BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2523—2526 (1970)

Ring-opening Reactions of Cyclic Ethers. VIII.[*1] Acid-catalyzed Ring-opening Reactions of Isobutylene Oxide in Alcohols

Shizen SEKIGUCHI, Kohji MATSUI and Yoshihiro YASURAOKA

Department of Synthetic Chemistry, Faculty of Engineering, Gunma University, Tenjin-cho, Kiryu, Gunma

(Received January 20, 1970)

The rates of the ring-opening reaction of isobutylene oxide have been measured in methyl, ethyl, *n*-propyl and isopropyl alcohols in the range from 10 to 40°C under conditions where the molar ratio of an alcohol to the epoxide was kept at 10 and the range of the concentration of boron trifluoride etherate was *ca.* 1.0×10^{-3} to *ca.* 4.0×10^{-3} mol/*l*. The rate equation is expressed as follows: $-\mathrm{d}[\text{epoxide}]/\mathrm{d}t=k_2[\mathrm{C_0}][\text{epoxide}]$, where $[\mathrm{C_0}]$ is the initial concentration of the catalyst and [epoxide] is the instantaneous concentration of the epoxide at time *t*. The rate constants (k_2) decreased in the order, $CH_3OH > C_2H_5OH > n\text{-}C_3H_7OH > i\text{-}C_3H_7OH$. The entropies of activation decreased in the same order, while the energies of activation were not appreciably changed. A plot of $\log k_2$ against $1/D$ (D, the dielectric constant of the mixture of each alcohol and the epoxide) was found to be linear, its slope being -61.2. The results support the fact that the reaction is bimolecular.

Although the acid-catalyzed ring-opening reactions of epoxides in various solvents, such as water, alcohol, *etc.*, have recently received intensive attention,[1,2] there have still been controversies on their mechanisms. Long *et al.* reportrd that the acid-catalyzed hydrolyses of epichlorohydrin, propylene and isobutylene oxides were unimolecular (A-1).[3] On the other hand, that of epichlorohydrin was shown by le Noble and Muffy.[4] to proceed by

---

[*1] Part VII: S. Sekiguchi, H. Inoue, M. Hayashi and K. Matsui, *Kogyo Kagaku Zasshi*, **71**, 1943 (1968).

[1] R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

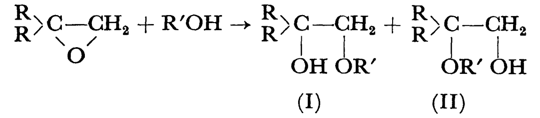
[2] S. Winstein and R. B. Henderson, "Heterocyclic Compounds," Vol. 1, ed. by R. C. Elderfield, John Wiley and Sons, Inc., New York, London (1950), p. 1.

[3] F. A. Long and J. G. Pritchard, *J. Amer. Chem. Soc.*, **78**, 2667, 6008 (1956).

[4] W. J. le Noble and M. Duffy, *J. Phys. Chem.*, **68**, 619 (1964).

a bimolecular process (A-2) and Koskikallio *et al.* gave the same conclusion for those of propylene oxide and isobutylene oxide.[5]

An unsymmetrical epoxide reacts with excess alcohol to give the following products:



$$\mathrm{R_2C\!-\!CH_2(\!-\!O\!-\!)} + \mathrm{R'OH} \rightarrow \underset{\text{(I)}}{\mathrm{R_2C(OH)\!-\!CH_2(OR')}} + \underset{\text{(II)}}{\mathrm{R_2C(OR')\!-\!CH_2(OH)}} \qquad (1)$$

In a previous paper*1 we determined the total amounts of I and II and the ratios (II/I) for the reaction of propylene oxide or isobutylene oxide with alcohols using boron trifluoride etherate as a catalyst. From the results obtained, we inferred that in the case of isobutylene oxide an A-1 reaction might perhaps take place. In the present investigation, kinetic measurements were carried out in excess alcohols using the same catalyst in order to obtain a closer insight into the reaction mechanism.

Results and Discussion

Reaction Products. In a previous investigation*1 the acid-catalyzed ring-opening reaction of isobutylene oxide was carried out in methyl, ethyl and isopropyl alcohols under conditions where the molar ratio of an alcohol to isobutylene oxide was kept at 10 and the concentration of boron trifluoride etherate was 1.2×10^{-3} mol/*l*. The values of II/I after three hours' reaction were found to be as follows:

Alcohol	Reaction temp. (°C)	II/I
CH_3OH	20	54.5
C_2H_5OH	20	42.4
	30	76.1
i-C_3H_7OH	20	II only
	30	II only

The figures indicate that II is the main product in the reactions.

