Tetrahedron Vol. 35, pp. 303–308
© Pergamon Press Ltd., 1979. Printed in Great Britain

0040-4020/79/0301-0303/$02.00/0

THE RING-OPENING REACTIONS OF PROPYLENE OXIDE AND PROPYLENE SULFIDE WITH DIBUTYLAMINE

Hiroshi Kakiuchi,* Takao Iijima and Hideaki Horie
Department of Applied Chemistry, Faculty of Engineering, Yokohama National University, Minami-ku, Yokohama, 233 Japan

(*Received in Japan* 10 *May* 1978)

Abstract—The rates of ring-opening of propylene oxide (PO) and propylene sulfide (PS) with dibutylamine (DBA) were measured in the range 40°–70°. The PO–DBA reaction in toluene (Tol) was too slow to be studied in detail. The PO–DBA reaction in DMSO–benzene mixtures was quicker and found to be competitive between the second-order dependent on the first order both in the PO concentration and in the DBA concentration, and the third-order by the participation of reaction products. The PS–DBA reactions both in Tol and in DMSO–Tol mixtures were found to obey the same kinetics as the PO–DBA reaction. The order of reactivity is PS > PO. The PS–DBA reaction in DMSO–Tol mixtures was accelerated and the increase in reactivity of PS was based on the selective solvation of thiolate anion by DMSO in the transition state. The pull process was shown to be an important factor in the base-catalyzed ring-opening.

In 3- and 4-membered cyclic compounds, the ring strain depends on the ring structure and the basicity of the ring, the extent of polarization of the bond between the carbon and heteroatom in the ring is influenced considerably by the heteroatom (O, S or NH) of the ring.[1] The ring strain and the basicity of the rings confer the great reactivity on 3-membered heterocycles in comparison with the 4-membered and the other heterocycles. In spite of the low basicity in cyclic ethers, oxiranes show greater ring-opening reactivity based on the larger ring strain than in other cyclic ethers. Therefore, oxirane is an interesting compound to clarify the degree of contribution of both the ring strain and the basicity to the ring-opening reactivity. There are many reports on the ring-opening reactions of oxirane with both electrophiles and nucleophiles.[2] In order to discuss the ring-opening of 3-membered heterocycles, it is considered necessary to study a 3-membered cyclic sulfide (thiirane) or a 3-membered cyclic imine (aziridine) in addition to oxirane and to consider the effects of heteroatoms in the ring on the reactivities.

The purpose of this paper was to study kinetically the ring-opening of oxirane and thiirane with a secondary amine in aprotic solvents. Propylene oxide (PO) was used as a oxirane, propylene sulfide (PS) as a thiirane and dibutylamine (DBA) as a secondary amine. These unsymmetric substituted 3-membered heterocycles give information on the orientation of the ring scission. A 3-membered cyclic imine, e.g. propylenimine, was not used, because aziridine is difficult to react with bases.[3]

RESULTS

Dibutylamine was used as a secondary amine because of facility in the kinetic study. The ring-opening of PO with DBA was studied in various solvents at 60° where the initial concentration of PO and DBA was *ca.* 1.5 M and *ca.* 3.0 M, respectively. The ring-opening of PO with DBA was too slow and made the kinetic study in such nonpolar aprotic solvents as toluene (Tol) difficult. The reactions of PO with DBA were carried out in 1,4-dioxane, chlorobenzene, nitrobenzene and dimethyl sulfoxide (DMSO) as solvents. The reaction rate of PO with DBA was larger in DMSO and decreased in the following order, chlorobenzene, 1,4-dioxane, nitrobenzene and Tol. In the other solvents except DMSO, the reactions of the PO–DBA system were too slow to be studied in detail.

