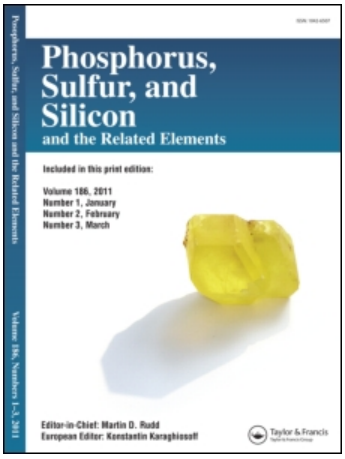

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PYROLYSIS OF α- and β-HETEROATOMS SUBSTITUTED ETHYL PHENYL SULFOXIDES

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A study on the mechanism of the thermal decomposition of α- and β-heteroatoms substituted ethyl phenyl sulfoxides was carried out using 1-chloroethyl phenyl sulfoxide (1); two diastereomeric 1-acetoxyethyl (substituted phenyl) sulfoxides (2a) and (2b); and 2-chloroethyl phenyl, 2-bromoethyl phenyl, and 2-methoxyethyl phenyl sulfoxides (3, 4, 5). The rate of pyrolysis of 1 was 4.8 times faster at 160°C than that of ethyl phenyl sulfoxide used as a reference, while those of 2a and 2b were 107 and 155 times faster, respectively. The results indicate that the lone pair of electrons on the α-heteroatoms has a larger rate acceleration effect than the electronegativity of them. The substituent effects of the phenyl group of 2a and 2b gave positive Hammett ρ-values ($\rho_a = 0.76$ and $\rho_b = 0.80$ vs. σ). Activation parameters for 2a and 2b are as follows: 2a, $\Delta H^{\ddagger} = 112$ kJmol^{-1}, $\Delta S^{\ddagger} = -20$ JK^{-1}mol^{-1}; 2b, $\Delta H^{\ddagger} = 107$ kJmol^{-1}, $\Delta S^{\ddagger} = -29$ JK-1mol^{-1}. Large deuterium kinetic isotope effects for 1-acetoxyethyl-2,2,2-$\mathbf{d}_3$ phenyl sulfoxides (2ad and 2bd) were observed ($\mathbf{k}_H/\mathbf{k}_D = 3.5 \sim 4.1$). These results suggest that the pyrolysis of α-heteroatom substituted ethyl phenyl sulfoxides proceeds via a five-membered transition state deviated to E1-like in character. On the other hand, from the results of kinetics for the pyrolysis of 3, 4, and 5, no effect by the β-halogen atoms or some deceleration effect by the β-methoxy group was observed. Thus the reaction seems to proceed via an E1-like mechanism.

Keywords Elimination; isotope effect; kinetics; mechanism; pyrolysis; sulfoxide

INTRODUCTION

Pyrolysis of sulfoxides bearing at least one β-hydrogen atom has been shown to proceed via an intramolecular cis elimination (Ei)[1] affording olefins.[2–8] Kinetic investigations for the Ei reaction of the sulfoxides have revealed that both C—S bond fission and β-proton transfer are important, and thus a concerted mechanism has been suggested from the observations of positive Hammett ρ-values[8,9] for the substituent effect on the *S*-phenyl group and large deuterium kinetic isotope effects on β-position.[10,11] However, we recently demonstrated that the transition state is variable depending on the substituent on the α- or β-position of the sulfoxides. For example, introduction of a phenyl group on the α-position of ethyl phenyl sulfoxide causes the transition state to deviate to one in which the C—S

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Dedicated to Professor Naomichi Furukawa on the occasion of his 70th birthday.

