777. *The Low-temperature Polymerisation of Isobutene. Part IV.* Exploratory Experiments.*

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We report results on the polymerisation of isobutene by titanium tetrachloride which were obtained while developing a satisfactory technique and apparatus. Only molecular weights are given and discussed. Reactions in hexane with trifluoroacetic acid as co-catalyst gave higher molecular weights and a lower E_M value than those found in earlier studies with trichloroacetic acid as the co-catalyst. In both ethyl bromide and ethyl chloride the molecular weights and E_M values were the same, and independent of the nature of the co-catalyst (water or trifluoroacetic acid); and at about −70° the molecular weights were independent of monomer concentration. Approximate values of k_m/k_p have been obtained. The results of Norrish and Russell on the polymerisation of isobutene in ethyl chloride by stannic chloride and water have been analysed: the relatively low rates and molecular weights obtained in that system are due to slow initiation, and a fast transfer reaction with free stannic chloride monohydrate. Values of relative transfer and termination coefficients have been calculated.

We have polymerised isobutene in liquid carbon dioxide in an all-glass apparatus at about −50° with aluminium bromide and with titanium tetrachloride.

Only one study of the kinetics of the low-temperature cationic polymerisation of isobutene is sufficiently rigorous to be accepted.[1-3] However, this deals with the comparatively slow reaction catalysed by stannic chloride and sheds little light on the fast polymerisations catalysed by, *e.g.*, boron fluoride, titanium tetrachloride, or aluminium chloride. Earlier kinetic studies with titanium tetrachloride[4,5] were carried out by techniques which are now known to be inadequate, though the general qualitative conclusions are probably sound.

The object of the present work was to devise a method for following the very fast polymerisations catalysed by titanium tetrachloride, to obtain reproducible rates and molecular weights, and to work out the kinetics and chemistry of the reaction. Although the rates of these reactions could not be measured with the required precision, the molecular weights of the products were reasonably consistent; this confirmed previous experience that the rate of this polymerisation is far more difficult to reproduce than the molecular weights of the reaction products. These preliminary results form the subject of this paper.

The irreproducibility of the rates was traced to the presence of micromolar quantities of water, and a technique was evolved by which the polymerisation rate could be measured and reproducible rates obtained. Detailed kinetic studies were then carried out with controlled quantities of water, various alkyl chlorides being used as solvents and titanium tetrachloride as catalyst, in the temperature range +20° to −95°. The results of these rigorous studies will form the subject of subsequent papers in this series.

Experimental

General Considerations.—Earlier experience had shown that the rigorous exclusion of moisture and other impurities would be required. A high-vacuum technique was therefore chosen. The most serious technical difficulty was the lack of a greaseless tap, rapid and delicate

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* Part III, Flett and Plesch, *J.*, 1952, 3355.

[1] Norrish and Russell, *Nature*, 1947, **160**, 543.

[2] Norrish and Russell, *Trans. Faraday Soc.*, 1952, **48**, 91.

[3] Russell, in " Cationic Polymerisation and Related Complexes," ed. P. H. Plesch, Heffer and Sons, Cambridge, 1953, p. 114.

[4] Plesch, Polanyi, and Skinner, *J.*, 1947, 257.

[5] Plesch, *J.*, 1950, 543.

in action, incorrodible, vacuum-tight, and completely reliable for long periods. No commercial device available when this work was started (1954) was satisfactory; our own solution of the problem has been published.[6]

Technique.—Preliminary experiments and earlier work showed that the polymerisation was so fast that none of the conventional methods of following the reaction could be used. Furthermore, we needed to work at low temperatures. Therefore, the adiabatic calorimetry technique was selected and refined.

The experiments reported here were carried out with apparatus and techniques essentially similar to those finally adopted and described.[7] All reagents were handled in a vacuum system. Solvent and isobutene were condensed into the vessel, and the reactions were started by magnetically breaking phials containing solutions of catalyst and/or of co-catalyst. The polymers were recovered either by precipitation or by steam-distillation.

