112.   *Cationic Polymerisation of Oxacyclobutanes.   Part II.**

By J. B. Rose.

A kinetic investigation of the polymerisation of oxa*cyclo*butane, catalysed by boron trifluoride, is described.   Water, ethanol, and hydroxyl-terminated polymer are cocatalysts for the reaction.   The rate of polymerisation obeys the equation, rate $= k[M][BF_3][R \cdot OH]$ (R = H, Et, polymer chain) provided that, with 0·1M-boron trifluoride as the catalyst, the concentration of cocatalyst is not greater than 0·01M.   When the concentration of water was increased from 0·01M to 0·03M the rate passed through a maximum, after which further increase in the concentration of water brought about a marked decrease in rate.   Increase in the concentration of water above 0·01M also changed the order of reaction with respect to monomer progressively from 1 to 2.   The molecular weight of the polymer (as indicated by its intrinsic viscosity) decreased steadily as the concentration of cocatalyst was increased. From the above data, polymerisation mechanisms are proposed involving chain propagation *via* oxonium ions.   The method of kinetic measurement also enabled the heat of polymerisation, which provides a measure of the ring-strain energy of the oxa*cyclo*butane ring, to be determined.   Investigation of the polymerisation of 3 : 3-dimethyloxa*cyclo*butane indicated that it followed a course analogous to that of the parent compound.

IN the presence of boron trifluoride both oxa*cyclo*butane and its 3 : 3-dimethyl analogue are polymerised to a mixture of a cyclic tetramer and a linear polymer.*   The present investigation was undertaken to determine the factors affecting both the rate of polymerisation and the molecular weights of the polymers produced.   The temperature was chosen so that linear polymer was the principal product.   All chemicals were handled *in vacuo*, and the kinetic measurements were made by measuring the rate at which the heat of reaction was evolved under isothermal conditions.

EXPERIMENTAL

Materials.—Oxa*cyclo*butane, 3 : 3-dimethyloxa*cyclo*butane, ethyl chloride, methyl chloride, and boron trifluoride were obtained, purified, and stored as in Part I.   Ethanol, used as a cocatalyst, was dried by Smith's method.[1]   Poly(oxa*cyclo*butane) of low molecular weight had $[\eta]$ *ca.* 0·05 dl. g.$^{-1}$, and was prepared as in Part I.
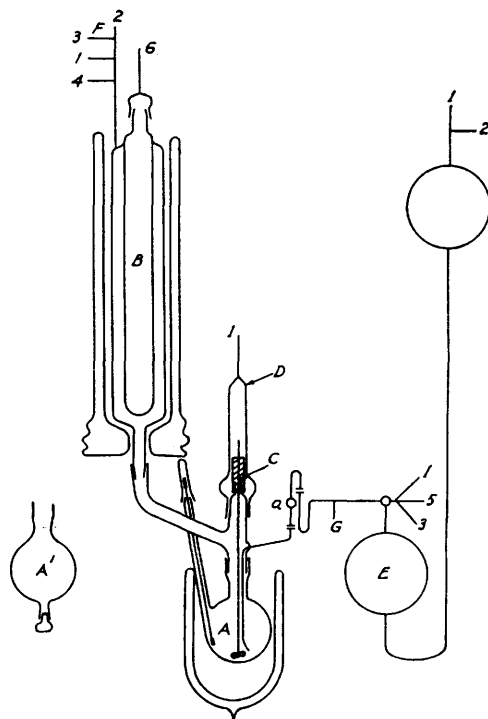
Apparatus.—This is shown in Fig. 1, and was designed so that the reaction vessel, *A* (*ca.* 300

    * Part I, preceding paper.
   [1] Smith. *J.*, 1927, 1288.

ml. capacity), could be charged with reactants *in vacuo*, then filled with dry nitrogen and the polymerisation carried out at atmospheric pressure. The condenser, B, and the reaction vessel, A, were insulated thermally by vacuum jackets, while the tubes connecting them, and the mouth of the vacuum flask surrounding A, were lagged with cotton-wool. A pentane thermometer projected into A, but was attached to a sealed glass tube containing soft iron so that it could be withdrawn by means of a magnet. The stirrer gland, C, which was made of " Neoprene " and lubricated with Silicone grease, effectively prevented ingress of moisture during polymerisation when a slight positive pressure of nitrogen was maintained in A, but was surrounded by the adaptor, D, when a vacuum was required in the apparatus. The gas pipette,

Fig. 1.

Fig. 2.

Vol. of CO_2 evolved in 5 min. (l.)

○, Methyl chloride.
△, Methyl chloride–ethyl chloride.

1, To pump.
2, To atmosphere.
3, To nitrogen supply.
4, To monomer and solvent supplies.
5, To BF_3 supply.
6, To flow meter.
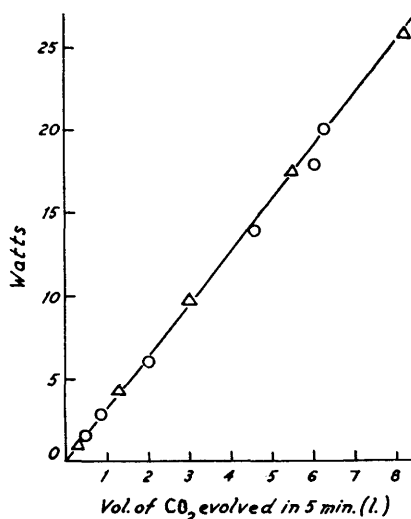
E (1·2 l. capacity), was filled with dry mercury. All ducts opening to the atmosphere were protected by long guard tubes packed with calcium hydride to prevent the entry of moisture. The nitrogen used was dried by being passed through a similar tube.

