JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

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VOLUME 78 JUNE 26, 1956 NUMBER 12

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

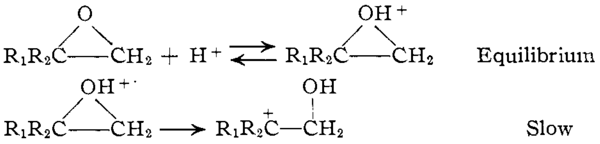
Hydrolysis of Substituted Ethylene Oxides in H_2O^{18} Solutions[1]

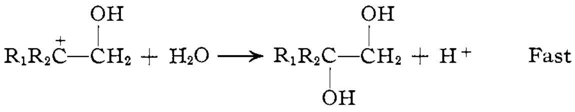
BY F. A. LONG AND J. G. PRITCHARD

RECEIVED NOVEMBER 17, 1955

Propylene and isobutylene oxides have been hydrolyzed in O^{18}-labeled water under acidic, basic and neutral conditions. The detailed paths of the hydrolysis have been established by a mass spectrometric analysis of the resulting glycols. The base-catalyzed reaction occurs predominantly at the primary carbon for propylene oxide and exclusively so for isobutylene oxide. In contrast the acid-catalyzed reaction occurs exclusively at the branched carbon for isobutylene oxide and predominantly so for propylene oxide. It is concluded that the basic reaction goes by an SN2 mechanism and that the acid-catalyzed reaction involves a carbonium ion mechanism. Data are also given for the kinetics of the hydrolysis of isobutylene oxide at 25° in the *p*H range of from 3 to 14.

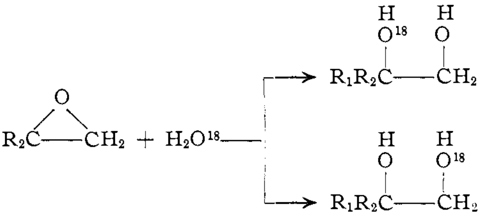
It is well known that there are at least three kinetically distinguishable paths for the hydrolysis of ethylene oxide in aqueous solution.[2-7] There is an acid-catalyzed hydrolysis, a base-catalyzed hydrolysis and a *p*H independent, "water" reaction. It will be shown in the next paper of this series[8] that in solutions of perchloric acid the acid-catalyzed hydrolysis of ethylene oxide and of several substituted oxides follows the Hammett acidity function, H_0. In accord with similar hydrolysis studies[9-11] this result indicates that a water molecule is not involved in the rate-determining step and suggests that the mechanism involves a carbonium ion as





$$R_1R_2\overset{+}{C}-\overset{OH}{CH_2} + H_2O \longrightarrow R_1R_2\underset{OH}{C}-\overset{OH}{CH_2} + H^+ \qquad \text{Fast}$$

To establish any mechanism it is desirable to obtain other evidence than that available from kinetic studies. For the hydrolysis of unsymmetrically substituted ethylene oxides one valuable piece of supplementary evidence is the detailed course of the hydrolysis as shown by reaction with O^{18}-labeled water. The two alternates



are possible for each of the three kinetically distinguishable hydrolysis paths.

In order to determine which of the above paths is actually involved it is necessary to hydrolyze the oxide in H_2O^{18} and then to measure the O^{18}-content in each of the hydroxyl groups of the resulting glycol. In favorable cases this can be done by a direct mass spectrometric analysis of the glycols themselves. The general procedure is similar to that employed by Long and Friedman in their study of the hydrolysis of lactones.[12]

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[1] Work supported by a grant from the Atomic Energy Commission.

[2] J. N. Bronsted, M. Kilpatrick and M. Kilpatrick, THIS JOURNAL, **51**, 428 (1929).

[3] H. J. Lichtenstein and G. H. Twigg, *Trans. Faraday Soc.*, **44**, 905 (1948).

[4] A. M. Eastham and G. A. Latremouille, *Can. J. Research*, **30**, 169 (1952).

[5] W. C. J. Ross, *J. Chem. Soc.*, 2257 (1950).

[6] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 301.

[7] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 341.

[8] J. G. Pritchard and F. A. Long, THIS JOURNAL, **78**, 2667 (1956).

[9] D. McIntyre and F. A. Long, *ibid.*, **76**, 3240 (1954).

