>J. Chem. Soc.</u>, 3609 (1955).

(98) V. Gold and D. P. N. Satchell, <u>ibid.</u>, 3619 (1955).

(99) D. P. N. Satchell, <u>ibid.</u>, 3911 (1956).

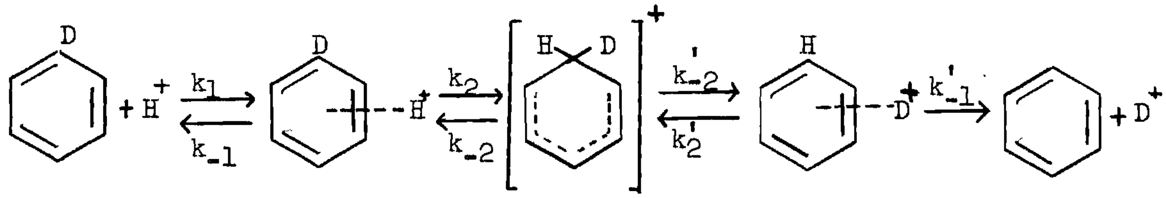
(100) V. Gold and D. P. N. Satchell, <u>ibid.</u>, 2743 (1956).

(101) L. P. Hammett, <u>Physical Organic Chemistry</u>, McGraw-Hill Book Co., Inc., New York, N. Y., (1940).

(102) V. Gold and F. A. Long, <u>J. Am. Chem. Soc.</u>, <u>75</u>, 4543 (1953).

(103) R. J. Gillespie and D. G. Norton, <u>J. Chem. Soc.</u>, 971 (1953).

mechanisms[97,98,104,111] have been postulated which agree with the observed linearity of rates with Hammett's acidity function. The most plausible mechanism according to Gold and Satchell[97] is



I II III IV V

Structure (III), where the entering and leaving atoms occupy equivalent positions are referred to as "inner" or σ complexes and structures (II) and (IV) as "outer" or π complexes[105,106].

Brown and Brady[106], investigating the equilibria between hydrogen chloride and aromatic hydrocarbon, with and without added aluminum chloride, suggested that the conjugate acid of benzene formed in the first case was an "inner" complex and in the second an "outer" complex. Only the interaction which leads to an inner complex can result in hydrogen isotope exchange between DCl and benzene[107]. Evidence for the existence of σ complexes has been presented by Olah and Kuhn[108]. A similar

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(104) P. B. D. de la Mare, E. D. Hughes, C. K. Ingold and Y. Pocker, J. Chem. Soc., 2930 (1954).

(105) R. S. Mulliken, J. Phys. Chem., 56, 801, 821 (1952).

(106) H. C. Brown and J. O. Brady, J. Am. Chem. Soc., 74, 3570 (1952).

(107) A. Klit and A. Langseth, Physik. Chem., 65, 176 (1936).

(108) G. A. Alah and S. J. Kuhn, J. Am. Chem. Soc., 80, 6535 (1958).

mechanism was originally proposed by Taft[109] to explain the dependence of rate of hydration of isobutene on Hammett's acidity function.

Gold and Satchell have presented evidence that the attacking species involved in the exchange reaction is larger than a hydrogen cation. Thus for protium-deuterium exchange reaction the partial rate factors referring to the _ortho_, _meta_ and _para_ positions in toluene[8] have been found to be 83, 1.9 and 83 respectively. The corresponding partial rate factors for bromination by HOBr in acidic medium were 76, 2.5 and 59. For nitrations it was found to be 42, 2.5 and 58 whereas for bromination by molecular bromine the partial rate factors for the _ortho_ and _para_ positions were found to be 450 and 1990 respectively. The higher _ortho/para_ ratio for bromination compared with nitration has been attributed by de la Mare and Harvey[110] to decreased steric effect.

The rates of acid-catalyzed hydrogen-isotope exchanges between _p_-deuteroanisole and solvent systems such as CH_3COOH, CH_3COOH-$ZnCl_2$, $ZnCl_2$-HCl-CH_3COOH have been investigated recently by Satchell[111]. He found that the rate of exchange in such solvents parallels to a close approximation the extent of ionization of indicators such as 4-chloro-2-nitroaniline and _p_-nitrodiphenylamine.

The kinetic isotope effect in hydrogen exchange reactions has

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(109) R. W. Taft, Jr., _J. Am. Chem. Soc._, _74_, 5372 (1952).

(110) P. B. D. de la Mare and J. T. Harvey, _J. Chem. Soc._, 36 (1956).

(111) D. P. N. Satchell, _ibid._, 1927 (1956).

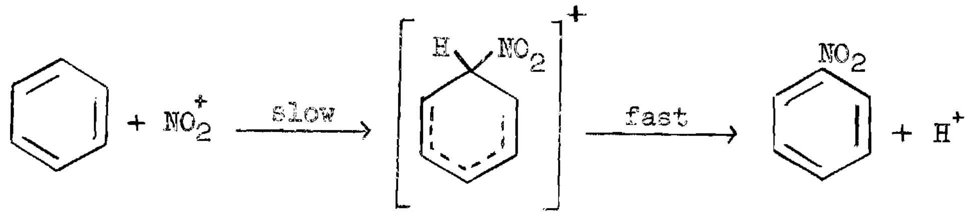
been determined recently by Melander[112] using both tritium and deuterium derivatives of toluene. The following results were obtained.

Position	$\frac{k_T}{k_D}$
Toluene-*ortho*	.53
Toluene-*meta*	.59
Toluene-*para*	.52
Benzene	.65

The fact that the *meta* position in toluene is somewhat more reactive than a single position in benzene[100] suggests that the ratio of k_T/k_D increases with decreasing reactivity. It is not clear whether this is a general rule or not.

Deuterium Isotope Effects in Electrophilic Aromatic Substitution.-- Early attempts to determine deuterium and tritium isotope effects in electrophilic aromatic substitutions were undertaken by Melander[5,6], who conducted a number of nitrations of aromatic compounds and their tritium analogues using relatively high proportions of nitric acid and aromatic compound to sulfuric acid. Since no detectable tritium isotope effect was observed, he concluded that the rate-controlling stage of the reaction, is not the abstraction of the proton. He considered that nitrations take place according to the two-step mechanism with the first step rate-determining.

(112) L. Melander and N. Olsson, *Acta Chem. Scand.*, 10, 879 (1956).



In the sulfonation of benzene and its tritium analogue, an isotope effect (k_T/k_H) of 0.55 at 0° was obtained[4], which corresponds to an unusually small isotope effect if the splitting of a C-H bond is rate-determining. Bonner, Bowyer and Williams[113] confirmed Melander's mechanism of nitration of aromatic compounds. Thus, within the limits of experimental error, they found that the rates of nitration of nitrobenzene in 97.4 per cent sulfuric acid and 86.7 per cent sulfuric acid are identical with the rates of nitration of pentadeuteronitrobenzene in the same media. Lauer and Noland[114] arrived at a similar conclusion upon studying the nitration of benzene containing 91.5 per cent monodeuterobenzene. They found that the expected 74.9 mole per cent of monodeuteronitrobenzene was formed, which agrees with a mechanism that demands the absence of deuterium isotope effect.

Bonner and Wilkins[115] have observed a small, but definite isotope effect in the cyclodehydration of 2-(2,4,6-trideuteroanilino)-pent-2-en-4-one and its protium analogue. The authors considered this reaction to be an intramolecular electrophilic substitution.

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(113) T. G. Bonner, F. Bowyer and G. Williams, J. Chem. Soc., 3274 (1952).

(114) W. M. Lauer and W. E. Noland, J. Am. Chem. Soc., 75 3689 (1953).

(115) T. G. Bonner and J. M. Wilkins, J. Chem. Soc., 2358 (1955).

In halogenation of aromatic compounds, Robertson[116] has pointed out that the proton loss is probably rapid and not rate-determining. Melander[6] found that in the iodine-catalyzed bromination of toluene and of tritiated toluene the rates were identical with either isotope. The rate of bromination of benzene and hexadeuterobenzene by aqueous hypobromous acid was studied by de la Mare, Dunn and Harvey[117]; no deuterium isotope effect was obtained. However, in the bromination of 2-naphthol-6,8-disulphonic acid by molecular bromine a deuterium isotope effect of 2.0 was found[118].

Zollinger[119] has studied the azo coupling reaction of 2-naphthol-6,8-disulphonic acid and the 1-deutero-2-naphthol-6,8-disulphonic acid with 4-chlorobenzene diazonium ion. He found that the reaction is strongly base catalyzed and the relative reaction rates gave an isotope effect of 6.55. In the diazo coupling reaction of related compounds a rather similar deuterium isotope effect was obtained.

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(116) P. W. Robertson, J. Chem. Soc., 1267 (1954).

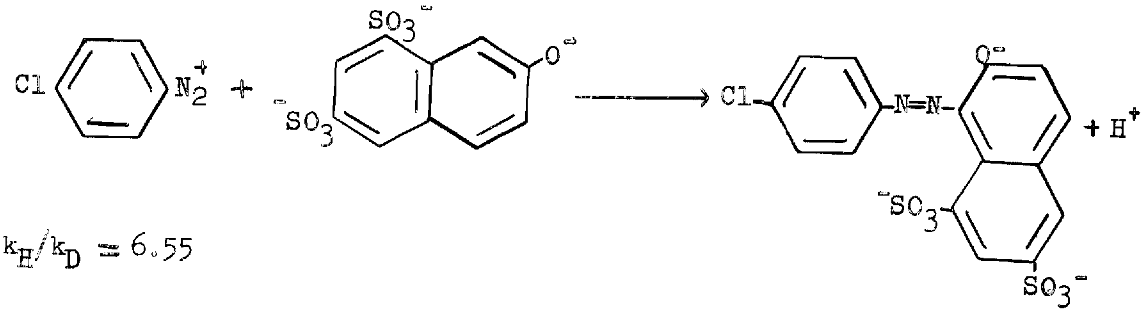
(117) P. B. D. de la Mare, T. M. Dunn and J. T. Harvey, J. Chem. Soc., 923 (1957).

(118) H. Zollinger, Experienta, 12, 165 (1956).

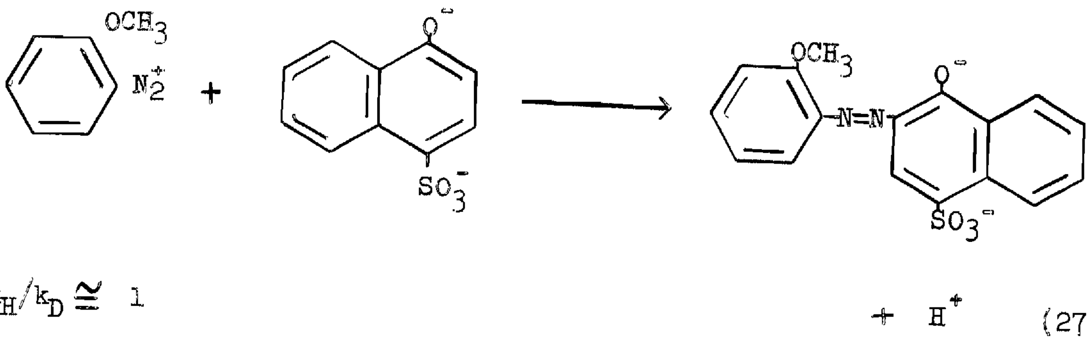
(119) a. H. Zollinger, Helv. Chim. Acta, 38, 1603 (1955).

b. Ibid., p. 1620.

c. Ibid., p. 1619.

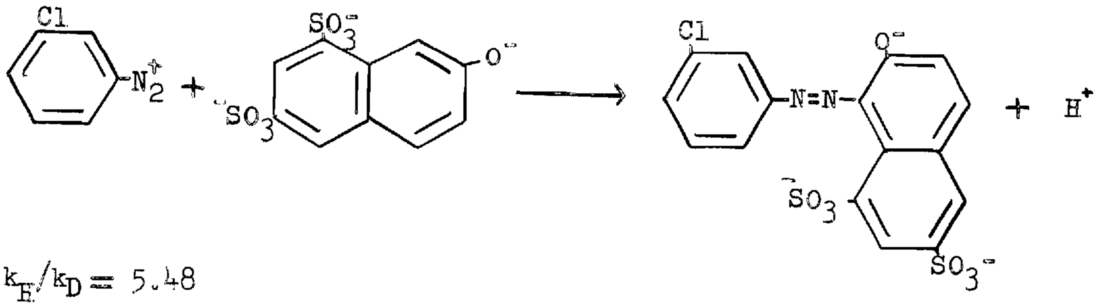


$k_H/k_D = 6.55$



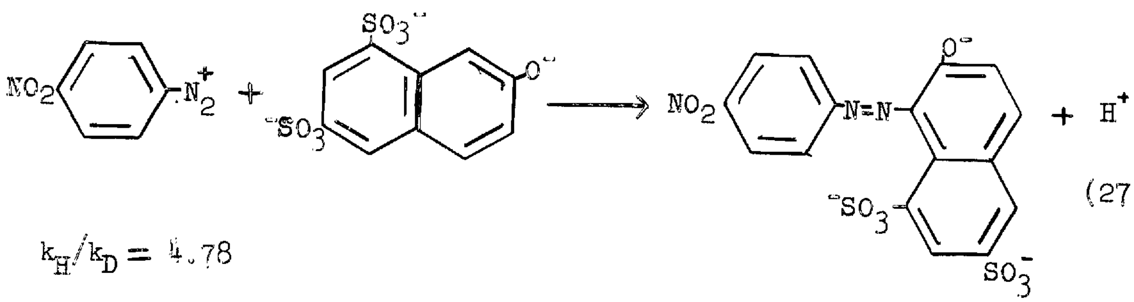
$k_H/k_D \cong 1$

(27 a)



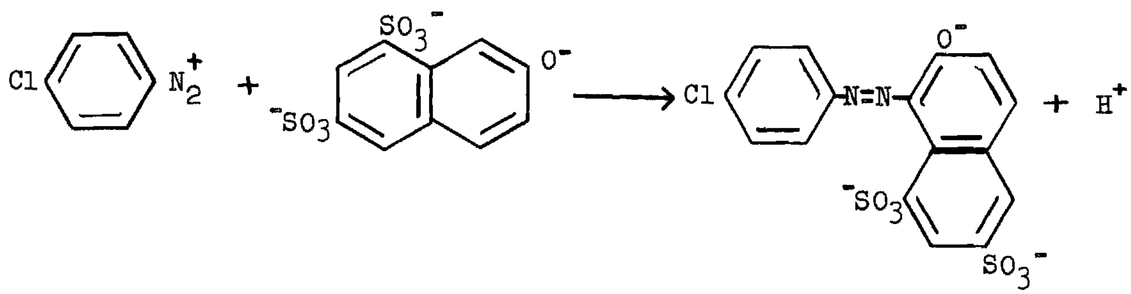
$k_H/k_D = 5.48$

(27 b)



(27 b)

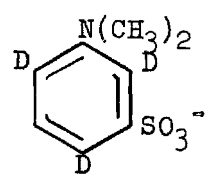
$k_H/k_D = 4.78$



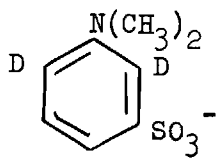
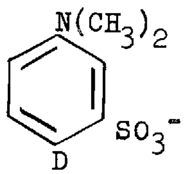
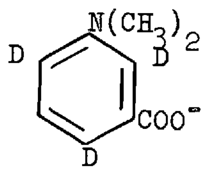
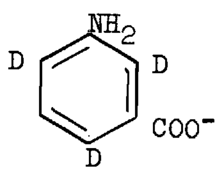
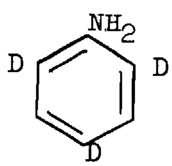
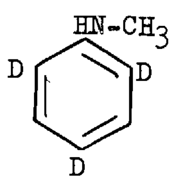
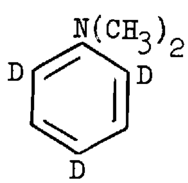
Base	k_H / k_D
55.6 M Water	6.55
0.0232 M Pyridine	6.01
0.905 M Pyridine	3.62

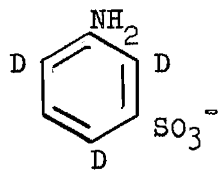
(27 c)

Shilov and Weinstein[120] have studied the iodination of 2,4,6-trideuteroaniline and related compounds. They found that the introduction of a sulphonic group in the *meta* position diminishes the magnitude of the isotope effect appreciably. Such a decrease in isotope effect was ascribed to "energetic peculiarities" of the reacting aromatic molecule. The following compounds were iodinated by these authors.

Compound	k_H/k_D
	1

(120) E. Shilov and F. Weinstein, Nature, 132, 1300 (1958) .

Compound	k_H/k_D
	1
	1
	1.4
	4.8
	3.5
	3.2
	3.0

Compound	k_H/k_D
	2.0

Farrell and Mason[121] have reported an isotope effect of 1.8 for the bromination of dimethylaniline and its 2,4,6-trideutero derivative.

(121) P. G. Farrell and S. F. Mason, Nature, 183 (1959).

CHAPTER III

SOURCE, PREPARATION, AND PURIFICATION OF MATERIALS

Anisole.--Eastman Kodak Co., white label grade anisole was purified as follows: Anisole (500 g.) was washed with 200 ml. of 10% solution of sodium hydroxide. The anisole was next washed with five 200 ml. portions of distilled water, and was dried over "Drierite" overnight. The anisole was then distilled through a three-foot column packed with 3/16 inch glass helices, and the fraction boiling at 154° under atmospheric pressure (742 mm.) was collected (ca. 350 g.). About ten grams of pure sodium metal was added to the distillate and the mixture was refluxed for three hours. The anisole was distilled from the sodium metal through the same fractionating column and the fraction boiling at 154° under atmospheric pressure (742 mm.) was collected (ca. 250 g.). The anisole was finally redistilled through the same column at 11 mm. pressure. The portion boiling at 43° was collected and placed in sealed tubes for further use.

Anisole-2,4,6-d_3.--Sodium metal 1.23 g. (53.4 mmoles) was placed in a 500 ml. three-necked round-bottom flask fitted with a nitrogen inlet, separatory funnel, and a condenser which was attached to a calcium chloride tube. Heavy water (18 ml. of 88.8% purity D_2O) was added very slowly while the flask was cooled. A solution of 10 g. (101.3 mmoles) of phenol-2,4,6-d_3 (half of which was neutralized previously with sodium deuteroxide prepared by the reaction of sodium metal with excess D_2O) in

40 ml. of heavy water was added to the flask dropwise followed by 13.45 g. (106.3 mmoles) of dimethyl sulfate. The solution was shaken vigorously for an hour and was then boiled overnight under reflux. The anisole layer was separated and the aqueous layer was extracted with two 10 ml. portions of diethyl ether. The ether extracts were combined with the anisole and dried over "Drierite". The ether was evaporated and the anisole distilled through a one-foot Vigreux column. The main portion boiled at 33.5-34° under reduced pressure (ca. 6.8 g.).

Kinetic experiments, however, showed that the deuterated anisole was appreciably contaminated with phenol-2,4,6-d_3. For purification, about two grams of sodium metal was added to the deuterated anisole and the mixture was refluxed for two hours. The anisole was then distilled from the sodium through the Vigreux column under reduced pressure at 35° (ca. 3.0 g.). The deuterated anisole was stored in sealed tubes for future use.

Calcium Chloride.--Mallinkrodt, Analytical Reagent, anhydrous calcium chloride was used without further purification.

Carbon Tetrachloride.--A commercial grade of carbon tetrachloride from Dow Chemical Co. was purified by distillation over potassium permanganate. The distillate was extracted with a 10% solution of sodium hydroxide and next with a dilute solution of sulfuric acid, then dried over calcium chloride and distilled through a one half foot column packed with glass helices. The portion boiling at 77° was collected.

Calcium Sulfate.--Hamond "Drierite", anhydrous calcium sulfate, was used without further purification.

Deuterium Chloride.--A solution of deuterium chloride in heavy water was prepared by the method of Langseth and Klit[122]. Twelve ml. of 99.5% heavy water was added dropwise from a funnel into a 100 ml. three-necked round-bottom flask containing 25 ml. of purified thionyl chloride. Nitrogen was continuously swept through the apparatus. The gases evolved, sulfur dioxide and deuterium chloride, were passed through two traps cooled by a mixture of acetone and solid carbon dioxide. Since the boiling point of sulfur dioxide is -10° and the freezing point is -75.5°, and deuterium chloride has a boiling point of -85° and a freezing point of -115°, all of the solid sulfur dioxide can be separated without contaminating the deuterium chloride. The deuterium chloride was then bubbled through a sintered glass bulb into 80 ml. of heavy water (99.5% in D_2O). Sweeping with nitrogen was continued until no more deuterium chloride was evolved. The concentration of the deuterium chloride solution was determined by titration with a standard sodium hydroxide solution and was found to be 3.660 M. A check for oxidizing agents was performed by addition of a little of the deuterium chloride solution to a solution of potassium iodide acidified with sulfuric acid. No visible blue color was observed upon addition of a starch solution.

Diethyl Ether.--Merck Reagent grade diethyl ether, stored in a brown bottle over sodium wire, was used without further purification.

Dimethyl Sulfate.--Dimethyl sulfate was purchased from Matheson Coleman and Bell, Inc. and was used without further purification.

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(122) A. E. Langseth and A. Klit, Kgl. Danske Videnskab Selskab, Mat. fys. Medd., 13, 15 (1937).

Heavy Water.--Heavy water (99.5% in D_2O) was purchased from the Liquid Carbonic Co., 767 Industrial Road, San Carlos, California.

Hydrochloric Acid.--du Pont C. P. Reagent grade hydrochloric acid was used without further purification.

Iodine.--Merck Resublimed-U.S.P. iodine was used without further purification. Dilute iodine solutions for kinetic runs were prepared as follows: A saturated solution of iodine in carbon tetrachloride (200 ml.) was extracted with three aliquots of redistilled water, the fourth and the subsequent extracts were used for the kinetic experiments. This method was adopted in order to eliminate, as much as possible, any extraneous triiodide ion present in the original iodine-carbon tetrachloride solution.

Concentrated stock iodine-sodium iodide solution was prepared by dissolving enough iodine and sodium iodide such that all the iodine was essentially converted to triiodide. This stock solution was then diluted to desired concentrations for runs with thallium perchlorate.

Linseed Oil.--Raw, refined, unboiled linseed oil was used without further purification.

Magnesium Sulfate.--Mallinckrodt, Analytical Reagent, anhydrous magnesium sulfate was used without further purification.

Mercuric Iodide.--Baker Analyzed Reagent mercuric iodide, was used without further purification.

Nitrogen.--Marks, Compressed Cylinder of nitrogen gas was used without further purification.

4-Nitrophenol.--Eastman Kodak Co., Rochester, N. Y., p-nitrophenol was purified by recrystallization from water. The product after the sixth recrystallization melted at 114° (uncorr.).

4-Nitrophenol-2,6-d_2.--The method used for the preparation of 4-Nitrophenol-2,6-d_2 is essentially that of Ingold and coworkers[93,94]. According to this method maximum deuteration is obtained when one half of the phenol is present as the phenoxide ion. Sodium deuteroxide was prepared by dropwise addition of 87 grams of 93% heavy water from a dropping funnel to 1.27 grams (55.21 mmoles) of sodium metal placed in a 200 ml. three-necked round-bottom flask fitted by means of ground-glass joints with a nitrogen inlet and an air condenser, and cooled in an ice bath. The sodium deuteroxide was then divided into two equal volumes and to each portion 7.0 grams (50.4 mmoles) of p-nitrophenol was added. The resulting solutions were placed in sealed tubes under nitrogen atmosphere and were then heated in a five liter flask containing two liters of boiling water. The tubes were then opened and the deuterium oxide was removed by distillation under vacuum. To the solid residue 15.0 grams of 99.5% heavy water was added and the solution was placed in sealed tubes under nitrogen atmosphere and was likewise heated for another fifteen days. The tubes were reopened and the solution was titrated with 3.6601 M deuterium chloride solution until just acidic to litmus paper. The deuterium oxide was next removed by distillation under vacuum, and the solid residue was dried for two hours under vacuum at 80°. The dry solid residue* weighed 13.0 grams.

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*Calculations show that approximately 4.3 grams of this residue is sodium chloride.

About four grams of this residue was sublimed at 130-140° and a pressure of 30 microns. At the end the sublimation temperature was raised to 180° and thus about 2.6 grams of pure 4-Nitrophenol-2,6-d_2, m.p. 114° (uncorr.), was isolated.

To the remainder of the solid residue (about 9 grams), a solution of 1.05 grams of sodium metal in 99.5% heavy water was added and the solution was again placed in sealed tubes under nitrogen atmosphere and was heated for thirty days. The tubes were then opened, titrated with deuterium chloride, and the heavy water removed under vacuum. The solid residue was dried, and then sublimed in a sublimating apparatus under reduced pressure. The weight of pure 4-nitrophenol-2,6-d_2 was 4.2 grams, melting at 114° (uncorr.). The recorded melting point for p-nitrophenol is 114°[123].

Perchloric Acid.--Baker Analyzed Reagent, 70-72%, perchloric acid was used without further purification. The exact concentration was determined by titration against standard sodium hydroxide solution.

Potassium Acid Phthalate.--Baker Analyzed potassium acid phthalate was used without further purification.

Potassium Dichromate.--Merck Reagent, potassium dichromate was used without further purification.

Potassium Iodate.--Baker Analyzed Reagent potassium iodate was used without further purification.

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(123) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, Systematic Identification of Organic Compounds, page 326, 4th Edition (1956), John Wiley and Sons, N. Y.,

Potassium Permanganate.--Baker Analyzed Reagent potassium permanganate was used without further purification.

Phenol.--Baker Analyzed Reagent phenol, was purified by distillation through a three-foot column packed with 3/16 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 a three-foot column packed with 3/16 inch glass helices. The portion boiling at 75-81° under 15-20 millimicrons was collected and sealed under nitrogen in glass vials.

Phenol-2,4,6-d_3.-- Phenol-2,4,6-d_3 was prepared by the general procedure of Ingold and coworkers[93]. The preparation of sodium deuteroxide is analogous to those described previously.

A solution of 50 grams of pure phenol (521.2 mmoles) in 200 grams of 99.25% heavy water containing 6.18 grams of sodium, was sealed in equal amounts in two tubes under nitrogen atmosphere and heated in boiling water for 96 hours. The tubes were then allowed to stand at room temperature for eighteen more days during this period an orange color was observed in the solutions. This solution was added dropwise to the sodium metal while the flask was continuously swept with nitrogen gas. The heavy water was then distilled under atmospheric pressure using an oil bath and the resulting salt was dried under vacuum. Deuterium chloride (30 ml. of 9.084 M) was then added cautiously to the salt, followed by 200 grams of 99.5% of deuterium oxide. The resulting solution was then placed in sealed tubes under nitrogen atmosphere and was heated for eight more days.

The tubes were then allowed to stand at room temperature for two days after which they were broken open and the solution was placed in 500 ml. separatory funnel. The solution was then titrated with deuterium chloride solution until just acidic to litmus paper. The deuterated phenol was then extracted with ten 50 ml. aliquots of ether, and the combined ether extracts were dried over anhydrous sodium sulfate. The ether was then removed by distillation and the deuterated phenol was distilled under vacuum using a half-foot column packed with 3/16 inch glass helices. The portion boiling at 54° under reduced pressure was collected (ca. 34.54 grams). About 7.35 grams of this deuterated phenol was stored in sealed tubes under nitrogen atmosphere and to the remainder (27.2 grams), a solution of 100 grams of 99.5% heavy water containing 3.73 grams (162.0 mmoles) of sodium metal was added in an analogous manner as described previously. The solution was then placed in sealed tubes under nitrogen and was re-equilibrated at the temperature of a boiling-water bath for seventeen days. The tubes were then broken open and the deuterated phenol was recovered from the solution in exactly the same way as described previously. The deuterated phenol that boiled at 44-45° under reduced pressure was collected (ca. 12.5 grams), and was stored in sealed tubes under nitrogen atmosphere for further use.

Silver Perchlorate.--Anhydrous silver perchlorate purchased from the G. Frederick Smith Chemical Co. was dried under vacuum at 80°.

Sodium Metal.--Baker Reagent Grade freshly cut sodium metal was used without further purification.

Sodium Carbonate.--Mallinckrodt Analytical Reagent anhydrous sodium carbonate was used without further purification.

Sodium Hydroxide.--Fisher Certified Reagent Grade sodium hydroxide was used without further purification. However, for the preparation of a standard solution of sodium hydroxide, it was purified as follows: A solution of 50 grams of sodium hydroxide in 50 ml. of redistilled water was filtered through a sintered-glass funnel. The concentrated sodium hydroxide solution was then diluted to the desired concentration. The molarity of this solution was determined by titration using potassium acid phthalate as a standard and phenolphthalein as indicator[124].

Sodium Iodide.--Baker Analyzed Reagent sodium iodide was dried in vacuum at 100° and was used directly for kinetic experiments. For stopping the reactions, a saturated solution of Merck, U.S.P. sodium iodide was used without further purification.

Sodium Perchlorate.--Hydrated sodium perchlorate purchased from the Amend Drug Co. was heated in the oven for 12 hours and then dried in vacuum (25 mm) at 130-140° for four hours.

A second portion of sodium perchlorate was prepared by reacting perchloric acid with solid sodium hydroxide. Near the end point a solution of sodium hydroxide was used to titrate the solution to neutral

(124) I. M. Kolthoff and E. B. Sandell, Textbook of Quantative Inorganic Analysis, Third Edition, New York; The Macmillian Co., 1952, p. 526.

using a Beckman pH meter. The solution was then evaporated to dryness and then dried for nine hours in an electric oven under vacuum (25 mm) at 130-140°. Sodium perchlorate monohydrate decomposes to give anhydrous sodium sodium perchlorate at 130°[125].

Sodium Thiosulfate.--Merck Reagent sodium thiosulfate was used without further purification. To prepare a standard sodium thiosulfate solution, about 75 grams of sodium thiosulfate was dissolved in three liters of freshly redistilled water. To this solution 0.30 grams of sodium carbonate was added and the solution was allowed to stand overnight before standardization. Either potassium iodate or potassium dichromate in sulfuric acid was used as a standard[126]. The results agreed within the limits of experimental error.

Sulfuric Acid.--du Pont C.P. sulfuric acid was used without further purification.

Thallium Metal.--Fisher Scientific Co. thallium metal was used without further purification.

Thallium Perchlorate.--Thallium perchlorate C.P. was purchased from the City Chemical Corporation, N. Y., dried under vacuum at 80°, and was used without further purification. Another batch of thallium perchlorate was prepared by refluxing with stirring an equimolecular mixture of

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(125) N. A. Lange, Handbook of Chemistry, Sixth Edition, Sandusky: Handbook Publishers, Inc., 1946, p. 256.

(126) I. M. Kolthoff and E. B. Sandell, Textbook of Quantative In-Organic Analysis, Third Edition, New York; Mcmillian Co., 1952, p. 594.

recovered thallium iodide and silver perchlorate. After six days the solution was filtered while hot, cooled, and the white crystals of thallium perchlorate were removed by filtration. After two recrystalizations, the thallium perchlorate was dried under vacuum for two hours at 80°.

Thionyl Chloride.--Eastman Kodak white label grade thionyl chloride was purified by the standard procedure of Martin and Fieser[127].

Water.--Distilled water was redistilled freshly over potassium permanganate (10 grams) and sodium hydroxide (50 grams) in batches of four liters each.

(127) E. L. Martin and L. F. Fieser, Organic Synthesis, John Wiley and Sons, Inc., New York, N. Y., Coll. Vol. II, 1943, p. 570.

CHAPTER IV

EXPERIMENTAL TECHNIQUES FOR KINETIC MEASUREMENTS

The multiple flask technique was employed throughout the course of the experimental work. However, slight modifications were made as the work was in progress. Kinetic runs were ordinarily carried out in 50 ml. or 100 ml. red, low actinic, volumetric flasks fitted with ground-glass stoppers which were lightly lubricated with silicone grease. All the stock solutions were thermostated in a Sargent constant temperature water bath Model S-W 3c-82055 equipped with automatic thermo-regulator. For kinetic experiments on p-nitrophenol and anisole, the bath temperature was set at $50.0 \pm 0.1^{\circ}$ as determined by a thermometer calibrated by the Bureau of Standards. The temperature of the bath was found to stay constant within 0.02° as determined by a $0-100^{\circ}$ thermometer calibrated in tenths of a degree. For kinetic experiments on phenol, the bath temperature was set at $25.0^{\circ} \pm 0.1$ as determined by a thermometer calibrated by the Bureau of Standards and was cooled with a coil through which cold water was circulated.

Generally, a stock solution of sodium iodide and perchloric acid along with enough sodium perchlorate (of such a concentration that the ionic strength of the solution became 0.3000 M) was first introduced into the reaction flasks at 50.0°. Next, the iodine solution was added and finally 5.0 ml. or 10.0 ml. of 4-nitrophenol. The flask was then shaken vigorously and the zero time of reaction was taken when one half of the solution of 4-nitrophenol had drained into the flask. To stop the reaction, a freshly prepared saturated solution of sodium iodide (one ml. per 50 ml. of reaction mixture) was injected into the reaction flasks with a syringe, the time was recorded, and the flask was shaken vigorously. The contents of the reaction flasks were rinsed into Erlenmeyer flasks and titrated to a starch end-point with sodium thiosulfate solution[128] (generally 0.006 M) delivered from a 10.0 ml. burette. Usually, a kinetic run was performed in nine reaction flasks, three of which contained all of the reactants except 4-nitrophenol and were used as blanks in order to determine the initial stoichiometric concentration of iodide. These blanks were determined at time intervals near the beginning, middle and end of the kinetic run. The blanks were found to remain constant at low iodide concentrations. However, in runs at high iodide ion concentration (0.0003 M or higher), the iodine titer showed a tendency to increase with time. When the flasks and the stock solutions of such runs were flushed with nitrogen gas, the blanks were found to remain constant, within the limits of experimental error. Therefore, this technique of flushing with nitrogen gas was employed for all the runs reported in this thesis at 0.00030 M or higher iodide concentration.

A slight modification was adopted in kinetic runs with anisole. As in the previous case, stock solutions of sodium iodide, perchloric acid and sodium perchlorate were introduced into the reaction flasks. To these solutions 25.0 ml. or 50.0 ml. of stock anisole was introduced

(128) I. M. Kolthoff and E. B. Sandell, Textbook of Quantitative Inorganic Analysis, Third Edition, New York; The Macmillian Co., 1952, p. 590.

followed with 10.0 ml. or 20.0 ml. of stock iodine solution. The zero time of the reaction was taken when half of the iodine solution was drained into the reaction flask. This modification was necessary in order to reduce the uncertainty in timing the start of the reaction.

The technique for performing kinetic runs with phenol is identical to that of 4-nitrophenol except that the reaction was run at 25° instead of 50°.

Kinetic Runs in The Presence of Thallium Perchlorate.--Thallium perchlorate was used in kinetic runs in order to maintain a fairly low and constant iodide ion concentration. However, a major source of difficulty is encountered in the use of thallium perchlorate. It is established that crystalline thallium iodide reacts with iodine and forms molecular complexes in the solid phase[129,130]:

$$6TlI + I_2 \longrightarrow Tl_6I_8$$

This reaction occurs at 25° at iodine concentrations greater than 0.76 x 10^{-5} M. At iodine concentrations greater than 3.3 x 10^{-4} M a second complex is formed

$$Tl_6I_8 + 5I_2 \longrightarrow 6TlI_3$$

in which the per cent iodine tied up as a complex is still greater. Thus, it was found necessary to perform kinetic runs in the presence of

(129) W. Maitland and R. Abegg, Z. anorg. Chem., 49, 341 (1906).

(130) A. G. Sharpe, J. Chem. Soc., 2165 (1952).

thallium ions at iodine concentrations below 3.3×10^{-4} M in order to keep major portions of iodine from being precipitated as TlI_3. It was necessary to use iodine concentrations usually above 2.0×10^{-4} M in order to have sufficient iodine for accurate titration. Generally, a stock solution of perchloric acid, sodium perchlorate and thallium perchlorate was pipetted into 50.0 ml. reaction flask thermostated at 50.0°. To the reaction flasks containing this stock solution was added a small amount (1 ml.) of sodium iodide (0.0002 M) and then iodine solution of such a concentration that the final stoichiometric concentration of iodine would be below 3.3×10^{-4} M. The sodium iodide was added in order to form enough crystal seeds to induce the precipitation of all additional iodide ions formed throughout the course of the reaction. The reactants were usually allowed to equilibrate for about one-half hour before the addition of 5.0 ml. of 4-nitrophenol. The reaction was stopped by pouring the contents of the flask into an Erlenmeyer flask containing an excess of standardized sodium thiosulfate solution. The contents of the reaction flask were rinsed with water and then 2.0 ml. of a saturated solution (at room temperature) of sodium iodide in water was added. The flask was shaken for a few minutes to ensure complete precipitation of thallium iodide and the solution was filtered through two medium porosity filter papers on a Buchner funnel under mild suction. Five ml. of starch solution was added and the pale yellow solution was back-titrated with standardized iodine-sodium iodide solution until a pale blue-green color was attained and then back-titrated to a yellow solution with sodium thiosulfate. The same technique was employed in runs with anisole except that the reaction was started by the introduction of 25.0 ml. of anisole. In kinetic experiments with phenol and thallium perchlorate, the reaction temperature was maintained at 25.0°.

Calculation of Apparent Rate Constants.--It was initially assumed that the reaction of 4-nitrophenol and anisole with iodine is first order in stoichiometric iodine and first order in substrate. This assumption was later confirmed by experiment. A similar kinetic order has been established for phenol. The apparent rate constants were calculated by the integrated rate equation

$$k_{app} = \frac{2.303}{(b-a)t} \log \frac{a(b-x)}{b(a-x)}$$

in which *a* and *b* designate the initial stoichiometric molar concentration of iodine and substrate respectively and *x* is the molar concentration of stoichiometric iodine consumed at time *t*.[131] The units of k_{app} are (liter)(mole^{-1})(sec.$^{-1}$) or l./mole sec. In a typical run, this equation was used to calculate the apparent rate constants at various intervals and the calculated rate constants were extrapolated to zero time.

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(131) A. A. Frost and R. G. Pearson, Kinetics and Mechanism, New York: John Wiley and Son, Inc., 1953, p. 17.

CHAPTER V

KINETIC MEASUREMENTS IN AQUEOUS PERCHLORIC ACID AND SODIUM PERCHLORATE SOLUTION

The mechanism of the iodination of phenol in water containing acetate-acetic acid buffer proposed by Grovenstein and Henderson has the following rate expression at high iodide ion concentration

$$\text{rate} = \frac{k_1 [PhOH][I_3^-][H_2O]}{[H^+][I^-]^2} + \frac{k_2 [PhOH][I_3^-][HOAC]}{[H^+]^2 [I^-]^2}$$

However, at low iodide ion concentrations, their rate expression assumes the form:

$$\text{rate} = k_1' [PhOH] [I_2] + \frac{k_2' [PhOH][I_2]}{[H^+]}$$

in which k_1' and k_2' designate the rate constant for iodination by molecular iodine of phenol and phenoxide ion respectively.

The mechanism of iodination of phenol in acetate-acetic acid buffer proposed by Berliner leads to the following rate expression.

$$\frac{k_3' [PhOH][I_2]}{[H^+] [I^-]} + \frac{k_4' [PhOH][I_2][HOAC]}{[H^+]^2 [I^-]}$$

According to Berliner, this expression holds at the entire iodide ion range and even at high iodide ion concentrations where approximately all the stoichiometric iodine is converted to triiodide ion.

$$I_2 + I^- \overset{K}{\rightleftarrows} I_3^-$$

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

The two mechanisms are kinetically indistinguishable at high iodide ion concentrations. However, at low iodide ion concentrations, if the reaction proceeds according to Grovenstein's mechanism, it is expected that Berliner's rate constants should decrease with decreasing iodide ion concentration.

