

**412. *The Kinetics of Ionic Polymerisation. Part X.\****  
***Low-temperature Polymerisation of Vinyl Ethers in Hexane.***

By D. D. ELEY and A. F. JOHNSON.

The system n-butyl vinyl ether–boron trifluoride–hexane in the extremely dry state showed no polymerisation at  $-78$  and  $25^\circ$ . This monomer cannot, therefore, be its own cocatalyst. Water added to the mixture started polymerisation after an induction period, so the boron trifluoride hydrates were examined.  $\text{BF}_3 \cdot \text{H}_2\text{O}$  was found to be a very active catalyst, probably heterogeneous in nature, but  $\text{BF}_3 \cdot 2\text{H}_2\text{O}$  was less active. The “polyphase polymerisation” system,  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ –isobutyl vinyl ether–hexane, followed  $[\text{P}_1]_0^2[\text{C}]$  kinetics, whilst  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ –isobutyl vinyl ether–toluene/hexane, a homogeneous stereospecific polymerising system, also gave  $[\text{P}_1]_0^2[\text{C}]$  kinetics. Homogeneous mechanisms are postulated to explain the last two cases. Polymerisation occurs at lower temperatures in hexane as compared with ether as solvent; the explanation advanced is that hexane fails to solvate the initial ion-pair, leading to a relatively more positive entropy of initiation, and hence a more rapid rate.

IN the “polyphase polymerisation” of Schildknecht *et al.*<sup>1</sup> crystalline polymers (characterised as isotactic<sup>2</sup>) were obtained by dropwise addition of boron trifluoride

\* Part IX, preceding Paper.

<sup>1</sup> Schildknecht, Gross, and Zoss, *Ind. Eng. Chem.*, 1949, **41**, 1998, 2981.

<sup>2</sup> Natta, Bassi, and Corradini, *Makromol. Chem.*, 1956, **18/19**, 213.

diethyl etherate to isobutyl vinyl ether in liquid propane at  $-78^{\circ}$ . This system is heterogeneous in that (a) the catalyst is only partly soluble in the solvent, and (b) the polymer is precipitated as it is formed, to give a "proliferous mass." Nevertheless, Schildknecht<sup>3</sup> favours a diffusion-controlled propagation step occurring homogeneously in the viscous polymeric medium surrounding the catalyst drop. For the less reactive monomers, such as methyl vinyl ether, the polyphase reaction requires the addition of an activator (chloroform or methylene dichloride).<sup>4</sup> Okamura *et al.*<sup>5</sup> showed that the activator makes the polymer soluble in the mixed medium. In this way they prepared isotactic polymers under homogeneous conditions. In the present Paper we describe a preliminary attempt to study these reactions under conditions suitable for kinetic investigation.

### EXPERIMENTAL

Catalyst solution, monomer, and the solvent n-hexane were all subjected to the elaborate vacuum drying procedure described in Part IX, and were measured into the reaction vessel from burettes and through greaseless valves. In some experiments dilatometers with magnetic stirrers were used, but in most cases the polymerisation was followed *in vacuo*, in an adiabatic calorimeter as described by Biddulph and Plesch.<sup>6</sup> In this case, the catalyst solution was contained in an evacuated bulb in the calorimeter. Reaction was started by breaking the bulb with a magnetic breaker. Typical traces are shown in Fig. 1, and the heat of mixing of the catalyst is clearly seen as an initial temperature spike. Polymerisations were usually followed over the first 10% of the reaction, and conditions adjusted to keep the rise in temperature for this percentage change to about  $2.5^{\circ}$ . The temperature-sensing element was a platinum resistance thermometer, and progress curves were observed with a potentiometric recorder. The effect of rise in temperature is to maintain the rate in opposition to the deceleration due to decrease in monomer concentration, and give a somewhat extended pseudo-zero-order initial rate. No molecular weight studies were made.

For "extreme drying" all internal surfaces were treated with dichlorodimethylsilane, to give a hydrophobic film. The three reactants were separately measured out into a vessel (J in Fig. 1, Part IX) and then distilled into the reaction vessel through several vessels containing sodium films inserted at point X.