[10] F. A. Long and M. Purchase, *ibid.*, **72**, 3267 (1950).

[11] V. Gold and J. Hilton, *J. Chem. Soc.*, 843 (1955).

[12] F. A. Long and L. Friedman, THIS JOURNAL, **72**, 3692 (1950).

The Mass Spectra.—Table I gives the mass spectra of propylene and isobutylene glycols and indicates the chemical nature of the various fragment ions. It is clear that the decomposition paths in the mass spectrometer are very similar for the two molecules. In neither case is there much intensity from the parent glycol ions. For both molecules the major peak results from a split between the hydroxylated or "glycol" carbons to give the heavier ion, CH_3RCOH^+ (mass 45 from propylene glycol; mass 59 from isobutylene glycol). As Fig. 1 shows, these fragments contain the branched alcohol group. Both molecules give a sizable peak for the loss of one methyl group (mass 61 for propylene glycol; mass 75 for isobutylene glycol). Both molecules also give sizable peaks at mass 31.

Table I

Mass Spectra of 1,2-Glycols

	Propylene glycol		Isobutylene glycol	
Mass	Intensity[a]	Fragment	Intensity[a]	Fragment
26	1.3		1.2	
27	10.0		8.1	
28	4.4		3.9	
29	9.1		34.3	
30	0.7		2.8	
31	10.3	CH_2OH^+	64.6	CH_2OH^+
32	0.6		22.2	
33	1.32	$CH_3OH_2^+$, $CH_2O^{18}H^+$	0.40	$CH_3OH_2^+$, $CH_2O^{18}H^+$
39	0.8		5.1	
40	0.1		0.5	
41	2.2		14.8	
42	1.7		2.8	
43	13.7		14.5	
44	6.7		0.8	
45	*100*	CH_3CHOH^+	4.1	
46	2.3		0.1	
47	0.28	$CH_3CHO^{18}H^+$	0.2	
55	0.5		4.4	
56	0.1		0.3	
57	2.2		24.5	
58	0.5		1.6	
59	0.6		*100*	$(CH_3)_2COH^+$
60	0.1		3.5	
61	4.4	$CHOHCH_2OH^+$	0.25	$(CH_3)_2CO^{18}H^+$
62	0.01		...	
63	0.018	$CHOHCHO^{18}H^+$	...	
73	...		2.1	
74	...		0.4	
75	0.2		13.9	$CH_3COHCH_2OH^+$
76	1.0 (parent)		0.5	
77	0.1		0.08	$CH_3COHCH_2O^{18}H^+$
78	0.1		...	

[a] Normalized to intensity 100 for most abundant peak.

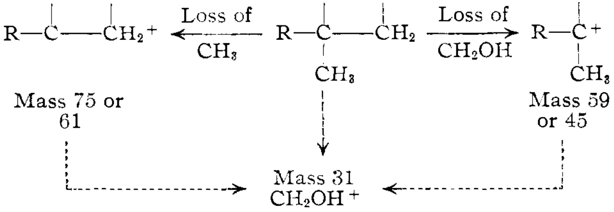

Fig. 1.—Origin of principal mass spectrometer peaks from isobutylene glycol ($R = CH_3$) and propylene glycol ($R = H$).

Analysis for O^{18}-content can best be done by utilizing the ions resulting from loss of a methyl group along with those from the "glycol" split. The natural O^{18}/O^{16} ratio is 0.002 and the enriched water has a ratio of 0.015.[13] Since two oxygen atoms are present in the ions of masses 61 and 75 from propylene and isobutylene glycol, respectively, the predicted values of the 63/61 and 77/75 ratios from the mass spectra of these two glycols are 0.004 if none of the oxygen is enriched above the natural level, 0.017 if one oxygen is enriched and 0.030 if both oxygens are enriched. The intensity ratios 47/45 and 61/59, for propylene and isobutylene glycol, respectively, give the O^{18}/O^{16} ratio for the branched alcohol fragments derived from the "glycol" split (see Fig. 1). Since these fragments contain only one oxygen atom, these intensity ratios should vary only between 0.002 and 0.015, the values for natural samples and those of maximum enrichment, respectively. From a knowledge of the degree of enrichment of both oxygen atoms together and of the oxygen of the branched alcohol group alone, the O^{18}-content of the primary alcohol group is easily calculated.

