Reaction of $K^+TCNE^{\cdot -}$ with Acid.—$K^+TCNE^{\cdot -}$ (1.00 g., 5.98 mmoles) was added to 10 ml. of ice-cold 6 *N* hydrochloric acid. The suspension was stirred 1 minute, and the white precipitate which formed was collected on a filter and dried. The product (0.63 g., 64% yield) was shown to be a 1:1 mixture of TCNE and tetracyanoethane by comparison of its infrared spectrum with that of an equimolar mixture of authentic TCNE and tetracyanoethane.

Stability of $K^+TCNE^{\cdot -}$ to Heat.—A sample of $K^+TCNE^{\cdot -}$ was heated in an atmosphere of nitrogen at 150° for 3 hours. The infrared spectrum of the product showed it to be substantially unchanged. Another sample was heated at 200° for 3 hours. The infrared spectrum of this product indicated gross decomposition. To test the stability of solid $K^+TCNE^{\cdot -}$ to atmospheric oxygen and water vapor, a crystalline sample was allowed to stand in an open beaker. Periodic examination of the crystals by infrared spectroscopy showed no appreciable decomposition in 1 month.

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[Contribution No. 62, Exploratory Research Laboratory Dow Chemical of Canada, Ltd., Sarnia, Ontario, Can.]

Aromatic Substitution XII.[1] Steric Effects in Nitronium Salt Nitrations of Alkylbenzenes and Halobenzenes

By George A. Olah and Stephen J. Kuhn

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The observed differences in isomer distributions and relative reactivities in the nitrations of alkylbenzenes and halobenzenes with a number of stable nitronium salts such as $NO_2^+BF_4^-$, $NO_2^+ClO_4^-$, $NO_2^+PF_6^-$, $NO_2^+AsF_6^-$ and $NO_2^+HS_2O_7^-$ in tetramethylene sulfone and nitromethane solution are discusssed. It is suggested that these differences are due to steric effects caused by solvent participation and ion pair interactions.

Introduction

The nitronium tetrafluoroborate ($NO_2^+BF_4^-$) nitration of alkylbenzenes[2] and halobenzenes[3] has been discussed previously. It was pointed out that solvent participation and ion pair interaction play a certain role in the isomer distributions and relative reactivities of the reactions. In the present paper this question is further discussed on the basis of extended experimental work.

Results

Competitive nitration of benzene with alkylbenzenes and with halobenzenes was carried out with different stable nitronium salts. The nitronium salts used were $NO_2^+BF_4^-$, $NO_2^+ClO_4^-$, $NO_2^+PF_6^-$, $NO_2^+AsF_6^-$ and $NO_2^+HS_2O_7^-$. The use of these stable nitronium salts in nitrations was discussed previously[4] together with details of their preparation and handling. Two solvent systems were used for the kinetic nitrations: tetramethylene sulfone and nitromethane.

The solubility of $NO_2^+BF_4^-$ in tetramethylene sulfone at 25° is about 7%.[4] The solubility in nitromethane is, however, very low (less than 0.2%), and nitrations with $NO_2^+BF_4^-$ in nitromethane solution could be carried out only in very high dilutions with considerable preparative difficulties. $NO_2^+PF_6^-$ and $NO_2^+AsF_6^-$ are quite soluble both in tetramethylene sulfone and nitromethane. The nitromethane solutions can reach concentrations of more than 50% (by weight). The solubilities of nitronium perchlorate and hydrogen disulfate are again negligible in nitromethane, and do not allow investigation of homogeneous nitrations. $NO_2^+SbF_6^-$ although it is quite soluble was not investigated in kinetic nitrations, due to secondary reactions caused by SbF_5 with the solvents.

The method of competitive nitrations and the gas–liquid chromatographic analysis of the products was identical with that previously described.[2,3]

The results of these competitive nitrations are summarized in Tables I and II.

Discussion of Results

The differences in nitrations of alkylbenzenes and halobenzenes with different stable nitronium salts in tetramethylene sulfone and nitromethane solutions can best be discussed treating separately the observed differences on substrate-selectivity (*e.g.*, relative rates) and positional-selectivity (*e.g.*, isomer distribution).

