

313. *The Mechanism of Aromatic Side-chain Reactions with Special Reference to the Polar Effects of Substituents. Part VIII. The Polar Effects of Halogens.*

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THE theory of the mechanism of quaternary-salt formation previously developed (J., 1935, 1840, and references there cited) and the data on which it was based have shown that, in the interaction of benzyl bromide with pyridine in dry acetone, the introduction of any nuclear substituent which causes an increase in electron availability at the side-chain C-Br linking increases the velocity of reaction, since it favours the inherently more probable (*a*) type of initiation of the necessary electron cycle (incipient anionisation of the bromine). On the other hand, introduction of a substituent group which has an electron-attractive power not greater than that of a *p*-nitro-group decreases this inherent probability and hence the velocity of reaction. It follows, therefore, that within such prescribed limits, the velocity with which a substituted benzyl bromide reacts with pyridine will provide reliable information concerning the total polar effect of the substituent. This criterion has now been applied to determine (1) the polar effects of certain unipolar groups in the

m-position, and (2) the polar effects of ambipolar (see J., 1935, 1840, footnote) halogen substituents.

The new data are in Table I, in which the relevant data for the *p*-substituents are included for purposes of comparison.

TABLE I.

Kinetic data for the interaction of $R \cdot C_6H_4 \cdot CH_2Br$ with pyridine in dry acetone
($c_a = c_p = 0.025M$).

R.	$k_p \times 10^4$ (l./g.-mol.-sec.).		E (kg.-cals.).	R.	$k_p \times 10^4$ (l./g.-mol.-sec.).		E (kg.-cals.).
	20°	40°			20°	40°	
(H)	1.22	4.82	12.5*	<i>p</i> -F.....	1.48	5.78	12.5
<i>p</i> -NO ₂ ...	1.12	4.33	12.3*	<i>p</i> -Cl	1.27	5.10	12.7
<i>m</i> -NO ₂ ...	0.99	3.53	11.5	<i>p</i> -Br	1.30	5.19	12.6
<i>p</i> -Me	2.02	7.98	12.5†	<i>p</i> -I	1.48	5.43	11.9
<i>m</i> -Me	1.43	5.15	11.7	<i>m</i> -F	0.95	3.62	12.5
<i>p</i> -Bu γ	1.65	6.47	12.5†	<i>m</i> -Cl	1.08	4.07	12.1
<i>m</i> -Bu γ ...	1.22	4.82	12.5	<i>m</i> -Br	1.07	3.77	11.5
				<i>m</i> -I	1.14	4.13	11.8

* J., 1935, 519.

† *Ibid.*, p. 1840.

The velocity of the *m*-nitrobenzyl bromide is less than that of the *p*-isomeride, thus confirming an earlier preliminary result (J., 1933, 1130). This observation, considered in conjunction with the data already obtained for the *o*-nitro- (this vol., p. 399) and 2:4-dinitro-derivatives (J., 1935, 1840), makes it very difficult to escape from the conclusion that the electron attraction exerted by a nitro-group in the *m*-position functions almost exclusively to reduce the probability of the (*a*) type of initiation, whereas the greater electron attraction of this group in the *p*-position is just sufficient for its effect in favouring the (*b*) type of initiation (incipient electrostriction of the base) to be recognisable. Thus the minimum velocity in the graded polar series, known to occur between the unsubstituted parent and its *p*-nitro-derivative, is now located more exactly at *m*-nitrobenzyl bromide.

Only two *m*-alkyl substituents were examined. The velocity of *m*-tert.-butylbenzyl bromide is experimentally indistinguishable from that of benzyl bromide itself, but the introduction of a methyl group in the *m*-position causes a small but definite increase in the reaction velocity. Thus from the *m*-, as from the *p*-position, the total electron release by a methyl group is greater than that of a tert.-butyl. This confirms the earlier conclusion (J., 1935, 1847) that the postulated new type of electron release by alkyl groups is of a permanent (mesomeric) character.

The effect of all four halogens in both the *m*- and the *p*-position has been investigated. The problem of the polar characteristics of this group has been thoroughly studied by Bennett and his collaborators (J., 1935, 1815, *et seq.*), whose communication appeared whilst this work was in progress. The data now obtained confirm the findings of these authors to the extent that it must be admitted that the total electron release of fluorine ($-I, +M, +E$) is at least as great as that of iodine.

The velocity of all the *m*-halogenobenzyl bromides is less than that of the unsubstituted parent, but (with the possible exception of fluorine) is not less than that of the *m*-nitro-derivative (*i.e.*, the minimum velocity). Thus the total polar effect of any halogen substituent in the *m*-position must be one of electron attraction away from the side chain. The velocity order $m-I > Br \approx Cl > F$ is in agreement with the view (Bennett, *loc. cit.*) that mesomeric and electromeric effects are of minor importance in the *m*-position.

