266. *Polymerisation of Epoxides. Part I. Some Kinetic Aspects of the Addition of Alcohols to Epoxides catalysed by Sodium Alkoxides.*

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The kinetics of the base-catalysed addition of alcohols to ethylene oxide have been studied. These reactions are of first order in ethylene oxide. Apparent orders of less than unity in the catalyst (sodium alkoxide) concentration are ascribed to incomplete dissociation, the ion-pair being much less reactive than the free alkoxide ion. In most cases the rate depends upon the concentration of alcohol, but this is ascribed to the effect of the latter on the degree of dissociation of the sodium alkoxide. There is no evidence to suggest that the reaction is termolecular, *i.e.*, that it involves the necessary presence of an alcohol molecule in the transition complex.

Apparent rate constants are given for the addition of various alcohols to ethylene oxide, the pure alcohol acting as the solvent. True rate constants have been measured for the addition of methanol to several epoxides in solution in pure methanol, and reveal a marked retardation by alkyl substitution.

ALTHOUGH there have been many kinetic studies of addition reactions involving olefin oxides,[1] the addition of alcohols catalysed by the corresponding alkoxide ions has not been investigated in detail. Boyd and Marle [2] studied the addition to olefin oxides of

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[1] See Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, pp. 341—344.

[2] Boyd and Marle, *J.*, 1914, **105**, 2117.

phenols catalysed by their sodium salts, and concluded that reaction occurs between the phenoxide ion and the olefin oxide. By analogy with this reaction the addition of an alcohol is likely to involve the reactions

$$RO^- + C_2H_4O \longrightarrow RO{\cdot}CH_2{\cdot}CH_2{\cdot}O^-$$

$$RO{\cdot}CH_2{\cdot}CH_2{\cdot}O^- + ROH \rightleftharpoons RO{\cdot}CH_2{\cdot}CH_2{\cdot}OH + RO^-$$

Apart from its intrinsic interest, this class of reaction is of importance in its relation to the base-catalysed polymerisation of olefin oxides,[3] which is thought to proceed through the following steps:

$$B^- + C_2H_4O \longrightarrow B{\cdot}CH_2{\cdot}CH_2{\cdot}O^- \rightleftharpoons B{\cdot}CH_2{\cdot}CH_2{\cdot}OH$$

$$B{\cdot}CH_2{\cdot}CH_2{\cdot}O^- + C_2H_4O \longrightarrow B(CH_2{\cdot}CH_2{\cdot}O)_2^- \rightleftharpoons B(CH_2{\cdot}CH_2{\cdot}O)_2H$$

$$B(CH_2{\cdot}CH_2{\cdot}O)_n^- + C_2H_4O \longrightarrow B(CH_2{\cdot}CH_2{\cdot}O)_{n+1}^- \rightleftharpoons B(CH_2{\cdot}CH_2{\cdot}O)_{n+1}H$$

Except for the initial reaction, all the steps are of the above type, and the initial reaction is also similar when B^- is an alkoxide ion. In a system giving low-molecular-weight polymers, the rates of the successive steps, other than the first, are[4] closely similar, but no detailed kinetic study has been made.

In the addition of amines to ethylene oxide in aqueous solutions, Eastham[5] concludes that the water plays an important part, while in pyridine solution a proton-source (the pyridinium ion) is essential. Thus the rate of addition of an alcohol to an olefin oxide may depend on the alcohol concentration as well as on that of the olefin oxide and the catalyst. In the first section of this paper we report a kinetic investigation of the addition of various alcohols to ethylene oxide, catalysed by the corresponding alkoxide ions. The overall reaction, if excess of alcohol is present, is $ROH + C_2H_4O \longrightarrow RO{\cdot}C_2H_4{\cdot}OH$ and is accompanied by a decrease in volume, making possible the use of dilatometry. This method was shown to be satisfactory by parallel experiments in which the concentration of ethylene oxide was determined analytically. In preliminary experiments the rates of reaction of ethylene oxide with various alcohols were found, the pure alcohol being the solvent. The initial concentrations of ethylene oxide were 1—2M, alcohol being in at least five-fold excess. Under these conditions good first-order plots were obtained up to 90% consumption of ethylene oxide, and Table 1 shows the first-order velocity constants $k_1 = -\mathrm{d}\ln[C_2H_4O]/\mathrm{d}t$ and the corresponding concentrations of the sodium alkoxide catalyst. Except where stated, in these and subsequent experiments the temperature was 29·8°. In similar experiments with *tert.*-butyl alcohol and *cyclo*hexanol the value of k_1 was found to increase with the extent of reaction.