Materials.—Isobutene. Isobutene (I.C.I.), said to be more than 99% pure, was dried by distilling it at least twice *in vacuo* through a trap containing molten sodium at 350°. Specimens of the purified material were analysed by gas–liquid chromatography and by infrared spectroscopy; neither technique showed any detectable impurity. The isobutene was stored as liquid in the apparatus described.[7]

Hexane. Hexane was purified by shaking it with two portions of 20% oleum; it was washed successively with water, aqueous sodium hydroxide, and water, and dried successively with calcium chloride and calcium hydride. It was distilled through an efficient column, and the fraction collected (b. p. 67—69°) was transparent down to 2200 Å. It was distilled into the reservoir attached to the polymerisation apparatus, out-gassed, and kept there over calcium hydride.

Ethyl bromide. This was purified by standard methods and distilled off phosphoric oxide through a Vigreux column with a reflux ratio of 5 : 1, and the fraction of b. p. 37·9°/745 mm. was collected (lit., b. p. 38·0°/760 mm.). It was distilled into the reservoir and kept there over phosphoric oxide which could be agitated by a magnetic stirrer.

Ethyl chloride. Ethyl chloride (I.C.I) was passed from the cylinder through towers containing sodium hydroxide pellets and phosphoric oxide and condensed in the reservoir of the polymerisation apparatus, containing calcium hydride. It had a triple point of −133·4° (lit., f. p. −138·3°).

Titanium tetrachloride. Titanium tetrachloride (British Titan Products) was distilled once in air and then twice *in vacuo*, generous head and tail fractions being discarded each time. Solutions in hexane or methylene dichloride were made up and charged into phials as previously described.[8] The concentrations of these solutions were determined by analysing several phials from each batch. The contents of the phials, kept in the dark, remained colourless for many months.

Trifluoroacetic acid. This was generated from the potassium salt by addition of concentrated sulphuric acid in a vacuum system, and purified by bulb-to-bulb distillations. Solutions in hexane were made up and filled into phials as described.[8]

Determination of Molecular Weight.—The polymers were dissolved in distilled and dried commercial di-isobutene. Viscosities were determined at 25° by using Craig and Henderson's viscometer.[9] Concentrations were determined by drying measured volumes of polymer solution to constant weight. Molecular weights were calculated from the intrinsic viscosities by Flory's equation.[10]

RESULTS

Hexane as Solvent.—Using hexane as solvent, we could prepare non-reacting mixtures of titanium tetrachloride and isobutene, which could be made to react by adding trichloro- or trifluoro-acetic acid. With both these co-catalysts the reaction rates were rather irreproducible. An Arrhenius plot of the molecular weights of the polymers is shown in Fig. 1, whence an " activation energy of molecular weight," $E_M = -3 \pm 1{\cdot}5$ kcal./mole, is obtained.

We found that at low temperatures the addition of millimolar quantities of trifluoroacetic

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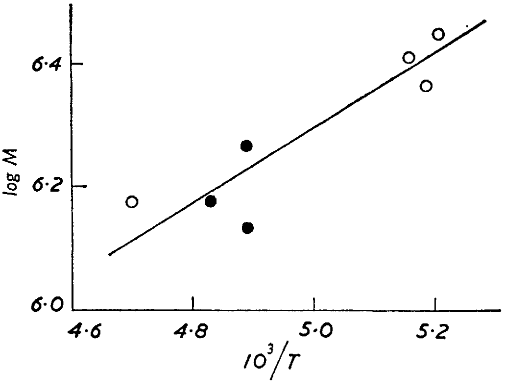
[6] Biddulph and Plesch, *Chem. and Ind.*, 1956, 569.
[7] Biddulph and Plesch, *Chem. and Ind.*, 1959, 1482.
[8] Biddulph and Plesch, *Chem. and Ind.*, 1956, 567.
[9] Craig and Henderson, *J. Polymer Sci.*, 1956, **19**, 215.
[10] Flory, *J. Amer. Chem. Soc.*, 1943, **65**, 372.

