161. *The Kinetics of Halogen Substitution. Part VIII. Halogen Addition. Part XV. Benzyl and Allyl Chloride, Bromide, and Cyanide.*

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The order of reactivity, per molecule, is $PhH > Ph{\cdot}CH_2Cl > Ph{\cdot}CH_2Br > Ph{\cdot}CH_2{\cdot}CN$ for chlorine substitution, and

$$CH_2{:}CH_2 \gg CH_2{:}CH{\cdot}CH_2Cl > CH_2{:}CH{\cdot}CH_2Br > CH_2{:}CH{\cdot}CH_2{\cdot}CN$$

for bromine addition. The theories relating to these reactions are discussed.

The rates of aromatic substitution, as well as the orientation of the products, are of importance in elucidating the mechanisms involved in the process. This has been demonstrated by Ingold and his co-workers for nitration by the competitive method (*J.*, 1938, 905, 918, 929), and for chlorination, in the present series of investigations, for alkylbenzenes and halogenonaphthalenes (*J.*, 1943, 279; 1948, 100). The benzyl halides and in general compounds of the type $Ph{\cdot}CH_2X$ may also be investigated by this method. Whilst the present work was in progress there appeared a paper by Ingold and Shaw (*J.*, 1949, 575) on the relative rates of nitration of benzyl chloride and ethyl phenylacetate.

Our preliminary rate measurements of the chlorination of benzyl chloride in acetic acid solution showed variations greater than might be accounted for by experimental error. It was found further that in the presence of mercuric chloride these rates were lowered, whereas mercuric chloride accelerated the chlorination of toluene under the same conditions. The conclusion was that in the relatively very slow reaction with benzyl chloride nuclear substitution was accompanied by an atom-chain reaction involving side-chain substitution, and that the mercuric chloride acted as a chain-breaker. It was also ascertained that in the mixed solvent, 20% aqueous acetic acid, which would be expected to eliminate the chain-reaction, the ratio of the toluene and benzyl chloride rates was the same as in acetic acid containing mercuric chloride. The use of such a mixed solvent for the determination of comparative rates involves the risk, for benzyl chloride and bromide, of concomitant hydrolysis with the formation of a more reactive compound. No autocatalysis, however, could be detected in the chlorination of benzyl chloride, and in particular the per cent. absorption–time curves for benzene and benzyl chloride remained proportionate throughout the experimental range. Another possible disturbance is that in the benzyl bromide reaction there might be simultaneous substitution of bromine by chlorine. Such a reaction would be expected to proceed with acceleration, but here also there was no evidence of autocatalysis. It is known, moreover, that replacements of this type tend to take place more especially when there is considerable electron-accession to the point of attack, *e.g.*, in a compound such as *p*-$Me\cdot C_6H_4\cdot CH_2Br$.

Herewith are the relative initial rates of chlorination, in 20% water–acetic acid at 25°, of benzene and the compounds, $Ph\cdot CH_2X$.

PhH	$Ph\cdot CH_2Cl$	$Ph\cdot CH_2Br$	$Ph\cdot CH_2\cdot CN$
1	0·76	0·61	0·17

Accurate percentages of *o*-, *p*-, and *m*-substitution products are known for nitration, but not for chlorination of some of the compounds examined. The values for *m*-nitration are for $Ph\cdot CH_2Cl$ (15%), $Ph\cdot CH_2Br$ (7%), and $Ph\cdot CH_2\cdot CN$ (14%), and it is not to be expected that there should be a large difference for chlorination. At all events the reactions are proceeding chiefly to give *p,o*-chloro-compounds, and the relative rates in the foregoing table are substantially those for substitution in these positions. The relative rate of nitration of benzene to that of benzyl chloride, molecule per molecule, found by Ingold and Shaw (*loc. cit.*) was 1 : 0·302, indicating that benzyl chloride is more deactivated on nitration than on chlorination. In nitration the reagent is the ion NO_2^+, and in chlorination the chlorine molecule, and benzyl chloride with its permanent dipole is likely to hinder the approach of the positive ion more than the neutral molecule. A similar difference in reactivities was found between nitration and halogenation for aromatic compounds containing halogen in the nucleus (*J.*, 1948, 104).

