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Aromatic Substitution. IX.¹ Nitronium Tetrafluoroborate Nitration of Halobenzenes in Tetramethylene Sulfone Solution

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Identical reaction conditions as described previously for alkylbenzene nitrations were used in the investigation of the nitronium tetrafluoroborate nitration of halobenzenes in tetramethylene sulfone solution. Relative reactivities compared with benzene and isomer distributions were determined using a gas chromatographic method. The relative rates of nitrations of halobenzenes show fair agreement with complex stabilities with π -complex forming agents. A secondary isotope effect, similar to that observed in nitrations of benzene-*d*₆ and toluene-*d*₈ was observed in nitration of 4-D-fluorobenzene. The mechanism of the reaction is discussed in view of the experimental results.

Introduction

In the previous paper of this series¹ the nitronium tetrafluoroborate nitration of alkylbenzenes in tetramethylene sulfone solution was discussed. This work was now extended to similar investigation of the nitration of halobenzenes.

Results

Competitive nitrations of benzene and halobenzenes were carried out (as described in detail previously) by treating equimolar quantities of the aromatics in tetramethylene sulfone solutions, kept at a constant temperature bath of $25 \pm 0.5^\circ$. A solution of nitronium tetrafluoroborate in tetramethylene sulfone was dropped into the well-stirred solution of the substrates. The mole ratio of the combined aromatic substrate:nitronium tetrafluoroborate was 10:1, this a practically constant excess of the aromatics was maintained. Under the experimental conditions used, a quantitative mononitration takes place. No traces of dinitro products or any other by-product was detectable in the reaction products either by gas chromatographic or spectroscopic methods. The mixtures were analyzed by gas chromatography. From the areas of the individual peaks (obtained by the use of an electronic printing integrator), mol % figures were calculated for each product after first determining relative response data following the method of Messner, Rosie and Argabright.²

The observed reactivities of the halobenzenes relative to that of benzene, together with the isomer distributions of the mononitro products, are summarized in Table I. (All data reported represent the average of at least three parallel experiments.)

TABLE I
COMPETITIVE NITRATION OF HALOBENZENES AND BENZENE WITH NO₂BF₄ IN TETRAMETHYLENE SULFONE SOLUTION AT 25°

Aromatic	Relative reactivity $k_{Ar}/k_{benzene}$	Isomer distribution, %		
		<i>Ortho</i>	<i>Meta</i>	<i>Para</i>
Benzene	1.0			
Fluorobenzene	0.45	8.5	..	91.5
Chlorobenzene	.14	22.1	0.7	76.6
Bromobenzene	.12	25.7	1.1	73.2
Iodobenzene	.28	36.3	.. ^a	63.7

^a Not detectable due to peak interference on chromatograph.

(1) Part VIII, G. A. Olah, S. J. Kuhn and S. H. Flood, *J. Am. Chem. Soc.*, **83**, 4571 (1961).

(2) A. E. Messner, D. M. Rosie and P. A. Argabright, *Anal. Chem.*, **31** [2], 230 (1959).

The analysis of mixtures of known composition which were dissolved in identical amounts of solvents and treated similarly as in the case of competitive nitrations, showed that the ratio of the peak areas obtained in gas-liquid chromatography was proportional, within 3%, to the ratio of the quantities of the materials. Peak areas, as obtained by the use of the electronic integrator, were found in good agreement with those measured as a control for a number of experiments by constructing triangles made up of tangents to the Gaussian curves and the intercepts on the base line or by weighing the cut-out peaks and determining the areas from the weights.

Thus, the gas-liquid chromatographic method used was found reliable to the extent required and it was also shown that no significant losses of products take place during the preparation of the reaction mixtures for analysis (water washings).

In a set of alternate experiments, water washing of the nitration mixtures for removal of the acid formed and simultaneously of the major part of the solvent, tetramethylene sulfone, was omitted. Instead the nitration mixtures were neutralized with anhydrous ammonia, precipitated ammonium fluoroborate was filtered off and the reaction solutions were directly analyzed by gas-liquid chromatography. Comparison of data obtained by this method with those obtained by washing out the reaction mixture with water to remove acid showed no significant differences.

