104. *The Low-temperature Polymerisation of* iso*Butene. Part II.**

By P. H. Plesch.

The polymerisation of *iso*butene in hexane solution by titanium tetrachloride with water and trichloroacetic acid as co-catalysts was investigated at temperatures between −90° and 0°, by an adiabatic technique. The kinetic data, which are of a preliminary nature, show that the reaction is of the first order with respect to the co-catalyst. There are indications that the activation energy of chain initiation is probably less than 4 kcals./mole and that the activation energy of chain termination may be as high as 10 kcals./mole. This is interpreted in terms of the rearrangement of the ion pair at the growing end of the polymer chain when termination takes place. Analytical data indicate that the co-catalyst may be built into the end of the chain at termination. The polarised-molecule theory is shown to be inapplicable to this system, and the carbonium ion theory is developed. The S-shaped reaction curves obtained under certain conditions are explained in terms of a slow build-up of the concentration of growing chains.

The polymerisation of *iso*butene at low temperatures by Friedel–Crafts catalysts has been the subject of numerous investigations, which have been reviewed recently (Heiligmann, *J. Polymer. Sci.*, 1949, **4**, 183; Plesch, *Research*, 1949, **2**, 267; *Proc. Roy. Dublin Soc.*, Symposium on Friedel–Crafts Polymerisations, in the press). In this laboratory we have mainly used titanium tetrachloride as catalyst (Plesch, Polanyi, and Skinner, *J.*, 1947, 257, who quote also Seymour, Thesis, Manchester, 1943; A. G. Evans *et al.*, *Nature*, 1946, **157**, 102; Plesch, *Nature*, 1947, **160**, 868) and the outcome of the early work with this halide and of parallel work with boron trifluoride (Evans, *loc. cit.*; A. G. Evans, Meadows, and Polanyi, *Nature*, 1947, **160**, 869; Evans and Polanyi, *J.*, 1947, 252; Evans and Meadows, *J. Polymer Sci.*, 1949, **4**, 359) was the conclusion that in these reactions a third component, called the co-catalyst, was essential. It was found that atmospheric moisture acted as such a co-catalyst. The reactions by means of which this effect was investigated at low temperatures were carried out adiabatically in hexane solution and were followed by recording the temperature rise caused by the heat of polymerisation.

When the reaction was initiated by passing a brisk stream of moist air through a non-reacting solution of *iso*butene and titanium tetrachloride in hexane, the reaction curves (time–temperature plots) were always S-shaped (Plesch, Polanyi, and Skinner, *loc. cit.*, Figs. 3 and 4). Frequently it was found that a given dose of moist air would induce a reaction which would cease before all the monomer had been consumed. In such cases a second dose of moist air would induce a further reaction (*loc. cit.*, Fig. 4). Although the detailed course of the reactions was not reproducible, an examination of the temperature dependence of the initial and maximum rate of reaction showed a certain regularity, as can be seen from Figs. 1 and 2 below. These results suggest that the rate of the polymerisation co-catalysed by water vapour has a positive temperature coefficient. This is the direct opposite of what had been found in our rough preliminary experiments (*loc. cit.*) and by other workers (*e.g.*, Thomas *et al.*, *J. Amer. Chem. Soc.*, 1940, **62**, 276; Waterman *et al.*, *Rec. Trav. chim.*, 1934, **53**, 699). An explanation of this will be suggested in the Discussion below.

* Part I, *J.*, 1947, 257.

Although the discovery of the rôle of water in these polymerisations had made clear at least one of the possible causes of the irreproducibility, which seemed to characterise the polymerisation of *iso*butene, the deliberate use of water vapour as co-catalyst had not lead to any appreciable degree of reproducibility in these reactions. The reasons for this are not difficult to find.

Water vapour introduced into a hydrocarbon solution at a temperature far below 0° must form a dispersion of ice and therefore its action could not be envisaged as anything but heterogeneous. This view was supported by the milky appearance of the final polymer solution. Even if the water had been initially in a molecularly disperse form in the reaction mixture it must be presumed that the titanium tetrachloride–water complex which is postulated as the real initiator of the reaction (Plesch, Polanyi, and Skinner, *loc. cit.*) would not be soluble in the mixture of *iso*butene and hexane and would tend to form aggregates. Thus the rate and extent of reaction would depend on the size and number of these aggregates and on the rate at which they settled out on the walls and fittings of the reaction vessel.

FIG. 1.

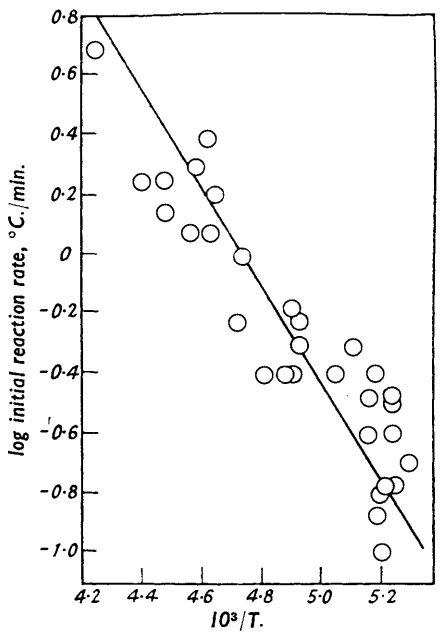


FIG. 2.

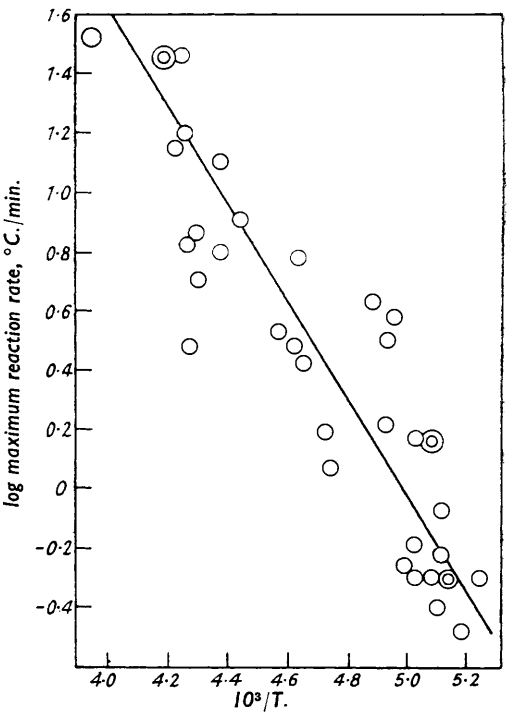


FIG. 1.—*Adiabatic polymerisation of* isobutene (2·5 *moles/l.*) *by* $TiCl_4$ ($4{\cdot}8 \times 10^{-2}$ *mole/l.*), *co-catalysed by water vapour. Initial rate as a function of temperature.*
FIG. 2.—*Maximum rate as a function of temperature. Otherwise as for Fig.* 1.