The time-conversion curves in the ring-opening reaction of PO with DBA in DMSO–benzene mixtures were S-shaped as shown in Fig. 1. The kinetic studies of

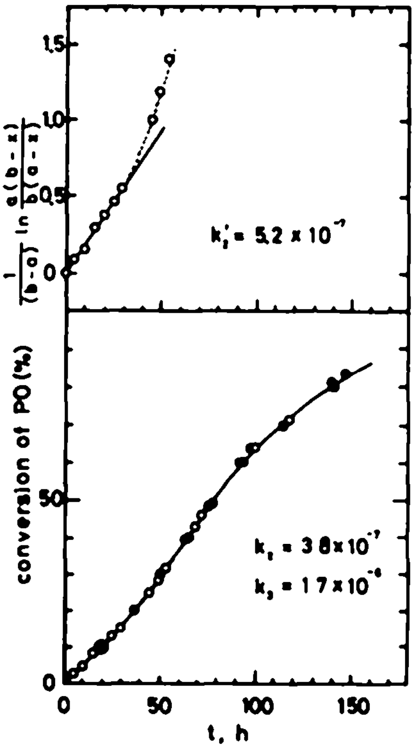
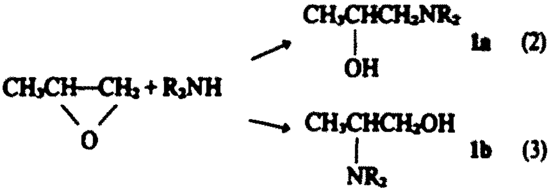


Fig. 1. The time-conversion curve in the reaction of PO with DBA in DMSO–benzene mixtures at 50° and its initial second-order plot: ○, found; ●, calc.

amine-catalyzed ring-opening of oxiranes have been reported in the reaction of oxiranes and various secondary amines in aqueous solution,[4] and in the reaction of PO with aniline in ethanol,[5] where the reaction rate was shown to obey the second-order kinetics dependent on the first order both in the oxirane concn and in the amine concn. The reaction of PO with DBA in DMSO–benzene mixtures obeyed approximately the second-order kinetics dependent on the first order of PO and DBA, respectively, only in the initial period, but the reaction was accelerated with an increase of the conversion per cent of PO and the obedience to second-order ones was found not to hold. Such behavior has been found in the ring-opening of PO with diethylamine (DEA) in bulk where Tiltacher[6] analyzed the reaction rate according to eqn (1). In the PO–DEA system the acceleration of the reaction was explained in terms of contribution of the second term which means the participation of the reaction product (RP) in the ring scission

$$-\frac{d(PO)}{dt} = k_2(PO)(DEA) + k_3(PO)(DEA)(RP) \quad (1)$$

where (PO), (DEA) and (RP) were the concn of PO, DEA and the reaction product at time t, respectively. The reaction product was 1-diethylamino-2-propanol, 1a ($R = C_2H_5$), a normal isomer produced as 1:1 adduct of PO and DEA. An abnormal product, 1b, was negligible under neutral or basic conditions.



$$CH_3CH\overset{O}{—}CH_2 + R_2NH \rightarrow CH_3\underset{OH}{CH}CH_2NR_2 \quad \mathbf{1a} \quad (2)$$

$$CH_3CH\overset{O}{—}CH_2 + R_2NH \rightarrow CH_3\underset{NR_2}{CH}CH_2OH \quad \mathbf{1b} \quad (3)$$

The reaction product of the ring-opening in the PO–DBA system was 1-dibutylamino-2-propanol, 1a, ($R = n\text{-}C_4H_9$). The rate constants in the PO–DBA reaction were calculated according to eqn (1) in the same manner as in the PO–DEA reaction.

When a and b were the initial concn of PO and DBA, respectively, and x the concn of PO consumed, eqn (1) was expressed by the following equation*

$$-\frac{d(a-x)}{dx} = k_2(a-x)(b-x) + k_3(a-x)(b-x)x. \quad (4)$$

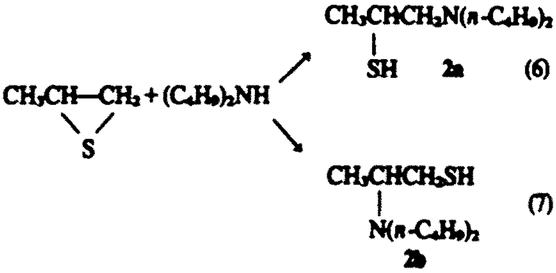
Integrating eqn (4) and substituting the initial conditions, eqn (4) became

$$t = \frac{\ln[(b-x)/b]}{(k_2+k_3b)(b-a)} - \frac{\ln[(a-x)/a]}{(k_2+k_3a)(b-a)} + \frac{k_3\ln[(k_2+k_3x)/k_2]}{(k_2+k_3a)(k_2+k_3b)} \quad (5)$$

where k_2 was approximately calculated from the slope of linear second-order plot of the first term on the right side of eqn (4) in the initial reaction of PO with DBA.