*Materials.*—Vinyl ethers and catalyst solutions were prepared and dried as described in Parts VIII and IX (preceding papers). Commercial hexane was purified by the method of Morgan and Lowry;<sup>7</sup> it was finally fractionally distilled from sodium, and the middle fraction collected. Boron trifluoride dihydrate,  $\text{BF}_3 \cdot 2\text{H}_2\text{O}$ , was prepared by passing boron trifluoride gas through a melting-toluene trap into purified water. The boric acid first precipitated was redissolved as more gas was passed. After passage of the stoichiometric quantity of gas, the dihydrate, purified by four fractional crystallisations from water, had m. p.  $6.1^{\circ}$ . Further passage of gas gave the monohydrate,  $\text{BF}_3 \cdot \text{H}_2\text{O}$ , which was similarly purified.<sup>8</sup>

### RESULTS

*Boron Trifluoride Catalyst.*—The components, boron trifluoride gas, n-hexane, and n-butyl vinyl ether, were intensively dried over sodium films and condensed into dilatometers. Monomer concentrations varied from 0.19 to 2.31 moles  $\text{l}^{-1}$ , and catalyst concentrations from 1.08 to 2.01 millimoles  $\text{l}^{-1}$ . Four runs were made at  $-78^{\circ}$ , followed by heating to  $25^{\circ}$ , and three runs at  $25^{\circ}$ ; there was no polymerisation in any experiment within 24 hours. Addition of moist air initiated polymerisation.

Attempts were made to add definite amounts of water to this system, but water was adsorbed on to glass surfaces even after treatment with dichlorodimethylsilane, and reproducibility was poor at both  $-78$  and  $25^{\circ}$ . For this reason the method was discontinued.

<sup>3</sup> Schildknecht, *Ind. Eng. Chem.*, 1958, **50**, 107.

<sup>4</sup> Zoss, U.S.P. 2,616,879 (1952).

<sup>5</sup> Okamura, Higashimura, and Yamamoto, *J. Polymer. Sci.*, 1958, **33**, 510.

<sup>6</sup> Biddulph and Plesch, *Chem. and Ind.*, 1959, 1482.

<sup>7</sup> Morgan and Lowry, *J. Phys. Chem.*, 1930, **34**, 2385.

<sup>8</sup> Topchiev, Zavgorodami, and Paushkin, "Boron Fluoride," Pergamon, London, 1959, pp. 50 *et seq.*

**Boron Trifluoride-Water Mixtures.**—An evacuated phial containing the boron trifluoride-water solution (0.2 ml.) was broken under hexane (100 ml.) containing  $0.154 \text{ mole l.}^{-1}$  of *n*-butyl vinyl ether in the calorimeter, at  $25^\circ$ . Catalyst solutions with molar ratios ( $\text{BF}_3 : \text{H}_2\text{O}$ ) from 1:10 to 1:10,460 were examined. The reaction possessed an induction period, between addition of catalyst and onset of measurable temperature rise, which increased linearly with the water content (Fig. 2), followed by a rate of temperature rise, which appeared to be

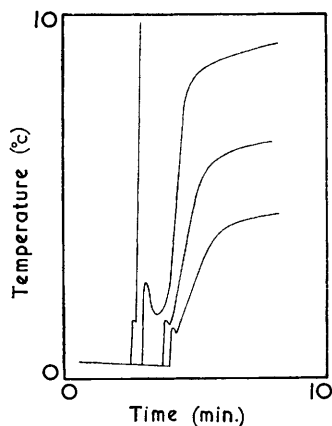


FIG. 1. Typical temperature-time traces.

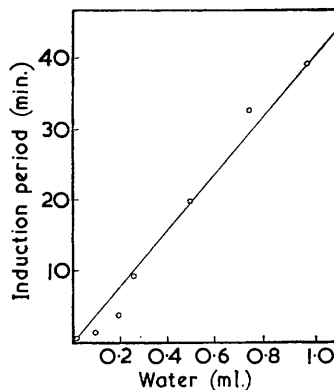


FIG. 2. Plot of induction period against water content for  $3.23 \times 10^{-3} \text{M}$ -boron trifluoride in hexane (100 ml.), at  $-25^\circ$ .