The method of competitive reaction rate determination can be applied only if the observed relative rates are dependent on the aromatic substrate. Changing the concentration of either of the aromatic components in competitive experiments in tetramethylene sulfone solution from the 1:1 ratio to 3:1 and 1:3 showed that the relative rate ratio remains almost unchanged if a first-order dependence on the aromatic concentration is accepted (Table II).

Increasing the speed and efficiency of stirring had almost no effect on the relative reactivities observed. Changing the temperature of the reactions had only a slight effect in accordance with a regular dependence of the relative rates on temperature.

In tetramethylene sulfone solution, the relative reactivity change of fluorobenzene/benzene was observed between +10 and +55° (the relatively high freezing point of the solvent prohibited determinations at lower temperatures).

TABLE II
CONCENTRATION VARIATION OF FLUOROBENZENE AND
BENZENE IN COMPETITIVE NITRATIONS

fluorobenzene:benzene	Ratio of	Obsd. relative rate	$k_{\text{C}_6\text{H}_5\text{F}}/k_{\text{C}_6\text{H}_6}$
3	1	1.32	0.44
2	1	0.88	.44
1	1	.45	.45
1	2	.24	.48
1	3	.14	.42
Average			0.45

TABLE III
TEMPERATURE DEPENDENCE OF COMPETITIVE NITRATION OF
FLUOROBENZENE AND BENZENE

Temp., °C.	$k_{\text{fluorobenzene}}/k_{\text{benzene}}$	—Isomer distribution, %—		
		<i>Ortho</i>	<i>Meta</i>	<i>Para</i>
10	0.41	6.4	..	93.6
15	.43	7.8	..	92.2
20	.44	8.4	..	91.6
25	.45	8.5	..	91.5
30	.48	8.6	..	91.4
35	.50	8.5	..	91.5
40	.51	8.7	..	91.3
45	.52	9.1	..	90.9
50	.53	9.6	..	90.4

The temperature dependence of the reaction indicates that with increasing temperature, the selectivity decreases.

Addition of water up to an equimolar amount of the combined aromatic substrate had no effect on the observed relative reactivities.

Discussion of Results

The observed relative reactivities of halobenzenes and benzene show good agreement with relative stabilities of complexes of halobenzenes with Ag^+ , Br_2 , I_2 , ICl , SO_2 , picric acid, HCl and HF , which are considered as π -complex-forming agents.

Table IV shows a comparison of the relative rates of $\text{NO}_2^+\text{BF}_4^-$ nitration in tetramethylene sulfone solutions with relative stabilities of complexes of halobenzenes. Differences may partly be due to varying steric hindrance.

TABLE IV
COMPARISON OF RELATIVE STABILITIES OF COMPLEXES OF
HALOBENZENES AND NITRATION RATES WITH $\text{NO}_2^+\text{BF}_4^-$

Aromatic	Ag^+	Br_2	I_2	ICl	SO_2	HCl	NO_2^+
Benzene	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Fluorobenzene	0.18	0.74	0.45
Chlorobenzene	.29	0.86	0.50	..	0.58	.50	.14
Bromobenzene	.40	1.13	0.86	0.59	..	.41	.12
Iodobenzene	2.08	1.53	1.540	.28
Reference	a	b	c	d	e	f	f

^a L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **72**, 3113 (1950). ^b R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 4677 (1950). ^c L. J. Andrews and R. M. Keefer, *ibid.*, **74**, 4500 (1952). ^d L. J. Andrews and R. M. Keefer, *ibid.*, **73**, 4169 (1951). ^e H. C. Brown and J. D. Brady, *ibid.*, **71**, 3573 (1949); ^f Present work.

The Question of Relative Basicity of Halobenzenes.—Contrary to the well investigated relative basicities of alkylbenzenes, there are only few data available on relative π -complex basicities of halobenzenes and no data at all on δ -complex basicities. Halobenzenes do not form σ -complexes with $\text{HF} + \text{BF}_3$ (or $\text{AlCl}_3 + \text{HCl}$ or $\text{AlBr}_3 + \text{HBr}$) under conditions similar to that of σ -complex formation of

alkylbenzenes. Therefore, no empirical sequence of relative sigma basicities is available. Recently, however, it was observed³ that $\text{HF} + \text{SbF}_5$ forms a fairly stable benzenonium complex with fluorobenzene.

