678. *The S_N Mechanism in Aromatic Compounds. Part II.*[*]

By JOSEPH MILLER.

A wide range of substituent effects has been surveyed. Substituent rate factors are defined and the results are expressed in terms of these factors.

THE structure of aromatic compounds with the π-electrons distributed in molecular orbitals externally to the ring framework of σ-bonded atoms leads to the commonly observed attack by electrophilic reagents. That suitable substituents or ring hetero-atoms may lead to attack by nucleophilic reagents has been known for many years; *e.g.*, Pisani (*Compt. rend.*, 1854, **39**, 852) recorded the attack by water and ammonia on picryl chloride.

Since the activation consists in denuding a point or points in the ring of the shielding π electrons, activating groups are electron-attracting, particularly those operating by the tautomeric mechanism since then the very important electromeric effects operate, and further such groups stabilise the *cyclo*pentadiene anion type structure of the transition state (see Part I*). The S_N2 mechanism follows from this since the S_N1 heterolysis can only be facilitated by electron-repelling groups and thus a highly electronegative replaced group is required; S_N1 reactions in this field are therefore comparatively rare.

The kinetics of aromatic nucleophilic substitutions have received considerable attention particularly the halogenonitrobenzenes (Holleman *et al.*, *e.g.*, *Rec. Trav. chim.*, 1901, **20**, 292; 1916, **35**, 1; 1928, **47**, 329; 1933, **52**, 428, 901), and there have been many other references covering a wide field (*e.g.*, Singh and Peacock, *J. Phys. Chem.*, 1936, **40**, 669; Bennett and Vernon, *J.*, 1938, 1783; Mangini and Frenguelli, *Gazzetta*, 1939, **69**, 86; Bunnett and Levitt, *J. Amer. Chem. Soc.*, 1948, **70**, 2778; Brady and Cropper, *J.*, 1950, 507; Sugden and Willis, *J.*, 1951, 1380; Spitzer and Wheland, *J. Amer. Chem. Soc.*, 1940, **62**, 2996). Reactions of this type have been reviewed recently by the author (Part I *) and by Bunnett and Zahler (*Chem. Reviews*, 1951, **49**, 273). The latter list an order of substituent groups, and the former, on the basis of the known polar effects of groups (Ingold, *Rec. Trav. chim.*, 1929, **48**, 810), divides substituents into seven main classes. The present paper is a survey of some important substituent groups, ranging from powerful activating to powerful deactivating groups; further parts will deal with individual groups and sub-groups.

In order to gauge uncomplicated substituent effects, *para*-substituents are preferred. However, in order to obtain reasonable rates of attack in the temperature range 0—100°, it is necessary in many cases to have activating groups present. In the work now described, therefore, activating groups (NO_2) have always been present in the *ortho*-position(s), and the *p*-substituents have been varied. Further, the replaced group has always been chloro, the attacking reagent sodium methoxide, and the solvent dry methanol.

The substituent groups investigated have been NO_2, CO_2Me, CO_2^-, CH_3, Cl, NH_2. The compounds studied were (i) *o*-chloronitrobenzene, (ii) *p*-chloronitrobenzene, (iii) 2-chloro-1 : 3-dinitrobenzene, (iv) 1-chloro-2 : 4-dinitrobenzene, (v) methyl 4-chloro-3 : 5-dinitrobenzoate, (vi) 4-chloro-3 : 5-dinitrobenzoic acid, (vii) 4-chloro-3 : 5-dinitrotoluene, (viii) 2 : 5-dichloro-1 : 3-dinitrobenzene, and (ix) 4-chloro-3 : 5-dinitroaniline.

In this preliminary paper only sufficient activation energies are presented to give numerical values of the " substituent rate factor " (S.R.F.), *i.e.*, the ratio of the rates of reaction, Ar'X/ArX, with the same reagent R and at the same temperature, where Ar' differs from Ar only in that a hydrogen atom has been replaced by a substituent group. By definition the S.R.F. of H = 1.

---

[*] *Rev. Pure Appl. Chem.*, 1951, **1**, 171, is regarded as Part I.

The values obtained are given in Table 1.

TABLE 1.

