Pyrolysis of Sulfoxide Bearing Electron-Withdrawing Substituents on β-Position in S-Ethyl Group of Ethyl Phenyl Sulfoxide

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In order to obtain information concerning the reaction mechanism of the pyrolysis of a sulfoxide bearing an electron-withdrawing substituent on the β-position in the S-ethyl group of ethyl phenyl sulfoxide, 2-(substituted phenyl)ethyl aryl sulfoxides(1) and 2-cyanoethyl (substituted phenyl) sulfoxides(2) were pyrolyzed. The rate-enhancing effect of the β-phenyl group of 1 was small. The activation enthalpy and entropy of 1 were found to be 110 kJ mol^{-1} and -45 JK^{-1} mol^{-1}, respectively. Hammett plots for 1 gave positive trends for the substituents, both on the β-phenyl group (ρ=0.76) and on the S-phenyl group (ρ=0.32), though the ρ-value of the latter was about half of the former. On the other hand, the Hammett plot for 2 did not give a straight line, but a concave curve in which a series of substituents from the p-OCH$_3$ to p-Cl groups gave a negative trend (ρ=$-$0.49), while the p-NO$_2$ group afforded a positive trend. The pyrolytic rate of 2 was found to be about 23-times faster than that of 1 at 100 °C. The kinetic isotope effect for β-position hydrogen in the β-phenylethyl group of 1 was considerably large (k_H/k_D=4.3). From the obtained results, it was suggested that the pyrolysis of 1 and 2 proceeds via a nearly carbanion-like mechanism in a five-membered cyclic transition state.
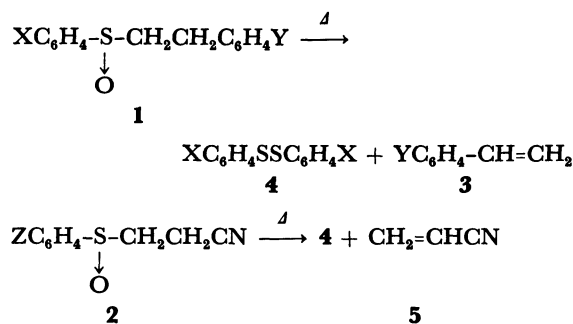
Sulfoxides having at least one hydrogen atom on the β-position carbon in the S-alkyl group are easily decomposed to give olefins, like N,N-dimethyl-2-phenylethylamine oxide,[1] at relatively lower temperatures than those in the pyrolysis of xanthates, i.e., a Chugaev elimination reaction.[2] From studies on the pyrolysis of various sulfoxides, it has been suggested that the reaction proceeds through a five-membered cyclic transition state:[6] That is, a concerted cis-elimination process, like a Cope reaction.[1,8] Three types of the Ei reaction mechanisms (an ideal cis-concerted[3] (i.e., the electron-delocarized state), an E1-like[4,5] and a radical pair[6] process) have been observed in the pyrolysis of various sulfoxides of different molecular structures. For example, Emerson et al.[3] concluded that the pyrolysis of s-butyl propyl sulfoxide proceeds via an ideal concerted mechanism from observations of the product distribution. In contrast, phenyl propyl sulfoxide[4] and phenyl t-butyl sulfoxide[5] are considered to decompose thermally via an E1-like process from observations of Hammett substituent effects.

On the other hand, Kingsbury and Cram[6] found that a stereospecific cis-elimination of 1,2-diphenylpropyl phenyl sulfoxides (7) is accompanied by a concomitant radical C–S bond cleavage. It is of interest to determine the mechanism regarding the pyrolysis of the sulfoxide bearing an electron-withdrawing group on the β-position in the S-ethyl group of ethyl phenyl sulfoxide; this has not yet been investigated kinetically.

Thus, 2-(substituted phenyl)ethyl phenyl sulfoxides (1) and 2-cyanoethyl (substituted phenyl) sulfoxides (2) were prepared and subjected to pyrolysis. In the present paper, we give a detailed account of a kinetic study of the pyrolysis of the reaction system as well as a possible mechanism.

