1116. *Aromatic Nucleophilic Replacement. Part IX.* The Reaction of 1-Halogeno-2,4-dinitrobenzenes with Sulphite Ion in Aqueous Ethanol.*

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Arrhenius parameters have been determined for the reactions of the four 1-halogeno-2,4-dinitrobenzenes with sulphite ion in 3 : 2 aqueous ethanol. Earlier observations made under similar conditions for halogenomononitrobenzenes are shown to be correlated with the decomposition of sulphite ion, to which too high a nucleophilic power was thus ascribed.

The new results are not consistent with the suggestion that there is a contribution by carbon 3*d*-orbitals in the transition state of these reactions, but they provide further evidence for the effects of dispersion forces.

REPLACEMENT of aromatic halogen by sulphite ion was investigated by Sprung[1] for chloro- and bromo-nitrobenzenes and -2,4-dinitrobenzenes. The results in the mononitro-series led to the assumption of a high nucleophilic power for the sulphite ion in aromatic nucleophilic substitution.[2] We have repeated these observations and find that in the mononitro-series Sprung was following the decomposition of the sulphite ion (cf. Experimental section). With the 1-halogeno-2,4-dinitrobenzenes, the situation is different, as reaction with sulphite ion is rapid and can be followed practically to completion (1-chloro-2,4-dinitrobenzene reacts at least $1{\cdot}3 \times 10^4$ times faster than *p*-chloronitrobenzene at 40°).

Runs were done simultaneously with a control containing sulphite ion only, to check that there was no decomposition of sulphite during the period of time the run was followed. Even at 30°, the highest temperature used in this series, there was no decomposition after 1·5 hours. For 1-bromo-2,4-dinitrobenzene, the rate of disappearance of sulphite and the rate of production of bromide ions were followed simultaneously; the agreement between the two rates measured by appearance of bromide and disappearance of sulphite, together with the known isolation of products[1] ensures that the reaction being followed is the replacement of halide by sulphite. Consistent with this and in agreement with Sprung's observations,[1] no reduction products or nitrite ion could be detected during a run. Our results are summarized in Table 1.

TABLE 1.

Reaction of sulphite ion in 60% aqueous ethanol with 1-X-2,4-dinitrobenzenes (rate constants in l. sec.^{-1} mole^{-1}).

X	F			Cl			Br			I		
Temp.	10·63°	20·26°	30·04°	10·03°	19·86°	30·04°	10·18°	20·08°	30·00°	10·53°	20·71°	30·01°
10^2k_2...	126	238	425	2·04	5·01	12·0	2·84	6·29	13·3	1·59	3·90	8·75

X	F	Cl	Br	I
10^2k_2 at 30°	425	12·0	13·3	8·75
E (kcal. mole^{-1})	10·7	15·1	13·3	15·0
$\log B$	8·34	9·97	8·74	9·76

The Table shows that at 30° the order of reactivity of the halogens is $\text{F} \gg \text{Br} \sim \text{Cl} > \text{I}$, the position of the bromo-compound being determined by a fall in activation energy not quite compensated by a corresponding decrease in the frequency factor. However, if the relative rates are calculated at widely different temperatures, the values in Table 2 are obtained. Thus the order of reactivity depends on the temperature. At 0° the sequence is $\text{F} \gg \text{Br} > \text{Cl} > \text{I}$, at 30° $\text{F} \gg \text{Br} \sim \text{Cl} > \text{I}$, and at 100° $\text{F} \gg \text{Cl} > \text{I} > \text{Br}$.

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* Part VII, *J.*, 1960, 4543; Part VIII, *Chem. and Ind.*, 1963, 119.

[1] Sprung, *J. Amer. Chem. Soc.*, 1930, **52**, 1650.

[2] Bunnett, *Chem. Rev.*, 1951, **49**, 273.

TABLE 2.