Procedure.—(1) The apparatus was evacuated overnight by means of a two-stage oil-pump pumping through a trap cooled in liquid nitrogen. (2) Measured quantities of monomer, cocatalyst (water or ethanol), and solvent were distilled, in this order, into the reaction vessel which was cooled in liquid nitrogen, the thermometer being withdrawn. When polymer of low molecular weight was used as the cocatalyst, it was placed in the reaction vessel when the apparatus was assembled, and heated to 130° while the apparatus was evacuated. Measurements of the intensity of the infrared absorption band at *ca.* 5100 cm.$^{-1}$, due to water, showed that the above treatment reduced the water content of the polymer to a negligible level. After the polymer had been dried, the other reactants were distilled into the reaction vessel without discharging the vacuum. (3) The condenser was filled with a mixture of solid carbon dioxide (700 g.) and ethanol (100 ml.), and dry nitrogen passed into the apparatus until the pressure inside it was 1 atm. Thereafter a flow of nitrogen was maintained across the junction, F.

The adaptor, D, could now be removed, allowing the stirrer to be connected to an electric motor. Then the reaction vessel was warmed until its contents, which were vigorously stirred, refluxed against the condenser, and the apparatus was insulated thermally as described in the previous paragraph. (4) A measured quantity of boron trifluoride was distilled from a constant-volume variable-pressure gas-burette into the tube, G, which was cooled in liquid nitrogen. It was then warmed so that it vaporised and displaced mercury from bulb, E, the upper bulb being evacuated. When the boron trifluoride had vaporised completely, the lower bulb was opened to the atmosphere so that the gas in the lower bulb was under pressure. (5) The reaction vessel having reached thermal equilibrium with its surroundings, polymerisation was initiated by injecting boron trifluoride from the bulb, E, into the reaction vessel *via* the tap, a, and immediately afterwards flushing the dead space between A and E with a slow stream of dry nitrogen. The complete operation took *ca.* 3 min., the boron trifluoride being absorbed during this period.

Polymers.—Three methods were used to isolate polymers of oxa*cyclo*butane. (*a*) The reactant product was poured into ether and, when most of the methyl chloride had evaporated, the ether extract was washed, first with sodium hydroxide solution and then with distilled water. After being dried (K_2CO_3), the polymer was isolated free from tetramer (the proportion of tetramer was $<10\%$) by crystallisation at $-80°$ (see Part I). (*b*) The product was poured into dry ether containing trichloroacetic acid (0.6 g.), and the resulting solution treated as in method (*a*). (*c*) This was used to stop the polymerisation before completion. The flask, A' (see Fig. 1), was used instead of the reaction vessel and at a predetermined time the stopper was removed and the reaction solution blown by nitrogen into a solution of sodium ethoxide in ethanol at $-20°$. The resulting mixture was poured into ether, the solution washed several times to remove ethanol and excess of alkali, and the polymer isolated as in method (*a*). Polymers of 3 : 3-di-methyloxa*cyclo*butane, which did not crystallise from ether at $-80°$, were isolated by method (*a*), the ether solution being evaporated to dryness to recover the polymer.

Intrinsic viscosities, $[\eta]$, of the polymers in benzene solution were measured at $20°$ with an Ostwald No. 1 viscometer. The plot of η_s/C against C, where η_s is the specific viscosity and C the concentration, gave straight lines in the concentration range 1.0—0.2 g. dl.$^{-1}$. Osmometric measurements gave a value of $20,000$ for the number-average molecular weight of a mixture of several polymers of oxa*cyclo*butane having $[\eta]$ ranging from 0.60 to 0.54 dl. g.$^{-1}$.

Polymers isolated by method (*a*) did not contain detectable quantities of chlorine or fluorine, but their infrared absorption spectra contained bands characteristic of the primary hydroxyl group at 3300 cm.$^{-1}$ (OH fundamental), 4700 cm.$^{-1}$ (OH overtone which was resolved from the corresponding band due to water at 5100 cm.$^{-1}$), and at 1045 cm.$^{-1}$ (C–O stretching vibration). No absorption characteristic of the $>C\ddot{:}CH_2$ group was detected. Polymers prepared by using low concentrations of cocatalyst and isolated by method (*b*) contained detectable quantities of chlorine (see Tables 5 and 7), but an increase in the concentration of water to 0.10 mole l.$^{-1}$ (the concentration of catalyst being 0.10 mole l.$^{-1}$) reduced the chlorine content of the polymer to 0.1%. Polymers isolated by method (*a*) from blank experiments, in which solutions of hydroxyl-terminated polymer in ether were treated with trichloroacetic acid both in the absence and in the presence of boron trifluoride, did not contain detectable quantities of chlorine. The intrinsic viscosities of polymers isolated by method (*c*) from repetitions of experiment 1 (see Table 1) in which the reaction was stopped after approximately 50%, 75%, and 100% of the monomer had reacted were 1.10, 0.90, 0.56 dl. g.$^{-1}$, respectively. The intrinsic viscosity of hydroxyl-terminated polymer was unchanged when a solution of the polymer in methyl chloride was treated with boron trifluoride.