For these reasons we attempted to find a co-catalyst which would make it possible to carry out the reaction under homogeneous conditions. We required a co-catalyst which would be soluble in a hydrocarbon medium and whose complexes with titanium tetrachloride would also be soluble in such a medium. It was evident that no inorganic substance was likely to fulfil both these conditions. Investigations in these laboratories running parallel to the work reported here had shown that acetic acid (Evans, Meadows, and Polanyi, *loc. cit.*) and *tert.*-butanol (Evans and Polanyi, *loc. cit.*) are capable of acting as co-catalysts to boron trifluoride in the polymerisation of gaseous *iso*butene at room temperature, but neither of these substances was found to be effective as co-catalyst to titanium tetrachloride in the low-temperature polymerisation of *iso*butene (Plesch, *Nature*, 1947, **160**, 868). On the contrary, they were found to act as inhibitors to this reaction. Diethyl ether and ethanol have been reported previously (Plesch, Polanyi, and Skinner, *loc. cit.*) to have a similar inhibiting effect.

The Present Investigation.

Qualitative Results. The Survey of Co-catalysts.—The qualitative results of the search for co-catalysts other than water are presented in Table I. According to our views on the nature of this polymerisation, a substance, in order to act as co-catalyst, must be capable of forming with the catalyst a complex which is a sufficiently strong acid to donate a proton to the monomer, thus converting it into a carbonium ion. It is well known that concentrated sulphuric acid will polymerise *iso*butene to a product of low molecular weight at room temperature, but we found that it would not do so at low temperatures. We thought that possibly sulphuric acid might form with the titanium tetrachloride a complex acid strong enough to initiate polymerisation at low temperatures, though of course such a complex could not be expected to be soluble in hexane. Experiment showed that concentrated sulphuric acid did indeed act as a very potent co-catalyst at −80°. Since the effect might have been due to the water contained in the sulphuric acid, 20% oleum which could not contain any water was tried and was found to be as effective as sulphuric acid. The reactions co-catalysed by sulphuric acid were very violent and virtually complete, and the product was of relatively low molecular weight, probably not above 20,000.

Table I.

T_o.	*iso*Butene concn., mols./l.	$TiCl_4$ concn., 10^{-2} mols./l.	Test substance, *X*.	Concn. of *X*, millimols./l.	Effect.
−87°	2	4·8	Conc. H_2SO_4	50	Vigorous polymn.
−86	2	0	,, ,,	50	No polymn.
−79	2	4·8	20% oleum	50	Vigorous polymn.
−68	2	4·8	,,	50	,,
−79	2	0	,,	50	No ,,
−25 to −120	0·62 to 2·5	0·2 to 5	$CCl_3{\cdot}CO_2H$ in hexane	0·25 to 6·5	Polymn.
−75	1·25	4·8	$CHCl_2{\cdot}CO_2H$ in hexane	1·9 9·5 [c]	Slight indication of polymn.; poisoning [b]
−75	1·25	4·8	$CH_2Cl{\cdot}CO_2H$ in hexane	>1·0 [d]	No polymn.; poisoning
−62	2·5	2·4	$CH_3{\cdot}CO_2H$ in hexane	0·85	No polymn.; poisoning
−60	2·5	2·4		0·85	
−76	2·5	2·4		8·5	
+20	2·5	2·4		8·5	

[a] T_o is the temperature of the reaction mixture when *X* was added. [b] "Poisoning" means that the addition of trichloroacetic acid or water vapour to a reaction mixture to which the reagent *X* had been added previously, caused no reaction, or only at a rate much smaller than that in the absence of *X*. [c] Two separate additions of this acid to the same reaction mixture were made. [d] An emulsion of the (liquid) acid in hexane was used.

Since it was thought that other strong acids might act in a similar manner, trichloroacetic acid was tried, and was indeed found to possess a strong co-catalytic activity. Its acid strength in water is of the same order as that of sulphuric acid and it has the advantage for the present purpose of being appreciably soluble in hexane even at −80°. The complexes which it forms with titanium tetrachloride also appear to be soluble in hexane. The main part of this paper is devoted to the results of polymerisation studies carried out with this co-catalyst.

Experimental.

Purification of Reagents.—Hexane. Commercial hexane was purified by standard methods; it was distilled from phosphoric oxide through a 3-ft. point column, and the fraction distilling between 67·5° and 68·5° was collected. It was stored over phosphoric oxide until introduced into the reservoir attached to the polymerisation apparatus.

Titanium tetrachloride. The commercial product was distilled in a stream of dry air until the intensity of the pale yellow colour could not be reduced by further fractionations. A weighed quantity was dissolved in the calculated quantity of pure dry hexane in the absence of atmospheric moisture, to give a 0·6M-solution (approx. 12% w/v). It was prepared in batches of about 200 ml. and stored in a reservoir connected to the polymerisation apparatus. The solution was almost colourless, clear, and free from deposit even after several months' storage. The colour of the titanium tetrachloride was caused by traces of iron and chromium.

iso*Butene.* This was a much appreciated gift from Messrs. I.C.I. (Billingham) Ltd., and was stated to be 99% pure. Before use it was distilled *in vacuo* from about −80° to liquid-air temperature until the liquid was perfectly clear and free from white flocks. For the experiments an amount of *iso*butene approximately equal to that required was collected in a roughly graduated trap, and the exact amount determined by weighing.

Trichloroacetic acid. The commercial, pure but deliquescent product was crystallised 4 times from hexane, and then dissolved in hexane to give an approx. N/10-solution. This was stored over phosphoric oxide and its strength was determined by titration. Such solutions could be thus stored for several weeks without undergoing change in concentration.

Apparatus and Technique.—The apparatus and technique used in the present series of polymerisation experiments were essentially the same as those previously described (Plesch, Polanyi, and Skinner, *loc. cit.*) which had been used for studying the co-catalytic effect of water vapour. The quantities of hexane, *iso*butene, and catalyst solution were always so adjusted that the volume of the whole batch was 200 ml. at room temperature.

The reaction was started by adding to the non-reacting solution of *iso*butene and titanium chloride in hexane a measured quantity of the co-catalyst solution from a pipette through an opening in the stopper of the reaction vessel. It was ascertained by control experiments that the amount of atmospheric moisture admitted to the reaction vessel during this addition of the co-catalyst was insufficient to cause measurable reaction.

The progress of the reaction was observed by noting the temperature of the reaction mixture on a pentane thermometer at definite time intervals. Since the polymerisation of *iso*butene is exothermic by more than 10 kcals./mole, the temperature changes accompanying this reaction provide an accurate and sensitive means of observation. For instance, the complete polymerisation of 7 g. of *iso*butene (0·125 mole) in 190 ml. of hexane gave a temperature rise of 14° in our apparatus.

At the end of the reaction 2—3 ml. of 90% ethanol were added to the polymer solution. This removed the catalyst by precipitating it as a pale yellow oil, leaving a clear and colourless solution of poly*iso*butene in hexane.

Measurement of Molecular Weight.—The mean molecular weight of the poly*iso*butene specimens obtained in the course of this work was calculated from the intrinsic viscosities of their solutions in hexane, by means of the formula (Houwink, *J. pr. Chem.*, 1940, **157**, 15) $[\eta] = KM^{a}$, where $[\eta]$ is the intrinsic viscosity, M is the mean molecular weight, and K and a are constants.