Results and Discussion

Reaction Products. Pyrolysis was carried out by heating a solution of the sulfoxide in dioxane in a sealed tube in a thermostat adjusted to within the range ± 0.05 °C of the desired temperature. Though the reaction products were not actually isolated, the products were identified by comparing their HPLC and GLPC with those of authentic samples. Thus, under these reaction conditions, the resultant products were found to be both substituted styrene (3) and substituted diphenyl disulfide (4); 2 produced both 4 and acrylonitrile (5). The disulfide 4 is probably formed via an initial formation of arenesulfenic acid followed by a dimerization process.[14,15]

$$XC_6H_4\text{-S-}CH_2CH_2C_6H_4Y \xrightarrow{\ \Delta\ }$$
$$\underset{O}{\overset{\downarrow}{}}$$
$$\mathbf{1}$$

$$XC_6H_4SSC_6H_4X + YC_6H_4\text{-CH=CH}_2$$
$$\mathbf{4} \qquad\qquad \mathbf{3}$$

$$ZC_6H_4\text{-S-}CH_2CH_2CN \xrightarrow{\ \Delta\ } \mathbf{4} + CH_2\text{=CHCN}$$
$$\underset{O}{\overset{\downarrow}{}}$$
$$\mathbf{2} \qquad\qquad\qquad\qquad \mathbf{5}$$

The NMR spectra of the product mixtures that resulted from the pyrolysis of sulfoxides 1 and 2 in CCl$_4$ in sealed tubes at 100 °C showed that the yields of 3 and 5 are nearly quantitative.

Kinetics. Kinetic measurements were carried out by following the intensity of the UV absorption (254 nm) by means of HPLC. In order to obtain pyrolytic information concerning the sulfoxide bearing a stronger electron-withdrawing group than the phenyl group

Table 1. The Kinetic Data for Pyrolysis of 2-Arylethyl Aryl Sulfoxides(1)
and 2-Cyanoethyl Aryl Sulfoxides(2)

$$XC_6H_4\text{-}S\text{-}CH_2CH_2C_6H_4Y$$
$$\downarrow$$
$$O \quad (1)$$

Sulfoxide		Temp	Rate constant[a]	
X	Y	°C	$\dfrac{k \times 10^5}{s^{-1}}$	
H	p-OCH$_3$	120.0	5.54±0.12	
H	p-CH$_3$	120.0	6.34±0.87	
H	m-CH$_3$	120.0	7.56±0.15	
H	H	100.0	1.41±0.03	$\Delta H^* = (110 \pm 3)$ kJ mol^{-1}
H	H	110.0	3.65±0.13	$\Delta S^* = (-45 \pm 9)$ J K^{-1} mol^{-1}
H	H	120.0	10.5 ±0.3	(at 100 °C)
H	H	130.0	22.3 ±0.3	
H	H	140.0	46.6 ±2.2	$\rho_X = +0.32$ ($\gamma = 0.963$)
H	p-Cl	120.0	11.2 ±0.3	
H	p-NO$_2$	120.0	36.0 ±0.3	$\rho_Y = +0.76$ ($\gamma = 0.987$)
p-CH$_3$	H	120.0	8.14±0.16	
m-CH$_3$	H	120.0	10.6 ±0.2	
p-Cl	H	120.0	11.1 ±0.6	
p-NO$_2$	H	120.0	18.2 ±0.2	
PhS(O)CH$_2$CD$_2$Ph		120.0	2.46±0.04	$k_H/k_D = 4.3$

$$ZC_6H_4\text{-}S\text{-}CH_2CH_2CN$$
$$\downarrow$$
$$O \quad (2)$$

Z	Temp	$k \times 10^4$	
	°C	s^{-1}	
p-OCH$_3$	100.0	5.03±0.53	
p-CH$_3$	100.0	4.38±0.17	
H	100.0	3.30±0.22	
p-Cl	100.0	2.92±0.15	$\rho_Z = -0.49$ ($\gamma = 0.971$)[b]
p-NO$_2$	100.0	4.96±0.20	

a) The rate constants were calculated by the least-squares method and the errors are standard diviations.   b) The datum for p-nitro derivative is not included in calculation.

on the β-position, 2 was also subjected to pyrolysis. The reaction rates of the sulfoxides were all correlated in a fine manner with a first-order equation with respect to the concentration of the substrate.

The kinetic data obtained are summarized in Table 1.

