537. *Acylation. Part XI.* The Addition of Hydrogen Bromide to Isopropenyl Acetate in Chlorobenzene.*

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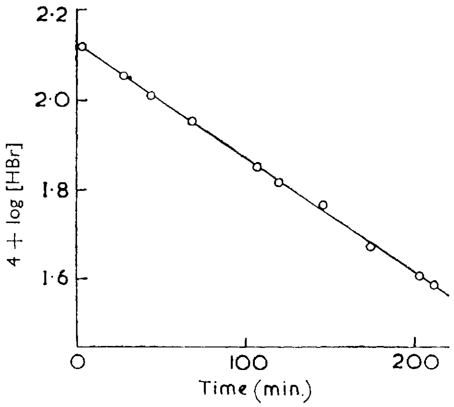
The polar addition of hydrogen bromide to isopropenyl acetate in chlorobenzene solution is kinetically of the first order in both reactants. Therefore facilitation of hydrogen bromide heterolysis through HBr_2^- formation does not occur in this context. Possible reasons are given.

In non-aqueous solvents isopropenyl acetate acylates hydrogen halides: [1,2]

$$CH_2{:}CMe{\cdot}CO{\cdot}CH_3 + HHal \longrightarrow Me_2CO + CH_3{\cdot}CO{\cdot}Hal.$$

Possible details of this process in acetic acid have been previously discussed.[2] We report here briefly the kinetics in chlorobenzene, a solvent of similar dielectric constant but lacking the hydrogen-bonding and co-ordinating properties of acetic acid.



Example of first-order disappearance of hydrogen bromide. (Initial [Ester] = 0·788M.)

In chlorobenzene hydrogen chloride reacts very slowly. Our experiments were therefore confined to hydrogen bromide. Specimen kinetic results are represented in the Table and Figure. Other features of the reaction are described in the Experimental section, where it is also shown that "abnormal" addition of hydrogen bromide is probably unimportant under the conditions used. The results have three main features: (i)

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* Part X. Satchell, *J.*, **1963**, 564.

[1] Hagermayer and Hull, *Ind. Eng. Chem.*, 1949, **41**, 2920.

[2] Jeffery and Satchell, *J.*, 1962, 1876.

reaction between hydrogen bromide and isopropenyl acetate is notably slower in chlorobenzene than in acetic acid;[2] (ii) the reaction is closely of the first order in ester (see Table); (iii) it is also of the first order in hydrogen bromide (see Figure). In addition, the rates are reproducible with different batches of starting materials, and the experimental first-order plots were excellent straight lines.

Reaction between hydrogen bromide and isopropenyl acetate in chlorobenzene at 25°.

$k_{obs.}$ = observed first-order rate constant.

[Ester] (M)	0·270	0·526	0·767	0·788	0·766 *
[HBr] (M)	0·0212	0·0206	0·0200	0·0133	0·0200 *
$10^3 k_{obs.}$ (min.$^{-1}$)	2·1	4·0	5·8	5·6	5·9

* Reaction initiated by addition of hydrogen bromide rather than ester.

The observed order in hydrogen bromide means that only one molecule of this substance enters the transition state, *i.e.*, that ion-pairs containing HBr_2^- are not involved (in chlorobenzene the dominant participation of free ions is most unlikely). Set against the background of previous work in non-aqueous media[3-6] this result is rather surprising. For, while few kinetic studies of any kind concerning hydrogen chloride and bromide have been reported, those which have, and which concern hydrogen chloride, usually contain evidence for the involvement of the interaction $[Cl \cdots HCl]^-$ at some stage; studies with hydrogen bromide, although very limited[3,5,6] and hardly compelling, also imply electrophilic stabilisation of bromide by hydrogen bromide as a common occurrence. The cleavage of hydrogen bromide in the present context would therefore be expected to be aided by another molecule of the acid. This would mean second-order dependence on hydrogen bromide. Yet we did not observe this in acetic acid,[2] nor do we now in chlorobenzene. In acetic acid the result is acceptable because bromide ions may be largely stabilised by hydrogen-bonding from the solvent; in chlorobenzene it seems significantly anomalous.

We know of one similar case of first-order involvement of hydrogen bromide. It concerns the catalysed depolymerisation of trioxan in decalin.[5] However, this process is significantly different from the present reaction since its rate increases as the co-ordinating power of the solvent is reduced. It is possible that complete ionisation of the catalyst is not necessary for the depolymerisation, and bromide stabilisation therefore is less important.

The most relevant comparison available is perhaps to the polar addition of hydrogen bromide to propene in heptane,[3] for the present reaction may proceed by addition to the double bond, followed by intramolecular rearrangement.[2,7] Although the propene results are qualitative, evidence exists for an order in hydrogen bromide greater than unity. An important feature is that water reduces this order (probably to unity). An obvious interpretation of our results is, therefore, that sufficient water was present in our (dried) materials to render stabilisation of bromide by hydrogen bromide unnecessary, water molecules taking the latter's place. This is possible. Two facts seem to us, however, to argue strongly against it. First, the rate could then reasonably be expected to depend on the amount of water present, and so become irreproducible. This is not the case. Secondly, the product acetyl bromide reacts with water, even in benzene,[8] at a significant rate. This would disturb the kinetics. The plots, however, are good straight lines.

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[3] Mayo and Katz, *J. Amer. Chem. Soc.*, 1947, **69**, 1339; Mayo and Savoy, *ibid.*, p. 1348.