At low iodide concentrations, the second order apparent rate constant (k_{app}) falls sharply as the reaction proceeds. Such a decrease in rate constant is expected since the iodide ion concentration increases throughout the course of the reaction. In order to obtain an apparent rate constant at a definite iodide ion concentration, the integrated rate constant was plotted versus the per cent reaction and the apparent rate constant at the initial stoichiometric iodide ion concentration (zero per cent reaction) was obtained. At initially high iodide ion concentration where the per cent increase in iodide ion concentration is small relative to the initial ion concentration, the apparent rate constants were rather constant, hence an average of the apparent rate constants was taken.

Berliner's rate constant k' was also calculated for each run from the extrapolated apparent rate constant. The rate constant k', is defined as follows

$$k' = \frac{k_{app}\ K\ [I_2][I^-]^2}{[I_3^-]}$$

In order to account for the iodide tied up as triiodide ion the rate constant k* defined as

$$k^* = k_{app}\frac{(I_2)}{[I_2]}$$

was calculated. The stoichiometric concentration of molecular species are designated by enclosure in parentheses ( ), and the actual concentration of a species by enclosure in square brackets[ ]. This designation is adopted throughout this thesis.

Kinetic Reaction of 4-Nitrophenol.--In order to determine the effect of iodide ion concentration on the rates of iodination of p-nitrophenol, a wide range of iodide ion concentration was studied. The first kinetic run was performed at 25.00×10^{-4} M Sodium iodide in the presence of perchloric acid and sodium perchlorate at 50° and ionic strength of 0.3000. The use of NaCl, as employed by Berliner[9], was avoided since it is possible that iodine may react with chloride ion for form I_2Cl^- or ICl[132]. The results (Table I, Run 32-V-1) indicate that there was no appreciable drop in the apparent rate constant throughout the reaction. This is rather expected in runs at relatively high iodide ion concentration since the amount of iodide ion formed during the reaction is relatively small. In

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(132) W. M. Latimer, The Oxidation States of Elements and Their Potentials in Aqueous Solutions . New York: Prentice Hall; 1952 p.65

order to avoid polyiodination, the concentration of p-nitrophenol was always kept at least four times as large as the iodine concentration. The average value of the apparent rate constant was found to be 10.94 $\pm 0.29 \times 10^{-4}$ l./mole sec. and the calculated value of k' was 51.2×10^{-7} sec.$^{-1}$ (See Table 1). Duplication of the same run gave an average rate constant of 11.18 $\pm 0.3 \times 10^{-4}$ l./mole sec. and the value of k' was 52.0×10^{-7} sec.$^{-1}$ (See Table 2, Run 39-V-1).

Iodination at higher iodide concentrations (65.0×10^{-4} M and 125×10^{-4} M) were performed. As in the previous case, the apparent rate constants were averaged since no appreciable drop in apparent rate constant was observed (See Table 3 and Table 4). A kinetic run at 5.0×10^{-4} M in sodium iodide was done under the same **experimental** conditions. A downward drift in the rate constants was prominent in this case. Extrapolation of the rate constant to zero time gave an apparent rate constant of 9.10×10^{-3} l./mole sec. and the calculated value of k' was 45.8×10^{-7} sec.$^{-1}$ (Table 7, Run 43-V-1). The same run when duplicated gave an extrapolated value of apparent rate constant of 8.70×10^{-3} l./mole sec. and a value of k' of 44.7×10^{-7} sec.$^{-7}$ sec.$^{-1}$ (Table 8, Run 55-V-1).

The iodination of p-nitrophenol at 2.50×10^{-4} M sodium iodide was run using the same concentrations of reactants except iodine. The plot of apparent rate constant versus per cent reaction when extrapolated to zero time gave an apparent rate constant of 17.91×10^{-3} l./mole sec., which gives a value of k' of 41.8×10^{-7} sec.$^{-1}$ (See Table 9, Run 51-V-1).

The iodination of p-nitrophenol at 1.00 x 10^{-4} M sodium iodide was run. A close examination (Table 10, Run 36-V-1) reveals that the rate constant falls in half at 50 per cent reaction. A plot of rate constants versus per cent reaction gave an extrapolated rate constant of 4.10 x 10^{-2} l./mole sec. or a value of k' of 33.6 x 10^{-7} sec.$^{-1}$. The experiment was repeated and the extrapolated rate constant was found to be 4.30 x 10^{-2} l./mole sec. and the value of k' was 39.6 x 10^{-7} sec.$^{-1}$ (Table 11, Run 37-V-1). Such a discrepancy in a set of similar runs was at first thought to be due to errors in one of the experiments. Therefore, another check was made and the rate constant was found to be 4.04 x 10^{-2} l./mole sec. and the value of k' was 34.7 x 10^{-7} sec.$^{-1}$. (Table 12, Run 42-V-1). A fourth check on the same run gave an extrapolated value of rate constant of 4.00 x 10^{-2} l.mole sec. and a calculated value of k' 38.2 x 10^{-7} sec.$^{-1}$ (Table 13, Run 46-V-1). A close examination of tables 10, 11, 12, and 13 reveals that the iodine concentration in runs 36-V-1 and 40-V-1 are approximately similar (4.90 x 10^{-4} M and 4.49 x 10^{-4} M, respectively) and the magnitude of k's are also comparable within the limits of experimental error. In Tables 11 and 13 the iodine concentrations (2.82 x 10^{-4} M and 2.02 x 10^{-4} M respectively) are fairly close and the values of k's are also close. The effect of iodine concentration on k' will be discussed later on in terms of the iodine-triiodide equilibrium.

The iodination of p-nitrophenol was studied at 0.50 x 10^{-4} M sodium iodide and 2.07 x 10^{-4} M iodine concentration. The rate constants fell sharply as the reaction proceeded. Extrapolation of rate constants to zero time gave a value of 6.60×10^{-2} l./mole sec. and a value of k' of 30.3×10^{-7} sec.$^{-1}$ (Table 14, Run 48-V-1). The same run was repeated and the extrapolated value of the apparent rate constant was 6.40×10^{-2} l./mole sec. or the value of k' was 29.0×10^{-7} sec.$^{-1}$. (Table 15, Run 80-V-1).

A run at 0.2500×10^{-4} M in sodium iodide was performed. The concentration of iodine in this case was lowered to 1.396×10^{-4} M in order that the increase in iodide ion concentration with reaction not overshadow the initial stoichiometric iodide concentration. However, it can be easily seen that at 20 per cent reaction the concentration of iodide ion doubles. Extrapolation of rate constants in this case gave a value of 8.75×10^{-2} l./mole sec. at zero time. The calculated value of k' was 21.4×10^{-7} sec.$^{-1}$ (Table 16, Run 81-V-1).

The iodination of p-nitrophenol at lower iodide ion was desirable. Thus a run at 0.100×10^{-4} M sodium iodide was performed. As in the previous case the iodine concentration was lowered to 1.017×10^{-4} M. In order to have enough titratable iodine, the reaction was run in 200 ml. volumeric flasks. The concentration of sodium thiosulfate was doubled in order to get good starch-iodine end points. Examination of Table 17 reveals that at 90 seconds approximately nine per cent of product was formed. Experimental error due to starting and stopping the reaction are exaggerated in this case due to the short period of reaction time. Another major souce of difficulty is that accurate extrapolation is not possible at this iodide ion concentration. Thus, at ten per cent reaction it can be seen that the concentration of stoichiometric iodide increases more than two fold and at 50 per cent reaction the stoichiometric iodide ion concentration is approximately 0.6 $x10^{-4}$ $\underline{M}$. The overall shape of the plot of rate constants versus per cent reaction is similar to a logarithmic plot. To obtain an accurate extrapolation, points beyond 30 per cent reaction were almost neglected and the extrapolated value was primarily based on 10 to 30 per cent reaction. Thus a value of apparent rate constant of 15.25 x 10^{-2} l./mole sec. was obtained. The calculated value of k' was 14.6 x 10^{-7} sec.$^{-1}$ (Table 17, Run 82-V-1). This experiment was checked and a value of k_{app} of 15.20 x 10^{-2} l./mole sec. was obtained and the calculated value of k' was 14.5 x 10^{-7} sec.$^{-1}$.

Due to difficulties in extrapolating at low iodide ion concentration, no firm conclusion could be reached regarding the effect of iodide ion concentration on reaction rate at low iodide concentrations. Therefore, the use of thallium ion to regulate the iodide ion concentration was next studied. In the presence of a high concentration of thallous ion, the iodide ion concentration should remain constant during a kinetic run if the solution is initially saturated in thallium iodide since any additional iodide ion formed during the reaction should precipitate as thallium iodide.

A preliminary experiment on iodination of p-nitrophenol in the presence of thallium ion under otherwise similar conditions was run. The results of such an experiment indicated that the reaction is too fast to be studied under the conditions used. The sources of error in this experiment were many. First, starting and stopping the reaction constituted the main source of error. The reaction was stopped by pouring the contents of the reaction flask into an excess of sodium thiosulfate in an Erlenmeyer flask. Another source of error in experiments with thallium perchlorate is that the starch end-points are not as sharp as in the previous experiments due to the formation of a greenish-blue color. Table 19 shows that there is a drop in the apparent rate constants. A plot of rate constants versus per cent reaction gave a value of 17.80×10^{-2} l./mole sec.

It is established that the reactivity of p-nitrophenoxide ion is greater than that of p-nitrophenol toward electrophilic substitution and the addition of acids to aqueous solution of p-nitrophenol depresses the ionization of the latter. Therefore, in order to obtain accurate measurement of reaction time, the iodination of p-nitrophenol was repeated in the presence of thallium perchlorate (0.050 M) at higher acidity (0.04910 M). The rate constants were constant throughout the run within the limits of experimental error. The rate constants were averaged and a value of $2.36 \pm 0.15 \times 10^{-2}$ l./mole sec. was obtained (See Table 20, Run 56-V-2). The same run was checked in order to see the reproducibility of the experiment and an average value of $2.26 \pm 0.14 \times 10^{-2}$ l./mole sec. was obtained (Table 21, Run 58-V-2). Further checks were done and the results were in fair agreement (See Table 22, Run 55-V-2, and Table 23, Run 138-V-1).

In order to understand the mechanism of iodination of p-nitrophenol, the effect of hydrogen ion on reaction rates had to be investigated. Thus the iodination of p-nitrophenol was studied at varying iodide ion concentration and at different acidities.

The first run was done in 25.00×10^{-7} M sodium iodide and 0.003273 M perchloric acid. A three fold decrease in hydrogen ion concentration increased the reaction velocity by approximately three fold. The apparent rate constants were averaged at this iodide ion concentration and gave a value of $3.23 \pm 0.12 \times 10^{-3}$ l./mole sec. and the calculated value of k' was 141.9×10^{-7} sec.$^{-1}$. (See Table 24, Run 87-V-1).

The iodination of p-nitrophenol at 0.003273 M perchloric acid was also studied at lower iodide ion concentrations. Unfortunately, it was not possible to perform runs below 0.5×10^{-4} M iodide ion concentrations, since at this acidity runs with lower iodide concentrations are too fast to be measured with the standard technique.

The effect of another three fold change in hydrogen ion concentration was investigated at different iodide ion concentrations. Thus the iodination of p-nitrophenol at 8.00×10^{-4} M in sodium iodide and 0.00109 M in perchloric acid was run. The apparent rate constants dropped slightly. Extrapolation of rate constants to zero time gave a value of 4.30×10^{-2} l./mole sec. The calculated value of k' was 419.6 $\times 10^{-7}$ sec.$^{-1}$. (Table 29, Run 97-V-1). The iodination of p-nitrophenol at this low acidity was studied at several iodide ion concentrations. The lowest iodide ion concentration investigated at this acidity was 1.00×10^{-4} M. However, the experimental results were unreliable. Thus in an experiment at 1.00×10^{-4} M in perchloric acid, the extrapolated value of apparent rate constant was o.262 l./mole sec. and the value of k' was 237.9 sec.$^{-1}$. (Table 35, Run 96-V-1). However, the same experiment when repeated under the same iodide ion and hydrogen ion concentration gave an extrapolated value of rate constant 0.348 l./mole sec. and the value of k' was 333.5×10^{-7} sec.$^{-1}$ (Table 36, Run 90-V-1). It seems reasonable to conclude that such experiments are unreliable. In order to be able to make accurate kinetic runs at such low hydrogen ion concentration, it is necessary to use a more efficient buffering system.

In order to have further insight about the dependence of reaction rate on hydrogen ion concentration, the iodination of p-nitrophenol was studied at higher hydrogen ion concentration (0.04910 M). Unfortunately, it was not possible to study the reaction at high iodide ion concentrations at this high perchloric acid concentration since the oxidation of iodide to iodine becomes more prominent at high acidities. Furthermore, the reaction is much slower at high acidities hence a comparison of rates between p-nitrophenol and its deuterated derivative at high iodide ion and high hydrogen concentration becomes difficult sine it is expected that hydrogen-deuterium exchange will take place at prolonged reaction intervals. For this reason, the iodination of p-nitrophenol at 0.04910 M perchloric acid was studied at fairly low iodide ion concentrations. (See Tables 37 and 38).

In order to confirm the reaction order with respect to p-nitrophenol the iodination of p-nitrophenol was carried out at 1.00×10^{-4} M sodium iodide, at two different p-nitrophenol concentrations and at exactly the same iodine and perchloric acid concentrations. Tables 39 and 40, show that a three fold change in p-nitrophenol concentration, does not effect the value of apparent rate constant or the value of k'. Comparison of Tables 39 and 40 with Tables 10, 11, and 12 show that within another three fold change in p-nitrophenol concentration, the values of k_{app} are essentially constant.

Kinetic Reactions of 4-Nitrophenol-2,6-d_2.--The preparation of

4-nitrophenol-2,6-d_2 is described in Chapter III. However, at this point it was essential to find whether complete deuteration was achieved. Thus, the iodination of twice equilibrated p-nitrophenol (this compound is designated as partially deuterated p-nitrophenol) was studied under the conditions of 65.0×10^{-4} M iodide ion, 0.009820 M perchloric acid and 0.3000 in ionic strength at 30°. Examination of Table 41, Run 103-V-1, reveals that the apparent rate constants fall as the reaction proceeds. This is, however, contrary to what is expected from runs at high iodide ion concentration, since the increase in iodide ion concentration, is negligible compared t the intital stoichiometric iodide ion concentration. However, such a drop in apparent rate constants is to be expected for the reaction of iodine and partially deuterated p-nitrophenol. The extrapolated value of rate constant was 4.95×10^{-5}. This value was compared with the corresponding value of rate constant on p-nitrophenol (see Table 3, Run 54-V-1) and a deuterium isotope effect (k^H_{app}/k^D_{app}) of 4.01 was obtained. Similarly, the iodination of partially deuterated p-nitrophenol at 25.00×10^{-4} M sodium iodide was studied under similar experimental conditions (See Table 42, Run 102-V-1). The fall in apparent rate constants was also significant in this case. The rate constants were plotted versus per cent reaction and an extrapolated value of 2.55×10^{-4} l./mole sec. was obtained. Comparison of this value with the average rate constant obtained in the iodination of p-nitrophenol at the same iodide ion and hydrogen ion concentration (Table 1, Run 32-V-1) gave a deuterium isotope effect of 4.34.

The iodination of 4-nitrophenol-2,6-d_2 (prepared by three equilibrations with heavy water) was next studied at 25.00×10^{-4} M sodium idodide, in order to see whether any change in the magnitude of deuterium isotope effect may result. As contrasted to the previous run (Table 42), the apparent rate constants remained fairly constant and when averaged gave a value of $2.06 \pm 0.06 \times 10^{-4}$ l./mole sec. and the value of k' was 9.56×10^{-7} sec.$^{-1}$ (Table 43, Run 104-V-1). Comparison of these values with that of p-nitrophenol (Table 1, Run 32-V-1) gives a value of 5.32 for the deuterium isotope effect. Thus it may be concluded that the deuterated p-nitrophenol obtained by two equilibrations with heavy water was contaminated with some undeuterated compound.

The iodination of 4-nitrophenol-2,6-d_2 in 5.00×10^{-4} M sodium iodide was done at 0.009820 M perchloric acid. The rate constants were plotted versus per cent reaction to give a value of extrapolated rate constant of 2.00×10^{-3} l./mole sec. The calculated value of k' was 10.6×10^{-7} sec.$^{-1}$. (Table 44, Run 132-V-1). The magnitude of deuterium isotope effect (k^H_{app}/k^D_{app}) was 4.55. The same experiment was repeated as a check and the value of extrapolated rate constant was found to be 2.08×10^{-3} l./mole sec., and the calculated value of k' was 9.81×10^{-7} sec.$^{-1}$ (See Table 45, Run 13-V-1).

The iodination of 4-nitrophenol-2,6-d_2 in 1.000×10^{-4} M sodium iodide was performed. The plot of apparent rate constants versus per cent reaction and extrapolated to zero time gave an apparent rate constant of 8.67×10^{-3} l./mole sec. The calculation of k' gave a value of 8.20×10^{-7} sec.$^{-1}$. The kinetic isotope ratio of (k^H_{app}/k^D_{app}) gave a value of 4.65. This isotope ratio is close to that obtained in 5.00 $\times 10^{-4}$ M sodium iodide solution.

The iodination of 4-nitrophenol-2,6-d_2 in 0.5000 x 10^{-4} M sodium iodide was performed. The apparent rate constants were extrapolated to zero time and a value of 15.8 x 10^{-3} l./mole sec. was obtained. The calculated value of k' was 7.32 x 10^{-7} sec.$^{-1}$ (See Table 47, Run 109-V-1). The same run was repeated and the value of extrapolated k_{app} was found to be 14.50 x 10^{-3} l./mole sec. The calculated value of k' was 6.20 x 10^{-7} sec.$^{-1}$ (Table 48, Run 105-V-1). A comparison with the corresponding protio compound (Table 15, Run 30-V-1) gives a kinetic isotope effect (k^H_{app}/k^D_{app}) of 3.85.

To have more conclusive evidence regarding the drop in deuterium isotope effect, the iodination of 4-nitrophenol-2,6-d_2 was performed at the lower iodide ion concentration of 0.2500 x 10^{-4} M. The apparent rate constants plotted versus per cent reaction and extrapolated to zero time gave a value of 2.62 x 10^{-2} l./mole sec. The calculation of k' gave a value of 6.25 x 10^{-7} sec. $^{-1}$ (See Table 49, Run 107-V-1). The k' value at 0.2500 x 10^{-4} M sodium iodide for the protium compound as indicated in Table 16, was 8.75 x 10^{-2} l./mole sec. The kinetic isotope ratio of (k^H_{app}/k^D_{app}) was 3.34. This isotope ratio is still lower than the previous value.

The iodination of deuterated p-nitrophenol at 0.1000 x 10^{-4} M sodium iodide was done. As expected, the rate constants fell sharply as the reaction proceeded. The extrapolated rate constant was found to be 7.80 x 10^{-2} l./mole sec. and the value of k' was 7.41 x 10^{-7} sec. $^{-1}$. (Table 50, Run 106-V-1). A comparison with the corresponding run on the protio compound gave a deuterium isotope effect of 1.96.

The iodination of 4-nitrophenol-2,6-d_2 in the presence of thallium perchlorate (0.0500 M) was performed in perchloric acid solution (0.0491 M). A slight downward drift was observed. However, to compare the apparent rate constant with that of protio compound, an average of the rate constant was taken and was found to be $0.974 \pm 0.064 \times 10^{-2}$ l./mole sec. (Table 51, Run 57-V-2). The same run was repeated and an average rate constant of $0.820 \pm 0.043 \times 10^{-2}$ was obtained. (Table 57, Run 139-V-1). Comparison of this two values with that of protium compound in Table 20, gave a value of 2.43 and 2.88 respectively for the magnitude of deuterium isotope effect.

Table 1

Run 32-V-1, p-Nitrophenol in 25.00 x 10^{-4} M Sodium Iodide Solution at 50.0°

(p-Nitrophenol)$_o$ - 0.007699 M

$(I_2)_o$ - 0.0005124 M

$(NaI)_o$ - 25.00 x 10^{-4} M

$(HClO_4)$ - 0.009820 M

$(NaClO_4)$ - 0.2877 M

$(Na_2S_2O_3)$ - 0.006990 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^4 (l./mole sec.)	Per cent reaction
(blank)	7.33		0.00
13,662	6.53	11.09	10.98
22,420	6.07	10.99	17.19
33,252	5.53	11.11	24.50
44,374	5.02	11.21	31.20
73,310	4.05	10.61	44.37
73,555	4.01	10.75	45.07
114,912	2.97	10.08	58.23

Average value of rate constant (k_{app}) = 10.94 ± 0.29 x 10^{-4} l./mole sec.

k' = 51.2 ± 1.4 x 10^{-7} sec.$^{-1}$

k^* = 2.29 x 10^{-3} l./mole sec.

$1/k^* \times [H^+]$ = 44.5 x 10^3 sec.

$[I^-]_o$ = 22.323 x 10^{-4} mole/l.

Table 2

Run 39-V-1, p-Nitrophenol in 25.00 x 10^{-4} M Sodium Iodide Solution at 50.0°

(p-Nitrophenol)$_o$ - 0.007699 M

$(I_2)_o$ - 0.0005250 M

$(NaI)_o$ - 25.00 x 10^{-4} M

$(HClO_4)$ - 0.009820 M

$(NaClO_4)$ - 0.2877 M

$(Na_2S_2O_3)$ - 0.005991 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^4 (l./mole sec.)	Per cent reaction
(blank)	8.76		0.00
12,735	7.86	11.09	10.27
20,840	7.35	11.04	16.09
27,380	6.90	11.39	21.23
36,957	6.31	11.65	27.96
84,340	4.42	10.74	49.54

Average value of rate constant (k_{app}) = 11.18 ± 0.30 x 10^{-4} l./mole sec.

k' = 52.0 x 10^{-7} sec.$^{-1}$

k^* = 2.33 x 10^{-3} l./mole sec.

$1/k^* [H^+]$ = 43.7 x 10^3 sec.

$[I^-]_o$ = 22.260 x 10^{-4} mole/l.

Table 3

Run 54-V-1, p-Nitrophenol in 65.00×10^{-4} M Sodium Iodide Solution at 50.0°

(p-Nitrophenol)$_o$ - 0.007699 M

$(I_2)_o$ - 0.0004570 M

$(NaI)_o$ - 65.00×10^{-4} M

$(HClO_4)$ - 0.009820 M

$(NaClO_4)$ - 0.2837 M

$(Na_2S_2O_3)$ - 0.005991 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^5 (l./mole sec.)	Per cent reaction
(blank)	7.63		0.00
68,473	6.90	19.11	9.56
152,455	5.97	21.03	21.75
240,778	5.24	20.47	31.32
329,057	4.54	19.84	39.14
423,270	3.95	19.82	47.05
593,894	3.12	18.94	57.26

Average value of rate constant (k_{app}) = $19.87 \pm 0.42 \times 10^{-5}$ l./mole sec.

k' = 49.1×10^{-7} sec.$^{-1}$

k^* = 0.798×10^{-3} l./mole sec.

$1/k^* [H^+]$ = 12.8×10^4 sec.

$[I^-]_o$ = 61.567×10^{-4} mole/l.

Table 4

Run 56-V-1, p-Nitrophenol in 125.00 x 10^{-4} M Sodium Iodide Solution at 50.0°

(p-Nitrophenol)$_o$ - 0.007699 M

$(I_2)_o$ - 0.0003980 M

$(NaI)_o$ - 125.00 x 10^{-4} M

$(HClO_4)$ - 0.009820 M

$(NaClO_4)$ - 0.2777 M

$(Na_2S_2O_3)$ - 0.005991 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^5 (l./mole sec.)	Per cent reaction
(blank)	6.65		0.00
249,060	5.95	6.02	10.52
503,003	5.26	6.08	20.90
850,405	4.41	6.33	33.60
1,372,375	3.45	6.29	48.12
1,803,560	2.88	6.13	56.60

Rate constant extrapolated to zero time (k_{app}) = 6.17 ± 0.11 x 10^{-5} l./mole sec.

k' = 52.4 x 10^{-7} sec.$^{-1}$

k^* = 0.431 x 10^{-3} l./mole sec.

$1/k^* [H^+]$ = 23.7 x 10^4 sec.

$[I^-]_o$ = 121.59 x 10^{-4} mole/l.

Table 5

Run 52-V-1, p-Nitrophenol in 12.00 x 10^{-4} M Sodium Iodide Solution at 50.0°

(p-Nitrophenol)$_o$ - 0.007699 M

(I_2)$_o$ - 0.0003690 M

(NaI)$_o$ - 12.00 x 10^{-4} M

($HClO_4$) - 0.009820 M

($NaClO_4$) - 0.2890 M

($Na_2S_2O_3$) - 0.005991 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^4 (l./mole sec.)	Per cent reaction
(blank)	6.17		0.00
5,973	5.46	26.6	11.50
11,343	4.90	26.5	20.50
19,496	4.17	25.2	31.30
26,520	3.67	24.9	39.54
31,417	3.32	25.2	45.30

Rate constant extrapolated to zero time (k_{app}) = 27.4 x 10^{-4} l./mole sec.

k' = 44.9 x 10^{-7} $sec.^{-1}$

k^* = 4.17 x 10^{-3} l./mole sec.

$1/k^* [H^+]$ = 24.5 x 10^3 sec.

$[I^-]_o$ = 10.726 x 10^{-4} mole/l.

Table 6

Run 53-V-1, p-Nitrophenol in 12.00 x 10^{-4} M Sodium Iodide Solution at 50.0°

(p-Nitrophenol)$_o$ - 0.007699 M

$(I_2)_o$ - 0.0003680 M

$(NaI)_o$ - 12.00 x 10^{-4} M

$(HClO_4)$ - 0.009820 M

$(NaClO_4)$ - 0.2890 M

$(Na_2S_2O_3)$ - 0.005991 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^4 (l./mole sec.)	Per cent reaction
(blank)	6.15		0.00
6,173	5.40	27.4	12.19
10,755	4.93	26.8	19.83
16,765	4.40	26.1	28.45
25,428	3.72	25.9	39.51
35,660	3.13	24.9	49.11

Rate constant extrapolated to zero time (k_{app}) = 28.3 x 10^{-4} l./mole sec.

k' = 46.3 x 10^{-7} sec.$^{-1}$

k^* = 4.30 x 10^{-3} l./mole sec.

$1/k^* [H^+]$ = 23.6 x 10^3 sec.

$[I^-]_o$ = 10.730 x 10^{-4} mole/l.

Table 7

Run 43-V-1*, p-Nitrophenol in 5.000×10^{-4} M Sodium Iodide Solution at 50.0°

(p-Nitrophenol)$_o$ - 0.007699 M

(HClO$_4$) - 0.009820 M

$(I_2)_o$ - 0.0004840 M

(NaClO$_4$) - 0.2852 M

(NaI)$_o$ - 5.000×10^{-4} M

($Na_2S_2O_3$) - 0.005991 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	8.08		0.00
1,755	7.17	8.86	11.26
2,448	6.92	8.26	14.35
4,088	6.27	8.12	22.40
5,750	5.56	7.91	31.19
10,530	4.52	7.22	44.06

Rate constant extrapolated to zero time (k_{app}) = 9.10×10^{-3} l./mole sec.

k' = 45.8×10^{-7} sec.$^{-1}$

k^* = 11.0×10^{-3} l./mole sec.

$1/k^* [H^+]$ = 9.26×10^3 sec.

$[I^-]_o$ = 4.1774×10^{-4} mole/l.

*This run was performed in ordinary distilled water, in which iodine was dissolved directly.

Table 8

Run 55-V-1, p-Nitrophenol in 5.000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(p-Nitrophenol)$_0$ - 0.007699 M

$(I_2)_0$ - 0.0004330 M

$(NaI)_0$ - 5.000 x 10^{-4} M

$(HClO_4)$ - 0.009820 M

$(NaClO_4)$ - 0.2852 M

$(Na_2S_2O_3)$ - 0.005991 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	7.22		0.00
1,786	6.40	8.80	11.36
2,888	6.05	7.98	16.20
4,643	5.52	7.56	23.54
6,138	5.09	7.10	28.31
14,116	3.53	6.53	50.20
19,119	2.95	6.04	58.20

Rate constant extrapolated to zero time (k_{app}) = 8.70 x 10^{-3} l./mole sec.

k' = 44.7 x 10^{-7} sec.$^{-1}$

k^* = 10.5 x 10^{-3} l./mole sec.

$1/k^* [H^+]$ = 9.70 x 10^3 sec.

$[I^-]_0$ = 4.2540 x 10^{-4} mole/l.

Table 9

Run 51-V-1, p-nitrophenol in 2.500×10^{-4} M Sodium Iodide Solution at 50°

(p-Nitrophenol)$_o$ - 0.007699 M

$(HClO_4)$ - 0.009820 M

$(I_2)_o$ - 0.0004056 M

$(NaClO_4)$ - 0.2899 M

$(NaI)_o$ - 2.500×10^{-4} M

$(Na_2S_2O_3)$ - 0.005991 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	6.77		0.00
931	6.01	16.7	11.22
1,527	5.54	16.0	17.06
2,218	5.18	15.0	22.45
2,950	4.90	13.7	26.64
4,328	4.27	13.6	36.07
6,688	3.50	12.7	47.60
9,263	3.15	10.7	52.84

Rate constant extrapolated to zero time (k_{app}) = 17.9×10^{-3} l./mole sec.

k' = 41.9×10^{-7} sec.$^{-1}$

k^* = 19.8×10^{-3} l./mole sec.

$1/k^* [H^+]$ = 5.14×10^3 sec.

$[I^-]_o$ = 2.1190×10^{-4} mole/l.

Table 10

Run 36-V-1, p-Nitrophenol in 1.000×10^{-4} M Sodium Iodide Solution at 50.0^{o}

(p-Nitrophenol)$_o$ - 0.007699 M

$(I_2)_o$ - 0.0004900 M

$(NaI)_o$ - 1.000×10^{-4} M

$(HClO_4)$ - 0.009820 M

$(NaClO_4)$ - 0.2901 M

$(Na_2S_2O_3)$ - 0.005991 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	8.18		0.00
400	7.30	3.70	10.15
896	6.59	3.15	19.44
1,410	6.01	2.86	26.53
2,229	5.37	2.48	34.35
3,575	4.45	2.24	45.59
8,185	2.91	1.64	63.71

Rate constant extrapolated to zero time (k_{app}) = 4.10×10^{-2} l./mole sec.

k' = 33.6×10^{-7} sec.$^{-1}$

k^{*} = 41.5×10^{-3} l./mole sec.

$1/k^{*} \times [H^{+}]$ = 2.45×10^{3} sec.

$[I^{-}]_o$ = 0.8090×10^{-4} mole/l.

Table 11

Run 37-V-1*, p-Nitrophenol in 1.000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(p-Nitrophenol)$_o$ - 0.007699 M

$(I_2)_o$ - 0.0002820 M

$(NaI)_o$ - 1.000 x 10^{-4} M

$(HClO_4)$ - 0.009820 M

$(NaClO_4)$ - 0.2901 M

$(Na_2S_2O_3)$ - 0.005991 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	9.41		0.00
355	8.45	3.95	10.20
592	7.94	3.74	15.62
1,026	7.28	3.19	22.63
1,711	6.16	3.24	34.58
3,138	5.02	2.62	46.65
8,193	2.76	1.97	70.67

Rate constant extrapolated to zero time (k_{app}) = 4.30 x 10^{-2} l./mole sec.

k' = 39.6 x 10^{-7} sec.$^{-1}$

k^* = 44.8 x 10^{-3} l./mole sec.

$1/k^* [H^+]$ = 2.27 x 10^3 sec.

$[I^-]_o$ = 0.8830 x 10^{-4} mole/l.

*This run was performed in ordinary distilled water in which iodine was dissolved directly.

Table 12

Run 42-V-1, p-Nitrophenol in 1.000×10^{-4} M Sodium Iodide Solution at 50.0°

$(\text{p-Nitrophenol})_o$ = 0.007699 M

$(HClO_4)$ = 0.009820 M

$(I_2)_o$ = 0.0004490 M

$(NaClO_4)$ = 0.2901 M

$(NaI)_o$ = 1.000×10^{-4} M

$(Na_2S_2O_3)$ = 0.005991 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	7.50		0.00
372	6.75	3.68	10.00
556	6.47	3.46	13.73
975	5.96	3.07	20.53
1,684	5.17	2.89	31.06
4,095	3.76	2.22	49.86

Rate constant extrapolated to zero time (k_{app}) = 4.04×10^{-2} l./mole sec.

k' = 34.7×10^{-7} sec.$^{-1}$

k^* = 42.0×10^{-3} l./mole sec.

$1/k^* [H^+]$ = 2.42×10^3 sec.

$[I^-]_o$ = 0.8254×10^{-4} mole/l.

Table 13

Run 46-V-1, p-Nitrophenol in 1.000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(p-Nitrophenol)$_o$ - 0.007699 M

($HClO_4$) - 0.009820 M

$(I_2)_o$ - 0.0002020 M

($NaClO_4$) - 0.2901 M

$(NaI)_o$ - 1.000 x 10^{-4} M

($Na_2S_2O_3$) - 0.005991 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	6.73		0.00
406	6.03	3.58	10.40
665	5.67	3.40	15.75
1,016	5.25	3.20	21.89
1,462	4.92	2.68	26.02
2,325	4.06	2.77	38.94
3,285	3.48	2.48	46.46

Rate constant extrapolated to zero time (k_{app}) = 4.00 x 10^{-2} l./mole sec.

k' = 38.2 x 10^{-7} sec.$^{-1}$

k^* = 41.8 x 10^{-3} l./mole sec.

$1/k^* \left[H^+\right]$ = 2.44 x 10^3 sec.

$\left[I^-\right]_o$ = 0.9135 x 10^{-4} mole/l.

Table 14

Run 48-V-1, 4-Nitrophenol in 0.5000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(4-Nitrophenol)$_o$ = 0.007699 M

$(I_2)_o$ = 0.0002070 M

$(NaI)_o$ = 0.5000 x 10^{-4} M

$(HClO_4)$ = 0.009820 M

$(NaClO_4)$ = 0.2990 M

$(Na_2S_2O_3)$ = 0.005991 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	6.91		0.00
355	5.97	5.37	13.60
560	5.50	5.33	20.40
936	5.20	3.96	24.70
1,135	4.80	4.07	29.82
1,723	4.03	3.85	39.85
2,350	3.63	3.41	45.82

Rate constant extrapolated to zero time (k_{app}) = 6.60 x 10^{-2} l./mole sec.

k' = 30.3 x 10^{-7} sec.$^{-1}$

k^* = 6.16 x 10^{-2} l./mole sec.

$1/k^* \left[H^+\right]$ = 1.65 x 10^3 sec.

$\left[I^-\right]_o$ = 0.4450 x 10^{-4} mole/l.

Table 15

Run 80-V-1, 4-Nitrophenol in 0.5000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(4-Nitrophenol)$_o$ = 0.007699 M

$(I_2)_o$ = 0.0003060 M

$(NaI)_o$ = 0.5000 x 10^{-4} M

$(HClO_4)$ = 0.009820 M

$(NaClO_4)$ = 0.2901 M

$(Na_2S_2O_3)$ = 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	10.16		0.00
387	8.67	5.43	14.66
602	7.95	5.30	21.75
927	7.46	4.34	26.57
1,505	6.72	3.59	33.86
2,169	5.53	3.49	43.86
2,641	5.48	2.91	44.36

Rate constant extrapolated to zero time (k_{app}) = 6.40 x 10^{-2} l./mole sec.

k' = 29.0 x 10^{-7} sec.$^{-1}$

k^* = 61.5 x 10^{-3} l./mole sec.

$1/k^* [H^+]$ = 1.66 x 10^3 sec.

$[I^-]_o$ = 0.4360 x 10^{-4} mole/l.

Table 16

Run 81-V-1, 4-Nitrophenol in 0.2500×10^{-4} M Sodium Iodide Solution at 50.0°

(4-Nitrophenol)$_o$ = 0.007699 M

(HClO$_4$) = 0.009820 M

$(I_2)_o$ = 0.0001396 M

(NaClO$_4$) = 0.2902 M

(NaI)$_o$ = 0.2500×10^{-4} M

($Na_2S_2O_3$) = 0.012038 M

200 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	4.64		0.00
180	4.15	8.04	10.56
342	3.83	7.32	17.45
575	3.42	6.90	26.29
900	3.05	6.07	34.26
1,299	2.65	5.61	42.89
2,061	2.10	5.02	54.74

Rate constant extrapolated to zero time (k_{app}) = 8.75×10^{-2} l./mole sec.

k' = 21.4×10^{-7} sec.$^{-1}$

k^* = 91.06×10^{-3} l./mole sec.

$1/k^* \left[H^+\right]$ = 1.12×10^3 sec.

$\left[I^-\right]_o$ = 0.2350×10^{-4} mole/l.

Table 17

Run 82-V-1, 4-Nitrophenol in 0.1000×10^{-4} M Sodium Iodide Solution at 50.0°

(4-Nitrophenol)$_o$ = 0.007699 M

$(HClO_4)$ = 0.009820 M

$(I_2)_o$ = 0.0001017 M

$(NaClO_4)$ = 0.2902 M

$(NaI)_o$ = 0.1000×10^{-4} M

$(Na_2S_2O_3)$ = 0.012038 M

200.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	3.38		0.00
164	3.08	13.38	8.87
295	2.85	13.48	15.68
450	2.35	10.86	21.89
627	2.22	10.52	30.47
1,195	1.62	8.72	34.32

Rate constant extrapolated to zero time (k_{app}) = 15.25×10^{-2} l./mole sec.

k' = 14.6×10^{-7} sec.$^{-1}$

k^* = 153.2×10^{-3} l./mole sec.

$1/k^* \left[H^+\right]$ = 6.65×10^2 sec.

$\left[I^-\right]_o$ = 0.0953×10^{-4} mole/l.

Table 18

Run 108-V-1, 4-Nitrophenol in 0.1000 x 10^{-4} M Sodium Iodide Solution at 50.0°

$(4\text{-Nitrophenol})_o$ = 0.007699 M

$(HClO_4)$ = 0.009820 M

$(I_2)_o$ = 0.0001144 M

$(NaClO_4)$ = 0.2902 M

$(NaI)_o$ = 0.1000 x 10^{-4} M

$(Na_2S_2O_3)$ = 0.012038 M

200.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	3.80		0.00
120	3.40	12.11	10.53
219	3.19	10.41	16.05
435	2.84	8.71	25.26
687	2.58	7.35	32.10
992	2.24	6.95	41.05
1,249	1.95	6.96	48.00

Rate constant extrapolated to zero time (k_{app}) = 15.20 x 10^{-2} l./mole sec.

k' = 14.5 x 10^{-7} sec.$^{-1}$

k^* = 153.1 x 10^{-3} l./mole sec.

$1/k^* \left[H^+\right]$ = 6.65 x 10^2 sec.

I^-_o = 0.0947 x 10^{-4} mole/l.

Table 19

Run 49-V-2, 4-Nitrophenol in 0.0500 M Thallium Perchlorate Solution at 50.0°

(4-Nitrophenol)$_o$ = 0.007699 M

$(I_2)_o$ = 0.0002100 M

(NaI) = 0.00015 M

$(TlClO_4)_o$ = 0.0500 M

$(HClO_4)$ = 0.009820 M

$(NaClO_4)$ = 0.1902 M

$(Na_2S_2O_3)$ = 0.006019 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	3.49		0.00
83	3.16	15.60	9.45
148	2.96	14.50	15.18
237	2.70	12.08	22.60
547	2.38	9.13	31.80

Rate constant extrapolated to zero time (k_{app}) = 17.80 x 10^{-2} l./mole sec.

