2. **Competitive Nitrations in Nitromethane.**—Benzene (0.25 mole) and 0.25 mole of alkyl or halobenzenes were dissolved in 50 g. of nitromethane. A solution of 0.05 mole of nitronium salt dissolved in 60 g. of nitromethane was added to the vigorously stirred substrate solution. Since $NO_2^+BF_4^-$ is only slightly soluble in nitromethane, a very dilute solution must be used in these experiments. The resulting mixtures were washed twice with 50 ml. of water, dried over $CaCl_2$ and analyzed by gas-liquid chromatography.

3. **Nitrations in Mixed Solvents.**—The nitronium salt (0.05 mole) was dissolved in 60 g. of one of the solvents (nitromethane, tetramethylene sulfone) and this solution was used in the competitive nitration of 0.25 mole of benzene and 0.25 mole of mesitylene dissolved in 70 g. of the other solvent under conditions identical with previous nitrations.

4. **Nitrations in Toluene.**—Toluene (0.05 mole) was added in small portions to 0.05 mole of solid nitronium salt, while the temperature was kept around 25°. The mixtures obtained were washed twice with 25 ml. of water, dried over $CaCl_2$ and analyzed by gas-liquid chromatography.

The determination of relative rates and isomer distribution were carried out by gas-liquid chromatography using a Perkin-Elmer model 154C gas chromatograph as described in an earlier paper in this series.[2]

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Aromatic Substitution. XIII.[1a] Comparison of Nitric Acid and Mixed Acid Nitration of Alkylbenzenes and Benzene with Nitronium Salt Nitrations

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A comparison of nitric acid and mixed acid nitrations of alkylbenzenes and benzene in nitromethane, acetic acid, acetic anhydride, tetramethylene sulfone and sulfuric acid solutions with nitronium salt nitrations was carried out. In sulfuric acid solutions or in concentrated organic solutions using mixed acid, where detectable amounts of NO_2^+ are present, nitrations show a low substrate but high positional selectivity, in complete agreement with previous observations of nitrations with preprepared NO_2^+ salts. In dilute organic solutions of the acids there is no spectroscopically (Raman and infrared) detectable amount of nitronium ion and the slow kinetic step of these reactions must be considered to be the formation of NO_2^+. The interaction with the aromatic substrate must be taking place even before the nitronium ion is completely formed and its weaker electrophile precursor shows higher substrate selectivity. Cryoscopic investigation of tetramethylene sulfone solutions of $NO_2^+BF_4^-$ gave evidence of very limited ion separation. Therefore, nitrations with nitronium salts in organic solvents cannot be considered as interaction of the free NO_2^+ ion with aromatics, but as nucleophilic displacement of the solvated $NO_2^+BF_4^-$ ion pair by the aromatics. An interaction of this type is in accordance with substantial activation energy needed for the formation of an oriented π-complex type activated state, suggested for nitronium salt nitrations previously.

Introduction

Our present knowledge of the nature of electrophilic aromatic nitration goes back to Euler[2] who first suggested NO_2^+ as the active nitrating agent. Hantzsch,[3] Walden,[4] Ri and Eyring,[5] Ingold, Lapworth and co-workers,[6] Price[7] and Chedin,[8] added to the theory of NO_2^+ nitration, but it was not until 1946 that NO_2^+ was finally established as the active nitrating agent. Kinetic and spectroscopic evidence obtained from the work of Bennett, Brand and Williams,[9] Westheimer and Kharasch[10] and in particular by Ingold, Hughes and their co-workers[11] were the major contributions to the mechanism of aromatic nitrations.

Since much of this work is widely known and has been repeatedly reviewed, no further review seems to be necessary.

Results and Discussion

Nitronium salts have become easily available and have been developed as preparative nitrating agents.[12] The use of nitronium salts in tetramethylene sulfone[13] and nitromethane[5] solution has allowed investigation of the kinetics and mechanism of the nitration of aromatics (benzene, alkylbenzene, halobenzenes). All of these nitrations are very fast, but by employing Ingold's competitive nitration technique, it was possible to compare relative reactivity of aromatics. The relative rates show first-order dependence on the aromatic substrates and thus permit a comparison of relative reactivities under competitive conditions. Nitronium salts in organic solutions with reactive aromatic substrates show small substrate but high positional selectivity.[13,14] The relative reactivities correspond to known π-complex but not to σ-complex stabilities of the substrates. It was of some interest to try to compare these results with classical nitric acid nitrations, in which nitronium ion has been suggested to be the active nitrating species. Therefore an attempt was made to compare nitronium salt nitrations with nitric acid nitrations, carried out in organic media (acetic anhydride, acetic acid, nitromethane, tetramethyl-

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ene sulfone) and with mixed acid nitrations in the same solvent systems.

