

THE RING-OPENING REACTIONS OF PROPYLENE OXIDE WITH CHLOROACETIC ACIDS

HIROSHI KAKIUCHI* and TAKAO IJIMA

Department of Applied Chemistry, Faculty of Engineering, Yokohama National University, Mimami-ku, Yokohama, 232, Japan

(Received in Japan 27 April 1979)

Abstract—The association constants, K_a , of dichloroacetic acid (DCA) with ethers (tetrahydrofuran, tetrahydropyran, dibutyl ether, 1,4-dioxane) were measured in CCl_4 from 20°–40° using near IR spectra. A linear relationship between $\log_{10}K_D$ and $\log_{10}K_p$ was found, where K_p was the association constant of phenol with ethers. On the basis of their relationship the association constants of DCA with propylene oxide (PO) were estimated from those of phenol with PO. Furthermore, the ring-openings of PO with chloroacetic acids (trichloroacetic acid (TCA) or DCA) were studied kinetically in toluene. It was found that the PO-TCA reactions obeyed the second-order kinetics dependent on the first order both in the PO concn and in the TCA concn, and that the PO-DCA reactions obeyed the third-order kinetics on the first order in the PO concn and on the second order in the DCA concn. The elementary reaction rate constants were estimated on the basis of measured rate constants and estimated equilibrium constants and activation enthalpies were obtained from their temp dependence to be 13.5 kcal/mol in the PO-TCA reaction and 19.7 kcal/mol in the PO-DCA reaction. The mechanism was based on the activation enthalpy of elementary reaction and it was concluded that the main factor governing the reaction was the extent of activation of the protonated oxirane (the extent of polarization of the C–O bond in the oxirane ring).

Oxirane has considerable ring-opening reactivity due to both the ring strain and the basicity of the O atom in the ring. There are many reports on the ring-opening of oxirane with either nucleophiles or electrophiles.¹ A kinetic study is useful in the investigation of the ring-opening of oxirane. In the protonic-acid catalysed ring-opening of oxirane there is a preliminary equilibrium between the O atom in the ring and the protonic acid followed by the ring-opening of the protonated oxirane as rate-determining step.² In such a reaction the measured rate constant contains the above equilibrium constant. In order to clarify the mechanism of the ring-opening, we believed that it is necessary to evaluate the above equilibrium constant, to analyse the elementary reaction rate constant and to speculate on the behavior of the protonated oxirane in the transition state. However, it is impossible to measure directly the association constant of a strong acid with oxirane owing to its great reactivity. In the preceding paper³ we found that there was a linear relationship between $\log_{10}K_p$ and $\log_{10}K_T$, where K_p and K_T are the association constant of phenol with ethers and that of TCA with ethers, respectively. On the basis of this relationship, the association constant of TCA with oxirane was estimated from that of phenol with oxirane.

The purpose of this paper is to estimate indirectly the association constant of dichloroacetic acid (DCA) with oxirane, to study kinetically the ring-opening of oxirane with the protonic acid (TCA and DCA), to analyse the elementary reaction rate constant and to investigate the ring-opening reactivity of oxirane. Propylene oxide (PO) was used as an oxirane, which provided information on the orientation of the ring scission.

EXPERIMENTAL

Reagents. Ethers, CCl_4 and TCA were purified as described.³ DCA was a reagent grade and distilled twice under reduced pressure just before use for each IR measurement. Other reagents were purified by the usual method.

Measurements of the association constants of dichloroacetic acid with ethers. All spectral measurements were made in CCl_4 under flushing dry air by use of a Hitachi Model 230 double beam IR spectrometer with water-jacketed cells of path-length 20 mm. Details on measurements were described in the preceding paper.³ The integrated intensity, A , of the free OH band of DCA and dissociation constants, K_a , of the DCA dimer in CCl_4 were obtained at five temps, 20°, 25°, 30°, 35° and 40°. The initial formal concns of DCA were in the range of ca. 4×10^{-4} to 4×10^{-3} M and at least ten solns were measured for each temp. In the equilibria of DCA with ethers the concns of the monomeric DCA, C_i , were obtained from the integrated intensity, A , of the free DCA and association constants, K_D , were calculated from eqn (1).

$$K_D = \frac{[C_{0,t} - C_i - (2C_i^2/K_a)]}{[C_i][B_{0,t} - C_{0,t} + C_i + (2C_i^2/K_a)]} \quad (1)$$

where B_0 and C_0 are the initial formal concns of ethers and DCA, respectively, and the subscript t designates the temp at which measurement was made. In all cases the initial formal concns of ethers and DCA were ca. 10^{-2} – 10^{-3} and ca. 10^{-3} M, respectively, and corrected only for density changes of CCl_4 is the same manner as in the TCA-ethers system.³ For each DCA-ether pair, 2–3 solns were measured.