X	F	Cl	Br	I
10^3k_2 at 0°	602	7·62	11·8	5·75
k_2 at 100°	111·8	13·2	8·41	9·47

The order of reactivity of the halogens was recently discussed by Parker and Read[3] and a tentative correlation made between the reactivity sequence and the size of the reagent; the sequence $Cl > Br > I$ was found with small reagents (NH_3, OMe^-, OEt^-), the sequence $Br > Cl > I$ with larger ones ($Ph{\cdot}NH_2$, piperidine), and the sequence $Br > I > Cl$ with still larger reagents, *e.g.*, PhS^-. While in a very broad sense this correlation exists, yet in fact the relative rate ratios, and in some cases the actual reactivity sequence,[2,4] depend very much on the temperature at which the comparison is made, as $d \log k/dt = E/\boldsymbol{R}T^2$. The variation in the reactivity sequence with different nucleophiles was ascribed by Parker and Read to a contribution to the lowering of transition energy by overlap with carbon 3*d*-orbitals, which permits synchronous approach of reagent and expulsion of halogen; the amount of this contribution is considered to increase with the size of the attacking reagent since partial bonds can then be formed at greater distances. Such would not be the case if the reaction was solely through an intermediate complex. As Parker and Read's mechanism involves the partial breaking of carbon–halogen bonds in the rate-determining stage, the k_F/k_{Cl} ratios should be lower, and the k_I/k_F and k_I/k_{Cl} ratios higher for bulky reagents than for smaller ones.

A survey of the ten reactions listed by Parker and Read,[3] together with the results presented here, shows that in general these predictions are not borne out; in particular, they would require the effective volume of piperidine to be less than that of ammonia.

The relative nucleophilic power of the sulphite ion can be obtained by comparison of our results with those of Lulofs,[5] as in Table 3. For 1-chloro-2,4-dinitrobenzene, direct rate comparisons can be made in aqueous-methanolic and -ethanolic solutions. In both cases, sulphite is more reactive, the relevant rate ratios being $k\ (SO_3^{2-})/k\ (OR^-)$ (R = Et or Me) being 2·93 and 2·31. While direct comparisons cannot be made for the bromo- and the iodo-compound, sulphite ion is clearly the most reactive, for the alkoxy-rates quoted are for solvents containing a greater alcohol content and the rate of these reactions decreased on addition of water.[5] Thus, while the sulphite ion is a good nucleophile in aromatic nucleophilic substitution, its previous very high rating[2] cannot be substantiated. In the aliphatic series the rate ratios $k\ (SO_3^{2-})/k\ (OH^-)$ towards halogeno-acetates range from 52 to 204 (Table 4).

TABLE 3.

Rate constants, at 15°, for the reactions of alkoxide ions * and sulphite ions with 1-X-2,4-dinitrobenzenes (k_2 in l. sec.$^{-1}$ mole^{-1}).

X	Cl	Br	I
10^2k_2 (SO_3^{2-})	3·28,† 2·49 ‡	4·22 †	2·40 †
10^2k_2 (OR^-)	1·12,§ 1·08 **	0·942 ¶	0·359 ‖

* In aqueous-alcoholic solvents, the nucleophiles are OR^- and OH^-, and the constants quoted are for the composite reactions. As the predominant product formed is the ether,[6] we have termed them "alkoxide" reactions. The rates quoted are Lulofs's figures, converted into l. sec.$^{-1}$ mole^{-1} and divided by two.[7] † 60% Aq. EtOH. ‡ 60% Aq. MeOH. § 61·6% Aq. EtOH. ¶ 74·1% Aq. EtOH. ‖ 89·2% Aq. EtOH. ** 59·4% Aq. MeOH. [x% ROH = x vol. of ROH + (100 − x) vol. of H_2O.]

This high nucleophilic power compared with hydroxide or alkoxide ions is not to be

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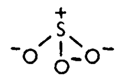
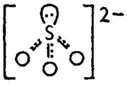
[3] Parker and Read, *J.*, 1962, 9.
[4] Bolto, Miller, and Williams, *J.*, 1955, 2926.
[5] Lulofs, *Rec. Trav. chim.*, 1901, **20**, 292.
[6] Bunnett and Davies, *J. Amer. Chem. Soc.*, 1954, **76**, 3011.
[7] Lorang, *Rec. Trav. chim.*, 1927, **46**, 891.

expected either from its basicity[8] pK_a ~7 or from an electronic structure of which (A) is one canonical form. We believe that the most probable structure of the sulphite ion is (B), formed from sulphur sp^3-hybridisation with a considerable amount of pd-π-bonding.