Rate Constants. The rates of the reactions were followed by measuring a decrease in the concentration of isobutylene oxide under conditions where the molar ratio of an alcohol to the epoxide was kept at 10 and the range of the concentration of boron trifluoride etherate was *ca.* 1.0×10^{-3} to *ca.* 4.0×10^{-3} mol/*l*.

The data of a decrease in the concentration of the epoxide were found to obey the standard first-order kinetic equation:

$$k_1 = \frac{1}{t}\log\frac{a}{a-x} \qquad (2)$$

where a is the initial concentration and x is the instantaneous concentration at time t of the epoxide, respectively. When k_1 was plotted against the initial concentration of the catalyst for the reaction with ethyl alcohol, a straight line was obtained as shown in Fig. 1. Similar results were obtained for other alcohols.

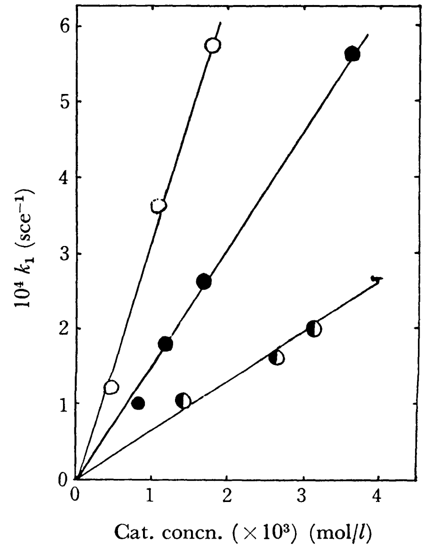


Fig. 1. Relation between rate constants and catalyst concentrations (EtOH).
○ 40°C, ● 30°C, ◐ 20°C

From the results the following equation was obtained.

$$k_1 = k_2[\mathrm{C_0}] \qquad (3)$$

where $[\mathrm{C_0}]$ is the initial concentration of the catalyst.

Therefore, the rate equation can be written as

$$\frac{-\mathrm{d[epoxide]}}{\mathrm{d}t} = k_2[\mathrm{C_0}]\,[\mathrm{epoxide}] \qquad (4)$$

The results of the rate measurements are tabulated in Table 1 together with the activation parameters.

It is evident from the results in Table 1 that the variations in the rates of the ring-opening reaction of isobutylene oxide are largely due to changes in the entropy of activation ($\Delta S^{\neq}$).

In their discussion of the acid-catalyzed hydration of olefins, Taft *et al.*[6,7] suggested that an A-1 reaction should be characterized by relatively more positive entropies of activation than an A-2 reaction.

---

[5] J. Koskikallio and E. Whalley, *Trans. Faraday Soc.*, **55**, 815 (1959).

[6] R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **74**, 5374 (1952).

[7] R. W. Taft, Jr., E. L. Purlee, P. Riesz and G. A. De Frazio, *ibid.*, **77**, 1584 (1955).

Table 1. RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE RING-OPENING REACTION OF ISOBUTYLENE OXIDE IN ALCOHOLS

Alcohol	10°C	k_2 $l\cdot mol^{-1}\cdot sec^{-1}$			E kcal·mol^{-1}	$\Delta S^{\neq}$ (20°C) e.u.
		20°C	30°C	40°C		
CH_3OH	1.20×10^{-1}	3.25×10^{-1}	6.60×10^{-1}	—	14.4	−13.5
C_2H_5OH	—	6.71×10^{-2}	1.58×10^{-1}	3.30×10^{-1}	14.9	−15.0
n-C_3H_7OH	—	2.75×10^{-2}	6.25×10^{-2}	1.50×10^{-1}	14.8	−17.9
i-C_3H_7OH	—	1.23×10^{-2}	2.97×10^{-2}	6.00×10^{-2}	14.9	−18.7

Table 2. VALUES OF $\Delta S^{\neq}$ FOR SEVERAL ACID-CATALYZED HYDROLYSES IN AQUEOUS SOLUTION

Substrate	Mechanism	$\Delta S^{\neq}$ (e.u.)
Ethyl orthoformate[a]	A-1	+5.8
Sucrose[b]	A-1	+7.9
Methylal[c]	A-1	+7.3
Dimethoxymethane[d]	A-1	+6.8
Dialkoxyethane[d]	A-1	$+7.0\sim+13$
Alkyl-1,3-dioxolane[e]	A-1	$-3.8\sim+7.9$
Benzaldehyde diethyl acetals[f]	A-1	$+7.0\sim+2.0$
2-(Substituted phenyl)-1,3-dioxolanes[f]	A-1	$-6.9\sim-9.6$
Methyl orthobenzoate[g]	A-1	+8.4
Ethyl orthobenzoate[h]	A-1	−0.3
Ethyl orthoacetate[h]	A-1	+5.5 (40% dioxane)
Methoxymethyl acetate[i]	A-1	+3.7
Methoxymethyl formate[i]	A-1	+2.7
Methyl acetate[b]	A-2	−21.3
Ethyl acetate[b]	A-2	−23.0
γ-Valerolactone[j]	A-2	−24.6
γ-Butyrolactone[j]	A-2	−20.9

