268. *Some Reactions of Cyclopropane and a Comparison with the Lower Olefins. Part IV.* Friedel–Crafts Polymerisation.*

By C. F. H. Tipper and D. A. Walker.

Cyclopropane polymerises in heptane between 0° and $-78°$ in the presence of aluminium bromide and hydrogen bromide to give products of low molecular weight (<700). The polymers, whose molecular weight fell with rise of temperature, appeared to be mainly long-chain alkanes with a terminal double bond. A precipitate was formed and there was a continuous loss of aluminium.

The kinetics have been investigated dilatometrically. The rate of polymerisation was a maximum with equal concentrations of $AlBr_3$ and HBr, and was then proportional to the concentrations both of catalyst–cocatalyst and of cyclopropane. The overall activation energy was 6 kcal. mole^{-1}.

The suggested mechanism involves the initial reaction of cyclopropane, aluminium bromide, and hydrogen bromide to give two complexes, one of which initiates the reaction, the other being inactive and precipitated. Propagation, monomer transfer, and termination occurred by the formation of a growing chain–monomer complex, which could rearrange in several ways.

The lower olefins have been polymerised under a wide variety of conditions with a number of different types of catalyst.[1] In particular Fontana and Kidder [2] found that, in n-butane at $-78°$, propene rapidly yields polypropene in the presence of aluminium bromide and hydrogen bromide. Ivin [3] studied the mercury-photosensitised reaction of cyclopropane in the gas-phase, and showed that the low polymer formed contained methyl and unsaturated groups and ring structures, but otherwise the polymerisation of this compound has not been reported. However, since cyclopropane readily undergoes the normal Friedel–Crafts reaction with benzene (Part III), it seemed probable that it would polymerise under conditions similar to those of Fontana and Kidder. This has been found to be so, and the kinetics of the reaction and the nature of the products have been investigated.

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* Part III, *J.*, 1957, 1199.

[1] Stille, *Chem. Rev.*, 1958, **58**, 541.

[2] Fontana and Kidder, *J. Amer. Chem. Soc.*, 1948, **70**, 3745; *Ind. Eng. Chem.*, 1952, **44**, 1688; Fontana, Herold, Kinney, and Miller, *ibid.*, p. 2955.

[3] Ivin, *J.*, 1956, 2241.

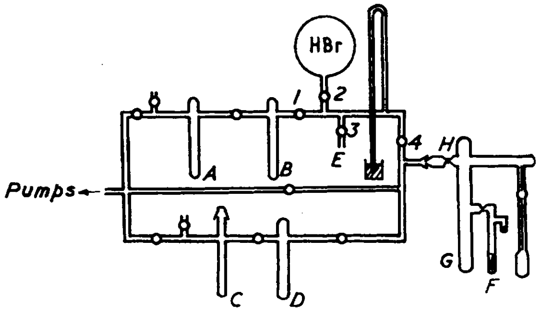
EXPERIMENTAL

Materials.—Traces of substances such as water affect Friedel–Crafts polymerisations, so great care was taken in the purification and handling of all reactants.

The solvent, n-heptane, was washed several times with, successively, concentrated sulphuric acid, sodium hydrogen carbonate solution, and distilled water, and dried with anhydrous sodium sulphate and by refluxing for 24 hr. over sodium. Finally it was fractionally distilled in dry nitrogen, the middle fraction being collected. Gas-chromatography showed that this contained a small proportion of branched isomers. Nitroethane was purified in the same way as nitromethane (Part III). Greenish-yellow commercial aluminium bromide was refluxed and then distilled from pure aluminium chippings in a stream of dry nitrogen into a flask containing more chippings. It was then distilled *in vacuo* into ampoules in approximately 5 g. samples. These were sealed. When required, one was broken *in vacuo* and the solid was distilled into smaller ampoules each containing 0·2 g. of pure white crystalline bromide.