The question of relative basicities of halobenzenes is more complex than that of the alkylbenzenes. Halobenzenes have two different donor centers. They can act as π -donors involving the ring π -system and as n -donors involving the unshared halogen pairs. Consequently, complex stabilities could be dependent on two different types of complex formation. As an example, we can take the iodobenzene + Ag^+ system in which n - and not π -complexing could account for the high relative stability observed.

Brown and co-workers⁴ measured the solubilities of HCl in halobenzenes by vapor pressure measurements and found the solubilities, thus the correlated basicity, to follow the order of $\text{C}_6\text{H}_6 > \text{C}_6\text{H}_5\text{F} > \text{C}_6\text{H}_5\text{Cl} > \text{C}_6\text{H}_5\text{Br} > \text{C}_6\text{H}_5\text{I}$.

Watanabe⁵ found the ionization potentials of halobenzenes to be in the order of fluorobenzene 9.19, chlorobenzene 9.07, bromobenzene 8.98 and iodobenzene 8.73 e.V.

As it is generally accepted that the lowering of the ionization potential means increased basicity of an aromatic, the relative order of basicity is $\text{C}_6\text{H}_5\text{I} > \text{C}_6\text{H}_5\text{Br} > \text{C}_6\text{H}_5\text{Cl} > \text{C}_6\text{H}_5\text{F}$.

It should, however, be kept in mind that the ionization potential of benzene is 9.245 e.V., thus higher than that of all halobenzenes. Assuming the generally accepted $-I > +T$ effect of halogens in halobenzenes, no simple correlation of relative basicities of halobenzenes and benzene is possible based on ionization potentials.

A comparison of the shift of the infrared fundamental H-X stretching frequency of a number of proton donors such as HCl , HBr , HI , $\text{C}_6\text{H}_5\text{OH}$, CH_3OH , $n\text{-C}_4\text{H}_9\text{OH}$ and pyrrole, was reported by Josien and Sourisseau⁶ for chlorobenzene and bromobenzene. In order to get information on all the halobenzenes and thus establish a relative order of basicity similar to Cook's⁷ method of determining the relative basicities of the alkylbenzenes, these investigations were extended by us to include fluorobenzene and iodobenzene. We also included phenylacetylene and methanol-*d* as acids. Table V summarizes the data obtained using a Perkin Elmer, Model 221-G, grating spectrophotometer with sodium chloride optics. In all the cases investigated, the spectroscopically observed shifts followed the decreasing order $\text{C}_6\text{H}_6 > \text{C}_6\text{H}_5\text{I} > \text{C}_6\text{H}_5\text{Br} > \text{C}_6\text{H}_5\text{Cl} > \text{C}_6\text{H}_5\text{F}$.

Kinetic Isotope Effect.—As in the case of the nitronium tetrafluoroborate nitration of benzene-*d*₆ and toluene-*d*₈, also in the case of the nitration of 4-D-fluorobenzene, a small secondary reverse isotope effect was observed.

Competitive nitration of benzene and 4-D-fluorobenzene, compared with that of benzene and fluoro-

(3) Unpublished results of G. A. Olah and S. W. Tolgyesi.

(4) H. C. Brown and J. D. Brady, *J. Am. Chem. Soc.*, **74**, 3570 (1952).

(5) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

(6) M. L. Josien and G. Sourisseau, "Hydrogen Bonding," Ed. D. Hadzi, Pergamon Press, New York, N. Y., 1959, p. 135.

(7) D. Cook, *J. Chem. Phys.*, **25**, 788 (1956).