10^5k_2, measured or, where shown in parentheses, calc. from Arrhenius parameters

Compound *	0·0°	15·0°	25·0°	26·35°	30·2	35·0°	71·0°	75·3°	81·6°	100·8°
(i)	$(0{\cdot}0_3323)$	—	—	—	(0·0240)	—	—	3·62	6·82	37·4
(ii)	$(0{\cdot}0_3920)$	—	—	—	(0·0741)	—	8·42	—	23·5	137·3
(iii)	(3·61)	—	—	90·5	138	226	—	—	(15,700)	—
(iv)	200	1060	2960	—	(4890)	—	—	—	(322,500)	—
(v)	3610	—	—	—	—	—	—	—	—	—
(vi)	57·0	—	—	—	—	—	—	—	—	—
(vii)	—	—	—	—	18·6	—	—	—	—	—
(viii)	51·8	—	—	—	—	—	—	—	—	—
(ix)	—	—	—	—	—	—	—	—	23·0	—

		S.R.F. at			
Compound *	Substituent	0·0°	30·2°	81·6°	S.R.F. (calc. from results of other workers)
(i)	—	—	—	—	—
(ii)	—	—	—	—	—
(iii)	o-NO_2	$1{\cdot}12 \times 10^4$	$5{\cdot}75 \times 10^3$	$2{\cdot}30 \times 10^3$	$1{\cdot}17 \times 10^3$ at 85° [a]
(iv)	o-NO_2	$2{\cdot}17 \times 10^5$	$6{\cdot}59 \times 10^4$	$1{\cdot}37 \times 10^4$	$2{\cdot}81 \times 10^4$ at 85° [a]
	p-NO_2	$6{\cdot}19 \times 10^5$	$2{\cdot}04 \times 10^5$	$4{\cdot}73 \times 10^4$	$7{\cdot}55 \times 10^4$
(v)	p-CO_2Me	$1{\cdot}00 \times 10^3$	—	—	—
(vi)	p-CO_2^-	$1{\cdot}58 \times 10^1$	—	—	$1{\cdot}54 \times 10^1$ at 25° [b]
(vii)	p-CH_3	—	$1{\cdot}35 \times 10^{-1}$	—	$1{\cdot}76 \times 10^{-1}$ at 50° [c]
(viii)	p-Cl	$1{\cdot}43 \times 10^1$	—	—	8·65 at 0° [a]
(ix)	p-NH_2	—	—	$1{\cdot}46 \times 10^{-3}$	—

[a] Holleman *et al.*, *Rec. Trav. chim.*, 1916, **35**, 1; 1920, **39**, 435. [b] Rouche (*Bull. Acad. Sci. roy. Belg.*, 1921, 534) with a mononitrofluorobenzoic acid. [c] Bevan, Hughes, and Ingold (unpublished; quoted by Bunnett and Zahler, *loc. cit.*), using sodium ethoxide in ethanol.

* For numbered compounds, see p. 3550.

Since the rate of attack on the monohalogenobenzenes has not yet been measured in the present work, the values for *o*- and *p*-chloronitrobenzene can give only the ratio p-NO_2/o-NO_2 in the absence of other substituents. This value varies from 3·45 at 81·6° to 3·67 at 100·8°; it may be compared with the value obtained by Holleman *et al.* (*locc. cit.*), *viz.*, 3·72 at 85°.

The rate constants for *o*- and *p*-chloronitrobenzene and 1-chloro-2 : 4- and 2-chloro-1 : 3-dinitrobenzene give good straight-line plots of $\log_{10} k_2$ against $1/T$. From these are obtained values of activation energies (E) and frequency factors (B) given in Table 2. Holleman's values (*loc. cit.*, 1916) are also shown; the latter are for two temperatures only except for 1-chloro-2 : 4-dinitrobenzene, for which, however, the values do not give a straight line.

TABLE 2.

			(Holleman *et al.*)	
Compound	E (cal.)	$\log_{10} B$	E (cal.)	$\log_{10} B$
o-Chloronitrobenzene	23,500	10·30	23,200	12·0
p-Chloronitrobenzene	23,950	11·12	23,000	12·5
2-Chloro-1 : 3-dinitrobenzene	19,770	11·37	17,900	11·8
1-Chloro-2 : 4-dinitrobenzene	17,430	11·26	16,800	12·5

The values in Table 2 are sufficient for calculation of the S.R.F.s of *p*-substituents, and also include values for the *o*-nitro-group. Most compounds were directly compared with 2-chloro-1 : 3-dinitrobenzene and the steric effects are constant. 1-Chloro-2 : 4-dinitrobenzene may be compared with both *o*- and *p*-chloronitrobenzene to give the S.R.F. of both *o*- and p-NO_2 groups, and comparison of 2-chloro-1 : 3-dinitrobenzene with *o*-chloronitrobenzene gives the S.R.F. of an o-NO_2 group when another such group is already present. The ratio p-NO_2/o-NO_2 at 81·6° then becomes 20·6. This will be discussed in a later paper.

