148. *The S_N Mechanism in Aromatic Compounds. Part XVI.**

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The very powerful activation by two types of cationic groups for aromatic S_N reactions has been compared with that of the dipolar nitro-group. The importance of the conjugative (*T*) effect is shown by the order of activating power, $N_2^+ \gg \overset{+-}{NO_2} \gg NMe_3^+$, the N_2^+ being the most activating group recorded in these reactions.

The influence of the first insertion of an activating group into a halogenobenzene is shown to be considerably greater than subsequent insertion of the same group, both rate constants and activation energy being considered.

In the course of this work the replacement of fluorine in fluorobenzene has been measured, and also the effect of varying ionic strength on the reactions between an anion and a cation in both methanol and water.

In the classification of substituents in aromatic S_N reactions by one of us,[1] class (i) refers to groups with a positive pole attached to the ring. It was subdivided into classes (i) (*a*) and (*b*) according to whether the substituent could exhibit only $-I$ or $-I,-T$ effect. For the resultant effect at *ortho*- and *para*-positions the latter subclass was predicted to have the greater activating power. Some preliminary results have been published.[2] The general discussion and predictions are now confirmed, the trimethylammonium and the diazonium group being used as representatives of classes (i) (*a*) and (*b*).

Table 1 records the rate constants, and Table 2 the derived quantities for the replacement of the halogen atom in (i) fluorobenzene, (ii) *p*-fluorobenzenediazonium borofluoride, (iii) *p*-fluoronitrobenzene, (iv) *o*-bromonitrobenzene, (v) (*a*) and (*b*) 4-bromo-*NNN*-trimethyl-3-nitroanilinium chloride, (vi) 1-bromo-2 : 4-dinitrobenzene. Replacement is by methoxyl group in methanol except for (ii) and (v) (*b*) which are by hydroxyl group in water. In the

Table 1.*

Rate constant, 10^5k_2 (l. mole^{-1} sec.$^{-1}$)

Compound	(*a*) at temperatures shown in parentheses					(*b*) calc. at : 0°	50°	100°
(i) †	4·01	8·08	15·1	—	—	$0·0_{10}101$	$0·0_6216$	$0·0_3318$
	(193·5°)	(202·5°)	(210·5°)					
(ii)	77·7	150	318	319	—	[170]	—	—
	[88·8]	[170]	[364]	[365]		{170,000}	—	—
	(−4·8°)	(0°)	(4·9°)	(5·2°)				
(iii)	58·7	104	188	218	5210	0·626	264	22,000
	(35·55°)	(40·2°)	(47·3°)	(48·05°)	(82·0°)			
(iv)	6·23	36·9	123	456	—	$0·0_3137$	0·185	36·0
	(81·8°)	(100·1°)	(113·7°)	(130·2°)				
(v) (*a*) ‡	47·6	152	439	454	—	—	—	—
	[151]	[505]	[1540]	[1590]		[5·28]	[2650]	[251,000]
	(25·0°)	(35·2°)	44·95°)	(45·5°)				
(*b*)	11·9	123	187	—	—	—	—	—
	[13·8]	[142]	[217]			$[0·0_2529]$	[4·83]	[708]
	(59·4°)	(82·4°)	(86·8°)					
(vi)	138	710	1180	1950	—	138	17,900	632,000
	(0°)	(15·0°)	(20·0°)	(25·0°)				

* Values in brackets are corrected to zero ionic strength. Values in braces are corrected to zero ionic strength, and estimated for OMe⁻ in MeOH by using the corrected relationship of (v) (*a*) and (*b*). Values of k_2 are accurate to ± 2%.

† Bevan and Bye (*J.*, 1954, 3091) have reported values for fluorobenzene at two temperatures which they regard as subject to some doubt.

‡ A similar result for the 4-chloro-compound (not corrected for ionic-strength effects) has been reported by Bunnett *et al.* (*J. Amer. Chem. Soc.*, 1953, **75**, 642).

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* Part XV, *J.*, 1955, 2929.

[1] Miller, *Rev. Pure Appl. Chem.* (*Australia*), 1951, **1**, 171.

[2] Bolto and Miller, *Chem. and Ind.*, 1953, 640.

TABLE 2 (see footnote to Table 1.)

