411. *The Kinetics of Ionic Polymerisation. Part IX.* Polymerisation of n-Butyl Vinyl Ether Initiated by a Boron Trifluoride Etherate, in the Corresponding Ether.*

By D. D. Eley and Anne Seabrooke.

The polymerisation of n-butyl vinyl ether catalysed by a boron trifluoride etherate in the corresponding ether as solvent has been investigated for four ethers. Third-order ($[P_1]^2[C]$) kinetics were found, as in earlier work with the diethyl etherate in diethyl ether. The overall rate of polymerisation decreased with the etherates in the order anisole > di-isopropyl > diethyl > di-n-butyl > tetrahydrofuran, the last named giving zero reaction in the extremely dry state. The di-n-butyl, di-isopropyl, and diethyl ethers all showed spontaneous termination at 25°, whilst anisole gave monomer transfer. The strongly negative entropies of activation for initiation are attributed to solvation effects of the ether solvent on the ion-pair. Addition of water to the n-butyl vinyl ether–boron trifluoridetetrahydrofuran–tetrahydrofuran system gave a maximum velocity at a 1 : 1 molar ratio $H_2O : BF_3$. Where induction periods occurred they are attributed to residual moisture.

In an earlier Paper [1] dealing with the system n-butyl vinyl ether–boron trifluoride diethyl etherate–diethyl ether, the initiation reaction (rate constant k_i) proposed was:

$$BF_3,Et_2O + CH_2{:}CH{\cdot}O{\cdot}C_4H_9 \longrightarrow (BF_3,EtO)^- Et{\cdot}CH_2{\cdot}\overset{+}{C}H{\cdot}O{\cdot}C_4H_9$$

This initiation step is supported by the use of isotopically labelled ethyl groups in the catalyst, which gave rise to a fraction of polymer chains containing labelled ethyl.[2] In the propagation reaction (k_p) monomer molecules add to this carbonium ion. The termination reaction at low monomer concentrations was established as spontaneous termination (k_t), the most probable mechanism being proton transfer to the anion, giving rise to a terminal double bond in the polymer:

$$\sim\!\!\sim\!CH_2{\cdot}\overset{+}{C}H{\cdot}O{\cdot}C_4H_9 \ (BF_3,EtO)^- \longrightarrow \sim\!\!\sim\!CH{:}CH{\cdot}O{\cdot}C_4H_9 + BF_3,EtOH$$
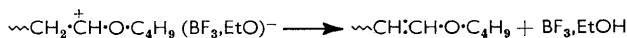
At higher monomer concentrations proton transfer to monomer could occur, the chains then being terminated by transfer (k_m).

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* Part VIII, preceding Paper.

[1] Coombes and Eley, *J.*, 1957, 3700.

[2] Kennedy, *J. Polymer. Sci.*, 1959, **38**, 263.

In this Paper we extend the investigation to four further boron trifluoride etherates, using the same ether as solvent so as to obviate complications due to ether exchange. A complete vacuum-handling technique was used, in which monomer, solvent, and catalyst were dried and mixed in the absence of greased taps.

Experimental

Apparatus.—In Fig. 1 is shown part of the vacuum apparatus used for preparation and purification of the reactants, and for subsequent filling of the dilatometer. Boron trifluoride gas, generated in A by heating calcium fluoroborate, was purified by distillation *in vacuo* from trap B to C.[1] A measured volume (bulb E) of boron trifluoride, at a pressure measured on a mercury manometer attached at D, was passed through the mercury cut-off F into purified ether contained in H. Vessel I contained purified solvent ether, which could be distilled previously through the magnetically-breakable seal M into H. Thereafter, the vapour pressure of the solvent was used to drive the catalyst solution over into the 10-ml. burette G, where it was stored over the greaseless valve T (Biddulph and Plesch [3]). Catalyst solution could then be measured into vessel J as required, and hence distilled into the dilatometer K.
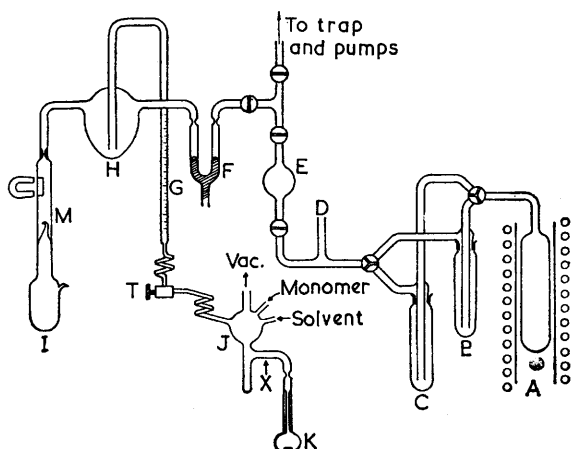

FIG. 1. Apparatus for preparation of the catalysts.

