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Auth: Lt ORD-9152:RED/18 July 1968

December 27, 1954

Chief, Bureau of Ordnance
Department of the Navy
Washington 25, D. C.

Attention: Dr. T. L. Brownyard, Re2c

Subject: A Study of Mechanism and Reactivity in Carbon-Carbon
Condensations of Aliphatic Polynitrocompounds.

Progress Report No. 1

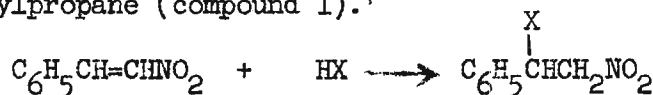
July 1, 1954 - December 21, 1954

Contract NOrd-14840

Dear Sir:

While the subject contract was entered into on April 30 and the project activated on July 1, Dr. Lloyd A. Kaplan, the Research Associate on the project, did not begin work until August 30 and his clearance did not come through until late in September. Therefore we are now reporting on the progress made during the three months' work carried out since that time.

The overall scope of investigation for this project is described in the original research proposal in rather general terms. Our present specific plans are as follows: We intend to investigate the addition of nitroform to β -nitrostyrene to give 1,1,1,3-tetranitro-2-phenylpropane (compound I).



Compound I

(In the equations used in this report the " $\text{C}(\text{NO}_2)_3$ " group will be abbreviated as "X")

The reactions kinetics will be studied at various acidities in order to learn whether acid or basic catalysis exists and whether any such catalysis is general or specific. Correlations with Hammett's acidity functions will also be sought. We hope to be able to determine equilibrium constants for the reaction under various conditions and to make studies at various temperatures in order to permit the calculation of energies of activation and perhaps energies of reaction. We would like then to extend some of this work to ring-substituted β -nitrosyrenes in order to learn more about the nature of electronic effects by use of the Hammett equation.

We are beginning our work by studies in the solvent methanol. This solvent was chosen because it dissolves not only the reactants and product but also most of the acids and bases we may wish to test for catalytic activity. Since it is a fairly good ion-solvating medium, the activity coefficients of dissolved electrolytes should not vary too widely in reasonably dilute solutions. The reaction is being followed by use of an ultraviolet spectral method. The adduct (compound I) does

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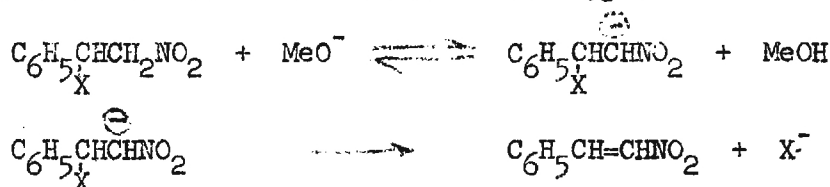
Chief, Bureau of Ordnance

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December 27, 1954

not absorb greatly at wave lengths longer than 3000 Å while *p*-nitro-styrene has an absorption maximum at 3100 Å and the nitroform anion one at 3500 Å. Our first attempts to determine the spectrum of compound I in methanol gave variable results and further experiments showed that this was due to dissociation to *β*-nitrostyrene and nitroform. We therefore decided to begin our study by investigating this reverse reaction since information could thereby be obtained about the forward reaction from consideration of equilibrium principles.

The dissociation of I in pure methanol proceeds quite rapidly at first, being well under way in less than one minute at 25°. Later the reaction slows down as the liberated nitroform increases the acidity of the reaction solution. When dissolved in methanol that is 0.05 M in HCl, compound I does not dissociate significantly in four days at 25°. The dissociation reaction is therefore base-catalyzed. Methoxide ion (concentration about 5×10^{-9} M in pure methanol) must be the catalyst since it is the only base present whose concentration is appreciably less in methanolic HCl than in pure methanol. Certainly the most reasonable reaction mechanism then is of the type:



We plan to study the reaction kinetically in the presence and absence of certain buffers to see if the above mechanism fits the experimental data quantitatively, to see if it needs modification (to explain general base catalysis, for example) and to learn something about the relative magnitudes of the rate constants for the various steps of the reaction. For this reason we are now determining the extinction coefficients of the reactants and products at various wave lengths and checking the applicability of Beer's law. We are also determining the ionization constants of trifluoroacetic acid in methanol so that we may use trifluoroacetate buffers (which should be capable of giving us pH's in a desired region).

Yours very truly,

JH:wr

Jack Hine,
Project Director

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for P. K. Calaway, Acting Director
Engineering Experiment Station

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GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

176th: Lt ORD-9152: AED/83
18 July 1966

March 16, 1955

Chief, Bureau of Ordnance
Department of the Navy
Washington 25, D.C.

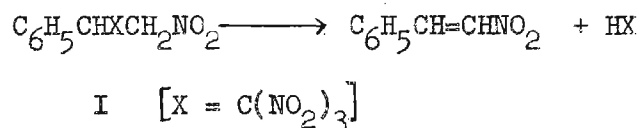
Attention: Dr. T. L. Brownyard, Re2c

Subject : Progress Report No. 2, Project No. A-159, Contract NOrd-14840
A Study of Mechanism and Reactivity in Carbon-Carbon Condensations of Aliphatic Polynitrocompounds
December 28, 1954 - March 15, 1955

Gentlemen:

The work during the current period may be summarized as follows:

Kinetic studies of the decomposition of 1,1,1,3-tetranitro-2-phenylpropane (I) to β -nitrostyrene and nitroform



show that the reaction is general base catalyzed, that is, that it is catalyzed by all of the bases present rather than merely the conjugate base of the solvent. These data give considerable information about the mechanism of this reaction and also the reverse reaction (the synthesis of I).

Progress Report No. 1 presented results of a preliminary investigation of the use of a trifluoroacetic acid-sodium trifluoroacetate buffer. However, further work disclosed that the trifluoroacetic acid esterifies with the solvent, methanol, at a rate comparable to the reaction rate and so the use of this buffer was abandoned. Trichloroacetic acid also esterified but some qualitative data obtained with trichloroacetate buffers showed that the reaction was very probably general base catalyzed.

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Semicarbazide-semicarbazide hydrochloride buffers were tried until it was found that semicarbazide destroys the β -nitrostyrene formed.

The use of p-chloroaniline-p-chloroaniline hydrochloride buffers was discontinued when it was found that they decomposed to give colored products which interfered with the spectrophotometric method of following the reaction.

However, a suitable buffer has been found in pyridine-pyridine hydrochloride. The buffer was present in the reaction mixtures in considerable excess over compound I so that the nitroform liberated brought about no significant change in the pyridine concentration or the buffer ratio (pyridine to pyridine hydrochloride) even though it was essentially all present as the nitroform anion at the pH's used. Since the concentrations of the bases pyridine, methoxide ion and methanol thus remain constant throughout a run, the reaction would be expected to obey the first order kinetic equation.

$$k = \frac{2.303}{t} \log \frac{D_{\infty}}{D_{\infty} - D}$$

where k is the first order rate constant, t the time in minutes, D_{∞} the optical density at infinite time and D the optical density at time t . Application of this equation to the experimental data gave satisfactory agreement, the rate constants within a given run usually having an average deviation from the mean of about 3%. When the buffer ratio was kept constant and the buffer concentration doubled at constant ionic strength (this should not change the methoxide ion concentration) the value of k almost doubled. Thus the reaction was quite strongly general base catalyzed (catalyzed by all of the bases in the solution rather than specifically catalyzed by methoxide ion, the conjugate base of the solvent). The observation, described in Progress

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Report No. 1, that I dissociates at a negligible rate in 0.05M hydrochloric acid, shows that catalysis by the base methanol is not important. Therefore, under our reaction conditions, the rate equation should be

$$-\frac{d(I)}{dt} = k_p (C_5H_5N) (I) + k_m (MeO^-)(I)$$

That is, the first order rate constants may be expressed by:

$$k = k_p (C_5H_5N) + k_m (MeO^-)$$

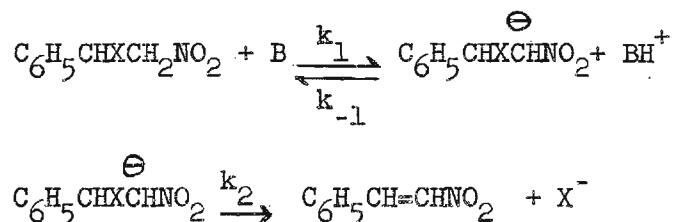
From the values of k obtained from the first five satisfactory runs and the values of (C_5H_5N) and (MeO^-) known for these runs, the "best" values of k_p and k_m were calculated by the method of least squares. These values (for methanol solution at 25°) are:

$$k_p = 0.487 \text{ mol}^{-1} \text{ l. min}^{-1}$$

$$k_m = 1.68 \times 10^7 \text{ mol}^{-1} \text{ l. min}^{-1}$$

These values are capable of reproducing the five k values used with an average deviation of less than 3%.

If the reaction mechanism is



k_2 must not be negligible compared to k_{-1} , because if it were, the reaction would be specific methoxide ion catalyzed.

Other possible reaction mechanisms include a one-step concerted elimination reaction of the E2 (Ingold, "Structure and Mechanism in Organic Chemistry," Cornell, 1953, Chapter VIII) type, and a scheme like that above except that BH^+ takes part in the second step, donating a proton to X^- . A detailed discussion is probably not warranted at the present time, but the

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reaction scheme as shown with k_2 comparable to or larger than k_{-1} is preferred.

The mechanism of the formation of I from nitroform and β -nitrostyrene under these conditions will be the reverse of that for the decomposition reaction.

After obtaining additional and perhaps more accurate data of the type we have described, there appear to be three reasonable paths for future work:

1. Investigate the reaction under conditions of higher acidity and higher reactant concentrations where the preparation of I is a synthetically useful reaction.
2. Try to distinguish between the remaining possible mechanisms.
3. Study derivatives of I with substituents on the ring.

Very truly yours,

Jack Hine
Project Director

Approved:

Frederick Bellinger, Head
Chemical Sciences Division

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A-159

GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station
Atlanta, Georgia

Auth: Lt. ORD-9152: AED/83
16 July 1968

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June 1, 1955

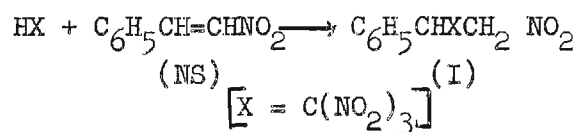
Chief, Bureau of Ordnance
Department of the Navy
Washington 25, D.C.

Attention: Dr. T. L. Brownyard, Re2c

Subject : Progress Report No. 3, Project No. A-159, Contract NOrd-14840
A Study of Mechanism and Reactivity in Carbon-Carbon
Condensations of Aliphatic Polynitrocompounds
March 16 - May 26, 1955

Dear Sir:

During the current period we have studied the mechanism of the addition
of nitroform to β -nitrostyrene under the type of conditions where the reac-
tion is synthetically useful.



To summarize: the equilibrium constant, kinetic form and rate constant for
the reaction in methanol at 40° have been studied. From the resultant data
plus those obtained previously on the reverse reaction, further conclusions
about the reaction mechanism may be drawn.

Because of its relation to several phases of our work, we have deter-
mined the ionization constant of nitroform in methanol at several ionic
strengths. Our results were not as reproducible as we would like, but our
investigations have not disclosed the cause of the unreproducibility.
Nevertheless we believe the following values to be reliable within about
10 per cent.

$$K_i = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]} = 5.8 \times 10^{-4} \text{ at } \mu = 0.1$$

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Progress Report No. 3, Project No. A-159

and $K_1 = 10.2 \times 10^{-4}$ at μ (ionic strength) = 0.2 both at 25°. Our values at 40° are about 3 per cent higher and hence within the experimental error of those obtained at 25°.

We soon learned that the reactions to be studied proceeded too slowly at 25° C., the temperature used in our earlier work, so we have used a temperature of 40° C. In order to determine the equilibrium constant,

$$K = \frac{[I]}{[HX][NS]}$$

equilibrium has been approached both from the side of the reactants and that of the products. Unfortunately, the occurrence of a relatively slow side reaction made it impossible to let the reactions go to "infinite" time. Therefore K was determined essentially by interpolation between the values obtained in decomposition experiments on I and those obtained in synthetic experiments from NS and HX, with small corrections being made for the slow side reaction. We obtain

$$K = 15 \pm 1 \text{ l. mole}^{-1}$$

The kinetics of the reaction are now being studied. From our preliminary results, the formation of I appears to be about first order in NS and around half order in HX. The decomposition of I in 0.02 N methanolic HCl seems to be a first-order reaction accompanied by a side reaction. We are also studying the pyridine-pyridine hydrochloride catalyzed decomposition of I at 40° in order to obtain activation energies and catalytic constants at 40°. Our studies of the reaction kinetics will probably occupy us for most of the rest of the contract period.

Yours very truly,

Approved:

Frederick Bellinger
Head, Chemical Sciences Division

Jack Hine
Project Director

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ENGINEERING DEPARTMENT
of the Georgia Institute of Technology
Atlanta, Georgia

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Ltr. ORD-9152: AED/83

18 July 1966

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FINAL REPORT

PROJECT NO. A-159

A STUDY OF MECHANISM AND REACTIVITY IN CARBON-CARBON
CONDENSATIONS OF ALIPHATIC POLYNITROCOMPOUNDS

By

LLOYD A. KAPLAN and JACK HINE

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DEPARTMENT OF THE NAVY

BUREAU OF ORDNANCE

CONTRACT NO. NOrd-14840

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APRIL 30, 1954, to JULY 31, 1955

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DEPARTMENT OF THE NAVY

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CONTRACT NO. NOrd-14840

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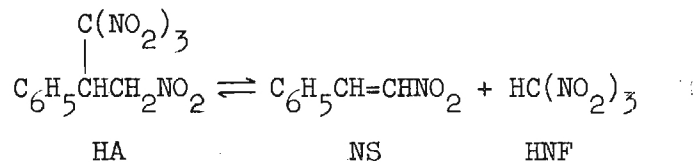
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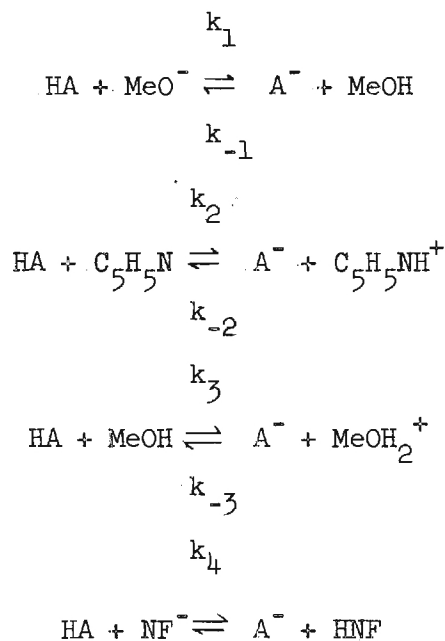
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I. ABSTRACT

The mechanism of the decomposition of 1,1,1,3-tetranitro-2-phenylpropane (HA) and of the reverse reaction, the addition of nitroform (HNF) to β -nitrostyrene (NS), has been studied in methanol solution.



The kinetics of the decomposition of HA in a pyridine-pyridine hydrochloride buffer have been studied at two temperatures. The kinetics of the decomposition of HA in methanolic hydrogen chloride and of the addition of HNF to NS in pure methanol have also been studied. The equilibrium constant for the reaction has been determined. The data obtained support the following reaction mechanism:

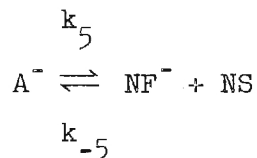


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From the kinetics of the decomposition of HA, k_2 and k_3 were determined accurately and k_1 was determined approximately. From these data, the ionization constant of nitroform and the equilibrium constant for the reaction as a whole, k_5 was determined. The study of the kinetics of the addition of HNF to NS gave a maximum value of k_4 . From an estimate of the ionization constant of HA as an acid, values of k_{-1} , k_{-2} , k_{-3} , k_5 , and a maximum value for k_{-4} could be calculated. Both the relative and the absolute magnitudes of these k 's are shown to be in reasonable agreement with the relevant published kinetic data on aliphatic nitrocompounds.

The fact that k_{-4} is smaller than k_{-2} , although nitroform is a stronger acid than pyridinium ion, is in agreement with the generalization that acids with the acidic proton bonded to carbon donate this proton more slowly than equally strong acids with acidic protons on oxygen and nitrogen.

The evidence against alternate reaction mechanisms and modifications of the mechanism described is pointed out.

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II. INTRODUCTION

This research was initiated to gain further knowledge about the theoretical organic chemistry of aliphatic polynitrocompounds for use in the investigation of high explosives of this type. The particular reactions studied in detail were the decomposition of 1,1,1,3-tetranitro-2-phenylpropane (HA) and the reverse reaction, the Michael addition of nitroform (HNF) to β -nitrostyrene (NS). In 1951 Ingold stated that no example of the Michael reaction had been studied kinetically.¹ More recently at the Naval Ordnance Laboratory, Kamlet and Glover have studied the kinetics of the Michael addition of barbituric acid to β -nitrostyrene.²

1. C. K. Ingold, Structure and Mechanism in Organic Chemistry. Cornell University Press, Ithaca, New York, 1953, Sec. 446.
2. M. J. Kamlet and D. J. Glover, Abstracts of Papers, 127th ACS Meeting, Cincinnati, Ohio, March 27-April 7, 1955, p. 35N.

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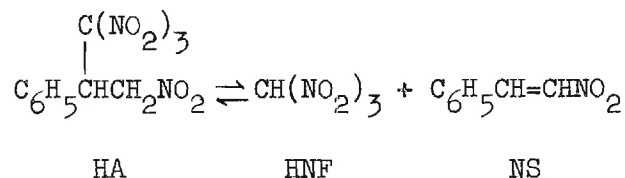
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III. RESULTS

The object of this investigation was a study of the mechanism of the reactions involved in the equilibrium between 1,1,1,3-tetranitro-2-phenylpropane (HA) and nitroform (HNF) and β -nitrostyrene (NS).



Preliminary spectrophotometric measurements in dilute methanol solution showed that, under these conditions, the equilibrium lies almost entirely on the side of nitroform and nitrostyrene. HA was found to dissociate at a negligible rate in hexane at room temperature, but it dissociated readily in ether, dioxane, and methanol, the rate increasing with changing solvent in the order named. Methanol was chosen as the solvent for the following work because of solubility considerations and ease of purification and because its hydroxylic character simplifies the study of acid and base catalysis.

Before studying the reaction kinetics, it was necessary to determine the spectra and extinction coefficients of the adduct, β -nitrostyrene, nitroform, and the nitroform anion. The spectrum of β -nitrostyrene was determined in methanol, but because of its ease of dissociation in methanol, the spectrum of the adduct was determined in hexane. The determination of the spectra of nitroform and its anion was complicated by the fact that nitroform is a fairly strong acid in methanol solution, so that solutions made by dissolving nitroform in pure methanol contain a significant fraction in each of the two forms. The material is easily obtained completely in the form of the anion by the addition

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of an excess of sodium methoxide and is changed very largely into undissociated nitroform by the addition of strong acid. The spectra obtained in this way are summarized in Table I and are shown in detail in Tables XI and XII.

TABLE I

ULTRAVIOLET SPECTRA OF REACTANTS AND PRODUCTS

<u>Compound</u>	<u>λ_{\max}</u> ($m\mu$)	<u>Slit</u> (mm)	<u>Solvent</u>	<u>ϵ^a</u>
Nitroform	b	--	MeOH-HCl	---
Nitroform anion	350	0.50	MeOH-NaOMe	15150
β -Nitrostyrene	310	0.64	MeOH	16400
Adduct	b	--	n-hexane	---

a. Determined from plot of optical density versus concentration.
b. Has no absorption maximum between 300 and 410 $m\mu$.

However, even in solutions of methanolic hydrogen chloride that were approximately 1 M and with formal nitroform concentrations of 6×10^{-4} M, there was enough nitroform anion present to have a measurable absorption at 350 $m\mu$. The change in optical density with hydrogen chloride concentration at λ_{\max} is tabulated in Table II.

