The Meyer Reaction of Phenylnitromethane in Acid

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ABSTRACT

The rate of formation of benzoic acids from phenylnitromethanes has been determined in different concentrations of mineral acid. The reaction rate reaches a maximum in 2 - 5 M acid. By a study of the reactions of the aci-form of phenylnitromethane, an explanation was found for the maximum: the aci-form undergoes two competing reactions in acid, one a tautomerization to give back the nitro-form via the aci-anion, and the other a dehydration of the protonated aci-form to give benzonitrile oxide. The dehydration is rate-limiting for the overall reaction up to the maximum, and is accelerated by increasing the concentration of acid. Beyond the maximum, the rate-limiting step for the overall reaction is the initial formation of the aci-form, a process that is inhibited by increasing the concentration of acid.

The reaction of benzonitrile oxides with sulfuric acid to form benzohydroxamic acid and the hydrolysis of benzohydroxamic acid in sulfuric acid have also been studied.

RESUME

On a étudié la vitesse de la formation des acides benzoïques par la réaction des phénylnitrométhanes avec de différentes concentrations d'acide. La vitesse de la réaction atteint un maximum dans une concentration d'acide de 2 - 5 M. En étudiant les réactions de la forme aci du phénylnitrométhane, on a trouvé l'explication de ce maximum: les deux réactions concurrentes de la forme aci sont la tautomérisation redonnant la forme nitro via l'anion de la forme aci, et la déshydratation menant a l'oxyde de benzonitrile, via la protonation de la forme aci. La vitesse de la déshydratation est augmentée par une augmentation de la concentration d'acide et contrôle la vitesse de la réaction globale jusqu'au maximum. Au-dessus du maximum, la vitesse de la réaction globale est contrôlée par la formation initiale de la forme aci, qui est ralentie par une augmentation de la concentration d'acide.

On a étudié aussi la réaction de l'oxyde de benzonitrile avec l'acide sulfurique, menant a l'acide benzohydroxamique, et la réaction de l'acide benzohydroxamique avec l'acide sulfurique menant a l'acide benzoïque.

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To Annette, Barry and Alan

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ABSTRACT

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On a étudié aussi la réaction de l'oxyde de benzonitrile avec l'acide sulfurique, menant a l'acide benzohydroxamique, et la réaction de l'acide benzohydroxamique avec l'acide sulfurique menant a l'acide benzoïque.

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PREFACE

The research reported in this thesis was undertaken under the direction of Dr. J. T. Edward, as part of a continuing programme of study in his laboratory of reactions in strong acid media. The particular aims of the research reported here will be outlined in the general introduction that follows this preface.

Following the general introduction, the main body of this thesis has been divided into three parts, each of which has been written in the form of a scientific paper to be submitted with little alteration to the Canadian Journal of Chemistry. The main body of the thesis is followed by an appendix containing the raw data from the kinetic studies described in the text.

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GENERAL INTRODUCTION

The Meyer rearrangement-hydrolysis

The reaction of a nitroalkane with hot mineral acid to form a carboxylic acid and a salt of hydroxylamine was first reported by Meyer (1) in 1873, soon after the first synthesis of a nitroalkane (2). The reaction of a nitroalkane with hot sulfuric acid is now used for the commercial production of hydroxylamine (3). In this general introduction is presented a brief survey of the literature pertinent to the mechanism of this reaction, followed by a statement of the aims of the research reported in the main body of this thesis.

It may be noted here that this reaction of nitroalkanes with hot acid has often been called a "hydrolysis" (4-7). In fact, hydrolysis is only one step in the overall reaction, being preceded by a tautomerization and a rearrangement. For convenience, the reaction is herein called "the Meyer rearrangement-hydrolysis" or "the Meyer reaction of nitroalkanes", in spite of the number of reactions that already bear the name of that prolific chemist (8).

The three steps

The early review of Hass and Riley (4) proposed the reaction scheme now generally accepted (5,6,7,9) for the reaction of nitroalkanes in hot acid: tautomerization to the *aci*-form (equation [1]), rearrangement to the hydroxamic acid (equation [2]), and finally hydrolysis

$$[1] \qquad RCH_2NO_2 \longrightarrow RCH{=}NO_2H$$

$$[2] \qquad RCH{=}NO_2H \longrightarrow RCONHOH$$

$$[3] \qquad H_3O^+ + RCONHOH \longrightarrow NH_3OH^+ + RCOOH$$

to the observed products (equation [3]). The first of these three steps was identified by Junell (10,11,12) as the rate-determining step: the rates of bromination of nitromethane and nitroethane in hot dilute sulfuric acid were the same as the rates of their reaction with acid to form a carboxylic acid and hydroxylamine. The product of the bromination in hot acid was the bromonitroalkane, demonstrating that the bromination of the _aci_-form is faster than the Meyer reaction of the _aci_-form. Bamberger and Rust (13) found that the _aci_-forms of nitroethane and phenylnitromethane were converted quickly into acetohydroxamic acid and benzohydroxamic acid when treated with cold 12% hydrochloric acid. At the same time, they reported the isolation of a very small yield of benzohydroxamic acid from the reaction of phenylnitromethane with hot 65% sulfuric acid. The confirmation of a hydroxamic acid as an intermediate in the Meyer reaction was made by Lippincott and Hass (14) who isolated a 44% yield of propiohydroxamic acid from the reaction of 1-nitropropane with hot concentrated sulfuric acid, in which the water activity was low enough to slow the subsequent hydrolysis of the hydroxamic acid. It has been known for some time (15,16) that hydroxamic acids are hydrolyzed in hot aqueous acid to carboxylic acids and hydroxylamine.

Although the mechanism of the Meyer reaction was agreed to be composed of these three steps ([1]-[3]), some details of the reaction mechanism remained obscure.

Rate profile maxima

In the most recent work on the Meyer reaction, Cundall and Locke (9) studied the rate of the reaction of nitromethane in different concentrations of hot hydrochloric acid. The rate reached a maximum at 4 M hydrochloric acid, then decreased slightly before beginning an increase with increasing acid concentration up to 10 M hydrochloric acid, the highest concentration studied. The rate of the reaction in sulfuric and perchloric acids was reported to demonstrate a similar increase with increasing acid concentration. Cundall and Locke proposed an explanation for the maximum in the rate profile, but the explanation was not in accord with recent work, as will be shown below.

Similar rate profiles have been widely used as a diagnostic tool in studies of reaction mechanisms (17,18) in spite of a continuing debate on their interpretation (19,20,21). The observation of a maximum in the rate profile for a reaction provides special assistance to interpretation of the profile (18,22). An acid-catalyzed hydrolysis may show a maximum in the rate profile because the substrate (S) has been almost completely protonated at that acid concentration (equation [4]). Any further

$$[4] \qquad S + H^+ \rightleftharpoons SH^+$$

$$[5] \qquad SH^+ + H_2O \longrightarrow \text{products}$$

increase in the acid concentration only serves to reduce the activity of water in the medium, slowing the rate of the nucleophilic attack by water on the protonated substrate (equation [5]) (23).

A different explanation was given by Bunton for the maximum observed in the rate of hydrolysis of some phosphate esters (24) and carboxylic anyhydrides (25). Bunton determined the aqueous activity coefficients of these substrates in different concentrations of acid and found a decrease in the activity coefficient beginning at an acid concentration near the point of the maximum in the rate profile. Such a decrease, coupled with the decrease in water activity in increasing concentrations of acid, can account for the observed decrease in rate after the maximum in the rate profile.

Another explanation for a rate maximum was offered by Martin et al (26) for the hydrolysis in acid of 2-methyl-Δ^2-thiazoline. An initial slow reaction of the protonated substrate with water produces a hydrated intermediate that may react with acid to give back protonated substrate, or react with water to form products. An increase in the acid concentration forms a greater concentration of protonated substrate, but also increases the rate of the back-reaction and decreases the water activity, giving rise to a maximum in the rate profile.

Since it was found by Gillespie (27) that nitromethane is only 21% protonated in 100% sulfuric acid, the maximum in the rate profile for the Meyer reaction of nitromethane cannot be due to essentially complete protonation of the substrate in 4 M hydrochloric acid. Cundall and Locke (9) proposed that the formation of a hydrogen-bonded complex of nitromethane assists the tautomerization, and that the formation of this hydrogen-bonded complex is nearly complete in 4 M acid. There is some evidence that such hydrogen-bonded complexes of nitro compounds do exist in acid (28-31). However, Haldna (28) found that the rate of tautomerization of the hydrogen-bonded complex of nitromethane must be the same as the rate of tautomerization of uncomplexed nitromethane: the rate of bromination (k_r) of nitromethane in sulfuric acid up to 5.3 M decreased with the fourth power of the water activity (a_{H_2O}) (equation [6]), as would be expected if the water were

$$k_r = k_o \, a^4_{H_2O} \qquad [6]$$

accepting a proton from unprotonated nitromethane. The explanation for the maximum in the rate profile for the Meyer reaction of nitromethane must lie elsewhere.

The reactions of the *aci*-form

Since Junell (10) showed that the Meyer rearrangement-hydrolysis of nitroethane took place through the slow formation of the *aci*-form, the reactions of the *aci*-form of nitroalkanes should be identical with the Meyer reaction of nitroalkanes. Mention has already been made of the work of Bamberger and Rust (13) who isolated acetohydroxamic acid from the reaction of *aci*-nitroethane with cold 12% hydrochloric acid. However, it is known that *aci*-nitroethane reacts with cold dilute acid to form acetaldehyde, an example of the Nef reaction (6). Moreover, in very weak acid, *aci*-nitroethane tautomerizes to the *nitro*-form (32).

The relation between these three reactions indicates their mechanisms: in water or weak acid, the aci-form tautomerizes via the anion, as shown by many workers (32-35). The nitro-form is stable in cold acid (equations [7] and [8]). In more concentrated acid, according to the mechanism proposed by Hawthorne (36) and by Kornblum and Brown (37), the protonated

$$[7] \qquad H_2O + RCH{=}NO_2H \rightleftharpoons RCH{=}NO_2^{-} + H_3O^{+}$$

$$[8] \qquad H_3O^{+} + RCH{=}NO_2^{-} \longrightarrow RCH_2NO_2 + H_2O$$

$$[9] \qquad H_3O^{+} + RCH{=}NO_2H \rightleftharpoons RCH{=}\overset{+}{N}(OH)_2 + H_2O$$

$$[10] \qquad 2H_2O + RCH{=}\overset{+}{N}(OH)_2 \longrightarrow R\underset{\substack{|\\ OH}}{C}H{-}N(OH)_2 + H_3O^{+}$$

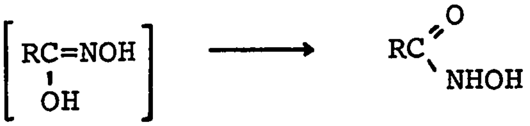
$$[11] \qquad R\underset{\substack{|\\ OH}}{C}H{-}N(OH)_2 \rightleftharpoons R\underset{\substack{|\\ OH}}{C}H{-}N{=}O + H_2O$$

$$[12] \qquad 2\ R\underset{\substack{|\\ OH}}{C}H{-}N{=}O \longrightarrow 2RCHO + N_2O + H_2O$$

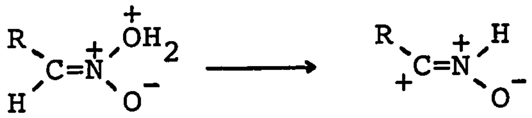
aci-form reacts with water (equations [9] and [10]) to form a hydrated intermediate. The hydrated intermediate loses water to form a coloured nitroso compound that decomposes to the aldehyde and nitrous oxide (equations [11] and [12]).

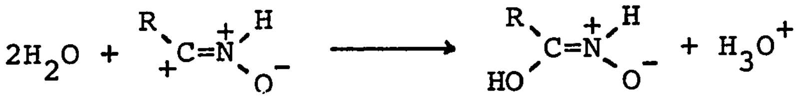
In even more concentrated acid, a hydroxamic acid is formed from the aci-form (13,37). Hydroxamic acids are also obtained as by-products from some Nef reactions (6). Noland (6) and Smith (7) proposed formation of hydroxamic acid from the hydrated intermediate (equation [13]) in a reaction competing with equation [11].

$$[13] \qquad R\underset{\substack{|\\ OH}}{C}H{-}N(OH)_2 \longrightarrow \left[R\underset{\substack{|\\ OH}}{C}{=}NOH \right] + H_2O$$

[14] 

Another mechanism proposed (6,7,9) for the formation of hydroxamic acid is a Beckmann-type rearrangement of the O-protonated aci-form (equations [15]-[17]).

[15] 

[16] 

[17] 

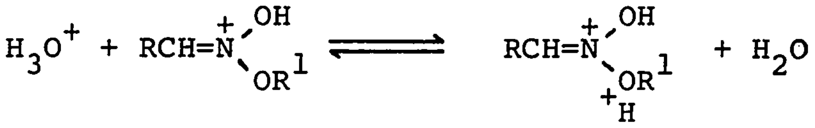
Noland (6) and Cundall and Locke (9) also proposed the possibility of a nitrile oxide intermediate, $RC\equiv\overset{+}{N}-O^-$, as an intermediate in the formation of the hydroxamic acid (equations [18]-[20]).

[18] $RCH=\overset{+}{N}(OH)_2 \longrightarrow RCH=\overset{+}{N}=O + H_2O$

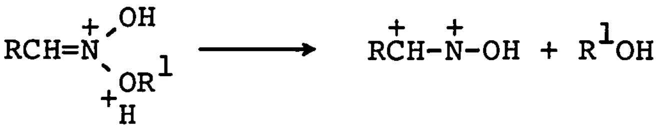
[19] $H_2O + RCH=\overset{+}{N}=O \longrightarrow RC\equiv\overset{+}{N}-O^- + H_3O^+$

[20] $H_2O + RC\equiv\overset{+}{N}-O^- \longrightarrow RCONHOH$

Phenyl-aci-nitromethane and its substituted derivatives do not undergo the Nef reaction in cold dilute acid (32). Instead of aldehyde, a quantitative yield of the nitro-form was obtained (37). Hawthorne (36) attributed this failure of the Nef reaction to resonance stabilization by the phenyl group of the protonated *aci*-form, but not of the transition state leading to the Nef products. Kornblum and Brown (37) observed that the *aci*-form of *p*-nitrophenylnitromethane gave only the *nitro*-form in cold 4 *N* sulfuric acid, but that the ethyl ester of *p*-nitrophenyl-*aci*-nitromethane under the same conditions gave an 80% yield of *p*-nitrobenzaldehyde along with some *p*-nitrobenzohydroxamic acid. In 31 *N* sulfuric acid, both the *aci*-form and the ethyl ester of the *aci*-form produced excellent yields of *p*-nitrobenzohydroxamic acid. Because the *aci*-ester does not have the possibility of tautomerization to the *nitro*-form in dilute acid, protonation of the *aci*-ester is followed by attack of water (as in equation [10]) to form the Nef products. Kornblum (37) suggested that the formation of the benzohydroxamic acid requires a double protonation of the *aci*-form

[21] 

$$H_3O^+ + RCH{=}\overset{+}{N}\begin{array}{l}OH\\OR^1\end{array} \rightleftharpoons RCH{=}\overset{+}{N}\begin{array}{l}OH\\\underset{+H}{OR^1}\end{array} + H_2O$$

[22] 

$$RCH{=}\overset{+}{N}\begin{array}{l}OH\\\underset{+H}{OR^1}\end{array} \longrightarrow \overset{+}{RCH}\text{-}\overset{+}{N}\text{-}OH + R^1OH$$

[23] 

$$H_2O + \overset{+}{RCH}\text{-}\overset{+}{N}\text{-}OH \longrightarrow RC{\equiv}\overset{+}{N}\text{-}OH + H_3O^+$$

(equations [21]-[23]; $R^1=C_2H_5$ or H). This accounted for the low ratio of hydroxamic acid to aldehyde formed from the *aci*-ester in 4 *N* sulfuric acid, compared to that formed in 31 *N* sulfuric acid. However, this change in ratio could be explained as well by the decrease in water activity, assuming a monoprotonated *aci*-form.

Nitrile oxide as an intermediate

In the preceding section was mentioned the proposal (6,9,37) of a nitrile oxide intermediate in the rearrangement of an *aci*-form to a hydroxamic acid. A nitrile oxide was also proposed as an intermediate in the rearrangement of a secondary *nitro* compound in acid (38), and in the reaction of some α-nitroketones with acid (39). It has been known for some time that nitrile oxides react with acid to form hydroxamic acids (40,41). A number of nitrile oxides have been synthesized (42-44) but there has been no experimental evidence of a nitrile oxide intermediate during the course of the Meyer rearrangement-hydrolysis of a nitroalkane.

The nitro-aci tautomerization

The *nitro*-*aci* tautomerization has been rarely studied in acid. Hass and Riley (4) concluded that the tautomerization was acid-catalyzed on the basis of the work of Lowry and Magson (45) in 1908 on the racemization of nitrocamphor in benzene. The racemization was not acid-catalyzed in alcohol solution (46). Feuer and Nielson (47) found that the epimerization of 2,5-dinitro-1,6-hexanediol in benzene was catalyzed by acid, but the epimerization of the dimethyl ether was not. Feuer and Nielson proposed acid catalysis for the tautomerization of 1-nitrooctane in 1 *N* hydrochloric acid (48) but presented no evidence for it. Smith (7) and Cundall and Locke (9) proposed acid-catalyzed tautomerization as the rate-determining step of the Meyer rearrangement-hydrolysis of nitroalkanes, on the basis of the rate increase observed with an increase in acid concentration. However, Reitz (49) found that the rate of bromination of nitromethane decreased in deuterated acid. Acid-catalyzed reactions usually show a rate increase in deuterated acid (50) due to the greater acidity of the deuteronium ion, but this is not always the case (51,52).

The tautomerization from the aci-form to the nitro-form has been extensively studied, by conductimetric and titrimetric methods (32-35). In every case, the results were explained by prior ionization to the aci-anion (equations [7] and [8]), a process not catalyzed by acid. The principle of microscopic reversibility would indicate a similar mechanism for the nitro-aci tautomerization.

The aims of this research

The research reported in this thesis was undertaken to determine if the rate profile for the Meyer rearrangement-hydrolysis of phenylnitromethane in acid passed through a maximum, with the further possibility of finding the cause of the maximum and clarifying the details of the initial tautomerization. Since the benzoic acid produced by the Meyer reaction absorbs in the ultraviolet (u.v.), the reaction was followed by u.v. spectrophotometry. The results of this study are given in Part III.

A prerequisite for the interpretation of the results of that initial study of the overall reaction was a knowledge of the kinetics of the reaction of the _aci_-form of the phenylnitromethanes. Since these compounds also absorb in the u.v., the reactions were followed by u.v. spectrophotometry. During the course of that study, reported in Part I of this thesis, the intermediate benzonitrile oxides were observed for the first time during the reaction of the _aci_-forms.

To complete the kinetic scheme for the Meyer reaction of phenylnitromethane, a brief study of the kinetics of the reactions in acid of benzonitrile oxides and benzohydroxamic acid was undertaken, and is reported in Part II.

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PART I

The reactions of phenyl-*aci*-nitromethane in acid

Abstract

Phenyl-aci-nitromethane reacts in aqueous sulfuric acid at room temperature to form phenylnitromethane and benzohydroxamic acid. The relative amounts of these two products depend on the concentration of the acid. Benzohydroxamic acid is formed by reaction of the intermediate, benzonitrile oxide, with water.

Solvent effects, substituent effects and isotope effects have been studied to determine mechanisms for these reactions of phenyl-aci-nitromethane.

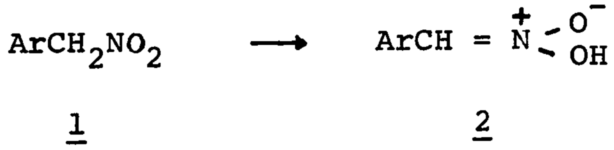
Le phényl-aci-nitrométhane au contact de l'acide sulfurique à température ambiante, donne deux produits: le phénylnitrométhane et l'acide benzohydroxamique. Un changement dans la concentration de l'acide sulfurique fait varier la proportion des deux produits. L'acide benzohydroxamique provient de la réaction de l'intermédiaire, l'oxyde de benzonitrile, avec l'eau.

L'influence du solvant et des substituants et les effects isotopiques ont été étudiés dans le but de découvrir le mécanisme de ces réactions.

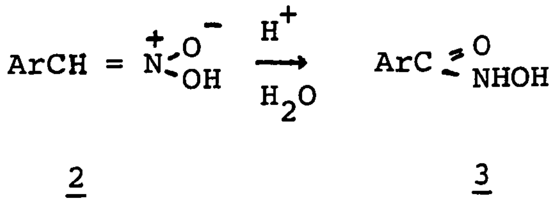
Introduction

Primary nitroalkanes in hot concentrated mineral acids give a carboxylic acid and hydroxylamine. This reaction was first reported by Victor Meyer in 1873 (1), and is now used commercially for the production of hydroxylamine.