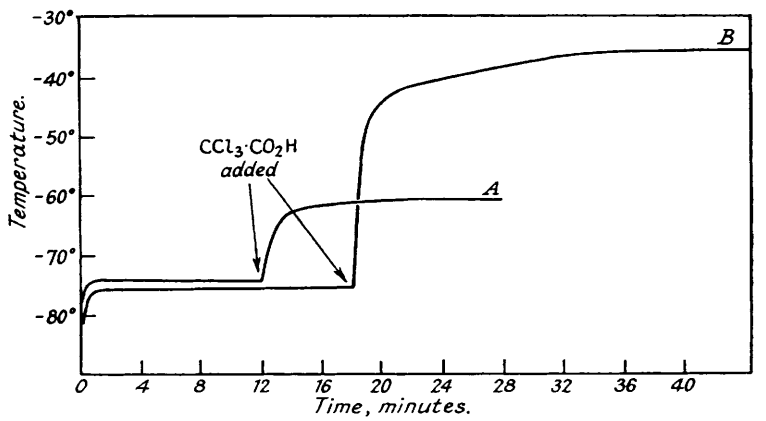
The intrinsic viscosity of the unfractionated polymer was determined as follows: After reaction a small portion of the mixture discharged from the reaction vessel was made up into an approx. 1% w/v solution in hexane, and this was diluted, *e.g.*, to $\frac{1}{2}$, $\frac{1}{4}$, and $\frac{1}{8}$. The flow times of not less than three such solutions were measured in the usual manner in a B.S.S. 188 No. 1 U-tube viscometer at 25°, and from it and the flow time of the pure solvent the specific viscosity $\eta_{sp.}$ was calculated. After the timing, the content of the viscometer was weighed in a tared weighing-bottle, dried to constant weight (16 hours at 90—110°), and re-weighed. Hence the concentration c of the polymer was found. The plot of $\log(\eta_{sp.}/c)$ against c, extrapolated to $c = 0$, gave the intrinsic viscosity $[\eta]$, from which the molecular weight was calculated by the above formula, with $K = 3{\cdot}6 \times 10^{-4}$ and $a = 0{\cdot}64$. As these constants had been obtained by Flory (*J. Amer. Chem. Soc.*, 1943, **65**, 372) for solutions of poly*iso*butene in di-*iso*butene it was ascertained by experiment that there was no significant difference between the intrinsic viscosities of poly*iso*butene in this solvent and in hexane.

Duplicate determinations of the molecular weights obtained in this way agree to within 5%, but their relation to the true weight-average and number-average molecular weights is somewhat doubtful, as the measurements were carried out on unfractionated specimens, whereas the constants in the formula had been obtained from measurements on carefully fractionated polymer samples.

Polymerisation with Trichloroacetic Acid as Co-catalyst.

General.—The polymerisation of *iso*butene by titanium tetrachloride and trichloroacetic acid has been studied under a variety of conditions. It was found that the polymerised solutions were always much less opaque than those which had been produced with water vapour as co-

Fig. 3.

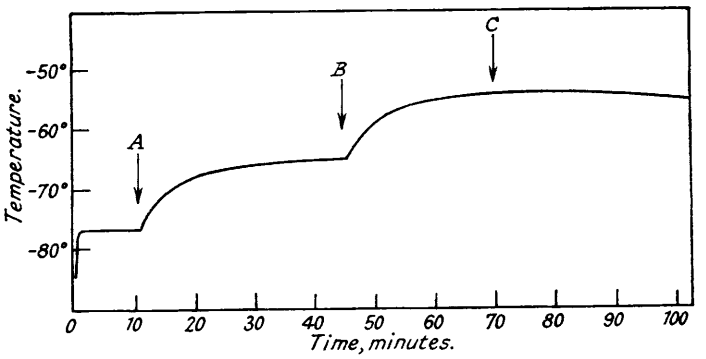


Adiabatic polymerisation of isobutene. *Typical time–temperature curves. Catalyst:* $TiCl_4$ (48 *millimoles/l.*). *Concn. of* isobutene: A 2·5, B 0·62 *mole/l. Concn. of* $CCl_3{\cdot}CO_2H$: A 1·65, B 3·3 *millimoles/l. Catalyst added at time* = 0.

catalyst, and the orange-red crystalline sediment, which had always been present when water was used, was absent from the solutions polymerised with trichloroacetic acid.

Whereas the curves showing the progress of reaction with time (time–temperature curves) obtained with water-vapour co-catalysis were always S-shaped, the rate of the reactions induced by trichloroacetic acid decreased monotonically from the start, provided that the molar ratio

FIG. 4.



Adiabatic polymerisation of isobutene *in hexane solution by* $TiCl_4$ *and* $CCl_3{\cdot}CO_2H$. *Concn. of* isobutene, 10% (*v*/*v*, i.e., ~0·25 *mole*/200 *c.c.*), *and of* $TiCl_4$, 1% (*w*/*v*, i.e., $9{\cdot}8 \times 10^{-3}$ *mole*/200 *c.c.*). *The* $TiCl_4$ *was added at* t = 0. *The quantities of trichloroacetic acid added were at* A $6{\cdot}6 \times 10^{-5}$ *mole*, B $3{\cdot}3 \times 10^{-4}$ *mole, and at* C $6{\cdot}6 \times 10^{-4}$ *mole*.

FIG. 5.

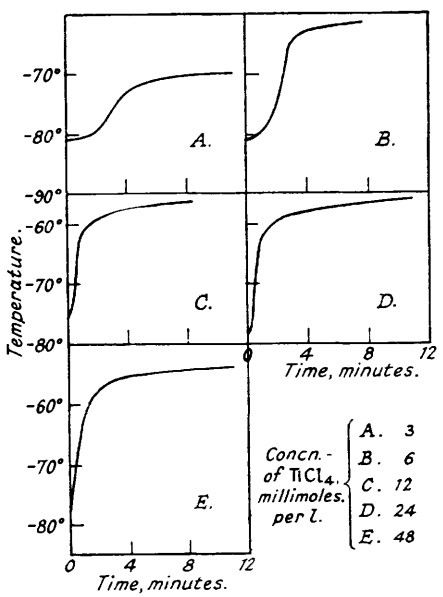


FIG. 6.

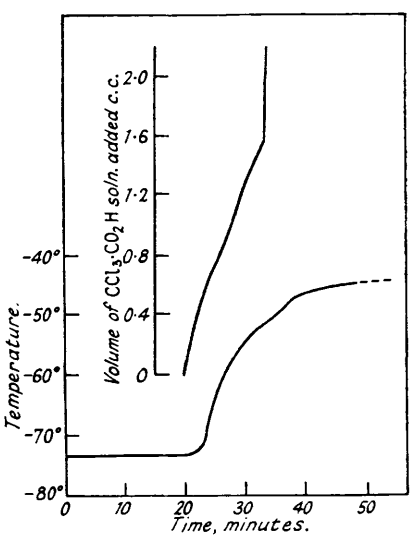


FIG. 5.—*The effect of varying the catalyst : co-catalyst ratio. Concn. of* isobutene 1·25 *mole*/*l. Concn. of* $CCl_3{\cdot}CO_2H$ 3·3 *millimoles*/*l.*

FIG. 6.—*Slow addition of a solution of* $CCl_3{\cdot}CO_2H$ ($1{\cdot}2 \times 10^{-3}$ *mole*/*c.c.*) *in hexane to* 200 *c.c. of* isobutene *solution* (1·25 *moles*/*l.*) *containing* $4{\cdot}8 \times 10^{-2}$ *mole*/*l. of* $TiCl_4$.

titanium tetrachloride/trichloroacetic acid was greater than about 4 (for starting temperatures near −80°) (Figs. 3 and 4). For reactions in which this ratio was less than 4, the time–temperature curves became the more pronouncedly S-shaped, the lower the value of this ratio (see Fig. 5).