TABLE II

EFFECT OF ACIDITY ON ABSORPTION OF NITROFORM AT 350 $m\mu$

<u>Conc. Nitroform (formal)</u>	<u>Conc. MeOH $\frac{1}{2}$ HCl</u>	<u>O.D., $\lambda = 350 m\mu$</u>
5.97×10^{-4} M	0.9699 M	0.022
5.97×10^{-4}	0.4384	0.029
6.74×10^{-4}	0.4384	0.042
6.74×10^{-4}	0.03975	0.093

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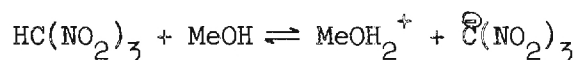
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Further proof of the fact that small amounts of nitroform anion were causing deviations from 100 per cent transmission at 350 μ in the spectrum of nitroform in methyl oxonium chloride can be found by inspecting the complete spectrum given in Table XII. From 270 to 330 μ the optical density continually decreases. Then it increases at 340 to 360 μ , after which it once again decreases. This is the region for the maximum absorption of nitroform anion.

The application of Beer's Law to solutions of β -nitrostyrene and nitroform anion at their absorption maxima gave straight-line plots of concentration versus optical density that passed through the origin. The extinction coefficients listed in Table I were obtained from the slopes of these graphs.

Preliminary experiments designed to study the dissociation of the adduct in pure methanol showed that the reaction proceeded very rapidly at first and then slowed down as the methoxide ion concentration of the solvent was reduced by the nitroform produced in the reaction. Data from a typical run are reproduced in Table III. It should be noted that the optical density of the solution in this case represents the combined absorption of β -nitrostyrene and nitroform anion since both of these species absorb at 310 μ . These data are purely qualitative, since as the acidity of the medium increases not only is the rate of the reaction reduced but so is the fraction of nitroform present as the anion. This is due to the shifting of the equilibrium



to the left with increasing methyl oxonium ion concentration. No attempt was made to correct for the partial dissociation of nitroform in this instance.

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TABLE III

DISSOCIATION OF ADDUCT IN METHANOL^a

<u>Time</u> (min)	<u>O.D.</u>	<u>Time</u> (min)	<u>O.D.</u>
1.5	0.398	26.5	0.833
6.5	0.614	36.5	0.889
11.5	0.701	46.5	0.928
16.5	0.764	61.5	0.967
21.5	0.818		

a. $\lambda = 310 \text{ m}\mu$, slit = 0.64 mm, conc. adduct (formal) = $1.099 \times 10^{-4} \text{ M}$.

Since the rate of dissociation of the adduct in pure methanol was initially too rapid and since the manner in which the rate decreased with time promised to be rather complicated, several runs were tried in solutions of methanolic hydrogen chloride. For hydrogen chloride concentrations between 0.05 M and 4×10^{-3} M, the adduct did not dissociate to any appreciable extent at 25° during one-day intervals. At a concentration of 4×10^{-5} M, about 30 per cent of the adduct dissociated after 19 hours. Since the effect of adding hydrogen chloride to methanol is to reduce the concentration of methoxide ion formed from the autoprotolysis of methanol, it seemed evident that the dissociation of the adduct was a base-catalyzed reaction, and that catalysis by the base methanol was negligible compared to catalysis by the base methoxide ion in neutral methanol solution.

In an effort to determine whether the reaction was subject to general base catalysis (the rate being affected by all bases present in the reaction medium) or specific base catalysis (the reaction subject to catalysis solely by the

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conjugate base of the solvent, methoxide ion), it was decided to determine the rate of dissociation of the adduct in various buffer systems. Several systems were tried before one was found that was completely suitable. One important point to be considered in choosing a buffer is the pK of the buffer acid since the pH^3 of the solution is equal to this pK when the buffer ratio is unity and since buffers are not conveniently used at buffer ratios differing from unity by more than a factor of about ten.

Selections were made to keep the pH between the values of 4 and 7, since preliminary work showed that the dissociation should proceed at a convenient rate under these conditions. The first two systems tried were trifluoroacetic acid-sodium trifluoroacetate and trichloroacetic acid-sodium trichloroacetate. Although the pK for trifluoroacetic acid in methanol had not been determined previously, we felt that this could be done by a method based on that of Stearns and Wheland.⁴ The pK for trichloroacetic acid in methanol had been reported to be 4.9.⁵

However, the possible use of these two buffer systems was ruled out when it was found that both of these acids underwent self-catalyzed esterification reactions in methanol. Trifluoroacetic acid solutions in methanol could not be standardized by titration with base because of a variable, fading end point. This result was attributable to the hydrolysis of the methyl trifluoroacetate by the base used in the titration.

This same effect was detected with trichloroacetic acid buffers in methanol although it was not as pronounced. For example, a solution containing 3. Throughout this report pH will be defined as $-\log[\text{MeOH}_2^+]$ rather than using any definition referring to aqueous solution.

4. R. S. Stearns and G. W. Wheland, *J. Am. Chem. Soc.* 69, 2025 (1947).

5. I. M. Kolthoff and L. S. Guss, *J. Am. Chem. Soc.* 60, 2516 (1938).

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5.45×10^{-2} moles/l. of trichloroacetic acid was prepared by weighing out the appropriate amount of acid and dissolving it in a small amount of methanol. To this solution was added enough 0.1062 M sodium methoxide to half neutralize the acid present. This left 2.725×10^{-2} moles/l. of trichloroacetic acid and made the ratio $\frac{\text{CCl}_3\text{COO}^-}{\text{CCl}_3\text{COOH}}$ equal to unity. Rapid titration of an aliquot of this solution with 0.0139 N aqueous sodium hydroxide gave an initial end point that was equivalent to a concentration of only 2.462×10^{-2} M of trichloroacetic acid.

Even though this buffer system was not suitable for quantitative work, a determination of the rate of dissociation of the adduct in a "one-to-one" buffer produced some interesting results. Approximately a tenfold increase in the buffer concentration produced roughly a tenfold increase in the rate of dissociation of the adduct. This showed that the reaction was probably general base catalyzed since the increase in buffer concentration at constant buffer ratio increases the trichloroacetate ion concentration but not the methoxide ion concentration. These data are given in Table XIII.

The next buffer system studied was the semicarbazide-semicarbazidium ion system. The pK for semicarbazide hydrochloride in methanol had not been determined although its value in water is 3.43. Since acids of charge type, plus one, (such as the semicarbazidium ion) tend to have pK's about one unit higher in methanol than in water,⁶ the pK in methanol should be around 4.4 to 4.5.

The system was excellent from a spectral viewpoint since neither species absorbed in the region from 300 to 400 mμ. However, one disadvantage caused

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6. H. Goldschmidt and E. Mathiesen, Z. Physik. Chem. 119, 465 (1926).

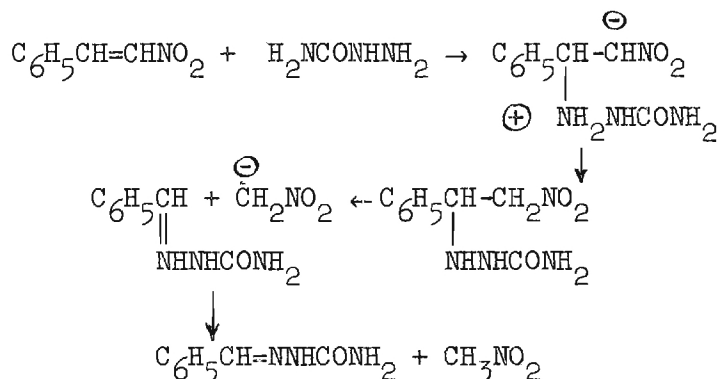
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this system to be discarded. One of the products, β -nitrostyrene, was decomposed by this buffer. This decomposition may have the following mechanism:



A third system tried was the p-chloroaniline-p-chloroanilinium chloride. p-Chloroanilinium ion has been found to have an acidity constant of 1.2×10^{-5} in methanol.⁶ The spectra of solutions of p-chloroaniline in methanolic hydrogen chloride, methoxide ion in methanol and in pure methanol were determined to see whether or not the absorption of p-chloroanilinium ion or p-chloroaniline would interfere with that of β -nitrostyrene or nitroform anion. These results are summarized in Table IV with complete data being in Table XIV.

TABLE IV

SPECTRAL SUMMARY OF p-CHLOROANILINE-p-CHLOROANILINIUM BUFFER

Species	λ_{max} (m μ)	Slit (mm)	Solvent
p-Chloroaniline	298	0.70	NaOMe-MeOH
p-Chloroaniline	260	0.92	NaOMe-MeOH
p-Chloroanilinium	260	0.92	HCl-MeOH

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From a consideration of the spectrum of p-chloroaniline, it was decided to follow the rate of dissociation of the adduct at 370 mμ. This wavelength was chosen for two reasons. The extinction coefficient of p-chloroaniline at 310 mμ was quite large, being 1119. At the concentrations required for a suitable buffer, about 10^{-3} M, the solution would have too high an optical density to measure accurately the change produced by a small amount of β-nitrostyrene. In addition, changes in the pH of the medium would affect the concentration of p-chloroaniline, producing a corresponding variation in the optical density.

Three hundred and seventy millimicrons was selected as the new wavelength since nitroform anion absorbs strongly at this point although it is not at its λ_{max} . Then too, at this wavelength the ratio $\frac{\epsilon_{\text{NF}}}{\epsilon_{\text{NS}}}$ is at a maximum. This reduces the relative value of the absorption of β-nitrostyrene to a minimum. This is especially desirable since it was found that the optical density of a solution of β-nitrostyrene tends to decrease slightly on standing. This effect is less pronounced in low-actinic glassware and at pH's less than 7. In low actinic glassware, a neutral methanolic solution of β-nitrostyrene transmitting 10.0 per cent at 310 mμ was transmitting 12.3 per cent 24 hours later. The same solution in Pyrex-774 was transmitting 17.5 per cent after standing for 24 hours. Apparently, the decomposition is catalyzed by light as well as by bases.

We next undertook a study of the stability of this buffer and solutions of it containing nitroform. While solutions of p-chloroaniline and p-chloroanilinium in methanol were stable for 15 hours, the addition of nitroform to this solution caused a reaction to take place with the formation of colored products. This buffer system was, therefore, discarded.

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The last buffer system selected was the pyridinium chloride system, and it was found to be quite suitable for this work. A determination of the spectra of pyridine and pyridinium chloride in methanol showed that both species were optically transparent between 310 and 410 $m\mu$. Solutions of pyridine and pyridinium chloride in methanol were very stable, showing essentially no change in the optical density over a 24-hour period.

A series of experiments were then performed to determine the degree of ionization of nitroform in pyridine-pyridinium buffers at various buffer ratios. These results are summarized in Table V.

TABLE V

DEGREE OF DISSOCIATION OF NITROFORM IN PYRIDINE BUFFERS AT 25°

Buffer Ratio $\frac{[Py]}{[PyH^+]}$	1/1	1/2	1/3	a
$\lambda = 350 m\mu$, O.D.	0.468	0.458	0.455	0.468
$\lambda = 370 m\mu$, O.D.	0.237	0.234	0.230	0.237

Formal concentration of nitroform = 3.125×10^{-4} M in all solutions.

a. Control, rendered alkaline with NaOMe, $Conc_{OMe^-} = 7.69 \times 10^{-3}$ M.

All solutions were 0.1 M in $NaClO_4$. $K_{PyH^+} = 2.9 \times 10^{-6}$.

From the above data, it can be seen that nitroform exists completely as the anion in a pyridine buffer with a ratio of Py/PyH^+ equal to unity. Since this is the case, it is safe to assume that where the ratio Py/PyH^+ is greater than unity, all the nitroform in solution will still be present as the anion. Therefore, by working within this buffer range, there is no need to apply a

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correction to the observed concentration of nitroform anion due to the presence of undissociated nitroform in solution. This fact made possible the use of the following expression:

$$\text{Optical Density} = C (\epsilon_{\text{NF}^-} + \epsilon_{\text{NS}})$$

where C = concentration of nitroform anion or β -nitrostyrene,

ϵ_{NF^-} = molar extinction coefficient of nitroform anion, and

ϵ_{NS} = molar extinction coefficient of β -nitrostyrene.

Since nitroform is not completely dissociated in pyridine-pyridinium chloride mixtures with a buffer ratio, Py/PyH^+ , less than unity, the determination of the ionization constant of nitroform in this buffer was attempted. The values obtained at a constant ionic strength, 0.1, varied by about tenfold. This large error was due to the almost complete dissociation of nitroform in the pyridine buffer. In buffers with a ratio of 0.20 and 0.33, nitroform is at least 95 per cent dissociated. The determination of a small amount of undissociated nitroform in such a mixture by difference is subject to considerable error. Therefore, the degree of dissociation of nitroform in methanolic hydrogen chloride at 25° and 40° was determined. It was found that the values of the ionization constant obtained in this manner were much more precise. These data are reproduced in Table VI.

The optical densities of the solution listed in Table V were found to be unchanged after the solutions had stood for a period of 24 hours at room temperature. Therefore, it will be assumed that nitroform and nitroform anion are both stable in the presence of a pyridine-pyridinium chloride buffer. However,

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it should be noted that a coincidental decomposition of either species, nitroform or nitroform anion, to yield products having similar absorption spectra and extinction coefficients can not be completely ruled out. However, this is exceptionally improbable since the per cent transmission was checked at two wavelengths for the 24-hour period.

TABLE VI

IONIZATION CONSTANT OF NITROFORM IN METHANOL AT VARIOUS IONIC STRENGTHS

$10^3 [\text{HCl}]$	O.D.	$10^5 [\text{HNF}_f]$	$10^5 [\text{NF}^-]$		μ	$10^4 K_{\text{HNF}}$	
			25°	40°		25°	40°
1.81	0.132	13.34	0.89	--	~0.002	1.32	--
1.81	0.326	13.34	2.20	--	0.04	3.61	--
1.90	0.338 ^a	9.73	2.32	2.28	0.1	5.94	5.89
2.37	0.283 ^b	9.73	1.91	1.91	0.1	5.79	5.89
1.86	0.484 ^c	9.73	3.26	3.23	0.2	9.37	9.53
2.33	0.408 ^d	9.73	2.75	2.77	0.2	9.15	9.53
1.81	0.959	13.34	6.46	--	0.5	17.6	--

a. O.D. = 0.344 at 40°.

b. O.D. = 0.284 at 40°.

c. O.D. = 0.479 at 40°.

d. O.D. = 0.411 at 40°.

Further proof of the stability of solutions of β -nitrostyrene and nitroform in this buffer can be found in the agreement of the calculated and observed values of the optical density at infinite time in the kinetic runs of the following section.

The rate of decomposition of HA in methanol solution buffered with pyridine-pyridinium chloride was followed by measuring the change in optical density with time at a wavelength of 370 m μ . This was equal to the sum of the optical

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densities of the nitroform anion and β -nitrostyrene liberated by the dissociation of the adduct. A reasonably constant value for the experimental rate constant was obtained by using the following modification of the first order rate expression:

$$K = \frac{2.303}{t} \log \frac{D_{\infty}}{D_{\infty} - D}$$

where D_{∞} = optical density at infinite time and

D = optical density at time t .

A graph of $\log \frac{D_{\infty}}{D_{\infty} - D}$ versus time gave the usual straight-line plot obtained by graphing \log concentration versus time, the slope of which was equal to $k/2.303$. The reaction is thus shown to follow first order kinetics. The data from eight such runs are summarized in Table VII.

Before the decomposition of the adduct in solutions of hydrogen chloride in methanol was studied, the equilibrium constant for the dissociation of the adduct in methanol was determined. Because of a slow side reaction, no doubt the decomposition of β -nitrostyrene, it was not possible to equilibrate the reaction mixtures to infinite time. The procedure was to attempt to follow both the decomposition and the synthetic reactions as long as possible and then plot the calculated equilibrium constant versus time for each run. (See Fig. 1.)

The value of the equilibrium constant (K_E) at infinite time is 0.063 where $K_E = \frac{[HNF][NS]}{[HA]}$. This value was obtained by interpolation between the asymptotic portions of the two curves. The data from a typical determination are given in Table VIII.

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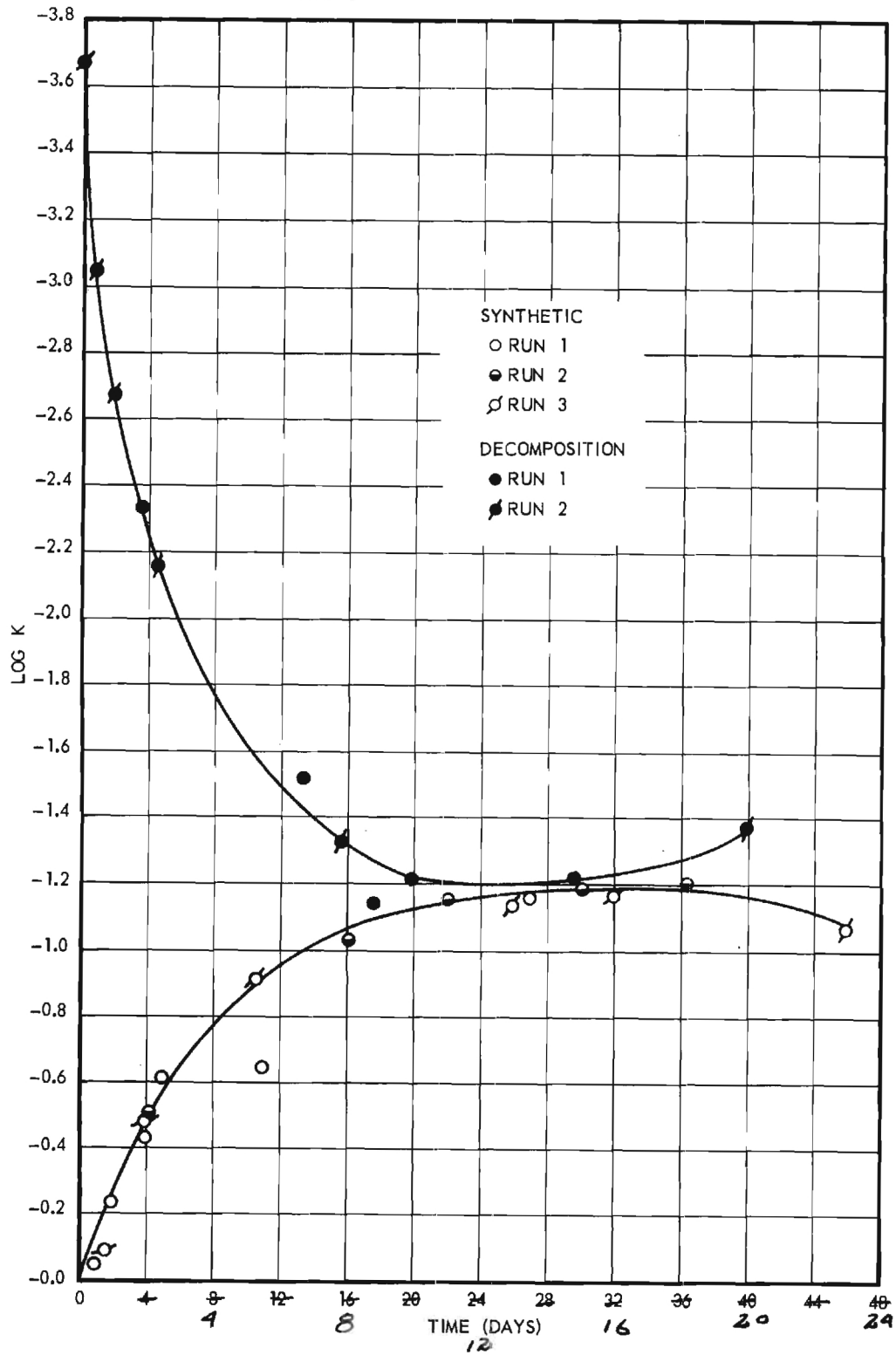


Figure 1. Plot of $\text{Log } K_E$ Versus Time at 40° .

