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KINETICS OF AROMATIC NITRATION

Berkeley, California

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KINETICS OF AROMATIC NITRATION

Reid Clark Miller and Theodore Vermeulen

October 15, 1963

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KINETICS OF AROMATIC NITRATION

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Berkeley, California

October 15, 1963

ABSTRACT

Heterogeneous nitration rates of the aromatic organic compound 1, 3-bis(trifluoromethyl)benzene in a well-agitated batch system have been measured in an extensive range of very concentrated mixed acids (aqueous HNO_3 and H_2SO_4), with each run at essentially constant acid composition. The observed conversions correlated well with a first-order dependence on the fraction of aromatic unconverted.

Solubilities of the aromatic compound have been measured over the range of acid compositions. By eliminating solubility from the kinetic results, the apparent rate coefficient along the H_2SO_4-H_2O base line is found to have a maximum value near 92 weight-percent H_2SO_4. The coefficient also exhibits a maximum on the HNO_3-H_2SO_4 base line at approximately 55 weight-percent H_2SO_4.

The nitration rates are correlated in a manner that indicates, at any given mixed-acid composition, (a) the nonideality of the reaction medium expressed by the activity-coefficient behavior; and (b) the ability of the medium to convert HNO_3 to NO_2^+, the attacking species in the nitration sequence. To apply this correlation to aromatics having varying resistance to nitration, the correlation has been extended to the dilute mixed-acid region, using equilibrium equations based on the nitronium-ion mechanism. This correlation is generally applicable, except for effects that are not a direct result of the state of the acid medium--such as a change in aromatic solubility, a change in aromatic reactivity through complexing or protonation, or a change in the nitration mechanism characteristic of the particular aromatic.

From the nitration kinetics, values of the Hammett acidity function at 25°C are estimated for mixed-acid compositions, as interpolations between previously determined experimental values along the HNO_3-H_2O and H_2SO_4-H_2O base lines.

I. INTRODUCTION

A. Historical Background

Nitration of aromatic compounds has been studied extensively since early in this century. This reaction has been used as an example of the more general mechanism of aromatic substitution, since it is an irreversible reaction and introduction of only one nitro group is usually possible. Commercial applications of this reaction are also very important, especially in the explosives and dyestuffs industries.

By far the most common medium for nitration is "mixed acid," some composition of the ternary system HNO_3-H_2O-H_2SO_4. To elucidate the sequence of elementary steps involved in the nitration of aromatics with mixed acid, it has been necessary to follow two lines of experimentation. One involved nonkinetic studies to determine in what form the nitric acid exists in the various solvents of interest; the other, kinetic studies to determine which of the possible nitrating agents existent in the mixture is the actual reactant.

From early work, many mechanisms were proposed. Until recently the most prevalent one involved addition of a molecule of nitric acid across a double bond in the ring of the aromatic, with subsequent elimination of water leaving the $-NO_2$ group attached to the ring. However, it was shown that aromatics with electron-withdrawing (electrophilic) groups attached to the ring are nitrated more slowly than benzene and mainly in the meta position, while those with electron-releasing (nucleophilic) groups are nitrated more rapidly than benzene and mainly in the ortho and para positions. These positions of preferred nitration are the positions of highest electron density in each case.

The addition-elimination path is no longer held to; rather it is generally accepted that aromatic nitration occurs through substitution of an electrophilic agent for a hydrogen of the ring. The ability of possible nitrating agents, each represented as X-NO_2, to attack the aromatic ring is proportional to the electron affinity of X; hence we can arrange a series of possible agents in the order of increasing nitrating power[1]: $EtONO_2 \langle HONO_2 \langle AcONO_2 \langle NO_3NO_2 \langle ClNO_2 \langle H_2ONO_2^+ \langle NO_2^+$.

From studies of the physical and chemical properties of nitric acid in solution with water, sulfuric acid, and organic solvents, Hantzsch concluded that nitric acid exists in several different forms such as ionized true acid (H^+, NO_3^-), pseudo acid ($HO\text{-}NO_2$), and the ions $H_2NO_3^+$ and $H_3NO_3^{++}$ in sulfuric acid solutions.[2] The ratio of the depression of the freezing point of sulfuric acid by a given solute to the depression caused by the same concentration of nondissociated solute is known as the van't Hoff i-factor; this i-factor for nitric acid was determined by Hantzsch to be on the order of three, which would correspond to the equation

$$HNO_3 + 2H_2SO_4 \rightleftharpoons H_3NO_3^{++} + 2HSO_4^- .$$

He also determined from ultraviolet absorption that nitrate ion was not present in the sulfuric acid solutions. The high electrical conductivity of the solutions indicated ionization, which both Hantzsch and Usanovich[3] attributed to $H_2NO_3^+$ and $H_3NO_3^{++}$ ions.

Other authors considered that nitric acid exists as nitronium ion (NO_2^+) both in anhydrous nitric acid and in solutions of nitric acid and sulfuric acid.[4,5,6] Gillespie et al.,[7] repeating the experiments of Hantzsch with improved methods, have shown that the i-factor for nitric acid is very close to 4 instead of 3, indicating that the ionization proceeds as

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^- .$$

The existence of the species NO_2^+ has been confirmed through x-ray crystallography studies of solid NO_2ClO_4,[8] and N_2O_5.[9] Goddard, Hughes, and Ingold have shown[10] that the salt formed from nitric and perchloric acids is an equimolecular mixture of (NO_2^+) (ClO_4^-) and (H_3O^+) (ClO_4^-) instead of the compound ($H_3NO_3^{++}$) (ClO_4^-)$_2$ postulated by Hantzsch. Both NO_2ClO_4 and N_2O_5 were found to contain identical linear triatomic species as well as ClO_4^- and NO_3^- respectively. This linear triatomic species must then be NO_2^+.

Several other nitronium salts have been identified,[11] all of which exhibit a Raman-spectrum line at 1400 cm^{-1}. Millen has shown that

the species responsible for this line gives no other Raman lines, and must then be either a diatomic or a linear triatomic species.[12] By measuring the intensities of the Raman line at 1400 cm^{-1}, Chedin has determined the concentration of NO_2^+ in mixed acid solutions,[13] as shown in Fig. 1. Vapor-pressure measurements of HNO_3 in H_2O-H_2SO_4 mixtures agree with these results[1]; starting with pure water as a solvent, the vapor pressure of nitric acid gradually increases because of repression of the ionization to nitrate ions, and then decreases again in more concentrated sulfuric acid as ionization to nitronium ion proceeds. Freezing-point data indicate that about 1% by weight nitronium ion exists in anhydrous nitric acid. The Raman line at 1400 cm^{-1} is present in anhydrous nitric acid, but cannot be detected upon dilution with water to 95% by weight HNO_3 or less.

Martinsen early established that aromatic nitration in the solvent sulfuric acid was a second-order reaction, first-order in nitric acid and first-order in aromatic.[14] This has been confirmed many times for many different aromatic compounds. Martinsen also showed that the rate of nitration of nitrobenzene increased with sulfuric acid concentration to a maximum at approximately 90% sulfuric, and then decreased; this was confirmed later by several other workers for various aromatics.

In 1933 Hetherington and Masson found[15] that in the two-phase nitration of nitrobenzene, reaction ceased at certain specified mixed acid concentrations, which are shown in Fig. 1. It may be seen that the line drawn through these concentrations corresponds well with the limit of detection of the nitronium ion.

Westheimer and Kharasch[16] demonstrated that the plot of the logarithm of the rate constant versus percent sulfuric acid up to the maximum in the curve parallels the plot of the fraction of the indicator pp'p''-trinitrotriphenylcarbinol converted to its positive ion. This indicator is known to ionize as

$$R_3COH + 2H_2SO_4 \rightleftharpoons R_3C^+ + H_3O^+ + 2HSO_4^- .$$

Deno and Stein have confirmed this from 10 to 55%m H_2SO_4.[38] Westheimer and Kharasch also showed that the maximum in the rate

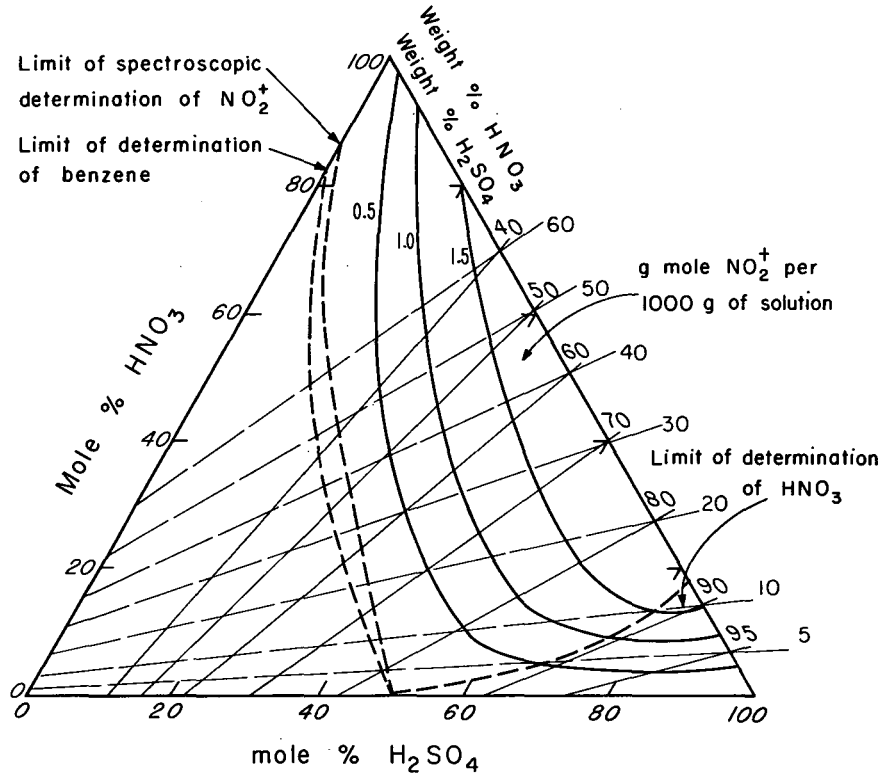

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Fig. 1. Nitronium ion concentration in mixed acids.

curve occurs at a constant value of the acidity of the medium as specified by the Hammett acidity function, rather than at a constant sulfuric acid concentration.

Bennett et al. postulated that NO_2^+ is the nitrating agent from 50 mole % aqueous sulfuric acid all the way to oleum solutions.[17] They found that the rate constant for nitration rises in media above 90% by weight sulfuric acid when (a) initial nitric acid is increased, (b) initial aromatic concentration is increased, and (c) bisulfate is added. The rate constant decreased in media below 90% sulfuric for all three of the above. They postulated a mechanism consistent with the above observations with the rate-determining step involving a ternary collision of NO_2^+, aromatic, and bisulfate ions. However, the above mentioned results do not positively identify the attacking species in nitration.

More definite evidence has come about as a result of the work of Hughes, Ingold, and co-workers.[18] Using acetic acid and nitromethane as solvents for nitric acid, they found that the more reactive aromatics exhibited pseudo-zero-order kinetics, the less reactive aromatics exhibited pseudo-first-order kinetics, and some of intermediate reactivity exhibited intermediate kinetics. They concluded, for the pseudo-zero-order reactions, that the aromatic must not be involved in the rate-determining step. The slow step must therefore be the formation of the attacking species; this could not be HNO_3 or $H_2NO_3^+$ because the HNO_3 would already be present, and formation of $H_2NO_3^+$ involves only a proton transfer, which should be almost instantaneous. Hence the rate-determining step must involve the breaking of a bond, as occurs in the formation of NO_2^+. They argue that the formation of NO_2^+ is a two-step process because added nitrate retards the pseudo-zero-order reaction greatly while water has a much smaller retarding effect.

Melander showed that the bond between the $-NO_2$ group and the ring must be very nearly completely formed before the hydrogen is removed, by noting that substitution of tritium into the ring has no effect on the rate of nitration.[19] If we assume that a basic species is

necessary for removal of the hydrogen, then the cation formed by the aromatic and NO_2^+ must be an intermediate.

Consistent with the above observations, Hughes, Ingold, and Reed prescribe the following mechanism,[18] nearly the same as Bennett's except for details of the last step, for nitration in nitric acid or organic solvents:

$$HNO_3 + HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^- ,$$

$$H_2NO_3^+ \rightleftharpoons NO_2^+ + H_2O ,$$

$$H_2O + HNO_3 \rightleftharpoons H_2O \cdot HNO_3 ,$$

$$ArH + NO_2^+ \longrightarrow \left[Ar\text{-}H \atop \diagdown NO_2 \right]^+ \xrightarrow[NO_3^-]{} ArNO_2 + HNO_3 .$$

In the presence of acids stronger than nitric, the ionization to nitronium ion can be represented by Gillespie's equilibrium reaction.

The decrease in the rate of nitration above 90% sulfuric acid is attributed to conversion of the aromatic to the conjugate acid, and to increased polarity of the medium, which should decrease the rate of attack of NO_2^+ on the uncharged aromatic.