The shape of the time–temperature curve is also influenced by the rate at which the co-catalyst is added to the reaction mixture. By adding it at a small and constant rate, S-curves can be produced even in the presence of excess of catalyst (see Fig. 6).

When the co-catalyst is added at the usual very high rate, *e.g.*, 1 ml. in less than 5 seconds in the presence of excess of catalyst, the reaction rate is greatest at the very start of the reaction. Although temperature readings were taken every 15 seconds, the finite time required for the co-catalyst to enter the mixture—even when this is well stirred, as it always was—introduced a considerable error into the determination of the maximum reaction rate when this was given by the temperature rise during the first 15 seconds from the addition of the co-catalyst.

The reproducibility of the maximum reaction rate was much greater than in the experiments carried out with water as co-catalyst. The reproducibility decreased as this rate increased, a feature which can be accounted for in terms of the finite time of mixing discussed above, and of the experimental difficulties and inaccuracies. Even in cases where the maximum (initial) rates were in close agreement, the later course of the reactions was not exactly reproducible so that the extent of reaction and the time required for the reaction to cease were variable for a given set of conditions.

FIG. 7.

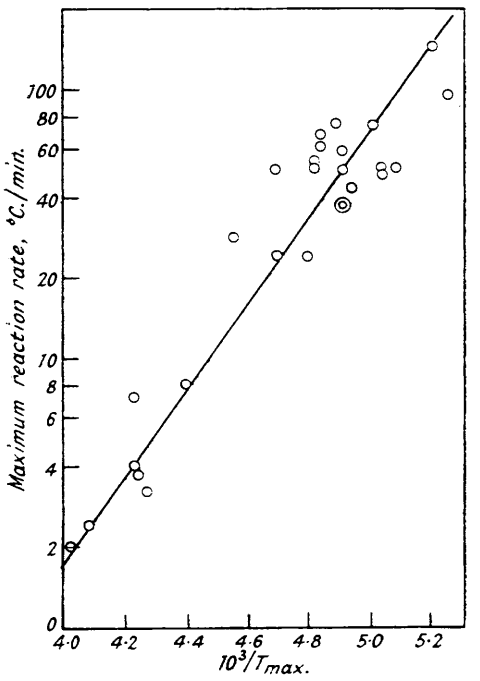


FIG. 8.

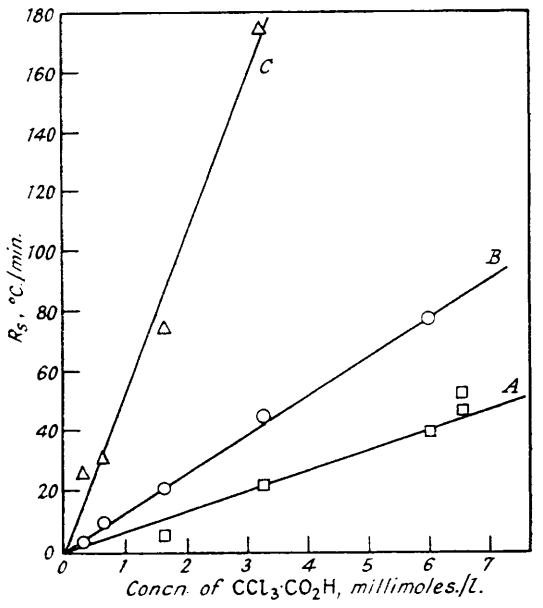


FIG. 7.—*The maximum reaction rate as a function of temperature.* iso*Butene concn.* 1·25 *moles/l.*, $TiCl_4$ *concn.* $4{\cdot}8 \times 10^{-2}$ *mole/l.* $CCl_3{\cdot}CO_2H$ *concn.* 6×10^{-3} *mole/l.*

FIG. 8.—*The standardised maximum reaction rate* R_s *as a function of co-catalyst concn. for three* iso*butene concns. :* A 0·62, B 1·25, C 2·5 *moles/l.* $TiCl_4$ *concn.* 48 *millimoles/l.*

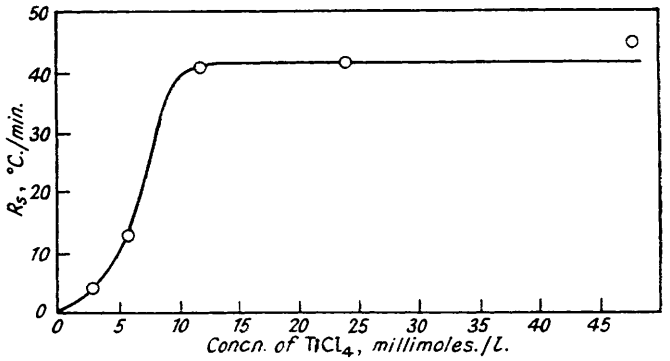
The reproducibility of the molecular weights was considerably greater than in the experiments with water co-catalysts. The sensitivity of the molecular weight to temperature and to monomer concentration is probably responsible for the degree of irreproducibility remaining in the present experiments.

The kinetic results to be presented below must be regarded as preliminary for the reason that they were obtained from adiabatic experiments. None the less they provide some new information about the mechanism of this polymerisation. In the present investigations we have determined the influence of the concentrations of *iso*butene, titanium tetrachloride, and trichloroacetic acid, and of the starting temperature of the reaction, on the maximum reaction rate and the molecular weight.

Variation of the Maximum Reaction Rate with Temperature.—The logarithm of the maximum reaction rate was plotted against the reciprocal of the absolute temperature $T_{max.}$ at which the maximum rate occurred (Fig. 7). In very fast reactions this was not very well defined. For all the experiments represented in Fig. 7 the *iso*butene concentration was 1·25 moles/l. (10% v/v)

and the catalyst (titanium tetrachloride) and co-catalyst (trichloroacetic acid) concentrations were $4{\cdot}8 \times 10^{-2}$ and 6×10^{-3} moles/l. respectively (1% and 0·5% w/v respectively). These results indicate a negative " activation energy " of about −7·5 kcals./mole for the over-all reaction.

FIG. 9.