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TABLE VII

RATE CONSTANTS FOR THE DECOMPOSITION
OF THE ADDUCT IN METHANOL WITH A PYRIDINE BUFFER

Run ^a	10^4 [Adduct]	10^3 [Py]	10^3 [PyH ⁺]	Py/PyH ⁺	10^5 k sec ⁻¹ ^b
1	1.385	4.141	4.147	1.00	3.58 ± 0.02
2	1.241	2.455	1.228	2.00	2.40 ± 0.12
3	1.554	4.910	2.456	2.00	4.68 ± 0.10
4	1.314	9.076	3.025	3.00	7.67 ± 0.05
5	0.930	18.15	6.050	3.00	15.35 ± 0.47
6	1.684	2.046	0.682	3.00	5.18 ± 0.10
7	1.396	3.758	1.698	2.21	8.97 ± 0.14
8	1.755	4.163	1.387	3.00	9.53 ± 0.05

a. Runs 1 through 5 at 25° C, runs 6 through 8 at 38° ± 0.2°. All solutions made 0.1 M with NaClO₄ to equalize salt effects.

b. Average of all values of k from 10 to 75 per cent reaction.

It was not possible to determine the rate of decomposition of the adduct in methanolic hydrogen chloride at 25° because of the simultaneous decomposition of the β -nitrostyrene formed. At higher temperatures this competing reaction did not introduce a significant error. Therefore, the rate of decomposition was followed at 40°. The change in optical density at 310 and 350 m μ , of solutions of the adduct in methanolic hydrogen chloride made 0.1 M with sodium perchlorate was measured at various time intervals. From the two optical-density measurements and the molar extinction coefficients of β -nitrostyrene and nitroform anion, it was possible to calculate the increase in the concentration of β -nitrostyrene with time. This is equal to a corresponding decrease in the concentration of HA. Substitution of these values into the usual form of the first order

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rate expression gave good first order rate constants. These data are summarized in Table IX.

TABLE VIII

REACTION BETWEEN β -NITROSTYRENE AND NITROFORM IN METHANOL

Time (days)	$10^2 [\beta\text{-Nitrostyrene}]$	$10^2 [\text{Nitroform}]^a$	$10^3 [\text{Adduct}]^a$	K_E^b
0.8	6.08	4.44	3.31	0.816
2.0	5.70	4.07	7.11	0.326
5.25	5.09	3.47	14.23	0.241
13.0	4.56	3.01	18.51	0.0742
16.0	4.49	2.92	19.21	0.0682
22.0	4.70	3.14	17.13	0.0862

a. Undissociated nitroform remaining after time t . The amount of nitroform reacted was taken to be equal to the amount of β -nitrostyrene that had reacted. The adduct formed was equal to the amount of β -nitrostyrene that had reacted.

b. This is the equilibrium constant for the reaction:



TABLE IX

DECOMPOSITION OF THE ADDUCT IN METHYL OXONIUM CHLORIDE AT 40°

$10^4 [\text{Adduct}]$	$10^2 [\text{MeOH}_2^+ \text{Cl}^-]$	$10^7 k \text{ sec}^{-1}$
1.949	0.48	6.28 ± 0.11
2.719	2.21	9.52 ± 0.19
2.300	9.03^a	11.69 ± 0.39

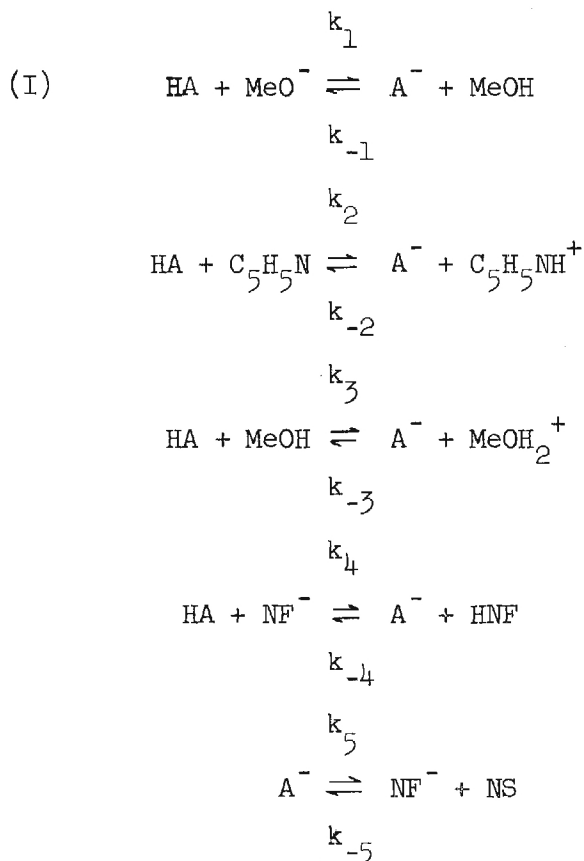
a. No NaClO_4 added in this run; $\mu = 0.090$.

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IV. DISCUSSION

The most reasonable reaction mechanism appears to be



where A^- is $\text{C}_6\text{H}_5\overset{\ominus}{\underset{\text{C}(\text{NO}_2)_3}{\text{CHCHNO}_2}}$

and k_{-1} and k_3 will be treated as first order rate constants. The following equilibrium constants will also be used.

$$K_{\text{HNF}} = \frac{[\text{MeOH}_2^+][\text{NF}^-]}{[\text{HNF}]}$$

$$K_P = \frac{[\text{C}_5\text{H}_5\text{NH}^+][\text{OMe}^-]}{[\text{C}_5\text{H}_5\text{N}]}$$

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$$K_M = [\text{MeOH}_2^+][\text{MeO}^-]$$

$$K_{HA} = \frac{[\text{MeOH}_2^+][\text{A}^-]}{[\text{HA}]}$$

It is obvious from the data of Table VII that the decomposition reaction in pyridine buffers is general base catalyzed with most of the catalysis due to pyridine. This shows that $k_2[\text{C}_5\text{H}_5\text{N}]$ is larger than either $k_1[\text{MeO}^-]$ or k_3 . Application of the steady-state treatment to that part of the reaction due to pyridine gives the equation

$$V = \frac{k_2 k_5 [\text{C}_5\text{H}_5\text{N}][\text{HA}]}{k_{-2}[\text{C}_5\text{H}_5\text{NH}^+] + k_5}$$

Thus, the first order rate constant for the reaction of HA could be represented

$$k = \frac{k_2[\text{C}_5\text{H}_5\text{N}]}{(k_{-2}/k_5)[\text{C}_5\text{H}_5\text{NH}^+] + 1} \quad (1)$$

if all of the reaction were due to pyridine.

Assuming catalysis by the bases methanol and methoxide ion to negligible and neglecting $k_{-2}[\text{C}_5\text{H}_5\text{NH}^+]$ in comparison to k_5 , a least squares calculation gives values of k_2 whose predictions of k are in error by an average of 5 per cent. Since the average percentage of deviation in the experimental determination of the rate constants was about 2 per cent, it seems quite probable that this lack of strict proportionality between pyridine concentration and reaction rate requires an explanation. Each of three specific versions of mechanism I appears to give such an explanation.

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Mechanism Ia suggests that catalysis by bases other than pyridine is negligible under the conditions used, but that $k_{-2}[\text{C}_5\text{H}_5\text{NH}^+]$ may not be neglected in comparison to k_5 .⁷ Thus, with the values: $k_2^{25^\circ} = 0.0101$, $k_2^{38^\circ} = 0.0252$, and $k_{-2}/k_5 = 40$, the first order rate constants of Table VII may be calculated with an average deviation of about 3 per cent.

Mechanism Ib hypothesizes that $k_{-2}[\text{C}_5\text{H}_5\text{NH}^+]$ is negligible compared to k_5 , but that some of the reaction is due to catalysis by methoxide ions. It may be shown that

$$\frac{k_2[\text{C}_5\text{H}_5\text{N}]}{k_{-1}[\text{MeO}^-]} = \frac{k_{-2}[\text{C}_5\text{H}_5\text{NH}^+]}{k_{-1}} \quad (2)$$

Therefore, if most of the reaction is due to pyridine as in the present case, k_{-1} must be smaller than $k_{-2}[\text{C}_5\text{H}_5\text{NH}^+]$ and, hence, negligible compared to k_5 . Hence, the first order rate constant would be represented

$$k = k_{-1}[\text{MeO}^-] + k_2[\text{C}_5\text{H}_5\text{N}]. \quad (3)$$

Using K_p , values of k_{-1} and k_2 were calculated by a least squares method, the percentage of deviations from the experimental being minimized.⁸ These values,

7. The observations of general base catalysis shows that k_5 may not be neglected in comparison to $k_{-2}[\text{C}_5\text{H}_5\text{NH}^+]$. If $k_{-2}[\text{C}_5\text{H}_5\text{NH}^+]$ were very much larger than k_5 , the reaction would be specific methoxide ion catalyzed.
8. K_p was calculated from the acidity constant ($\text{pK } 5.55$) of the pyridinium ion [H. Goldschmidt and E. Mathieson, Z. physik. Chem. **119**, 439 (1926)] and $K_M^{25^\circ}$ (pK_M 16.66) [N. Bjerrum, A. Unmack, and L. Zechmeister, Kgl. Danske Videnskab, Math. fys. Medd. **5**, No. 11 (1925); C. A. **19**, 3196 (1925)]. The value of pK_M was corrected to 15.97 for $\mu = 0.1$ by the assumption that

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$k_1^{25^\circ} = 5.68 \times 10^4$, $k_1^{38^\circ} = 5.81 \times 10^4$, $k_2^{25^\circ} = 8.105 \times 10^{-3}$, and $k_2^{38^\circ} = 21.96 \times 10^{-3}$ (all in $\text{l. mole}^{-1} \text{ sec}^{-1}$) reproduced the k 's in Table VII with an average deviation of about 2 per cent.⁹

Mechanism Ic also involves the assumption that $k_{-2}[\text{C}_5\text{H}_5\text{NH}^+]$ is negligible compared to k_5 and further assumes catalysis by the base methanol while neglecting any methoxide ion catalysis. Since an equation of the type of (2) may be used to show that with these assumptions $k_{-3}[\text{MeOH}_2^+]$ may be neglected in comparison to k_5 under the reaction conditions employed, it may be seen that

$$k = k_2[\text{C}_5\text{H}_5\text{N}] + k_3. \quad (4)$$

A least squares treatment gives the values $k_2^{25^\circ} = 0.00819$, $k_2^{38^\circ} = 0.02117$, $k_3^{25^\circ} = 3.7 \times 10^{-6}$, and $k_3^{38^\circ} = 8.58 \times 10^{-6}$; capable of reproducing the rate constants of Table VII with an average deviation of about 2.5 per cent.

Although mechanisms Ia, Ib, and Ic do not differ greatly in their agreement with the data in Table VII, the data on the decomposition reaction in methanolic hydrogen chloride solution (Table IX) showed that the deviations

8. changing ionic strength had the same effect as observed on pK_{HNF} . (See Table VI.) Since no temperature coefficient was available for the acidity constant of the pyridinium ion, the same pK_P (10.42) was used at both temperatures.
9. While the assumption that K_P has the same value at 38° as at 25° can have no effect on the ability (or inability) of equation (3) to fit the experimental data, it does affect the magnitude of $k_1^{38^\circ}$ obtained. If $K_P^{38^\circ}$ is smaller than $K_P^{25^\circ}$, the value of $k_1^{38^\circ}$ will be larger than that listed. The ionization constants of some amines increase with increasing temperature, while others decrease. E.g., see the data of D. H. Everett and W. F. K. Wynne-Jones, Proc. Roy. Soc. (London) A 177, 499 (1941).

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of the rate constants of Table VII from strict proportionality to the pyridine concentration are largely due to the operation of mechanism Ib.

The rate constants of Table IX are seen to continue to fall, with increasing acidity, throughout the range studied. It might be suggested that this decrease is due to the decreasing methoxide ion concentration, with the first order rate constant following the equation

$$k = k_1[\text{MeO}^-] + k_3.$$

The optimum values calculated by a least squares method to fit the data in Table IX are $k_1^{40^\circ} = 5.65 \times 10^6$ and $k_3^{40^\circ} = 6.60 \times 10^{-7}$. However, these values give an average deviation of more than 10 per cent predicting the rate constants of Table IX. Furthermore, the value of $k_1^{40^\circ}$ required is more than one hundred times as large as the $k_1^{38^\circ}$ calculated on the assumption that mechanism Ib operates in pyridine buffer. If mechanism Ia and/or Ic operate in addition to or instead of Ib, the calculated $k_1^{38^\circ}$ would be even smaller. Therefore, it seems unlikely that methoxide catalysis is significant in the runs described in Table IX.

A more reasonable explanation for the decrease in rate is the assumption that under the more acidic conditions used in these runs an appreciable fraction of the intermediate A^- ions formed is reconverted to HA. In other words

$$k = \frac{k_3}{r_3[\text{MeOH}_2^+] + 1} \quad (5)$$

where $r_3 = k_{-3}/k_5$. With the values $k_3^{40^\circ} = 1.194 \times 10^{-6}$ and $r_3^{40^\circ} = 10$, Eq. (5) reproduces the rate constants of Table IX with an average deviation of 1.8 per cent.

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Since

$$\frac{k_3}{k_2[C_5H_5N]} = \frac{k_{-3}[MeOH_2^+]}{k_{-2}[C_5H_5NH^+]}$$

$$\frac{k_{-2}}{k_5} = \frac{r_3 k_2 K_M}{k_3 K_P}.$$

From this relationship and the values of K_M and K_P used previously,⁸ k_{-2}/k_5 may be calculated to be 2.5 in contrast to the value of about 40 required by the exclusive operation of mechanism Ia for the reaction in the presence of pyridine buffers. Although this value of k_{-2}/k_5 is subject to the errors present in K_M and K_P , we believe there is another strong argument against mechanism Ia. Namely, the value of 40 for k_{-2}/k_5 would make k_{-2} , the rate constant for the donation of a proton from pyridinium ion to the base A^- , four times as large as k_{-3} , the rate constant for the donation of a proton from the methyl oxonium ion to the same base.

The fact that mechanism I_c requires values of $k_3^{25^\circ}$ and $k_3^{38^\circ}$ much larger than the $k_3^{40^\circ}$ determined more directly from the data of Table IX shows that catalysis by the base methanol is very slight in the pyridine buffer reaction.

The establishment of K_E (Fig. 1) permits a determination of the value of an additional rate constant, k_{-5} , since

$$\frac{k_3 k_5}{k_{-3} k_{-5}} = \frac{[NS][MeOH_2^+][NF^-]}{[HA]}$$

and

$$k_{-5} = \frac{k_3}{r_3 K_E K_{HNF}} = 3.23 \times 10^{-3}.$$

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The kinetics of the addition of nitroform to β -nitrostyrene may now be discussed. If mechanism I operates for the decomposition reaction, it must, of course, also operate (in reverse) for the addition reaction. In the decomposition reactions, the concentrations of HNF and NF^- never reached any significant level (the reactions were run in quite dilute solutions) so that the terms involving k_4 and k_{-4} could always be neglected. In order to get the addition reaction to proceed to an appreciable extent, however, it is necessary to use relatively high concentrations of nitroform. While these higher concentrations make the solution sufficiently acidic to neglect the k_1 and k_{-1} terms, the k_4 and k_{-4} terms are considered in deriving a kinetic equation, as follows. From the steady-state approximation

$$[\text{A}^-] = \frac{k_3[\text{HA}] + k_4[\text{HA}][\text{NF}^-] + k_{-5}[\text{NS}][\text{NF}^-]}{k_{-3}[\text{MeOH}_2^+] + k_{-4}[\text{HNF}] + k_5} \quad (6)$$

therefore,

$$\frac{d[\text{HA}]}{dt} = \frac{(r_3 k_{-5} K_{\text{HNF}} [\text{NS}][\text{HNF}] - k_3[\text{HA}])(1 + [\text{NF}^-]k_4/k_3)}{r_3[\text{MeOH}_2^+] + r_4[\text{HNF}] + 1} \quad (7)$$

where $r_4 = k_{-4}/k_5$. Since the terms $[\text{NF}^-]k_4/k_3$, $r_3[\text{MeOH}_2^+]$, and $r_4[\text{HNF}]$ are not too large compared to one, the values of $[\text{NF}^-]$, $[\text{MeOH}_2^+]$, and $[\text{HNF}]$ ($[\text{HNF}]$ in the denominator but not in the numerator) may be taken as their average during a run. That is, in a given run, there is a constant, C,

$$C = \frac{1 + [\text{NF}^-]k_4/k_3}{r_3[\text{MeOH}_2^+] + r_4[\text{HNF}] + 1}$$

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Calculations show that C never varies from its average value by as much as 0.5 per cent in our runs. If $x = [HA]$ and $a = [HNF]_0$ (this is the concentration of HNF actually present in the undissociated form, not the formal concentration), then the approximation $[HNF] = (a - x)$ is never in error by as much as 0.2 per cent in our runs. With these approximations Eq. (7) becomes

$$\frac{dx}{dt} = C[A(a - x)(b - x) - k_3x] \quad (8)$$

where $A = r_3 k_{-5} K_N$ and $b = [NS]$. Integration of (8) gives

$$2.3 \log \frac{(D + B - 2Ax)(D - B)}{(D - B - 2Ax)(D + B)} = BCt \quad (9)$$

where $B = \sqrt{A^2(a - b)^2 + 2k_3A(a + b) + k_3^2}$ and $D = A(a + b) + k_3$. Since terms containing k_4 and k_{-4} are found only in the constant C, a plot of the logarithmic term in Eq. (9) versus time should give a straight line whether k_{-4} and k_4 are significant or not. From the values already determined for r_3 , k_3 , k_{-5} , and K_{HNF} and the data on an individual kinetic run on the addition reaction, such plots were made. (See Fig. 2.) The run described by solid circles was carried out at an ionic strength of only about 4×10^{-3} (due to the ionized nitroform) rather than 0.1 at which the values of r_3 , k_3 , k_{-5} , and K_{HNF} were determined. However, only reactions between ions should be greatly affected by the change in ionic strength. Only r_3 and K_{HNF} relate to reactions of this type, and since these values will change in opposite directions, the reaction rate should not change greatly with changing ionic strength. The points in Fig. 2 lie fairly near straight lines, in support of the proposed reaction mechanism. However, the straight lines shown were not chosen to fit

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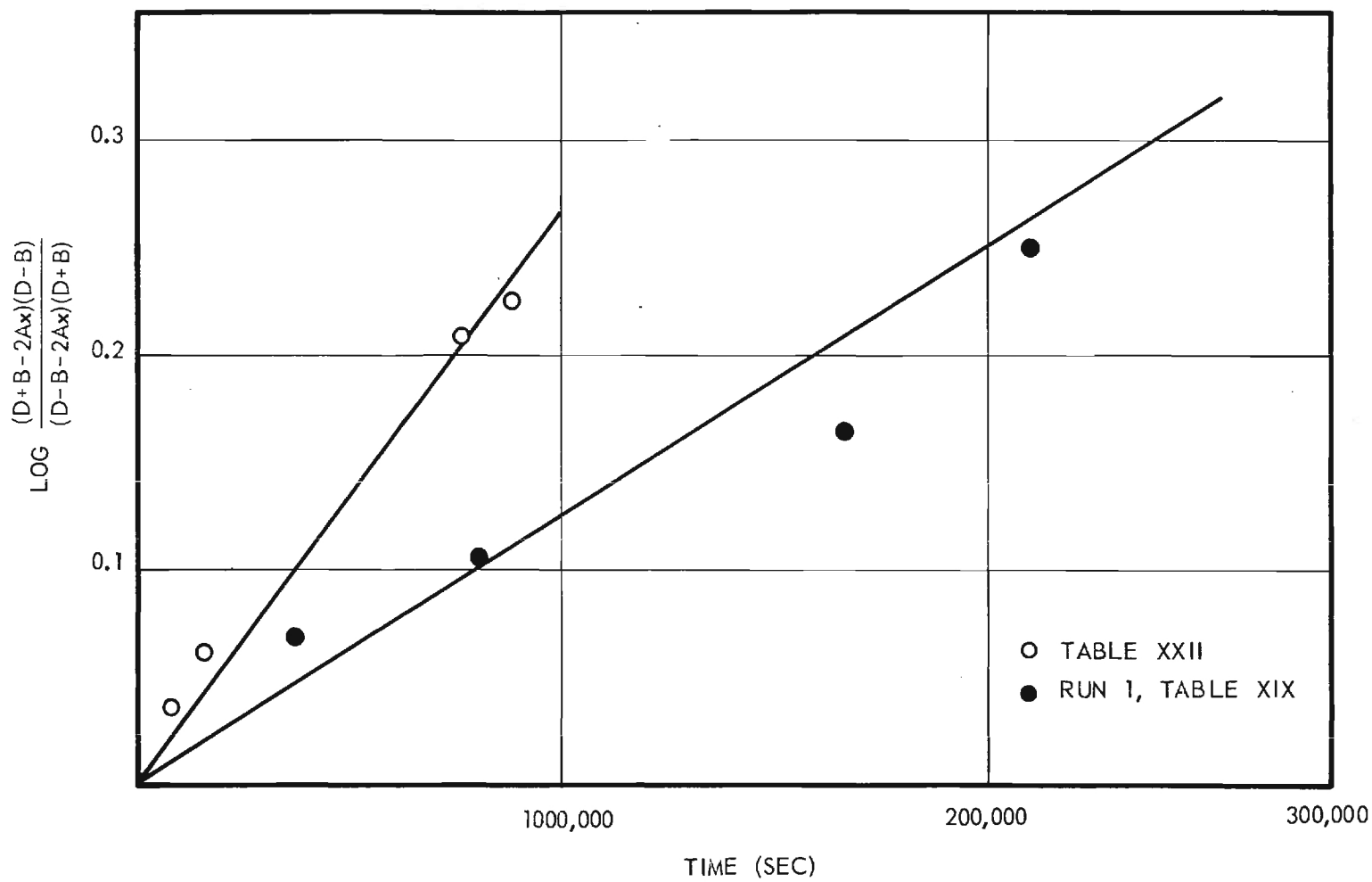


Figure 2. Kinetic Plot for Addition of Nitroform to β -Nitrostyrene.