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bond cleavage is more progressed than proton transfer, that is, a partially positive charge is developed on the α-carbon (E1-like).[12] On the other hand, introduction of β-phenyl group causes deviation to the carbanion-like, and stronger electron-withdrawing CN group on the β-carbon results in a negative ρ-value ($\rho = -0.49$) for the substituent effect on the *S*-phenyl group.[13] Meanwhile, introduction of carbonyl group[14] on the α-carbon shows that conjugation of the carbonyl group with the developing C—C π-bond stabilizes the transition state and increase the acidity of the β-proton to accelerate the reaction greatly. In a series of systematic investigations has been undertaken to analyze the character of the Ei-reaction and its transition state with the sulfoxides. It was of interest to investigate how electronegativity and the lone-pair electrons on the α- and β-heteroatoms affect competitively the pyrolytic mechanism of the ethyl phenyl sulfoxide. Thus, 1-chloroethyl phenyl sulfoxide (**1**); 1-acetoxyethyl (substituted phenyl) sulfoxides (**2a**, **2b**); 1-acetoxyethyl-2,2,2-d_3 phenyl sulfoxides(**2ad**, **2bd**); and 2-chloroethyl phenyl, 2-bromoethyl phenyl, and 2-methoxyethyl phenyl sulfoxides (**3**, **4**, **5**) were prepared and subjected to pyrolysis. This article gives a detailed account of the effect of the α- and β-heteroatoms of the pyrolysis of sulfoxides.

RESULTS

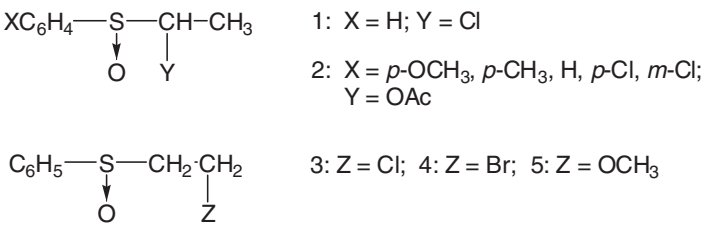
Synthesis of α- and β-Heteroatoms Substituted Ethyl Phenyl Sulfoxides and Their Diastereomers

The sulfoxide **1** was prepared by treating ethyl phenyl sulfoxide with sulfuryl chloride,[15] and two diastereomers **2a** and **2b** were obtained by oxidizing the corresponding sulfides, which were prepared by the Pummerer reaction[16] of ethyl aryl sulfoxides with acetic anhydride, and with hydrogen peroxide. The mixture of **2a** and **2b** was separated by repeated column chromatography, whereas the purification of **1** by column chromatography gave only one isomer. All of **2a** was eluted initially and displayed a quartet ^{1}H NMR methine signal at higher field than **2b** eluted last. Though the stereochemical assignment of **2a** and **2b** is not complete, the two diastereomers are distinguishable by the following consideration. Figure 1 shows the plots of ^{1}H NMR chemical shifts of methine protons of **2a** and **2b** against Hammett σ-values. Two series of the methine signals of the higher field and the lower one showed a fairly good linear relationship. Therefore, it can be assumed that the same diastereomers are on the same line. Thus, the chemical shifts of the methine protons of **2** were found to be available to distinguish the diastereomers.

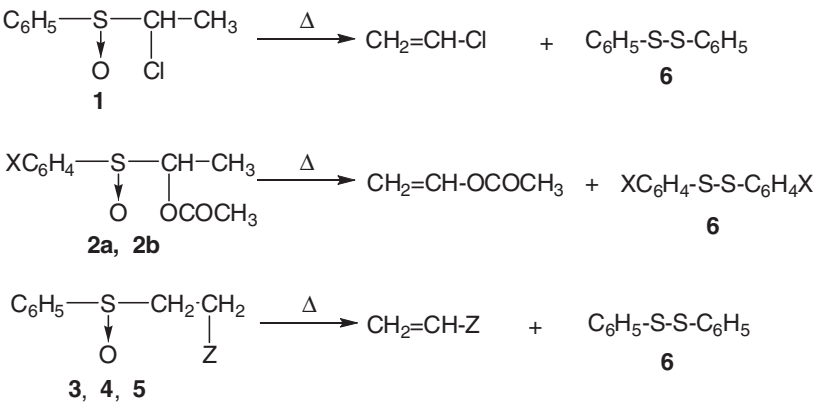
On the other hand, 2-chloroethy phenyl **3** and 2-bromoethyl phenyl sulfoxides **4** were prepared by the oxidation of the corresponding sulfides[17,18] with hydrogen peroxide in acetic acid. The sulfoxides **3** and **4** were then treated with sodium methoxide to give 2-methoxyethyl phenyl sulfoxide (**5**) (Scheme 1).[19]

