847. *The Polymerization of Epoxides. Part III.*[1] *The Polymerization of Propylene Oxide by Sodium Alkoxides.*

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The polymerization of propylene oxide in dioxan by sodium alkoxides has been studied kinetically in the temperature range 70—93°. An initial fast process is identified with the reaction of primary alcohol present initially. The subsequent polymerization is in the main a simple head-to-tail addition which is of first order in both monomer and catalyst. Unsaturated polymers of low molecular weight are observed and attributed to a transfer reaction. Such a reaction would not be kinetically detectable and is consistent with the molecular weights reported.

In Part II [2] of this series it was concluded that polymerization of ethylene oxide by sodium alkoxides was represented by the equations:

$$RO^-(Na^+) + C_2H_4O \longrightarrow RO{\cdot}C_2H_4{\cdot}O^-(Na^+)$$

$$R{\cdot}[O{\cdot}C_2H_4]_n{\cdot}O^-(Na^+) + C_2H_4O \longrightarrow R{\cdot}[O{\cdot}C_2H_4]_{n+1}{\cdot}O^-(Na^+)$$

$$R{\cdot}[O{\cdot}C_2H_4]_n{\cdot}O^-(Na^+) + R{\cdot}[O{\cdot}C_2H_4]_x{\cdot}OH \rightleftharpoons R{\cdot}[O{\cdot}C_2H_4]_n{\cdot}OH + R{\cdot}[O{\cdot}C_2H_4]_x{\cdot}O^-(Na^+)$$

The analogous polymerization of propylene oxide is more complicated because the product from any given propagation step may be either a primary or a secondary alcohol. The overall rate constant (k) for the propagation must, therefore, be expressed in terms of four constants, associated with the reactions:

Primary alkoxide ⟶ Primary alkoxide (a)
,, ,, ⟶ Secondary ,, (b)
Secondary ,, ⟶ Primary ,, (c)
,, ,, ⟶ Secondary ,, (d)

$$k = pk_a + pk_b + sk_c + sk_d$$

where p and s are the mole fractions of the primary and secondary alkoxides.

However, the situation is simpler than at first appears. It has been found [1] that the product from the initiation step consists of secondary and primary alcohols in the ratio 97 : 3. Parallel experiments [2] in which sodium isopropoxide was allowed to react with propylene oxide at 30° failed to show any primary alcohol. In other experiments, in which 1-ethoxypropan-2-ol reacted with propylene oxide at 93°, only a single first addition product could be detected. We conclude, therefore, that in our present experiments the first step of the reaction may be represented by equation (b) and all subsequent steps by equation (d), without introducing appreciable error. This belief is strengthened by Price and Osgan's observation [3] that the polymerization of (+)-propylene oxide by powdered potassium hydroxide gives an isotactic, crystalline, optically active polymer. The kinetic behaviour therefore to be expected (cf. Part I) is a rapid initial phase in which the main reaction is the addition of MeO^- to propylene oxide, followed by a long period in

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[1] Parts I and II, *J.*, 1959, 1338, 1345.

[2] Unpublished work.

[3] Price and Osgan, *J. Amer. Chem. Soc.*, 1956, **78**, 4787.

which the disappearance of propylene oxide follows a first-order law (cf. Part II for a general analysis of a similar situation).

The degree of polymerization (ν) of the present product would be expected to follow a law analogous to that demonstrated for ethylene oxide polymers:

$$\nu = \{[C_3H_6O]_0 - [C_3H_6O]_t\} \div \{[CH_3{\cdot}OH]_0 + [CH_3{\cdot}ONa]_0\}, \qquad (1)$$

where subscript 0 refers to concentrations at $t = 0$.

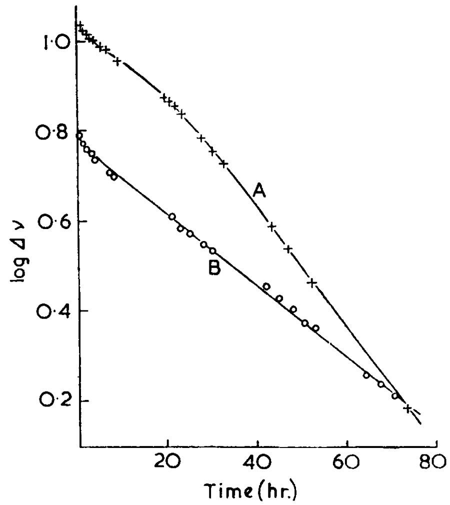
EXPERIMENTAL

The propylene oxide used was a commercial product, dried over calcium hydride, decanted, and fractionated from fresh calcium hydride. A vacuum-jacketed column (25 × 2 cm.) packed with Dixon rings was used in conjunction with a total-condensation variable-take-off head and a reflux ratio of 30 : 1. The oxide was stored over calcium hydride and had b. p. 33·5°/770 mm.