Hydrogen bromide, prepared by the action of bromine on tetrahydronaphthalene,[4] was condensed in a trap and fractionated *in vacuo*, the middle fraction being stored in a blackened bulb attached to the apparatus. Cyclopropane from a cylinder was washed with a solution of mercuric sulphate in sulphuric acid and dried [$CaCl_2$, then $Mg(ClO_4)_2$]. It yielded only one peak when analysed chromatographically. Propene from a cylinder was dried in the same way. " AnalaR " iodine was distilled *in vacuo* into very small ampoules. Conductivity water and " AnalaR " methanol and trichloroacetic acid were not further purified. " AnalaR " toluene was treated as the heptane.

FIG. 1.



Kinetic Measurements.—The rate of polymerisation was measured dilatometrically. Reactants were mixed and the dilatometer filled *in vacuo* in the apparatus shown in Fig. 1.

The volume between taps 1, 2, 3, and 4 was determined for different levels of mercury in the manometer by means of a flask of known volume attached at *E*. Traps *B* and *D* were graduated in 0·1 ml. Purified cyclopropane (or propene) was condensed in trap *A* and degassed, and a middle fraction transferred to trap *B in vacuo*. *B* was calibrated for use at −78° by distilling out measured volumes of cyclopropane into ampoules immersed in liquid nitrogen. The weights of cyclopropane could then be determined. The effective density was 0·98 g./ml. Purified heptane was placed in trap *C* and a middle fraction transferred to *D in vacuo*.

The dilatometer (vol. ~5 ml.) had a small bulb to allow for expansion at the top of the standard capillary on which a reference mark was scratched. The same dilatometer was used for any one series of experiments. It was cleaned by washing several times with concentrated nitric acid and then with distilled water.

The weighed ampoule containing aluminium bromide (in tube *F*) was broken by a ball-bearing and the contents distilled into tube *G in vacuo*. *F* was sealed off, and the broken ampoule removed and reweighed. A known volume of heptane was distilled *in vacuo* into *G* from tube *D* at room temperature. The bromide was dissolved, and known volumes of hydrogen bromide and cyclopropane were condensed into *G*. If desired, known amounts of water, methanol, or toluene could be added from a graduated trap attached at *E*, or iodine or trichloroacetic acid in the same manner as for the aluminium bromide. When all the reactants were present in *G* it was sealed off at *H in vacuo*, and placed in a bath at −78°, at which temperature the

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[4] Mayo and Walling, *J. Amer. Chem. Soc.*, 1949, **71**, 3845.

reaction was very slow. When the mixture had melted, vigorous shaking produced a clear yellow solution, some of which was then poured into the dilatometer, also at −78°, until it was filled to just below the mark. Since the amount of aluminium bromide could not be controlled exactly, the amounts of the solvent and other reactants were adjusted so that, though the total volume varied, the actual concentrations in *G* and thus in the dilatometer were as required. The dilatometer was sealed off above the expansion bulb and clamped in a standard position in a solid CO_2–alcohol mixture at $-78{\cdot}0° \pm 0{\cdot}1°$. When thermal equilibrium was attained the distance between the level of liquid and the reference mark was measured to $\pm 10^{-2}$ mm. with a cathetometer. To determine the rate at higher temperatures the dilatometer was removed to a suitable constant-temperature bath. At various times it was reimmersed in the mixture at −78° and the fall in liquid level measured.

Analyses.—The amount of catalyst remaining in solution during the reaction was found by filtering the mixture and determining the aluminium as the oxide. Added iodine was determined by extracting the reaction mixture with water and titrating the aqueous layer with 0·01N-sodium thiosulphate.

The residue in tube *G* after the dilatometer had been filled was maintained at the reaction temperature long enough for polymerisation to be complete. When *G* was opened, some gas, presumably unchanged cyclopropane, was released from solution; the products were then transferred to a separating funnel containing 50% hydrochloric acid. When a number of such residues from experiments under the same conditions had been collected they were extracted several times with the acid, then with water, and the heptane, water, etc., removed *in vacuo* at 100°. The distillate was collected and examined by gas-chromatography after being rigorously dried. The polymer left was dissolved in cyclohexane and precipitated by addition of methanol–concentrated hydrochloric acid. This was repeated several times. Finally solvent was removed *in vacuo* and the molecular weight of the pure polymer determined by the depression of the freezing point of cyclohexane. The infrared spectrum was obtained with a Grubb-Parsons double-beam spectrometer, no solvent being necessary, and the polymer was tested for halides by the Beilstein test.