An Arrhenius plot for 2-phenylethyl phenyl sulfoxide afforded a good straight line; the activation enthalpy (110 kJ mol^{-1}) and a considerably small activation entropy (-45 J K^{-1} mol^{-1}) were obtained. A comparison of the pyrolytic rate of 1 to that of other sulfoxides are listed in Table 2.

The pyrolytic rate of 2-cyanoethyl phenyl sulfoxide (2) was found to be 200-times faster than that of ethyl phenyl sulfoxide (6), while that of 1 was only 8-times faster than that of 6. This finding reveals that the rate-enhancing effect of the β-phenyl group in the reaction system is rather small.

Kinetic Isotope Effect. The kinetic isotope effect using 2-phenylethyl-2,2-d_2 phenyl sulfoxide was mea-

Table 2. The Relative Rates of Pyrolysis of Sulfoxides at 100 °C in Dioxane

Sulfoxide	Rate constant $\dfrac{k \times 10^5}{s^{-1}}$	Relative rate
PhS(O)CH$_2$CH$_3$	0.165	1
PhS(O)CHCH$_3$ (threo)	43.5	264
Ph (erythro)	83.9	508
PhS(O)CH$_2$CH$_2$Ph	1.41	8.55
PhS(O)CH$_2$CH$_2$CN	33.0	200

sured and the effect was found to be $k_H/k_D = 4.3$ (120 °C). The large kinetic isotope effect apparently reveals that the reaction process involves C–H bond breaking in a rate-determining step.

The magnitude of the effect is larger than those for the pyrolysis of heptyl-2-d phenyl sulfoxide ($k_H/k_D = 2.9$)[10] and cis- and trans-N,N-dimethylcyclooctyl-2-

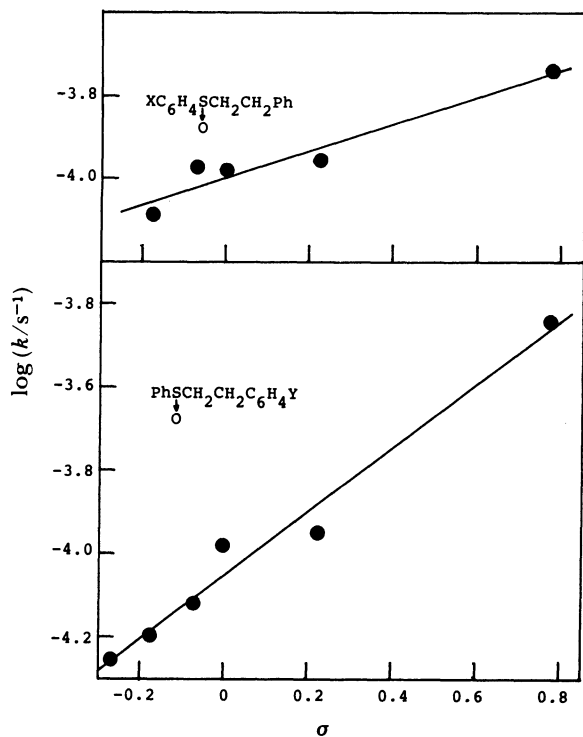Fig. 1. Hammett relations for the pyrolysis of 2-(substituted phenyl)ethyl phenyl sulfoxides and 2-phenylethyl (substituted phenyl) sulfoxides (1).
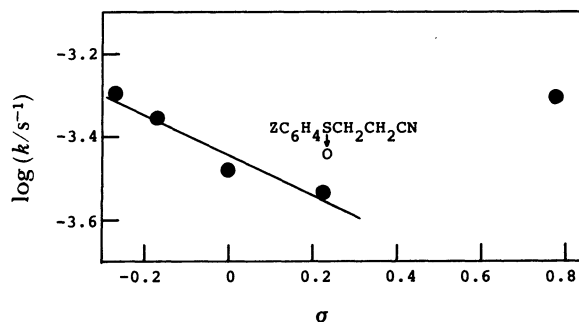

Fig. 2. Hammett relation for the pyrolysis of 2-cyanoethyl (substituted phenyl) sulfoxides (2).