There appears formally to be a third intensity ratio of interest since the glycol structures suggest that a direct split of the "glycol" carbon atoms could lead to the ion CH_2OH^+ of mass 31. Both spectra show large intensity at this mass, but for two reasons the 33/31 intensity ratio is not useful for O^{18}-analysis. Firstly, the natural glycols both exhibit an abnormally high 33/31 ratio (0.12 for propylene glycol and 0.006 for isobutylene glycol) The conclusion is that ions other than $CH_2O^{18}H^+$ contribute to the intensity at mass 33. Secondly, fragments of mass 31 can result from decomposition of the heavier fragments from each glycol, masses 45 and 59, which contain the branched alcohol group (see Fig. 1). In fact, the mass spectra of secondary and tertiary butyl alcohols show that this type of decomposition is a likely process.[14] Fortunately, the ratios 47/45 and 63/61 for propylene glycol and 61/59 and 77/75 for isobutylene glycol are uncomplicated in the sense that the origins of the peaks are unambiguous and that the values of the ratios for the natural glycols are close to those predicted from the natural O^{18}/O^{16} ratio of 0.002. Hence these ratios appear entirely suitable for analysis.

Kinetic Study of the Hydrolysis of Isobutylene Oxide and Propylene Oxide.—In order to determine the most desirable conditions for the H_2O^{18} hydrolysis experiments, a kinetic study of the hydrolysis of isobutylene oxide was carried out at 25° over the *p*H range 3 to 14. This was supplemented by a similar study of propylene oxide in the acid-catalyzed region. The results for isobutylene oxide are shown in Fig. 2 and indicate clearly a rapid acid-catalyzed reaction, a well defined base-catalyzed reaction at *p*H values greater than 12, and a *p*H independent "water" reaction in the *p*H range 7 to 11. Table II gives the second-order rate coefficients for these reactions, together with estimated data on ethylene oxide and propylene oxide. As might be expected, the rates of the base-catalyzed and "water" reactions are much

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[13] The H_2O^{18} was obtained from the Stuart Oxygen Company, by agreement of the Atomic Energy Commission. The isotopic ratio, O^{18}/O^{16}, was found to be 0.0154.

[14] Spectra no. 287 and 289, Catalogue of Mass Spectral Data, Amer. Pet. Inst., Research Project No. 44, Carnegie Institute of Technology.

less sensitive to change of structure than are those for the acid-catalyzed reactions.

TABLE II

SECOND-ORDER RATE COEFFICIENTS[a] FOR THE HYDROLYSIS OF OXIDES AT 25°

Oxide	Based catalyzed	Water reaction	Acid catalyzed
Isobutylene	8.7×10^{-5}	2.0×10^{-8}	6.8
Propylene	*ca.* 10^{-4}[b]	*ca.* 10^{-8}[b]	6×10^{-2}[c]
Ethylene	1.1×10^{-4} [3]	1.0×10^{-8} [3]	9×10^{-3} [4]

[a] Units: l. mole^{-1} sec.$^{-1}$. [b] Interpolated values. [c] Estimated from results at 0° from ref. 8.

Hydrolysis in H_2O^{18}.—Tables III and IV give conditions for the H_2O^{18} hydrolysis of propylene and isobutylene oxides together with preliminary exchange tests on the glycols. The reaction times and concentrations of catalysts were chosen to ensure almost complete reaction. After the hydrolyses, samples of the product glycols were recovered and analyzed in the mass spectrometer.

TABLE III

HYDROLYSIS OF 1.3 MOLAR PROPYLENE OXIDE IN H_2O^{18} SOLUTION

Expt. no.	Solute	Catalyst concn.	Reaction time (hr.)	Reaction temp. (°C.)	Intensity ratios × 10^2 47/45	63/61
1	Glycol	....	..	..	0.20	0.38
2	Glycol	0.2 *M* NaOH	6	100	0.30	0.37
3	Oxide	0.12 *M* $HClO_4$	16	25	1.20	1.70
4	Oxide	0.25 *M* $HClO_4$	15	25	1.12	1.70
5	Oxide	1.1 *M* NaOH	5	45	0.55	1.75
6	Oxide	0.2 *M* NaOH	6	100	.49	1.73
7	Oxide	10^{-5} *M* NaOH	38	100	.77	1.70
8	Oxide	10^{-5} *M* NaOH	80	100	.69	1.71