Kinetic Method.—Polymerisations were followed by measuring the rate at which heat was evolved, and transferred by the refluxing solvent to the condenser. This was effected by measurement of the volume of carbon dioxide evolved from the freezing mixture in the condenser, at intervals during the reaction, by means of a gas-meter which could be read to 0.01 l. The total volume of carbon dioxide evolved provided a direct measure of the heat of reaction, while the rate of evolution measured the reaction rate. Blanks were run immediately before and after the polymerisation, and the mean value obtained (*ca.* 0.3 l. min.$^{-1}$) used to correct for heat entering the system owing to imperfect insulation. The method was calibrated by replacing the pentane thermometer (see Fig. 1) by a small electric heater, and comparing the rate of carbon dioxide evolution with the wattage of the heater. Heat evolution in the reaction vessel was registered almost immediately on the flow-meter, and the volume of carbon dioxide evolved was proportional to the energy dissipated by the heater (see Fig. 2). The refluxing solvent was methyl chloride, or ethyl chloride–methyl chloride ($1 : 1$).

Rate measurements made at the start of the reaction were disturbed because the catalyst, which dissolved relatively slowly, was not added instantaneously. Therefore an arbitrary zero of time was taken after the catalyst had been added, and first- and second-order integrated rate constants were calculated according to the equations $k_1 = 2 \cdot 303\{\log_{10} a/(a - x)\}/t$ and $k_2 = x/(a - x)ta$, respectively, where $a = V_\infty - V_0$ and $x = V_t - V_0$, V_∞ being the total volume of carbon dioxide evolved, V_0 that evolved up to the zero of time, and V_t that evolved by time t (measured from the arbitrary zero of time). For the tabulated results the starting monomer concentration was calculated from the volumes of monomer and solvent used, while the "initial" monomer concentration is equal to the "starting" concentration $\times V_0/V_\infty$. Values quoted in the Tables are the average values of k_1 or k_2 for each experiment, a series of constants being calculated for values of x up to 70—80% of a. The deviation from the mean value was *ca.* $\pm 5\%$.

Kinetic Results.—(a) *Polymerisation of oxacyclobutane in methyl chloride solution at* $-22°$. Both the order and the rate of the reaction were markedly affected by the concentration of water present in the system (see Table 1). Continual increase in the concentration of added water caused the rate to rise to a maximum and then to decrease, while the apparent order of reaction changed progressively from 1 to 2. The intrinsic viscosities of the polymers decreased as the concentration of added water was increased.

The region ([H₂O] added ranging from zero to $0 \cdot 0066$ mole l.$^{-1}$) in which the reaction obeyed a first-order rate law was investigated in greater detail, as now to be described.

Variation of both the concentration of monomer at the start of the reaction and the "initial" monomer concentration (Table 2) had only a slight effect on k_1, but the intrinsic viscosity of the polymers increased with increasing monomer concentration. This increase in k_1 is largely

TABLE 1. *Effect of added water on the polymerisation.*

(Starting [monomer] $= 1 \cdot 62$ mole l.$^{-1}$; [BF₃] $= 0 \cdot 10$ mole l.$^{-1}$.)

Expt.	[H₂O] added (mole l.$^{-1}$)	Reaction order	Rate * (mole min.$^{-1}$)	k_1 (min.$^{-1}$)	k_2 (min.$^{-1}$ mole^{-1} l.)	$[\eta]$ (dl. g.$^{-1}$)
1	Nil	1	0·051	0·083	—	0·60
1 (a)	Nil	1	0·053	0·085	—	0·54
2	0·0066	1	0·132	0·212	—	0·47
3	0·010	>1 <2	*ca.* 0·20	—	—	0·54
4	0·030	>1 <2	0·36	—	—	0·52
5	0·050	>1 <2	0·20	—	—	0·50
6	0·070	>1 <2	0·15	—	—	0·46
7	0·080	2	0·13	—	0·325	0·42
8	0·090	2	0·04	—	0·106	0·38
9	0·120	2	0·02	—	0·054	0·34
10	0·150	—	Rate too slow to be measured	—		0·16

* The rate quoted is that when the monomer concentration was $0 \cdot 62$ mole l.$^{-1}$, and in expts. 1, 2, 7, 8, and 9 was calculated from the corresponding rate constants. In expts. 3, 4, 5, and 6 the rate was obtained from experimental plots of monomer concentration against time by drawing tangents.

accounted for by the automatic increase in the concentration of water which accompanies an increase in monomer concentration, owing to the relatively inadequate method (as compared with that used for the solvent) of drying the monomer. The reaction is therefore of first order with respect to monomer.

TABLE 2. *Effect of monomer concentration on* k_1.

([BF₃] $= 0 \cdot 10$ mole l.$^{-1}$; no water added.)

Expt.	Starting [monomer] (mole l.$^{-1}$)	Initial [monomer] (mole l.$^{-1}$)	k_1 (min.$^{-1}$)	$[\eta]$ (dl. g.$^{-1}$)	Expt.	Starting [monomer] (mole l.$^{-1}$)	Initial [monomer] (mole l.$^{-1}$)	k_1 (min.$^{-1}$)	η (dl. g.$^{-1}$)
11	0·81	0·30	0·067	0·39	1a	1·62	1·12	0·085	0·54
1	1·62	0·90	0·083	0·60	12	2·44	1·08	0·088	0·69

Variation in the concentration of boron trifluoride caused only random fluctuations in the value of $k_1/[BF_3]$ (Table 3), indicating that the reaction was of first order with respect to boron trifluoride.

Addition of small quantities of water or of ethanol to the reaction (Tables 4 and 5) caused the rate constant, k_1, to increase according to the equations, $k_1 = C_{H_2O}\{[H_2O] + 0 \cdot 0045\}$ and $k_1 = 0 \cdot 084 + C_{EtOH}[EtOH]$. Water and ethanol are therefore cocatalysts and, if it is assumed that the concentration of water remaining in the reactants after drying was $0 \cdot 0045$ mole l.$^{-1}$,

the reaction is of first order with respect to the cocatalyst. The value of 0·0045 mole l.$^{-1}$ corresponds to slightly less than one part of water (by vol.) per 10,000 parts of reaction mixture. Addition of water causes only a slight decrease in $[\eta]$ but addition of ethanol brings about a considerable decrease.