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the data but were calculated from Eq. (9) on the assumption that the terms $[NF^-]$, k_4/k_3 and $r_4[HNF]$ were negligible. From the agreement observed, it is believed that most of the reaction goes through the path governed by k_3 and k_{-3} and not more than one fifth of it through the path governed by k_4 and k_{-4} .

From the ionization constant of HA, it is possible to calculate some other of the rate constants of mechanism I. The rapidity of the base-catalyzed decomposition prevents a determination of this ionization constant. However, it was estimated by the method of Branch and Calvin.¹⁰ Using their inductive constants and as a reference compound, nitroethane,¹¹ the pK of HA may be estimated as 3.4 in aqueous solution. There appears to be a correlation between the extent to which the ionization constants of acids decrease upon going from water to methanol and the degree of concentration of charge in the anion of the acid. The pK's of carboxylic acids increase by about 4.9 units on the average while those of nitroform and picric acid increase by about 3.0 units.¹² We estimated that aliphatic mononitrocompounds should have pK's about 4.5 units greater in methanol than in water. We believe that the resultant estimate of the pK of HA in methanol (7.9) is reliable within one or two units.

In order to get somewhat better values of k_1 and k_2 than those calculated on the assumption of the exclusive operation of mechanism Ib for the reaction in pyridine buffers, the correction necessary for catalysis by the base

- - - - -
10. G. E. K. Branch and M. Calvin, The Theory of Organic Chemistry. Prentice Hall, Inc., New York, 1941, Chap. VI.
 11. G. W. Wheland and J. Farr, J. Am. Chem. Soc. **65**, 1433 (1943) report pK = 8.6 in water.
 12. I. M. Kolthoff, J. J. Lingane, and W. D. Larson, J. Am. Chem. Soc. **60**, 2512 (1938); I. M. Kolthoff and L. S. Guss, ibid., **61**, 330 (1939); L. D. Goodhue and R. M. Hixon, ibid., **56**, 1329 (1934); Navord Report 1717.

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methanol in these runs has been estimated. Assuming that the activation energy for k_3 is near that for k_2 , $k_3^{25^\circ} = 0.04 \times 10^{-5}$ and $k_3^{38^\circ} = 0.10 \times 10^{-5}$. Values were then obtained of k_1 and k_2 listed in Table X from the equation

$$k = k_1[\text{MeO}^-] + k_2[\text{C}_5\text{H}_5\text{N}] + k_3$$

and the data in Table VII, by the method of least squares.

From the estimated value of pK_{HA} , values of k_{-1} , k_{-2} , k_{-3} , and k_5 at 40° were estimated, since our values of k_2 , k_3 , K_{HNF} , and K_{E} are fairly reliable at this temperature. These values (Table X) all contain the uncertainty in the estimate of K_{HA} , but this does not affect their relative magnitudes. In addition, k_1 , k_{-1} , and k_{-2} are affected by inaccuracies in K_{P} and K_{M} ; and k_1 and k_{-1} cannot be very accurate because such a small fraction of the reaction in pyridine buffers is due to methoxide catalysis. For these reasons, the fact the least squares treatments gave a $k_1^{38^\circ}$ smaller than $k_1^{25^\circ}$ cannot be considered significant evidence against the proposed reaction mechanism.

As an independent check on mechanism I, it is useful to consider whether the magnitudes of the k 's of Table X are reasonable in view of what is known about the kinetics of related reactions. The estimates of k_4 and k_{-4} are believed to be conservative. Therefore, it appears very probable that k_{-4} is smaller than k_{-2} , i.e., although nitroform is more than 100 times as strong an acid as the pyridinium ion, it donates protons to A^- more slowly. While this may at first seem surprising, it is actually in good agreement with the generalization that acidic protons attached to carbon are donated to bases more slowly than equally acidic protons attached to oxygen or nitrogen. Thus, the ammonium ion ($\text{pK}_{\text{a}} \sim 10$) undergoes deuterium exchange in acidic aqueous solution

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TABLE X

RATE CONSTANTS FOR MECHANISM I

Determined	Estimated from pK_{HA}
$k_1^{25^\circ} \sim 5.2 \times 10^4$	$k_{-1}^{40^\circ} \sim 2 \times 10^{-3}$
$k_1^{38^\circ} \sim 5.1 \times 10^4$	$k_{-2}^{40^\circ} \sim 25$
$k_2^{25^\circ} 8.097 \times 10^{-3}$	$k_{-3}^{40^\circ} \sim 10^2$
$k_2^{38^\circ} 2.189 \times 10^{-2}$	$k_{-5} \sim 10$
$k_3^{40^\circ} 1.194 \times 10^{-6}$	$k_{-4}^{40^\circ} < 1$
$k_4^{40^\circ} < 2 \times 10^{-5}$	
$k_{-5} 3.23 \times 10^{-3}$	

at 0° ¹³ millions of times more rapidly than nitroethane ($pK \sim 8.6$) would under these conditions.¹⁴ This relative inefficiency of nitroform at bringing about general acid-catalyzed reactions is a factor which may be of importance in a number of other cases.

The rate constants observed for the removal of a proton from nitroethane by various bases are: $k = 1.25 \times 10^{-7} \text{ sec}^{-1}$ for water,¹⁴ $k = 3.57 \times 10^{-4}$ liters

13. A. I. Brodskii and L. V. Sulima, Doklady Akad. Nauk S.S.S.R. 74, 513 (1950); Cf. Louis Kaplan and K. E. Wilzbach, J. Am. Chem. Soc. 76, 2593 (1954); and C. G. Swain, J. T. McKnight, M. M. Labes, and V. P. Kreiter, ibid., 76, 4243 (1954).
14. R. G. Pearson and R. L. Dillon, ibid., 72, 3574 (1950).

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mole⁻¹ sec⁻¹ for pyridine,¹⁵ $k = 8.04$ liters mole⁻¹ sec⁻¹ for hydroxide ions,¹⁶ all in aqueous solution at 34.85°.

Pearson and coworkers' observations that pyridine is 2860 times as reactive as water toward nitroethane compared to our finding that pyridine is 2220 times as reactive as methanol toward HA is reasonable (even though methanol is a weaker base than water¹⁷) since the stronger acid HA should be less selective in its reactions. The relative magnitude of k_1 and the absolute magnitudes of all of our k 's are believed to be in the general area expected, when the following factors are considered: Reactions like those governed by k_2 and k_3 , in which there is charge formation in the transition state, should proceed more rapidly in water than in methanol.¹⁸ Reactions like those of the hydroxide and methoxide ions with nitrocompounds should be faster in methanol.¹⁸ The methoxide ion is a slightly weaker base than the hydroxide ion,¹⁹ and nitroethane is a weaker acid than HA.

The open circles of Fig. 3 constitute a Brønsted-type plot of the rate constants for the donation of a proton from various acids to A⁻ versus the logarithms of the acidity constants of these acids.²⁰ The solid points are

15. R. G. Pearson and F. V. Williams, ibid., 75, 3073 (1953).
 16. Extrapolated from the data of R. P. Bell and J. C. Clunie, Proc. Roy. Soc. (London) A 212, 16 (1952).
 17. H. Goldschmidt and A. Thuesen, Z. physik. Chem. 81, 30 (1912); H. Goldschmidt and P. Dahll, ibid., 108, 121 (1924).
 18. This follows from the theory of solvent effects described by C. K. Ingold, Structure and Mechanism in Organic Chemistry. Cornell University Press, Ithaca, New York, 1953, Sec. 25. For specific supporting data, see ref. (15).
 19. J. Hine and M. Hine, J. Am. Chem. Soc. 74, 5266 (1952).
 20. In these Brønsted plots, the rate constants for water and methanol are treated as second order. E.g., k_{-1} was divided by 25, the concentration of methanol in pure methanol. A small correction for the change in solvent was necessary for the data of Pearson and Williams on substituted pyridines in 30 per cent ethanol. It was assumed that these reactions would go 37 per cent faster in pure water since the reaction of pyridine itself does.

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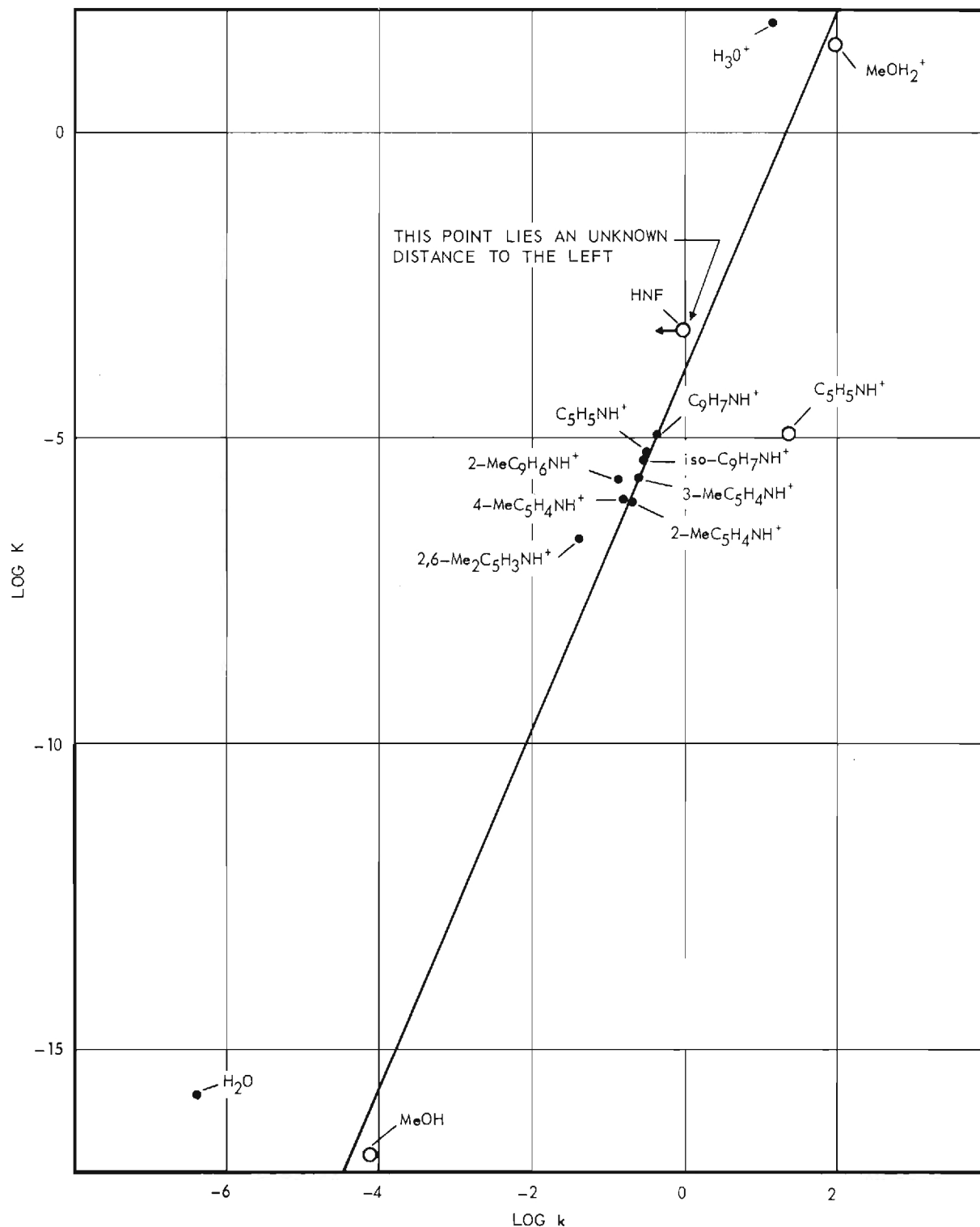


Figure 3. Bronsted-Type Plot of Logs of Acidity Constants of Acids Versus Logs of Rate Constants for Proton Donation to: ● the Nitroethane Anion; ○ A7.

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an analogous plot of rate constants for the reaction of the nitroethane anion with pyridinium ions, water, and the hydronium ion calculated from the data of Pearson and Williams.^{15,20}

Following these workers, we have drawn the best line through the points representing pyridinium ions and ignoring such di-orthosubstituted ions as 2,6-dimethylpyridinium and 2-methylquinolinium, which react slowly because of steric hindrance. The acids, water, and hydronium ion are too unreactive to fall on this line. According to Bell, hydronium ions and hydroxide ions are usually less reactive than would be expected from the Brønsted relation.²¹ Furthermore, if hydroxide ions are less reactive than expected from the Brønsted equation in any proton removal, then water must be a less reactive acid than expected in the reverse proton donation.²² In at least qualitative agreement with the data of Pearson and Williams, it is seen that if a line parallel to the line drawn through the nitroethane data was drawn through our points for the pyridinium ion, the acids methanol and methyl oxonium ion would be too unreactive to fall on it. Nitroform is found to be much less reactive than would be expected from its acidity. While the most reasonable explanation for this fact appears to be the general slowness of proton donations from carbon previously noted,¹³ the possibility of steric hindrance should not be overlooked. Whatever the explanation, this relative inability of nitroform to participate in general acid-catalyzed reactions is probably of importance in a number of instances, particularly in reactions in relatively

21. R. P. Bell, Acid-Base Catalysis. Oxford University Press, London, 1941, p. 93.

22. The generalization of Bell²¹ that water usually follows the Brønsted equation might well be reexamined on the basis of this "microscopic reversibility" argument.

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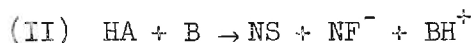
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nonpolar solvents where all acid-catalyzed reactions are general acid catalyzed. Even in the present case where methanol is the solvent, if nitroform had been reactive enough for its point in Fig. 3 to lie on a line joining the points for pyridinium and methyloxonium ions, the addition reaction described by the circles of Fig. 2 would have been more than four times as rapid as observed. The only rate constant determined with sufficient precision at two temperatures to warrant calculating activation parameters was k_2 , for which $\Delta H^\ddagger = 13.5$ kcal./mole and $\Delta S^\ddagger = -16.8$ e.u. was calculated from the absolute rate equation²³

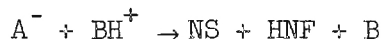
$$k = \frac{kT}{h} e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R}.$$

A comparison of these data with those of Pearson and Williams¹⁵ shows that the greater reactivity of HA than nitroethane toward pyridine is partly an entropy and partly an enthalpy effect.

There are other reaction mechanisms such as a concerted one-step E2 type²⁴ elimination reaction (II)



and



which explain the observed general base catalysis but not the data of Table

IX.

23. S. Glasstone, K. J. Laidler, and H. Eyring, The Theory of Rate Processes. McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p.14.

24. C. K. Ingold, op. cit., Sec. 30a.

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V. EXPERIMENTAL WORK

Purification of Methanol

Synthetic methanol was purified by refluxing over magnesium methoxide according to the procedure of Vogel.²⁵ After removing a forerun, the methanol collected boiled at 64.5°.

Preparation of β -Nitrostyrene

Five-tenths of a mole (30.5 g.) of nitromethane and 0.5 mole (53 g.) of benzaldehyde were condensed in aqueous methanol according to the procedures described in Organic Syntheses.²⁶ The crude material was recrystallized from absolute ethanol yielding 50 g. of yellow needles, m.p. 55° to 56° (uncorr). For spectral measurements, this material was recrystallized two more times from absolute ethanol. No change in the melting point was observed.

Preparation of Nitroform

Potassium nitroform was prepared by the reaction of an aqueous alkaline solution of glycerine with tetranitromethane according to the procedure of Macbeth and Orr.²⁷ The crude salt was filtered with suction, washed with absolute ethanol, and sucked dry. The salt was stored under n-hexane as it was found to decompose violently on storing dry.

The nitroform was liberated from the potassium salt in the following manner: About 100 grams of potassium nitroform was placed in a 500-cc 3-necked flask with standard taper joints. The flask was equipped with a gas inlet tube, tru-bore stirrer, and drying tube. To the potassium salt was added 300 cc

25. A. I. Vogel, Textbook of Practical Organic Chemistry, Second Edition. Longmans Green & Co., London, p. 168.

26. Organic Syntheses, Coll. Vol. I. John Wiley, New York, p. 413.

27. A. K. Macbeth and W. B. Orr, J. Chem. Soc., 534 (1932).

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of n-hexane, and dry hydrogen chloride was slowly passed into the well-stirred mixture. When the color of the suspended salt changed from bright yellow to a very pale yellow, the gas stream was stopped and a slow stream of dry nitrogen was passed through the mixture to remove the excess hydrogen chloride. The reaction mixture was then filtered with suction through a sintered glass funnel, and the filtrate was placed in a dry-ice acetone bath after first protecting it against moisture with a drying tube. A white solid crystallized out. This was rapidly collected on a fritted glass funnel and stored in a glass stoppered flask. This material melted at room temperature to yield a liquid containing two layers (n-hexane and nitroform). To purify it further, it was distilled through a 9-cm Vigreux column into glass ampoules under reduced pressure, b.p. 48° to 49° (15 mm). The distillate was a clear liquid, with a slight yellow cast, which crystallized on standing at room temperature. Distilled nitroform was used for all spectral measurements. Samples which had a yellow color were redistilled before being used. In order to weigh out a sample, the nitroform was melted by placing the stoppered ampoule in a water bath at 40° and then withdrawing some of the liquefied nitroform with a hypodermic syringe. The weight of the sample taken was obtained by difference.

Trichloroacetic Acid

Trichloroacetic acid was purified by distillation of the reagent grade acid under reduced pressure. The distillate crystallized rapidly on standing to yield a solid, m.p. 57° to 58° (uncorr).

Pyridine

Pyridine was purified by the distillation of reagent grade pyridine through a 3-foot by 1/2-inch column packed with 1/8-inch glass helices after

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first refluxing it over potassium hydroxide pellets. The material boiling at 114.5° to 115° (ratio 7:1) was collected and used in this work.

