The Kinetics of Ionic Polymerisations. Part V.* The Inhibition by Pyridine and 2-Iodopyridine of Polymerisation of n-Butyl Vinyl Ether Catalysed by Iodine.

By D. D. ELEY and J. SAUNDERS.

The polymerisation of *n*-butyl vinyl ether catalysed by iodine is inhibited by pyridine and 2-iodopyridine. The results may be described in terms of a ternary 1 : 1 : 1-complex, and a number of these complexes have been prepared. The formation equilibrium constants are deduced from the kinetics of inhibition and a structure is postulated.

True velocity constants for the polymerisation of the different vinyl ethers have been calculated from the apparent velocity constants quoted in Part III, and the values of the iodine–vinyl ether complex formation constant K_c have been revised. These data are given in an Appendix.

THE initiation of vinyl ether polymerisation by iodine has been attributed to the unstable I^+ ion reacting with the double bond to form a carbonium ion (Part I, Eley and Richards, *Trans. Faraday Soc.*, 1949, **45**, 425). If this is so we should expect the addition of pyridine to inhibit the initiation step by forming a PyI^+ ion. While co-ordination of this type serves to stabilise the iodine cation (cf. Sidgwick, " The Chemical Elements and Their Compounds," 1950, Vol. II, p. 1241) it will at the same time be expected to destroy its activity as an electrophilic catalyst. Here we study the subject quantitatively, both with pyridine and with 2-iodopyridine which we expect to be a somewhat weaker electron donor than pyridine itself.

EXPERIMENTAL

The monomer used was *n*-butyl vinyl ether, the catalyst iodine, and the solvent diethyl ether. These materials were purified as described in Part I (*loc. cit.*). The polymerisations were followed in dilatometers at 25°.

* Part IV, preceding paper.

" AnalaR " pyridine was first dried (KOH, then P_2O_5), and then distilled twice *in vacuo*; it had $d_4^{25} = 0.971$, $n_D^{21.5} = 1.5046$, and was used as a solution in diethyl ether.

2-Iodopyridine was kindly supplied by Professor Wilson Baker and Dr. R. F. Curtis. It was purified by repeated distillation *in vacuo*, giving a colourless product, $d_4^{25} = 1.928$ g./c.c., $n_D^{20.5} = 1.6242$. It was used in ethereal solution.

RESULTS

The results of the kinetic investigations are shown in Table 1 and Fig. 1. It is noteworthy that with 2-iodopyridine a small amount of the base actually increased the rate of reaction by about 25%. When pyridine was used there was evidence for the formation of small amounts of an orange-brown deposit or red crystals in the reaction mixture. With 2-iodopyridine a yellow-orange cloudiness developed in the mixture at 25°, but redissolved without leaving any solid deposit. In some experiments with iodine, *cyclo*hexyl vinyl ether, and pyridine, a transparent red liquid was formed at 0°, and when the temperature was raised a deep red crystalline sediment was obtained, insoluble in distilled water and diethyl ether but soluble in alcohol. It was decomposed by aqueous sodium thiosulphate and gave a positive starch–iodide test.

As a result of these observations the formation of crystalline complexes at room temperature in the system pyridine–iodine–X was examined, where X was a vinyl ether or other compound.
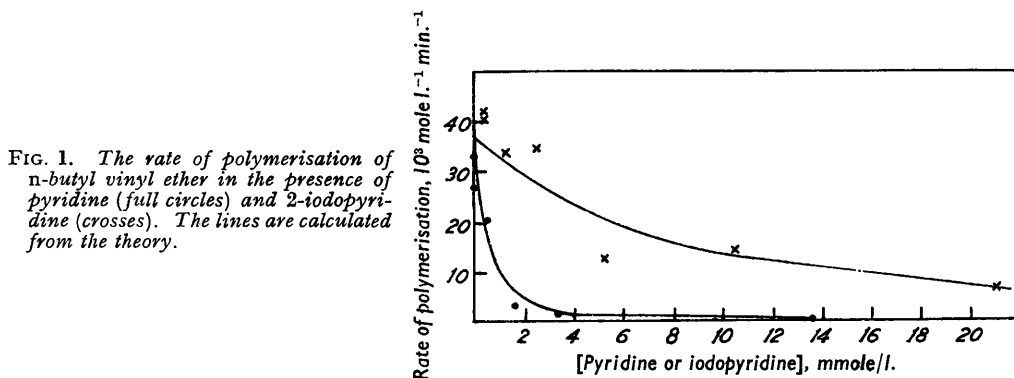