TABLE 1.

[Alcohol] (M)	10[NaOR] (M)	10^5k_1 (sec.$^{-1}$)	10^5k_2 (l. mole^{-1} sec.$^{-1}$)	[Alcohol] (M)	10[NaOR] (M)	10^5k_1 (M)	10^5k_2 (l. mole^{-1} sec.$^{-1}$)
$CH_3{\cdot}OH$	2·63	5·63	21·4	$CH_3{\cdot}O{\cdot}C_2H_4{\cdot}OH$ ...	3·54	6·62	18·7
$C_2H_5{\cdot}OH$	0·68	3·74	55·0	$C_2H_5{\cdot}O{\cdot}C_2H_4{\cdot}OH$ ...	1·17	1·77	15·1
n-$C_3H_7{\cdot}OH$	1·25	7·30	58·5	$CH_3{\cdot}[O{\cdot}C_2H_4]_2{\cdot}OH$...	2·67	3·15	11·8
n-$C_4H_9{\cdot}OH$	0·97	4·57	47·1	$C_2H_5{\cdot}[O{\cdot}C_2H_4]_2{\cdot}OH$	2·72	4·51	16·6
$HO{\cdot}[CH_2]_2{\cdot}OH$ ...	1·76	3·71	21·1	$C_2H_5{\cdot}[OC_2H_4]_3{\cdot}OH$...	2·09	2·36	11·3
$HO{\cdot}[CH_2]_3{\cdot}OH$ ...	0·62	3·94	63·6				

The variation of k_1 with the concentration of the catalyst was investigated for certain alcohols, and some of the results are shown in Fig. 1. In the methanol–sodium methoxide system the reaction is strictly of first order in sodium methoxide, but in all the other cases the order in catalyst is slightly less than unity, as can be seen from the curvature of the plots. Other experiments were performed to find the effect of the concentration of the alcohol upon the rate, 1 : 4-dioxan being used as an inert diluent. In a series of

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[3] Perry and Hibbert, *J. Amer. Chem. Soc.*, 1940, **62**, 2599.

[4] Miller, Bann, and Thrower, *J.*, 1950, 3623.

[5] Eastham, *ibid.*, 1952, 1936.

experiments in which the alcohol concentration was varied, comparison was made through a second-order constant, $k_2 = k_1/[\text{NaOR}]$, as shown in Table 1. For a given alcohol, variations in the catalyst concentration were not large, so that the errors introduced on account of the non-integral order in the catalyst were small. Fig. 2 shows plots of k_2' against x for various alcohols, where x is the ratio of the concentration of alcohol (in mole l.^{-1}) to its concentration when the pure alcohol is used as solvent, and k_2' is the ratio of k_2 at alcohol concentration x to k_2 when $x = 1$. The plots are similar for ethanol, propan-1-ol, butan-1-ol, and 2-ethoxyethanol, but these differ considerably from methanol, while the behaviour with glycol is intermediate between these extremes. Since the dielectric constant of the solvent is reduced when the concentration of alcohol is decreased, at least two effects may be responsible for the changes in k_2 with x. Hence, several sets of experiments were done in which the alcohol concentration was varied, the dielectric constant being maintained at approximately the same value for experiments in a given set by the use of 1 : 4-dioxan ($D \simeq 2$) and nitrobenzene ($D \simeq 34$);* some results are shown in Fig. 3. We attach little significance to the linearity of the plots obtained, for although $k_2 = A + B[\text{ROH}]$, where A and B are constants, A is negative for butan-1-ol. In similar experiments k_2 was found at a constant alcohol concentration with various values of the dielectric constant of the solution (Fig. 4). Again there is little variation in the rate of addition of methanol but a large change for other alcohols. Other experiments showed a negative salt effect for propan-1-ol and butan-1-ol, but the rate of addition of methanol was unaffected by the presence of added salt. In all three cases the reaction took place in the pure alcohol as solvent, and sodium perchlorate was the salt added.