Pyrolysis Products

The pyrolysis of **2a** and **2b** was carried out in CCl_4 in sealed NMR tubes at 100°C, and then ^{1}H NMR analysis showed the formation of vinyl acetate at $\delta = 4.4 \sim 5.0$ and $6.95 \sim 7.4$ ppm in agreement with those of an authentic sample. Scheme 2 shows the pyrolytic products of **1**, **2a**, **2b**, and **3–5**. The sulfoxide **1** afforded vinyl chloride and diaryl disulfide (**6**), while **2a** and **2b** gave vinyl acetate and **6**. Although the pyrolytic products were not actually isolated, the products were identified by comparing their HPLC and GLPC retention times with those of the authentic samples. The disulfides **6** may be generated via an initial formation of arenesulfenic acid followed by dimerization process.[20,21]



Scheme 1



Scheme 2 Pyrolysis of sulfoxides.

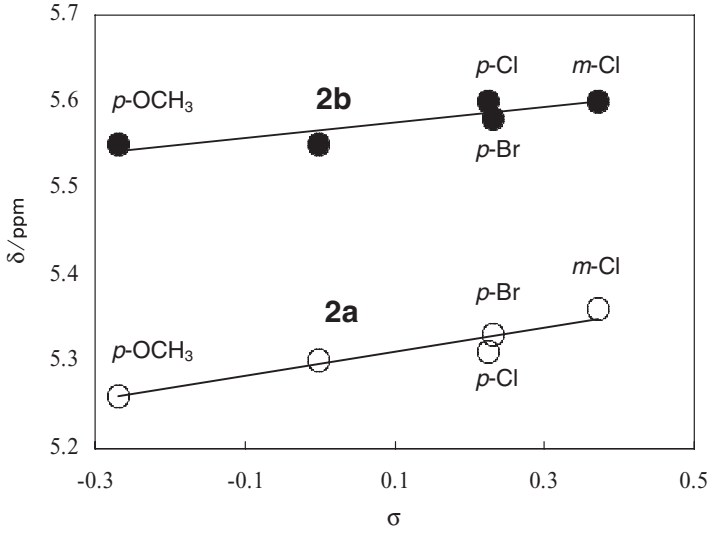


Figure 1 Dependence of ^{1}H NMR methine signals of two diastereomers of 1-acetoxyethyl aryl sulfoxides (substituted **2a** and **2b**) on Hammett σ-values. Solvent: CCl_4.

Kinetics

Kinetic experiments were carried out in dry dioxane at the desired temperature for **1**, **2a**, and **2b** (90∼130°C) and for **3**∼**5** (140∼180°C), and decreasing amounts of the sulfoxides was followed by measuring the intensity of the UV absorption (254 nm) by HPLC. The rates of the pyrolysis were all correlated with first-order kinetics ($r = 0.999$) and have been listed in Table I. Table II shows activation parameters and relative rates at 160°C compared with those for the reference sulfoxide. The rate of the pyrolysis of **1** was found to be 4.8 times faster than that of the reference sulfoxide, while those of **2a** and **2b** were 107 and 155 times faster, respectively. On the other hand, the effect of the β-heteroatoms is small and rather slows the rates. Specifically, the rate of the reaction of **5** is 0.27 times faster than that for the reference. These effects will be discussed later. Activation entropies for the reaction of **2** are in the range of –20∼−29 $JK^{-1}mol^{-1}$ and are somewhat larger than that of 2-phenylethyl phenyl sulfoxide (–34.5 $JK^{-1}mol^{-1}$) [13] but smaller than that of 1-phenylethyl phenyl sulfoxide (–6 or –4 $JK^{-1}mol^{-1}$).[12]

