

The Kinetics of Ionic Polymerisations. Part IV. The Action of Iodine Chloride and Iodine Bromide on n-Butyl Vinyl Ether.*

By D. D. ELEY and J. SAUNDERS.

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The polymerisation of *n*-butyl vinyl ether catalysed by iodine monochloride or iodine monobromide obeys third-order kinetics, as found earlier for iodine, but the apparent velocity constant for both interhalogen compounds is only 8 l.² mole.⁻² min.⁻¹ compared with 1800 for iodine. In the case of iodine monobromide, 15% of the observed catalytic velocity is probably due to iodine formed by decomposition, and the true velocity constants probably lie in the order $I_2 > ICl > IBr > Br_2$. These facts are discussed in relation to the halogen-addition reaction, and a mechanism involving a carbonium ion as a common intermediate is proposed.

THE polymerisation of 2-ethylhexyl vinyl ether catalysed by iodine was found to be of first order in monomer and of second order in iodine, and it was suggested that the first step involved the bimolecular ionisation of iodine to give I^+ and I_3^- ions, the I^+ adding to the double bond of the monomer to give a reactive carbonium ion which entered into an ionic polymerisation chain-reaction (Parts I and II, Eley and Richards, *Trans. Faraday Soc.*, 1949, 45, 425, 436). These kinetics held in light petroleum, diethyl ether, and ethylene dichloride, and subsequently were found valid for other vinyl ethers with the additional proviso that at high monomer concentrations the rate became of zero order in monomer, or even started to decrease. This latter behaviour was attributed to binding of iodine in a catalytically inactive π -complex with the double bond of the monomer (Part III, Eley and Saunders, *J.*, 1952, 4167).

Polymers isolated by pumping off monomer and solvents at 60° contained no iodine. At the end of a polymerisation run only 20–50% of the iodine added was titratable, the rest being bound in the polymer as di-iodide or π -complex, and dissociating therefrom at 60°. Bromine analysis showed rather less than one double bond per polymer molecule, which was attributed to some iodination of the "dead" polymer having occurred. Qualitative experiments in this laboratory by A. R. Richards (unpublished report, June 1947) had established that iodine monochloride and bromine acted as catalysts but gave a much slower rate than iodine. This is in contrast to the halogenation of allyl acetate in acetic acid, which follows the same third-order law with rate constants in the relative order: $I_2 (1) < IBr (3 \times 10^3) < Br_2 (10^4) < ICl (10^5) < BrCl (4 \times 10^6)$ (White and Robertson, *J.*, 1939, 1509). It is therefore of great interest to investigate quantitatively the catalytic action of interhalogen compounds on the polymerisation of vinyl ether.

* Part III, *J.*, 1952, 4167.

EXPERIMENTAL

The technique used was that of Eley and Richards (*loc. cit.*), the polymerisations being followed in evacuated, sealed dilatometers at 25°. The dilatometers were opened at 30–40% polymerisation, and the reaction stopped by addition of excess of aqueous sodium thiosulphate, except in the case of the iodine bromide runs. Densities and cryoscopic molecular weights of all polymers were determined (Eley and Saunders, *loc. cit.*).

In runs with iodine bromide the reaction mixture at 30% polymerisation was titrated with sodium thiosulphate to determine "combined halogen." Specimens were analysed for total halogen commercially.

In all runs *n*-butyl vinyl ether was the monomer and diethyl ether the solvent, and these were purified as described in Part I (*loc. cit.*). Iodine monochloride and iodine monobromide

FIG. 1. The time course of polymerisation catalysed by iodine bromide. $[M] = 0.86M$. $[C] = 32.23 \text{ mm}$.