Substituent		Substituent rate factor at 0°	50°	100°	Activation energy (E) (cal.)	Frequency factor ($\log_{10} B$)
H		1	1	1	34,900	12·0
p-N_2^+		{$1{\cdot}68 \times 10^{16}$}	—	—	[21,300]	[14·3]
					{$19{,}1_{50}$}	{15·6}
p-NO_2		$6{\cdot}20 \times 10^{10}$	$1{\cdot}33 \times 10^{9}$	$6{\cdot}92 \times 10^{7}$	21,200	$11{\cdot}7_5$
H		1	1	1	$25{,}2_{50}$	$11{\cdot}3_5$
p-NMe_3^+	(*a*)	[$3{\cdot}85 \times 10^{4}$]	[$1{\cdot}43 \times 10^{4}$]	[$6{\cdot}97 \times 10^{3}$]	[$21{,}7_{50}$]	[$13{\cdot}1_5$]
	(*b*)	—	—	—	[23,900]	[$11{\cdot}8_5$]
p-NO_2		$1{\cdot}14 \times 10^{6}$	$1{\cdot}01 \times 10^{5}$	$1{\cdot}72 \times 10^{4}$	17,100	10·8

manner discussed in the Experimental section, corrections to zero ionic strength are made for (ii), (v) (*a*) and (*b*), and the comparison of (v) (*a*) and (*b*) used to estimate rates and Arrhenius parameters for reaction of (ii) with methoxyl group in methanol.

Discussion of Results.—It is now generally accepted, particularly from the work of Roberts *et al.*,[3] that replacement of halogen in halogenobenzenes by the amino-group takes place by a mechanism involving rearrangement, and thus different from that in the simpler aromatic S_N reactions. The reaction with methoxyl group, however, may well proceed by simple nucleophilic displacement, and it is noteworthy that *p*-difluorobenzene reacts with sodium hydroxide to form *p*-fluorophenol, and that Heppolette and Miller[4] have shown, admittedly for an activated displacement, that the substituent rate factor of fluorine is approximately 1. If then the methanolysis of fluorobenzene is a simple displacement, the substituent rate factors obtained by comparison with it are actual values; if not, then they are ***minimum*** values, since reaction with rearrangement would necessarily proceed faster than the direct displacement.

The activating order, $N_2^+ \gg NO_2 \gg NMe_3^+$, was obtained by a separate comparison of N_2^+ and NO_2, and NO_2 and NMe_3^+. The first comparison is in the series with no other substituents, while the latter is in one having another powerfully activating substituent also present. Reference to the nitro-group shows that the second series is less sensitive to substituent effects, though the values may be used to make a reasonable estimate from one series to the other. Numerical ratios are: $-I,-T$ cation to $-I,-T$ dipole about $2{\cdot}7 \times 10^5$, while the ratio $-I,-T$ dipole to $-I$ cation (less sensitive series) is about 30, and may be estimated as not more than 10^3 if in the more sensitive series. The relative position of nitro-group and trimethylammonium ion is opposite to that in aromatic S_E reactions,[5] illustrating the importance of the electromeric (E) component of the conjugative (T) effect. In comparing the nitro-group with the two cations, the obvious measurement of rate of replacement of halogen in *p*-halogenotrimethylanilinium ion (even with less activating and more easily replaced fluorine) was not attempted owing to expected concurrent and probably faster displacement of trimethylammonium ion,[6] so that following the displacement of the fluoro-group would be impracticable. The change from fluorine to bromine in changing from the more sensitive to the less sensitive series is regarded as unimportant since comparison of the 1-halogeno-2 : 4-dinitrobenzenes[7] with the *o*-halogenonitrobenzenes[8] shows that the activating power of the second nitro-group is very little affected by the nature of the halogen displaced, and thus negligible in comparison with the very marked separation shown here, *viz.*, for substituent rate factors at 0° being $6{\cdot}20 \times 10^{10}$ for the *p*-nitro-group in the first series, and $1{\cdot}14 \times 10^6$ in the second.

The variation of the Arrhenius parameters is in accord with that deduced from the rate constants. Substitution of the diazonium ion into the *para*-position lowers the activation

[3] Roberts, Simmons, Carlsmith, and Vaughan, *J. Amer. Chem. Soc.*, 1953, **75**, 2390.

[4] Heppolette and Miller, *ibid.*, p. 4265.

[5] Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Co., 1953, p. 234; Bonner, James, Lowen, and Williams, *Nature*, 1949, **163**, 955.

[6] Cf. Heppolette and Miller, ref. 4; Bolto and Miller, in preparation.

[7] Beckwith, Miller, and Leahy, *J.*, 1952, 3552.