Nitration with Nitric Acid in Organic Solvents.—With nitric acid (used both as solvent and as nitrating agent) Ingold has found that nitrations are first order with respect to aromatic compounds. Although, according to Raman spectroscopic observations,[11] anhydrous nitric acid contains approximately 1% of nitronium ion, solutions of nitric acid in organic solvents such as nitromethane contain no detectable amount of nitronium ion. Ingold, Hughes and co-workers have found that sufficiently reactive aromatic compounds (benzene, toluene, ethylbenzene, etc.) exhibit, in nitrations in nitromethane solutions, zeroth order kinetics, *i.e.*, the reaction rates are independent of the nature or concentration of the substrate indicating that the aromatic compound takes no part in the rate-determining step. This step must therefore be limited to the nitric acid (with the possible assistance of the solvent) and was found to be the formation of NO_2^+.

The necessary condition in the formation step of the nitronium ion is that the rate of the recombination of nitronium ion with water should be much slower than the rate of reaction of the nitronium ion with the aromatic compound. In nitromethane solution there will be at the start of the reaction a minute concentration of water arising from the ionic self-dehydration of the nitric acid. During the reaction this will be increased, but the water concentration will always be much less than that in the partly aqueous solution. In nitromethane solution the zeroth order rate was observed by Ingold and Hughes in almost all cases involving compounds with reactivities equal to or greater than that of benzene. The addition of small quantities of water to nitromethane has little effect on the zeroth order rate. This is expected, since water does not enter into the pre-equilibrium step and therefore does not reduce the concentration of the nitracidium ion. When more water is added, a point is reached where the water competes with the aromatic compound for the limited supply of the nitronium ion. The kinetics then change to a first-order form.[15]

The relative reactivity of toluene and benzene in competitive nitration with nitric acid in nitromethane was found by Ingold[11] to be 21, using a dilatometric technique. Employing gas–liquid chromatography as an analytical method, the nitric acid nitration of benzene, toluene, ethylbenzene, *p*-xylene and mesitylene were compared in competitive experiments (Table I). The results are in excellent agreement with Ingold's data for the toluene:benzene reactivity ratio and also establish high substrate selectivity and the usual isomer distributions in the nitration of the other alkylbenzenes.

Table I

Competitive Nitration of Benzene and Alkylbenzenes with Nitric Acid in Organic Solvents at 25°

Aromatic	Solvent	$k_{Ar}/k_{benzene}$	Isomer distribution, % *ortho*	*meta*	*para*
Benzene	Acetic anhyd.	1.0			
Toluene[11,16]		27	61.4	1.6	37.0
Ethylbenzene[16]		23	45.9	3.3	50.8
p-Xylene		>1000			
Mesitylene		>1000			
Benzene	Nitromethane	1.0			
Toluene		26.4	61.5	3.1	35.4
Ethylbenzene		22.6	48.3	2.3	49.5
p-Xylene		>1000			
Mesitylene		>1000			
Benzene	Acetic acid	1.0			
Toluene		28.8	56.9	2.8	40.3
p-Xylene		>1000			
Mesitylene		>1000			
Benzene	Tetramethylene sulfone	1.0			
Toluene		17	61.9	3.5	34.7
Mesitylene		>1000			

Nitric acid nitration of toluene and benzene in acetic anhydride and acetic acid solutions was investigated by Ingold and Hughes during their systematic study of nitrations.[11] Knowles, Norman and Radda[16] redetermined relative rates and isomer distribution in nitric acid nitrations of toluene and benzene in acetic anhydride solution at 0°, using gas–liquid chromatographic analysis, and extended the work to additional alkylbenzenes. Their data again show excellent correlation with Ingold's work and as summarized in Table I, indicate high substrate selectivity.

Nitric acid nitrations in acetic acid and tetramethylene sulfone solution gave results closely similar to those obtained in nitromethane and acetic anhydride solutions.

The concentration of nitric acid in the organic solutions was in every instance about 20% by weight. In all cases the systems, as indicated by Raman and infrared spectra of solutions of comparable concentration, do not contain any detectable amount of NO_2^+. No free NO_2^+ could be detected in a solution of HNO_3 in acetic anhydride but there was spectroscopic evidence of the formation of acetyl nitrate. It seems improbable that

$$(CH_3CO)_2O + HNO_3 \longrightarrow CH_3COONO_2 + CH_3COOH$$

free NO_2^+ could exist in acetic anhydride for any significant period of time, since nitronium salts themselves react very vigorously with acetic anhydride to form acetyl nitrate. Vandoni and Viola[17] arrived at the same conclusion from vapor pressure measurements of acetic anhydride and absolute nitric acid at −10°. This reaction has also been shown to occur by Raman[18] and infrared[19] spectroscopic investigations. The nature of acetyl nitrate as a nitrating agent has been discussed recently by Bordwell and Garbisch[20] whose data are consistent with previous observations.