Table 3. Solvent Effect on Pyrolysis of 2-Phenylethyl Phenyl Sulfoxide at 120 °C

Solvent	Dielectric constant	Rate constant $k \times 10^5$ / s^{-1}	Relative rate
Dioxane	2.21	10.5 ±0.3	1
Benzene	2.27	9.00±0.34	0.86
DMSO	48.9	6.02±0.22	0.57
Acetonitrile	37.5	4.13±0.08	0.39
Ethanol	24.3	1.73±0.08	0.16

d-amine oxide ($k_H/k_D = 3.5$) in benzene,[7] which proceed via a five-membered cyclic transition state.[8]

Substituent Effect. The substituent effects for the pyrolysis of **1** and **2** were studied in dioxane. Figure 1 shows Hammett plots for **1** with both β-aryl and S-aryl substituents at 120 °C.

As is apparent from Fig. 1, log k nicely correlates with σ-values, showing a positive trend for both the X-side ($\gamma = 0.96$) and the Y-side ($\gamma = 0.99$). The ρ-value for the Y-side was +0.76, while that for the X-side ($\rho = +0.33$) was only about half of the Y-side. Thus, in the pyrolysis of **1**, electron-withdrawing substituents are apparently more favorable than electron-releasing types. On the other hand, the Hammett relation for **2** did not afford a straight line, but a concave curve in which a series of the substituents from the p-OCH₃ to p-Cl groups gave a negative trend ($\rho = -0.49$, $\gamma = 0.97$), while the p-NO₂ group, as a strong electron-withdrawing substituent, afforded a positive trend. The effect for **2** is shown in Fig. 2.

It appears at first sight that, due to the negative trend, that pyrolysis proceeds via another mechanism than that for **1**. However, since the effect corresponding to that of X-substituents in **1** is small, the pyrolysis mechanism should also be the same as that for **1**. The result of a Hammett relation for **2** together with the behavior of the p-NO₂ substituent will be discussed later.

Solvent Effects. Pyrolysis was carried out in five kinds of solvents; the obtained rate constants are summarized in Table 3. The pyrolysis was not much affected by solvent change. Though it seems that an increase in the solvent polarity tends to cause a retardation of pyrolysis, the rates of pyrolysis are not correlated to the dielectric constants and the effect is small. This indicates that the transition state of the reaction is not ionic. This observation is similar to those for the pyrolysis of sulfilimines[11] and sulfoxides **7**,[6] except for reactions in protic solvents. The small decrease in the rate for reactions in dipolar aprotic solvents is interpreted in view of the more solvation in the starting state by a dipole-dipole interaction than in the transition state. Meanwhile, a large rate retardation in the pyrolysis of sulfoxides and sulfilimines in protic solvents has been shown.[8] Kingsbury and Cram reported that the pyrolysis of sulfoxide **7** in methanol is 1000-times slower than that in dioxane.[6] Though the rate difference in both solvents is not so large, hydrogen-bonding to the sulfoxide oxygen in the starting state apparently prevents pyrolysis. Recently, we demonstrated the effect of hydrogen-bonding in the pyrolysis of aryl ethyl sulfilimines in protic solvents.[16]

From the above results the following conclusion can be obtained. In the first place, the considerably large β-hydrogen kinetic isotope effect rules out a radical pair mechanism, since the free radical mechanism involving the rate-determining C–S bond cleavage is not in accord with the large kinetic isotope effect.

Secondarily, an E1-like mechanism is also ruled out because of the positive ρ-value for Y-substituents and the small ρ-value for X-substituents. For example, recently it has been found that the pyrolysis of 1-phenylethyl phenyl sulfoxide, which has been revealed to proceed via an E1-like mechanism, gives relatively large positive ρ-values for S-phenyl substituents and negative ρ-values for electron-releasing substituents on 1-phenyl group.[9]

Oae et al.[11] proposed that the pyrolysis of S-(1- and 2-phenylethyl)-S-phenyl-N-tosylsulfilimines proceeds via an E1-like cis-concerted mechanism in view of the following results: A small kinetic isotope effect $(k_H/k_D=2.9)$, a substituent effect of the opposite relation giving a positive ρ-value for S-aryl substituents against a negative one for 1-aryl substituents, a large rate acceleration by α-phenyl group and a small rate-enhancing effect of β-phenyl group [$k_{Ph}/k_H=2000$ for PhS(NTs)CH(R)CH$_3$, $k_{Ph}/k_H=1.5$ for PhS(NTs)-CH$_2$CH$_2$R (R=H and Ph)].