Anhydrous Sodium Perchlorate

Anhydrous sodium perchlorate was prepared by recrystallization of reagent grade sodium perchlorate monohydrate from water. Cornec and Dickely²⁸ found the transition temperature for sodium perchlorate monohydrate to anhydrous sodium perchlorate to be 53°. The solubility of the monohydrate in water was about twice that of anhydrous sodium perchlorate between 50° and 100°. ²⁸ Therefore, it should be possible to prepare the anhydrous salt by crystallization from a saturated solution at a temperature above 53°. The following procedure was employed: An almost saturated solution of the monohydrate was prepared at 95° to 100° and was allowed to cool slowly by gradually reducing the hot-plate current. Crystallization commenced when the solution had cooled to 85°. After cooling to 75°, the solution was rapidly suction filtered, the crystals sucked dry and placed in a vacuum desiccator over phosphorus pentoxide at 8 to 10 mm. After drying for 8 to 10 hours, the product was ground to a powder and returned to the desiccator for 12 hours in vacuo. The anhydrous salt was stored in a desiccator over phosphorus pentoxide.

Titration of the anhydrous salt with Karl Fischer's Reagent to determine the percentage of water gave the following results.

Standardization of Karl Fischer's Reagent

Fifteen cubic centimeters of anhydrous methanol (equivalent to 0.26 ml of Karl Fischer's Reagent) were delivered into a 50-cc volumetric flask. A weighed quantity of water was then added, and the resulting solution was

28. E. Cornec and J. Dickely, Bull. Soc. Chim. de France 41, Series 4, 1017 (1923).

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titrated with Karl Fischer's Reagent until a permanent iodine color remained.

The following results were obtained:

48.906 mg water required	9.26 ml K. F. R.	5.281 mg H ₂ O/ml K. F. R.
52.894 mg water required	9.96 ml K. F. R.	<u>5.316</u> mg H ₂ O/ml K. F. R.
	Average titre	5.299 ± 0.018 (< 1%)

Determination of Water in Sodium Perchlorate

A weighed sample of anhydrous sodium perchlorate was added to 15 cc of methanol (equivalent to 0.26 ml of Karl Fischer's Reagent), and the resulting solution was titrated with Karl Fischer's Reagent. A burette was filled with the reagent which was standardized and then used to titrate the sodium perchlorate samples in methanol. In this manner, the absorption of water by the reagent during a given series of titrations was held to a minimum. The burette was protected with a drying tube containing indicating drierite.

The following results were obtained:

841.8 mg NaClO ₄ required	0.07 ml K. F. R.	Percentage of H ₂ O = 0.044
1013.2 mg NaClO ₄ required	0.09 ml K. F. R.	Percentage of H ₂ O = 0.047

The neutrality of the salt was checked in the following manner: Twenty-cubic-centimeter aliquots of methanol and 1 M sodium perchlorate in methanol were titrated with 0.01039 N NaOH using 0.3 per cent bromthymol blue in ethanol as the indicator.

For methanol--ml 0.01039 N NaOH, 0.39, 0.35

For 1 M NaClO₄--ml 0.01039 N NaOH, 0.31, 0.33

The foregoing procedure was repeated using 0.3 per cent bromphenol blue in ethanol as the indicator and titrating with 0.010 N MeOH₂⁺Cl⁻ to test for weak bases in the sodium perchlorate solution.

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CONFIDENTIALFor methanol--ml 0.010 N $\text{MeOH}_2^+\text{Cl}^-$, 0.30, 0.35For 1 M NaClO_4 --ml 0.010 N $\text{MeOH}_2^+\text{Cl}^-$, 0.31, 0.40

Spectral data on β -nitrostyrene and the nitroform anion are tabulated in Table XI and plotted in Figs. 4 through 6. Spectral data on the adduct are given in Table XII.

TABLE XI

SPECTRAL DATA ON β -NITROSTYRENE AND THE NITROFORM ANION

λ (m μ)	Slit (mm)	β -Nitrostyrene		Nitroform Anion	
		Optical Density	ϵ	Optical Density	ϵ
250	1.175	0.130	2851	0.394	4452
260	0.92	0.162	3553	0.277	3130
270	0.82	0.253	5548	0.185	2090
280	0.76	0.396	8684	0.147	1661
290	0.72	0.554	12149	0.152	1718
300	0.68	0.682	14956	0.175	1977
310	0.64	0.726	16921	0.243	2746
320	0.60	0.648	14211	0.412	4655
330	0.56	0.472	10351	0.733	8282
340	0.52	0.276	6053	1.131	12780
350	0.50	0.132	2895	1.319	14904
360	0.50	0.062	1359	1.102	12452
370	0.50	0.031	680	0.668	7548
380	0.50	0.016	351	0.376	4249
390	0.50	0.008	175	0.233	2633
400	0.50	0.004	88	0.155	1813
410	0.50	0.001	22	0.111	1254

$$\text{Conc}_{\text{NS}} = 4.56 \times 10^{-5} \text{ m/l. } \text{Conc}_{\text{NF}} = 8.85 \times 10^{-5} \text{ m/l.}$$

$$\text{Conc}_{\text{OMe}} = 0.1860 \text{ m/l.}$$

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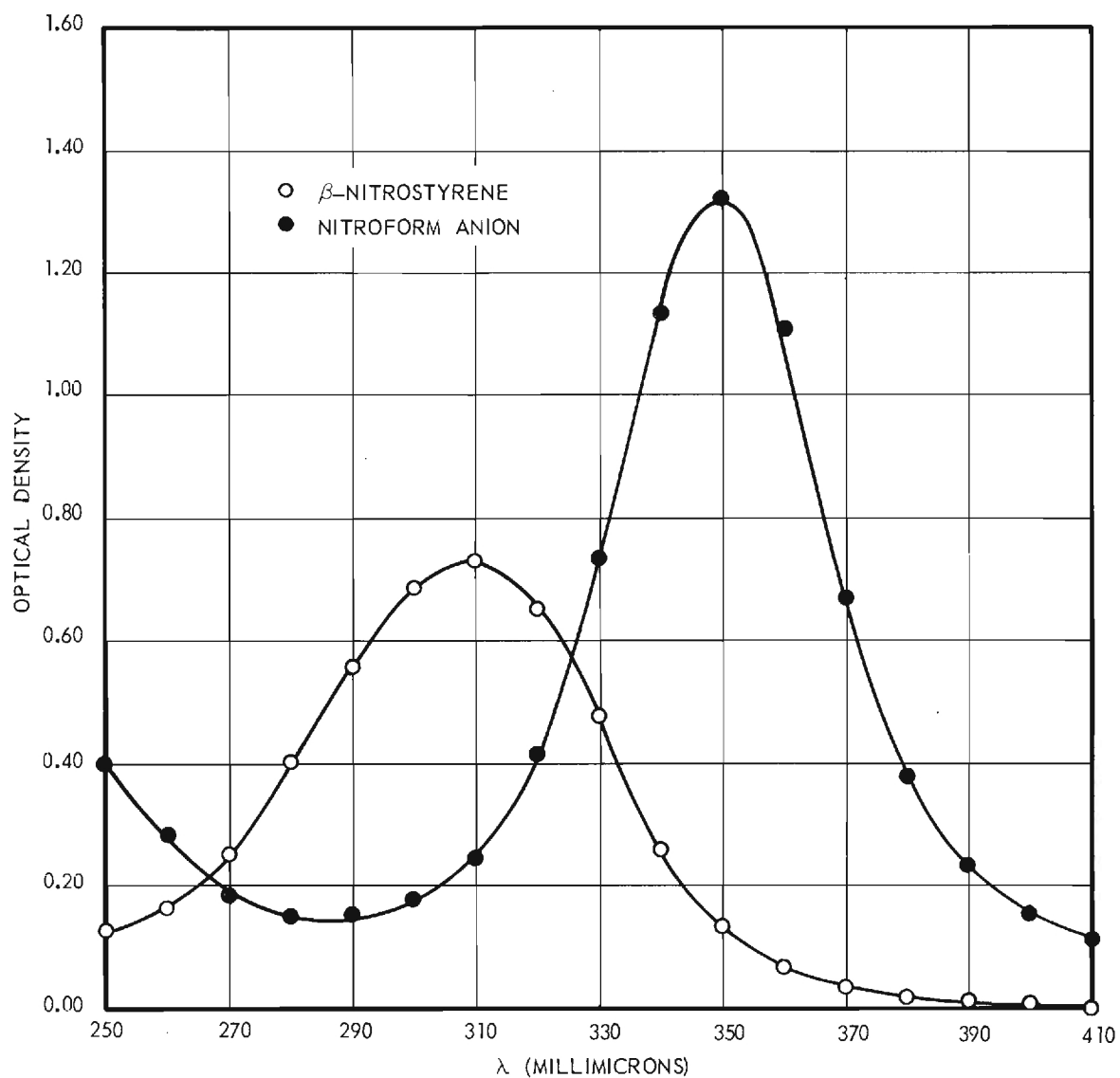


Figure 4. Spectra of β -Nitrostyrene and the Nitroform Anion in Methanol.

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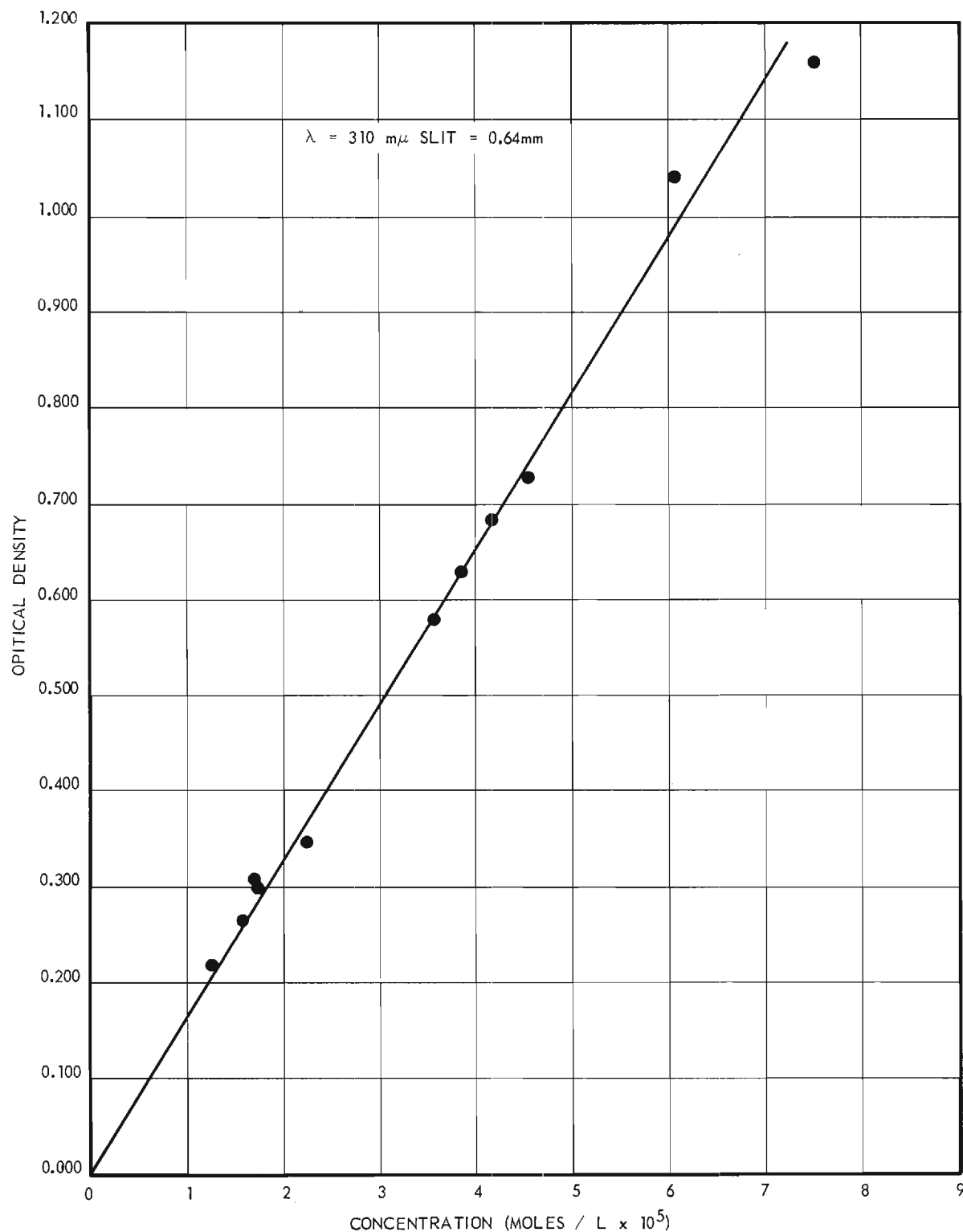


Figure 5. Plot of Optical Density Versus Concentration of β -Nitrostyrene in Methanol.

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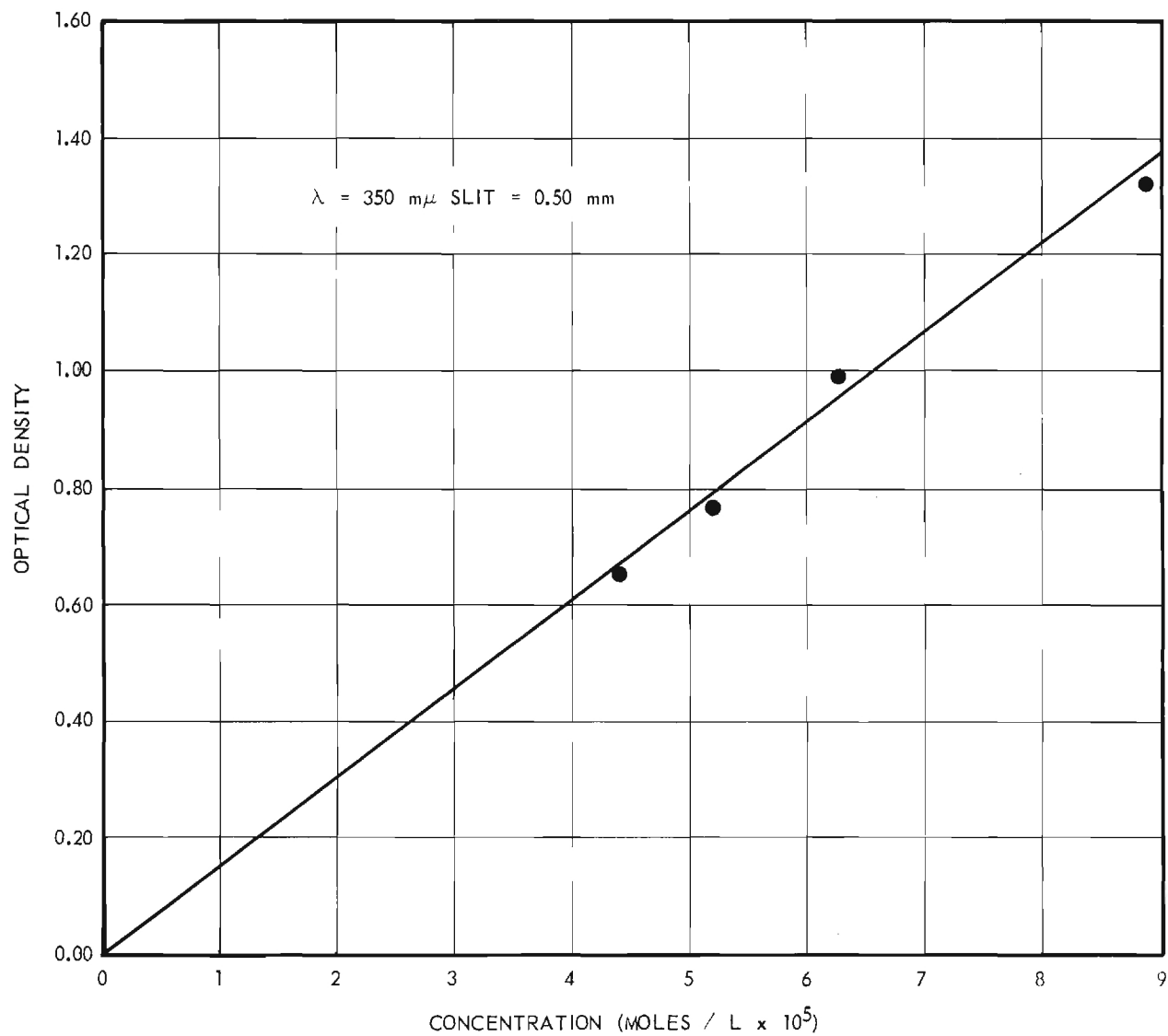
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Figure 6. Plot of Optical Density Versus Concentration of Nitroform Anion in Methanol.

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TABLE XII

SPECTRAL DATA ON HA AND NITROFORM

λ (m μ)	Slit (mm)	Adduct (n-Hexane) [†]	Nitroform ^{††} (methanol)
		Optical Density	Optical Density
270	0.82	0.047	0.078
280	0.76	0.027	0.056
290	0.72	0.016	0.042
300	0.68	0.006	0.031
310	0.64	0	0.025
320	0.60	0.002	0.021
330	0.56	0	0.019
340	0.52	0	0.022
350	0.50	0	0.022
360	0.50	0	0.020
370	0.50	0	0.012
380	0.50	0	0.009
390	0.50	0	0.005
400	0.50	0	0.005

[†]Concentration = 9×10^{-5} moles/l.^{††}Concentration Nitroform = 5.97×10^{-4} m/l.Concentration MeOH₂⁺Cl⁻ = 0.9699 m/l.Dissociation of the Adduct in Methanol

Three and three-tenths milligrams (1.099×10^{-5} moles) of the adduct was weighed into a 100-cc low actinic glass volumetric flask and rapidly diluted to the mark with absolute methanol that had been thermostatted at 25°. After shaking thoroughly, a sample was transferred to a 1.00-cm silica cell, and measurements of the optical density were made at various time intervals. A thermostatted Beckman spectrophotometer (Model DU) was used at a wavelength

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of 310 mμ (slit = 0.64 mm). The time interval from the start of the addition of methanol to the sample till the first reading was taken was 1.5 minutes. The measured optical densities together with the time intervals are reproduced in Table III (page 8).

Dissociation of the Adduct in Methanolic Hydrogen Chloride

A solution of methanolic hydrogen chloride was prepared by passing anhydrous hydrogen chloride into absolute methanol in a two-necked standard taper flask protected against moisture with a drying tube. This stock solution was diluted until titration of an aliquot showed it to be 0.047 molar.

Fourteen and seven-tenths milligrams (4.90×10^{-6} moles) of the adduct was weighed (by transfer from a slightly larger weighed sample) into a 100-cc low actinic glass volumetric flask. The sample was diluted to volume with 0.047 molar methanolic hydrogen chloride and thoroughly mixed. A sample was taken, and the optical density was measured at 310 mμ (slit = 0.64). After 2.5 minutes, the time required for mixing, the optical density was 0.002. There was essentially no change in the optical density, within ± 0.002 units, during the next 30 minutes. Four days after this solution was prepared, it was found to have an optical density of 0.009.

A similar study in which 1.67×10^{-5} moles of the adduct were diluted to 100 cc with 3.81×10^{-3} molar $\text{MeOH}_2^+\text{Cl}^-$ yielded similar results. The optical density of this solution remained constant over a period of 4 hours, after which time the measurements were discontinued.

When the dissociation of 1.15×10^{-6} moles of the adduct in 100 cc of 3.81×10^{-5} molar hydrogen chloride was followed spectrophotometrically at 25°, it was found to dissociate slightly after a period of 19 hours. The following data were obtained:

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<u>Time</u> (min)	<u>O.D.</u>	<u>Time</u> (min)	<u>O.D.</u>
2.0	0.000	100.0	0.000
15.0	0.000	520.0	0.032
30.0	0.000	1135.0	0.052

$\lambda = 310$, slit 0.64 mm

If all the nitroform produced is present in the undissociated form, then about 30 per cent of the HA has dissociated.

Dissociation of the Adduct in Trichloroacetic Acid-Trichloroacetate Buffer

Preparation of Buffers

Two samples of redistilled, Merck reagent grade trichloroacetic acid were weighed into 100-cc volumetric flasks. Approximately 25 cc of absolute methanol was added and the samples dissolved. The appropriate amount of standard sodium methoxide solution was added from a burette, and the solutions were diluted to volume.