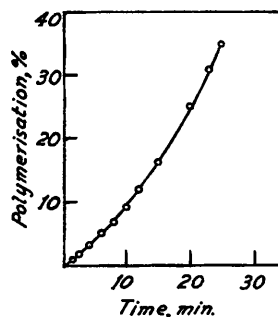
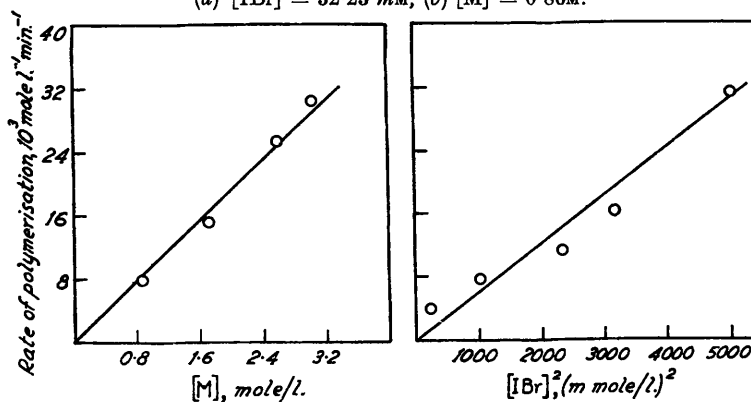


FIG. 2. Effect of catalyst and monomer concentrations on the initial rate with iodine bromide. (a) $[IBr] = 32.23 \text{ mm}$, (b) $[M] = 0.86M$.



were purified by two sublimations (Palmer and Wiig, *J. Amer. Chem. Soc.*, 1952, **74**, 2785), the second into evacuated bulbs which were sealed off for storage. Each bulb contained enough catalyst for two runs, and the ethereal catalyst solution was prepared freshly each day in nitrogen in a dry box. These iodine halides are sensitive to traces of moisture (Cornog and Karges, *J. Amer. Chem. Soc.*, 1932, **54**, 1882), and not only slowly decompose but also react with diethyl ether in both cases liberating iodine (Gillam and Morton, *Proc. Roy. Soc.*, 1931, *A*, **132**, 152; Gillam, *Trans. Faraday Soc.*, 1933, **29**, 1132), so that it is imperative to use fresh solutions.

RESULTS

Reaction Velocity.—No induction periods were observed. With iodine monochloride the initial 2–10% of the polymerisation–time curve was linear, and then fell off as expected from mass-action considerations. The results were similar to those observed earlier with iodine. With iodine monobromide the initial linear period was followed by a gradual increase in velocity of polymerisation (Fig. 1), an effect which we have never found before.

The effects of catalyst and monomer concentration on the initial rate of polymerisation in the iodine monobromide case enables us to conclude that

$$-d[M]/dt_{\text{initial}} = k[C]^2[M], \text{ and } k_{\text{IBr}} = 8.2 \text{ l.}^2 \text{ mole.}^{-2} \text{ min.}^{-1}.$$

[C] is the total concentration of iodine monobromide in the mixture. For iodine monochloride the rate was also proportional to $[C]^2$ but the effect of monomer concentration was not determined. The same kinetic law as for iodine monobromide being assumed, $k_{\text{ICl}} = 8.3 \text{ l.}^2 \text{ mole.}^{-2} \text{ min.}^{-1}$.

The Iodine Bromide Polymers.—These were transparent mobile liquids varying from water-white to orange. The densities (d_4^{20}) varied from 0.9056 to 0.9562, an average for all polymers being 0.9321. In the series of runs recorded in Fig. 2 the products at 30% polymerisation contained 53.3 to 76.6% of the initial catalyst concentration as "combined halogen" as determined by titration. The molecular weights varied from 300 to 850 in no systematic fashion. The total halogen in a polymer of molecular weight (M) 650 was 5.69%, and in one of M 350 was 1.9%, as determined by microanalysis. The first figure corresponds to 2I/7 chains or 1Br/2 chains and the second to 1I/19 chains or 1Br/12 chains. The halogens were not distinguished in the microanalyses.

The Iodine Chloride Polymers.—These were transparent yellow to orange, mobile liquids, of density varying from 0.9348 to 0.9849, the average for all specimens being 0.9618.