Table 20

Run 56-V-2, 4-Nitrophenol in 0.0500 M Thallium Perchlorate Solution at 50.0°

(4-Nitrophenol)$_o$ = 0.007699 M

$(I_2)_o$ = 0.0002730 M

$(NaI)_o$ = 0.000200 M

$(TlClO_4)_o$ = 0.0500 M

$(HClO_4)$ = 0.04910 M

$(NaClO_4)$ = 0.2019 M

$(Na_2S_2O_3)$ = 0.006019 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	4.54		0.00
607	4.11	2.13	9.47
1,149	3.74	2.20	17.62
1,986	3.09	2.50	31.90
2,820	2.58	2.60	43.17
4,864	1.83	2.45	59.69

Average value of rate constant (k_{app}) = 2.360 ± 0.15 x 10^{-2} l./mole sec.

Table 21

Run 58-V-2, 4-Nitrophenol in 0.0500 M Thallium Perchlorate Solution at 50.0°.

(4-Nitrophenol)$_o$ - 0.007699 M

$(I_2)_o$ - 0.0002910 M

$(NaI)_o$ - 0.000200 M

$(TlClO_4)_o$ - 0.0500 M

$(HClO_4)$ - 0.04910 M

$(NaClO_4)$ - 0.2011 M

$(Na_2S_2O_3)$ - 0.006019 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec)	Per cent reaction
(blank)	4.84		0.00
620	4.25	2.73	12.19
1107	3.98	2.30	17.77
1823	3.55	2.22	26.65
2539	3.11	2.27	35.74
3373	2.65	2.34	45.24
4267	2.50	2.03	48.34
5511	2.14	1.95	55.78

Average value of rate constant (k_{app}) = 2.26 0.14 x 10^{-2} l./mole sec.

Table 22

Run 55-V-2, p-Nitrophenol in 0.0500 M Thallium Perchlorate Solution at 50.0°

(p-Nitrophenol)$_o$ = 0.007699 M

$(I_2)_o$ = 0.0003240 M

$(NaI)_o$ = 0.000200 M

$(TlClO_4)_o$ = 0.0500 M

$(HClO_4)$ = 0.04910 M

$(NaClO_4)$ = 0.2019 M

$(Na_2S_2O_3)$ = 0.006019 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	5.39		0.00
689	4.58	3.07	15.03
1,088	4.40	2.43	18.37
2,373	3.56	2.28	33.95
2,890	3.24	2.31	39.89
3,754	2.72	2.38	49.50
4,388	2.29	2.57	57.50

Average value of rate constant (k_{app}) = 2.51 ± 0.19 x 10^{-2} l./mole sec.

Table 23

Run 138-V-1, p-Nitrophenol in 0.0500 M Thallium Perchlorate Solution at 50.0°

(p-Nitrophenol)$_o$ = 0.007699 M

$(I_2)_o$ = 0.0002600 M

$(NaI)_o$ = 0.000200 M

$(TlClO_4)$ = 0.0500 M

$(HClO_4)$ = 0.04910 M

$(NaClO_4)$ = 0.2011 M

$(Na_2S_2O_3)$ = 0.006019 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	4.32		0.00
692	3.83	2.26	11.34
1,275	3.42	2.39	20.83
2,105	2.96	2.34	31.48
2,776	2.43	2.48	41.01
3,773	2.16	2.24	47.57
5,478	1.71	2.10	58.49
7,520	1.20	1.72	70.87

Average value of rate constant (k_{app}) = 2.22 x 0.17 x 10^{-2} l./mole sec.

Table 24

Run 87-V-1, p-Nitrophenol in 25.00 x 10^{-4} M Sodium Iodide Solution at 50.0°

(p-Nitrophenol)$_o$ = 0.007699 M

(HClO$_4$) = 0.003273 M

(I_2)$_o$ = 0.0006960 M

(NaClO$_4$) = 0.2942 M

(NaI)$_o$ = 25.00 x 10^{-4} M

($Na_2S_2O_3$) = 0.006019 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	5.78		0.00
2,920	5.35	3.46	7.44
6,946	4.85	3.31	16.09
8,768	4.68	3.16	19.03
11,362	4.40	3.15	23.87
13,048	4.25	3.10	26.47

Average value of rate constant (k_{app}) = 3.23 ± 0.12 x 10^{-3} l./mole sec.

k' = 141.9 x 10^{-7} $sec.^{-1}$

k^* = 6.62 x 10^{-3} l./mole sec.

$1/k^* [H^+]$ = 46.1 x 10^3 sec.

$[I^-]_o$ = 21.436 x 10^{-4} mole/l.

Table 25

Run 85-V-1, p-Nitrophenol in 5.000×10^{-4} M Sodium Iodide Solution at 50.0°

$(\text{p-Nitrophenol})_o$ = 0.007699 M

$(I_2)_o$ = 0.0002680 M

$(NaI)_o$ = 5.000×10^{-4} M

$(HClO_4)$ = 0.003273 M

$(NaClO_4)$ = 0.2962 M

$(Na_2S_2O_3)$ = 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	8.92		0.00
501	8.10	2.49	9.19
758	7.85	2.19	11.99
1,212	7.15	2.37	19.84
1,734	6.70	2.15	24.88
2,676	5.60	2.28	37.22
3,463	5.35	1.93	40.00

Average value of rate constant (k_{app}) = $2.24 \pm 0.14 \times 10^{-2}$ l./mole sec.

k' = 123.4×10^{-7} sec.$^{-1}$

k^* = 27.3×10^{-3} l./mole sec.

$1/k^* \, [H^+]$ = 11.2×10^3 sec.

$[I^-]_o$ = 4.514×10^{-4} mole/l.

Table 26

Run 84-V-1, p-Nitrophenol in 2.500 x 10^{-4} M Sodium Iodide Solution at 50.0°

(p-Nitrophenol)$_o$ = 0.007699 M

(HClO$_4$) = 0.003273 M

(I_2)$_o$ = 0.0002030 M

(NaClO$_4$) = 0.2965 M

(NaI)$_o$ = 2.500 x 10^{-4} M

($Na_2S_2O_3$) = 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	9.74		0.00
503	8.20	4.45	15.89
832	7.25	4.63	25.64
1,068	6.95	4.13	28.72
1,420	6.27	4.06	35.69
1,958	5.40	3.82	45.55

Rate constant extrapolated to zero time (k_{app}) = 4.90 x 10^{-2} l./mole sec.

k' = 120.0 x 10^{-7} sec.$^{-1}$

k^* = 54.2 x 10^{-3} l./mole sec.

$1/k^* \, [H^+]$ = 5.64 x 10^3 sec.

$[I^-]_o$ = 2.213 x 10^{-4} mole/l.

Table 27

Run 88-V-1, p-Nitrophenol in 1.000×10^{-4} M Sodium Iodide Solution at 50.0°

(p-Nitrophenol)$_o$ = 0.007699 M

$(I_2)_o$ = 0.0003120 M

$(NaI)_o$ = 1.000×10^{-4} M

$(HClO_4)$ = 0.003273 M

$(NaClO_4)$ = 0.2966 M

$(Na_2S_2O_3)$ = 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	10.35		0.00
97	9.52	11.22	8.02
177	9.02	10.12	12.85
300	8.40	9.08	18.84
529	7.38	8.36	28.69
759	6.65	7.64	35.75
1,273	5.43	6.58	47.53

Rate constant extrapolated to zero time (k_{app}) = 11.70×10^{-2} l./mole sec.

k' = 106.4×10^{-7} sec.$^{-1}$

k^* = 122.0×10^{-3} l./mole sec.

$1/k^* \, [H^+]$ = 2.50×10^{3} sec.

$[I^-]_o$ = 0.8720×10^{-4} mole/l.

Table 28

Run 89-V-1, p-Nitrophenol in 0.5000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(p-Nitrophenol)$_o$ = 0.007699 M

$(I_2)_o$ = 0.0003010 M

$(NaI)_o$ = 0.5000 x 10^{-4} M

$(HClO_4)$ = 0.003273 M

$(NaClO_4)$ = 0.2967 M

$(Na_2S_2O_3)$ = 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	10.00		0.00
74	9.15	15.63	8.50
96	8.93	15.39	10.70
163	8.40	13.95	16.00
300	7.43	12.94	25.71
552	6.42	9.78	35.80
920	5.10	9.61	49.00

Rate constant extrapolated to zero time (k_{app}) = 16.85 x 10^{-2} l./mole sec.

k' = 75.6 x 10^{-7} sec.$^{-1}$

k^* = 173.0 x 10^{-3} l./mole sec.

$1/k^* \times [H^+]$ = 1.77 x 10^3 sec.

$[I^-]_o$ = 0.4379 x 10^{-4} mole/l.

Table 29

Run 97-V-1, p-Nitrophenol in 8.000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(p-Nitrophenol)$_o$ = 0.007699 M

$(I_2)_o$ = 0.0003010 M

$(NaI)_o$ = 8.000 x 10^{-4} M

$(HClO_4)$ = 0.001091 M

$(NaClO_4)$ = 0.2981 M

$(Na_2S_2O_3)$ = 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	10.01		0.00
480	8.62	4.06	13.89
698	8.06	4.05	19.48
921	7.60	3.91	24.07
1,334	6.81	3.78	31.97
1,908	6.10	3.40	39.06
2,389	5.25	3.55	47.55

Rate constant extrapolated to zero time (k_{app}) = 4.30 x 10^{-2} l./mole sec.

k' = 419.6 x 10^{-7} sec.$^{-1}$

k^* = 58.2 x 10^{-3} l./mole sec.

$1/k^* \left[H^+\right]$ = 17.4 x 10^3 sec.

$\left[I^-\right]_o$ = 7.213 x 10^{-4} mole/l.

Table 30

Run 94-V-1, p-Nitrophenol in 6.000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(p-Nitrophenol)$_o$ = 0.007699 M

$(I_2)_o$ = 0.0002690 M

$(NaI)_o$ = 6.000 x 10^{-4} M

$(HClO_4)$ = 0.001091 M

$(NaClO_4)$ = 0.2989 M

$(Na_2S_2O_3)$ = 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	8.97		0.00
300	7.75	5.35	13.60
483	7.37	5.30	17.84
658	6.92	5.14	22.85
885	6.35	5.10	29.21
1,122	5.73	5.00	36.12
1,480	5.12	4.96	42.92

Rate constant extrapolated to zero time (k_{app}) = 5.60 x 10^{-2} l./mole sec.

k' = 385.2 x 10^{-7} sec.$^{-1}$

k^* = 70.9 x 10^{-3} l./mole sec.

$1/k^* \left[H^+\right]$ = 12.9 x 10^3 sec.

$\left[I^-\right]_o$ = 5.433 x 10^{-4} mole/l.

Table 31

Run 92-V-1, p-Nitrophenol in 4.000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(p-Nitrophenol)$_o$ - 0.007699 M

$(I_2)_o$ - 0.0003070 M

$(NaI)_o$ - 4.000 x 10^{-4} M

$(HClO_4)$ - 0.001091 M

$(NaClO_4)$ - 0.2989 M

$(Na_2S_2O_3)$ - 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	10.20		0.00
232	8.59	7.43	12.25
345	8.35	7.68	18.14
703	7.02	6.98	31.17
1,084	5.73	6.88	43.82
1,485	4.75	6.74	53.43

Rate constant extrapolated to zero time (k_{app}) = 7.85 x 10^{-2} l./mole sec.

k' = 327.0 x 10^{-7} sec.$^{-1}$

k^* = 92.2 x 10^{-3} l./mole sec.

$1/k^* \, [H^+]$ = 9.94 x 10^3 sec.

$[I^-]_o$ = 3.546 x 10^{-4} mole/l.

Table 32

Run 98-V-1, p-Nitrophenol in 3.000 x 10^{-4} Sodium Iodide Solution at 50.0°

(p-Nitrophenol)$_o$ - 0.007699 M

$(I_2)_o$ - 0.0002890 M

$(NaI)_o$ - 3.000 x 10^{-4} M

$(HClO_4)$ - 0.001091 M

$(NaClO_4)$ - 0.2986 M

$(Na_2S_2O_3)$ - 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant (l./mole sec.)	Per cent reaction
(blank)	9.60		0.00
121	8.35	0.150	13.65
147	8.30	0.129	14.17
227	8.06	0.103	16.64
357	7.05	0.114	27.09
467	6.75	0.094	28.60
654	5.85	0.096	38.10
871	5.10	0.092	46.03

Rate constant extrapolated to zero time (k_{app}) = 0.130 l./mole sec.

k' = 391.8 x 10^{-7} sec.$^{-1}$

k^* = 147.0 x 10^{-3} l./mole sec.

$1/k^* \left[H^+\right]$ = 6.24 x 10^3 sec.

$\left[I^-\right]_o$ = 2.666 x 10^{-4} mole/l.

Table 33

Run 95-V-1, p-Nitrophenol in 2.000 x 10^{-4} Sodium Iodide Solution at 50.0°

(p-Nitrophenol)$_o$ - 0.007699 M

$(I_2)_o$ - 0.0003110 M

$(NaI)_o$ - 2.000 x 10^{-4} M

$(HClO_4)$ - 0.001091 M

$(NaClO_4)$ - 0.2989 M

$(Na_2S_2O_3)$ - 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant (l./mole sec.)	Per cent reaction
(blank)	10.32		0.00
120	8.70	0.185	15.70
177	8.26	0.165	19.90
241	7.82	0.150	24.23
309	7.24	0.143	28.66
420	6.50	0.139	35.96
604	5.62	0.124	43.63

Rate constant extrapolated to zero time (k_{app}) = 0.190 l./mole sec.

k' = 362.0 x 10^{-7} sec.$^{-1}$

k^* = 206.4 x 10^{-3} l./mole sec.

$1/k^* \, [H^+]$ = 4.44 x 10^3 sec.

$[I^-]_o$ = 1.754 x 10^{-4} mole/l.

Table 34

Run 91-V-1, p-Nitrophenol in 2.000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(p-Nitrophenol)$_o$ - 0.007699 M

$(I_2)_o$ - 0.0001910 M

$(NaI)_o$ - 2.000 x 10^{-4} M

$(HClO_4)$ - 0.001091 M

$(NaClO_4)$ - 0.2989 M

$(Na_2S_2O_3)$ - 0.01204 M

200.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant (l/mole sec.)	Per cent reaction
(blank)	6.36		0.00
132	5.28	0.183	16.98
195	4.93	0.170	22.48
293	4.35	0.169	31.60
480	3.68	0.149	42.14
708	2.95	0.142	53.61

Rate constant extrapolated to zero time (k_{app}) = 0.210 l./mole sec.

k' = 421.5 x 10^{-7} sec.$^{-1}$

k^* = 228.8 x 10^{-3} l./mole sec.

$1/k^* \, [H^+]$ = 4.01 x 10^3 sec.

$[I^-]_o$ = 1.842 x 10^{-4} mole/l.

Table 35

Run 96-V-1, p-Nitrophenol in 1.000×10^{-4} M Sodium Iodide Solution at 50.0^{o}

(p-Nitrophenol)$_o$ - 0.007699 M

$(I_2)_o$ - 0.0001340 M

$(NaI)_o$ - 1.000×10^{-4} M

$(HClO_4)$ - 0.001091 M

$(NaClO_4)$ - 0.2989 M

$(Na_2S_2O_3)$ - 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant (l./mole sec)	Per cent reaction
(blank)	10.43		0.00
58	9.30	0.257	10.83
81	8.88	0.259	14.87
115	8.35	0.252	19.94
156	7.70	0.250	26.17
226	7.05	0.226	32.41
305	6.05	0.230	41.99

Rate constant extrapolated to zero time (k_{app}) = 0.262 l./mole sec.

k' = 237.9×10^{-7} sec.$^{-1}$

k^* = 273.1×10^{-3} l./mole sec.

$1/k^*$ $[H^+]$ = 3.36×10^{3} sec.

$[I^-]_o$ = 0.8710×10^{-4} mole/l.

Table 36

Run 90-V-1, p-Nitrophenol in 1.000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(p-Nitrophenol)$_0$ - 0.007699 M

($HClO_4$) - 0.001091 M

(I_2)$_0$ - 0.0001910 M

($NaClO_4$) - 0.2989 M

(NaI)$_0$ - 1.000 x 10^{-4} M

($Na_2S_2O_3$) - 0.01204 M

200.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant (l./mole sec)	Per cent reaction
(blank)	6.36		0.00
74	5.33	0.311	16.20
119	4.80	0.307	24.53
158	4.62	0.264	27.36
244	3.95	0.255	37.89
366	3.28	0.237	48.43

Rate constant extrapolated to zero time (k_{app}) = 0.348 l./mole sec.

k' = 333.5 x 10^{-7} sec.$^{-1}$

k^* = 363.3 x 10^{-3} l./mole sec.

$1/k^*$ $[H^+]$ = 2.52 x 10^3 sec.

$[I^-]_0$ = 0.9180 x 10^{-4} mole/l.

Table 37

Run 61-V-1, p-Nitrophenol in 1.000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(p-Nitrophenol)$_o$ - 0.0007699 M

$(I_2)_o$ - 0.0002630 M

$(NaI)_o$ - 1.000 x 10^{-4} M

$(HClO_4)$ - 0.04910 M

$(NaClO_4)$ - 0.2510 M

$(Na_2S_2O_3)$ - 0.006019 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	4.37		0.00
1,830	3.88	8.24	11.20
3,300	3.66	6.81	16.25
4,852	3.38	6.73	22.65
6,823	3.15	6.09	27.92
9,262	3.02	5.37	30.90
12,615	2.56	5.40	41.42
15,065	2.35	5.26	46.22

Rate constant extrapolated to zero time (k_{app}) = 9.65 x 10^{-3} l./mole sec.

Table 38

Run 60-V-2, p-Nitrophenol in 0.5000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(p-Nitrophenol)$_o$ - 0.007699 M

$(I_2)_o$ - 0.0002648 M

$(NaI)_o$ - 0.5000 x 10^{-4} M

$(HClO_4)$ - 0.04910 M

$(NaClO_4)$ - 0.2503 M

$(Na_2S_2O_3)$ - 0.006019 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	4.40		0.00
1,025	3.97	13.07	9.77
1,995	3.72	11.09	15.45
3,400	3.42	9.66	22.27
4,562	3.22	8.93	26.82
6,115	3.02	8.05	31.30
8,910	2.63	7.56	40.23
12,760	2.35	6.44	46.59

Rate constant extrapolated to zero time (k_{app}) = 16.40 x 10^{-3} l./mole sec.

Table 39

Run 131-V-1, p-Nitrophenol in 1.000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(p-Nitrophenol)$_o$ - 0.002566 M

$(I_2)_o$ - 0.0002101 M

$(NaI)_o$ - 1.000 x 10^{-4} M

$(HClO_4)$ - 0.009820 M

$(NaClO_4)$ - 0.2901 M

$(Na_2S_2O_3)$ - 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	6.98		0.00
984	6.36	3.71	8.88
2,040	5.72	3.84	18.05
2,908	5.42	3.43	22.35
3,788	5.18	3.10	25.79
5,028	4.63	3.23	33.67
7,067	4.20	2.86	39.83

Rate constant extrapolated to zero time (k_{app}) = 3.90 x 10^{-2} l./mole sec.

k' = 37.07 x 10^{-7} sec.$^{-1}$

k^* = 40.7 x 10^{-3} l./mole sec.

$1/k^*$ $[H^+]$ = 2.50 x 10^3 sec.

$[I^-]_o$ = 0.9103 x 10^{-4} mole/l.

Table 40

Run 130-V-1, p-Nitrophenol in 1.000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(p-Nitrophenol)$_o$ - 0.0007699 M

$(I_2)_o$ - 0.0002101 M

$(NaI)_o$ - 1.000 x 10^{-4} M

$(HClO_4)$ - 0.009820 M

$(NaClO_4)$ - 0.2901 M

$(Na_2S_2O_3)$ - 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	6.98		0.00
3,734	6.30	3.62	9.74
5,915	5.95	3.58	14.76
7,915	5.67	3.49	18.77
11,212	5.27	3.38	24.50
13,372	5.10	3.17	26.93
22,456	4.27	2.67	38.83

Rate constant extrapolated to zero time (k_{app}) = 3.90 x 10^{-2} l./mole sec.

k' = 37.07 x 10^{-7} sec.$^{-1}$

k^* = 40.7 x 10^{-3} l./mole sec.

$1/k^* \, [H^+]$ = 2.50 x 10^3 sec.

$[I^-]_o$ = 0.9103 x 10^{-4} mole/l.

Table 41

Run 103-V-1, 4-Nitrophenol-2,6-d_2 in 65.00 x 10^{-4} M Sodium Iodide Solution at 50.0°

(4-Nitrophenol-2,6-d_2)$_o$* - 0.007699 M

(I_2)$_o$ - 0.0006838 M

(NaI)$_o$ - 65.00 x 10^{-4} M

($HClO_4$) - 0.009820 M

($NaClO_4$) - 0.2837 M

($Na_2S_2O_3$) - 0.006019 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^5 (l./mole sec.)	Per cent reaction
(blank)	11.36		0.00
255,370	10.33	4.86	9.06
599,290	9.15	4.52	18.66
927,470	8.37	4.33	25.60
1,360,650	7.20	4.43	36.00
2,128,280	5.85	4.15	48.00

Rate constant extrapolated to zero time (k_{app}) = 4.95 x 10^{-5} l./mole sec.

*Partially deuterated p-Nitrophenol

Table 42

Run 102-V-1, 4-Nitrophenol-2,6-d_2 in 25.00 x 10^{-4} M Sodium Iodide Solution at 50.0°

(4-Nitrophenol-2,6-d_2)$_o$* - 0.007699 M

($HClO_4$) - 0.009820 M

(I_2)$_o$ - 0.0005750 M

($NaClO_4$) - 0.2877 M

(NaI)$_o$ - 25.00 x 10^{-4} M

($Na_2S_2O_3$) - 0.006019 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^4 (l./mole sec.)	Per cent reaction
(blank)	9.56		0.00
34,220	8.97	2.42	6.17
71,340	8.43	2.30	11.82
109,435	7.82	2.24	17.07
162,270	7.46	1.89	20.89
255,135	6.45	1.81	29.66
418,045	5.20	1.79	43.29
1,358,995	1.80	1.62	80.37

Rate constant extrapolated to zero time (k_{app}) = 2.55 x 10^{-4} l./mole sec.

*Partially deuterated p-Nitrophenol

Table 43

Run 104-V-1, 4-Nitrophenol-2,6-d_2 in 25.00 x 10^{-4} M Sodium Iodide Solution at 50.0°

(4-Nitrophenol-2,6-d_2)$_o$ - 0.007699 M

(I_2)$_o$ - 0.0005290 M

(NaI)$_o$ - 25.00 x 10^{-4} M

($HClO_4$) - 0.009820 M

($NaClO_4$) - 0.006019 M

($Na_2S_2O_3$) - 0.006019 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^4 (l./mole sec.)	Per cent reaction
(blank)	8.78		0.00
75,255	7.77	2.12	11.50
156,810	6.79	2.15	22.66
248,130	5.95	2.06	32.23
355,032	5.06	2.05	42.36
439,120	4.53	1.90	46.83

Average value of rate constant (k_{app}) = 2.06 ± 0.06 x 10^{-4} l./mole sec.

k' = 9.56 x 10^{-7} sec.$^{-1}$

k^* = 4.26 x 10^{-4} l./mole sec.

$1/k^*$ $[H^+]$ = 23.9 x 10^4 sec.

I^-_o = 22.244 x 10^{-4} mole/l.

Table 44

Run 132-V-1, 4-Nitrophenol-2,6-d_2 in 5.000×10^{-4} M Sodium Iodide Solution at 50.0°

(4-Nitrophenol-2,6-d_2)$_o$ - 0.007699 M

($HClO_4$) - 0.009820 M

(I_2)$_o$ - 0.0003471 M

($NaClO_4$) - 0.2901 M

(NaI)$_o$ - 5.000×10^{-4} M

($Na_2S_2O_3$) - 0.006311 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	5.50		0.00
7,690	4.85	2.13	12.73
12,970	4.60	1.80	16.36
20,630	4.22	1.68	23.27
25,947	3.97	1.64	27.82
35,480	3.58	1.59	34.91
43,447	3.35	1.50	39.09

Rate constant extrapolated to zero time (k_{app}) = 2.00×10^{-3} l./mole sec.

k' = 10.6×10^{-7} sec.$^{-1}$

k^* = 2.43×10^{-3} l./mole sec.

$1/k^*$ $[H^+]$ = 41.8×10^3 sec.

$[I^-]_o$ = 4.386×10^{-4} mole/l.

Table 45

Run 136-V-1, 4-Nitrophenol-2,6-d_2 in 5.000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(4-Nitrophenol-2,6-d_2)*$_o$ - 0.007699 M

(HClO$_4$) - 0.009820 M

(I_2)$_o$ - 0.0006470 M

(NaClO$_4$) - 0.2852 M

(NaI)$_o$ - 5.000 x 10^{-4} M

($Na_2S_2O_3$) - 0.006019 M

ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	10.75		0.00
5,840	9.84	1.95	8.55
12,327	9.07	1.80	15.63
19,913	8.37	1.65	22.14
25,104	7.90	1.61	26.51
32,908	7.25	1.58	32.56
55,128	5.94	1.42	44.74
69,003	5.30	1.36	50.70

Rate constant extrapolated to zero time (k_{app}) = 2.08 x 10^{-3} l./mole sec.

k' = 9.81 x 10^{-7} sec.$^{-1}$

k^* = 2.48 x 10^{-3} l./mole sec.

$1/k^*$ $[H^+]$ = 41.0 x 10^3 sec.

$[I^-]_o$ = 3.9507 x 10^{-4} mole/l.

*This compound was partially deuterated.

Table 46

Run 110-V-1, 4-Nitrophenol-2,6-d_2 in 1.000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(4-Nitrophenol-2,6-d_2)$_o$ - 0.007699 M

(HClO$_4$) - 0.009820 M

(I_2)$_o$ - 0.0002221 M

(NaClO$_4$) - 0.2900 M

(NaI)$_o$ - 1.000 x 10^{-4} M

($Na_2S_2O_3$) - 0.006019 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	3.68		0.00
1,560	3.35	7.85	8.97
3,113	3.10	7.17	15.76
5,727	2.75	6.64	25.27
6,905	2.65	6.20	27.90

Rate constant extrapolated to zero time (k_{app}) = 8.67 x 10^{-3} l./mole sec.

k' = 8.20 x 10^{-7} sec.$^{-1}$

k^* = 9.04 x 10^{-3} l./mole sec.

$1/k^* \left[H^+\right]$ = 11.3 x 10^3 sec.

$\left[I^-\right]_o$ = 0.9060 x 10^{-4} mole/l.

Table 47

Run 109-V-1, 4-Nitrophenol-2,6-d_2 in 0.5000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(4-Nitrophenol-2,6-d_2)$_o$ - 0.007699 M

$(I_2)_o$ - 0.0002170 M

$(NaI)_o$ - 0.5000 x 10^{-4} M

$(HClO_4)$ - 0.009820 M

$(NaClO_4)$ - 0.2902 M

$(Na_2S_2O_3)$ - 0.006019 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	3.60		0.00
806	3.30	14.1	8.33
1,593	3.08	12.8	14.44
3,254	2.72	11.2	24.44
5,160	2.42	8.9	30.00

Rate constant extrapolated to zero time (k_{app}) = 15.8 x 10^{-3} l./mole sec.

k' = 7.32 x 10^{-7} sec.$^{-1}$

k^* = 16.1 x 10^{-3} l./mole sec.

$1/k^* \left[H^+\right]$ = 6.32 x 10^3 sec.

$\left[I^-\right]_o$ = 0.4530 x 10^{-4} mole/l.

Table 48

Run 105-V-1, 4-Nitrophenol-2,6-d_2 in 0.5000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(4-Nitrophenol-2,6-d_2)$_o$ - 0.007699 M

(I_2)$_o$ - 0.0004045 M

(NaI)$_o$ - 0.5000 x 10^{-4} M

($HClO_4$) - 0.009820 M

($NaClO_4$) - 0.2902 M

($Na_2S_2O_3$) - 0.006019 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	6.72		0.00
873	6.18	12.5	8.03
1,890	5.73	10.9	14.73
3,047	5.38	9.5	19.94
4,707	4.97	8.4	26.04
6,995	4.48	6.9	31.07

Rate constant extrapolated to zero time (k_{app}) = 14.5 x 10^{-3} l./mole sec.

k' = 6.20 x 10^{-7} sec.$^{-1}$

k^* = 14.8 x 10^{-3} l./mole sec.

$1/k^* \left[H^+ \right]$ = 6.88 x 10^3 sec.

$\left[I^- \right]_o$ = 0.4187 x 10^{-4} mole/l.

Table 49

Run 107-V-1, 4-Nitrophenol-2,6-d_2 in 0.2500 x 10^{-4} M Sodium Iodide Solution at 50.0°

(4-Nitrophenol-2,6-d_2)$_o$ - 0.007699 M

$(I_2)_o$ - 0.0001238 M

$(NaI)_o$ - 0.2500 x 10^{-4} M

$(HClO_4)$ - 0.009820 M

$(NaClO_4)$ - 0.2902 M

$(Na_2S_2O_3)$ - 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	4.12		0.00
717	3.64	2.24	11.65
1,267	3.30	1.99	19.90
1,885	3.14	1.87	23.79
2,915	2.80	1.72	32.04

Rate constant extrapolated to zero time (k_{app}) = 2.62 x 10^{-2} l./mole sec.

k' = 6.25 x 10^{-7} sec.$^{-1}$

k^* = 26.6 x 10^{-3} l./mole sec.

$1/k^* \left[H^+ \right]$ = 3.83 x 10^3 sec.

$\left[I^- \right]_o$ = 0.2340 x 10^{-4} mole/l.

Table 50

Run 106-V-1, 4-Nitrophenol-2,6-d_2 in 0.1000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(4-Nitrophenol-2,6-d_2)$_o$ - 0.007699 M

$(I_2)_o$ - 0.0001189 M

$(NaI)_o$ - 0.1000 x 10^{-4} M

$(HClO_4)$ - 0.009820 M

$(NaClO_4)$ - 0.2902 M

$(Na_2S_2O_3)$ - 0.01204 M

200.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	3.95		0.00
346	3.44	5.21	12.91
550	3.28	4.40	16.96
1,105	3.03	3.12	23.29
1,953	2.66	2.63	32.66
3,253	2.30	2.04	39.79

Rate constant extrapolated to zero time (k_{app}) = 7.80 x 10^{-2} l./mole sec.

k' = 7.41 x 10^{-7} sec.$^{-1}$

k^* = 78.4 x 10^{-3} l./mole sec.

$1/k^* \left[H^+\right]$ = 1.30 x 10^3 sec.

$\left[I^-\right]_o$ = 0.0945 x 10^{-4} mole/l.

Table 51

Run 57-V-2, 4-Nitrophenol-2,6-d_2 in 0.05000 M Thallium Perchlorate Solution at 50.0°

$(\text{4-Nitrophenol-2,6-}d_2)_o$ - 0.007699 M

$(HClO_4)$ - 0.04910 M

$(I_2)_o$ - 0.0002470 M

$(NaClO_4)$ - 0.2011 M

$(NaI)_o$ - 0.000200 M

$(Na_2S_2O_3)$ - 0.006019 M

$(TlClO_4)_o$ - 0.0500 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	4.11		0.00
1,531	3.63	1.06	11.67
2,549	3.44	0.92	16.30
4,310	2.89	1.07	29.68
5,858	2.70	0.94	34.30
9,678	2.12	0.89	48.40

Average value of rate constant (k_{app}) = 0.97 ± 0.06 x 10^{-2} l./mole sec.

Table 52

Run 139-V-1, 4-Nitrophenol-2,6-d_2 in 0.0500 M Thallium Perchlorate Solution at 50.0°

$(4\text{-Nitrophenol-2,6-}d_2)_o$ - 0.007699 M

$(I_2)_o$ - 0.0002630 M

$(NaI)_o$ - 0.00020 M

$(TlClO_4)_o$ - 0.0500

$(HClO_4)$ - 0.04910 M

$(NaClO_4)$ - 0.2011 M

$(Na_2S_2O_3)$ - 0.006019 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	4.37		0.00
2,058	3.87	0.77	11.44
3,695	3.41	0.88	21.97
5,291	3.02	0.77	26.88
7,277	2.63	0.81	36.32
9,593	2.19	0.87	46.97

Average value of rate constant (k_{app}) = 0.82 ± 0.04 x 10^{-2} l./mole sec.

Kinetic Reactions of Anisole.--Having studied the kinetics of iodination of p-nitrophenol, it was of interest to investigate the iodination of anisole in order to see whether or not it exhibits similar iodide ion dependence, and to study its deuterium isotope effect.

It was first necessary to determine the reaction order with respect to anisole concentration. Thus a kinetic run at 0.0040 M in anisole and 0.500×10^{-4} M in sodium iodide was performed at 50°. The acidity of the solution was 0.009783 M at an ionic strength of 0.3000. The apparent rate constants plotted as usual versus per cent reaction and extrapolated to zero time, a value of 7.35×10^{-3} l./mole sec. was obtained (Table 53, Run 6-V-3). The same reaction was performed at the same acidity and iodine concentration but at a different anisole concentration (0.002995 M). The extrapolated value of apparent rate constant in this case was 7.06×10^{-3} l./mole sec. (See Table 54, Run 7-V-3.)

The iodination of anisole at a lower concentration was desirable. Thus a run at 0.001997 M in anisole and 0.500×10^{-4} M in sodium iodide was performed. The rate constants were plotted versus per cent reaction and extrapolated to zero time a value of 6.63×10^{-3} l./mole sec. was obtained (Table 55, Run 4-V-3). The same reaction at still lower concentrations of anisole (0.0009978 M and 0.0004996 M), gave extrapolated rate constants of 6.80×10^{-3} and 6.70×10^{-3} l. mole^{-1} sec.$^{-1}$, respectively. (See Table 56, Run 5-V-3, and Table 58, Run 8-V-3, respectively). Over the eight fold change of concentration of anisole the apparent second-order rate constant had an average value of 6.91×10^{-3} l. mole^{-1} sec.$^{-1}$ with an average deviation of 0.24×10^{-3} l. mole^{-1} sec.$^{-1}$ Thus, it is safe to conclude that the reaction is first order with respect to anisole. The iodination of anisole was then investigated at different iodide ion concentrations but at constant acidity and ionic strength.

A kinetic run at high iodide ion concentration (10.0×10^{-4} M) was performed. The apparent rate constants were essentially unchanged hence they were averaged and a value of $1.869 \pm 0.067 \times 10^{-4}$ l./mole sec. was obtained. The calculated value of k' was 27.0×10^{-8} sec.$^{-1}$ (Table 58, Run 116-V-2). The same reaction at 5.000×10^{-4} M sodium iodide was performed. The apparent rate constants showed a slight downward drift. Thus when extrapolated to zero time a value of 5.45×10^{-4} l./mole sec. was obtained. The value of k' was 30.0×10^{-8} sec.$^{-1}$ (Table 59, Run 115-V-2). A comparison of this value of k' with that of its previous run shows that k' increased by nine per cent. This is, however, contrary to what is expected. Thus, the same run was repeated at lower iodine and anisole concentration. The apparent rate constants were averaged since at this low iodine concentration, the increase in iodide ion due to the reaction is negligible. The average value of apparent rate constant was $5.149 \pm 0.325 \times 10^{-4}$ l./mole sec., and the value of k' was 30.2×10^{-8} sec.$^{-1}$. (Table 60, Run 11-V-3).

The iodination of anisole was studied in the presence of thallium perchlorate in 0.009783 M perchloric acid. The experimental technique in performing this run was identical to that of p-nitrophenol in the presence of thallium ions. Examination of Table 67, reveals that the apparent rate constants drop significantly throughout the course of the reaction. The exact cause of such a drop is unknown, however it is possible that a reaction like

$$6TlI + I_2 \longrightarrow Tl_6I_8$$

may take place. Such a reaction would introduce an appreciable error in calculating the iodine concentration. However, for comparison of rate constants with the corresponding deuterated anisole, it seems logical to adopt the extrapolation technique in both cases. The extrapolated value in Table 67, Run 17-V-3, was found to be 2.21 x 10^{-2} l./mole sec. The same run was repeated and gave an extrapolated value of 1.88 x 10^{-2} l./mole sec. (See Table 68, Run 49-V-3).

In order to be able to perform kinetic runs at lower iodide ion concentration, the thallium concentration was raised four fold (0.2000 M). Thus from the relationship between the solubilities and solubility products of thallium iodide, it is expected that the concentration of iodide ion should drop by approximately four fold (neglecting any specific salt effects). Examination of Table 69, Run 39-V-3, reveals that the apparent rate constants show a significant downward drift. Hence the apparent rate constants were plotted versus per cent reaction and when extrapolated to zero time a value of 7.20 x 10^{-2} l./mole sec. was obtained.

A kinetic run at 0.5149 M thallium perchlorate was done. In this run no sodium perchlorate was introduced since the concentration of thallium ions is greater than 0.300. The rate constants dropped significantly, and when extrapolated to zero time gave a value of 13.00 x 10^{-2} l./mole sec. (See Table 70, Run 50-V-3). The same run at the same thallium ion concentration was repeated. The apparent rate constants dropped also; however, it was decided to take an average of the rate constants since in the corresponding run on the deuterated derivative an average had been taken. The average value given in Table 71 is 12.90 ± 1.00 x 10^{-2} l./mole sec.

At this point, it was decided to perform a run on anisole, at essentially zero iodide ion concentration (0.0100 x 10^{-4} M). Table 72, reveals that extrapolation is not possible in this case. Such a run could be meaningful when compared with a corresponding run on deuterated anisole under identical conditions. Unfortunately, experiments at such low iodide ion concentration are irreproducible. Thus in an experiment (Table 72, Run 46-V-3) the apparent rate constant at 9.86 per cent reaction was 8.91 x 10^{-2} l./mole sec. The rate constant at a comparable per cent reaction obtained in another experiment was 2.22 x 10^{-2} l./mole sec. A third experiment gave a value of 5.32 x 10^{-2} l./mole sec. at essentially ten per cent reaction. Such large deviations of rate constants performed under essentially identical experimental conditions can be attributed to several factors. First, it is possible that the initial iodide ion concentration is unknown and varies from one experiment to another regardless of the number of extractions of the iodine-CCl_4 solu- with purified water. Second, the presence of extremely small amounts of chlorine or other oxidizing agents in the solution will change the initial iodide ion concentration due to oxidation. Although apparently the necessary precautions were taken to avoid such impurities, it is possible that still some chlorine will distil from the permanganate sodium hydroxide solution from which the distilled water was redistilled.

Furthermore, the rate constant at ten per cent reaction is affected appreciably by the initial stoichiometric iodine concentration, since at higher iodine concentrations, the per cent increase in iodide ion concentration is greater than the reaction performed at lower iodine concentration. Moreover, the accuracy in reactions at low iodine concentration is small due to the relatively small volume of sodium thiosulfate required for titration. It is interesting, however, to note that the main difficulty in such experiments is in the first twenty per cent reaction, since the relative change in iodide ion concentration afterwards is less and hence the rate constants become comparable.

Kinetic Reactions of Anisole-2,4,6-d_3.--The first kinetic run was performed at 5.000 x 10^{-4} M sodium iodide in the presence of perchloric acid (0.009783 M) and sodium perchlorate at 50^{o} and ionic strength of 0.3000. The purpose of this run was to determine the magnitude of maximum isotope effect by comparison with the corresponding run of the protio compound. The results in Table 73, Run 37-V-3, show that the apparent rate constants remain essentially constant throughout the reaction. Therefore, an average of the rate constants was taken and was found to be 1.589 ± 0.099 x 10^{-4} l./mole sec. The calculated value of k' was 9.35 x 10^{-8} sec.$^{-1}$. The k_{app} value at 5.000 x 10^{-4} M sodium iodide for the protio compound as indicated in this chapter (Table 60, Run 11-V-3) was 5.149 x 10 l./mole sec. The kinetic deuterium isotope effect, $(k^{H}_{app})/(k^{D}_{app})$ was found to be 3.24.

