(0.1 mole) was dissolved in 200 g. of tetramethylene sulfone, 0.1 mole of the Lewis acid halide (BF_3, BCl_3, PF_5, AsF_5, $TiCl_4$) was then introduced into the solution while the temperature was kept around 15°. The N_2O_4 catalyst solution thus obtained was added dropwise to a stirred solution of 0.5 mole of the aromatic to be nitrated in 50 ml. of tetramethylene sulfone. After the addition was completed, the reaction mixture was heated slowly under reflux condenser, generally to 100° and kept there for an hour. After cooling, the reaction mixture was poured on crushed ice, the organic layer separated, washed twice with water, dried with calcium chloride and distilled. The products obtained were analyzed by gas–liquid chromatography.

Nitration of Aromatics with N_2O_5 + Lewis Acid Catalyst in Tetramethylene Sulfone Solution.—Dinitrogen pentoxide (0.1 mole) was dissolved in 200 g. of tetramethylene sulfone; 0.1 mole of the Lewis acid halide (BF_3, PF_5, AsF_5, $TiCl_4$) was introduced, while keeping the temperature between 10–20°. The N_2O_5–catalyst solution obtained then was added to a well-stirred solution of 0.5 mole of the aromatic to be nitrated in 50 ml. of tetramethylene sulfone, and kept at 10–15°. The nitration takes place very fast and is practically completed after the addition is finished. The mixture was stirred at room temperature for another 15 minutes, then poured on crushed ice. The organic layer was separated, washed twice with water and the nitro product isolated as previously.

Nitration of Aromatics with NO_2BF_4 in Tetramethylene Sulfone Solution.—The aromatic (0.5 mole) was dissolved in 100 ml. of tetramethylene sulfone and a solution of 20 g. (0.15 mole) of nitronium tetrafluoroborate in 300 ml. of tetramethylene sulfone (0.5 molar solution) was added to the stirred solution with external cooling at a rate such as to allow the temperature to remain between 15–25°. After the addition was completed, the reaction mixture was stirred at room temperature for another 10 minutes. In the case of deactivated aromatics, longer reaction times and higher temperatures are needed. The reaction mixture then was diluted with 500 ml. of water, the organic layer separated, washed twice with water, dried with $CaCl_2$ and the excess aromatic removed by distillation. The nitro products now were isolated either by fractionation or crystallization. For details of the reaction times, temperatures and yields obtained, see Tables I–V.

Picryl Fluoride.—A mixture of 60 g. of 100% H_2SO_4, 0.15 mole of $NO_2{}^+HS_2O_7{}^-$ and 9.3 g. (0.05 mole) of 2,4-dinitrofluorobenzene was heated to 110–120° and kept at this temperature for 12 hours. After cooling, the reaction mixture was poured on crushed ice. The organic material was extracted with 120 g. of a 1:1 mixture of toluene and Freon 113 and diluted with ligroin until separation of crystals started. The mixture then was left standing overnight in a refrigerator. The separated crystals were filtered and dried in a vacuum desiccator; m.p. 128–130°, yield 4.6 g., 40% of the theoretical. *Anal.* Calcd.: C, 31.17; H, 0.84; N, 18.18; F, 8.21. Found: C, 31.12; H, 0.90; N, 18.02; F, 8.11.

Previously[29] we reported the melting point of picryl fluoride as 35°. In a personal communication Dr. R. E. Parker of the University of Southampton, England, called our attention to the fact that picryl fluoride prepared under conditions similar to those used by us previously, gives, after repeated recrystallization, a product with a melting point of +130°. This was found entirely correct and the previous low melting point could have been due to impurities of 2,4-dinitrofluorobenzene present.

The infrared spectrum (obtained as a mixed Nujol–Fluorolube mull on a Perkin–Elmer model 221-G spectrophotometer) showed the bands at 3117m, 3090sh, 1715w, 1618s, 1547s, 1410m, 1335s, 1310w, 1176m, 1078s, 940m, 924m, 910m, 776m, 730m, 720s, 695m μ (s = strong, m = medium, w = weak). The spectrum agrees well with that of picryl chloride, the 1078 band being obviously a C–F stretching frequency.

Identical results were obtained in nitrations using NO_2BF_4 dissolved in 100% H_2SO_4. BF_3 evolution is observed, $BF_4{}^-$ being obviously replaced by $HSO_4{}^-$ or $HS_2O_7{}^-$.

Aromatic Substitution. VIII.[1] Mechanism of the Nitronium Tetrafluoroborate Nitration of Alkylbenzenes in Tetramethylene Sulfone Solution. Remarks on Certain Aspects of Electrophilic Aromatic Substitution[2]

By George A. Olah, Stephen J. Kuhn and Sylvia H. Flood

Ingold's method of competitive nitration has been used in order to determine relative reactivities of alkylbenzenes and benzene in homogeneous mononitrations with nitronium tetrafluoroborate in tetramethylene sulfone solutions. Relative reactivities and isomer distributions were determined by gas–liquid chromatography. The obtained relative rates show a good correlation with relative π-complex stabilities of alkylbenzenes (Ag^+, Br_2, I_2, ICl, picric acid, HCl, HF), but not with σ-complex stabilities (HF + BF_3). The reaction mechanism is considered to involve oriented (or localized) π-complex formation between $NO_2{}^+$ and the aromatics as the main rate-determining step. This is in accordance with the fact that partial rate factors and empirical selectivity factors are not applicable to present systems (primary competition is between donor molecules as such and not individual positions of those). The nitration of benzene-d_6 and toluene-d_8 shows a small secondary reverse kinetic isotope effect (the heavy compound reacting faster). The mechanism of the investigated nitration of alkylbenzenes with nitronium tetrafluoroborate is discussed in the light of the obtained experimental data.

Introduction

The idea that the actual nitrating agent in aromatic nitrations under certain conditions might be the nitronium ion was first suggested by von Euler as early as 1903[3] and has since been supported by numerous other authors.[4]

In a series of fundamental papers, Ingold, Hughes and co-workers[5,6] investigated the kinetics and

(1) Part VII, *J. Am. Chem. Soc.*, **83**, 4564 (1961).

(2) Partly presented as a paper at the 140th National Meeting of the American Chemical Society in Chicago. Ill., September, 1961.

(3) H. von Euler, *Ann.*, **330**, 280 (1903); *Z. angew. Chem.*, **35**, 580 (1922).

(4) P. Walden, *Angew. Chem.*, **37**, 390 (1924); T. Ri and E. Eyring, *J. Chem. Phys.*, **8**, 433 (1940); C. C. Price. *Chem. Revs.*, **29**, 51 (1941).

(5) C. K. Ingold, E. D. Hughes, *et al.*, *Nature*, **158**, 448 (1946), *J. Chem. Soc.*, 2400 (1950), and subsequent papers.