TABLE 1. *Polymerisation in ethyl bromide.*

Expt. No.	$-T_i$ *	$[i\text{-}C_4H_8]$ (mmole/l.)	$[TiCl_4]$ (mmole/l.)	$10^{-5}M$	Expt. No.	$-T_i$*	$[i\text{-}C_4H_8]$ (mmole/l.)	$[TiCl_4]$ (mmole/l.)	$10^{-5}M$
				Variation of temperature					
67	103·1°	180	4·98	86	64	70·5°	175	4·98	8·2
68	101·2	177	,,	144	71	42·9	172	,,	2·2
62	71·8	177	,,	7·0	70	37·8	176	,,	0·91
				Variation of monomer concentration					
30	71·4	920	5·68	5·8	31	65·4	360	5·68	2·04
62	71·8	177	4·98	7·0	50	59·4	236	11·4	4·2
64	70·5	175	,,	8·2	45	63·4	116	8·51	4·3
65	70·3	123	,,	9·5	47	62·7	116	11·4	2·74
66	72·5	120	,,	6·2	46	66·6	112	,,	3·1
57	71·5	120	2·74	5·1					
61	72	117	4·98	5·1					

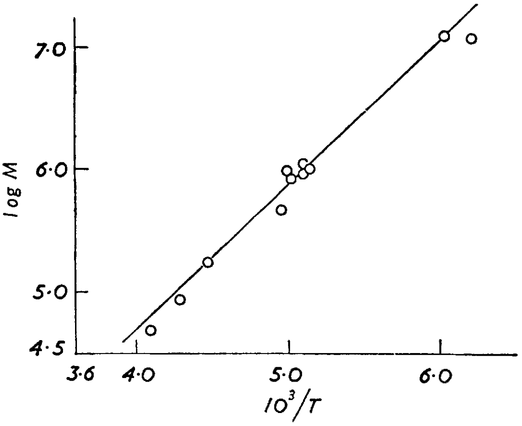
* In Tables 1—3 T_i is the initial temperature.

FIG. 1. *Polymerisation in hexane solution. Dependence of molecular weight on temperature.*



$[i\text{-}C_4H_8]$ = 940 mmoles/l.; $[TiCl_4]$ = 5·68 mmoles/l.; $[CF_3\cdot CO_2H]$ = 0·81 (○) and 1·22 (●) mmoles/l.

FIG. 2. *Polymerisation in ethyl chloride solution. Dependence of molecular weight on temperature.*



(Concentrations as in Table 2.)

TABLE 2. *Polymerisation in ethyl chloride.*

$[i\text{-}C_4H_8] = 0·173 \pm 0·003$ mole/l.

Expt. No.	$-T_i$ *	$[TiCl_4]$ (mmole/l.)	$10^{-5}M$	Expt. No.	$-T_i$ *	$[TiCl_4]$ (mmole/l.)	$10^{-5}M$
93	112·1°	7·36	120	85	73·4°	2·49	9·77
94	107·5	,,	126	95	71·4	7·36	4·78
89	78·2	2·49	10·2	87	50·0	2·49	4·48
90	77·6	7·36	11·5	92	40·3	7·36	0·87
88	77·4	2·49	9·55	91	30·8	,,	0·50
86	74·0	,,	8·31				

TABLE 3. *Polymerisation in ethyl chloride with trifluoroacetic acid as co-catalyst.*

Expt. No.	$-T_i$*	$[i\text{-}C_4H_8]$ (mmole/l.)	$[TiCl_4]$ (mmole/l.)	$[CF_3\cdot CO_2H]$ (mmole/l.)	$10^{-5}M$
Fig. 2	75°	173	—	0	~9 [a]
96	71·1	177	7·36	0·0105	8·30
97	75·6	115	4·98	,,	8·04
99	75·6	88	,,	,,	8·71
100 [b]	74·6	90	,,	,,	7·48
	73	104	,,	,,	
	73	94	,,	,,	

[a] This value is taken for comparison from Fig. 2. [b] In this experiment three portions of isobutene were added and polymerised successively in the same reaction mixture; the molecular weight is that of the whole batch of polymer recovered at the end.

acid to approximately M-solutions of isobutene (in the absence of titanium tetrachloride) caused no observable polymerisation during periods of up to 15 min.