FIG. 2. A typical contraction–time graph; 1 cm. contraction approximates to 10% polymerisation.

Monomer and solvent were handled similarly. After initial purification (see later) they were dried *in vacuo* in two separate reservoirs (see Biddulph and Plesch,[4] Fig. 3). Solvent was dried over calcium hydride, and monomer over sodium. They were then separately distilled into two separate 30-ml. burettes with greaseless valves, which allowed definite volumes to be measured into vessel J.

The 9-ml. dilatometer (K), with magnetic stirrer,[5] was sealed to the vacuum apparatus, and, after evacuation to 10^{-5} mm., cooled to $-195°$. Measured volumes of monomer, some of the solvent, catalyst solution, and the remainder of the solvent were cold-distilled into the dilatometer in that order. Anisole and n-butyl vinyl ether had to be run directly into the dilatometer since they distilled very slowly. The dilatometer was then sealed off and stored in liquid nitrogen. In the case where extreme drying was required all three reactants were distilled through one or more vessels containing sodium films and inserted at point X.

To start a reaction, a dilatometer with its frozen reactants was clamped in the thermostat and the stirrer magnet switched on. The dilatometer was flat-bottomed to help rapid attainment of temperature equilibrium. The capillary of the dilatometer (some 2% of the total volume) projected above the thermostat liquid. This liquid was " Methcol " cooled by a stream of nitrogen gas from liquid nitrogen, and temperatures from -78 to $10°$ were maintained to $\pm 0.5°$. An ordinary water-thermostat was used for 25°.

[3] Biddulph and Plesch, *Chem. and Ind.*, 1956, 569.
[4] Biddulph and Plesch, *Chem. and Ind.*, 1959, 1482.
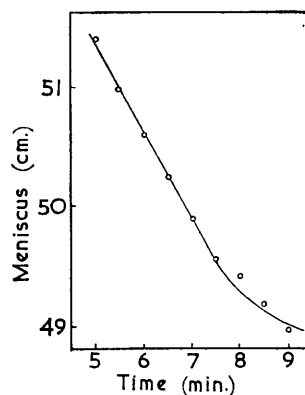[5] Colclough and Dainton, *Trans. Faraday Soc.*, 1958, **54**, 886.

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A typical contraction–time graph is shown in Fig. 2. In calculating the rate of polymeris-ation from the graph, we take $d_4^{25} = 0.944$ g. c.c.$^{-1}$ as an average value for polymer in the molecular-weight range 3500—10,000. The earlier value of 0.905 g. c.c.$^{-1}$ [1,6] referred to the molecular weight range 650—1200. We found a definite tendency for an increase in d_4^{25} with molecular weight, *viz.*, 0.9386 (4390), 0.9625 (8600), 0.9958 (14,600). The effect of temperature on the density was neglected in the rate calculations. We have every reason to expect a good approximation to ideal behaviour, and a linear relation between contraction and percentage conversion.

Polymers.—Separate runs were performed in evacuated tubes; the reactions were stopped at 30% polymerisation by addition of 5% aqueous sodium hydroxide. The polymers were isolated and their molecular weight determined from the viscosity of benzene solutions, using the previous Staudinger constant of 3.8×10^{-4} l. base mole^{-1}.[1]

Materials.—Boron fluoride and n-butyl vinyl ether were purified as described in Part VII.[1] Di-isopropyl ether and di-n-butyl ether were each shaken successively with acidified ferrous sulphate to remove peroxides, concentrated sulphuric acid, water, and potassium hydroxide solution, dried over potassium hydroxide and then sodium, and distilled; the middle fraction was transferred to the drying flask on the vacuum apparatus. Tetrahydrofuran was dried over sodium, and distilled. Anisole was purified according to the method of Bien, Krauss, and Fuoss,[7] dried over calcium chloride and then sodium, and distilled.
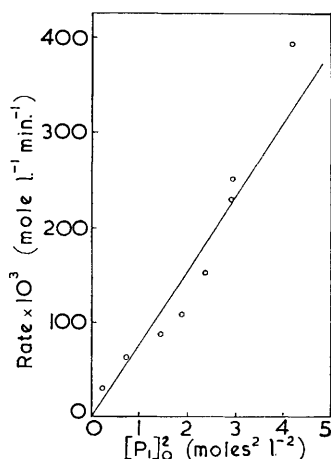