It has been claimed (2,3) that the rate-determining step in the Meyer reaction (illustrated in equations [1] - [3] for a phenylnitromethane) is the acid catalyzed formation of the aci-form 2 of the nitroalkane 1

[1] 

$$\underset{\underline{1}}{\mathrm{ArCH_2NO_2}} \longrightarrow \underset{\underline{2}}{\mathrm{ArCH} = \overset{+}{\mathrm{N}} {<}^{\mathrm{O}^-}_{\mathrm{OH}}}$$

[2] 

$$\underset{\underline{2}}{\mathrm{ArCH} = \overset{+}{\mathrm{N}} {<}^{\mathrm{O}^-}_{\mathrm{OH}}} \xrightarrow[\mathrm{H_2O}]{\mathrm{H^+}} \underset{\underline{3}}{\mathrm{ArC} {\lessgtr}^{\mathrm{O}}_{\mathrm{NHOH}}}$$

$$[3] \quad \underset{\underline{3}}{\mathrm{ArCONHOH}} + \mathrm{H_2O} \longrightarrow \underset{\underline{4}}{\mathrm{ArCO_2H}} + \mathrm{NH_2OH}$$

(equation [1]), followed by its rapid transformation into a hydroxamic acid 3 (equation [2]), which is then hydrolyzed to a carboxylic acid 4 and hydroxylamine (equation [3]). However, the nature of the steps involved in the transformation summarized in equation [2] has remained obscure. Recently Cundall and Locke (3) have investigated the kinetics of the hydrolysis of nitromethane, and have proposed two possible mechanisms (one involving a nitrile oxide intermediate). However, they were unable to distinguish between these two alternatives.

In this and the following two papers we report on our studies of the mechanism of the Meyer reaction of phenylnitromethane, which in hot concentrated acid is converted into benzoic acid and hydroxylamine (4). The presence of the phenyl group makes it possible to study this reaction conveniently by ultraviolet (u.v.) spectrophotometry. In this paper we report on the mechanism of the reactions of phenyl-*aci*-nitromethane (**2**; Ar = Ph) and substituted phenyl-*aci*-nitromethanes; i.e., on the mechanism of some of the reactions summarized by equation [2], and the mechanism of **2** → **1**, the reverse of equation [1].

Experimental

Materials

Phenylnitromethane was prepared by alkaline nitration of phenylacetonitrile (5). Nitration of phenylnitromethane with fuming nitric acid was used to prepare *m*-nitrophenylnitromethane, m.p. 96-97.5°C (lit. 92-94°C (6)). *p*-Methylphenylnitromethane, b.p. 76-78°C/2mm (lit. 99°C/3mm) was prepared by the reaction of α-chloro-p-xylene with silver nitrite in diethyl ether (7). *o*-Methylphenylnitromethane, b.p. 86-89°C/2mm (lit. 137-39°C/23mm) was synthesized in a similar manner from α-chloro-o-xylene, and characterized by formation of the benzal derivative, m.p. 93.5-94°C (lit. 92°C (8)).

The sodium salt of phenylnitromethane was prepared by addition of a methanol solution of phenylnitromethane to an equivalent amount of sodium methoxide in methanol. The solution was partially evaporated to precipitate the *aci*-salt, filtered, and the precipitate washed well with anhydrous ether. The white powder obtained was dried *in vacuo*. A stock solution of the sodium salt of phenylnitromethane was prepared by dissolving 7.5 mg of the salt in 0.01 *N* sodium hydroxide solution (10 ml).

The salts and the stock solutions of *m*-nitrophenylnitromethane, *p*-methylphenylnitromethane, and *o*-methylphenylnitromethane were prepared by a similar procedure.

Kinetic runs

For each run, a 1.00 ml aliquot of the *aci*-salt stock solution at the reaction temperature was added to 25.00 ml of dilute sulfuric acid at the reaction temperature. After mixing, a spectrophotometer cell was rinsed with the reaction mixture, was then filled, and was placed in the temperature-controlled cell block of a Unicam SP800 spectrophotometer. After an equilibration period of one minute, the u.v. spectra of the cell contents were obtained as a function of time by scanning at intervals. "Infinity" readings were obtained after at least seven half-lives. The *pseudo*-first-order rate constant (k_ψ) was calculated from the data for the optical density *versus* time by a least-squares computer program. The concentration of the sulfuric acid was determined by titration of the reaction mixture with standard sodium hydroxide solution.

Phenyl-aci-nitromethane-α-d

Phenylnitromethane (194 mg) was dissolved in 2.5 N sodium deuteroxide in deuterium oxide (1 ml). The progress of the exchange was followed by proton magnetic resonance spectroscopy. After heating to 70°C for 6 hr, the resonance from the α-proton (τ 2.9) had been reduced to 10% of the starting value. A 4 μl aliquot of this solution was added to 25.00 ml of dilute sulfuric acid and the kinetics were followed as above.

Isolation of benzonitrile oxide

A solution of 100 mg of the sodium salt of phenylnitromethane in 0.01 N sodium hydroxide solution (2 ml) was added to 3.5 M sulfuric acid (8 ml), resulting in a 2.8 M concentration of sulfuric acid. Ninety seconds after mixing, the solution was shaken with an equal volume of carbon tetrachloride; the organic layer was separated and cursorily dried over magnesium sulfate. The infrared (i.r.) spectrum of the carbon tetrachloride solution was found to be identical with the spectrum of a solution of authentic benzonitrile oxide, prepared by the procedure of Wiley and Wakefield (9).

A similar extraction, carried out only thirty seconds after mixing, showed only a small peak at 2280 cm^{-1}, where benzonitrile oxide absorbs strongly, and a peak at 1650 cm^{-1} due to the *aci*-nitro group (10).

The first procedure above was repeated for the isolation of *m*-nitrobenzonitrile oxide from *m*-nitrophenyl-*aci*-nitromethane, but the medium used was 6.2 M sulfuric acid instead of 2.8 M. The i.r. spectrum of m-nitrobenzonitrile oxide in carbon tetrachloride showed characteristic absorptions at 2295, 1538, 1380 and 1350 cm^{-1}; these were observed also in the spectrum of authentic m-nitrobenzonitrile oxide (9).

Results and Discussion

Effect of Acid Concentration

Kornblum and Graham (11) isolated phenylnitromethane in 81% yield after addition of an excess of 20% hydrochloric acid to a strongly basic solution of phenylnitromethane at 5°C, and Kornblum and Brown (12) isolated p-nitrophenylnitromethane in 93% yield after the aci-form had been allowed to react with 3.5 N sulfuric acid for 45 min. However, when the sodium salt of p-nitrophenylnitromethane was added to 85% sulfuric acid at room temperature, a 86% yield of p-nitrobenzohydroxamic acid was isolated after a few minutes. Alkylhydroxamic acids have frequently been isolated from the Meyer reaction in concentrated acid, in which their hydrolysis to a carboxylic acid and hydroxylamine is slow (13).

It is evident, then, that phenyl-aci-nitromethane in acid can give either phenylnitromethane or the Meyer reaction products, depending on whether the acid is weak or strong.

Branch and Jaxon-Deelman (14) studied the transformation of phenyl-aci-nitromethane (2; Ar = Ph) to phenylnitromethane (1; Ar = Ph) in weak aqueous acid at 0°C. They came to the conclusion that the tautomerization proceeds by ionization of the aci-form (2) to the anion (5) (equation [4]) which is then C-protonated by the solvent to form the nitro tautomer (1) (equation [5]):

$$[4]\quad \underset{}{H_2O} + \underset{\underline{2}}{ArCH{=}NO_2H} \rightleftharpoons \underset{\underline{5}}{ArCH{=}NO_2^-} + \underset{\underline{3}}{H_3O^+}$$

$$[5]\quad \underset{\underline{5}}{ArCH{=}NO_2^-} + H_3O^+ \longrightarrow \underset{\underline{1}}{ArCH_2NO_2} + H_2O$$

We studied the kinetics of the disappearance of phenyl-aci-nitromethane in acid by u.v. spectroscopy at 274 nm. The rate of disappearance of the aci-form increased with increasing acidity (Table I). It was evident from the u.v. spectra (Fig. 1) that the nitro-form was not the only product from the reaction in 2 M sulfuric acid at 25.1°C. The spectra showed clearly the decay of the aci-form (λ_{max} 274 nm), the formation and subsequent decay of an intermediate having a u.v. peak at 241 nm, and finally the formation of benzohydroxamic acid, having a peak at 230 nm. Phenylnitromethane, the other product from the aci-form, showed only end-absorption. On heating the reaction mixture to 70°C for two days, both benzohydroxamic acid and phenylnitromethane were converted to benzoic acid (λ_{max} 230 nm), so that the peak at 230 nm increased by about 50%. Using the extinction coefficients at 230 nm of phenylnitromethane, benzohydroxamic acid and benzoic acid, it was possible to calculate the rates of formation of phenylnitromethane (k_{-1}) and of the intermediate leading to benzohydroxamic acid (k_2) (15) (Table I and Fig. 2).

TABLE I

Rate constants for reactions of phenyl-*aci*-nitromethane in sulfuric acid at 25.1°C

H_2SO_4 Conc'n ($\underline{M}$)	10^4k_ψ[a] (sec^{-1})	10^4k_{-1}[b] (sec^{-1})	10^4k_2[c] (sec^{-1})
0.010	23.4	20±1	3±1
0.520	27.5	22±1	6±1
1.45	35.2	18±2	17±2
1.70	37.9	16±2	22±2
1.99	44.1	14±3	30±3
2.51	66.	13±3	53±3
2.92	102.	15±5	87±5
3.14	113.	10±5	103±5
3.82	263.	10±10	258±15
4.01	325.	25±18	300±18

---

[a] pseudo-first-order rate constant for disappearance of the *aci*-form.

[b] pseudo-first-order rate constant for formation of the *nitro*-form.

[c] pseudo-first-order rate constant for formation of benzonitrile oxide.

FIGURE 1

The u.v. spectra showing the reaction of 0.00018 M phenyl-*aci*-nitromethane in 1.99 M sulfuric acid.

A. after 60 seconds at 25.1°C.

B. after 3000 seconds at 25.1°C.

C. after 2 days at 70°C.

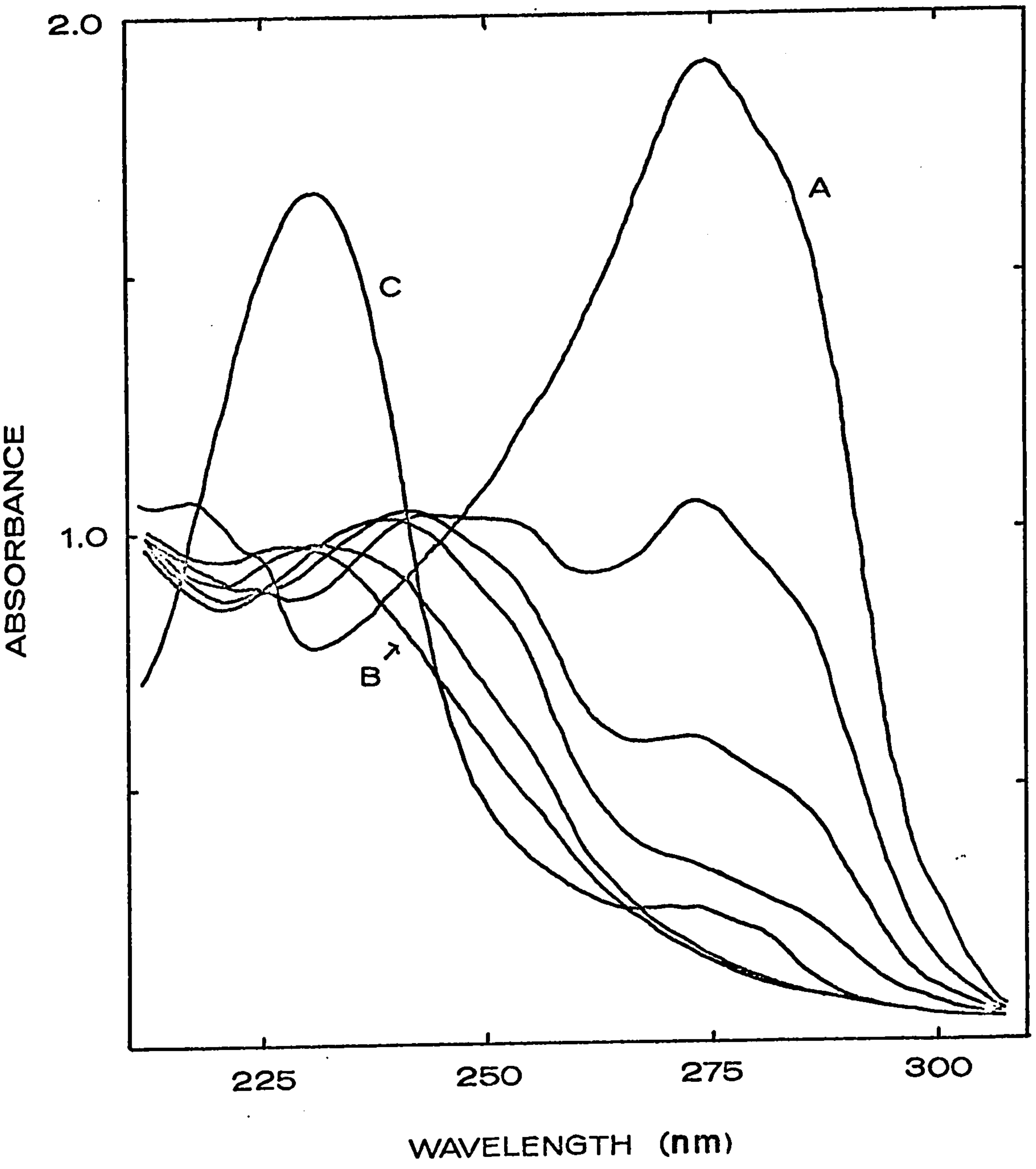

2.0
1.0
ABSORBANCE
225
250
275
300
WAVELENGTH (nm)
A
B
C

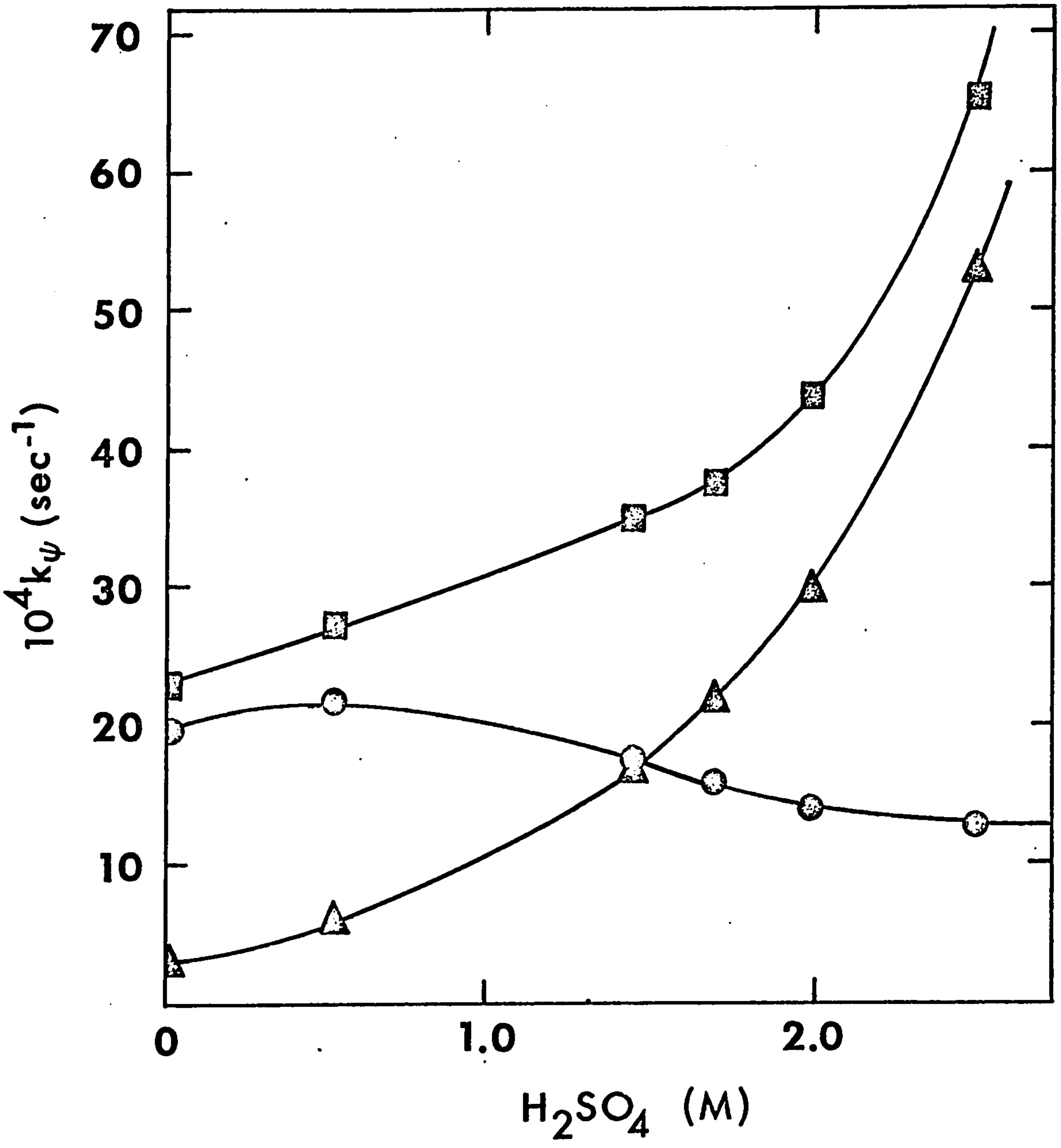
FIGURE 2

Rate profiles for the reaction of phenyl-*aci*-nitromethane in sulfuric acid at 25.1°C.

■ pseudo-first-order rate constants for the disappearance of the *aci*-form.

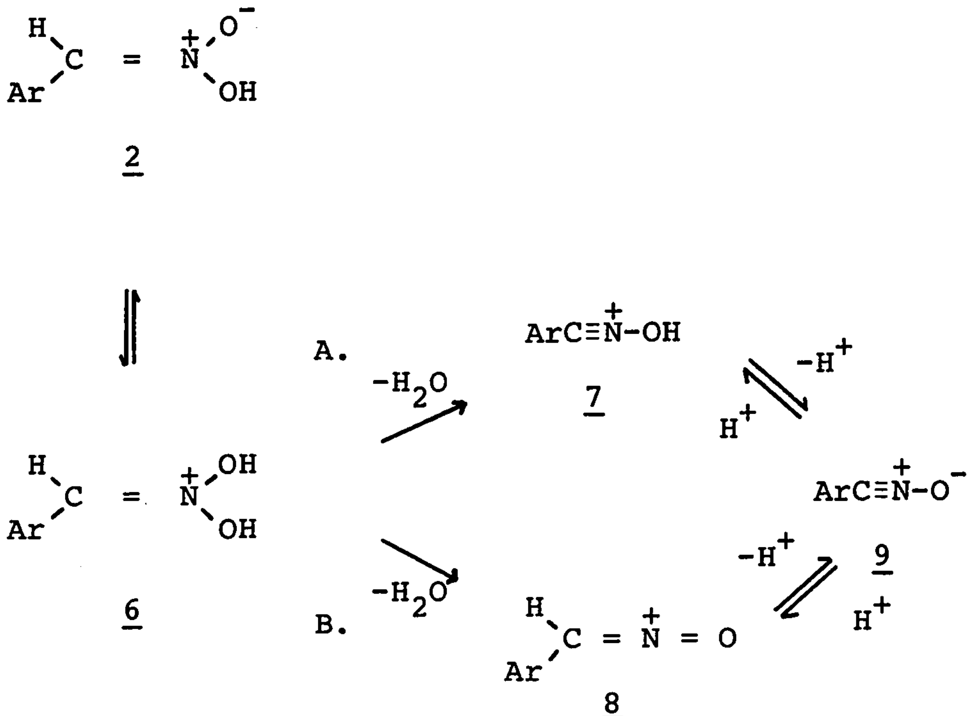
● pseudo-first-order rate constants for the formation of the *nitro*-form.

▲ pseudo-first-order rate constants for the formation of benzonitrile oxide.


70
60
50
40
30
20
10
$10^4 k_\psi$ (sec^{-1})
0
1.0
2.0
H_2SO_4 (M)

The intermediate was extracted from a more concentrated reaction mixture into carbon tetrachloride and identified as benzonitrile oxide (9) by infrared spectroscopy. It is shown in a following paper that benzonitrile oxide is hydrolyzed in acid cleanly to benzohydroxamic acid under the conditions of temperature and acid concentration employed in the present study.

Two mechanisms may be postulated (Reaction Scheme I) for the conversion of phenyl-aci-nitromethane (2) to benzonitrile oxide (9). Cundall and Locke (3) proposed path B, without any experimental evidence to support the proposal,



REACTION SCHEME I

as well as another path not involving a nitrile oxide. However, an alternative pathway (A) to benzonitrile oxide may be envisaged. These two paths A and B are discussed below, and a choice between them is made. For the present it is sufficient to note that both mechanisms involve the formation of the protonated aci compound 6, and hence both require acid-catalysis for the formation of the nitrile oxide 9, as is observed (Fig. 2).