The values of k_2 and k_3 were calculated on the basis of the approximate value of k_2 by the curve-fitting method. Figure 1 shows the initial second-order plot and the calcd and found values in the conversion per cent of PO at 50°. The calcd ones were obtained from k_2, k_3 and the initial conditions by use of eqn (5). There is a good agreement between the calcd and found ones at any time t. The calcd values of rate constants are shown in Table 1. Arrhenius plots of k_2 and k_3 gave straight lines as shown in Fig. 2 and activation energies, E_a, were obtained from the temperature dependence of reaction rates. Activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, were obtained from the Eyring equation (Table 1).

The ring-opening of PS with DBA proceeded as in the PO–DBA reaction system.



$$CH_3CH\overset{S}{—}CH_2 + (C_4H_9)_2NH \rightarrow CH_3\underset{SH}{CH}CH_2N(n\text{-}C_4H_9)_2 \quad \mathbf{2a} \quad (6)$$

$$CH_3CH\overset{S}{—}CH_2 + (C_4H_9)_2NH \rightarrow CH_3\underset{N(n\text{-}C_4H_9)_2}{CH}CH_2SH \quad \mathbf{2b} \quad (7)$$

In the PS–DBA reaction system a normal product was 1 - dibutylamino - 2 - propanethiol, 2a and an abnormal product, 2 - dibutylamino - 1 - propanethiol, 2b. The normal product appeared in larger amounts under basic conditions in the same process as in the PO–DBA system. However, the usual chemical analysis could not distinguish between primary thiols and secondary thiols. It was useful for spectroscopy techniques to analyze two kinds of the above isomer, 2a and 2b. In the NMR spectra of products of the PS–DBA system thiol protons

Table 1. Rate constants and activation parameters for the reaction of PO with DBA in DMSO–benzene mixtures[a]

temp.[b] (°C)	$k_2 \times 10^7$ ($M^{-1}s^{-1}$)	$k_3 \times 10^7$ ($M^{-2}s^{-1}$)
40	2.1	8.5
50	3.8	17
60	7.2	21
70	13.5	36
$\Delta H^{\neq}$ (Kcal/mol)	13.2	7.8
$\Delta S^{\neq}$ (e.u.)	-47.1	-60.9
$\Delta H^{\neq}$ [c] (Kcal/mol)	17.2	13.1
$\Delta S^{\neq}$ [c] (e.u.)	-44.2	-53.7

[a] DMSO/benzene = 10/7(vol/vol). The initial concns of PO and DBA are 1.47 and 3.05 M, resp. [b] ± 0.1°C.
[c] Cited from ref.6.

---

*The initial molar ratio (DBA/PO) was ca. 2. In excess of DBA the reaction proceeded quantitatively as shown in eqn (2). The concn of RP was equal to that of PO consumed.

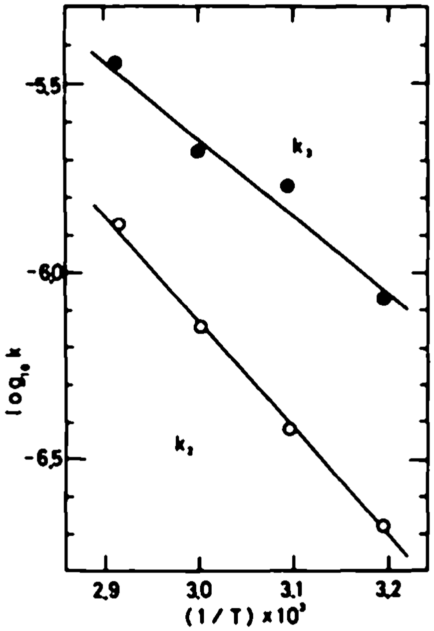


Fig. 2. Arrhenius plots for the reaction of PO with DBA in DMSO–benzene mixtures: ○, k_2; ●, k_3.

