The Kinetics of Aromatic Halogen Substitution. Part X. The Intermediates involved in Halogenation in Acetic Acid Solution.*

By P. W. ROBERTSON.

[Reprint Order No. 4820.]

The influence of electrolytes on halogenation by solutions of halogen in acetic acid solution indicates that positive halogen ions and halogen acetates play no part in the reactions. Electrolytes appear to act by an activity effect promoting the anionisation of a halogen atom from the intermediate, ArH,X_2. The differences between mechanisms involving X_2 and X^+ are discussed.† Measurements of the influence of added hydrogen bromide on the rate of bromination of mesitylene show that the termolecular reaction, $A + 2Br_2$, is changed with excess of hydrogen bromide into a bimolecular reaction, $A + Br_2$, catalysed by hydrogen bromide.

THROUGHOUT the present series of investigations, and in the parallel series on halogen addition, we have interpreted the experimental evidence as indicating that the initial halogen attack is by a neutral halogen molecule. In certain kinetic studies the possible participation of other entities has been examined in detail. Bartlett and Tarbell (*J. Amer. Chem. Soc.*, 1936, **58**, 466), for instance, have shown that, in the action of bromine on stilbene in methyl-alcoholic solution, the compound BrOMe plays no part. Again, Bradfield and Brynmor Jones (*Trans. Faraday Soc.*, 1941, **37**, 734) and Bradfield, Davies, and Long (*J.*, 1949, 1389) concluded that, in the bromination of phenol ethers in acetic acid solution containing 25% of water, the electrophilic reagent is the bromine molecule, Br_2, or Br_4, rather than such possible intermediaries as BrOH, BrOAc, or " positive " bromine. Similarly for chlorination it was concluded by Bradfield and Brynmor Jones (*Trans. Faraday Soc.*, 1941, **37**, 726) that no mechanism other than the direct interaction between chlorine and the phenol ether comes into play. Our own studies, more particularly with regard to the effect of electrolytes on the rates (Parts I, II, and V, *J.*, 1943, 276, 279 ; 1949, 294), are in agreement with this interpretation. Such a view, however, has not been universally accepted. For instance, Baker (" Hyperconjugation," Oxford Univ. Press, 1952, p. 52), discussing our results, writes " . . . in halogenation many different potential sources of Cl^+ may be acting simultaneously, and until it is possible to study both comparative rate and orientation data under experimental conditions when only a single halogenating entity is operative, no reliable conclusions can be drawn." With reference to bromination in acetic and aqueous acetic acid it is stated by Ingold (" Structure and Mechanism in Organic Chemistry," G. Bell and Sons Ltd., London, 1953, p. 289) : " In these media it seems certain that molecular bromine is one of the effective bromine carriers; but there are complications that have not been fully elucidated; and it is not clear what part, if any, the expected carrier acetyl hypobromite plays in these brominations." Certain results, hitherto unpublished, which are of diagnostic value with regard to the mechanisms of bromination, are now presented, together with a formal review of the evidence that has a bearing on the nature of both chlorination and bromination.

In chlorination the rates are not disturbed by the concurrence of higher-order reactions as in bromination, nor is there intervention, to any appreciable extent, of the subsidiary reaction, $Cl_2 + HCl \rightleftharpoons HCl_3$. Added electrolytes show a small positive catalysis, which is in the order of their conductivities, $HClO_4 > LiCl \approx HCl > NaOAc$, becoming very slight for the last compound. This is considered (Part V, *loc. cit.*) to be a salt (activity) effect, such as is found in other halogenation reactions, addition as well as substitution, in acetic acid solution. These activity effects become less in aqueous acetic acid in accordance with theoretical expectation.

The slight influence of Cl^- ions (*i.e.*, as added LiCl or HCl) shows that a mechanism

---

* Part IX, *J.*, 1953, 782. † In this paper, except where otherwise specified, the symbol X^+ is used to imply either the free ion or the form in which it is covalently attached to a solvent molecule HOAc, or possibly H_2O in the aqueous solutions.

involving Cl^+ ions is not possible. The equilibrium, $Cl^+ + Cl^- \rightleftharpoons Cl_2$, is displaced almost completely to the right, so that the concentration of Cl^+ ions in the reacting mixtures must be virtually zero. The possibility that there might be initially an exceedingly small concentration of very highly reactive Cl^+ ions is also excluded, since in that case the HCl formed in the substitution would immediately destroy the reactive reagent, and the initial bimolecular rate would fall off rapidly. Actually the bimolecular coefficients gradually increase owing to the catalytic effect of the HCl formed in the reaction.