Nitration with Nitric Acid in Sulfuric Acid.—In sulfuric acid, nitric acid is converted rapidly and completely to nitronium ion. The formation of NO_2^+ therefore cannot be rate determining in nitrations carried out with nitric acid in sulfuric acid and the rate of nitration may be expected to depend on the concentration and the nature of the

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aromatic compound and the concentration of nitronium ion.

Mixed acid nitration of aromatic hydrocarbons using only excess of aromatics as solvent or using sulfuric acid as solvent is not entirely suitable for kinetic investigations. Mixed acid forms a heterogeneous system with aromatic hydrocarbons; therefore competitive nitrations can be carried out only under conditions not suitable for kinetic work. Increasing the velocity of stirring (by applying a vibrational stirrer) allowed some informative experiments to be carried out with this system. The data (Table II) are, of course, only informative because of differences in rate of diffusion into the acid layer and of solubility and because some dinitration takes place.

TABLE II

COMPETITIVE NITRATION OF BENZENE AND ALKYLBENZENES WITH MIXED ACID AT 25°

Heterogeneous, non-kinetic conditions

		ortho	*meta*	*para*
Benzene	1.0			
Toluene	1.24	56.4	4.8	38.4
o-Xylene	1.02	3-Nitro-*o*-xylene		55%
		4-Nitro-*o*-xylene		45%
m-Xylene	0.80	2-Nitro-*m*-xylene		14%
		4-Nitro-*m*-xylene		86%
p-Xylene	1.09			
Mesitylene	0.68			

With all the shortcomings of the heterogeneous nitration technique, these informative results show, however, marked resemblance to nitronium salt nitrations, but not to nitric acid nitration in organic solvents.

In addition to the above-mentioned factors influencing heterogeneous reactions, lower relative rates and *ortho* isomer ratios point to the fact that in mixed acid the NO_2^+ salt must be solvated to a substantial degree by solvent acid; steric factors therefore may play an increasingly important role.

Nitration with Mixed Acid in Organic Solvents.—Spectroscopic investigation of solutions of mixed acid in organic solvents (to be discussed later) shows that the NO_2^+ ion concentration in tetramethylene sulfone solution drops at around 60 volume per cent. acid below the spectroscopically determinable limit. In acetic acid the limiting concentration is about 50 volume per cent. and in nitromethane about 25 volume per cent. mixed acid.

Homogeneous nitrations of benzene and alkylbenzenes with mixed acid can be carried out in organic solvents, such as tetramethylene sulfone and acetic acid. Nitromethane cannot be used, because upon the addition of the hydrocarbon the acid layer separates from the previously homogeneous solution. Acetic anhydride, as mentioned previously, reacts very vigorously with mixed acid to form acetyl nitrate, and cannot be used as solvent. Competitive nitration of benzene and alkylbenzenes was carried out by adding the solutions of mixed acid to the stirred solution of the substrates at 25°. Two different sets of experiments were carried out. In one a 30% solution of mixed acid in the solvent was used as nitrating agent, in the other a 75% solution. According to spectroscopic data in the 30% solutions there is no detectable amount of NO_2^+, whereas in the 75% solutions 5–7.5 weight per cent. NO_2^+ is present.

The nitration data obtained are summarized in Tables III and IV.

TABLE III

COMPETITIVE NITRATION OF BENZENE AND ALKYLBENZENES WITH 30% SOLUTION OF MIXED ACID IN TETRAMETHYLENE SULFONE AND ACETIC ACID AT 25°

Aromatic	Solvent	$k_{Ar}/k_{benzene}$	Isomer distribution, % *ortho*	*meta*	*para*
Benzene	Tetramethylene	1.0			
Toluene	sulfone	28	62.0	3.4	34.6
Ethylbenzene		24	50.3	3.6	46.1
Isopropylbenzene		13.8	43.2	4.5	52.3
p-Xylene		> 500			
Mesitylene		>1000			
Benzene	Acetic acid	1.0			
Toluene		21	56.5	3.1	40.4
p-Xylene		> 500			
Mesitylene		>1000			

TABLE IV

COMPETITIVE NITRATION OF BENZENE AND ALKYLBENZENES WITH 75% SOLUTION OF MIXED ACID IN TETRAMETHYLENE SULFONE AND ACETIC ACID AT 25°

Aromatic	Solvent	$k_A/k_{benzene}$	Isomer distribution, % *ortho*	*meta*	*para*
Benzene	Tetramethylene	1.0			
Toluene	sulfone	1.60	56.3	2.6	41.0
Ethylbenzene		1.35	44.7	2.0	53.3
o-Xylene		0.9			
m-Xylene		1.1	15.3%	2-NO_2-*m*-xylene	
p-Xylene		1.8	84.7%	4 NO_2-*m*-xylene	
Mesitylene		0.33			
Benzene	Acetic acid	1.0			
Toluene		2.13	58.1	1.9	40.0
m-Xylene		1.27	16.3%	2-NO_2-*m*-xylene	
			83.8%	4-NO_2-*m*-xylene	