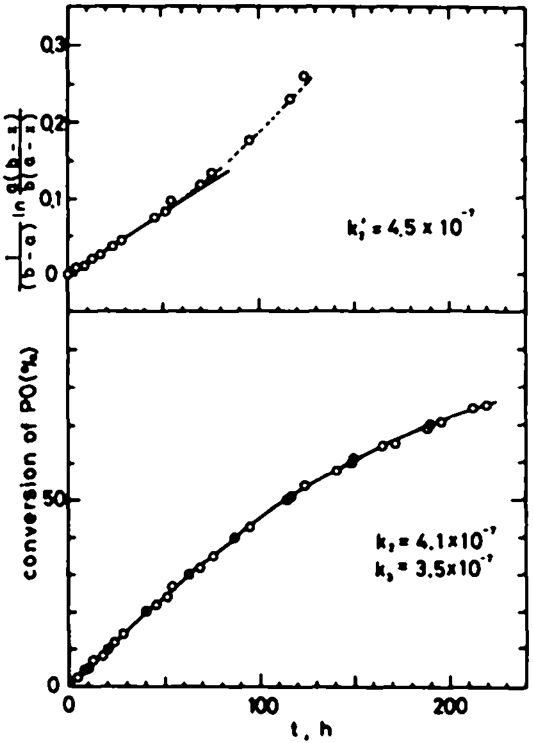


Fig. 3. The time-conversion curve in the reaction of PS with DBA in Tol at 50° and its initial second-order plot: ○, found; ●, calc.

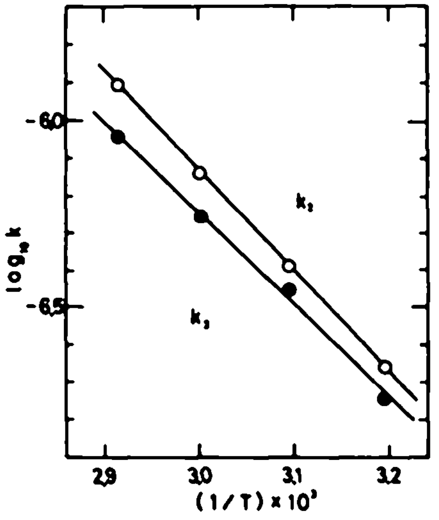


Fig. 4. Arrhenius plots for the reaction of PS with DBA in Tol: ○, k_2; ●, k_3.

and methylene protons of the Bu group were overlapped and the product ratio (2a:2b) could not be determined. Attempts to separate these NMR signals by a shift reagent failed. In the mass spectra of products the molecular ion peak could not be observed owing to the ease of fragmentation, but the characteristic fragment ion peak of the secondary thiol (M^+–SH) could be detected.[7] The larger amount of product was considered normal, 2a. It has been reported that normal products were obtained both in the reaction of PS with aniline in ethanol as solvent[3] and in the reaction of PS with secondary amines in 1,4-dioxane,[8] and therefore our estimation was reasonable. However, the reaction of eqn (7) was thought to proceed partly as the smaller fragment ion peak characteristic of the primary thiol (M^+–H_2S) was also observed.

The ring-opening of the PS–DBA system in Tol was much faster than that of the PO–DBA system and could be studied kinetically. There are few papers on the kinetics of base-catalyzed ring-opening reactions of thiirane[3,8] in which the reaction has been reported to obey the second-order kinetics dependent on the first order both in the thiirane concn and in the amine concn. Figure 3 shows an example of the time-conversion curves in the ring-opening of PS with DBA in Tol. The acceleration of the reaction was also observed in the PS–DBA system and the rate constants, k_2 and k_3, were calculated by eqn (8) in the same manner as in the PO–DBA reaction.

$$-\frac{d(PS)}{dt} = k_2(PS)(DBA) + k_3(PS)(DBA)(RP) \qquad (8)$$

where PS, DBA and RP are the concn of PS, DBA and the reaction product at time t, respectively.

Arrhenius plots are shown in Fig. 4. Rate constants and activation parameters are collected in Table 2.