[8] Bolto, Miller, and Williams, *J.*, 1955, 2926.

energy by 13,600 cal. and multiplies the frequency factor by $10^{2\cdot3}$. Allowing that one reaction is with methoxyl in methanol and the other with hydroxyl in water, and using the comparison in this paper for the trimethylanilinium ion, we may estimate the true changes in the parameters as a decrease in activation energy of 15,750 cal. and rise in frequency factor as $\times 10^{3\cdot6}$. The marked lowering of the energy term is characteristic of $-I,-T$ activation in this field, and the rise in frequency factor is appropriate for attack by an anion on a cation. While the trimethylammonium ion as a *para*-substituent also caused a considerable increase ($\times 10^{1\cdot8}$) in frequency factor, the absence of the $-T$ effect is demonstrated by a markedly smaller drop in activation energy (3500 cal.). Again some allowance must be made for the difference in sensitivity of the two series. For the *p*-nitro-group the activation energy changes are 13,700 and 8150 cal. lower, with frequency factors little affected, being $10^{0\cdot25}$ and $10^{0\cdot55}$ lower. An estimated lowering of activation energy of not more than 6000 cal. may thus be made for the trimethylammonium ion as a *para*-substituent into fluorobenzene, compared with 15,750 (see above) for the diazonium ion.

EXPERIMENTAL

Rate constants were measured as in our previous papers at not less than three temperatures (20—40° range usually) for each compound. Values of k_2 were obtained graphically, and those of the Arrhenius parameters by a least-squares analysis of not less than six separately determined values of $\log_{10} k_2$ and reciprocal temperature. Estimated probable error in activation energy (E) is ± 400 cal. and of $\log_{10} B$ (frequency factor) $\pm 0\cdot30$, the " probable errors " by least squares being always less than this. For the diazonium ion, mainly because of the short range of temperature measurements, the probable error is larger and may be as much as about 1000 cal. in E and 1·0 in log B. For this reason calculated values at 50° and 100° for this compound were not given. In the case of fluorobenzene concentrations (0·15M) were higher than usual (0·05M) owing to the slow replacement of halogen even at 200°; also, in order to avoid waiting for infinity readings, equimolar concentrations of aromatic compound and reagent were used. As far as the runs were followed (about 50% of reaction) good second-order kinetics were obeyed, and the rate constants thus obtained fitted well the straight-line relations of $\log_{10} k_2$ and reciprocal temperature. To confirm that the reaction of the diazonium ion really was displacement of fluorine as the ion (apart from lack of visible evolution of gas) the runs at 0° were checked by determination of fluoride ion. The procedure used was that of Treadwell and Köhl,[9] involving a conductometric titration of fluoride against aluminium in aqueous alcohol, and in which the presence of sodium was advantageous. The end-points nevertheless were not such as to give a high order of accuracy, and the closeness of the results to those made by the standard procedure (before and after correction for ionic-strength effects) must be regarded as somewhat fortuitous (1·72 and $1\cdot68 \times 10^{-3}$ after correction), though confirming the reaction as being simple displacement of fluorine. The highest temperature used for the diazonium ion was 5·2°.

Effect of Ionic Strength (μ).—By the Brönsted equation the reaction between ions of unlike charge is given by $\log k = \log k_0 + 2Az_Az_B\sqrt{\mu}$, where k = rate constant; z_A and z_B = valencies of ion and cation; A = Debye constant = $\boldsymbol{N}^2\boldsymbol{e}^3(\pi/500)^{1/2}/2\cdot3026(\boldsymbol{R}DT)^{3/2}$, D being the dielectric constant of the solvent, and T the absolute temperature. On use of Albright and Gosting's values [10] of D for methanol at 25° (also for 35° and 45°) the Brönsted equation becomes $\log k = \log k_0 - 3\cdot786\sqrt{\mu}$. Similarly for water, Erben's equation [11] for relating D and T being used, the Brönsted equation at 86·8° becomes $\log k = \log k_0 - 1\cdot186\sqrt{\mu}$. Rates were determined experimentally at five ionic strengths for the anilinium salt at 25° in methanol, and at three ionic strengths at 86·8° in water.

With methanol a curve was obtained, which approximated to two intersecting straight lines with slopes 2·50 up to $\sqrt{\mu} = 0\cdot159$, and 0·570 for higher values. With water a straight line with slope 0·239 was obtained to values of $\sqrt{\mu}$ as low as could be measured. The curvature for methanol was as expected, and differences between initial slopes and theoretical values may be ascribed, at least partly, to ions' being non-spherical and to distance of the charge from the point of attack. Since the Debye constant A may be written as $B/(DT)^{3/2}$, and corresponding values of D and T are known, corrections were readily made at other temperatures. In view of

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[9] Treadwell and Köhl, *Helv. Chim. Acta*, 1925, **8**, 500; 1926, **9**, 470.

