35. *The Kinetics of Halogen Addition to Unsaturated Compounds. Part VI. The Allyl Halides: Lithium Chloride and Hydrogen Bromide Catalysis.*

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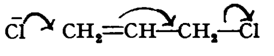
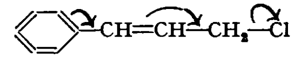
Allyl chloride and bromide add bromine in acetic acid solution at a slower rate than allyl benzoate, and their reactions are accelerated by hydrogen bromide and considerably so by lithium chloride. These anomalies are not shown by γ-phenylallyl chloride and allyl benzoate. A theory, involving nucleophilic attack on the γ-carbon atom of the system, is proposed. Evidence is also produced to show that HBr_3 addition, when there is considerable electron accession to the ethylenic system, may take place by an electrophilic mechanism.

ALLYL chloride and bromide differ in certain respects from related compounds in their mode of bromine addition. Nozaki and Ogg (*J. Amer. Chem. Soc.*, 1942, **68**, 709) showed that addition of bromine to the former in acetic acid solution is much accelerated by lithium chloride, and implied that such behaviour is typical. They accordingly formulated a general mechanism for bromine addition, involving the simultaneous attack by an ion (OAc^-, Cl^-, or Br^-) and the bromine molecule. The normal influence of lithium chloride in electrophilic addition of bromine in acetic acid solution appears to be a small acceleration. As acetic acid has a low dielectric constant, and lithium chloride acts as a strong electrolyte in this solvent, a salt effect is possible, and this has been proposed to explain the similar relatively small acceleration observed by us for bromine and chlorine substitution (J., 1943, 279). On the other hand, lithium chloride considerably accelerates bromine addition to allyl chloride and bromide. The ratios of the rates of catalysed reactions for M/80-acid + M/80-bromine + M/20-lithium chloride to the uncatalysed reactions in acetic acid at 24° are :

$CH_2{:}CH{\cdot}CH_2Br$	$CH_2{:}CH{\cdot}CH_2Cl$	$CHPh{:}CH{\cdot}CH_2Cl$	$CH_2{:}CH{\cdot}CH_2{\cdot}OBz$
5·5	6·3	1·3	1·9

The accelerations with allyl bromide and allyl chloride are so considerable that a change in mechanism is indicated, and correspondingly there is a change, as determined from the initial rates at different concentrations, with respect to A + Br_2 (where A = the acid), from third-order towards second-order kinetics. Especially significant is the difference between allyl chloride and its γ-phenyl derivative. An attack by the chloride ion

(A.) 

(B.) 

on allyl chloride (cf. Hughes, *Trans. Faraday Soc.*, 1941, **37**, 630) may be represented by (A). The ion thus formed, owing to its negative charge, would be susceptible to electrophilic attack by bromine. With (B), on the other hand, tautomeric displacement through the phenyl group reduces the positive charge on the γ-carbon atom, and so lessens the attack by chloride ions. Consequently, the mechanism for the action of bromine on allyl chloride in the presence of lithium chloride could be expressed by

$$A + Cl^- \rightleftarrows \bar{A}Cl \xrightarrow{Br_2} AClBr + Br^-$$

Nozaki and Ogg (*loc. cit.*) find that hydrogen bromide accelerates bromine addition to allyl chloride in acetic acid solution, and they regard this as the normal behaviour. Some compounds, however, may show the reverse effect, as is illustrated by the following ratios of velocities for M/80-reactants plus M/20-hydrogen bromide to the uncatalysed reactions in acetic acid at 24° :

$CH_2{:}CH{\cdot}CH_2Br$	$CH_2{:}CH{\cdot}CH_2Cl$	$CHPh{:}CH{\cdot}CH_2Cl$	$CH_2{:}CH{\cdot}CH_2{\cdot}OBz$
2·1	2·3	0·27	0·67

These reactions were further examined with different amounts of hydrogen bromide, and these results are shown as bimolecular coefficients :

$[HBr]/[Br_2]$.	0.	1.	4.	8.	16.
(I) $CH_2{:}CH{\cdot}CH_2Cl$, k_2 (x = 20)	1·6	3·6	3·8	3·8	—
(II) $CH_2{:}CH{\cdot}CH_2Br$, k_2 (x = 20)	1·0	—	2·2	2·2	—
(III) $CH_2{:}CH{\cdot}CH_2{\cdot}OBz$, k_2 (x = 20)	13·8	13·5	9·2	8·5	8·3
(IV) $CHPh{:}CH{\cdot}CH_2Cl$, k_2 (x = 50)	58	—	16	14	—

As the rates become constant with increasing amounts of hydrogen bromide, it is concluded that the catalysed reactions take place by HBr_3 addition. It is apparent that the reactions of compounds (I) and (II), which show considerable catalysis by lithium chloride, are accelerated by hydrogen bromide, and the reverse is true for (III) and (IV), the reactions of which are not considerably catalysed by lithium chloride. For (I) and (II), this is regarded as indicating a nucleophilic attack by HBr_3. The theoretical rates of nucleophilic addition are (I) > (II) > (III). There thus appears to be a change in mechanism in the series, and HBr_3 addition to allyl benzoate is therefore considered to be electrophilic in character (as for ββ-dimethylacrylic acid, Part V). Similarly, the nucleophilic rates should be (I) > (IV), and the reverse effect is explained if HBr_3 addition to phenylallyl chloride proceeded by an electrophilic mechanism. With regard to (I), although the nucleophilic mode of reaction appears to be dominant, it is reasonable to assume, by comparison with (III), that it is accompanied by a certain amount of simultaneous electrophilic HBr_3 addition. With reference to this dual mechanism, allyl chloride shows in its reactivity an analogy with benzyl chloride, which for similar reasons, *viz.*, the electron-repelling and electron-attracting power of the CH_2Cl group, undergoes *op*- as well as *m*-substitution.