An example of the PS–DBA reaction in DMSO–Tol mixtures is shown in Fig. 5. Rate constants were calculated by eqn (8). Arrhenius plots are shown in Fig. 6. Kinetic results are collected in Table 2. In the PS–DBA reaction system the reaction rates in DMSO-Tol mixtures were considerably higher than those in Tol (Table 2).

To clarify the solvent effect of DMSO, the measurements of dielectric constants, ϵ, were carried out in various compositions of DMSO–Tol mixtures and the relation between the reaction rate of the PS–DBA system and the dielectric constants of mixtures was investigated. Dielectric constants were determined at 25° by a heterodyne apparatus. Figure 7 shows that there is a linearity between the dielectric constants of mixtures and the weight fraction of DMSO and that the dielectric constant of three component mixtures (DMSO–Tol–

Table 2. Rate constants and activation parameters for the reaction of PS with DBA

solvent	in Tol[a]		in DMSO-Tol[b]	
temp.[c] (°C)	$k_2 \times 10^7$ ($M^{-1}s^{-1}$)	$k_3 \times 10^7$ ($M^{-2}s^{-1}$)	$k_2 \times 10^5$ ($M^{-1}s^{-1}$)	$k_3 \times 10^4$ ($M^{-2}s^{-1}$)
40	2.2	1.8	—	—
45	—	—	3.1	1.5
50	4.1	3.5	3.5	1.7
55	—	—	4.0	1.9
60	7.2	5.5	5.4	3.0
70	12.5	9.0	—	—
$\Delta H^{\ddagger}$ (Kcal/mol)	11.7	10.8	6.8	8.8
$\Delta S^{\ddagger}$ (e.u.)	-51.7	-54.8	-57.8	-48.5

[a] The initial concns of PS and DBA are 1.49 and 3.46 M, resp. [b] DMSO/Tol = 10/7 (vol/vol). The initial concns of PS and DBA are 1.47 and 3.09 M, resp. [c] ± 0.1°C.

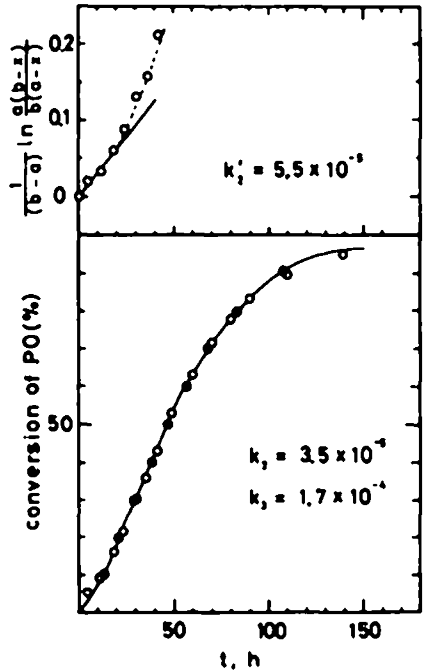


Fig. 5. The time-conversion curve in the reaction of PS with DBA in DMSO-Tol mixtures at 50° and its initial second-order plot: ○, found; ●, calc.

DBA) lies in the identical line. On the basis of the above fact, the dielectric constants of reaction mixtures can be evaluated from the DMSO weight fraction. Table 3 shows the solvent effect on the reaction rate of ring-opening of PS with DBA in various DMSO-Tol mixtures where the dielectric constants of reaction mixtures were estimated from the weight fraction of DMSO by use of Fig. 7. The reaction rate increased with an increase in the dielectric constant of mixtures. The PS–DBA reaction in DMSO as a solvent was so rapidly accelerated that the rate constant could not be obtained.

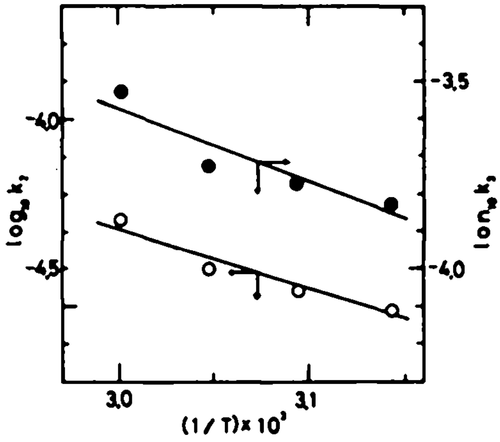


Fig. 6. Arrhenius plots for the reaction of PS with DBA in DMSO-Tol mixtures: ○, k_2; ●, k_3.