Ethyl Bromide as Solvent.—The polymers were precipitated during the reactions, but were soluble in ethyl bromide at room temperature. The polymerisations were generally very fast, and the rates not reproducible. Occasionally, abnormally slow reactions occurred and the products of these always had abnormally low molecular weights. Apart from these " freaks," the molecular weights were reasonably consistent (Table 1). From these results $E_M = -5{\cdot}5 \pm 0{\cdot}5$ kcal./mole. Any variation of molecular weight with monomer concentration appears to be very slight between $-72°$ and $-60°$.

Ethyl Chloride as Solvent.—The polymer precipitated during reaction. The rates and the extent of polymerisation (yield) were irreproducible especially at the higher temperatures. This we attribute to the presence of uncontrolled quantities of residual water which is consumed during the reaction. However, the molecular weights were fairly consistent. The data shown in Table 2 and Fig. 2 give $E_M = -5{\cdot}5 \pm 0{\cdot}5$ kcal./mole, and show that the molecular weight is independent of the catalyst concentration.

Some experiments at about $-75°$ with trifluoroacetic acid as co-catalyst (Table 3) showed that this did not affect the molecular weight, and that the latter is independent of the monomer concentration under these conditions. In these experiments the monomer was consumed completely.

We found even our lowest polymers, of molecular weight about 5×10^4, to be virtually insoluble in ethyl chloride, whereas Russell [2,3] states that polyisobutenes of molecular weight less than about 10^6 were soluble; we have been unable to trace the cause of this discrepancy.

DISCUSSION

Theory.—For this discussion the polymerisation of isobutene will be interpreted according to the following theoretical picture:

Catalyst and co-catalyst react to give a complex acid:

$$x\mathrm{TiCl_4} + y\mathrm{HA} \longrightarrow (\mathrm{TiCl_4})_x(\mathrm{HA})y$$

For HA = H_2O nothing is known about x and y, but for simplicity we shall assume that both are unity. For HA = $CF_3{\cdot}CO_2H$, earlier work [11] has suggested that $x = 1$ and $y = 2$.

Initiation is assumed to occur by transfer of a proton from the complex acid to the monomer, and the rate-determining step is either a bimolecular process, *e.g.*,

$$\mathrm{TiCl_4,OH_2} + \mathrm{C_4H_8} \longrightarrow \mathrm{C_4H_9{}^+TiCl_4OH^-}$$

or a unimolecular isomerisation of a complex between the acid and the monomer.

The propagation (rate constant k_p) is regarded as a bimolecular reaction between carbonium ion and monomer.

The true (kinetic) termination (rate constant k_t) is an isomerisation of the ion-pair to give poly(isobutyl alcohol) or trifluoroacetate, according to the co-catalyst, titanium tetrachloride being regenerated.

Many types of transfer are possible, but the only one for which we have evidence is proton transfer to monomer (k_m):

$$\mathrm{H{\cdot}[C_4H_8]_n{\cdot}CH_2{\cdot}C(CH_3)_2{}^+} + \mathrm{C_4H_8} \longrightarrow \mathrm{H{\cdot}[C_4H_8]_n{\cdot}CH_2{\cdot}C(CH_3){:}CH_2} + \mathrm{C_4H_9{}^+}$$

In these terms the degree of polymerisation DP is given by

$$1/\mathrm{DP} = k_m/k_p + k_t/k_p[\mathrm{M}]$$

The " activation energy of molecular weight," E_M, is given by

$$E_M = 2{\cdot}3\boldsymbol{R}\ \mathrm{d}\log \mathrm{DP}/\mathrm{d}(1/T) = E_p - 2{\cdot}3\boldsymbol{R}\ \mathrm{d}\log(k_t + k_m[\mathrm{M}]/\mathrm{d}(1/T)$$

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[11] Brackman and Plesch, *J.*, 1958, 3563.

Thus E_M cannot be simply interpreted without a knowledge of the temperature-dependence of k_t and k_m.