Kinetic measurements. The reaction was carried out under dry N_2 in 100 ml 4-necked flask equipped with a thermometer, a stirrer and a cooler. The temp was controlled within $\pm 0.1^\circ$ in a thermostat. Reaction rates were measured by the determination of the residual PO under the following glc conditions: for PO-TCA system; internal standard, CHCl_3 ; Silicon DC 550 20%, 150 cm \times 3 mm; column temp, 85°; carrier gas, He 50 ml/min; for PO-DCA system; internal standard, CH_2Cl_2 or Benzene; Diethylene glycol succinate 20%, 150 cm \times 3 mm; column temp, 60°; carrier gas, He 50 ml/min.

Product analyses

The reaction of PO with TCA. TCA (23.0 g, 0.14 mol) was dissolved in toluene (50 ml), refluxed gently under N_2 , a PO toluene soln (8.1 g, 0.14 mol in 10 ml) added dropwise for 30 min and then refluxed for 1 hr. After the reaction was over, the soln was washed three times with cold water, dried over MgSO_4 , and the solvent was evaporated. The crude product in a 94% yield

was then distilled, yield 38% (11.9 g), b.p. 76.0°–76.2°/0.09 Torr. (Found: C, 27.06; H, 3.43; Cl, 48.19. Calc. for $C_3H_7O_3Cl_3$: C, 27.11; H, 3.19; Cl, 48.03%). This material was analysed to be a mixture of (2-hydroxy)propyl trichloroacetate, 1a (53%) and iso-(2-hydroxy)propyl trichloroacetate, 1b (47%) as follows. In NMR spectrum (CCl_4) the signals of two Me protons were partly overlapped (δ 1.25, d and δ 1.35, d), but the methine proton of 1b ($CHOCOCCl_3$, δ 5.04, m) was well separated from other protons. And then the product ratio of 1a and 1b was analysed based on the integral value of methine proton of 1b. The mixtures in kinetic runs were treated in the same manner as the synthesis of authentic sample and analysed by NMR.

The ring-opening of PO with DCA. DCA (31.2 g, 0.243 mol) was dissolved in toluene (20 ml), a PO toluene soln (11.2 g, 0.193 mol in 30 ml) added dropwise at room temp. during 2 hr and then stirred at 50°–60° for 22 hr. After the reaction was over, the residual DCA was neutralized with dil Na_2CO_3 aq extracted six times with $CHCl_3$, dried over $MgSO_4$ and the solvent was evaporated. The crude product was distilled, yield 36% (13.1 g), b.p. 82°/0.7 Torr. In NMR spectrum (CCl_4) both the signals of two Me protons (δ 1.21, d and δ 1.28, d) and those of two methine protons ($CHCl_2COO$, δ 5.98, s, and δ 6.01, s) were partly overlapped, but methine proton ($CHOCOCHCl_2$, δ 5.00, m) was well separated. This material was analysed to be a mixture of (2-hydroxy)propyl dichloroacetate, 2a, and iso-(2-hydroxy)propyl dichloroacetate, 2b, by NMR. The product ratio (66:34) obtained from the integral values of Me protons on the basis of the methine proton agreed with that (66:34) obtained from the methine protons ($CHCl_2CO$).

RESULTS

Estimation of the association constants of dichloroacetic acid with propylene oxide. The integral in-

tensity, A , of the free OH band of DCA in ca. 3508 cm^{-1} and the dissociation constants of DCA dimer, K_d , are shown in Table 1. The integrated intensity of DCA was approximately constant and its average value 3.88×10^4 agreed with that of TCA (3.95×10^4). The temp. dependence of dissociation of the DCA dimer, K_d , was obtained by the least squares method and expressed by the following equation

$$\log_{10} K_d = 5.20 - 2.37 \times 10^3(1/T) \quad (2)$$

where T is a absolute temp. (°K).