Except for the work of Hetherington and Masson, all of the above mentioned work was carried out with polar aromatics that were completely soluble in the nitrating media. For such relatively nonpolar aromatics as benzene, toluene, and chlorobenzene, which are only slightly soluble in nitrating media, nitration is controlled by the rates at which they dissolve[20] unless agitation is sufficient to maintain equilibrium distribution of the aromatics between the phases.

Significant data on the nitration of immiscible aromatics are obtained from the studies of Lewis and Suen[21] with benzene, and McKinley and White[22] and Kobe et al.[23] with toluene. Hougen and Watson[24] have derived a rate equation for heterogeneous nitration and have used it to correlate the data of Lewis and Suen and also those of McKinley and White. The results of these two-phase studies in sulfuric acid indicate that an irreversible second-order reaction does occur, but that the rate in the organic phase is negligible compared

with the rate in the acid phase. No maximum is found in the rate curve as in homogeneous reactions, because solubility of aromatics increases rapidly from 90% to 100% sulfuric acid and obscures any effects that would decrease the rate.[25]

The form of second-order rate equation adaptable to the experimental observations is

$$R = k\,(HNO_3)_a\,(ArH)_o\,, \qquad (1)$$

where the rate R is moles converted per unit of time per unit volume of acid phase. The mole fraction of nitric acid, $(HNO_3)_a$, is measured in the acid phase, while $(ArH)_0$ is the mole fraction of unnitrated aromatic in the organic phase. The apparent rate coefficient k is a function of both temperature and composition of the acid phase. If it is assumed that the quantity of aromatic soluble in the acid phase is small compared with the total aromatic phase, we may write Eq. (1) as

$$R = \frac{-N_0}{V_a}\,\frac{d(ArH)_o}{dt} = k\,(ArH)_o\,(HNO_3)_a\,, \qquad (2)$$

where N_0 is the total number of moles of aromatic in the reactor, V_a the volume of the acid phase, and t the time. Letting g be the fraction of aromatic converted, we may write

$$\frac{N_0}{V_a}\,\frac{dg}{dt} = k\,(1-g)\,x_N\left(1 - \frac{N_0}{N_N}\,g\right), \qquad (3)$$

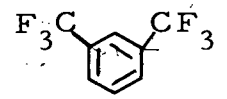
where x_N is the initial mole fraction, and N_N the initial total moles, of nitric acid in the acid phase. Upon integration we obtain

$$\left[\frac{N_0}{V_a\,x_N(1 - N_0/N_N)}\right]\ln\left[\frac{1 - N_0 g/N_N}{1-g}\right] = kt. \qquad (4)$$

This equation assumes during any reaction: (a) constant composition of the acid medium, (b) very slight solubility of the aromatic phase in the acid phase, (c) equilibrium distribution of all components between the phases, and (d) availability of all the nitric acid in the acid phase.

B. Statement of the Problem

In order to give a kinetic interpretation of heterogeneous nitration of aromatics in concentrated mixed acids, we undertook to study the nitration rate over a very wide range of acid compositions. The aromatic chosen for these experiments was 1, 3-bis(trifluoromethyl)-benzene, for which the Lewis structure may be drawn as



This aromatic was chosen because it is extremely resistant to nitration,[26, 27] only one nitration product should result, and it is only slightly soluble in concentrated mixed acids.

We have nitrated the above aromatic in a wide range of mixed acid solutions in a well-agitated batch system, following the reaction by refractive index of the organic phase. Solubilities of both the unnitrated and nitrated aromatics have been measured in this range of acid compositions for use in interpretation of the kinetic results. A few preliminary nitrations of the compounds benzotrifluoride and nitrobenzene have been made in an attempt to find aromatics with the proper range of reactivity to provide kinetic data in the region between the dilute acids used for nitrating benzene and toluene and the very concentrated acids of this study.

II. EXPERIMENTAL

In order to determine the effect of mixed-acid composition, the rate of nitration of 1,3-bis(trifluoromethyl)benzene was studied in batch runs in a stirred 500-ml baffled glass flask, pictured in Fig. 2. The aromatic was used as obtained from Hooker Electrochemical Company. The acids used for preparation of the mixed acids were 70%w HNO_3, 90%w HNO_3, 96%w H_2SO_4, 30%w oleum, and solid SO_3 recovered from bottles of 30%w oleum. (The symbols %w and %m will be used to denote weight-percent and mole-percent, respectively.) The compositions of all acids were determined before mixing, by titration with standard NaOH and by density measurement. The NaOH was standardized by titration against primary standard potassium acid phthalate. Total acid and density determinations were also made of all mixed acids before use. The compositions of acids prepared with solid SO_3 were determined by total NO_3^- and SO_4^{--}, as 1,4-diphenyl-3,5-endoanilodihydrotriazole nitrate and barium sulfate, and checked by total acid titration.

The apparatus assembly is shown in Figs. 3 and 4. The reaction flask was suspended in a well-agitated and thermostated stainless-steel water bath, measuring $14 \times 14 \times 10$ inches, insulated with styrofoam. The temperature of the bath could be maintained constant within 0.1 deg C by means of an immersion heater regulated by an on-off temperature controller. The mixed acid was measured into this reaction flask through the neck for the reflux condenser, with the flask suspended in the bath. The aromatic compound was measured into a graduated cylinder that also was suspended in the bath. The bath was then brought to a temperature slightly below the desired reaction temperature. When the thermometer in the reaction flask showed that the acid had essentially reached bath temperature, the aromatic was quickly transferred to the reaction flask and stirring was started. Stirring was provided by a glass impeller driven by a small electric motor at between 250 and 300 revolutions per minute. The reaction flask was a 500-ml round-bottom three-necked boiling flask with four equally spaced vertical baffles (creases).

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Fig. 2. Reaction flask.

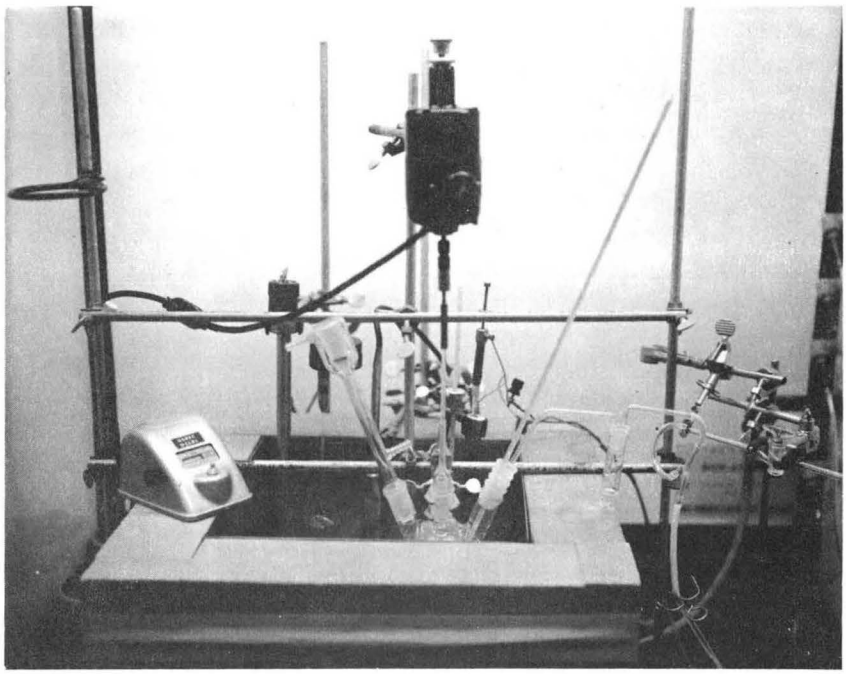

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Fig. 3. Apparatus assembly.

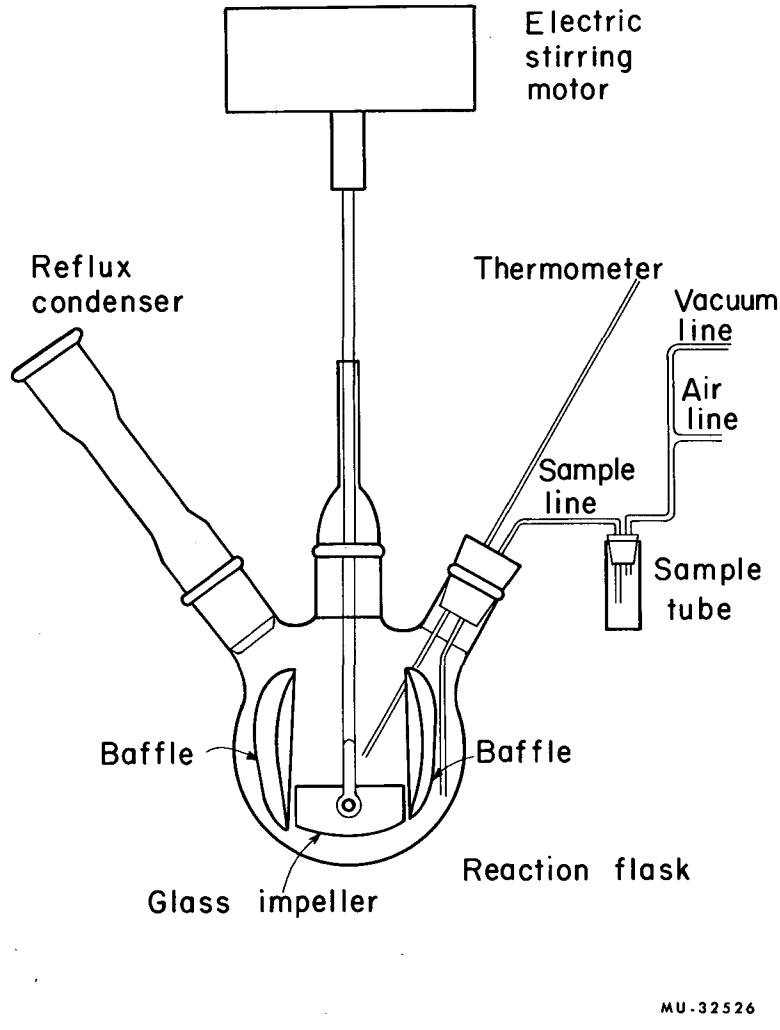

Fig. 4. Reactor assembly.

The flask diameter was 4.0 inches, the impeller was 2.0 inches long, and the creases protruded inward 0.6 inch, leaving only a 0.4-inch clearance between the impeller and the creases. Immediately after the stirring was begun, a slight temperature rise, on the order of 1 to 2 °C, would occur in the reaction flask, due to the heat of reaction of the aromatic. After three or four minutes the temperature of the flask could be held constant within 0.1 °C, at a value balancing the heat release and the heat transfer, for the remainder of the reaction.

At specified time intervals, samples of the dispersed reaction mixture were withdrawn through the sample line, without interruption of the stirring, by opening a valve on the vacuum line. As soon as the sample reached the sample tube, the tube was removed from the sampling system and placed in an ice bath to cool it quickly to a temperature near 0°C. Upon withdrawal of a sample, the phases always separated very rapidly--within a few seconds of the time they left the reaction flask. After completion of each run, portions of the organic phase from each sample tube were transferred to smaller tubes, and the refractive index was measured at 18°C. (A calibration curve for refractive index is shown in Fig. A-I of the Appendix.)

The solubility of the unnitrated aromatic in unreactive acid solutions was measured by means of a volumetric difference method. A 250-ml round-bottom boiling flask was equipped with a nipple on the bottom for connection with a large syringe. A 1-ml calibrated capillary pipet was attached to a ground glass joint fitted for the neck of the flask. Acid was allowed to enter the flask, partially filling the syringe and completely filling the flask. The capillary pipet was fitted into the neck of the flask, and the acid level was brought up to the bottom of the calibrations by pushing the acid out of the large syringe. The aromatic compound was added at the top of the capillary pipet by means of a small syringe. The volume of aromatic was noted, and the liquid level then drawn down into the 250-ml flask by use of the large syringe. The solution was agitated with a magnetic stirrer for several minutes, and the phases were allowed to separate completely. The aromatic was then pushed up into the capillary, and the

volume again measured. This procedure of mixing and measuring the volume undissolved was continued until no further change in aromatic volume could be noted. If the solubility was more than 1 ml, more additions of aromatic were made with the volume of each noted.

In the reactive acid mediums, the above procedure for solubility would not work, for extensive nitration would take place even at room temperature owing to the small amounts of aromatic present compared to nitric acid. Since the $-NO_2$ group on the aromatic nitro product absorbs in the ultraviolet range, a procedure was developed to utilize this property for measurement of solubilities. The acid was quickly saturated with the aromatic by violent shaking in a separatory funnel, with a great excess of aromatic over the amount soluble in the acid. The phases were then separated and the saturated acid heated for a period of time that would ensure complete conversion to the nitro compound. A known amount of this acid was diluted 1:1 by volume, to greatly decrease the solubility of aromatic. The aromatic nitro compound was then extracted from the acid with a known amount of cyclohexane. The cyclohexane was washed with dilute caustic and then with water to remove all traces of acid. Extraction efficiency was determined to be about 90% by weighing known amounts of aromatic into the acid, going through the extraction procedure, and comparing the amount recovered, as determined by a spectrophotometer, with the amount added. The concentration of nitro compound in the cyclohexane was determined by measuring the optical density at 3500Å with a Cary Type-14 spectrophotometer. A calibration curve was made by weighing portions of the nitro compound into volumetric flasks, and diluting to volume with cyclohexane. The curve is shown in Fig. A-II of the Appendix. The above procedure, but without the nitration step, was also used to measure the solubility of the nitro compound in various mixed acids, relying upon the low rate for further nitration in order to assure the purity of the extracted material. This procedure could also be used effectively to measure the solubility of nitratable aromatics in aqueous sulfuric acid by saturating with aromatic, adding some nitric acid, and reacting to complete conversion of the aromatic before extraction.