However, in system 1, the substituent effect on the β-phenyl group gave a positive Hammett correlation in both ρ_Y and ρ_X; also, the kinetic isotope effect for β-hydrogen gave a large value. Thus, the present data suggest that the pyrolysis of both 1 and 2 proceed via a nearly carbanion-like internal concerted cis-elimination.

The small rate-enhancing effect of the β-phenyl group might reveal that pyrolysis proceeds via an E1-like mechanism, since some E2 reactions[12] and Cope eliminations,[13] which are presumed to proceed via a nearly carbanion like mechanism, show large rate-enhancements by the β-phenyl group.[12,13] For the above reason, the small enhancement effect appears to be somewhat inconsistent with the nearly carbanion like mechanism; however, it may be explaind as follows. In general, the pyrolysis of the alkyl aryl sulfoxides tends to proceed, essentially, via an E1-like mechanism, which should give a positive Hammett ρ-value in the substituent effect on the S-phenyl group. On the other hand, in the nearly carbanion-like mechanism, the basicity of a sulfoxide-oxygen atom should affect the rate of the reaction giving a negative Hammett ρ-value for the substituent effect on the S-phenyl group. In the pyrolysis of 1 the ρ-value still shows a positive trend like other sulfoxides,[4] though the trend becomes considerably small. This small positive ρ-value is attributed to the substituent effect on the S-phenyl group being more susceptible to C-S bond cleavage than proton abstraction. In other words, the 2-phenyl group as a relatively weak electron-withdrawing substituent is insufficient to give a negative trend in the Hammett relation for S-phenyl substituents.

Therefore, the sulfoxide bearing a stronger electron-withdrawing group at the β-position can be expected to give a negative Hammett ρ-value. Thus, the
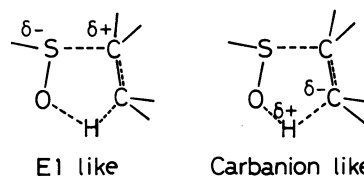

Fig. 3. E1-like and Carbonion-like cyclic transition states.

Hammett relation on the pyrolysis of 2 indicated a negative trend. The result reveals that the transition state is apparently changed to a nearly carbanion-like type by the CN group as a stronger electron-withdrawing group than the phenyl type. Meanwhile, the positive trend for the p-Cl to the p-NO$_2$ group in the Hammett plot may be explained as follows. The substituent, the p-NO$_2$ group, is so strong in electron-withdrawing that the rate-enhancing effect by the CN group on the β-position might be weakened; thus, the reaction was conversely accelerated.

The Hammett relation for 2 apparently suggests that the transition state is gradually changed from a nearly carbanion-like to an E1-like type in going from p-CH$_3$ to p-NO$_2$ substituents (Fig. 2). Thus, it can be concluded that the pyrolysis of sulfoxides bearing electron-withdrawing substituents on the β-position carbon in the S-ethyl group proceeds via a nearly carbanion-like mechanism in a five-membered cyclic transition state (Fig. 3).

Experimental

Measurements. All the melting points are uncorrected. The IR spectra were determined on a JEOL-810 spectrometer. The ^{1}H NMR spectra were recorded with a Hitachi R-24B spectrometer in CDCl$_3$ or CCl$_4$ using TMS as an internal standard. The HPLC analysis were carried out with a JASCO FAMILIC-100N and UVIDEC-100 SYSTEM apparatus by using silica gel (SS-10) and styrene-divinylbenzene copolymer (HP-01) columns (CH$_3$CN/H$_2$O, hexane/THF as eluting solution). The peak area were measured by a TAKEDA-RIKEN TR-2217 integrater. The MS spectra were taken with JEOL-JMS-D 300 mass spectrometer.