Effects on Substrate-selectivity. (a) **Tetramethylene Sulfone as Solvent.**—Only slight differences in relative reactivity over benzene were observed. These are in accordance with possible steric interference depending on the size of the anion involved. BF_4^- and ClO_4^- are isosteric and close similarities are expected. PF_6^- and AsF_6^- are larger than the fluoroborate or perchlorate ions and this may explain the observed decrease in relative rates. This is most predominant in the case of the mesitylene:benzene ratio, where the steric interference indeed should be the largest. $HS_2O_7^-$, the largest of all anions investigated, shows also the lowest relative rates. It is significant to compare the mesitylene:benzene ratio, which is given in Table III for the nitronium salts investigated.

(b) **Nitromethane as Solvent.**—Relative rates of competitive nitration of alkylbenzenes and benzene using nitromethane as solvent are generally lower then those observed in tetramethylene sulfone solution. Again the most predominant differences can be observed by comparing the mesitylene: benzene ratios.

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TABLE I

COMPETITIVE NITRATION OF BENZENE, ALKYLBENZENES AND HALOBENZENES WITH NITRONIUM SALTS IN TETRAMETHYLENE SULFONE SOLUTION AT 25°

	$NO_2^+BF_4^-$				$NO_2^+ClO_4^-$				$NO_2^+PF_6^-$			
	Rel.	Isomer, %			Rel.	Isomer, %			Rel.	Isomer, %		
Aromatic	rate	*ortho*	*meta*	*para*	rate	*ortho*	*meta*	*para*	rate	*ortho*	*meta*	*para*
Benzene	1.00				1.00				1.00			
Toluene	1.67	65.4	2.8	31.8	1.60	66.2	3.4	30.4	1.40	67.6	1.4	31.0
o-Xylene	1.75	79.7% 3-NO_2-*o*-xylene			1.64	77.1% 3-NO_2-*o*-xylene			1.46	74.4% 3-NO_2-*o*-xylene		
		20.3% 4-NO_2-*o*-xylene				22.9% 4-NO_2-*o*-xylene				25.6% 4-NO_2-*o*-xylene		
m-Xylene	1.65	17.8% 2-NO_2-*m*-xylene			1.52	15.0% 2-NO_2-*m*-xylene			1.48	12.4% 2-NO_2-*m*-xylene		
		82.2% 4-NO_2-*m*-xylene				85.0% 4-NO_2-*m*-xylene				87.6% 4-NO_2-*m*-xylene		
p-Xylene	1.96				1.98				1.60			
Mesitylene	2.71				3.25				1.60			
Fluorobenzene	0.45	8.5	..	91.5	0.46	11.7	..	88.3	0.54	14.2	..	85.8
Chlorobenzene	0.14	23.8	1.0	75.2	0.20	22.7	..	76.3	0.21	29.2	..	70.8

	$NO_2^+AsF_6^-$				$NO_2^+HS_2O_7^-$			
	Rel.	Isomer, %			Rel.	Isomer, %		
Aromatic	rate	*ortho*	*meta*	*para*	rate	*ortho*	*meta*	*para*
Benzene	1.00				1.00			
Toluene	1.52	65.5	2.6	31.9	1.48	62.1	3.2	34.7
o-Xylene	1.60	74.8% 3-NO_2-*o*-xylene			1.10	68.65% 3-NO_2-*o*-xylene		
		25.2% 4-NO_2-*o*-xylene				31.35% 4-NO_2-*o*-xylene		
m-Xylene	1.71	12.1% 2-NO_2-*m*-xylene			1.23	14.6% 2-NO_2-*m*-xylene		
		87.9% 4-NO_2-*m*-xylene				85.4% 4-NO_2-*m*-xylene		
p-Xylene	1.85				1.72			
Mesitylene	1.65				0.90			
Fluorobenzene	0.39				.41			
Chlorobenzene	0.12	27.0		73.0	.14	30.4		69.6

