267. *Polymerisation of Epoxides. Part II.*[1] *The Polymerisation of Ethylene Oxide by Sodium Alkoxides.*

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The polymerisation of ethylene oxide in solution in 1 : 4-dioxan is catalysed by solutions of sodium in an excess of a simple alcohol, ROH. The dependence of the rate of polymerisation and the molecular weight of the product upon reactant concentrations has been investigated. These experiments support the suggestion that the initiation and propagation reactions are, respectively,

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

and that there is no termination reaction. Both the ion-pair, RO^-Na^+, and the ion, RO^-, are catalysts, the reaction of the ion-pair being dominant at low initial concentrations of the conjugate alcohol.

Deviations from the kinetic predictions of this simple scheme are discussed in terms of the relative reactivity and basicity of the anions RO^- and $R{\cdot}[O{\cdot}C_2H_4]_n{\cdot}O^-$.

ETHYLENE OXIDE is conveniently polymerised by bases, and the reaction sequence takes a particularly simple form when an alkoxide ion RO^- is used as initiator:

$$RO^- + C_2H_4O \longrightarrow RO{\cdot}C_2H_4O^-$$
$$RO{\cdot}C_2H_4O^- + C_2H_4O \longrightarrow R{\cdot}[O{\cdot}C_2H_4]_2{\cdot}O^- \text{ etc.}$$

No termination reaction is expected, but a series of proton-exchange reactions arise from the presence of excess of alcohol, usually added to increase the solubility of the catalyst. If, as we expect, these exchange reactions are much faster than the polymerisation, their effect on the kinetics of polymerisation will be negligible unless the alcohol added differs markedly in acid strength from the polyether alcohols. In most experiments now described we used sodium methoxide as catalyst, with a small excess of free methanol. In most cases 1 : 4-dioxan was also present as an inert diluent.

From Part I[1] it is clear that under these conditions the catalyst will be only partially ionised. Moreover, as reaction proceeds, the nature of the solvent changes, especially if no diluent is added, so that the degree of ionisation is not necessarily constant. This effect, together with the small change in the nature of the reacting ions, is likely to cause variations in the velocity constants observed at different stages of the polymerisation. Since it seems scarcely possible to predict the exact quantitative pattern, we begin by assuming that all the polymerisation steps have the same constant rate. Subsequently we shall discuss the extent to which our experimental results show deviations attributable to this over-simplification.

Simple Reaction Scheme.—If each individual reaction has the same bimolecular velocity constant k, the overall rate of reaction is given by

$$-\mathrm{d}[C_2H_4O]/\mathrm{d}t = k[C_2H_4O]\sum_{n=0}^{\infty}[R{\cdot}[O{\cdot}C_2H_4]_n{\cdot}O^-] \quad . \quad . \quad . \quad . \quad (1)$$

In this form we have implicitly assumed complete ionisation. To be more realistic we should divide $k\sum[R{\cdot}[O{\cdot}C_2H_4]_n{\cdot}O^-]$ into two terms, representing the separate contributions of ions and ion-pairs. So long as the degree of ionisation remains constant, we shall not introduce error by retaining the simple form. Since no ions are formed or lost during the polymerisation, the summation gives simply c_0, the initial concentration of catalyst used, and eqn. (1) reduces to

$$-\mathrm{d}[C_2H_4O]/\mathrm{d}t = kc_0[C_2H_4O] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

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[1] Part I, preceding paper.

Disappearance of ethylene oxide should therefore follow a first-order law, with a constant proportional to the catalyst concentration.