On the other hand, the formation of phenylnitromethane from phenyl-aci-nitromethane is inhibited by high acidities (Fig. 2). This evidence is in accord with the mechanism proposed in equations [4] and [5] (14,16), high acidities preventing the formation of the anion 5 and hence the nitro compound 1.

Isotope Effects

In an attempt to discriminate between the two possible paths A and B in the formation of the nitrile oxide 9 from the aci compound 2, we have determined the rates for the reactions of α-deuterio-aci-phenylnitromethane in acid solution. Significant stretching of the carbon-deuterium bond in the rate-controlling step would cause at least a two-fold decrease in the reaction rate (17). The results (Table II) indicate that the α-hydrogen bond is not stretched in the transition state for the rate-determining step in the formation of the nitrile oxide. These results would seem to exclude path A, since the step 6 → 7 would certainly be the slow step in this mechanism. The evidence can be construed as evidence in support of reaction path B if the dehydration 6 → 8 is the slow step in the reaction.

No primary isotope effect would be expected for the

TABLE II

Isotope effects for reactions of phenyl-aci-nitromethane in sulfuric acid at 25.1°C

Compound	H_2SO_4 Conc'n (M)	$10^4 k_\psi$[a] (sec^{-1})	$10^4 k_{-1}$[b] (sec^{-1})	$10^4 k_2$[c] (sec^{-1})
$\phi CD{=}NO_2H$	0.520	27.5±0.4	21±1	7±1
$\phi CH{=}NO_2H$	0.520	27.5±0.4	22±1	6±1
$\phi CD{=}NO_2H$	2.09	46.4±1.6	18±3	28±3
$\phi CH{=}NO_2H$	2.09[d]	46.8±1.6	14±3	33±3

[a] pseudo-first-order rate constant for disappearance of the aci-form.

[b] pseudo-first-order rate constant for formation of the nitro-form.

[c] pseudo-first-order rate constant for formation of benzonitrile oxide.

[d] value interpolated from rate data in Table I.

tautomerization 1 → 2, if it proceeds by the mechanism of equation [1], and none is found (Table II).

Substituent Effects

The rate of disappearance of m-nitrophenyl-aci-nitromethane in sulfuric acid at room temperature was followed by u.v. spectrophotometry at 285 nm (Table III and Fig. 3). In dilute acid, the disappearance of this substituted aci-form was faster than the disappearance of the unsubstituted aci-form. Cooke and Macbeth (16) observed a similar increase in tautomerization rates of other substituted phenyl-aci-nitromethanes in water when the substituents were electron-withdrawing. This can be understood in terms of the mechanism of equations [4] and [5], if the effect of the electron-withdrawing substituent in making the substituted aci-form a stronger acid, and hence increasing the concentration of the anion 5 (equation [4]) is more important than its effect in decreasing the rate of protonation of 5 to form 1 (equation[5]).

In dilute acid, the m-nitro group can be expected not only to accelerate the conversion of the aci-form 2 to the nitro form 1, but to retard the formation of m-nitrobenzonitrile oxide 9 (and thence of m-nitrobenzohydroxamic acid) by making the aci-form 2 a weaker base in the reaction 2 → 6 (Reaction Scheme I). For these reasons, no m-nitrobenzonitrile oxide or m-nitrobenzohydroxamic acid are observed as products in dilute acid (< 4 M). However, at high enough acid concentrations the rate of formation of the nitro compound is sufficiently depressed (by repression of reaction [4]), and

TABLE III

Pseudo-first-order rate constants (k_ψ) for disappearance of substituted phenyl-aci-nitromethanes in sulfuric acid at 25.4°C

H_2SO_4 Conc'n ($\underline{M}$)	$\underline{p}$-methyl- $10^4 k_\psi$ (sec^{-1})	$\underline{o}$-methyl- $10^4 k_\psi$ (sec^{-1})	$\underline{m}$-nitro- $10^4 k_\psi$ (sec^{-1})
0.010	12.3	30.9	138.
0.520	18.4	40.5	----
1.12	27.2	50.	----
1.45	34.7	54.	----
1.73	-----	67.	----
2.09	54.	82.	----
2.37	74.	97.	124.
2.69	101.	-----	----
2.92	-----	188.	104.
3.14	146.	-----	----
4.01	-----	-----	78.
4.83	-----	-----	78.
5.69	-----	-----	108.
6.49	-----	-----	270.

FIGURE 3

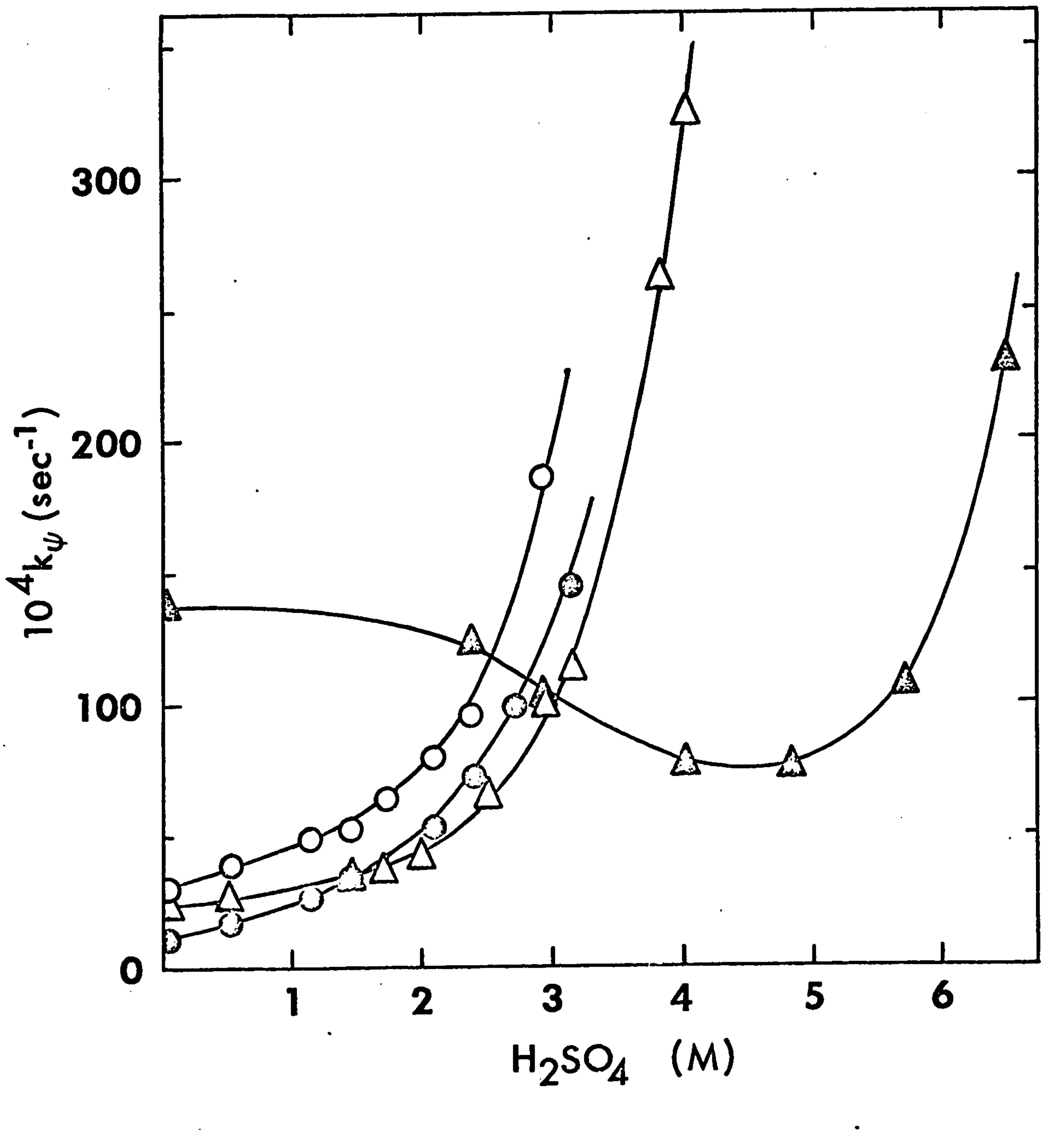
Rate profiles for the disappearance of phenyl-aci-nitromethanes in sulfuric acid.

△ phenyl-aci-nitromethane (25.1°C).

○ o-methylphenyl-aci-nitromethane (25.4°C).

● p-methylphenyl-aci-nitromethane (25.4°C).

▲ m-nitrophenyl-aci-nitromethane (25.4°C).



300
200
100
0
1
2
3
4
5
6
$10^4 k_\psi$ (sec^{-1})
H_2SO_4 (M)

the rate of formation of the nitrile oxide sufficiently enhanced (by protonation of *2* → *6*), for *m*-nitrobenzonitrile oxide (λ_{max} 243 nm) to become apparent in the reaction mixture. It rapidly adds water to form *m*-nitrobenzohydroxamic acid (λ_{max} 215 nm). Some *m*-nitrobenzonitrile oxide was extracted from a concentrated solution of the *aci*-compound in 6.2 *M* sulfuric acid, and identified by its i.r. spectrum.

The rates of disappearance of *p*-methylphenyl-*aci*-nitromethane and *o*-methylphenyl-*aci*-nitromethane in sulfuric acid were determined by following the decay of their absorption peaks at 280 nm (Table III and Fig. 3). Even in 1 *M* sulfuric acid, some *o*- and *p*- methylbenzonitrile oxide is observed during the reaction of both substituted *aci*-forms, so the observed rate of disappearance is a combination of the rate of tautomerization to the *nitro*-form and the rate of dehydration to *o*- and *p*- methylbenzonitrile oxide. It is evident from the results that both of these reactions are accelerated by the proximity of the methyl group to the reaction site. The molecular model of the *ortho*-substituted *aci*-form shows some crowding, which is relieved on dehydration by path A or B of reaction scheme I. The strain is also relieved on tautomerization to the *nitro*-form. A steric acceleration of the tautomerization in water has already been observed for *o*-chloro- and *o*-bromophenyl-*aci*-nitromethane (16).

Activation Parameters

The entropies of activation calculated for the disappearance of phenyl-*aci*-nitromethane in acid are negative

(Table IV) over a range of acid concentration. It must be kept in mind that the disappearance of the aci-form takes place by two paths: tautomerization to the nitro-form and dehydration to benzonitrile oxide. As the acid concentration is increased, the increase in the entropy of activation is due to the greater contribution of the dehydration path to the disappearance. Such a process would be expected to have a higher entropy of activation than the proton transfer necessary for tautomerization (18).

There is little change in the enthalpy of activation for the disappearance as the acid concentration is increased. This indicates that for a particular acid concentration, the ratio of the rates of the two reactions (tautomerization and dehydration) would remain approximately constant as the temperature is raised.

Conclusions

This study has shown that the pseudo-first-order rate constant (k_ψ) for the disappearance of phenyl-aci-nitromethane (2) in acid is made up of two rate constants: k_{-1} for the tautomerization to the nitro form (1), and k_2 for the dehydration to benzonitrile oxide (9):

$$\underset{\underline{1}}{ArCH_2NO_2} \quad \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \quad \underset{\underline{2}}{ArCH{=}NO_2H} \quad \xrightarrow{k_2} \quad \underset{\underline{9}}{ArC{\equiv}\overset{+}{N}{-}O^-} \quad + \quad H_2O$$

The mechanisms of these reactions have been discussed, and account for the fact that while in dilute acid $k_{-1} > k_2$, in

TABLE IV

Activation parameters for disappearance of phenyl-*aci*-nitromethane in sulfuric acid

Temp. (°C)	H_2SO_4 Conc'n ($\underline{M}$)	10^4k_ψ (sec^{-1})	$\Delta H_\ddagger$ (kcal/mole)	$\Delta S_\ddagger$ (e.u.)
25.1	0.520	27.5	17±1	-14±1
34.2	0.520	63.7		
25.1	1.70	37.9	19±1	- 7±1
34.2	1.70	96.		
25.1	2.51	65.7	18±1	- 7±1
34.2	2.51	165.		

strong acid $k_2 \gg k_{-1}$. The activation parameters indicate that the relative rates would not change greatly with temperature.

Acknowledgments

For work in this and the following two papers, we are pleased to acknowledge the skillful technical assistance of James Tong, the grant of a McConnell Fellowship by McGill University (to P.H.T.) for 1968-70, and the financial support of the Defence Research Board of Canada.

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PART II

The reactions in acid of benzonitrile oxide and benzohydroxamic acid

Abstract

The kinetics of the transformation of benzonitrile oxide in dilute sulfuric acid into benzohydroxamic acid have been followed by u.v. spectrophotometry at a temperature near room temperature. A mechanism is proposed on the basis of the effects of substituents and sulfuric acid concentration.

The rate profile for the hydrolysis of benzohydroxamic acid in hot dilute sulfuric acid has been obtained.

The results of these studies are applied to the detailed mechanism of the Meyer rearrangement-hydrolysis of phenylnitromethane in acid.

La cinétique de formation de l'acide benzohydroxamique à partir de l'oxyde de benzonitrile dans l'acide sulfurique a été étudiée à la température ambiante. Afin de proposer un mécanisme pour cette réaction on a étudié l'influence de divers substituants et de différentes concentrations d'acide.

La vitesse de l'hydrolyse de l'acide benzohydroxamique a été étudiée à 68.8°C en variant la concentration de l'acide sulfurique.

Les conclusions de ces études sont appliquées au mécanisme de la réaction de Meyer sur le phénylnitrométhane.

Introduction

In an example of the Meyer reaction, phenylnitromethane forms benzoic acid and hydroxylamine when heated in mineral acid (1). The slowest step in the reaction sequence

[1] $\mathrm{ArCH_2NO_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ArCH = NO_2H}$

[2] $\mathrm{ArCH = NO_2H} \xrightarrow[k_2]{} \mathrm{ArC \equiv \overset{+}{N} - O^{-} + H_2O}$

[3] $\mathrm{ArC \equiv \overset{+}{N} - O^{-} + H_2O} \longrightarrow \mathrm{ArCONHOH}$

[4] $\mathrm{ArCONHOH + H_2O} \longrightarrow \mathrm{ArCO_2H + NH_2OH}$

is the formation of phenyl-*aci*-nitromethane (equation [1]) (2), and in the preceding paper (3) we have studied the rate at which phenyl-*aci*-nitromethane reverts to phenylnitromethane (k_{-1} of reaction [1]) and the rate at which it is dehydrated to benzonitrile oxide (k_2 of reaction [2]). It is already known that benzonitrile oxide in acid solution adds water to form benzohydroxamic acid (equation [3]) (4) (which has been isolated in small yield from the reaction of phenylnitromethane in hot acid (5)), and that benzohydroxamic acid is hydrolyzed to benzoic acid and hydroxylamine (equation [4]) (6), but no kinetic studies have been reported for these reactions. We now report these, as a part of an overall study of the Meyer reaction of phenylnitromethane described in this and two accompanying papers (3,7).

Experimental

Preparation of benzonitrile oxide

Benzohydroximoyl chloride (m.p. 50-52°C) was prepared by the chlorination of benzaldoxime in hydrochloric acid (8). A solution of 30 mg of benzohydroximoyl chloride in 5 ml of carbon tetrachloride was shaken with 5 ml of water, the organic layer was drawn off and dried with magnesium sulfate at 0°C. The infrared (i.r.) spectrum of this solution showed the same distinctive absorptions at 2290, 1368, 1096, and 1029 cm^{-1} that are found in the spectrum of authentic benzonitrile oxide prepared using sodium carbonate solution (8). The carbon tetrachloride solution was extracted with water and the ultraviolet (u.v.) spectrum of the extract showed an absorption at 245 nm with a slight shoulder at 253 nm. This is identical with the spectrum of authentic benzonitrile oxide in water.

The addition of aqueous sodium carbonate to this solution of benzonitrile oxide in the spectrophotometer cell initiated a change in the u.v. spectrum, which passed with an isosbestic point from an absorption with λ_{max} 245 nm to one with λ_{max} 268 nm. The product was identified as benzohydroxamate anion on the basis of its u.v. spectrum and the spectrum of benzohydroxamic acid obtained on acidification (λ_{max} 230 nm).

Kinetic runs on the benzonitrile oxides

1) From benzohydroximoyl chloride:

A 10^{-3} *M* stock solution of benzonitrile oxide was prepared by dissolving 15 mg benzohydroximoyl chloride in 25 ml distilled water. A one ml aliquot of this stock solution at the reaction temperature was added to 25.00 ml dilute sulfuric acid, which was pre-equilibrated at the reaction temperature. After mixing, a one cm spectrophotometer cell was rinsed with the reaction mixture, was then filled, and placed in the temperature-controlled cell block of a Unicam SP800 spectrophotometer. After an equilibration period of at least one minute, the u.v. spectrum was scanned at recorded time intervals. The spectrum at "infinite" time was recorded after at least seven half-lives. The optical densities (A) were measured from the spectra at 243 nm, and the first-order rate constant was obtained from a computer-calculated least-squares plot of $\ln(A_t - A_\infty)$ versus time. The concentration of the sulfuric acid solution was determined after the run by titration of the reaction mixture with standard alkali. A similar procedure was used for preparation of m-nitrobenzonitrile oxide from m-nitrobenzohydroximoyl chloride for the kinetic experiments in dilute sulfuric acid.

2) From phenyl-aci-nitromethane:

The procedure used to determine the rate of reaction of phenyl-aci-nitromethane in acid solution has been described in the preceding paper (3). At some acid concentrations, the u.v. spectra still show the presence of benzonitrile oxide after at least 90% of the phenyl-aci-nitromethane has reacted. The disappearance of this benzonitrile oxide has been followed by repetitive scanning at recorded time intervals with an equilibrium reading taken after at least seven half-lives. The data for the optical density versus time were treated as above to obtain the first-order rate constant.

A similar procedure was used to follow the reactions of m-nitrobenzonitrile oxide at 245 nm, o-methylbenzonitrile oxide at 250 nm, and p-methylbenzonitrile oxide at 256 nm.

Hydrolysis of benzohydroxamic acid

One ml of an aqueous stock solution of benzohydroxamic acid was added to 25.00 ml of dilute sulfuric acid to produce a final concentration of benzohydroxamic acid of 0.0007 M. Two ml aliquots of this reaction mixture were measured into screw-capped glass vials. These sample tubes were heated in a thermostatted water bath to 68.8°C. After an equilibration period of forty-five minutes, tubes were removed at different time intervals, cooled in ice and quenched with three ml of cold 9 N sodium hydroxide solution. The samples were then scanned with the Unicam SP800 to determine benzohydroxamate anion at 270 nm. The sample for determination at "infinite" time was withdrawn after at least seven half-lives. The data for the optical density and time were treated as above to obtain the first-order rate constant.

Results and Discussion

(A) Preparation of benzonitrile oxide and substituted derivatives

In concentrated solution, unhindered benzonitrile oxides dimerize quickly to form furoxans (9). Dilute solutions of unhindered benzonitrile oxides are stable enough for their infrared spectra to be recorded (8). We have found that 10^{-3} M solutions of benzonitrile oxide in water are stable for hours, but that they react rapidly to form benzohydroxamic acid on addition of sulfuric acid. The addition of sodium carbonate to an aqueous solution of benzonitrile oxide results in the formation of benzohydroxamate anion in a few minutes.

A stock solution of benzonitrile oxide was prepared by dissolving benzohydroximoyl chloride in water: water is sufficiently basic to bring about the immediate formation of benzonitrile oxide from benzohydroximoyl chloride under these conditions. An aliquot of the stock solution was added to a sulfuric acid solution and the disappearance of benzonitrile oxide was followed by u.v. spectrophotometry.

In the same manner, it was possible to prepare a stock solution of _m_-nitrobenzonitrile oxide from _m_-nitrobenzohydroximoyl chloride. However, it was found more convenient to prepare this nitrile oxide by allowing _m_-nitrophenyl-_aci_-nitromethane to react in strong acid solution. The products of this reaction are _m_-nitrophenylnitromethane, which is stable (under the conditions of the reaction), and _m_-nitrobenzonitrile oxide, which reacts further to form _m_-nitrobenzohydroxamic acid. The latter reaction can be followed by u.v. spectrophotometry.

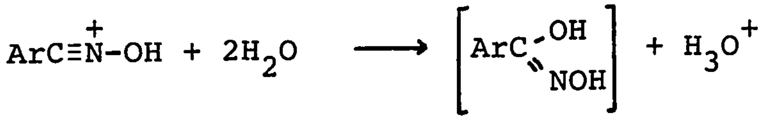
Both _p_-methylbenzonitrile oxide and _o_-methylbenzonitrile oxide were prepared in similar fashion from the corresponding methylphenyl-_aci_-nitromethanes.