Procedures and Materials. All the reactions were monitored by TLC (MERCK, Kieselgel 60 GF), and the substrates were separated by column chromatography using Merck kieselgel 60 silica gel, Wako Activated Alumina (200 mesh). All the substrates obtained were identified by IR, ^{1}H NMR, GC, MS, and elemental analyses. The computations were performed on the NEC 9801-F computer. Elemental analyses were carried out by Chemical Analysis Center in Toyama Medical and Pharmaceutical University. All reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Co. Ltd., or Aldrich Chemical Co. The reagents and solvents used were further purified by general methods.

Preparation of Sulfoxides. 2-(Substituted phenyl)-ethyl phenyl sulfoxides were prepared by treating methyl

phenyl sulfoxide with LDA and with substituted benzyl chlorides in dry ether at $-78\ ^\circ$C, and were extracted with chloroform. The extracts were dried and evaporated. The residues were purified by column chromatography (a mixture of ether and hexane as eluent). Ethyl phenyl sulfoxide and 2-phenylethyl (substituted phenyl) sulfoxides were prepared by oxidizing the corresponding sulfides with hydrogen peroxide in acetic acid, and was isolated through SiO_2-column chromatography (chloroform as eluent), or was recrystallized from ether-methanol. 2-Cyanoethyl (substituted phenyl) sulfoxides (**2**) were prepared by oxidizing the corresponding sulfides obtained in the method described below with hydrogen peroxide, and was worked up as described above. The sulfides were prepared by treating acrylonitrile and substituted benzenethiol in benzene under the presence of a minute amount of triethylamine.

Preparation of 2-Phenylethyl-2,2-d_2 Phenyl Sulfoxide. 2-Phenylethyl-2,2-d_2 phenyl sulfoxide were prepared by treating methyl phenyl sulfoxide with LDA and with benzyl-α,α-d_2 chloride in dry ether at $-78\ ^\circ$C.

Benzyl-α,α-d_2 Alcohol: Methyl benzoate was treating by lithium aluminium deuteride in the usual way; after the solution was extracted with ether and the solvent evaporated, the residue was distilled under reduced pressure. Yield 60%.

Benzyl-α,α-d_2 Chloride: The deuterated alcohol was converted into the corresponding chloro compound with thionyl chloride. Yield 60%.

2-(Substituted Phenyl) ethyl Phenyl Sulfoxides (1):
p-OCH$_3$: ^{1}H NMR (CDCl$_3$) $\delta=2.89$—3.25 (4H, m, CH$_2$-CH$_2$), 3.58 (3H, s, OCH$_3$), 6.57—7.65 (9H, m, C$_6$H$_5$, C$_6$H$_4$); IR (neat) 1030 cm^{-1} (S=O). Found: C, 68.32; H, 6.18%. Calcd for C$_{15}$H$_{16}$O$_2$S: C, 69.20; H, 6.19%.

p-CH$_3$: ^{1}H NMR (CDCl$_3$) $\delta=2.20$ (3H, s, CH$_3$), 2.56—2.98 (4H, m, CH$_2$CH$_2$), 6.85 (5H, s, C$_6$H$_5$), 7.26—7.53 (4H, m, C$_6$H$_4$); IR (KBr) 1040 cm^{-1} (S=O). Found: C, 73.00; H, 6.54%. Calcd for C$_{15}$H$_{16}$OS: C, 73.73; H, 6.60%. Mp 46.0 — 47.5 $^\circ$C.

m-CH$_3$: ^{1}H NMR (CDCl$_3$) $\delta=2.30$—2.80 (4H, m, CH$_2$-CH$_2$), 2.58 (3H, s, CH$_3$) 7.09—7.60 (9H, m, C$_6$H$_5$, C$_6$H$_4$); IR (neat) 1040 cm^{-1} (S=O).

p-Cl: ^{1}H NMR (CDCl$_3$) $\delta=2.70$—3.30 (4H, m, CH$_2$-CH$_2$), 7.20 (5H, s, C$_6$H$_5$), 7.06 — 7.61 (4H, m,C$_6$H$_4$); IR (KBr) 1040 cm^{-1} (S=O). Found: C, 63.71; H, 5.04%. Calcd for C$_{14}$H$_{13}$ClOS: C, 63.51; H, 4.95%. Mp 62.5 — 63.5 $^\circ$C.

p-NO$_2$: ^{1}H NMR (CDCl$_3$) $\delta=2.85$ — 3.45 (4H, m, CH$_2$CH$_2$), 8.22—9.15 (9H, m, C$_6$H$_5$, C$_6$H$_4$); IR (KB$_r$) 1040 cm^{-1} (S=O). Found: C, 61.24; H, 4.69; N, 4.60%. Calcd for C$_{14}$H$_{13}$NO$_3$S: C, 61.07; H, 4.76; N, 5.09%. Mp 111.5 — 113.0 $^\circ$C.