The dissociation constant of the DCA dimer in CCl_4 was measured by using IR spectra,⁴⁻⁶ but there was poor agreement among these results. The association constant, K_D , of DCA with ether was calculated from eqn (1). It was assumed that the dissociation constant of the DCA dimer was not influenced in the presence of ethers and that the species of the DCA-ether association existed as a 1:1 complex in excess of ethers. The results in the DCA-ether systems are collected in Table 2. The ethers used were THF, THP, BuE and 1,4-Dox. The association constant of DCA with ether has not been reported.

Figure 1 shows a relationship of the association constant, K_p , of phenol with ethers and those, D_D , of DCA with ethers in CCl_4 . The plot of the logarithm of K_p vs that of D_D shows a linearity, where both K_p and D_D contain all the values measured on all the ethers used except 1,4-Dox in the temp range 20°–40°. The relation-

Table 1. Integrated intensities of monomer band, A , half-intensity band widths, $\Delta\nu_{1/2}$ and dissociation constants, K_d , of DCA dimer

temp. (°C)	20	25	30	35	40
$A \times 10^{-4}$ (intens. unit)	4.02	3.93	3.81	3.85	3.78
$\Delta\nu_{1/2}$ (cm^{-1})	45.8	46.3	45.8	46.2	46.7
$K_d \times 10^3$ (M)	0.395	0.584	0.782	1.06	1.42

Table 2. Association constants and thermodynamic parameters for DCA-ethers system

ether	$K_D \times 10^{-2}$ ^a (M^{-1})	$-\Delta H$ (kcal/mol)	$-\Delta F_{298}$ (kcal/mol)	$-\Delta S_{298}$ (e. u.)
THF	9.63 ± 0.69	7.07 ± 0.57	4.07 ± 0.04	10.06 ± 2.07
THP	7.33 ± 0.29	5.57 ± 0.33	3.91 ± 0.02	5.57 ± 1.17
BuE	3.06 ± 0.24	6.39 ± 0.54	3.39 ± 0.05	10.04 ± 1.97
1,4-Dox	1.31 ± 0.05	4.76 ± 0.34	2.89 ± 0.02	6.27 ± 1.21
PO	4.33 ^b	5.31 ^b	3.60 ^b	5.73 ^b

^a At 25°. ^b Estimated values.

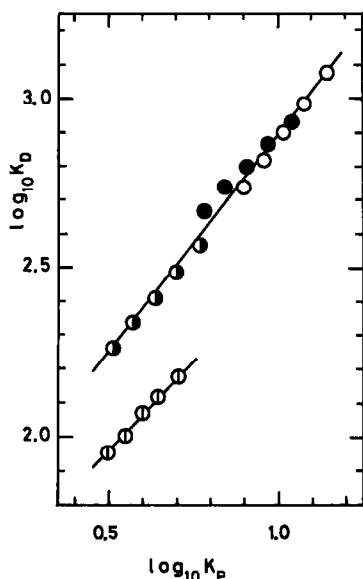


Fig. 1. The relationship between the association constants of phenol with ethers, K_p , and those of DCA with ethers, K_D : O, THF; ●, THP; ○, BuE; ◇, 1,4-Dox.

ship is expressed by eqn (3) and its correlation coefficient is 0.993.

$$\log_{10} K_D = 1.282 \log_{10} K_p + 1.609. \quad (3)$$

The association constant of DCA with PO was estimated from eqn (3) on the basis of the association constant of phenol with PO. The estimated association constants of the DCA-PO system are shown in Table 2. The relationship of K_p with K_D corresponds with that of K_p with K_T .† The slope of the linear line in the former was smaller than that in the latter. The slope of the linear line is believed to decrease with the acidity of carboxylic acid.

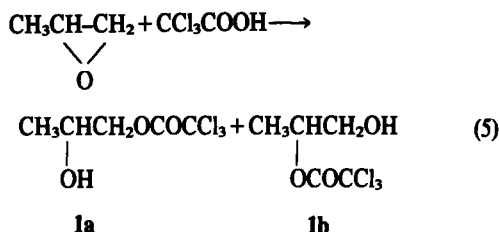
†The relationship of K_p with K_T was expressed as follows.³
 $\log_{10} K_T = 1.460 \log_{10} K_p + 1.726$

The ring-opening reactions of propylene oxide with chloroacetic acids. The ring-opening of PO with TCA was studied kinetically in toluene as a solvent at 0°–40°. The initial concns of PO and TCA were *ca.* 0.076–0.126 M and 0.104–0.268 M, respectively, and the initial mole ratios (TCA/PO) were controlled more than unity. The reactions of PO with TCA were found to obey the second-order kinetics dependent on the first order both in the PO concn and in the TCA concn,

$$-\frac{d(b-x)}{dt} = k_2(a-x)(b-x) \quad (4)$$

where $(a-x)$ and $(b-x)$ were the concn of TCA and PO at time t , respectively.