FIG. 3. Effect of monomer concentration on the rate of polymerisation for boron trifluoride di-n-butyl etherate; $[C] = 7.76 \times 10^{-3}$M.
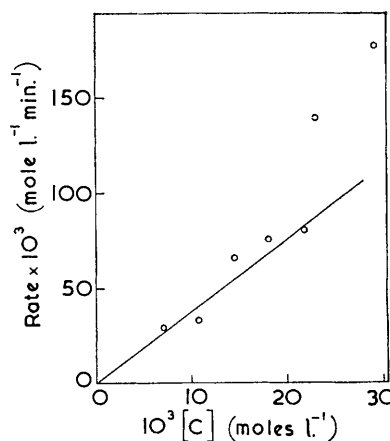
FIG. 4. Effect of catalyst concentration on the rate of polymerisation for boron trifluoride di-n-butyl etherate; $[P_1] = 0.601$M.

RESULTS

Boron Trifluoride Di-n-butyl Etherate in Diethyl Ether.—After immersion of the dilatometer in the thermostat there was an induction period before the meniscus started to fall. At monomer concentration $[P_1] = 1.718$M, and catalyst concentration $[C] = 11.6 \times 10^{-3}$M, this varied from 7.5 min. at $-5°$ to 30.5 min. at $-34°$. At constant temperature the induction period (defined as the length of time between immersion of the dilatometer in the thermostat and the commencement of the fall of the meniscus) increased with catalyst or monomer con-centration, approximately as the reciprocal of the subsequent rate of polymerisation. The results are considered in the Discussion section.

Figs. 3 and 4 establish the kinetic law [1] at 25°, for the rate of polymerisation R_p:

$$R_p = -d[P_1]/dt = k[P_1]^2[C], \quad k = 10.2 \ l.^2 \ mole^{-2} \ min.^{-1}.$$

[6] Eley and Saunders, *J.*, 1952, 4167.
[7] Bien, Krauss, and Fuoss, *J. Amer. Chem. Soc.*, 1960, **56**, 1934.

The activation energy calculated from Fig. 5 is $E = 8.7 \pm 0.6$ kcal. mole^{-1} (-5 to $-34°$).

Fig. 6 may be interpreted in terms of the usual equation [1] for average degree of polymerisation, $\overline{\text{D.P.}}$, of the polymer.

$$\overline{\text{D.P.}} = k_p[P_1]/(k_t + k_m[P_1])$$

The present results provide no evidence for solvent-transfer effects, so no term for this is included in the equation. Clearly, spontaneous termination is dominant over monomer
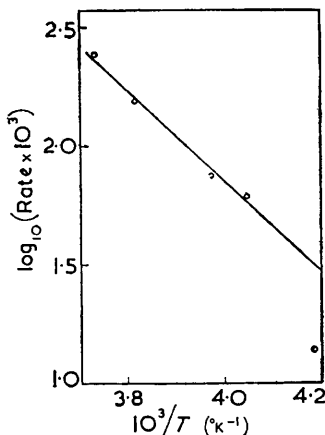

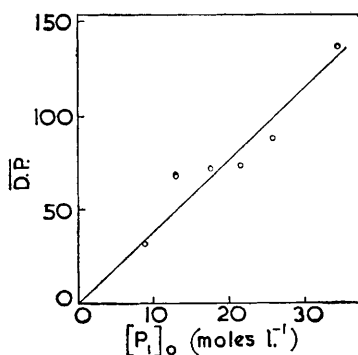FIG. 5. Activation energy for boron trifluoride di-n-butyl etherate; $[P_1] = 1.718$M, $[C] = 11.6 \times 10^{-3}$M.