TABLE V
SHIFT OF INFRARED FUNDAMENTAL H-X STRETCHING FREQUENCIES OF PROTON DONORS IN HALOBENZENES

Donors	HCl	HBr	HI	C ₆ H ₅ OH	CH ₃ OH	CH ₃ OD	n-C ₆ H ₅ OH	Pyrrole	Phenyl- acetylene
Gas, cm. ⁻¹	2886 ± 1	2558 ± 1	2230 ± 1	3654 ± 1	3687 ± 2	2720 ± 2 ^a	3680 ± 2	3530 ± 2	3340 ± 2
CCl ₄ , cm. ⁻¹	2831 ± 1	2518 ± 1	2204 ± 1	3610 ± 2	3645 ± 2	2689 ± 2 ^b	3640 ± 2	3495 ± 2	3315 ± 2
Acceptors									
C ₆ H ₅ F	2810 ± 2	2518 ± 2	2190 ± 2	3606 ± 2	3643 ± 2	2687 ± 2	3630 ± 2	3488 ± 2	3307 ± 2
C ₆ H ₅ Cl	2779 ± 2	2481 ± 3	2182 ± 3	3578 ± 2	3624 ± 3	2677 ± 2 ^b	3616 ± 3	3475 ± 2	3304 ± 2
C ₆ H ₅ Br	2769 ± 2	2476 ± 3	2176 ± 3	3568 ± 3	3618 ± 3	2669 ± 2	3610 ± 3	3470 ± 2	3302 ± 2
C ₆ H ₅ I	2761 ± 2 ^d	2468 ± 2	2167 ± 2	3559 ± 2	3610 ± 2	2667 ± 2 ^b	3609 ± 2	3467 ± 2	3300 ± 2
C ₆ H ₆	2756 ± 2 ^d	2452 ± 2	2164 ± 3	3557 ± 2	3607 ± 2	2660 ± 2 ^c	3606 ± 3	3460 ± 2	3299 ± 2

Data for chlorobenzene and bromobenzene (with the exception of those for phenylacetylene and CH₃OD) are from M. L. Josien and G. Sourisseau.⁷ Those for fluoro- and iodobenzene are from the present investigation. ^a E. F. Barker and G. Bosschietter *J. Chem. Phys.*, **6**, 563 (1938). ^b M. Tamres *J. Am. Chem. Soc.*, **74**, 3375 (1952). ^c W. Gordy *J. Chem. Phys.*, **7**, 93 (1939); L. H. Jones and R. M. Badger *J. Am. Chem. Soc.*, **73**, 3132 (1951). ^d Corrected value.

benzene, gave the following results (analyzed by gas-liquid chromatography).

$$k_{C_6H_5F}/k_{C_6H_6} = 0.45 \quad k_D/k_H = 1.14 \pm 0.03$$

$$k_{4-D-C_6H_4F}/k_{C_6H_6} = 0.51$$

As *p*-substitution in nitration of fluorobenzene takes place to an extent of 91.5%, the observed kinetic isotope effect should be corrected accordingly and is slightly larger ($k_D/k_H = 1.22$).

The previously established kinetic isotope effect for the nitration of C₆D₆¹ was again observed in competitive nitration of C₆D₆ with fluorobenzene

$$k_{C_6H_5F}/k_{C_6H_6} = 0.45 \quad k_{D/H} = 1.16 \pm 0.03$$

$$k_{C_6H_5F}/k_{C_6D_6} = 0.39$$

The explanation for the observed small isotope effect for the nitration of 4-D-C₆H₄F most probably is that in the transition state, the initial sp² carbon hydrogen bond must have been changed at least somewhat in the direction toward sp³. Owing to the low frequency of the out-of-plane bending mode of aromatic carbon-hydrogen bonds, it could be expected that this would increase the zero-point energy and, consequently, cause a secondary α -isotope effect with the heavy molecule reacting faster. The opposed hyperconjugative effect of the carbon-hydrogen bond removed somewhat from the ring plane with the p-orbitals of the other five carbon atoms, will tend to decrease the zero-point energy but will not cancel it completely.

Streitwieser recently demonstrated⁸ that aromatic deuterium is electropositive relative to protium in the normal state. It is effectively electron donating relative to hydrogen, presumably because of anharmonicity effects. This finding is in agreement with the observed secondary kinetic isotope effect in our investigated nitrations.