FIG. 1. *The rate of polymerisation of n-butyl vinyl ether in the presence of pyridine (full circles) and 2-iodopyridine (crosses). The lines are calculated from the theory.*

Preparation of Complexes.—The reactant X was added to the red-brown solution of iodine in pyridine, with the results shown. All these components were necessary for *complex* formation. The calculated analytical figures are for 1 : 1 : 1–I_2 : pyridine : X.

X = n-*Butyl vinyl ether.* A deep red oil was formed which crystallised as a grey-brown solid, insoluble in diethyl ether and stable up to 40—50°.

X = *cycloHexyl vinyl ether plus diethyl ether.* Red needles and a little red oil were formed. The complex was insoluble in ether, but soluble in pyridine and alcohol. It was stable if separated, but liquefied after a few days if kept in contact with supernatant liquor.

X = *cycloHexyl vinyl ether.* Pale yellow needles and red microcrystals were formed, which changed to a viscous red oil if kept in contact with supernatant liquor. The crystals were soluble in pyridine, chloroform, and nitrobenzene.

X = 2-*Ethylhexyl vinyl ether.* A red oil was formed which slowly gave chocolate-coloured crystals, insoluble in ethyl ether, and melting with decomposition at 30° with liberation of iodine. The complex gave conducting solutions in acetone and pyridine, the specific conductance of the almost saturated solution being respectively 3.2×10^{-4} and 1.5×10^{-4} mho, at 18°.

X = *Ethyl vinyl ether.* A yellow oil was formed which became red and gave pale grey crystals, insoluble in ethyl ether, but soluble in pyridine, acetone, etc. They were stable to 40—50° (Found : C, 27·65; H, 3·3; I, 60·35; N, 4·1; O, 4·6. Required : C, 26·7; H, 3·2; I, 62·7; N, 3·5; O, 3·93%).

X = *isoButyl vinyl ether.* A deep red oil was formed, slowly crystallising to a deep red solid, insoluble in ethyl ether.

X = 2-*Chloroethyl vinyl ether.* A red oil was formed together with pale yellow crystals. This complex was formed more slowly than with the other vinyl ethers (Found : C, 25·5; H, 3·35; Hal, 60·8; N, 3·0. Required : C, 24·6; H, 2·7; Hal, 65·9; N, 3·2%).

X = Divinyl ether. A red oil was formed, crystallising as a pale yellow transparent solid, insoluble in ethyl ether and non-polar solvents, but soluble in polar solvents (Found : C, 27·5; H, 3·0; I, 61·9; N, 4·1. Required : C, 26·8; H, 2·7; I, 63·0; N, 3·5%).

X = Acrylonitrile. Chocolate-brown prismatic crystals were slowly formed, but no oil. It was noticed that the crystal habit was different from that of the vinyl ether complexes (Found : C, 25·2; H, 2·0; N, 6·8. Required : C, 24·9; H, 2·1; N, 7·25%).

X = α-Methylstyrene. The complex was a red oil, giving no crystals, and was only slowly formed in the presence of excess of monomer. It was sparingly soluble in diethyl ether, and soluble in alcohol.

X = Diethyl ether. A little red oil was observed, which was only formed if ether was present in excess.

*X = Dibutyl ether.* Some red oil was formed, but only in the presence of excess of ether.

X = Anisole. No complex was obtained.

X = Water. A large yield of orange crystals was obtained which were soluble in pyridine and very soluble in ethyl ether.