<u>Buffer A</u>	<u>Buffer B</u>
0.8905 g. CCl_3COOH	9.2250 g. CCl_3COOH
25.67 cc 0.1062 M NaOMe	28.64 cc 0.9846 M NaOMe
$\text{Conc}_{\text{CCl}_3\text{COOH}} = 2.725 \times 10^{-2} \text{ M}$	$\text{Conc}_{\text{CCl}_3\text{COOH}} = 2.82 \times 10^{-1} \text{ M}$
$\text{Conc}_{\text{CCl}_3\text{COO}^-} = 2.725 \times 10^{-2} \text{ M}$	$\text{Conc}_{\text{CCl}_3\text{COO}^-} = 2.82 \times 10^{-1} \text{ M}$

Determination of the Rate of Dissociation

Two samples of the adduct were weighed out into 50-cc low actinic glass flasks and diluted to volume with the appropriate buffer which had previously been

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thermostatted at 25°. Samples were transferred to matched silica spectrophotometer cells, and the optical density was measured at various times at a wavelength of 310 mμ (slit = 0.64 mm). No correction was applied for the absorption of nitroform anion since this was a qualitative run. The results obtained are listed in Table XIII.

TABLE XIII

DISSOCIATION OF HA IN $\text{CCl}_3\text{COOH}-\text{CCl}_3\text{COONa}$ BUFFER

Run A		Run B	
wt. of sample = 0.003360 g.		wt. of sample = 0.003962 g.	
dilute to 50 cc with Buffer A		dilute to 50 cc with Buffer B	
Conc _{Adduct} = 2.24×10^{-4} m/l.		Conc _{Adduct} = 2.64×10^{-4} m/l.	
Time	O.D.	Time	O.D.
(min)		(min)	
3.0	0.076	3.0	0.107
5.0	0.076	5.0	0.120
13.0	0.076	7.0	0.131
28.0	0.091	12.0	0.166
43.0	0.102	17.0	0.199
358.0	0.305	27.0	0.268
388.0	0.328	37.0	0.332
418.0	0.347	47.0	0.398
598.0	0.462	57.0	0.457

Determination of the Spectrum of Semicarbazide and Semicarbazide Hydrochloride

Semicarbazide hydrochloride (Eastman white label) was recrystallized from aqueous alcohol. The product collected on a fritted funnel, washed once with absolute MeOH, once with ether, and sucked dry; m.p. 172° dec. (uncorr).

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The spectra of semicarbazide and semicarbazidium ion were determined as follows:

A 0.365900-gram sample (3.28×10^{-3} moles) of semicarbazide hydrochloride was weighed out and diluted to exactly 250 cc with absolute methanol. Two 25-cc aliquots of this solution were taken. The first was diluted to exactly 50 cc with absolute methanol, and the second aliquot was diluted to exactly 50 cc with 0.06203 molar sodium methoxide in methanol. The solutions were thoroughly mixed, samples withdrawn, placed in 1.00-cm silica cells, and the optical density was determined from 300 to 390 m μ . The results are tabulated below:

	Conc _B = 6.55×10^{-3} m/l.					Conc _{BH⁺} = 6.55×10^{-3} m/l.				
	Conc _{OMe⁻} = 0.03102									
λ	300	310	320	330	340	350	360	370	380	390
Slit	0.68	0.64	0.60	0.56	0.52	0.50	0.50	0.50	0.50	0.50
O.D. _B	0.000	0.000	0.001	0.001	0.001	0.000	0.000	0.000	0.001	0.001
O.D. _{BH⁺}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Methanol was used in the reference cell.

Determination of the Stability of β -Nitrostyrene in Semicarbazide Buffer

Two 10-cc aliquots of a 1.82×10^{-4} molar β -nitrostyrene solution were placed in 100-cc low actinic glass volumetric flasks. To the first was added, by pipette, 25 cc of 0.1125 M semicarbazide hydrochloride and 14.18 ml of 0.09917 M sodium methoxide in methanol. It was then diluted to 100 cc with absolute methanol. The second aliquot of β -nitrostyrene was diluted to 100 cc with absolute methanol. The solutions were thoroughly mixed, samples withdrawn,

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and the change in optical density with time measured for each sample at 310 mμ (slit = 0.64 mm). Methanol was used in the reference cell. The following results were obtained.

	<u>Solution A</u>	<u>Solution B</u>
Conc _{NS}	1.82×10^{-5} m/l.	1.82×10^{-5} m/l.
Conc _{Semicarbazide HCl} (formal)	2.81×10^{-2} m/l.
Conc _{OMe} - (formal)	1.41×10^{-2} m/l.
Conc _{Semicarbazide}	1.41×10^{-2} m/l.
Conc _{Semicarbazide HCl}	1.40×10^{-2} m/l.
<u>Time</u> (min)	<u>Optical Density</u>	<u>Optical Density</u>
40	0.222	0.308
145	0.147	0.306
1375	0.063	0.284

Determination of the Spectrum of p-Chloroaniline and p-Chloroanilinium Chloride

A 0.054683-gram (4.29×10^{-4} moles) sample of p-chloroaniline, freshly distilled (in vacuo) Eastman white label, was weighed into a 100-cc volumetric flask and diluted to the mark with absolute methanol. Three 5-cc aliquots were withdrawn and placed in 50-cc volumetric flasks. The first was diluted to the mark with absolute methanol. The second was diluted to volume with 0.01062 molar sodium methoxide in methanol. The third aliquot was made up to volume with 0.5547 molar methanolic hydrogen chloride. The solutions were mixed, samples withdrawn and placed in 1.00-cm silica cells, and the spectra were determined in the usual manner. Methanol was used in the first reference cell, 0.09558 molar sodium methoxide was used in the second reference cell, and

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0.4992 molar $\text{MeOH}_2^+\text{Cl}^-$ was used in the third reference cell. The spectral data are shown in Table XIV and Fig. 7.

TABLE XIV

SPECTRAL DATA ON p-CHLOROANILINE

λ (m μ)	Slit (mm)	<u>p-Chloroaniline^a</u> Optical Density	<u>p-Chloroaniline^b</u> Optical Density	<u>p-Chloroanilinium^c</u> Optical Density
250	1.175	---	---	0.068
260	0.92	1.481	1.507	0.096
270	0.82	0.291	0.288	0.071
280	0.76	0.372	0.367	0.011
290	0.72	0.588	0.587	0.004
298	0.70	0.658	0.668	0.002
300	0.68	0.471	0.660	0.001
310	0.64	0.194	0.480	0.001
320	0.60	0.027	0.199	0
330	0.56	0	0.031	0
340	0.52	0	0.002	0
350	0.50	0	0.001	0
360	0.50	0	0.001	0
370	0.50	0	0.001	0
380	0.50	0	0.001	0
390	0.50	0	0.001	0
400	0.50	0	0	0
410	0.50	0	0.001	0

a. p-Chloroaniline, 4.29×10^{-4} M in methanol.

b. p-Chloroaniline, 4.29×10^{-4} in 0.1062 M OMe^- , $\text{Conc}_{\text{OMe}^-} = 0.09558$ M.

c. p-Chloroaniline, 4.29×10^{-4} in 0.5547 M $\text{MeOH}_2^+\text{Cl}^-$, $\text{Conc}_{\text{MeOH}_2^+\text{Cl}^-} = 0.4992$ M.

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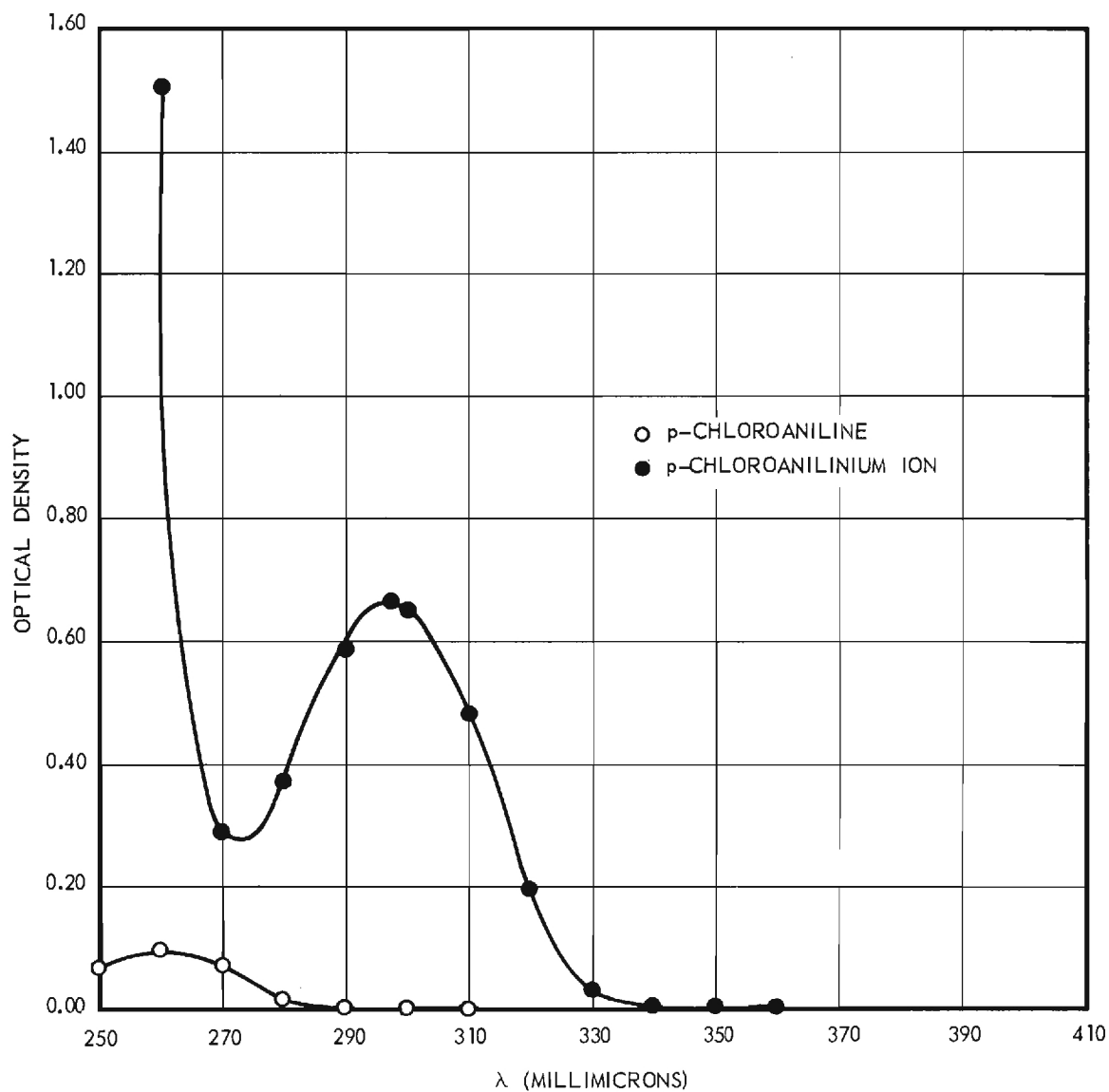
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Figure 7. Spectra of p-Chloroaniline and p-Chloroanilinium Ion.

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~~CONFIDENTIAL~~~~CONFIDENTIAL~~Determination of the Spectra and the Stability of Solutions of Pyridine in Methanol, Methoxide Ion (Methanol), and Hydrogen Chloride (in Methanol)

The following solutions were prepared in methanol, and their spectra were determined in the usual manner:

Pyridinium Chloride-- 2.968×10^{-2} molar pyridine and 0.0768 molar $\text{MeOH}_2^+\text{Cl}^-$

Pyridine in OMe⁻-- 6.145×10^{-2} molar pyridine and 0.0775 molar OMe^-

Pyridine in MeOH-- 6.145×10^{-2} molar pyridine

Between 310 and 410 mμ, each of these solutions was found to be optically transparent (had an optical density of 0.002 or less).

On standing for 48 hours, the optical densities of these solutions did not change by more than 0.003 unit. Therefore, these solutions were considered to be stable.

Determination of the Degree of Ionization of Nitroform in Various Pyridine BuffersPreparation of the Buffers

A 0.4856-gram (6.139×10^{-3} moles) sample of pyridine was weighed into a 100-cc volumetric flask and was diluted to volume with methanol. Three 15-cc aliquots of this stock solution were delivered into 100-cc volumetric flasks, and the following volumes of 0.1024 molar $\text{MeOH}_2^+\text{Cl}^-$ were added from a microburette after first diluting the aliquot with about 25 cc of methanol. (To the first, 4.500 cc; the second, 6.000 cc; and the third, 6.744 cc.) The solutions were then diluted to volume giving the following concentrations.

	Buffer No. 1	Buffer No. 2	Buffer No. 3
Pyridine	4.601×10^{-3} m/l.	3.055×10^{-3} m/l.	2.123×10^{-3} m/l.
Pyridinium	4.608×10^{-3} m/l.	6.144×10^{-3} m/l.	6.906×10^{-3} m/l.
Ratio Py/PyH ⁺	1	0.5	0.33

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~~CONFIDENTIAL~~~~CONFIDENTIAL~~Optical Density of Nitroform in Above-Mentioned Buffers

A 0.059000-gram sample (3.906×10^{-4} moles) of nitroform was weighed out and was diluted to exactly 200 cc with absolute methanol. A 10-cc aliquot of this solution was diluted to exactly 100 cc with methanol to yield a 1.953×10^{-4} molar solution of nitroform in methanol. Four 8-cc aliquots of this solution were placed in 50-cc volumetric flasks, and then 5 cc of 1 molar sodium perchlorate solution in absolute methanol was added to each flask. Three of these samples were diluted to volume with the buffers described in the previous section. The fourth sample was diluted to volume with methanol after first adding 5 cc of 7.69×10^{-2} molar sodium methoxide in methanol. This last solution acted as a control. The data obtained are given in Table XV.

TABLE XV

DEGREE OF DISSOCIATION OF NITROFORM IN PYRIDINE BUFFERS

	<u>Buffer No. 1</u>	<u>Buffer No. 2</u>	<u>Buffer No. 3</u>	<u>Control</u>
$10^3 [\text{C}_5\text{H}_5\text{N}]$	3.404	2.268	1.704	---
$10^3 [\text{C}_5\text{H}_5\text{NH}^+]$	3.410	4.546	5.110	---
$10^5 [\text{HNF}]_{\text{formal}}$	3.125	3.125	3.125	3.125
$[\text{NaCOO}_4]$	0.1	0.1	0.1	0.1
Buffer Ratio	1	0.5	0.33	a
λ_{350}^b 0 hrs	0.468	0.458	0.455	0.468
24 hrs	0.468	0.463	0.457	
λ_{370}^b 0 hrs	0.237	0.234	0.230	0.237
24 hrs	0.237	0.236	0.231	

a. $[\text{OMe}^-] = 7.69 \times 10^{-2}$.

b. Slit 0.5 mm.

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~~CONFIDENTIAL~~~~CONFIDENTIAL~~Determination of the Ionization Constant of Nitroform

Two stock solutions of nitroform about 10^{-3} M were prepared by weighing out the appropriate amount of freshly distilled nitroform and by diluting to volume with absolute methanol. Five-milliliter aliquots of one of these stock solutions were transferred to each of three volumetric flasks. To the first two flasks was added an accurately measured amount of 0.02 or 0.005 M methanolic hydrogen chloride (enough to allow from 20 to 60 per cent of the nitroform to be present as nitroform anion). To the resulting mixture was added enough 1 M sodium perchlorate in methanol to adjust the ionic strength to the desired value. The solutions were then diluted to volume with methanol. The third aliquot was diluted to volume to 0.1 M sodium methoxide in methanol. The optical densities of the three solutions were determined at 350 mμ.

From the optical density of the nitroform-sodium methoxide solution, the formal concentration of nitroform was calculated using the extinction coefficient of nitroform anion at 350 mμ; $\epsilon_{NF^-} = 14847$. The optical densities of the nitroform-methanolic hydrogen chloride solutions gave the amount of nitroform anion present in these mixtures. Substituting these values and the concentration of methanolic hydrogen chloride added initially into the following expression gave the values listed in Table VI (page 15).

$$K_{HNF} = \frac{[H^+][NF^-]}{[HNF]_{\text{formal}} - [NF^-]}$$

Fig. 8 is a plot of $\log K_{HNF}$ versus the square root of the ionic strength. The data of Navord Report 1717 are included in this plot.

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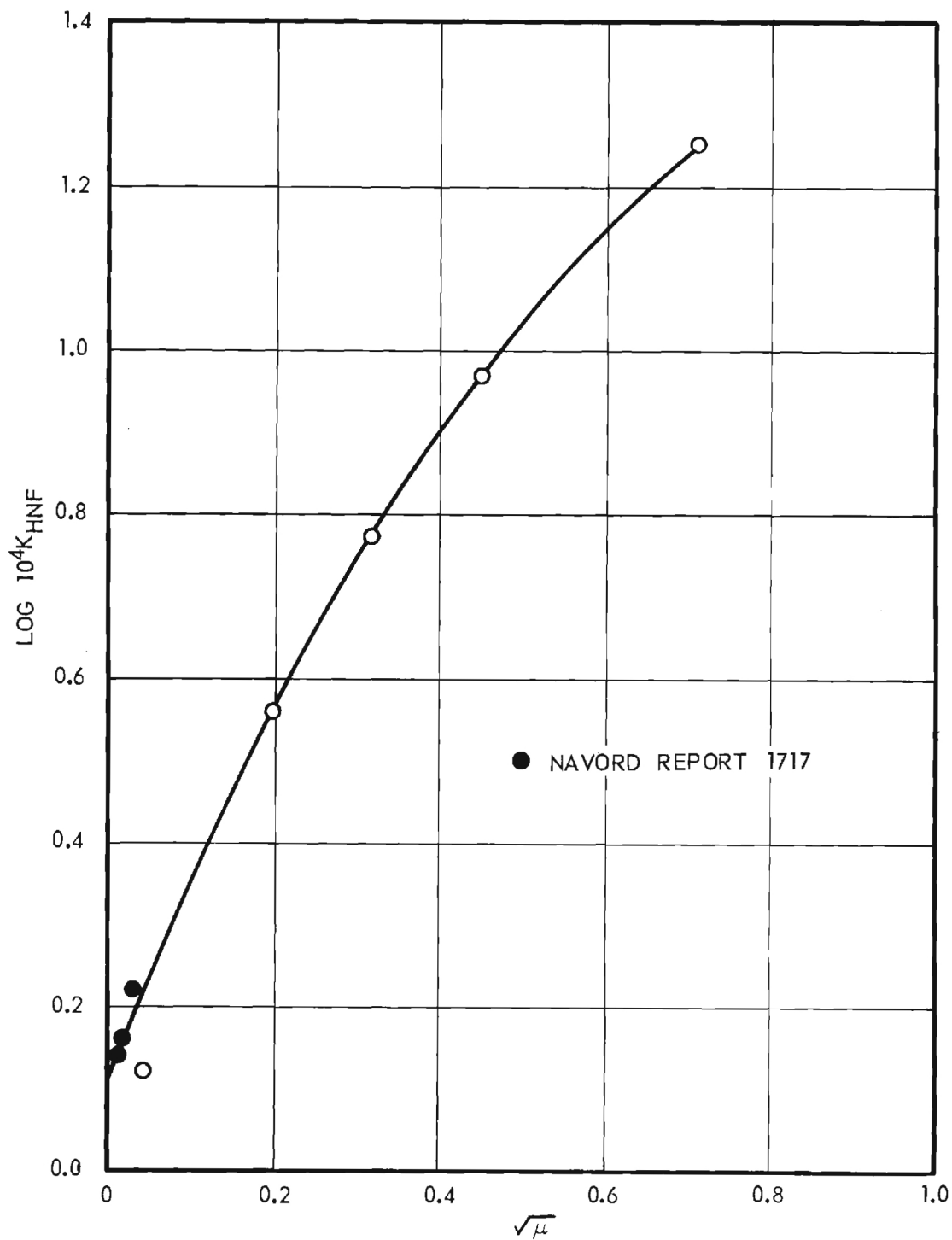


Figure 8. Plot of $\text{Log } K_{\text{HNF}}$ Versus $\sqrt{\mu}$ in Methanol at 25° .

