Tetrahedron Letters No. 20, pp. 1659-1662, 1971. Pergamon Press. Printed in Great Britain.

CHLORINATION ACCOMPANYING BROMINATION IN THE REACTION BETWEEN BROMINE AND ALKYLBENZENES IN THE PRESENCE OF LITHIUM CHLORIDE.[1] THE ROLE OF THE EQUILIBRIUM:

$$2Cl^- + Br_2 \rightleftharpoons 2Br^- + Cl_2$$

Enrico Baciocchi and Luigi Mandolini
Istituto Chimico, Università di Roma, and Centro C.N.R.
dei Meccanismi di Reazione, 00185 Roma, Italy

(Received in UK 23 March 1971; accepted in UK for publication 6 April 1971)

It has recently been shown that electrophilic side-chain bromination of hexamethylbenzene in acetic acid occurs by a step-wise mechanism, where the slow step is the base-catalysed decomposition of the intermediate σ-complex.[2] In connection with further investigation of this reaction to determine the catalytic effect of different bases, we have now found that catalysis by lithium chloride is apparently much more effective than catalysis by sodium acetate in the initial part of the reaction, despite the fact that CH_3COO^- is a much stronger base than Cl^-. Moreover, in the presence of lithium chloride, side-chain chlorinated and brominated products are formed in the reaction between bromine and hexamethylbenzene. Data and comments on these findings are reported here.

Hexamethylbenzene (0.01M) was made to react with bromine (4×10^{-3}M) in acetic acid, in the dark, at 30°. Plots of bromine concentration versus time are reported in Figure 1 and refer to runs carried out without any salt added (Figure 1A), in the presence of lithium chloride (0.05M) (Figure 1B), and of sodium acetate (0.05M) (Figure 1C).

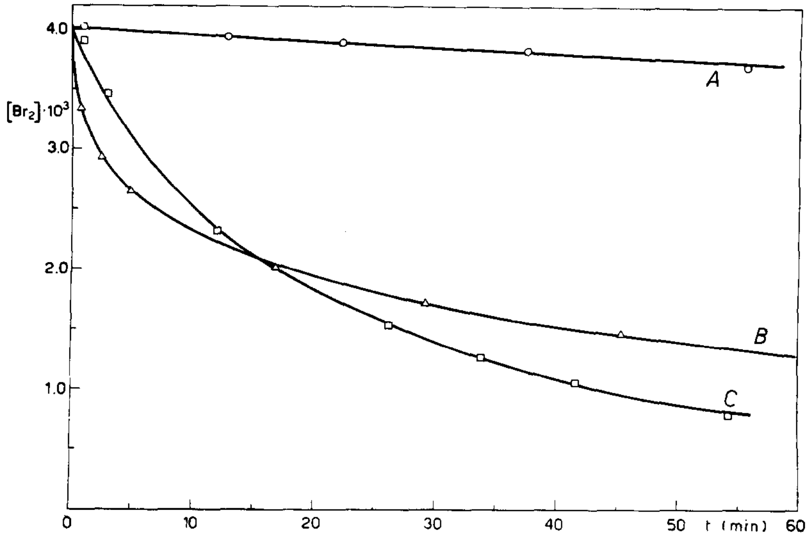

FIG. 1. Plots of $[Br_2]$ vs time for runs under various conditions (see text)

Comparison of Figures 1B and 1C clearly shows that the initial disappearance of Br_2 is much faster in the presence of LiCl than in the presence of an equal concentration of CH_3COONa. Times taken to reach 20% reaction are 70 and 250 sec., respectively. However, the decrease in rate as the reaction proceeds is much greater in the former case, as is shown by the fact that Figures 1B and 1C intersect at about 45% of reaction. The rapid fall in the rate-accelerating effect of LiCl is attributed to an anti-catalytic effect of Br^- ions which are formed in the course of the reaction. Accordingly, in the presence of LiBr, the initial rate-accelerating effect of LiCl decreases significantly. Times taken to reach 20% reaction are 25 sec. with LiCl (0.1M), and 145 sec. with LiCl (0.1M) and LiBr (2×10^{-3}M). The crude reaction product isolated at the end of the reaction was treated with NaOH in EtOH and the liberated halides were determined potentiometrically. It was found that side-chain chlorinated and brominated compounds were formed in a ratio of about 4 : 1. The possibility that such a ratio was due to an exchange reaction between Cl^- and previously formed bromomethylpentamethylbenzene was not tested; however, it seems very unlikely considering the short reaction times and low temperature used.