FIG. 6. Effect of monomer concentration on $\overline{\text{D.P.}}$ of polymer; $[C] = 9.22 \times 10^{-3}$M, 25°, boron trifluoride di-n-butyl etherate.
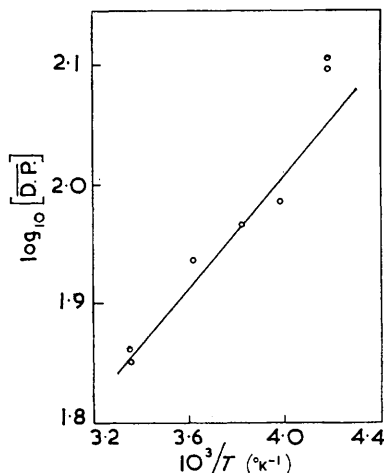

FIG. 7. Activation energy for molecular weight for boron trifluoride di-n-butyl etherate; $[P_1] = 1.718$M, $[C] = 11.6 \times 10^{-3}$M.

transfer, *i.e.*, $k_t > k_m[P_1]$, and the slope of the line gives $k_p/k_t = 39.4$ l. mole^{-1}. The polymers were colourless viscous liquids.

The variation of $\overline{\text{D.P.}}$ with temperature (Fig. 7) gives an " activation energy for molecular weight," $E_{\text{D.P.}} = -1.1 \pm 0.5$ kcal. mole l.$^{-1}$.

Boron Trifluoride Di-isopropyl Etherate in Di-isopropyl Ether.—This etherate is a solid, m. p. 68°,[8] and its sparingly soluble character in di-isopropyl ether limited experiments to catalyst concentrations in the range 20—50mM. On lowering the temperature to 15°, catalyst started to crystallise out, so activation energies could not be determined. At 25° no

[8] Brown and Adams, *J. Amer. Chem. Soc.*, 1942, **64**, 2257.

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induction periods were observed, reaction starting as soon as thermal equilibrium was established, 3—5 minutes after the dilatometer had been immersed in the thermostat. The tendency for catalyst solution to deposit crystals [5] on the walls of the dilatometer led to a somewhat greater spread of results than previously, but the data determined fitted the expression:

$$-d[P_1]/dt = k[P_1]^2[C], \quad k = 46\cdot7 \ l.^2 \ mole^{-2} \ min.^{-1}.$$

At 25° and $[C] = 3\cdot0 \times 10^{-3}$ mole l.$^{-1}$, $\overline{D.P.}$ increased linearly with $[P_1]$, the slope giving $k_p/k_t = 43\cdot5$ l. mole^{-1}. The polymers were colourless viscous liquids, $\overline{D.P.}$ 52—126.

Boron Trifluoride Anisolate in Anisole.—In the presence of moist air this system gave long induction periods during which the solution became intensely coloured and finally opaque. A wide range of colours (brown, yellow, green, pink, and mauve) were observed, and the subsequent polymerisation rates were very irreproducible. The effects recalled those observed on adding water to the boron trifluoride diethyl etherate system.[1] Using the present vacuum technique, shorter induction periods, of 6—24 minutes, were observed, the solution remained colourless up to 80—90% polymerisation, and the rates were reproducible. The final products
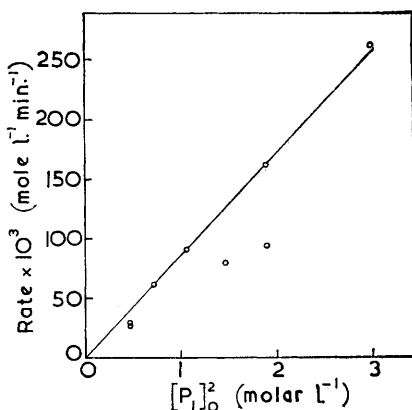

FIG. 8. Effect of monomer concentration on rate of polymerisation; boron trifluoride anisolate, $[C] = 1\cdot33 \times 10^{-3}$M, —30°.
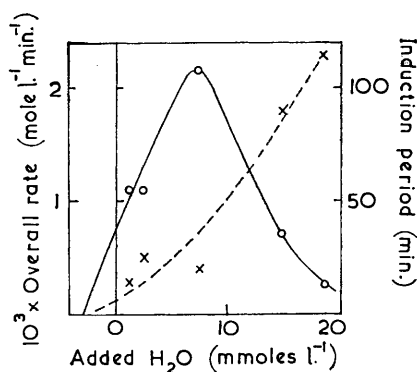

FIG. 9. Effect of added water on the polymerisation rate in boron trifluoride–tetrafuran; $[P_1] = 1\cdot718$M, $[C] = 11\cdot5 \times 10^{-3}$M, 25°.

The broken line and the crosses denote induction period.

were only slightly coloured. Measurable rates were achieved at —30°, and the effect of monomer concentration, but not of catalyst concentration, was determined (Fig. 8).