Arrhenius plot of the rate constant, k_2 , gave a straight line and activation energy, E_a , was calculated from the temp. dependence of reaction rates by the least squares method. Activation parameters were obtained from the Eyring eqn (Table 3). The protonic-acid catalysed ring-opening of PO, one of the unsymmetric substituted oxirane, is known to give two kinds of isomers where its product ratio changes dependent on the reaction conditions.¹ The products were a normal product, 1a, and an abnormal product, 1b, and the product ratios were analysed by NMR spectra as shown in Table 4.



The ring-opening of PO with DCA was carried out in toluene at 30°–50°, where the initial concns of PO and DCA were *ca.* 0.070–0.288 M and 0.242–0.565 M, respectively. The reaction of PO with DCA was found to obey the third-order kinetics dependent on the first order in

Table 3. Rate constants and activation parameters for the ring-opening of PO

acid	TCA		DCA		
	temp. (°C)	$k_2 \times 10^3$ (M ⁻¹ .s ⁻¹)	number of expts	$k_3 \times 10^3$ (M ⁻² .s ⁻¹)	number of expts
	0	0.399 ± 0.047	2	—	—
	20	1.19 ± 0.16	3	—	—
	30	1.73 ± 0.28	3	0.537 ± 0.049	3
	40	2.68 ± 0.17	2	1.09 ± 0.09	3
	45	—	—	1.76 ± 0.12	3
	50	—	—	2.45 ± 0.19	4
ΔH^\ddagger (kcal/mol)		7.4 ± 0.3		14.3 ± 0.4	
ΔS^\ddagger (e. u.)		-46.7 ± 1.3		-26.4 ± 1.4	

Table 4. Product ratios in the ring-opening of PO

temp. (°C)	PO-TCA		PO-DCA	
	1a	1b	2a	2b
0	61	39	—	—
20	57	43	—	—
30	52	48	53	47
40	46	54	54	46
50	—	—	56	44

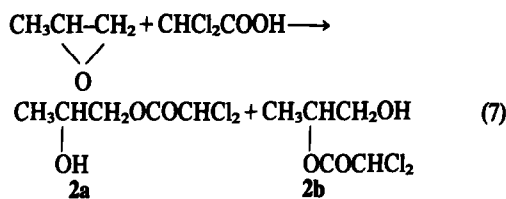
the PO concn and on the second order in the DCA concn,

$$-\frac{d(b-x)}{dt} = k_3(c-x)^2(b-x) \quad (6)$$

where $(c-x)$ and $(b-x)$ were the concns of DCA and PO at time t , respectively.

The temp. dependence of reaction rates showed a straight line. Activation parameters were calculated in the same manner as in the PO-TCA reaction. Results were collected in Table 3.

The reaction of PO with DCA proceeded as shown in eqn (7). The product ratios of two kinds of isomers were analysed by NMR spectra (Table 4).



DISCUSSION

In a few papers on the kinetic study of the ring-opening of oxirane with protonic acids in nonaqueous solvents, hydrogen halides were mainly used.^{2,7,8} However, it is difficult to determine the equilibrium