The concentrations mentioned above refer only to the concentration of the nitrating acid ($H_2SO_4 + HNO_3$) in the solvent. Upon addition of the substrates in the same solvent the actual concentration is further reduced (see Experimental part). Since it was established in previous work that NO_2^+ nitrations of benzene and alkylbenzenes are very fast, it was suggested that NO_2^+ ions present in the solutions of the nitrating agent will react with the substrate before any substantial changes due to dilution of the solution, leading to formation of nitric acid and decrease of the amount of NO_2^+. In competitive rate determinations the actual amount of nitration taking place is of no importance; therefore only slight interference is to be expected because of the formation of some nitric acid, which reacts much more slowly than NO_2^+ ions.

Mixed acid nitration of benzene and alkylbenzenes in dilute (30%) tetramethylene sulfone and acetic acid solution showed close similarity to nitric acid nitrations in the same solvents (high substrate and high positional selectivity).

Nitrations with concentrated (75%) solutions of mixed acid showed good agreement with previously reported nitrations of benzene and alkylbenzenes with NO_2^+ salts.

Thus nitrations with mixed acid, when carried out in concentrated organic solutions containing spectroscopically demonstrated amounts of NO_2^+, show close similarities with nitronium salt nitrations. Mixed acid nitrations in more dilute organic solutions, not containing detectable amounts of NO_2^+, however, show much higher substrate selectivity (but practically unchanged isomer distributions), similar to results reported by Ingold and Hughes for kinetic nitrations with nitric acid in these solvents, or to those obtained in nitric acid nitrations in the present work. It must be concluded therefore that (a) nitrations in dilute organic solutions involve the formation of the active nitrating agent as the rate-determining step and (b) the interaction of aromatic substrates with the nitrating agent involves not free NO_2^+, but a weaker electrophilic precursor of it, probably $H_2NO_3^+$. NO_2^+ as such is formed only after it is already associated with the aromatic substrate. This may explain why, as Ingold found, the reaction of NO_2^+ is much faster with aromatics, than with water.

The experimental data point to the fact that the reaction of NO_2^+ with water in organic solvents cannot be considered as markedly slower than the reaction of NO_2^+ with the aromatic substrates.

The availability of stable nitronium salts allows direct competitive experiments on the nitration rate of water, benzene, toluene (and fluorobenzene). Using tetramethylene sulfone as solvent, competitive nitrations of equimolar quantities of hydrocarbon and water were carried out with $NO_2^+BF_4^-$. The products were analyzed by gas–liquid chromatography. The data are summarized in Table V.

Table V

Competitive Nitration of Benzene (Toluene, Fluorobenzene) and Water with $NO_2^+BF_4^-$ in Tetramethylene Sulfone Solution at 25°

Water	1.0
Benzene	1.17
Toluene	1.77
Fluorobenzene	0.55

Under these conditions benzene reacts only very slightly faster than water with $NO_2^+BF_4^-$. The above data also permit calculation of the relative toluene:benzene and fluorobenzene:benzene nitration rates. These are: $k_{\text{toluene}}:k_{\text{benzene}} = 1.52$, $k_{\text{fluorobenzene}}:k_{\text{benzene}} = 0.47$. The correspondence with previous data measured in direct competitive nitration of the aromatics[13] (*e.g.*, 1.67 and 0.45) is quite good.

Infrared and Raman Spectroscopic Investigation of Nitronium Tetrafluoroborate and of Mixed Acid Solutions in Organic Solvents.—No apparent difference in the infrared and Raman absorption of NO_2^+ in nitronium salts was observed whether the spectra of solid salts or their solutions in organic solvents with varying dielectric constants, such as tetramethylene sulfone, nitromethane or acetic acid, were taken. The identity of the spectra under such varying conditions is best explained by assuming that as in the crystal lattice, where NO_2^+ is in strong coulombic interaction with the anion, a somewhat similar situation also exists in solution. This suggestion of NO_2^+ being present in solution in the form of ion pairs (or higher associated ion clusters, which of course in turn can be solvated) is further substantiated by cryoscopic investigation of the solutions.

Raman and infrared spectroscopic investigations of solutions of nitric acid in the organic solvents used in these investigations (acetic acid, acetic anhydride, nitromethane and tetramethylene sulfone) gave no evidence of the presence of free NO_2^+ ions. These observations are in agreement with previous data.

In order to gain further information on mixed acid solutions in organic solvents, systems suitable for homogeneous kinetic nitrations, it was necessary to determine by Raman and infrared spectroscopy the NO_2^+ concentrations of these solutions at different concentrations.