(A)





(B)

This structure provides the sulphur atom with a convenient orbital for bond formation and make it comparatively highly polarizable; these two factors account for the exclusive formation of sulphonates, rather than organic sulphites, whenever sulphite ions displace halogen from an organic halide. The polarizability of the sulphite ion can be regarded as due either to the normal effect of the presence of low-energy d-orbitals[9] or an increase in the O–S π-bonding, giving a result similar to Edward's α effect,[9] utilizing d- instead of p-orbitals.

The interaction of polarizable nucleophiles, and the polarizabilities of the leaving group and groups situated near the reaction centre, have been discussed by Bunnett[10] in terms of dispersion forces. As the order of polarizability of the halogens is I > Br > Cl > F, this should be the order of reactivity due to this effect for a given nucleophile towards a halogen series. However, this effect is frequently masked by others such as variation in bond strength of the leaving group and charge density at the reaction site. To demonstrate the polarizability effect, Bunnett compares k (Y)/k (OR$^-$) ratios for a halogen series, assuming as a first approximation that the effect of change in bond strengths and charge densities will be the same for reagent Y as for OR$^-$, so that the variation in the ratios for different halogens is due to the polarizability effect. Values of these ratios for sulphite ion and other nucleophiles towards substrate 1-halogen-2,4-dinitrobenzene are assembled in Table 4 and towards substrate halogenoacetate ion in Table 5.

TABLE 4.

A comparison of k(Y)/k(OMe$^-$) ratios for 1-halogeno-2,4-dinitrobenzenes as substrate in methanol at 0°.

Halogen	Rate coefficients (l. sec.$^{-1}$ mole^{-1})					$\frac{k\ (\text{PhS}^-)}{k\ (\text{OMe}^-)}$	$\frac{k\ (\text{SO}_3^{2-})}{k\ (\text{OMe}^-)}$	$\frac{k\ (\text{Z})}{k\ (\text{OMe}^-)}$ ‡	$10^4 \frac{k\ (\text{NH}_3)}{k\ (\text{OMe}^-)}$
	OMe$^-$ *	Z *†	PhS$^-$ *	SO$_3^{2-}$	NH$_3$ ‡				
F	1·76	1·5	103·4	$6·02 \times 10^{-1}$	$5·42 \times 10^{-4}$	59	0·342	0·85	3·08
Cl	$2·00 \times 10^{-3}$	$1·95 \times 10^{-3}$	3·89	$7·62 \times 10^{-3}$	$1·57 \times 10^{-7}$	1950	3·81	0·98	0·79
Br	$1·38 \times 10^{-3}$	$1·97 \times 10^{-3}$	6·68	$1·18 \times 10^{-2}$	$1·44 \times 10^{-7}$	4840	8·55	1·43	1·05
I	$3·08 \times 10^{-4}$	$4·57 \times 10^{-4}$	5·17	$5·75 \times 10^{-3}$	$4·53 \times 10^{-8}$	16,800	18·7	1·48	1·47

* Ref. 10. † Z = piperidine. ‡ Calc. from the results of Reinheimer, Taylor, and Rohrbaugh, *J. Amer. Chem. Soc.*, 1961, **83**, 835.

TABLE 5.

Rate of reaction of hydroxide and sulphite ions with halogenoacetates at 25° (k_2 in l. sec.$^{-1}$ mole^{-1}).

Halogen	10^5k (OH$^-$) *	k (SO$_3^{2-}$) †	k (SO$_3^{2-}$)/k (OH$^-$)
Cl	0·145	$7·68 \times 10^{-5}$	52·9
Br	6·06	$7·57 \times 10^{-3}$	125
I	6·48	$1·32 \times 10^{-2}$	204

* Calc. from results of Darienko and Sapozhnikov, *Izvest. Vysshikh Ucheb. Zavedenii, Khim. i Khim. Tekhnol.*, 1960, **3**, 461. † Backer and Mels, *Rec. Trav. chim.*, 1930, **49**, 457.