(6) C. K. Ingold, E. D. Hughes, *et al.*, ref. 5, also E. D. Hughes, C. K. Ingold and R. B. Pearson. *J. Chem. Soc.*, 4357 (1958).

mechanism of aromatic nitration. This work provided definite kinetic, spectroscopic (Millen) and cryoscopic (Gillespie) evidence for the existence of NO_2^+ and proved it to be the effective nitrating agent in the nitrations investigated.
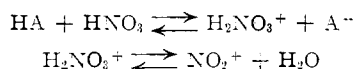
The detailed picture of the attack of the nitronium ion on the aromatic compound is mainly based on the work of Melander[7] who found no kinetic isotope effect in the nitration of tritiated aromatics. Similar results were obtained later for deuterated aromatics.[8] In order to have measurable reaction rates, this work was generally carried out on dinitration of benzene or mononitration of nitrobenzene.

We have reported previously[9] the application of a number of isolated, stable nitronium salts as preparative nitrating agents. First of all, nitronium tetrafluoroborate was found suitable and the method was extended to a general nitration method.[10]
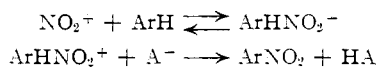
$$ArH + NO_2^+BF_4^- \longrightarrow ArNO_2 + HF + BF_3$$

The structure of isolated stable nitronium salts used as nitrating agents was found by infrared investigation to be the expected linear $O{=}\overset{+}{N}{=}O$.[11]

We suggested previously[9] that the nitronium tetrafluoroborate nitration method offers good possibilities for the investigation of the mechanism of aromatic nitrations. The first two kinetic steps of Ingold's generally accepted nitration scheme with acid-catalyzed nitric acid are eliminated, a preprepared stable nitronium salt being used as nitrating agent. Thus a possibility appears to investigate the effective reaction of the nitronium ion with the aromatic, generally considered according to Ingold as a two-step reaction.

$$HA + HNO_3 \rightleftharpoons H_2NO_3^+ + A^-$$

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

$$NO_2^+ + ArH \rightleftharpoons ArHNO_2^-$$

$$ArHNO_2^+ + A^- \longrightarrow ArNO_2 + HA$$

Results

Ingold's method of competitive nitration[12] was used to determine the relative reactivity of alkylbenzenes over benzene in nitrations with nitronium tetrafluoroborate in homogeneous tetramethylene sulfone solutions.

The competitive method of comparing reaction rates does not require an accurate knowledge of the reaction kinetics, provided we assume that both hydrocarbons are nitrated by the same nitrating agent or agents and that the rates of nitration are of the first order with respect to the hydrocarbon concentrations.[13]

Competitive nitrations of benzene and alkylbenzenes were carried out (as described in detail in the Experimental section) by treating equimolar quantities of the aromatics in tetramethylene sulfone solutions, kept in a constant temperature bath at $+25 \pm 0.5°$, by dropping a solution of nitronium tetrafluoroborate in tetramethylene sulfone into the well stirred solution of the substrates. The mole ratio of the combined aromatic substrate: nitronium tetrafluoroborate was 10:1; thus 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, either by gas–liquid chromatography or spectroscopic methods, in the reaction products. The mixtures were analyzed by gas–liquid chromatography. Details of the analytical determination are given in the Experimental part. From the areas of the individual peaks (obtained by the use of an electronic printing integrator), mole % figures were calculated for each product after first determining relative response data following the method of Messner, Rosie and Argabright.[14]

The obtained relative reactivities of a number of alkylbenzenes over those of benzene, together with the isomer distributions of the mononitro products, are summarized in Table I. (All data were obtained as the average of at least three parallel experiments.)

TABLE I

COMPETITIVE NITRATION OF ALKYLBENZENES AND BENZENE WITH NO_2BF_4 IN TETRAMETHYLENE SULFONE SOLUTION AT 25°

Ar	$k_{Ar}/k_{benzene}$	Isomer distribution, %			ortho:para ratio
		ortho	meta	para	
Benzene	1.00				
Toluene	1.67	65.4	2.8	31.8	2.05
o-Xylene	1.75	3-Nitro-o-xylene, 79.7%			
		4-Nitro-o-xylene, 20.3%			
m-Xylene	1.65	2-Nitro-m-xylene, 17.8%			
		4-Nitro-m-xylene, 82.2%			
p-Xylene	1.96				
Mesitylene	2.71				
Ethylbenzene	1.60	53.0	2.9	44.1	1.20
n-Propylbenzene	1.46	51.0	2.3	46.7	1.09
i-Propylbenzene	1.32	23.4	6.9	69.7	0.34
n-Butylbenzene	1.39	50.0	2.0	48.0	1.04
t-Butylbenzene	1.18	14.3	10.7	75.0	0.19

The method of competitive reaction rate determination can be applied only if the observed relative rates are dependent on the aromatic substrate.[13] As our observed relative rates show only small selectivity concerning the nature of the aromatic substrate, it could have been attributed to a very fast reaction taking place when the solution of nitronium salt reagent is dropped into the solution of the mixed aromatic substrate. Thus the NO_2^+ would have no possibility of reaching uniform distribution in the solution of the substrates before entering nitration and the observed relative rates may be influenced rather by statis-

(7) L. Melander, Acta. Chem. Scand., 3, 95 (1949), Nature, 163, 599 (1949); Arkiv. Kemi, 2, 213 (1950).

(8) T. C. Bonner, F. Bowyer and G. Williams, J. Chem. Soc. 2605 (1950); W. M. Lauer and W. E. Noland, J. Am. Chem. Soc. 75, 3689 (1953).

(9) G. Olah and S. Kuhn, Chemistry & Industry, 98 (1956); G. Olah, S. Kuhn and A. Mlinko, J. Chem. Soc., 4257 (1956).

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

(11) D. Cook, S. J. Kuhn and G. A. Olah, J. Chem. Phys., 33, 1669 (1960).

(12) C. K. Ingold and F. R. Shaw, J. Chem. Soc., 2918 (1927); C. K. Ingold, A. Lapworth, E. Rothstein and D. Ward, ibid., 1959 (1931), and subsequent papers.

(13) For a discussion of the competitive method of nitration, see M. J. S. Dewar, T. Mole and E. W. T. Warford, ibid., 3576 (1956).

(14) A. E. Messner, D. M. Rosie and P. A. Argabright, Anal. Chem., 31, 230 (1959).

tical factors than real competition.[15] In order to clarify this possibility and also to determine the accuracy of the method used, we carried out experiments to establish whether real competitive reaction actually occurs under our experimental conditions and whether the methods employed provide results which could establish small differences between the alkylbenzenes investigated.

(1) 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 fluoborate 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.

	$k_{Ar}/k_{benzene}$	
Aromatic	Water washed	Neutralized with NH₃
Benzene	1.0	1.0
Toluene	1.67	1.63
p-Xylene	1.96	2.01
m-Xylene	1.65	1.71
Mesitylene	2.71	2.75

(2) Preparative separation of larger scale competitive reactions, run under identical conditions, was carried out by fractional distillation (using a laboratory column rated at 50 theoretical plates) of the reaction mixtures or by preparative scale separation by gas-liquid chromatography using a 3 m × 1″ aluminum column and individual samples up to 3 ml. It was possible to obtain on the average a 98% material balance. Individual fractions were also identified by infrared spectroscopy. It was found in these experiments also that under the experimental conditions used (tenfold excess of aromatic), only mononitration takes place (no traces of dinitro products or other higher boiling products were detected) and the rest of the substrate aromatics was recovered unchanged. Small losses amounting to 2% of the combined material balance must be accounted for as mechani-

(15) We are grateful to Professor H. C. Brown for pointing out this possibility and for his suggestions to clarify this point.

cal losses (probably taking place during water washing of the mixtures).