All the spectroscopic data were obtained using a nitric acid:sulfuric acid mole ratio of 1:1 prepared from 90% nitric acid, 15% oleum and 96% sulfuric acid. Raman spectra were obtained using a Hilger photoelectric/photographic instrument with 4358 Å. excitation; the inverse dispersion in this region is 7 Å./mm. when photoelectric recording is used and 16 Å./mm. for photographic recording. The intensity was obtained photoelectrically and all solutions were scanned immediately after preparation.

Infrared spectra were obtained using a prism-grating instrument constructed by Herscher[21]; slit widths of the order of 2 cm.$^{-1}$ were used. Solutions were held between AgCl plates and, although the film thicknesses were not known, the qualitative intensity data obtained were reproducible and satisfactory for our purposes.

The results are illustrated in Fig. 1, in which the relative concentration of NO_2^+ ion is plotted against the volume percentage of mixed acid in the organic solvent. Unity on the NO_2^+ concentration scale is 5.6 molar. For the tetramethylene sulfone and the acetic acid solutions the Raman band of the NO_2^+ ion at 1400 cm.$^{-1}$ [22] was used as the concentration measure, and all solutions were run under identical conditions. Also run under these same conditions was a nitric–sulfuric acid mixture in which the sulfuric acid was in sufficient excess to convert the nitric acid entirely into the NO_2^+ ion. In this way the NO_2^+ ion concentration in all solutions was estimated. Uncertainties are of the order of ±4%. A linear relation between intensity and concentration was assumed and no corrections for refractive index effects were applied, but these are not expected to be large enough to influence the conclusions reached. Curves a and b show that the limit of detection of NO_2^+ is attained at a higher mixed-acid concentration in acetic acid solvent than in tetramethylene sulfone. Photographic Raman spectra, in which the sensitivity is greater, confirmed the approximate limits and further confirmation was derived from the infrared peak-intensity measurements made on

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[21] L. W. Herscher, *Spectrochim. Acta*, **11**, 901 (1959).

[22] D. J. Millen, *Nature*, **158**, 480 (1946).

the band at 2375 cm.$^{-1}$, which is due to the asymmetric stretching mode of the NO_2^+ ion.[23,24]

Nitromethane has an intense Raman band near 1400 cm.$^{-1}$ so that the concentration range covered by the Raman data was very limited. Curve c in Fig. 1 was drawn using the infrared-band peak intensities at 2375 cm.$^{-1}$. In this case, the NO_2^+ ion could be detected down to about 25% mixed acid concentration which is considerably beyond the limits for the other two solvents. Here again, a linear dependence of peak band intensity upon concentration is assumed; the curve probably carries an uncertainty of less than ±10% of the measured quantity.

No determination of mixed-acid solutions in acetic anhydride was possible, because of the very explosive reaction with the solvent leading to the formation of acetyl nitrate. In a few low concentrations, however, spectra were obtained, but showed no NO_2^+.

Cryoscopic Measurements of Tetramethylene Sulfone Solutions of $NO_2^+BF_4^-$.—Cryoscopic investigations were carried out with a technique similar to that developed by Gillespie.[25]

Cooling was effected by immersing the cryoscopic cell in a controlled temperature bath. A calibrated platinum resistance thermometer attached to a recorder was used. Accuracy of the temperature determinations was 0.01°. In the experiments the customary super-cooling correction was found small enough to be ignored.

The freezing point of tetramethylene sulfone (twice distilled, with a specific conductivity of 1×10^{-7} ohm^{-1}/cm.$^{-1}$) was found to be 27.6°.

The molal freezing point depression of tetramethylene sulfone used in our experiments, as determined using naphthalene as solute, was 64.8 ± 0.8°. Using $NO_2^+BF_4^-$ as solute in concentrations of about 3 mole per cent. the ion pair dissociation constant was determined (from the average of four determinations) to be: i = obsd./calcd. molar depression = 66.1/64.8 = 1.02, corresponding to 2% dissociation, but within the limit of the experimental error.

The molal freezing point depression of tetramethylene sulfone, as determined in the case of solute naphthalene, is slightly smaller and the specific conductivity somewhat higher then that reported by Burwell and Langford.[26] It is probable that differences in the purity of the tetramethylene sulfone used are responsible for the differences. Attempts to use 3-methyltetramethylene sulfone, which has a lower freezing point (−1.9°) in cryoscopic investigations, were less satisfactory. Substitution of the symmetrical cyclic sulfone decreases the molar freezing point depression to 10.1 ± 0.3°. Solvent properties of 3-methyltetramethylene sulfone for nitronium salts are also considerably poorer than those of the symmetrical tetramethylene sulfone.