It has also been suggested that chlorine acetate may be an intermediate in the reactions, either as such or as the protonated molecule. In the first instance the expected mode of formation would be represented :

$$Cl_2 + HOAc \rightleftharpoons ClOAc + H^+ + Cl^- \rightleftharpoons HCl + ClOAc$$

As the chlorine is in very large excess over the chlorine acetate, then, the kinetic form being $-d[Cl_2]/dt = k[ArH][Cl_2]$, this equilibrium would have to be established rapidly. The addition to the solution of HCl (or of H^+ or Cl^- ions) would cause displacement to the left and so reduce the rate of reaction. Since HCl does not have this effect, it follows that chlorine acetate is not an essential intermediate.

A second possible route is through the rapidly established equilibrium

$$Cl_2 + HOAc \rightleftharpoons ClOAcH^+ + Cl^-$$

Again, a reaction proceeding by this route, and having the kinetic form, $-d[Cl_2]/dt = k[ArH][Cl_2]$, would be impeded by Cl^- ions, as is contrary to the facts. Hence $ClOAcH^+$, like Cl^+ and ClOAc, cannot be regarded as an essential intermediate.

Such theoretical conclusions have now received direct experimental confirmation, since recently chlorine acetate has been prepared in acetic acid solution, and its kinetics have been investigated by de la Mare, Ketley, and Vernon (*Research*, 1953, **6**, 12*S*). Its solutions are immediately decomposed by Cl^- ions, and in its reactions it is " enormously catalysed by mineral acids." It thus differs markedly from a solution of chlorine, for which acids and bases (NaOAc) are not specific, and Cl^- ions have merely a slight positive effect.

In general, similar arguments can be used to prove that neither Br^+ ions nor bromine acetate can be intermediates in the bromination by bromine in acetic acid solution. Although no kinetic experiments on bromine acetate have been reported, it is very probable that it would react in a similar manner to chlorine acetate, and show strong acid catalysis. This is not a characteristic of aromatic bromination; the influence of added electrolytes is relatively small, and, as for chlorination, in the order of their relative conductivities, *viz.*, $HClO_4$ ($\approx LiClO_4$) > LiCl > NaOAc.

Whereas in chlorination the effect of Cl^- ions is in accord with the non-intervention of chlorine acetate in the reactions, their effect in bromination offers less certain evidence, since with bromine acetate, or Br^+ ions, they would form bromine chloride, which is a more reactive reagent than bromine. Such a possible ambiguity in interpretation may be avoided by the study of the effect of Br^- ions on the reaction. Accordingly, we report data on the bromination of mesitylene in the presence of varying amounts of HBr. The investigation is confined to the early stages of the reaction, and, in accordance with previous practice, the times at $x = 10\%$ bromine absorption are taken as a measure of the relative initial rates (Figs. 1, 2).

The interpretation of these experimental results is that added HBr gradually converts the third-order bromination ($A + 2Br_2$) into a reaction of the second order ($A + Br_2$). This is in part due to the removal of the bromine as unreactive HBr_3, thus eliminating the third-order reaction, which is favoured by a high concentration of bromine, but more especially to the establishment of a second-order reaction catalysed by hydrogen bromide. Under the conditions when the relative rates become approximately constant with increasing amounts of HBr, the equilibrium in the reaction, $HBr + Br_2 \rightleftharpoons HBr_3$, is shifted largely to the right, so that the rate expression becomes $\sim k[A][Br_2][HBr]$. This, however, does not mean that the HBr is taking an integral part in the reaction, one molecule being involved for each molecule of bromine, but that its catalytic effect happens to be equivalent per molecule to one molecule of bromine under the experimental conditions. The rate expression is more correctly ($k + k'$[HBr])[A][Br_2], and there is also a contribution from the reaction whose rate is given by ($k + k''$[HBr_3])[A][Br_2].