Attention is now turned to the relative rates of chlorination of the three compounds $Ph\cdot CH_2X$. Chlorine has a greater inductive effect than bromine, but the difference between the dipole moments of $Ph\cdot CH_2Cl$ (1·85 D.) and $Ph\cdot CH_2Br$ (1·86 D.) is inconsiderable. In benzyl chloride the carbon atoms in the ring should be somewhat more deactivated than in benzyl bromide, and the superior reactivity of the chloride is consequently caused by the greater hyperconjugation of the hydrogen atoms in the chloromethyl group. Benzyl cyanide, on the other hand, has a greater dipole moment (3·52 D.), so that in this compound the deactivation must be more considerable than in the benzyl halides. The rate of chlorination, however, is not greatly inferior, so the hyperconjugation effect here must be large. This involves the weakening of the C–H bond by the CN group, and in this connection it is known that benzyl cyanide forms a sodium salt, $Ph\cdot CHNa\cdot CN$.

If groups such as chloromethyl act in aromatic substitution by a hyperconjugation effect reduced by an opposing inductive effect, they may be expected to act in a similar manner in causing halogen addition to ethylene compounds. The previously measured rates of bromine addition to the allyl halides in acetic acid solution are now compared with that of allyl cyanide, the velocities being calculated as second order coefficients at 25° for reactants at M/80 (x = 10% absorption) :

$CH_2:CH\cdot CH_2Cl$	$CH_2:CH\cdot CH_2Br$	$CH_2:CH\cdot CH_2\cdot CN$
$k_2 = 1{\cdot}6$	$k_2 = 1{\cdot}1$	$k_2 = 0{\cdot}23$

In our earlier communication (*J.*, 1945, 131) the rate order, allyl chloride > allyl bromide, was considered to be anomalous, and it was suggested that it might have been caused by intervention of solvent molecules in the reaction; but the same rate ratio is found, not only in acetic acid and aqueous acetic acid solutions, but also for the reactions in the polar aprotic solvent chlorobenzene. In the non-polar carbon tetrachloride these rates appear to be reversed (Juvala, *Ber.*, 1930, **63**, 1998), but we find it difficult to obtain reproducible results for these compounds in this solvent, even in an atmosphere of dry nitrogen.

The allyl cyanide reaction in acetic acid solution is autocatalytic like those of the bromide and chloride owing to the formation of hydrogen bromide caused by the participation of solvent molecules. The following third order coefficients for bromine addition to allyl cyanide, reactants M/80, in acetic acid at 25°, show this effect.

x, %	10	20	30	40	50	60
k_3	20	23	28	33	40	53

Correspondingly, the reaction is largely catalysed by the lithium halides, as is seen from the initial rates, now calculated as second order coefficients :

	No catalyst.	LiCl, M/20.	LiBr, M/20.
$k_2(x = 10)$	0·23	2·4	1·2

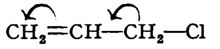
Thus for allyl cyanide, like other compounds of the type $CHR':CH_2$, where R′ is a group with $+T, -I$ characteristics, LiCl is superior to LiBr as a catalyst, and as the $-I$ effect (measured by the dipole moment) is large, the catalysis is considerable (cf. *J.*, 1949, 294).

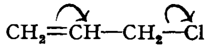
The rate of bromine addition to ethylene has now been determined by a revised technique, specially applicable to volatile reactants, and this will be described in a later communication. These measurements have, for reasons of solubility, been made in a mixed solvent composed of chloroform and carbon tetrachloride, and the rate of bromine addition to allyl bromide was measured in the same solvent. On combining these results with those shown above for the reactions in acetic acid, the following relative rates are obtained :

$CH_2{:}CH_2$	$CH_2{:}CH{\cdot}CH_2Cl$	$CH_2{:}CH{\cdot}CH_2Br$	$CH_2{:}CH{\cdot}CH_2{\cdot}CN$
1	0·019	0·013	0·0027

A comparison of this series with the one obtained for the chlorination of the benzyl compounds reveals that the order of reactivity is the same, but with a different deactivation effect in the two series. These results are consistent with the operation of a mechanism with similar electron requirements in the two reactions; but the deactivation by the CH_2X group is more considerable in the allyl compounds, where the dipole is nearer to the point of attack. The same effect has been observed for the compounds PhBr and $CH_2{:}CHBr$, since the bromine atom has the same $+T, -I$ characteristics as the CH_2X groups at present being investigated.