A kinetic run at 3.000 x 10^{-4} M in sodium iodide was performed. The apparent rate constants were averaged and found to be 2.585 ± 0.067

x 10^{-4} l./mole sec. The calculated value of k' was 8.41 x 10^{-8} sec.$^{-1}$ (Table 74, Run 38-V-3). Comparison of this value of k_{app} with the corresponding value of the protio compound (Table 61, Run 12-V-3) gives a value of 3.17 for the deuterium isotope effect.

The iodination of anisole-2,4,6-d_3 was studied at lower iodide ion concentration (1.000 x 10^{-4} M). The rate constants were plotted versus per cent reaction and when extrapolated to zero time gave a value of 10.40 x 10^{-4} l./mole sec. The calculated value of k' was 10.29 x 10^{-8} sec.$^{-1}$ (Table 75, Run 29-V-3). The magnitude of deuterium isotope effect was 2.82.

Thus far it can be concluded that the maximum kinetic isotope effect is approximately 3.2, and the drop in the isotope effect is probably insignificant. Therefore, runs at lower iodide ion were necessary to determine whether or not such a drop is meaningful.

A kinetic run at 0.500 x 10^{-4} M in sodium iodide was performed. As expected, the apparent rate constants dropped appreciably. The apparent rate constants plotted versus per cent reaction and extrapolated to zero time gave a value of 22.20 x 10^{-4} l./mole sec. The calculated value of k' was 10.65 x 10^{-8} sec.$^{-1}$ (Table 76, Run 27-V-3). Comparison of this value of k_{app} with the corresponding value on the protio compound (Table 55, Run 4-V-3) gave an isotope effect of 2.91.

The iodination of anisole-2,4,6-d_3 was studied at 0.2500 x 10^{-4} M sodium iodide. The extrapolated value of rate constant was 3.48 x 10^{-3} l./mole sec. and the calculated value of k' was 8.32 x 10^{-8} sec.$^{-1}$ (Table 77, Run 30-V-3). The kinetic isotope effect was 3.14.

The kinetic isotope effect at even lower iodide ion concentrations had to be determined, in order to see whether or not any appreciable drop may result. Therefore, a kinetic run at 0.175 x 10^{-4} M in sodium iodide was performed. The apparent rate constants plotted versus per cent reaction and extrapolated to zero time gave a value of 3.80 x 10^{-3} l./mole sec. The calculated value of k' was 6.38 x 10^{-8} sec.$^{-1}$ (Table 78, Run 31-V-3). The magnitude of deterium isotope effect was 3.39.

A kinetic run at 0.100 x 10^{-4} M in sodium iodide was done. As expected, the apparent rate constants dropped sharply. The rate constants were plotted versus per cent reaction. Extrapolation of the rate constants to zero time gave a value of 5.80 x 10^{-3} l./mole sec. The calculated value of k' was 5.50 x 10^{-8} sec.$^{-1}$ (Table 79, Run 32-V-3). Comparison of this value of k_{app} with the corresponding value on protio compound (Table 66, Run 13-V-3) gives an isotope effect of 2.98. The same run was repeated (Table 80, Run 48-V-3) and the value of kinetic isotope effect was 2.87.

It can be concluded that in a fifty fold change in stoichiometric iodide concentration, no appreciable change in deuterium isotope effect has resulted. It was felt that perhaps further lowering in iodide ion concentration might throw light on the mechanism of iodination. Therefore, a kinetic run was performed in the presence of thallium perchlorate (0.050 M). As in the corresponding protio run, the apparent rate constants dropped significantly. The rate constants were therefore plotted versus per cent reaction and extrapolated to zero time gave a value of 6.80 x 10^{-3} l./mole sec. (See Table 81, Run 41-V-3). Comparison of this value of k_{app} with the corresponding k_{app} of the protio compound (Table 67, Run 17-V-3) gives a deuterium isotope effect of 2.95.

It was, of course, desirable to measure the deuterium isotope effect at lower iodide ion concentrations. Therefore a kinetic run at 0.2000 M in thallium perchlorate was performed. In order to have good comparison with the protio run, the iodine concentration was adjusted to exactly the same value as reported in Table 69. The rate constants were plotted versus per cent reaction, and the extrapolated value of k_{app} was found to be 2.60×10^{-2} l./mole sec. The magnitude of deuterium isotope effect was 2.76. (Table 82, Run 40-V-3).

The iodination of anisole-2,4,6-d_3 at higher thallium ion concentration was necessary, in order to see whether or not any more drop in deuterium isotope effect may result. Therefore, a kinetic run at 0.5149 M in thallium perchlorate was performed. The iodine concentration was maintained at exactly the same value as in the corresponding protio run (Table 70, Run 50-V-3). The extrapolated value of apparent rate constant was 10.70×10^{-2} sec.$^{-1}$. (Table 83, Run 51-V-3). Surprisingly, the magnitude of the deuterium isotope effect was 1.21. The same run was repeated under similar conditions as reported in Table 71 for protio compound, and the apparent rate constants were averaged since the rate constants of corresponding protio run was also averaged. The value of k_{app} was found to be $10.3 \pm 0.5 \times 10^{-2}$ (Table 84, Run 54-V-3). The kinetic isotope effect was 1.25.

The drop in kinetic isotope effect is significant, and the interpretation in terms of the mechanism of iodination of anisole will be given in Chapter VI.

The iodination of anisole-2,4-6-d_3 at extremely low iodide ion concentration (0.0100×10^{-4} M) was performed. No extrapolation was possible in this case. However, this run was important in the sense that it makes possible to determine the deuterium isotope effect at various per cent reaction. Thus, comparison of Table 85, Run 47-V-3 with Table 72 on protio compound, gives a deuterium isotope effect of 2.45 at 9.5 per cent reaction. At 13 per cent reaction, the magnitude of deuterium isotope effect increases to 2.98. It should be pointed out that this experiment was performed at the same time and with the same solution of the corresponding protio run in Table 85. Therefore comparison of deuterium isotope effect in this case is justified.

Experiments in the Presence of Silver Perchlorate.--The iodination of anisole at extremely low iodide ion concentrations was desirable. In order to maintain a constant iodide concentration, it was decided to use silver ions as regulator, since any iodide ion beyond the solubility of silver iodide will be precipitated. The major difficulty in such a reaction is that iodine, in the presence of silver ion, is converted to iodate, which is incapable of iodination. Bell and Gelles[133] have discussed the kinetics of iodate formation from iodine in presence of silver ion, and have reported that at high hydrogen ion concentrations, the rate of iodate formation is slowed appreciably. Thus a kinetic run at 2.00×10^{-4} *M* in silver perchlorate, 0.100 *M* in perchloric acid was performed at 50° and an ionic strength of 0.3000. The reaction was started by introduction of iodine, and was stopped by injecting 2 ml. of saturated sodium iodide solution. Table 86 reveals that iodate formation competes with iodination of anisole. Therefore, it was decided to perform another run at higher acidity (1.000 *M*). Table 87 shows that after

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

Table 53

Run 6-V-3, Anisole in 0.5000×10^{-4} M Sodium Iodide Solution at 50.0°

$(Anisole)_o$ - 0.004001 M

$(I_2)_o$ - 0.0001204 M

$(NaI)_o$ - 0.5000×10^{-4} M

$(HClO_4)$ - 0.009783 M

$(NaClO_4)$ - 0.2902 M

$(Na_2S_2O_3)$ - 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	4.00		0.00
8,130	3.28	6.13	18.00
11,728	3.10	5.46	22.50
12,060	3.08	5.44	23.00
17,944	2.86	4.69	28.50
32,985	2.33	4.13	41.75
40,770	2.24	3.58	44.00

Rate constant extrapolated to zero time (k_{app}) = 7.35×10^{-3} l./mole sec.

k' = 35.6×10^{-8} $sec.^{-1}$

k^* = 75.4×10^{-4} l./mole sec.

$1/k^*$ = 132.6 mole sec./l.

$[I^-]_o$ = 0.4721×10^{-4} mole/l.

Table 54

Run 7-V-3, Anisole in 0.5000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(Anisole)$_o$ - 0.002995 M

$(I_2)_o$ - 0.0001204 M

$(NaI)_o$ - 0.5000 x 10^{-4} M

$(HClO_4)$ - 0.009783 M

$(NaClO_4)$ - 0.2902 M

$(Na_2S_2O_3)$ - 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	4.00		0.00
9,122	3.38	6.20	15.50
12,962	3.25	5.38	18.75
19,545	2.97	5.11	25.75
33,760	2.57	4.42	35.75
41,792	2.42	4.06	39.50
77,500	2.00	3.02	50.00

Rate constant extrapolated to zero time (k_{app}) = 7.06 x 10^{-3} l./mole sec.

k' = 34.2 x 10^{-8} sec.$^{-1}$

k^* = 72.4 x 10^{-4} l./mole sec.

$1/k^*$ = 138.1 mole sec./l.

$[I^-]_o$ = 0.4721 x 10^{-4} mole/l.

Table 55

Run 4-V-3, Anisole in 0.5000 x 10^{-4} M Sodium Iodide Solution at 50.0°

$(Anisole)_o$ - 0.001997 M

$(I_2)_o$ - 0.0001159 M

$(NaI)_o$ - 0.5000 x 10^{-4} M

$(HClO_4)$ - 0.009783 M

$(NaClO_4)$ - 0.2902 M

$(Na_2S_2O_3)$ - 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	3.85		0.00
7,190	3.52	6.29	8.57
14,368	3.29	5.52	14.55
14,305	3.29	5.52	14.55
21,200	3.09	5.23	19.74
28,615	2.90	4.99	24.68
36,300	2.70	4.93	29.87
45,000	2.55	4.64	33.77
78,340	2.13	3.84	44.68

Rate constant extrapolated to zero time (k_{app}) = 6.63 x 10^{-3} l./mole sec.

k' = 32.1 x 10^{-8} sec.$^{-1}$

k^* = 67.8 x 10^{-4} l./mole sec.

$1/k^*$ = 147.5 mole sec,/l.

$[I^-]_o$ = 0.4737 x 10^{-4} mole/l.

Table 56

Run 5-V-3, Anisole in 0.5000 x 10^{-4} M Sodium Iodide Solution at 50.0°

$(Anisole)_o$ - 0.0009978 M

$(I_2)_o$ - 0.0001159 M

$(NaI)_o$ - 0.5000 x 10^{-4} M

$(HClO_4)$ - 0.009783 M

$(NaClO_4)$ - 0.2902 M

$(Na_2S_2O_3)$ - 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	3.85		0.00
17,121	3.46	6.33	10.13
29,695	3.27	5.58	15.06
44,440	3.04	5.40	21.04
77,805	2.72	4.56	29.35
100,270	2.53	4.29	34.29
176,138	2.00	3.85	48.05

Rate constant extrapolated to zero time (k_{app}) = 6.80 x 10^{-3} l./mole sec.

k' = 32.9 x 10^{-8} sec.$^{-1}$

k^* = 69.5 x 10^{-4} l./mole sec.

$1/k^*$ = 143.9 mole sec./l.

$[I^-]_o$ = 0.4737 x 10^{-4} mole/l.

Table 57

Run 8-V-3, Anisole in 0.5000×10^{-4} M Sodium Iodide Solution at 50.0°

(Anisole)$_o$ - 0.0004996 M

(HClO$_4$) - 0.009783 M

(I$_2$)$_o$ - 0.0001180 M

(NaClO$_4$) - 0.2902 M

(NaI)$_o$ - 0.5000×10^{-4} M

(Na$_2$S$_2$O$_3$) - 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	3.92		0.00
34,840	3.55	5.76	9.44
34,995	3.55	5.76	9.44
78,595	3.30	4.47	15.82
113,895	3.04	4.59	22.45
187,750	2.74	3.97	30.10
339,080	2.25	3.48	42.60

Rate constant extrapolated to zero time (k_{app}) = 6.70×10^{-3} l./mole sec.

k' = 32.5×10^{-8} sec.$^{-1}$

k^* = 68.7×10^{-4} l./mole sec.

$1/k^*$ = 145.6 mole sec./l.

$[I^-]_o$ = 0.4729×10^{-4} mole/l.

Table 58

Run 116-V-2, Anisole in 10.00 x 10^{-4} M Sodium Iodide Solution at 50.0°

$(\text{Anisole})_o$ - 0.004000 M

$(I_2)_o$ - 0.0002648 M

$(\text{NaI})_o$ - 10.00 x 10^{-4} M

$(HClO_4)$ - 0.009783 M

$(NaClO_4)$ - 0.2892 M

$(Na_2S_2O_3)$ - 0.006019 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^4 (l./mole sec.)	Per cent reaction
(blank)	4.44		0.00
96,820	4.10	1.822	7.65
165,195	3.87	1.952	12.84
241,175	3.65	1.947	17.79
420,895	3.26	1.797	26.57
599,940	2.80	1.908	36.93
792,285	2.52	1.788	43.24

Average value of rate constant (k_{app}) = 1.869 ± 0.067 x 10^{-4} l./mole sec.

k' = 27.0 x 10^{-8} sec.$^{-1}$

k^* = 2.94 x 10^{-4} l./mole sec.

$1/k^*$ = 340.1 mole sec./l.

$[I^-]_o$ = 9.179 x 10^{-4} mole/l.

Table 59

Run 115-V-2, Anisole in 5.000×10^{-4} M Sodium Iodide Solution at 50.0°

$(\text{Anisole})_o$ - 0.004000 M

$(I_2)_o$ - 0.0002654 M

$(\text{NaI})_o$ - 5.000×10^{-4} M

$(HClO_4)$ - 0.009783 M

$(NaClO_4)$ - 0.2897 M

$(Na_2S_2O_3)$ - 0.006019 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^4 (l./mole sec.)	Per cent reaction
(blank)	4.41		0.00
31,075*	4.12	5.50	6.57
68,070	3.90	4.53	11.56
118,995	3.53	4.69	19.95
164,485	3.30	4.44	25.17
240,395	2.94	4.27	33.33
332,435	2.61	4.00	40.81

Rate constant extrapolated to zero time (k_{app}) = 5.45×10^{-4} l./mole sec.

k' = 30.0×10^{-8} sec.$^{-1}$

k^* = 6.66×10^{-4} l./mole sec.

$1/k^*$ = 1502 mole sec./l.

$[I^-]_o$ = 4.5189×10^{-4} mole/l.

*This point was neglected in the plot since points earlier than 10 per cent reaction are likely to be inaccurate.

Table 60

Run 11-V-3, Anisole in 5.000×10^{-4} M Sodium Iodide Solution at 50.0°

$(Anisole)_o$ - 0.002000 M

$(I_2)_o$ - 0.0001234 M

$(NaI)_o$ - 5.000×10^{-4} M

$(HClO_4)$ - 0.009783 M

$(NaClO_4)$ - 0.2897 M

$(Na_2S_2O_3)$ - 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^4 (l./mole sec.)	Per cent reaction
(blank)	4.10		0.00
89,673	3.75	5.023	8.54
155,100	3.43	5.794	16.34
240,890	3.18	5.315	22.44
328,130	3.00	4.800	26.83
500,525	2.55	4.811	37.80

Average value of rate constant (k_{app}) = $5.149 \pm 0.325 \times 10^{-4}$ l./mole sec.

k' = 30.2×10^{-8} $sec.^{-1}$

k^* = 6.33×10^{-4} l./mole sec.

$1/k^*$ = 1580 mole sec./l.

$[I^-]_o$ = 4.7664×10^{-4} mole/l.

Table 61

Run 12-V-3, Anisole in 3.000×10^{-4} M Sodium Iodide Solution at 50.0°

(Anisole)$_o$ - 0.002000 M

$(I_2)_o$ - 0.0001213 M

$(NaI)_o$ - 3.000×10^{-4} M

$(HClO_4)$ - 0.009783 M

$(NaClO_4)$ - 0.2899 M

$(Na_2S_2O_3)$ - 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^4 (l./mole sec.)	Per cent reaction
(blank)	4.03		0.00
88,515	3.48	8.35	13.65
154,124	3.10	8.58	23.08
240,055	2.70	8.42	33.00
326,520	2.41	8.00	40.20
413,517	2.10	8.01	47.89
499,647	1.86	7.88	53.84

Average value of rate constant (k_{app}) = $8.21 \pm 0.25 \times 10^{-4}$ l./mole sec.

k' = 28.9×10^{-8} sec.$^{-1}$

k^* = 10.08×10^{-4} l./mole sec.

$1/k^*$ = 992 mole sec./l.

$[I^-]_o$ = 2.8616×10^{-4} mole/l.

Table 62

Run 15-V-3, Anisole in 1.000 x 10^{-4} M Sodium Iodide Solution at 50.0°

$(Anisole)_o$ - 0.002000 M

$(I_2)_o$ - 0.0001174 M

$(NaI)_o$ - 1.000 x 10^{-4} M

$(HClO_4)$ - 0.009783 M

$(NaClO_4)$ - 0.2901 M

$(Na_2S_2O_3)$ - 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	3.90		0.00
18,695	3.50	2.92	10.26
32,524	3.28	2.68	15.90
45,952	3.04	2.73	22.05
75,574	2.70	2.45	30.77
98,184	2.48	2.54	36.41
167,987	1.87	2.23	52.05

Rate constant extrapolated to zero time (k_{app}) = 2.90 x 10^{-3} l./mole sec.

k' = 28.9 x 10^{-8} $sec.^{-1}$

k^* = 30.19 x 10^{-4} l./mole sec.

$1/k^*$ = 330 mole sec./l.

$[I^-]_o$ = 0.9479 x 10^{-4} mole/l.

Table 63

Run 14-V-3, Anisole in 0.2500×10^{-4} M Sodium Iodide Solution at 50.0°

$(\text{Anisole})_o$ - 0.002000 M

$(I_2)_o$ - 0.0001171 M

$(\text{NaI})_o$ - 0.2500×10^{-4} M

$(HClO_4)$ - 0.009783 M

$(NaClO_4)$ - 0.2902 M

$(Na_2S_2O_3)$ - 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	3.89		0.00
5,628	3.53	8.70	9.25
9,290	3.30	8.91	15.17
12,569	3.15	8.45	19.02
18,912	2.92	7.64	24.94
32,785	2.50	6.83	35.73
46,076	2.32	5.69	40.36

Rate constant extrapolated to zero time (k_{app}) = 10.86×10^{-3} l./mole sec.

k' = 25.9×10^{-8} sec.$^{-1}$

k^* = 109.7×10^{-4} l./mole sec.

$1/k^*$ = 91.2 mole sec./l.

$[I^-]_o$ = 0.2366×10^{-4} mole/l.

Table 64

Run 16-V-3, Anisole in 0.175×10^{-4} M Sodium Iodide Solution at 50.0°

$(Anisole)_o$ - 0.001999 M

$(I_2)_o$ - 0.0001309 M

$(NaI)_o$ - 0.1750×10^{-4} M

$(HClO_4)$ - 0.009783 M

$(NaClO_4)$ - 0.2902 M

$(Na_2S_2O_3)$ - 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	4.35		0.00
4,226	3.97	10.82	8.74
8,285	3.75	8.97	13.79
11,900	3.58	8.24	17.70
20,453	3.28	6.96	24.60
30,317	3.00	6.19	31.03
71,777	2.40	4.22	44.82

Rate constant extrapolated to zero time (k_{app}) = 12.90×10^{-3} l./mole sec.

k' = 21.4×10^{-8} $sec.^{-1}$

k^* = 130.0×10^{-4} l./mole sec.

$1/k^*$ = 76.9 mole sec./l.

$[I^-]_o$ = 0.1645×10^{-4} mole/l.

Table 65

Run 85-V-2, Anisole in 0.100 x 10^{-4} $\underline{M}$ Sodium Iodide Solution at 50.0°

$(\text{Anisole})_o$ - 0.004000 $\underline{M}$

$(I_2)_o$ - 0.0001014 $\underline{M}$

$(\text{NaI})_o$ - 0.1000 x 10^{-4} $\underline{M}$

$(HClO_4)$ - 0.009783 $\underline{M}$

$(NaClO_4)$ - 0.2989 $\underline{M}$

$(Na_2S_2O_3)$ - 0.006019 $\underline{M}$

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	3.37		0.00
881	3.18	16.43	5.64
1,890	3.05	13.17	9.49
4,732	2.76	10.54	18.10
6,645	2.61	9.66	22.55
11,256	2.30	8.52	31.75
14,365	2.17	7.70	35.60

Rate constant extrapolated to zero time (k_{app}) = 15.70 x 10^{-3} l./mole sec.

k' = 15.1 x 10^{-8} sec.$^{-1}$

k^* = 1.58 x 10^{-2} l./mole sec.

$1/k^*$ = 63.3 mole sec./l.

$[I^-]_o$ = 0.09530 x 10^{-4} mole/l.

Table 66

Run 13-V-3, Anisole in 0.1000 x 10^{-4} M Sodium Iodide Solution at 50.0°

$(Anisole)_o$ - 0.002000 M

$(I_2)_o$ - 0.0001243 M

$(NaI)_o$ - 0.1000 x 10^{-4} M

$(HClO_4)$ - 0.009783 M

$(NaClO_4)$ - 0.2902 M

$(Na_2S_2O_3)$ - 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	4.13		0.00
3,401	3.74	14.58	9.44
6,389	3.49	13.27	15.50
11,857	3.22	10.58	22.03
17,027	3.00	9.63	27.36
19,285	2.90	9.25	29.78

Rate constant extrapolated to zero time (k_{app}) = 17.30 x 10^{-3} l./mole sec.

k' = 16.4 x 10^{-8} sec.$^{-1}$

k^* = 1.737 x 10^{-2} l./mole sec.

$1/k^*$ = 57.6 mole sec./l.

$[I^-]_o$ = 0.0943 x 10^{-4} mole/l.

Table 67

Run 17-V-3, Anisole in 0.0500 M Thallium Perchlorate Solution at 50.0°

$(Anisole)_o$ - 0.001999 M

$(HClO_4)$ - 0.009783 M

$(I_2)_o$ - 0.0002684 M

$(NaClO_4)$ - 0.2402 M

$(NaI)_o$ - 2.000 x 10^{-4} M

$(Na_2S_2O_3)$ - 0.006019 M

$(TlClO_4)_o$ - 0.0500 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	4.46		0.00
1,417	4.20	2.12	5.83
2,926	3.95	2.09	11.43
6,642	3.46	1.94	22.42
8,641	3.32	1.74	25.56
14,922	2.91	1.47	34.75

Rate constant extrapolated to zero time (k_{app}) = 2.21 x 10-2 l./mole sec.

Table 68

Run 49-V-3, Anisole in 0.0500 M Thallium Perchlorate Solution at 50.0°

$(\text{Anisole})_o$ - 0.002002 M

$(I_2)_o$ - 0.002251 M

$(\text{NaI})_o$ - 2.000 x 10^{-4} M

$(\text{TlClO}_4)_o$ - 0.0500 M

(HClO_4) - 0.009783 M

(NaClO_4) - 0.2402 M

$(\text{Na}_2\text{S}_2\text{O}_3)$ - 0.06019 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	3.74		0.00
2,067	3.48	1.74	6.95
3,493	3.32	1.72	11.23
6,942	3.01	1.58	19.52
10,694	2.84	1.31	26.74
17,943	2.43	1.23	35.03
34,540	1.75	1.14	53.21
44,990	1.51	1.08	59.63

Rate constant extrapolated to zero time (k_{app}) = 1.88 x 10^{-2} l./mole sec.

Table 69

Run 39-V-3, Anisole in 0.2000 M Thallium Perchlorate Solution at 50.0°

(Anisole)$_o$ = 0.001999 M

$(I_2)_o$ = 0.0002007 M

(NaI)$_o$ = 2.000 x 10^{-4} M

$(TlClO_4)_o$ = 0.2000 M

$(HClO_4)$ = 0.009783 M

$(NaClO_4)$ = 0.09022 M

$(Na_2S_2O_3)$ = 0.006311 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	3.18		0.00
1,536	2.65	5.99	16.67
2,511	2.48	5.01	22.01
3,815	2.27	4.49	28.61
6,956	1.97	3.52	38.05
13,920	1.55	2.66	48.74

Rate constant extrapolated to zero time (k_{app}) = 7.20 x 10^{-2} l./mole sec.

Table 70

Run 50-V-3, Anisolein 0.5149 M Thallium Perchlorate Solution at 50.0°

$(Anisole)_o$ - 0.0008006 M

$(I_2)_o$ - 0.0002065 M

$(NaI)_o$ - 2.000 x 10^{-4} M

$(TlClO_4)_o$ - 0.5149 M

$(HClO_4)$ - 0.009783 M

$(NaClO_4)$ - 0.000 M

$(Na_2S_2O_3)$ - 0.006019 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	3.43		0.00
755	3.19	12.15	7.00
1,981	2.85	11.98	16.91
3,715	2.45	11.77	28.57
6,123	2.19	9.65	36.15
9,162	1.76	9.80	48.69
12,135	1.51	9.29	55.97
16,160	1.33	8.08	61.22

Rate constant extrapolated to zero time (k_{app}) = 13.00 x 10^{-2} l./mole sec.

Table 71

Run 53-V-3, Anisole in 0.5149 M Thallium Perchlorate Solution at 50.0°

(Anisole)$_o$ - 0.0008006 M

$(I_2)_o$ - 0.0002386 M

$(NaI)_o$ - 2.000 x 10^{-4} M

$(TlClO_4)_o$ - 0.5149 M

$(HClO_4)$ - 0.009783 M

$(NaClO_4)$ - 0.000 M

$(Na_2S_2O_3)$ - 0.006150 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	3.88		0.00
1,257	3.36	14.6	13.40
3,134	2.80	13.6	27.83
4,565	2.53	12.4	34.79
5,945	2.21	12.7	43.04
7,957	2.09	10.9	47.14

Average value of rate constant (k_{app}) = 12.9 ± 1.0 x 10^{-2} l./mole sec. and extrapolated value of rate constant k_{app} = 16.3 x 10^{-2} l./mole sec.

Table 72

Run 46-V-3, Anisole in 0.0100 x 10^{-4} M Sodium Iodide Solution at 50.0°

$(Anisole)_o$ - 0.002002 M

$(HClO_4)$ - 0.009783 M

$(I_2)_o$ - 0.00008848 M

$(NaClO_4)$ - 0.2902 M

$(NaI)_o$ - 0.0100 x 10^{-4} M

$(Na_2S_2O_3)$ - 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	2.94		0.00
584	2.65	8.91	9.86
900	2.56	7.71	12.93
2,482	2.38	4.27	19.05
4,620	2.20	3.15	25.17
7,938	2.00	2.44	31.97
18,810	1.27	1.11	56.80

Rate constant extrapolated to zero time (k_{app}) = 14.4 x 10^{-2} l./mole sec.

Table 73

Run 37-V-3, Anisole-2,4,6-d_3 in 5.000×10^{-4} M Sodium Iodide Solution at 50.0°

(Anisole-2,4,6-d_3)$_o$ - 0.002001 M

$(I_2)_o$ - 0.0001224 M

$(NaI)_o$ - 5.000×10^{-4} M

$(HClO_4)$ - 0.009783 M

$(NaClO_4)$ - 0.2897 M

$(Na_2S_2O_3)$ - 0.006311 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^4 (l./mole sec.)	Per cent reaction
(blank)	3.88		0.00
333,564	3.46	1.361	10.82
584,970	3.24	1.549	16.49
842,275	2.90	1.741	25.26
1,016,065	2.79	1.638	28.09
1,445,015	2.40	1.683	38.14
1,883,080	2.17	1.564	44.07

Average value of rate constant (k_{app}) = $1.589 \pm 0.098 \times 10^{-4}$ l./mole sec.

k' = 9.35×10^{-8} sec.$^{-1}$

k^* = 1.963×10^{-4} l./mole sec.

$1/k^*$ = 5100 mole sec./l.

$[I^-]_o$ = 4.7680×10^{-4} mole/l.

Table 74

Run 38-V-3, Anisole-2,4,6-d_3 in 3.000×10^{-4} M Sodium Iodide Solution at 50.0°

(Anisole-2,4,6-d_3)$_o$ - 0.002001 M

$(I_2)_o$ - 0.0001193 M

$(NaI)_o$ - 3.000×10^{-4} M

$(HClO_4)$ - 0.009783 M

$(NaClO_4)$ - 0.2899 M

$(Na_2S_2O_3)$ - 0.006311 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^4 (l./mole sec.)	Per cent reaction
(blank)	3.78		0.00
583,980	2.80	2.587	25.93
841,265	2.40	2.735	36.51
1,014,805	2.25	2.590	40.47
1,444,545	1.90	2.418	49.00
1,882,194	1.45	2.598	61.64

Average value of rate constant (k_{app}) = $2.585 \pm 0.067 \times 10^{-4}$ l./mole sec.

k' = 8.41×10^{-8} sec.$^{-1}$

k^* = 2.95×10^{-4} l./mole sec.

$1/k^*$ = 3394 mole sec./l.

$[I^-]_o$ = 2.8537×10^{-4} mole/l.

Table 75

Run 29-V-3, Anisole-2,4,6-d_3 in 1.000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(Anisole-2,4,6-d_3)$_o$ - 0.001999 M

$(I_2)_o$ - 0.0001225 M

$(NaI)_o$ - 1.000 x 10^{-4} M

$(HClO_4)$ - 0.009783 M

$(NaClO_4)$ - 0.2901 M

$(Na_2S_2O_3)$ - 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^4 (l./mole sec.)	Per cent reaction
(blank)	4.07		0.00
58,233	3.64	9.67	10.57
86,400	3.47	9.30	14.74
173,270	3.07	8.21	24.57
225,175	2.75	8.79	32.43
282,315	2.63	7.85	35.38
364,328	2.43	7.19	40.29

Rate constant extrapolated to zero time (k_{app}) = 10.40 x 10^{-4} l./mole sec.

k' = 10.3 x 10^{-8} sec.$^{-1}$

k^* = 10.88 x 10^{-4} l./mole sec.

$1/k^*$ = 919 mole sec./l.

$[I^-]_o$ = 0.9458 x 10^{-4} mole/l.

Table 76

Run 27-V-3, Anisole-2,4,6-d_3 in 0.5000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(Anisole-2,4,6-d_3)$_o$ - 0.002009 M

$(I_2)_o$ - 0.0001369 M

$(NaI)_o$ - 0.5000 x 10^{-4} M

$(HClO_4)$ - 0.009783 M

$(NaClO_4)$ - 0.2902 M

$(Na_2S_2O_3)$ - 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^4 (l./mole sec.)	Per cent reaction
(blank)	4.55		0.00
20,114	4.20	19.81	7.69
67,992	3.63	16.68	20.22
111,871	3.32	12.64	24.55
157,365	2.95	11.88	31.07
246,268	2.65	9.81	38.08

Rate constant extrapolated to zero time (k_{app}) = 22.20 x 10^{-4} l./mole sec.

k' = 10.6 x 10^{-8} sec.$^{-1}$

k^* = 22.7 x 10^{-4} l./mole sec.

$1/k^*$ = 441 mole sec./l.

$[I^-]_o$ = 0.4692 x 10^{-4} mole/l.

Table 77

Run 30-V-3, Anisole-2,4,6-d_3 in 0.2500 x 10^{-4} M Sodium Iodide Solution at 50.0°

(Anisole-2,4,6-d_3)$_o$ - 0.001999 M

(I_2)$_o$ - 0.0001213 M

(NaI)$_o$ - 0.2500 x 10^{-4} M

($HClO_4$) - 0.009783 M

($NaClO_4$) - 0.2902 M

($Na_2S_2O_3$) - 0.006019 M

ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	4.03		0.00
12,120	3.80	2.42	5.71
22,813	3.58	2.62	11.17
38,055	3.32	2.57	17.62
57,060	3.15	2.17	21.84
79,985	2.95	1.96	26.79
105,263	2.72	1.88	32.51

Rate constant extrapolated to zero time (k_{app}) = 3.48 x 10^{-3} l./mole sec.

k' = 8.32 x 10^{-8} sec.$^{-1}$

k^* = 35.2 x 10^{-4} l./mole sec.

$1/k^*$ = 284 mole sec./l.

$[I^-]_o$ = 0.2361 x 10^{-4} mole/l.

Table 78

Run 31-V-3, Anisole-2,4,6-d_3 in 0.175 x 10^{-4} M Sodium Iodide Solution at 50.0°

(Anisole-2,4,6-d_3)$_o$ - 0.001999 M

(HClO$_4$) - 0.009783 M

(I_2)$_o$ - 0.0001198 M

(NaClO$_4$) - 0.2902 M

(NaI)$_o$ - 0.175 x 10^{-4} M

($Na_2S_2O_3$) - 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	3.98		0.00
8,120	3.76	3.50	5.53
15,067	3.62	3.18	9.05
27,035	3.44	2.72	13.57
38,298	3.22	2.78	19.10
56,235	3.00	2.54	24.62
78,987	2.77	2.32	30.40

Rate constant extrapolated to zero time (k_{app}) = 3.80 x 10^{-3} l./mole sec.

k' = 6.38 x 10^{-8} sec.$^{-1}$

k* = 38.6 x 10^{-4} l./mole sec.

1/k* = 259 mole sec./l.

$[I^-]_o$ = 0.1654 x 10^{-4} mole/l.

Table 79

Run 32-V-3, Anisole-2,4,6-d_3 in 0.1000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(Anisole-2,4,6-d_3)$_o$ - 0.001991 M

(I_2)$_o$ - 0.0001120 M

(NaI)$_o$ - 0.1000 x 10^{-4} M

($HClO_4$) - 0.009783 M

($NaClO_4$) - 0.2902 M

($Na_2S_2O_3$) - 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	3.72		0.00
2,935	3.60	5.75	3.23
6,665	3.49	4.87	6.18
12,227	3.37	4.10	9.41
25,434	3.15	3.31	15.32
49,012	2.73	3.19	26.61
87,510	2.35	2.67	36.83

Rate constant extrapolated to zero time (k_{app}) = 5.80 x 10^{-3} l./mole sec.

k' = 5.50 x 10^{-8} sec.$^{-1}$

k^* = 57.0 x 10^{-4} l./mole sec.

$1/k^*$ = 176 mole sec./l.

$[I^-]_o$ = 0.0984 x 10^{-4} mole/l.

Table 80

Run 48-V-3, Anisole-2,4,6-d_3 in 0.1000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(Anisole-2,4,6-d_3)$_o$ - 0.001619 M

$(I_2)_o$ - 0.0001171 M

$(NaI)_o$ - 0.1000 x 10^{-4} M

$(HClO_4)$ - 0.009783 M

$(NaClO_4)$ - 0.2902 M

$(Na_2S_2O_3)$ - 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	3.89		0.00
18,142	3.38	4.78	13.11
35,347	3.05	4.29	21.59
46,835	2.93	3.77	24.68
76,272	2.68	3.06	31.11
89,717	2.55	2.95	34.45

Rate constant extrapolated to zero time (k_{app}) = 6.00 x 10^{-3} l./mole sec.

k' = 5.69 x 10^{-8} sec.$^{-1}$

k^* = 6.02 x 10^{-3} l./mole sec.

$1/k^*$ = 166 mole sec./l.

$[I^-]_o$ = 0.09460 x 10^{-4} mole/l.

Table 81

Run 41-V-3, Anisole-2,4,6-d_3 in 0.0500 M Thallium Perchlorate Solution at 50.0°

(Anisole-2,4,6-d_3)$_o$ - 0.002001 M

$(I_2)_o$ - 0.0002739 M

$(NaI)_o$ - 2.000 x 10^{-4} M

$(TlClO_4)_o$ - 0.0500 M

$(HClO_4)$ - 0.009783 M

$(NaClO_4)$ - 0.2402 M

$(Na_2S_2O_3)$ - 0.006311 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	4.34		0.00
6,260	4.08	4.95	5.95
12,760	3.78	5.47	12.90
20,747	3.55	4.91	18.20
28,238	3.37	4.46	22.35
40,029	3.13	4.16	27.88
72,387	2.58	3.70	40.55

Rate constant extrapolated to zero time (k_{app}) = 6.80 x 10^{-3} l./mole sec.

Table 82

Run 40-V-3, Anisole-2,4,6-d_3 in 0.2000 M Thallium Perchlorate Solution at 50.0°

(Anisole-2,4,6-d_3)$_o$ = 0.002001 M

$(I_2)_o$ = 0.0002007 M

$(NaI)_o$ = 2.000 x 10^{-4} M

$(TlClO_4)_o$ = 0.2000 M

$(HClO_4)$ = 0.009783 M

$(NaClO_4)$ = 0.09022 M

$(Na_2S_2O_3)$ = 0.006311 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	3.18		0.00
1,372	2.98	2.37	6.29
2,335	2.88	2.13	8.88
5,235	2.67	1.68	16.00
13,906	2.28	1.21	28.30
24,507	1.88	1.08	40.88
30,336	1.75	1.01	44.97

Rate constant extrapolated to zero time (k_{app}) = 2.60 x 10^{-2} l./mole sec.

Table 83

Run 51-V-3, Anisole-2,4,6-d_3 in 0.5149 M Thallium Perchlorate Solution at 50.0°

$(\text{Anisole-2,4,6-}d_3)_o$ = 0.0006479 M

$(I_2)_o$ = 0.0002065 M

$(NaI)_o$ = 2.000 x 10^{-4} M

$(TlClO_4)_o$ = 0.5149 M

$(HClO_4)$ = 0.009783 M

$(NaClO_4)$ = 0.0000 M

$(Na_2S_2O_3)$ = 0.006019 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	3.43		0.00
3,572	2.78	9.39	18.95
5,962	2.48	8.70	27.41
8,750	2.22	8.19	35.28
12,047	1.97	7.69	42.57
16,084	1.73	7.22	49.56
19,105	1.66	6.48	51.60

Rate constant extrapolated to zero time (k_{app}) = 10.70 x 10^{-2} l./mole sec.

Table 84

Run 54-V-3, Anisole-2,4,6-d_3 in 0.5149 M Thallium Perchlorate Solution at 50.0°

(Anisole-2,4,6-d_3)$_o$ - 0.0006479 M

$(I_2)_o$ - 0.0002386 M

$(NaI)_o$ - 2.000 x 10^{-4} M

$(TlClO_4)_o$ - 0.5149 M

$(HClO_4)$ - 0.009783 M

$(NaClO_4)$ - 0.0000 M

$(Na_2S_2O_3)$ - 0.006150 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	3.88		0.00
2,090	3.41	9.7	12.11
2,717	3.22	10.9	17.01
4,418	2.97	9.8	23.45
5,853	2.64	10.8	31.96
7,863	2.43	9.9	37.37

Average value of rate constant (k_{app}) = 10.3 ± 0.5 x 10^{-2} l./mole sec.

Table 85

Run 47-V-3, Anisole-2,4,6-d_3 in 0.0100 M Sodium Iodide Solution at 50.0°

(Anisole-2,4,6-d_3)$_o$ - 0.002005 M

$(I_2)_o$ - 0.00008848 M

$(NaI)_o$ - 0.0100 M

$(HClO_4)$ - 0.009783 M

$(NaClO_4)$ - 0.2902 M

$(Na_2S_2O_3)$ - 0.006019 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	2.94		0.00
755	2.71	5.39	7.82
1,400	2.66	3.58	9.52
2,748	2.55	2.59	13.27
6,130	2.48	1.39	15.65
16,810	2.32	0.71	21.09
36,355	2.03	0.51	30.95
64,990	1.75	0.40	40.48

Rate constant extrapolated to zero time (k_{app}) = 10.1 x 10^{-2} l./mole sec.