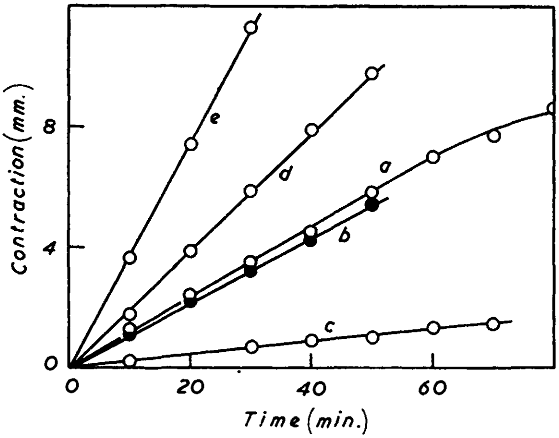


Fig. 2. *Typical results of the dilatometric measurement of the rate of cyclopropane polymerisation.*

a, $[AlBr_3] = [HBr] = 0{\cdot}039$M; [cyclopropane] = 5·4M; temp. = −45·0°.
b, as for (*a*) +5·4 mole/l. of toluene.
c, $[AlBr_3] = [HBr] = 0{\cdot}039$M; [cyclopropane] = 1·0M; temp. = −45·0°.
d, $[AlBr_3] = [HBr] = 0{\cdot}073$M; [cyclopropane] = 5·4M; temp. = −45·0°.
e, $[AlBr_3] = [HBr] = 0{\cdot}039$M; [cyclopropane] = 5·4M; temp. = −10·0°.

Results.—*Kinetics.* The polymerisation of propene being rapid even at −78°, rate measurements were made with cyclopropane only.

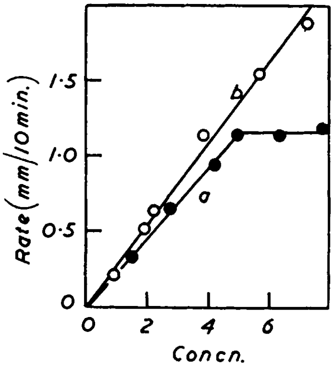
A lag of about 20 min. occurred between the filling of the dilatometer and the actual beginning of a kinetic experiment, during which time a pale yellow solid was precipitated. Despite this, the rate of reaction remained constant for at least 50 min., only then decreasing slowly (Fig. 2), and the initial rates were reproducible to within 10% under the same conditions. One set of conditions (curve *a*, Fig. 2) was taken as a reference for all the kinetic measurements, and this reference experiment was repeated before any series was performed.

No reaction took place in nitroethane. With heptane no appreciable reaction occurred at −45° in the absence of hydrogen bromide, and the rate was proportional to the co-catalyst concentration up to a molar ratio of $1AlBr_3 : 1HBr$. Further addition had no further effect (Fig. 3*a*). The rate was also proportional to the concentration of a 1 : 1 $AlBr_3$–HBr mixture

(Fig. 3*b*), and to the cyclopropane concentration except when this was very high (Fig. 4), when the fast rate was difficult to measure since the high proportion of cyclopropane repeatedly broke the thread in the capillary of the dilatometer. The variation of the rate with temperature is shown in Fig. 5. The overall activation energy of polymerisation was 6 ± 1 kcal. mole^{-1}.

FIG. 3. *Variation of the rate of cyclopropane polymerisation with catalyst concentration.*

[Cyclopropane] = 5·4M; temp. = $-45·0°$.
a, HBr varied; [$AlBr_3$] = 0·039M.
b, $AlBr_3$ + HBr varied at a constant molar ratio of 1 : 1.
Concn. = 10[HBr]/[$AlBr_3$] + [HBr] *or* 10^2[$AlBr_3$,HBr].



The addition of water, methanol, or trichloroacetic acid to the aluminium bromide–cyclopropane–heptane mixture caused complete inhibition in the presence or absence of hydrogen bromide, a pale yellow oil and a pink precipitate separating with the last two additives respectively. The addition of the same amount of toluene as cyclopropane had little effect on the rate at $-45°$ (Fig. 2), though at room temperature the reaction was extremely rapid.