TABLE 3. *Effect of boron trifluoride concentration on k_1.*

(Starting [monomer] = 1·62 mole l.$^{-1}$; no water added.)

Expt.	Initial [monomer] (mole l.$^{-1}$)	[BF$_3$] (mole l.$^{-1}$)	k_1 (min.$^{-1}$)	k_1/[BF$_3$] (min. mole^{-1} l.)	$[\eta]$ (dl. g.$^{-1}$)
13	1·08	0·05	0·035	0·70	0·72
1	0·90	0·10	0·083	0·83	0·60
1a	1·12	0·10	0·085	0·85	0·54
14	1·15	0·13	0·094	0·72	—
15	0·86	0·16	0·113	0·71	0·49
16	0·78	0·18	0·131	0·73	0·51
17	0·57	0·20	0·170	0·85	0·44

TABLE 4. *Effect of added water on k_1.*

(Starting [monomer] = 1·62 mole l.$^{-1}$; [BF$_3$] = 0·10 mole l.$^{-1}$.)

Expt.	Initial [monomer] (mole l.$^{-1}$)	[H$_2$O] added (mole l.$^{-1}$)	k_1 (min.$^{-1}$)	k/([H$_2$O] + 0·0045) (min.$^{-1}$ mole^{-1} l.)	$[\eta]$ (dl. g.$^{-1}$)
1	0·90	Nil	0·083	18·4	0·60
1a	1·12	Nil	0·085	18·9	0·54
18	0·85	0·0022	0·136	20·3	0·52
19	0·77	0·0037	0·154	18·8	0·50
20	0·65	0·0058	0·194	18·8	—
2	0·62	0·0066	0·212	19·1	0·47

Average value for C_{H_2O} = 91·1 g. min.$^{-1}$ mole^{-1} l.

TABLE 5. *Effect of ethanol on k_1.*

(Starting [monomer] = 1·62 mole l.$^{-1}$; [BF$_3$] = 0·10 mole l.$^{-1}$.)

Expt.	Initial [monomer] (mole l.$^{-1}$)	[EtOH] (mole l.$^{-1}$)	k_1 (min.$^{-1}$)	$(k_1 - 0·084)$/[EtOH] (min.$^{-1}$ mole^{-1} l.)	$[\eta]$ (dl. g.$^{-1}$)	[Cl] † (%)
1	0·90	Nil	0·083	—	0·60°	—
1a	1·12	Nil	0·085	—	0·54	0·2
21	1·00	0·0021	0·115	14·8	0·42	0·2
22	1·07	0·0036	0·131	13·1	0·40	0·2
23	0·82	0·0067	0·175	13·7	0·35	0·3
24 *	—	0·030	—	—	0·27	—

Average value for C_{EtOH} = 13·9 min.$^{-1}$ mole^{-1} l.

* The order of this reaction was >1<2.

† The polymers were isolated by method (*b*), and their chlorine content is listed in this column.

Hydroxyl-terminated polymer was also a cocatalyst (Table 6), but as the molecular weight of the polymer was not known with any degree of certainty, the effectiveness of its cocatalysis could not be measured.

TABLE 6. *Effect of hydroxyl-terminated polymer on k_1.*

(Starting [monomer] : 1·62 mole l.$^{-1}$; [BF$_3$] = 0·10 mole l.$^{-1}$.)

Expt.	Initial [monomer] (mole l.$^{-1}$)	[Polymer] (g. l.$^{-1}$)	k_1 (min.$^{-1}$)	$[\eta]$ (dl. g.$^{-1}$)
1	0·90	Nil	0·083	0·60
25	0·82	10·7	0·164	0·38
26	0·98	11·0	0·173	0·35

(b) *Polymerisation of oxacyclobutane and* 3 : 3-*dimethyloxacyclobutane at* −9°, *a mixture of methyl chloride and ethyl chloride being used as the solvent.* Poly-(3 : 3-dimethyloxacyclobutane) crystallised when this monomer was polymerised in methyl chloride solution at −22°. However, a homogeneous reaction mixture was obtained when ethyl chloride–methyl chloride (1 : 1, by vol.) was used as the solvent. A brief investigation, restricted to the region in which the reactions obeyed first-order rate laws, indicated that for both monomers the addition of small quantities of water (Tables 7 and 8) brought about a linear increase in rate of polymerisation. Expts. 30 and 31 (Table 8) indicate that the polymerisation of 3 : 3-dimethyloxacyclobutane is of first order with respect to boron trifluoride.

Heats of Polymerisation.—The total volume of carbon dioxide evolved from the condenser during each experiment was corrected for the heat of solution of the catalyst, and the value obtained converted into kcal. by means of the conversion factor obtained from Fig. 2 (100w = 6·3 l. min.$^{-1}$, *i.e.*, 1 l. = 6/6·3 × 4·185 = 0·228 kcal.). The heat of solution of the catalyst, obtained by measurement of the volume of carbon dioxide evolved when boron trifluoride was dissolved in a solution of polymer, was equivalent to 0·7 l. of carbon dioxide per 0·01 mole of boron trifluoride dissolved. In Table 9 the heat of polymerisation of oxa*cyclo*butane is compared with that of its 3 : 3-dimethyl analogue.