R_s *as a function of the* $TiCl_4$ *concn.* iso*Butene concn.*, 1·25 *moles/l.* $CCl_3{\cdot}CO_2H$ *concn.*, $3{\cdot}3 \times 10^{-3}$ *mole/l.*

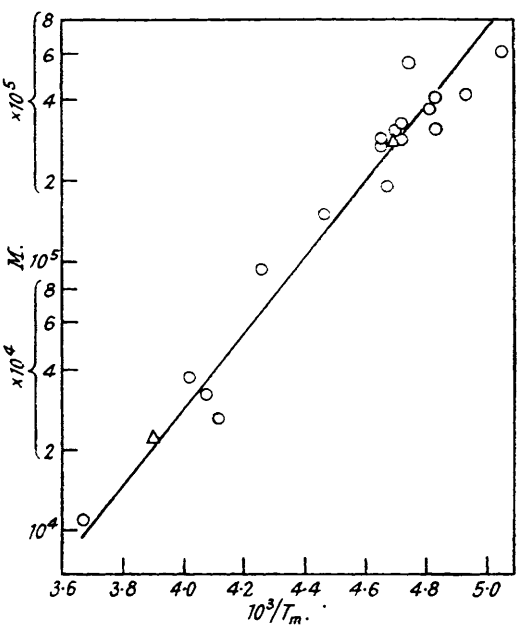
Effects of the Concentrations of the Three Reactants on the Maximum Reaction Rate.—While studying these effects it was impossible to adjust conditions in such a manner that the maximum rate always occurred at the same temperature. For this reason the observed maximum rate occurring at an absolute temperature $T_{max.}$ was adjusted to the fixed standard temperature −75° by means of the " activation energy " of −7·5 kcals./mole reported above. In this way the standardised maximum reaction rates R_s were obtained.

Variation of R_s *with Co-catalyst Concentration.*—This is shown in Fig. 8 for three different concentrations of *iso*butene. In these experiments the titanium tetrachloride concentration was constant at $4{\cdot}8 \times 10^{-2}$ mole/l. and the temperatures at which the maximum reaction rate occurred were in the region −70° to −85°. R_s is seen to increase linearly with the co-catalyst concentration.

Owing to the uncertainties inherent in the experimental method the slopes of the lines shown in Fig. 8 should not be considered as more than a first approximation. The ratios of these slopes indicate that the polymerisation is probably of an order greater than unity with respect to *iso*butene, but it would not be justifiable to attempt an evaluation of the exact order from the present data.

Dependence of the Standardised Maximum Reaction Rate R_s *on the Titanium Tetrachloride Concentration.*—For constant *iso*butene and co-catalyst concentrations, this dependence is shown in Fig. 9. Beyond a certain point the rate appears to be independent of the catalyst concentration.

FIG. 10.



The mean mol. wt. of the polymer as a function of the mean absolute temperature during the reaction. iso*Butene concn.* 1·25 *moles/l.* $CCl_3{\cdot}CO_2H$ *concn.* 3·3 *millimoles/l.* $TiCl_4$ *concn.* 48 *millimoles/l.* (○), 24 *millimoles/l.* (△).

Yield of the Polymerisation.—For a fixed catalyst concentration of $4{\cdot}8 \times 10^{-2}$ mole/l. the polymerisation of a 5% v/v solution of *iso*butene goes to at least 90% completion for T_0 (the starting temperature) in the region of −75°, provided that the trichloroacetic acid concentration

is greater than about $1\cdot2 \times 10^{-3}$ mole/l. For higher concentrations of *iso*butene the yields were not reproducible, probably in consequence of the high viscosity of these solutions.

Effect of Temperature on the Molecular Weight of the Polymer.—In Fig. 10 the logarithm of the molecular weight is plotted against the reciprocal of the mean temperature T_m during the experiment. T_m is the arithmetic mean between the starting temperature T_0 and the final temperature of the reacted solution at the end of the polymerisation.

TABLE II.

The variation of molecular weight with monomer and co-catalyst concentration.

In all the experiments recorded in this table the titanium tetrachloride concentration was $4\cdot8 \times 10^{-2}$ mole./l.

Expt. no.	$-T_m$.	Concn. of *iso*butene, mols./l.	Concn. of $CCl_3{\cdot}CO_2H$, millimol./l.	Observed mol. wt. (M) $\times 10^{-3}$.	M_s $\times 10^{-3}$.	Mean M_s $\times 10^{-3}$.
154	60°	1·25	0·66	286	950	600
158	74			250	280	
159	73			460	550	
151	70	1·25	1·65	420	640	800
152	61			325	1000	
156	58			190	750	
149	60	1·25	3·3	305	1000	840
153	61			280	880	
177	65			370	840	
181	66			310	650	
150	66			400	820	
155	58	1·25	6·6	270	1000	—
157	62			580	1600	
178	60			280	950	
166	69	0·62	1·65	430	720	—
164	68		3·3	280	500	
165	68		6·6	285	500	
167	69		6·6	240	400	
163	61	2·5	0·33	400	1250	—
161	55		1·65	280	1350	
162	56		3·3	255	960	

TABLE III.

Specimen no.	Co-catalyst	Mol. wt.[a] $\times 10^{-3}$.	Found.[b] C, %.	H, %.	Cl, %.	Calc.[c] Cl, %.
121	H_2O	20	—	—	0	0
119	,,	22	—	—	0	0
77	,,	243	85·2	14·4	0	0
206.I[e]	$CCl_3{\cdot}CO_2H$	11	—	—	1·7 2·1	1·0
206.II[f]	,,	11	—	—	0·2 0·6	1·0
189	,,	22·4 28[d]	—	—	0·2 0·7	0·48
194.I	,,	26	85·2 85·1	12·6 14·2	0·3	0·4
194.II	,,	26	85·3 85·3	14·0 14·2	0·3	0·4
156	,,	190	85·5	14·5	0	0·056

[a] Molecular weight before precipitation of the polymer. [b] Micro-analyses by Messrs. Weiler and Strauss, Oxford, England. [c] Assuming the presence of one trichloroacetate group per molecule. [d] Molecular weight after two precipitations. [e] Reaction mixture washed three times with distilled water, dried, and evaporated in a high vacuum. [f] Reaction mixture precipitated in methanol–acetone mixture, washed with acetone, and evaporated in a high vacuum.

Effects of the iso*Butene and Co-catalyst Concentrations on the Molecular Weight.*—Table II records results showing these effects. Since the mean temperature during the polymerisation has such a great effect on the molecular weight, the measured values of the molecular weight (M) were adjusted to the standard temperature −75° by means of T_m, the mean temperature

during the reaction, and the relation between T_m and M is represented in Fig. 10. The standardised molecular weights thus obtained are designated by M_s.

It is seen from the table that M_s shows only a slight increase with the co-catalyst concentration but that it increases with the *iso*butene concentration. In view of the uncertainties involved in the calculation of the M_s values, and considering that these refer to the mean molecular weight of the end-product of the reaction, it would not be justifiable to draw any definite conclusions from these data as to the exact relationship between the molecular weight and the monomer concentration.

Analysis of the Polymer.—A certain number of polymer samples were analysed for chlorine. The main practical difficulty was to make sure that the polymer was free from trichloroacetic acid and from hydrolysis products of titanium tetrachloride.