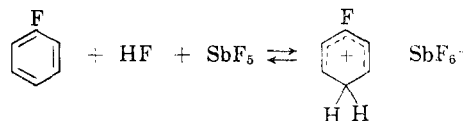
Conclusions

Correlation of the observed relative reactivities of halobenzenes, obtained in homogeneous nitrations with nitronium tetrafluoroborate in trimethylene sulfone solution, with relative stabilities of certain π -complexes of the halobenzenes gave a fair agreement. No data are available on σ -complex forming ability of halobenzenes (HF + BF₃). It seems that under conditions where the alkylbenzenes give stable benzenonium ions, no similar complex formation takes place with halobenzenes.

(8) H. S. Klein and A. Streitwieser, Jr., *Chemistry & Industry*, 180 (1961).

The reason for this must be not only the lower π -electron density of the ring in halobenzenes, but the absence of alkyl groups capable of stabilizing through conjugation (in the *o*- and *p*-positions) benzenonium ion formation.

The recent observation on the preparation of a stable benzenonium complex from fluorobenzene + HF + SbF₅³



is in agreement with the fact that the fluorine substituent can effect, through conjugation, a considerable stabilization of the benzenonium ion in the *p*-position. N.m.r. investigation of the complex in liquid SO₂ solution showed, that protonation had taken place nearly exclusively in the 4-position. Known π -complex stability data of halobenzenes, as shown in Table IV, give a fair correlation with relative rates of nitration of halobenzenes. These data, however, relate always to the over-all donor-acceptor complex stabilities with different acceptors and could also involve a considerable amount of n -complexing, instead of ring π -complexing. Therefore, it is easily understandable why the observed relative nitration rates (involving always the ring π -electron system) are lower (first of all in the case of bromo- and iodobenzene) than relative complex stabilities, say with Ag⁺.

The anomalous behavior of iodobenzene in complex formations with silver salts showing considerably higher stabilities than the other halobenzenes was discussed previously by Andrews and Keefer.¹⁵ They gave a reasonable explanation for the anomalous behavior by suggesting that in the complex formation the silver ion bonds to the iodine atom (and not the aromatic π -sextet) Ar-I \rightarrow Ag⁺. The existence of such complexes is not surprising since structurally they are similar to the known diphenyliodonium salts and iodobenzene dichloride.

The stabilities of the π -complexes do not change greatly with the nature of the halogen substituents (see data of Table IV). It is obvious that the absolute value of the density of the π -electron donor system could not change drastically by inductive and conjugative effects of one halogen atom. Thus it can be explained that the relative reactivities observed in NO₂⁺BF₄⁻ nitrations in the present

TABLE VI
 ISOMER DISTRIBUTION IN THE MONONITRATION OF HALOBENZENES

Halobenzene	Nitrating agent	Solvent	Temp., °C.	Ortho	Meta	Para	Ortho:para ratio	Analytical method ^e	Reference
Fluorobenzene	HNO ₃	H ₂ SO ₄	18	12.4	..	87.6	0.14	F.p.	^a
	HNO ₃	Acetic anhydride	25	8.7	..	91.3	.095	G.L.C.	^b
	NO ₂ BF ₄	TMS	25	8.5	..	91.5	.087	G.L.C.	^c
Chlorobenzene	HNO ₃	H ₂ SO ₄	18	30.1	..	69.9	.43	F.p.	^a
	Acetyl nitrate	Nitromethane	25	29.6	0.9	69.5		Isotopic dilution	^d
	NO ₂ BF ₄	TMS	25	22.7	0.7	76.6		G.L.C.	^c
Bromobenzene	HNO ₃	H ₂ SO ₄	18	37.6	..	62.4		F.p.	^a
	Acetyl nitrate	Nitromethane	25	36.5	1.2	62.4		Isotopic dilution	^d
	NO ₂ BF ₄	TMS	25	25.7	1.1	73.2		G.L.C.	^c
Iodobenzene	HNO ₃	H ₂ SO ₄	18	41.1	..	58.7		F.p.	^a
	Acetyl nitrate	Nitrate methane	25	38.3	1.8	59.7		Isotopic dilution	^d
	NO ₂ BF ₄	TMS	25	36.3	..	63.7		G.L.C.	^c