Rate data and the nature of the reaction products may be rationalised by assuming the intervention of equilibrium (1) in the systems containing LiCl and Br_2. The value of the equilibrium constant in acetic acid should not be

$$2Cl^- + Br_2 \rightleftharpoons 2Br^- + Cl_2 \qquad (1)$$

far from the value of 10^{-10}, calculated on the basis of the redox potentials[3] in water of the couples Cl_2/Cl^- and Br_2/Br^-. According to this figure, it is possible to estimate that under the conditions used (e.g., $[Br_2] = 4 \times 10^{-3}M$, $[LiCl] = 0.1M$) the chlorine concentration is about $1 \times 10^{-5}M$. Since the reactivity of Cl_2 in electrophilic side-chain halogenation exceeds that of Br_2 by a factor[2,4] of more than 10^6, the estimated concentration of chlorine is sufficient to account for both the surprisingly high initial rate observed in the reactions carried out in the presence of LiCl, and the formation of relevant amounts of chlorinated materials. Of course, as the reaction proceeds, Br^- ions are formed and these rapidly produce a decrease in the chlorine concentration (which depends on $[Br^-]^{-2}$); as a consequence a rapid decrease in the rate is observed.

Further, definite confirmation of the possible intervention of equilibrium (1) in the bromination reactions in the presence of LiCl has been obtained by a study of the products formed in the reaction between mesitylene and bromine. Mesitylene ($10^{-3}M$), Br_2 ($10^{-4}M$) and LiCl (0.5M) were made to react in acetic acid. Examination of the crude reaction product, carried out by gas chromatographic analysis, showed the presence of bromomesitylene and chloromesitylene in practically equimolar amounts. Since in this case no exchange reaction can occur between bromomesitylene and LiCl, the chloromesitylene must have come from the reaction of mesitylene with Cl_2, formed according to eq. (1).

Although some quantitative aspects of the problem remain to be studied, the above observations clearly show that Br_2 and LiCl in acetic acid can behave as a chlorinating system towards aromatic substrates for which chlorine reactivity is sufficiently greater than that of bromine. The fact that no rate-accelerating effect by LiCl has been observed in previous studies[5] dealing with salt effects in aromatic bromination is probably due to the fact that in such studies the bromine concentrations were higher than in the present experiment with mesitylene. This causes the bromination to occur according to third-order kinetics with a subsequent reduction in the difference in rate between Cl_2 and Br_2. Moreover, under these conditions, after a small percentage of the reaction has occurred, sufficient Br^- ions are produced to reduce the concentration of chlorine to practically zero.

Finally, the addition of bromine to certain olefins is strongly catalysed by LiCl.[6] Among the diverse hypotheses which have been proposed to explain this, it has been suggested,[7] without any experimental support however, that there is possible formation of the more reactive BrCl by reaction between Br_2 and Cl^- ions. In the light of the present results, we believe that the intervention of equilibrium (1) should be given careful consideration as a possible cause of the observed rate-accelerating effect of LiCl.

Acknowledgement. Grateful acknowledgement is made to Professor G. Illuminati for useful discussions.

REFERENCES

1. Part XXIV of the series "Substitutions in Polymethylbenzenes." Part XXIII E.Baciocchi and L.Mandolini, J.Chem.Soc.(B), 1361 (1967).
2. E.Baciocchi, M.Casula, G.Illuminati and L.Mandolini, Tetrahedron Letters, 1275 (1969).
3. G.N.Lewis and M.Randall, "Thermodynamics", 2nd ed, International Student Edition, McGraw-Hill Book Co., New York, (1965), p. 371.
4. E.Baciocchi, A.Ciana, G.Illuminati and C.Pasini, J.Amer.Chem.Soc., **87**, 3953 (1965).
5. P.W.Robertson, J.Chem.Soc., 1267 (1954); R.M.Keefer, A.Ottenberg and L.J.Andrews, J.Amer.Chem.Soc., **78**, 255 (1956).
6. P.B.D. de la Mare and R.Bolton, "Electrophilic Addition to Unsaturated Systems", Elsevier Publishing Co., London (1966), p. 119.
7. H.P.Braendlin and E.T.McBee, "Friedel-Crafts and Related Reactions," G.A. Olah, ed., Vol. III, Part 2, Interscience Publishers, New York (1964), p. 1566.