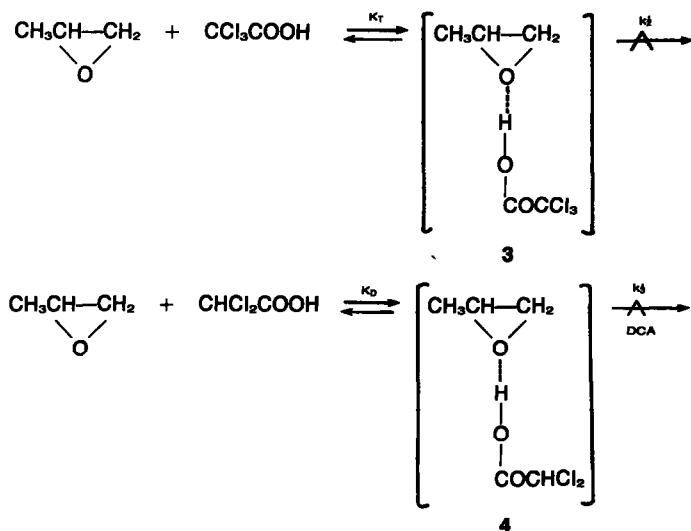
constant of oxirane with hydrogen halides. The ring-opening of oxirane with the carboxylic acid in nonaqueous solvent has been studied kinetically only in the reaction of PO with acetic acid.⁹ We clarified that the equilibrium constant of PO with the strong carboxylic acid could be estimated by IR spectrometry.³ Accordingly, the ring-opening of oxirane with the carboxylic acid is believed to be interesting, for the elementary reaction rate constant of ring-opening of the protonated oxirane can be obtained on the basis of the estimated equilibrium constant.

In this paper we estimated the association constant of PO with DCA and studied kinetically the ring-opening of PO with chloroacetic acids (TCA and DCA). They gave the different kinetics dependent on the acidity of chloroacetic acids and proceeded in the different mechanism. The reaction of PO with TCA obeyed the second-order kinetics on the first order both in the PO concn and in the TCA concn, which suggested that the protonated PO in the PO-TCA reaction could be cleaved unimolecularly in the transition state. On the other hand, the reaction of PO with DCA gave the third-order kinetics on the first order in the PO concn and on the second order in the DCA concn. The observed second-order dependence of the rate on DCA implied that the 1:1 adduct of PO with DCA was less reactive than that of PO with TCA and that a second molecule of DCA participated in the transition state of the rate-determining step. These mechanisms are shown in Scheme 1. In such mechanisms the stability of the 1:1 complex of PO with chloroacetic acid (3 or 4) is thought to govern the reactivity to a considerable extent. We believe that the analysis of elementary rate of the ring cleavage provides information on the stability of the protonated oxirane.

The measured rate constants k are the apparent ones and contain the equilibrium constants. If the ring scission is the rate-determining step, as usually assumed, the apparent rate constant is expressed as the product of the equilibrium constant, K , and the elementary reaction rate constant, k' .

In the reaction of PO with TCA the apparent rate constant k_2 is expressed by eqn (8),

$$k_2 = k_2'K_T \quad (8)$$



Scheme 1.

In the PO-DCA reaction system the apparent rate constant k_3 is expressed as follows,

$$k_3 = k'_3 K_D \quad (9)$$

Elementary rate constants were calculated from the above equations on the basis of the estimated association constants of PO with chloroacetic acids. Arrhenius plots are shown in Fig. 2. Elementary reaction rate constant and activation parameters are collected in Table 5. Since the ring-opening polymerisabilities of cyclic compounds were studied thermodynamically by Dainton *et al.*,¹⁰ the change in the enthalpy has been thought to correlate with the ring strain. Isaacs¹¹ reported that the difference in the activation enthalpy correlated with that in the ring strain of the reactants in the reaction of PO and propylene sulfide with aniline.

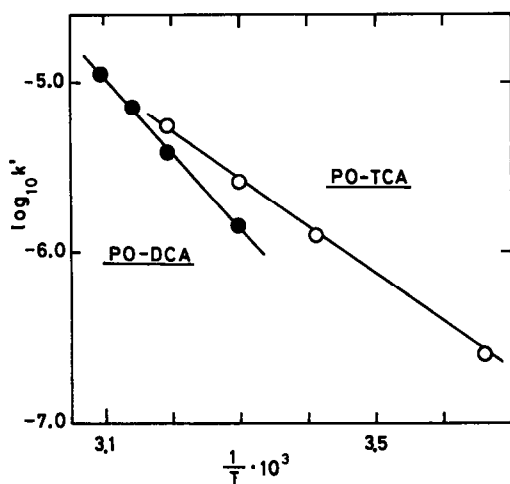


Fig. 2. Arrhenius plots of the elementary rate constants for the ring-opening of the protonated PO: O, PO-TCA reaction; ●, PO-DCA reaction.