TABLE IV

HYDROLYSIS OF 1.0 *M* ISOBUTYLENE OXIDE IN H_2O^{18} SOLUTION

Expt. no.	Solute	Catalyst concn.	Reaction time (hr.)	Reaction temp. (°C.)	Intensity ratios × 10^2 61/59	77/75
9	Glycol	....	..	..	0.25	0.58
10	Glycol	0.1 *M* $HClO_4$	$^1/_4$	25	.24	.52
11	Glycol	0.2 *M* NaOH	6	100	.27	.56
12	Oxide	0.12 *M* $HClO_4$	$^1/_4$	25	1.58	1.77
13	Oxide	0.1 *M* $HClO_4$	$^1/_4$	25	1.55	1.65
14	Oxide	0.2 *M* NaOH	6	100	0.35	1.86
15	Oxide	0.2 *M* NaOH	6	100	0.38	1.76
16	Oxide	10^{-3} *M* NaOH	80	100	1.44	1.95
17	Oxide	10^{-4} *M* NaOH	80	100	1.29	1.77

Tables III and IV also give the observed values of the intensity ratios which are needed to determine the paths of hydrolysis. Experiments 1 and 9 show that the observed ratios for the natural glycol samples are close to those expected for the normal O^{18}/O^{16} ratio of 0.002. Experiments 2, 10 and 11 show that there is no significant exchange of oxygen between the hydroxyl groups of the glycols and the solvent water, under the conditions of the hydrolyses. We conclude that the results for the oxides can legitimately be interpreted as reflecting the hydrolysis paths.

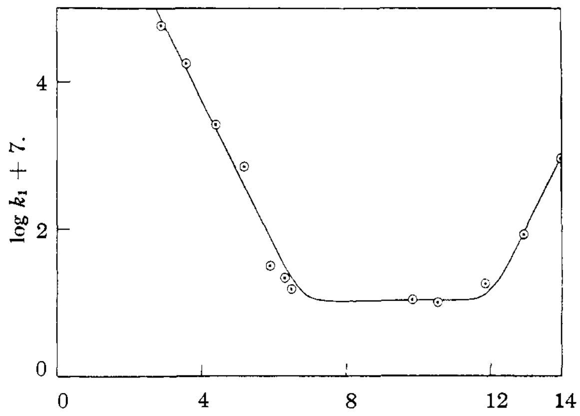


Fig. 2.—Observed first-order rate coefficient, k_1 (sec.$^{-1}$), for hydrolysis of isobutylene oxide at 25° plotted against $-\log C_{H^+}$.

The only correction which is necessary for calculation of the O^{18}/O^{16} ratio from the data of Tables III and IV is a small subtraction to take account of the fact that the ratios for the natural glycols are slightly higher than expected. Specifically the corrections are: propylene glycol, −0.06 for the 47/45 ratio; no correction for the 63/61 ratio; isobutylene glycol, −0.05 for the 61/59 ratio, −0.16 for the 77/75 ratio. The "per cent. reaction" figures of Table V are calculated from these corrected ratios.

TABLE V

DIRECTION OF REACTION OF OXIDES WITH H_2O^{18}

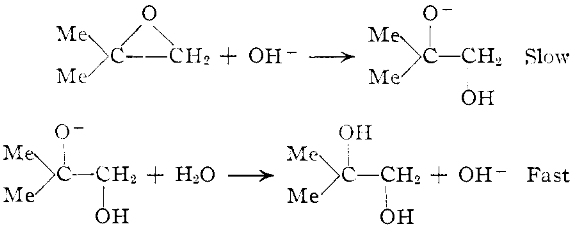
Expt. no.	Oxide	Hydrolysis condition	% of entering oxygen At primary carbon	At branched carbon
3	Propylene	Acid	26	74
4	Propylene	Acid	34	66
5	Propylene	Basic	78	22
6	Propylene	Basic	82	18
7	Propylene	Neutral	61	39
8	Propylene	Neutral	67	33
12	Isobutylene	Acid	0	100
13	Isobutylene	Acid	1	99
14	Isobutylene	Basic	92	8
15	Isobutylene	Basic	90	10
16	Isobutylene	Neutral[a]	9	91
17	Isobutylene	Neutral[a]	20	80

[a] Actually found to involve considerable acid contribution; see text.