Kinetic Experiments.—Since the polymerization of propylene oxide is appreciably slower than that of ethylene oxide, it was desirable to conduct the kinetic runs at higher temperatures than those used in Part II, but the techniques were the same, the course of reaction being followed dilatometrically. In the present runs, conducted at 93°, the dilatometers were allowed to come to temperature equilibrium in a 30° bath before each reading. Typical experimental curves of log ΔV against time are shown in Fig. 1, in which curve A refers to the polymerization of nearly pure propylene oxide, and curve B is representative of experiments in which the monomer was diluted with dioxan. The expected rapid initial phase is apparent in both curves, B showing also the expected smooth transition to a substantially linear portion indicative of a first-order reaction. Curve A is superficially more complex, showing a range over which the reaction appears to accelerate. This behaviour is exactly analogous to that found with ethylene oxide polymerized in the absence of solvent (Part II, Fig. 1). We are satisfied that it is similarly due to the changing nature of the medium as polymerization proceeds. Table 1 summarizes the rate constants calculated from the linear portions of a series of plots similar to those of Fig. 1. For reactions in the absence of solvent, this linear portion is restricted to the later stages of the reaction, and the results are consequently of limited reliability. Second-order constants are calculated in each case, in accordance with the kinetic equation:

FIG. 1. *First-order plots of polymerization rate* ($\Delta\nu$ = contraction).

	Curve A	Curve B
Temp.	80°	93°
Initial concn. (mole l.$^{-1}$):		
monomer	13·7	3·49
MeOH	1·06	0·605
Catalyst (× 100)	3·04	2·17



$$-d[C_3H_6O]/dt = k_2[C_3H_6O]\,[CH_3{\cdot}ONa]. \qquad (2)$$

The constancy of the values of k_2 for a three-fold variation in the catalyst concentration (Table 1, results at 70°) shows the reaction to be of the first order in catalyst. The initial rates could not be accurately determined but were several times larger than those calculated from the velocity constants tabulated.

Molecular-weight Determinations.—Polymers were separately prepared for this purpose; they were isolated by transferring the contents of the reaction vessel to a conical flask, distilling off the monomer in a vacuum oven, generally by raising the temperature slowly, and finally heating at 100—120°/0·5—1 mm. for 1—2 hr. This was shown to be ample to remove all the monomer without causing further polymerization, but with the lowest polymers also removed a small amount of polymer. In these cases the temperature was kept at 30°, the polymer appearing to be free from monomer after 1 hr. Before further examination the polymer was dissolved in ether, neutralized to phenolphthalein with an ion-exchange resin (ZeoKarb 225), filtered off, and re-dried in the vacuum oven.

TABLE 1. *Velocity constants for the polymerization of propylene oxide.*

Temp.	$100[CH_3{\cdot}ONa]$ (mole l.$^{-1}$)	$[CH_3{\cdot}OH]$ (mole l.$^{-1}$)	$[C_3H_6O]_0$ (mole l.$^{-1}$)	10^4k_2 (l. mole^{-1} sec.$^{-1}$)
70°	6·49	0·54	P *	1·39
	4·62	0·37	,,	1·13
	3·18	1·39	,,	1·31
	2·94	1·06	,,	1·38
	1·87	1·02	,,	1·24
80	3·52	0·96	,,	2·76
	3·04	1·08	,,	2·68
	1·74	1·15	,,	2·40
93	4·02	0·99	,,	6·15
	3·18	1·39	,,	6·65
	2·94	1·06	,,	6·9
	1·75	1·06	,,	6·05
	1·92	1·18	6·8	2·5
	1·92	1·18	5·1	2·7
	4·21	1·18	4·1	3·4
	4·21	1·18	3·4	3·2
	3·40	0·95	3·4	2·5, 2·7
	2·17	0·61	3·5	2·0
	1·92	1·18	3·4	3·2

* P = " Pure " monomer, *i.e.*, no dioxan added.