Just as in the compounds $Ph{\cdot}CH_2X$, there is the possibility of either *o*-, *p*-, or *m*-substitution, so also in the allyl compounds two modes of reaction, (I) and (II), are possible. According to

(I.) 
$CH_2{=}CH{-}CH_2{-}Cl$

(II.) 
$CH_2{=}CH{-}CH_2{-}Cl$

(I), hyperconjugation operates, whilst in (II) the mechanism is dependent on the inductive effect of the CH_2Cl group, reinforced by halogen-hyperconjugation. Certainly, Kharasch has shown that hydrogen iodide and normal hydrogen bromide addition to the allyl bromide takes place entirely by method (I); but other reagents that add to the double link may behave differently. In the case of bromine addition an approximate estimate may be made of the relative contributions of the two reactions. From a consideration of the velocities of halogen addition to $CHPh{:}CH{\cdot}CO_2H$ and $CH_2{:}CH{\cdot}CO_2H$, the same ratio of velocities being assumed for $CHPh{=}CH{\cdot}CH_2Cl$ and allyl chloride reacting as $CH_2{=}CH{\cdot}CH_2Cl$, bromine addition proceeding by method (II) would represent 12% of the total reaction. Although, therefore, bromine addition to the compounds $CH_2{:}CH{\cdot}CH_2X$ is directed chiefly by mechanism (I), just as in the compounds $Ph{\cdot}CH_2X$ halogen substitution is chiefly in the *p*,*o*-positions, there may also be an appreciable contribution from reaction by method (II).

EXPERIMENTAL.

The following compounds were used in the investigations: benzyl chloride, b. p. 178—178·5°/758 mm.; benzyl bromide, b. p. 195—197°/749 mm.; benzyl cyanide, b. p. 233—234°/760 mm.; benzene, m. p. 5°; allyl cyanide, b. p. 116—117°/753 mm.

The technique for the experiments was as previously described. Herewith is a typical bromine addition reaction :

M/80-Allyl cyanide + M/80-Br_2 in acetic acid at 25°; reaction mixture 10 ml.; 1-ml. samples titrated with KI and N/80-$Na_2S_2O_3$:

Time (mins.)	0	31·0	120	271	0	60·6	183	330
Titre (ml.)	1·99	1·86	1·39	0·88	1·99	1·67	1·16	0·79

From combined graph, $x = 10\%$, $t = 37$ mins.

Other measurements in acetic acid at 25° are : M/80-allyl cyanide + M/80-Br_2; (i) + M/20-LiCl, $x = 10$, $t = 3·74$; (ii) + M/20-LiBr, $t = 7·2$. In 10% aqueous acetic acid at 0°, M/80-allyl chloride + M/80-Br_2, $x = 50$, $t = 5·4$; M/80-allyl bromide + M/80-Br_2, $x = 50$, $t = 8·4$. In chlorobenzene at 25°, M/40-allyl chloride + M/40-Br_2, $x = 20$, $t = 76$; M/40-allyl bromide + M/40-Br_2, $x = 20$, $t = 112$.

Herewith is a typical chlorine-substitution reaction : M/2-Benzyl bromide + M/20-Cl_2 in 20% aqueous acetic acid at 25°; reaction mixture 10 ml.; 2-ml. samples titrated with KI + N/10-$Na_2S_2O_3$.

Time (mins.)	0	20·7	54·1	0	30·0	45·1	0	75·0
Titre (ml.)	1·98	1·77	1·50	1·95	1·66	1·50	1·97	1·42
Blank (ml.)	1·96	1·91	1·86	1·94	1·89	1·83	1·98	1·92

From combined graph, $x = 10\%$, $t = 25·7$ mins.

Other results (expressed in minutes) in 20% aqueous acetic acid at 25° : M/2-Benzene + M/20-Cl_2, $x = 10$, $t = 15·5$; M/2-benzyl chloride, + M/20-Cl_2, $x = 10$, $t = 20·4$; M/2-benzyl cyanide + M/20-Cl_2, $x = 10$, $t = 92·1$.

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