Assuming $x = 1$ in $R_p = k[P_1]^2[C]^x, k(-30°) = 65$ l.^{2} mole^{-2} min.$^{-1}$. Variation of $[P_1]$ from 0·430 to 2·570M at $[C] = 2\cdot2 \times 10^{-3}$M and —30°, gave no systematic variations in $\overline{D.P.}$, which lay in the range 64·7—104·0, so it was concluded that monomer transfer was dominant, with $k_p/k_m = 77\cdot5$. The polymers were all colourless, very viscous liquids. Since boron trifluoride di-n-butyl etherate gave a similar $\overline{D.P.}$ at —30°, *viz.*, 110, we may neglect any solvent transfer by the anisole.

Boron Trifluoride–Tetrahydrofuran in Tetrahydrofuran.—Although tetrahydrofuran itself is polymerised by boron fluoride [9] a blank run under the conditions of these experiments ($[C] = 65 \times 10^{-3}$M) gave only 1% polymerisation of tetrahydrofuran in 3 hours. Addition of n-butyl vinyl ether to this system gave a polymerisation which was so extremely slow that it suggested cocatalysis by traces of water. Therefore, an additional vessel containing a sodium film was incorporated between vessel J and the dilatometer K, at point X. In the final cold-distillation, the vapours of monomer, solvent, and catalyst were all successively passed over this sodium film. Two test runs ($[P_1] = 0\cdot859$M, $[C] = 10\cdot5 \times 10^{-3}$M; and $[P_1] = 1\cdot718$M, $[C] = 31\cdot5 \times 10^{-3}$M) showed no polymerisation at 25° during 24 hours under these conditions of extreme dryness. On addition of water a volume contraction occurred, pointing to a water cocatalysis.

[9] Hamann, *Angew. Chem.*, 1951, **19**, 231,

A series of runs were carried out with the normally dried reagents, with addition of quantities of water at 25° (Fig. 9). The maximum rate occurred at a 1:1 ratio of water to boron trifluoride. Addition of more water caused a marked increase in the induction period before reaction. The intercept on the axis in Fig. 9 corresponds to a residual water content in the normally dried reagents of 3×10^{-3} mole l.$^{-1}$ (0·68 mg. l.$^{-1}$). Addition of isopropyl ether also initiated polymerisation.

The $\overline{\mathrm{D.P.}}$ of the product at $[\mathrm{P_1}] = 1\cdot718\mathrm{M}$, $[\mathrm{C}] = 11\cdot5 \times 10^{-5}\mathrm{M}$, and 25° showed no systematic variation from 48 ± 7 with water content. The products were colourless viscous liquids.

The third-order constant at the maximum velocity in Fig. 9 is $k_{\mathrm{max.}} = 0\cdot064$ l.^{2} mole^{-2} min.$^{-1}$.

DISCUSSION

Induction Periods.—When water is added to the tetrahydrofuran or diethyl etherate systems induction periods are found which increase with the amount of added water. This suggests that quite generally induction periods arise in these polymerisations from the
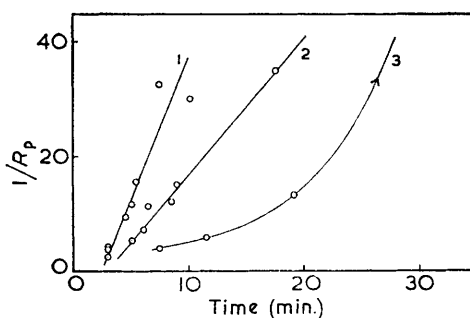

FIG. 10. Correlation between induction period and $1/R_{\mathrm{p}}$, where R_{p} is the overall rate of polymerisation, for boron trifluoride di-n-butyl etherate. 1, Effect of [C]; 2, effect [P$_1$]; 3, effect of T.

traces of water present (68 mg. per litre of solvent, even in carefully dried systems). These traces of water then react completely with the initial ion-pairs within a time which will vary inversely as the velocity of initiation or generation of these ion-pairs, $k_{\mathrm{i}}[\mathrm{P_1}][\mathrm{C}]$. The onset of induction periods at 25° over the range of catalysts is not inconsistent with this view, as can be seen from the following figures for induction period and k_{i}; diethyl etherate, 0 min., 0·88 l. mole^{-1} min.$^{-1}$; di-isopropyl etherate, 0 min., 1·14; < di-n-butyl etherate, 0·5 min., 0·126; < anisole, 0·10 min. at $-30°$, <0·36. Within a given catalyst system, since overall velocity of polymerisation (R_{p}) will run parallel to velocity of initiation, we may expect a correlation between induction period and $1/R_{\mathrm{p}}$ (*e.g.*, Fig. 10).