Reactions in Hexane.—The polymers obtained when using trifluoroacetic acid as co-catalyst can be compared with those obtained by one of us using trichloroacetic acid as co-catalyst,[5] although in the earlier work the intrinsic viscosity measurements were made on hexane solutions of the polymers, whereas we now use di-isobutene. We have found that polyisobutenes have almost the same intrinsic viscosity in hexane as in di-isobutene.[12] The molecular weights found in this work are all higher than those obtained previously. This is probably correlated with the greater acid strength of the co-catalyst, which presumably gives a greater strength to the complex acid formed with titanium tetrachloride.[13] This would agree with other observations [14] that in the polymerisation of styrene by various acids the molecular weight of the polymer increases with the strength of the acid. However, the difference may also be partly due to the isobutene's having been much more rigorously purified than that used in previous work.

The value of $E_M = -3 \pm 1{\cdot}5$ kcal./mole is significantly smaller than that ($-7{\cdot}5$) found with trichloroacetic acid.[5] Unfortunately, this difference cannot be interpreted without information on the temperature-dependence of k_t and k_m. Over the temperature range studied, the molecular weights are significantly greater than those obtained in ethyl bromide and ethyl chloride.

Reactions in Ethyl Bromide.—In these experiments the co-catalyst was probably residual water, but part, at any rate, of the irreproducibility may also have been due to traces of hydrogen bromide. At 20° the equilibrium constant for the reaction $C_2H_5Br \rightleftharpoons C_2H_4 + HBr$ is $K_p = 1{\cdot}96 \times 10^{-8}$ atm.[15] The vapour pressure of ethyl bromide at that temperature is $\sim$400 mm. This means that for the liquid at that temperature the equilibrium concentration of hydrogen bromide is $\sim 3 \times 10^{-3}$ mole/l. Although, of course, the equilibrium concentration of hydrogen bromide is very much smaller at the low temperatures of our experiments, it is not certain that equilibrium would have been attained in every experiment, and therefore some interference with the polymerisation by traces of hydrogen bromide might be expected, possibly through the formation of some t-butyl bromide. This is a serious reason for avoiding in future the use of this solvent.

The most significant conclusion is that below about —60° the molecular weight is independent of monomer concentration. It follows that in these reactions the DP is governed by the transfer to monomer (k_m) and that unimolecular termination (k_t) and any unspecified transfer or termination reactions not involving monomer are insignificant. On this basis the data in Table 1 give k_m/k_p at *ca.* —63° as about 2×10^{-4} and at *ca.* —71° as about 8×10^{-5}.

We have no evidence to indicate whether or not ethyl bromide is a co-catalyst.

Reactions in Ethyl Chloride.—Our results have shown that this substance is not a co-catalyst, because reactions which had been stopped by the consumption of the adventitious water could be made to continue by addition of, *e.g.*, trifluoroacetic acid.

The molecular weights obtained at —70° without and with trifluoroacetic acid are not significantly different, and with the acid the molecular weights are independent of monomer (and probably also of catalyst) concentration at that temperature. Both these features indicate that, just as in ethyl bromide solution, the principal chain-breaking mechanism must be transfer to monomer. It follows from the data in Table 3 that at about —74° k_m/k_p is approximately 7×10^{-5}. The very close agreement between the magnitudes of the molecular weights and of the values of E_M obtained with both solvents suggests that the reaction mechanisms are similar. Over the whole temperature range concerned the dielectric constant of ethyl bromide is about two units smaller than that of ethyl chloride—

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[12] Plesch, unpublished work.

[13] Plesch, *Sci. Proc. Roy. Dublin Soc.*, 1950, **25**, 154.

[14] Brown and Mathieson, *J.*, 1957, 3612.

[15] Lane and Linnett, *Proc. Roy. Soc.*, 1953, *A*, **216**, 361.

which suggests that it is not primarily the dielectric constant of a solvent which determines its effect on cationic polymerisations. With trifluoroacetic acid as catalyst the molecular weights obtained in hexane were appreciably greater than those obtained with the same co-catalyst in ethyl chloride.