The average value of ΔH for the polymerisation of oxa*cyclo*butane in methyl chloride solution at $-22°$ (Expts. 1—25) was 20·0 kcal. mole^{-1}.

TABLE 7. *Effect of added water on the rate of polymerisation of oxacyclobutane.*

(Starting [monomer] = 0·81 mole l.$^{-1}$; [BF$_3$] = 0·040 mole l.$^{-1}$.)

Expt.	Initial [monomer] (mole l.$^{-1}$)	[H$_2$O] added (mole l.$^{-1}$)	k_1 (min.$^{-1}$)	k_1/([H$_2$O] + 0·0025) (min.$^{-1}$ mole l.$^{-1}$)	$[\eta]$ (dl. g.$^{-1}$)	[Cl] * (%)
27	0·66	Nil	0·076	30·4	0·43	0·5
28	0·60	0·00072	0·117	36·3	—	0·3
29	0·60	0·00122	0·127	34·2	—	0·2
30	0·58	0·00161	0·143	34·8	0·41	0·4

* The polymers were worked up by method (*b*) and their chlorine contents are listed in this column.

TABLE 8. *Effect of boron trifluoride concentration and of added water on the rate of polymerisation of 3 : 3-dimethyloxacyclobutane.* *

(Starting [monomer] = 0·81 mole l.$^{-1}$.)

Expt.*	Initial [monomer] (mole l.$^{-1}$)	[BF$_3$] (mole l.$^{-1}$)	[H$_2$O] added (mole l.$^{-1}$)	k_1 (min.$^{-1}$)	k_1/([H$_2$O] + 0·0024) (min.$^{-1}$ mole l.$^{-1}$)
31	0·44	0·040	Nil	0·111	—
32	0·61	0·020	Nil	0·053	21·9
33	0·55	0·020	0·00067	0·069	22·3
34	0·29	0·020	0·00111	0·078	22·1

* $[\eta]$ was *ca.* 2 dl. g.$^{-1}$ in all four experiments, but this value is of little significance as the polymers became partially cross-linked during isolation.

TABLE 9. *Heats of polymerisation at* $-9°$, *a mixture of ethyl chlorine and methyl chloride being used as the solvent.*

(Starting [monomer] = 0·81 mole l.$^{-1}$.)

(*a*) Oxa*cyclo*butane

Expt.	27	28	29	30
[BF$_3$] (mole l.$^{-1}$)	0·040	0·040	0·040	0·040
Vol. of CO$_2$ evolved (l.) *	13·5	13·6	13·8	13·8
ΔH (kcal. mole^{-1})	19·0	19·1	19·4	19·4

(*b*) 3 : 3-Dimethyloxa*cyclo*butane

Expt.	31	32	33	34
[BF$_3$] (mole l.$^{-1}$)	0·040	0·020	0·020	0·020
Vol. of CO$_2$ evolved (l.) *	11·3	11·4	11·2	11·6
ΔH (kcal. mole^{-1})	15·8	16·0	15·7	16·3

* This volume of gas was evolved when 200 ml. of a 0·81 mole l.$^{-1}$ solution of monomer was polymerised, correction having been made for the heat of solution of the catalyst.

DISCUSSION

The kinetic measurements show that water has a marked effect on the nature of this reaction, complex variations in both rate and order occurring as the concentration of water is changed. However, provided that the concentration of water does not exceed a limiting value, the kinetics of the reaction are described by equation (1), where [H$_2$O] and [BF$_3$] are the concentrations of these reactants added to the system. This was demonstrated
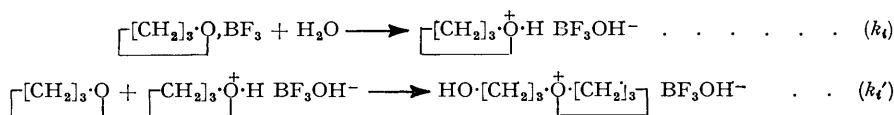
$$-d[M]/dt = \text{const.} \times [M][BF_3]([H_2O] + C) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

for the polymerisation of oxa*cyclo*butane in methyl chloride solution, and for both oxa*cyclo*butane and its 3 : 3-dimethyl analogue, a methyl chloride–ethyl chloride being used as the solvent. These data do not show that water is an essential cocatalyst, for reaction occurs
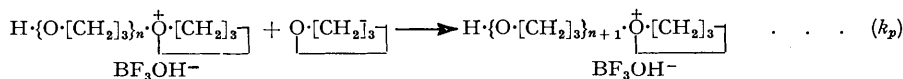
without addition of water. However, Farthing and Reynolds [2] have shown that boron trifluoride is unable to initiate the polymerisation of 3 : 3-bischloromethyloxa*cyclo*butane in an exhaustively dried system, but polymerisation commences on addition of water. Therefore, for discussion of the experiments described in this paper, it appears reasonable to assume that reaction takes place without addition of water because the system is not completely dry, and in equation (1), C is equal to the concentration of water present owing to incomplete drying. A qualitative indication of the polymers' relative molecular weights was obtained from measurements of their intrinsic viscosities. These measurements show that the molecular weight increases with increasing monomer concentration, but decreases as the concentration of added water is increased. The molecular weight also decreases with increasing conversion of monomer into polymer, implying that this polymerisation does not take place by a mechanism of the type described by Hibbert and Perry [3] for the base-catalysed polymerisation of ethylene oxide, in which step-wise addition of monomer to hydroxyl-terminated polymer occurs, and the molecular weight increases as the polymerisation proceeds :