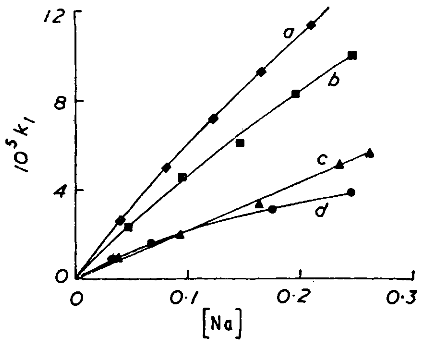

FIG. 1. *Reactions in*: *a propan*-1-*ol*, *b butan*-1-*ol*, *c methanol*, *and d* 70% *butanol*–30% *dioxan*.

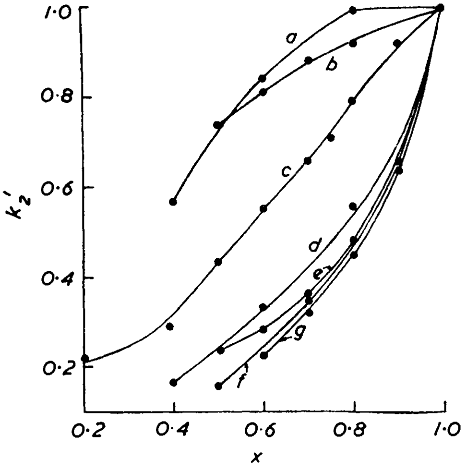

FIG. 2. *Plots of k_2' against x in*: *a water*, *b methanol*, *c ethylene glycol*, *d ethanol*, *e* 2-*ethoxyethanol*, *f propan* 1-*ol*, *and g butan*-1-*ol*.

We conclude that the free alkoxide ion is a more effective catalyst than the sodium alkoxide ion-pair (see also ref. 2), and that under our conditions dissociation of the sodium alkoxide is virtually complete only in solutions of sodium methoxide in pure methanol and in methanol-rich mixtures with 1 : 4-dioxan. Other evidence [6-8] about the extent of

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* There was no evidence of reaction between the alkoxide and nitrobenzene, although in later experiments on the polymerisation of ethylene oxide in presence of nitrobenzene there was a slow loss of catalyst.

[6] Jones and Hughes, *J. Amer. Chem. Soc.*, 1934, 1197.

[7] Ogston, *Trans. Faraday Soc.*, 1936, **32**, 1679.

[8] Hovorka and Sims, *J. Amer. Chem. Soc.*, 1937, **59**, 92.

dissociation of alkoxides and other salts in solution in alcohols confirms this view. The large decrease in k_2 for reactions in propan-1-ol and butan-1-ol as the dielectric constant falls, at constant alcohol concentration (Fig. 4), is probably due at least in part to a decrease in the degree of dissociation of the catalyst. In methanol solutions, changes in the relatively large dissociation constant of sodium methoxide will little affect the degree of dissociation, which is near unity. For these solutions, the experiments in which the dielectric constant remains the same and the methanol concentration is varied (Fig. 3) suggest that the alcohol concentration does not enter into the rate equation. If this is also true of other alcohols, the rapid decrease in k_2 with the alcohol concentration, when the dielectric constant is kept the same by addition of nitrobenzene, shows that the degree of dissociation of the catalyst depends upon the nature of the solvent molecules present as well as on the bulk dielectric constant. The alcohols are more effective than nitrobenzene, presumably on account of the strong solvating power of their hydroxyl groups.[9] Finally, the salt effects observed with propan-1-ol and butan-1-ol are probably due mainly to a decrease in the degree of dissociation of the catalyst in the presence of the sodium ions added. Again, the degree of dissociation of sodium methoxide is likely to be little altered.