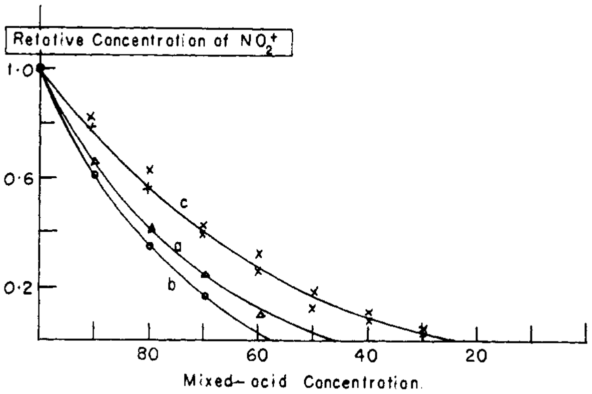

Fig. 1.—Variation of NO_2^+ ion concentration with the concentration of mixed acid (nitric:sulfuric, 1 mole:1 mole) in organic solvents: a, in sulfolane; b, in acetic acid; c, in nitromethane. Curves a and b were determined by Raman measurements using the 1400 cm.$^{-1}$ band while curve c was derived from infrared measurements on the 2375 cm.$^{-1}$ band. Unity on the NO_2^+ concentration scale was determined to be 5.6 molar (~25.8 weight per cent.).

The existence of nitronium tetrafluoroborate in tetramethylene sulfone solution predominantly in the form of ion pairs is not too surprising and provides an explanation for the cryoscopic results. Foster[27] observed a similar behavior in nitromethane solution of nitronium perchlorate. Although our previously reported conductivity measurements[12] of nitronium tetrafluoroborate in tetramethylene sulfone solution have shown specific conductance varying linearly with the concentration of the solutions, it must be now restated that these conductivity values in all probability were due not to the separated ions, but to the presence in fairly concentrated solutions of conducting ion triplets. Foster was able to demonstrate, following the molar conductance against the volume of solutions, that the conductivity curve goes through a minimum. The explanation generally advanced to account for this type of minima is, that in fairly concentrated solutions (where all of our conductivity measurements with $NO_2^+BF_4^-$ were reported) conducting ion triplets are present. Foster observed that on dilution these are converted into ion pairs which are non-conducting. On even further dilution the ion pairs split up into separate ions.

Conclusions

There is in our opinion no discrepancy between the classical nitration work of Ingold and Hughes and our data obtained with stable nitronium salt nitrations. With nitronium salts in suitable organic solvents the kinetic step of formation of NO_2^+ is eliminated. In nitric acid nitrations in nitromethane, acetic anhydride, acetic acid and tetramethylene sulfone solutions, where Raman and infrared spectroscopy do not show any NO_2^+, the formation of NO_2^+ or its precursor certainly is a slow kinetic step. The effect of aromatic substrates on the formation of NO_2^+ is shown in the considerably increased substrate selectivity over that obtained with NO_2^+ salts. On the basis of

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(23) R. Teranishi and J. C. Decius, *J. Chem. Phys.*, **22**, 896 (1954).

(24) D. Cook, S. J. Kuhn and G. A. Olah, *ibid.*, **33**, 1669 (1960).

(25) R. J. Gillespie, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2473 (1950).

(26) R. L. Burwell, Jr., and C. H. Langford, *J. Am. Chem. Soc.*, **81**, 3799 (1959).

(27) P. W. Foster, unpublished results, personal communication.

the experimental data it is suggested that in these nitrations a weaker nitrating species than NO_2^+ must be involved in the primary interaction with the aromatic substrates. This incipient nitronium ion then attaches itself to the aromatics in a step giving high substrate selectivity. Whether the incipient nitronium ion is the nitracidium ion ($H_2NO_3^+$), protonated acetyl nitrate (CH_3COO-HNO_2^+) or probably a transition state of any of those unstable species to NO_2^+, in which water is loosened, but not yet completely eliminated, is difficult to say and no direct physical evidence is available.

Nitric acid nitrations in nitromethane, acetic acid, acetic anhydride (in the last of course acetyl nitrate is formed and must be considered the starting material for the formation of NO_2^+ or its precursor), or in tetramethylene sulfone solution all must be considered specific nitration systems not containing detectable amounts of NO_2^+. Nitric acid in sulfuric acid (in which it is completely ionized), or mixed acid in concentrated organic solutions (containing NO_2^+) indeed nitrates as NO_2^+, which is solvated by the acid to a certain degree. Dilute organic solutions of mixed acid (not containing detectable amounts of NO_2^+) behave similarly to nitric acid nitrations.