Table 86

Run 42-V-3, Anisole in 2.00 x 10^{-4} M Silver Perchlorate Solution at 50.0°

$(Anisole)_o$ - 0.001999 M

$(HClO_4)$ - 0.1000 M

$(I_2)_o$ - 0.000294 M

$(NaClO_4)$ - 0.1998 M

$(AgClO_4)_o$ - 2.00 x 10^{-4} M

$(Na_2S_2O_3)$ - 0.006311 M

100.0 ml. of reaction mixture per flask

Time (sec.)	Titer (ml.)	Apparent per cent reaction
(blank)	9.33	0.00
320	7.97	14.60
540	6.67	29.45
759	6.65	29.73
1,424	8.00	14.26

Table 87

Run 43-V-3, Anisole in 2.00 x 10^{-4} M Silver Perchlorate Solution at 50.0°

$(\text{Anisole})_o$ = 0.001999 M

$(HClO_4)$ = 1.000 M

$(I_2)_o$ = 0.000138 M

$(NaClO_4)$ = 0.000 M

$(AgClO_4)_o$ = 2.000 x 10^{-4} M

$(Na_2S_2O_3)$ = 0.006311 M

100.0 ml. of reaction mixture per flask

Time (sec.)	Titer (ml.)	Apparent per cent Reaction
(blank)	4.37	0.00
40	1.55	64.60
59	1.65	62.28
103	1.56	64.44
88*	3.05	30.12
178*	2.80	35.98
480*	2.96	32.37
1,760*	3.05	30.12

*These points were measured at 0°C.

Table 88

Run 44-V-3, Anisole in 2.00 x 10^{-4} M Silver Perchlorate Solution at 0.0°

$(Anisole)_o$ - 0.0003999 M

$(I_2)_o$ - 0.000142 M

$(AgClO_4)_o$ - 2.000 x 10^{-4} M

$(HClO_4)$ - 1.000 M

$(NaClO_4)$ - 0.00 M

$(Na_2S_2O_3)$ - 0.006311 M

100.0 ml. of reaction mixture per flask

Time (sec.)	Titer (ml.)	Apparent Per cent Reaction
(blank)	4.48	0.00
20	1.05	76.53
86	0.87	80.60
1,727	0.65	85.60
19*	0.95	78.79

*The concentration of anisole at this point was one-half the original concentration.

103 seconds the iodine titer becomes essentially constant. The same reaction was performed at zero degrees, and the iodine titer again remained constant after three minutes. Another experiment at lower anisole concentration was performed in order to have longer reaction time. The iodine titers were irregular (See Table 88), therefore, it was decided to abandon the thought of using silver perchlorate as an iodide ion regulator.

Kinetic Reactions of Phenol.--The iodination of phenol was studied by Kilby[134], who concluded that the values of k' do not drop with decreasing iodide ion concentration. He furthermore found that the kinetic isotope effect in the iodination of phenol-2,4,6-d_3 does not change with decreasing the iodide ion concentration. His reported maximum deuterium isotope effect was approximately 4.

It was of interest, however, to reinvestigate his experiments under modified experimental conditions, and see if a higher deuterium isotope effect is obtainable.

The first run was done as a check of Kilby's experiment at 5.000×10^{-4} M sodium iodide and 0.0174 M perchloric acid at 25° and ionic strength 0.300. The apparent rate constants were plotted versus per cent reaction and extrapolated to zero time gave a value of 9.50×10^{-3} l./mole sec. The calculated value of k' was 46.41×10^{-7} sec.$^{-1}$ (Table 89, Run 60-V-3). This value was in good agreement with that 45.3×10^{-7} sec.$^{-1}$ reported by Kilby[134].

A second run at 0.500×10^{-4} M in sodium iodide was performed at

(134) D. C. Kilby, Kinetic Study of The Mechanism of iodination of Phenol, M. S. Thesis, Georgia Institute of Technology, 1958, p. 95.

25^{o}. As expected, the apparent rate constants dropped sharply. The rate constants when extrapolated to zero time gave a value of 10.30 x 10^{-2} l./mole sec. and the calculated value of k' was 48.57 x 10^{-7} sec.$^{-1}$ (Table 90, Run 62-V-3). It seemed that further lowering in initial iodide ion concentration was necessary. Therefore, another run at 0.250 x 10^{-4} M in sodium iodide was run. The extrapolated value of k_{app} was 19.85 x 10^{-2} l./mole sec. and the calculated value of k' was 45.96 x 10^{-7} sec.$^{-1}$ (Table 91, Run 63-V-3). The same reaction was run at 0.1000 x 10^{-4} M sodium iodide and the apparent rate constants were plotted versus per cent reaction. Extrapolation of rate constants to zero time gave a value of 46.50 x 10^{-2} l./mole sec. and the calculated value of k' was 42.48 x 10^{-7} sec.$^{-1}$ (See Table 92, Run 61-V-3).

Analysis of Tables 89, 90, 91, 92, shows that within fifty fold change in stoichiometric iodide ion concentration, the values of k' remained essentially constant. Such a result is contrary to that observed in the case of p-nitrophenol and anisole. It was felt that further lowering of iodide ion conceneration might cause the values of k' to drop. Therefore, a kinetic run at 0.0200 x 10^{-4} M in sodium iodide was performed. Due to the fast reaction rate at this low iodide ion concentration, the acidity of the reaction medium was increased five fold (0.0870 M) in order to have measurable rates. Unfortunately, as can be seen in Table 93, the rate constants cannot be extrapolated to zero time since at ten per cent reaction the iodide ion concentration is already five times greater than the initial stoichiometric iodide concentration.

A kinetic run in the presence of thallium perchlorate (0.0500 M) was performed at 0.0870 M in perchloric acid. The rate constants dropped appreciably. Extrapolation of rate constants to zero time gave a value of 0.77 l./mole sec. (Table 94, Run 74-V-3).

Kinetic Reactions of Phenol-2,4,6-d_3.--The iodination of phenol-2,4,6-d_3 was studied in order to determine the magnitude of deuterium isotope effect. It was at first necessary to determine whether or not the compound was completely deuterated. Therefore, a kinetic run at 5.000 x 10^{-4} M in sodium iodide was performed using phenol-2,4,6-d_3 which was twice equilibrated with heavy water (see Chapter III for preparation of phenol-2,4,6-d_3). The rate constants dropped with per cent reaction. Extrapolation of rate constants to zero time gave a value of 14.20 x 10^{-4} l./mole sec. The calculated value of k' was 7.126 x 10^{-7} sec.$^{-1}$ (Table 95, Run 64-V-3). The magnitude of deuterium isotope effect, $(k^H_{app})/(k^D_{app})$ was 6.69.

Another kinetic run was performed in the presence of 5.000 x 10^{-4} M sodium iodide using phenol-2,4,6-d_3 which was equilibrated with heavy water three times. The rate constants were plotted versus per cent reaction and extrapolated to zero time gave a value of 14.35 x 10^{-4} l./mole sec. The calculated value of k' was 7.201 x 10^{-7} sec.$^{-1}$ (Table 96, Run 65-V-3). The deuterium isotope effect in this case was 6.62. It can, therefore, be concluded that complete deuteration of phenol can be achieved by two equilibrations with heavy water.

The iodination of phenol-2,4,6-d_3 was studied at 0.500 x 10^{-4} M sodium iodide. The extrapolated value of apparent rate constant was 15.90 x 10^{-3} l./mole sec. and the calculated value of k' was 7.506 x 10^{-7} (Table 97, Run 66-V-3). The magnitude of kinetic isotope effect in this case was 6.55.

A kinetic experiment at 0.250 x 10^{-4} M in sodium iodide was performed using relatively low iodine concentration. The rate constants were plotted versus per cent reaction and extrapolated to zero time gave a value of 3.00 x 10^{-2} l./mole sec. The calculated value of k' was 6.930 x 10^{-7} sec.$^{-1}$ (Table 98, Run 68-V-3) and the kinetic isotope effect $(k^{H}_{app})/(k^{D}_{app})$ was 6.62. A similar experiment was performed at 0.100 x 10^{-4} M in sodium iodide. Extrapolation of rate constants to zero time gave a value of 6.85 x 10^{-2} l./mole sec. The value of k' was 6.287 x 10^{-7} sec.$^{-1}$ (Table 99, Run 67-V-3); and the kinetic isotope effect was 6.78. At this point it can be concluded that within fifty fold change in stoichiometric iodide ion concentration, neither the values of k' nor the magnitude of the isotope effect dropped to any appreciable extent.

The iodination of phenol-2,4,6-d_3 was done at 0.0200 x 10^{-4} M sodium iodide. As in the case of the corresponding protio compound (See Table 93, Run 72-V-3), the acidity of the medium was increased five fold (0.0870 M). It can be seen from Table 100 that extrapolation of rate constants to zero time is not possible. However, qualitative comparison of deuterium isotope effect is possible. Thus at 7.43 per cent reaction the magnitude of deuterium isotope effect is 4.68. At 27 per cent reaction the magnitude of deuterium isotope effect increases to approximately 6.

A kinetic run in the presence of thallium perchlorate (0.0500 M) was performed in 0.0870 M perchloric acid. The extrapolated value of apparent rate constants was 11.40 x 10^{-2} l./mole sec. (Table 101, Run 75-V-3). The magnitude of deuterium isotope effect was 6.75.

It was of interest to determine the magnitude of the deuterium isotope effect at 50^{o}. Therefore, the iodination of phenol was first studied at 5.000×10^{-4} M sodium iodide and 0.0174 M in perchloric acid at 50^{o} and an ionic strength of 0.300. As can be seen in Table 102, Run 70-V-3, the apparent rate constants were averaged and a value of $12.79 \pm 0.680 \times 10^{-2}$ l./mole sec. was obtained. The calculated value k' was 63.53×10^{-6} sec.$^{-1}$. The iodination of phenol-2,4,6-d_3 was also carried out under identical conditions. The average value of apparent rate constant was $2.413 \pm 0.121 \times 10^{-2}$ l./mole sec. The calculated value of k' was 11.99×10^{-6} sec.$^{-1}$ (Table 103, Run 71-V-3) and the magnitude of kinetic isotope effect was 5.30.

Table 89

Run 60-V-3, Phenol in 5.000 x 10^{-4} M Sodium Iodide Solution at 25.0°

(Phenol)$_o$ - 0.001969 M

$(I_2)_o$ - 0.0005394 M

$(NaI)_o$ - 5.000 x 10^{-4} M

$(HClO_4)$ - 0.01740 M

$(NaClO_4)$ - 0.2821 M

$(Na_2S_2O_3)$ - 0.006150 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	8.77		0.00
4,555	8.14	9.29	7.18
8,158	7.70	8.25	12.20
14,161	7.09	7.85	19.16
20,605	6.60	7.27	24.74
29,267	5.96	7.04	32.04
53,155	4.75	6.31	45.84

Rate constant extrapolated to zero time (k_{app}) = 9.50 x 10^{-3} l./mole sec.

k' = 46.41 x 10^{-7} sec.$^{-1}$

k^* = 12.26 x 10^{-3} l./mole sec.

$1/k^*$ $[H^+]$ = 4.69 x 10^3 sec.

$[I^-]_o$ = 3.7851 x 10^{-4} mole/l.

Table 90

Run 62-V-3, Phenol in 0.5000×10^{-4} M Sodium Iodide Solution at 25.0°

$(Phenol)_o$ - 0.001969 M

$(I_2)_o$ - 0.0001276 M

$(NaI)_o$ - 0.5000×10^{-4} M

$(HClO_4)$ - 0.01740 M

$(NaClO_4)$ - 0.2826 M

$(Na_2S_2O_3)$ - 0.006150 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	4.15		0.00
675	3.66	9.50	11.81
1,050	3.47	8.70	16.39
1,643	3.26	7.99	21.45
2,269	3.05	6.95	26.51
3,281	2.75	6.44	33.73
4,463	2.48	5.94	40.24
6,355	2.13	5.43	48.67

Rate constant extrapolated to zero time (k_{app}) = 10.30×10^{-2} l./mole sec.

k' = 48.6×10^{-7} sec.$^{-1}$

k^* = 106.3×10^{-3} l./mole sec.

$1/k^* \left[H^+\right]$ = 5.41×10^{2} sec.

$\left[I^-\right]_o$ = 0.4568×10^{-4} mole/l.

Table 91

Run 63-V-3, Phenol in 0.2500 x 10^{-4} M Sodium Iodide Solution at 25.0°

$(Phenol)_o$ - 0.001969 M

$(I_2)_o$ - 0.0001276 M

$(NaI)_o$ - 0.2500 x 10^{-4} M

$(HClO_4)$ - 0.01740 M

$(NaClO_4)$ - 0.2826 M

$Na_2S_2O_3)$ - 0.006150 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	4.15		0.00
335	3.70	17.42	10.84
595	3.47	15.36	16.39
915	3.27	13.30	21.20
1,285	3.10	11.64	25.30
1,874	2.85	10.31	31.33
2,652	2.61	8.99	37.11
4,288	2.16	7.88	47.95

Rate constant extrapolated to zero time (k_{app}) = 19.85 x 10^{-2} l./mole sec.

k' = 46.0 x 10^{-7} sec.$^{-1}$

k^* = 201.6 x 10^{-3} l./mole sec.

$1/k^* [H^+]$ = 285 sec.

$[I^-]_o$ = 0.2280 x 10^{-4} mole/l.

Table 92

Run 61-V-3, Phenol in 0.1000 x 10^{-4} M Sodium Iodide Solution at 25.0°

$(Phenol)_o$ - 0.001969 M

$(I_2)_o$ - 0.0001338 M

$(NaI)_o$ - 0.1000 x 10^{-4} M

$(HClO_4)$ - 0.01740 M

$(NaClO_4)$ - 0.2826 M

$(Na_2S_2O_3)$ - 0.006150 M

ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	4.35		0.00
126	4.00	34.02	8.05
270	3.75	28.13	13.79
431	3.63	21.49	16.55
750	3.38	17.27	22.30
1,149	3.14	14.55	27.82
1,715	2.84	12.81	34.71
3,083	2.38	10.11	45.29

Rate constant extrapolated to zero time (k_{app}) = 46.50 x 10^{-2} l./mole sec.

k' = 42.5 x 10^{-7} sec.$^{-1}$

k^* = 468.2 x 10^{-3} l./mole sec.

$1/k^* [H^+]$ = 123 sec.

$[I^-]_o$ = 0.09074 x 10^{-4} mole/l.

Table 93

Run 72-V-3, Phenol in 0.0211 x 10^{-4} M Sodium Iodide Solution at 25.0°

$(Phenol)_o$ - 0.001969 M

$(I_2)_o$ - 0.0001076 M

$(NaI)_o$ - 0.0200 x 10^{-4} M

$(HClO_4)$ - 0.0870 M

$(NaClO_4)$ - 0.2130 M

$(Na_2S_2O_3)$ - 0.00615 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	3.50		0.00
126	3.30	23.56	5.71
288	3.19	16.34	8.86
888	2.99	9.06	14.57
1943	2.72	6.64	22.29
2859	2.52	5.88	28.00
4387	2.30	4.91	34.29

No accurate extrapolation is possible in this case.

Table 94

Run 74-V-3, Phenol in 0.0500 M Thallium Perchlorate Solution at 25.0°

$(Phenol)_o$ - 0.001969 M

$(I_2)_o$ - 0.0002091 M

$(NaI)_o$ - 2.000 x 10^{-4} M

$(TlClO_4)$ - 0.0500 M

$(HClO_4)$ - 0.08700 M

$(NaClO_4)$ - 0.1630 M

$(Na_2S_2O_3)$ - 0.006150 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant (l./mole sec.)	Per cent reaction
(blank)	3.40		0.00
90	2.99	0.7033	10.29
184	2.69	0.6548	20.88
351	2.41	0.5066	29.12
569	2.04	0.4667	40.00
799	1.99	0.3489	41.47
1173	1.60	0.3372	52.94
1587	1.41	0.2960	58.53
1962	1.25	0.2607	63.25

Rate constant extrapolated to zero time (k_{app}) = 0.77 l./mole sec.

Table 95

Run 64-V-3, Phenol-2,4,6-d_3 in 5.000×10^{-4} M Sodium Iodide Solution at 25.0°

(Phenol-2,4,6-d_3)$_o$* - 0.002052 M

(HClO$_4$) - 0.01740 M

$(I_2)_o$ - 0.0004938 M

(NaClO$_4$ - 0.2821 M

$(NaI)_o$ - 5.000×10^{-4} M

($Na_2S_2O_3$) - 0.006150 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^4 (l./mole sec.)	Per cent reaction
(blank)	8.03		0.00
28,240	7.43	13.46	7.47
61,338	6.82	13.22	15.07
101,086	6.20	12.83	22.79
153,866	5.58	11.99	30.51
205,516	5.05	11.56	37.11
238,710	4.75	11.34	40.85
278,029	4.48	10.87	44.21

Rate constant extrapolated to zero time (k_{app}) = 14.20×10^{-4} l./mole sec.

k' = 7.126×10^{-7} sec.$^{-1}$

k* = 1.842×10^{-3} l/mole sec.

$1/k^*$ $[H^+]$ = 31.2×10^3 sec.

$[I^-]_o$ = 3.8689×10^{-4} mole/l.

*This phenol was deuterated with two equilibrations in heavy water.

Table 96

Run 65-V-3, Phenol-2,4,6-d_3 in 5.000×10^{-4} M Sodium Iodide Solution at 25.0°

(Phenol-2,4,6-d_3)$_o$ - 0.002161 M

$(I_2)_o$ - 0.0004983 M

$(NaI)_o$ - 5.000×10^{-4} M

$(HClO_4)$ - 0.01740 M

$(NaClO_4)$ - 0.2821 M

$(Na_2S_2O_3)$- 0.006150 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^4 (l./mole sec.)	Per cent reaction
(blank)	8.03		0.00
27,963	7.38	14.07	8.09
61,079	6.82	12.60	15.07
100,748	6.23	11.98	22.42
153,699	5.62	11.16	30.01
205,170	5.12	10.63	36.24
238,522	4.80	10.51	40.22
277,390	4.43	10.53	44.83

Rate constant extrapolated to zero time (k_{app}) = 14.35×10^{-4} l./mole sec.

k' = 7.20×10^{-7} sec.$^{-1}$

k^* = 1.86×10^{-3} l./mole sec.

$1/k^*$ $[H^+]$ = 20.9×10^3 sec.

$[I^-]_o$ = 3.8689×10^{-4} mole/l.

Table 97

Run 66-V-3, Phenol-2,4,6-d_3 in 0.5000 x 10^{-4} M Sodium Iodide Solution at 25.0°

(Phenol-2,4,6-d_3) - 0.002161 M

$(I_2)_o$ - 0.0001273 M

$(NaI)_o$ - 0.5000 x 10^{-4} M

$(HClO_4)$ - 0.01740 M

$(NaClO_4)$ - 0.2826 M

$(Na_2S_2O_3)$ - 0.006150 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^3 (l./mole sec.)	Per cent reaction
(blank)	4.14		0.00
5,125	3.57	13.41	13.77
11,399	3.14	11.29	25.00
15,675	2.19	10.51	29.71
21,488	2.63	9.88	36.47
26,408	2.47	9.16	40.33

Rate constant extrapolated to zero time (k_{app}) = 15.90 x 10^{-3} l./mole sec.

k' = 7.51 x 10^{-7} sec.$^{-1}$

k^* = 16.4 x 10^{-3} l./mole sec.

$1/k^*$ $[H^+]$ = 3.51 x 10^3 sec.

$[I^-]_o$ = 0.4568 x 10^{-4} mole/l.

Table 98

Run 68-V-3, Phenol-2,4,6-d_3 in 0.2500×10^{-4} M Sodium Iodide Solution at 25.0°

(Phenol-2,4,6-d_3)$_o$ - 0.002161 M

$(I_2)_o$ - 0.0001273 M

$(NaI)_o$ - 0.2500×10^{-4} M

$(HClO_4)$ - 0.01740 M

$(NaClO_4)$ - 0.2826 M

$(Na_2S_2O_3)$ - 0.006150 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	4.14		0.00
1,563	3.76	2.86	9.18
3,047	3.57	2.26	13.77
5,053	3.33	2.00	19.57
6,418	3.17	1.94	23.43
10,395	2.82	1.73	31.88
15,852	2.51	1.48	39.37
20,513	2.31	1.34	44.20

Rate constant extrapolated to zero time (k_{app}) = 3.00×10^{-2} l./mole sec.

k' = 6.93×10^{-7} sec.$^{-1}$

k^* = 30.4×10^{-3} l./mole sec.

$1/k^*$ $[H^+]$ = 1.89×10^3 sec.

$[I^-]_o$ = 0.2280×10^{-4} mole/l.

Table 99

Run 67-V-3, Phenol-2,4,6-d_3 - 0.1000 x 10^{-4} M Sodium Iodide Solution at 25.0°

(Phenol-2,4,6-d_3)$_o$ - 0.002161 M

$(I_2)_o$ - 0.0001273 M

$(NaI)_o$ - 0.1000 x 10^{-4} M

$(HClO_4)$ - 0.01740 M

$(NaClO_4)$ - 0.2826 M

$(Na_2S_2O_3)$ - 0.006150 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	4.14		0.00
445	3.92	5.72	5.31
839	3.77	5.19	8.94
1,665	3.55	4.28	14.25
2,450	3.42	3.62	17.39
4,352	3.10	3.10	25.12
6,050	2.98	2.54	28.02
10,050	2.62	2.13	36.71

Rate constant extrapolated to zero time (k_{app}) = 6.85 x 10^{-2} l./mole sec.

k' = 6.29 x 10^{-7} sec.$^{-1}$

k^* = 68.9 x 10^{-3} l./mole sec.

$1/k^*$ $[H^+]$ = 835 sec.

$[I^-]_o$ - 0.09115 x 10^{-4} mole/l.

Table 100

Run 73-V-3, Phenol-2,4,6-d_3 in 0.0200 x 10^{-4} M Sodium Iodide Solution at 25.0°

(Phenol-2,4,6-d_3)$_o$ - 0.002075 M

(HClO$_4$) - 0.0870 M

(I_2)$_o$ - 0.0001076 M

(NaClO$_4$) - 0.2130 M

(NaI)$_o$ - 0.0200 x 10^{-4} M

($Na_2S_2O_3$) - 0.00615 M

100.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	3.50		0.00
347	3.37	5.15	3.71
920	3.24	4.06	7.43
2,935	3.10	3.48	11.43
5,348	2.91	1.67	16.86
8,620	2.75	1.35	21.43
14,760	2.55	1.04	27.14

No accurate extrapolation is possible in this case.

Table 101

Run 75-V-3, Phenol-2,4,6-d_3 in 0.0500 M Thallium Perchlorate Solution at 25.0°

(Phenol-2,4,6-d3)$_o$ - 0.002075 M

$(I_2)_o$ - 0.0002091 M

$(NaI)_o$ - 2.000 x 10^{-4} M

$(TlClO_4)_o$ - 0.0500 M

$(HClO_4)$ - 0.08700 M

$(NaClO_4)$ - 0.1630 M

$(Na_2S_2O_3)$ - 0.006150 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	3.40		0.00
622	3.01	9.51	11.47
605	3.00	10.04	11.76
1,151	2.79	8.36	17.94
2,178	2.52	7.28	25.33
2,913	2.23	7.12	34.41
4,110	2.01	6.31	40.88

Rate constant extrapolated to zero time (k_{app}) = 11.40 x 10^{-2} l./mole sec.

Table 102

Run 70-V-3, Phenol in 5.000×10^{-4} M Sodium Iodide Solution at 50.0°

$(Phenol)_o$ - 0.002227 M

$(I_2)_o$ - 0.0005166 M

$(NaI)_o$ - 5.000×10^{-4} M

$(HClO_4)$ - 0.0174 M

$(NaClO_4)$ - 0.2821 M

$(Na_2S_2O_3)$ - 0.00615 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	8.40		0.00
430	7.40	13.43	11.90
687	6.80	14.14	19.05
1,017	6.30	13.10	25.00
1,428	5.76	12.35	31.43
1,853	5.07	12.89	39.64
2,258	4.72	12.16	43.81
3,339	3.81	11.47	54.46

Average value of rate constant $(k_{app}) = 12.79 \pm 0.68 \times 10^{-2}$ l./mole sec.

$k' = 63.53 \times 10^{-6}$ sec.$^{-1}$

$k^* = 15.38 \times 10^{-2}$ l./mole sec.

$1/k^* [H^+] = 3.74 \times 10^2$ sec.

$[I^-]_o = 4.1305 \times 10^{-4}$ mole/l.

Table 103

Run 71-V-3, Phenol-2,4,6-d_3 in 5.000 x 10^{-4} M Sodium Iodide Solution at 50.0°

(Phenol-2,4,6-d_3)$_o$ - 0.002212 M

$(I_2)_o$ - 0.0005166 M

$(NaI)_o$ - 5.000 x 10^{-4} M

$(HClO_4)$ - 0.01740 M

$(NaClO_4)$ - 0.2821 M

$(Na_2S_2O_3)$ - 0.00615 M

50.0 ml. of reaction mixture per flask

Time elapsed (sec.)	Titer (ml.)	Rate constant x 10^2 (l./mole sec.)	Per cent reaction
(blank)	8.40		0.00
1,327	7.80	2.536	7.14
2,120	7.60	2.172	9.52
3,737	6.88	2.470	18.10
5,105	6.36	2.541	24.29
7,040	5.88	2.466	30.00
9,345	5.20	2.292	38.10

Average value of rate constant (k_{app}) = 2.413 ± 0.121 x 10^{-2} l./mole sec.

k' = 11.99 x 10^{-6} sec.$^{-1}$

k^* = 2.903 x 10^{-2} l./mole sec.

$1/k^*$ $[H^+]$ = 19.8 x 10^2 sec.

$[I^-]_o$ = 4.1305 x 10^{-4} mole/l.

CHAPTER VI

THE MECHANISM OF IODINATION OF p-NITROPHENOL

Introduction.--Experiments in tables 12, 39, and 40 indicate that for comparisons at equal hydrogen and iodide ion concentrations, the iodination of p-nitrophenol is first order in both stoichiometric concentration of iodine and of substrate. Hence, the second-order rate constants were calculated on this basis. These rate constants were found to be highly dependent upon the iodide ion concentration. Since the rate constants were calculated by using the stoichiometric concentrations of reactants, and ignoring the iodine tied up as triiodide, then it is justified to consider these constants as apparent rate constants, designated as k_{app}.

It was demonstrated in Chapter V that the apparent rate constant is dependent on both iodide and hydrogen ion concentration. Thus, when the stoichiometric iodide ion concentration was lowered by 250 fold, the rate constant k^* increased by approximately 65 fold whereas the values of k^* dropped by three fold (see Table 104). Furthermore, the values of k^* and k^0 (as previously defined) follow a trend indicating that k_{app} follows a non-integral iodide ion dependence. Alternatively, k^* has an iodide ion dependence between inverse first-order and zero-order.

Table 106 demonstrates the hydrogen ion dependence. It can be seen that, at constant iodide ion concentration (1.00×10^{-4} M), the

Table 104

Effect of Iodide Ion Concentration on the Rate of Iodination of p-Nitrophenol

All runs were made in aqueous solution, 0.009820 M in perchloric acid, at an ionic strength of 0.3000 at 50.0°.

$[I^-]$ (mole/l.)	k_{app} (l./mole sec.)	k^* (l./mole sec.)	$k^*[I^-] = k'$ (sec.$^{-1}$)	Ref. Table
121.6×10^{-4}	6.17×10^{-5}	0.431×10^{-3}	52.4×10^{-7}	4
61.6×10^{-4}	19.9×10^{-5}	0.798×10^{-3}	49.1×10^{-7}	3
22.6×10^{-4}	119×10^{-5}	2.333×10^{-3}	52.0×10^{-7}	2
10.7×10^{-4}	282×10^{-5}	4.300×10^{-3}	46.3×10^{-7}	6
4.25×10^{-4}	870×10^{-5}	10.5×10^{-3}	44.7×10^{-7}	8
2.1×10^{-4}	1791×10^{-5}	19.8×10^{-3}	41.9×10^{-7}	9
0.8×10^{-4}	4100×10^{-5}	41.5×10^{-3}	33.6×10^{-7}	10
0.46×10^{-4}	6600×10^{-5}	68.0×10^{-3}	30.3×10^{-7}	14
0.24×10^{-4}	8750×10^{-5}	91.0×10^{-3}	21.4×10^{-7}	16
0.095×10^{-4}	15250×10^{-5}	153.2×10^{-3}	14.6×10^{-7}	17

Table 105

Effect of Iodide Ion Concentration on the Rate of Iodination of 4-Nitrophenol-2,6-d_2

All runs were made in aqueous solution, 0.009820 M in perchloric acid, at an ionic strength of 0.3000 at 50.0°.

$[I^-]$ (mole/l.)	k_{app} (l./mole sec.)	k^* (l./mole sec.)	$k^*[I^-] = k'$ (sec.$^{-1}$)	Ref. Table
22.244×10^{-4}	2.06×10^{-4}	0.43×10^{-3}	9.56×10^{-7}	43
4.386×10^{-4}	20.0×10^{-4}	2.43×10^{-3}	10.66×10^{-7}	44
0.906×10^{-4}	86.7×10^{-4}	9.06×10^{-3}	8.20×10^{-7}	46
0.453×10^{-4}	158×10^{-4}	16.2×10^{-3}	7.32×10^{-7}	47
0.234×10^{-4}	262×10^{-4}	26.7×10^{-3}	6.25×10^{-7}	49
0.0945×10^{-4}	780×10^{-4}	79.5×10^{-3}	7.41×10^{-7}	50

Table 106

Effect of Hydrogen Ion Concentration on the Rate of Iodination of p-Nitrophenol

All runs were made in aqueous solution at an ionic strength of 0.3000 at 50.0°.

$[I^-] \times 10^4$ (mole/l.)	$[H^+]$ (mole/l.)	k_{app} (l./mole sec.)	$k_{app}[H^+]$ (sec.$^{-1}$)	Reference Table
21.436	0.003273	0.00323	0.0000106	24
7.213	0.001091	0.0430	0.0000469	29
5.433	0.001091	0.0560	0.0000611	30
4.514	0.003273	0.0224	0.0000733	25
3.546	0.001091	0.0785	0.0000856	31
2.666	0.001091	0.1300	0.0001418	32
2.213	0.003273	0.0490	0.0001600	26
1.754	0.001091	0.190	0.0002073	33
1.842	0.001091	0.210	0.0002291	34
0.8710	0.001091	0.262	0.0002860	35
0.9180	0.001091	0.348	0.0003810	36
0.8720	0.003273	0.117	0.0003820	27
0.9135	0.009820	0.040	0.0003940	13
0.9110	0.04910	0.00965	0.0004738	37
0.4370	0.003273	0.1685	0.0005520	28
0.4210	0.04910	0.0164	0.0008052	38

values of $k_{app} \times [H^+]$ remained essentially constant over a nine fold change in hydrogen ion concentration. However, if a wider range of iodide ion concentration is considered, then the rate is not quite inversely proportional to hydrogen ion concentration. The order becomes somewhere between inverse first-order and zero-order dependence.

The problem now becomes one of incorporating both the iodide ion and hydrogen ion dependence into a rate equation and then considering various mechanisms which would give rise to the derived rate equation.

<u>Mechanism I</u>.--Part of the iodide ion dependence must be attributable to the formation of triiodide through the equilibrium

$$I_2 + I^- \overset{K_1}{\rightleftharpoons} I_3^- \; ; \; K_1 = \frac{[I_3^-]}{[I_2]\,[I^-]}^{1} \qquad (1)$$

It can be seen from the equilibrium expression that the concentration of iodine is inversely proportional to the concentration of iodide ion.

If one considers the possible hydrolysis of iodine in an aqueous medium then,

$$I_2 + 2H_2O \overset{K_2}{\rightleftharpoons} HOI + H_3O^+ + I^- \; ;$$

$$K_2 = \frac{[HOI]\,[H_3O^+]\,[I^-]}{[I_2]\,[H_2O]^2} \qquad (2)$$

$$HOI + H_3O^+ \overset{K_3}{\rightleftharpoons} H_2OI^+ + H_2O \; ; \qquad (3)$$

---

(1) The equilibrium constants defined throughout this thesis are expressed in terms of concentrations rather than activities.

or $$I_2 + H_2O \overset{K_5}{\rightleftharpoons} H_2OI^+ + I^- ;$$ (4)

then $$[HOI] = \frac{K_2 [I_3^-] [H_2O]^2}{K_1 [I^-]^2 [H_3O^+]}$$ (3')

$$[H_2OI^+] = \frac{K_3 K_2 [I_3^-] [H_2O]}{K_1 [I^-]^2}$$ (4')

$$[H_2OI^+] = \frac{K_5 [I_3^-] [H_2O]}{K_1 [I^-]^2}$$ (5)

It can be seen that the concentration of H_2OI^+ is directly proportional to the concentration of iodine and inversely proportional to the concentration of iodide ion. Since the concentration of I^+ is directly proportional to the concentration of H_2OI^+, these two iodinating agents are indistinguishable under most conditions.

The inverse hydrogen ion dependence implies that the transition state complex of the rate-determining step has one less proton under the reaction conditions specified than do the assumed reactants.

One possible mechanism fulfilling these requirements is (Mechanism I).

$$ArOH \overset{K_4}{\rightleftharpoons} ArO^- + H^+ ; \quad K_4 = \frac{[ArO^-][H^+]}{[ArOH]}$$ (6)

$$ArO^- + H_2OI^+ \xrightarrow[\text{slow}]{k_1} \text{products}$$ (7)

$$\text{rate} = k_1 \left[ArO^-\right]\left[H_2OI^+\right] \qquad (7')$$

then from substitution of (5) and (6) into (7')

$$\text{rate} = \frac{K_5K_4k_1}{K_1} \times \frac{\left[ArOH\right]\left[I_3^-\right]\left[H_2O\right]}{\left[H^+\right]\left[I^-\right]^2} \qquad (8)$$

Since the reaction was run in aqueous medium, then equation (8) may be modified to (8') by substituting equation (1) in (8)

$$\text{rate} = \frac{K_5K_4k_1 \left[ArOH\right]\left[I_2\right]}{\left[I^-\right]\left[H^+\right]} \qquad (8')$$

The same expression results also when I^+ is assumed to be the halogenating agent.

Thus far, it may be seen that such a mechanism leads to an expression which accounts for an inverse first-power iodide and hydrogen ion dependence.

Substitution of Equation (8) into equation (9),

$$\text{rate} = k_{app}\ (ArOH)(I_2), \qquad (9)$$

gives $$k_{app}\ (ArOH)(I_2) = \frac{K_5K_4k_1}{K_1} \times \frac{\left[ArOH\right]\left[I_3^-\right]\left[H_2O\right]}{\left[H^+\right]\left[I^-\right]^2} \qquad (10)$$

On the assumption that under acidic conditions

$$\left[ArOH\right] = (ArOH)$$

we obtain by rearranging equation (10)

$$\frac{k_{app}\ K_1\left[I^-\right]^2\ (I_2)}{\left[I_3^-\right]} = K_5K_4k_1\ \frac{\left[H_2O\right]}{\left[H^+\right]} = k' \qquad (11)$$

Equation (11) is similar to the one proposed by Berliner which demands that k' be constant in a medium of constant hydrogen ion concentration at different iodide ion concentrations. If a weaker acid such as acetic acid were used, a somewhat different equation would hold for Berliner's mechanism.

Figure 1 shows that the values of k' at constant hydrogen ion concentration are indeed constant only at high iodide ion concentrations and then start gradually dropping with decreasing iodide ion concentration. Furthermore, it is of interest to note that mechanism I cannot distinguish between H_2OI^+ and I^+ as possible halogenating species, and that distinction between a one step termolecular and two stage process is not possible in this case.

On the basis of the observed drop of k' it seems reasonable to eliminate mechanism I as a possibility.

Mechanism I'.--For a somewhat similar mechanism which involves iodination of unionized p-nitrophenol by hypoiodous acidium ion, i.e.,

$$ArOH + H_2OI^+ \xrightarrow[\text{slow}]{k_o} \text{products}, \qquad (12)$$

it can be shown that

$$\text{rate} = \frac{k_o K_5 [ArOH][I_2][H_2O]}{[I^-]} \qquad (13)$$

or

$$\text{rate} = \frac{k_o K_5 [ArOH][I_3^-][H_2O]}{K_1 [I^-]^2} \qquad (14)$$

Equation (13) accounts for zero-order hydrogen ion dependence.

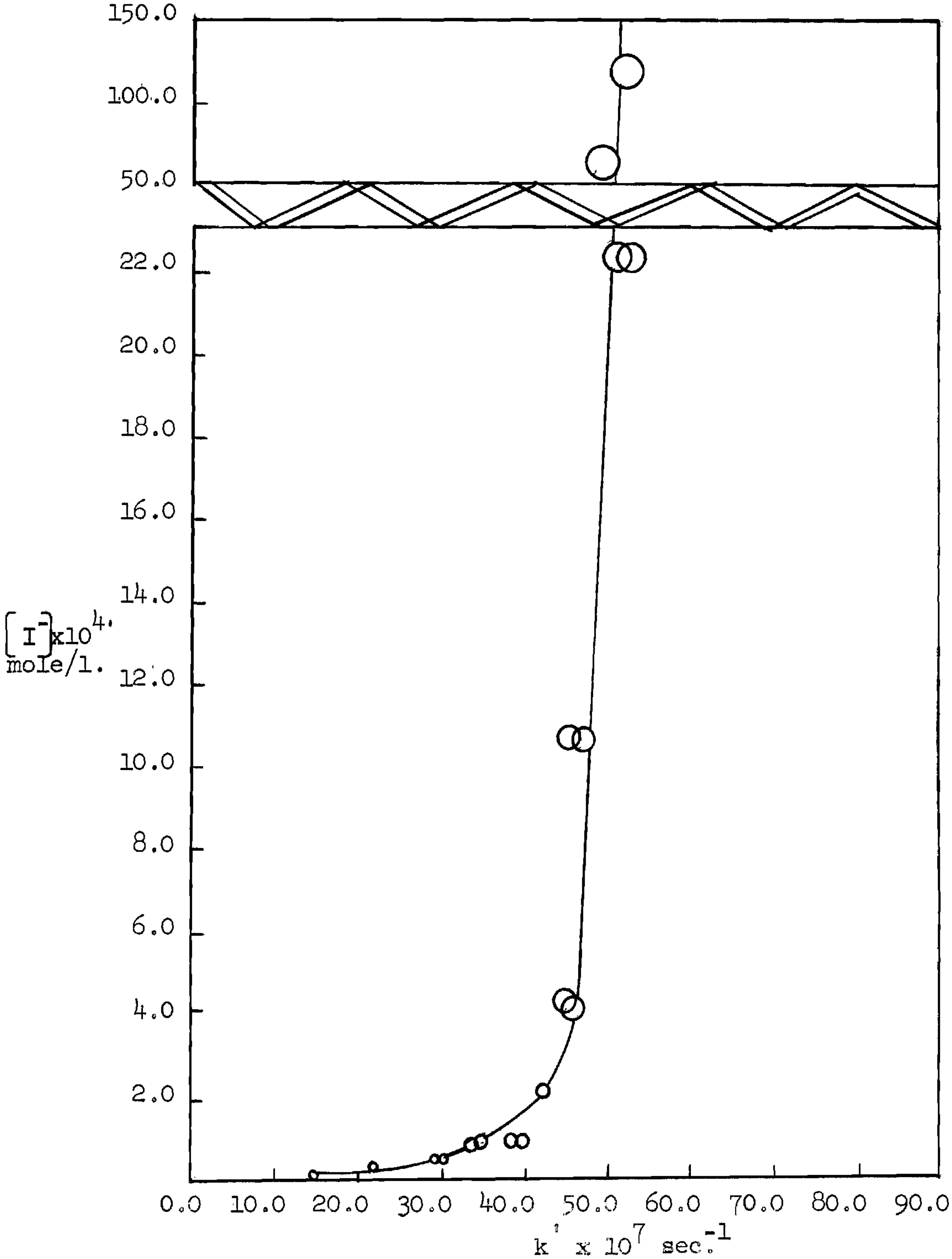


Fig. 1.- p-Nitrophenol in 0.009820 M perchloric acid

Substitution of equation (9) in (14) and the assumption that

$$\left[ArOH\right] = (ArOH)$$

gives equation (15),

$$K_5 k_o \left[H_2O\right] = \frac{k_{app}\, K_1 \left[I^-\right]^2 (I_2)}{\left[I_3^-\right]} = k' \qquad (15)$$

Such an equation demands that k' be constant at varying hydrogen and iodide ion concentrations. On the basis of the variations in k' observed, it is also reasonable to eliminate mechanism I' as a possibility.