The polymer solutions were freed from titanium tetrachloride by adding 2—3 ml. of ethanol to the solutions at the end of the reactions. This reacted with the titanium tetrachloride, and the product separated as a yellow oil. The polymer was then precipitated in a large excess of 90% ethanol and the visco-elastic mass of polymer was well kneaded in a fresh batch of ethanol. It was then dissolved in hexane to give an approx. 20% solution, precipitated again in ethanol, kneaded in ethanol, and again dissolved in hexane. The solution was then evaporated *in vacuo* at room temperature. When the bulk of the hexane had been removed, evacuation by way of a liquid-air trap was continued for 24 hours, at a pressure less than 10^{-3} mm. Hg. The colourless and transparent polymer thus obtained was used for analysis. The results of the analyses are shown in Table III. In one case (No. 194) the original polymer solution was divided into two portions, one of which (194.I) was precipitated in boiling water and the polymer so obtained dissolved in hexane and then precipitated in ethanol and thereafter treated as described. The second portion (194.II) was treated in the usual way with two ethanol precipitations. There is no difference between the chlorine contents of these two specimens. The absence of chlorine from specimens 119 and 121 which were prepared by water co-catalysis shows that where any chlorine was found in the polymers it could not have originated from end-groups derived from the catalyst. This is further supported by the absence of an incombustible residue. The absence of chlorine from the specimens 77 and 156 rules out the possibility of physical entrainment of chlorine compounds in polymer micelles, since this effect would be much greater in polymers of higher molecular weight. The precipitation process necessarily removes some of the fractions of lowest molecular weight (this is shown in specimen 189) and thus it is understandable that the measured chlorine content of the polymers is slightly less than that to be expected from the molecular weight determined before precipitation.

The data presented in Table III thus indicate that chlorine is present only in the polymer when trichloroacetic acid was used as co-catalyst.

Discussion.

The Mechanism of the Polymerisation.—The mechanism of the polymerisation of *iso*butene by Friedel–Crafts catalysts is now believed to involve reaction between carbonium ions and monomer. The original carbonium-ion theory of Whitmore (*Ind. Eng. Chem.*, 1934, **26**, 94), Hunter and Yohe (*J. Amer. Chem. Soc.*, 1933, **55**, 1248), and Brunner and Farmer (*J.*, 1937, 1039) was developed by Polanyi and his collaborators (*J.*, 1947, 252, 257) who showed that a co-catalyst, as well as the halide catalyst, was required to bring about polymerisation. This was confirmed by Norrish and Russell (*Nature*, 1947, **160**, 543). It has been shown again in the present work that a co-catalyst is essential for the reaction and therefore the older theories such as those of Price (*Annals N.Y. Acad. Sci.*, 1943, **44**, 368; "Reactions at Carbon-Carbon Double Bonds" New York, 1946) and Eyring and his collaborators (*Annals N.Y. Acad. Sci.*, 1943, **44**, 382), which ignored this, cannot apply to the systems investigated by us.

According to our present views, the initiating species is a complex between catalyst and co-catalyst, which is formed by the reaction (I) shown in the scheme below.

The complex is thought to react with a molecule of monomer according to reaction (II) in which XA^-H^+ represents the complex ion pair. This is the initiation step which involves the transfer of a proton from the catalytic complex to a molecule of monomer.

The propagation of the polymerisation is believed to take place by the combination of the carbonium ion formed in the initiating step with a molecule of the monomer, with transference of the charge to the end of the chain thus formed (Polanyi and his collaborators, *loc. cit.*). This is represented in reaction (III). In the previous attempts at formulating the propagation mechanism, the question of the fate of the anion was left open. It is clear, however, that in the system under consideration the anion cannot be separated to any considerable distance

from the carbonium ion. If one uses the method of Fuoss and Kraus (*J. Amer. Chem. Soc.*, 1933, **55**, 1019) to calculate the degree of dissociation of the ion pair

$$-CH_2\cdot(CH_3)_2C^+\cdot(Cl_3C\cdot CO_2\cdot TiCl_4)^-$$

in hexane at $-80°$, one obtains a value of the order of 10^{-22}. Therefore in the course of chain propagation the anion must remain in the vicinity of the carbonium-ion end of the growing polymer chain. A. G. Evans and Meadows (*J. Polymer Sci.*, 1949, **4**, 359), approaching the problem in a rather different manner, reached the same conclusion. This is an additional reason why the older theories (Price, *loc. cit.*; Eyring, *loc. cit.*; Heiligmann, *J. Polymer Sci.*, 1949, **4**, 183) which involve considerable charge separation cannot be applicable to this system.

The termination of the chains could take place by several different mechanisms : The ion pair at the growing end of the polymer chain may undergo a unimolecular rearrangement to give an ester (or alcohol if the co-catalyst is water) (Norrish and Russell, *loc. cit.*) as shown in reaction (IV*a*). In this case the halide will remain co-ordinated on to the oxygen of the terminal group. It will only be removed by treating the polymer with, *e.g.*, water which can break up the co-ordination complex. This was shown by Staudinger (" Die hochmolekularen organischen Verbindungen," Berlin, 1932) with polystyrene prepared with stannic chloride as catalyst, and is confirmed by our observation that addition of water to a clear polymerised reaction mixture which had been freed from excess of titanium tetrachloride by the addition of alcohol produced a tenuous but quite definite white precipitate presumed to be titanium oxide.

The suggested mechanism accounts for the consumption of the co-catalyst in the course of the reaction, which is indicated by experiments such as that represented in Fig. 4 and it is supported by the analytical evidence given in Table III.

The formation of *tert.*-butyl trichloroacetate by a bimolecular reaction between monomer and the ion pair, leaving the polymer with a terminal double bond [reaction (IV*b*)], is a possibility which cannot be neglected, especially at higher temperatures. It would also account for the consumption of the co-catalyst.*

The alternative is the loss of a proton from the growing end of the polymer chain, leaving a terminal double bond. This process could take place in three different ways : (*a*) A unimolecular decomposition of the terminal ion-pair in which the catalytic complex is regenerated [reaction (V*a*)]. (*b*) A bimolecular reaction with monomer, leading to chain transfer [reaction (V*b*)]. (*c*) A bimolecular reaction with the terminal double bond of a dead polymer molecule formed by process (IV*b*), (V*a*), or (V*b*) in which the catalytic complex is regenerated as in (*a*) [reaction (V*c*)].

The complete reaction is thus represented by the scheme on following page.

If for the moment the transfer reactions (V) are neglected, the set of differential equations describing this reaction scheme with the termination mechanism (IV*a*) is as set out below.

This is analogous to the schemes used by Eley and Pepper (*Trans. Faraday Soc.*, 1947, **43**, 112; cf. Pepper, *ibid.*, 1949, **45**, 397, and Eley and Richards, *ibid.*, p. 425).

$$-\mathrm{d[AH]}/\mathrm{d}t = k_c c[\mathrm{AH}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$-\mathrm{d[CAH]}/\mathrm{d}t = -\frac{\mathrm{d[AH]}}{\mathrm{d}t} - k_i m[\mathrm{CAH}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$-\mathrm{d}m/\mathrm{d}t = k_i m[\mathrm{CAH}] + k_p m\mathrm{M}^* \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\mathrm{dM}/\mathrm{d}t = k_t \mathrm{M}^* \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\mathrm{dM}^*/\mathrm{d}t = k_i m[\mathrm{CAH}] - k_t \mathrm{M}^* \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Where concentrations are as follows : m *iso*butene, c titanium tetrachloride, [AH] trichloroacetic acid, [CAH] initiating complex, M* growing polymer chain, and M dead polymer chain.