Discussion of the Results

With propylene oxide, the acid-catalyzed hydrolysis leads predominantly to entry of the O^{18} on the secondary carbon atom. In contrast, hydroxide ion clearly attacks the propylene oxide molecule predominantly at the primary position in the epoxide ring. For isobutylene oxide, this change in path is even more marked in that the acid- and base-catalyzed reactions go almost entirely at the tertiary and primary carbons, respectively.

The normal expectation is that the base-catalyzed hydrolysis would involve nucleophilic attack by the hydroxide ion. For steric reasons this would be expected to occur predominantly at the primary carbon atom of the epoxide ring.[15,16] In addition the electron releasing properties of the methyl groups of propylene and isobutylene oxides would favor nucleophilic reaction at the primary carbon, leading to the mechanism below[17]

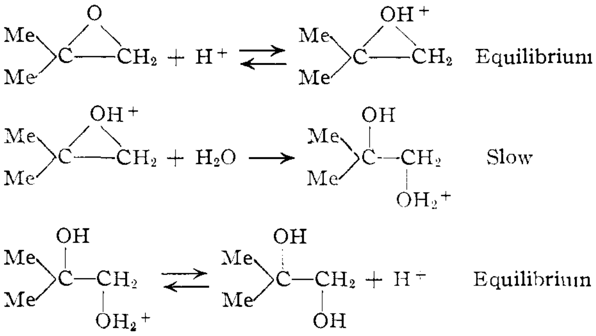


Quite evidently, our results with isobutylene glycol are consistent with this proposal in that, within experimental error, the base-catalyzed reaction leads only to entrance of O^{18} at the primary position. For propylene oxide, the same reaction predominates but a significant amount of attack at the secondary position is indicated.

A similar mixture of primary and secondary substitution was obtained by Bartlett and Ross[18] in their studies of the base-catalyzed reaction of methanol with butadiene monoxide. For this case, the investigators reached the conclusion that, at both carbon atoms, the reaction involved nucleophilic attack. The fact (Table V) that with propylene oxide the amount of reaction at the secondary carbon is independent of the hydroxide ion concentration again suggests a bimolecular nucleophilic attack at both of the carbon atoms. This is consistent with the finding[19] that for nucleophilic attack of chloride ion labeled with Cl^{36} on 2,3-dichloropropane-1-ol a significant amount (24%) of attack takes place at the secondary position although the predominant attack is at the terminal (3) carbon atom. Apparently nucleophilic attack on propane structures is not entirely limited sterically to the primary position.

Studies of the "water" reaction were deliberately made with unbuffered solutions since it is known that normal buffer components frequently react with oxides[2,5] and hence can complicate the hydrolysis. The experiments were started at *p*H values as high as were possible without producing a contribution from the base-catalyzed reaction. Even so it was found that during the 80-hour reaction period the *p*H drifted down to a value of about four, probably due to reaction of hydroxide ion with the glass. This *p*H change should not complicate the "water" reaction of propylene oxide since the acid catalyzed reaction is comparatively slow, *cf.* Table II. Hence the data of Table V can be interpreted as showing that about 65% of the nucleophilic attack by water occurs at the primary carbon of the propylene oxide ring. This value is consistent with the weaker nucleophilic character of water compared to hydroxide ion. With isobutylene oxide, it is very probable that the observed *p*H drift resulted in a large fraction of the hydrolysis being due to the acid catalyzed reaction. As Fig. 2 shows, at *p*H values of from 6 to 4 the acid-catalyzed reaction is distinctly faster than the "water" reaction. Because of this it is unsafe to reach any conclusions from the results of Experiments 16 and 17.