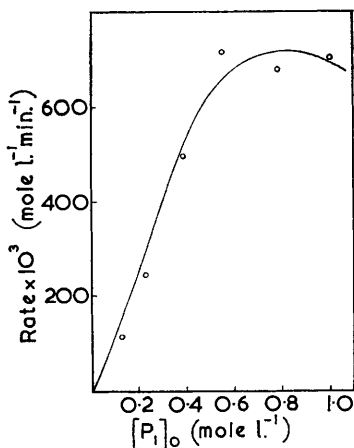


FIG. 3. Rate for  $\text{BF}_3 \cdot \text{H}_2\text{O}$  ( $3.76 \times 10^{-2} \text{M}$ )-*n*-butyl vinyl ether-hexane at  $-35^\circ$  as a function of initial concentration,  $[\text{P}_1]_0$ .

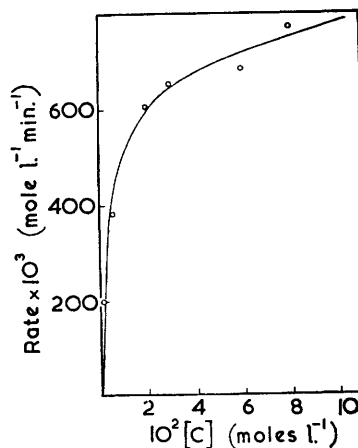


FIG. 4. Rate for  $\text{BF}_3 \cdot \text{H}_2\text{O}$ -*n*-butyl vinyl ether ( $0.385 \text{M}$ )-hexane at  $-35^\circ$  as a function of catalyst concentration,  $[\text{C}]$ .

approximately independent of water content, of  $4.0 \pm 2.0 \times 10^{-2} \text{ deg./sec}$ . However, the reproducibility was inadequate for kinetic studies, so it was decided to examine the separately prepared boron fluoride hydrates as catalysts.

**Boron Trifluoride Monohydrate-*n*-Butyl Vinyl Ether-Hexane.**—Reaction rates were measurable at  $-35^\circ$ , and, after an induction period of about 150 seconds, reaction started, giving a stationary rate over 10% of the polymerisation. The catalyst can only be partly soluble in the hexane, but the results suggest that the stirring is adequate to give a reproducible dispersion of catalyst.

In Figs. 3 and 4 the overall rate of polymerisation,  $R_p$ , is plotted against  $[\text{P}_1]_0$  and  $[\text{C}]$ .

For the case of  $[P_1]_0$  a maximum rate is reached at  $0.720 \text{ mole l.}^{-1} \text{ min.}^{-1}$ , and a similar trend holds for  $[C]$  at  $10^{-1} \text{ mole l.}^{-1}$ . The Arrhenius plot in Fig. 5 gives an overall activation energy (in the region of maximum velocity) of  $E = 4.1 \text{ kcal. mole}^{-1}$ .

*Boron Trifluoride Dihydrate-n-Butyl Vinyl Ether-Hexane.*—The rates with this system were lower at all temperatures than with the monohydrate (cf. Fig. 5). The apparent activation energy is  $E = 36 \text{ kcal. mole}^{-1}$ . This is subject to considerable error, as the adiabatic calorimeter is only intended for study of reactions with small activation energies. At the lowest temperatures the reaction became very clearly heterogeneous.

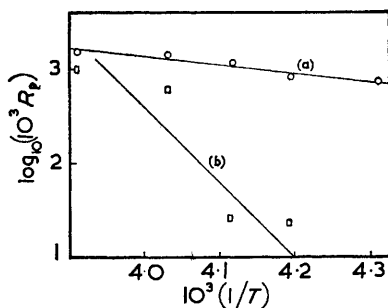


FIG. 5. (a) Arrhenius plot for  $\text{BF}_3 \cdot \text{H}_2\text{O}$  ( $3.76 \times 10^{-2} \text{M}$ )—*n*-butyl vinyl ether ( $0.77 \text{M}$ )—hexane. (b) Similar, for  $\text{BF}_3 \cdot 2\text{H}_2\text{O}$ .