If we make the usual stationary state assumption, *i.e.*, put M* = constant, and also assume that k_p and k_t are independent of chain length, we get for the rate of reaction

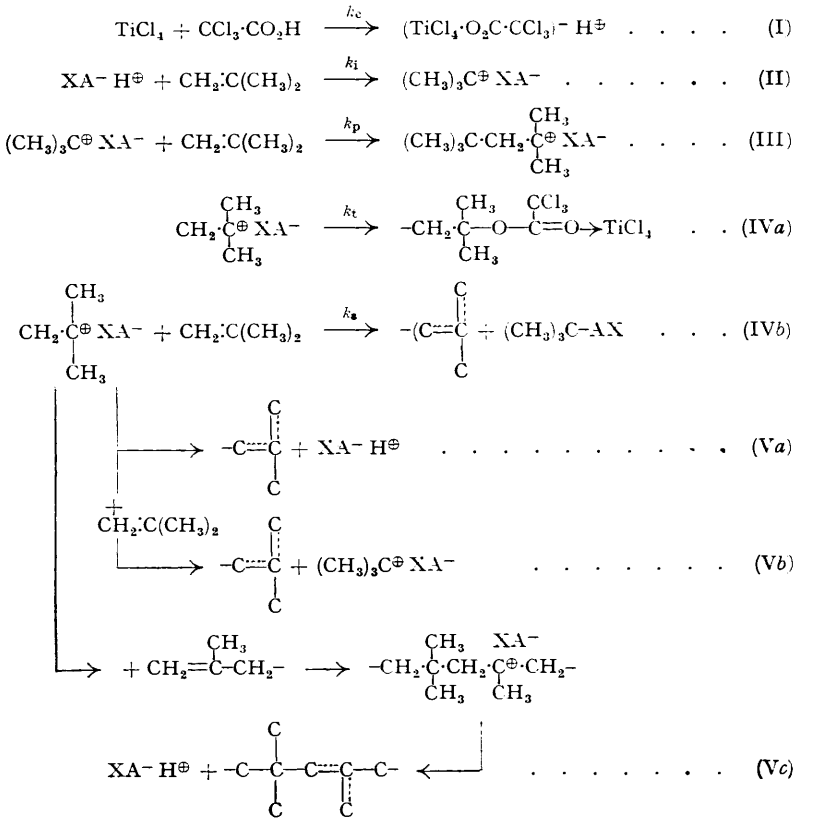
$$-\frac{\mathrm{d}m}{\mathrm{d}t} = \frac{k_i k_p}{k_t} \cdot m^2[\mathrm{CAH}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

when $k_p m/k_t \gg 1$.

If we make the plausible assumption that reaction (I) goes practically to completion in the presence of excess of titanium tetrachloride, the unknown term [CAH] can be replaced by the known co-catalyst concentration [AH].

* *iso*Butene and trichloroacetic acid react rapidly to give the *tert.*-butyl ester (Scovill, Burke, and Lankelma, *J. Amer. Chem. Soc.*, 1944, **66**, 1039).

It is indeed found in the present work that the maximum reaction rate is proportional to the first power of the co-catalyst concentration, but the correlation cannot be regarded as definitely established until isothermal measurements are available. The order of the reaction with respect to monomer cannot be derived unambiguously from the present set of measurements, though it is probably greater than unity.



The dotted lines in this scheme indicate alternative positions for the double bond.

The molecular weight of the polymer is given by

$$M = M^0 m(k_p/k_t) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where M^0 is the molecular weight of the monomer. The present data indicate that the molecular weight depends on the monomer concentration and is independent of the co-catalyst concentration; but again the data do not permit one to deduce exactly how the monomer concentration affects the molecular weight.

If termination takes place by reaction (IV*b*) the maximum reaction rate is given by

$$-\mathrm{d}m/\mathrm{d}t = k_i m[\mathrm{CAH}]$$

if $k_p/k_s \gg 2$. The molecular weight is given by

$$M = M^0 k_p/k_s$$

The facts that the observed order of the reaction rate with respect to monomer concentration is between 1 and 2, and that the molecular weight depends on a power of m rather less than 1, may indicate that both termination mechanisms (IV*a*) and (IV*b*) play a part in this reaction.

Although the present data on the concentration-dependence of the rate and molecular weight do not provide much information, the temperature dependence of these quantities yields some interesting results. Considering first the reaction with termination (IV*a*), we assume that the

number-average molecular weight of the final polymer is given by equation (7), and denote by E_i, E_p, and E_t the activation energies corresponding to the three rate constants. We then find from Figs. 7 and 10 that

$$E(\text{rate}) \equiv E_i + E_p - E_t$$

and

$$E(\text{Mol. wt.}) \equiv E_p - E_t$$

are equal within the limits of accuracy of the present experiments and have a value of $-7{\cdot}5 \pm 2$ kcals./mole.

Thus if the mechanism outlined above is correct we may assign an upper limit of about 4 kcals./mole to E_i, and it may well be very much less than this.

Since there is a great similarity between the initiation and propagation reactions, it is probable that E_p is also a very small quantity. Thus it appears that E_t may well be as high as 6—10 kcals./mole.

The reason for this high activation energy may be found in the drastic rearrangement which must take place in the ion pair during the termination act. In the course of chain propagation the configuration of the anion is probably such that the trichloroacetate residue is co-ordinated symmetrically with both its oxygen atoms to the titanium tetrachloride. When the termination takes place, this symmetrical arrangement is disturbed, and both ions must rearrange themselves so that a covalent bond can be formed between them.

If the termination (IV*b*) applies, a similar argument with E_s in place of E_t leads to the same conclusions about E_i and E_p. The value of E_s estimated in this way is the same as that of E_t. Its interpretation is also the same as that of E_t, since the main difference between termination mechanisms (IV*a*) and (IV*b*) is that the latter involves both the making and breaking respectively of two double bonds of very similar constitution which would hardly affect the energetics of the reaction.

It is necessary to examine more closely the assumption made above, that a stationary state is established during the course of the reactions. There can be little doubt that during the period of maximum rate, whenever it may occur, this is approximately true. But in some reactions (Fig. 5) there was an initial period of acceleration and during this, conditions are not stationary. It may therefore be of interest to discuss the conditions under which S-shaped reaction curves are obtained.

The Origin of the S-Curves.—If we compare the results obtained with water as co-catalyst (Plesch, Polanyi, and Skinner, *loc. cit.*) which were summarised on p. 543 and the results obtained with trichloroacetic acid as co-catalyst, we see that the most striking differences between the two sets of experiments are the different shapes of the curves showing the progress of reaction with time, and the opposite sign of the temperature coefficient of the polymerisation velocity. Whereas the time–temperature curves for reactions co-catalysed by water vapour were invariably S-shaped, those for trichloroacetic acid co-catalysis showed a monotonically decreasing reaction rate unless the concentration of catalyst was smaller than about four times the concentration of co-catalyst. The third condition under which S-curves are obtained is the slow addition of the co-catalyst (Fig. 6). If we ask the question : What is the feature which is common to the different circumstances which give rise to S-shaped curves ?, we find that in each case there is a good reason to assume that the rate of formation of the chain-initiating species is low, so that the maximum concentration of growing polymer chains is built up slowly. This explanation of sigmoid reaction curves was previously suggested by Eley and Pepper (*loc. cit.*) for the polymerisation of *n*-butyl vinyl ether by stannic chloride.