III. RESULTS AND DISCUSSION

A. Nitration of 1, 3-Bis(Trifluoromethyl)Benzene

1. Interpretation of Experiments

a. Rate plots. We now rewrite Eq. (4) in the abbreviated form

$$A \ln \psi = kt . \qquad (5)$$

Plots of the experimental run data as $A \ln \psi$ versus t were found to be straight lines for all the nitrations performed, except those using sulfuric acid concentrations above about 64%m. The method of least squares was used to find the statistically best linear fit for each run, the slope giving the value of k. A typical run is shown as Run 43 in Fig. 5; the nonzero intercept observed here will be discussed later.

In acids stronger than 64%m, the plots obtained were concave upward; plots of moles converted versus time were straight lines, as shown in Fig. 6. Near the origin a slight induction effect occurred, for which two possible reasons can be cited: (a) the initial rise in temperature due to heat of reaction, and (b) the greater solubility of the nitrated aromatic, perhaps causing incomplete transfer of the nitro compound back to the organic phase.

The nonlinearity of the semilogarithmic plot, and linearity of the Cartesian plot, will be seen to result from an increase in k as the reaction proceeds. This effect was greater for runs with the lowest HNO_3 content, since lower ratios of HNO_3 to aromatic had to be used to allow proper handling of samples. Each run was used only to obtain the rate of reaction at the initial acid composition. The slope corresponding to this condition could have been taken from either the semilogarithmic or the linear plot; the linear plots of moles converted versus time were selected because they appeared to give a more accurate slope.

The compositions of the mixed acids were calculated from the compositions and quantities of the acids used. Total acid content from these calculations agreed with the results of the titrations of the mixed acids with an average deviation of 0.6% and a maximum deviation of 1.5%. The percentage of water is the greatest in error; with only the small amounts by weight of water present, small errors in total acid

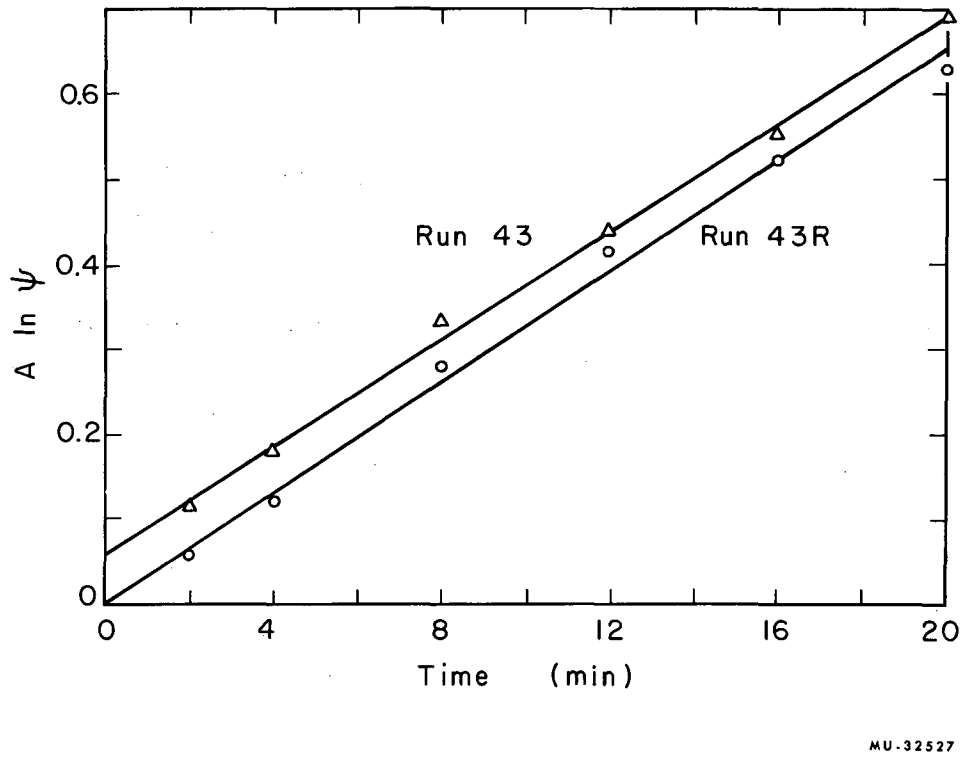

Fig. 5. Typical nitration of 1, 3-bis(trifluoromethyl)benzene.

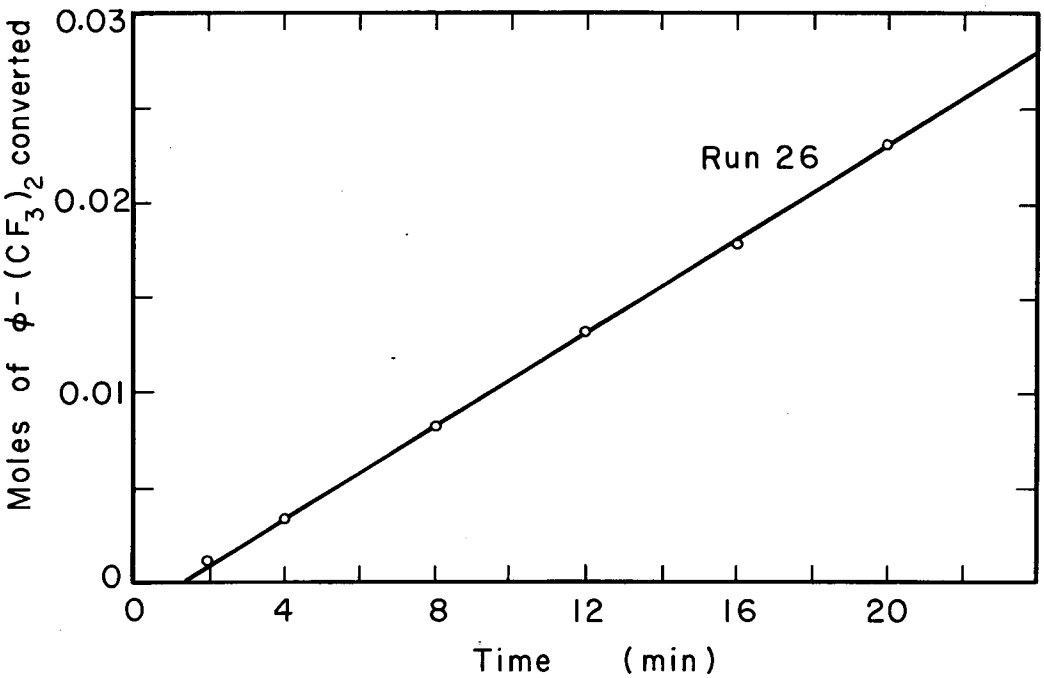

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Fig. 6. Nitration of 1, 3-bis(trifluoromethyl)benzene in very concentrated H_2SO_4.

titrations can cause a much larger error in the mole percent water calculated.

The results of all the nitrations of 1, 3-bis(trifluoromethyl)benzene are presented in Table A-I of the Appendix. From pairs of runs at the same acid composition but different temperatures (Runs 12 and 13, 52 and 53), an overall activation energy of 18.1 ± 0.3 kcal/g-mole was calculated, and this activation-energy value was then used to correct all k values to 50°C. The lines of constant k (at 50°C) obtained by interpolation and smoothing of the results are shown in Fig. 7 as a function of composition of the mixed acid. (The error in acid composition should not affect the general trends of the data, particularly as much of the error is eliminated in the interpolation and smoothing of the data required for the construction of Fig. 7.)

It is felt that mass-transfer resistances played no significant part in these heterogeneous reactions. Run 26 was made at a much slower stirring rate (100 to 150 rpm) than the rate used in all other nitrations (250 rpm); subsequently this run was repeated as Run 27 with stirring much more vigorous (350 rpm). The values of k from the two runs deviate from each other by about 18%, most of which is felt to be due to the slowness with which equilibrium mixing was attained at the slower stirring rate. The 18.1 kcal/g-mole activation energy also indicates that mass-transfer resistance is not appreciable.

b. Solubility of aromatic in acid. The solubility of 1, 3-bis-(trifluoromethyl)benzene as a function of mixed-acid composition is represented in Fig. 8. This plot was made by interpolating and cross-plotting from a limited number of data shown in Table A-II of the Appendix. Although the solubility measurements are believed to be accurate to ±5%, the interpolations made may introduce a total uncertainty of around 15%.

As mentioned in the experimental section, the course of the reaction was followed by measuring the refractive index of the organic phase. This method of analysis requires that the distribution of nitro compound greatly favor the aromatic phase over the acid phase at the phase-separation temperature used (0°C). The distribution was tested

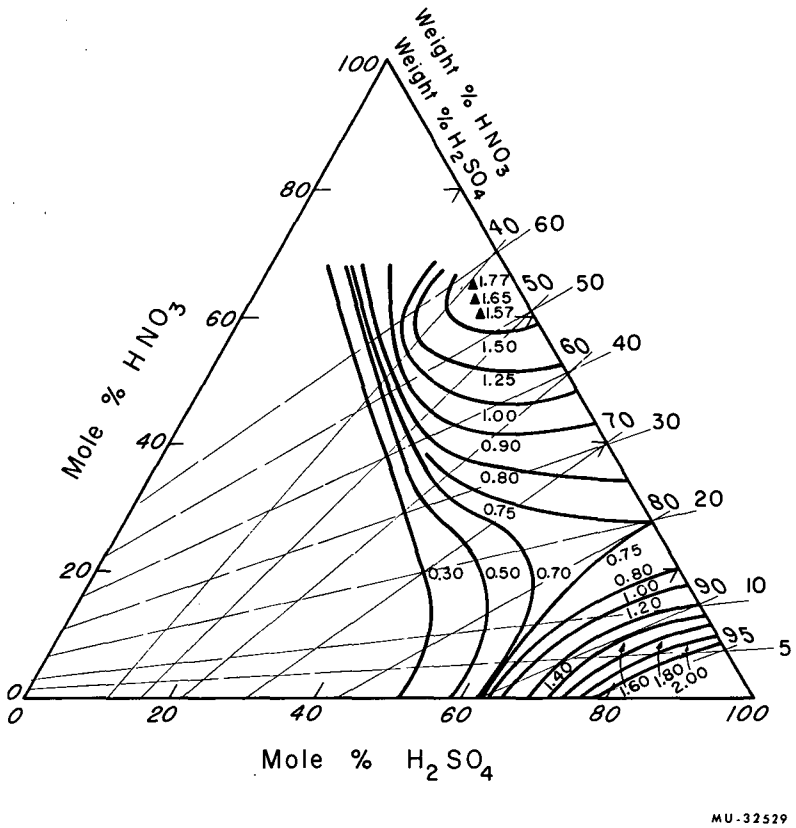

Fig. 7. Experimental values of k (at 50°C) for the rate equation $R = k(HNO_3)_a(ArH)_o$, moles per hour per liter of acid phase.