The presence of alcohol will give rise to the series of reactions

$$R\cdot[O\cdot C_2H_4]_n\cdot O^- + R\cdot[O\cdot C_2H_4]_x\cdot OH \rightleftharpoons R\cdot[O\cdot C_2H_4]_n\cdot OH + R\cdot[O\cdot C_2H_4]_x\cdot O^-$$

where n and x take all integral values from zero to infinity. Since these reactions leave the total ion concentration unchanged, they cannot affect the observed overall rate if our assumption of equal reactivity of all ions is valid. However, the alcohol will affect the molecular weight. Each alcohol molecule, equally with each alkoxide ion, is a potential growing point for a polymer. The total concentration of polymer chains will therefore remain constant during most of the reaction, and equal to $[ROH]_0 + c_0$, where $[ROH]_0$ is the initial alcohol concentration. The number-average degree of polymerisation ν at time t is therefore given simply by

$$\nu = \{[C_2H_4O]_0 - [C_2H_4O]_t\} \div \{[ROH]_0 + c_0\} \quad . \quad . \quad . \quad . \quad (3)$$

where $[C_2H_4O]_t$ represents the concentration of ethylene oxide at time t. This counts each ion and alcohol molecule as a potential chain, so that, in averaging, free alcohol is counted as polymer. The molecular-weight distribution, for a polymerisation following this simple scheme, was worked out by Flory[2] for a system free from alcohol; he showed that a Poisson distribution was to be expected, defined by

$$N_x = \frac{N_m}{(x-1)!}\left(\frac{N_m}{N_c}\right)^{(x-1)} e^{-(N_m/N_c)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where N_x = number of polymer molecules each containing x molecules of ethylene oxide, N_m = total ethylene oxide molecules consumed, and N_c = number of catalyst molecules.

Physically, the reason for this very sharp distribution is that all the polymer chains are present throughout the reaction, competing equally for the ethylene oxide. This condition will still be satisfied in the presence of alcohol, *provided* the proton-exchange reaction is rapid. It is easy to show that eqn. (4) is to be generalised to

$$N_x = N_m \nu^{(x-1)} e^{-\nu}/(x-1)! \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Summarising, we are led by the simple reaction scheme to three conclusions: (1) first-order disappearance of monomer, with a rate constant proportional to catalyst concentration; (2) a number-average degree of polymerisation given by eqn. (3) and unaffected by temperature or presence of diluent; (3) a Poisson distribution of molecular weight.

Deviations from the Simple Scheme.—Departures from this scheme might be expected from three sources: (*a*) The progressive change in the medium during polymerisation might affect the velocity constants of all the steps. (*b*) The reaction between catalyst and monomer will in general have a rate constant different from that of subsequent steps; differences between the remaining rate constants are likely to be small and will not be further considered. (*c*) If free alcohol is present its acid dissociation constant may be different from that of the polyether alcohols. Formal analysis of these factors is deferred to the Appendix; here we shall discuss only their broad effects.

(*a*) Changes in the velocity constants produced by the changing medium are likely to be independent of degree of polymerisation, so that the only effect to be expected is a departure from first-order behaviour. This will occur progressively during polymerisation and will be more marked in absence of diluent than in its presence.

(*b*) If the initiation process is much faster than propagation, the first step will be virtually complete before any higher polymer is produced, but thereafter polymerisation will proceed as in the simple scheme. Apart from a rapid disappearance of monomer in the early stages, no abnormality will therefore be observed. A slow initiation process will have more serious consequences. There will clearly be an initial period of acceleration

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[2] Flory, *J. Amer. Chem. Soc.*, 1940, **62**, 1561.

while catalyst is converted into polymer ion, but additional complication will arise because some chains will now grow considerably before others have started to grow. It is physically obvious that this must broaden the molecular-weight distribution since the late starters have a shortened period of growth. On the other hand, the number-average molecular weight will be unchanged, and in consequence the *weight* average will be somewhat increased.

(*c*) The effect of adding an alcohol whose acid dissociation constant differs from that of the polyether alcohol can be seen by considering the equilibria $ROH + R\cdot[O\cdot C_2H_4]_n\cdot O^- \rightleftharpoons RO^- + R\cdot[O\cdot C_2H_4]_n\cdot OH$. We shall discuss only the case in which the added alcohol is the one whose sodium salt is used as catalyst. If this is a much stronger acid than the polymer alcohol, the equilibrium will be displaced to the right and will therefore tend to prevent the growth of any polymer chains until all the alcohol has been incorporated. If the acid strength of the alcohol is sufficient, the total reaction will be split into two consecutive stages: (i) conversion of all ROH into $RO\cdot C_2H_4\cdot OH$, followed by (ii) a simple polymerisation of C_2H_4O by RO^- in presence of $RO\cdot C_2H_4\cdot OH$. In this case the molecular-weight distribution will be sharp [Poisson type in the limiting case where (i) and (ii) are completely separate]. The effect on the overall rate of disappearance of monomer will depend on the rate of stage (i). If this were fast compared with the subsequent propagation, the initial reaction would be fast. In fact this situation is unlikely to arise, since the ready ionisation of ROH would be associated in general with a *slow* reaction of RO^- with ethylene oxide. These two effects would then reinforce one another to produce a slow initial reaction, accelerating when most of the alcohol has been incorporated.