The elementary reaction of ring-opening of the protonated PO is the nucleophilic substitution of the protonated PO and its activation enthalpy is thought to reflect the energy difference between the protonated PO and the transition state of the ring-opening step. The activation enthalpy of ring-opening of the protonated PO in the PO-TCA reaction is considerably smaller than that in the PO-DCA reaction. This fact suggests that the oxirane ring protonated by TCA is activated to a larger extent than that by DCA. Such an activation can be explained as follows: the oxirane ring protonated by the stronger acid, TCA, weakens its C-O bond, and consequently the partial positive charge of the C atom increases, and such an increase in the partial positive charge enables the gegen anion ($^{\ominus}\text{OCOC}\text{Cl}_3$) to attack the oxirane ring. In such reactions, it is believed that the carbonium ion can not be produced, as it can be solvated to a very slight extent in nonpolar aprotic solvents, and that the ring-opening proceeds in the $\text{S}_{\text{N}}2$ type mechanism. The large negative value of the activation entropy agrees also with the $\text{S}_{\text{N}}2$ type mechanism. The observed second-order kinetics in the PO-TCA reaction could be reasonably explained as the result of activation of elementary reaction of the ring-opening in the reaction of PO with DCA was larger than that in the reaction of PO with TCA and the kinetics in the former showed the second-order dependence on DCA. These results suggest that the 1:1 complex of PO with DCA is activated to a lesser extent and that the ring cleavage process of participation of two molecules of DCA is predominant in the transition state. Accordingly, the reaction of PO with TCA was accelerated to a larger extent owing to the development of the partial positive charge in the oxirane ring due to the protonation (the pull process), but in the PO-DCA reaction the attack of another molecule of DCA toward the protonated oxirane (the push process) is more important in the transition state. The free energy change in the PO-TCA reaction system is schematically shown in Fig. 3. The energy level A of the protonated

Table 5. Estimated elementary rate constants, k' , for the ring-opening of protonated PO

acid	T C A			D C A		
	temp. (°C)	$k_2 \times 10^3$ ($\text{M}^{-1} \cdot \text{s}^{-1}$)	$K_T \times 10^{-2}$ (M^{-1})	$k'_2 \times 10^6$ (s^{-1})	$k_3 \times 10^3$ ($\text{M}^{-2} \cdot \text{s}^{-1}$)	$K_D \times 10^{-2}$ (M^{-1})
0	0.399	20.1	0.199	—	—	—
20	1.19	9.38	1.27	—	—	—
30	1.73	6.66	2.60	0.537	3.74	1.44
40	2.68	4.84	5.54	1.09	2.83	3.85
45	—	—	—	1.76	2.47	7.13
50	—	—	—	2.45	2.17	11.3
ΔH^\ddagger (kcal/mol)	7.4		13.5 ^a	14.3		19.7 ^a
ΔS^\ddagger (e.u.)	-46.7		-39.6 ^a	-26.4		-20.5 ^a

^a The activation parameters of elementary reaction of the ring-opening.

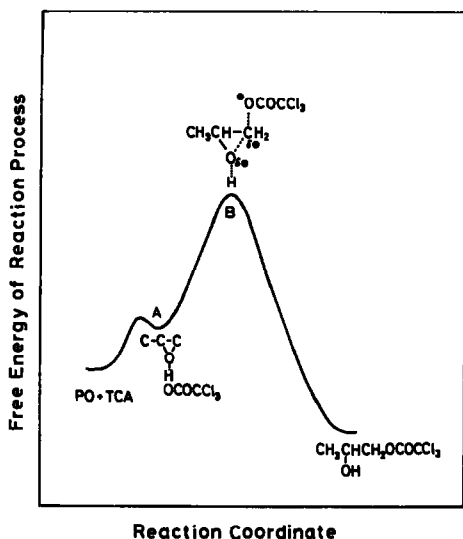
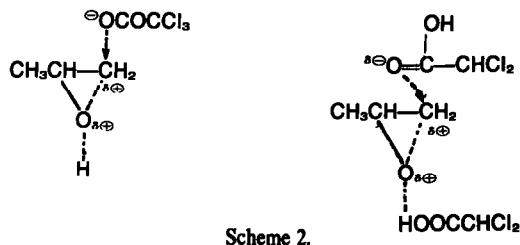


Fig. 3. Energy profile of ring-opening in the PO-TCA reaction system.

oxirane would be lower in the PO-DCA reaction system. Considering the transition state shown in Scheme 2, the energy level *B* of the PO-DCA reaction is thought to be a higher than that of the PO-TCA reaction, because the nucleophilicity of $^{\ominus}\text{OCOCCl}_3$ is greater than that of DCA molecule.[†]

We reported that the reaction of PO with hydrogen chloride in toluene obeyed the second-order kinetics dependent on the first order with respect to both the PO and HCl concns.⁷ But the mechanism could not be discussed in detail, as the preliminary equilibrium constant



Scheme 2.