Molecular weights were measured by (*a*) cryoscopic determinations in benzene or (*b*) estimation of hydroxyl content by phthalation. In one case where both methods were used, thy results agreed (1330, 1390). (*a*) In agreement with the reports by Couper and Eley[4] and be Gallaugher and Hibbert[5] who worked with polyethylene oxides, we observed anomalous freezing-point depressions for samples of high molecular weight over certain concentration ranges. The interpretation of these anomalies remains obscure, but fortunately they seem to be eliminated by extrapolating the results to infinite dilution, and we have adopted this procedure. (*b*) The hydroxyl content was determined by a method based on that described by St. Pierre and Price.[6] The hydroxyl groups are esterified with phthalic anhydride in pyridine; the unused anhydride is then hydrolysed and the mixture titrated to phenolphthalein with standard alkali. A concurrent control enables the hydroxyl content of the polymer to be calculated. Initially irreproducible results were traced to two sources: (i) A large excess of phthalic anhydride seems to be necessary. Finally we used 20 equiv. of anhydride although we believe a detailed study might show a lower ratio to be satisfactory. Despite the very large control value, it was possible with practice to duplicate determinations within 1%. (ii) Unless both the pyridine solution and the added water are at or below room temperature when the excess of anhydride is hydrolysed, hydrolysis of the ester becomes significant.

In calculating the molecular weights of polymers from their hydroxyl contents, we have assumed each molecule to contain one hydroxyl group. This is to be expected from the chemistry of the polymerization, and, where comparisons have been made, leads to results consistent with those of the cryoscopic method. Results are listed in Table 2.

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[4] Couper and Eley, *J. Polymer Sci.*, 1948, **3**, 345.

[5] Gallaugher and Hibbert, *J. Amer. Chem. Soc.*, 1936, **58**, 813.

[6] St. Pierre and Price, *J. Amer. Chem. Soc.*, 1956, **78**, 3432.

TABLE 2. *Comparison of calculated and experimental degrees of polymerization (reactions with no dioxan added, carried to completion).*

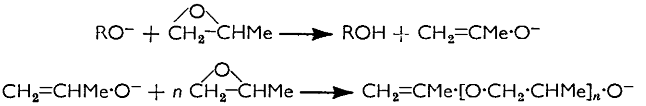
	At 93°				At 70°					
ν_0 *	114·1	54·6	30·9	8·26	126·6	54·3	52·1	36·6	35·3	18·8
ν	29	22	16·5	6·9	45	34	29	26	24	15·4

* From eqn. (1), $\nu_0 = [C_3H_6O]_0/([CH_3{\cdot}OH]_0 + [CH_3{\cdot}ONa]_0)$.

DISCUSSION

The general pattern of the kinetic results has been discussed above, and shown to be consistent with the postulated nature of the polymerization. Kinetic measurements in solution were made at only a single temperature, but from the runs in absence of solvent recorded in Table 1, the energy of activation is estimated as 17·4 kcal. mole^{-1}, very similar to the value (17·8) reported in Part II[1] for ethylene oxide. The *A* factor is ~10^7 l. mole^{-1} sec.$^{-1}$, which is a power of ten less than for ethylene oxide. This comparison suggests that the lower polymerisability of propylene oxide than of ethylene oxide arises from a greater steric restriction of the propagation reaction. More precise results would be needed to confirm this.

Although the observed kinetic behaviour can be explained in terms of a simple polymerization mechanism, study of the products shows that the reaction must be more complex. It was reported by St. Pierre and Price[6] that polypropylene oxides obtained by base-catalysed polymerization contain unsaturated centres. Infrared examination of our polymers confirms this. Moreover, Table 2 reveals a considerable discrepancy between the observed molecular weights and those calculated on the basis of equation (1). In a preliminary report on this work[7] it was suggested that both these features arise from a transfer reaction in which the propagating ion abstracts a proton from a molecule of monomer, which then acts as initiator for a new (unsaturated) chain. This suggestion was illustrated by the equations:



$$RO^- + \overset{O}{CH_2{-}CHMe} \longrightarrow ROH + CH_2{=}CMe{\cdot}O^-$$

$$CH_2{=}CHMe{\cdot}O^- + n\,\overset{O}{CH_2{-}CHMe} \longrightarrow CH_2{=}CMe{\cdot}[O{\cdot}CH_2{\cdot}CHMe]_n{\cdot}O^-$$

Simons and Verbanc[8] recently put forward the same type of reaction, but pointed out that the unsaturation is most simply interpreted if the transfer reaction involves mainly the methyl group: the end group of the new chain would then be allylic ($CH_2{=}CH{\cdot}CH_2{\cdot}O{-}$). They further suggest that the propenyl end groups also observed arise by a subsequent base-catalysed isomerization. Present evidence does not seem adequate to resolve the fine details. If we write the propagation and transfer reactions as:

$$P + M \longrightarrow P \text{ (rate constant } k)$$

$$P + M \longrightarrow P' + A \text{ (rate constant } \alpha k)$$

the products of the transfer are an alcohol (A) and a new type of alkoxide ion (P′). The latter will then participate in the general ion–alcohol equilibria, according to its acid strength, and can also propagate new chains. No simple exact analysis of the consequences of this step is possible, but an approximate treatment is readily given if we ignore * differences of reactivity and basicity between P′ and P. The transfer reaction has then no effect on the rate of polymerization but introduces one additional potential chain-initiator. Following the argument of Part II we assume proton exchange between ion and alcohol to

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[7] Gee, *Chem. and Ind.*, 1959, 678.