$$OH \cdot [CH_2 \cdot CH_2 \cdot O]_n \cdot H + \overline{ CH_2 \cdot CH_2 \cdot O} \longrightarrow OH \cdot [CH_2 \cdot CH_2 \cdot O]_{n+1} \cdot H$$
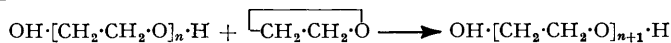
Taking the observed dependence of molecular weight on monomer concentration into account, it may be concluded from equation (1) that polymerisation proceeds by a chain mechanism in which the rate of initiation does not depend on the concentration of monomer. Boron trifluoride is only slightly soluble in methyl chloride, but dissolves readily in a solution of oxa*cyclo*butane in methyl chloride owing, presumably, to the formation of a co-ordination compound whose concentration will be that of the boron trifluoride added. A two-stage initiation mechanism, the rate of which does not depend on monomer concentration, is as follows :

$$\overline{[CH_2]_3 \cdot O}, BF_3 + H_2O \longrightarrow \overline{[CH_2]_3 \cdot \overset{+}{O} \cdot H} \ BF_3OH^- \quad . \quad . \quad . \quad . \quad (k_i)$$

$$\overline{[CH_2]_3 \cdot O} + \overline{[CH_2]_3 \cdot \overset{+}{O} \cdot H} \ BF_3OH^- \longrightarrow HO \cdot [CH_2]_3 \cdot \overset{+}{O} \cdot \overline{[CH_2]_3} \ BF_3OH^- \quad . \quad . \quad (k_i')$$

The chain is then propagated *via* the tertiary oxonium ion :

$$H \cdot \{O \cdot [CH_2]_3\}_n \cdot \overset{+}{O} \cdot \overline{[CH_2]_3} + O \cdot \overline{[CH_2]_3} \longrightarrow H \cdot \{O \cdot [CH_2]_3\}_{n+1} \cdot \overset{+}{O} \cdot \overline{[CH_2]_3} \quad . \quad . \quad . \quad (k_p)$$
$$ BF_3OH^- BF_3OH^-$$

In accordance with current theory,[4] the anion, BF_3OH^-, is assumed to be closely associated with its cation, the two forming an ion-pair. The reactions of the oxonium ions with monomer are considered, by analogy with the acid-catalysed substitution reactions of ethylene oxide,[5] to involve nucleophilic attack by monomer at the α-carbon atom of the oxonium ion. The secondary oxonium ion should be kinetically distinguishable from the tertiary one, because hydrogen bonding to the anion, possible in the former but not in the latter, reduces the effective positive charge on the oxygen atom and therefore the reactivity at the α-carbon. This distinction is substantiated by the observation [6] that tertiary oxonium ions are among the strongest alkylating agents known, but secondary oxonium ions are far less electrophilic, *e.g.*,[6] secondary salts, $R_2\overset{+}{O}H\overset{-}{X}$ where X is halogen, are known, but attempts to prepare the salt $R_3\overset{+}{O}\overset{-}{I}$ lead to a mixture of alkyl iodide and dialkyl ether.

Polymers isolated from reaction products that had been treated with sodium hydroxide were found to contain primary hydroxyl groups, but in no case could halogen or $>C:CH_2$ groups be detected. However, when the reaction product was treated with trichloro-acetic acid the polymers isolated always contained chlorine. These facts suggest that

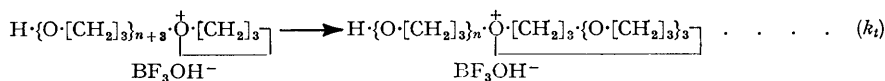[2] Farthing and Reynolds, *J. Polymer Sci.*, 1954, **12**, 503.
[3] Hibbert and Perry, *J. Amer. Chem. Soc.*, 1940, **62**, 2599.
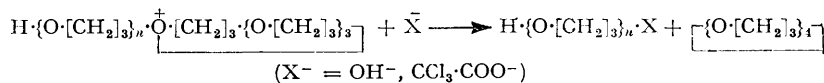[4] Pepper, *Quart. Rev.*, 1954, **8**, 88.
[5] Ingold, "Structure and Mechanism in Organic Chemistry," Bell and Son Ltd., London, 1953, p. 345.
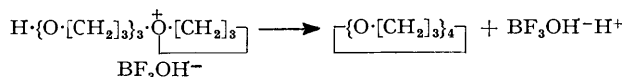[6] Burwell, *Chem. Rev.*, 1954, **54**, 615.

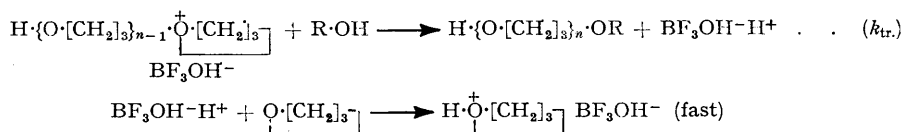termination occurs through the formation of a strainless, and therefore relatively unreactive, oxonium ion :

$$H \cdot \{O \cdot [CH_2]_3\}_{n+3} \cdot \overset{+}{O} \cdot [CH_2]_3 \quad \longrightarrow \quad H \cdot \{O \cdot [CH_2]_3\}_n \cdot \overset{+}{O} \cdot [CH_2]_3 \cdot \{O \cdot [CH_2]_3\}_3 \quad \cdots \cdots \cdots (k_t)$$
$$\text{BF}_3\text{OH}^- \qquad\qquad \text{BF}_3\text{OH}^-$$