(3) Gas–liquid chromatographic analytical data showed good agreement with infrared and mass spectroscopic controls, being well within the limit of ±3.0% error.

(4) Non-isomerizing reaction conditions were present for any of the nitrations with the exception of that of isopropyl- and t-butylbenzene. In these cases, when pure o- or p-nitroalkylbenzene isomers were added to a tenfold excess of benzene, which was nitrated under our standard conditions, isomerization giving rise to m-nitroalkylbenzene was observed. The o-isomers were isomerized more easily than the p-isomers and the nitro-t-butylbenzenes more easily than the nitroisopropylbenzenes. Consequently, the higher m-isomer ratios obtained in the nitration of isopropyl and t-butylbenzene must be attributed, in addition to the steric influence of the bulky alkyl groups in the o-positions, at least partly to secondary isomerization of the o- and p-isomers through HBF_4, which is formed in the reactions and is quite stable as the conjugate acid in tetramethylene sulfone solutions. The low relative reactivities of isopropyl- and tert-butylbenzene must also be partially due to some intermolecular isomerization (disproportionation).

(5) 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 toluene/benzene was observed between +10 and +55° (the relatively high freezing point of the solvent prohibited determinations at lower temperatures) (Table II).

TABLE II

TEMPERATURE DEPENDENCE OF COMPETITIVE NITRATION OF TOLUENE AND BENZENE

(Benzene = 1.0)

		Isomer distribution, %		
t. °C.	$k_{toluene}/k_{benzene}$	ortho	meta	para
10	1.85	65.6	2.9	31.5
15	1.75	65.6	3.0	31.4
20	1.72	65.4	3.3	31.3
25	1.67	65.4	2.8	31.8
30	1.55	65.0	2.9	32.1
35	1.32	65.8	2.7	31.5
40	1.29	64.9	2.9	32.2
45	1.24	63.7	3.0	33.3
50	1.18	63.1	3.2	33.7
55	1.13	62.6	3.4	34.0

The temperature dependence of the reaction indicates that with increasing temperature, the selectivity decreases. The isomer ratios observed, however, are almost unchanged. No significant change of relative reactivities was observed.

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

(7) Changing the concentration of either of the aromatic components in competitive experiments in tetramethylene sulfone solution from the 1:1

ratio to 4:1 and to 1:4 showed that the relative rate ratio remains almost unchanged if a first-order dependence on the aromatic concentration is accepted (Table III).

<div align="center">TABLE III

CONCENTRATION VARIATION OF TOLUENE AND BENZENE IN COMPETITIVE NITRATIONS</div>

Toluene:benzene	Obsd. rel. reactivity	$k_{toluene}/k_{benzene}$
4:1	6.40	1.60
3:1	5.13	1.71
2:1	3.40	1.70
1:1	1.67	1.67
1:1.5	1.11	1.66
1:2	0.81	1.62
1:3	.62	1.86
1:4	.45	1.80
	Average	1.70

The experimental data obtained point to the fact that the observed relative reactivities are due to competition of NO_2^+ with the aromatic substrates, the reactions being first order in aromatic substrates. Statistical distribution which takes place in a fast reaction without any selectivity cannot explain the above data, although it is necessary to state that the reactions are indeed very fast even in high dilutions.

Discussion of Results

The observed relative reactivities of alkylbenzenes and benzene show good agreement with relative stabilities of complexes of alkylbenzenes with Ag^+, Br_2, I_2, ICl, SO_2, picric acid, HCl and HF (which are considered as π-complex-forming agents) but not with relative stabilities of $HF + BF_3$, $AlCl_3 + HCl$, $AlBr_3 + HBr$ complexes (considered as σ-complex-forming agents).

Table IV shows a comparison of the relative rates of $NO_2^+BF_4^-$ nitration in tetramethylene sulfone solutions with relative stabilities of complexes of alkylbenzenes. Small differences may be due to varying steric hindrance with different reference acids.

It thus appears that the nitronium tetrafluoroborate nitration of alkylbenzenes in homogeneous solutions gives relative rates which correspond to relative π-complex but not to σ-complex stabilities. In view of the well known work of Brown and co-workers[16] showing that σ-complex stabilities and not π-complex stabilities correspond to the observed relative rates of electrophilic aromatic substitutions, we felt that our experimental observations needed further explanation.

All our competitive nitrations showing low selectivity of the aromatic substrate gave isomer distributions of the mononitro products (as shown in Table I) corresponding to usual directing effects in previously reported nitrations) with no unusual increase of the m-isomers.

Isomer distributions reported for the mononitration of toluene and alkylbenzenes are compared with the results of the present work in Tables V and VI.

(16) For a summary see K. L. Nelson and H. C. Brown in "The Chemistry of Petroleum Hydrocarbons," Vol. III, Reinhold Publishing Corp., New York, N. Y., 1955, p. 465.

Calculation of partial rate factors[12] and empirical selectivity factors[17] cannot be carried out from our data of relative reactivity and corresponding isomer distribution of alkylbenzene nitrations. When an attempt was made to calculate partial rate factors, the values for m_f were found to be 0.14 for toluene, 0.14 for ethylbenzene, 0.10 for n-propylbenzene, 0.08 for n-butylbenzene. These values are obviously impossible for an alkylbenzene if we assume that individual positions are competing because there is no way of explaining how one position (such as a m-position) in an alkylbenzene could be deactivated ten times relative to a benzene position.

This discrepancy, however, can be explained and is even to be expected, if we assume that π- and not σ-complex formation is the main rate-determining step in our NO_2^+ nitrations. Partial rate factors and empirical selectivity factors in our view can be used only if, in a certain reaction, competition takes place between individual positions in the molecules involved and not between π-electron systems, as entities, of reacting molecules. In the competition between molecules involving their π-electron systems as an entity (which we suggest is the case observed in our present work), the calculation of partial rate factors and selectivity factors is meaningless.

The stabilities of the π-complexes do not change greatly with increasing number and position of alkyl 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 hyperconjugative effects of alkyl groups. Thus it can be explained that the relative reactivities observed in NO_2BF_4 nitrations in the present work show only small differences of the same order of magnitude for benzene and alkylbenzenes, even for di- and trialkylbenzenes such as mesitylene, etc. This order of selectivity of the aromatic substrate is entirely different from reactions where relative stabilities of intermediate σ-complexes in individual positions are involved. These, of course, frequently show relative reactivities in positions *ortho* and *para* to alkyl groups (which are highly stabilized by conjugation) thousand times greater than that of an individual benzene position.