TABLE II

COMPETITIVE NITRATION OF BENZENE, ALKYLBENZENES AND HALOBENZENES WITH NITRONIUM SALTS IN NITROMETHANE SOLUTION AT 25°

	$NO_2^+BF_4^-$				$NO_2^+PF_6^-$				$NO_2^+AsF_6^-$			
	Rel.	Isomer, %			Rel.	Isomer, %			Rel.	Isomer, %		
Aromatic	rate	*ortho*	*meta*	*para*	rate	*ortho*	*meta*	*para*	rate	*ortho*	*meta*	*para*
Benzene	1.00				1.00				1.00			
Toluene	1.19	64.7	3.2	32.1	0.91	64.8	1.9	33.3	0.97	66.6	2.1	31.3
Ethylbenzene					.76	55.4	6.1	38.5				
t-Butylbenzene					.62	12.2	13.5	74.3				
o-Xylene					.74	68.6% 3-NO_2-*o*-xylene						
						31.4% 4-NO_2-*o*-xylene						
m-Xylene	0.96	14.6% 2-NO_2-*m*-xylene			.77	14.6% 2-NO_2-*m*-xylene			0.54	12.2% 2-NO_2-*m*-xylene		
		85.4% 4-NO_2-*m*-xylene				85.44% 4-NO_2-*m*-xylene				87.8% 4-NO_2-*m*-xylene		
p-Xylene					.81				.53			
Mesitylene	1.22				.41				.42			
Fluorobenzene					.73	12.3	..	87.7	.73	11.6	..	88.4
Chlorobenzene					.50	30.7	..	69.3	.40	28.6	..	71.4
Bromobenzene					.39	34.1	..	65.9				

TABLE III

COMPARISON OF COMPETITIVE NITRATION OF MESITYLENE AND BENZENE IN TETRAMETHYLENE SULFONE SOLUTION AT 25°

	$k_M:k_B$		$k_M:k_B$
$NO_2^+ClO_4^-$	3.25	$NO_2^+AsF_6^-$	1.65
$NO_2^+BF_4^-$	2.71	$NO_2^+HS_2O_7^-$	0.90
$NO_2^+PF_6$	1.60		

TABLE IV

COMPARISON OF COMPETITIVE NITRATION OF MESITYLENE AND BENZENE IN NITROMETHANE SOLUTION AT 25°

	$k_M:k_B$
$NO_2^+BF_4^-$	1.22
$NO_2^+PF_6^-$	0.41
$NO_2^+AsF_6^-$	0.42

The mechanism of nitronium salt nitrations in tetramethylene sulfone previously was interpreted[2,3] in terms of a rate-determining activated state of the oriented π-complex type. Low substrate selectivities observed in nitromethane solution show a similar pattern. Differences due to basicities of alkylbenzenes must be compensated to a large degree, or even overshadowed by steric requirements because of higher association of the reagents (ion pair nature) in nitromethane, or more stable complexing with the solvent.

No differences in the spectra of nitronium salts in either tetramethylene sulfone or nitromethane could be demonstrated by infrared and Raman spectroscopic investigation of the solutions, as compared with spectra of the crystalline complexes as mulls. No shift of the 2380 cm.$^{-1}$ infrared or the

1400 cm.$^{-1}$ Raman-band of NO_2^+ could be observed. However, no differences are expected, if the complexes are present in the solutions in the form of closely associated ion-pairs.

That the solvent must complex the nitronium salts to a certain degree was obvious from the solubility of these ionic salts in non-aqueous organic solvents to the observed degree. Also the considerable differences observed with different nitronium salts would be difficult to explain otherwise. The high solubility of $NO_2^+PF_6^-$ and $NO_2^+AsF_6^-$ (as well as $NO_2^+SbF_6^-$) must also be due partly to the higher association of these salts as compared with $NO_2^+BF_4^-$.[4]

A further proof of complexing of the nitronium salts by solvent was obtained from experiments in which solutions of nitronium hexafluorophosphate in one of the solvents (nitromethane or tetramethylene sulfone) were used for nitrating aromatics dissolved in an approximately equal amount of the other solvent. The data obtained (Table V) point to the fact that a nitromethane solution of $NO_2^+PF_6^-$ gave, in the nitration of a toluene: benzene mixture dissolved in approximately the same amount of tetramethylene sulfone, the same relative reactivities as nitration using nitromethane alone as solvent. This was also observed in reversed experiments for tetramethylene sulfone.

Table V

Competitive Nitration of Mesitylene and Benzene in Mixed Solvents

NO_2PF_6 in solvent	Aromatics in solvent	$k_M : k_B$
Tetramethylene sulfone	Tetramethylene sulfone	1.60
Nitromethane	Nitromethane	0.43
Nitromethane	Tetramethylene sulfone	0.37
Tetramethylene sulfone	Nitromethane	1.62

Effects on Orientation-selectivity.—Tables I and II show that nitration of aromatics with prepared nitronium salts shows low substrate selectivity and high positional selectivity in both tetramethylene sulfone and nitromethane solutions. Only minor change in the isomer distribution of the nitration of toluene can be observed when the same nitronium salt is used in tetramethylene sulfone or nitromethane. The relative amounts of *ortho* isomers are slightly decreased when nitromethane was used instead of tetramethylene sulfone. With increasing size of the anion of the nitronium salts, the amount of the *ortho* isomer also decreases slightly. This is best observed in the case of the $NO_2^+HS_2O_7^-$ nitration of toluene where the *ortho* isomer formed was found to be 62.1% compared to 66–67% of *ortho* isomer in nitrations with other nitronium salts. There seems to be a parallel between substrate selectivity and positional selectivity changes (affecting the *o*-positions), both due mainly to steric factors.