(B) The reaction in acid of the benzonitrile oxides. Effect of acid concentration

In sulfuric acid, benzonitrile oxide reacts cleanly to form benzohydroxamic acid. This is shown by the u.v. spectra, which during the reaction exhibit a sharp isosbestic point at a wavelength between those of the absorption peaks of starting material at 245 nm and of product at 228 nm. Increasing the acid concentration of the medium causes an increase in the rate of the reaction (Table I). This marked effect of acid concentration suggests an equilibrium protonation preceding the nucleophilic attack by water.

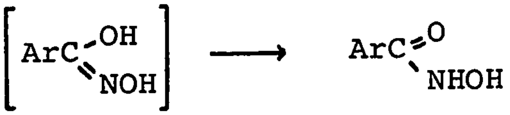
[5] $$\mathrm{ArC{\equiv}\overset{+}{N}{-}O^{-}} + \mathrm{H_3O^{+}} \rightleftharpoons \mathrm{ArC{\equiv}\overset{+}{N}{-}OH} + \mathrm{H_2O}$$

[6]



$$\mathrm{ArC{\equiv}\overset{+}{N}{-}OH} + \mathrm{2H_2O} \longrightarrow \left[\mathrm{ArC}\begin{array}{l}\mathrm{{-}OH}\\ \mathrm{{=}NOH}\end{array}\right] + \mathrm{H_3O^{+}}$$

[7]



$$\left[\mathrm{ArC}\begin{array}{l}\mathrm{{-}OH}\\ \mathrm{{=}NOH}\end{array}\right] \longrightarrow \mathrm{ArC}\begin{array}{l}\mathrm{{=}O}\\ \mathrm{{-}NHOH}\end{array}$$

The carbonyl form of benzohydroxamic acid has already been identified, by u.v. and i.r. spectroscopy (10,11), as the stable tautomer.

Over the range of acid concentrations studied, the rates of reaction of benzonitrile oxide are slightly slower than the rates of its formation from the aci-form. This accounts for the observation of benzonitrile oxide as an intermediate during the reaction of the aci-form, as described in the preceding paper (3).

Substituent effects

With increasing acid concentration, m-nitrobenzonitrile oxide exhibits an increase in the rate of reaction (Table II). However, compared to unsubstituted benzonitrile oxide, the onset of the rapid increase in the rate of reaction is delayed until higher acid concentrations. This behaviour may be explained by reference to equations [5] and [6]: the

TABLE I

Pseudo-first-order rate constants (k_ψ) for the reaction of benzonitrile oxide in sulfuric acid

Temperature (^{o}C)	H_2SO_4 Conc'n (M)	10^4k_ψ (sec^{-1})
20.6	1.45	5.0 [a]
"	2.51	11.8 [a]
"	3.36	22.7 [a]
"	4.07	39.6 [a]
25.1	1.45	7.8 [b]
"	1.70	8.8 [b]
"	1.99	12.6 [b]
"	2.51	19.7 [b]
"	4.01	46.0 [b]
35.0	0.195	2.09 [a]
"	1.45	19.2 [a]

[a] benzonitrile oxide prepared from benzohydroximoyl chloride (see Experimental).

[b] benzonitrile oxide prepared from phenyl-*aci*-nitromethane.

TABLE II

Pseudo-first-order rate constants (k_ψ)
for the reaction of m-nitrobenzonitrile oxide
in sulfuric acid

Temperature (°C)	H_2SO_4 Conc'n (M)	$10^4 k_\psi$ (sec^{-1})
20.6	1.45	2.32[a]
"	4.07	7.1[a]
"	4.53	10.0[a]
"	5.69	14.6[a]
25.4	5.69	23.4[b]
"	6.49	35.9[b]
"	7.33	56.6[b]
"	9.18	136.[b]

[a] m-nitrobenzonitrile oxide prepared from m-nitrobenzohydroximoyl chloride (see Experimental).

[b] m-nitrobenzonitrile oxide prepared from m-nitrophenyl-aci-nitromethane.

electron-withdrawing group makes the m-nitrobenzonitrile oxide less basic that unsubstituted benzonitrile oxide, requiring a more strongly acidic medium to form the same concentration of protonated substrate. On the other hand, the rate of reaction [6] is subject to an increase when Ar is substituted with an electron-withdrawing group, because of the enhanced electrophilicity of the substituted compound. The two effects (on reactions [5] and [6]) are in opposition, but in the present instance the effect of the m-nitro group on reaction [5] is greater than its effect on reaction [6], so that a slower reaction results. A similar result has been reported for the acid-catalyzed hydrolysis of benzalanilines (12) and benzamides (13). Jencks (14) has recently discussed this balance between the substituent effects for a rate-determining step and a preceding equilibrium.

Up to a concentration of at least 9 M sulfuric acid, the rate of destruction of m-nitrobenzonitrile oxide is slower than its rate of formation from the aci-form, so m-nitrobenzonitrile oxide should be observed spectroscopically if it is an intermediate during the reaction of m-nitrophenyl-aci-nitromethane in acid. Consequently, failure to observe m-nitrobenzonitrile oxide during the reaction of m-nitrophenyl-aci-nitromethane in sulfuric acid of less than 4 M concentration (3) indicates that in these acid concentrations $k_{-1} >> k_2$.

Steric effects

The rate profiles for p-methylbenzonitrile oxide and *o*-methylbenzonitrile oxide (Table III) illustrate the rate decrease caused by the proximity of a methyl group to the reaction site. The steric effect lends support to the designation of reaction [6] as the rate-determining step in the hydrolysis of nitrile oxides, since the formation of *o*-methylbenzohydroxamic acid would be slowed by hindrance to nucleophilic attack by water.

Activation parameters

The rates of reaction of benzonitrile oxide in 1.45 *M* sulfuric acid at 20.6°C, 25.1°C, and 35.0°C (Table I) have been used to calculate the approximate enthalpy and entropy of activation for the reaction: $\Delta H_{=}$ = 17 kcal/mole, and $\Delta S_{=}$ = -16 e.u. The entropy of activation is negative, as expected for a nucleophilic attack of water in the rate-determining step (15). Similar values are obtained from the data in Table II for *m*-nitrobenzonitrile oxide in 5.69 *M* sulfuric acid: $\Delta H_{\ddagger}$ = 17 kcal/mole, and $\Delta S_{\ddagger}$ = -13 e.u.

(C) The Hydrolysis of Benzohydroxamic Acid

The rates of hydrolysis of benzohydroxamic acid in sulfuric acid were obtained at 68.8°C by quenching aliquots of the reaction mixture in base (Table IV). This procedure permitted determination of the resulting benzohydroxamate anion by u.v. spectrophotometry at 270 nm, where benzoate anion does not interfere (10). Over the range of acid concentrations, the rates observed are greater than the rates of the Meyer rearrangement-hydrolysis of phenylnitromethane at 68.8°C (7); this accounts for the failure under these conditions to

TABLE III

Pseudo-first-order rate constants (k_ψ)
for the reaction of methylbenzonitrile oxides
with sulfuric acid at 25.4°C

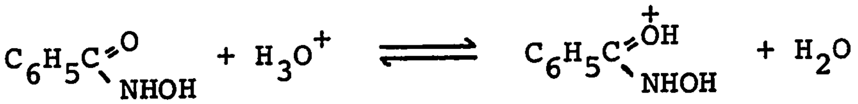
H_2SO_4 Conc'n (*M*)	*p*-methyl 10^4k_ψ (sec^{-1})	*o*-methyl 10^4k_ψ (sec^{-1})
0.520	-	5.5
1.12	9.2	6.7
1.45	12.7	7.4
1.73	-	8.9
2.09	20.4	12.4
2.37	31.5	16.4
2.69	38.6	-
2.92	-	25.0
3.14	55.6	-

TABLE IV

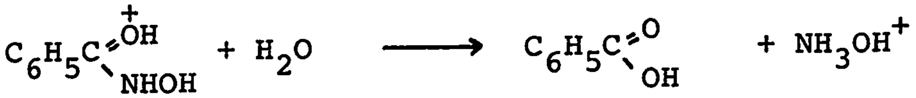
Pseudo-first-order rate constants (k_ψ)
for hydrolysis of benzohydroxamic acid
in sulfuric acid at 68.8°C

H_2SO_4 Concentration (M)	10^5k_ψ (sec^{-1})
.195	2.32
.520	6.39
1.12	12.2
1.73	17.4
2.37	24.6
3.14	37.1
4.53	32.0

observe benzohydroxamic acid as an intermediate. The rate of hydrolysis of benzohydroxamic acid, like that of benzamide (16), passes through a maximum as the acid concentration is increased, and probably involves a similar mechanism (16,17):

[8] 

$$C_6H_5C(=O)NHOH + H_3O^+ \rightleftharpoons C_6H_5C(=\overset{+}{O}H)NHOH + H_2O$$

[9] 

$$C_6H_5C(=\overset{+}{O}H)NHOH + H_2O \longrightarrow C_6H_5C(=O)OH + NH_3OH^+$$

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PART III

The *nitro*-*aci* tautomerization

Abstract

The rate-acidity profiles for the Meyer rearrangement-hydrolysis of phenylnitromethane in sulfuric, perchloric and hydrochloric acid show a maximum near 3 M acid. Ring-substituted phenylnitromethanes also show a maximum in their rate profiles, at slightly different acid concentrations. These maxima arise because the slow formation of the aci-form is followed by two competing reactions: fast tautomerization back to the nitro-form, and fast rearrangement-hydrolysis to the Meyer products. The rearrangement is rate-limiting in dilute acid and is acid-catalyzed, causing the rate increase. In more concentrated acid, the rate-limiting step is the nitro to aci tautomerization, which is not acid-catalyzed, and which goes more slowly as the activity of water decreases.

The tautomerization was studied by means of primary and solvent deuterium isotope effects, and was found to occur through proton abstraction by water, through a transition state closely resembling the products.

En variant la concentration d'acide sulfurique, hydrochlorique, ou perchlorique, on obtient un maximum aux environs de 3 M acide dans la vitesse de la réaction de Meyer sur le phénylnitrométhane. Avec les phénylnitrométhanes substitués on obtient aussi un maximum de vitesse, mais à de différentes molarités d'acide.

La présence de ce maximum peut être expliquée par ce schéma de réaction: la formation lente de la forme aci,

suivie par deux réactions rapides et concurrentes: une réaction de tautomérisation redonnant la forme nitro, et une réaction de réarrangement menant finalement aux produits Meyer. Au-dessous du maximum, la réaction de réarrangement, catalysée par l'acide, contrôle la vitesse de la réaction globale menant aux produits Meyer. Au-dessus du maximum, la réaction de tautomérisation redonnant la forme nitro est supprimée par l'acide, de sorte que la vitesse de la réaction globale de Meyer est contrôlée par la formation lente de la forme aci. Celle-ci est ralentie à mesure qu'on augmente la concentration de l'acide.

Afin d'éclaircir le mécanism de la formation lente de la forme aci, on a étudié les effets produits par une substitition de deutérium dans le solvant ou dans de phénylnitrométhane. Les resultats indiquent que l'abstraction du proton α par l'eau passe par un état de transition ressemblant fortement aux produits.

Introduction

The work done up to 1955 on the Meyer reaction (1) (a rearrangement-hydrolysis) has been reviewed by Noland (2), who proposed the formation of the *aci*-nitroalkane (equation [1]) as the slow step, followed by a series of rapid reactions in the acidic medium. This mechanism was based on the work of Junell (3), who showed that the rate of hydrolysis of nitroethane was the same as its rate of bromination. Our study of the reaction of phenyl-*aci*-nitromethane in acid (4) has shown that, at least for phenylnitromethane in dilute acid, this reaction scheme must be modified by the addition of a fast back-reaction from phenyl-*aci*-nitromethane to phenylnitromethane (equation [2]). The identification of benzonitrile oxide formed by the mechanism of equations [3] - [5], as an intermediate in the rearrangement of phenyl-*aci*-nitromethane to benzohydroxamic acid was also reported at that time. The mechanism of the hydration

[1] $RCH_2NO_2 \xrightarrow{k_1} RCH{=}NO_2H$

[2] $RCH{=}NO_2H \xrightarrow{k_{-1}} RCH_2NO_2$

[3] 

$$H_3O^+ + RCH{=}NO_2H \rightleftharpoons RCH{=}\overset{+}{N}\begin{matrix}OH\\OH\end{matrix} + H_2O$$

[4] 

$$RCH{=}\overset{+}{N}\begin{matrix}OH\\OH\end{matrix} \longrightarrow RCH{=}\overset{+}{N}{=}O + H_2O$$

[5] $H_2O + RCH{=}\overset{+}{N}{=}O \rightleftharpoons RC{\equiv}\overset{+}{N}{-}O^- + H_3O^+$

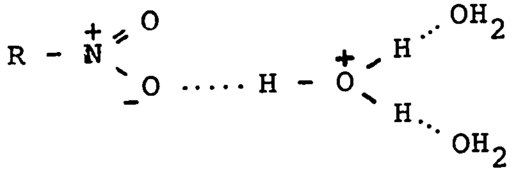
[6] $RC{\equiv}\overset{+}{N}{-}O^- + H_3O^+ \rightleftharpoons RC{\equiv}\overset{+}{N}{-}OH + H_2O$

[7] $2H_2O + RC{\equiv}\overset{+}{N}{-}OH \longrightarrow RCONHOH + H_3O^+$

[8] $H_3O^+ + RCONHOH \longrightarrow RCOOH + NH_3OH^+$

of benzonitrile oxide (equations [6] and [7]), and of the hydrolysis of benzohydroxamic acid (equation [8]) were discussed in a second paper (5). In the present paper we consider reaction [1], the rate-determining step under some (but as it will be shown, not all) conditions of the reaction.

The details of this rate-determining step may be tested by following the dependence of the overall reaction rate on the acidity of the medium. Cundall and Locke (6) found that the rate profile for the Meyer reaction of nitromethane in hydrochloric acid passed through a maximum at 4 M hydrochloric acid. After a slight decline, the rate continued to increase with increasing acidity up to 10 M hydrochloric acid, the highest concentration studied. A possible explanation for the maximum at 4 M acid in the rate profile could have been the essentially complete protonation of nitromethane at that acidity; however, Gillespie (7) had already reported that nitromethane is only 21% protonated in 100% sulfuric acid. Alternatively, the maximum could be explained by the essentially complete formation of a hydrogen-bonded complex (8,9,10,11), in 4 M acid:



Similar hydrogen-bonded complexes of ketones in moderate concentrations of acid have been proposed (12), and may be intermediates in the enolization of ketones in acid (13). However, Haldna (8) has presented evidence that the formation of a hydrogen-bonded complex of nitromethane does not affect the rate of bromination of nitromethane in dilute sulfuric acid, and we show in this paper that the maximum in the rate of formation of Meyer products from phenylnitromethane also is not explained by formation of such a complex.

Experimental

Materials

The preparation of phenylnitromethane, m-nitrophenylnitromethane, p-methylphenylnitromethane and o-methylphenylnitromethane has been described in a previous paper (4). p-Nitrophenylnitromethane, m.p. 89-91.5°C (lit. 89-90.5°C) (14) and p-chlorophenylnitromethane, m.p. 31-31.5°C (lit. 33°C) (15), were prepared by reaction of the substituted benzyl halide with silver nitrite in diethyl ether. 2,4,6-Trimethylphenylnitromethane, m.p. 74-74.5°C, was prepared from 2,4,6-trimethylbenzyl chloride and silver nitrite in diethyl ether (14) and was characterized by its i.r. spectrum (1550 cm^{-1} and 1367 cm^{-1}) and its p.m.r. spectrum (singlet 3.17τ for 2 protons, singlet 4.60τ for 2 protons, and two singlets 7.68τ and 7.75τ with total 9 protons).

Anal. Calcd. for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31. Found: C, 67.19; H, 7.35.

All the phenylnitromethanes were stored at -20°C until used.

Deuteriosulfuric acid (99%D) of spectroscopic quality was obtained from Merck, Sharp and Dohme of Canada, Limited.

Phenylnitromethane-α,α-d_2 was prepared by the exchange of phenylnitromethane in alkaline deuterium oxide (16). After acidification with deuteriosulfuric acid, the deuterated phenylnitromethane was extracted out with carbon tetrachloride. The organic solution was dried and evaporated. Analysis for residual hydrogen in the deuterated phenylnitromethane by p.m.r. spectroscopy showed an isotopic purity of 97%D at the alpha-position.

Procedures for kinetic runs

(A) Sufficient phenylnitromethane was dissolved in water or 50% ethanol to give a 0.003 M solution. A four ml aliquot of this stock solution was added to 100.0 ml of dilute mineral acid in a stoppered flask. The flask was then immersed in a thermostatted water bath (±0.05°C) and allowed to warm up for forty-five minutes. (Separate experiments showed that thermal equilibrium was reached in less than this time.) Five ml aliquots were withdrawn at recorded time intervals, cooled in ice and scanned with a Unicam SP800 spectrophotometer. The aliquot for "infinite" time was withdrawn after at least seven half-lives.

Alternatively, the reaction mixture was subdivided into screw-capped vials before heating to the reaction temperature.

The optical densities (A) at the wave length of λ_{max} for the (substituted) benzoic acid produced were measured. An exception to this general procedure was made for 2,4,6-

trimethylphenylnitromethane, the reaction of which was followed at 244 nm, since mesitoic acid shows only end absorption in dilute acid.

The pseudo-first-order rate constants were calculated by a computer-assisted least-squares plot of ln $(A_\infty - A_t)$ versus time.

The concentration of the mineral acid solutions was determined after the runs by titration with standard alkali.

(B) The runs in deuteriosulfuric acid were carried out by adding 10 μl of a 1 vol.% solution of phenylnitromethane in ethanol to 10 ml dilute deuteriosulfuric acid and transferring, after mixing, to a u.v. cell. The cell was kept in a thermostatted cell block at the reaction temperature (± 0.1°C) for one hour, and then removed at recorded time intervals for optical density determination at a fixed wavelength near λ_{max} for benzoic acid. The readings were made in the heated cell compartment of a Beckman DB spectrophotometer. The data were treated as above. Comparative runs were made at the same time under the same conditions with protiosulfuric acid.

Determination of distribution coefficients

A stock solution of the phenylnitromethane to be studied was made in n-hexane, with optical density approximately 2.0 at a chosen wavelength near λ_{max}. A ten ml aliquot of this solution was shaken with a measured aliquot of dilute sulfuric acid in a flask held at 25.0°C in a water bath. The amount of dilute sulfuric acid used was varied to obtain approximately 50% partition. The hexane layer was withdrawn and scanned with a Unicam SP800 spectrophotometer to determine the concentration of the phenylnitromethane present. The distribution coefficient, D, was calculated (17) using the equation:

$$D = \frac{nA}{(A_o - A)}$$

where A_o is the optical density of the hexane solution before equilibration with the sulfuric acid solution, A is the optical density after equilibration, and n is the ratio of the volumes used (aqueous/organic).

An estimate of the distribution coefficient in pure water (D_{aq}) was made by extrapolation from dilute acid solutions, and used to calculate the aqueous activity coefficient ($\underline{f}_s$) of the phenylnitromethane (18) in different concentrations of acid:

$$\underline{f}_s = D/D_{aq}$$

Formation of benzaldehyde from phenylnitromethane

A mixture of 200 mg phenylnitromethane and 50 ml 11.5 M sulfuric acid was heated with frequent mixing to 80°C for three hours. A brown gas was visible over the reaction mixture during this time. After cooling, the reaction mixture was poured over 100 g crushed ice and extracted with carbon tetrachloride. The extract was dried with magnesium sulfate and evaporated. The i.r. and p.m.r. spectra indicated that the product was a mixture of 80% phenylnitromethane and 20% benzaldehyde.

Results and Discussion

Effect of acid concentration

The kinetics of the Meyer reaction of phenylnitromethane were studied in hot sulfuric, perchloric and hydrochloric acids (Table I). In each case, the rate profile passed through a maximum at an acid concentration far below that required to protonate most of the phenylnitromethane.

The rates of the rearrangement-hydrolysis of *p*-methylphenylnitromethane, *p*-chlorophenylnitromethane, and *m*- and *p*-nitrophenylnitromethane in sulfuric acid at 68.8°C were also determined (Table II and Figure 1). The rate profile for each of these compounds exhibited a maximum at a slightly different acid concentration.

The rate of the reaction of *o*-methylphenylnitromethane was considerably slower than that of *p*-methylphenylnitromethane (Table II). The rate for 2,4,6-trimethylphenylnitromethane was even slower. Since the rate of reaction of the *aci*-form is actually increased by ortho substituents (4,15), these steric effects must be operative in the transition state leading to the *aci*-form.

Reaction in very concentrated acid

In sulfuric acid from 7 to 13 *M*, and in perchloric acid from 7 to 11 *M*, a different reaction of phenylnitromethane was observed at 78.6°C: the formation of benzaldehyde. Within this acidity range, the rate of formation of benzaldehyde increased rapidly with increasing acid concentration. Above 11 *M* perchloric acid and 13 *M* sulfuric acid, undetermined brown reaction products were also formed.