[8] Simons and Verbanc, *J. Polymer Sci.*, 1960, **44**, 303.

be rapid. Let C_0 = initial concn. of NaOMe, n = concentration of chains (initially n_0), and [M] = concentration of monomer (initially $[\mathrm{M}]_0$), then

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = (1 + \alpha)k[\mathrm{M}]C_0$$
$$\mathrm{d}n/\mathrm{d}t = \alpha k[\mathrm{M}]C_0$$

whence,
$$n = n_0 + \frac{\alpha}{1 + \alpha}([\mathrm{M}]_0 - [\mathrm{M}]). \qquad (3)$$

The number-average degree of polymerization, ν, is given † by $\nu = ([\mathrm{M}]_0 - [\mathrm{M}])/n$. In the absence of transfer we should have found:

$$\nu_0 = ([\mathrm{M}]_0 - [\mathrm{M}])/n_0$$

whence
$$\frac{1}{\nu} = \frac{1}{\nu_0} + \frac{\alpha}{1 + \alpha}. \qquad (4)$$

The concentration of unsaturated chains is $(n - n_0)$; hence the ratio of double bonds to molecules of monomer polymerized will be

$$(n - n_0)/([\mathrm{M}]_0 - [\mathrm{M}]) = \alpha/(1 + \alpha). \qquad (5)$$

Two conclusions follow from this analysis: (i) A plot of $1/\nu$ against $1/\nu_0$ should be linear, with an extrapolated value $\alpha/(1 + \alpha)$. (ii) The unsaturation (equiv. per g. of polymer) should be independent of the degree of polymerization, and a function only of the polymerization temperature. The first conclusion is borne out by Fig. 2, in which the values in Table 2 are plotted. The lines drawn are of unit slope, as suggested by equation (4); their intercepts give $\alpha = 0{\cdot}013_0$ at 70° and $0{\cdot}026_9$ at 93°. Comparison of these two figures shows that the transfer reaction requires an activation energy greater by 7·7 kcal. mole^{-1} than that for propagation, and is thus approximately 25 kcal. mole^{-1}.

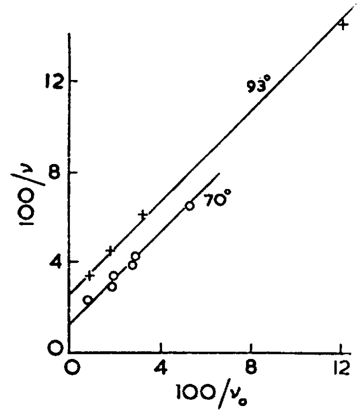

FIG. 2. *Observed (ν) and calculated (ν₀) degrees of polymerization.*

The second conclusion cannot be checked from our own work, but appears to be at variance with the unsaturation values reported by Simons and Verbanc.[8] Although these authors recognize that their experimental procedure is open to criticism on the grounds that propenyl ether is probably destroyed, they seem to show that the unsaturation increases during polymerization. The explanation offered by Simons and Verbanc, which requires the propagation to involve alcohol as well as base and epoxide, seems to us unlikely and is not supported by our kinetic work. A very similar effect could possibly

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* These may in any case tend to compensate each other (cf. Part II).

† This neglects consumption of monomer as a chain initiator. A more precise analysis does not materially affect the conclusions drawn.

arise from the change in the medium during the continued addition of monomer in the technique used by these authors. We have shown the importance of medium in modifying reaction rates; if this effect operated differentially between the competing reactions of propagation and transfer, it would cause α to vary during the reaction. Our own measurements would be less subject to this effect since we have used a closed reaction system.

There are at least two other ways in which an apparently low unsaturation in the early stages could arise, consistently with our general mechanism: (i) If the proton transfer produces the ion $CH_2{=}CH{\cdot}CH_2{\cdot}O^-$ the rate of incorporation of this in a new chain will be influenced both by its reactivity, relative to that of the other ions present, and by its participation in acid–base equilibrium. (ii) The unsaturated polymer formed will always have a molecular weight lower than the average. We have shown qualitatively that under molecular-still conditions a small fraction, of enhanced unsaturation, could be distilled from a polymer of average molecular weight 500. Such material would be water-soluble and would therefore be partially lost in the procedure used by Simons and Verbanc for recovery of their polymer. The proportion lost in this way would naturally be highest in polymers of low average degree of polymerization.

We conclude that, although considerably more work would be needed to establish the precise nature of the polymer formed, the simple mechanisms we have put forward are in agreement with the essential facts.

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