2-Phenylethyl (Substituted Phenyl) Sulfoxides (1). **p-CH$_3$:** ^{1}H NMR (CDCl$_3$) $\delta=2.32$ (3H, s, CH$_3$), 2.37—2.98 (4H, m, CH$_2$CH$_2$), 7.05 (5H, s, C$_6$H$_5$), 6.92—7.50 (4H, m, C$_6$H$_4$); IR (neat) 1050 cm^{-1} (S=O). Found: C, 72.60; H, 6.44%. Calcd for C$_{15}$H$_{16}$OS: C, 73.73; H, 6.60%.

m-CH$_3$: ^{1}H NMR (CDCl$_3$) $\delta=2.35$ (3H, s, CH$_3$), 2.62—3.35 (4H, m, CH$_2$CH$_2$), 7.09 (5H, s, C$_6$H$_5$), 6.90—7.63 (4H, m, C$_6$H$_4$); IR (neat) 1055 cm^{-1} (S=O). Found: C, 72.95: H, 6.50%. Calcd for C$_{15}$H$_{16}$OS: C, 73.73; H, 6.60%.

p-Cl: ^{1}H NMR (CDCl$_3$) $\delta=2.70$—3.30 (4H, m, CH$_2$CH$_2$), 7.20 (5H, s, C$_6$H$_5$), 7.06 — 7.61 (4H, m, C$_6$H$_4$); IR

(neat) 1050 cm^{-1} (S=O). Found: C, 62.57; H, 4.97%. Calcd for C$_{14}$H$_{13}$ClOS: C, 63.51; H, 4.95%.

p-NO$_2$: ^{1}H NMR (CDCl$_3$) $\delta=2.75$—3.68 (4H, m, CH$_2$CH$_2$), 7.18 (5H, s, C$_6$H$_5$), 7.69—8.39 (4H, m C$_6$H$_4$); IR (KBr) 1055 cm^{-1} (S=O). Found: C, 61.09; H, 4.84; N 5.38% . Calcd for C$_{14}$H$_{13}$NO$_3$S: C, 61.07; H, 4.76; N, 5.09%. Mp 101.5—103.0 $^\circ$C.

2-Cyanoethyl (Substituted Phenyl) Sulfoxides (2). **p-OCH$_3$:** ^{1}H NMR (CDCl$_3$) $\delta=3.90$ (3H, s, OCH$_3$), 2.50—3.30 (4 H, m, CH$_2$CH$_2$), 7.05 — 7.70 (4H, m, C$_6$H$_4$); IR (neat) 1050 cm^{-1} (S=O).

p-CH$_3$: ^{1}H NMR (CDCl$_3$) $\delta=2.48$ (3H, s, CH$_3$), 2.39—3.35 (4 H, m, CH$_2$CH$_2$), 7.55 (4 H, s, C$_6$H$_4$); IR (KBr) 1050 cm^{-1} (S=O). Found: C, 62.29; H, 5.63; N, 7.29%. Calcd for C$_{10}$H$_{11}$NOS: C, 62.15; H, 5.74; N, 7.25%. Mp 49.5 — 50.1 $^\circ$C.

H: ^{1}H NMR (CDCl$_3$) $\delta=2.24$—3.35 (4 H, m, CH$_2$CH$_2$), 7.58 (5H, s, C$_6$H$_5$); IR (KBr) 1045 cm^{-1} (S=O). Found: C, 60.47; H, 5.01; N, 7.59%. Calcd for C$_9$H$_9$NOS: C, 60.31; H, 5.60; N, 7.81%. Mp 64.0 — 65.0 $^\circ$C.