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

Two factors must be considered in answering this question. The first is the fact that the greater the reactivity of an electrophilic substituting agent, the smaller its selectivity.[18] 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 *ortho*, two *meta* and one *para* 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 activa-

(17) H. C. Brown and C. R. Smoot, J. Am. Chem. Soc., 78, 6255 (1956).

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

TABLE IV

COMPARISON OF RELATIVE STABILITIES OF COMPLEXES OF ALKYLBENZENES (p-XYLENE = 1) WITH NITRATION RATES

Benzene ring substituents	Ag^{+a}	Br$_2$[b]	I$_2$[c]	ICl[c]	SO$_3$[d]	Picric[e] acid	HCl[f]	HF[g]	NO$_2^+$ nitration rate	HF + BF$_3$[h]	Halogenation rate[f]
H	0.98	0.46	0.48	0.36	0.35	0.70	0.61	0.40	0.51		0.0005
CH$_3$	1.04	0.64	.52	.57	0.59	0.84	0.92	0.62	.85	0.01	0.157
o-(CH$_3$)$_2$	1.26	1.01	.87	.82	1.23	1.03	1.13	..	.89	2.00	2.1
m-(CH$_3$)$_2$	1.19	0.96	1 00	.92	1.11	0.98	1.26	0.92	.84	20.00	200.0
p-(CH$_3$)$_2$	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
1,3,5-(CH$_3$)$_3$	0.70		2.65	3.04	1.57	1.12	1.59	1.76	1.38	2800	80,000
C$_2$H$_5$	0.86			0.58		0.74	1.06		.82		0.13
n-C$_3$H$_7$						.98			.74		
i-C$_3$H$_7$	0.89			0.58		.60	1.24		.67		0.08
n-C$_4$H$_9$						.57			.71		
t-C$_4$H$_9$	0.79			0.58		.51	1.36		.60		0.05

[a] N. Ogimuchi, L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **78**, 2210 (1956); L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954).　[b] R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **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. D. Anderson and D. L. Hammick, *J. Chem. Soc.*, 1089 (1950).　[f] H. C. Brown and J. D. Brady, *J. Am. Chem. Soc.*, **71**, 3573 (1949); **74**, 3570 (1952).　[g] E. L. Mackor, A. Hofstra and J. H. van der Waals, *Trans. Faraday Soc.*, **422**, 186 (1958); D. A. McCaulay and A. P. Lien, "Conference on Hyperconjugation, Indiana University," Pergamon Press, New York, N. Y., 1959, p. 118.　[h] D. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.*, **73**, 2013 (1951).

TABLE V

ISOMER DISTRIBUTIONS IN MONONITRATIONS OF TOLUENE

Nitrating agent	Solvent	Temp., °C.	ortho	Isomer, % meta	para	ortho:para ratio	Analytical method[i]	Reference
HNO$_3$	Acetic anhydr.	0	61.4	1.6	37.0	1.66	G.L.C.	[a]
HNO$_3$	Acetic anhydr.	0	58.11	3.7	38.2	1.52	F.p.	[b]
HNO$_3$	Acetic anhydr.	30	58.4	4.4	37.2	1.57	F.p.	[b]
HNO$_3$	Acetic anhydr.	30	58.5	4.4	37.1	1.58	F.p.	[c]
HNO$_3$	H$_2$SO$_4$	25–50	62	5.0	33	1.88		[d]
HNO$_3$	H$_2$SO$_4$		58.45	4.4	37.15	1.57	Distln.	[e]
HNO$_3$	90% acetic acid	45	56.5	3.5	40.0	1.41	I.R.	[f]
C$_6$H$_5$COONO$_2$	CH$_3$CN	0	59	5	37	1.59	I.R.	[g]
NO$_2$BF$_4$	Tetramethylene sulfone	25	65.4	2.8	31.8	2.05	G.L.C.	[h]
NO$_2$BF$_4$	Nitromethane	25	65.7	3.2	31.1	2.11	G.L.C.	[h]
NO$_2$PF$_6$	Tetramethylene sulfone	25	67.6	1.4	31.0	2.18	G.L.C.	[h]
NO$_2$ClO$_4$	Tetramethylene sulfone	25	66.2	3.4	30.4	2.18	G.L.C.	[h]
N$_2$O$_5$	Tetramethylene sulfone	25	65.1	3.1	31.8	2.04	G.L.C.	[h]

[a] J. R. Knowles, R. O. C. Norman and G. K. Radda, *J. Chem. Soc.*, 4885 (1960).　[b] C. K. Ingold, *et al.*, *ibid.*, 1959 (1931).　[c] Holleman *et al.*, *Rec. trav. chim.*, **33**, 11 (1914).　[d] P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution: Nitration and Halogenation," Academic Press, Inc., New York, N. Y., 1959, p. 50.　[e] K. L. Nelson and H. C. Brown, *J. Am. Chem. Soc.*, **73**, 5605 (1951).　W. W. Jones and M. Russel, *J. Chem. Soc.*, 921 (1947).　[f] H. Cohn, E. D. Hughes, M. H. Jones and M. A. Peeling, *Nature*, **169**, 291 (1951).　[g] R. Halvarson and L. Melander, *Arkiv. Kemi*, **11**, 77 (1957).　[h] Present work.　[i] G.L.C. = gas-liquid chromatography; I.R. = infrared spectroscopy; F.p. = freezing point method.

TABLE VI

ISOMER DISTRIBUTIONS IN MONONITRATION OF ALKYLBENZENES

Aromatic	Nitrating agent	Solvent	Temp., °C.	ortho	Isomer, % meta	para	ortho:para ratio	Analytical method	Reference
Toluene	HNO$_3$	H$_2$SO$_4$		58.45	4.4	37.15	1.57	Distln.	[a]
Toluene	HNO$_3$	Acetic anhydr.	0	61.4	1.6	37.0	1.66	G.L.C.	[b]
Toluene	NO$_2$BF$_4$	TMS[d]	25	65.4	2.8	31.8	2.05	G.L.C.	[c]
Ethylbenzene	HNO$_3$	H$_2$SO$_4$		45.0	6.5	48.5	0.93	Distln.	[a]
Ethylbenzene	HNO$_3$	Acetic anhydr.	0	45.9	3.3	50.8	0.90	G.L.C.	[b]
Ethylbenzene	NO$_2$BF$_4$	TMS	25	53.0	2.9	44.1	1.20	G.L.C.	[c]
Isopropylbenzene	HNO$_3$	H$_2$SO$_4$		30.0	7.7	62.3	0.48	Distln.	[a]
Isopropylbenzene	HNO$_3$	Acetic anhydr.	0	28.0	4.5	67.5	.42	G.L.C.	[b]
Isopropylbenzene	NO$_2$BF$_4$	TMS	25	23.4	6.9	69.7	.34	G.L.C.	[c]
t-Butylbenzene	HNO$_3$	H$_2$SO$_4$		15.8	11.5	72.7	.22	Distln.	[a]
t-Butylbenzene	HNO$_3$	Acetic anhydr.	0	10.0	6.8	83.2	.12	G.L.C.	[b]
t-Butylbenzene	NO$_2$BF$_4$	TMS	25	14.3	10.7	75.0	.19	G.L.C.	[c]

[a] K. L. Nelson and H. C. Brown, *J. Am. Chem. Soc.*, **73**, 5605 (1951).　W. W. Jones and M. Russel, *J. Chem. Soc.*, 921 (1947).　[b] J. R. Knowles, R. O. C. Norman and G. K. Radda, *J. Chem. Soc.*, 4885 (1960).　[c] Present work.　[d] TMS = tetramethylene sulfone.