Turning now to the acid-catalyzed reaction, if it occurs through an A-2 mechanism as shown below, *i.e.*, one involving rate-determining nucleophilic attack by water, one would again expect substitution to occur at the primary carbon atom



However, for the A-1, carbonium ion mechanism suggested earlier, the expectation would be for substitution to occur at the branched carbon atom, since, quite generally, secondary and tertiary carbonium ions are more stable than primary ones. The fact that, for the acid-catalyzed hydrolysis, the substitution is predominantly at the branched carbon atom for propylene oxide and is entirely so for isobutylene is then a strong argument for the carbonium ion mechanism. Several other types of evidence are in accord with this conclusion; they will be discussed in the subsequent paper.

Experimental

Reagent grade epoxides were purified by distillation, giving propylene oxide of b.p. 35°, $n^{25}D$ 1.3638, and isobutylene oxide of b.p. 52°, $n^{25}D$ 1.3700. Isobutylene glycol isolated from an acid-catalyzed hydrolysis of the oxide had b.p. 79° (10 mm.), $n^{27}D$ 1.4307. This material and reagent grade propylene glycol were used for the mass spectra studies and for experiments 1 and 2 of Table III, and 9, 10 and 11 of Table IV. The rate studies of Fig. 2 were done at 25° using a straightforward dilatometric procedure.[10] Initial concentration of oxide was approximately 0.1 molar. First-order rate coefficients were calculated by the Guggenheim procedure.

The hydrolyses in H_2O^{18} were all carried out with 10 cc. of H_2O^{18} (O^{18}/O^{16} = 0.0154) and 1 cc. of oxide. The sodium hydroxide solutions were made up by reaction of the appropriate weight of sodium metal with the H_2O^{18} under toluene. The perchloric acid solutions were made up by adding the required amount of 70% acid to the H_2O^{18}. Since the concentrated acid contains natural water this procedure causes a slight decrease in the O^{18}-content of the final solution. However, the change is so small that it has been ignored in making the calculations of Table V. After hydrolysis the resulting solutions of glycol were neutralized with a concentrated solution of acid or base, the excess water was distilled off and the salt formed was filtered from the glycol. The observed mass spectra served as a direct check on the identity and purity of the glycols. In all cases the only significant contaminant was water, which of course does not interfere with the O^{18}-analysis.

Mass spectra of the glycols were run in a Consolidated Model 21-401 machine using 75 volt bombarding electrons. The rather large leak rate of this machine resulted in high intensities for the principal ions even though at room tem-

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[15] O. R. Boyd and E. R. Marle, *J. Chem. Soc.*, **93**, 838 (1908); **105**, 2117 (1914).

[16] H. C. Chitwood and B. T. Freure, THIS JOURNAL, **68**, 680 (1946).

[17] *Cf.* reference 7.

[18] P. D. Bartlett and S. D. Ross, *This Journal*, **70**, 926 (1948).

[19] P. B. D. de la Mare and J. G. Pritchard, *J. Chem. Soc.*, 1644 (1954).

perature the vapor pressure of the glycols is very low. Analysis for O^{18} was made by scanning several times through the peak regions of interest and averaging the observed "isotopic" intensity ratios. Typical observed values for natural isobutylene glycol were 61/59 = 32.0/12500 and 77/75 = 8.2/1728. The combination of high intensities and good reproducibility leads us to believe that the final percentage reaction figures of Table V are correct to about ±5%.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Kinetics and Mechanism of the Acid-catalyzed Hydrolysis of Substituted Ethylene Oxides[1]

BY J. G. PRITCHARD AND F. A. LONG

RECEIVED NOVEMBER 17, 1955

The kinetics of the acid-catalyzed hydrolysis of ten simple epoxides have been studied at 0°, by a dilatometric procedure, in aqueous perchloric acid with acid concentrations ranging up to 3.5 molar. The rates vary widely with substituent; at constant acid concentration the rate for isobutylene oxide is faster than that for epibromohydrin by about 10^4. For the seven oxides whose rates could be studied in concentrated solutions of acid, log k_1 was found to increase linearly with $-H_0$. On this basis it is concluded that the hydrolysis goes by an A-1 mechanism involving a carbonium ion intermediate. This conclusion is supported by evidence from several other sources.