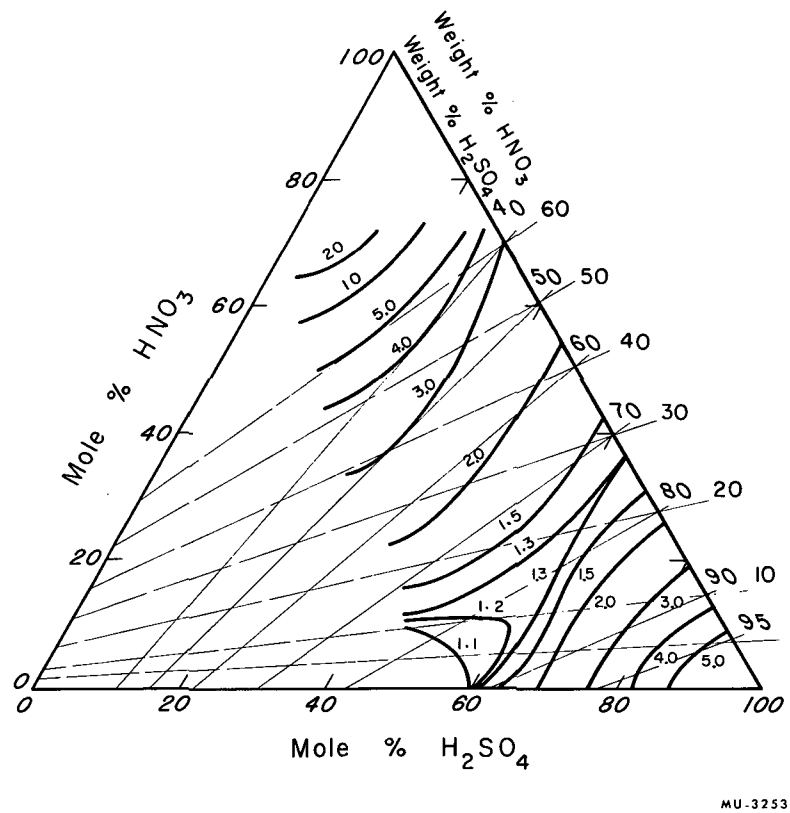

Fig. 8. Solubility of 1, 3-bis(trifluoromethyl)benzene in mixed acids at 23°C, g aromatic per liter of acid.

by mixing several partially nitrated aromatic mixtures with acids of various compositions at room temperature, and subsequently noting any changes of refractive index in the aromatic. The fraction of nitro compound in the aromatic phase was reduced only slightly in regions of unnitrated-aromatic solubility greater than 4 g/liter (as shown in Fig. 8), and was not affected elsewhere. In this high-solubility region, the k values obtained were not corrected for this effect and are therefore probably low by an extent of 1 to 10%. Some solubility values for the nitro-aromatic are also given in Table A-II.

c. Reactivity in 70%m nitric acid. Since the nitrated aromatic is completely miscible with 70%m HNO_3, it was questioned whether some nitration would occur in this acid at reasonable temperatures, contrary to the results indicated by Run 34. This was checked by mixing some purified aromatic with 70%m HNO_3, heating to 75°C for thirty minutes, and extracting the aromatic from the acid with cyclohexane as was done in the solubility measurements. The spectrophotometer showed no absorption at 3500Å, thus matching the purified unnitrated aromatic dissolved directly in cyclohexane. The purified aromatic was not the purchased material subjected to distillation, but instead was recovered by distillation from the organic phases of the nitration runs. Thus, this redistilled aromatic was free from any impurities that may have nitrated more easily than 1, 3-bis(trifluoromethyl)benzene.

d. Impurity in the feed aromatic. In all nitration runs, except the one in 70%m HNO_3 and a few near the sulfuric acid corner of the three-component mixed-acid diagram, the refractive index of the organic phase showed a very rapid conversion of about 1 to 2%, which appears as a nonzero intercept (cf. Run 43 in Fig. 5). It was postulated that this very rapid initial reaction was due to the presence of small amounts of more easily nitrated impurities in the 1, 3-bis(trifluoromethyl)benzene. The inability to detect nitrated impurities in the high-HNO_3 and high-H_2SO_4 ranges could be attributed either to conversion of the impurity into an unreactive species or to complete solubility of nitrated impurities in the acid phase. The most probable

impurity in 1, 3-bis(trifluoromethyl)benzene as prepared by Hooker Electrochemical Company would appear to be benzotrifluoride,[28] the mononitro derivative of which we found to be more than ten times as soluble in concentrated acid as 1, 3-bis(trifluoromethyl), 5-nitrobenzene. Since the refractive index of 1-trifluoro, 3-nitrobenzene is 1.4740, compared with 1.3828 for 1, 3-bis(trifluoromethyl)benzene, a 0.25% impurity of the former in the latter would appear as about a 1% conversion of the latter to its nitro product.

Confirmation that impurities were causing the rapid initial conversion was obtained by repeating the above-described experiment for determining the reactivity in 70%m HNO_3, but using the purchased aromatic as used in the nitration runs. Two samples of the acid were saturated with aromatic, and extracted to see if some nitro compound had been formed. The first was not heated, whereas the second was heated to 50°C for thirty minutes. Both showed identical absorption at 3500Å, amounting to about 1%m conversion had it been 1, 3-bis(trifluoromethyl), 5-nitrobenzene. Since the latter was obviously not the absorbing compound, an accurate quantitative estimation of the amount of impurities from this method was impossible. The impurities are evidently nitrated very rapidly compared with 1, 3-bis(trifluoromethyl)-benzene; they should not affect the slopes of the kinetic curves obtained, but only cause the intercept to be displaced from the origin. This was confirmed by performing Run 43 again, using the purified aromatic. This is shown as Run 43R on Fig. 5; it can be seen that the slope has not been affected to any appreciable extent.

2. Kinetic Interpretation of Rate Data

a. Development of an aromatic-independent relative rate coefficient. If irreversible attack of nitronium ion on the aromatic ring is assumed to be rate-determining in the nitration sequence, we know from transition-state theory that the rate must be given by

$$R = k_0'(NO_2^+)(ArH)_a \frac{\gamma_{NO_2^+}(\gamma_{ArH})_a}{\gamma_0^{\ddagger}}, \qquad (6)$$

where k_0' is the true rate constant, not a function of the composition of the medium. For mass-transfer equilibrium between phases we have

$$(a_{ArH})_a = (a_{ArH})_o \tag{7}$$

if the same standard state is used for both phases. We choose the pure aromatic as the standard state. Then the distribution coefficient K is given by

$$K = \frac{(ArH)_a}{(ArH)_o} = \frac{1}{(\gamma_{ArH})_a} . \tag{8}$$

Thus, to conform to Eq. (1), we must write

$$R = k_0' \frac{\gamma_{NO_2^+}(NO_2^+)}{\gamma_0^{\ddagger}\,(HNO_3)_a}(HNO_3)_a(ArH)_o , \tag{9}$$

and we see that the apparent rate coefficient k is actually given by

$$k = k_0' \frac{\gamma_{NO_2^+}(NO_2^+)}{\gamma_0^{\ddagger}\,(HNO_3)_a} . \tag{10}$$

A function proportional to (NO_2^+), except for variations in the activity coefficients, is obtained by multiplying k by $(HNO_3)_a$ and dividing by K:

$$\frac{k(HNO_3)_a}{K} = k_0' \frac{\gamma_{NO_2^+}(\gamma_{ArH})_a}{\gamma_0^{\ddagger}}(NO_2^+) . \tag{11}$$

Figure 9 is a plot of this quantity as a function of mixed-acid composition, with an arbitrary numerical scale made by dividing the actual values by 100. In general appearance the contours of Fig. 9 resemble rather closely the nitronium-ion profiles of Fig. 1. However, they are seen to be different in two respects: they deviate from the horizontal as the acid composition becomes greater than about 70%m H_2SO_4; and the difference between the values in the upper right and

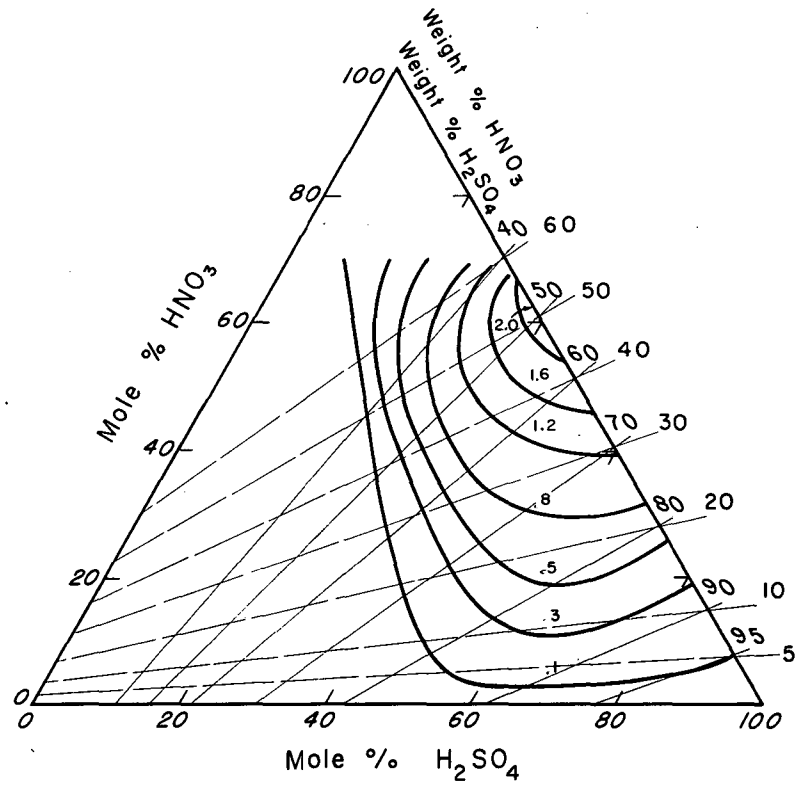

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Fig. 9. Values of $(10^{-2})k_0'(\gamma_{NO_2^+})(\gamma_{ArH})(NO_2^+)/\gamma_0^{\ddagger}$ at 50°C for the rate equation $R = k_0'(a_{NO_2^+})(a_{ArH})a/\gamma_0^{\ddagger}$.

lower right portions is too great to be ascribed solely to the change in concentration of nitronium ion.

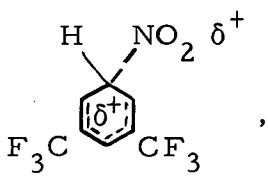
If the function of Eq. (11), or Fig. 9, is divided by $(HNO_3)_a$ along the 5%m HNO_3 line and along the HNO_3-H_2SO_4 base line, we obtain Figs. 10 and 11 respectively. This quantity, which we shall denote as k_0, is the one generally reported as the apparent rate coefficient in the homogeneous nitration of aromatics:

$$k_0 = \frac{k}{K} = k_0' \frac{\gamma_{NO_2^+} (\gamma_{ArH})_a (NO_2^+)}{\gamma_0^{\ddagger} (HNO_3)_a} . \qquad (12)$$

Figure 10, with the maximum k_0 occurring near 92%w H_2SO_4, is seen to be very similar to the reported homogeneous results,[14] which show a peak at about 90%w.

What has not been noted previously is that the apparent rate coefficient also increases to a maximum from pure H_2SO_4 along the HNO_3-H_2SO_4 base line, as shown by Fig. 11. The maximum along the H_2O-H_2SO_4 base line is known to occur at an H_0 value of about -8.3. Paul and Long give an H_0 value of -11.1 for 100% H_2SO_4,[29] while recent work by Dawber and Wyatt indicates an H_0 value of -6.3 for 100% HNO_3.[30] From these values it seems very reasonable that the H_0 value could be -8.3 near 55%m HNO_3, where the maximum k_0 occurs on the HNO_3-H_2SO_4 base line.

b. Activity coefficients. The general similarity between Figs. 1 and 9 suggests that, to a first approximation, $\gamma_{NO_2^+} \gamma_{ArH}/\gamma_0^{\ddagger}$ is nearly constant. As $\gamma_{NO_2^+}$ should not vary greatly from unity, it is indicated that $\gamma_0^{\ddagger}$ is proportional to γ_{ArH} over a good portion of the range. Since the activated complex should have the structure[31]



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its activity coefficient probably bears a close relation to the activity coefficients of both NO_2^+ and the aromatic; we therefore assume a

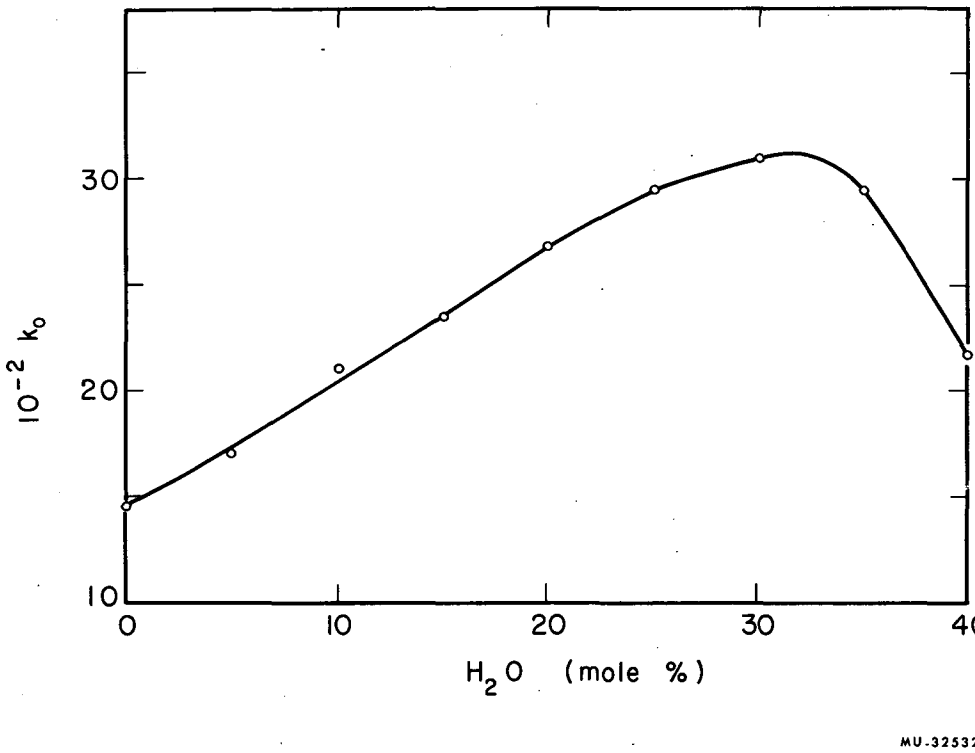

Fig. 10. The apparent rate coefficient k_0 along the 5%m HNO_3 line.