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~~CONFIDENTIAL~~~~CONFIDENTIAL~~Rate of Dissociation of the Adduct in Pyridine-Pyridinium Chloride Buffers

A 0.002080-gram (6.92×10^{-6} moles) sample of the adduct was weighed into a 50-cc low actinic glass volumetric flask. To this was added 25 cc of a pyridine-pyridinium buffer that had been thermostatted at 25° C. Then 5 cc of 1 M sodium perchlorate in methanol was added, and the mixture was diluted to volume with the buffer solution. The solution was thoroughly shaken, a sample was withdrawn for optical-density measurements, and the remainder was placed in the thermostat at 25° C. Methanol was used in the reference cell, and the cell compartment was also thermostatted at 25° C. Four minutes elapsed from the time the buffer was first added till the time the first reading was taken. All optical-density measurements were taken at 370 mμ (slit = 0.5 mm). The following concentrations of reactants were present in solution:

$$\text{Conc}_{\text{Adduct}} = 1.385 \times 10^{-4} \text{ M}$$

$$\text{Conc}_{\text{Pyridine}} = 4.141 \times 10^{-3} \text{ M}$$

$$\text{Conc}_{\text{Pyridinium}^+ \text{Cl}^-} = 4.147 \times 10^{-3} \text{ M}$$

$$\text{Conc}_{\text{NaClO}_4} = 0.1 \text{ M}$$

$$\text{Buffer ratio} = 1$$

The data obtained are summarized in Table XVI and Fig. 9.

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TABLE XVI

DECOMPOSITION OF HA IN PYRIDINE BUFFERS AT 25°

$10^{-1} t \text{ sec}^a$	Optical Density	$\log \frac{D_{\infty}}{D_{\infty} - D}$	$10^5 k \text{ sec}^{-1}^a$
24	0.013	0.00498	(4.78)
396	0.151	0.0614	3.57
456	0.173	0.0715	3.62
1236	0.411	0.1931	3.60
1356	0.441	0.2111	3.58
1476	0.468	0.2281	3.57
1596	0.496	0.2465	3.55
1656	0.510	0.2560	<u>3.57</u>
			Avg. 3.58 ±0.02

a. A value for t_{240} is given and then only values from 10 to 75 per cent reacted. This is the region from which the average value of k was calculated.
 $D_{\infty} = 1.150$, $D_{\infty} \text{ calcd} = 1.140$.

Rate of Dissociation in Pyridine-Pyridinium Buffer at Constant Buffer Ratio
but Varying Buffer Concentration

The solutions were made up as in the previous run with the following concentrations being present:

	Run 2	Run 3
Adduct	$1.241 \times 10^{-4} \text{ m/l.}$	$1.554 \times 10^{-4} \text{ m/l.}$
Pyridine	$2.455 \times 10^{-3} \text{ m/l.}$	$4.910 \times 10^{-3} \text{ m/l.}$
Pyridinium	$1.228 \times 10^{-3} \text{ m/l.}$	$2.456 \times 10^{-3} \text{ m/l.}$
Sodium Perchlorate	0.1 M	0.1 M
Buffer Ratio	2.00	2.00

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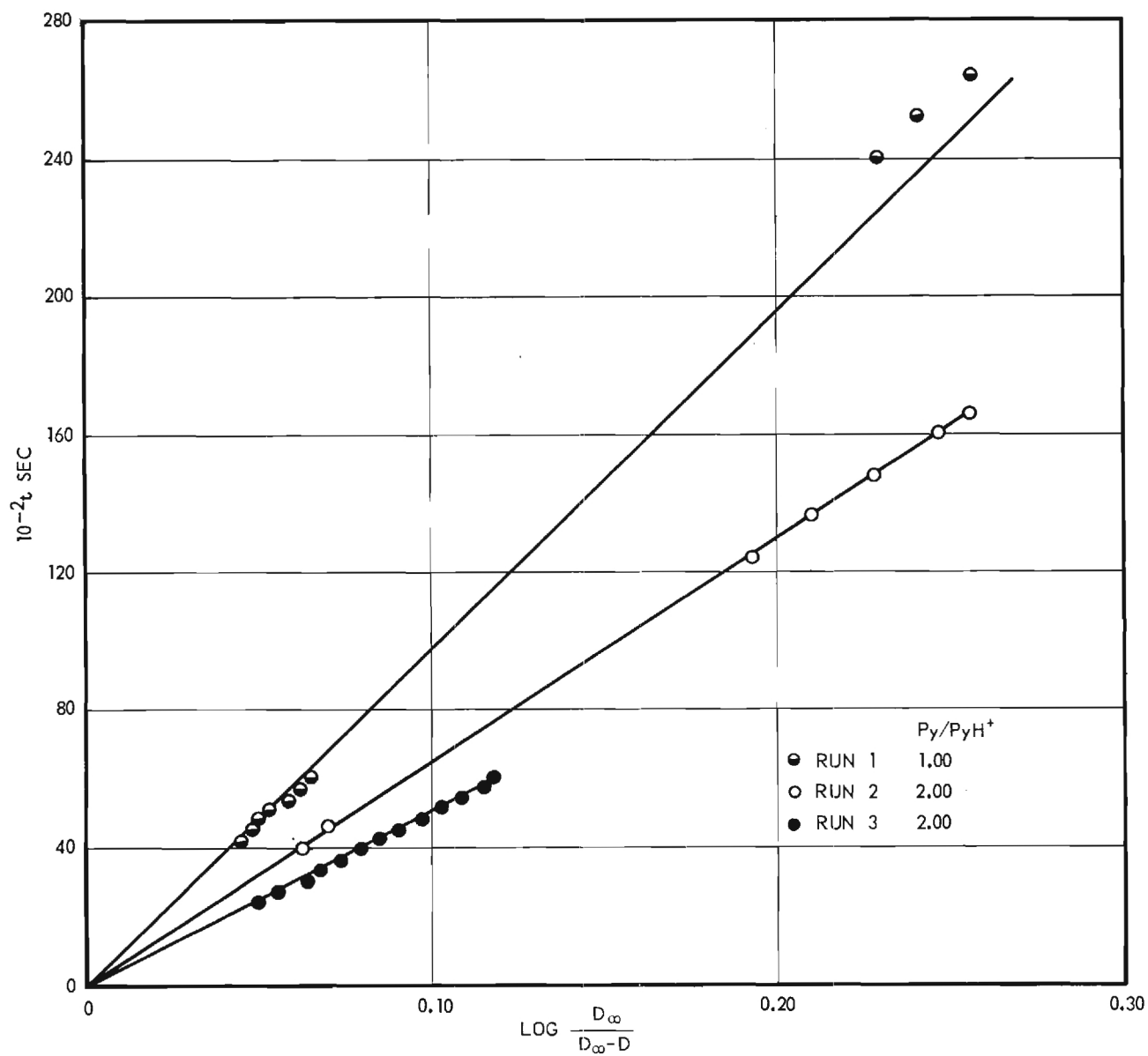
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Figure 9. Decomposition of HA in Methanolic Pyridine-Pyridine Hydrochloride Buffers at 25°C.

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	Run 4	Run 5
Adduct	1.314×10^{-4} m/l.	9.300×10^{-5} m/l.
Pyridine	9.076×10^{-3} m/l.	1.815×10^{-2} m/l.
Pyridinium	3.025×10^{-3} m/l.	6.050×10^{-3} m/l.
Sodium Perchlorate	0.1 M	0.1 M
Buffer Ratio	3.00	3.00

The change in optical density with time was measured at 370 mμ (slit = 0.5mm), and the following data were obtained. The initial reading is given along with those values of the optical density corresponding to 10 to 75 per cent reacted. The results are summarized in Table XVII and Fig. 9 and 10.

Decomposition of HA in Pyridine-Pyridinium Chloride Buffers at 38°

Following the procedure used in runs 1 through 5, the rate of decomposition of the adduct in pyridine-pyridinium chloride buffers was determined at 38° by thermostating the cell compartment of the spectrophotometer. Water was continuously pumped through a water jacket (Beckman No. 2021) from an external bath. The temperature was determined by inserting a thermocouple into a cell filled with methanol that had been allowed to equilibrate in the cell compartment. By this method, the temperature was found to be constant to within $\pm 0.1^\circ$ (effectively no change in the potentiometer reading but the accuracy of the absolute value was ± 0.3 degree).

The solutions were prepared as described in the runs at 25°, except that the buffer was thermostatted at 38° before adding it to the adduct. The following solutions were prepared. The data obtained are summarized in Table XVIII and Fig. 11.

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TABLE XVII

DECOMPOSITION OF HA IN PYRIDINE-PYRIDINIUM CHLORIDE BUFFERS AT 25°

$10^{-2} t \text{ sec}^a$	Run 2			Run 3		
	O.D.	$\log \frac{D_{\infty}}{D_{\infty} - D}$	$10^5 k \text{ sec}^{-1}^a$	O.D.	$\log \frac{D_{\infty}}{D_{\infty} - D}$	$10^5 k \text{ sec}^{-1}^a$
3	0.003	0.001258	(0.965)	0.026	0.00894	(0.685)
24	---	--	---	0.140	0.05034	4.83
27	---	--	---	0.155	0.05610	4.78
30	---	--	---	0.177	0.06468	4.97
33	---	--	---	0.186	0.06826	4.77
36	---	--	---	0.201	0.07427	4.75
39	---	--	---	0.215	0.07993	4.72
42	0.102	0.04568	2.50	0.229	0.08569	4.70
45	0.108	0.04852	2.48	0.243	0.09146	4.68
48	0.113	0.05088	2.43	0.258	0.09785	4.70
51	0.119	0.05377	2.43	0.272	0.10384	4.68
54	0.131	0.05956	2.53	0.285	0.10948	4.67
57	0.137	0.06251	2.53	0.299	0.11564	4.67
60	0.143	0.06547	2.51	0.312	0.11813	4.53
240	0.420	0.22986	2.20	0.833	0.45754	4.38
252	0.436	0.24155	2.20	0.860	0.48466	<u>4.43</u>
264	0.456	0.25665	<u>2.23</u>	Average		4.68 ± 0.10
Average			2.40 ± 0.12			
$D_{\infty} = 1.015, D_{\infty} \text{ calcd} = 1.022$				$D_{\infty} = 1.357, D_{\infty} \text{ calcd} = 1.279$		

(Continued)

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TABLE XVII (Continued)

DECOMPOSITION OF HA IN PYRIDINE-PYRIDINIUM CHLORIDE BUFFERS AT 25°

$10^{-2} t \text{ sec}^a$	Run 4			Run 5		
	O. D.	$\log \frac{D_{\infty}}{D_{\infty} - D}$	$10^5 k \text{ sec}^{-1}^a$	O.D.	$\log \frac{D_{\infty}}{D_{\infty} - D}$	$10^5 k \text{ sec}^{-1}^a$
3	0.027	0.01094	(8.40)	0.036	0.02090	(16.05)
9	---	--	--	0.092	0.05528	14.17
12	---	--	--	0.121	0.07482	14.37
15	0.117	0.04961	7.62	0.153	0.09691	14.88
21	0.159	0.06856	7.52	0.208	0.13767	15.10
27	0.201	0.08920	7.62	0.258	0.1784	15.22
33	0.243	0.11059	7.72	0.304	0.2196	15.33
39	0.281	0.1307	7.72	0.347	0.2620	15.47
45	0.318	0.1511	7.73	0.387	0.3056	15.63
51	0.349	0.1691	7.63	0.421	0.3464	15.65
57	0.385	0.1909	7.72	0.456	0.3929	15.87
63	0.418	0.2122	7.75	0.483	0.4325	15.82
69	0.445	0.2302	7.68	0.510	0.4760	15.88
75	0.474	0.2504	7.68	0.538	0.5263	<u>16.17</u>
81	0.502	0.2709	<u>7.70</u>	Average		15.35 \pm 0.47
Average			7.67 \pm 0.05			

 $D_{\infty} = 1.075$, $D_{\infty \text{ calcd}} = 1.095$ $D_{\infty} = 0.785$, $D_{\infty \text{ calcd}} = 0.775$

a. A value for t_{300} is given and then only values from 10 to 75 per cent reacted. This is the region from which the average value of k was calculated.

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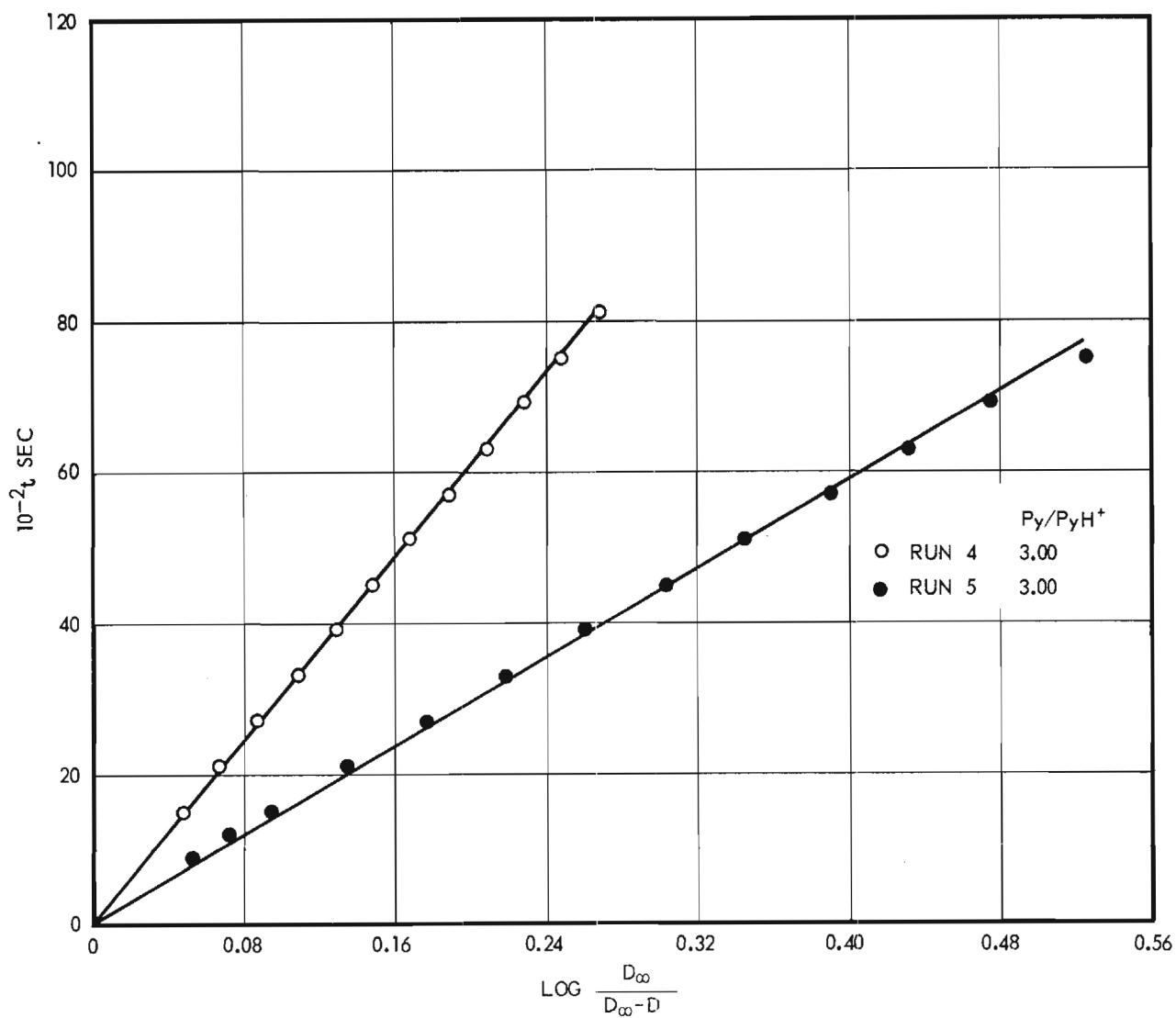
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Figure 10. Decomposition of HA in Methanolic Pyridine-Pyridine Hydrochloride Buffers at 25°C.

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Run	10^4 [Adduct]	10^3 [Py]	10^3 [PyH ⁺]	[NaClO ₄]	Py/PyH ⁺
6	1.684	2.046	0.682	0.1	3.00
7	1.396	3.758	1.698	0.1	2.21
8	1.755	4.163	1.387	0.1	3.00

TABLE XVIII

DECOMPOSITION OF HA IN PYRIDINE-PYRIDINIUM CHLORIDE BUFFERS AT 38°

$10^{-2}t$ sec ^a	O.D.	$\log \frac{D_{\infty}}{D_{\infty} - D}$	10^5k sec ^{-1a}	$10^{-2}t$ sec ^a	O.D.	$\log \frac{D_{\infty}}{D_{\infty} - D}$	10^5k sec ^{-1a}
<u>Run 6</u>							
3	0.022	0.00702	5.38	66	0.400	0.1498	5.23
15	0.098	0.03218	4.93	72	0.427	0.1620	5.18
21	0.133	0.04427	4.85	78	0.460	0.1773	5.23
27	0.176	0.05964	5.08	84	0.488	0.1909	5.23
33	0.220	0.07591	5.30	96	0.545	0.2199	5.28
39	0.249	0.08697	5.13	102	0.569	0.2327	5.25
57	0.353	0.1291	5.22	126	0.664	0.2874	5.25
60	0.370	0.1364	5.23	186	0.865	0.4323	<u>5.35</u>
Average							5.18
							±0.10

 $D_{\infty} = 1.301$, $D_{\infty \text{ calcd}} = 1.372$

(Continued)

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TABLE XVIII (Continued)

DECOMPOSITION OF HA IN PYRIDINE-PYRIDINIUM CHLORIDE BUFFERS

$10^{-2}t \text{ sec}^a$	O.D.	$\log \frac{D_{\infty}}{D_{\infty} - D}$	$10^5 k \text{ sec}^{-1}^a$	O.D.	$\log \frac{D_{\infty}}{D_{\infty} - D}$	$10^5 k \text{ sec}^{-1}^a$
Run 7				Run 8		
3	0.037	0.01841	(14.13)	0.046	0.01406	(10.80)
9	0.093	0.03667	9.38	0.119	0.03731	9.55
12	0.119	0.04747	9.12	0.157	0.04995	9.58
15	---	---	---	0.193	0.06228	9.57
18	---	---	---	0.228	0.07456	9.53
21	---	---	---	0.261	0.08650	9.48
24	---	---	---	0.294	0.09878	9.48
27	---	---	---	0.328	0.1119	9.55
30	---	---	---	0.358	0.1235	9.48
75	0.556	0.2874	8.83	---	---	---
78	0.572	0.2991	8.83	---	---	---
87	0.616	0.3337	8.83	---	---	---
90	0.634	0.3485	8.92	---	---	---
103.8	---	---	---	0.914	0.4347	9.65
106.8	---	---	---	0.921	0.4406	9.50
109.8	---	---	---	0.939	0.4558	9.57
111	0.721	0.4289	8.90	---	---	---
112.8	---	---	---	0.951	0.4661	9.52
115.8	---	---	---	0.959	0.4732	9.42
147	0.830	0.5689	8.92	---	---	---
Average			8.97	Average		
			± 0.14			
$D_{\infty} = 1.140$				$D_{\infty} = 1.412$		
$D_{\infty} \text{ calcd} = 1.445$				$D_{\infty} \text{ calcd} = 1.445$		

a. A value for t_{300} is given and then only values from 10 to 75 per cent reacted. This is the region from which the average value of k was calculated.