The S.R.F. values obtained show that substituent effects are very large, and will be sensitive to small variations in group-activating power. Although the groups chosen do not cover the complete range accessible through compounds prepared with reasonable facility, the S.R.F.s already measured cover a range of more than 3×10^7.

The results are in agreement with the activating powers of substituents predicted by the author (Part I, *loc. cit.*).

EXPERIMENTAL

Thermostats were controlled to ±0·02° or better. The methanol used was dried by distilling it once from concentrated sulphuric acid then twice from aluminium amalgam through a column. It was tested for moisture content by Weaver's method (*J. Amer. Chem. Soc.*, 1914, **36**, 2463), and shown to contain not more than 0·001%.

A typical run is for 2-chloro-1 : 3-dinitrobenzene at 26·35°, shown herewith.

Titre (ml.)	$10^5 (b - x)$ (moles/l.)	$10^5 (a - x)$ (moles/l.)	t (sec.)	$10^4 k_2$	Titre (ml.)	$10^5 (b - x)$ (moles/l.)	$10^5 (a - x)$ (moles/l.)	t (sec.)	$10^4 k_2$
4·96	7935	4662	0	—	8·58	6106	2833	8,100	8·897
5·24	7795	4527	422	9·168	9·50	5641	2368	11,220	9·154
5·49	7670	4397	832	8·964	10·08	5348	2075	13,860	9·137
5·72	7552	4279	1190	9·282	10·69	5039	1766	17,100	9·231
6·02	7400	4127	1790	8·883	11·15	4808	1535	20,400	9·132
6·34	7238	3965	2400	8·913	11·54	4612	1339	23,700	9·085
6·99	6910	3637	3715	9·094	11·95	4405	1132	28,260	8·941
7·45	6678	3405	4800	9·010	14·19	3273	0	—	—
7·90	6451	3178	6005	8·966	14·19				

Average value : $k_2 = 9{\cdot}05 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$.

Preparation of Materials.—*o*- and *p*-Chloronitrobenzene and 1-chloro-2 : 4-dinitrobenzene were commercial products, purified by recrystallisation, and had m. p.s 32·5°, 83°, and 50·5°, respectively. 2-Chloro-1 : 3-dinitrobenzene was made from chlorobenzene in four stages, the first according to Lindemann and Wessel (*Ber.*, 1925, **58**, 1221) and the others according to Welsh (*J. Amer. Chem. Soc.*, 1941, **73**, 3276). The final product had m. p. 87°. 4-Chloro-3 : 5-dinitrobenzoic acid and its methyl ester were prepared from *p*-chlorobenzoic acid by Ullmann and Kuhn's method (*Annalen*, 1909, **366**, 92). The final products had m. p. 160° and 105°, respectively. 4-Chloro-3 : 5-dinitrotoluene was prepared in three stages from aceto-*p*-toluidide; the first two stages were according to Brady, Day, and Rolt (*J.*, 1921, **121**, 521), and the last was a Sandmeyer reaction, nitrosylsulphuric acid being used as diazotising agent. The final product had m. p. 114—115°. 2 : 5-Dichloro-1 : 3-dinitrobenzene was prepared by dinitration of *p*-chlorophenol by concentrated sulphuric and nitric acids, followed by substitution of chloro for hydroxy according to Ullmann and Sane (*Ber.*, 1911, **44**, 3731). The final product had m. p. 105°. 4-Chloro-3 : 5-dinitroaniline was made from the corresponding acid *via* the chloride and azide (Lindemann and Wessel, *loc. cit.*).

The author acknowledges financial assistance from the Commonwealth Research Grant to Australian Universities.

UNIVERSITY OF WESTERN AUSTRALIA, NEDLANDS, W.A. [*Received, April 1st*, 1952.]