The expected electrophilic order for the relative velocities of uncatalysed bromine addition to allyl compounds in acetic acid is benzoate ≫ bromide > chloride, whereas the experimental result is benzoate ≫ chloride > bromide. Bromine addition to allyl bromide and allyl chloride, owing to hydrogen bromide formed in the reaction by the partial addition of acetate ions in the process, is autocatalytic. This autocatalysis is more pronounced for allyl chloride than the bromide, and thus tends to reverse the relative order of these two compounds; but this alone does not seem sufficient to cause the reversal in rate. There is the further possibility that the velocities of these two compounds are determined in part by a nucleophilic attack by the solvent. In this connection, it is significant that the order remains unaltered for the bimolecular bromine addition in aqueous acetic acid. In carbon tetrachloride there is the normal electrophilic order, as is seen from the initial rates (l.g.-mol.$^{-1}$, min.$^{-1}$) at 15° : allyl bromide, k_2 ($x = 20$), 0·030; allyl chloride, k_2 ($x = 20$), 0·017 (Juvala, *Ber.*, 1930, **63**, 1998).

EXPERIMENTAL.

The compounds used were allyl bromide, b.p. 67—68°/754 mm.; allyl chloride, b.p. 44·0—44·5°/744 mm.; γ-phenylallyl chloride, b.p. 122°/18 mm. Owing to their sensitivity to light, allyl chloride and bromide were weighed in a dim light. The solutions in acetic acid were stable, showing identical rates when freshly prepared and after being kept. The semi-micro technique was employed, and reactions were carried out in the dark. Data for a typical experiment were :

M/50-*Allyl chloride* + M/50-*bromine in acetic acid at* 24°.

Reaction mixture, 10 ml.; 2-ml. samples titrated with 0·02N-$Na_2S_2O_3$.

Time, mins.	0	1·6	4·4	8·0
Titre, ml.	3·97	3·67	3·23	2·64

From curve : at $x = 20\%$, $t = 4·7$; second expt., $x = 20\%$, $t = 4·8$.

Other results for allyl chloride in acetic acid at 25° are : times (mins.) for $x = 20$: reactants 0·04M, $t = 1·06$; 0·0125M, $t = 12·7$; 0·0125M + 0·05M-HCl, $t = 10·2$; 0·0125M + 0·05M-H_2SO_4, $t = 8·4$; 0·0125M + 0·05M-HBr, $t = 5·3$; 0·0125M + 0·05M-LiCl, $t = 2·0$.

The order for the reaction between allyl chloride and bromine (0·04—0·02M) was $n = 3·2$, somewhat higher than the values, 3·0—3·1, obtained for other compounds over this concentration range. This higher value is possibly to be attributed to the disturbing effect of hydrogen bromide catalysis. Nozaki and Ogg (*loc. cit.*, Table II) give rates that show for the same range $n = 3·7$, whereas the rates (Tables III and IV) show $n = 3·3$. Since the reaction is autocatalytic, owing to hydrogen bromide formation, it is necessary to evaluate n for the same initial percentage change. As a result of this autocatalysis the reaction shows rising bimolecular coefficients : M/80-allyl chloride + M/80-bromine, k_2 ($x = 10$) 1·5; k_2 ($x = 50$) 1·8. Nozaki and Ogg (Table I) show for the same reaction at 0·008M, constant bimolecular coefficients (*ca.* 0·020, with seconds as the time unit), whereas the conventional method of calculation (times from $x = 0$) gives from the smoothed curve k_2 ($x = 20$), 0·026; k_2 ($x = 60$), 0·050.

Allyl bromide + bromine ($x = 20$) : 0·04M, $t = 1·48$; 0·02M, $t = 6·6$; 0·0125M, $t = 19·3$; 0·0125M + 0·05M-HBr, $t = 9·2$; 0·0125M + 0·1M-LiCl, $t = 1·75$.

γ-Phenylallyl chloride + bromine ($x = 50$) : 0·0125M, $t = 1·39$; 0·125M + 0·05M-HBr, $t = 4·9$; 0·0125M + 0·1M-HBr, $t = 5·6$; 0·0125M + 0·05M-LiCl, $t = 1·0$; 0·0125M + 0·05M-HCl, $t = 1·37$.

Allyl benzoate + bromine ($x = 20$) : 0·0125M, $t = 1·45$; 0·0125M + 0·05M-HBr, $t = 2·13$; 0·0125M + 0·1M-HBr, $t = 2·30$; 0·0125M + 0·2M-HBr, $t = 2·27$. In these experiments fission of hydrogen bromide is excluded, as the same rates were found immediately on adding hydrogen bromide to the allyl benzoate in acetic acid, and on keeping the solutions.

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