[4] *E.g.*, Patai and Zabricky, *J.*, 1961, 5479; Hart and Cassis, *J. Amer. Chem. Soc.*, 1954, **76**, 1634; Andrews and Keefer, *ibid.*, 1961, **83**, 3708; Gelles, Hughes, and Ingold, *J.*, 1954, 2918; de la Mare, Ingold, and Pocker, *J.*, 1954, 2937; Leimu and Salomaa, *Acta Chem. Scand.*, 1947, **1**, 353; Swain and Pegues, *J. Amer. Chem. Soc.*, 1958, **80**, 812; Pocker, *J.*, 1960, 1292.

[5] Bell and Burnett, *Trans. Faraday Soc.*, 1939, **35**, 474; Bell and Skinner, *J.*, 1952, 2955.

[6] Satchell, *J.*, 1963, 555.

[7] Wasserman and Wharton, *J. Amer. Chem. Soc.*, 1960, **82**, 661; Euranto and Kujanpaa, *Acta Chem. Scand.*, 1961, **15**, 1209.

[8] Satchell, unpublished observations.

We prefer one or other of the following rationalisations. They both involve stabilisation of the halide ion by the dipolar ester itself. In chlorobenzene and in the presence of a notable excess of isopropenyl acetate (see Table), hydrogen bromide may form (rapidly and in effectively stoicheiometric amount) a 1 : 1 addition complex with the latter which suffers hydrogen bromide cleavage only on interaction with another molecule of ester:

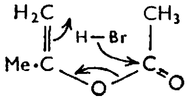
$$CH_2{=}CMe{\cdot}OAc + HBr \rightleftharpoons \text{Complex (C)} \qquad \text{Fast, K}$$

$$CH_2{=}CMe{\cdot}OAc + C \xrightarrow{k} CH_3{\cdot}CBrMe{\cdot}OAc + CH_2{=}CMe{\cdot}OAc \qquad \text{Slow}$$

$$CH_3{\cdot}CBrMe{\cdot}OAc \longrightarrow COMe_2 + AcBr \qquad \text{Fast}$$

$$-\mathrm{d}[\mathrm{HBr}]/\mathrm{d}t = k[\mathrm{C}][\mathrm{Ester}] \approx k[\mathrm{HBr}]_{\mathrm{unreacted}}. \quad [\mathrm{Ester}] = k_{\mathrm{obs.}}[\mathrm{HBr}]$$

This scheme preserves the observed orders and leaves little hydrogen bromide free in the system. Second-order terms in this substance are therefore not to be expected. Similar complexes (*e.g.*, π-complexes between acids and olefins) have often been postulated. Alternatively the equilibrium's position may lie to the left (when [C] = K[HBr][Ester]), being followed directly by a slow (k') intramolecular rearrangement which does not require the help of another hydrogen bromide molecule (cf. A). The orders are again preserved($-\mathrm{d}[\mathrm{HBr}]/\mathrm{d}t = k'[\mathrm{C}]$).


(A)

EXPERIMENTAL

Materials.—" AnalaR " chlorobenzene was dried over, and distilled from phosphorus pentoxide. The ester was a previous sample.[2] Anhydrous hydrogen bromide was prepared as before.[6]

Kinetic Solutions.—Reaction mixtures were made up from a stock solution of hydrogen bromide in chlorobenzene, chlorobenzene, and ester. To provide convenient rates, and to simplify the kinetic form, the ester always had a concentration at least ten times that of the hydrogen bromide. The appearance of the products was followed by observing spectrophotometrically the increase in light absorption at 2950 Å where the solvent, the ester, and hydrogen bromide all absorb negligibly. Thus the rate of loss of hydrogen bromide could be determined. The ground-glass stoppered spectrophotometer-cell served as reaction vessel. Measurements were made with a Beckman D.U. spectrophotometer fitted with thermostat-controlled cell compartment.

Addition of hydrogen bromide to a sample of redistilled chlorobenzene results in the relatively rapid formation of a yellow colour. The resulting solution has strong absorption at 2950 Å. The passage of dry nitrogen through the chlorobenzene sample before addition of hydrogen bromide restricts whatever reaction is involved to very small proportions. Oxidation of hydrogen bromide by dissolved oxygen may underlie the colour formation. Because of it, in the kinetic work both the solvent and the ester were de-oxygenated with dry nitrogen immediately before use. The reproducibility of the rates on different occasions, and for different orders of mixing (which was within ±3%), is illustrated in the Table. A typical first-order plot for loss of hydrogen bromide is shown in the Figure.

Stoicheiometry.—That the observed reaction produces the expected products [1] in high yield is indicated by two observations: (1) The difference between the initial and the final light absorptions in any run corresponded reasonably to that expected on the basis of synthetic product mixtures. (2) The removal of aliquot parts of the reaction mixture at the beginning and the end of the reaction, their extraction with water, and subsequent titration of the aqueous solution for acid content (to phenolphthalein), show (*a*) that the titratable acid at the end is exactly twice that at the beginning and (*b*) that effectively no acidity is lost on dilution of a stock solution of hydrogen bromide with more chlorobenzene. Result (*a*) is expected if the rapidly hydrolysable acetyl bromide is formed quantitatively from hydrogen bromide. It seems therefore that the reaction of hydrogen bromide involves little abnormality. The simplicity of the kinetics also points to this. Result (*b*) shows that, whatever the initial side-reaction is, it probably involves the loss of very little hydrogen bromide.

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