For a given series of nucleophiles the $k_{\text{I}}/k_{\text{Br}}$ and $k_{\text{I}}/k_{\text{Cl}}$ ratios, due to this effect, should be greater the more polarizable the reagent. Again, to a first approximation, the effect of

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[8] Stewart and Donnally, *J. Amer. Chem. Soc.*, 1932, **54**, 3559.
[9] Edwards and Pearson, *J. Amer. Chem. Soc.*, 1962, **84**, 16.
[10] Bunnett, *J. Amer. Chem. Soc.*, 1957, **79**, 5969.

change of charge density can be eliminated by comparing $(k_I/k_{Br})_Y/(k_I/k_{Br})_{OMe^-}$ and $(k_I/k_{Cl})_Y/(k_I/k_{Cl})_{OMe^-}$ values; moreover, the magnitude of the second ratio should always be greater than that of the first. Values of these ratios are assembled in Table 6.

TABLE 6.

Comparison of rate ratios for various reagents at 0°. Substrate: 1-halogeno-2,4-dinitrobenzene.

Reagent	PhS⁻	SO_3^{2-}	NH_3	Piperidine	OMe⁻
k_I/k_{Br} (= A)	0·78	0·487	0·314	0·231	0·22
A (Y)/A (OMe⁻)	3·5	2·24	1·43	1·07	1
k_I/k_{Cl} (= B)	1·32	0·755	0·288	0·23	0·15
B (Y)/B (OMe⁻)	8·8	5·03	1·92	1·53	1

Tables 4—6 [with the exception of the ratio $k(NH_3)/k(OMe^-)$ towards 1-fluoro-2,4-dinitrobenzene] reveal sequences in agreement with the operation of dispersion forces. The sulphite ion has a good polarizability, occupying an expected position between thiophenoxide and amines in this respect. The high value of $k(NH_3)/k(OMe^-)$ for 1-fluoro-2,4-dinitrobenzene in comparison with other halogens is not unexpected; we ascribe it to rate-enhancing hydrogen bonding in the transition state between the fluorine atom and a primary amine as described by Bamkole, Bevan, and Hirst.[11]

The effect of change of solvent on the rate of a reaction is given by the Hughes–Ingold theory of solvent action.[12] In the reactions of sulphite ion with 1-halogeno-2,4-dinitrobenzenes, formation of the transition state leads to dispersal of the charge present in the ground state, so that the theory leads to the prediction that the rate will decrease as the polarity of the solvent increases. The effect of changing the solvent medium on the rate of reaction of 1-chloro-2,4-dinitrobenzene is illustrated in Table 7. If we here take 60% aqueous ethanol as standard, the solvent polarity has been increased in two ways: by increasing the water content and by replacing ethanol by methanol. Both changes decrease the rate, as predicted by the theory. A similar effect of the same order of magnitude has been observed by Lulofs [5] for the reaction between ethoxide ion and 1-chloro-2,4-dinitrobenzene in aqueous ethanol.

TABLE 7.

Effect of change of solvent polarity on the rate of reaction of 1-chloro-2,4-dinitrobenzene with sulphite ion at 30°.

(Rate constants in l. sec.$^{-1}$ mole^{-1}.)

	60% Aq. EtOH	50% Aq. EtOH *	60% Aq. MeOH
$10k_2$	1·20	1·02	1·02

* From ref. 1.

EXPERIMENTAL

Commercial *p*-chloronitrobenzene and 1-fluoro-, 1-chloro-, and 1-bromo-2,4-dinitrobenzene were purified by crystallization, m. p.s being 82° (from alcohol), —, 50·5—51° (from alcohol), and 71·5—72° (from di-isopropyl ether), respectively. 1-Iodo-2,4 dinitrobenzene,[13] when recrystallised from alcohol and then several times from light petroleum (b. p. 60—80°) had m. p. 83°.

Ethanol.—Sodium (10 g.) and diethyl phthalate (27·5 g.) were dissolved in absolute alcohol, which was then refluxed for 2 hr. and distilled.

Methanol.—Magnesium (5 g.) and iodine (0·5 g.) were dissolved in " AnalaR " methanol (1 l.). which was then refluxed for 0·5 hr. and distilled.

Kinetic Measurements.—Thermostat temperatures were steady within 0·02°. Solutions of " AnalaR " sodium sulphite in 20% aqueous alcohol were estimated by method (*a*) below.