The converse case of an alcohol which is *less* acidic than the polymer alcohol is likely to be associated with high reactivity of RO^-, which will therefore be converted rapidly into the first adduct $RO\cdot C_2H_4\cdot O^-$. As this will have little tendency to react with ROH, further propagation will follow and extensive polymerisation will occur before all the original alcohol is incorporated. After the early rapid reaction, polymerisation will appear kinetically normal, but the product will have a broader molecular-weight distribution.

Experimental Results.—Most of the results to be described were obtained by a dilatometric technique, checked in a few cases by chemical determination of unchanged ethylene oxide at appropriate intervals. The rather considerable contractions involved (23% in absence of solvent) lead to a minor complication in the apparent kinetic pattern. We assume the rate equation to hold in terms of concentrations: $-\mathrm{d}[C_2H_4O]/\mathrm{d}t = k[C_2H_4O][\text{catalyst}]$. If V is the volume at time t, N the number of moles of monomer unchanged at time t, and N_c the number of moles of catalyst originally added, this gives $-\mathrm{d}(N/V)/\mathrm{d}t = kNN_c/V^2$. We assume $V = V_\infty + \alpha N$, where α is a constant and V_∞ the final volume when polymerisation is complete.

Defining $(V - V_\infty)$ as ΔV, we can easily show that the rate equation can be written

$$-\mathrm{d}\ln(\Delta V)/\mathrm{d}t = kN_c/V_\infty = kc_\infty \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where c_∞ is the *final* concentration of catalyst. It is assumed that c_∞ differs from c_0 only by reason of the contraction. This assumption has been experimentally verified in most runs. We have also confirmed that the reaction goes to completion, *i.e.*, that no unchanged ethylene oxide remains.

This method of analysis has been used to study changes of temperature and reactant concentrations on the course of the polymerisation. If eqn. (6) holds, a plot of log (ΔV) against t should be linear. The results of two typical experiments are plotted in Fig. 1, in which curve *A* refers to polymerisation of nearly pure ethylene oxide (1M-methanol added to keep the catalyst in solution), while curve *B* is more representative of our normal polymerisation procedure, in which monomer was diluted by dioxan. The former displays considerable curvature, while the latter is linear over substantially all of the reaction.

The results of a considerable number of experiments are summarised in Table 1, in which two second-order velocity " constants " are given for each run. The first is derived from the initial slope of log ΔV *versus* t; the " later " value from the slope at a time equal to twice that required for half the total contraction. The trend shown in Fig. 1 is typical: the velocity constant is usually substantially constant during a reaction except when the initial monomer concentration is high. Moreover, its value is constant over considerable ranges of the concentrations of catalyst (expts. 8—12) and monomer (expts. 2—7). The second-order constant increases with the methanol concentration as shown by expts. 13—16 (cf. also expts. 17 and 18).

Fig. 1.