[10] Albright and Gosting, *J. Amer. Chem. Soc.*, 1946, **68**, 1063.

[11] Erben, *Bull. Soc. chim. France*, 1951, 515.

the similarity in shape of the diazonium and anilinium ions as regards relative position of halogen and N^+, analogous (and in any case small in water) corrections could be made for the diazonium salt. All slopes are in the theoretical direction.[12]

Tables 3 and 4 give the values of $\log_{10} k$ and $\sqrt{\mu}$ used for the anilinium ion in methanol at 25° and in water at 86·8°, respectively.

TABLE 3. *Anilinium salt in methanol at 25°.*

$-\log_{10} k$	$\sqrt{\mu}$	$-\log_{10} k$	$\sqrt{\mu}$
3·3299	0·340	3·2157	0·167
3·3228		3·1534	0·132
3·3144		3·0571	$0{\cdot}093_5$
3·2746	0·242		

TABLE 4. *Anilinium salt in water at* 86·8°.

$-\log_{10} k$	$\sqrt{\mu}$	$-\log_{10} k$	$\sqrt{\mu}$
2·7214	0·268	2·6973	0·147
2·7359		2·7013	
		2·6921	0·115

A typical run, the anilinium salt at 25·0° with OMe^- in methanol, is given as Table 5, and the full set of rate constants for the same compound is shown as Table 6. Corrections to zero ionic strength are not included in these two Tables.

TABLE 5. *Anilinium salt with* OMe^- *in methanol at* 25·0°.

Titration values ...	9·31	9·98	10·59	10·96	11·65	12·04	12·39	12·87	13·20	15·86
log term	0·1438	0·1575	0·1725	0·1831	0·2069	0·2234	0·2407	0·2694	0·2936	—
Time (hr.)	0	1	2	3	4·5	6	7·5	9·4	11·5	∞

$$k_2 = 4{\cdot}76_6 \pm 0{\cdot}04_2 \times 10^{-4} \text{ l. mole}^{-1} \text{ sec.}^{-1}.$$

TABLE 6. *Anilinium salt with* OMe^- *in methanol* ($\mu = 0{\cdot}116$).

$10^5 k_2$	46·8	47·6	48·5	150	155	441	443	439	434	454
Temp.	25·0°			35·2°		44·95°				45·5°

Preparation of Materials.—Commercial fluorobenzene was purified by distillation and had b. p. 85—85° (lit. 84—85°). *p*-Fluoronitrobenzene was prepared as in Part VII.[13]

p-*Fluorobenzenediazonium borofluoride.* *p*-Fluoronitrobenzene was reduced with iron filings and methanol containing 10% (v/v) of hydrochloric acid (conc.). The diazonium borofluoride was made in the usual way from the crude reduction product (obtained in 59% yield), and recrystallised from acetone–ether below 40°. The product had m. p. 154·5° (decomp.) [lit. 154·5° (decomp.)].

o-Bromonitrobenzene was prepared as in Part XIV.[8] 4-Bromo-*NN*-dimethyl-3-nitroaniline was made from dimethylaniline by bromination[14] and nitration by Clemo and Smith's method[15] except that absolute nitric acid was used.

4-*Bromo-NNN-trimethyl*-3-*nitroanilinium picrate and chloride.* These were made from the tertiary amine by the method used by Zaki and Fahim[16] for a similar compound. The *picrate*, recrystallised from water, had m. p. 189·5° (sealed tube) (Found: N, 14·4. $C_{15}H_{14}O_9N_5Br$ requires N, 14·4%). The chloride, recrystallised from methanol–ether, had m. p. 179° (sealed tube).

1-Bromo-2 : 4-dinitrobenzene was made as described in Part III.[7]

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[12] Cf. La Mer and Kammer, *J. Amer. Chem. Soc.*, 1931, **53**, 2832.

[13] Briner, Miller, and (in part) Liveris and Lutz, *J.*, 1954, 1265.

[14] Cumming, Hopper, and Wheeler, " Systematic Organic Chemistry," Constable and Co., London, 1931, p. 353.

[15] Clemo and Smith, *J.*, 1928, 2421.

[16] Zaki and Fahim, *J.*, 1942, 270.