Large kinetic isotope effects using 1-acetoxyethyl-2,2,2-d_3 phenyl sulfoxides (**2ad** and **2bd**) were observed for both **2ad** and **2bd** at 110∼130°C ($k_H/k_D = 3.5$∼4.1). The values are smaller than those for the pyrolysis of 2-phenylethyl-2,2-d_2 phenyl sulfoxide ($k_H/k_D = 4.4$ at 100°C), [13] which proceeds via a carbanion-like mechanism and for that of 1-phenylethyl-2,2,2-d_3 phenyl sulfoxide (4.77∼5.15 at 100∼80°C),[12] which proceeds via an E1-like mechanism. However, the values are larger than that for the reaction of heptyl-2d phenyl sulfoxide ($k_H/k_D = 2.9$), which proceeds via a typical concerted five-membered cyclic transition state.[11]

In order to obtain more detailed data for the effect of the α-heteroatoms on the transition state, the effect of substituents X on the *S*-phenyl group in **2a** and **2b** was examined. The kinetic data with respect to X are listed in Table I, and the Hammett relation is shown in Figure 2. The Hammett plots for both substituted **2a** and **2b** gave separate but

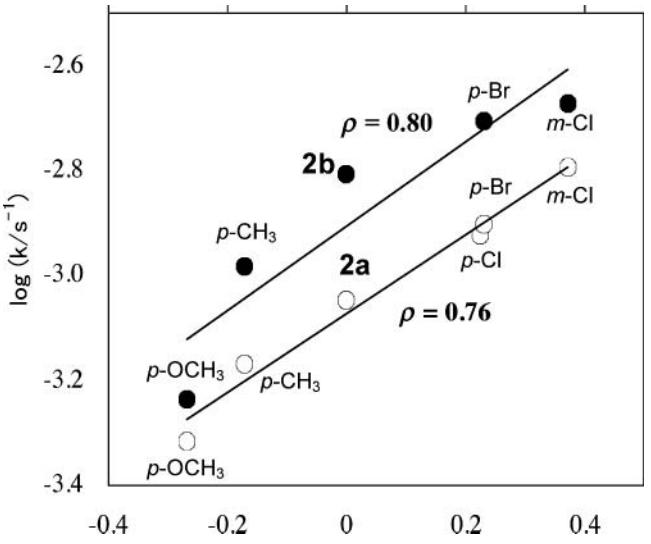
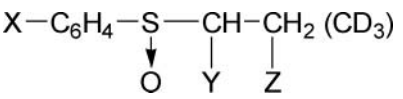


Figure 2 Hammett plots for the rates of pyrolysis of two diastereomers of 1-acetoxyethyl aryl sulfoxides (substituted **2a** and **2b**) at 100°C in dioxane.

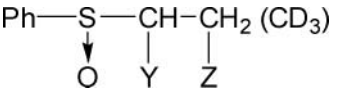
Table I Rate constants of pyrolysis of α- and β-heteroatoms substituted ethyl phenyl sulfoxides in dioxane