A combined mechanism (I'') of the form

$$\text{rate} = k_1(ArO^-)(H_2OI^+) + k_o(ArOH)(H_2OI^+)$$

leads to the expression

$$K_5 K_4 k_1 \frac{\left[H_2O\right]}{\left[H^+\right]} + K_5 k_o \left[H_2O\right] = k' \qquad (16)$$

This mechanism can also be neglected on the grounds of a similar argument. Another possible mechanism is (I''')

$$ArO^- + H_2OI^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArOI + H_2O$$

$$ArOH + H_2OI^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ArOI + H^+ + H_2O$$

$$ArOI \xrightarrow[\text{slow}]{k_3} A'rOI + H^+$$

Such a mechanism as Mechanism I''', which involves the attack of H_2OI^+ on p-nitrophenoxide ion in a fast step followed by a slow abstraction of a proton, may account for the observed hydrogen ion dependency as well as the observed deuterium isotope effect. However, the iodide ion dependency is similar to that of mechanism (I) which demands that k' be constant at varying iodide ion concentrations. On the basis of the observed drop of k', mechanism (I''') is also eliminated.

Mechanism II.--To account for the non-integral iodide ion dependence and the observed trend in the values of k' and k*, it is possible to postulate a second mechanism (II) which involves iodination via molecular iodine and hypoiodous acidium ion or iodine cation. Such a possibility leads to the rate expression

$$\text{rate} = k_1'' \left[H_2OI^+\right]\left[ArO^-\right] + k_o' \left[I_2\right]\left[ArOH\right] + k_o'' \left[I_2\right]\left[ArO^-\right] \quad (17)$$

where $[ArOH]$ and $[ArO^-]$ represent the concentration of p-nitrophenol and p-nitrophenoxide ions respectively. Terms for attack of H_2OI^+ as well as any species of similar iodide ion dependence upon both p-nitrophenol and p-nitrophenoxide ion might also be included in equation (17), but at constant hydrogen ion concentration, in any event, all such expressions reduce to

$$\text{rate} = k_o'' \left[ArOH\right]\left[I_2\right] + \frac{k_1''' \left[ArOH\right]\left[I_2\right]}{\left[I^-\right]} \quad (18)$$

where k_o'' and k''' include any hydrogen ion dependency. Substitution of equation (18) into equation (9), and the assumption that

$$(ArOH) = [ArOH]$$

at acidities as used in the present work leads to the relation

$$k_{app} \frac{(I_2)}{[I_2]} = k^* = k_o'' + \frac{k_1'''}{[I^-]} \qquad (19)$$

Hence, for this mixed mechanism to hold, a plot of k^* versus $1/[I^-]$ should give a straight line. Such a plot at constant hydrogen ion concentration is shown in Figure 2 and the deviation from linearity argues against this mechanism for the iodination of p-nitrophenol.

Mechanism III.—To account for the observed iodide ion and hydrogen ion dependency of k_{app}, mechanism III is postulated.

$$ArHOH \overset{fast}{\rightleftharpoons} ArHO^- + H^+ ; \quad K_4 = \frac{[ArHO^-][H^+]}{[ArHOH]} \qquad (6)$$

$$ArHO^- + I_2 \overset{k_1}{\rightleftharpoons} ArHOI + I^- \qquad (20)$$

$$ArHOH + I_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ArHOI + H^+ + I^- \qquad (21)$$

$$ArHOI^{(1)} \longrightarrow ArOI^- + H^+ \qquad (22)$$

(1) To be sure the proton formed here is affixed to some base; this step is assumed to be subject to general base catalysis.

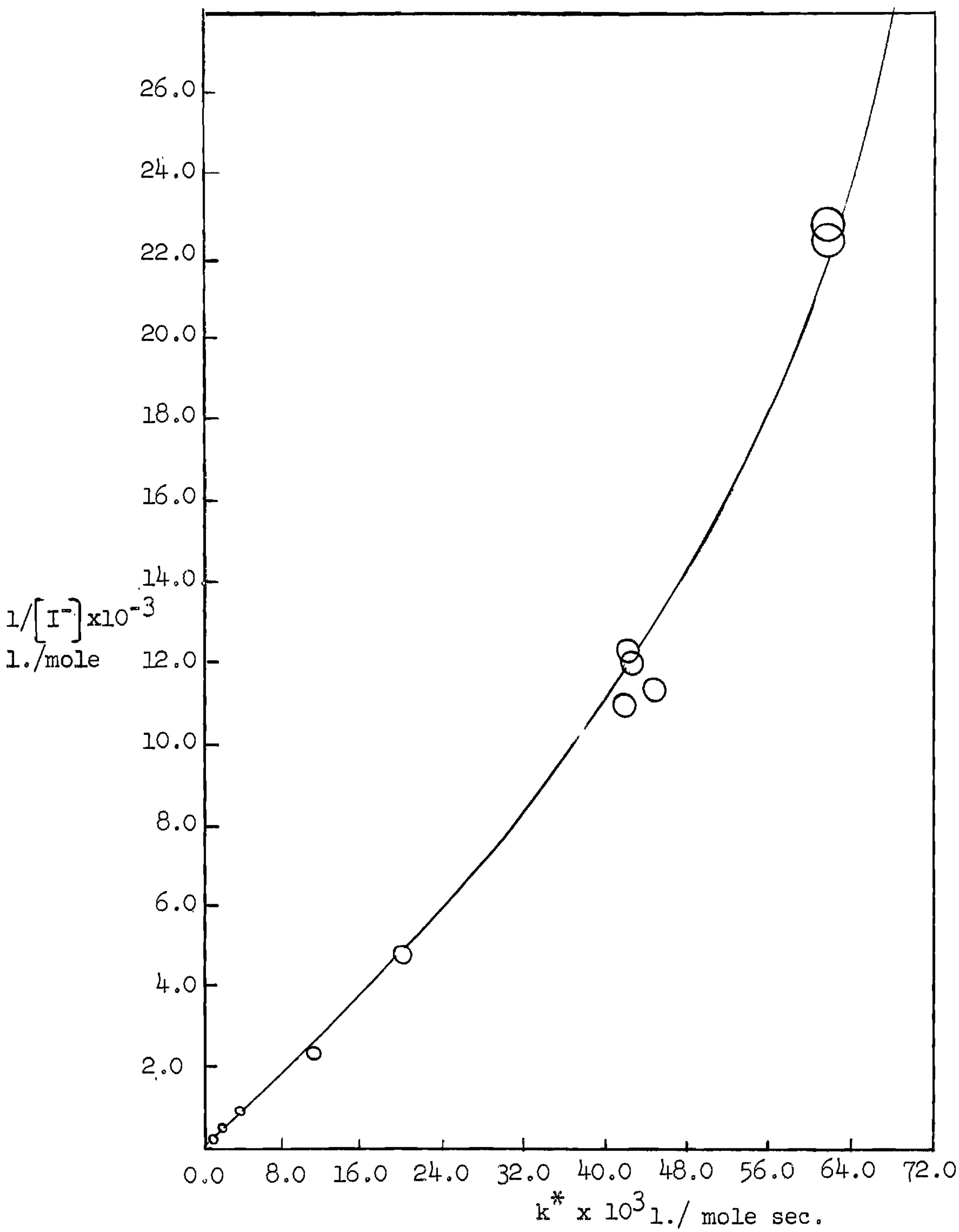
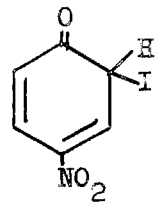


Fig. 2.- p-Nitrophenol
in 0.009820 M perchloric acid

where ArHOI is a reactive intermediate having an <u>ortho</u> quinoid type structure



Such an intermediate is assumed to be formed in small concentration relative to ArOH. Then application of steady state approximation gives

$$k_1 [ArHO^-][I_2] + k_2 [ArHOH][I_2] = k_{-1} [ArHOI][I^-] + k_{-2} [ArHOI][H^+][I^-] + k_3 [ArHOI] \quad (23)$$

Equation (23) can be rearranged to

$$[ArHOI] = \frac{k_1 [ArHO^-][I_2] + k_2 [ArHOH][I_2]}{k_{-1} [I^-] + k_{-2} [H^+][I^-] + k_3} \quad (24)$$

Substitution of equation (6) in (24) gives

$$[ArHOI] = \frac{k_1 K_4 [ArHOH][I_2] + k_2 [ArHOH][I_2][H^+]}{\left\{k_{-1} [I^-] + k_{-2} [H^+][I^-] + k_3\right\} [H^+]} \quad (25)$$

since

$$\text{rate} = k_3 [ArHOI] = k_{app}(I_2)(ArHOH) \quad (26)$$

substitution of (25) into (26) gives

$$k_{app} \frac{(I_2)\left[H^+\right]}{\left[I_2\right]} = k^* \left[H^+\right] = \frac{k_1 \times K_4 + k_2 \left[H^+\right]}{\frac{k_{-1}}{k_3}\left[I^-\right] + \frac{k_{-2}}{k_3} \times \left[H^+\right]\left[I^-\right] + 1} \qquad (27)$$

Application of equilibrium statistics and the principle of microscopic reversibility[135] to reactions (6), (20) and (21) leads to the relationship

$$\frac{k_1 K_4}{k_{-1}} = \frac{k_2}{k_{-2}} \qquad (28)$$

From equations (27) and (28) there may be obtained

$$\frac{1}{k^* \left[H^+\right]} = \frac{k_{-1}\left[I^-\right]}{k_3 k_1 K_4} + \frac{1}{k_2 \left[H^+\right] + k_1 K_4} \qquad (29)$$

According to equation (29) a plot of $1/(k^* \left[H^+\right])$ versus $\left[I^-\right]$ should give a series of parallel straight lines for each hydrogen ion concentration. Figure 3 shows that the data do indeed fall rather well upon a straight line all the way down to an initial iodide ion concentration of essentially zero. However, it is of interest to note that nearly all the points at various hydrogen ion concentration coincide on a single straight line rather than on a series of parallel lines. This is probably correct only at low hydrogen ion concentrations where $k_2 \left[H^+\right] \ll k_1 K_4$. At high hydrogen ion concentrations where $k_2 \left[H^+\right] \gg k_1 K_4$, a series of parallel lines is to be expected.

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(135) A. A. Frost and R. G. Pearson, Kinetics and Mechanism, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 202.

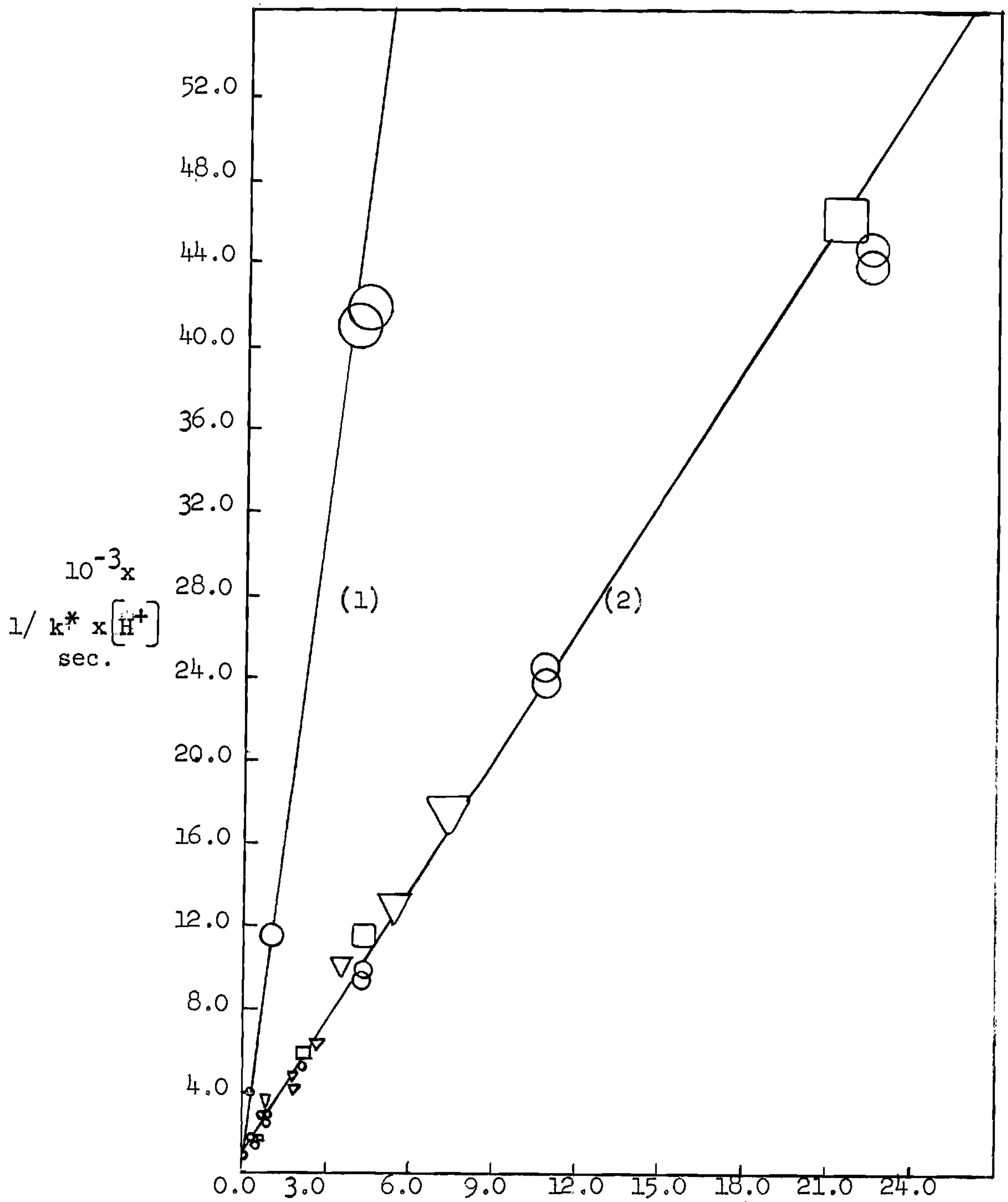


Fig. 3.– $[I^-] \times 10^4$ mole/l.

Legend: (1) 4-Nitrophenol-2,6-d_2 in 0.009820 M $HClO_4$.
(2) ◯ p-Nitrophenol in 0.009820 M perchloric acid
□ p-Nitrophenol in 0.003273 M perchloric acid
△ p-Nitrophenol in 0.001091 M perchloric acid

It is therefore reasonable to conclude that at low hydrogen ion concentrations, the overall reaction rate is independent of hydrogen ion concentration, i.e., the main species which undergoes iodination is p-nitrophenoxide ion. Hence, equation (29) may be modified to

$$\frac{1}{k^{*}\left[H^{+}\right]} = \frac{k_{-1}\left[I^{-}\right]}{k_3 k_1 K_4} + \frac{1}{k_1 K_4} \qquad (30)$$

By extrapolating the plot of $1/(k^{*}\left[H^{+}\right])$ versus $\left[I^{-}\right]$ to zero iodide ion concentration, the value of k_1K_4 may be obtained from the intercept. The slope of such plot corresponds to $k_{-1}/k_3k_1K_4$ l./mole sec. The graphical values of k_1K_4 and $k_{-1}/k_3k_1K_4$ were found to be 500 sec.$^{-1}$ and 2059 x 10^4 l./mole sec. respectively.

It is of interest to note that a similar plot for the iodination of 4-nitrophenol-2,6-d_2 gives about the same intercept but a different slope. A similar intercept is not unusual since the magnitude of secondary isotope effects are small, therefore, the magnitude of k_1K_4 is similar in p-nitrophenol and its corresponding deuterated derivative.

The presence of deuterium isotope effect presents a strong evidence in favor of mechanism (III), since it was assumed that the proton removal is the slow step. Furthermore, according to mechanism (III) the maximum deuterium isotope expected should be at high iodide ion concentrations, where k' is essentially constant. However, at low iodide ion concentrations it is expected that the magnitude of the isotope effect should drop with decreasing iodide ion concentration to essentially 1 at zero iodide ion concentration. Such a prediction is primarily based on the reversibility of the first step. At high iodide ion concentration the intermediate ArHOI is formed at small, near equilibrium concentration and the rate determining step is the reaction of equation (22). Since this reaction involves loss of a proton bound to carbon, a large (primary) isotope effect is expected. At very small iodide ion concentrations reactions (20) and (21) should not be appreciably reversed and hence these reactions correspond to the rate determining steps of the reaction. Since these reactions do not involve proton loss from the positions which are substituted with deuterium, only a small(secondary) isotope effect is expected. At intermediate values of iodide ion concentrations intermediate values are expected for the isotope effect.

The drop in the magnitude of deuterium isotope effect can also be presented mathematically. Thus, assuming that appreciable isotope effect exists only for the step (22), and neglecting secondary isotope effects and the effect of isotopic substitution upon ionization constant of p-nitrophenol

$$\mathrm{ArHOI} \xrightarrow{k_{3H}} \mathrm{ArOI}^- + \mathrm{H}^+ \qquad (22)$$

$$\mathrm{ArDOI} \xrightarrow{k_{3D}} \mathrm{ArOI}^- + \mathrm{D}^+ \qquad (22')$$

there will be two equations analogous to (29), one for the deutero and the other for the protio compound. Division of one by the other gives:

$$\frac{k^*_D\,[H^+]_D}{k^*_H\,[H^+]_H} = \frac{k_{-1}\,[I^-]_H / k_1 k_{3H} K_4 \;+\; 1/(k_2\,[H^+]_H + k_1 K_4)}{k_{-1}\,[I^-]_D / k_1 k_{3D} K_4 \;+\; 1/(k_2\,[H^+]_D + k_1 K_4)}$$

If $[H^+]$ and $[I^-]$ are the same for the deutero and the protio compounds, and if $k_2 \left[H^+\right]$ is negligible relative to $k_1 K_4$, equation (31) may be reduced to

$$\frac{k^*_D}{k^*_H} \quad \frac{\left\{k_1 \left[I^-\right] / k_{3H}\right\} + 1}{\left\{k_{-1} \left[I^-\right] / k_{3D}\right\} + 1} \tag{32}$$

Thus, according to equation (32), at relatively high iodide ion concentrations, when $\frac{k_{-1}\left[I^-\right]}{k_{3H}} \gg 1$ and $\frac{k_{-1}\left[I^-\right]}{k_{3D}} \gg 1$, then

$$\frac{k^*_D}{k^*_H} = \frac{k_{3D}}{k_{3H}} \tag{33}$$

or

$$\frac{k^*_H}{k^*_D} = \frac{\frac{k_{3H}}{k_{-1}}}{\frac{k_{3D}}{k_{-1}}} = 5.94^* \tag{34}$$

substitution equation (34) in equation (32)

$$\frac{k^*_H}{k^*_D} \quad \frac{5.94 \times \frac{k_{-1}\left[I^-\right]}{k_{3H}} + 1}{\frac{k_{-1}}{k_{3H}} \times \left[I^-\right] + 1} \tag{35}$$

(*) This value was calculated from the ratio of the slopes of protio and deutero compounds in figure 3.

Since the value of k_{-1}/k_{3H} can be determined from the slope and intercept of figure 3, then the magnitude of deuterium isotope effect can be calculated at any iodide ion concentration. The results of such calculations are tabulated in Table 107 along with the experimentally determined deuterium isotope effects. The calculated values seem to be in fair agreement with those determined experimentally. Moreover, it can be seen that the magnitude of the deuterium isotope effect diminishes with decreasing iodide ion concentration. Thus, within 250 fold change in the stoichiometric iodide ion concentration, the magnitude of the isotope effect $(k^*_H/k^*_D)^{\#}$ dropped from 5.3 to essentially 2. Such a drop is definitely significant specially when the same drop was obtained in the presence of thallium perchlorate, which eliminates some of the doubt about the possibility of inaccurate extrapolation at low iodide ion concentrations.

The preceding discussion therefore strongly supports mechanism III for the iodination of p-nitrophenol.

Rediscussion of the Mechanism of Iodination of p-Nitrophenol.--An alternative mathematical distinction between mechanism (III) and (I) is possible by evaluating the rate constants at each per cent reaction according to the iodide dependencies demanded by mechanisms III and I.

Such an evaluation is useful in the sense that no extrapolation of apparent rate constants needs to be done. Such extrapolations are especially apt to be inaccurate at low iodide ion concentrations.

(#) The deuterium isotope effect in this chapter is expressed in terms of rate constants k^*, which are corrected for triiodide formation.

Table 107

Effect of Iodide Ion Concentration on the Magnitude of Deuterium Isotope Effect.

Reference Table Protio	Deutero	$(I^-)_o \times 10^4$ (mole/l.)	$k^*_H \times 10^3$ l.mole^{-1} sec.$^{-1}$	$k^*_D \times 10^3$ l.mole^{-1} sec.$^{-1}$	$\left(\frac{k^*_H}{k^*_D}\right)_{found}$	$\left(\frac{k^*_H}{k^*_D}\right)_{calc.}$
1	43	25.000	2.29	0.43	5.32	5.89
8	44	5.000	10.50	2.43	4.33	5.68
13	46	1.000	41.80	9.04	4.62	4.94
14	47	0.500	61.60	16.14	3.76	4.25
15	48	0.500	61.50	14.81	4.16	4.23
16	49	0.250	91.00	26.62	3.47	3.48
18	50	0.100	153.20	78.40	1.95	2.43
21	51	$TlClO_4$ = 0.0500	22.60[a]	9.74[a]	2.32[a]	
		$TlClO_4$ = 0.0500	25.10[a]	8.20[a]	3.06a	

(a) Apparent second-order rate constants were used for evaluation of deuterium isotope effect since the actual iodide ion concentration is not known at 50.0°.

From mechanism (III) equation (25) we have the relationship

$$\left[ArHOI\right] = \frac{k_1K_4\left[ArHOH\right]\left[I_2\right] + k_2\left[ArHOH\right]\left[I_2\right]\left[H^+\right]}{\left\{k_{-1}\left[I^-\right] + k_{-2}\left[H^+\right]\left[I^-\right] + k_3\right\}\left[H^+\right]} \qquad (25)$$

If we assume that the concentration of p-nitrophenol, and of hydrogen ion remain constant throughout a given run, and if we assume that the ratio of actual to stoichiometric iodide ion concentration is also equal to a constant value (B) throughout a particular run, then we may derive

$$\text{rate} = \frac{\left[ArHOH\right]\left((I_2)_o + (B-1)(I^-)_o + \chi(B-2)\right) \cdot \left(k_3k_1K_4 + k_3k_2\left[H^+\right]\right)}{B\left[H^+\right]\left\{\left[(I^-)_o + \chi\right]\left[k_{-1} + k_{-2}\left[H^+\right]\right] + \frac{k_3}{B}\right\}} \qquad (36)$$

where χ = concentration of iodine reacted.

It can also be shown that

$$I_2 = (I_2)_o + (B-1)(I^-)_o + (B-2)\chi \qquad (37)$$

Equation (36) can be reduced to

$$\frac{dx}{dt} = \frac{(B-2)\left[ArHOH\right]\left\{k_3k_1K_4 + k_3k_2\left[H^+\right]\right\}}{B\left[H^+\right]\left\{k_{-1} + k_{-2}\left[H^+\right]\right\}} \cdot \frac{\left\{\frac{(I_2)_o + (B-1)(I^-)_o}{(B-2)} + \chi\right\}}{\left\{\chi + (I^-)_o + \frac{k_3}{B\left\{k_{-1} + k_{-2}\left[H^+\right]\right\}}\right\}} \qquad (38)$$

Integration of equation (26) leads to

$$gt = (h-c)\ \ln\left(\frac{c+\chi}{c}\right) + \chi \qquad (39)$$

where $$g = \frac{(B-2)}{B} \quad \frac{k_3 k_1 K_4}{k_{-1}} \quad \frac{[ArHOH]}{[H^+]}$$

$$c = \frac{(I_2)_o + (B-1)(I^-)_o}{(B-2)}$$

$$h = (I^-)_o + \frac{k_3 k_1 K_4}{k_{-1} \; B \left\{ k_2 \, [H^+] + k_1 K_4 \right\}}$$

and t = time elapsed in seconds.

Since, in equation (39), the values of g, c, t and x are known, then it can be solved for h from which the value of $1/(k_2 [H^+] + k_1 K_4)$ can be calculated. For such a calculation an accurate value of the ratio $k_{-1}/k_3 k_1 K_4$ had to be determined. From equation (29) it can be seen that if the approximate value of the intercept, (which in this case is $1/(k_2 [H^+] + k_1 K_4)$) is known, then the slope of the line which is the derived ratio can be calculated at each iodide ion concentration since

$$\frac{\dfrac{1}{k^* [H^+]} - 500}{[I^-]_o} = \frac{k_{-1}}{k_3 k_1 K_4} \qquad (40)$$

Thus, the values of $k_{-1}/k_3 k_1 K_4$ were calculated and when averaged gave a value of $2161 \pm 139.2 \times 10^4$ l./mole sec. (see Table 108). When a different intercept was assumed, the magnitude of the ratio did not change appreciably.

According to mechanism (III), it is expected that any any per cent reaction, the value of $1/(k_2 [H^+] + k_1K_4)$ is constant at varying iodide ion concentrations provided that the hydrogen ion concentration is constant. Inspection of Table 109, reveals that the values of the intercept $1/(k_2 [H^+] + k_1K_4)$ are essentially constant although at certain points a fairly large deviation in these values is present. Such a deviation may be justified since the magnitude of the intercept is quite sensitive to experimental error.

If the iodination of p-nitrophenol proceeds via mechanism (I), i.e.,

$$I_2 + H_2O \overset{K_5}{\rightleftharpoons} H_2OI^+ + I^- \qquad (4)$$

$$ArO^- + H_2OI^+ \xrightarrow[\text{slow}]{k_1} \text{products} \qquad (7)$$

$$ArOH + H_2OI^+ \xrightarrow[\text{slow}]{k_1'} \text{products} \qquad (12)$$

then

$$\frac{-d(I_2)}{dt} = k_1 [ArO^-][H_2OI^+] + k_1' [ArOH][H_2OI^+] \qquad (41)$$

or

$$\frac{-d(I_2)}{dt} = \frac{k_1K_4 [ArOH][H_2OI^+]}{[H^+]} + k_1' [ArOH][H_2OI^+] \qquad (42)$$

substitution equation (4) into (42)

$$\frac{-d(I_2)}{dt} = \frac{k_1K_4K_5 [ArOH][I_2]}{[H^+][I^-]} + \frac{k_1'K_5 [ArOH][I_2]}{[I^-]} \qquad (43)$$

Table 108

Evaluation of the Magnitude of $k_{-1}/k_3k_1K_4$ for the Iodination of p-Nitrophenol in 0.009820 M Perchloric acid at 50.0°.

Reference Table	$[I^-]_o$ mole/l.	$\frac{1}{k^*[H^+]}$	$\frac{1}{k^*[H^+]} - 500$	$\frac{\frac{1}{k^*[H^+]} - 500}{[I^-]_o} = \frac{k_{-1}}{K_4k_3k_1}$
16	0.2345×10^{-4}	1,116	616	2630×10^4
14	0.4450×10^{-4}	1,528	1,028	2310×10^4
13	0.9135×10^{-4}	2,346	1,846	2020×10^4
9	2.1190×10^{-4}	5,151	4,651	2190×10^4
8	4.254×10^{-4}	9,697	9,196	2160×10^4
6	10.730×10^{-4}	23,981	23,481	2190×10^4
2	22.323×10^{-4}	44,021	43,520	1950×10^4
3	61.567×10^{-4}	127,607	127,107	2060×10^4
4	121.59×10^{-4}	236,376	235,876	1940×10^4
				Av. $2161 \pm 139 \times 10^4$

Table 109

Mathematical Evaluation of the Mechanism of Iodination of p-Nitrophenol

Ref. Table	$(I^-)_o \times 10^4$	$B_{av.}$	Per cent reaction	$\frac{1}{k_2 [H^+] + k_1K_4}$	$k_1K_5K_4 + k_1'K_5 [H^+] \times 10^8$
18	0.1000	0.950	0.00	- - - -	1.422*
"	"	"	10.53	507.7	1.185
"	"	"	16.05	574.9	1.924
"	"	"	25.26	649.2	2.064
"	"	"	31.10	668.1	2.048
"	"	"	41.05	718.4	2.356
"	"	"	48.00	628.7	2.653
17	0.1000	0.960	0.00	- - - -	1.434*
"	"	"	8.87	458.0	1.851
"	"	"	15.68	376.1	1.262
"	"	"	21.89	465.9	2.232
"	"	"	30.47	597.0	1.960
"	"	"	34.32	565.7	2.309
"	"	"	52.07	425.7	3.079
16	0.2500	0.947	0.00	- - - -	2.101*
"	"	"	10.56	564.2	2.503
"	"	"	17.45	584.1	2.643
"	"	"	26.29	515.5	2.968
"	"	"	34.26	571.1	3.000
"	"	"	42.89	538.3	3.204
"	"	"	54.74	494.3	3.448
14	0.5000	0.950	0.00	- - - -	2.975*
"	"	"	13.60	581.4	1.147
"	"	"	20.40	443.0	3.582
"	"	"	24.70	1010.0	2.830
"	"	"	29.82	794.5	3.208
"	"	"	39.85	674.3	3.461
15	0.5000	0.930	0.00	- - - -	2.848*
"	"	"	14.66	425.0	3.614
"	"	"	21.75	193.0	4.191
"	"	"	26.57	443.0	3.771
"	"	"	33.86	660.2	3.556
"	"	"	43.86	352.0	4.088
"	"	"	44.36	915.7	3.438

(*) These values were calculated from the extrapolated values of k' at zero per cent reaction.

By making the same assumptions as above for mechanism III, we may rewrite equation (43) as

$$\frac{dx}{dt} = \left\{\frac{k_1K_4K_5b}{B\,[H^+]} + \frac{k_1'K_5b}{B}\right\}\left\{\frac{(I_2)_o + (B-1)(I^-)_o + (B-2)x}{(I^-)_o + x}\right\} \qquad (44)$$

in which $b = [ArOH]$

Integration of equation (44) leads to

$$lt = (h-c)\ln\left(\frac{c+x}{c}\right) + x \qquad (45)$$

in which

$$c = \frac{(I_2)_o + (B-1)(I^-)_o}{(B-2)}$$

$$l = \frac{k_1K_4K_5b + k_1'K_5b\,[H^+]\,(B-2)}{B\,[H^+]}$$

$$h = (I^-)_o$$

$$t = \text{time elapsed in seconds}$$

From equation (45) the value of $\underline{l}$ may be calculated from which the value of $k_1K_4K_5 + k_1'K_5\,[H^+]$ can be calculated as well.

Since the value of $k_1K_4K_5 + k_1'K_5\,[H^+]$ is somewhat related to Berliner's rate constant k' through equation (16') i.e.,

$$\frac{K_5K_4k_1}{[H^+]} + K_5k_o = k' \qquad (16')$$

in which the concentration of H_2O is neglected, k' can be calculated.

If the iodination of p-nitrophenol proceeds via mechanism (I"), then the values of $k_1K_4K_5/\left[H^+\right] + k_oK_5$ or alternatively k', ought to be constant in the entire range of iodide ion concentration.

Inspection of Table 109 reveals, however, that the values of $k_1K_4K_5 + k_1'K_5\left[H^+\right]$ or $k'\left[H^+\right]$ decrease with diminishing iodide ion concentration. On these grounds as well, therefore, it seems reasonable to exclude mechanism (I) or its modifications as possibilities.

The variation of B throughout a run is given in Table 110. Calculations with different magnitudes of B in a particular run showed that the effect of small variations of B on the magnitude of the rate constants calculated by either mechanism is negligible. Therefore, an average value of B was taken at each particular iodide ion concentration.

Table 110

Variation of B in Run 108-V-1, Table 18

Per cent reaction	$(I_2) \times 10^4$	$[I_3^-] \times 10^4$	$[I^-] \times 10^4$	$(I^-) \times 10^4$	$\frac{[I^-]}{(I^-)} = B$
0.00	1.14400	0.005285	0.09472	0.10000	0.9472
10.53	1.02354	0.010399	0.21012	0.22046	0.9531
16.05	0.96039	0.012588	0.27102	0.28361	0.9556
20.00	0.91520	0.014040	0.31480	0.32880	0.9574
25.26	0.85503	0.015517	0.37345	0.38897	0.9601
32.10	0.77878	0.016771	0.45045	0.46722	0.9641
41.05	0.67439	0.017750	0.55186	0.56961	0.9688
48.00	0.59488	0.01784	0.63128	0.64912	0.9725
					Av. = 0.9598

CHAPTER VII

THE MECHANISM OF IODINATION OF ANISOLE

Introduction.--Experiments in tables 53, 54, 55, 56, and 57 indicate that at constant iodide ion concentration, the iodination of anisole is first order in stoichiometric concentration of both iodine and anisole. Hence, as in the case of p-nitrophenol, the apparent rate constants were calculated on this basis. The rate constants, as demonstrated in Chapter V, were found to be dependent on iodide ion concentration.

At low iodide ion concentrations the apparent rate constants were extrapolated to zero per cent reaction in order to obtain a value of k_{app} at a definite $[I^-]$, whereas at relatively high iodide ion concentrations an average was taken. Hydrogen ion dependence in this case was assumed to be nil, since it is evident that no ionization is possible, and this assumption was verified by experiment.

The iodide ion dependency can be demonstrated in terms of the rate constants k^* and k'. Thus, when the stoichiometric iodide ion concentration was lowered by 100 fold, the rate constant k^* increased by approximately two fold (See Table 111). As in the case of p-nitrophenol, k_{app} follows a non-integral iodide ion dependence, somewhere between an inverse second-order and zero-order dependence. Alternatively, k^* has an iodide ion dependence between inverse first-order and zero-order.

Table 111

Effect of Iodide Ion Concentration on the Rate of Iodination of Anisole

$[I^-] \times 10^4$ (mole /l.)	k_{app} (l./mole sec.)	$k^* \times 10^4$ (l./mole sec.)	$k^* x [I^-] = k'_a$	Ref. Table
9.1790	1.87×10^{-4}	2.94	27.0×10^{-8}	58
4.5189	5.45×10^{-4}	6.66	30.0×10^{-8}	59
4.7664	5.15×10^{-4}	6.33	30.2×10^{-8}	60
2.8616	8.21×10^{-4}	10.08	28.9×10^{-8}	61
0.9479	2.90×10^{-3}	30.19	28.9×10^{-8}	62
0.437	6.63×10^{-3}	67.8	32.1×10^{-8}	55
0.2366	10.86×10^{-3}	109.7	25.9×10^{-8}	63
0.1645	12.90×10^{-3}	130.0	21.4×10^{-8}	64
0.0953	15.70×10^{-3}	158.0	15.1×10^{-8}	65
0.0943	17.30×10^{-3}	173.7	17.4×10^{-8}	66

Table 112

Effect of Iodide Ion Concentration on the Rate of Iodination of Anisole-2,4,6-d_3

$[I^-] \times 10^4$ (mole/l.)	k_{app} (l./mole sec.)	$k^* \times 10^4$ (l./mole sec.)	$k^* [I^-] = k'_a$ (sec.$^{-1}$)	Ref. Table
4.7680	1.59×10^{-4}	1.96	9.35×10^{-8}	73
2.8537	2.59×10^{-4}	2.95	8.41×10^{-8}	74
0.9458	10.40×10^{-4}	10.88	10.30×10^{-8}	75
0.4692	22.20×10^{-4}	22.70	10.60×10^{-8}	76
0.2361	3.48×10^{-3}	35.20	8.32×10^{-8}	77
0.1654	3.80×10^{-3}	38.60	6.38×10^{-8}	78
0.0948	5.80×10^{-3}	57.00	5.50×10^{-8}	79
0.0946	6.00×10^{-3}	60.20	5.69×10^{-8}	80

To account for the iodide ion dependence, we considered the following mechanisms which are analogous to the ones described in Chapter VI.

$$ArOMe + H_2OI^+ \xrightarrow[\text{slow}]{k_{1a}} \text{products} \qquad (7'')$$

$$\text{rate} = k_{1a} [ArOMe][H_2OI^+] \qquad (7''')$$

substitution equation (5) Chapter VI in (7''') we obtain

$$\text{rate} = \frac{K_5 k_{1a}}{K_1} \times \frac{[ArOMe][I^-_3][H_2O]}{[I^-]^2} \qquad (8'')$$

Since the reaction was run in aqueous medium, then the concentration of water may be neglected in this case also. Substitution equation (1) in (8'')

$$\text{rate} = \frac{K_5 k_{1a} [ArOMe][I_2]}{[I^-]} \qquad (8''')$$

Equation (8''') thus gives an inverse first-power iodide ion dependence.

Equation (7''') can be modified to a relationship which involves k_{app}:

$$\text{rate} = k_{app}(ArOMe)(I_2) = k_{1a}[ArOMe][H_2OI^+] \qquad (9')$$

then

$$k_{app}(ArOMe)(I_2) = \frac{K_5 k_{1a}}{K_1} \times \frac{[ArOMe][I_3][H_2O]}{[I^-]^2} \qquad (10')$$

rearranging equation (10')

$$\frac{k_{app}K_1 \left[I^-\right]^2 (I_2)}{\left[I^-_3\right]} = K_5 k_{1a} \left[H_2O\right] = k' \qquad (11')$$

Equation (11') is rather similar to the one proposed by Berliner, which demands that k' be constant at varying iodide ion concentrations. Figure 4 however, shows that the values of k' are only constant at high iodide ion concentrations and then start dropping with decreasing iodide ion concentration. Mechanism I, therefore, is unlikely either as a two-stage process or as a termolecular reaction.

Mechanism II.--To account for the non-integral iodide ion dependence and the observed trend in the values of k' and k^*, it is possible to postulate a second mechanism (II) which involves iodination via molecular iodine and hypoiodous acidium ion or iodine cation. Such a possibility leads to the rate equation

$$\text{rate} = k \left[I_2\right]\left[ArOMe\right] + k_o \left[H_2OI^+\right]\left[ArOMe\right] \qquad (17')$$

Equation (17') may be reduced to

$$\text{rate} = k \left[ArOMe\right]\left[I_2\right] + \frac{k'_o \left[ArOMe\right]\left[I_2\right]}{\left[I^-\right]} \qquad (18')$$

As a test of this mechanism, since

$$\text{rate} = k_{app} (ArOMe)(I_2)$$

$$\text{and } [ArOMe] = (ArOMe)$$

then

$$k_{app} \frac{(I_2)}{[I_2]} = k^{*} = k + \frac{k'_o}{[I^-]} \tag{19'}$$

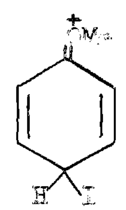
Hence for this mixed mechanism to hold, a plot of k^{*} versus $1/[I^-]$ should give a straight line. Such a plot is shown in figure 5 and the deviation from linearity argues against this mechanism for iodination of anisole.

Mechanism III.--To account for the observed iodide ion dependency of k_{app}, mechanism III is postulated.

$$ArOMe + I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArOMeI^{+} + I^{-} \tag{46}$$

$$ArOMeI^{+} \xrightarrow{k_3} Ar'OMeI + H^{+} \tag{47}$$

where $ArOMeI^{+}$ is a reactive intermediate having a para quinoid type structure[a]:



Such an intermediate is assumed to be formed in small concentration relative to ArOMe. Then on the basis of the steady state approximation:

$$k_1 [ArOMe][I_2] = k_{-1} [ArOMeI^{+}][I^{-}] + k_3 [ArOMeI^{+}] \tag{48}$$

(a) It is assumed that predominant substitution takes place at the para position.