If we assume that an activated state of the oriented π-complex type is formed irreversibly in nitrations with nitronium salts, one must explain from where forces resisting its formation to that extent come. The NO_2^+ ion, even in nitrations with nitronium salts, is not present (at least in the organic solvents investigated) as separated ion. Cryoscopic investigations (involving solutions of about 3 weight per cent. concentration in tetramethylene sulfone, in contrast to more concentrated, about 7 weight per cent. solutions used in relative rate determinations) suggest that ion separation, if any, is very limited in tetramethylene sulfone solution of $NO_2^+BF_4^-$ ($<2\%$). The nitronium salt consequently is predominantly present in the form of ion pairs; triplets or even higher associated ions are suggested from the conductivity measurements of Foster[27] in nitronium perchlorate solutions of nitromethane. Therefore substantial activation energy is needed to separate the NO_2^+ from the strong coulombic interaction in the ion pair (with possible additional solvation of the ion pairs by the solvent) and allow it to react with the aromatic ring as a π-donor. The reaction itself accordingly can best be characterized as *nucleophilic displacement by the basic aromatic hydrocarbon on the solvated* $NO_2^+BF_4^-$ *ion pair* (*or higher associated ion clusters*).

Whereas our investigations were carried out on benzene and alkylbenzenes (relatively strongly basic aromatics with only one donor center, *e.g.*, the aromatic π-sextet), most of the kinetic investigations using sulfuric acid as solvent were carried out previously with nitrated aromatics or quaternary ammonium salts, which are relatively resistant to nitration and thus give measurable rates. At the same time they permit homogeneous solutions, not possible with hydrocarbons. It is suggested that differences in the nature of the aromatic substrates may have more profound consequences than so far generally realized. Nitro aromatic compounds have in contrast to aromatic hydrocarbons not one, but two, nucleophilic centers: the polar nitro group and the ring π-sextet. The latter is weaker in donor properties and does not allow ring protonation with strong Friedel–Crafts acids capable of protonating alkylbenzenes. Thus no direct analogy can be drawn from nitration of such different substrates. It should be mentioned that a somewhat similar observation was made previously by Williams and Lowen,[28] who found that compounds containing an activated aromatic nucleus (benzene, alkylbenzenes) may be nitrated rapidly by nitric acid–sulfuric acid–water mixtures, containing more than 50 mole % of water, in which the nitronium ion cannot be detected spectroscopically. Deactivated aromatics (like nitrobenzene) failed to be nitrated in the same media. The entity which nitrates nitrobenzene in 80% sulfuric acid is according to Westheimer and Kharasch[10] in all probability the nitronium ion. However the reagent which nitrates more active aromatic molecules at a speed much greater in the same medium and which is also effective in more aqueous media, still needs to be identified. It may be the nitracidium ion or the nitronium ion present in small concentration, or any intermediate state between the two limiting cases, the aromatic substrate interacting with the precursor of NO_2^+ before it is entirely preformed.

The nitrations of aromatics with $NO_2^+BF_4^-$ and related nitronium compounds in organic solvents in our opinion should be considered as nitrations with *nitronium salts* and not free NO_2^+ nitrations. All evidence points to the fact that the salt (*e.g.*, ion pair or solvated ion pair) is the nitrating species and not the free NO_2^+ ion.

If the previous argument is pursued for nitration with mixed acid in organic solvents, then again we must first consider the nature of the nitrating species. Nitrations involving relatively dilute solutions of mixed acid in organic solvents do not involve spectroscopically detectable amounts of NO_2^+ (whatever its state of association). However, this does *not* exclude the presence of subspectroscopic amounts of NO_2^+ present in equilibrium. Therefore the over-all observed nitration rates could include nitration by NO_2^+ (present probably as solvated ion pair, but formed prior to the interaction of the precursor with the substrate), as well as nitration by a weaker electrophile not involving predissociation into the nitronium species prior to interaction with the aromatic substrate. Any degree of transition between the limiting cases is possible depending on the reaction conditions (reagent, solvent, catalyst and substrate). The same consideration must also hold for the nature of the transition state. With strong electrophiles it is in nature closer to an oriented π-complex than to a σ-complex. With a weaker electrophile it can alter to resemble more a σ-complex. According to our observations these effects influence first of all substrate selectivity (*e.g.*, relative reactivities) but not positional selectivity, because

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(28) G. Williams and A. M. Lowen, *J. Chem. Soc.*, 3312 (1950).

besides some steric effects (discussed previously) the positional orientation remains predominant *ortho–para*, with the *meta* isomer generally present only in very small amounts. No simple linear correlation between positional and substrate selectivity can be derived from our experimental observations.

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Experimental

The purity of materials used was similar to that previously described.[12–14]

Nitrations with 100% Nitric Acid in Organic Solvents. (a) **Nitromethane.**—Benzene (0.25 mole) and 0.25 mole of alkylbenzenes were dissolved in 50 g. of nitromethane and treated with 0.2 mole of 100% HNO_3 dissolved in 10 g. of nitromethane. The reaction mixture was stirred for an hour at 25°, washed 3 times with 25 ml. of water, dried over $CaCl_2$, and analyzed by gas–liquid chromatography.