The Initiation Rate.—The rate of polymerisation in terms of the individual rate constants, k_{i} for initiation, k_{p} for propagation, and k_{t} for spontaneous termination, is:[1]

$$-\mathrm{d}[\mathrm{P_1}]/\mathrm{d}t = (k_{\mathrm{i}}k_{\mathrm{p}}/k_{\mathrm{t}})[\mathrm{P_1}]^2[\mathrm{C}].$$

Hence, for the case of two etherates, where $\overline{\mathrm{D.P.}} = k_{\mathrm{p}}[\mathrm{P}]/k_{\mathrm{t}}$, k_{i} at 25° can be calculated and compared with the earlier result for the diethyl etherate.[1] For anisole, $\overline{\mathrm{D.P.}} = k_{\mathrm{p}}/k_{\mathrm{m}}$, but we may still derive an upper limit for k_{i}. It is reasonable to assume that k_{i} for anisole

TABLE 1.

Initiation rates at 25°.

Etherate	$k_{\mathrm{i}}k_{\mathrm{p}}/k_{\mathrm{t}}$ *	k_{p}/k_{t} †	$k_{\mathrm{p}}/k_{\mathrm{m}}$	k_{i} ‡
Diethyl	16·5	18·7	—	0·88
Di-isopropyl	49·7	43·5	—	1·14
Di-n-butyl	10·2	39·5	—	0·26
Anisole ($-30°$)	65·0	—	77·5	<0·36
Tetrahydrofuran	0·0	—	—	—

* l.^{2} mole^{-2} min.$^{-1}$,   † l. mole^{-1},   ‡ l. mole^{-1} min.$^{-1}$.

at 25° would be very much larger than for the other ethers, because of the immeasurably high polymerisation velocity at this temperature.

To discuss the influence of the ether on k_i we shall assume that the main effects arise in the activation energy, E_i, of the initiation step, which in turn is taken as proportional to the ΔH_i change in this step. In summary, then:

$$BF_3,OR^1R^2 + P_1 \longrightarrow (BF_3,OR^1)^- R^2P_1^+$$

and

$$\Delta H_i = D(BF_3,OR^1\text{-}R^2) - D(R^2\text{-}P_1) + E_\pi + I(R^2P_1) - E(BF_3,OR^1) - X$$

where D denotes dissociation energy, E_π the energy to open the π-part of the double bond in monomer P_1, I ionisation potential, E electron affinity, and X the sum of a coulombic energy of the two ions and a term for the solvent interaction with the ion-pair. Except for anisole, R_1 is the same as R_2.

We may expect negligible changes in the difference quantity $D(BF_3,OR^1\text{-}R^2) - D(R^2\text{-}P_1)$, and in the relatively small quantity $E(BF_3,OR^1)$ with changes in the nature of radical R^2. The discussion of Kaufmann and Koski [10] predicts that the effect of the hydrocarbon radical R^2 in lowering the ionisation potential of R^2P_1 increases in the order, R^2 = methyl 27·2 < ethyl 29·7 < isopropyl 33 < butyl 33·2 < phenyl 49·3 kcal. mole^{-1}. If this is the determining factor in decreasing ΔH_i, and hence also E_i, for initiation, we should expect an order of increasing k_i for the ethers of: methyl < ethyl < isopropyl < butyl < anisole. Except for butyl this is the observed order, and it may be that the large size of this radical has the effect of increasing the radius of the ion-pair and lowering the contribution of the coulombic term to X. This would then act to increase ΔH_i and lower the rate, thus explaining the observed anomaly. Because of the assumptions involved this explanation of the relative order of catalysts is still only tentative in character.