In excess toluene alone, steric effects due to solvent participation or ion pair interactions are easily demonstrated. The nitronium salt reacts practically instantaneously with toluene and no solubility data could be determined, but the solubility of the ionic salt in the hydrocarbon must be very low. A comparison of the isomer distribution of nitrotoluenes obtained using excess toluene as solvent with data of nitration in tetramethylene sulfone and nitromethane solutions is given in Table VI.

Table VI

Comparison of Isomer Distribution of Nitration of Toluene in Different Solvents at 25°

Nitrating agent	Solvent	Isomer distribution, % *ortho*	*meta*	*para*
$NO_2^+BF_4^-$	Tetramethylene sulfone	65.4	2.8	31.8
	Nitromethane	64.7	3.2	32.1
	Toluene	53.8	3.2	43.0
$NO_2^+ClO_4^-$	Tetramethylene sulfone	66.2	3.4	30.4
	Toluene	55.0	3.4	41.6
$NO_2^+PF_6^-$	Tetramethylene sulfone	67.6	1.4	31.0
	Nitromethane	64.8	1.9	33.3
	Toluene	55.0	2.2	42.8
$NO_2^+HS_2O_7^-$	Tetramethylene sulfone	62.1	3.2	34.7
	Toluene	49.2	3.6	47.3

It is worthwhile to mention that according to observations of Fischback and Harris[5] mixed acid ($HNO_3 + H_2SO_4$) nitration of toluene at −15° gives an isomer distribution of 47.5% *ortho*, 1.1% *meta* and 51.4% *para* isomer, as compared with the isomer distribution at 25°: 57.4% *ortho*, 3.9% *meta* and 38.7 *para*. It was suggested that the low *ortho* ratio at lower temperatures is due to the higher degree of solvation of the nitronium ion.

Friedel–Crafts nitration[4] of toluene with $NO_2Cl + TiCl_4$ and $NO_2Cl + AgBF_4$ in tetramethylene sulfone, nitromethane or toluene solutions similarly gave significantly different isomer distributions (Table VII).

Table VII

Nitrating agent	Catalyst	Solvent	Temp., °C.	Isomer distribution, % *ortho*	*meta*	*para*	*ortho*: *para*
NO_2Cl	$TiCl_4$	TMS	25	61.3	4.2	34.5	1.78
NO_2Cl	$TiCl_4$	Toluene	25	41.4	3.1	55.5	0.75
NO_2Cl	$AgBF_4$	CH_3NO_2	15	68.5	2.1	29.4	2.33

The $NO_2Cl + AgBF_4$ nitration is a typical nitronium tetrafluoroborate nitration with *in situ* preparation of the nitronium salt. $NO_2Cl + TiCl_4$ in tetramethylene sulfone solution also shows a typical nitronium nitration ratio, although ionization may be less complete. When toluene is used as solvent, it is suggested that primarily only a 1:1 donor–acceptor addition compound is formed, which then reacts with the aromatic as a considerably bulkier nitrating agent than NO_2^+ giving a much lower *ortho*:*para* ratio.

Experimental

The alkylbenzenes and halobenzenes used were commercial materials of highest available purity. Nitromethane was Eastman Kodak Co. spectro grade. Tetramethylene sulfone was obtained from Shell Chemical Co. and purified by fractional distillation under reduced pressure. Nitronium salts were prepared in this Laboratory.[4]

1. **Competitive Nitrations in Tetramethylene Sulfone.**—Benzene (0.25 mole) and 0.25 mole of alkyl- or halobenzenes were dissolved in 70 g. of tetramethylene sulfone. A solution of 0.05 mole of nitronium salt in 60 g. of tetramethylene sulfone was added dropwise to the vigorously stirred reaction mixture and the temperature was kept at 25 ± 0.5°. After stirring for 15 minutes the mixtures were neutralized with NH_3 gas, filtered and analyzed by gas-liquid chromatography.

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(5) B. C. Fischback and G. H. Harris, personal communication.

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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