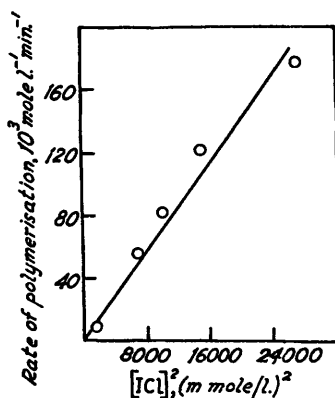


FIG. 3. Effect of catalyst concentration on the initial rate with iodine chloride. $[M] = 0.86\text{M}$.

Two polymer specimens had M 350 and 650, and the latter gave on microanalysis 9.4% of halogen, *i.e.*, 1I/2 chains or 5Cl/3 chains.

In two cases the polymers deposited a yellow crystalline sediment, which had m. p. 100–110° [Found: C, 5.0%; H, 0.4% (Mr. B. S. Noyes, Bristol)]. Insufficient was available for halogen analysis. These data suggest that the compound was iodoform, m. p. 119° (Calc.: C, 3.05; H, 0.26%), contaminated with polymer.

DISCUSSION

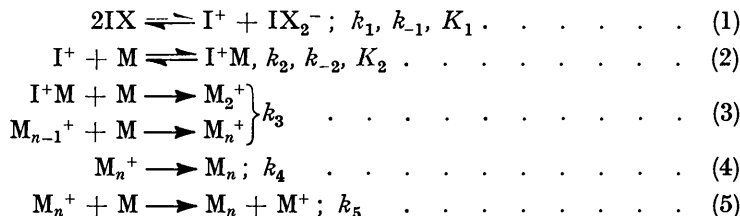
The Velocity.—The iodine monochloride and iodine monobromide polymerisations have kinetics identical with those of the iodine polymerisation of *n*-butyl vinyl ether (Eley and Saunders, *loc. cit.*) but the third-order velocity constant of about 8 for the first two catalysts is to be compared with a value of 1800 for iodine. Now, a certain amount of iodine is present even in fresh iodine halide solutions, formed by the dissociation $3\text{IX} \rightleftharpoons \text{I}_2 + \text{IX}_3$. At 25° the chloride is 0.42% decomposed (Cornog and Karges, *loc. cit.*) and the bromide 8% in the vapour phase and 9.5% in carbon tetrachloride solution (Yost, Anderson, and Skoog, *J. Amer. Chem. Soc.*, 1933, **55**, 552). If these figures apply to the ethereal solution we expect catalysis due to the free iodine, the apparent rate constants being given by $[\text{I}_2]^2 \times 1800 = (1.4 \times 10^{-3})^2 \times 1800 = 0.00353$ for iodine chloride and $(0.0267)^2 \times 1800 = 1.28$ for iodine bromide. It is clear that the value of 8.3 observed for the iodine chloride is 2350 times greater than the value estimated on a basis of catalysis by its free-iodine content, and we therefore attribute this catalysis to the iodine monochloride itself. On the other hand the value for iodine monobromide is only 6.4 times the estimated rate for the free iodine present, so that about 85% of the reaction rate is due

to iodine bromide and 15% to the free iodine. Furthermore, the reaction velocity increases with time in this case only, which strongly suggests the iodine monobromide to be decomposing as polymerisation proceeds. We therefore conclude that the true third-order constant for iodine monobromide is less than 8.2, so that $k_{I_2} = 1800 > k_{ICl} = 8.3 > k_{IBr} \sim 7 > k_{I_2}$, is the order of decreasing catalytic activity. Since bromine in carbon tetrachloride may be used quantitatively to brominate the double bond of monomeric vinyl 2-ethylhexyl ether (Richards, unpublished) we may conclude that this is an even less active catalyst for polymerisation than iodine monobromide.

The Polymers.—The average degree of polymerisation (D.P.) of the polymer produced by iodine monobromide and iodine monochloride of 5.2 is rather less than the value of 9.8 found earlier for iodine, but the factor of 2 may be neglected compared with the factor of 220 found for the overall velocities of polymerisation. Thus, since the material chains in these cases are ended by transfer (Eley and Richards, *loc. cit.*) we may suppose the ratio of propagation rate to transfer rate to be hardly affected by the catalyst, and the difference in overall velocity to be due to differences in the initiation steps.