TABLE I

Pseudo-first-order rate constants (k_{ψ})
for formation of
benzoic acid from phenylnitromethane in acid

Temp. (°C)	Acid	Acid Conc'n ($\underline{M}$)	$10^5 k_{\psi}$ (sec^{-1})
68.8	H_2SO_4	.85	4.30
"	"	1.54	5.80
"	"	2.56	6.82
"	"	3.23	5.00
"	"	4.20	3.44
"	"	5.69	1.68
"	"	7.18	1.18
74.8	$HClO_4$	.235	2.96
"	"	.494	4.93
"	"	.75	6.18
"	"	1.09	7.6
78.6	"	1.03	9.7
"	"	1.84	9.1
"	"	2.91	5.68
"	"	3.80	3.27
"	"	4.64	1.95
"	"	5.45	1.42
"	"	7.12	.69
68.8	HCl	.469	2.46
"	"	1.14	4.08
"	"	3.04	4.21
"	"	4.82	3.20
"	"	7.78	2.15

TABLE II

Pseudo-first-order rate constants (k_ψ) for the rearrangement-hydrolysis of substituted phenylnitromethanes in sulfuric acid at 68.8°C.

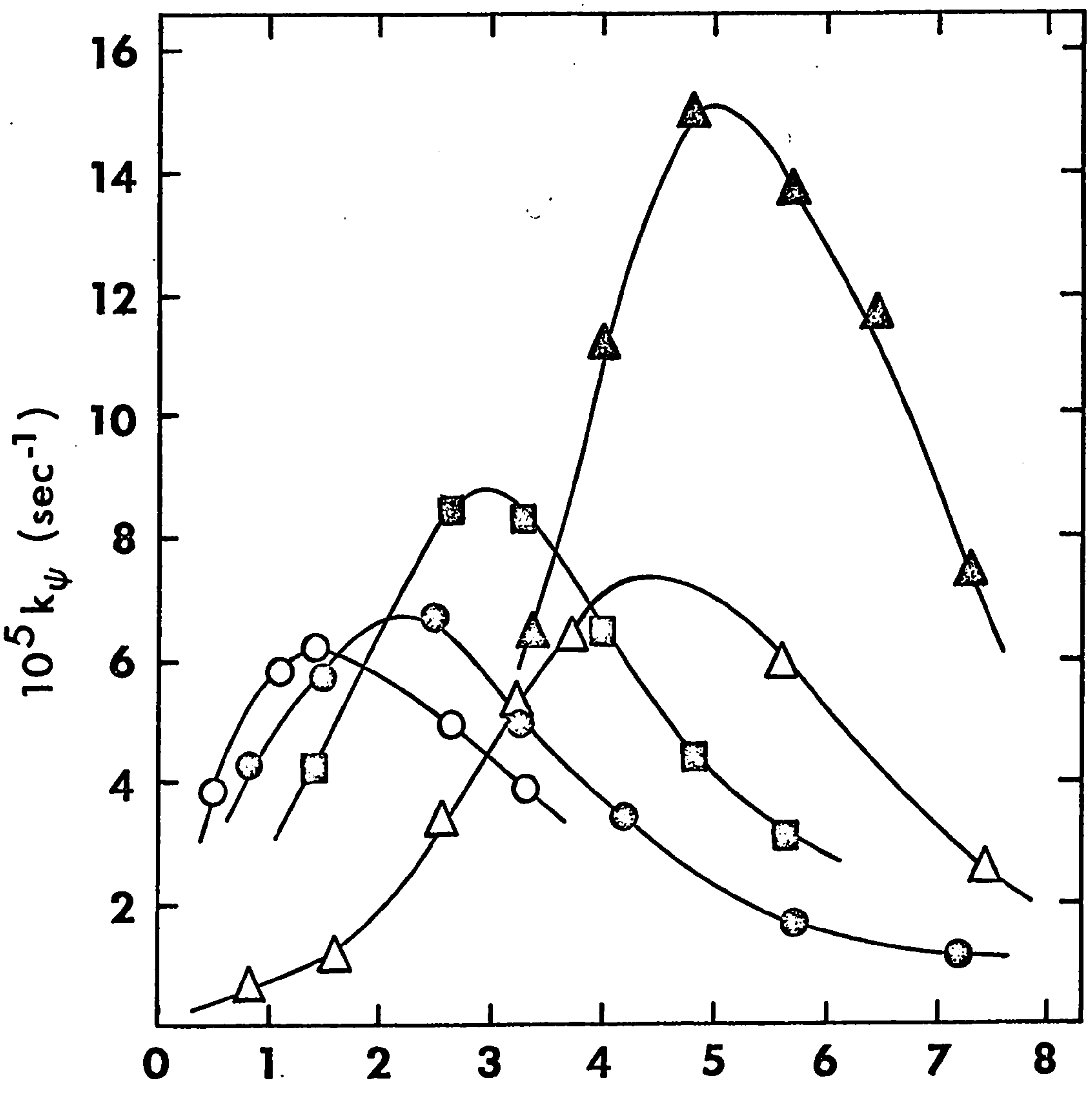
Substituent	H_2SO_4 Conc'n (*M*)	$10^5 k_\psi$ (sec^{-1})
p-methyl-	0.51	3.95
	1.11	5.84
	1.40	6.17
	2.69	4.98
	3.36	3.95
p-chloro-	1.40	4.27
	2.69	8.5
	3.36	8.3
	4.01	6.5
	4.83	4.51
	5.69	3.10
m-nitro-	0.85	0.65
	1.54	1.20
	2.56	3.32
	3.23	5.30
	3.74	6.41
	5.62	5.98
	7.45	2.59
p-nitro-	3.36	6.4
	4.01	11.2
	4.83	15.0
	5.69	13.8
	6.47	11.6
	7.33	7.4
o-methyl-	0.52	0.97
	1.73	1.47
	2.37	1.52
2,4,6-trimethyl-	0.52	0.82[a]
	2.32	1.09[a]

[a] rates measured at 70.0°C.

FIGURE 1

Rate profiles for the formation of benzoic acids from phenylnitromethanes in sulfuric acid at 68.8°C.

● phenylnitromethane
○ *p*-methylphenylnitromethane
■ *p*-chlorophenylnitromethane
△ *m*-nitrophenylnitromethane
▲ *p*-nitrophenylnitromethane



16
14
12
10
8
6
4
2
$10^5 k_\psi$ (sec^{-1})
0
1
2
3
4
5
6
7
8
H_2SO_4 (M)

The formation of benzaldehyde does not take place via the *aci*-form. The reaction of the sodium salt of *aci*-phenylnitromethane with acid in this concentration range produces only benzohydroxamic acid from a cold and benzoic acid from a hot solution.

Both hot perchloric acid and hot sulfuric acid in this concentration range are oxidizing agents (19,20). The observation of a brown gas, probably nitrogen tetroxide, during the formation of benzaldehyde, lends support to the hypothesis that oxidation of the methylene group takes place:

$$[9] \qquad PhCH_2NO_2 \longrightarrow PhCHOHNO_2 \longrightarrow PhCHO + HNO_2$$

This reaction was not studied further.

Activity coefficient changes

A decrease in substrate activity coefficient with increasing acid concentration ("salting-in") has been presented as part of the explanation for a maximum in the rate profile for the hydrolysis of some carboxylic anhydrides (21) and some aryl phosphates (22). The aqueous activity coefficients of phenylnitromethane and of some substituted derivatives were determined at room temperature in sulfuric acid solutions by partition between the acid solutions and *n*-hexane (18). It was found that the variation of log f_s with the molarity of sulfuric acid was not linear. An initial increase above zero ("salting-out") was followed by a later decrease ("salting-in") as the medium became more acidic. Similar behaviour has been observed with many other organic compounds in sulfuric acid (17).

Phenylnitromethane and p-methylphenylnitromethane showed an increase in activity coefficient up to a maximum in 3 M sulfuric acid, followed by a smooth decrease. In 6 M sulfuric acid, the activity coefficient had dropped below that in pure water. The nitro-substituted phenylnitromethanes were "salted-in" in 2 M sulfuric acid. Since the nitro-substituted phenylnitromethanes show a maximum in the rate profile for the Meyer reaction at a higher acidity than unsubstituted phenylnitromethane, we must conclude that "salting-in" of the substrate cannot account for the rate decrease observed after the maximum in the rate profile. Haldna has reported that the formation of a hydrogen-bonded complex with nitro groups in acid does not cause an abnormal change in activity coefficients for these compounds (23).

Bunnett-Olsen plot

Bunnett and Olsen (24) have tested a linear free energy relationship applicable to reactions of weakly basic substrates in acid. An estimate of the involvement of water in the transition state of such reactions is provided by the slope, ϕ, obtained from a plot of ($\log k_\psi + H_o$) versus ($H_o + \log [H^+]$). The parameter, ϕ, was shown to assume a value less than zero when water was not involved in the transition state, from zero to 0.33 when water was acting as a nucleophile, and above 0.58 when water was taking part as a proton transfer agent. The Bunnett-Olsen plots of our results for the rearrangement-hydrolysis of phenylnitromethane and p-methylphenylnitromethane are linear and give ϕ values greater than 0.58 (Table III). The plots for the other substituted phenylnitromethanes are linear at high acidity, but show a deviation from linearity at low acidity. Bennett predicted such deviations from linearity when a side-reaction competes with the reaction being studied. In paper I of this series (4), we reported a parallel reaction of phenyl-aci-nitromethanes in acid: the rearrangement to benzohydroxamic acid, which is the predominant reaction of phenyl-aci-nitromethane in concentrated acid (> 3 M), is surpassed in rate in more dilute acid by the tautomerization to phenylnitromethane. It was also found that an electron-withdrawing group assisted the tautomerization and inhibited the rearrangement, until a higher acidity was reached. This predominance of tautomerization at low acid concentrations for phenylnitromethanes having electron-withdrawing substituents is the cause of the deviations from linearity in the Bunnett-Olsen plots.

The nitro-aci tautomerization

In paper I of this series (4), the tautomerization rates and the rearrangement rates of phenyl-aci-nitromethane were determined over a range of acid concentration at 25.1°C. In the Meyer rearrangement-hydrolysis of phenylnitromethane, phenyl-aci-nitromethane is formed slowly, then undergoes these two fast competing reactions.

$$[10] \qquad ArCH_2NO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArCH{=}NO_2H \xrightarrow{k_2} \text{products}$$

TABLE III

Bunnett-Olsen plots for the rearrangement-hydrolysis of phenylnitromethanes at 68.8°C

Substituent	Acid range	ϕ-value	Correlation Coefficient
unsubst.	0.85 - 7.2 <u>M</u> H_2SO_4	1.68	.9987
"	1.0 - 5.5 <u>M</u> $HClO_4$[a]	2.06	.9976
"	0.45 - 4.8 <u>M</u> HCl	1.99	.9984
<u>p</u>-methyl-	0.5 - 3.4 <u>M</u> H_2SO_4	1.95	.9996
<u>p</u>-chloro-	2.69 - 5.69 <u>M</u> H_2SO_4	1.73	.9989
<u>m</u>-nitro-	3.23 - 7.45 <u>M</u> H_2SO_4	1.42	.9982
<u>p</u>-nitro-	4.83 - 7.33 <u>M</u> H_2SO_4	1.45	.9994

[a] rates measured at 78.6°C.

A similar reaction scheme has been analyzed by Rocek and co-workers (25) who called the reaction characterized by k_2 the "rate-limiting" step, the last step in the reaction sequence that affects the overall rate. Although this step is faster than the initial step (k_1), the rate of the reaction depends on both k_1 and k_2, because of the very fast back-reaction (k_{-1}) that is competing.

In the case of phenylnitromethane, it was found that the ratio k_2/k_{-1} was relatively insensitive to temperature changes (4). Applying this ratio to the overall rate (k_{ov}) observed for the Meyer reaction of phenylnitromethane at 68.8°C, it is possible to determine the rate k_1 of the nitro-aci tautomerization (26):

$$k_1 = k_{ov} \times \frac{k_2+k_{-1}}{k_2} \tag{11}$$

The results of these calculations (Table IV) show the inhibiting effect of increasing sulfuric acid concentration in the range 0.85 - 7.18 M on the tautomerization of phenylnitromethane to phenyl-aci-nitromethane.

It has often been proposed that tautomerization between nitro and aci forms, (like the tautomerization between keto and enol forms), is acid-catalyzed (5,27,28). However, there is much experimental evidence that dilute acids inhibit the tautomerization of the aci to the nitro form (equation [2]) (15,29-31), and so, on the principle of microscopic reversibility, inhibit the reverse reaction [1]. Direct evidence for the effect of acid in inhibiting reaction

TABLE IV

Pseudo-first-order rate constants for tautomerization (k_1) of phenylnitromethane to phenyl-aci-nitromethane in sulfuric acid at 68.8°C.

H_2SO_4 Concentration (M)	10^5k_1 (sec^{-1})
.85	16.
1.54	11.
2.56	8.5
3.23	4.6
4.20	3.3
5.69	1.7
7.18	1.2

[1] has been produced by Haldna et al (8), and is confirmed by the present work. Haldna showed that the rate of bromination (k_r) of nitromethane in sulfuric acid up to 5.3 $\underline{M}$ decreased with decreasing water activity (a_{H_2O}) according to equation [12], where k_o is constant.

[12] $$k_r = k_o a^4_{H_2O}$$

Our results for the tautomerization of phenylnitromethane (Table IV) follow a similar correlation with the fourth power of the water activity over the range 1.5 - 5.7 $\underline{M}$ sulfuric acid, indicating the involvement of water as a proton acceptor (8).

Further information about the tautomerization was obtained from a study of the Meyer reaction in an acidity range where the tautomerization alone is the rate-determining step ($k_1 \cong k_{ov}$). This condition is fulfilled at acid concentrations above those required for the maximum in the rate profile. In these concentrations the large negative entropy of activation (Table V) indicates a mechanism in which there is a large increase in solvent ordering in the transition state (32); as would be required for the abstraction of a proton by water.

Primary isotope effect

The reaction of phenylnitromethane-α,α-d_2 is slower than that of the undeuterated phenylnitromethane (Table VI), as would be expected if the rate-determining step is the tautomerization (equation [1]), which involves stretching of the carbon-hydrogen bond. The maximum primary isotope effect

TABLE V

Activation parameters for the rearrangement-hydrolysis of phenylnitromethane in sulfuric acid

Acid Conc'n (<u>M</u>)	Temp. (°C)	10^5k_ψ (sec^{-1})	$\Delta H_{\ddagger}$ (kcal/mole)	$\Delta S_{\ddagger}$ (e.u.)
2.92	63.1	3.66	21±1	-16±1
"	"	3.75		
"	72.1	8.7		
"	78.3	14.6		
"	"	14.7		
"	88.5	33.6		
"	"	34.6		
4.68	63.1	1.79	22±1	-16±1
"	78.3	7.97		
"	88.5	16.8		

TABLE VI

Kinetic isotope effects on the rearrangement-hydrolysis in sulfuric acid at 78.3°C

	Acid Conc'n ($\underline{M}$)	$10^5 k_\psi$ (sec^{-1})	k_H/k_D
$C_6H_5CH_2NO_2$	2.92	14.6	2.6 ± 0.1
$C_6H_5CD_2NO_2$	"	5.6	
$C_6H_5CH_2NO_2$	4.68	8.0	2.5 ± 0.1
$C_6H_5CD_2NO_2$	"	3.3	

(k_H/k_D) expected at 78°C is 5, corresponding to a transition state with departing hydrogen symmetrically disposed between the carbon and the abstracting oxygen (33). The lower values observed for phenylnitromethane tautomerization indicate a transition state in which the departing hydrogen is bound more strongly to either the carbon or the oxygen. In view of the instability of the *aci*-phenylnitromethane in acid, application of the Hammond postulate (34,35) to this system would predict a transition state close to the *aci*-form or its anion: i.e. predict that the departing hydrogen is bound more strongly to oxygen.

Solvent isotope effect

The effect of carrying out the Meyer reaction of phenylnitromethane in deuteriosulfuric acid varies greatly, depending on the concentration of the acid (Table VII).

These isotope effects cannot be due to differential solvation of the initial state, since we have determined distribution coefficients of phenylnitromethane in isooctane/sulfuric acid and isooctane/deuteriosulfuric acid. The isotope effect ($f_{\underline{s}}(H_2O)/f_{\underline{s}}(D_2O)$) on the activity coefficient of the starting material in 4.0 *M* acid is 1.03. An isotope effect of 1.06 ($f_{\underline{s}}(H_2O)/f_{\underline{s}}(D_2O)$) has been reported on the activity coefficient of nitromethane in water (36).

At high acid concentrations, the solvent isotope effect influences the rate-determining tautomerization of phenylnitromethane to phenyl-*aci*-nitromethane. Here the reaction is slowed in deuterated solvent by the lower

TABLE VII

Solvent isotope effects on the rearrangement-hydrolysis of phenylnitromethane at 74.8°C

Acid	Conc'n (M)	$10^5 k_\psi$ (sec^{-1})	k_{H_2O}/k_{D_2O}
H_2SO_4	0.51	5.25	0.63
D_2SO_4	"	8.35	
H_2SO_4	1.11	10.5	1.07
D_2SO_4	"	9.8	
H_2SO_4	1.71	12.8	1.46
D_2SO_4	"	8.74	
H_2SO_4	2.31	12.4	1.71
D_2SO_4	"	7.26	
H_2SO_4	3.00	10.5	1.79
D_2SO_4	"	5.88	
H_2SO_4	4.00	7.05	1.86
D_2SO_4	"	3.79	
H_2SO_4	5.30	3.84	1.96
D_2SO_4	"	1.96	

basicity of deuterium oxide, which makes it less effective in proton abstraction (37). Swain and Rosenberg (38) predicted values for the solvent isotope effect (k_{H_2O}/k_{D_2O}) on a proton abstraction from a carbon acid such as ketones and nitroalkanes: 1.0 for zero transfer of the proton in the transition state, 1.4 for half-transfer, and 2.0 for complete transfer of the proton to water in the transition state. Bunton and Shiner (35) calculated a solvent isotope effect of 1.4 for a symmetrical "free-proton" transition state for enolization of a ketone. The relatively large values (up to 1.96) obtained for the tautomerization of phenylnitromethane indicate a transition state with considerable proton transfer, close to hydronium ion and the aci-form or its anion.

The reaction scheme is more complex in dilute acid. Here the aci-form is formed slowly, but is transformed back into the nitro-form more quickly than into the Meyer reaction products. The rate-limiting step now for the Meyer reaction is the loss of water from the protonated aci-form (equation [4]) (4). Reactions with a protonation equilibrium prior to the rate-limiting step are usually faster in deuterated solvent because of the increased acidity of deuteronium ion, and this is observed in the Meyer reaction, as shown in Table VII. As the rate-limiting step changes over to tautomerization (equation [1]) in more concentrated acid, the value of the isotope effect changes to approach the value found for the tautomerization.

Conclusion

The Meyer rearrangement-hydrolysis of phenylnitromethane in acid proceeds through tautomerization to phenyl-*aci*-nitromethane. In dilute acid, the tautomerization is followed by a rate-limiting acid-catalyzed reaction of the *aci*-form (equation [4]), which causes the observed increase in rate with increasing acidity. As the medium is made more acidic, the rate-limiting step changes to the tautomerization (equation [1]), which is inhibited in acid, so that the rate decreases with increasing acidity. The tautomerization is not acid-catalyzed, and proceeds by proton abstraction from the α-carbon by water, through a transition state closely resembling the products.

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SUMMARY AND CLAIMS TO ORIGINAL RESEARCH

In the main body of this thesis is presented a detailed mechanism of the Meyer rearrangement - hydrolysis of phenylnitromethane in acid. The proposed mechanistic scheme includes the tautomerization to the *aci*-form, which is shown to be inhibited by acid, in contrast with the mechanism of *nitro*-*aci* tautomerization proposed recently by some other workers. A new explanation is provided for the maximum observed in the profile of rate *versus* acid concentration for the Meyer reaction of phenylnitromethane. It has been proven that benzonitrile oxide is an intermediate in the Meyer reaction of phenylnitromethane, the first experimental evidence for a nitrile oxide intermediate in the Meyer reaction of a nitroalkane.

A mechanism is proposed for the reactions with mineral acids of benzonitrile oxides and benzohydroxamic acid.

The conclusions drawn above are based on the following original kinetic studies:

rate profiles for the Meyer rearrangement - hydrolysis of phenylnitromethane and of substituted derivatives of phenylnitromethane,

rate profiles for the reactions in acid of phenyl-*aci*-nitromethane and three substituted derivatives, rate profiles for the reaction in acid of benzonitrile oxide and three substituted derivatives,

and a rate profile for the hydrolysis in acid of benzohydroxamic acid.

APPENDIX

APPENDIX

The following pages contain the raw data, derived rates and statistical parameters for the kinetic experiments described in the main body of the thesis. The data are presented in separate tables for each compound studied, in the order that the results appear in the text. A detailed index is included in the List of Tables.

The following headings have been used in the tables that follow:

time (s) = elapsed time in seconds, not necessarily from the time of mixing.

time (m) = elapsed time in minutes, not necessarily from the time of mixing.

dA = the absolute value of the difference between the optical density at the time stated and the optical density at "infinite time", expressed in units of 0.0133 OD units (obtained by direct measurement of the difference on the recorded spectra using a transparent metric rule).

dA (OD units) = the same absolute value of the optical density difference referred to above, but expressed in OD units.