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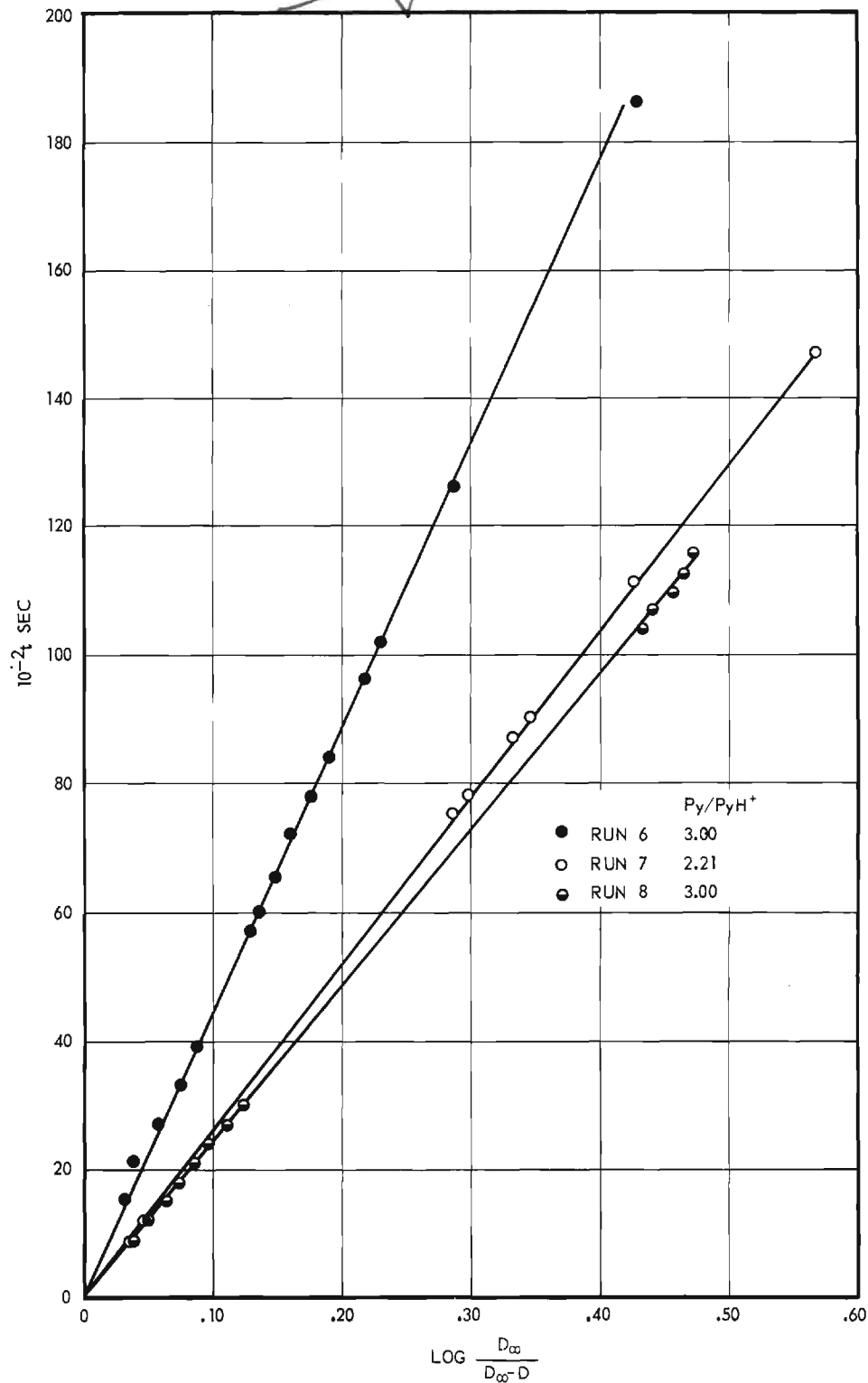


Figure 11. Decomposition of HA in Methanolic Pyridine-Pyridine Hydrochloride Buffers at 38°.

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~~CONFIDENTIAL~~~~CONFIDENTIAL~~Determination of the Equilibrium Constant for the Reaction $HA \rightleftharpoons HNF + NS$ By the Synthetic Route

Twenty-five milliliter aliquots of stock solutions of β -nitrostyrene and nitroform (about 0.1 M) were pipetted into a 50-cc low actinic glass volumetric flask. After mixing, the flask was placed in a thermostat at 40°. Measurements were made by taking a 5-cc aliquot and diluting it to 50 cc with methanolic hydrogen chloride (about 0.5 M) at 40°. This procedure quenched the reaction. A 5-cc aliquot of this solution was then diluted to 100 cc with methanol at 40°. The final dilution was made by taking a 5-cc aliquot of the second dilution and diluting it to 50 cc at 40° with methanol. This gave a dilution factor of 2000. Optical density measurements were made on the last solution at 310 and 350 m μ . The slit widths used were 0.64 and 0.50 mm respectively. The results are summarized in Table XIX.

By the Decomposition of the Adduct

An accurately weighed sample of the adduct (about 1.5 grams, 0.005 mole) in a 50-cc low actinic glass volumetric flask was diluted to volume with methanol at 40°. After mixing, the flask was placed in a thermostat at 40°. Optical-density measurements were made at 310 m μ (0.64 mm) and 350 m μ (0.50 mm) after first diluting the reaction mixture as described previously.

The results are summarized in Table XX.

Rate of Decomposition of the Adduct in Methanolic Hydrogen Chloride

A sample of the adduct (about 3×10^{-5} moles) was accurately weighed into a 100-cc low actinic glass volumetric flask. To this sample were added required amounts of 0.2 M methanolic hydrogen chloride and enough 1 M sodium perchlorate in methanol to bring the ionic strength up to 0.1. The solutions

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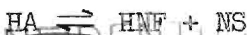
TABLE XIX

DETERMINATION OF K_E BY REACTION OF HNF AND NS

	<u>Optical Density</u>					
<u>Time</u>	<u>λ_{310}</u>	<u>λ_{350}</u>	<u>10^2[NS]</u>	<u>10^2[HNF]^a</u>	<u>10^3[HA]^a</u>	<u>K_{HA}^b</u>
(days)						
			<u>Run 1</u>			
0.0	---	---	7.13	9.09	---	---
0.5	0.565	0.237	6.52	8.48	6.12	0.901
1.0	0.538	0.229	6.25	8.22	8.84	0.581
2.0	0.509	0.222	5.89	7.88	12.36	0.375
2.5	0.472	0.209	5.45	7.46	16.76	0.242
5.5	0.462	0.194	5.37	7.37	17.64	0.225
13.5	0.338	0.176	3.85	5.94	32.84	0.0699
			<u>Run 2</u>			
2.1	0.524	0.199	6.14	5.18	10.20	0.312
8.1	0.426	0.162	4.98	4.08	21.74	0.0935
11.1	0.396	0.137	4.66	3.78	24.92	0.0709
15.1	0.390	0.144	4.58	3.71	25.78	0.0658
18.2	0.387	0.143	4.53	3.67	26.22	0.0633
			<u>Run 3</u>			
0.8	0.520	0.199	6.08	4.44	3.31	0.813
2.0	0.488	0.187	5.70	4.07	7.11	0.327
5.3	0.431	0.144	5.09	3.41	14.23	0.122
13.0	0.388	0.135	4.56	3.01	18.51	0.0741
16.0	0.380	0.125	4.49	2.92	19.21	0.0685
23.0	0.398	0.131	4.70	3.13	17.13	0.0862

a. Undissociated nitroform remaining after time t. The amount of nitroform reacted was taken to be equal to the amount of β -nitrostyrene that has reacted. The adduct formed was equal to the amount of β -nitrostyrene that had reacted.

b. This is the equilibrium constant for the reaction

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were thermostatted at 25° before use. In the case of run 3, 0.02 M methanolic hydrogen was used. The solutions were then diluted to volume with methanol at 25°. An optical-density measurement was made immediately after mixing by withdrawing a sample and measuring its optical density at 310 and 350 mμ.

TABLE XX

DETERMINATION OF K_E BY REACTION OF HA

Time (days)	Optical Density		$10^2[\text{NS}]^a$	$10^2[\text{HMF}]^b$	$10^2[\text{HA}]^c$	K_{HA}^d
	λ_{310}	λ_{350}				
Run 1						
1.8	0.180	0.065	2.12	1.64	7.55	0.00461
6.7	0.367	0.156	4.26	3.88	5.41	0.0305
8.8	0.483	0.178	5.66	5.10	4.00	0.0725
9.9	0.457	0.163	5.38	4.93	4.29	0.0617
14.8	0.458	0.176	5.35	4.91	4.31	0.0610
Run 2						
0.05	0.042	0.012	0.498	0.419	9.88	0.000211
0.4	0.080	0.022	0.960	0.836	9.42	0.000895
1.0	0.125	0.045	1.47	1.29	8.91	0.00213
2.3	0.223	0.082	2.61	2.33	8.77	0.00699
7.8	0.458	0.199	5.31	4.52	5.07	0.04474
20.0	0.424	0.155	4.98	4.60	5.40	0.0424

a. Calculated from observed optical density.

b. Undissociated nitroform formed after time t. The amount of nitroform produced was assumed to be equal to the amount of β -nitrostyrene formed.

c. The amount of adduct remaining obtained by the difference between the initial concentration and the amount of β -nitrostyrene formed.

d. This is the equilibrium constant for the reaction

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The slit widths were 0.64 and 0.50 mm, respectively. The flask was then placed in a thermostat at 40°, and the reaction was followed by measuring the change in the optical density of the reaction mixture at these wavelengths in a thermostatted Beckman D. U. spectrophotometer.

The concentration of β -nitrostyrene was calculated from the initial optical-density readings at 25°. This value was subtracted from the formal concentration of adduct to give the actual concentration at t_0 . Succeeding calculated concentrations of β -nitrostyrene were also corrected by subtracting this value from them. The rate constants were calculated by subtracting the concentration of adduct at t_0 and concentration of β -nitrostyrene at t_t into the usual form of the first order rate expression.

The data obtained are summarized in Table XXI and Fig. 12.

The Addition of Nitroform to β -Nitrostyrene

A 1.0518-gram sample (0.007059 mole) of β -nitrostyrene was weighed into a 50-cc low actinic glass volumetric flask, and 20 cc of a 1.0380 molar nitroform solution in methanol was added. Five cubic centimeters of a 1 M solution of sodium perchlorate in methanol was added, and the solution was made up to volume with methanol. After shaking thoroughly, it was placed in a thermostat at 40°, and samples were periodically withdrawn to determine the optical density at 310 (slit = 0.64 mm) and 350 m μ (slit = 0.50 mm).

The following dilution procedure was used:

Five cubic centimeters of the reaction mixture was diluted to 100 cc with 0.5 M methanolic hydrogen chloride. A second dilution was made by taking 5 cc of the above solution and diluting to 100 cc with 0.5 M methanolic hydrogen chloride. The optical-density measurements were made on a solution prepared

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by diluting 5 cc of the second dilution to 50 cc with methanolic hydrogen chloride. This gave a dilution factor of 4000.

The data obtained are summarized in Table XXII.

TABLE XXI

DECOMPOSITION OF HA IN METHANOLIC HYDROGEN CHLORIDE

<u>$10^{-3} t \text{ sec}$</u>	<u>Optical Density</u>		<u>$10^4 [\text{NS}]^a$</u>	$\log \frac{[\text{HA}]_0}{[\text{HA}]_0 - [\text{NS}]}$	<u>$10^7 k \text{ sec}^{-1}$</u>
	<u>λ_{310}</u>	<u>λ_{350}</u>			
<u>Run 1</u>					
0.0	0.096	0.022	0.058	---	---
77.4	0.284	0.056	0.114	0.02210	6.58
81.0	0.285	0.055	0.115	0.02227	6.33
97.2	0.362	0.062	0.139	0.02706	6.41
104.4	0.335	0.065	0.145	0.02828	6.25
126.0	0.383	0.074	0.174	0.03415	6.25
174.6	0.483	0.096	0.234	0.04662	6.14
185.4	0.509	0.101	0.250	0.04999	6.22
262.8	0.660	0.131	0.341	0.06971	<u>6.11</u>
				Average	6.28
					± 0.11

$$[\text{HA}]_{\text{formal}} = 2.358 \times 10^{-4}$$

$$[\text{NS}]_0 = 0.058 \times 10^{-4}$$

$$[\text{HA}]_0 = 2.300 \times 10^{-4}$$

$$[\text{MeOH}_2^+] = 0.09027$$

$$a. \text{ Corrected for } [\text{NS}]_0 = 0.058 \times 10^{-4}$$

(Continued)

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TABLE XXI (Continued)

DECOMPOSITION OF HA IN METHANOLIC HYDROGEN CHLORIDE

$10^{-3} t \text{ sec}$	Optical Density		$10^4 [\text{NS}]^a$	$\log \frac{[\text{HA}]_0}{[\text{HA}]_0 - [\text{NS}]}$	$10^7 k \text{ sec}^{-1}$
	λ_{310}	λ_{350}			
Run 2					
0.0	0.113	0.027	0.0680	---	--
39.6	0.280	0.061	0.1009	0.01645	9.56
50.4	0.321	0.072	0.1252	0.02044	9.33
57.6	0.356	0.080	0.1464	0.02395	9.58
81.0	0.446	0.103	0.2005	0.03334	9.47
118.8	0.588	0.131	0.2861	0.04829	9.36
136.8	0.648	0.143	0.3226	0.05492	9.25
205.2	0.914	0.208	0.5065	0.08962	10.06
				Average	9.52 ± 0.19
$[\text{HA}]_{\text{formal}} = 2.787 \times 10^{-4}$				$[\text{HA}]_0 = 2.719 \times 10^{-4}$	
$[\text{NS}]_0 = 0.068 \times 10^{-4}$				$[\text{MeOH}_2^+] = 0.02210$	
a. Corrected for $[\text{NS}]_0 = 0.068 \times 10^{-4}$					
Run 3					
0.0	0.075	0.017	0.0450	---	---
50.4	0.253	0.065	0.1062	0.02428	11.08
57.6	0.291	0.072	0.1293	0.02784	11.14
81.0	0.375	0.103	0.1791	0.04183	11.89
118.8	0.509	0.142	0.2587	0.06194	12.00
136.8	0.565	0.161	0.2915	0.07048	11.86
205.2	0.799	0.231	0.4306	0.10854	12.19
				Average	11.69 ± 0.39
$[\text{HA}]_{\text{formal}} = 1.994 \times 10^{-4}$				$[\text{HA}]_0 = 1.949 \times 10^{-4}$	
$[\text{NS}]_0 = 0.045 \times 10^{-4}$				$[\text{MeOH}_2^+] = 0.0048$	
a. Corrected for $[\text{NS}]_0 = 0.045 \times 10^{-4}$					

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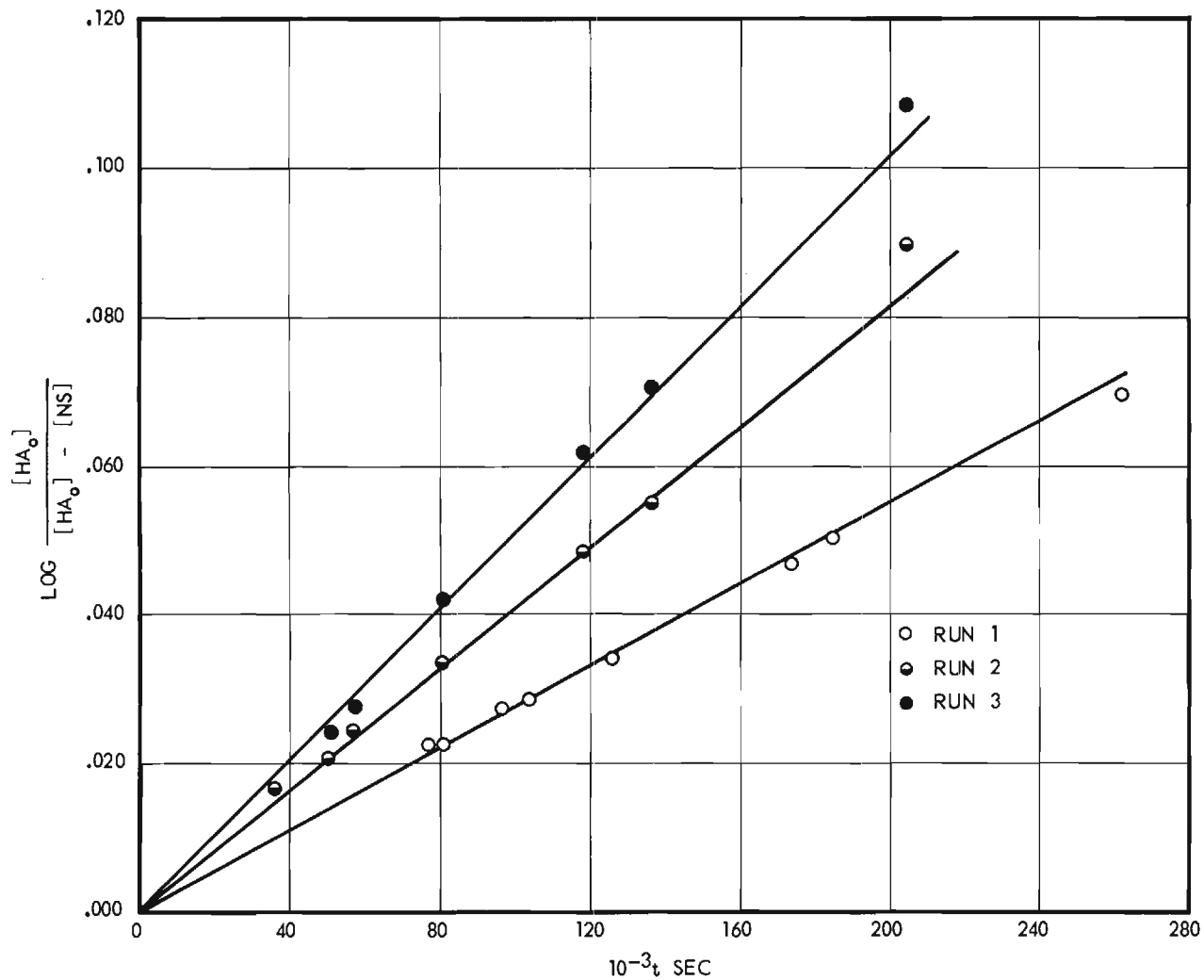
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Figure 12. Decomposition of HA in Methanolic Hydrogen Chloride Solution at 40°.

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TABLE XXII

ADDITION OF HNF TO NS

<u>Time</u>	<u>Optical Density</u>		<u>[NS]^a</u>
	<u>λ_{310}</u>	<u>λ_{350}</u>	
0.0	0.583	0.135	0.1402
2.5	0.538	0.113	0.1340
4.5	0.503	0.119	0.1208
21.5	0.366	0.081	0.0884
24.5	0.356	0.076	0.0860

a. $[\text{HNF}]_{\text{formal}} = 0.4152.$

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VI. RECOMMENDATIONS

The study of the decomposition and formation of HA has yielded a surprising amount of detailed information about the reaction. Since the reaction seems suitable for detailed study and since this type of study often yields information of general character that could not be obtained in any general qualitative survey of reactions, its further study is recommended as follows:

1. The decomposition reaction should be studied in other buffers in order to make a Brønsted plot and in order to permit a more accurate determination of k_1 .

2. As a completely independent test of the proposed reaction mechanism, the kinetics of the deuterium exchange of HA should be studied under most of the conditions where the decomposition reaction has been investigated.

3. From the magnitude of k_5 estimated in Table X, it should be possible to determine this rate constant directly if a method designed for relatively rapid reactions were used. One such method was described by Bell and Clunie.¹⁶ Thus, if the decomposition of HA were studied in increasingly basic solutions, the rate would not continue to increase with increasing methoxide concentration indefinitely. Instead, the point would be reached where A^- was formed rapidly and quantitatively, and the reaction rate would be controlled by k_5 , the rate constant for the decomposition of A^- . The determination of k_5 would permit a reliable calculation of K_{HA} and, therefore, make accurate values of k_{-1} , k_{-2} , and k_{-3} obtainable.

4. The reactions of ring-substituted derivatives of HA should give added information about the charge distribution in several transition states.

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VII. PERSONNEL AND ACKNOWLEDGMENTS

This work was carried out by Lloyd A. Kaplan, Assistant Research Chemist, under the supervision of Jack Hine, Project Director. We should like to express our gratitude to Dr. D. V. Sickman and Dr. M. J. Kamlet for stimulating discussion of this work.

Respectfully submitted:

Lloyd A. Kaplan
Assistant Research Chemist

Jack Hine
Project Director

Approved: *A*

for Paul K. Calaway, Director
Engineering Experiment Station

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