When the reaction product is treated with a nucleophilic reagent, X⁻, the oxonium ion is destroyed, producing tetramer and polymer containing X as an end group:

$$H \cdot \{O \cdot [CH_2]_3\}_n \cdot \overset{+}{O} \cdot [CH_2]_3 \cdot \{O \cdot [CH_2]_3\}_3 + \bar{X} \longrightarrow H \cdot \{O \cdot [CH_2]_3\}_n \cdot X + \{O \cdot [CH_2]_3\}_4$$
$$(\text{X}^- = \text{OH}^-, \text{CCl}_3 \cdot \text{COO}^-)$$

Tetramer can be produced without the formation of polymer, so that no direct relation exists between the proportions in which the two are produced :

$$H \cdot \{O \cdot [CH_2]_3\}_3 \cdot \overset{+}{O} \cdot [CH_2]_3 \quad \longrightarrow \quad \{O \cdot [CH_2]_3\}_4 + \text{BF}_3\text{OH}^- \text{H}^+$$
$$\text{BF}_3\text{OH}^-$$

Nucleophilic attack on the tertiary oxonium ion by the cocatalyst must be regarded as a chain transfer reaction, for it generates the acid, $\text{BF}_3\text{OH}^- \text{H}^+$, which would rapidly re-form the secondary oxonium ion by proton transfer to monomer :

$$H \cdot \{O \cdot [CH_2]_3\}_{n-1} \cdot \overset{+}{O} \cdot [CH_2]_3 + \text{R} \cdot \text{OH} \longrightarrow H \cdot \{O \cdot [CH_2]_3\}_n \cdot \text{OR} + \text{BF}_3\text{OH}^- \text{H}^+ \quad \cdot \quad (k_{\text{tr.}})$$
$$\text{BF}_3\text{OH}^-$$

$$\text{BF}_3\text{OH}^- \text{H}^+ + \text{O} \cdot [CH_2]_3 \longrightarrow H \cdot \overset{+}{O} \cdot [CH_2]_3 \quad \text{BF}_3\text{OH}^- \quad \text{(fast)}$$

The degree of chain transfer, as indicated by the decrease in molecular weight that accompanies an increase in the cocatalyst concentration, is small when the cocatalyst is water, but becomes considerable when ethanol is used. This is to be expected because the nucleophilic power of ethanol is greater than that of water.

Stationary concentrations of both the secondary and the tertiary oxonium ions containing strained rings, being assumed, the mechanism postulated in the previous two paragraphs leads to equations (2) and (3), which accord with the experimental observations :

$$d[M]/dt = (k_i k_p / k_t) \ [M][BF_3][R \cdot OH] \quad \cdots \cdots \cdots (2)$$

$$\overline{\text{D.P.}} = k_p[M]/(k_t + k_{\text{tr.}}[R \cdot OH]) \quad \cdots \cdots \cdots (3)$$

However, although the kinetics of the polymerisation are described by the third-order equation (2), individual reactions obey the first-order equation (4), where k_1 depends on the concentrations of water and boron trifluoride present at the start of the reaction:

$$-d[M]/dt = k_1[M] \quad \cdots \cdots \cdots \cdots (4)$$

The effective concentrations of water and boron trifluoride must therefore remain sensibly unchanged during the period in which the kinetic measurements are made. Polymerisations where the concentrations of water, boron trifluoride, and monomer used were 0·10, 0·0045, and 1·62 mole l.⁻¹, respectively, gave polymer having a molecular weight of 20,000. The concentration of boron trifluoride used was therefore greatly in excess of the concentration of polymer produced (0·0047 mole l.⁻¹), but the concentration of water was slightly less than that of the polymer. Thus it appears that, on the basis of the mechanism postulated above, individual reactions should obey a second-order rate law. However, during polymerisation one hydroxyl group is formed for every water molecule used up, and as both ethanol and hydroxyl-terminated polymer are cocatalysts, the primary hydroxyl group can replace water in the initiating process. Further, hydroxyl groups regenerate themselves when they cocatalyse initiation, so that the concentration of cocatalyst (water

plus hydroxyl groups) remains constant throughout the polymerisation, and the first-order rate dependence is qualitatively explained.

The hydroxyl group is quantitatively a less effective cocatalyst than water, so that the explanation given in the previous paragraph must be examined in greater detail. The first-order integrated constant, k_1, for polymerisations cocatalysed by a mixture of ethanol and water is given by

$$k_1 = 19 \cdot 1[H_2O] + 13 \cdot 9[EtOH] \quad \text{(where } [BF_3] = 0 \cdot 10 \text{ mole l.}^{-1}) \quad . \quad (5)$$

If it is assumed that the cocatalytic reactivity of hydroxyl groups attached to polymer molecules is the same as that of ethanol (this appears reasonable, for the hydroxyl group is primary in both cases, and the difference in reactivity between water and ethanol is small), the rate coefficient k_t at time t will vary according to
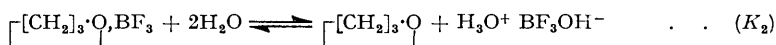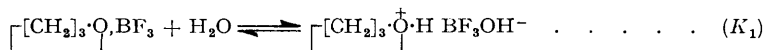
$$k_t = 19 \cdot 1x + 13 \cdot 9\{[H_2O] - x\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $[H_2O]$ is the concentration of water at the start and x the concentration remaining at time t. To a first approximation the concentration of water used, $[H_2O] - x$, is given by equation (7) where p is the concentration of polymer and V_{H_2O} and V_{ROH} are the average rates of polymerisation catalysed by water and hydroxyl respectively :
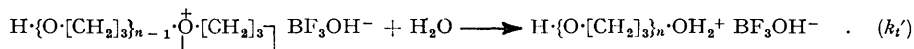
$$[H_2O] - x = pV_{H_2O}/(V_{H_2O} + V_{ROH}) = \frac{p \times 19 \cdot 1([H_2O]) + x)/2}{19 \cdot 1([H_2O] + x)/2 + 13 \cdot 9([H_2O] - x)/2} \quad (7)$$