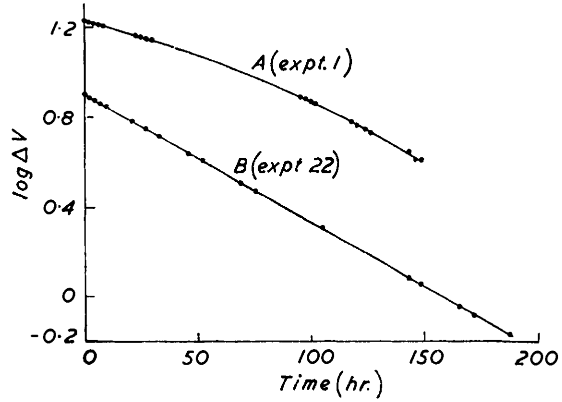
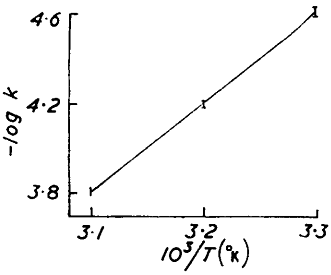
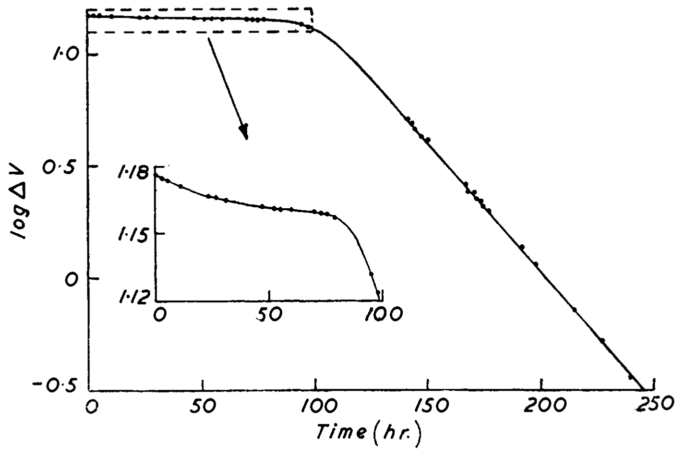


Fig. 2.



Taking mean values of the initial velocity constants at 30°, 40°, and 50°, including only experiments with $[CH_3{\cdot}OH] \simeq 1{\cdot}0\text{M}$ and with $[C_2H_4O] < 10\text{M}$, we have plotted log k against $1/T$ (Fig. 2) and this gives an activation energy of $17{\cdot}8 \pm 1$ kcal. mole^{-1} with a temperature-independent factor of 2×10^8 l. mole^{-1} sec.$^{-1}$. These values are similar to those reported in Part I for the first step.

Fig. 3.



In a few experiments methanol was replaced by a different alcohol, and some typical results are shown in Table 2: the results do not differ in any important way. Use of phenol (expt. 33) leads to a very different result, shown in more detail in Fig. 3. The slow initial reaction reported by previous workers [3] is fully confirmed (inset to Fig. 3).

An attempt was made to vary the dielectric constant of the medium by addition of

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[3] Patat, Cremer, and Bobleter, *Monatsh.*, 1952, **83**, 322.

1—4M-nitrobenzene, but this led to slow destruction of catalyst, the final concentration being close to zero in each case. Initial polymerisation rates were not markedly affected.

Molecular weights were estimated for most of the polymers obtained and in Tables 1 and 2 these are compared with values calculated from eqn. (3). The experimental values are derived from measurements of intrinsic viscosities in dioxan solution, by using the equation

$$[\eta](\text{ml. g.}^{-1}) = 0{\cdot}083M^{0{\cdot}59} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This equation was based on viscosity determinations of a series of polyethylene oxide samples kindly supplied by Messrs. Oxirane. Their molecular weights ranged from 300 to 5100 and had been determined by acetylation. Since these materials had been prepared by sodium-catalysed polymerisation, our use of the viscosity method is simply a convenient interpolation procedure to permit of the rapid determination of a large number of molecular weights. Although no high precision is claimed for our figures, the agreement between experimental and calculated values is very striking, and persists through all the changes of temperature and composition. This remained true even though many of the polymerisation tubes were given a final period of heating at 60—80° to accelerate the last few per cent. of reaction.

DISCUSSION

Comparison of our findings with the theoretical analysis presented above shows that most of our results are consistent with the simplest reaction scheme. The molecular-weight evidence, coupled with the observations that all the monomer reacts but no catalyst is lost, shows the absence of either transfer or termination reactions and of polymer–polymer reactions. We have no evidence of molecular-weight distribution, but other workers [4] have analysed low-molecular-weight polyethylene oxides and found their compositions to be consistent with eqn. (5).