The failure of tetrahydrofuran–boron trifluoride to catalyse may be associated with the non-mobile character of the anion, which will remain covalently bound to the monomer.
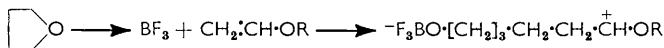
Imoto and Aoki [11] found that boron trifluoride diethyl etherate and boron trifluoride–tetrahydrofuran acted on styrene monomer in benzene as solvent to give the same results as those reported here. With n-butyl vinyl ether in benzene as solvent, however, they found [11] boron trifluoride–tetrahydrofuran to be more active than the diethyl etherate. Both catalysts showed induction periods, and kinetic order as high as 4 in the catalyst. Imoto and Aoki [11] suggest that vinyl ether displaces tetrahydrofuran to act as its own cocatalyst. This suggestion, although logical for hydrocarbon solvents, is clearly inapplicable to the present system, where use of the catalytic ether as solvent makes its displacement by the vinyl ether unlikely on mass-action grounds.

Entropy of Activation for the Initiation Step.—Deriving the energy of activation for initiation, $E_i = E - E_{D.P.}$, the entropy of activation $\Delta S_i^\ddagger$ can be calculated by the usual equation. The present Paper allows this to be derived for the boron fluoride di-n-butyl etherate, and the results are given in Table 2, with two earlier values [1] for comparison.

TABLE 2.

Activation entropy of initiation step.

Catalyst	k_i (mole^{-1} min.$^{-1}$)	E_i (kcal. mole^{-1})	$\Delta S_i^\ddagger$ (cal. deg.$^{-1}$ mole^{-1})
BF$_3$,Et$_2$O, nBVE	0·88	9·2	−35·0
BF$_3$,Bu$^n_2$O, nBVE	0·26	9·8	−28·6
SnCl$_4$,H$_2$O, octyl vinyl ether	0·20	13·3	−27·2

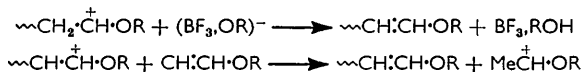[10] Kaufmann and Koski, *J. Amer. Chem. Soc.*, 1960, **82**, 3263.
[11] Imoto and Aoki, *Makromol. Chem.*, 1961, **48**, 72.

The value of some -30 cal. deg.$^{-1}$ mole^{-1} suggests a fairly extensive solvation of the ion-pair, the effect being largest for the ion-pair of smallest radius, *i.e.*, boron trifluoride diethyl etherate.

The Effect of Traces of Water.—In the case of boron trifluoride diethyl etherate, which is very active in the anhydrous state, water was without effect on the rate, but it did give rise to induction periods and lowered the $\overline{\text{D.P.}}$ of the product.[1]

In the case of boron trifluoride–tetrahydrofuran, which was inactive, water gave rise to a relatively slow catalytic polymerisation, the maximum observed rate constant of 0.064 l.^{2} mole^{-2} min.$^{-1}$ being much smaller than the overall rate constants in Table 1. Water is thus a cocatalyst for the inactive tetrahydrofuran complex, but the system is still relatively less active than the other ethers. The optimum ratio of $1:1$ for water to boron trifluoride suggests that the active catalyst is the complex BF_3,H_2O, as in the isomerisation of butenes.[12]

Termination and Transfer.—The relative speed of the reactions,

$$\text{ᴧᴧCH}_2\cdot\overset{+}{\text{CH}}\cdot\text{OR} + (BF_3,OR)^- \longrightarrow \text{ᴧᴧCH:CH·OR} + BF_3,ROH$$

$$\text{ᴧᴧCH}\cdot\overset{+}{\text{CH}}\cdot\text{OR} + \text{CH:CH·OR} \longrightarrow \text{ᴧᴧCH:CH·OR} + \text{Me}\overset{+}{\text{CH}}\cdot\text{OR}$$

depends on the relative proton affinities of counter-ion and monomer. The present results, and earlier work on iodine catalysis,[13] require proton affinities to fall into two groups, in comparison to the proton affinity of monomer: $(BF_3,OMe)^-$ (from anisole), $(BF_3,OEt)^-$ I_3^- < alkyl vinyl ether monomer < $(BF_3,OPr^i)^-$ $(BF_3,OBu)^-$; $(SnCl_4,X)^-$ $(X = OH)$. In the case of stannic chloride it has been suggested that the cocatalyst was the monomer, but it may well have been water, since a trace of hydrate was probably present in the stannic chloride [13] (cf. Colclough and Dainton [5]).

THE UNIVERSITY, NOTTINGHAM.   [*Received July 2nd* 1963.]

[12] Clayton and Eastham, *J. Amer. Chem. Soc.,* 1957, **79**, 5368.
[13] Eley and Richards, *Trans. Faraday Soc.,* 1949, **45**, 436.