(b) **Acetic Acid.**—Benzene (0.25 mole) and 0.25 mole of alkylbenzene were dissolved in 60 g. of acetic acid and treated with 0.2 mole of nitric acid dissolved in 30 g. of acetic acid. The mixture was stirred for 3 hours at 25°, washed twice with 200 ml. of water, dried over $CaCl_2$ and analyzed by gas–liquid chromatography.

(c) **Acetic Anhydride.**—Benzene (0.25 mole) and 0.25 mole of alkylbenzene were dissolved in 70 g. of acetic anhydride and treated with a solution of 0.2 mole of nitric acid in 30 g. of acetic anhydride while the temperature was kept at 25°. The mixture was stirred at 25° for an hour, then washed twice with 200 ml. of water, dried over $CaCl_2$ and analyzed by gas–liquid chromatography.

(d) **Tetramethylene Sulfone.**—Benzene (0.25 mole) and 0.25 mole of alkylbenzenes were dissolved in 60 g. of tetramethylene sulfone and treated with 0.2 mole of nitric acid dissolved in 50 g. of sulfuric acid at 25°. The solution was stirred for 2 hours at 25°, then washed twice with 250 ml. of water, dried over $CaCl_2$ and analyzed by gas–liquid chromatography.

Nitration with HNO_3 + H_2SO_4 without Solvent.—To a well stirred (vibrational stirrer) mixture of 0.25 mole of benzene and 0.25 mole of alkylbenzene, a mixture of 3.15 g. (0.05 mole) of 100% HNO_3 and 9.8 g. (0.1 mole) of 100% H_2SO_4 was added dropwise while the temperature of the mixture was kept at 25°. Reaction time was 25 minutes. The reaction mixture was washed with 50 ml. of ice-water, then twice with 25 ml. of water, dried over $CaCl_2$ and analyzed by gas–liquid chromatography.

Nitration with HNO_3 + H_2SO_4 in Tetramethylene Sulfone Solution.—The used nitric acid:sulfuric acid mole ratio was 1:1. Nitrations have been carried out with mixed acid solution in tetramethylene sulfone: (a) in which the mixed acid concentration was 30% by volume and (b) in which the mixed acid concentration was 75% by volume.

Benzene (0.25 mole) and 0.25 mole of alkylbenzene were dissolved in 70 g. of tetramethylene sulfone and treated with 0.1 mole of mixed acid as a tetramethylene sulfone solution (30 or 75%) was added dropwise. The reaction mixture was stirred and kept at 25°. After 15 minutes the reaction mixture was washed with 150 ml. of water. The organic layer was dried over $CaCl_2$ and analyzed by gas–liquid chromatography.

Nitration with HNO_3 + H_2SO_4 in Acetic Acid Solution.—The nitric acid:sulfuric acid mole ratio was 1:1. Nitrations have been carried out with mixed acid solutions in acetic acid: (a) in which the mixed acid concentration was 30% by volume and (b) in which the mixed acid concentration was 75% by volume.

Benzene (0.25 mole) and 25 mole of alkylbenzene were dissolved in 60 g. of 100% acetic acid and to this solution a 30% 0.1 mole of mixed acid as acetic acid solution (30 or 75%) was added. The stirred reaction mixture was kept at 25° for 30 minutes, washed twice with 200 ml. of water, dried over $CaCl_2$ and analyzed by gas–liquid chromatography.

Competitive Nitration of Aromatics and Water with NO_2^+-BF_4^- in Tetramethylene Sulfone Solution.—Water (0.25 mole) and 0.25 mole of aromatics (benzene, toluene, fluorobenzene) were dissolved in 70 g. of tetramethylene sulfone and to this stirred solution 0.05 mole of $NO_2^+BF_4^-$ dissolved in 60 g. of tetramethylene sulfone was added dropwise at 25°. After the addition of the $NO_2^+BF_4^-$ solution the reaction mixture was stirred for 10 minutes. Thereafter it was either neutralized with anhydrous ammonia or washed with water and analyzed by gas–liquid chromatography.

In both cases the relative rates were determined from the amount of nitroaromatics formed in the competitive reactions compared with control runs using identical conditions but with no water as competing substrate present or by the decrease of the amount of the aromatic substrate as compared to internal reference, according to the method described by Knowles, Norman and Radda.[16]

Gas–Liquid Chromatographic Analysis.—The analysis of the nitration mixtures was carried out on a Perkin–Elmer model 154-C vapor fractometer, using a thermistor detector equipped with a Perkin–Elmer model 194 electronic printing integrator. A 4 meter by 6-mm. stainless steel column packed with polypropylene glycol (UCON LB-500-X) supported on diatomaceous earth was used. Details of analysis and observed retention times have been described previously.[13]

In low conversion nitrations part of the solvent and excess aromatics was distilled off in order to concentrate solutions to obtain sufficiently large nitroaromatic peaks.