Over quite a wide range of conditions, the kinetic behaviour also accords closely with the simple pattern of eqn. (2). The significance of this requires further discussion, and the deviations cannot be ignored. Comparing the two curves in Fig. 1, we attribute the departure from linearity of *A* to large changes in the nature of the medium. After 140 hours' reaction, the concentration of ethylene oxide in *A* is similar to the initial concentration in *B*, but the solvent is a polyether alcohol of average molecular weight *ca.* 600. In the presence of much dioxan as an inert diluent these large changes of medium are avoided.

In the series of expts. 1—7 the initial dielectric constants are estimated to range from *ca.* 13 to 5. None of the experiments reported in Tables 1 and 2 took the dielectric constant outside this range, so this factor does not appear to be important. The effect of alcohol concentration is therefore to be attributed specifically to the hydroxyl groups. In line with the conclusions of Part I, we interpret this in terms of the incomplete dissociation of the sodium alkoxide ion-pair. Evidently, the degree of dissociation of sodium methoxide is small at low methanol concentrations. The constant found at low alcohol concentrations appears to be due mainly to catalysis by the undissociated ion-pair, for if the reaction were due solely to free methoxide ions, the second-order " constant " should depend approximately on the inverse square-root of the catalyst concentration. As shown by expts. 8—12 (Table 1), this is not so. Thus we conclude that at 30° the bimolecular rate constant for $CH_3{\cdot}O^-Na^+$ with ethylene oxide is *ca.* 2×10^{-5} l. mole^{-1} sec.$^{-1}$, which is roughly one-tenth of that for the free methoxide ion reported in Part I.

The simple kinetic behaviour is now seen as a consequence of the fact that most of our experiments have been confined to conditions under which the effective catalyst is an ion-pair, and in which changes in medium during reaction are of little importance. The fact that the initial stages show normal reaction rates demonstrates further that there can be

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[4] Miller, Bann, and Thrower, *J.*, 1950, 3623; Weibull and Nycander, *Acta Chem. Scand.*, 1954, 8, 847.

no major differences of reactivity between the first and subsequent stages.* The strikingly different behaviour of phenol illustrates the consequences of using an acidic compound and follows the pattern predicted by the theoretical analysis.

TABLE 1. *Polymerisation of ethylene oxide in dioxan by sodium methoxide.*

Expt.	Temp.	Initial $[C_2H_4O]$ (M)	100 × Final [NaOMe] (M)	Initial $[CH_3{\cdot}OH]$ (M)	10^5k (l. mole^{-1} sec.$^{-1}$) Initial	Later	Mol. wt. Calc.	Obs.
1	30°	18·6 *	6·95	0·97	2·9	6·0	830	790
2		13·2	6·45	0·97	2·3	3·5	600	590
3		10·6	6·3	0·99	2·6	3·5	475	490
4		8·5	6·1	1·00	2·6	3·0	390	375
5		6·4	5·95	1·00	2·6	2·5	300	285
6		4·8	5·85	1·00	2·6	2·4	230	255
7		3·2	5·7	0·99	2·6	2·3	170	210
8		7·5	11·2	0·77	2·7	3·1	410	470
9		7·5	7·2 †	0·81	2·1	3·8	410	375
10		7·5	5·2	0·83	2·4	2·6	410	380
11		7·5	3·6 †	0·85	2·2	3·6	410	375
12		7·5	2·6	0·85	2·4	2·5	410	355
13		8·7	3·5	0·60	2·3	2·4	635	580
14		8·7	3·7	1·87	3·5	3·3	230	210
15		8·7	3·4	2·52	4·3	4·0	180	170
16		8·7	3·5	3·15	5·1	4·7	150	125
17		4·5	7·2	1·26	3·15	2·8	180	215
18		4·5	7·25	3·46	5·8	5·3	90	—
19	40	10·6	6·35	1·00	6·4	8·8	475	440
20		8·6	6·2	1·00	6·1	7·3	390	375
21		6·5	6·0	1·01	6·4	6·95	300	295
22		4·9	5·9	1·01	6·3	6·35	230	190
23		3·2	5·7	0·99	6·45	6·05	170	170
24	50	6·9	5·35	0·58	15·4	17·2	515	390
25		5·1	5·1	0·57	15·6	17·2	395	460
26		5·1	5·1	1·07	14·8	15·8	230	—
27		5·1	5·1	1·82	17·9	17·7	150	155
28		5·1	5·1	3·07	25·8	25·7	100	60

* No added dioxan. † KOMe catalyst.