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

The second fact to be considered must be the nature of the π-complexes involved in the rate-determining interaction. It is necessary to be aware of the fact that whatever the nature of the primary interaction between a strong electrophile (NO_2^+) with the aromatic substrate should be, in the case of substituted benzenes (*e.g.*, aromatics showing a non-uniform π-electron distribution), the outer complex must be an oriented one. The electrophilic substituent thus does not move around unhindered on Dewar's π-electron orbits but has statistically a larger probability of being found in the vicinity of the higher electron density points of the ring. In other words, the π-complex formation should be considered as first suggested by Brown, an oriented π-complex.[19] If the π-complex formation is considered in this way, it is quite obvious that subsequent transition of the reagent (NO_2^+) along the reaction path from the outer to an inner complex intermediate, followed by proton elimination, could give regular *ortho-para* orientations in a low selectivity electrophilic aromatic substitution without any larger increase of the *m*-isomer.

Due to inductive and hyperconjugative effects of the alkyl groups, the region of the *o*- and *p*-positions in alkylbenzenes have a higher electron density than that of the *m*-positions. If the π-electron cloud is represented—as in a very simplified descriptive way it sometimes is—as a double "tube" above and below the plane of the ring, there is a bulging of the "tube" around these positions as if someone were blowing into it (*i.e.*, the electron contributing power of the alkyl groups), but the effect is not uniformly distributed, showing up only around certain positions. This effect is obviously further increased by polarization by a strong electrophile (NO_2^+). Since two *ortho*, but only one *para* positions are affected, the oriented π-complex formation (and subsequent substitution) statistically would be expected to give an *ortho:para* ratio of 2:1. However, as the inductive effect diminishes with the distance, the region of the *o*-positions should have a somewhat higher electron density than that of the *p*-position. This could give rise to slightly higher *ortho:para* ratios than 2:1. Indeed, our toluene nitrations show an *ortho:para* ratio of 2.05 (in tetramethylene sulfone solutions at 25°). With increasing steric hindrance of the alkyl substituents, the *ortho:para* ratio diminishes. Bulky alkyl substituents such as isopropyl and *t*-butyl have a very considerable steric effect on *o*-substitution, as expected (Table I).

The *ortho:para* ratios observed indirectly prove that the NO_2^+ is not solvated to any high degree in tetramethylene sulfone solution. Otherwise, a considerably higher steric *ortho* effect should be expected even in the case of the nitration of

(19) H. C. Brown and H. Jungk, *J. Am. Chem. Soc.*, **77**, 5579 (1955); **78**, 2182 (1956).

toluene. It was recently demonstrated[20] that a considerable decrease in the *ortho:para* ratio (to as low as 0.92) arises from steric interaction between the methyl group of toluene and a nitronium ion which has become bulky because of solvation with sulfuric acid in nitrations with a nitric–sulfuric acid at −15°. As the NO_2BF_4 nitration in tetramethylene sulfone solution does not show any such steric *ortho* hindrance, the nitrating species (NO_2^+) must exist as a loosely solvated or unsolvated ion-pair, if not as free nitronium ions. Electric conductivity measurements of tetramethylene sulfone solutions of NO_2BF_4, although carried out so far on a very qualitative bases,[3] seem to be in agreement with this suggestion.

Steric considerations of the *ortho* effect of bulky alkyl groups in nitrations with nitronium ion (NO_2^+) must consider the orientation of the nitronium ion in the transition state. This determines the effective size of the substituting agent and hence the sensitivity of the reaction to steric hindrance. The atoms in the nitronium ion are initially linear and finally trigonal. Thus, in the transition state, they should be represented by a slightly bent structure.[21]

The Question of Kinetic Isotope Effect in Electrophilic Aromatic Nitration.—Proton elimination in electrophilic aromatic nitration was found by Melander[22] using tritiated compounds, and by subsequent investigators,[23] using deuterated compounds to be not rate determining as no kinetic isotope effect was observed. The absence of a kinetic isotope effect was also frequently quoted against a simple SE2 type mechanism in electrophilic aromatic substitutions as originally suggested by Hammond[24] because such a reaction, for obvious reasons, should show a large isotope effect due to zero point energy differences of C–H, C–T and C–D bonds in the intermediate.

The question of whether a small kinetic isotope effect should be possible in an electrophilic aromatic nitration has been recently discussed by Melander.[25] He explained why isotopic substitution can have only negligible influence on the ratio of the addition step and why the proton elimination step should show no or only a very small kinetic isotope effect, the direction of which is also impossible to predict.

It is obvious that in a reaction similar to the one observed by us with $NO_2^+BF_4^-$ nitration, the primary addition step should have practically no dependence on isotopic substitution. As the primary addition step of NO_2^+ to the aromatic is influenced only by the over-all π-donor ability of the molecule, differences between molecules such as C_6H_6 and C_6D_6 in π-electron properties should be practically non-existent.

(20) Personal communication, B. C. Fishback and G. H. Harris.

(21) P. B. C. de la Mare and J. H. Ridd, "Aromatic Substitution. Nitration and Halogenation," Academic Press, Inc., New York, N. Y., 1959, p. 72.

(22) L. Melander, *Arkiv. Kemi*, **2**, 211 (1950).

(23) W. M. Lauer and W. E. Noland, *J. Am. Chem. Soc.*, **75**, 3689 (1953); T. G. Bonner, F. Bowyer and G. Williams, *J. Chem. Soc.*, 2605 (1953).

(24) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(25) L. Melander, "Kinetic Isotope Effects," Roland Press, New York, N. Y., 1960, p. 112.

Using Cook's[26] method of determining the relative basicities of alkylbenzenes by the shift of the main infrared H–Cl absorption frequency of HCl in the aromatic substrate, we found no difference for C_6H_6 and C_6D_6, both showing ν_{H-Cl} to be at 2765 cm.$^{-1}$. Even if a slight difference of basicity should exist, the effect on ν_{H-Cl} must be less than ± 1.5 cm.$^{-1}$ which was our experimental limit by the use of a Perkin-Elmer, model 221-G, grating spectrophotometer with sodium chloride optics.

Whether the proton elimination step gives rise to any kinetic isotope effect in nitrations with NO_2^+-BF_4^- was investigated in simple competitive experiments.

Benzene and benzene-d_6 as well as toluene and toluene-d_8 were competitively nitrated in tetramethylene sulfone solution with $NO_2^+BF_4^-$. In control experiments it was found that under our experimental conditions, HBF_4, which is formed as a by-product of the nitrations, does not affect hydrogen–deuterium exchange to any detectable amount (using infrared and mass spectroscopy).