It is clear that hydrogen bromide acts as a positive catalyst. This result, together with the facts that the reaction is not strongly acid-catalysed and that its rate is not reduced by added sodium acetate, indicate that neither bromine acetate nor Br^+ ions can be intermediates in aromatic bromination in pure acetic acid. A similar conclusion was reached by Bradfield, Davies, and Long (*loc. cit.*) for 25% aqueous acetic acid, and our kinetic measurements in this mixed solvent have been carried out within the concentration range containing 10—20% of water.

FIG. 1. *Mesitylene* M/80 + *bromine* M/80.

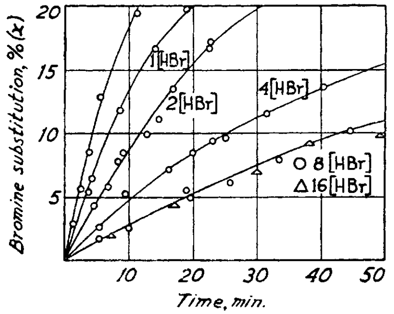
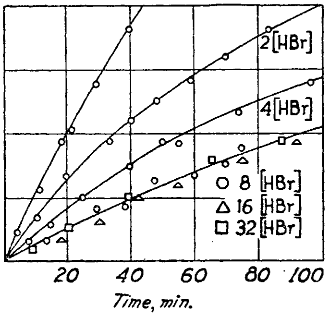


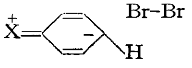
FIG. 2. *Mesitylene* M/160 + *bromine* M/160.



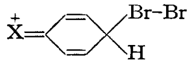
Not only is the effect of catalysts in halogenation not in accord with the intervention of halogen acetates, but it is in agreement with a mechanism according to which there is a direct electrophilic attack by the halogen molecule on the organic compound. For example, the reaction with bromine would proceed :

$$ArH + Br_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ArH,Br_2 \xrightarrow{k_3} Br^- + ArHBr^+ \xrightarrow{k_4} ArBr + H^+$$

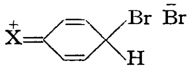
The structures (I), (II), and (III) are among those that contribute to the intermediate.



(I)



(II)



(III)

The final stage (k_4) is too rapid to affect the rate * which consequently becomes equal to $(k_1/k_2)k_3$[ArH][Br_2]. The magnitude of k_3 will be increased by any factor that promotes the anionisation of the bromine, *viz.*, (*a*) added water (solvating effect), (*b*) electrolytes (activity effect), (*c*) iodine, which acts as IBr and forms the IBr_2^- ion, and (*d*) increase in the concentration of the bromine, which promotes the formation of Br_3^- ions.†

When the environmental factors are kept constant, and a comparison is made in a series of compounds PhX, where the group X has $+T$ characteristics, the electronic flow from X influences the rate by its effect on k_1/k_2. The impulse is relayed from atom to atom, as indicated in the resonance structures (I—III), and finally assists in the anionisation of the bromine. A change in the group X thus involves a change, in the same sense, in both k_1/k_2 and k_3. In this way may be explained the large spread in rates observed for such reactions, the relative values varying for instance from 10^{18} for Ph·NMe_2 to unity for

---

[*] This is probable since sodium acetate, a base in acetic acid, causes little acceleration. Melander (*Arkiv Kemi*, 1950, **2**, 213) by an independent method proved that the removal of the proton was not a rate-determining stage in aromatic bromination.

[†] The effects represented by *a* and *b* are in competition with *d*, and tend to reduce the reaction order, as is found experimentally. Consequently, in acetic acid solution the third-order reaction would appear to proceed, $A + Br_2 \rightleftharpoons A,Br_2 \xrightarrow{Br_2}$ Products, in preference to the alternative scheme, $A + Br_4 \rightleftharpoons Br_2 + A,Br_2 \longrightarrow$ products, which shows similar kinetics (Part I, *loc. cit.*; Part IV, *J.*, 1948, 100).