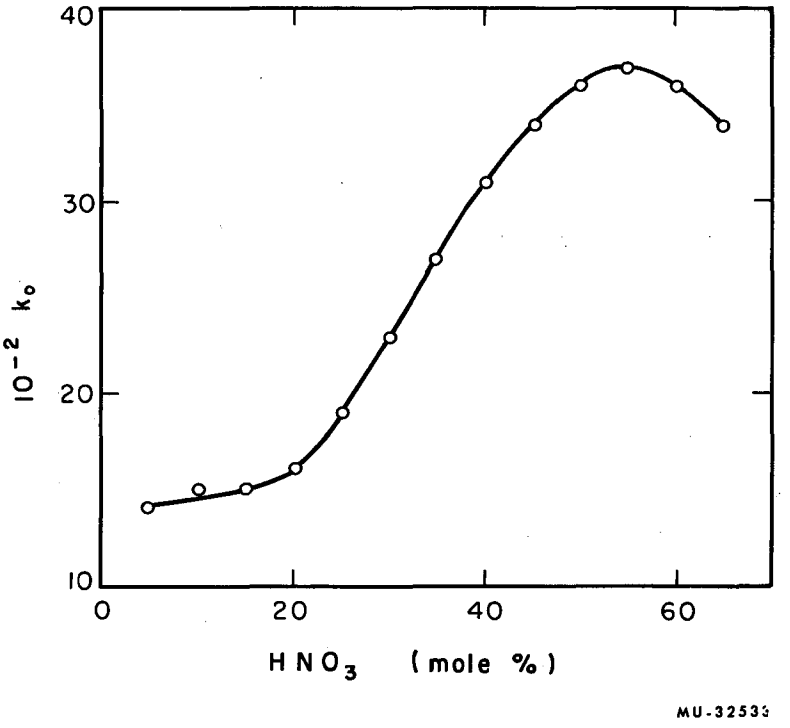

Fig. 11. The apparent rate coefficient k_0 for the HNO_3-H_2SO_4 base line.

linear combination of the form

$$\gamma_0^{\ddagger} = A\gamma_{ArH} + B\gamma_{NO_2^+} . \qquad (13)$$

The actual values of the constants A and B are unknown, but their probable effect can be illustrated. Possible values, based roughly on the relative molecular size of the two reactants, might be $A = 0.75$ and $B = 0.25$. From the solubility measurements, γ_{ArH} is in the range of 500 to 5000 in the acids of interest. By comparison with ion behavior in aqueous solution, we would not expect $\gamma_{NO_2^+}$ to be greatly different from unity for these acids; Eq. (12) would then suggest that $\gamma_0^{\ddagger}$ is proportional to γ_{ArH}, and that the activated complex should behave mainly as an organic molecule in the acid phase.

In the organic phase we know that γ_{ArH} is nearly unity, and we would expect the value of $\gamma_{NO_2^+}$ to be quite high. Thus

$$\gamma_0^{\ddagger} \propto \gamma_{NO_2^+} , \qquad (14)$$

and the activated complex would behave as an inorganic ion in the organic phase. As stated in the introduction, results of two-phase nitrations indicate that reaction in the organic phase is very slow in comparison with reaction in the aqueous phase. Since under mass-transfer equilibrium the activities of the reactants are identical in both phases, the much slower rate of nitration in the organic phase must be due to a much larger value of $\gamma_0^{\ddagger}$ in this phase. According to the above arguments, this would indicate

$$(\gamma_{NO_2^+})_o \gg (\gamma_{NO_2^+})_a . \qquad (15)$$

Let us assume that the rate is only 1/100 as great in the organic phase. To satisfy this relationship we would need values of $(\gamma_{NO_2^+})_o$ in the region of 10^5 to 10^6, or $(NO_2^+)_o$ values only about 10^{-5} to 10^{-6} times those of $(NO_2^+)_a$.

Plots of γ_{ArH} along the 5%m HNO_3 line and the HNO_3-H_2SO_4 base line taken from the solubility measurements are shown in

Figs. 12 and 13 respectively. Also shown for the same acids is a function proportional to $\gamma_0^{\ddagger}$ calculated from

$$\gamma_0^{\ddagger} \propto \frac{(NO_2^+)\,\gamma_{NO_2^+}}{k(HNO_3)_a}, \qquad (16)$$

using (NO_2^+) values extrapolated from the available Raman-spectrum data and assuming $\gamma_{NO_2^+}$ is constant. We see that $\gamma_0^{\ddagger}$ is not strictly proportional to γ_{ArH} in this range. Possible explanations for this lack of proportionality are as follows:

(a) The increased dielectric constant as pure H_2SO_4 is approached[1] has rendered the positive charge associated with NO_2^+ more diffuse owing to its increased ability to polarize the surrounding molecules, resulting in a decrease in $\gamma_{NO_2^+}$.

(b) The increase in solubility (decrease in γ_{ArH}) occurs by converting the aromatic to a less reactive species, about which we can say the following:

(i) Protonation is improbable, since pK_a, the thermodynamic ionization constant, should be greater than the value of 12.7 given for dinitrobenzene[32] owing to the relative ease of proton association with $-NO_2$ groups.

(ii) Hydrogen bonding with molecular H_2SO_4 seems possible; in fact, the increase in solubility toward anhydrous H_2SO_4 roughly parallels the increase in molecular H_2SO_4 concentration given by Brand[32] and the increase in H_2SO_4 vapor pressure given by Gmitro and Vermeulen.[33]

Figure 11 is very similar to Fig. 10, up to about 35%m HNO_3. The same arguments as used above could be invoked for the lack of proportionality between $\gamma_0^{\ddagger}$ and γ_{ArH} in this region. The most striking feature occurs as the solvent changes from H_2SO_4 to HNO_3; the proportionality becomes quite good, indicating that the aromatic exists in a relatively free and reactive state.

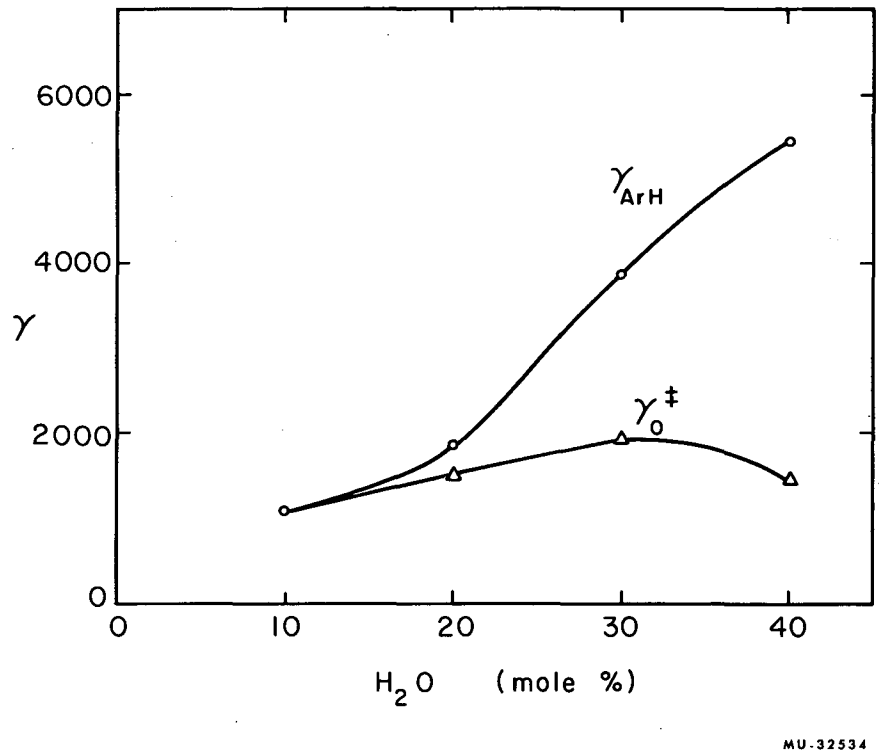

Fig. 12. Activity coefficients for the 5%m HNO_3 line.

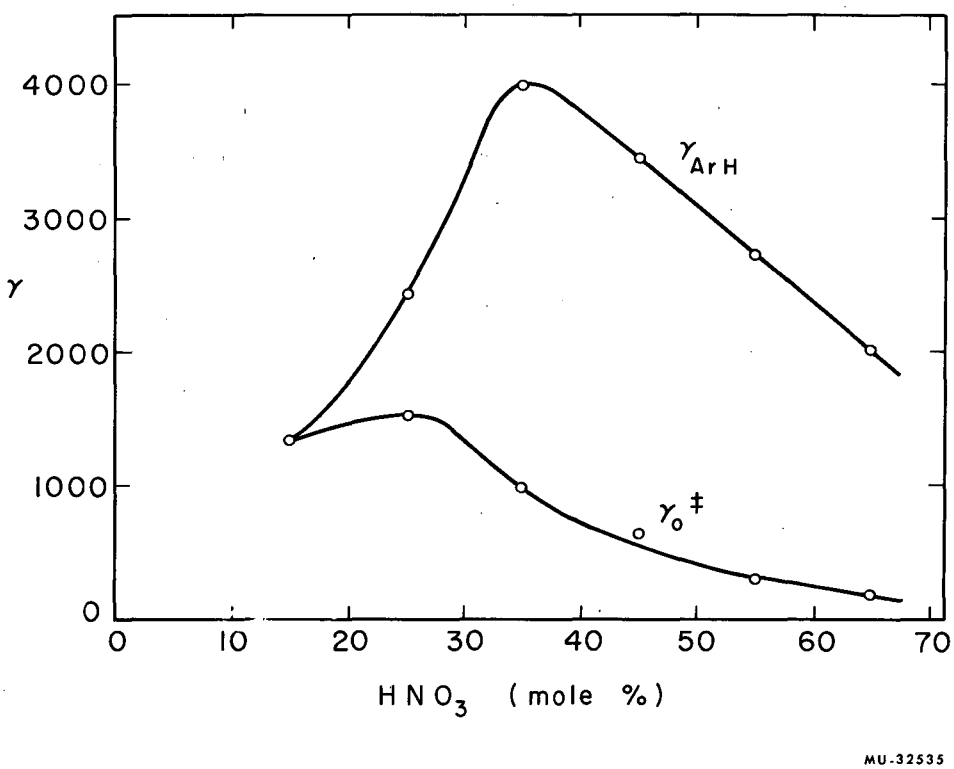

Fig. 13. Activity coefficients for the HNO_3-H_2SO_4 base line.

B. General Kinetic Analysis

1. Extrapolation of Experimental Results

By using aromatics of varying ease of substitution it would be possible to construct a diagram similar to Fig. 9 encompassing nearly the entire range of mixed acid compositions. Some workers have postulated that $H_2NO_3^+$,[18] or molecular nitric acid itself,[34] may be the attacking species in such media as aqueous HNO_3, where nitronium ion has seemed not to exist; however, we believe that the NO_2^+ mechanism is the important process for nitration in the presence of H_2SO_4, even in relatively dilute media. Equation (4) could be used to correlate nitration experiments for the entire diagram, so long as the assumptions involved in the derivation are satisfied.

Nitration rates could be predicted from such a diagram simply by establishing the proportionality at convenient reference conditions for the aromatic in question. For heterogeneous nitrations, as reported in this paper, the solubility would have to be accounted for separately, unless the compound is nitrated in a region where solubility changes are small. Such a region has been established for several aromatics of widely varying polarities along the H_2SO_4-H_2O base line from about 20 to 60%w (4.4 to 21.6%m) H_2SO_4.[35,36]

Indications from our preliminary runs with trifluoromethylbenzene and nitrobenzene (shown in Table I), as well as the results of Lewis and Suen[21] and McKinley and White[22] mentioned previously, are that more narrowly limited ranges of acid compositions are accessible for study of aromatics more reactive than 1, 3-bis(trifluoromethyl)benzene, because reaction rate changes very rapidly with acid composition, and the range of reaction rates measurable in a glass batch-reactor is rather limited.

From the nitration data available at present, we could not convincingly bridge the gap in acid compositions between our work and the McKinley-White and Lewis-Suen results. Below we attempt to bridge this gap by using equilibrium equations based on the nitronium-ion mechanism.

Table I. Preliminary nitrations of other aromatics.

Aromatic	H_2SO_4 (%m)	HNO_3 (%m)	T (°C)	k_T (moles/liter hr)
Trifluoro-methylbenzene	30.0	15.1	71	8.53
	33.0	23.9	33	>20[a]
	0.0	52.1	50	0.36
	0.0	60.8	35	>20[a]
Nitrobenzene	30.0	15.1	75	<0.1[b]
	33.0	23.9	30	16.4
	0.0	70.0	50	Measurable

[a] Too rapid for measurement.
[b] Too slow for measurement.