A. G. Evans and Meadows (*J. Polymer Sci.*, 1949, **4**, 359) have shown that in the polymerisation of *iso*butene by boron trifluoride and acetic acid (AcOH) the complex BF_3,AcOH is very much more active than the complex $BF_3(AcOH)_2$, and that the latter may be entirely inactive. We may assume by analogy that in our system we have the equilibria

$$TiCl_4 + 2CCl_3{\cdot}CO_2H \rightleftharpoons TiCl_4,2CCl_3{\cdot}CO_2H \quad . \quad . \quad . \quad . \quad . \quad (a)$$

$$TiCl_4,2CCl_3{\cdot}CO_2H + TiCl_4 \rightleftharpoons 2(TiCl_4,CCl_3{\cdot}CO_2H) \quad . \quad . \quad . \quad . \quad (b)$$

where the 1 : 1 complex is the initiating species. It is evident that, when the concentration of the acid is small compared to that of the halide, almost all the acid will be present in the form of the active complex so that the initial rate of chain initiation will be the maximum. If the concentration of acid is increased during the reaction by adding the acid slowly to the reaction mixture, the number of growing chains will increase with time and an acceleration of the reaction will be observed, as was indeed found (Fig. 6).

On the other hand, if the concentration of the catalyst is of the same order as that of the co-catalyst, an appreciable fraction of the latter will be in the form of the inactive complex. The consumption of the active complex by chain initiation will shift the equilibrium, so that more of it is formed and thus the concentration of growing chains increases with time and the reaction curve is sigmoid. Fig. 5 shows how the S-character of the reaction curves becomes more pronounced as the ratio catalyst : co-catalyst is diminished, as is to be expected from this hypothesis.

The S-shaped curves obtained with water vapour as co-catalyst can be explained on the same basis, since the rate of formation of the initiating complex from titanium tetrachloride and an ice dispersion in the circumstances of the experiment can only have been very low. Accordingly, if we conclude that in these experiments the formation of the complex was the rate-governing step, we can now explain the positive temperature coefficient of the over-all reaction rate with water as co-catalyst; for the interaction of a finely divided solid phase (ice) with titanium tetrachloride in solution can be expected to be accelerated by an increase in the temperature so that we may in fact expect a quasi-autocatalytic effect.

It might be thought, by analogy with free-radical polymerisation that the acceleration may be due to the slow consumption of inhibiting impurities. Though this would certainly enhance the effect, it cannot account for it entirely. For if impurities alone were responsible for the effect, a second reaction induced, after partial reaction, in a system in which polymerisation had ceased through consumption of co-catalyst would be expected to show no acceleration. That this is not so is shown by Plesch, Polanyi, and Skinner (*loc. cit.*, Fig. 4), the second reaction showing well-developed acceleration.

The increase in polymerisation rate with decreasing temperature which was found by previous workers (Waterman, *et al.*, *loc. cit.*; Thomas *et al.*, *loc. cit.*; Bresler, *Doklady*, 1945, **47**, [vi], 410), and in the preliminary experiments in more or less open vessels (Plesch, Polanyi, and Skinner, *loc. cit.*), can be explained tentatively by the supposition that the lower the initial temperature of the reaction mixture, the more atmospheric moisture would condense in the system, and hence that there would be a greater number of particles to participate in the heterogeneous reaction. However, the ill-defined conditions of these experiments make it pointless at present to discuss further the undoubtedly very spectacular explosive polymerisations which take place at very low temperatures.

Norrish and Russell (*loc. cit.*) attempted to explain the acceleration of ionic polymerisations in terms of the inhibition of mutual termination of carbonium and carbanion polymerisation chains by the increasing viscosity of the medium. This theory cannot apply to polymerisations in hydrocarbon media because of the impossibility of separating the ions, even if the possibility of the existence of carbanion polymerisation chains were admitted. In any case, Eley and Pepper (*loc. cit.*) have shown that in the polymerisation of *n*-butyl vinyl ether by stannic chloride in light petroleum the acceleration sets in before there is any marked increase in viscosity. Bresler (*loc. cit.*) also found that ionic polymerisations carried out isothermally could become explosive.

The Chain-transfer Reactions.—Each of the reactions (V) represented in the scheme above is equivalent to a chain-transfer mechanism, because in each case either the catalytic complex or an actual growing chain is reproduced. Eley and Richards (*loc. cit.*) have recently shown that chain transfer can occur in the ionic polymerisation of vinyl ethers. Horrex and Perkins (*Nature*, 1949, **163**, 486) have shown that chain transfer probably takes place in the low-temperature polymerisation of *iso*butene by boron trifluoride when this is inhibited by olefins, and A. G. Evans and Meadows (*loc. cit.*) have found that in the polymerisation of gaseous *iso*butene by boron trifluoride and acetic acid at room temperature there is a very high degree of chain transfer. The same phenomenon has been found in the course of the present work. Approximately 1×10^{-3} mole of $TiCl_4,CCl_3{\cdot}CO_2H$ complex in contact with gaseous *iso*butene at room temperature produced about 2×10^{-2} mole of polymer of mean molecular weight 400. In the polymerisations carried out at low temperatures the number of moles of polymer produced is usually smaller than the number of moles of co-catalyst. The presence of double bonds in the polymers formed at higher temperatures which was found by Dainton and Sutherland (*J. Polymer Sci.*, 1949, **4**, 37) and which was confirmed by Flett and Plesch (in the press) for poly*iso*butenes of mean molecular weight up to at least 10^5 can be considered as evidence of chain transfer only if the number of moles of polymer is greater than the number of moles of co-catalyst. In view of the possible occurrence of termination (IV*b*), the mere presence of double bonds is not evidence for chain transfer.

The presence of other olefins during the polymerisation of *iso*butene reduces the molecular

weight of the polymer without necessarily affecting the rate (Horrex and Perkins, *loc. cit.*; Thomas *et al.*, *loc. cit.*). Therefore if olefins are produced as products of the normal reaction we could expect a self-poisoning effect by reaction (V*c*). Since according to this scheme the catalytic complex is regenerated there will probably be no effect on the rate but anomalous molecular weights and disappearance of terminal double bonds as the reaction goes to completion might be observable. Double bonds resulting from reaction (V*c*) are probably too inaccessible to take part in any further reaction.

Further work on co-catalysts and inhibitors for this polymerisation is in progress, and the kinetics of isothermal polymerisations are being studied.

I would like to express my gratitude to Professor M. Polanyi, F.R.S., for his help and encouragement in this work, and to my colleagues for many helpful discussions. I thank also Messrs. Imperial Chemical Industries (Billingham) Ltd. for kindly supplying the *iso*butene, the Anglo-Iranian Oil Co. Ltd. for funds which materially assisted the progress of this work, and the Editor of " *Research* " for permission to reproduce Fig. 4.

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