a) F. Bresica and V. K. Lamer, *J. Amer. Chem. Soc.*, **62**, 612 (1940).
b) E.A. Moelwyn-Hughes, "Kinetics of Reactions in Solution," Second Edition, Oxford University Press, Oxford, (1947), p. 321.
c) D. McIntyre and F. A. Long, *J. Amer. Chem. Soc.*, **76**, 3240 (1954).
d) J. Koskikallio and E. Shalley, *Trans. Faraday Soc.*, **55**, 809 (1959).
e) P.Salomaa and A.Kankaanperä, *Acta Chem. Scand.*, **15**, 871 (1961).
f) T. H. Fife and L. K. Jao, *J. Org. Chem.*, **30**, 1492 (1965).
g) J. G. Fullington and E. H. Cordes, *ibid.*, **29**, 970 (1964).
h) R.H. Dewolfe and J.L. Jensen, *J. Amer. Chem. Soc.*, **85**, 3264 (1963).
i) P. Salomaa, *Suomen Kemistilehti*, **B33**, 11 (1960).
j) F. D. Coffin and F. A. Long, *J. Amer. Chem. Soc.*, **74**, 5767 (1952).

Schaleger and Long[8] reported that the entropies of activation should be used as a criterion of mechanism for acid-catalyzed reactions in aqueous solution.

Whalley[9] further deduced that (i) if $\Delta S^{\neq}$ was less than zero then the reaction was probably A-2 and (ii) if $\Delta S^{\neq}$ was greater than zero the mechanism could be either A-1 or A-2. Stimson *et al.*[10,12] showed that the hydrolyses of *t*-butyl benzoate and *t*-butyl formate in acidified 60% acetone-water gave the $\Delta S^{\neq}$ values of +9.5 and −23.7 e.u., respectively, indicating that the former hydrolysis proceeds by an A-2 mechanism and the latter by an A-2 mechanism and that the hydrolysis of *t*-butyl 2,4,6-trimethylbenzoate in acidified 90% ethanol-water gave an $\Delta S^{\neq}$ of +8.1 by an A-1 mechanism.

Further examples that show the relation between $\Delta S^{\neq}$ and mechanism are listed in Table 2. The data in Table 2 show that the $\Delta S^{\neq}$ values fall into two groups, corresponding to the two types of mechanism. The $\Delta S^{\neq}$ values in Table 1 are closer to the value for the A-2 reactions rather than for the A-1 reactions. Therefore, we conclude that A-2 mechanism holds for the acid-catalyzed ring-opening reaction of isobutylene oxide.

Relationship between Rate Constants and Dielectric Constants of Media. The relationship between reaction rates and dielectric constants of media (D) have so far been studied by many investigators. Hiromi[12] further developed the theories of Kirkwood[13] and Laidler *et al.*[14] and concluded that the slope in a plot of logarithms of k_2 against reciprocals of dielectric constants of media was less than about −150 for A-1 reactions and greater than about −100 for A-2 ones. Hiromi's theory was applied by Parker *et al.*[15] to elucidate the mechanism of the reaction of benzylamine with 1,2-epoxyethylbenzene.

---

[8] L. L. Schaleger and F. A. Long, "Advances in Physical Organic Chemistry," Vol. 1, ed. by V. Gold, Academic Press Inc., London (1963), p. 1.

[9] E. Whalley, *Trans. Faraday Soc.*, **55**, 798 (1959).

[10] V. R. Stimson, *J. Chem. Soc.*, **1955**, 4020.

[11] V. R. Stimson and E. J. Watson, *ibid.*, **1954**, 2848.

[12] K. Hiromi, This Bulletin, **33**, 1251 (1960).

[13] J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

[14] K. J. Laidler and P. A. Landskroener, *Trans. Faraday Soc.*, **52**, 200 (1956).

[15] R. E. Parker and B. W. Rockett, *J. Chem. Soc.*, **1965**, 2569.