FIG. 4. *Variation of the rate of polymerisation with concentration of cyclopropane.* [$AlBr_3$] = [HBr] = 0·039M; temp. = $-45·0°$.

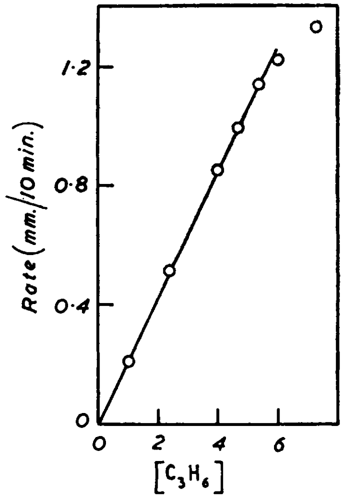
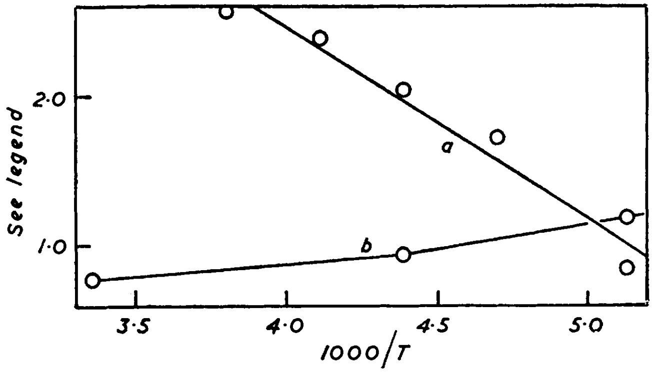


FIG. 5. *Variation of the rate of cyclopropane polymerisation and of the degree of polymerisation with temperature.*



[$AlBr_3$] = [HBr] = 0·039M; [cyclopropane] = 5·4M.
Ordinate: *a*, $\log_{10}$ [Rate (mm./10 min.) + 2]; *b*, $\log_{10}$ D.P.

Iodine retarded the polymerisation, the effect increasing with increasing concentration as shown in Fig. 6.

Analyses. The variation of the concentration of aluminium bromide in the solution as the reaction proceeded is shown in Fig. 7. Precipitation was rapid at first, but the loss of catalyst became much slower as the reaction proceeded. On separation, the precipitate formed a red oil very rapidly at room temperature. The concentration of free iodine fell to zero during an experiment when iodine was added, but the quantitative results were erratic. Whereas the purified heptane or heptane recovered from a solution of aluminium bromide kept at room temperature gave three peaks when analysed chromatographically, the solvent recovered from the reaction mixture was separated into five components, the two new ones being lower-boiling hydrocarbons in trace amounts. The polymers were oils whose viscosity increased as the reaction temperature decreased. Under the reference conditions the molecular weight of the polycyclopropane (deep yellow) decreased as the temperature increased (658, 366, and 244 at −78°, −45°, and 25° respectively; degrees of polymerisation D.P. 15·7, 8·7, and 5·8). A plot of $\log_{10}$ D.P. against $1/T$ was not straight (Fig. 5), but the overall activation energy, calculated from the values at the two lower temperatures, since at 25° side reactions probably occurred, was −1·6 kcal. mole^{-1}. Variation of the catalyst concentration had little effect on the molecular weight of the cyclopropane polymer at −45°. The polypropene, which was a very pale straw colour, had M 364 at this temperature.

The infrared spectra of the polycyclopropane exhibited large peaks at 3·49, 6·93, and 7·33 μ, which suggest that it was a paraffinic hydrocarbon, and a band at 13·7—8 μ indicating a methylene chain containing four or more carbon atoms. There was probably little branching. A large peak at 15·6 μ and smaller ones at 9·66 and 11·25 μ showed that there was probably a $>$C=CH$_2$ end-group. As the temperature increased and the molecular weight of the polymer fell, the bond at 13·7—13·8 μ became less apparent and the peak at 15·6 μ more so. This tends to confirm the structural suggestions above. A peak at 5·88 μ was probably due to a C=O grouping, produced by slight oxygen uptake during extraction of the polymer. The spectrum of the polypropene was not markedly different. None of the polymers gave a positive Beilstein test and therefore bromide was absent.