^a A. F. Holleman, "Die direkte Einführung von Substituenten in den Benzolkern," Leipzig, 1910, p. 475; A. F. Holleman, *Chem. Revs.*, **1**, 187 (1925). ^b J. R. Knowles, R. O. C. Norman and G. K. Radda, *J. Chem. Soc.*, 4885 (1960). ^c Present work. ^d J. D. Roberts, J. K. Sanford, F. L. J. Sixma, H. Cerfontain and R. Zagt, *J. Am. Chem. Soc.*, **76**, 4525 (1954). ^e TMS = tetramethylene sulfone, G.L.C. = gas-liquid chromatography, F.P. = freezing point method.

work show only small differences of the same order of magnitude for benzene and halobenzenes. (The halobenzenes take part with their π -sextet as entities in the rate-determining π -complex-forming step.) This order of selectivity of the aromatic substrate is different from reactions where relative stabilities of intermediate σ -complexes in individual positions are involved. These, of course, frequently show relative reactivities of orders of magnitude smaller than that of an individual benzene position.

It is difficult at the present time to give a "general" order of basicity of halobenzenes based on the available data. In present investigations interaction with NO₂⁺ as acceptor acid was established. Only an informative correlation with relative basicities observed in one system should not necessarily mean a similar relative order against another acceptor, with considerably changed steric and other properties. Any oversimplification of the problem, particularly in view of the two distinctive donor systems of halobenzenes (π - and n -donor), seems to us without proper foundation.

The next question to be answered is how the low substrate selectivity, corresponding to relative π -complex stabilities, compares with the observed isomer distributions.

The greater the reactivity of an electrophilic substituting agent, the smaller its selectivity.⁹ This means low selectivity with different aromatics and also a simultaneous change of the isomer distribution toward the statistical value (40% *ortho*, 40% *meta* and 20% *para*, representing two *o*-, two *m*- and one *p*-position in a monosubstituted benzene). This generally is demonstrated by an increase in the concentration of the *m*-isomer. The obvious explanation is the decreasing role of small activation energy differences of different individual positions compared to the over-all activation energy of the reaction. This, again, is valid only if the reaction is dependent on relative stability of σ -complexes but *not* if competition of individual molecules is involved (according to relative π -complex stability). In this case, a low selectivity with different aromatic substrates (halobenzenes in

the present investigation) is possible without necessarily involving a change of the isomer distribution in the direction of statistical distribution (demonstrated by an increase of the *m*-isomer).

Our competitive nitrations showing low selectivity of the halobenzenes gave isomer distributions of the mononitro products showing no significant amount of the *m*-isomers.

Isomer distributions reported for the mononitration of halobenzenes are compared with the results of the present work in Table VI.

Concerning the directing effect in the nitration of halobenzenes, the nature of the π -complexes involved in the rate-determining interaction must be considered. It is necessary to be aware of the fact that whatever the nature of the primary interaction between a strong electrophile (NO₂⁺) and the aromatic substrate should be, in the case of substituted benzene (*e.g.*, aromatics showing a non-uniform π -electron distribution) the outer complex must be an oriented one. The electron distribution of the halobenzene may give an explanation for the nature of the oriented π -complex formation and subsequent directing effect in nitration. The $-I > +I$ effect of the halogen atoms results in the region of the *o*-positions generally to some degree of neutralization of the two opposed effects. As the inductive effect diminishes with the distance in the *p*-position, the conjugate effect becomes predominant.¹⁰ This is best shown by comparing the *ortho/para* ratios of nitrohalobenzenes obtained, which gives a sequence quite obviously opposed to the steric *ortho* effect.

	Ortho/para
Fluorobenzene	0.09
Chlorobenzene	.30
Bromobenzene	.35
Iodobenzene	.57

The over-all effect can be further increased by polarization by the strong electrophile, NO₂⁺.