A (OD units) = the actual optical density at the time stated, measured in OD units.

C = the concentration of the mineral acid used in the run, determined by titration with standard alkali.

S = the concentration of the table title compound at the beginning of the run.

T = temperature of the run; controlled ±0.05°C during the run.

L = wavelength at which the reaction was followed; expressed only to the nearest 0.5 nm, but held constant during the run to ±0.3 nm.

t = time at which the "infinite time" reading of the optical density was taken, when the reaction was assumed to be at equilibrium (at least seven half-lives). For some runs, this "infinite time" value of the optical density, A, is given here in parentheses.

dt (G) = time interval between the two sets of optical density readings used to determine the rate constant by the Guggenheim method, when used. In the few cases that this method was used, the heading dA stands for the absolute value of the difference in optical density over this time "dt".

cc = correlation coefficient for the integrated first-order rate plot; 0.994 for all runs included; 0.999 for 80% of all runs included.

rate = pseudo-first-order rate constant calculated by the method of least-squares from the integrated first-order rate equation.

sd = standard deviation for the rate constant given above, expressed in the same units as the numerical portion of the rate constant. For the runs with seven points or more (80% of the runs included), the probable error for 99% confidence limits is approximated by four times the standard deviation. For example, for a run with the following results:

rate = 5.00×10^{-5} sec^{-1}

sd = .05

the true rate constant within 99% confidence limits would be:

$$(5.00 \pm 4(0.05)) \times 10^{-5} \text{ sec}^{-1}$$
$$= (5.0 \pm 0.2) \times 10^{-5} \text{ sec}^{-1}.$$

APPENDIX

PART I

Phenyl-_aci_-nitromethanes in sulfuric acid

PART I

TABLE I

Phenyl-aci-nitromethane

C = 0.010 M

S = 0.00018 M

T = 25.1°C

L = 274 nm

t = 2.8 hr

cc = .9994

rate = 23.4×10^{-4} sec^{-1}

sd = .09

time (s)	dA
62	128.8
130	108.2
196	92.3
255	79.3
318	67.5
383	57.0
441	49.2
506	42.0
591	34.0
660	29.0
800	20.8
900	16.5
1000	13.0
1100	10.3
1300	6.6
1550	3.8
1800	2.3

C = 0.520 M

S = 0.00018 M

T = 25.1°C

L = 274 nm

t = 2.0 hr

cc = .9999

rate = 27.5×10^{-4} sec^{-1}

sd = .05

182	133.2
243	114.0
303	97.0
416	70.2
473	59.1
541	48.9
605	41.5
667	34.5
736	28.4
805	23.9
875	19.5
941	16.3
1043	12.2
1173	8.9
1258	6.9
1358	5.4

TABLE I (cont.)

Phenyl-aci-nitromethane

C = 1.45 M

S = 0.00018 M

T = 25.1°C

L = 274 nm

t = 1.3 hr

cc = .9998

rate = 35.2 x 10^{-4} sec^{-1}

sd = .10

time (s)	dA
134	126.7
216	95.6
298	71.0
382	51.7
461	39.0
546	28.7
638	20.7
722	15.5
825	10.7
930	7.8
1058	5.0

C = 1.70 M

S = 0.00018 M

T = 25.1°C

L = 274 nm

t = 2.8 hr

cc = .9997

rate = 37.9 x 10^{-4} sec^{-1}

sd = .14

time (s)	dA
39	133.0
100	106.9
200	72.3
300	48.0
400	32.5
500	22.2
600	15.0
750	9.0
900	5.2

C = 1.99 M

S = 0.00018 M

T = 25.1°C

L = 274 nm

t = 2.8 hr

cc = .9998

rate = 44.1 x 10^{-4} sec^{-1}

sd = .15

time (s)	dA
21	130.5
100	95.5
180	66.2
260	45.6
340	32.0
440	20.2
540	12.9
800	4.4

TABLE I (cont.)

Phenyl-aci-nitromethane

C = 2.51 M
S = 0.00018 M
T = 25.1°C
L = 274 nm
t = 1.0 hr
cc = .9987
rate = 65.7 x 10^{-4} sec^{-1}
sd = .49

time (s)	dA
18	103.8
89	66.3
169	38.7
243	24.0
320	14.5
399	8.7
482	5.5
562	3.3
643	1.5

C = 2.92 M
S = 0.00019 M
T = 25.1°C
L = 276 nm
t = 1.8 hr
cc = .9997
rate = 102. x 10^{-4} sec^{-1}
sd = .58

68	121.5
76	111.7
86	98.8
98	89.0
110	79.0
121	70.5
131	63.6
142	56.9
157	49.0
177	39.7

C = 3.14 M
S = 0.00019 M
T = 25.1°C
L = 276 nm
t = 1.5 hr
cc = .9999
rate = 113. x 10^{-4} sec^{-1}
sd = .30

59	124.0
69	111.5
78	99.5
88	89.7
98	80.0
108	71.8
117	64.2
128	56.9
140	48.9
153	42.3
211	22.2
260	12.8
315	7.0

TABLE I (cont.)

Phenyl-aci-nitromethane

C = 3.82 M
S = 0.00019 M
T = 25.1°C
L = 276 nm
t = 1.8 hr
cc = .9997
rate = 263. x 10^{-4} sec^{-1}
sd = 2.0

time (s)	dA
70	88.2
78	70.0
86	56.4
94	45.2
102	36.3
110	29.2
118	23.7
127	19.0
135	15.6
169	6.5

C = 4.01 M
S = 0.00019 M
T = 25.1°C
L = 276 nm
t = 9 min
cc = .9999
rate = 330. x 10^{-4} sec^{-1}
sd = 1.3

15	71.5
24	52.9
33	39.0
41	29.8
50	22.5
58	17.5
66	13.1
73	10.5
82	7.7
90	5.9
98	4.7

C = 4.01 M
S = 0.00019 M
T = 25.1°C
L = 276 nm
t = 4.0 hr
cc = .9998
rate = 316. x 10^{-4} sec^{-1}
sd = 1.9

13	46.3
21	35.6
29	27.6
38	20.9
46	16.2
54	12.2
63	9.5
71	7.3
79	5.8

TABLE I (cont.)

Phenyl-aci-nitromethane

C = 0.520 M

S = 0.00018 M

T = 34.2°C

L = 274 nm

t = 2.0 hr

cc = .9995

rate = 63.7 x 10^{-4} sec^{-1}

sd = .29

time (s)	dA
84	80.3
146	53.6
211	35.0
276	23.1
338	15.2
404	10.0
462	7.0
562	3.5
672	2.0

C = 1.70 M

S = 0.00018 M

T = 34.2°C

L = 275 nm

t = 2.0 hr

cc = .9997

rate = 96.4 x 10^{-4} sec^{-1}

sd = .36

time (s)	dA
72	111.5
130	62.5
187	35.5
245	20.0
303	11.0
364	6.5
425	3.8
486	2.0

C = 2.51 M

S = 0.00018 M

T = 34.2°C

L = 275 nm

t = 2.0 hr

cc = .9999

rate = 165. x 10^{-4} sec^{-1}

sd = .55

time (s)	dA
26	66.0
87	24.8
141	10.5
197	4.0
255	1.5

TABLE II

Phenyl-aci-nitromethane-α-d

C = 0.520 M

S = 0.00019 M

T = 25.1°C

L = 280 nm

t = 2.0 hr

cc = .9996

rate = 27.5 x 10^{-4} sec^{-1}

sd = .10

time (s)	dA
115	124.5
188	98.4
260	79.0
335	62.7
409	50.5
485	40.9
562	32.8
637	27.0
718	22.0
1065	8.5
1238	5.6
1449	3.0

C = 2.09 M

S = 0.00019 M

T = 25.1°C

L = 280 nm

t = 1.5 hr

cc = .9978

rate = 46.4 x 10^{-4} sec^{-1}

sd = .40

time (s)	dA
46	117.5
108	79.5
169	56.0
231	40.7
292	30.5
355	23.0
418	17.0
482	12.8
556	9.8
631	7.0
773	3.8

TABLE III

m-Nitrophenyl-aci-nitromethane

C = 0.010 M

S = 0.00013 M

T = 25.4°C

L = 270 nm

t = 1.3 hr

cc = .9987

rate = 138. x 10^{-4} sec^{-1}

sd = 1.4

time (s)	dA
41	47.3
114	16.0
157	8.4
200	5.3
253	2.5

C = 2.37 M

S = 0.00013 M

T = 25.4°C

L = 275 nm

t = 2.0 hr

cc = .9989

rate = 124. x 10^{-4} sec^{-1}

sd = 1.0

40	51.2
85	29.9
130	18.4
176	10.8
221	5.8
301	2.0

C = 2.92 M

S = 0.00013 M

T = 25.4°C

L = 275 nm

t = 2.5 hr

cc = .9996

rate = 104. x 10^{-4} sec^{-1}

sd = .51

36	54.8
108	27.0
154	17.5
198	10.6
253	5.9
330	2.6

TABLE III (cont.)

m-Nitrophenyl-aci-nitromethane

C = 4.01 M

S = 0.00013 M

T = 25.4°C

L = 275 nm

t = 2.0 hr

cc = .9988

rate = 77.9×10^{-4} sec^{-1}

sd = .73

time (s)	dA
44	75.3
126	42.0
206	22.6
287	12.5
366	6.0

C = 4.83 M

S - 0.00013 M

T = 25.4°C

L = 275 nm

t = 2.5 hr

cc = .9998

rate = 78.4×10^{-4} sec^{-1}

sd = .28

47	63.8
131	31.8
212	17.7
287	9.7
383	4.5

C = 5.69 M

S = 0.00013 M

T = 25.4°C

L = 285 nm

t = 4.0 hr

cc = .9997

rate = $108. \times 10^{-4}$ sec^{-1}

sd = 1.3

43	53.7
108	27.3
166	14.9
226	7.8
287	3.8

TABLE III (cont.)

m-Nitrophenyl-aci-nitromethane

C = 6.49 M

S = 0.00017 M

T = 25.4°C

L = 285 nm

t = 1.7 hr

cc = .9995

rate = 270. x 10^{-4} sec^{-1}

sd = 4.5

time (s)	dA
27	43.1
58	17.7
91	7.1
127	2.9

TABLE IV

p-Methylphenyl-aci-nitromethane

C = 0.010 M

S = 0.00008 M

T = 25.4°C

L = 285 nm

t = 2.0 hr

cc = .9999

rate = 12.3 x 10^{-4} sec^{-1}

sd = .04

time (s)	dA
37	101.5
97	95.5
200	84.9
267	78.6
337	72.0
406	65.8
475	60.5
543	55.7
610	51.2
709	45.7
815	39.7
922	34.7
1058	29.2
1175	25.2
1352	20.1
1543	16.0
1813	11.7

C = 0.520 M

S = 0.00008 M

T = 25.4°C

L = 285 nm

t = 3.8 hr

cc = .9999

rate = 18.4 x 10^{-4} sec^{-1}

sd = .07

39	93.2
98	84.8
161	75.8
225	67.3
288	59.9
350	53.0
414	47.2
480	41.8
553	36.4
720	26.8
819	22.1
950	17.3
1100	13.0
1385	8.0
1771	4.0

TABLE IV (cont.)

p-Methylphenyl-aci-nitromethane

C = 1.12 M
S = 0.00008 M
T = 25.4°C
L = 285 nm
t = 3.5 hr
cc = .9999
rate = 27.2 x 10^{-4} sec^{-1}
sd = .12

time (s)	dA
28	91.0
87	78.6
147	68.0
207	57.4
270	48.5
331	41.3
393	34.5
494	26.4
583	20.4
701	14.7
942	7.7

C = 1.45 M
S = 0.00008 M
T = 25.4°C
L = 285 nm
t = 3.0 hr
cc = .9997
rate = 34.7 x 10^{-4} sec^{-1}
sd = .25

time (s)	dA
30	93.7
90	78.5
150	64.8
210	52.8
269	43.1
328	35.0
387	28.5
449	22.9
510	18.2
571	14.8
700	9.3

C = 2.09 M
S = 0.0008 M
T = 25.4°C
L = 285 nm
t = 4.0 hr
cc = .9995
rate = 54.2 x 10^{-4} sec^{-1}
sd = .56

time (s)	dA
32	79.6
91	60.4
150	44.8
209	32.9
269	23.7
329	16.9
389	12.1
450	8.3
511	6.2

TABLE IV (cont.)

p-Methylphenyl-aci-nitromethane

C = 2.37 M
S = 0.00008 M
T = 25.4°C
L = 285 nm
t = 2.5 hr
cc = .9996
rate = 73.8 x 10^{-4} sec^{-1}
sd = .66

time (s)	dA
27	81.0
45	72.5
62	64.4
79	57.4
139	37.7
199	24.7
258	15.5
320	9.8
381	5.8
443	3.9

C = 2.69 M
S = 0.00008 M
T = 25.4°C
L = 285 nm
t = 2.0 hr
cc = .9997
rate = 101. x 10^{-4} sec^{-1}
sd = .78

time (s)	dA
30	72.2
48	60.8
65	51.8
82	43.8
100	37.2
160	20.3
220	11.0
279	5.8

C = 3.14 M
S = 0.00008 M
T = 25.4°C
L = 285 nm
t = 1.5 hr
cc = .9998
rate = 146. x 10^{-4} sec^{-1}
sd = 1.0

time (s)	dA
43	52.0
60	41.3
77	32.5
93	25.5
111	19.7
168	8.4

TABLE V

<u>o-Methylphenyl-aci-nitromethane</u>

C = 0.010 M

S = 0.00016 M

T = 25.4°C

L = 280 nm

t = 3.0 hr

cc = .9989

rate = 30.9 x 10^{-4} sec^{-1}

sd = .18

time (s)	dA
70	127.2
125	115.9
188	86.9
246	71.3
302	59.1
357	49.4
416	40.8
473	34.3
529	29.0
618	22.3
771	13.5
1257	3.4

C = 0.520 M

S = 0.00016 M

T = 25.4°C

L = 297.5 nm

t = 1.5 hr

cc = .9997

rate = 40.5 x 10^{-4} sec^{-1}

sd = .13

51	58.8
105	45.4
161	36.8
217	30.5
272	24.8
334	19.0
434	12.0
518	8.4
633	5.4
762	3.3
928	1.7

C = 1.12 M

S = 0.00016 M

T = 25.4°C

L = 300 nm

t = 1.0 hr

cc = .9992

rate = 50.4 x 10^{-4} sec^{-1}

sd = .69

65	42.5
121	33.5
177	25.7
233	19.6
292	14.7
350	10.4
412	7.7
478	5.4
536	3.8
631	2.3

TABLE V (cont.)

o-Methylphenyl-aci-nitromethane

C = 1.45 M

S = 0.00016 M

T = 25.4°C

L = 297.5 nm

t = 2.5 hr

cc = .9995

rate = 54.3×10^{-4} sec^{-1}

sd = .25

time (s)	dA
48	54.0
102	39.6
157	29.7
212	21.6
267	16.3
327	11.3
384	8.2
490	4.6
636	2.3

C = 1.73 M

S = 0.00016 M

T = 25.4°C

L = 297.5 nm

t = 3.0 hr

cc = .9996

rate = 66.7×10^{-4} sec^{-1}

sd = .25

time (s)	dA
44	53.8
108	35.9
160	27.0
214	18.2
271	12.6
326	8.4
380	5.7
433	4.1
488	3.0
574	1.6

C = 2.09 M

S = 0.00016 M

T = 25.4°C

L = 297.5 nm

t = 2.5 hr

cc = .9997

rate = 82.0×10^{-4} sec^{-1}

sd = .30

time (s)	dA
63	42.5
120	28.5
172	18.7
225	12.0
278	7.7
332	4.8
388	3.0
478	1.5

TABLE V (cont.)

o-Methylphenyl-aci-nitromethane

C = 2.37 M
S = 0.00016 M
T = 25.4°C
L = 300 nm
t = 2.0 hr
cc = .9981
rate = 97.4 x 10^{-4} sec^{-1}
sd = 1.1

time (s)	dA
44	35.9
98	21.3
152	11.7
205	6.6
259	4.2
314	2.7

C = 2.92 M
S = 0.00016 M
T = 25.4°C
L = 300 nm
t = 1.3 hr
cc = .9994
rate = 188. x 10^{-4} sec^{-1}
sd = 1.4

47	25.2
106	8.1
159	3.3
217	1.0

APPENDIX

PART II

Benzonitrile oxides and benzohydroxamic acid in sulfuric acid

PART II

TABLE VI

Benzonitrile oxide

C = 0.195 M

S = 0.00015 M

T = 35.0°C

L = 243 nm

t = 5 hr

cc = .9993

rate = 2.10 x 10^{-4} sec^{-1}

sd = .011

time (s)	dA
595	57.0
892	54.4
1188	51.0
1486	48.0
1782	45.0
2080	42.7
2396	39.7
2674	37.5
2973	34.9
3260	32.6

C = 1.45 M

S = 0.00015 M

T = 35.0°C

L = 243 nm

t = 2.0 hr

cc = .9994

rate = 19.2 x 10^{-4} sec^{-1}

sd = .10

446	31.1
595	24.0
743	18.0
892	13.5
1040	10.1
1188	7.9
1486	4.5
1782	2.3
2080	1.5
2396	0.8

C = 1.45 M

S = 0.00018 M

T = 25.1°C

L = 250 nm

t = 2.3 hr

cc = .9993

rate = 7.78 x 10^{-4} sec^{-1}

sd = .12

722	17.1
825	15.8
930	14.7
1058	13.1
2142	5.9
2462	4.3

TABLE VI (cont.)

Benzonitrile oxide

C = 1.70 M

S = 0.00015 M

T = 25.1°C

L = 245 nm

t = 1.7 hr

cc = .9995

rate = 8.76 x 10^{-4} sec^{-1}

sd = .13

time (s)	dA
100	20.3
250	18.0
400	16.0
1000	9.0
1700	5.1

C = 1.99 M

S = 0.00015 M

T = 25.1°C

L = 250 nm

t = 3.0 hr

cc = .9999

rate = 12.6 x 10^{-4} sec^{-1}

sd = .07

time (s)	dA
40	25.3
140	22.7
400	16.6
840	9.4
1853	2.6

C = 2.51 M

S = 0.00015 M

T = 25.1°C

L = 250 nm

t = 3.5 hr

cc = .9988

rate = 19.7 x 10^{-4} sec^{-1}

sd = .34

time (s)	dA
320	29.2
399	25.8
482	21.5
562	19.2
643	16.0
726	12.7
810	11.5
1227	5.0

TABLE VI (cont.)

Benzonitrile oxide

C = 4.01 M

S = 0.00015 M

T = 25.1°C

L = 250 nm

t = 2.5 hr

cc = .9992

rate = 46.0 x 10^{-4} sec^{-1}

sd = .77

time (s)	dA
154	27.0
209	20.5
273	14.8
332	11.5
391	8.8
454	6.8

C = 1.45 M

S = 0.00013 M

T = 20.6°C

L = 245 nm

dt (G) = 1.0 hr

cc = .9974

rate = 5.01 x 10^{-4} sec^{-1}

sd = .045

time (s)	dA
595	45.0
743	42.8
892	39.8
1040	37.5
1188	35.2
1337	33.0
1486	30.8
1635	28.5
1782	27.0
2080	24.0
2396	20.2
2674	16.9
2973	14.2
3260	12.0

C = 2.51 M

S = 0.00013 M

T = 20.6°C

L = 243 nm

t = 2.0 hr

cc = .9995

rate = 11.8 x 10^{-4} sec^{-1}

sd = .05

time (s)	dA
446	39.0
595	33.4
743	27.7
892	23.6
1040	19.8
1188	16.1
1486	11.2
1782	7.9
2080	5.6
2396	4.1
2674	3.0
2973	1.9

TABLE VI (cont.)