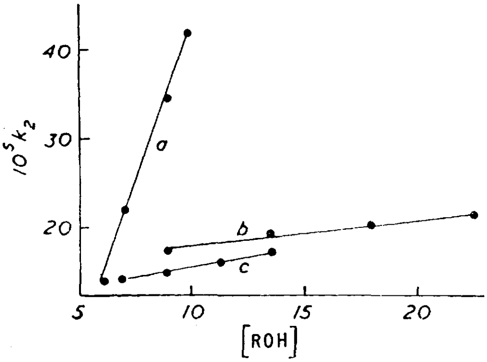

FIG. 3. *Plots of k_2 against* [ROH] *in*: *a butan-1-ol* (D = 17), *b methanol* (D = 29·5), *and c methanol* (D = 19).

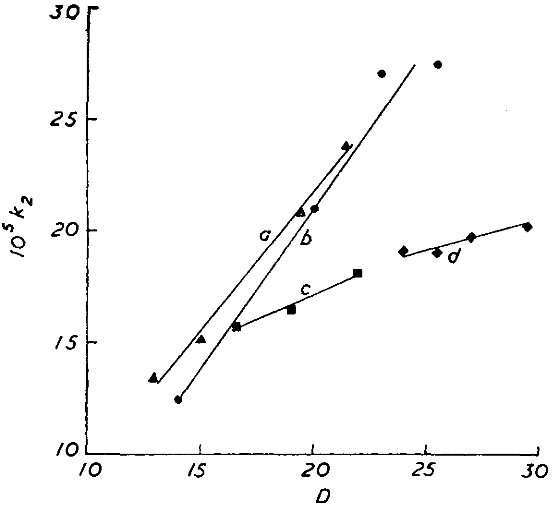

FIG. 4. *Effect of dielectric constant in*: *a butan-1-ol* (7·0M), *b propan-1-ol* (7·3M), *c methanol* (11·2M), *d methanol* (17·9M).

In their interpretation of the analogous reaction between alkali-metal ethoxides and

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[9] Hughes and Hartley, *Phil. Mag.*, 1933, **15**, 610.

alkyl halides,[10] Acree and his co-workers showed that it is possible to obtain true second-order velocity constants in systems in which the alkoxide is incompletely dissociated. In our case we can write

$$k_1 = k_{(\mathrm{RO}^-)}\alpha c + k_{(\mathrm{RONa})}(1 - \alpha)c$$

where $k_{(\mathrm{RO}^-)}$ and $k_{(\mathrm{RONa})}$ are the second-order velocity constants for the reaction of the free alkoxide ion and the sodium alkoxide ion-pair, respectively, with ethylene oxide, c is the concentration of the catalyst, and α is its corresponding degree of dissociation. Three parameters are involved in this equation, the two velocity constants and K, the equilibrium constant for dissociation of the ion-pair, which relates α to c. However, for all the systems studied we find that several widely-varying sets of values of these parameters satisfy the equation over the range of values of c employed. For most alcohols this range was small, owing to the low solubility of the catalyst. Further, K and to a less extent the two velocity constants are likely to vary with c. We conclude that it is impossible to evaluate these velocity constants without knowing values for K at appropriate concentrations of the catalyst.