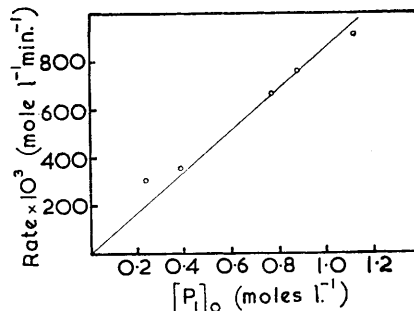


FIG. 6. Rate for  $\text{BF}_3 \cdot 2\text{H}_2\text{O}$  ( $3.76 \times 10^{-2} \text{M}$ )—*n*-butyl vinyl ether—hexane plotted against monomer concentrations.

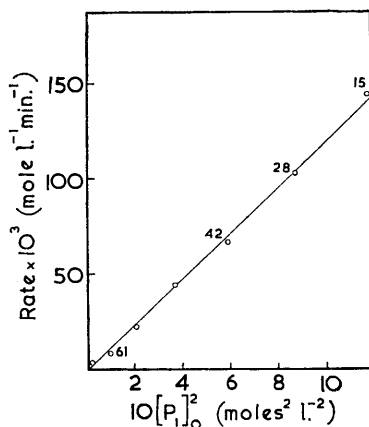


FIG. 7. Rate for  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  ( $3.23 \times 10^{-3} \text{M}$ )—*i*-isobutyl vinyl ether—hexane plotted against monomer concentration, at  $-70.5^\circ$ . The numbers beside the points are the corresponding induction periods in minutes.

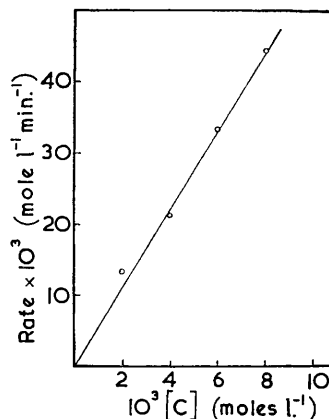


FIG. 8. Rate for  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ —*i*-isobutyl vinyl ether ( $0.618 \text{M}$ )—hexane plotted against catalyst concentration, at  $70.5^\circ$ .

The reaction rate at  $-25^\circ$  was proportional to the monomer concentration, as shown in Fig. 6. The usual induction period at  $-25^\circ$  was about 300 sec., roughly independent of  $[P_1]_0$  at  $[C] = 3.76 \times 10^{-2} \text{ mole l.}^{-1}$ .

*The "Polyphase Polymerisation."*—It was not possible to measure kinetics exactly under Schildknecht's conditions. Instead, an evacuated bulb containing boron trifluoride diethyl etherate solution was broken under the rapidly stirred solution of isobutyl vinyl ether in hexane in the calorimeter. Reaction set in after a definite induction period, which was 15–61 minutes and is marked against the points in the rate graph of Fig. 7. This induction period decreased as the overall rate,  $R_p$ , increased. Figs. 7 and 8 show that at  $-70.5^\circ$  the kinetics are accurately

$$R_p = -d[P_1]/dt = k[P_1]^2[C].$$

The data in the Arrhenius plot (Fig. 9) give an activation energy  $E = 7.3$  kcal. mole<sup>-1</sup>. In drawing the line, the two points off the line at the right-hand side have been ignored, but clearly there is considerable error in this activation energy, which is perhaps to be expected for a definitely heterogeneous system.