Apart from the acrylonitrile complex which was stable all the above complexes showed appreciable decomposition after 5 months' storage in stoppered tubes in the dark. The colour darkened and an odour developed which in a number of cases appeared to be that of the alcohol corresponding to the side-chain in the ether, *e.g.*, *cyclo*hexyl vinyl ether (odour of *cyclo*hexanol). The *cyclo*hexyl vinyl ether complex after storage had C, 26·2; H, 2·9%.

DISCUSSION

Nature of the Complex.—The above work supports the notion that the complexes are $1Py : 1I_2 : 1X$. Where X is a vinyl ether, acrylonitrile, or α-methylstyrene relatively stable yellow or red needles are formed which decompose at 40—50°, and are probably ionic or highly polar as they are insoluble in ether and non-polar solvents, and dissolve in polar solvents to give conducting solutions. The complexes where X is a saturated ether seem to be much more slowly formed, and if an electron-attracting group is present in the saturated ether, as phenyl in anisole, no complex is formed at all. We take these results to mean that formation of the vinyl ether complex occurs through the olefinic group rather than the ether oxygen. The complex with water is obviously of a different type, and is probably similar to that described as PyI_2 by Waentig (*Z. physikal. Chem.*, 1909, **68**, 513) and Py_2I_2 by Chatelet (*Ann. Chim.*, 1934, **2**, 5; *Compt. rend.*, 1933, **196**, 1421, 1607). A range of complexes containing positive iodine, $Py_2I^+X^-$; PyI^+X^- and related complexes, have been prepared by Carlsohn (*Ber.*, 1935, **68**, 2209; *Angew. Chem.*, 1933, **46**, 747) and recently by Zingaro, Goodrich, Kleinberg, and VanderWerf (*J. Amer. Chem. Soc.*, 1949, **71**, 575; 1950, **72**, 5341). Here X is an acid radical, such as nitrate, acetate, etc., but in our complexes the third component is monomer. For iodine–pyridine solutions, conductivity (Audrieth and Birr, *J. Amer. Chem. Soc.*, 1933, **55**, 668), polarisation (Fairbrother, *J.*, 1948, 1051), and calorimetric studies (Markley and Skinner, *Trans. Faraday Soc.*, 1950, **46**, 621) suggest the formation of salts or ion pairs of the form $PyI^+ I^-$. Very recently Zingaro, VanderWerf, and Kleinberg, from absorption spectra and exchange with radio-iodine (*J. Amer. Chem. Soc.*, 1951, **73**, 88, 1865), postulated an equilibrium :

$$2I_2 + Py \rightleftharpoons PyI^+ + I_3^-$$
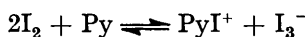
These considerations suggest that our complexes may probably be formulated as $(Py \ X \ I)^+ \ I^-$, and the results further suggest that in vinyl ethers the double bond rather than the ether group is involved, *e.g.*

$$\left\{ Py \longrightarrow I \ \ldots \ \begin{matrix} CH_2 \\ \| \\ CH_2-OR \end{matrix} \right\}^+ I^-$$
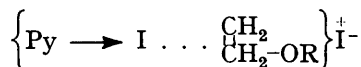
The bond between ethylene and the iodine atom is unlikely to be a donor link of the π electrons, since it is improbable that the empty $5d$ or $6s$ shell of the iodine atom will accept electrons in this way (the $5p$ shell is already completed by the electron pair from the nitrogen atom). Also, such a bond would involve a large accumulation of electrons on the iodine atom. Finally the formation of the complexes is not inhibited by the presence of electron-attracting side groups on the vinyl ether, chlorovinyl ether and divinyl ether

both giving complexes. A possible bond involves a donation of electrons from the complete $4d$ shell of the iodine atom to the empty antibonding π orbital of the ethylenic complex, as suggested by Dewar for Ag^+ and Br^+ (*Bull. Soc. chim.*, 1951, **18**, C79). Such a link might serve to stabilise the $N{\rightarrow}I$ bond by transferring electron density from the iodine atom to the ethylenic compound. It would not be expected to activate the double bond for polymerisation (Eley, " Cationic Polymerisation and Related Complexes," Cambridge, 1953, p. 67, Ed. Plesch). The relationship of these complexes to the binary complexes of iodine and ethylenic substances (Andrews and Keefer, *J. Amer. Chem. Soc.*, 1952, **74**, 458; Freed and Sancier, *ibid.*, p. 1273; Ketelaar and Van der Stolpe, *Rec. Trav. chim.*, 1952, **71**, 805) requires further investigation.