For the (most critical) case that $[H_2O] = 0 \cdot 0045$ mole l.$^{-1}$ the value of p at the end of the reaction is $0 \cdot 0047$ mole l.$^{-1}$. Substituting $[H_2O] \simeq p = a$, we obtain a quadratic equation in x and a, the positive solution of which is $x = 0 \cdot 30a$. Therefore at the start of the polymerisation $k_t = 0 \cdot 088$ min.$^{-1}$ and at the finish $k_t = 0 \cdot 072$ min.$^{-1}$. Thus k_t decreases by 18% during the complete reaction or by 9% during the period, from 30% to 80% conversion, in which the rate measurements were made. However, the rate constant, k_1, is an integrated constant, and therefore an average value of the instantaneous rate constants, k_t, in the time interval 0—t, so that in practice variations in k_1 may be expected to be within the experimental error ($\pm 5\%$). It is a necessary consequence of cocatalysis by hydroxyl-terminated polymer that combination of the tertiary oxonium ion with its anion does not occur to any detectable extent, for this would cause the molecular weight to increase with increasing conversion of monomer into polymer, whereas the opposite was shown to occur.

Increase in the total concentration of water present in the system from $0 \cdot 012$ to $0 \cdot 035$ mole l.$^{-1}$ ($[BF_3] = 0 \cdot 10$ mole l.$^{-1}$) causes the rate of polymerisation to pass through a maximum, after which further increase in the water concentration decreases the rate. There is a marked decrease in the molecular weight, and the order of reaction with respect to monomer changes from unity ($[H_2O] \leqslant 0 \cdot 012$ mole l.$^{-1}$) to 2 ($[H_2O] \geqslant 0 \cdot 085$ mole l.$^{-1}$). These facts may be explained if it is assumed that proton transfer from the secondary oxonium ion to water increases in importance as the concentration of water increases. Under these conditions the reaction of the secondary oxonium ion with monomer may control the rate of initiation, and the mechanistic scheme must be modified by replacing the first reaction (rate constant k_1) by two equilibria :

$$[CH_2]_3 \cdot \overset{}{O}, BF_3 + H_2O \rightleftharpoons [CH_2]_3 \cdot \overset{+}{O} \cdot H \ BF_3OH^- \quad . \quad . \quad . \quad . \quad (K_1)$$

$$[CH_2]_3 \cdot \overset{}{O}, BF_3 + 2H_2O \rightleftharpoons [CH_2]_3 \cdot \overset{}{O} + H_3O^+ \ BF_3OH^- \quad . \quad . \quad (K_2)$$

Reaction of the cocatalyst with the tertiary oxonium ion now becomes the most important termination step :

$$H \cdot \{O \cdot [CH_2]_3\}_{n-1} \cdot \overset{+}{O} \cdot [CH_2]_3 \ BF_3OH^- + H_2O \longrightarrow H \cdot \{O \cdot [CH_2]_3\}_n \cdot OH_2^+ \ BF_3OH^- \quad . \quad (k_t')$$

A stationary concentration of tertiary oxonium ions being assumed, these modifications to the kinetic scheme lead to equations (8) and (9) :

$$-d[M]/dt = (K_1 k_i' k_p / k_t')[BF_3, M][M]^2 \qquad (8)$$

$$\overline{D.P.} = k_p[M]/k_t'[H_2O] \qquad (9)$$

Boron trifluoride dihydrate is the most stable complex present, so that $K_2 \gg K_1$. Thus $[BF_3, M] = [BF_3]_s - [BF_3, 2H_2O]$, and to a first approximation $[BF_3, 2H_2O] = \frac{1}{2}[H_2O]_s$, where the subscript s denotes stoicheiometric, as opposed to equilibrium, reactant concentrations. Equation (8) now becomes :

$$-d[M]/dt = (K_1 k_i' k_p / k_t')([BF_3]_s - \tfrac{1}{2}[H_2O]_s)[M]^2$$

This provides a qualitative explanation (it cannot be quantitatively correct, for boron trifluoride dihydrate catalyses the reaction, although the rate was too slow to be measured when $[BF_3, 2H_2O] = 0.10$ mole l.$^{-1}$) of the kinetic and molecular-weight data obtained for polymerisations where $[H_2O]_s \gg 0.085$ mole l.$^{-1}$ and $[BF_3]_s = 0.10$ mole l.$^{-1}$. The maximum rate occurs during the transition from one mechanism, whose kinetics are described by equation (2), to the mechanism postulated in this paragraph.

Values of 19·3 and 16·1 kcal. mole^{-1} were obtained for the heats of polymerisation of oxa*cyclo*butane and 3 : 3-dimethyloxa*cyclo*butane respectively, the reaction being carried out in MeCl–EtCl solution at $-9°$. It is of interest that this variation is comparable in both magnitude and direction with the difference between the values, estimated by Dainton, Devlin, and Small,[7] for the (hypothetical) heats of polymerisation of *cyclo*butane and its 1 : 1-dimethyl analogue to liquid polymers at 25°. The polymerisation of oxa*cyclo*butane involves the production of a strainless chain from strained rings containing the same number of bonds, so that the heat of polymerisation provides some measure of the strain energy of the oxa*cyclo*butane ring.

[7] Dainton, Devlin, and Small, *Trans. Faraday Soc.*, in the press.