Fig. 6.—*Effect of added iodine on the rate of polymerisation of cyclopropane.* [AlBr$_3$] = [HBr] = 0·039M; [cyclopropane] = 5·4M; temp. = −45·0°.

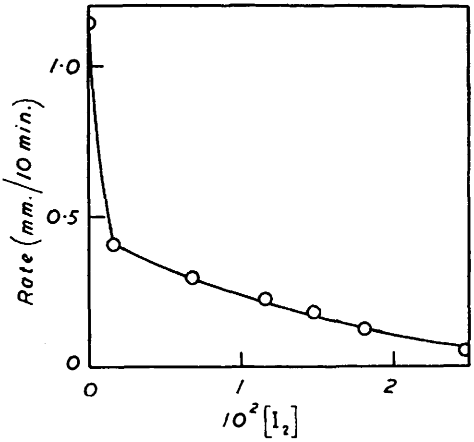
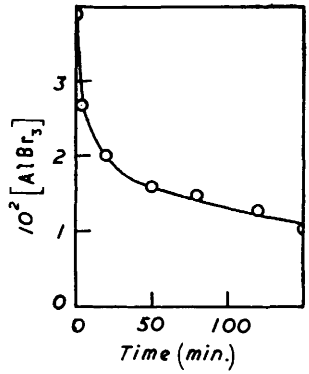


Fig. 7. *Variation of the aluminium bromide concentration in the solution during an experiment.* [HBr] = 0·039M; [cyclopropane] = 5·4M; temp. = −45·0°.



At −45° the polymer produced in the presence of iodine was a brown oil, M 200. The spectrum was somewhat indeterminate but indicated a paraffinic structure. No peaks were present above about 9 μ and the peak at 5·88 μ was very small. The Beilstein test was positive, and thus it is probable that the product was mainly an alkyl iodide, about $C_6H_{11}I$.

DISCUSSION

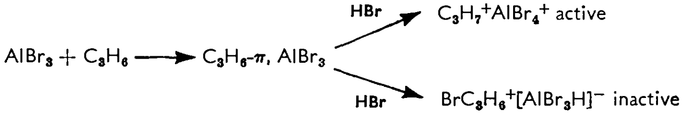
Although precipitation occurred, the fact that the rate plots were linear and the rates reproducible indicates that the polymerisation was homogeneous, the precipitate being inactive, but not just catalyst thrown down from a supersaturated solution. The formation of a Friedel–Crafts tar also shows that it contained organic groups as well as aluminium. Fontana and Kidder [2] found that with propene at −78° there was an induction period followed by a rapid rise in rate to a sharp maximum. A white precipitate was formed, and the rate fell to a steady value after which no further precipitation appeared to occur, though no aluminium analyses were reported. Filtering off the precipitate had no effect on the steady rate, and precipitation could be prevented by operating a " semi-continuous " process. If there was an induction period and sharp rate change with cyclopropane, they could not be observed, owing to the time lag between mixing the reactants and beginning the rate measurements.

The polymerisation of cyclopropane and propene almost certainly proceeds by a carbonium-ion mechanism in a similar way to other Friedel–Crafts polymerisations.[5] Fontana and Kidder [2] found that the kinetics of polymerisation of propene at $-78°$ were very similar to those of polymerisation of cyclopropane reported here except that the dependence on olefin concentration was of the form $[C_3H_6]/(1 + K[C_3H_6])$. They suggested that the rate-determining step was the rearrangement of a growing chain–monomer complex to give a higher carbonium ion:

$$(a)\ M_n^+C^- + M \rightleftharpoons M_n^+C^-M;\quad (b)\ M_n^+C^-M \longrightarrow M_{n+1}^+C^-$$

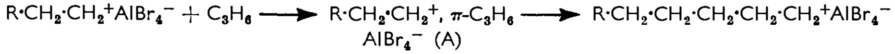
They identified the overall activation energy of 10·3 kcal. mole^{-1} with that of step (*b*) and did not include a termination reaction. They considered that the ionic species was partly precipitated at the beginning of the reaction owing to the non-polar nature of the solvent, but that very soon the solubilising effect of the hydrocarbon chains prevented further loss. The activation energy of the rate-determining growth step seems high for a polymerisation which is rapid at $-78°$, and at any rate with cyclopropane the results seem to be better explained on the basis of a " normal " type of chain mechanism, especially as not all the monomer was used up when the reaction had stopped.