The nitration mixtures were analyzed by mass spectroscopy. A secondary isotope effect of $k_D/k_H = 1.17$ was observed for the toluene-d_8 nitration and a similar effect of 1.12 in the benzene-d_6-nitration (by comparing the amounts of nitrobenzene and nitrobenzene-d_5 as well as nitrotoluene and nitrotoluene-d_7 formed in the competitive experiments).

To substantiate the observed small kinetic isotope effects, competitive nitrations of benzene and toluene-d_8 as well as of benzene-d_6 and toluene were carried out with NO_2BF_4 in tetramethylene sulfone solutions. The mononitro products obtained could, in these cases, be analyzed by gas–liquid chromatography.

$k_{toluene}/k_{benzene-d_6} = 1.45$ $k_D/k_H = 1.15$

$k_{toluene-d_8}/k_{benzene} = 2.02$ $k_D/k_H = 1.21$

$k_{toluene}/k_{benzene} = 1.67$

The kinetic isotope effects obtained by the mass spectroscopic and gas-liquid chromatographic method thus show good agreement.

The small, but well reproducible isotope effect which was observed, indicates that the transition state of the over-all reaction is not entirely reached before the pertinent carbon-hydrogen bond has lost at least an appreciable part of its zero point energy. However, it is not necessary to assume the existence of a true intermediate or, what amounts to the same thing, of a minimum in the potential energy curve. In the reverse reaction (proton elimination) we bring up the hydrogen to its normal position by gaining at least enough energy in σ-bond formation to balance out at least a part of the loss due to stretching of the carbon-substituent bond.

One must still explain, however, how isotopic substitution can have such a negligible influence on the rate of addition step and why a secondary isotope effect is observed (the heavy compound reacting faster). In the transition state, the initial sp^2 carbon-hydrogen bond must have been changed in character at least somewhat toward that of sp^3

bonding. Owing to the low frequency of the out of plane aromatic carbon–hydrogen vibrations, it could be expected that the transition from sp^2 to sp^3 should increase the zero point energy and consequently cause a secondary reverse isotope effect with the heavy molecule reacting faster.[25] On the other hand, hyperconjugation of the carbon–hydrogen bond removed from the ring plane with the π-orbitals of the other five carbon atoms will tend to decrease the zero point energy and the two effects will cancel each other to a certain degree.[27] We think that in our present investigation, the appearance of a secondary reverse isotope effect (with the heavy compound reacting faster to some extent) proves that hyperconjugation is not sufficiently strong to compensate the increase of zero point energy due to change from sp^2 hybridization on the carbon atom to be substituted.

The fact that we used completely deuterated compounds in our kinetic isotope investigations (benzene-d_6 and toluene-d_8) should have very little secondary effect on the observed kinetic effects. Secondary isotope effects due to hyperconjugation with the π-electron system are excluded in these cases, since the carbon–hydrogen bonds are situated in the ring plane and thus their orbitals are orthogonal to the carbon π-orbitals. Deuteration of the side chain in deuteriotoluene should also have only a very minor effect on the strength of hyperconjugation compared to the effect of the methyl group in toluene.[28]

The observation of a kinetic isotope effect made it interesting to carry out some investigation to see the effect of the proton acceptor bases on the rate of the reaction. Under our experimental conditions, however, only relative reaction rates were measured in competitive experiments. Thus, no accurate comparison based on absolute reaction rates was possible. Carrying out competitive nitration of toluene and benzene with different nitronium salts, as nitronium tetrafluoroborate, nitronium hydrogen disulfate, nitronium hexafluorophosphate and nitronium perchlorate under otherwise identical conditions in tetramethylene sulfone solution, gave the results

	$NO_2^+PF_6^-$	$NO_2^+HS_2O_7^-$	$NO_2^+ClO_4^-$	$NO_2^+BF_4^-$
$k_{toluene}/k_{benzene}$	1.40	1.45	1.60	1.67

These results show that the acceptor base (BF_4^-, $HS_2O_7^-$, PF_6^-, ClO_4^-) has some influence on the relative reaction rates in accordance with what should be expected if the proton elimination is at least partially rate determining. The small differences observed can also be a consequence of steric effects due to the fact that different nitronium salts could be more or less complexed (solvated) by the solvent. Differences in the ion-pair *versus* free nitronium ion availability could also influence the reactivities (the size of the anion affecting different steric effects). Differences observed in different solvents can be attributed to similar reasons. This question will be discussed in a subsequent paper.

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

(27) A. Strietwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958).

(28) C. G. Swain, T. E. C. Knee and A. J. Kresge, *ibid.*, **79**, 505 (1957).

The Role of Reaction Intermediates in the Mechanism of the Reaction.—An outstanding area of confusion, as pointed out by Hammond,[24] is found in the field of reaction mechanisms in the evaluation of the importance of complexes of various types which may be formed between reactants.

There are two ways in which information, gained either by experimentation or inference, as to the stability of complexes can be of aid in the discussion of reaction rates and mechanisms. If one can measure independently the equilibrium constant for the formation of the complex, or of a similar complex in a closely related system, a close correspondence between the formation constants and the reaction rates will be expected if the structure of the complex is similar to that of the transition state.

In the more likely event that some type of addition complex which is similar in structure to the transition state can be imagined, the complex (hypothetical perhaps) may well provide a concrete basis for the discussion of relative reactivities. The role of postulate is that of enabling one to use discrimination in the choice of the complexes which will serve as useful models for transition states.

Electrophilic aromatic substitution represents a reaction in which there has been extensive discussion of the possible importance of complexes formed from the electrophile and the aromatic substrate.

The general status of theories relating mechanism of electrophilic aromatic substitutions was reviewed in a previous paper.[29]

It has been shown by Dewar[30] that the free energies of activation for electrophilic substitution in a series of aromatic hydrocarbons are linearly proportional to the atom localization energies of the most reactive position in the hydrocarbon and that the relative free energies of substitution in the various positions of a polycylic aromatic nucleus give a similar correlation with the atom localization energy values of these positions. The atom localization energy of a given position in an aromatic hydrocarbon, which is the difference in π-electron energy between the hydrocarbon (e.g., benzene) and the corresponding Wheland intermediate[31] (vide infra, II) or benzenonium ion, is obtained[32] in terms of the empirical carbon–carbon resonance integral (β) which has a value of about 20 kcal./mole in the Hückel approximation[33] of the resonance energies of the aromatic hydrocarbons. (As the benzenonium ion type intermediate itself is a highly conjugated system with substantial resonance stabilization, only a part of the over-all resonance energy of the aromatic is needed to reach this stage.)

In a number of cases, the apparent β-values are smaller than the Hückel values from which Dewar

concluded that the Wheland intermediate (or benzenonium ion) (e.g., II) is only partly formed (e.g., I) in the transition state of the aromatic substitution.