As an alternative attempt to obtain a value of $k_{(\mathrm{RO}^-)}$ for the prop-1-oxide ion we investigated the kinetic behaviour of mixtures of propan-1-ol and methanol, the dielectric constant being maintained at 23·0. In such mixtures the degree of dissociation of sodium prop-1-oxide is likely to be near to unity, on account of the high solvating power of the methanol, so that the total concentration of anions can be taken equal to the catalyst concentration c. If k_m' and k_p' are the bimolecular velocity constants for the reaction of ethylene oxide with the methoxide and prop-1-oxide ions, respectively, in the mixed solvent and k_2 is the observed second-order velocity constant, then

$$k_2c = k_\mathrm{m}'[\mathrm{MeO}^-] + k_\mathrm{p}'[\mathrm{Pr^nO}^-]$$

whence
$$k_2 = k_\mathrm{m}' + (k_\mathrm{p}' - k_\mathrm{m}')[\mathrm{Pr^nO}^-]/([\mathrm{MeO}^-] + [\mathrm{Pr^nO}^-])$$

Since the acid dissociation constant of methanol is 8·0 times greater than that of propan-1-ol,[11] it follows that

$$k_2 = k_\mathrm{m}' + (k_\mathrm{p}' - k_\mathrm{m}')[\mathrm{Pr^nOH}]/(8{\cdot}0[\mathrm{MeOH}] + [\mathrm{Pr^nOH}])$$

Taking $k_\mathrm{m}' = 19{\cdot}3 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$ when $D = 23$, we use this equation to calculate k_p', the results being summarised in Table 2. The approximate constancy of k_p' so calculated shows that the concentration of propan-1-ol does not enter into the rate equation under these conditions. This confirms our belief that for alcohols other than methanol the large variations in the second-order velocity constant with the concentration of the alcohol are due to the effect upon the dissociation constant of the sodium alkoxide ion-pair, and that the reaction can be regarded as bimolecular.

TABLE 2.

$[\mathrm{MeOH}]/[\mathrm{Pr^nOH}]$	$[\mathrm{Pr^nOH}]$ (M)	10^5k_2 (obs.) (l. mole^{-1} sec.$^{-1}$)	$[\mathrm{MeO}^-]/c$	$10^5k_\mathrm{p}'$ (calc.) (l. mole^{-1} sec.$^{-1}$)
0·462	9·9	46·7	0·787	148
1·85	5·5	28·8	0·934	169
7·70	2·2	21·4	0·984	150

The average value of $k_\mathrm{p}' = 156 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$ may be compared with the lower values found in propan-1-ol at various catalyst concentrations. These results have been analysed on two alternative assumptions: (*a*) that the ion-pair is unreactive and that the dissociation constant K of the ion-pair depends on c; (*b*) that K is independent of c, and

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[10] Robertson and Acree, *J. Amer. Chem. Soc.*, 1915, **37**, 1902; Marshall and Acree, *J. Phys. Chem.*, 1915, **19**, 589.

[11] Hine and Hine, *J. Amer. Chem. Soc.*, 1952, **74**, 5266.

the ion-pair is catalytically active. Results of the two calculations, both made by using $k_p' = 156 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$, are given in Table 3; k_p'' is the velocity constant for the reaction of the ion-pair Pr^{n}ONa.

TABLE 3.

		Assumption (*a*)		Assumption (*b*)		
c (M)	10^5k_2 (l. mole^{-1} sec.$^{-1}$)	α	*K* (mole l.$^{-1}$)	α	*K* (mole l.$^{-1}$)	$10^5k_p''$ (l. mole^{-1} sec.$^{-1}$)
0·040	67	0·430	0·0130	0·202	$2 \cdot 05 \times 10^{-3}$	44·5
0·125	58·5	0·375	0·0285	0·125	$2 \cdot 25 \times 10^{-3}$	
0·210	55	0·353	0·0405	0·094	$2 \cdot 05 \times 10^{-3}$	

It seems likely that the true state of affairs is intermediate between (*a*) and (*b*). In Part II (following paper) we present evidence that the ion-pair MeONa has approximately one-tenth of the activity of MeO$^-$. If a similar ratio holds here, k_p'' is probably 10—15 l. mole^{-1} sec.$^{-1}$. An increase in *K* as *c* increases is to be expected, arising from the greater ionic strength; in very dilute solutions *K* is probably less than 0·010 mole l.$^{-1}$. For comparison, the limiting dissociation constant[7] of potassium ethoxide in ethanol at 25° is 0·0189 mole l.$^{-1}$; a somewhat lower value is probable for sodium prop-1-oxide in propan-1-ol.