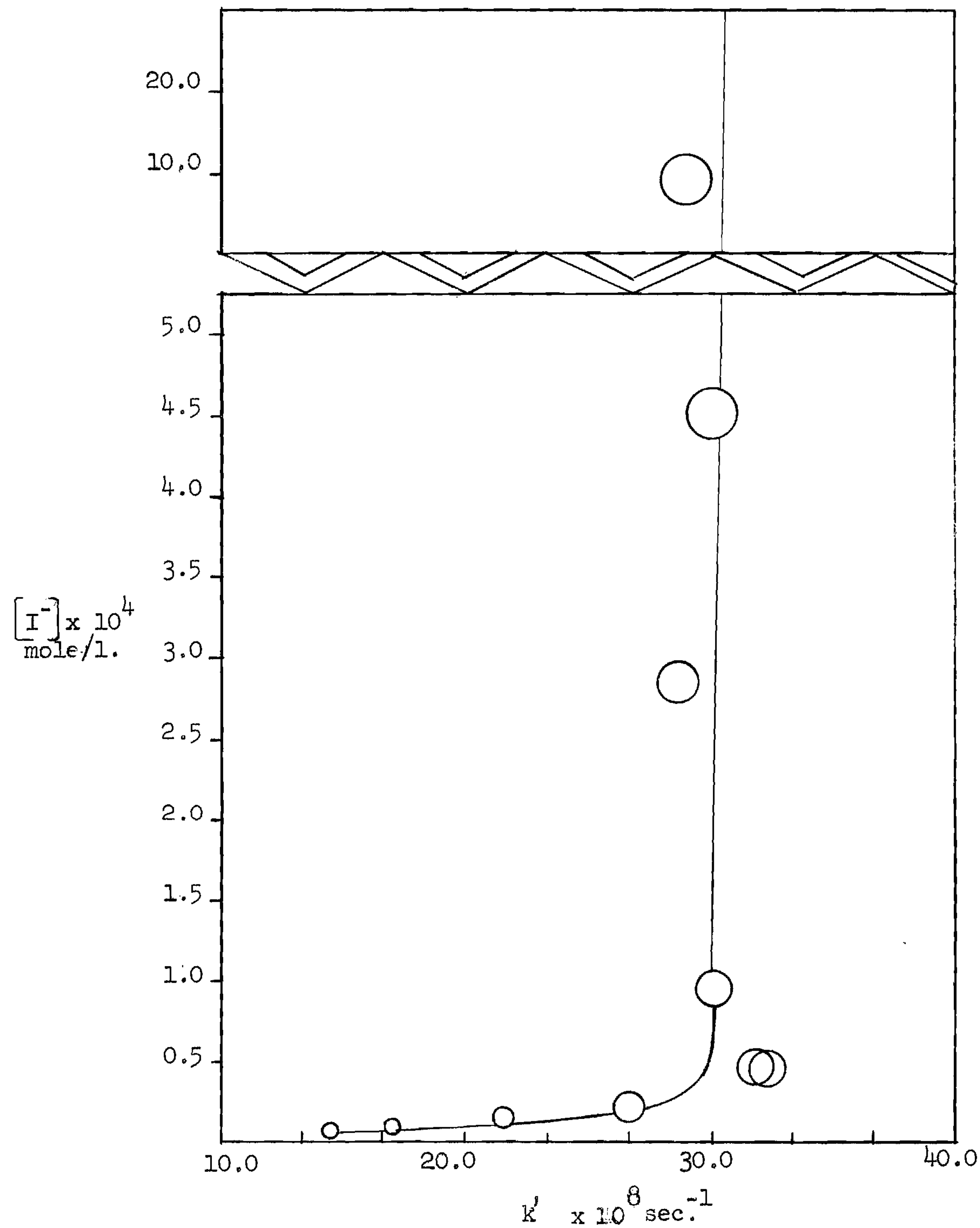


Fig. 4.—Anisole in 0.009783 M perchloric acid

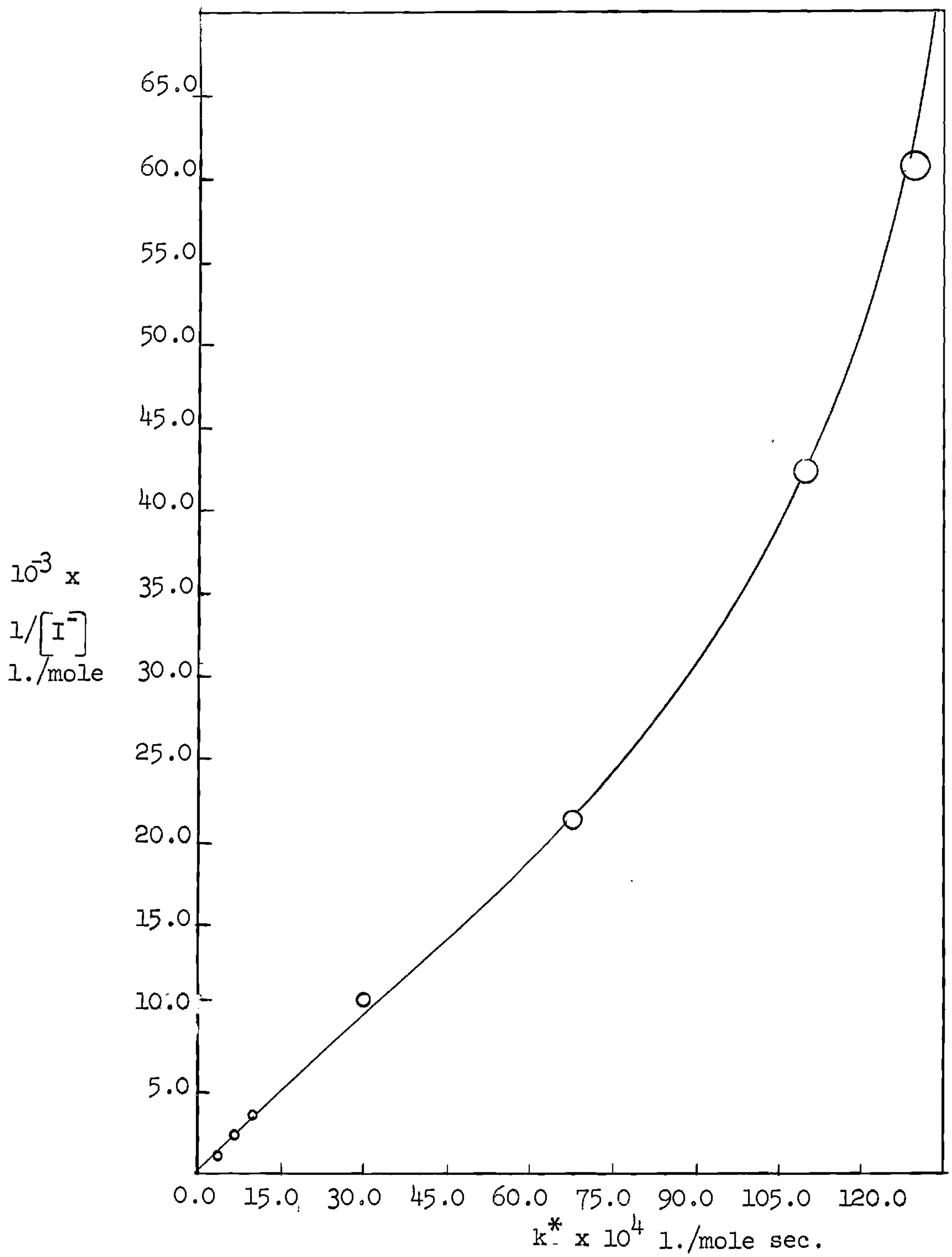


Fig. 5.- Anisole in 0.009783 M perchloric acid

solving for $ArOMeI^{+}$ gives

$$\left[ArOMeI^{+}\right] = \frac{k_1 \left[ArOMe\right]\left[I_2\right]}{k_{-1}\left[I^{-}\right] + k_3} \tag{49}$$

since

$$\text{rate} = k_3 \left[ArOMeI^{+}\right] = k_{app}\,(I_2)(ArOMe) \tag{50}$$

Substitution of equation (49) in (50) gives

$$k_{app}\,(I_2)(ArOMe) = \frac{k_3 k_1 \left[ArOMe\right]\left[I_2\right]}{k_{-1}\left[I^{-}\right] + k_3}$$

On the basis that $(ArOMe) = \left[ArOMe\right]$

then

$$k_{app}\,(I_2) = \frac{k_3 k_1 \left[I_2\right]}{k_{-1}\left[I^{-}\right] + k_3} \tag{51}$$

or

$$k_{app}\frac{(I_2)}{\left[I_2\right]} = k^{*} = \frac{k_3 k_1}{k_{-1}\left[I^{-}\right] + k_3} \tag{52}$$

Equation (52) can be rearranged to

$$\frac{1}{k^{*}} = \frac{k_{-1}\left[I^{-}\right]}{k_3 k_1} + \frac{1}{k_1} \tag{53}$$

According to equation (53) a plot of $1/k^{*}$ versus $\left[I^{-}\right]$ should give a straight line. Figure 6 shows that the data do indeed fall on a straight line. By extrapolating this plot to zero iodide ion

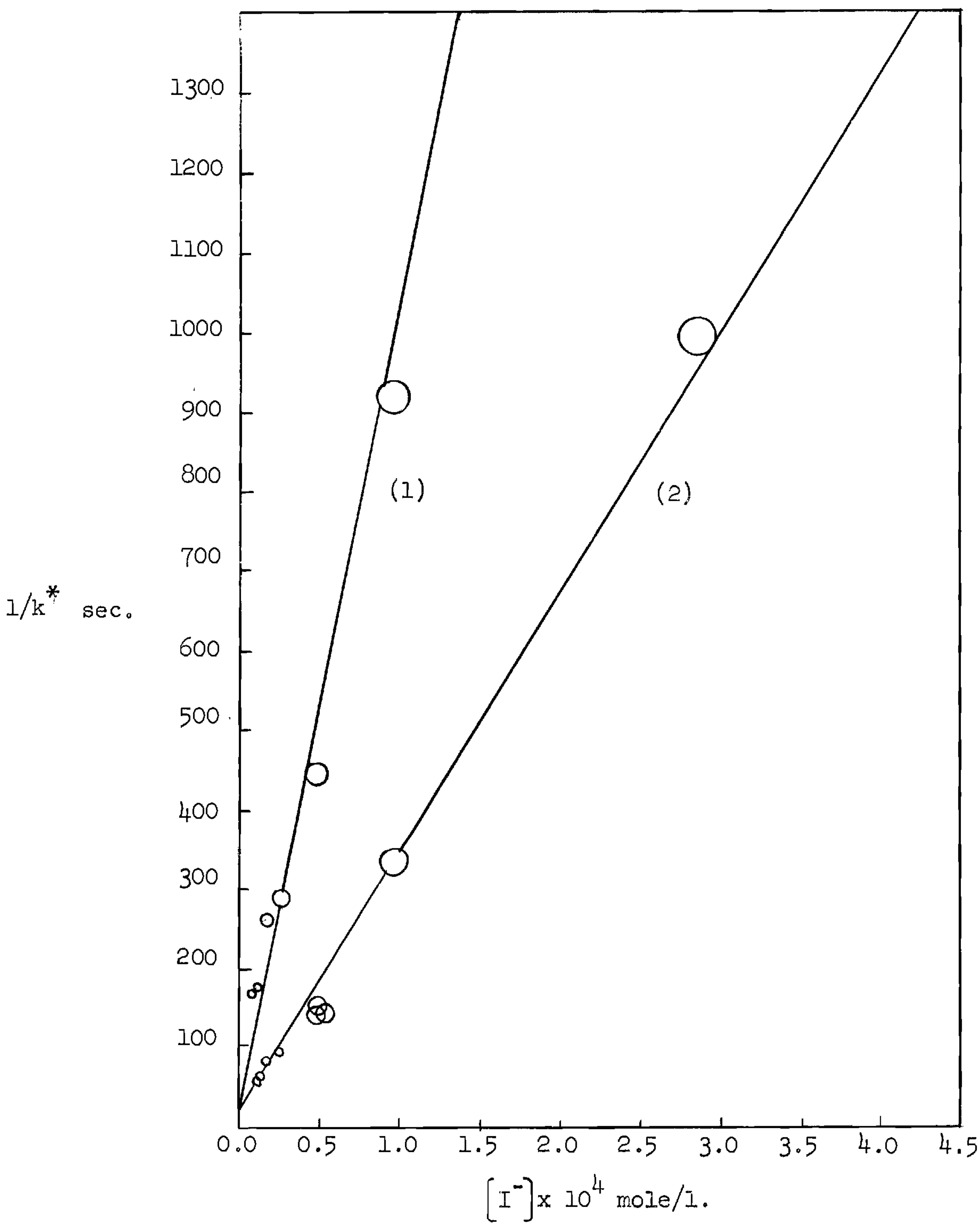


Fig. 6

(1) Anisole-2,4,6-d_3 in 0.009783 M perchloric acid
(2) Anisole in 0.009783 M perchloric acid

concentration, the value of k_1 may be obtained from the intercept. The slope of such a plot corresponds to k_{-1}/k_3k_1. The graphical values of k_1 and k_{-1}/k_3k_1 were found to be 30 l./mole sec. and 296.2 x 10^4 sec.$^{-1}$ respectively.

A similar plot for the iodination of anisole-2,4,6-d_3 gave approximately the same intercept but a different slope. Such a case is not unusual since it is expected that k_1 be the same for both anisole and its deuterated derivative.

The presence of a deuterium isotope effect provides strong evidence in favor of mechanism (III), since it was assumed that proton removal is the slow step. As in the case of p-nitrophenol, it is expected that the maximum deuterium isotope effect be at high iodide ion concentrations, where k' is essentially constant. However, at low iodide ion concentrations, it is expected that the magnitude of the isotope effect drop with decreasing iodide ion concentration. The justification for such a prediction is similar to that for p-nitrophenol.

The deuterium isotope effect as a function of iodide ion concentration can be accounted for mathematically. Thus, rewriting equation (32) in Chapter VI

$$\frac{k^*_D}{k^*_H} = \frac{\left\{k_{-1}\left[I^-\right]/k_{3H}\right\} + 1}{\left\{k_{-1}\left[I^-\right]/k_{3D}\right\} + 1} \qquad (32)$$

At high iodide ion concentrations where

$$\frac{k_{-1}\left[I^-\right]}{k_{3H}} \gg 1$$

and

$$\frac{k_{-1}\left[I^-\right]}{k_{3D}} \gg 1,$$

then

$$\frac{k^*_D}{k^*_H} = \frac{k_{3D}}{k_{3H}} = 3.2 \qquad (33')$$

Equation (32) can then be rewritten as

$$\frac{k^*_H}{k^*_D} = 3.2 \times \frac{\dfrac{k_{-1}\left[I^-\right]}{k_{3H}} + 1}{\dfrac{k_{-1}\left[I^-\right]}{k_{3H}} + 1}$$

Thus, it can be seen that the magnitude of the isotope effect can be readily calculated at any iodide ion concentration provided that the magnitude of k_{-1}/k_{3H} is known. This ratio can be calculated from the slope and intercept of the plot of $1/k^*$ versus $\left[I^-\right]$. The calculated value of k_{-1}/k_{3H} was found to be 888.6×10^5 l./mole. The results of such calculations are tabulated in Table 113 along with the experimentally determined deuterium isotope effects. It can be seen that the deuterium isotope effect remains essentially constant although deviations are observed which are believed to be due to experimental errors. Furthermore, it is of interest to note that the calculated values also remain essentially constant. This can be interpreted in terms of the reversibility of the first step and the ratio of k_{-1}/k_3. Since it is

Table 113

Effect of Iodide Ion Concentration on the Magnitude of Deuterium Isotope Effect in the Iodination of Anisole.

Reference Table Protio	Deutero	$(I^-)_o$ mole/l.	$k^*_H \times 10^4$ l./mole sec.	$k^*_D \times 10^4$ l./mole sec.	$\left(\frac{k^*_H}{k^*_D}\right)_{found}$	$\left(\frac{k^*_H}{k^*_D}\right)_{calc.}$
59	73	5.000×10^{-4}	6.66	1.96	3.40	3.20
60		5.000×10^{-4}	6.33		3.23	3.20
61	74	3.000×10^{-4}	10.08	2.95	3.42	3.20
62	75	1.000×10^{-4}	30.19	10.9	2.77	3.20
55	76	0.500×10^{-4}	67.8	22.7	2.98	3.20
63	77	0.250×10^{-4}	109.7	35.2	3.12	3.20
64	78	0.175×10^{-4}	130.0	38.6	3.36	3.20
65	79	0.100×10^{-4}	158.2	57.0	2.78	3.19
66	80	0.100×10^{-4}	173.7	60.2	2.88	3.19
67	81	$Tl^+ = 0.0500$	221.0[a]	68.0[a]	3.25[a]	
68		$Tl^+ = 0.0500$	188.0[a]		2.77[a]	
69	82	$Tl^+ = 0.2000$	720.0[a]	260.0[a]	2.77[a]	
70	83	$Tl^+ = 0.5149$	1300[a]	1070[a]	1.21[a]	
71	84	$Tl^+ = 0.5149$	1290[a]	1030[a]	1.25[a]	
		1×10^{-6}				3.17
		1×10^{-7}				2.98
		1×10^{-8}				2.04
		1×10^{-9}				1.18

(a) Apparent second order rate constants were used for evaluations of deuterium isotope effect since the actual iodide ion concentration was not known.

evident that the magnitude of this ratio is much greater than in the case of p-nitrophenol, it seems evident that much lower iodide ion concentrations need to be used to obtain any appreciable drop in deuterium isotope effect. Calculations according to equation (32) show that at an iodide ion concentration of the order of 10^{-8} there should be an experimentally detectable drop in the magnitude of deuterium isotope effect. The experimental data at 0.5149 M thallium perchlorate, however, reveal that the isotope effect diminished to essentially 1.25. According to equation (32), such a drop seems somewhat unreasonable. However, experiments at such a high thallium perchlorate solution are apt to be in greater error than others. First, the ionic strength of the medium is higher than the standard reaction conditions. The heterogeneous nature of the reaction probably introduces another source of error. Furthermore, the reaction

$$6TlI + I_2 \longrightarrow Tl_6I_8$$

is more prominent in this case. And finally the magnitude of k_{-1}/k_3 could be in some error as well.

Based on the drop in the magnitude of k', it seems reasonable to exclude mechanism I and accept mechanism III as a possible path for the iodination of anisole.

Rediscussion of the Mechanism of Iodination of Anisole.--An altervative mathematical distinction between mechanism (III) and (1) is possible by evaluating the various rate constants at a certain per cent reaction.

From mechanisms (III) equation (49) we have the relationship

$$\left[ArOMeI^{+}\right] = \frac{k_1 \left[ArOMe\right]\left[I_2\right]}{k_{-1}\left[I^{-}\right] + k_3} \qquad (49)$$

Assuming that the concentration of anisole remains constant throughout the reaction and that the ratio of actual to stoichiometric iodide ion concentration is also equal to a constant value (B) throughout a particular run, then

$$I_2 = (I_2)_o + (B-1)(I^-)_o + (B-2)\,\chi \qquad (37)$$

$$\frac{dx}{dt} = \frac{k_3 k_1 \left[ArOMe\right] (I_2)_o + (B-1)(I^-)_o + (B-2)\,\chi}{Bk_{-1}\left[(I^-)_o + \chi\right] + k_3} \qquad (54)$$

where χ = concentration of iodine reacted.

Integration of equation (54) leads to

$$gt = (h-c)\ \ln\left(\frac{c+\chi}{c}\right) + \chi \qquad (55)$$

where

$$g = (B-2)\left[ArOMe\right] x \frac{k_3 k_1}{Bk_{-1}}$$

$$c = \frac{(I_2)_o + (B-1)(I^-)_o}{(B-2)}$$

$$h = (I^-)_o + k_3/Bk_{-1}$$

and t = time elapsed in seconds.

Since in equation (55), the values of $\underline{g}$, $\underline{c}$, $\underline{t}$, and $\underline{\chi}$ are known, then the equation can be solved for $\underline{h}$ from which the value of k_3/k_{-1}

can be calculated. To calculate the value of k_1 or $1/k_1$ which corresponds to the intercept of figure 6, an accurate knowledge of the magnitude of the slope is necessary. From equation (53), it can be seen that if the approximate value of the intercept is known, then the slope of the line can be calculated at each iodide ion concentration since

$$\text{slope} = \frac{(1/k^*) - 20}{[I^-]} = \frac{k_{-1}}{k_3 k_1}$$

Thus, the values of the slope were calculated and when averaged gave a value of 324×10^4 sec.^{-1} (See Table 114). When a different intercept was assumed, the magnitude of the slope did not change appreciably.

According to mechanism (III), it is expected that at any per cent reaction, the values of $1/k_1$ be constant at varying iodide ion concentrations. Table 115, reveals that the intercept $1/k_1$ is essentially constant although at certain points a fairly large deviation in these values are present. Such a deviation, as mentioned previously, is due to sensitivity of the intercept to experimental errors.

If the iodination of anisole proceeds via mechanism (I), then

$$\text{rate} = k_{1a}\,[\text{ArOMe}]\,[H_2OI^+] = \frac{K_5 k_{1a}\,[\text{ArOMe}]\,[I_2]}{[I^-]} \qquad (7'')$$

By making the same assumptions as for Mechanism (III), we may rewrite equation (7'') as

Table 114

Evaluation of the Magnitude of k_{-1}/k_3k_1 for the Iodination of Anisole at 50.0°

Reference Table	$[I^-]_o \times 10^4$ mole/liter	$\frac{1}{k^*}$	$\frac{1}{k^*} - 20$ [a]	$\frac{\frac{1}{k^*} - 20}{[I^-]} = \frac{k_{-1}}{k_3k_1}$
58	9.1790	3398	3378	370×10^4
59	4.5189	1500	1480	328×10^4
60	4.7664	1576	1556	327×10^4
61	2.8616	991	971	328×10^4
62	0.9479	330	310	327×10^4
65	0.4737	148	128	269×10^4
63	0.2366	91	71	301×10^4
64	0.1645	77	57	346×10^4
				Av. = $324 \pm 20 \times 10^4$

(a) An intercept of 20 l./mole sec. was used in calculating the slope since it gave a value with the least deviation in k_{-1}/k_3k_1.

$$\frac{dx}{dt} = \frac{K_5 k_{1a} \left[ArOMe\right] \quad (I_2)_o + (B-1)(I^-)_o + (B-2)\chi}{B\left[(I^-)_o + \chi\right]} \qquad (56)$$

or

$$\frac{dx}{dt} = \frac{K_5 k_{1a} \left[ArOMe\right] \left\{\frac{(I_2)_o + (B-1)(I^-)_o}{(B-2)} + \chi\right\}}{B\left\{(I^-)_o + \chi\right\}} \qquad (57)$$

Integration of equation (57) leads to

$$lt = (h-c) \ln \left(\frac{c + \chi}{c}\right) + \chi \qquad (58)$$

in which

$$c = \frac{(I_2)_o + (B-1)(I^-)_o}{(B-2)}$$

$$l = \frac{K_5 k_{1a} (B-2) \left[ArOMe\right]}{B}$$

$$h = (I^-)_o$$

$$t = \text{time elapsed in seconds}$$

From equation (58) the value of <u>l</u> may be calculated and from this, the value of $k_{1a}K_5$ can be calculated as well. From equation (11'), it can be seen that the value of $k_{1a}K_5$ is the same as Berliner's rate constant k', in which the concentration of H_2O is neglected.

If the iodination of anisole proceeds by mechanism (I), then the values of k_1K_5 ought to be constant in the entire range of iodide ion concentration.

Inspection of table 115, reveals however, that the magnitude of $k_{1a}K_k$ or k' decrease with diminishing iodide ion concentration. On these grounds, therefore, it is reasonable to exclude mechanism (I) as a possibility.

Table 115

Mathematical Evaluation of the Mechanism of Iodination of Anisole

Reference Table	$(I^-)_o \times 10^4$ mole/l.	$B_{av.}$	per cent reaction	$\frac{1}{k_1}$	$k' \times 10^8$ or $k_{1a}K_5 \times 10^8$
65	0.1000	0.960	0.00	--	15.1
65	0.1000	0.960	5.64	20.9	20.3
65	0.1000	0.960	9.49	25.3	20.3
65	0.1000	0.960	18.10	33.1	19.9
65	0.1000	0.960	22.55	34.6	20.4
65	0.1000	0.960	31.75	30.5	22.5
65	0.1000	0.960	35.60	36.8	21.9
64	0.1750	0.950	0.00	--	21.4
64	0.1750	0.950	8.74	19.3	24.7
64	0.1750	0.950	13.79	27.1	23.2
64	0.1750	0.950	17.70	19.6	23.4
64	0.1750	0.950	24.60	35.6	23.2
64	0.1750	0.950	31.03	38.3	23.4
64	0.1750	0.950	44.82	78.9	20.4
63	0.2500	0.950	0.00	--	25.9
63	0.2500	0.950	9.25	20.16	25.4
63	0.2500	0.950	15.17	5.57	29.3
63	0.2500	0.950	19.02	4.23	29.7
63	0.2500	0.950	24.94	4.73	29.7
63	0.2500	0.950	35.73	- 0.23	29.8
63	0.2500	0.950	40.36	16.38	27.9
55	0.5000	0.960	0.00	--	32.1
55	0.5000	0.960	8.57	-14.38	33.6
55	0.5000	0.960	14.55	- 4.43	31.6
55	0.5000	0.960	19.74	- 4.76	31.7
55	0.5000	0.960	24.68	- 6.65	31.8
55	0.5000	0.960	29.87	-14.67	33.1
55	0.5000	0.960	33.77	- 9.92	32.3
55	0.5000	0.960	44.68	- 9.18	29.7

CHAPTER VIII

THE MECHANISM OF IODINATION OF PHENOL

<u>Introduction</u>.—Apparent second-order rate constants were calculated on the basis of the reaction being first order in the stoichiometric concentration of both phenol and iodine. Such rate constants remained constant throughout a run at high iodide ion concentration, and for such runs, an average value of k_{app} was taken. For runs at lower iodide ion concentration, however, the values of k_{app} fell throughout a run and therefore, k_{app} was extrapolated to zero per cent reaction in order to have a value of k_{app} at definite iodide ion concentration.

The iodide ion dependency is demonstrated in Chapter V. It can be seen that at constant hydrogen ion concentration during a 50 fold change in stoichiometric iodide ion concentration, the values of k' remain essentially constant whereas the values of k^* increase linearly with decreasing iodide ion concentration (see Table 116).

To account for the observed iodide ion dependence, the following mechanisms are considered.

<u>Mechanism I</u>.—

$$ArOH \overset{K_4}{\rightleftharpoons} ArO^- + H^+ \quad ; \quad K_4 = \frac{[ArO^-][H^+]}{[ArOH]} \qquad (6)$$

$$ArO^- + H_2OI^+ \xrightarrow[slow]{k_1} \text{products.}$$

Table 116

Effect of Iodide Ion Concentration on the Rate of Iodination of Phenol

All runs were made in aqueous solution, 0.01740 M in perchloric acid, at an ionic strength of 0.3000 at 25.0°.

k_{app} (l./mole sec.)	$k^* \times 10^3$ (l./mole sec.)	$[I^-] \times 10^4$ (mole/l.)	$k^*[I^-] \times 10^7 = k \times 10^7$ (sec.$^{-1}$)	Ref. Table
9.50×10^{-3}	12.26	3.7851	46.4	89
10.30×10^{-2}	106.3	0.4568	48.6	90
19.85×10^{-2}	201.6	0.2280	46.0	91
46.50×10^{-2}	468.2	0.0907	42.5	92

It can be seen that this mechanism is identical to one proposed in Chapter VI for the iodination of p-nitrophenol. As it was pointed out, according to this mechanism, it is expected that the values of k' be constant at varying iodide ion concentration. Table 116 reveals that the values of k' are essentially constant at constant hydrogen ion concentration. However, due to the presence of a deuterium isotope effect of 6.6, it seems reasonable to exclude this mechanism as a possibility.

Modifications of mechanism (I), i.e., those which involve the attack of H_2OI^+ on phenol and phenoxide ion in a slow step, followed by the subsequent rapid abstraction of proton, can also be eliminated on the basis of the observed deuterium isotope effect.

A mechanism (I''') which involves the attack of H_2OI^+ on phenol and phenoxide ion in a fast and reversible step followed by slow removal of proton i.e.

$$ArHOH \rightleftharpoons ArHO^- + H^+$$

$$ArHO^- + H_2OI^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArHOI + H_2O$$

$$ArHOH + H_2OI^+ \overset{k_2}{\rightleftharpoons} ArHOI + H_2O + H^+$$

$$ArHOI \xrightarrow[\text{slow}]{} ArOI + H^+$$

cannot be excluded in this case, since such a mechanism accounts for the iodide ion dependence as well as the observed deuterium isotope effect.

Mechanism II.--According to this mechanism, it is expected that both hypoiodous acidium ion and molecular iodine are the active halogenating species. And the rate of iodination can be represented as

$$\text{rate} = k_o'' [ArOH][I_2] + k_1''' \frac{[ArOH][I_2]}{[I^-]} \qquad (18)$$

where k_o'' and k_1''' include any hydrogen ion dependency. Equation (18) can be rearranged to a form including k_{app}

$$k_{app} \frac{(I_2)}{[I_2]} = k^* = k_o'' + \frac{k_1'''}{[I^-]} \qquad (19)$$

Hence, for this mixed mechanism to hold, a plot of k^* versus $1/[I^-]$ should give a straight line. Such a plot at constant hydrogen ion concentration is shown in figure 7. Within the range of iodide ion studied, the data fit well on a straight line. On this basis, mechanism II cannot also be excluded as a possibility.

Mechanism III.--

$$ArOH \rightleftharpoons ArO^- + H^+ \; ; \; K_4 = \frac{[ArO^-][H^+]}{[ArOH]} \qquad (6)$$

$$ArO^- + I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ar^{\ddagger}OI + I^- \qquad (20)$$

$$ArOH + I_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Ar^{\ddagger}OI + H^+ + I^- \qquad (21)$$

$$Ar^{\ddagger}OI \xrightarrow{k_3} ArOI^- + H^+$$

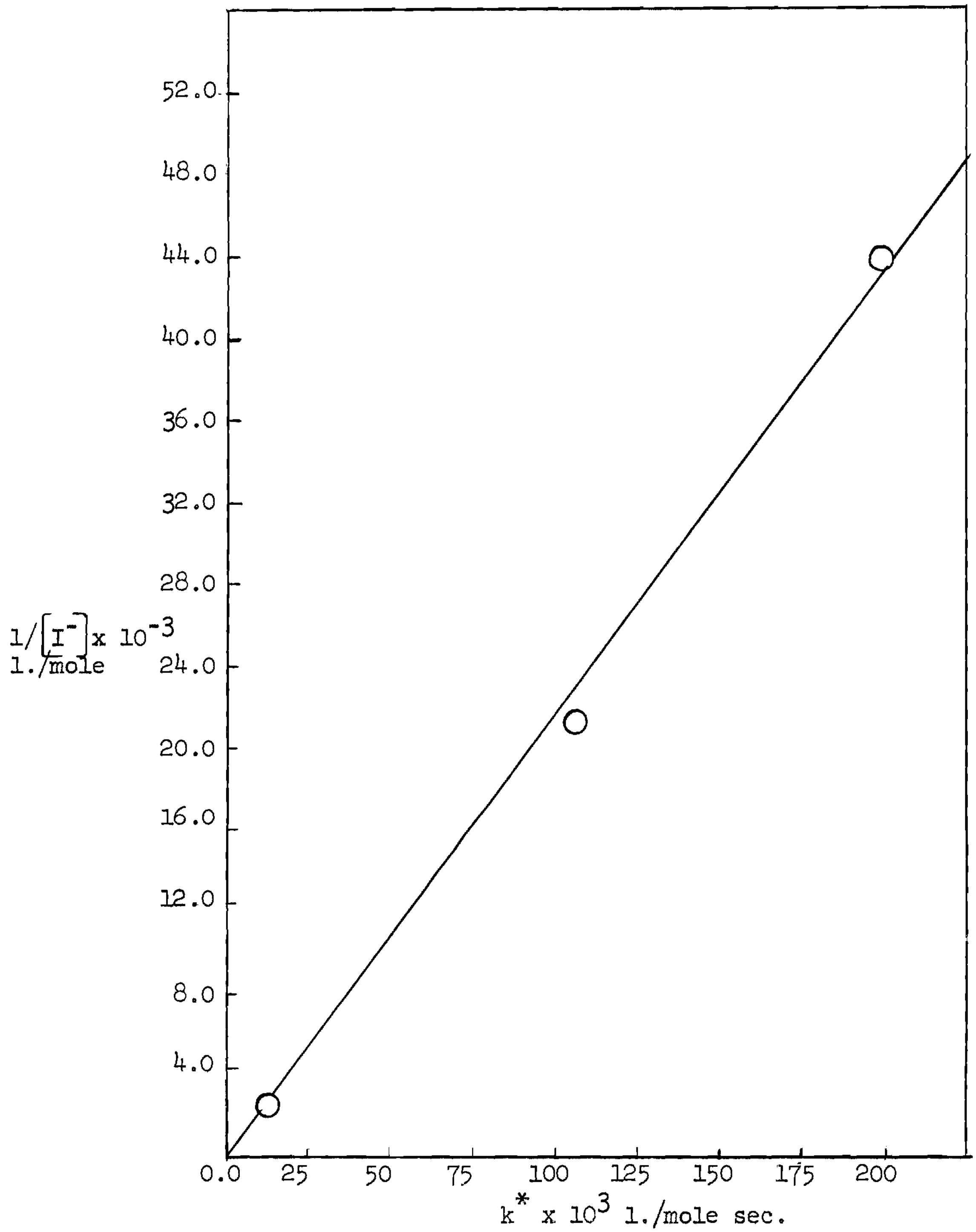
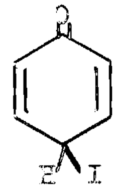


Fig 7.- phenol in 0.0174 M perchloric acid

where $\overset{\circ}{\mathrm{Ar}}\mathrm{OI}$ is a reactive intermediate having predominantly a <u>para</u> quinoid type structure



By making the same assumptions as in the case of p-nitrophenol, it can be shown that

$$\frac{1}{k^{*}[H^{+}]} = \frac{k_{-1}[I^{-}]}{k_3 k_1 K_4} + \frac{1}{k_2[H^{+}] + k_1 K_4} \qquad (29)$$

According to equation (29) a plot of $1/k^{*}[H^{+}]$ versus $[I^{-}]$ should give a straight line at constant hydrogen ion concentration. Figure 8 shows that the available data do indeed fall on a straight line which passes through the origin. Such a case can be justified since the second term of equation 29 is essentially zero, i.e., the value of $k_2[H^{+}] + k_1K_4 \gg 1$.

The presence of deuterium isotope effect cannot differentiate between certain of the previous mechanisms. However, if the iodination of phenol proceeds via mechanism III, it is expected that the deuterium isotope effect should drop with diminishing iodide ion concentrations. Inspection of Table 118 reveals, however, that the magnitude of deuterium isotope effect remains essentially constant. The constancy of this isotope effect can be justified in terms of the reversibility of the first step, i.e., the ratio $k_3/k_{-1}[I^{-}]$.

For purposes of discussion, the magnitude of $1/k_1K_4$ will be taken as unity. From equation (29) and the slope of Figure 8, the magnitude of k_3/k_{-1} is then estimated to be of the order of 10^{-7}. From equation

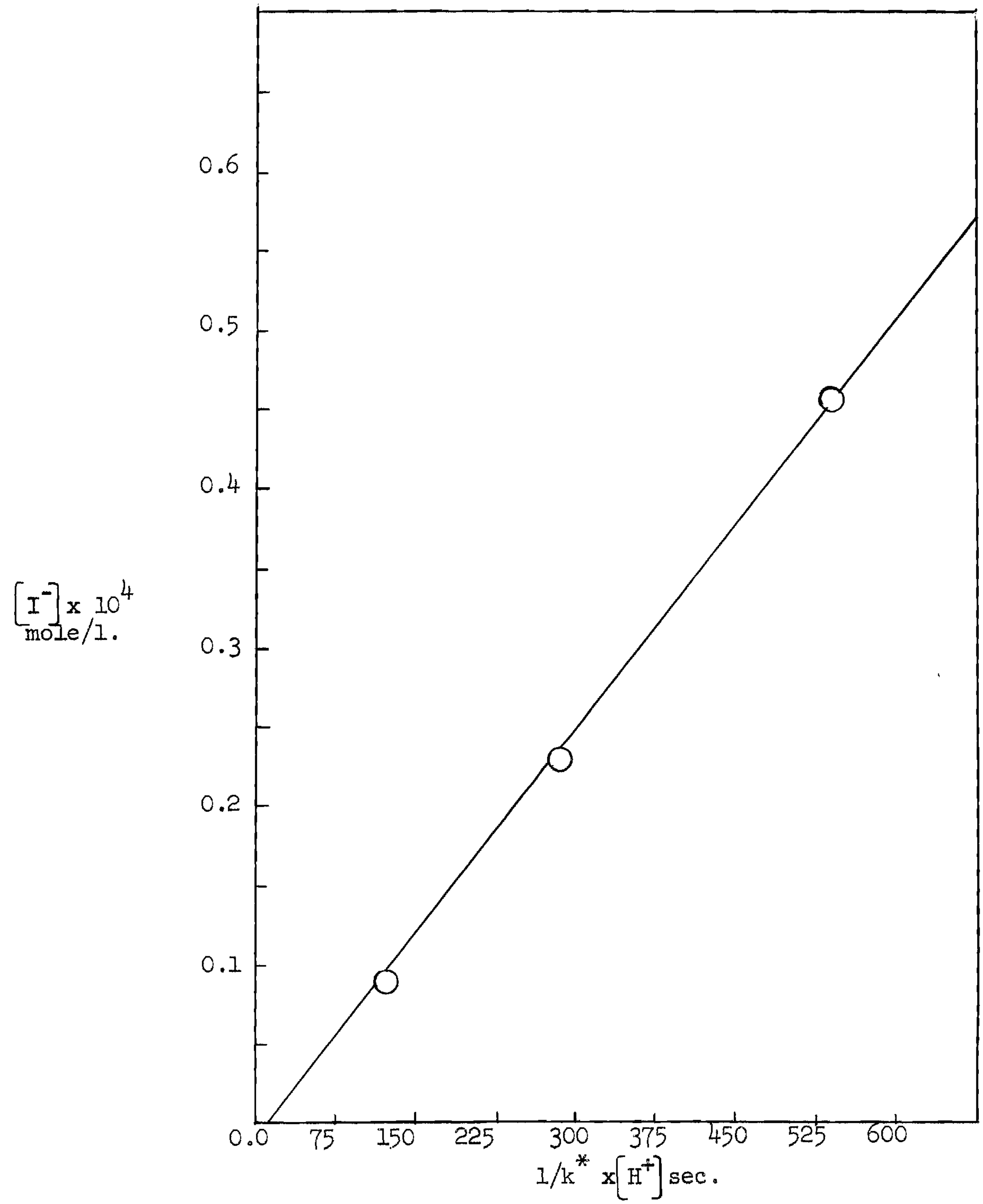


Fig. 8.- phenol in 0.0174 M perchloric acid

Table 117

Effect of Iodide Ion Concentration on the Rate of Iodination of Phenol-2,4,6-d_3

All runs were made in aqueous solution, 0.01740 M in perchloric acid, at an ionic strength of 0.3000 at 25.0°.

k_{app} (l./mole sec.)	$k^* \times 10^3$ (l./mole sec.)	$[I^-]_o \times 10^4$ (mole/l.)	$k^*[I^-] \times 10^7 = k' \times 10^7$ (sec.$^{-1}$)	Ref. Table
14.35×10^{-4}	1.86	3.8689	7.20	96
15.90×10^{-3}	16.4	0.4568	7.51	97
3.00×10^{-2}	30.4	0.2280	6.93	98
6.85×10^{-2}	68.9	0.09115	6.29	99

Table 118

Effect of Iodide Ion Concentration on the Magnitude of Deuterium Isotope Effect in the Iodination of Phenol.