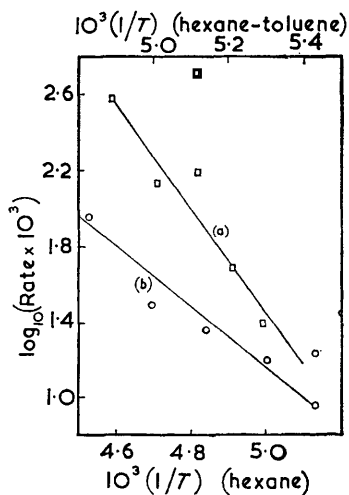


FIG. 9. Arrhenius plots. (a)  $\text{BF}_3\text{Et}_2\text{O}$  ( $3.96 \times 10^{-3}\text{M}$ )-isobutyl vinyl ether ( $0.232\text{M}$ )-mixture of toluene and hexane (50:50). (b)  $\text{BF}_3\text{Et}_2\text{O}$  ( $0.2 \times 10^{-3}\text{M}$ )-isobutyl vinyl ether ( $0.618\text{M}$ )-hexane (polyphase polymerisation).

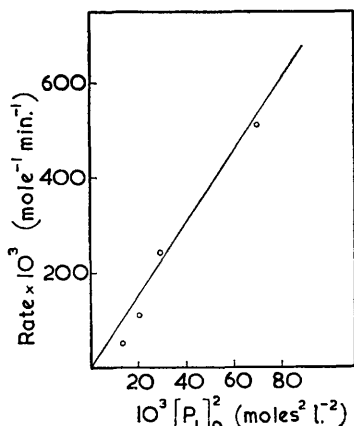


FIG. 10. Rate for  $\text{BF}_3\text{Et}_2\text{O}$  ( $3.96 \times 10^{-3}\text{M}$ )-isobutyl vinyl ether-mixture of toluene and hexane (50:50), as a function of monomer concentrations, at  $-68.7^\circ$ .

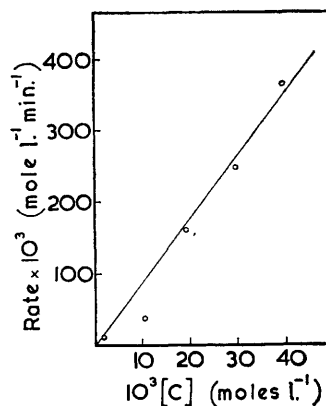


FIG. 11. Rate for  $\text{BF}_3\text{Et}_2\text{O}$ -isobutyl vinyl ether ( $0.23\text{M}$ )-mixture of toluene and hexane (50:50), as a function of catalyst concentration, at  $-68.7^\circ$ .

*Stereoregular Polymerisation in Toluene-Hexane Mixtures.*—In these experiments an evacuated bulb containing boron trifluoride etherate was broken into a solution of isobutyl vinyl ether in the mixed solvent toluene (50 ml.)-hexane (50 ml.). These conditions do not exactly reproduce the conditions of Okamura *et al.*<sup>5</sup> for homogeneity, which really require a bulb containing monomer to be broken into the catalyst solution. However, we expect a greater degree of homogeneity than in the polyphase system described previously.

The results in Figs. 10 and 11 suggest that the usual kinetic equation is applicable at  $-68.7^\circ$ :

$$R_p = -d[P_1]/dt = k[P_1]^2[C].$$

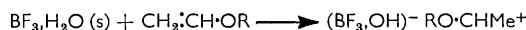
The Arrhenius plot in Fig. 9 gives an overall activation energy of  $E = 13.4$  kcal. mole<sup>-1</sup>.

## DISCUSSION

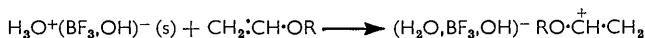
In the first place it is established that n-butyl vinyl ether will not act as its own cocatalyst with boron trifluoride in hexane. This is in contrast to the postulated cocatalysis by n-butyl vinyl ether monomer with boron trifluoride-tetrahydrofuran in benzene as solvent.<sup>9</sup> The addition of water caused a rapid reaction to set in, after an induction period which increased with the amount of water present. No doubt the water reacts with the initial ion-pair, to give a non-reactive product, *i.e.*, it acts as an inhibitor which is eliminated during the induction period at a rate dependent on the velocity of initiation. These results agree with similar ones in Part IX (preceding Paper).