Values of k_2 were found at various temperatures from 24·8° to 40·3° in the solvents methanol, propan-1-ol, and butan-1-ol. We find $k_m = \text{antilog}_{10}\ (10 \cdot 0 \pm 0 \cdot 6) \exp [(-18{,}000 \pm 800)/\boldsymbol{R}T]$, $k_p = \text{antilog}_{10}\ (7 \cdot 7 \pm 0 \cdot 6) \exp [(-15{,}200 \pm 800)/\boldsymbol{R}T]$, $k_b = \text{antilog}_{10}\ (7 \cdot 0 \pm 0 \cdot 4) \exp [(-14{,}400 \pm 600)/\boldsymbol{R}T]$ where k_m, k_p, and k_b are the second-order velocity constants for the reaction with ethylene oxide of sodium methoxide, prop-1-oxide, and but-1-oxide respectively in solution in the corresponding pure alcohol. For the reaction in methanol the pre-exponential factor and activation energy quoted are those for the reaction of the free methoxide ion. Since the degree of dissociation of the sodium alkoxide is less than unity in the other alcohols, these parameters can be regarded only as approximate values for the reaction of the free prop-1-oxide and but-1-oxide ions. However, for each alcohol the apparent activation energy found in a 1 : 1 alcohol–1 : 4-dioxan mixture was the same as that in the pure alcohol, although for 50% propanol and 50% butanol the second-order velocity constants were only about one-sixth of the value in the pure alcohol.

Comparison of the reactivity of different epoxides towards a given base is much more straightforward than comparing alcohols. A series of measurements have been made in methanol solution at 29·8°, where we feel it safe to assume that sodium methoxide is completely dissociated. In presence of excess of methanol, the measured second-order velocity constants k_2 are taken to be true bimolecular constants for the reaction between MeO$^-$ and the oxide. Col. 2 of Table 4 records the observed constants.

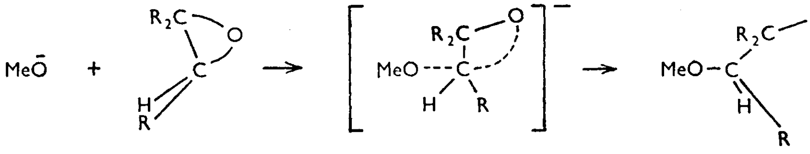
TABLE 4.

Oxide	10^5k_2	$10^5k_2'$	$10^5k_2''$	$10^5k_2'''$	Oxide	10^5k_2	$10^5k_2'$	$10^5k_2''$	$10^5k_2'''$
				(all in l. mole^{-1} sec.$^{-1}$)					
Ethylene	21·4	10·7	—	—	*trans*-But-2-ene	0·4	—	0·2	—
Propene	11·3	11·0	0·3	—	*cyclo*Hexene ...	1·2	—	0·6	—
*iso*Butene	9·7	9·7	—	0·0	*cyclo*Pentene ...	*ca.* 0·8	—	*ca.* 0·4	—
cis-But-2-ene ...	1·3	—	0·65	—					

In ethylene oxide, two equivalent ·CH$_2$· groups are available for attack by MeO$^-$. The constant k_2' given in col. 3 of Table 3 is the rate constant for attack at a single ·CH$_2$· group and is obtained, in the case of ethylene oxide, by halving k_2. Several of the other oxides are symmetrically disubstituted and thus contain no ·CH$_2$· group but two similar ·CHR· groups. Col. 4 of Table 3 records k_2'', the rate constant for MeO$^-$ + ·CHR·, obtained in these instances by halving k_2.