The Kinetics.—The above results suggest we are concerned with a ternary equilibrium of iodine, pyridine, and monomer to give inactive complex :

$$I_2 + Py + M \rightleftharpoons I_2PyM$$
$$[I_2] - x - y \quad [Py] \quad [M] \quad y$$
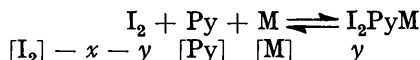
In addition there is the previously postulated equilibrium between iodine and monomer to give inactive complex :

$$I_2 + M \rightleftharpoons I_2M$$
$$[I_2] - x - y \quad [M] \quad x$$
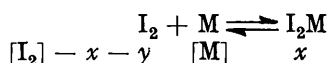
We define
$$K_p = \frac{y}{([I_2] - x - y)[Py] \cdot [M]} \text{ and } K_c = \frac{x}{([I_2] - x - y)[M]}$$

and deduce the concentration of free unbound iodine to be

$$[I_2]_f = \frac{[I_2]}{1 + K_c[M] + K_p[Py][M]} \qquad \cdots \cdots \quad (1)$$

The easiest procedure is to assume the kinetic expression with a true velocity constant k_t,

$$-d[M]/dt = k_t[I_2]_f{}^2[M]$$

then
$$k_t = 4000 \text{ l.}^2 \text{ mole}^{-2} \text{ min.}^{-1} \text{ (see appendix)}$$

From this equation we can calculate $[I_2]_f$ for the measured rates, at the given monomer concentration $[M] = 0.86$ mole l.$^{-1}$. A plot of $1/[I_2]_f$ against the concentration of pyridine should give a straight line, since from equation (1)

$$\frac{1}{[I_2]_f} = \frac{1 + K_c[M]}{[I_2]} + \frac{K_p[M] \cdot [Py]}{[I_2]}$$

Values of K_p so derived are : pyridine, $K_p = 1.9 \times 10^3$ l.^{2} mole^{-2}; 2-iodopyridine, $K_p \sim 100$ l.^{2} mole^{-2}.

The point at the highest pyridine concentration is neglected. It lies off the line and the experimental error will have a large effect for such a very small

<div align="center">TABLE 1.</div>

Inhibition by pyridine. [M] = 0.86 mole/l.; [I₂] = 4.37 mmole/l. at 25°.			Inhibition by 2-iodopyridine. [M] = 0.86 mole/l.; [I₂] = 4.37 mmole/l. at 25°.		
IPy, mmole/l.	Rate (obs.) mole l⁻¹. min⁻¹. ×10³	Rate (calc.) mole l⁻¹. min⁻¹. ×10³	IPy, mmole/l.	Rate (obs.) mole l⁻¹ min⁻¹. ×10³	Rate (calc.) mole l⁻¹ min⁻¹. ×10³
0	27·3	36·7	0·418	40·8	34·6
0	33·1	36·7	0·418	42·0	34·6
0·546	20·4	13·2	1·254	33·9	31·3
1·638	3·6	4·1	2·508	35·0	27·0
3·277	1·6	1·5	5·238	13·0	20·5
13·66	0·4	0·12	10·48	14·3	13·1
			20·95	6·6	6·6

reaction rate. For 2-iodopyridine it is necessary to neglect the four points at the lowest concentrations, as here the reaction velocity is *increased*. This effect, however, is well outside the experimental error. It cannot arise from iodine impurity in the iodopyridine since this was carefully removed, and the effect has not so far been explained. To compare

theory with experiment it is convenient to recalculate values of the reaction velocity as a function of pyridine concentration :

$$-\frac{d[M]}{dt} = k_t[I_2]_f{}^2[M] = \frac{k_t}{(1 + K_c[M] + K_p[Py][M])^2}[I_2]^2[M]$$