There is also another anomaly. Not only is the appropriate numerical value of β (3–12 kcal./mole) much less than that normally ascribed to the carbon resonance integral ($\sim$20 kcal./mole), but the value of β also varies from one reaction to another.[30,31] This can be reasonably explained by assuming that the Wheland structure II is *not* a transition state but a stable intermediate, the transition state I lying between the initial state and II.
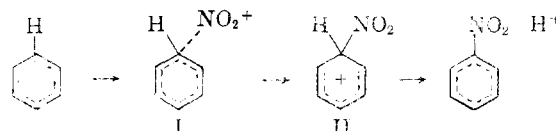
If the transition state has the same general configuration for various electrophilic reactions, β will not be the true resonance integral but the numerically smaller quantity $(\beta - \beta_t^*)$; moreover, this will vary with the reagent. Now β_t^* should be numerically greater, and $(\beta - \beta_t^*)$ numerically smaller, the more reactive the reagent. This relation holds in practice[30,34] and can be used to account for the empirical rule that the selectivity of substituting agents is smaller the greater their reactivity.[30]

The more powerful the substituent (which NO_2^+ certainly is in the present work), the less selective the substitution becomes. The transition state comes then much closer to the structure I than to the II, which was found in some cases to be actually a stable, isolable intermediate of the benzenonium ion type and not an activated state.[35]

The assumption that the transition state is I (represented as an oriented or localized π-complex), is in agreement with the fact that in it the C–N bond is comparatively long and weak and the C–H bond short and strong. Melander has shown[22] that the C–H bond cannot be appreciably stretched in the transition state for the nitration of toluene by the NO_2^+ ion.

The question of whether or not there is a non-isolable intermediate of high energy or an isolable intermediate of lower energy is trivial, since the real objective is to obtain information concerning the rate determining step of the reaction irrespective of precisely what the configuration of the transition state is.

Electrophilic aromatic substitutions are considered to follow a two-stage substitution mechanism as envisaged by Lapworth and expressly postulated by Pfeiffer and Wizinger and later by Wheland. Melander's nitrations having no isotope effect,[22] azo couplings observed by Zollinger[36] as either having or not having isotope effect of the tritium or deuterium atom, diarylethylene substi-

(29) G. A. Olah and S. J. Kuhn, *J. Am. Chem. Soc.*, **80**, 6535 (1958).

(30) M. J. S. Dewar, T. Mole and E. W. T. Warford, *J. Chem. Soc.*, 3581 (1956); M. J. S. Dewar and T. Mole, *J. Am. Chem. Soc.*, 342 (1957).

(31) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).

(32) F. H. Burkitt, C. A. Coulson and H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **47**, 553 (1951).

(33) C. A. Coulson, "Valence," Oxford University Press, New York, N. Y., 1952, p. 240.

(34) K. L. McEwan and H. C. Longuet-Higgins, *J. Chem. Phys.*, **24**, 771 (1956).

(35) G. A. Olah, et al., *Nature*, **178**, 694, 1344 (1956); *J. Am. Chem. Soc.*, **80**, 6535, 6540, 6541 (1958); Abstracts of Papers 138th A.C.S. Meeting, New York, N. Y., 1960, p. 3P; W. von E. Doering, M. Saunders, H. C. Baynton, E. F. Wodley and W. R. Edwards G. Laber, *Tetrahedron*, **4**, 178 (1958).

(36) H. Zollinger, *Helv. Chim. Acta* **38**, 1597, 1617, 1623 (1955).

tutions of Pfeiffer and Wizinger,[37] alkylbenzene alkylations and acylations of Olah and co-workers[35] taking place *via* intermediates capable of being isolated and present nitrations showing a small secondary isotope effect are all based on one and the same two-stage substitution mechanism.

The differences in reaction behavior are not inconsistent with the latter statement but are due to differences in energetics.

In the intermediate of a benzene substitution, the aromatic state of the starting material, which is particularly favorable from the standpoint of energetics, is no longer present. In the intermediate of the benzene substitution, two of the original six π-electrons, which are responsible for the stability of the aromatic state, have been used up in binding the electrophilic reagent, whereby the system loses stability.

Although in the classical chemical sense the intermediate must be looked upon as a very unstable particle (the concept of chemical stability depending on whether or not a chemical compound can be isolated or detected by chemical means), it is stable according to thermodynamic definition because it corresponds to an energy minimum. It is thus an intermediate proper and not a transition state. It appears important to us to stress this, because in some literature (even in very recent papers) this species is called a transition state. Isolation of stable benzenonium complexes[35] proved this point convincingly.

In view of the proceedings, the simplified energy profile of an S_E2 type electrophilic aromatic nitration with NO_2BF_4 can be represented as shown in Fig. 1. The two main maxima represent the two activated transition states leading to primary localized π-complex formation of the aromatic with NO_2^+ and the corresponding π-complex involved in proton elimination, showing a small kinetic isotope effect. (The corresponding π-complexes themselves are, of course, small minima, following near the transition states on the potential energy curve.) The main minimum is that of the σ-complex (or benzenonium ion) state, which is, however, considered as a stable reaction intermediate, capable of being isolated under specific conditions and not necessarily reached in the course of usual nitrations (by some sort of "tunneling"). In the present reaction, it certainly cannot be considered as a rate-determining transition state.

A stable benzenonium type intermediate of an aromatic nitration, $CF_3C_6H_5NO_2^+BF_4^-$, corresponding to the bottom of the energy valley, was indeed isolated previously at low temperature $(-50°)$ from benzotrifluoride, NO_2F and BF_3.[38] As pointed out by Glasstone, Laidler and Eyring,[39] it is possible for a system, in view of the thermal impulses which it receives from the outside, to by-pass the energy minimum of the intermediate state, *i.e.*, pass over the highest "summits" along the reaction path without really going through the bottom of the "valley."

(37) P. Pfeiffer and R. Wizinger, *Ann.*, **461**, 132 (1928); R. Wizinger, *Chimia*, **7**, 273 (1953).

(38) G. Olah, L. Noszko and A. Pavlath, *Nature*, **179**, 146 (1957).

(39) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw–Hill Book Co., Inc., New York, N. Y., 1941.
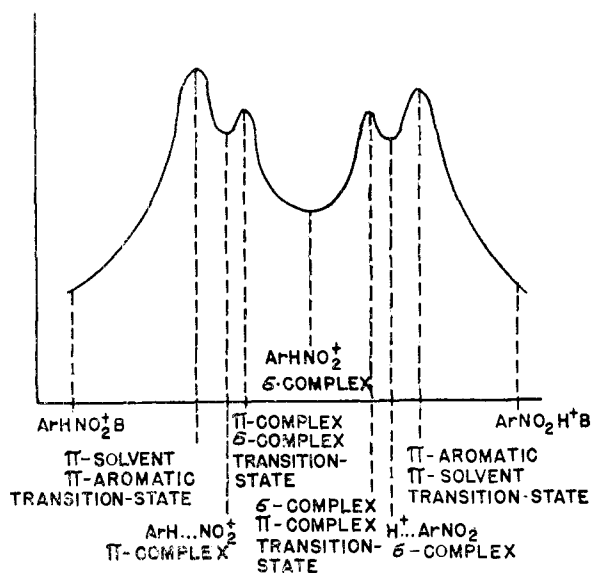
Fig. 1.