2. Nitronium-Ion Concentration

In mixed-acid solutions we may write the following equilibrium reactions:

$$HNO_3 + (H^+) \rightleftharpoons H_2NO_3^+, \qquad (a)$$

$$H_2NO_3^+ \rightleftharpoons NO_2^+ + H_2O, \qquad (b)$$

$$H_2O + (H^+) \rightleftharpoons H_3O^+, \qquad (c)$$

$$HNO_3 \rightleftharpoons (H^+) + NO_3^-. \qquad (d)$$

From these we see

$$(HNO_3)_T = (HNO_3)\left[1 + K_a h_0 + \frac{K_a K_b K_c h_0^2}{(H_3O^+)} + \frac{K_d}{h_0}\right], \qquad (17)$$

where $(HNO_3)_T = (HNO_3) + (H_2NO_3^+) + (NO_2^+) + (NO_3^-)$, and h_0 (proportional to the activity of H^+) is the Hammett acidity function, discussed further in the next section. We have assumed constancy of activity-coefficient ratios. We now obtain a NO_2^+ concentration of

$$(NO_2^+) = \frac{K_a K_b\, h_0 (HNO_3)_T}{(H_2O)\left[1 + K_a h_0 + \frac{K_a K_b K_c h_0^2}{(H_3O^+)} + \frac{K_d}{h_0}\right]}. \qquad (18)$$

If we assume that the mole fraction concentration of NO_2^+ is the only factor influencing the relative-rate quantity plotted in Fig. 9 in regions of less than complete conversion of HNO_3 to NO_2^+, we may span the region between our data and the dilute-acid data by calculating the reduction in NO_2^+ concentration over this region. We have selected the 5%m-HNO_3 line to make this bridge, as h_0[29] and p_{H_2O},[33] the partial pressure of water vapor, are available for extrapolation from the H_2SO_4-H_2O base line, and data on $(NO_3^-)/(HNO_3)$ and $(NO_2^+)/(HNO_3)$ are available for this region.[37] Deno and Stein have shown that the rate of nitration parallels the ionization of HNO_3 to NO_2^+ in the region of 10 to 55%m H_2SO_4.[38]

Rewriting Eq. (18) in a different form, we obtain

$$(NO_2^+) = \frac{K' h_0 (HNO_3)_T}{(H_2O)\left[1 + \frac{(H_2NO_3^+)}{(HNO_3)} + \frac{(NO_2^+)}{(HNO_3)} + \frac{(NO_3^-)}{(HNO_3)}\right]} . \qquad (19)$$

Values of h_0 were extrapolated from the base line up a constant %m-H_2O line, a line passing through 100% HNO_3, a constant %m-H_2SO_4 line, or some line intermediate to these, depending respectively upon whether the nitric acid present exists as NO_3^-, HNO_3, NO_2^+, or a combination of two of these. Values of p_{H_2O} extrapolated up lines of constant %m H_2O were used for (H_2O). It was assumed that $(H_2NO_3^+)/(HNO_3)$ was negligible compared with the other terms in the denominator. The constant K' of Eq. (19) was found to be 8.43×10^{-11} mm Hg by noting that the line with the value 1 (100 on true scale) in Fig. 9 is equivalent to about 3%m NO_2^+ in the region where all the nitric acid exists as NO_2^+.

The results of the nitronium-ion concentration calculations are shown in Table II. The dashed lines of Fig. 14 are drawn to be consistent with the results of the calculations along the 5%m-HNO_3 line, with slopes that form a smooth pattern between the results of McKinley and White and our data for 1, 3-bis(trifluoromethyl)benzene, both of which are also shown on Fig. 14. The lines are more closely spaced on the left side of the diagram than they are in the central portion; in the center, nitric acid exists predominantly as HNO_3, and the concentration of NO_2^+ is proportional to $h_0/(H_2O)$; on the left, nitric acid exists predominantly as NO_3^-, and the concentration of NO_2^+ is proportional to $h_0^2/(H_2O)$. This agrees with the fact that nitric acid is believed to be only slightly ionized to NO_3^- above 50%m HNO_3.[1]

We feel that this higher h_0 dependence in the dilute region is evidence that whatever quantity of $H_2NO_3^+$ is present does not become a significant factor in the nitration rate, since the concentration of $H_2NO_3^+$ in this region would be proportional only to h_0^2, and a higher dependence is needed to justify experimental data. As seen by Eq. (18), if a considerable part of the HNO_3 is converted to $H_2NO_3^+$,

Table II. Concentration of nitronium ion along the 5%m HNO_3 line.

H_2SO_4 (%m)	h_0(25°C)	p_{H_2O}(25°C) (mm Hg)	$\frac{(NO_2^+)}{(HNO_3)}$	$\frac{(NO_3^-)}{(HNO_3)}$	(NO_2^+)	$k_0' \frac{\gamma_{NO_2^+}\gamma_{ArH}}{\gamma_{0^\ddagger}}(NO_2^+)$
55.0	1.00×10^8	0.0090	0.56	0.00	3.00×10^{-2}	1.00×10^2
48.5	4.47×10^7	0.0200	0.11	0.00	8.50×10^{-3}	2.83×10^1
45.0	2.51×10^7	0.0429	0.00	0.00	2.47×10^{-3}	8.23×10^0
40.0	8.51×10^6	0.0785	0.00	0.00	4.57×10^{-4}	1.53×10^0
35.0	2.95×10^6	0.230	0.00	0.00	5.40×10^{-5}	1.80×10^{-1}
28.5	4.47×10^5	0.665	0.00	0.00	2.84×10^{-6}	9.47×10^{-3}
27.5	3.16×10^5	0.728	0.00	0.00	1.83×10^{-6}	6.10×10^{-3}
24.0	1.00×10^5	1.40	0.00	0.03	2.92×10^{-7}	9.77×10^{-4}
21.0	3.16×10^4	2.32	0.00	0.13	6.38×10^{-8}	1.70×10^{-4}
16.7	6.77×10^3	4.04	0.00	0.33	6.52×10^{-9}	1.76×10^{-5}

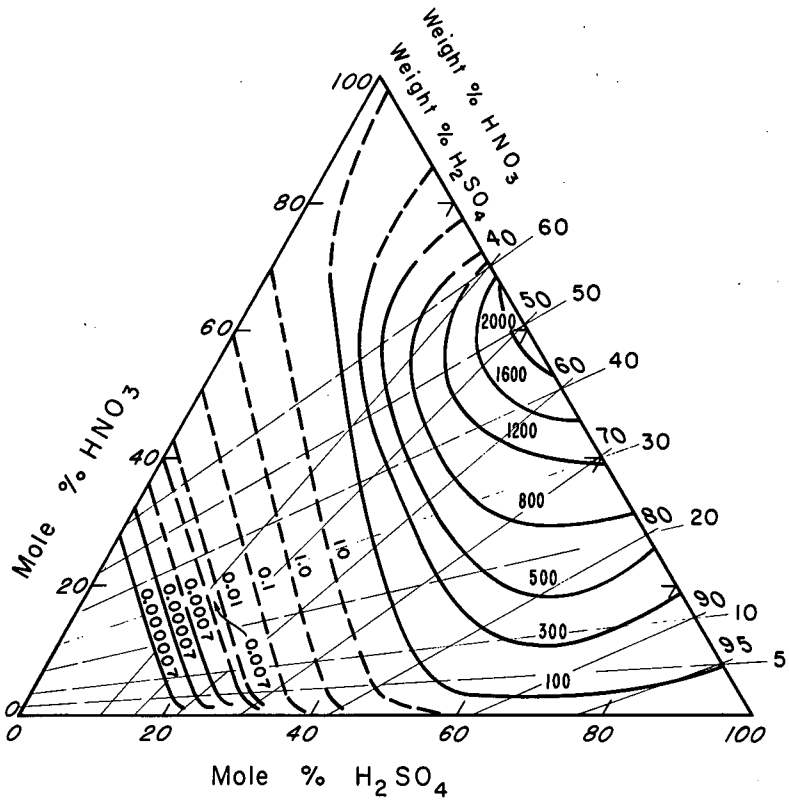

Fig. 14. Relative nitration rates in mixed acids; $k_0'(\gamma_{NO_2^+})(\gamma_{ArH})(NO_2^+)/\gamma_0^{\ddagger}$ values for the rate equation $R = k_0'(a_{NO_2^+})(a_{ArH})a/\gamma_0^{\ddagger}$.

the h_0 dependence of (NO_2^+) would be greatly reduced; thus, we can discount a significant conversion of HNO_3 to $H_2NO_3^+$ by the same argument as was used above to discount the latter's contribution to the reaction rate.

Dividing the values from Fig. 14 by $(HNO_3)_a$, we obtain the values of the apparent rate coefficient k_0 as a function of mixed-acid composition, as shown in Fig. 15.

An equation similar to Eq. (18), but derived with no assumptions regarding the constancy of activity coefficients, would be given as

$$(NO_2^+) = \frac{K_a K_b h_0 (HNO_3)_T}{\gamma_{H_2O}(H_2O)\left[1 + K_a h_0 + \frac{K_a K_b K_c h_0^2}{\gamma_{H_2O}(H_3O^+)} + \frac{\gamma_{HNO_3} K_d}{a_{H^+}(\gamma_{NO_3^-})}\right]} . \tag{20}$$

3. Hammett Acidity Scale

For protonation of a neutral base according to

$$B + H^+ \rightleftharpoons BH^+ , \tag{21}$$

Hammett[39] defines an acidity function H_0 such that

$$H_0 = pK_{BH^+} - \log\left[\frac{(BH^+)}{(B)}\right], \tag{22}$$

where K_{BH^+} is the thermodynamic ionization constant of BH^+;

$$H_0 = -\log h_0 = \log\left[\frac{\gamma_{BH^+}}{\gamma_B a_{H^+}}\right]. \tag{23}$$

This acidity function expresses the tendency of a solution to transfer a proton to a neutral base.

In the mixed-acid system,

$$h_0 = \frac{a_{H^+}(\gamma_{H_2O})}{\gamma_{H_3O^+}} = \frac{a_{H^+}(\gamma_{HNO_3})}{\gamma_{NO_2^+}} . \tag{24}$$

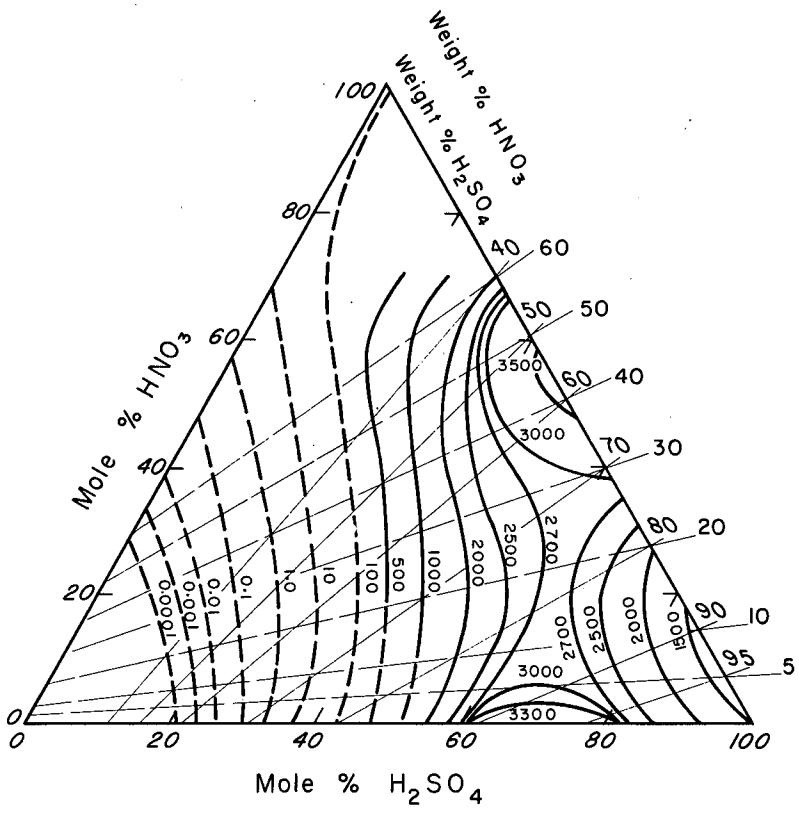

Fig. 15. Values of the apparent rate coefficient k_0 for the rate equation $R = k_0(HNO_3)_a(ArH)_a$.

It was found by Deno and Taft[40] that values of H_0 could be predicted in the range 74-98%w H_2SO_4 from vapor-pressure data of aqueous sulfuric acids according to the equation

$$H_0 = \log a_{H_2O} - \log (H_3O^+) - 5.00 , \qquad (25)$$

where 5.00 is a constant chosen to give the best fit with observed values. They give convincing proof for the use of a mole-fraction equilibrium constant, K', of 50 for the equation

$$H_2O + H_2SO_4 = H_3O^+ + HSO_4^-$$

below 90%w H_2SO_4. They used the Clausius-Clapeyron equation to extrapolate vapor pressure data in the range 150 to 280°C down to 25°C. Using the recently calculated values of vapor pressures of water above aqueous sulfuric acid solutions from Gmitro and Vermeulen,[33] we have found that H_0 values at 25°C may be predicted from these data according to the equation

$$H_0 = \log a_{H_2O} - \log (H_3O^+) - 5.06 , \qquad (26)$$

with an average deviation of 0.02 H_0 units from the observed values given by Paul and Long[29] in the region 75 to 99%w H_2SO_4. Table A-III of the Appendix gives the results of the calculations. (H_0 values for aqueous H_2SO_4 are shown as Fig. A-3 of the Appendix.)

With the success of the above method it would be interesting to extend it to the system H_2O-HNO_3-H_2SO_4 to predict H_0 values. From vapor pressures of nitric acid and water above mixed acids, we could also calculate $a_{NO_2^+}$ from

$$\log a_{NO_2^+} = \log (H_3O^+) + \log a_{HNO_3} - \log a_{H_2O} + B . \qquad (27)$$

Use of Eq. (27) is restricted by the inadequacy of partial-pressure data for concentrated mixed acids.