We must expect the boron trifluoride hydrates to be insoluble in hexane (Evans<sup>10</sup>). The monohydrate is shown to be more active, as for isobutene polymerisation.<sup>10</sup>

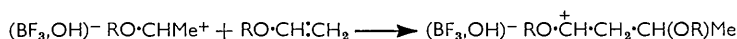
Dainton<sup>10</sup> postulated initiation, propagation, and termination for gaseous isobutene all to occur in the adsorbed film on the surface of the solid boron trifluoride monohydrate. We suggest that initiation so occurs for vinyl ethers in hexane, but that a more probable propagation reaction, avoiding any need for charge separation, may be an insertion mechanism (familiar in Ziegler catalysis). The initiation steps will then be, following Evans and Polanyi:<sup>11</sup>



or for the dihydrate, with its ionic structure:<sup>12</sup>



and propagation



The polymer molecule will therefore grow out into solution. It may be that the low activation energy of 4.1 kcal. mole<sup>-1</sup> for the monohydrate, as compared with a propagation activation for styrene of 8 kcal. mole<sup>-1</sup>,<sup>13</sup> may indicate a rate-limiting step of monomer diffusion through polymer chains to the active centre (as postulated by Schildknecht in another connection, that of polyphase polymerisation; see below). The activation energy for dihydrate catalysis, 36 kcal. mole<sup>-1</sup>, is open to a large error, but may reflect the decreased acid strength and an increased energy change in the initiation step, as compared with the monohydrate. Certainly Fig. 6 (dihydrate catalyst) shows no indication of a diffusion-limiting process, in contrast to Fig. 3 (monohydrate), but physical considerations (catalyst dispersion and solubility) were not necessarily comparable in both cases.

The polyphase and the homogeneous stereospecific polymerisations both follow  $[\text{P}_1]^2[\text{C}]$  kinetics. This law has been twice found for polymerisations catalysed by boron trifluoride etherates in ether at 25° under definitely homogeneous conditions (see Part IX), which tends to support Schildknecht's view that the rate-determining step is a homogeneous reaction in polyphase polymerisation. However, there is no evidence that the rate of our version of the polyphase polymerisation is limited by diffusion of monomer through polymer solution surrounding the active centres. The maximum rates achieved in our polyphase polymerisation were only  $150 \times 10^{-3}$  mole l.<sup>-1</sup> min.<sup>-1</sup>, to be compared with the value  $700 \times 10^{-3}$  mole l.<sup>-1</sup> min.<sup>-1</sup> for the  $\text{BF}_3 \cdot \text{H}_2\text{O}$  polymerisation, which we have suggested is diffusion limited. However, the true polyphase polymerisation, as carried out under Schildknecht's conditions, may be diffusion limited.

The overall activation energies in the boron trifluoride diethyl etherate-n-butyl vinyl ether-hexane polymerisations are around 7 kcal. mole<sup>-1</sup>, and the rates are measurable in

<sup>9</sup> Imoto and Aoki, *Makromol. Chem.*, 1961, **48**, 72.

<sup>10</sup> "Friedel-Crafts Polymerisation," ed. Pepper, *Sci. Proc. Royal Dublin Soc.*, 1950, pp. 145, 146.

<sup>11</sup> Evans and Polanyi, *J.*, 1947, 252.

<sup>12</sup> Klinkenberg and Ketelaar, *Rec. Trav. chim.*, 1935, **54**, 959.

<sup>13</sup> Hayes and Pepper, *Proc. Roy. Soc.*, 1961, *A*, **263**, 63.

the range  $-80$  to  $-40^{\circ}$ . On the other hand, the system boron trifluoride diethyl etherate-*n*-butyl vinyl ether-diethyl ether has an overall activation energy of 6 kcal. mole<sup>-1</sup> and a measurable rate at  $25^{\circ}$ .<sup>14</sup> Clearly, the overall entropy of activation in the first case must be much less negative, and one is led to conclude that solvation effects of the ion-pair by the solvent are much less in hexane as solvent than in diethyl ether. Where solvation does occur in hexane it must be by monomer, and this is clearly linked with the possible stereoregular character of the polymerisation in this solvent. Detailed studies of entropy of activation are being made on homogeneous stereoregular polymerisations in this laboratory at present, so we postpone further discussion for the present.

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<sup>14</sup> Coombes and Eley, *J.*, 1957, 3700.

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