It must also be considered that the nitronium ion itself must be more or less complexed by the solvent which could be considered as a base (B). Therefore, activation energy is required to break the NO_2^+–solvent π-complex before the NO_2^+ can complex with the aromatic substrate. The latter reaction then becomes rate determining and requires participation by the aromatic. The height of this first peak will be the main rate determining and will be dependent on the stability of the π-complex formed by the aromatic. The height of the peak relative to the second maximum (corresponding to the transition state of the proton elimination) is determined by the small kinetic isotope effect.

Our present investigations suggest a mechanism for the nitronium tetrafluoroborate nitration of alkylbenzenes, which seems to fit well into the conception for an electrophilic substitution "by-passing the intermediate" and involving two transition states of the oriented π-complex type as energy maxima of the reaction path. It should be emphasized that we consider the present investigation informative only as a specific example of an electrophilic aromatic substitution, *i.e.*, the interaction of a preprepared, stable cation (NO_2^+) with sufficiently reactive aromatics such as benzene and alkylbenzenes. We think that through these investigations some useful information was obtained about the nature of interaction of the electrophile (NO_2^+) with the aromatic substrates. For obvious reasons, however, no generalization from present observations for other electrophilic aromatic substitutions is possible; certainly not for reactions where the formation of the electrophilic reagent involves a slow kinetic step. This seems to be the case with most of the aromatic electrophilic substitutions and Friedel–Crafts reactions investigated so far. For these reactions relative reactivities corresponding to σ-complex stabilities were established and they seem to follow Brown's selectivity rules.

It is hoped in subsequent papers of this series to show that the present concept can be applied to

further examples of aromatic nitrations and that the outlined mechanism is operative, under suitable conditions, also for electrophilic aromatic substitutions (such as alkylations) involving other strong electrophiles.

Acknowledgment.—We are most grateful for having had the opportunity of discussing parts of the present papers with many colleagues and friends on different occasions, all of whom we thank for their interest and stimulating discussions. In particular, we express sincere gratitude to Professors H. C. Brown, M. J. S. Dewar, Sir Christopher Ingold and H. Zollinger, as well as D. A. McCaulay, for helpful discussions and suggestions. R. S. Gohlke (Chemical Physics Research Laboratory, The Dow Chemical Co., Midland, Mich.), kindly carried out the mass spectroscopic analyses and D. Cook, of this Laboratory, the infrared investigations.

Experimental

Benzene, alkylbenzenes, o-, m- and p-nitrotoluene, were commercial materials of highest available purity. p-Nitrotoluene was recrystallized to constant m.p.; the other isomers were purified by fractional distillation. Their purity was checked by gas–liquid chromatography.

$NO_2{}^+BF_4$ was prepared as described previously.[1]

Tetramethylene sulfone was a commercial product (Shell Development Co., Emeryville, Calif.). It was purified by being vacuum fractionated twice from solid NaOH. It gave a specific conductivity of 1.35×10^{-7} mho/cm.[40]

The o-, m- and p-nitro derivatives of alkylbenzenes (isopropylbenzene, n-propylbenzene, t-butylbenzene and n-butylbenzene) were samples available in this Laboratory, prepared by the nitration of the corresponding alkylbenzenes. The individual isomers were separated either by distillation on a Podbielniak column (if boiling point differences of the isomers made this possible) or were otherwise separated by preparative scale gas–liquid chromatography. The column (4 m. × 1″) was packed with UCON LB 550-X propylene glycol and operated at 195° with a carrier stream of nitrogen of 800 ml./min. The eluting material passed into a cold trap.

Benzene-d_6 and toluene-d_8 were obtained from Merck Chemical Ltd., Montreal, Canada. The purity of the products was 98% or higher (the main impurity of toluene-d_8 being $C_6H_5CD_2H$).

All operations involving nitronium salts were carried out with usual precautions to avoid moisture.

General Procedure for Competitive Nitration. (a) In Tetramethylene Sulfone Solution (Water Washing).— Benzene (0.25 mole) and 0.25 mole of alkylbenzene were dissolved in 70 g. of tetramethylene sulfone. Into this solution, 0.05 mole of NO_2BF_4, dissolved in 60 g. of tetramethylene sulfone, was added dropwise. The reaction mixture was vigorously stirred and the temperature was kept constant at 25 ± 0.5° 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 Tetramethylene 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

(40) R. L. Burwell and C. M. Langford, J. Am. Chem. Soc., **81**, 3799 (1959), reported on solvent properties of tetramethylene sulfone. They obtained a specific conductivity of 2×10^{-8} mho/cm.

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 ± 0.5° 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 fractometer, using a thermistor detector equipped with a Perkin–Elmer model 194 electronic printing integrator. A four meter by 0.25″ stainless steel column packed with polypropylene glycol (UCON LB 500-X) supported on diatomaceous earth was used. The column temperature was 195° for all mononitroalkylbenzene determinations; 60 ml. of hydrogen per minute was used for carrier gas. Samples of 100 μml. were generally injected.

The accuracy of the analytical method was checked by preparing and analyzing mixtures of the mononitroalkylbenzenes, alkylbenzenes 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 ±3% and was this large only in the case of the minor constituents. An error of less than ±1% was found for most constituents.

The observed retention times of mononitroalkylbenzenes are given in Table VII.

TABLE VII
RETENTION TIMES OF MONONITROALKYLBENZENES AT COLUMN TEMPERATURE 195°

Compound	Retention time, min.	Compound	Retention time, min.
Nitrobenzene	14	p-Nitro-n-butylbenzene	76
o-Nitrotoluene	17	Nitro-p-xylene	26
m-Nitrotoluene	21	Nitromesitylene	29
p-Nitrotoluene	23	o-Nitroethylbenzene	20
3-Nitro-o-xylene	30	m-Nitroethylbenzene	27
4-Nitro-o-xylene	43	p-Nitroethylbenzene	32
2-Nitro-m-xylene	18	o-Nitro-n-propylbenzene	30
4-Nitro-m-xylene	30	m-Nitro-n-propylbenzene	42
o-Nitroisopropylbenzene	24	p-Nitro-n-propylbenzene	50
m-Nitroisopropylbenzene	35	o-Nitro-t-butylbenzene	34
p-Nitroisopropylbenzene	43	m-Nitro-t-butylbenzene	46
o-Nitro-n-butylbenzene	45	p-Nitro-t-butylbenzene	59
m-Nitro-n-butylbenzene	64		

Determination of Kinetic Isotope Effects. (a) Competitive Nitration of C_6D_6:C_6H_6 and C_7D_8:C_7H_8.—Benzene (0.05 mole) and 0.05 mole of benzene-d_6 or identical amounts of toluene and toluene-d_8 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 ± 0.5° 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 mass spectroscopy.

(b) Competitive Nitration of C_6H_6:C_7D_8 and C_6D_6:C_7H_8.— Benzene (0.05 mole) and 0.05 mole of toluene-d_8 or identical amounts of toluene and 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. The mixture was stirred and the temperature was kept at 25 ± 0.5°. On completion of the reaction (15 min.), 50 ml. of 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.