PhH (Part IX). Such a spread in rate becomes greatly reduced in bromination *via* the Br^+ ion, which proceeds according to the scheme :

$$ArH + Br^+ \xrightarrow{k} ArHBr^+ \xrightarrow{\text{Rapid}} \text{Products}$$

As an example of such a difference in rate-ratio may be cited the cases of toluene and benzene, the value for Br_2 being 470 (Berliner and Berliner, *J. Amer. Chem. Soc.*, 1949, **71**, 1195), and for the Br^+ ion 20 (de la Mare, Ketley, and Vernon, *loc. cit.*).

When, however, for a compound PhX, where X has $+T$, $-I$ characteristics, the rate is less than the rate for benzene, then the inductive effect has a relatively greater influence on the rate than the tautomeric effect. Under these conditions the spread in rate, with reference to benzene, may become greater for the ionic than for the molecular mechanism. In an extreme case the rate relative to that of benzene may be even reversed. Thus fluorobenzene reacts less rapidly than benzene with acidified hypochlorous acid in acetic acid containing water (ionic mechanism ; de la Mare, Ketley, and Vernon, *loc. cit.*), whereas the reverse order has been found for chlorination by chlorine in aqueous acetic acid (Part IV). In this respect the reagent yielding positive chlorine behaves similarly to nitric acid, which on nitration reacts through the nitronium ion.

Another difference between the molecular and the ionic mode of bromination is in the amounts of *meta*-substitution. Although direct measurements have not been made, there is sufficient evidence to predict their magnitude. From the relative rates of bromination of mesitylene and pentamethylbenzene the partial rate factor in a position *meta* to a methyl group may be calculated to be 3·6. This value with toluene–benzene ratio for bromination gives the amount of *m*-bromotoluene formed in this reaction as 0·26%. On nitration (toluene to benzene, 25 : 1) there is 3·2% of *meta*-substitution, and it has been shown by Brown and Nelson (*J. Amer. Chem. Soc.*, 1953, **75**, 6292) that with decrease in the rate-ratio of toluene to benzene with different reagents the *meta*-substitution of toluene increases. Consequently, on bromination with the Br^+ ion (toluene to benzene, 20 : 1) the amount of *m*-bromotoluene formed must be more than 3·2%, *i.e.*, a considerably greater amount than that produced by molecular bromination.

These differences are characteristic and considerable, and strengthen the view that the participation of the ionic mechanism in halogenation by solutions of chlorine or bromine, if any at all, must be slight. The kinetic evidence based on the effect of electrolytes is, however, decisive, and neither in bromination by bromine nor in chlorination by chlorine can halogen acetate or positive halogen ion be considered to play a part. Thus, contrary to Baker's opinion (*op. cit.*), halogenation data are available for constitutional studies. In chlorination, certainly, our own experiments, as well as the earlier measurements of Orton, Bradfield, Brynmor Jones, and their co-workers, have been carried out under conditions where only a single halogen entity is operative. In bromination, on the other hand, reactions of different kinetic order may proceed simultaneously, but comparative measurements with a series of compounds have always been carried out under conditions in which the kinetic forms were identical. When comparisons have been possible with the corresponding rates of chlorination, similar rate-sequences have been observed, and even small differences in rate have been reproduced (see, *e.g.*, Orton, Bradfield, and Brynmor Jones, *J.*, 1929, 2810).

Experimental.—The experimental technique is as described in previous communications. The figures in the text are from measurements by (the late) R. M. Dixon. It was shown by I. J. Lambourne that pentamethylbenzene behaved in a similar manner to mesitylene, giving rates of bromination which became constant with increasing amounts of added hydrogen bromide. The rate-ratio for the two compounds with bromine (reactants M/80 and hydrogen bromide M/10) was 4·7, the previously found value (Part II, *loc. cit.*) for the reaction without hydrogen bromide being 4·3. This value was used for the calculation of the partial rate factor for a *meta*-position due to one methyl group in pentamethylbenzene, and consequently also in toluene, *viz.*, $\sqrt{3 \times 4{\cdot}3} = 3{\cdot}6$.

VICTORIA UNIVERSITY COLLEGE,
WELLINGTON, NEW ZEALAND.

[*Received, November 20th*, 1953.]