The lower *o*-isomer ratios obtained in nitrations of chloro-, bromo- and iodobenzenes with nitronium tetrafluoro-borate in tetramethylene sulfone

(10) For a more detailed discussion in the case of fluorobenzene, see G. Olah, A. Pavlath and G. Varsanyi, *J. Chem. Soc.*, 1823 (1957).

(9) M. J. S. Dewar, *Ann. Rept.*, **53**, 132 (1956).

solution, as compared with values obtained in previous conventional nitrations, may be partly due to steric effects. NO_2^+ , by dissolving the nitronium salt in tetramethylene sulfone, is complexed to some extent by the solvent and the main rate determining step, as pointed out previously,¹ is considered as the transition of the NO_2^+ -solvent complex to the NO_2^+ -aromatic π -complex. The complexed nitronium salt, being bulkier, could effect a larger steric *ortho* effect in the case of halobenzenes having a sufficiently large halogen substituent. The question of steric effects and solvent participation will be discussed in more detail in a forthcoming publication.

It is necessary to call attention to the fact that in the case of halobenzene nitrations, the $\text{NO}_2^+\text{BF}_4^-$ nitrations (in tetramethylene sulfone) differ less from the classical nitration results of Ingold¹¹ obtained with acetyl nitrate in acetic anhydride solution than in the case of the previously investigated alkylbenzenes. The differences are, however, significant as shown in Table VII and show again a considerably lower substrate selectivity without, however, any significant change in isomer distribution giving rise to a substantially increased *m*-isomer ratio.

TABLE VII

Aromatic	Relative rates of mononitrations with acetyl nitrate ¹¹ in acetic anhydride by Ingold	Relative rates of mononitrations with $\text{NO}_2^+\text{BF}_4^-$ in tetramethylene sulfone
Benzene	1.00	1.00
Fluorobenzene	0.15	0.45
Chlorobenzene	.033	.14
Bromobenzene	.030	.12
Iodobenzene	.18	.28

In a forthcoming paper of this series a more detailed comparison of our data obtained in homogeneous stable nitronium salt nitrations with classical conventional nitrations will be given and some explanations will be forwarded to account for observed differences.

Acknowledgments.—Dr. W. S. Tolgyesi prepared the 4-D-fluorobenzene used in the present investigation. We are grateful to Dr. D. Cook and Miss D. Anderson for the infrared spectra and Dr. E. B. Baker (Physical Research Laboratory, The Dow Chemical Co., Midland, Mich.) for the n.m.r. investigations.

Experimental

As nitronium tetrafluoroborate is very hygroscopic, all operations involving the nitronium salt preparation must be carried out with usual precautions to avoid moisture.

Materials.—Benzene, halobenzenes and nitrohalobenzenes were commercial materials of highest available purity. They were purified by fractionation in a laboratory column rated at 50 theoretical plates or by repeated crystallization to constant m.p. Their purity was checked by gas-liquid chromatography. $\text{NO}_2^+\text{BF}_4^-$ was prepared as described previously.¹² Tetramethylene sulfone was a commercial product (Shell Development Co., Emeryville, Calif.). It was purified by being twice vacuum fractionated. It gave a specific conductivity of 1.35×10^{-7} mho/cm.

General Procedure for Competitive Nitration. (a) In Tetramethylene Sulfone Solution (Water Washing).—Benzene (0.25 mole) and 0.25 mole of halobenzene were dissolved in 70 g. of tetramethylene sulfone. Into this solution, 0.05 mole of NO_2BF_4 , dissolved in 60 g. of tetra-

methylene sulfone, was added dropwise. The reaction mixture was vigorously stirred and the temperature was kept constant at $25 \pm 0.5^\circ$ during the reaction. The reaction time was generally 15 minutes. After that, 150 ml. of ether was added, the mixture was washed with 300 ml. of water and the separated organic layer was washed again with 200 ml. of water and dried with CaCl_2 . The resulting dry mixture was analyzed by gas-liquid chromatography.