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[11] Bamkole, Bevan, and Hirst, *Chem. and Ind.*, 1963, 119.

[12] Hughes and Ingold, *J.*, 1935, 252.

[13] Bennett and Vernon, *J.*, 1938, 1783.

Standard solutions of the organic halide in absolute alcohol were made by direct weighing. Solutions of the two reactants were brought to thermostat temperature, and equal volumes were mixed. Portions (10 c.c.) were withdrawn at intervals and (*a*), with the chlorides and bromides, were run into cold concentrated hydrochloric acid, sulphite being titrated with standard potassium iodate (Amaranth indicator) or (*b*), with the bromide and iodide, were run into acetone (20 c.c.) containing concentrated nitric acid (1 c.c.), halide ion being titrated potentiometrically with silver nitrate. In all cases a control of sodium sulphite in 60% aqueous alcohol was carried out simultaneously to check that no significant decomposition of sulphite occurred while the measurements were taken.

1-Fluoro-2,4-dinitrobenzene reacted too rapidly for the above method to be used, and its rate of reaction was followed by the "triple tube" technique.[14] Solutions (5 c.c.) of sulphite in 20% alcohol, and the fluoro-compound in absolute alcohol, were placed in the two bottom bulbs and concentrated hydrochloric acid (20 c.c.) in the top bulb. After the reactants had achieved thermostat-temperature, reaction was started by mixing the contents of the bottom two bulbs. At known times the reaction was stopped by adding the contents of the third bulb and the sulphite ion was estimated as in (*a*).

Tables 8 and 9 give typical results.

TABLE 8.

Reaction of *p*-chloronitrobenzene with sodium sulphite in 50% ethanol at 40·0°.

Initial [Chloride] = 0·0360M, $[SO_3^{2-}]$ = 0·0594M.
(Control solution of sulphite, 0·0594M.)

Time (hr.)	0	4	16	20	36	44	60	88
$10^2[SO_3^{2-}]$ (M) (reaction)	5·94	5·46	5·32	5·14	4·60	4·42	4·029	3·69
$10^2[SO_3^{2-}]$ (M) (control)	5·94	5·35	5·35	5·17	4·60	4·40	4·15	3·62

TABLE 9.

Determination of k_2 (l. sec.$^{-1}$ mole^{-1}) for the reaction of 1-bromo-2,4-dinitrobenzene with sulphite ion in 60% aqueous ethanol.

(*a*) Following the disappearance of sulphite ion:

Initial $[SO_3^{2-}]$ = 0·00914M, [Bromide] = 0·0135M. Temp. 10·18°.
"Concns." in c.c. of 0·00538N-KIO_3 per 10-c.c. sample.

Time (sec.)	0	326	754	923	1235	1525	1828	2426	3326	4527
[Bromide]	47·27	43·82	40·12	38·63	36·77	35·32	34·02	31·52	28·77	26·07
$[SO_3^{2-}]$	31·15	27·70	24·00	22·51	20·65	19·20	17·90	15·40	12·65	9·95
10^2k_2	—	2·97	2·97	3·08	2·99	2·92	2·85	2·85	2·81	2·79

Mean $k_2 = 2{\cdot}91 \times 10^{-2}$ (duplicate, $2{\cdot}88 \times 10^{-2}$).

(*b*) Following the appearance of bromide ions:

Initial $[SO_3^{2-}]$ = 0·01706M, [Bromide] 0·00763M. Temp. 10·53°.
"Concns." in c.c. of 0·00376N-$AgNO_3$ per 10-c.c. sample.

Time (sec.)	0	323	740	922	1228	1525	1824	2423	3023	3622	4228
[Sulphite]	43·35	40·69	37·69	36·71	35·24	34·41	33·39	31·29	30·39	29·44	28·59
[Bromide]	19·01	16·35	13·35	12·37	10·90	10·07	9·05	6·95	6·05	5·10	4·25
10^2k_2	—	2·97	3·16	3·13	3·11	2·91	2·88	3·07	2·86	2·80	2·79

Mean $k_2 = 2{\cdot}97 \times 10^{-2}$ (duplicate, $2{\cdot}95 \times 10^{-2}$).

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[14] Criegee, *Annalen*, 1932, **495**, 219.