DISCUSSION

The relative ring-opening reactivities of oxirane and thiirane have been compared only in the reaction of PO and PS with aniline in ethanol and then have been clarified that the reactivity of PO is greater than that of

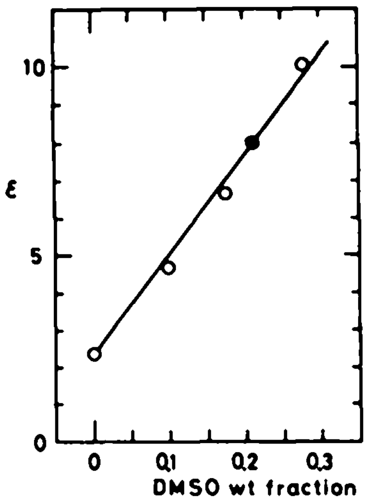


Fig. 7. Dependence of dielectric constants on DMSO weight fraction in DMSO–Tol mixtures at 25°: ○, Tol–DMSO; ●, Tol–DMSO–DBA (DBA wt fraction, 0.367).

Table 3. Solvent effects on rate constants for the reaction of PS with DBA at 60° in DMSO–Tol mixtures[a]

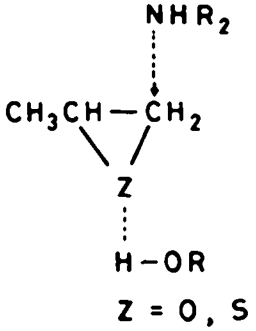
DMSO (wt fraction)	ε	$k_2 \times 10^{-5}$ ($M^{-1}s^{-1}$)	$k_3 \times 10^{-5}$ ($M^{-1}s^{-1}$)
0	2.38	0.072	0.055
0.080	4.20	1.0	1.0
0.146	6.08	2.0	4.2
0.189	7.17	3.0	3.3
0.265	9.19	5.4	30
0.889	ca.29[b]	ca.1×10^3	ca.8×10^3

[a] The initial concns of PS are 0.140 - 1.53 M. Those of DBA are 0.190 - 3.45 M. [b] Roughly extrapolated from the plot of ε vs. wt fraction of DMSO.

PS in the range 30°–50°,[4] in which E_a (kcal/mol) and $\Delta S^{\neq}$ (e.u.) have been reported to be 7.10 and −56.8 for the PO–aniline reaction, and 14.64 and −35.2 for the PS–aniline reaction. It was thought that the order of these reactivities would be reversed beyond 85° on the basis of activation parameters and that the reactivity of PS would be greater than that of PO. It is interesting that the base-catalyzed reaction of PS is far faster than that of PO in aromatic hydrocarbons in this paper, but the factors that govern the reactivity can not be discussed in detail as it is impossible to obtain detailed kinetic information in the PO–DBA reaction system.

The order of the reactivity is PS > PO also in DMSO–aromatic hydrocarbon mixtures. In the initial second-order reaction, the activation entropy for the PS–DBA reaction has a larger negative value than that for the PO–DBA reaction. This suggests that DMSO solvates more strongly the partial negative charge on the S atom produced by the nucleophilic attack in the transition state than that on the O atom.[9] Such a solvation of DMSO is liable to break the C–S bond to a more extent and increases the reactivity of PS. Reversely, it is believed that the partial negative charge on the O atom, the small anion with a localized charge, is more solvated in ethanol and that the relative reactivity of PO increases more than that of PS. The greater the extent of the solvation, the larger the negative values of the entropies of activation, and so the activation enthalpies would be compensated.

One of the important factors governing the ring-opening in ethanol is the H-bonding between the heteroatom of the ring and ethanol in the reactants. In a protonic solvent such as ethanol, there is the H-bonding of the OH group toward ethers and thioethers.[10] The amine-catalyzed ring-opening of 3-membered heterocycles have been explained to be nucleophilic substitutions. However, the H-bonding of a solvent is thought to govern the reactivity to some extent in such a ring-opening and then it should be considered that the amine-catalyzed ring-opening proceeds in a protic solvent by the push and pull mechanism as shown in Scheme 1.