TABLE 2. *Effect of variations in alcohol* ($T = 40°$).

Expt.	Initial $[C_2H_4O]$ (M)	100 × Final [NaOR] (M)	ROH	Initial [ROH] (M)	10^5k (l. mole^{-1} sec.$^{-1}$) Initial	Later	Mol. wt. Calc.	Obs.
29	8·6	6·8	MeOH	0·45	5·85	5·85	775	750
30	8·6	9·1	EtOH	0·43	7·2	8·9	790	820
31	8·6	4·7	Pr^nOH	0·47	7·5	8·25	805	850
32	8·6	7·5	$MeO{\cdot}C_2H_4{\cdot}OH$	0·44	5·0	8·6	835	930
33	7·9	7·4	PhOH	0·34	0·36	10·0	950	950

Experimental.—Methods and materials were generally similar to those of Part I.[1] The dilatometers were made by sealing a 20-cm. length of graduated tubing of cross-section either 0·25 or 0·13 sq. cm. to a bulb of capacity about 20 ml. A B14 cone sealed to the top of the dilatometer provided connection with a vacuum line or ethylene oxide distillation apparatus. After filling, by pipette or distillation, the contents were frozen in liquid nitrogen and the dilatometer was warmed to room temperature, shaken vigorously to ensure mixing of the contents, and placed in the thermostat.

Molecular weights were determined by diluting the reaction mixture with 1 : 4-dioxan and making viscosity measurements in an Ostwald viscometer, BSS 188, No. 1. It was found unnecessary to extrapolate η_{sp}/c to infinite dilution, values at a relative viscosity of 1·1 being indistinguishable from intrinsic viscosities. In a number of cases the polymer was separated from the reaction mixture by evaporation, and redissolved in dioxan; this procedure gave substantially identical results.

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* It is shown in the Appendix that this test is not highly sensitive, so it is difficult to draw quantitative conclusions.

APPENDIX

Deviations from the Simple Scheme.—If we neglect any effect of chain length on reactivity, the system of reactions to be analysed may be written:

$$\mathrm{C} + \mathrm{M} \longrightarrow \mathrm{P}_1 \qquad \text{velocity constant } \beta k$$
$$\mathrm{P}_x + \mathrm{M} \longrightarrow \mathrm{P}_{x+1} \qquad \text{velocity constant } k \ (x = 1 \text{ to } \infty)$$
$$\mathrm{P}_x + \mathrm{HC} \longrightarrow \mathrm{P}_x\mathrm{H} + \mathrm{C}$$

where C denotes the alkoxide ion RO^- used as catalyst (concentration c), M is ethylene oxide, and P_x is $R\cdot[O\cdot C_2H_4]_x\cdot O^-$. Writing [P] and [PH] for $\sum_{x=1}^{\infty}[P_x]$ and $\sum_{x=1}^{\infty}[P_xH]$, respectively, we have

$$[\mathrm{P}] + c = c_0, \text{ the initial concentration of the alkoxide catalyst} \quad . \quad . \quad . \quad (1)$$

$$[\mathrm{PH}] + [\mathrm{CH}] = [\mathrm{CH}]_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

We assume the proton exchange to be rapid and write an equilibrium constant K defined by

$$K = c\,[\mathrm{PH}]/[\mathrm{CH}][\mathrm{P}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From (1) and (2) this gives $[\mathrm{CH}] = [\mathrm{CH}]_0c/\{Kc_0 + (1 - K)c\}$ . . . . (4)