We take $k_t = 4000\ 1.^2\ \text{mole}^{-2}\ \text{min.}^{-1}$, $K_c = 0.41.\ \text{mole}^{-1}$, $K_p = 1.9 \times 10^3\ 1.^2\ \text{mole}^{-2}$, and obtain the figures given in the last column of Table 1, and the full curve in Fig. 1. Figures are also shown for 2-iodopyridine, calculated with the above data and the value $K_p = 100\ 1.^2\ \text{mole}^{-2}$.

APPENDIX

In Part III (*loc. cit.*) values of the apparent third-order constant k at *low* monomer concentrations, and K_c are listed. We now require the true velocity constants k_t which refer to the concentration of free iodine :

$$v = k_t[I]_f{}^2[M] = \frac{k_t[I_2]^2[M]}{(1 + K_c[M])^2}$$

and we have calculated these by fitting the theoretical formula to the experimental points over the whole range of monomer concentrations. Examples are given in Fig. 2 (*n*-butyl

FIG. 2. *Experimental points and theoretical curve* ($k_t = 4000$, $K_c = 0.4$) *for* n-*butyl vinyl ether.*
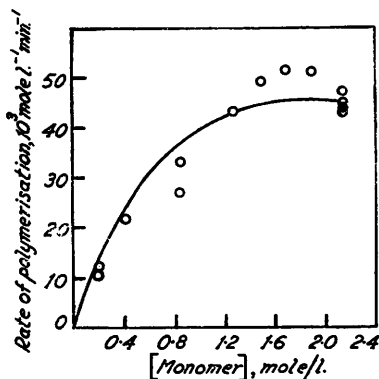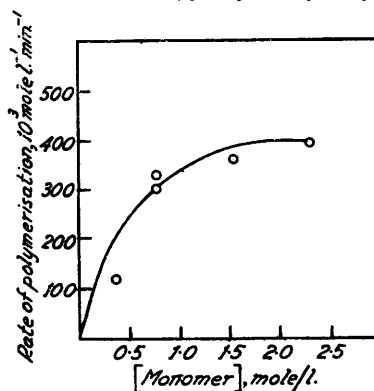
FIG. 3. *Experimental points and theoretical curve* ($k_t = 40,000$, $K_c = 0.5$) *for* cyclo*hexyl vinyl ether.*

vinyl ether) and Fig. 3 (*cyclo*hexyl vinyl ether), the solid lines being calculated by using the new k_t and K_c values in Table 2. There are noticeable deviations between the theoretical curve and the experimental points, part of which may be experimental error,

TABLE 2. *Kinetic constants for vinyl ether polymerisations.*

Monomer	k (Part III)	k_t (new)	K_c (Part III)	K_c (new)
	1.² mole⁻² min.⁻¹		1. mole⁻¹	
*cyclo*Hexyl	22,000	40,000	1·25	0·5
*iso*Butyl	1,900	4,000	1·25	0·8
2-Ethylhexyl	1,000	2,000	0·67	0·4
n-Butyl	1,800	4,000	0·5	0·4
Ethyl	1,900	5,000	0·31	0·31
2-Chloroethyl	90	125	<0·23	0·05

but part may be attributed to shortcomings in the theory : *e.g.*, neglect of activity coefficients in the equilibrium equations. The tendency is for the experimental points to rise more gradually and then turn over rather more abruptly than the theoretical curve at high concentrations, at least for the case of Fig. 2, and also for the *iso*butyl and 2-ethylhexyl ethers. The new values for k_t and K_c are given in Table 2 together with the values deduced for the apparent velocity constants k and K in the previous paper.

THE UNIVERSITY, BRISTOL.