Comparison with the Results of Norrish and Russell.—The system isobutene–ethyl chloride has been investigated by Norrish and Russell,[1-3] who used stannic chloride as catalyst and water as co-catalyst. One of the most striking differences between their results and ours is that our reactions, catalysed by titanium tetrachloride, were very much faster, a feature previously reported by Russell.[3] Under comparable conditions of concentrations and temperature our reactions had half-lives of the order of a few seconds, whereas with stannic chloride they are measured in hours. A similar difference has been found in the polymerisation of styrene.

Unpublished results on molecular weights, kindly communicated to us by Dr. K. E. Russell, are given in Table 4. It is evident from these that, in contrast to our system, the molecular weight increases linearly with the monomer concentration, and that at comparable concentrations the molecular weights obtained with stannic chloride are much smaller than those obtained by us with titanium tetrachloride. A " first Mayo plot " of 1/DP against 1/[M] for Russell's results shows an intercept $I_1 = (2 \pm 1) \times 10^{-5}$ which can be identified with k_m/k_p. The slope S_1 is $5{\cdot}4 \times 10^{-4}$. This is identified, according to the usual procedure, with $(1/k_p[M])(k_t + J)$, where $J = \sum k_{b_i}[X_i]$, and X_i is the i-th chain-breaking agent reacting with growing chains, with a rate constant k_{b_i}. It remains to ascertain the number and nature of the chain-breaking agents in this system. Fortunately, the data assembled by Norrish and Russell[2] in their Figs. 2 and 4, when represented as " second " and " third Mayo plots " of 1/DP against $[H_2O]$ and 1/DP against $[SnCl_4]$, show unambiguously that the only chain-breaking agent is the free monohydrate of stannic chloride. If this is represented by X, and the rate constant of its reaction with growing chains by k_x, $J = k_x[X]$. $[X] = [H_2O]$ when $[H_2O] < [SnCl_4]$, and $[X] = [SnCl_4]$ when $[H_2O] > [SnCl_4]$.

TABLE 4. *Polymerisation of isobutene in ethyl chloride by stannic chloride and water at —78·5°.*

(Unpublished results of K. E. Russell,* quoted by permission.)

$[i\text{-}C_4H_8]$ (mole %)	4·2	8	11·2	14	17·6	25
$[i\text{-}C_4H_8]$ (mole/l.)	0·712	1·33	1·84	2·27	2·83	3·93
$10^{-5}M$	0·712	1·28	1·44	2·45	2·81	5·03

$[SnCl_4] = 1{\cdot}15$, $[H_2O] = 0{\cdot}11$ mole %.

* The concentrations are given by Russell in moles %. The concentrations of isobutene in mole/l. have been computed by us, the volumes of ethyl chloride and isobutene being assumed to be additive. The concentrations of stannic chloride and of water have been calculated by us to be, respectively, 0·196 and 0·0188 mole/l. at the lowest isobutene concentration, and 0·182 and 0·0174 mole/l. at the highest.

The slope of the " second Mayo plot " is $S_2 = k_x/k_p[M] = 8{\cdot}4 \times 10^{-3}$, whence $k_x/k_p = 2{\cdot}71 \times 10^{-2}$. This, and S_1, give $k_t/k_p = 4{\cdot}9 \times 10^{-5}$ moles/l. The intercept I_2 of the " second Mayo plot " is $(k_t + k_m[M])/k_p[M] = 3{\cdot}78 \times 10^{-5}$, whence $k_m/k_p = 2{\cdot}25 \times 10^{-5}$, which is in excellent agreement with the value derived from the " first Mayo plot."

The slope S_3 and the intercept I_3 of that part of the " third Mayo plot " which relates to $[SnCl_4] < [H_2O]$, have the same interpretation as S_2 and I_2, and the values ($S_3 = 8 \times 10^{-3}$, $I_3 = 2 \times 10^{-5}$) are in satisfactory agreement with those of S_2 and I_2.

These calculations show that at —78·5° in the system isobutene–stannic chloride–water–ethyl chloride, by far the most important chain-breaking reaction is that with free stannic chloride monohydrate. The importance of this compound as a transfer agent, revealed by this analysis, implies that initiation by it must be a slow reaction. Moreover, the activation energy of the rate is large and positive ($E_R = 7$ kcal./mole), and DP is almost independent [15a] of temperature between −63° and −95°. This indicates that E_R is essentially E_i and thus supports the idea that initiation is slow. Thus, the low rate must be attributed to the slowness of the initiation, and the low value of DP to the efficiency of stannic chloride monohydrate as transfer agent.