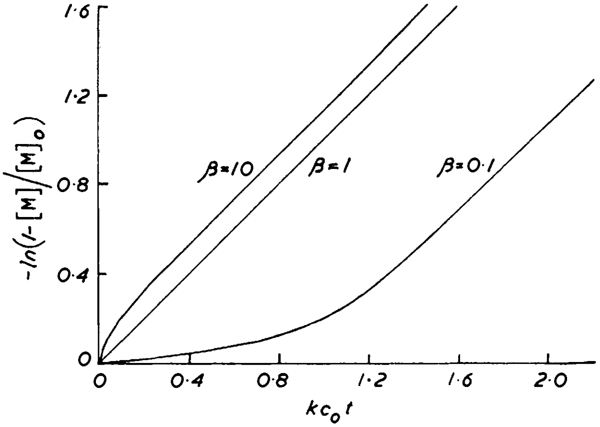
Since the proton exchange does not affect either [M] or the total of $(c + [\mathrm{CH}])$ we have:

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k[\mathrm{M}](\beta c + [\mathrm{P}]) = k[\mathrm{M}]\{c_0 + (\beta - 1)c\} \quad . \quad . \quad . \quad . \quad (5)$$

Since $-\mathrm{d}(c + [\mathrm{CH}])/\mathrm{d}t = \beta k[\mathrm{M}]c$, by using (4), we have

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{\beta k[\mathrm{M}]c\{Kc_0 + (1 - K)c\}^2}{Kc_0[\mathrm{CH}]_0 + \{Kc_0 + (1 - K)c\}^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

FIG. 4.



Division of (5) by (6) gives

$$\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}c} = \frac{\{c_0 + (\beta - 1)c\}(Kc_0[\mathrm{CH}]_0 + \{Kc_0 + (1 - K)c\}^2)}{\beta c\{Kc_0 + (1 - K)c\}^2} \quad . \quad . \quad . \quad (7)$$

which integrates to

$$[\mathrm{M}]_0 - [\mathrm{M}] = \frac{\beta - 1}{\beta}(c_0 - c) + \frac{\beta K - 1}{\beta}\cdot\frac{[\mathrm{CH}]_0(c_0 - c)}{\{Kc_0 + (1 - K)c\}} + \frac{c_0 + [\mathrm{CH}]_0}{\beta K}\ln\frac{c_0}{c}$$
$$+ \frac{[\mathrm{CH}]_0}{\beta K}\ln\left\{K + (1 - K)\left(\frac{c}{c_0}\right)\right\} \quad . \quad (8)$$

where $[\mathrm{M}]_0$ is the initial concentration of ethylene oxide. This is a generalisation of an equation obtained previously by Bauer and Magat [5] for the special case of $K = 1$, $[\mathrm{CH}]_0 = 0$. With the

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[5] Bauer and Magat, *J. Chim. phys.*, 1950, **47**, 55.

aid of (8) it is now possible to integrate eqn. (5) numerically, thus obtaining t and [M] as functions of c. It has been argued that if K is small, β is likely to be large, and *vice versa*. Illustrative solutions have therefore been obtained by setting $\beta K = 1$, which leads to useful simplifications. Writing y for $(1 - c/c_0)$, and z for $(1 - [\mathrm{M}]/[\mathrm{M}]_0)$, we see that equations (8) and (5) become

$$\frac{[\mathrm{M}]_0}{c_0} . z = \frac{\beta - 1}{\beta} y - \left(1 + \frac{[\mathrm{CH}]_0}{c_0}\right) \ln (1 - y) + \frac{[\mathrm{CH}]_0}{c_0} \ln \left\{1 + y\left(\frac{1}{\beta} - 1\right)\right\} \quad . \quad (9)$$

$$kc_0 \frac{\mathrm{d}t}{\mathrm{d}z} = \frac{1}{(1 - z)\{1 + (\beta - 1)(1 - y)\}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

In Fig. 4, $-\ln (1 - [\mathrm{M}]/[\mathrm{M}]_0)$ is plotted against kc_0t by using data calculated from equations (9) and (10) by putting $\beta = 10$, 1, and 0·1. With $\beta = 1$ the system reduces to the simple form and the reaction follows a first-order plot throughout. It is to be noted that this rate plot is not sensitive to β, especially if $\beta > 1$. The uncertainties inseparable from the early stages of a reaction being borne in mind, β could clearly be considerably greater than 1 without this being obvious from kinetic studies.

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