The hydrolysis of ethylene oxides in dilute aqueous solution of acids is known from the studies of Brönsted, Kilpatrick and Kilpatrick[2] to lead to the 1-2 glycols and to follow the rate law

$$\frac{-\mathrm{d}C_{\text{oxide}}}{\mathrm{d}t} = k_1 C_{\text{oxide}} \qquad (1)$$

where the first-order rate coefficient, k_1, is directly proportional to the hydrogen ion concentration. As noted in the previous paper of this series,[3] there are two likely mechanisms for this reaction, both of which would agree with the dilute solution kinetics.[4] One is an A-2 mechanism in which the conjugate acid of the oxide undergoes nucleophilic attack by a water molecule. The other is an A-1 mechanism for which the rate-determining step is unimolecular reaction of the conjugate acid of the oxide to give a carbonium ion.

A procedure which can be used to obtain evidence for these mechanisms is to study the hydrolysis in concentrated solutions of strong acids and see whether the rate is proportional to the Hammett acidity function, H_0.[5-10] This paper reports kinetic studies of the acid-catalyzed hydrolysis in aqueous solutions of perchloric acid at concentrations up to 3.5 molar. Still another type of evidence which bears on the mechanism is the effect of substituents on the rates, and to obtain data for this we have studied the hydrolysis of ten different epoxides.

Experimental

Hydrolysis rates were measured dilatometrically at 0° in a water-methanol bath whose temperature could be held constant to ±0.01°. Since the volume change for hydrolysis of epoxides is relatively large, adequate accuracy was obtained by the use of 50-ml. dilatometers of simple design. Epoxide concentrations varied from 0.05 to 0.2 molar. For all experiments pre-cooled epoxide was added to a pre-cooled and degassed solution of perchloric acid present in an upper chamber of the dilatometer, and the mixture was rapidly stirred and then transferred into the working chamber of the dilatometer by compressed air. Rate coefficients were calculated graphically using the Guggenheim procedure; Fig. 1 is a plot of typical data. Units of k_1 are sec.$^{-1}$ in all cases.

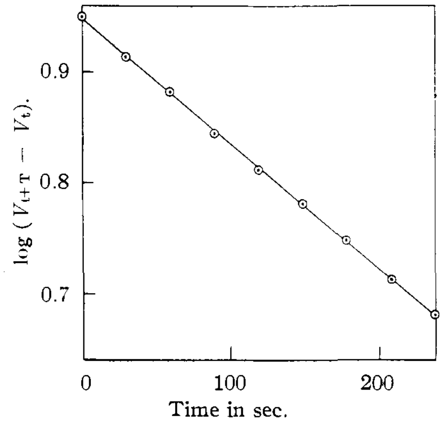

Fig. 1.—Guggenheim plot for reaction of 0.1 M ethylene oxide in 1.86 M aqueous perchloric acid at 0°.

At the end of each dilatometer run, the perchloric acid concentration of the reaction mixture was determined by titration of an aliquot with standardized sodium carbonate. Values of H_0 (at 25°) corresponding to the stoichiometric concentration of acid were taken from smoothed plots of the data of Hammett and Deyrup,[11] as corrected by Hammett and Paul.[12]

It is known that epoxides may undergo hydrolysis by a pH independent, "water" reaction. However, from the available data[3,5] it can be safely concluded that the contribution to the hydrolysis from the "water" reaction is negligible for all the experiments of the present study.

Solutions of perchloric acid were made up from reagent grade acid and redistilled water. The more common epoxides were reagent grade materials and were distilled before use. We are indebted to the Shell Development Company for samples of β-methylepichlorohydrin and β-methyl glycidol and to the Carbide and Carbon Chemical Company for

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[1] Work supported by a grant from the Atomic Energy Commission.

[2] J. N. Brönsted, M. Kilpatrick and M. Kilpatrick, THIS JOURNAL, **51**, 428 (1929).

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[5] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 273–277.

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[7] F. A. Long, W. F. McDevit and F. Dunkle, *J. Phys. Chem.*, **55**, 813, 829 (1951).

[8] R. W. Taft, Jr., THIS JOURNAL, **74**, 5372 (1952).

[9] D. McIntyre and F. A. Long, *ibid.*, **76**, 3240 (1954).

[10] V. Gold and J. Hilton, *J. Chem. Soc.*, 843 (1955).

[11] L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721 (1932).

[12] L. P. Hammett and M. Paul, *ibid.*, **56**, 827 (1934).