By use of Eq. (19), we have estimated H_0 values at 25°C for mixed acids in the region where most of the nitric acid exists as molecular HNO_3. The values of (NO_2^+) were determined by

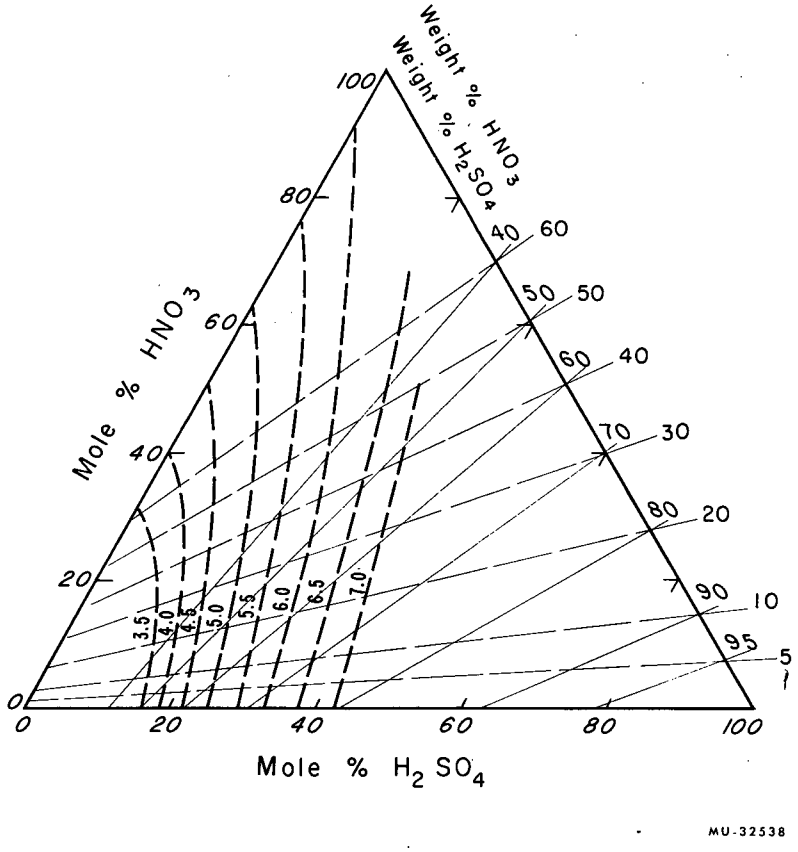

Fig. 16. Estimation of H_o values at 25°C for mixed acids.

multiplying the values from Fig. 14 by 3×10^{-4}, while values of p_{H_2O} were again obtained from the tables of Gmitro and Vermeulen[33] by extrapolation up lines of constant %m H_2O. These estimations are shown in Fig. 16 as interpolations between the values along the HNO_3-H_2O base line from Dawber and Wyatt,[30] and the values along the H_2SO_4-H_2O base line from Paul and Long.[29] Our method of prediction gives H_0 values at HNO_3 concentrations greater than 50%m HNO_3 along the HNO_3-H_2O base line that agree with the experimental values shown to within about 10% (as h_0).

4. Entropy of Activation

Using the activation energy of 14 000 kcal/g-mole for toluene from Hougen and Watson,[24] the 18 000 kcal/g-mole activation energy for 1, 3-bis(trifluoromethyl)benzene from our work, and relative rate values for the two compounds, we find that the transition state of the latter aromatic is more difficult to form, by approximately 20 entropy units, than the transition state of toluene. Thus, changes in activation energy by themselves do not seem to be indicative of the relative reactivity of these two aromatics.

IV. CONCLUSIONS

1. The effect of mixed-acid composition on the rate of nitration of aromatic compounds can be accounted for by the nitronium-ion mechanism throughout the entire range of acid compositions. A relative-rate correlation of data for the very concentrated mixed-acid range can be extended to the more dilute region by using equilibrium equations based on the nitronium-ion mechanism.

2. A maximum nitration rate, found previously in the range of H_2O-H_2SO_4 mixtures (at about 62%m H_2SO_4), has been found to extend through the three-component region to the HNO_3-H_2SO_4 binary mixture (at about 45%m H_2SO_4).

3. By use of the correlation obtained (Fig. 14), the nitration rate of any aromatic compound in any composition of mixed acid can be predicted, simply by establishing the proportionality between the aromatic in question and the scale of Fig. 14. However, any effect that is not a direct result of the state of the acid medium itself, such as a change in aromatic solubility, or a change in the reactivity of the aromatic through protonation, will have to be accounted for separately for the particular aromatic in question.

4. Hammett acidity functions can be predicted by a combination of vapor pressures of water above mixed acids and nitronium-ion concentrations from nitration results. These acidity functions at 25°C have been estimated from our extended nitration results along with vapor-pressure values extrapolated from the H_2SO_4-H_2O base line.

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NOTATION

g	Fraction of the aromatic converted
H_0	Hammett acidity function
h_0	Antilog $(-H_0)$
K	Distribution coefficient
K_a, K_b, K_c, K_d	Equilibrium constants for Eqs. (a), (b), (c), and (d)
k	Apparent rate coefficient
N	Total moles
p	Partial pressure
pK	Thermodynamic ionization constant
R	Rate of reaction, moles converted per unit volume per unit time
t	Time
γ	Activity coefficient
( )	Denotes mole-fraction concentration

Superscript

$\ddagger$	Refers to the activated complex

Subscripts

a	Refers to the acid phase
o	Refers to the organic phase
0	Refers to the rate-determining step in the nitration sequence
T	Refers to the total or stoichiometric quantity

APPENDIX

Table A-1. Experimental nitrations of 1,3-bis(trifluoromethyl)benzene.

Run number	Temperature (°C)	H_2SO_4 (mole%)	HNO_3 (mole%)	Density of acid	Moles HNO_3 per mole $(CF_3)_2$	k (moles per hour per liter of acid)	k corrected to 50°C
1	50.0	35.8	39.0	1.74	6.33	1.165	1.17
2	50.0	60.7	1.0	1.82	0.24	0.000[b]	0.00
3	50.0	39.7	35.3	1.73	5.65	0.737	0.737
4	50.0	51.3	48.2	1.78	6.02	0.960	0.960
5	50.0	54.0[a]	43.0	1.82	5.32	0.753	0.753
6	50.0	44.6	51.6	1.74	6.67	1.428	1.43
7	50.5	39.5	51.5	1.72	6.67	1.322	1.32
8	50.0	41.7	43.9	1.74	5.72	0.860	0.860
9	50.0	34.0	44.7	1.71	5.88	0.983	0.983
10	50.0	49.1	34.6	1.74	5.92	0.655	0.655
11	50.0	37.7	51.4	1.71	6.10	1.170	1.17
12	65.5	46.7	33.1	1.77	6.13	2.621	0.728
13	45.0	46.7	33.1	1.77	6.13	0.450	0.704
14	60.0	46.7	33.1	1.77	6.13	1.893	0.822
15	50.0	30.5	54.4	1.69	5.88	1.432	1.43
18	60.5	63.9	30.0	1.82	5.47	1.760[b]	0.733
19	60.5	69.6[a]	23.5	1.87	5.47	1.731	0.721
20	60.5	58.6	37.4	1.81	5.49	1.977	0.825
21	60.5	70.1	14.6	1.84	5.88	1.850[b]	0.771
22	65.5	74.7	7.3	1.84	2.93	4.960[b]	1.38
26	65.5	74.9	15.4	1.85	5.21	2.420[b]	0.677
27	65.5	74.9	15.4	1.85	5.21	2.970[b]	0.828
28	65.5	88.2	8.0	1.85	2.93	6.740[b]	1.88
29	65.5	66.9	6.5	1.83	2.93	3.630[b]	1.01
30	65.5	80.4	7.7	1.85	2.93	5.820[b]	1.62
31	65.5	59.2	12.2	1.81	5.88	2.150[b]	0.600
32	65.5	64.0	22.0	1.83	5.52	2.800[b]	0.782
33	65.5	48.7	10.2	1.76	2.98	1.049	0.293
34	65.0	0.0	72.8	1.49	11.9	0.000[c]	0.00
34a	80.0	0.0	72.8	1.49	11.9	0.000[c]	0.00
35	50.0	42.1	39.1	1.74	5.88	0.698	0.699
35a	60.0	42.1	39.1	1.74	5.88	2.060	0.897
36	74.3	48.9	10.1	1.76	3.97	1.694	0.240
37	65.0	54.3	21.2	1.78	5.92	2.048	0.593
38	57.5	29.8	64.3	1.68	9.48	3.339	1.77
39	51.3	20.8	65.7	1.64	20.8	1.102	0.979
40	50.0	38.4	58.7	1.73	8.30	1.501	1.501
41	61.9	13.1	66.6	1.59	22.4	2.259	0.837
42	52.0	25.3	56.6	1.66	5.92	2.334	1.96
43	60.0	34.6	41.5	1.70	6.03	1.896	0.827
43R	60.2	34.6	41.5	1.70	6.03	1.960	0.839
44	69.0	45.9	19.6	1.75	5.85	1.463	0.308
46	59.5	6.1	67.7	1.53	24.2	0.152	0.0687
47	50.1	23.8	60.0	1.65	9.60	1.335	1.32
48	60.0	9.5	67.3	1.55	11.6	0.812	0.353
49	55.2	19.1	55.9	1.61	9.60	0.580	0.371
50	68.2	14.9	52.3	1.58	19.2	0.0688	0.0153
51	49.6	33.3	59.9	1.71	8.52	1.525	1.57
52	45.5	31.5	62.1	1.70	8.73	1.122	1.67
53	55.8	31.5	62.1	1.70	8.73	2.707	1.65
54	65.3	55.4	27.3	1.79	5.52	2.595	0.731
55	74.5	41.0	22.9	1.73	5.52	1.653	0.231
56	80.0	57.0	10.1	1.79	4.77	5.110	0.477
57	78.7	63.7	6.5	1.81	3.30	7.340	0.756
57R	73.3	63.7	6.5	1.81	1.65	5.340	0.812
58	76.6	33.0	23.9	1.68	11.0	0.198	0.0238
59[d]	72.5	27.8	47.1	1.73	13.1	2.161	0.353
60[d]	72.6	41.9	33.7	1.75	8.92	4.230	0.690

[a] Third component SO_3 instead of H_2O.

[b] Taken from slopes of curves for moles converted versus time.

[c] Zeroes mean rate too slow for measurement.

[d] From unpublished results of C. Shih.

Table A-II. Solubility of reactant and product in mixed acids.

Acid composition		Solubility (g/liter)	
H_2SO_4 (%m)	HNO_3 (%m)	ϕ-$(CF_3)_2$	O_2N-ϕ-$(CF_3)_2$
100	0	8.4	—
80	0	3.6	115
60	0	1.1	30.4
0	70	74.8	—
11	70	24.3	—
21	70	8.2	91.3
30	40	3.2	45.0
50	20	1.6	—
60	40	1.4	33.3
70	30	1.6	—

Table A-III. Prediction of H_0 from vapor pressures.

H_2SO_4 (% w)	H_2SO_4 (%m)	Log (H_3O^+)	Log a_{H_2O}	H_0(observed) (Ref. 27)	A	H_0(calc.) A = 5.06
99.8	99.0	-1.967	-7.06	-10.36	5.27	-10.15
99.5	97.3	-1.574	-6.37	-10.03	5.23	- 9.86
99.0	94.4	-1.282	-5.84	- 9.74	5.18	- 9.62
98.5	92.5	-1.116	-5.51	- 9.50	5.11	- 9.45
98.0	90.0	-0.999	-5.28	- 9.36	5.08	- 9.34
97.0	85.6	-0.831	-4.94	- 9.14	5.03	- 9.17
96.0	81.5	-0.733	-4.69	- 8.98	5.02	- 9.02
95.0	77.7	-0.652	-4.46	- 8.86	5.05	- 8.87
94.0	74.2	-0.588	-4.28	- 8.75	5.06	- 8.75
93.0	70.9	-0.536	-4.10	- 8.63	5.07	- 8.62
92.0	67.9	-0.493	-3.94	- 8.52	5.07	- 8.50
91.0	65.0	-0.455	-3.79	- 8.39	5.06	- 8.39
90.0	62.3	-0.424	-3.64	- 8.27	5.05	- 8.28
88.0	57.3	-0.393	-3.34	- 8.03	5.08	- 8.01
86.0	53.0	-0.365	-3.06	- 7.71	5.01	- 7.76
84.0	49.1	-0.361	-2.78	- 7.51	5.09	- 7.48
82.0	45.5	-0.369	-2.51	- 7.24	5.10	- 7.19
80.0	42.3	-0.385	-2.27	- 6.97	5.08	- 6.95
78.0	39.4	-0.406	-2.04	- 6.72	5.09	- 6.69
76.0	36.7	-0.434	-1.82	- 6.45	5.06	- 6.45
74.0	34.4	-0.463	-1.66	- 6.19	4.99	- 6.26
72.0	32.1	-0.493	-1.50	- 5.93	4.92	- 6.07
70.0	30.0	-0.522	-1.35	- 5.65	4.82	- 5.89
65.0	25.4	-0.594	-1.03	- 5.04	4.60	- 5.50
60.0	21.6	-0.665	-0.79	- 4.46	4.33	- 5.19