Reference Table Protio	Deutero	$(I^-)_o \times 10^4$ (mole/l.)	$k^*_H \times 10^3$ l./mole sec.	$k^*_D \times 10^3$ l./mole sec.	$\left(\frac{k^*_H}{k^*_D}\right)_{found}$	$\left(\frac{k^*_H}{k^*_D}\right)^b_{calc.}$
89	96	5.000	12.26	1.86	6.60	6.6
90	97	0.500	106.3	16.4	6.47	6.6
91	98	0.250	201.6	30.4	6.62	6.6
92	99	0.100	468.2	68.9	6.78	6.6
94	101	Tl^+=0.0500[a]	770.0	114.0	6.75	

(a) This run was performed at 0.0870 M in perchloric acid.
(b) The calculation is based on the assumption of $1/(k_1K_4)$ = 1.00 sec.

32 of Chapter VI, with k^*_H/k^*_D taken as 6.6 it can be estimated that an iodide ion concentration of the magnitude of 10^{-7} is needed to have any appreciable experimentally detectable deuterium isotope effect.

On the basis of the available data, therefore, it is not possible to distinguish between mechanisms I, II and III. In order to have a clear cut distinction, the kinetics of iodination of phenol needs to be studied at extremely low iodide ion concentrations.

Rediscussion of the Mechanism of Iodination of Phenol.--An attempt was made to distinguish between mechanism III and I mathematically. Rewriting equation (39) of Chapter VI

$$gt = (h-c) \ln \left(\frac{c+\chi}{\chi}\right) + \chi \qquad (39)$$

where

$$g = \frac{B-2}{B} \times \frac{k_3 k_1 K_4}{k_{-1}} \times \frac{[ArOH]}{[H^+]}$$

$$c = \frac{(I_2)_o + (B-1)(I^-)_o}{(B-2)}$$

$$h = (I^-)_o + \frac{k_3 k_1 K_4}{k_{-1}\, B \left\{k_2 [H^+] + k_1 K_4\right\}}$$

The magnitude of $1/(k_2 [H^+] + k_1 K_4)$ can be determined in a similar way as in Chapter VI. According to mechanism (III), it is expected that at any per cent reaction, the values of $1/(k_2 [H^+] + k_1 K_4)$ be constant at varying iodide ion concentrations, provided that the hydrogen ion concentration is constant. Table 119 reveals however, that the values of $1/(k_2[H^+] + k_1K_4)$ at each per cent reaction are not constant, ranging from negative to positive values. The poor constancy of $1/(k_2[H^+] + k_1K_4)$ is, however, attributed to difficulties in calculating the unknown ratio which is represented as small differences between large numbers. Therefore, on the grounds of the available data, mechanism III cannot be excluded as a possibility. According to equation 45, Chapter VI, it is expected that the values of $k_1K_4K_5 + k_1'K_5[H^+]$, which is related to Berliner's rate constant k', be constant at constant hydrogen ion but varying iodide ion concentration. The results in Table 119 seem to be rather constant and therefore, on the grounds of the constancy of k' and $k_1K_5K_4 + k_1'K_5[H^+]$ it seems that mechanism (I"') is at least in satisfactory agreement with the available data.

Table 119

Mathematical Evaluation of the Mechanism of Iodination of Phenol

Ref. Table	$(I^-)_o \times 10^4$	$B_{av.}$	Per cent reaction	$\frac{1}{k_2[H^+] + k_1K_4}$	$k_1K_5K_4 + k_1'K_5[H^+]$ 10^8
92	0.1000	0.930	0.00	----	7.39[a]
"	"	"	8.05	-13.25	8.60
"	"	"	13.79	-11.51	10.36
"	"	"	16.55	+16.74	7.50- 7.20
"	"	"	22.30	+32.90	9.86
"	"	"	27.82	+45.80	7.33
"	"	"	34.71	+36.97	7.26
"	"	"	45.28	+51.70	
91	0.2500	0.930	0.00	----	8.00[a]
"	"	"	10.84	-48.5	9.21
"	"	"	16.39	-48.4	9.05
"	"	"	21.20	-31.2	8.59
"	"	"	25.30	- 3.3	8.05
"	"	"	31.33	+ 7.1	7.90
"	"	"	37.11	+33.5	7.56
"	"	"	47.95	+17.7	7.80
90	0.5000	0.930	0.00	----	8.46[a]
"	"	"	11.81	-71.6	9.15
"	"	"	16.39	-68.2	8.85
"	"	"	21.45	- 8.7	8.09
"	"	"	26.51	- 8.4	8.23
"	"	"	33.73	+ 5.7	8.23
"	"	"	40.24	+15.2	8.13
"	"	"	48.67	+15.6	8.12

(a) Calculated from extrapolation of k_{app} to zero per cent reaction.

Table 120

Evaluation of the Magnitude of $k_{-1}/k_3k_1K_4$ for the Iodination of Phenol in 0.01740 M Perchloric Acid at 25.0°

Reference Table	$[I^-] \times 10^4$ mole/l.	$\frac{1}{k^* [H^+]}$	$\frac{\frac{1}{k^* [H^+]}}{[I^-]} = \frac{k_{-1}}{k_3k_1K_4}$
89	3.7851	4688	1239×10^4
90	0.4568	541	1183×10^4
91	0.2280	280	1228×10^4
92	0.0974	123	1352×10^4
			Av. = $1250 \pm 51 \times 10^4$

CHAPTER IX

CONCLUSIONS

The rates of iodination of 4-nitrophenol, 4-nitrophenol-2,6-d_2, anisole, anisole-2,4,6-d_3, phenol and phenol-2,4,6-d_3 when measured in an aqueous solution of perchloric acid and sodium perchlorate were found, during a kinetic run, to remain first order in iodine and first order in substrate as long as the concentrations of iodide ion and hydrogen ion remained constant.

The iodination of 4-nitrophenol and 4-nitrophenol-2,6-d_2 showed an iodide ion dependence somewhere between inverse second and zero order dependence. The hydrogen ion dependence was found to be somewhere between inverse first order and zero order. This reaction when carried out in the presence of 4-nitrophenol-2,6-d_2 showed a maximum deuterium isotope effect of 5.2 which dropped to essentially 2 with diminishing iodide ion concentration. This evidence is consistent with a mechanism in which molecular iodine attacks p-nitrophenoxide ion or p-nitrophenol in a fast and reversible step, followed by slow and irreversible abstraction or proton by solvent, thus

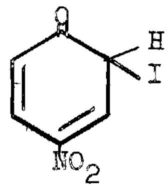
$$ArOH \rightleftharpoons ArO^- + H^+$$

$$ArOH + I_2 \rightleftharpoons ArOI + H^+ + I^-$$

$$ArO^- + I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArOI + I^-$$

$$ArOI \xrightarrow{Slow} ArOI^- + H^+$$

in which ArOI represents an intermediate having an orthoquinoid type structure



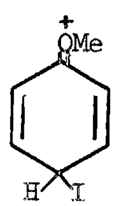
The iodination of anisole showed a similar iodide ion dependence although it was found that the reaction was independent of hydrogen ion concentration. A maximum deuterium isotope effect of 3.2 was observed. This isotope effect remained essentially constant, except at extremely low iodide ion concentrations attained by the use of high thallium perchlorate concentrations, when the deuterium isotope effect dropped to 1.25.

A mechanism consistent with the present evidence includes a rapid and reversible attack of molecular iodine on anisole followed by an irreversible abstration of proton.

$$\mathrm{ArOMe} + I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \overset{)}{\mathrm{Ar}}\mathrm{OMeI} + I^-$$

$$\overset{)}{\mathrm{Ar}}\mathrm{OMeI} \xrightarrow{k_3} \mathrm{ArOMeI} + H^+$$

Here $\overset{)}{\mathrm{Ar}}\mathrm{OMeI}$ designates an intermediate having a quinoid type structure such as



The iodination of phenol was studied at 25° .0. The apparent second order rate constant after correction for formation of inert triiode ion, showed an inverse first order iodide ion dependence at constant hydrogen ion concentration. A deuterium isotope effect of 6.6 was obtained and this isotope effect remained constant within a 50 fold change in stoichiometric iodide ion concentration.

The available data on iodination of phenol make it clear that a proton is being lost in the rate-determining step but cannot distinguish between molecular iodine or hypoidous acidium ion as the iodinating agent.

CHAPTER X

SUGGESTIONS FOR FUTURE EXPERIMENTAL WORK

A major aspect of the iodination of phenols is in definite need of further clarification by experimental means. It was seen in Chapter VI, that the iodination of p-nitrophenol proceeds exclusively via mechanism III, i.e., one which involves the attack of molecular iodine on p-nitrophenoxide ion to give an ortho-quinoid type intermediate which subsequently loses a proton. Furthermore, it is evident that the rate of conversion of the intermediate into product relative to conversion to reactants, i.e., k_3/k_{-1}, is relatively large compared to that of anisole and phenol. It is as yet unknown whether such effect is due to the presence of a nitro group on the aromatic molecule or to differences in the value of ortho as opposed to para quinoid intermediates.

It is, therefore, suggested that the kinetics of iodination of o-nitrophenol, 2,4-dichlorophenol and 2,6-dichlorophenol be investigated at varying hydrogen ion and iodide ion concentrations and that the deuterium isotope effect be studied as a function of iodide ion concentration in each case. If o-nitrophenol showed a different behavior from that of p-nitrophenol, then it may be concluded that the nature of the intermediate, whether it has a p-quinoid or o-quinoid type structure is the likely important factor. If, however, o-nitrophenol shows a behavior similar to p-nitrophenol, then it would appear that the nitro group has some effect in the reversibility of the first step.

The iodination of 2,4-dichlorophenol and 2,6-dichlorophenol along with their deuterated derivatives ought to clarify the factors effecting the reversibility of the first step in the iodination of phenols.

APPENDICES

APPENDIX A.

THE DETERMINATION OF THE EQUILIBRIUM CONSTANT FOR THE REACTION

$$I_2 + I^- \rightleftharpoons I_3^-$$

The iodine-triiodide equilibrium constant has been determined by a few investigators at different temperatures using different experimental techniques. Bray and MacKay[136] have measured the equilibrium constant in aqueous neutral solution at 25°. These workers found that, in saturated iodine solution (1.32×10^{-3} M), the iodine-triiodide equilibrium constant diminished with decreasing iodide ion concentration. Thus at 1.00 M, 0.100 M, 0.010 M, 0.005 M and 0.001 M iodide ion concentrations, the equilibrium constant was 763, 729.9, 714.3, 704 and 667 respectively. These equilibrium constants when extrapolated to zero iodide concentration gave a value of 654.6 at 25°. On the basis of the magnitude of the hydrolysis constant of iodine

$$I_2 + H_2O \rightleftharpoons HOI + HI \qquad K_1 = \frac{[HOI][HI]}{[I_2][H_2O]} = 0.6 \times 10^{-12}$$

these workers claimed that no acid need be added to suppress the hydrolysis of iodine. Furthermore, they found that in solutions which are not saturated in iodine, the equilibrium constant

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

(136) W. C. Bray and G. M. J. MacKay, *J. Am. Chem. Soc.*, **32**, 914 (1910).

increases as the concentration of iodine increases.

Bray and Mackay[137] have also measured the equilibrium constant in saturated iodine solutionm in the presence of acetic acid (0.10 M), and cupric ions (17.0×10^{-3} M). By the use of titrimetric procedure and assuming that there is no salt effect on saturation concentration of iodine, the authors reported a value of 769 at 25°.

Washburn and Strachon [138] have measured the equilibrium constant via partition of iodine between carbon tetrachloride and water at 25° and by varying iodine and iodide ion concentrations, they reported a value of 769.

Awtrey and Connick[139] have determined the equilibrium constant spectrophotometrically at different temperatures. A plot of their equilibrium constants versus the reciprocal of the absolute temperature gave a straight line from which the value of the equilibrium constant was found to be 373 at 50°. This, however, is in disagreement with the value reported by Davies and co-workers[140], who claimed to have measured accurate values for iodine-triiodide equilibrium constant and have reported a value of 490 at 50°. The partition of iodine between carbon tetrachloride and water was the general technique employed by these workers. They found that plots of

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(137) W. C. Bray and G. M. J. MacKay, ibid., 32, 1207 (1910).

(138) E. W. Washburn and E. K. Strachon, ibid., 35, 692 (1913).

(139) A. D. Awtrey and R. E. Connick, ibid., 73, 1842 (1951).

(140) M. Davies and E. Gwynne, ibid., 74, 2748 (1952).

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

at constant iodide ion concentration, versus free iodine gave approximately linear relationship which upon extrapolation to zero iodine concentration gave the equilibrium constant. The same type of plots were done at several iodide ion concentrations, and were found to have the same intercept, which they claimed to be the equilibrium constant. A careful examination of their plots, however reveals that the plots are not entirely linear especially at low iodine concentration, which makes one wonder whether their equilibrium constant is valid. The authors concluded that the formation of I_6^{--}

$$2I^- + 2I_2 \rightleftarrows I_6^{--}$$

is the probable cause of the deviation from linearity.

Redetermination of the equilibrium constant was made under experimental conditions similar to those of the kinetic runs, i.e., at ionic strength of 0.3000 and acidities of 0.009783 M. The iodine concentrations, however, were lower by at least ten fold from those of the kinetic experiments since the equilibrium is known to be in favor of triiodide formation, which exhibits relatively high extinction coefficient at 352 millimicrons.

A Beckman, Model DK, spectrophotometer, thermostated at 50.0 ± 0.5° was used for the determination of the equilibrium constant. For measuring the equilibrium constant at 25°, the same spectrophotometer was used and a constant temperature was maintained by circulating cold water through the thermostat. Calibrated Corex cells of optical path length 1.000 $\pm$ 0.001 cm. and 5.000 $\pm$ 0.001 cm. equipped with ground stoppers coated with a fine layer of silicone grease were used.

Two general procedures were used for the determination of the equilibrium constant. The results were in fair agreement with each other, however, they differed considerably from those reported by Davies and co-workers[140].

Procedure A.-- It was assumed that the total optical density of a solution at a given wave length is equal to the sum of the optical densities of each of the species present in the system at the wave lengths being observed. Hence such a system could be represented by the equation

$$D^{\lambda}_{tot} = e^{\lambda}_{I_3^-} \left[I_3^-\right] + e^{\lambda}_{I_2} \left[I_2\right]$$

where D^{λ}_{tot} represents the total optical density at wave length λ and $e^{\lambda}_{I_3^-}$ and $e^{\lambda}_{I_2}$ represent the extinction coefficient of triiodide and iodine respectively.

If the total optical density of solutions containing both free iodine and triiodide ion are known, and the extinction coefficients for each species are also known at two different wave lengths, it is possible to solve for the concentration of each species, and from them calculate the equilibrium constant.

Literature reports[139] indicate that both free iodine and triiodide ion absorb at 270, 287.5, 353 and 460 millimicrons with the following extinction coefficients

$m\mu$	$e_{I_3^-}$	e_{I_2}
270	17200	121
287.5	40000	95
353	26400	18
460	975	746

It was, however, desirable to redetermine the extinction coefficients of free iodine and triiodide ion at 352 and 462 millimicrons, at an ionic strength of 0.3000, and an acidity of 0.009810 M at 50.0°C.

Preliminary experiments indicated that the only species that absorb from 250-500 millimicrons are free iodine and triiodide ion with maxima at 270, 288, 352 and 462 millimicrons.

The extinction coefficient of triiodide ion had to be determined by approximation. If a solution is made 0.15000 M in iodide ion and 0.00002 M in iodine almost all of the iodine is tied up as triiodide ion but there is still a small contribution from free iodine. If it is assumed that the optical density is due entirely to triiodide ion then it is possible to calculate the extinction coefficient. Such an assumption was found to be correct since upon using higher iodide ion concentrations the extinction coefficient remained constant within the limits of experimental error.

Oxidation of iodide ion to iodine was observed; consequently high extinction coefficients resulted. Such oxidation was attributed to the presence of oxygen in the solutions. Experiments under nitrogen atmosphere with solutions freed of oxygen (by bubbling nitrogen through the solution) showed that oxidation was still in effect although at slower rate. The period of time required for the solutions in the thermostat to reach 50.0°C was found to be six minutes. Therefore the optical density was read immediately after thermal equilibrium was attained.

Some sample calculations will be shown to illustrate the method used and the summary of the results are tabulated in Table 121.

a. Determination of $e^{352}_{I_3^-}$, in 1.87341 x 10^{-5} M iodine, 0.15000 M sodium iodide, 0.009101 M perchloric acid and 0.1402 M sodium perchlorate at 50.0 ± 0.5°C.

$$D = 0.530$$

$$D = e^{\lambda}_{I_3^-} \left[I_3^-\right] \times 1$$

$$0.530 = e^{352}_{I_3^-} \times 1.87341 \times 10^{-5}$$

$$e^{352}_{I_3^-} = 28290$$

The extinction coefficient of triiodide ion at 462 millimicrons was similarly determined using 5.000 cm. cells.

$$D = 0.802$$

$$0.802 = e^{462}_{I_3^-} \left[1.24894 \times 10^{-5}\right] \times 5.001$$

$$e^{462}_{I_3^-} = 1284$$

The extinction coefficient of free iodine was also determined spectrophotometrically at 50.0°C. The loss of iodine during the transfer of the solutions to the cells was avoided by the use of a ground glass adapter fitted on a 100.0 ml. reaction flask with an inlet attached to a nitrogen cylinder and an outlet extending to the bottom of the cell. Hydrolysis of iodine was found to be suppressed almost completely by 0.0500 M perchloric acid, since higher acidities showed no change in optical density at a given iodine concentration.

Some sample calculations are shown below.

b. Determination of extinction coefficient of free iodine in 0.050 M perchloric acid, 0.2950 M sodium perchlorate and 1.1406 x 10^{-4} M iodine at 462 millimicrons and 50.0°C. in 5.000 ± .001 cm. cells.

$$D = 0.419$$

$$D = e_{I_2}^{\lambda} \left[I_2\right] \times 1$$

$$0.419 = e_{I_2}^{462} (1.1406 \times 10^{-4}) \times 5.001$$

$$e_{I_2}^{462} = 734.6$$

c. Determination of extinction coefficient of iodine at 50.0°C. in 0.2000 M perchloric acid*, 0.1000 M sodium perchlorate and 5.4171 x 10^{-4} M iodine at 352 millicrons in 5.000 ± 0.001 cm. cells.

$$D = 0.175$$

---

* A high perchloric acid concentration was used in this case, since the extinction coefficient of I_3^- at 352 is very large, and even a very small amount of triiodide will introduce a large error in the extinction coefficient of iodine.

$$D = e^{\lambda}_{I_2} \left[I_2\right] \times 1$$

$$0.175 = e^{352}_{I_2} \times 5.4171 \times 10^{-4} \times 5.001$$

$$e^{352}_{I_2} = 64.6$$

A second procedure for determination of extinction coefficient of iodine is recommended in the literature[139]. A 100.0 ml. mixture of 0.1000 M perchloric acid, 0.000015 M potassium iodate and 0.2000 M sodium perchlorate was sealed in a test tube and was allowed to stand in the bath at 50.0°C. for ten days. The contents of the flask were then transferred to 5.000 cm. cells and the optical density was determined.

The results were in agreement with the previous procedures at 352 millimicrons. However, they differed by 13 per cent at 462 millimicrons. (See Table 121).

The equilibrium constant was next determined spectrophotometerically at 352 millimicrons. Solutions of 0.009810 M perchloric acid, sodium perchlorate and sodium iodide with concentration range varying from 0.0050 M to 0.0010 M were introduced into 100.0 ml. volumetric flasks thermostated at 50.0°C. A definite volume of iodine of known concentration was then introduced to the mixture at 50.0°C followed by vigorous shaking. The solution was then transferred to a 1.000 cm. cell and the optical density recorded at 352 millimicrons.

A sample calculation for the equilibrium constant is illustrated below.

$$D^{352}_{tot} = e^{352}_{I_3^-} \times C_{I_3^-} + e^{352}_{I_2} \times C_{I_2}$$

$$\left(C_{I_2}\right)_{free} + \left(C_{I_3^-}\right)_{free} = \left(C_{I_2}\right)_{titrimetric}$$

at 0.0050 M sodium iodide concentration

$$0.1107 = 28681 \times \left(C_{I_3^-}\right) + 68 \times \left(C_{I_2}\right)$$

$$3.05163 \times 10^{-5} = \left(C_{I_3^-}\right)_{free} + \left(C_{I_2}\right)_{free}$$

$$C_{I_3^-} = 0.3799 \times 10^{-5}$$

$$C_{I_2} = 2.67173 \times 10^{-5}$$

$$C_{I^-} = 0.0004962$$

$$k = \frac{[I_3^-]}{[I_2]\,[I^-]} = \frac{0.3799 \times 10^{-5}}{2.67173 \times 10^{-5} \times .0004962} = 286$$

The equilibrium constants tabulated in Table 122 were calculated in a similar manner by assuming that the extinction coefficient of triiodide was 28681. Careful examination reveals that the results are not unifrom and, therefore, they were averaged and a value of 285 ± 20 was obtained. The same equilibrium constants were recalculated by assuming a value of 25860 for the extinction coefficient of triiodide a value which was obtained graphically (See procedure B). The equilibrium constants were higher in this case and when averaged gave a value of 353 ± 16. (See Table 123).

Table 121

Extinction Coefficients of I_2 and I_3^-

$e^{352}_{I_3}$	$e^{462}_{I_3^-}$	$e^{352}_{I_3}$	$e^{462}_{I_3}$
29940	1297	64.5	695
29440	1241	67.7	669
27084	1298	67.7	645
26115	Av=1279±25	68.8	634 *
29440		64.8	634 *
29180		Av=67.5 ± 1.5	651± 20
28290			
Av=28681±1090			

* Potassium iodate technique was employed in these runs

Table 122

Equilibrium Constant of

$I_2 + I^- \; I_3^-$

Extinction Coefficient of I_3^- at 352 mμ = 28681

Sodium Iodide	$(I_2) \times 10^5$	$[I_3^-] \times 10^5$	K
0.0050	2.80887	1.60070	266
0.0050	4.73996	2.61867	248
0.0040	5.21240	2.85920	306
0.0040	5.68795	2.71798	240
0.0030	2.80887	1.28553	283
0.0030	6.51550	3.07320	301
0.0030	6.74128	3.04815	279
0.0030	6.66359	2.99581	275
0.0020	2.80887	1.09292	320
0.0020	6.51550	2.46383	308
0.0015	5.61773	1.79014	316
0.0020	6.74128	2.40030	283
0.0010	7.81860	1.80242	305
0.0010	7.70432	1.71514	291
0.0010	7.46356	1.64567	288
			Av. value of k = 285 ± 20

Table 123

Equilibrium Constant of

$$I_2 + I^- \rightleftharpoons I_3^-$$

Extinction Coefficient of I_3^- at 352 mμ = 25860

Sodium Iodide	$(I_2)_{tit.} \times 10^5$	$[I_3^-] \times 10^5$	K
0.0050	2.80887	1.75779	345
0.0040	5.21240	3.18569	382
0.0040	6.59081	3.75101	334
0.0030	2.80887	1.42664	346
0.0030	6.51550	3.40934	370
0.0030	6.74128	3.38155	340
0.0030	6.66359	3.32348	335
0.0020	2.80887	1.21247	382
0.0020	6.51550	2.73359	366
0.0020	6.74128	2.66283	331
0.0015	5.61773	1.98539	374
0.0010	7.8186	1.99956	351
0.0010	7.70432	1.90273	334
0.0010	7.46356	1.82566	330
0.0010	8.78774	2.26894	350
			Av. value of k = 353 ± 16

Procedure B.-- The equilibrium constant was also determined graphically by the method described by D. L. Cason[141].

The equilibrium constant may be expressed as

$$K = \frac{[I_2]\,[I^-]}{[I_3^-]} \tag{1}$$

Then the total optical density at a given wave length may be expressed as

$$D = e_{I_3^-}\,[I_3^-] + e_{I_2}\,[I_2] + e_{I^-}\,[I^-] \tag{2}$$

The last term of the equation is negligible due to the low absorbency of the iodide anion. Then equation (2) may be reduced to

$$D = e_{I_3^-}\,[I_3^-] + e_{I_2}\,[I_2] \tag{3}$$

supposing that

$$[I_2] + [I_3^-] = C_o \tag{4}$$

where C_o is the titrimetric iodine concentration then equation (4) can be rewritten as

$$[I_2] = C_o - [I_3^-] \tag{5}$$

(141) D. L. Cason, Studies of Equilibrium Involving Chloro-Complexes of Iodine, Georgia Institute of Technology, M. S. Thesis. 1959, p. 5.

and equation(1)can be rewritten as

$$[I_2] = \frac{K\,[I_3^-]}{[I^-]} \tag{6}$$

Substituting the value of I_2 from equation(5) into(6)

$$[I_3^-] = \frac{[I^-]\,C^o}{K + [I^-]} \tag{7}$$

Similarly the iodine concentration may be expressed as

$$[I_2] = \frac{KC_o}{K + [I^-]} \tag{8}$$

Suppose that C_o is fixed in any given experiment then substitution of(7)and(8)into(2)gives

$$D = \frac{e_{I_3}\,[I^-]\,C_o}{K + [I^-]} + \frac{e_{I_2}\,KC_o}{K + [I^-]} \tag{9}$$

Let us define that

$$e_{I_3^-}C_o = D_{I_3^-} \tag{10}$$

$$e_{I_2}C_o = D_{I_2} \tag{11}$$

Then
$$D = D_{I_3^-} + \frac{K\,(D_{I_2} - D)}{[I^-]} \tag{12}$$

Since D_{I_2} is known then plotting D versus $[D_{I_2} - D]/(I^-)$ for a series of solutions having C_o fixed gives a line the slope of which will be K and the intercept on the D-axis will be $D_{I_3^-}$. If on the other hand $D_{I_3^-}$ is known then equation (12) may be expressed as

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

Thus, a series of solutions were prepared at constant concentration of iodine (4.249×10^{-5} M) and constant concentration of perchloric acid (0.009783 M) but at varying sodium iodide concentrations. The ionic strength of the solutions was adjusted by sodium perchlorate to 0.3000 at 50°, and the optical density was recorded immediately after thermal equilibrium was attained. By the use of equation (12), the optical density D was plotted versus $[D_{I_2} - D]/(I^-)$ for a series of solutions ranging from 0.0100 M to 0.00020 M in sodium iodide. The slope of the plot gave a value of 365 for the equilibrium constant and an extinction coefficient of 25600 was calculated from the intercept. Use of the actual iodide concentration $[I^-]$ in the term $[D_{I_2} - D] / (I^-)$ via the equilibrium constant reported by Davies and Gwynne[148], did not produce any appreciable change in the values of the equilibrium constant and extinction coefficient of triiodide ion. The experimental data are presented in Table 124.

It seems that the graphically determined equilibrium constant compares favorably with Table 123 but disagrees with Table 122. Such a discrepancy may be attributed to an error in determination of the extinction coefficient of triiodide ion. Therefore it is believed that the value 25600 obtained graphically is more reliable.

The iodine-triiodide equilibrium constant was also determined graphically at 25°, in perchloric acid (0.009783 M) and sodium perchlorate solution at an ionic strength of 0.3000. The iodine concentration was kept constant at 4.8595×10^{-5} M while the iodide ion concentration was varied from 0.0100 M to 0.00003 M. The experimental results are tabulated in Table 125. A plot of optical density D versus $[D_{I_2} - D]/(I^-)$ gave a straight line with a slope of 620, which represents the equilibrium constant, and an intercept from which the value of the triiodide extinction coefficient was found to be 28,000. (See Table 125).

The same experiment was repeated as a check in 4.755×10^{-5} M iodine solution. The equilibrium constant was found to be 610, while the extinction coefficient was found to be 29,000 at 25° (See Table 126).

From these experiments it can be seen that the values of the iodine-triiodide equilibrium constants are in general lower than those reported by Davies and Gwynne. Such a discrepancy can be explained in terms of the iodine concentration, as Bray and MacKay claimed that the equilibrium constant increases with increasing iodine concentration. Since the experiments reported in this chapter were performed at extremely low iodine concentrations, it seems reasonable to attribute the value of equilibrium constants to low iodine concentration.

It was then necessary to determine the effect of changes in the equilibrium constant on the values of K' for iodination of p-nitrophenol. Therefore the rate constants (k') were recalculated by assuming an equilibrium constant of 350. Table 127, reveals that the values of k' are slightly affected at high iodide ion concentrations whereas at low iodide ion concentrations the values of k's remained essentially the same. For practical purposes therefore, all the calculations in Chapter V were performed by assuming a value of 490 for the iodine-triiodide equilibrium constant.

Table 124

Graphical Determination of Iodine-triiodide Equilibrium Constant at 50°, and an Ionic Strength of 0.3000.

$(I_2)_o$ = 4.2494×10^{-5} M (HClO) = 0.009783

(I^-) (moles/liter)	Optical density D	$(D_{I_2} - D)/(I^-)$	$(D_{I_2} - D)/(I^-)$ corr.
0.01000	0.860	85.7	86.0
0.00800	0.812	101.1	101.6
0.00700	0.774	110.2	110.7
0.00600	0.738	122.5	123.3
0.00500	0.682	135.8	136.7
0.00400	0.634	157.8	159.0
0.00300	0.558	185.1	186.7
0.00200	0.444	220.6	223.0
0.00100	0.280	277.2	230.9
0.00080	0.233	287.7	292.7
0.00060	0.192	315.3	320.0
0.00040	0.142	347.9	359.2
0.00020	0.082	395.8	403.3

Equilibrium constant from slope = 365

Extinction coefficient = 25600 at 352 millimicrons

Table 125

Graphical Determination of Iodine-triiodide Equilibrium Constant at 25^{o}, and an Ionic Strength of 0.3000

$(I_2)_o$ = 4.8595 x x 10^{-5} M $(HClO_4)$ = 0.009783 M

(I_2) (mole/l.)	Optical Density	$(D_{I_2} - D)$	$(D_{I_2} - D)/(I^-)$
0.01000	1.190	1.187	119.3
0.00800	1.130	1.127	141.4
0.00600	1.045	1.042	174.0
0.00400	0.980	0.977	246.7
0.00200	0.758	0.755	335.5
0.00080	0.438	0.435	556.6
0.00060	0.367	0.364	626.2
0.00040	0.270	0.267	686.7
0.00020	0.159	0.155	801.0
0.00010	0.081 *	0.078	832.8
0.00005	0.043 *	0.040	838.0

Equilibrium constant from slope = 620

Extinction coefficient of I_3^- = 28000

* These optical densities were measured in 5.000 cm. cells and the recorded optical density was then divided by five.

Table 126

Graphical Determination of Iodine-triiodide Equilibrium Constant at 25^{o} and an Ionic Strength of 0.3000

$(I_2)_o = 4.7550 \times 10^{-5}$ $\underline{M}$ $(HClO_4) = 0.009783$

$(I^-)_o$ (moles/liter	Optical density	$D_{I_2} - D$	$[D_{I_2} - D]/(I^-)$
0.00500	1.044	1.034	209.7
0.00400	0.989	0.982	251.4
0.00300	0.879	0.871	298.0
0.00200	0.731	0.735	378.3
0.00100	0.504	0.505	523.0
0.00050	0.313	0.308	643.0
0.00025	0.176	0.168	728.4

Equilibrium constant from slope = 610

Extinction coefficient of I_3^- = 29000

Table 127

Effect of Iodine-triiodide Equilibrium Constant on k'

Table	Run	$K_{I_2 - I_3^-}$	$(I^-)_o \times 10^4$	$k' \times 10^7$
4	56-V-1	490	125.000	52.38
4	56-V-1	350	125.000	39.73
3	54-V-1	490	65.000	49.14
3	54-V-1	350	65.000	41.52
1	32-V-1	490	25.000	51.15
1	32-V-1	350	25.000	45.83
2	39-V-1	490	25.000	52.02
2	39-V-1	350	25.000	47.18
5	52-V-1	490	12.000	44.85
5	52-V-1	350	12.000	42.98
8	55-V-1	490	5.000	44.69
8	55-V-1	350	5.000	44.37
9	51-V-1	490	2.500	41.88
9	51-V-1	350	2.500	42.61
11	37-V-1	490	1.000	39.53
11	37-V-1	350	1.000	40.48
13	46-V-1	490	1.000	38.17
13	46-V-1	350	1.000	38.64
15	80-V-1	490	0.500	29.03
15	80-V-1	350	0.500	29.42
16	81-V-1	490	0.250	21.41
16	81-V-1	350	0.250	20.95
17	82-V-1	490	0.100	14.95
17	82-V-1	350	0.100	15.14

APPENDIX B

SAMPLE CALCULATION OF INTEGRATED RATE CONSTANTS

The rate constants were calculated from the integrated form of the second order rate equation, i.e.,

$$k = \frac{2.303}{t(a-b)} \times \frac{b(a-x)}{a(b-x)}$$

in which k is the rate constant (l./mole sec.), t is the time elapsed, a is the initial stoichiometric concentration of p-nitrophenol, anisole, or phenol, b is the initial stoichiometric concentration of iodine, and x is the molar concentration of iodine reacted at time t. The sample calculation will be on Run 81-V-1, Table 16.

a = 0.007699 M a-b = .0075594

b = 0.0001396 (200 ml. samples)

$(Na_2S_2O_3)$ = 0.012038 M

t(sec)	Titer (ml.)	(b-x)	(a-x)	(x)	$\frac{b(a-x)}{a(b-x)}$
180	4.15	0.0001249	0.0076843	0.000001258	1.1156
342	3.83	0.0001153	0.0076747	0.0000243	1.2069
575	3.42	0.0001029	0.0076623	0.0000367	1.3502
900	3.05	0.0000918	0.0076512	0.0000478	1.5113
1299	2.65	0.0000798	0.0076392	0.0000598	1.7358
2061	2.10	0.0000632	0.0076226	0.00007621	2.1869

$$k_{app} = \frac{2.303}{(0.00075594)\,t} \log \frac{b(a-x)}{a(b-x)}$$

t(sec)	$\frac{2.303}{(a-b)t}$	log $\frac{b(a-x)}{a(b-x)}$	$\frac{2.303}{(a-b)xt}$ log $\frac{b(a-x)}{a(b-x)}$
180	1.691	0.04750	0.0804
342	0.892	0.08217	0.0732
575	0.532	0.13039	0.0691
900	0.335	0.17935	0.0607
1299	0.235	0.23950	0.0562
2061	0.148	0.33983	0.0502

Extrapolated value of rate constant k_{app} = 0.0875 l./mole sec.

For the calculation of k' the following equation was employed.

$$k' = \frac{K\, k_{app} \times (I_2)_o \; [I^-]_o^2}{[I_3^-]_o}$$

in which K is the iodine-triiodide equilibrium constant at the designated temperature which is represented as

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

$(I_2)_o$ is the initial stoichiometric iodine concentration and $[I^-]_o$ is the initial actual iodide ion conrentration corrected for triiodide formation and $[I_3^-]_o$ is the initial triiodide concentration. The sample calculation will be on the same run represented above.

$$I_2 \quad + \quad I^- \quad \rightleftarrows \quad I_3^-$$

$$(1.396 \times 10^{-4} - x) \qquad (0.2500 \times 10^{-4} - x) \qquad x$$

$$K = \frac{x}{(1.396 \times 10^{-4} - x)(0.2500 \times 10^{-4} - x)} = 490 \text{ at } 50^{\circ}$$

$$x^2 - 22.054 \times 10^{-4}x + 0.3490 \times 10^{-8} = 0$$

Solving for **x** via the quadratic equation

then $$x = \frac{22.0540 \times 10^{-4} - \sqrt{(22.054 \times 10^{-4})^2 - 4x(0.3490 \times 10^{-8})}}{2}$$

$$x = \frac{22.0540 \times 10^{-4} - 22.0232 \times 10^{-4}}{2} = 0.01539 \times 10^{-4}$$

$$I^{-}_{o} = 0.25000 \times 10^{-4} - 0.01539 \times 10^{-4} = 0.23461 \times 10^{-4} \ \underline{M}$$

$$k' = \frac{(0.0875)(490)(1.396 \times 10^{-4})(0.23461 \times 10^{-4})^2}{(0.01539 \times 10^{-4})}$$

$$k' = 21.41 \times 10^{-7} \text{ sec.}^{-1}$$

All calculations of this type were made on an electric calculating machine with use of the numbers of significant figures shown.

APPENDIX C

Correction For Iodine Tied up as Tl_6I_8

Experiments in Tables 67, 68, 69, 70 and 83 indicate that the apparent rate constants for the iodination of anisole in the presence of thallous ions drop as the reaction proceeds. Such a drop in apparent rate constants is contrary to what is expected from reactions in a medium of constant iodide ion concentration. However, the possibility of Tl_6I_8 formation through the reaction

$$6TlI + I_2 \longrightarrow Tl_6I_8$$

may explain the drop in apparent rate constants since these rate constants were calculated on the assumption that all the titratable iodine in the reaction medium exists as free iodine available for iodination.

To correct for the iodine tied up as Tl_6I_8 we may write

$$\text{rate} = \frac{-d(I_2)}{dt} = k_{app} \left[ArOH\right]\left[I_2\right] \tag{1}$$

then

$$\frac{dx}{dt} = k_{app}\left[(ArOH)_o - x\right]\left[(I_2)_o - (Tl_6I_8)_o - \frac{7}{6}x\right] \tag{2}$$

where $\underline{x}$ designates the amount of iodine (mole/l.) reacted at time $\underline{t}$, $(ArOH)_o$ is the initial concentration (mole/l) of the substrate and $(Tl_6I_8)_o$ designates the initial amount of the solid complex Tl_6I_8, expressed in units of moles/l.

Equation (2) can be rewritten as

$$\frac{dx}{dt} = \frac{k_{app}}{6/7}\left[(ArOH)_o - x\right]\left[\frac{6}{7}\left\{(I_2)_o - Tl_6I_8\right\} - x\right] \tag{3}$$

Integration of equation (3) leads to

$$(k_{app}) = \frac{6}{7}\,\frac{2.303}{(b-a)t}\,\log\frac{a(b-x)}{b(a-x)} \tag{4}$$

where $b = (ArOH)_o$

$$a = \frac{6}{7}\left\{(I_2)_o - (Tl_6I_8)_o\right\}$$

Thus the apparent rate constants were calculated according to equation (4) at each per cent reaction and the results are tabulated in Table 128. Inspection of these results reveals that $(k_{app})_{corr.}$ is more nearly constant than k_{app} especially in the runs at highest thallium ion concentration ($Tl^+ = 0.5149$ M).

Table 128

Correction for Iodine Tied up as Tl_6I_8 in the Reaction $6TlI + I_2 \rightarrow Tl_6I_8$.

Reference Table	$(k_{app})_{calc} \times 10^2$ l./mole sec	$(k_{app})_{corr} \times 10^2$ l./mole sec.	Per cent reaction
67	2.12	2.45	5.83
67	2.09	2.43	11.43
67	1.94	2.32	22.42
67	1.74	2.08	25.56
67	1.47	1.83	37.75
		Av = 2.22 ± 0.21	
68	1.74	2.07	6.95
68	1.72	2.06	11.23
68	1.58	1.94	19.52
68	1.31	1.63	26.74
68	1.23	1.58	35.03
68	1.14	1.68	53.21
68	1.08	1.69	59.63
		Av = 1.81 ± .19	
69	5.99	7.64	16.67
69	5.01	6.36	22.01
69	4.49	5.83	28.61
69	3.52	4.79	38.05
69	2.66	3.63	48.74
		Av = 5.65 ± 1.15	
70	12.15	14.7	7.00
70	11.98	14.8	16.91
70	11.77	15.2	28.57
70	9.65	12.9	36.15
70	9.80	14.3	48.69
70	9.29	14.6	55.97
70	8.08	14.1	61.22
		Av = 14.4 ± 0.5	

Table 128
(continued)

83	9.39	11.7	18.95
83	8.70	11.2	27.41
83	8.19	10.9	35.28
83	7.69	10.7	42.57
83	7.22	10.6	49.56
83	6.48	9.8	51.60
		Av = 10.8 ± 0.5	

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