Benzonitrile oxide

C = 3.36 M

S = 0.00013 M

T = 20.6°C

L = 243 nm

dt (G) = 20 min

cc = .9999

rate = 22.7 x 10^{-4} sec^{-1}

sd = .12

time (s)	dA
297	28.5
446	20.0
595	14.6
743	10.5
892	7.5
1040	5.2
1188	3.8

C = 4.07 M

S = 0.00013 M

T = 20.6°C

L = 243 nm

dt (G) = 15 min

cc = .9987

rate = 39.6 x 10^{-4} sec^{-1}

sd = .89

297	20.2
446	11.4
595	6.8
743	3.8
892	1.9

TABLE VII

m-Nitrobenzonitrile oxide

C = 1.45 M

S = 0.00008 M

T = 20.6°C

L = 243 nm

dt (G) = 30 min

cc = 1.0000

rate = 2.32 x 10^{-4} sec^{-1}

sd = .013

time (s)	dA
149	9.0
297	8.7
446	8.4

C = 4.07 M

S = 0.00008 M

T = 20.6°C

L = 245 nm

dt (G) = 1.0 hr

cc = .9997

rate = 7.13 x 10^{-4} sec^{-1}

sd = .024

time (s)	dA
297	32.3
446	29.6
595	26.6
743	23.6
892	21.7
1188	17.2
1486	14.2
1782	11.2
2080	9.0
2396	7.5

C = 4.53 M

S = 0.00008 M

T = 20.6°C

L = 244 nm

t = 2.0 hr

cc = .9990

rate = 9.97 x 10^{-4} sec^{-1}

sd = .05

time (s)	dA
446	18.4
595	15.0
743	13.5
892	11.6
1188	9.0
1486	7.1
1782	5.2
2080	3.8
2396	2.6
2674	1.9
2973	1.5
3260	1.1

TABLE VII (cont.)

m-Nitrobenzonitrile oxide

C = 5.69 M
S = 0.00008 M
T = 20.6°C
L = 244 nm
t = 2.0 hr
cc = .9946
rate = 14.6 x 10^{-4} sec^{-1}
sd = .20

time (s)	dA
297	19.1
446	15.0
595	11.6
743	9.4
892	7.1
1188	4.9
1486	3.4
1782	1.9
2080	1.1
2396	0.8
2674	0.8

C = 5.69 M
S = 0.00013 M
T = 25.4°C
L = 250 nm
t = 3.0 hr
cc = .9996
rate = 23.4 x 10^{-4} sec^{-1}
sd = .23

287	22.1
348	19.9
406	17.3
468	14.7
531	12.7
641	9.7
768	7.2
920	5.0
1059	3.8

C = 6.49 M
S = 0.00013 M
T = 25.4°C
L = 245 nm
t = 2.0 hr
cc = .9990
rate = 35.9 x 10^{-4} sec^{-1}
sd = .52

161	32.9
223	27.6
289	21.7
352	16.8
414	13.3
479	10.5
543	8.4
664	5.2
797	3.6

TABLE VII (cont.)

m-Nitrobenzonitrile oxide

C = 7.33 M

S = 0.00013 M

T = 25.4°C

L = 245 nm

t = 1.5 hr

cc = .9993

rate = 56.6 x 10^{-4} sec^{-1}

sd = .89

time (s)	dA
116	23.8
175	16.7
238	11.6
302	7.9
365	5.5
468	3.3

C = 9.18 M

S = 0.00013 M

T = 25.4°C

L = 245 nm

t = 1.0 hr

cc = .9999

rate = 136. x 10^{-4} sec^{-1}

sd = .97

time (s)	dA
42	25.3
107	10.8
171	4.5
219	2.3

TABLE VIII

p-Methylbenzonitrile oxide

C = 1.12 M

S = 0.00008 M

T = 25.4°C

L = 255 nm

t = 3.5 hr

cc = .9998

rate = 9.18 x 10^{-4} sec^{-1}

sd = .10

time (s)	dA
942	8.4
1222	6.6
1598	4.7
2141	2.8

C = 1.45 M

S = 0.00008 M

T = 25.4°C

L = 256 nm

t = 3.0 hr

cc = .9988

rate = 12.7 x 10^{-4} sec^{-1}

sd = .25

700	10.4
830	8.9
1004	7.2
1328	4.9
1779	2.8
2012	1.9

C = 2.09 M

S = 0.00008 M

T = 25.4°C

L = 256 nm

t = 3.5 hr

cc = .9999

rate = 20.4 x 10^{-4} sec^{-1}

sd = .16

608	7.9
708	6.4
809	5.2
942	4.0

TABLE VIII (cont.)

p-Methylbenzonitrile oxide

C = 2.37 M

S = 0.00008 M

T = 25.4°C

L = 256 nm

t = 2.5 hr

cc = .9990

rate = 31.5 x 10^{-4} sec^{-1}

sd = .59

time (s)	dA
381	10.9
443	9.4
518	7.6
586	5.9
723	3.9
879	2.3

C = 2.69 M

S = 0.00008 M

T = 25.4°C

L = 256 nm

t = 2.0 hr

cc = .9998

rate = 38.6 x 10^{-4} sec^{-1}

sd = .37

time (s)	dA
279	12.3
341	9.9
420	7.3
550	4.3
667	2.8

C = 3.14 M

S = 0.00008 M

T = 25.4°C

L = 256 nm

t = 1.5 hr

cc = .9999

rate = 55.6 x 10^{-4} sec^{-1}

sd = .28

time (s)	dA
225	11.5
282	8.5
343	6.0
402	4.3
462	3.1

TABLE IX

o-Methylbenzonitrile oxide

C = 0.520 M

S = 0.00016 M

T = 25.4°C

L = 250 nm

t = 2.5 hr

cc = .9968

rate = 5.51×10^{-4} sec^{-1}

sd = .26

time (s)	dA
762	8.0
928	7.0
1068	6.4
1237	5.9

C = 1.12 M

S = 0.00016 M

T = 25.4°C

L = 250 nm

t = 2.0 hr

cc = .9982

rate = 6.72×10^{-4} sec^{-1}

sd = .079

631	20.0
769	18.4
1113	14.8
1479	11.8
1870	8.6

C = 1.45 M

S = 0.00016 M

T = 25.4°C

L = 250 nm

t = 2.5 hr

cc = .9999

rate = 7.39×10^{-4} sec^{-1}

sd = .022

636	29.2
1002	22.4
1560	15.0
1906	11.7
2698	6.3
3123	4.7

TABLE IX (cont.)

o-Methylbenzonitrile oxide

C = 1.73 M

S = 0.00016 M

T = 25.4°C

L = 250 nm

t = 3.0 hr

cc = 1.0000

rate = 8.94×10^{-4} sec^{-1}

sd = .022

time (s)	dA
488	38.1
574	35.6
875	27.0
1118	21.9
1454	16.1

C = 2.09 M

S = 0.00016 M

T = 25.4°C

L = 250 nm

t = 2.5 hr

cc = .9999

rate = 12.4×10^{-4} sec^{-1}

sd = .035

time (s)	dA
388	43.9
478	39.5
623	33.6
761	28.3
912	23.3
1166	17.0
1611	9.7

C = 2.37 M

S = 0.00016 M

T = 25.4°C

L = 250 nm

t = 2.0 hr

cc = .9999

rate = 16.4×10^{-4} sec^{-1}

sd = .030

time (s)	dA
259	53.8
314	49.4
369	45.6
459	39.4
600	31.3
825	22.2
1296	10.1
2368	1.7

TABLE IX (cont.)

o-Methylbenzonitrile oxide

C = 2.92 M

S = 0.00016 M

T = 25.4°C

L = 250 nm

t = 1.3 hr

cc = 1.0000

rate = 25.0×10^{-4} sec^{-1}

sd = .087

time (s)	dA
272	47.6
330	40.9
400	34.4
460	29.6
597	20.9
785	13.2

TABLE X

Benzohydroxamic acid

$C = 0.195$ M

$S = 0.0007$ M

$T = 68.8^{\circ}C$

$L = 270$ nm

$t = 51$ hr

cc = .9944

rate = 2.32×10^{-5} sec^{-1}

sd = .069

time (s)	dA
8	90.7
951	89.0
1903	86.8
3583	84.6
5275	80.8
8939	73.0
11011	70.9

$C = 0.520$ M

$S = 0.0007$ M

$T = 68.8^{\circ}C$

$L = 270$ nm

$t = 51$ hr

cc = .9977

rate = 6.39×10^{-5} sec^{-1}

sd = .16

23	88.2
966	81.5
1915	75.8
3597	67.0
5293	60.7
8987	48.2
11026	43.5

$C = 1.12$ M

$S = 0.0007$ M

$T = 68.8^{\circ}C$

$L = 270$ nm

$t = 44$ hr

cc = .9999

rate = 12.2×10^{-5} sec^{-1}

sd = .045

1343	86.5
2018	80.0
3270	68.7
4132	62.0
6072	48.0
9387	32.7

TABLE X (cont.)

Benzohydroxamic acid

C = 1.73 M
S = 0.0007 M
T = 68.8°C
L = 270 nm
t = 44 hr
cc = .9974
rate = 17.4×10^{-5} sec^{-1}
sd = .19

time (s)	dA
1311	79.5
1988	66.7
2535	61.5
3256	51.5
4095	47.0
5361	36.0
6056	33.5
8972	20.5

C = 2.37 M
S = 0.0007 M
T = 68.8°C
L = 265 nm
t = 51 hr
cc = .9984
rate = 24.6×10^{-5} sec^{-1}
sd = .22

time (s)	dA
35	57.1
993	41.3
1933	33.3
3607	25.0
5304	15.6
7551	8.0
9001	6.3
11043	3.7

C = 3.14 M
S = 0.0007 M
T = 68.8°C
L = 265 nm
t = 51 hr
cc = .9992
rate = 37.1×10^{-5} sec^{-1}
sd = .20

time (s)	dA
61	48.0
1033	33.0
1965	23.3
3634	12.1
7582	2.9
9041	1.7

TABLE X (cont.)

Benzohydroxamic acid

C = 4.53 M

S = 0.0007 M

T = 68.8°C

L = 265 nm

t = 51 hr

cc = .9952

rate = 32.1×10^{-5} sec^{-1}

sd = .48

time (s)	dA
46	34.7
1007	22.8
1950	15.0
3619	9.9
5317	5.0
7564	2.5
9023	1.5
11057	1.1

APPENDIX

PART III

Phenylnitromethanes in sulfuric, perchloric, hydrochloric and deuteriosulfuric acid

PART III

TABLE XI

Phenylnitromethane in sulfuric acid

C = 0.85 M
S = 0.00012 M
T = 68.8°C
L = 230 nm
t = 50 hr
cc = .9999
rate = 4.30 x 10^{-5} sec^{-1}
sd = .021

time (m)	dA (OD units)
11.0	.990
41.0	.915
67.0	.860
99.0	.790
139.0	.715
165.0	.670
200.0	.615
220.0	.580
268.0	.515
289.0	.480
313.0	.455
362.0	.400

C = 1.54 M
S = 0.00011
T = 68.8°C
L = 230 nm
t = 45 hr
cc = .9992
rate = 5.80 x 10^{-5} sec^{-1}
sd = .061

17.0	.960
31.5	.920
47.5	.870
61.5	.830
77.5	.790
94.0	.740
115.0	.680
135.5	.630
155.5	.610
176.5	.560
196.5	.520
215.5	.480
235.5	.450

C = 2.56 M
S = 0.00012 M
T = 68.8°C
L = 230 nm
t = 60 hr
cc = .9996
rate = 6.82 x 10^{-5} sec^{-1}
sd = .060

10.0	.980
40.0	.870
66.0	.800
98.0	.690
138.0	.590
164.0	.530
199.0	.460
219.0	.430
267.0	.345
288.0	.320
312.0	.295
388.0	.205

TABLE XI (cont.)

Phenylnitromethane in sulfuric acid

C = 3.23 M
S = 0.00011 M
T = 68.8°C
L = 231 nm
t = 45 hr
cc = .9994
rate = 5.00 x 10^{-5} sec^{-1}
sd = .048

time (m)	dA (OD units)
17.5	.940
32.0	.890
47.0	.875
61.0	.830
76.5	.800
93.0	.745
114.0	.710
134.5	.670
154.5	.630
175.5	.590
195.5	.550
215.0	.520
234.5	.490

C = 4.20 M
S = 0.00011 M
T = 68.8°C
L = 231 nm
t = 45 hr
cc = .9993
rate = 3.44 x 10^{-5} sec^{-1}
sd = .035

19.0	1.000
32.0	.970
47.0	.950
60.5	.920
76.0	.900
93.0	.875
114.0	.820
134.0	.790
154.5	.755
175.5	.730
195.5	.700
215.5	.670
234.5	.640

C = 5.69 M
S = 0.00011 M
T = 68.8°C
L = 232 nm
t = 6 days
cc = .9984
rate = 1.68 x 10^{-5} sec^{-1}
sd = .032

20.0	1.060
32.0	1.055
47.0	1.040
61.0	1.030
76.0	1.015
92.5	.990
113.5	.965
133.5	.945
154.0	.930
175.0	.910
195.0	.900
215.5	.870
234.0	.860

TABLE XI (cont.)

Phenylnitromethane in sulfuric acid

C = 7.18 M

S = 0.00012 M

T = 68.8°C

L = 233 nm

t = 80 hr

cc = .9943

rate = 1.18×10^{-5} sec^{-1}

sd = .036

time (m)	dA (OD units)
10.0	.895
39.0	.885
65.0	.860
97.0	.835
137.0	.820
163.0	.810
198.0	.780
218.0	.760
266.0	.735
287.0	.730
311.0	.725
416.0	.680

TABLE XII

Phenylnitromethane in perchloric acid

C = 0.235 M
S = 0.00016 M
T = 74.8°C
L = 236 nm
t = 72 hr (A = 1.310)
cc = .9994
rate = 2.96 x 10^{-5} sec^{-1}
sd = .022

time (s)	A (OD units)
359	.308
3270	.382
5563	.444
7683	.499
10124	.556
12917	.616
15183	.664
17111	.699
19298	.731

C = 0.494 M
S = 0.00016 M
T = 74.8°C
L = 236 nm
t = 72 hr (A = 1.409)
cc = .9996
rate = 4.93 x 10^{-5} sec^{-1}
sd = .029

time (s)	A (OD units)
329	.423
3243	.550
5537	.642
7662	.724
10101	.801
12892	.879
15158	.936
17085	.971
19271	1.022

C = 0.754 M
S = 0.00016 M
T = 74.8°C
L = 236 nm
t = 72 hr (A = 1.482)
cc = .9998
rate = 6.18 x 10^{-5} sec^{-1}
sd = .013

time (s)	A (OD units)
299	.447
3214	.616
5511	.728
7635	.824
10075	.914
12865	1.004
15133	1.066
17059	1.114
19247	1.161

TABLE XII (cont.)

Phenylnitromethane in perchloric acid

C = 1.09 M
S = 0.00016 M
T = 74.8°C
L = 236 nm
t = 72 hr (A = 1.319)
cc = .9995
rate = 7.59×10^{-5} sec^{-1}
sd = .073

time (s)	A (OD units)
269	.457
3184	.620
5478	.731
7610	.824
10046	.900
12839	.987
15104	1.041
17031	1.081
19221	1.108

C = 1.09 M
S = 0.00016 M
T = 74.8°C
L = 236 nm
t = 72 hr (A = 1.310)
cc = .9998
rate = 7.55×10^{-5} sec^{-1}
sd = .045

time (s)	A (OD units)
391	.452
3324	.611
5614	.721
7740	.813
10174	.893
12969	.971
15233	1.032
17169	1.066
19350	1.102

C = 1.03 M
S = 0.00015 M
T = 78.6°C
L = 230 nm
t = 5 days
cc = 1.0000
rate = 9.71×10^{-5} sec^{-1}
sd = .024

time (s)	dA
9	92.5
969	84.3
1805	77.5
3300	67.6
4770	58.0
6199	50.4
8636	40.2

TABLE XII (cont.)

Phenylnitromethane in perchloric acid

C = 1.84 M
S = 0.00015 M
T = 78.6°C
L = 230 nm
t = 5 days
cc = .9998
rate = 9.07 x 10^{-5} sec^{-1}
sd = .032

time (s)	dA
22	98.0
982	90.0
1820	83.3
3311	73.2
6212	56.5
8648	45.5
10868	36.3

C = 2.91 M
S = 0.00015 M
T = 78.6°C
L = 231 nm
t = 5 days
cc = .9994
rate = 5.68 x 10^{-5} sec^{-1}
sd = .033

34	101.0
998	95.7
1831	91.2
3321	83.3
4792	76.6
6222	71.5
8659	62.8
10880	53.9

C = 3.80 M
S = 0.00015 M
T = 78.6°C
L = 231 nm
t = 5 days
cc = 1.0000
rate = 3.27 x 10^{-5} sec^{-1}
sd = .006

47	108.0
1011	104.8
1846	102.0
3333	97.0
4805	92.4
6236	88.3
8673	81.3
10892	76.0

TABLE XII (cont.)

Phenylnitromethane in perchloric acid

C = 4.64 M

S = 0.00015 M

T = 78.6°C

L = 231 nm

t = 5 days

cc = .9983

rate = 1.95×10^{-5} sec^{-1}

sd = .005

time (s)	dA
61	110.9
1022	108.9
1861	107.2
3349	103.8
4817	101.1
6252	98.4
8686	93.6
10904	89.9

C = 5.45 M

S = 0.00016 M

T = 78.6°C

L = 231 nm

t = 11 days

cc = .9999

rate = 1.42×10^{-5} sec^{-1}

sd = .005

time (m)	dA
1.2	93.2
121.4	83.5
244.3	74.8
362.3	67.7
453.4	62.3
1382.4	27.8
1505.6	25.6
1742.4	21.1
1830.2	19.3

C = 7.12 M

S = .00016 M

T = 78.6°C

L = 231 nm

t = 11 days

cc = .9995

rate = 0.69×10^{-5} sec^{-1}

sd = .004

1.7	86.7
121.9	83.0
244.7	77.4
362.7	74.7
454.0	71.4
1382.8	49.1
1624.2	44.4
1742.8	42.0
1832.3	40.3

TABLE XII (cont.)

Phenylnitromethane in perchloric acid

C = 9.60 M

S = 0.00016 M

T = 78.6°C

L = 256 nm (benzaldehyde)

dt (G) = 1380 min

cc = .9996

rate = 8.52×10^{-5} sec^{-1}

sd = .12

time (m)	dA
2.5	99.7
122.8	57.3
245.5	29.0
454.6	10.1

TABLE XIII

Phenylnitromethane in hydrochloric acid

C = 0.469 M

S = 0.00013 M

T = 68.8°C

L = 231 nm

t = 49 hr

cc = .9990

rate = 2.46×10^{-5} sec^{-1}

sd = .036

time (m)	dA (OD units)
10.0	1.055
47.0	1.010
77.0	.960
108.0	.920
138.0	.875
168.0	.850
198.0	.805
228.0	.765
262.0	.730

C = 1.14 M

S = 0.00013 M

T = 68.8°C

L = 231 nm

t = 49 hr

cc = .9968

rate = 4.08×10^{-5} sec^{-1}

sd = .11

11.0	1.100
46.0	1.020
107.0	.870
137.0	.810
167.0	.745
197.0	.700
227.0	.645
261.0	.590

C = 3.04 M

S = 0.00013 M

T = 68.8°C

L = 231 nm

t = 49 hr

cc = .9973

rate = 4.21×10^{-5} sec^{-1}

sd = .10

12.0	1.165
46.0	1.060
76.0	1.000
107.0	.940
137.0	.875
167.0	.810
197.0	.740
227.0	.670
261.0	.620

TABLE XIII (cont.)