Scheme 1.

These reactions can be apparently explained by the second-order kinetics on the first order both in the 3-membered heterocycles concn and in the amine concn, but the apparent second-order rate constant should be presumed to contain the association constant of a protic solvent with 3-membered heterocycles. Such H-bonding has been thoroughly studied in the association of phenol with proton acceptors.[b] The association constant of PO with phenol is larger than that of PS with phenol. Accordingly, it is imagined that the H-bonding of PO with ethanol should be larger than that of PS with ethanol and that this kind of the pull process would increase the reactivity of PO. It is interesting that there is a good correspondence between the activation parameters of the PO–aniline reaction and those of the third-order reaction in the PO–DBA system where the reaction product acts as a proton donor in the pull process. The transition state of the latter may be similar to that of the former.

The PS–DBA reaction in Tol is accelerated to a small extent owing to the weak H-bonding of the S atom with products. The PS–DBA reaction in DMSO–Tol mixtures is accelerated by the third-order reaction in spite of the weak H-bonding and is thought to be specific in comparison with that in Tol. Such a solvent effect of DMSO was studied in detail as shown in Table 3. In the S_N2 reaction like the Menschutkin reaction, a dipolar molecular-dipolar molecular reaction, the reaction tends to be accelerated with an increase in the polarity of the solvent and a linearity has been found between the logarithm of the

---

[b] Ref. 1b. It has been reported that the association constant of PO with phenol at 30° is 4.70 and that of PS with phenol is 0.961.

rate constant and $(\epsilon - 1)/(2\epsilon - 1)$ according to Kirkwood equation where ϵ is the dielectric constant of the medium. However, in the PS–DBA reaction the deviation from the linearity of Kirkwood plot is significant in the high-dielectric-constant region of the medium (rich in DMSO) in which the reaction is greatly accelerated. Therefore, the thiolate anion is though to be selectively solvated in DMSO in the following ways: the weak partial negative charge on the S atom would be induced by both the H-bonding (the pull process) and the nucleophilic attack (the push process) in the transition state and then developed by the solvation of DMSO so that the C–S bond would be liable to be cleaved to a large extent. These results suggest the importance of the pull process in base-catalyzed ring-opening reactions.

EXPERIMENTAL

Reagents. PO was a commercial product, dried over calcium hydride and distilled before use. PS was prepared by the method of Ishii *et al.*,[11] dried over Na_2CO_3 and distilled twice before use. DBA was a commercial product, refluxed over calcium hydride under reduced pressure and distilled. Other reagents were purified by the usual method.

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 ±0.1° in a thermostat. Rate constants were measured by the determination of the residual 3-membered rings under the following gas chromatographic conditions: for PO; internal standard, benzene; column material, PEG 20 M 20% + KOH 5%, 150 cm × 3 mm; column temp., 70°; carrier gas, He 50 ml/min: for PS; internal standard, toluene or cyclohexane; column material, diethylene glycol succinate polyester 20%, 150 cm × 3 mm; column temp., 70°; carrier gas, He 50 ml/min.

Product analyses

The reaction of propylene oxide with dibutylamine. PO (8.3 g, 0.143 mol) and DBA (28.6 g, 0.221 mol) were dissolved in EtOH (20 ml) and refluxed for 8 hr, and the solvent and the residual DBA were evaporated. The crude product in a 94% yield was then distilled twice and **1a** was obtained in a 38% yield (10 g), b.p. 106°/1.8 Torr (lit.[12] b.p. 228.9°) (Found: C, 69.55; H, 14.00; N, 7.43. Calc. for $C_{11}H_{25}NO$, C, 70.53; H, 13.45; N, 7.47%). In glc (PEG 20 M + KOH, 150°) **1a** was contaminated by less than 1% of its isomer, **1b**. The products of PO with DBA in DMSO–benzene mixtures were analyzed by glc, but the product ratio of **1a** and **1b** could not be determined as **1b** was overlapped with DMSO. Judged from the above product ratio in EtOH and the previous papers[4,5] on the base-catalyzed ring-opening reaction, a very small amount of **1b** seemed to be produced also in DMSO–benzene mixtures.