It is believed that the halogen in the product has arisen from an attack by the catalyst on the double bond of the dead polymer. The interhalogen compounds are much more efficient in the addition reaction than iodine, which explains why no halogen was found in the latter case (Eley and Richards, Eley and Saunders, *loc. cit.*).

The Kinetic Scheme.—It is instructive to discuss the problem of halogen addition as well as polymerisation in the light of the kinetic scheme advanced in Parts I and II (*loc. cit.*) for this polymerisation :



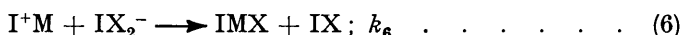
(where, *e.g.*, k_1 is the constant of the forward reaction, k_{-1} that of the reverse reaction, and K_1 the equilibrium constant).

In order to do this we need to consider the reverse reactions in steps (1) and (2) in addition to the forward constants usually considered. Now, polymerisation is very rapid, *i.e.*, $k_3 \gg k_1, k_2$, and the usual analysis holds :

$$-d[M]/dt = k_1 k_3 [IX]_f^2 [M] / k_4 \quad D.P. = k_3 [M] / (k_4 + k_5 [M])$$

where $[IX]_f$ is the concentration of free iodine or interhalogen *i.e.*, the total concentration less that bound as inactive complex with the double bond. While it is possible that, for a given total concentration of catalyst, $[ICl]_f < [I_2]_f$ because of the formation of a stronger inactive complex, this can hardly affect the velocity by a factor smaller than 0.5 [cf. values for benzene derivatives (Andrews and Keefer, *J. Amer. Chem. Soc.*, 1950, **72**, 5170; 1952, **74**, 4500)]. Therefore we conclude that the results for the overall velocity are due to a decrease of k_1 over the series $I_2 > ICl > IBr$.

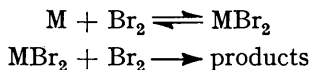
We now consider whether halogenation might follow the same route to I^+M , in the case of a monomer unreactive to polymerisation :



The overall velocity constants for halogenation of allyl acetate are much less than for polymerisation of *n*-butyl vinyl ether. Thus for iodine monochloride with allyl acetate in acetic acid $k = 0.045 \text{ l.}^2 \text{ mole}^{-2} \text{ min.}^{-1}$ (White and Robertson, *loc. cit.*) which is 200 times slower than the above polymerisation. The addition of iodine to allyl acetate is 10^5 times slower than the previous value, and therefore 4×10^9 times slower than the polymerisation of *n*-butyl vinyl ether by iodine. So allyl acetate is a much less reactive monomer than *n*-butyl vinyl ether, k_3 being negligible (no polymerisation). It should also be possible to

assume $k_{-1}, k_{-2} \gg k_6$, whereupon the kinetics of halogenation become $-d[IX]/dt = k_6[I^+M][IX_2^-] = k_6K_1K_2[IX]^2[M]$ as found experimentally. We should expect k_6 to increase with decreasing stability of the IX_2^- ion, which for varying X is $I > Br > Cl$ (Sidgwick, "The Chemical Elements and Their Compounds," II, 1193) and this result is also that found experimentally.

It may be remarked that White and Robertson favoured a two-stage process :



and this would be a mechanism quite distinct from polymerisation, and indeed it might be argued from our results that as polymerisation shows such different behaviour from halogenation, the latter can scarcely involve the same active carbonium ion as intermediate. However, it has been shown that halogenation kinetics may be reconciled with the carbonium ion intermediate. De la Mare's argument (*Quart. Reviews*, 1949, **3**, 133) against a pre-equilibrium of the form (1) in the case of bromination is that "addition of negative ions would greatly reduce the rate of addition (*e.g.*, $Br^+ + OAc^- \rightleftharpoons BrOAc$)." However, the only negative ion that could reduce the concentration of Br^+ produced by an equilibrium (1) would be Br_3^- and the appropriate test, which we hope to make later, would be to add $CsBr_3$ or $RbBr_3$.

THE UNIVERSITY, BRISTOL.

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