[†]The unimolecular ring cleavage of the 1:1 complex in the PO-TCA reaction is thought to be subject to the greater steric hindrance than the ring cleavage in the PO-DCA reaction. Such a steric hindrance would make the energy level of transition state of the former slightly higher. The $\text{S}_{\text{N}}1$ type substitution is known as an extreme mechanism of such a reaction. But it could not be decided whether the reaction proceeded in the usual $\text{S}_{\text{N}}2$ type or in the $\text{S}_{\text{N}}1$ type, as the information on retention of configuration or racemisation could not be obtained in the reaction of PO with TCA.

[‡]The product ratio of two kinds of propylene chlorohydrins was 67:33 (normal:abnormal) in toluene in the PO-HCl reaction.⁷

of protonation of the oxirane could not be obtained. The behavior of the PO-HCl reaction is very similar to that of the PO-TCA reaction in view of the kinetics, the apparent activation enthalpy (9.5 kcal/mol) and the regioselectivity of the ring cleavage.[‡]

The product ratios in Table 4 reflect the transition state in the carboxylic-acid catalysed ring-opening of oxirane in nonpolar solvents such as toluene. Long and Pritchard¹² studied the regioselectivity of ring cleavage in the perchloric-acid catalysed hydrolysis of PO at 25° and found that the abnormal product was predominant (ca. 70%), which was explained due to the stability of carbonium ion produced by the C-O bond scission of the oxirane ring. However, the nucleophilic substitution on the C atom of the protonated oxirane in nonpolar aprotic solvents proceeds in the $\text{S}_{\text{N}}2$ type mechanism, which is subject to the steric hindrance. In such reactions the protonations of the normal products increase compared with the reaction in aqueous soln. The increase in the normal product (1a and 2a) is due to such a steric hindrance in the nonpolar aprotic solvent.

In conclusion, the association constant of PO with DCA was estimated in the same manner as in that of PO with TCA. And then the activation enthalpy of the ring-opening step was estimated on the basis of the estimated equilibrium constant of PO with chloroacetic acids, where the estimated activation enthalpy of elementary reaction changed to a considerable extent dependent on the acidity of chloroacetic acids. Such a difference in the activation enthalpy could be explained based on the activation of protonated PO. It was clarified that the main factor giving the different kinetics was the extent of activation of the protonated oxirane.

Acknowledgements—The authors wish to express their thanks to Professor Minoru Hirota of Yokohama National University for his useful advice and kind permission to use an IR spectrophotometer for measurements of association constants.

REFERENCES

- R. E. Parker and N. S. Isaacs, *Chem. Rev.* **59**, 737 (1959).
- For example, G. Lamaty, R. Maleg, C. Selve, A. Sivade and J. Wyde, *J. Chem. Soc. Perkin Trans. 2*, 1119 (1975).
- T. Iijima and H. Kakiuchi, *Tetrahedron* **35**, 299 (1979).
- J. T. Harris and M. E. Hobbs, *J. Am. Chem. Soc.* **76**, 1419 (1954).
- D. Hadzi and J. Rajnvajn, *J. Chem. Soc. Faraday 1*, 151 (1973).
- J. A. Faniran, K. S. Patel and L. O. Nelson, *J. Phys. Chem.* **82**, 1018 (1978).
- H. Kakiuchi and T. Iijima, *Bull. Chem. Soc. Japan* **46**, 1569 (1973).
- G. Bellucci, G. Berti, G. Ingrassio, A. Vatteroni, G. Conti and R. Ambrosetti, *J. Chem. Soc. Perkin Trans. 2*, 627 (1978).
- N. S. Isaacs and K. Neelkantan, *Can. J. Chem.* **7**, 1043 (1968).
- F. S. Dainton, T. R. Devlin and P. A. Small, *Trans. Faraday Soc.* **51**, 1710 (1955).
- N. S. Isaacs, *Can. J. Chem.* **44**, 395 (1966).
- F. A. Long and J. G. Pritchard, *J. Am. Chem. Soc.* **78**, 2663 (1956).