Interpretation of the total rate constant for an unsymmetrical epoxide requires evidence of the ratio of the rates of attack at the two available points. This was obtained simply for propene and *iso*butene oxides by submitting the neutralised reaction products to vapour-phase chromatography. The former yielded 97% of the secondary alcohol $CHMe(OH)\cdot CH_2\cdot OMe$, and only 3% of $MeO\cdot CHMe\cdot CH_2\cdot OH$. It is concluded that attack at $\cdot CH_2\cdot$ and $\cdot CHMe\cdot$ is in the ratio 97 : 3, whence the values of k_2' and k_2'' for propene oxide shown in Table 3 were computed. The product from *iso*butene oxide appeared to be exclusively $CMe_2(OH)\cdot CH_2\cdot OMe$. It is concluded that $k_2' = k_2$ and that the rate constant k_2''' for attack at $\cdot CMe_2\cdot$ is too small to be measured by this method.

Table 3 reveals a very simple pattern, in that k_2' and k_2'' are approximately constant. Hence (i) the rate of attack at $\cdot CH_2\cdot$ is not materially changed by substitution at the adjacent carbon atom; (ii) $\cdot CAlk_2\cdot$ is inert. These findings are qualitatively consistent with the nucleophilic nature of the reaction. Attack of MeO^- will be approximately along the line of the C–O bond to be broken:



Alkyl substitution will retard this process by two independent mechanisms: (*a*) inductive transfer of a fractional negative charge to the adjacent carbon atom, (*b*) steric hindrance to the approaching ion. The available evidence is insufficient to indicate which effect is more important in the compounds studied.

EXPERIMENTAL

Epoxides other than ethylene and propene oxides were prepared by treating the corresponding chlorohydrins with alkali, as described for *cyclo*hexene oxide.[12] *iso*Butene chlorohydrin was prepared from 1-chloro-2-methylpropene,[13] *cyclo*hexene and *cyclo*pentene chlorohydrins from the olefins.[14] Samples of *cis*- and *trans*-but-2-ene oxides were kindly presented by Mr. R. Chapman, of these laboratories.

Other reagents were obtained commercially and were purified by conventional methods. The epoxides were dried (CaH_2) and redistilled. 1 : 4-Dioxan was dried by refluxing over sodium metal in the presence of fluorenone as indicator, distilled under nitrogen, and stored in a dark bottle under nitrogen. Alcohols were dried over magnesium metal and distilled.

Catalyst solutions were prepared by dissolving weighed amounts of sodium or potassium metal in the requisite alcohol. In some experiments, the concentration of the catalyst was determined by titration at the end of the experiment and in all cases agreed with the initial values. Initially, reaction mixtures were made up in an all-glass apparatus and the dilatometers were filled in the absence of air. This was later found to be unnecessary, and reaction mixtures were made up by pipette, contact with air being kept to a minimum.

The dilatometers consisted of a 10-ml. bulb to the top of which was sealed a 0·02-cm. diameter graduated capillary of length 30 cm. At the bottom of the bulb a U-tube led *via* a tap to a cylindrical mixing chamber. To avoid leakage through the tap the reaction solution on either side was displaced by mercury immediately after filling the bulb.

In a number of cases, parallel experiments were done in which the concentration of unchanged ethylene oxide was determined by titration, by using the addition reaction with hydrochloric acid.[15] Good agreement was found between velocity constants determined by the two methods. The volume change was not sufficient to require any correction to the concentrations of the reactants.

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[12] Osterberg, *Org. Synth.*, Coll. Vol. I, 179.

[13] Burgin, Hearne, and Rust, *Ind. Eng. Chem.*, 1941, **33**, 385.

[14] Coleman and Johnstone, *Org. Synth.*, Coll. Vol. I, 151.

[15] Lichtenstein and Twigg, *Trans. Faraday Soc.*, 1948, **44**, 905.