p-Cl: ^{1}H NMR (CDCl$_3$) $\delta=2.52$—3.50 (4H, m, CH$_2$CH$_2$), 7.62 (4H, s, C$_6$H$_4$); IR (KBr) 1045 cm^{-1} (S=O). Found: C, 50.62; H, 4.00; N, 6.66%. Calcd for C$_9$H$_8$NClOS: C, 50.59; H, 3.77; N, 6.55%. Mp 66.8 — 67.5 $^\circ$C.

p-NO$_2$: ^{1}H NMR (CDCl$_3$) $\delta=2.62$—3.25 (4H, m, CH$_2$CH$_2$), 7.79—8.58 (4H, m, C$_6$H$_4$); IR (KBr) 1050 cm^{-1} (S=O). Found: C, 47.95; H, 3.61; N, 12.59%. Calcd for C$_9$H$_8$N$_2$O$_3$S: C, 48.21; H, 3.60; N, 12.49%. Mp 114.0—115.0 $^\circ$C.

Kinetics. A pre-cooled solution of desired amount of a sulfoxide (7.0×10^{-3} mol dm^{-3}) in an anhydrous solvent was prepared and devided into a number of 10 µl of sealed capillary tubes, which were immersed in a constant temperature silicone oil bath ($\pm0.05^\circ$C), at appropriate time intervals, the tubes were taken out and frozen in ice bath to stop the reaction. The reaction rate was then calculated by following the decreasing peak area at UV 254 nm due to the recovered sulfoxide, which was separated from the reaction mixture by HPLC (column; HP-01, eluent; CH$_3$CN : H$_2$O=5 : 2) using diphenyl ether or diphenyl sulfide as an internal standard. The rate constants were calculated by a least-squares method using the 8—12 points accumulated during 70% completion of reaction. When the data were plotted as ln (V_0/V_0-V_t) vs. time (where V_0 is the initial volume of sulfoxide and V_t is the volume of sulfoxide at a particular time), a linear correlation was observed suggesting that the kinetics is of first order. Activation parameters were computer calculated by a least-squares method using ln k vs. $1/T$. The Hammett ρ-value was computed by the least-squares method using σ-values and the logarithmus of the rate constants.

References

1) A. C. Cope, T. T. Foster, and P. H. Toole, *J. Am. Chem. Soc.*, **71**, 3729 (1949).

2) D. V. Banthorpe, "Elimination Reaction," Elsvier, New York (1963), P. 167.

3) D. W. Emerson, A. R. Craig, and J. W. Potts, Jr., *J. Org. Chem.*, **32**, 102 (1967).

4) D. W. Emerson and T. J. Korniski, *J. Org. Chem.*, **34**, 4115 (1969).

5) J. R. Shelton and K. E. Davis, *Int. J. Sulfur Chem.*, **8**, 197 (1973).

6) C. A. Kingsbury and D. J. Cram, *J. Am. Chem. Soc.*, **82**, 1810 (1960).

7) R. D. Bach, D. Andrzejewski, and L. R. Dusold, *J. Org. Chem.*, **38**, 1742 (1973).

8) S. Oae and N. Furukawa, *Tetrahedron*, **33**, 2359 (1977).

9) T. Yoshimura, T. Sekioka, H. Mizuno, Y. Iizuka, M. Yoshizawa, and E. Tsukurimichi, 24th Symposium on Organic Radical Reactions and 34th Symposium on Organic Reaction Mechanisms, Sapporo, Japan, August 1983, Abstr., No. 3G08.

10) H. Kwart and T. J. George, *J. Am. Chem. Soc.*, **100**, 3927 (1978).

11) S. Oae, K. Harada, K. Tsujihara, and N. Furukawa, *Bull. Chem. Soc. Jpn.*, **46**, 3842 (1973).

12) E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, **1948**, 2038, 2044.

13) A. C. Cope, N. A. Lebel, H. H. Lee, and W. R. Moor, *J. Am. Chem. Soc.*, **79**, 4720 (1957).

14) F. A. Davis and R. H. Jenkins, Jr., *J. Am. Chem. Soc.*, **102**, 7967 (1980).

15) T.-L. Ju and J. L. Kice, *J. Org. Chem.*, **44**, 610 (1979).

16) E. Tsukurimichi, T. Yoshimura, and M. Kanda, *Nippon Kagaku Kaishi*, **1987**, 202.