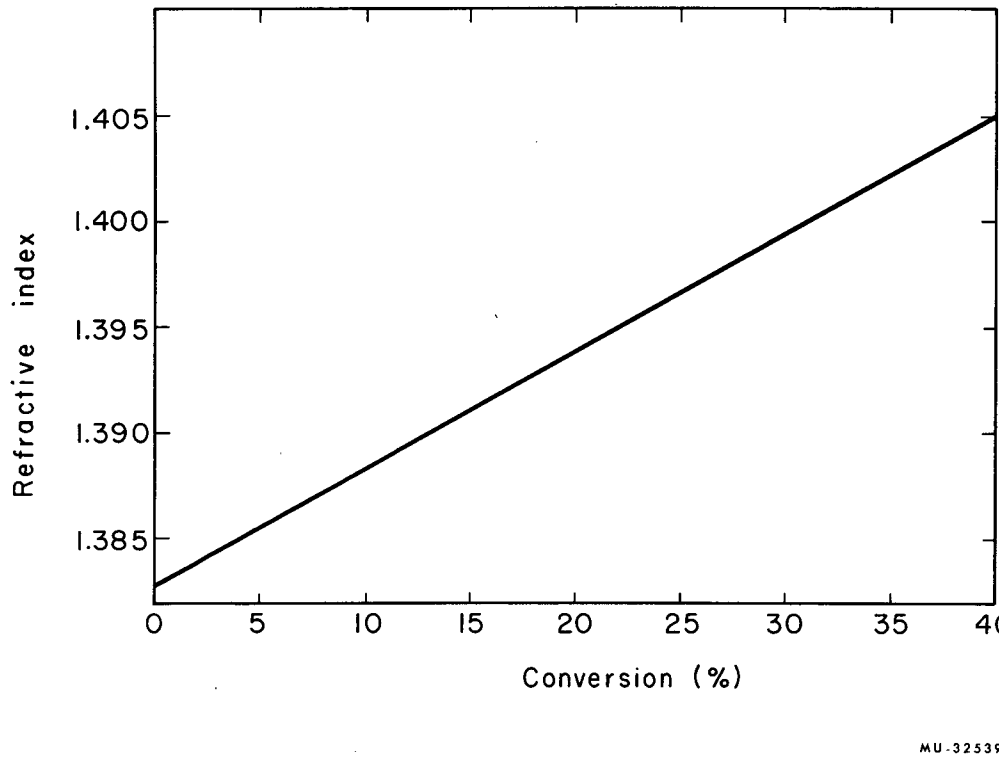

Fig. A-1. Refractive index versus percent conversion of 1, 3-bis(trifluoromethyl)benzene to 1, 3-bis(trifluoromethyl), 5-nitrobenzene (at 18°C).

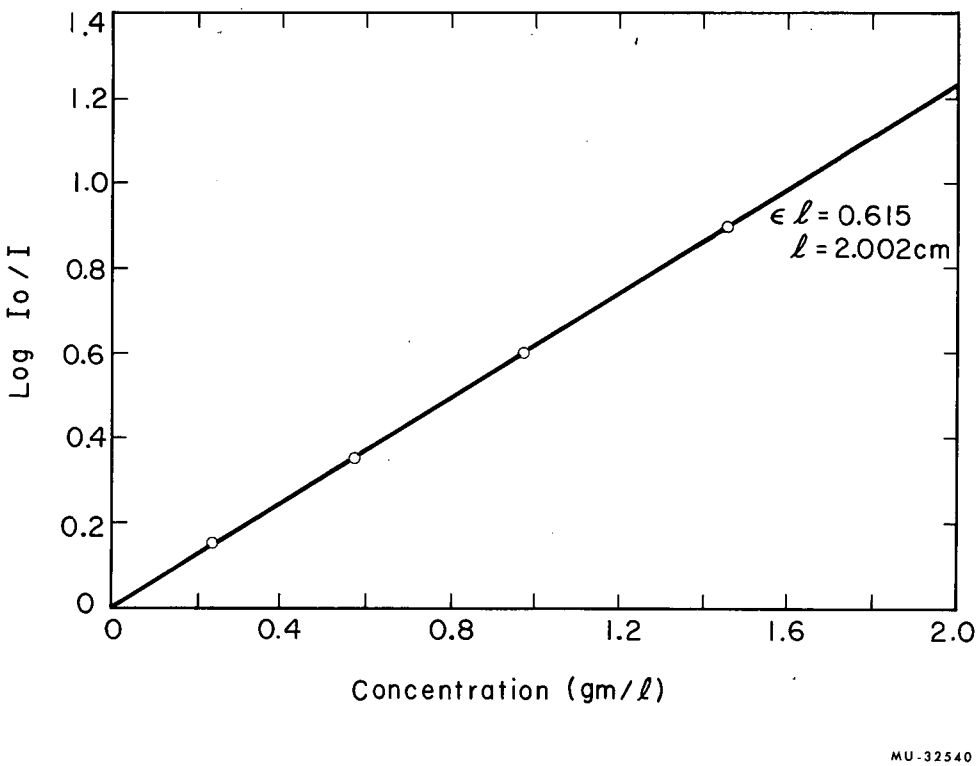

Fig. A-2. Optical density of mixtures of 1, 3-bis(trifluoromethyl), 5-nitrobenzene and cyclohexane at 3500Å.

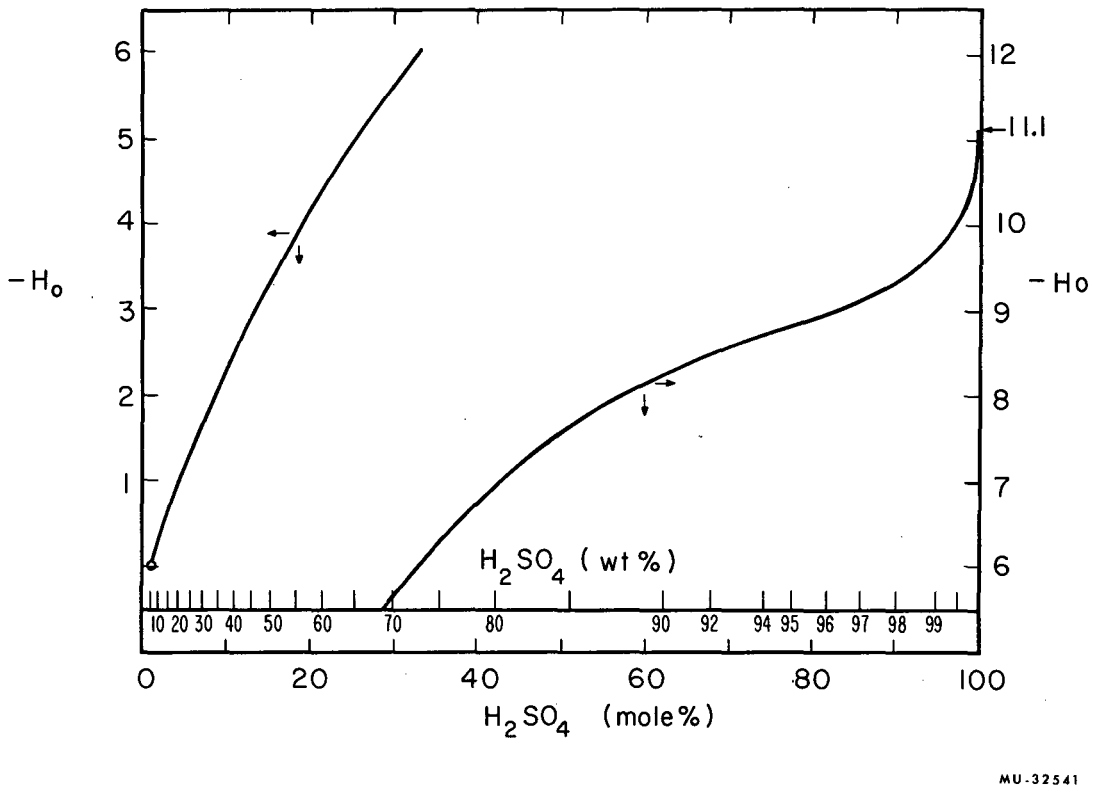

Fig. A-3. Hammett acidity functions for aqueous sulfuric acid (reference 29).

REFERENCES

1. R. J. Gillespie and D. J. Millen, Quart. Rev. (London) 2, 277 (1948).
2. A. V. Topchiev, Nitration of Hydrocarbons and Other Organic Compounds (Pergamon Press, New York, 1959), Chap. II.
3. M. Usanovich, Acta Physicochim. 2, 239 (1935); 3, 703 (1935).
4. H. Euler, Annalen 330, 280 (1903).
5. P. Walden, Z. angew. Chem. 37, 390 (1924).
6. T. Ri and H. Eyring, J. Chem. Phys. 8, 433 (1940).
7. R. J. Gillespie, J. Graham, E. D. Hughes, C. K. Ingold, and E. R. Peeling, Nature 158, 480 (1946).
8. E. G. Cox, G. A. Jeffery, and M. R. Truter, Nature 162, 258 (1948).
9. E. Grison, K. Ericks, and J. L. de Vries, Acta Cryst. 3, 290 (1950).
10. D. R. Goddard, E. D. Hughes, and C. K. Ingold, J. Chem. Soc., 2559 (1950).
11. D. R. Goddard, E. D. Hughes, and C. K. Ingold, Nature 158, 480 (1946).
12. D. J. Millen, J. Chem. Soc., 2600 (1950).
13. J. Chedin, Ann. Chim. 8, 295 (1937).
14. H. Martinsen, Z. Physik. Chem. 50, 385 (1904); 59, 605 (1907).
15. J. A. Hetherington and I. Masson, J. Chem. Soc., 105 (1933).
16. F. H. Westheimer and M. S. Kharasch, J. Am. Chem. Soc. 68, 871 (1946).
17. G. M. Bennett, J. C. D. Brand, D. M. James, T. J. Saunders, and Gwyn Williams, J. Chem. Soc., 474 (1947).
18. E. D. Hughes, C. K. Ingold, et al., J. Chem. Soc., 929 (1938); ibid., 2400 (1950); Nature 158, 448 (1946).
19. L. Melander, Nature 163, 499 (1949).
20. E. Gould, Mechanism and Structure in Organic Chemistry (Holt, Rinehart and Winston, Inc., New York, 1959), Chap. 11.
21. W. K. Lewis and T. J. Suen, Ind. Eng. Chem. 32, 1095 (1940).
22. C. McKinley and R. R. White, Trans. Am. Inst. Chem. Engrs. 40, 143 (1944).

23. A. J. Barduhn and K. A. Kobe, Ind. Eng. Chem. 48, 1305 (1956); H. M. Brennecke and K. A. Kobe, ibid., 1298 (1956).

24. O. A. Hougen and K. M. Watson, Chemical Process Principles, Part III (John Wiley and Sons, New York, 1947), p. 1052.

25. P. H. Groggins, Unit Processes in Organic Systhesis (McGraw-Hill Book Co., Inc., New York, 1952), Chap. I.

26. N. L. Drake, C. M. Eaker, and J. A. Garman, J. Am. Chem. Soc 68, 1602 (1946).

27. S. D. Ross, M. Markarian, and M. Schwarz, J. Am. Chem. Soc. 75, 4967 (1953).

28. R. L. Murray, W. S. Beanblossom, and B. H. Wojcik, Commercial Preparation of Bis(Trifluoromethyl) Benzenes, in Preparation, Properties, and Technology of Fluorine and Organic Fluoro Compounds (McGraw-Hill Book Co., Inc., New York, 1951), Chap. 22.

29. M. A. Paul and F. A. Long, Chem. Rev. 57, 1 (1957).

30. J. G. Dawber and P. A. H. Wyatt, J. Chem. Soc., 3589 (1960).

31. J. R. Knowles, R. O. C. Norman, and G. K. Radda, J. Chem. Soc., 4885 (1960).

32. J. C. D. Brand, J. Chem. Soc., 1002 (1950);
J. C. D. Brand, W. C. Horning, and M. B. Thornley, ibid., 1374 (1952).

33. J. I. Gmitro and T. Vermeulen, Vapor-Liquid Equilibria for Aqueous Sulfuric Acid, UCRL-10886, June 1963.

34. Z. Kecki, Tetrahedron 12, 23 (1961).

35. N. C. Deno and C. Perizzolo, J. Am. Chem. Soc. 79, 1345 (1957).

36. L. P. Hammett and R. P. Chapman, ibid. 56, 1282 (1934).

37. N. C. Deno, H. J. Peterson, and E. Sacher, J. Phys. Chem. 65, 199 (1961).

38. N. C. Deno and R. Stein, J. Am. Chem. Soc. 78, 578 (1956).

39. L. P. Hammett, Physical Organic Chemistry (McGraw-Hill Book Co., Inc., New York, 1940), Chap. IX.

40. N. C. Deno and R. W. Taft, J. Am. Chem. Soc. 76, 244 (1954).

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