In order to explain the anomalous effect of hydrogen chloride as cocatalyst on the kinetics of the alkylation of benzene with cyclopropane in the presence of aluminium chloride, it was necessary to postulate the formation of an inactive cyclopropane–catalyst complex (Part III). Thus, since the maximum rate of polymerisation was found with a catalyst–cocatalyst ratio of unity (Fig. 3), it is suggested that the aluminium bromide, hydrogen bromide, and cyclopropane reacted to give two 1 : 1 : 1 complexes. One initiated the polymerisation, and the other was inactive and, since it was ionic, precipitated from the non-polar solvent. It is possible that the first stage was the formation of a π-complex, of the type postulated as the intermediate in the reaction of cyclopropane and lithium aluminium hydride to give tripropylaluminium,[6] followed by addition of HBr in either of two ways leading to splitting of the ring, *viz.*,



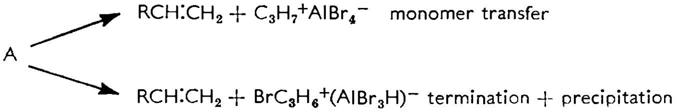
This is, of course, purely conjectural, though it is likely that n-propyl ions were the original growth centres.

Following Fontana and Kidder,[2] we may suppose that propagation occurred by the formation of a growing chain–monomer complex, which could rearrange to a higher carbonium ion:



$$R{\cdot}CH_2{\cdot}CH_2^+AlBr_4^- + C_3H_6 \longrightarrow \underset{AlBr_4^-\ (A)}{R{\cdot}CH_2{\cdot}CH_2^+,\ \pi\text{-}C_3H_6} \longrightarrow R{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2^+AlBr_4^-$$

It is usually assumed that the activation energy of propagation of Friedel–Crafts polymerisation is small,[5] and if the rate of the above process was high then the ion-pairs of lower molecular weight would not have had time to be precipitated. However, since the polymer formed had a low molecular weight and contained terminal double bonds, proton transfer probably also occurred in complex A



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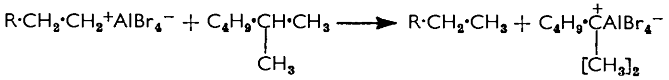
[5] Pepper, *Quart. Rev.*, 1954, **8**, 88.
[6] Tipper and Walker, *Chem. and Ind.*, 1957, 730.

In the presence of branched-chain hydrocarbons the molecular weight of polypropene was markedly less than with pure n-butane as solvent, probably owing to hydride-ion transfer to the growing carbonium ions.[2] This transfer may have occurred during the polymerisation of cyclopropane since small amounts of heptane isomers were present, *e.g.*,



$$\mathrm{R{\cdot}CH_2{\cdot}CH_2{}^{+}AlBr_4{}^{-} + C_4H_9{\cdot}\underset{\displaystyle CH_3}{\underset{|}{C}}H{\cdot}CH_3 \longrightarrow R{\cdot}CH_2{\cdot}CH_3 + C_4H_9{\cdot}\underset{\displaystyle [CH_3]_2}{\underset{|}{\overset{+}{C}}}AlBr_4{}^{-}}$$

This would account for the traces of hydrocarbons of low molecular weight detected in the solvent after reaction. Further hydride-ion transfer could have led to resonance-stabilised multiply charged carbonium-ion pairs.[2] The presence of these in the precipitate could have been responsible for the colour of the tar formed on warming. The organic part of any extracted with the polymer would have reacted with oxygen giving conjugated groupings responsible for the colour and the peak at 5·88 μ in the infrared spectra. However, hydride-ion transfer was actually of minor importance kinetically, since no appreciable branching was apparent in the polycyclopropane.