Although our own results on the comparable system isobutene–titanium tetrachloride–ethyl chloride are far less detailed than those of Norrish and Russell, they do indicate that all kinds of chain-breaking are relatively slow, and that initiation is fast. Herein appears to lie the main difference between the tetrachlorides of tin and titanium.

POLYMERISATIONS IN LIQUID CARBON DIOXIDE

It has been reported that when isobutene [16] and α-methylstyrene [17] are polymerised by aluminium halides, polymers of higher molecular weights are obtained with carbon disulphide than with alkyl halides as solvents. This prompted us to try liquid carbon dioxide as solvent for the polymerisation of isobutene. We have not been able to trace any publications on the use of this substance as a solvent for an organic reaction, although it has been mentioned in the patent literature. Since the triple point of carbon dioxide is at −56·5° and 5·01 atm., a special apparatus had to be devised, and experimentation was somewhat tedious. We therefore contented ourselves with a few qualitative experiments in which we found that the polymerisation of isobutene can indeed be carried out in liquid carbon dioxide.

Apparatus.—The polymerisation apparatus, made of 3-mm. Pyrex glass, consisted of a vertical tube fitted with a reciprocating stirrer operated by a solenoid. It had connected to it a sloping arm in which catalyst phials were held in position by magnetically retractable retainers, a manometer, and a side-arm with pressure-tap and ground socket to connect it to a vacuum manifold for evacuation and charging. The catalyst phials had to be made so heavy that they would sink and could thus be crushed by the stirrer.

Materials.—We found that with carbon dioxide from a cylinder there was no polymerisation when a phial containing aluminium bromide in ethyl bromide was broken in the solution containing isobutene. We therefore prepared carbon dioxide by heating " AnalaR " sodium hydrogen carbonate and dried it by passage through a trap cooled in solid carbon dioxide.

As catalyst we used solutions of aluminium bromide in ethyl bromide and solutions of titanium tetrachloride in isopropyl chloride. These were prepared, and filled into phials *in vacuo*.

The isobutene was purified as described above.

Procedure.—The apparatus was armed with two catalyst phials (in case one did not break) and evacuated, and approx. 0·27 mole of carbon dioxide and 0·03 mole of isobutene were condensed into it. When the contents were frozen solid, the apparatus was fitted with a wire-mesh guard-sleeve and transferred to a bath of alcohol at about −50°. When the contents were molten and the pressure was constant, the stirrer was started, and a catalyst phial dropped in. At the end of the reaction the reaction mixture was frozen solid, the bottom of the apparatus cut off, and the polymer recovered.

Results.—As soon as the catalyst phial was broken a white solid began to form. With aluminium bromide the reactions were extremely fast, the rise in temperature being shown by the increase in pressure—in one experiment to about 16 atm. The strong smell of isobutene when the discharged reaction mixture was being warmed showed that the reaction had been incomplete—presumably because the catalyst had become embedded in the polymer.

With titanium tetrachloride the reactions were slower than with aluminium bromide, and went virtually to completion.

Because the experiments were far from isothermal, and the conditions generally ill-defined, no particular value can be attached to the molecular weights, but those obtained with aluminium

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[15a] Russell, personal communication.

[16] Thomas and Arey, quoted in " Vinyl and Related Polymers," by C. E. Schildknecht, Wiley, New York, 1952, p. 546.

[17] Hersberger, Reid, and Heiligmann, *Ind. Eng. Chem.*, 1945, **37**, 1073.

bromide were much greater (~5 × 10^5) than those obtained with titanium tetrachloride (~3 × 10^4), which conforms with general experience. The infrared spectra of the polymers were normal.

Conclusion.—Our experiments show that carbon dioxide can be used as a solvent for cationic polymerisations. In comparative studies of solvent effects it may offer some advantages, since it is easy to purify, inert to metal halides, and very unlikely to participate in any transfer or termination reactions.

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