The reaction of propylene sulfide with dibutylamine. DBA (24.7 g, 0.191 mol) was dissolved in Tol (10 ml), refluxed gently under N_2, a PS toluene soln (8.7 g, 0.117 mol in 10 ml) added dropwise and then refluxed for 11 hr. The solvent and residual reactants (DBA and PS) were evaporated. The crude product was distilled; yield 49%, b.p. 81.9°–82.1°/1.8 Torr. In the NMR spectrum (CCl_4) SH and methylene protons of the Bu group were overlapped and those signals could not be separated by the shift reagent, $Eu(fod)_3$. In a mass spectrum a major product was assumed to be a normal isomer, **2a**, from the signal of $CH_3CHCH_2N(n\text{-}C_4H_9)_2$ (*m/e* 170, rel. intensity 2) by the elimination of HS from the secondary thiol group of **2a**.[7] On the other hand, a small signal of $CH_3CN(n\text{-}C_4H_9)_2{=}CH_2$ (169, 0.6) was observed by the elimination of H_2S from the primary thiol group of **2b**. The mixtures both in Tol and in DMSO–Tol were concentrated by the evaporation of the solvent and residual reactants, and analyzed. NMR and mass spectra of mixtures were very similar to those of the above synthesized sample, the mixtures of **2a** and **2b**. According to Snyder *et al.*,[13] in the reaction of PS with dipentylamine the 1:1 adduct, dipentylaminopropanethiol, was obtained in a 65% yield (b.p. 86°–87°/Torr), but the ratio of two kinds of isomers was obscure. In the reaction of isobutylene sulfide and DBA the product was reported to be normal, 1 - dibutylamino - 2 - methyl - 2 - propanethiol (b.p. 89°–90°/2.0 Torr).

Spectral and dielectric measurements. NMR spectra were measured with a TEOL TNM-60M spectrometer. Mass spectra were measured using a Hitachi RM-61 spectrometer. Measurements of dielectric constants in DMSO–Tol mixtures were carried out at 25° by use of a heterodyne apparatus.

Acknowledgements—The present work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education. The authors are grateful to Prof. Minoru Hirota of Yokohama National University of his kind permission to use a heterodyne apparatus for measurements of dielectric constants.

REFERENCES

[1] For the ring strain, see A. S. Pell and G. Pilcher, *Trans. Faraday Soc.* 61, 71 (1965). For the basicity of heterocycles, see E. Lippert and H. Prigge, *Liebigs Ann.* 659, 81 (1962).
[2] R. E. Parker and N. S. Isaacs, *Chem. Rev.* 59, 737 (1959).
[3] P. A. Gembitskii, N. M. Loim and D. S. Zhuk, *Russ. Che. Rev.* 35, 105 (1966).
[4] P. K. Sundaram and M. M. Sharma, *Bull. Chem. Soc. Japan* 42, 314 (1966).
[5] N. S. Isaacs, *Can. J. Chem.* 44, 395 (1966).
[6] H. Tiltscher, *Angew. Makromol. Chem.* 25, 1 (1974).
[7] E. J. Levy and W. A. Stahl, *Analyt. Chem.* 33, 707 (1961).
[8] A. Oddon and J. Wylde, *Bull. Soc. Chim. Fr.* 1603 (1967).
[9] A. J. Paker, *Chem. Rev.* 69, 1 (1969).
[10] *The Hydrogen Bond* (Edited by G. C. Pimentel and A. L. McCellan). Freeman, San Francisco (1960).
[11] H. Ito, S. Sakai and Y. Ishii, *Kogyo Kagaku Zasshi* 71 288 (1968).
[12] *Encyclopedia of Chem. Technol.* (Edited by R. E. Kirk and D. F. Othmer), Vol. 11, p. 166. The Interscience Encyclopedia, New York (1953).
[13] H. R. Snyder, J. M. Stewart and J. Z. Ziegler, *J. Am. Chem. Soc.* 69, 2675 (1947).