(b) In Tetramethyl Sulfone Solution (Neutralization of Acid with NH_3).—Benzene (0.25 mole) and 0.25 mole of the corresponding alkylbenzene were dissolved in 70 g. of tetramethylene sulfone. Into this solution, 0.05 mole of NO_2BF_4 dissolved in 60 ml. of tetramethylene sulfone, was added dropwise. The reaction mixture was vigorously stirred and the temperature kept constant at $25 \pm 0.5^\circ$ during the reaction. After the addition of the nitronium salt was completed, the mixture was stirred for another 15 minutes. The solution was then neutralized with anhydrous ammonia gas, precipitated ammonium fluoroborate was filtered off and the solution analyzed directly by gas-liquid chromatography.

Analytical Procedure.—Gas-liquid chromatography was carried out on a Perkin-Elmer model 154-C vapor fractionator, using a thermistor detector equipped with a Perkin-Elmer model 194 electronic printing integrator. A 4-meter by 0.25" stainless steel column packed with polypropylene glycol (UCON LB 500-X) supported in diatomaceous earth was used. The column temperature was 180° for all mononitroalkylbenzene determinations; 60 ml. of hydrogen per minute was used for carrier gas. Samples of 100 μ ml. were generally injected.

The accuracy of the analytical method was checked by preparing and analyzing mixtures of the mononitrohalobenzenes, halobenzenes and solvent of known composition approximating those obtained upon nitration of the same alkylbenzene mixtures under our experimental conditions. We found the error never exceeded $\pm 3\%$ and was this large only in the case of the minor constituents. An error of less than $\pm 1\%$ was found for most constituents.

Observed retention times of mononitrohalobenzenes are given in Table VIII.

TABLE VIII

RETENTION TIMES OF MONONITRO HALOBENZENES AT COLUMN TEMPERATURE 180°

Compound	Retention time, min.	Compound	Retention time, min.
Nitrobenzene	16	<i>o</i> -Nitrobromobenzene	59
<i>o</i> -Nitrofluorobenzene	17	<i>m</i> -Nitrobromobenzene	52
<i>p</i> -Nitrofluorobenzene	15	<i>p</i> -Nitrobromobenzene	54
<i>o</i> -Nitrochlorobenzene	36	<i>o</i> -Nitroiodobenzene	70
<i>m</i> -Nitrochlorobenzene	30	<i>p</i> -Nitroiodobenzene	65
<i>p</i> -Nitrochlorobenzene	32		

Determination of Kinetic Isotope Effects. (a) Competitive Nitration of $\text{C}_6\text{D}_6:\text{C}_6\text{H}_5\text{F}$.—Fluorobenzene (0.05 mole) and 0.05 mole of benzene-*d*₆ were dissolved in 35 g. of tetramethylene sulfone and into this solution, 0.01 mole of NO_2BF_4 in 15 g. of tetramethylene sulfone was added dropwise with constant stirring. The temperature was kept at $25 \pm 0.5^\circ$ during the whole reaction (15 minutes); 50 ml. of ether was then added and the reaction mixture was washed with 50 ml. of water. The separated organic layer was again washed with 30 ml. of water, then dried with CaCl_2 and analyzed by gas-liquid chromatography.

(b) Competitive Nitration of $\text{C}_6\text{H}_5:p\text{-D-C}_6\text{H}_4\text{F}$.—Benzene (0.05 mole) and 0.05 mole of *p*-D- $\text{C}_6\text{H}_4\text{F}$ prepared according to Hall, Piccolini and Roberts,¹³ were dissolved in 35 g. of tetramethylene sulfone and into this solution 0.01 mole of NO_2BF_4 in 15 g. of tetramethylene sulfone was added dropwise. The mixture was stirred and the temperature was kept at $25 \pm 0.5^\circ$. On completion of the reaction (15 minutes), 50 ml. ether was added and the reaction mixture was washed with 50 ml. of water. The separated organic layer was washed again with 30 ml. of water. After drying with CaCl_2 , the mixture was analyzed by gas-liquid chromatography.

(11) M. L. Bird and C. K. Ingold, *J. Chem. Soc.*, 918 (1938).

(12) S. J. Kuhn and G. A. Olah, *J. Am. Chem. Soc.*, **83**, 4564 (1961).

(13) C. E. Hall, R. Piccolini and J. D. Roberts, *ibid.*, **77**, 4540 (1955).