In the *p*-position all the possible electronic effects ($-I, +M$, and $+E$) of the halogens must be operative. The velocity of reaction of each of the *p*-halogenobenzyl bromides is greater than that of the unsubstituted parent; hence the total polar effect of any of these substituents must be one of electron release towards the side chain. The relative order is $p-F \approx I > Br > Cl$, the last inequality being almost negligible. This sequence differs somewhat from that found by Bennett *et al.* (*loc. cit.*) for the hydrolysis of *p*-halogenobenzyl chlorides with 50% aqueous acetone, *viz.*, $F \gg Cl > Br > I$, the first inequality being large. Since it has already been shown (Part III, *loc. cit.*) that a *p*-nitro-substituent

exerts a much greater retarding effect on the velocity of the pyridine reaction in 90% aqueous acetone than it does in the dry solvent, it is unlikely that the accelerating effect of *p*-fluorine observed by Bennett could be ascribed (as in the case of 2:4-dinitrobenzyl bromide) to any facilitating influence of its very powerful electron attraction on the electrostriction of the nucleophilic reagent. We agree with these authors that it must be due to its powerful electron release capacity. In the pyridine reaction this differentiation of fluorine is much less marked, either fluorine or iodine causing approximately the same degree of acceleration. From the combined data it would thus appear probable that the halogens possess a mechanism of electron release which varies according to the nature of the reaction and the experimental conditions, *i.e.*, an electromeric effect. If the order $F > Cl > Br > I$ is accepted for the inductive effect (electron attraction) and also for the mesomeric effect (polarisation), the data now obtained are consistent with the order $I > Br > Cl > F$ for the electromeric effect (polarisability) of the halogens. The *p/m* velocity ratios observed are :

	NO ₂ .	Me.	Bu ^γ .	F.	Cl.	Br.	I.
At 20°	1.13	1.41	1.35	1.56	1.18	1.19	1.22
At 40°	1.22	1.55	1.34	1.59	1.25	1.38	1.32

The ratio for fluorine is much smaller than that observed by Bennett.

The present results provide no information concerning the nature of the mesomeric and electromeric effects, but the author prefers to regard them as due to covalency increase (Ingold, *Chem. Reviews*, 1934, 15, 244). The mesomeric effect is thus regarded as a permanent polarisation arising from resonance between forms (I) and (II).



The electromeric effect is then regarded as the extent to which time-variable electron displacements, called into play by the demands of the reagent, can convert the mesomeric form into an activated phase approximating to type (II), thus localising the energy of the activated molecule at the reacting bond. These conclusions mean that the degree of permanent electron displacement which it is necessary to apply to the classical structure (I) in order to obtain a truer picture of the normal molecule decreases in the order $F > Cl > Br > I$, whereas the degree of polarisability involving time-variable electron displacements of the same type decreases in the order $I > Cl > Br > F$.

EXPERIMENTAL.

Preparation of Materials.—*m*-*tert*-Butylbenzyl bromide. The mixture of *m*- and *p*-*tert*-butyltoluenes obtained by the interaction of toluene and *tert*-butyl chloride in the presence of aluminium chloride was separated by the method of Shoesmith and McGechan (J., 1930, 2231). Bromination of *m*-*tert*-butyltoluene was effected at the b. p., and the product isolated in the usual manner. The bromide, purified by repeated fractional distillation in a vacuum, had b. p. 80°/0.6 mm. (Found : Br, 35.1. C₁₁H₁₅Br requires Br, 35.25%).

m-Methylbenzyl bromide, similarly prepared from *m*-xylene, had b. p. 59°/0.8 mm. (Found : Br, 42.8. Calc. for C₈H₉Br : Br, 43.2%). *m*-Nitrobenzyl bromide had m. p. 56.2°.

The halogenobenzyl bromides were either purchased or obtained by slow addition of bromine (1 mol.) to the *m*- or *p*-halogenotoluene at 140—150° and isolation of the product in the usual manner. Purification was effected by repeated fractional distillation in a good vacuum, a bath and a Claisen flask fitted with a fractionating column being used, or, in the case of solids, by repeated crystallisation from ligroin (b. p. 40—60°). The data relating to the samples used are briefly summarised below.

m-Fluorobenzyl bromide was obtained as a colourless liquid, b. p. 87.0°/17 mm. (Found : C, 45.2; H, 3.5; Br, 42.3. C₇H₆BrF requires C, 44.4; H, 3.2; Br, 42.3%).

p-Fluorobenzyl bromide, b. p. 38°/0.6 mm. (Found : C, 44.9; H, 3.5; Br, 41.7%), was obtained similarly. *p*-Chlorobenzyl bromide had m. p. 49°. *m*-Chlorobenzyl bromide had b. p. 55°/0.2 mm., m. p. 17.5° (Found : C, 40.7; H, 3.1; Br, 38.6. C₇H₆ClBr requires C, 40.9; H, 2.9; Br, 38.9%). *m*-Bromobenzyl bromide had m. p. 42.5—43° (Found : C, 34.0; H, 2.6. Calc. for

$C_7H_6Br_2$: C, 33.6; H, 2.4%). *p*-Bromobenzyl bromide had m. p. 62°. *m*-Iodobenzyl bromide had m. p. 50.8° (Found: C, 28.4; H, 2.2. C_7H_6BrI requires C, 28.3; H, 2.0%). *p*-Iodobenzyl bromide had m. p. 79°.

Velocity Measurements.—The technique was exactly the same as that described in Part IV (*loc. cit.*), the value of the velocity constants being determined as before from the slope of the straight line obtained by a plot of $x/(a - x)$ against time. In the case of the *p*-iodo-derivative separation of the quaternary salt restricted the observations to the first 10—15% of the reaction.

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