Phenylnitromethane in hydrochloric acid

C = 4.82 M

S = 0.00013 M

T = 68.8°C

L = 231 nm

t = 49 hr

cc = .9964

rate = 3.20×10^{-5} sec^{-1}

sd = .091

time (m)	dA (OD units)
13.0	1.150
45.0	1.075
75.0	1.010
106.0	.970
136.0	.910
166.0	.875
196.0	.825
226.0	.765
260.0	.700

C = 7.78 M

S = 0.00013 M

T = 68.8°C

L = 233 nm

t = 49 hr

cc = .9979

rate = 2.15×10^{-5} sec^{-1}

sd = .047

time (m)	dA (OD units)
15.0	1.090
45.0	1.050
75.0	1.015
106.0	.985
136.0	.930
166.0	.900
196.0	.870
226.0	.840
260.0	.790

TABLE XIV

p-Methylphenylnitromethane in sulfuric acid

C = 0.510 M
S = 0.00010 M
T = 68.8°C
L = 242 nm
t = 51 hr
cc = .9979
rate = 3.95 x 10^{-5} sec^{-1}
sd = .085

time (m)	dA (OD units)
0.0	.990
29.0	.920
59.0	.845
90.0	.805
122.0	.715
148.0	.695
179.0	.645
209.0	.600
239.0	.560

C = 1.11 M
S = 0.00010 M
T = 68.8°C
L = 241 nm
t = 51 hr
cc = .9999
rate = 5.84 x 10^{-5} sec^{-1}
sd = .034

0.0	.965
28.0	.880
58.0	.795
89.0	.710
121.0	.640
147.0	.575
178.0	.520
208.0	.470
238.0	.420

C = 1.40 M
S = 0.00010 M
T = 68.8°C
L = 242 nm
t = 51 hr
cc = .9997
rate = 6.17 x 10^{-5} sec^{-1}
sd = .050

0.0	.970
26.0	.870
56.0	.790
87.0	.700
119.0	.625
145.0	.570
176.0	.510
206.0	.450
236.0	.400

TABLE XIV (cont.)

p-Methylphenylnitromethane in sulfuric acid

C = 2.69 M
S = 0.00010 M
T = 68.8°C
L = 242 nm
t = 51 hr
cc = .9998
rate = 4.98×10^{-5} sec^{-1}
sd = .033

time (m)	dA (OD units)
0.0	.995
24.0	.925
54.0	.845
85.0	.765
117.0	.700
143.0	.640
174.0	.590
204.0	.540
234.0	.495

C = 3.36 M
S = 0.00010 M
T = 68.8°C
L = 242 nm
t = 51 hr
cc = .9999
rate = 3.95×10^{-5} sec^{-1}
sd = .019

time (m)	dA (OD units)
0.0	1.030
22.0	.980
52.0	.915
83.0	.845
115.0	.790
141.0	.740
172.0	.685
202.0	.640
232.0	.595

TABLE XV

p-Chlorophenylnitromethane in sulfuric acid

C = 1.40 M
S = 0.00006 M
T = 68.8°C
L = 242 nm
t = 48 hr
cc = .9999
rate = 4.27 x 10^{-5} sec^{-1}
sd = .025

time (s)	dA (OD units)
0	.788
1181	.750
2980	.690
4833	[illegible]0
6761	[illegible]90
8333	.550
10120	.510
11931	.470
13756	.440

C = 2.69 M
S = 0.00006 M
T = 68.8°C
L = 242 nm
t = 48 hr
cc = .9999
rate = 8.52 x 10^{-5} sec^{-1}
sd = .049

51	.622
1242	.568
3040	.490
4900	.416
6815	.352
8392	.306
10184	.264
12006	.224
13813	.196

C = 3.36 M
S = 0.00006 M
T = 68.8°C
L = 242 nm
t = 48 hr
cc = .9999
rate = 8.32 x 10^{-5} sec^{-1}
sd = .038

107	.634
1306	.576
3106	.500
4962	.428
6879	.362
8455	.318
10245	.272
12082	.234
13873	.204

TABLE XV (cont.)

p-Chlorophenylnitromethane in sulfuric acid

C = 4.01 M
S = 0.00006 M
T = 68.8°C
L = 243 nm
t = 48 hr
cc = .9999
rate = 6.52 x 10^{-5} sec^{-1}
sd = .029

time (s)	dA (OD units)
177	.678
1370	.628
3172	.562
5029	.498
6944	.438
8522	.393
10310	.352
12157	.310
13937	.278

C = 4.83 M
S = 0.00006 M
T = 68.8°C
L = 243 nm
t = 48 hr
cc = .9997
rate = 4.51 x 10^{-5} sec^{-1}
sd = .039

235	.690
1430	.650
3238	.604
5090	.552
7004	.504
8590	.468
10374	.432
12228	.402
13992	.372

C = 5.69 M
S = 0.00006 M
T = 68.8°C
L = 243.7 nm
t = 48 hr
cc = .9996
rate = 3.10 x 10^{-5} sec^{-1}
sd = .030

300	.738
1495	.706
3305	.664
5151	.628
7067	.592
8666	.564
10442	.538
12296	.506
14058	.478

TABLE XVI

m-Nitrophenylnitromethane in sulfuric acid

C = 0.85 M

S = 0.00007 M

T = 68.8°C

L = 232 nm

t = 7 days

cc = .9960

rate = 0.652 x 10^{-5} sec^{-1}

sd = .016

time (m)	dA (OD units)
10.0	.540
29.0	.533
50.0	.530
155.0	.509
241.0	.490
326.0	.477

C = 1.54 M

S = 0.00007 M

T = 68.8°C

L = 220 nm

t = 7 days

cc = .9964

rate = 1.20 x 10^{-5} sec^{-1}

sd = .026

time (m)	dA (OD units)
10.0	.775
29.0	.770
50.0	.760
82.0	.750
101.0	.730
132.0	.715
155.0	.710
178.0	.700
198.0	.685
219.0	.680
240.0	.660
261.0	.650
279.0	.645
300.0	.635
326.0	.620

TABLE XVI (cont.)

m-Nitrophenylnitromethane in sulfuric acid

C = 2.56 M

S = 0.00007 M

T = 68.8°C

L = 220 nm

t = 46 hr

cc = .9956

rate = 3.32 x 10^{-5} sec^{-1}

sd = .078

time (m)	dA (OD units)
9.0	.800
28.0	.760
49.0	.710
81.0	.710
100.0	.685
131.0	.635
154.0	.630
177.0	.595
197.0	.535
218.0	.535
239.0	.510
259.0	.495
277.0	.480
299.0	.450
325.0	.440
533.0	.275

C = 3.23 M

S = 0.00007 M

T = 68.8°C

L = 220 nm

t = 46 hr

cc = .9994

rate = 5.30 x 10^{-5} sec^{-1}

sd = .048

7.0	.770
27.0	.720
48.0	.690
80.0	.630
99.0	.595
130.0	.545
153.0	.510
176.0	.460
196.0	.440
216.0	.405
238.0	.380
258.0	.355
276.0	.335
298.0	.315
324.0	.290
544.0	.140

TABLE XVI (cont.)

m-Nitrophenylnitromethane in sulfuric acid

C = 3.74 M
S = 0.00006 M
T = 68.8°C
L = 220 nm
t = 27.5 hr
cc = .9970
rate = 6.41 x 10^{-5} sec^{-1}
sd = .18

time (m)	dA (OD units)
70.0	.690
101.0	.600
136.0	.550
163.0	.500
195.0	.435
232.0	.370
263.0	.325

C = 5.62 M
S = 0.00006 M
T = 68.8°C
L = 221 nm
t = 27.5 hr
cc = .9986
rate = 5.98 x 10^{-5} sec^{-1}
sd = .12

time (m)	dA (OD units)
69.0	.720
100.0	.645
135.0	.575
162.0	.525
194.0	.470
231.0	.410
262.0	.355

C = 7.45 M
S = 0.00006 M
T = 68.8°C
L = 221 nm
t = 51.5 hr
cc = .9987
rate = 2.59 x 10^{-5} sec^{-1}
sd = .050

time (m)	dA (OD units)
69.0	.780
100.0	.740
135.0	.710
162.0	.680
194.0	.645
231.0	.610
262.0	.575

TABLE XVII

p-Nitrophenylnitromethane in sulfuric acid

C = 3.36 M

S = 0.00006 M

T = 68.8°C

L = 267 nm

t = 24 hr

cc = .9987

rate = 6.43 x 10^{-5} sec^{-1}

sd = .059

time (s)	dA
2	10.0
1974	8.9
5506	7.0
9100	5.7
12676	4.3
14604	4.0

C = 4.01 M

S = 0.00006 M

T = 68.8°C

L = 267 nm

t = 24 hr

cc = .9967

rate = 11.2 x10^{-5} sec^{-1}

sd = .13

66	8.6
2037	7.0
3734	5.8
5570	4.6
7368	3.9
9167	3.4
10975	2.6
12775	2.1
14674	1.6

C = 4.83 M

S = 0.00006 M

T = 68.8°C

L = 267 nm

t = 24 hr

cc = .9994

rate = 15.0 x 10^{-5} sec^{-1}

sd = .18

130	7.3
2098	5.3
3799	4.2
5640	3.3
7440	2.3
9232	1.8
11043	1.4
12842	1.1
14751	0.8

TABLE XVII (cont.)

p-Nitrophenylnitromethane in sulfuric acid

C = 5.69 M
S = 0.00006 M
T = 68.8°C
L = 267 nm
t = 24 hr
cc = .9958
rate = 13.8 x 10^{-5} sec^{-1}
sd = .52

time (s)	dA
187	7.4
2170	5.4
3872	4.4
5706	3.1
7506	2.7
9295	2.1

C = 6.47 M
S = 0.00006 M
T = 68.8°C
L = 267 nm
t = 24 hr
cc = .9989
rate = 11.6 x 10^{-5} sec^{-1}
sd = .096

262	7.7
3937	4.7
5779	4.0
9374	2.5
12970	1.7
14903	1.4

C = 7.33 M
S = 0.00006 M
T = 68.8°C
L = 267 nm
t = 24 hr
cc = .9987
rate = 7.43 x 10^{-5} sec^{-1}
sd = .14

324	9.0
2427	7.8
4003	7.0
7651	5.2
9453	4.8
11248	4.0
13036	3.6
14977	3.0

TABLE XVIII

o-Methylphenylnitromethane in sulfuric acid

C = 0.520 M
S = 0.00013 M
T = 68.8°C
L = 232 nm
t = 7.5 days
cc = .9986
rate = .97 x 10^{-5} sec^{-1}
sd = .017

time (s)	dA
8	45.3
1066	45.2
3264	44.4
5203	43.4
6781	43.0
8381	42.3
10715	40.9
13234	40.0

C = 1.73 M
S = 0.00013 M
T = 68.8°C
L = 234 nm
t = 7.5 days
cc = .9968
rate = 1.47 x 10^{-5} sec^{-1}
sd = .023

42	59.4
1101	57.5
3293	56.1
5240	54.9
6820	52.9
8437	51.7
10747	50.2
13268	48.8

C = 2.37 M
S = 0.00013 M
T = 68.8°C
L = 235 nm
t = 7.5 days
cc = 1.0000
rate = 1.52 x 10^{-5} sec^{-1}
sd = .011

59	60.0
1118	58.8
3312	57.0
5257	54.9
6837	54.0
8455	52.5
10764	51.0
13284	48.9

TABLE XIX

o-Methylphenylnitromethane in perchloric acid

C = 7.12 M

S = 0.00016 M

T = 78.5°C

L = 259 nm (o-tolualdehyde)

t = 5 days

cc = 1.0000

rate = 1.86 x 10^{-5} sec^{-1}

sd = .029

time (s)	dA
8	41.0
2712	39.0
6477	36.2
9670	34.3

C = 8.30 M

S = 0.00016 M

T = 78.5°C

L = 260 nm (o-tolualdehyde)

t = 24 hr

cc = .9957

rate = 7.09 x 10^{-5} sec^{-1}

sd = .22

18	76.2
2725	62.5
6487	43.0
9678	39.1
13862	27.3
17301	23.6
20743	17.8
23371	13.4

C = 8.98 M

S = 0.00016 M

T = 78.5°C

L = 261 nm (o-tolualdehyde)

t = 24 hr

cc = .9954

rate = 23.6 x 10^{-5} sec^{-1}

sd = 1.0

28	46.0
2739	30.1
6495	11.1
13871	1.5
17309	1.0

TABLE XX

2,4,6-Trimethylphenylnitromethane in sulfuric acid

C = 0.520 M

S = 0.0009 M

T = 70.0°C

L = 244 nm

t = 7 days

cc = .9983

rate = 0.82 x 10^{-5} sec^{-1}

sd = .003

time (m)	dA (OD units)
0.0	.551
50.0	.539
100.0	.528
150.0	.519
200.0	.506
250.0	.488
300.0	.481
350.0	.467
400.0	.457
450.0	.444
500.0	.436
550.0	.424
600.0	.416
650.0	.403
700.0	.392
750.0	.381
800.0	.374
850.0	.362

C = 2.32 M

S = 0.0009 M

T = 70.0°C

L = 244 nm

t = 7 days

cc = .9947

rate = 1.09 x 10^{-5} sec^{-1}

sd = .004

20.0	.552
40.0	.544
60.0	.538
80.0	.529
100.0	.525
120.0	.519
140.0	.508
160.0	.502
180.0	.497
200.0	.489
220.0	.485
240.0	.477
260.0	.473
280.0	.467
300.0	.457
320.0	.455
340.0	.445
360.0	.442
380.0	.436

TABLE XXI

Phenylnitromethane in sulfuric acid

C = 2.92 M

S = 0.00012 M

T = 63.1°C

L = 231.5 nm

t = 4 days

cc = 1.0000

rate = 3.66 x 10^{-5} sec^{-1}

sd = .004

time (s)	dA
30	81.3
1701	76.5
3801	71.0
7376	62.2
9939	56.8
12378	51.7
14876	47.3
18579	41.3

C = 2.92 M

S = 0.00012 M

T = 63.1°C

L = 231.5 nm

t = 4 days

cc = 1.0000

rate = 3.75 x 10^{-5} sec^{-1}

sd = .006

46	80.8
1719	76.0
3819	70.6
7390	61.4
9952	56.0
12392	51.2
14888	46.5
20160	38.0

C = 2.92 M

S = 0.00012 M

T = 78.3°C

L = 232 nm

t = 5 days

cc = .9997

rate = 14.6 x 10^{-5} sec^{-1}

sd = .065

40	72.0
1034	62.2
2018	54.5
2978	48.0
4102	40.5
6106	30.5
9276	18.6

TABLE XXI (cont.)

Phenylnitromethane in sulfuric acid

C = 2.92 M
S = 0.00012 M
T = 78.3°C
L = 232 nm
t = 5 days
cc = .9997
rate = 14.7 x 10^{-5} sec^{-1}
sd = .063

time (s)	dA
59	72.5
1046	63.0
2033	54.9
3000	47.7
4113	40.8
5044	36.0
7706	24.0
9289	18.5

C = 2.92 M
S = 0.00015 M
T = 88.5°C
L = 232 nm
t = 2 days
cc = .9997
rate = 33.6 x 10^{-5} sec^{-1}
sd = .14

30	74.0
522	63.4
1100	52.4
1595	44.6
2960	27.7
3736	20.5
4352	16.2

C = 2.92 M
S = 0.00015 M
T = 88.5°C
L = 232 nm
t = 2 days
cc = .9993
rate = 34.6 x 10^{-5} sec^{-1}
sd = .22

46	75.4
534	64.8
1115	53.9
1618	46.0
2384	35.3
2975	28.0
4366	17.0

TABLE XXI (cont.)

Phenylnitromethane in sulfuric acid

C = 4.68 M
S = 0.00012 M
T = 63.1°C
L = 232 nm
t = 4 days
cc = 1.0000
rate = 1.79 x 10^{-5} sec^{-1}
sd = .010

time (s)	dA
59	83.0
1733	80.4
3842	77.7
7404	73.4
9965	69.9
12409	66.6
14904	63.2
21500	56.7

C = 4.68 M
S = 0.00012 M
T = 78.3°C
L = 232 nm
t = 5 days
cc = .9999
rate = 7.97 x 10^{-5} sec^{-1}
sd = .027

time (s)	dA
73	73.2
1056	67.8
2045	62.2
3021	58.0
4123	53.4
5057	49.4
6136	45.7
7724	39.6
9304	35.0

C = 4.68 M
S = 0.00015 M
T = 88.5°C
L = 232 nm
t = 2 days
cc = .9994
rate = 16.8 x 10^{-5} sec^{-1}
sd = .10

time (s)	dA
62	88.8
553	82.0
1131	74.3
1635	68.4
2400	60.6
2990	55.1
3770	48.4
4380	42.3

TABLE XXII

Phenylnitromethane-α,α-d_2 in sulfuric acid

C = 2.92 M
S = 0.00013 M
T = 78.3°C
L = 232 nm
t = 3 days
cc = .9940
rate = 5.56×10^{-5} sec^{-1}
sd = .21

time (s)	dA
43	43.9
1983	37.8
3296	34.9
5248	30.4
7480	27.2
9470	24.4
11463	23.0
13202	20.7

C = 2.92 M
S = 0.00013 M
T = 78.3°C
L = 232 nm
t = 3 days
cc = .9964
rate = 5.67×10^{-5} sec^{-1}
sd = .18

time (s)	dA
60	43.9
1997	37.7
3309	34.6
5258	31.2
7497	27.1
9480	25.0
13214	20.5

C = 4.68 M
S = 0.00013 M
T = 78.3°C
L = 232 nm
t = 3 days
cc = .9956
rate = 3.30×10^{-5} sec^{-1}
sd = .13

time (s)	dA
2009	36.1
3325	34.3
5268	31.9
7510	29.4
9491	27.8
13228	25.3

TABLE XXIII

Phenylnitromethane in deuteriosulfuric and sulfuric acid

C = 0.506 M H_2SO_4

S = 0.00009 M

T = 74.8°C

L = 232 nm

t = 48 hr (A = 0.907)

cc = .9997

rate = 5.25×10^{-5} sec^{-1}

sd = .038

time (s)	A (OD units)
85	.233
2363	.302
4513	.364
7060	.429
9719	.492
12175	.541
16075	.611
18995	.654
22584	.700

C = 0.508 M D_2SO_4

S = 0.00009 M

T = 74.8°C

L = 232 nm

t = 48 hr (A = 0.921)

cc = .9999

rate = 8.35×10^{-5} sec^{-1}

sd = .030

65	.318
2350	.422
4504	.506
7045	.587
9700	.656
12158	.703
16058	.763
18975	.797
22567	.828

C = 1.11 M H_2SO_4

S = 0.00009 M

T = 74.8°C

L = 232 nm

t = 24 hr (A = 0.958)

cc = .9995

rate = 10.5×10^{-5} sec^{-1}

sd = .099

188	.346
2168	.450
5134	.577
7327	.653
9630	.717
11900	.769
14530	.815
17150	.852
19590	.877
21970	.896

TABLE XXIII (cont.)

Phenylnitromethane in deuteriosulfuric and sulfuric acid

C = 1.11 M D_2SO_4
S = 0.00009 M
T = $74.8^{\circ}C$
L = 232 nm
t = 24 hr (A = 1.113)
cc = .9997
rate = 9.82×10^{-5} sec^{-1}
sd = .073

time (s)	A (OD units)
173	.479
2158	.587
5124	.717
7307	.792
9620	.863
11880	.920
14510	.958
17140	.993
19560	1.018
21960	1.037

C = 1.71 M H_2SO_4
S = 0.00009 M
T = $74.8^{\circ}C$
L = 232 nm
t = 24 hr (A = 0.914)
cc = .9996
rate = 12.8×10^{-5} sec^{-1}
sd = .11

223	.323
2198	.444
5164	.583
7347	.662
9660	.727
11930	.774
14560	.814
17190	.842
19620	.863
22010	.878

C = 1.71 M D_2SO_4
S = 0.00009 M
T = $74.8^{\circ}C$
L = 232 nm
t = 24 hr (A = 1.077)
cc = .9999
rate = 8.74×10^{-5} sec^{-1}
sd = .022

203	.418
2178	.529
5144	.653
7337	.728
9640	.790
11920	.843
14540	.890
17170	.928
19600	.958
21990	.979

TABLE XXIII (cont.)

Phenylnitromethane in deuteriosulfuric and sulfuric acid

C = 2.31 M H_2SO_4
S = 0.00009 M
T = 74.8°C
L = 232 nm
t = 24 hr (A = 0.958)
cc = .9999
rate = 12.4×10^{-5} sec^{-1}
sd = .059

time (s)	A (OD units)
243	.360
2228	.482
5194	.626
7377	.704
9690	.767
11960	.813
14600	.855
17220	.883
19650	.904
22040	.918

C = 2.31 M D_2SO_4
S = 0.00009 M
T = 74.8°C
L = 232 nm
t = 24 hr (A = 1.062)
cc = .9999
rate = 7.26×10^{-5} sec^{-1}
sd = .024

233	.392
2218	.482
5174	.594
7367	.661
9670	.724
11950	.774
14580	.826
17210	.867
19640	.900
22030	.923

C = 3.00 M H_2SO_4
S = 0.00009 M
T = 74.8°C
L = 232 nm
t = 24 hr (A = 0.967)
cc = .9999
rate = 10.5×10^{-5} sec^{-1}
sd = .055

293	.344
2258	.452
5224	.590
7407	.668
9720	.740
11990	.782
14630	.826
17250	.860
19690	.886
22080	.904

TABLE XXIII (cont.)

Phenylnitromethane in deuteriosulfuric and sulfuric acid

C = 3.00 M D_2SO_4

S = 0.00009 M

T = 74.8°C

L = 232 nm

t = 24 hr (A = 1.133)

cc = .9998

rate = 5.88×10^{-5} sec^{-1}

sd = .021

time (s)	A (OD units)
278	.454
2248	.527
5214	.623
7397	.683
9700	.740
11980	.788
14610	.838
17240	.882
19640	.917
22060	.943

C = 4.00 M H_2SO_4

S = 0.00009 M

T = 74.8°C

L = 232 nm

t = 30 hr (A = 0.986)

cc = .9999

rate = 7.05×10^{-5} sec^{-1}

sd = .017

120	.303
2395	.402
4562	.486
7090	.567
9757	.639
12210	.693
16119	.763
19031	.805
22625	.847

C = 4.00 M D_2SO_4

S = 0.00009 M

T = 74.8°C

L = 232 nm

dt (G) = 24 hr

cc = .9997

rate = 3.79×10^{-5} sec^{-1}

sd = .006

time (s)	dA (OD units)
101	.701
2380	.645
4537	.594
7075	.539
9738	.489
12194	.444
16094	.384
19012	.343
22603	.299

TABLE XXIII (cont.)

Phenylnitromethane in deuteriosulfuric and sulfuric acid

C = 5.30 M H_2SO_4

S = 0.00009 M

T = 74.8°C

L = 232 nm

dt (G) = 24 hr

cc = .9998

rate = 3.84×10^{-5} sec^{-1}

sd = .014

time (s)	dA (OD units)
150	.719
2427	.653
4602	.609
7125	.552
9800	.498
12250	.457
16160	.390
19070	.350
22670	.303

C = 5.30 M D_2SO_4

S = 0.00009 M

T = 74.8°C

L = 232 nm

dt (G) = 24 hr

cc = .9991

rate = 1.96×10^{-5} sec^{-1}

sd = .014

time (s)	dA (OD units)
137	.651
2410	.625
4587	.597
7110	.569
9779	.543
12231	.518
16138	.477
19050	.447
22648	.420