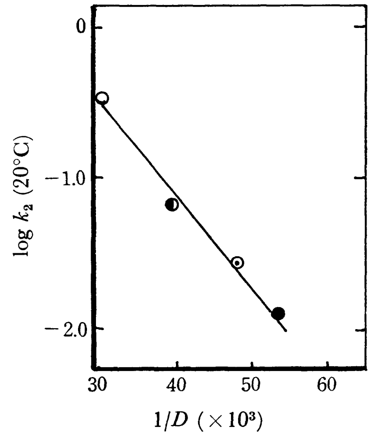


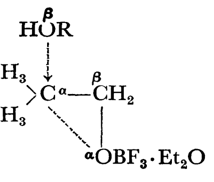
Fig. 2. Relation between rate constants and dielectric constants.
○ Methyl alcohol, ◐ Ethyl alcohol
⊙ n-Propyl alcohol ● Isopropyl alcohol

As shown in Fig. 2, the slope is −61.2, indicating that the reaction under investigation proceeds by a bimolecular process.

Our result is in agreement with the conclusion of Koskikallio *et al.*[5]

As shown in Table 1, the $\Delta S^{\neq}$ values for this ring-opening reaction are a little larger than those for the usual A-2 reactions and the rates increase in the increasing order of the polarity of alcohols.

As Parker *et al.*[1] proposed, we assume that the transition state for this ring-opening reaction is as follows:



where the extent to which bond breaking (C^{α}–O^{α}) has progressed is larger than the extent to which bond forming (C^{α}–O^{β}) has progressed. As the crowding in such a transition state should be less than the one in the usual bimolecular reaction, the lower $\Delta S^{\neq}$ values would be expected.

We conclude that this ring-opening reaction may be a borderline case between A-1 and A-2 reactions, but essentially is an A-2 reaction.

Experimental

Materials. *Alcohols.* Commercial reagents were purified by the usual procedures.

Boron Trifluoride Etherate. Commercial reagent of boron trifluoride etherate was distilled under a nitrogen atmosphere before use, bp 124.0—125.0°C.

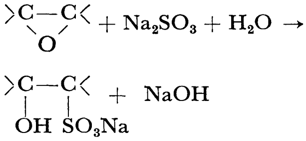
Isobutylene Oxide. Isobutylene chlorohydrin was prepared from isobutylene and hypochlorous acid according to the method of Michael *et al.*,[16] bp 63.0—65.0°C/74 mmHg (lit, 128—129°C[16]).

Found: C, 44.18; H, 8.20%. Calcd for C_6H_9OCl: C, 44.27; H, 8.31%.

The yield was 40% (based upon isobutylene).

Isobutylene oxide was prepared according to the method of Ishida,[17] bp 49.6—60.2°C (lit, bp 50°C[17]). The yield was 83% (based on isobutylene chlorohydrin). n_D^{20} 1.3732 (lit, 1.3730[17]).

Kinetic Measurements. The reaction was followed by the determination of isobutylene oxide according to the method of Swan.[18] About 1.0 g of a sample was pipetted out at different times from the reaction mixture and added to 30 m*l* of a saturated aqueous sodium sulfite solution. Sodium sulfite reacted smoothly and quantitatively with the epoxide, liberating an equivalent of sodium hydroxide.



$$\underset{\text{O}}{\text{>C—C<}} + Na_2SO_3 + H_2O \rightarrow \underset{\text{OH}\ \ \text{SO}_3\text{Na}}{\text{>C—C<}} + NaOH$$

The epoxide was determined by the titration of liberated sodium hydroxide with standard hydrochloric acid. A simple kinetic data for a representative run is shown in Table 3.

TABLE 3. SIMPLE KINETIC DATA FOR THE RING-OPENING REACTION OF ISOBUTYLENE OXIDE IN ETHYL ALCOHOL[a]

Time min	Sample pipetted g	Titer[b] HCl cc	Epoxide %	$10^2 k_1$ min^{-1}
0	—	—	13.52	—
14.63	0.9643	6.08	8.23	3.43
20.84	1.0949	5.67	7.09	3.31
26.70	1.1812	5.30	6.40	3.11
32.39	1.0100	3.45	4.47	3.40
38.58	1.0543	3.00	3.72	3.33
44.42	1.3086	3.13	3.14	3.27
50.38	1.2392	2.68	2.83	3.08
			Average:	3.37

a) Concentration of $BF_3 \cdot Et_2O$ was 3.55×10^{-3} mol/*l*.
b) Concentration of HCl was 0.1792 N.

Measurement of Dielectric Constants. Dielectric constants of the mixtures of isobutylene oxide and alcohols were measured by the phase difference compensation method with a Shibayama SS-207 type apparatus (Shibayama Scientific Co.).

---

[16] A. Michael and V. L. Leighton, *Ber.*, **39**, 2157 (1906).
[17] S. Ishida, This Bulletin, **33**, 924 (1960).
[18] J. D. Swan, *Anal. Chem.*, **26**, 878 (1954).