The main steps of the polymerisation can be summarised as follows ($\mathrm{M} \equiv \mathrm{C_3H_6}$, $\mathrm{C} \equiv \mathrm{AlBr_3 + HBr}$):

$$\begin{array}{lll}
1 & \mathrm{M + C \longrightarrow MC\ (active)} & \text{Initiation} \\
2 & \mathrm{M + C \longrightarrow CM\!\downarrow\ (inactive)} & \\
3 & \mathrm{M}_n\mathrm{C + M \longrightarrow M}_n\mathrm{CM} & \left.\right\} \text{Propagation} \\
4 & \mathrm{M}_n\mathrm{CM} \longrightarrow (a)\ \mathrm{M}_{n+1}\mathrm{C}\ \text{or}\ (b)\ \mathrm{M}_n + \mathrm{MC} & \\
5 & \mathrm{M}_n\mathrm{CM} \longrightarrow \mathrm{M}_n + \mathrm{CM}\!\downarrow & \text{Termination}
\end{array}$$

If the initial rate measured represented the rate of loss of cyclopropane then, since the loss by reaction 2 was negligible compared with that by 3:

$$\text{Rate} \propto -\mathrm{d}[\mathrm{C_3H_6}]/\mathrm{d}t = k_3[\mathrm{M}_n\mathrm{C}][\mathrm{M}].$$

Despite the relatively small degree of polymerisation, since monomer transfer was important:

$$k_3[\mathrm{M}_n\mathrm{C}][\mathrm{M}] = k_4[\mathrm{M}_n\mathrm{CM}]$$

at least to a first degree of approximation. If there was a stationary concentration of the complex $\mathrm{M}_n\mathrm{CM}$ then

$$k_1[\mathrm{M}][\mathrm{C}] = k_5[\mathrm{M}_n\mathrm{CM}]$$
$$-\mathrm{d}[\mathrm{C_3H_6}]/\mathrm{d}t = k_1k_4[\mathrm{M}][\mathrm{C}]/k_5 \propto \text{Rate}$$

as found experimentally. On this basis $E_1 + E_4 - E_5 = 6$ kcal. mole^{-1} and D.P. $= k_{4,a}/[k_{4,b} + k_5]$. Thus $E_{\mathrm{D.P.}} = -1{\cdot}6 = E_{4,a} - E_{4,b}$ or $E_{4,a} - E_5$, depending on whether chain-transfer or termination was the more important factor in determining the length of the polymer chains. This is of course not known, but if $E_{4,a}$ was very small, as seems probable, then $E_1 \approx 5$—10 kcal. mole^{-1}, which is not unreasonable for the activation energy of initiation.[5]

The results with added iodine suggest that it was very effective in terminating the chains, probably by the reaction

$$6\mathrm{M}_n\mathrm{CM} + \mathrm{I_2} \longrightarrow \mathrm{M}_{n+1}\mathrm{I} + \mathrm{I^{+}AlBr_4{}^{-}}$$

In this case, for stationary conditions,

$$k_1[\mathrm{M}][\mathrm{C}] = k_5[\mathrm{M}_n\mathrm{CM}] + k_6[\mathrm{M}_n\mathrm{CM}][\mathrm{I_2}]$$
$$\textit{i.e.},\ -\mathrm{d}[\mathrm{C_3H_6}]/\mathrm{d}t = k_1k_3[\mathrm{M}][\mathrm{C}]/(k_5 + k_6[\mathrm{I_2}])$$

and the experimental dependence of rate on iodine concentration was of this general form. The propagating carbonium ion cannot have reacted with toluene at —45°, but alkylation probably took place at room temperature as might be expected from the results reported in Part III.

Water, methanol, and trichloroacetic acid are often good co-catalysts for Friedel–Crafts polymerisations.[5] Their ineffectiveness in this case, and the iractual inhibiting action when hydrogen bromide was present, was probably due to the non-polar nature of the solvent. The co-catalysts other than HBr formed strongly bound complexes with aluminium bromide, which in heptane were unreactive towards cyclopropane. Nitroethane and aluminium bromide probably form a complex [cf. $AlCl_3,CH_3{\cdot}NO_2$],[6] preventing polymerisation in this solvent.

One of us (D. A. W.) thanks the University of Liverpool for a post-graduate scholarship.

Department of Inorganic and Physical Chemistry,
The University, Liverpool.

[*Received, October* 22*nd*, 1958.]