Compd. No.	Substituents X	Y	Z	Temp (°C)	Rate constant[a] ($k \times 10^4/s^{-1}$)		
	H	H	H	140.5	0.522	±0.022	
	H	H	H	150.0	0.945	±0.017	
	H	H	H	155.0	1.47	±0.02	
	H	H	H	160.0	2.15	±0.04	
1	H	Cl	H	160.0	10.4	±0.1	
2a	H	OAc	H	90.0	0.481	±0.010	
2b	H	OAc	H	90.0	0.935	±0.030	
2a	H	OAc	H	100.0	1.36	±0.01	
2b	H	OAc	H	100.0	2.35	±0.03	
2a	H	OAc	H	110.0	3.59	±0.03	
2b	H	OAc	H	110.0	5.84	±0.05	
2a	H	OAc	H	120.0	8.97	±0.04	
2b	H	OAc	H	120.0	15.6	±0.1	
2a	H	OAc	H	130.0	21.2	±0.1	
2b	H	OAc	H	130.0	33.8	±0.3	
2a	*p*-OCH_3	OAc	H	120.0	4.80	±0.04	$\rho_X = 0.76$ for (**2a**)
2b	*p*-OCH_3	OAc	H	120.0	5.78	±0.09	$\rho_X = 0.80$ for (**2b**)
2a	*p*-CH_3	OAc	H	120.0	6.78	±0.07	
2b	*p*-CH_3	OAc	H	120.0	10.4	±0.1	
2a	*p*-Cl	OAc	H	120.0	11.9	±0.1	
2a	*p*-Br	OAc	H	120.0	12.5	±0.1	
2b	*p*-Br	OAc	H	120.0	19.6	±0.1	
2a	*m*-Cl	OAc	H	120.0	16.0	±0.1	
2b	*m*-Cl	OAc	H	120.0	21.3	±0.5	
2ad	H	OAc	D	110.0	0.921	±0.006	$k_H/k_D = 3.90$
2bd	H	OAc	D	110.0	1.48	±0.07	$k_H/k_D = 3.95$
2ad	H	OAc	D	120.0	2.39	±0.03	$k_H/k_D = 3.75$
2bd	H	OAc	D	120.0	3.83	±0.03	$k_H/k_D = 4.07$
2ad	H	OAc	D	130.0	6.1	±0.07	$k_H/k_D = 3.53$
2bd	H	OAc	D	130.0	9.31	±0.13	$k_H/k_D = 3.63$
2ad	H	OAc	D	135.0	9.31	±0.13	
2ad	H	OAc	D	140.0	14.1	±0.2	
2bd	H	OAc	D	140.0	21.9	±0.6	
3	H	H	Cl	150.0	0.85	±0.05	
3	H	H	Cl	160.0	1.85	±0.06	
3	H	H	Cl	170.0	4.22	±0.04	
4	H	H	Br	140.0	0.413	±0.022	
4	H	H	Br	150.0	0.90	±0.03	
4	H	H	Br	160.0	2.03	±0.02	
5	H	H	OCH_3	160.0	0.58	±0.03	
5	H	H	OCH_3	170.0	1.35	±0.01	
5	H	H	OCH_3	180.0	3.12	±0.04	

[a]The rate constants were calculated by the least-squares method, and the errors are standard derivatives.

Table II Relative rates and activation parameters for the pyrolysis of α- and β-heteroatoms substituted ethyl phenyl sulfoxides and related sulfoxides in dioxane



Compd. No.	Substituents Y	Z	Relative rate (160°C)	Activation parameters (°C)[b] $\Delta H^{\ddagger}$/kJ · mol^{-1}	$\Delta S^{\ddagger}$/J · K^{-1} · mol^{-1}	
	H	H	1	105 ±7	−77 ± 16	(160)
1	Cl	H	4.8			
2a	OAc	H	107[a]	112 ± 1	−20 ± 1	(100)
2b	OAc	H	155	107 ± 2	−29 ± 5	(100)
2ad	OAc	D	0.68	117 ± 1	−20 ± 1	(100)
2bd	OAc	D		115 ± 1	−20 ± 1	(100)
	Ph	H	365 (Threof)[a,[12]]	113	−6	(90)
			678 (Erythreof)[a,[12]]	111	−4	(90)
3	H	Cl	0.86	121 ± 4	−39 ± 9	(160)
4	H	Br	0.94	115 ± 3	−54 ± 7	(160)
5	H	OCH_3	0.27	136 ± 3	−15 ± 6	(160)

[a]The rate constants were calculated by Arrhenius equation from the data at other temperatures.
[b]The temperature was used to calculate activation parameters from the Arrhenius plot ($\Delta H^{\ddagger} = Ea - RT$).

parallel lines, suggesting that the present ^{1}H NMR spectroscopic assumption (Figure 1) for the diastereomers was valid. The plots for both substituted **2a** and **2b** gave similar positive ρ-values ($\rho_X = 0.76$ for **2a** and $\rho_X = 0.80$ for **2b**). Both values are a little larger than those of aryl α-methylbenzyl sulfoxides ($\rho = 0.60$)[12] and aryl propyl sulfoxides ($\rho = 0.51$).[9] These results for kinetic isotope effect and substituent effect reveal that both the C—S bond cleavage and the proton transfer are important in the transition state, namely the reaction proceeds via a concerted process and the positive ρ-values suggest that the reaction of **2a** and **2b** proceeds via a mechanism deviated to E1-like.

DISCUSSION

Though the Ei-reaction of sulfoxides is generally recognized as a concerted process, there exists a variable in the amount of C—S bond cleavage versus proton migration from the β-carbon to the oxygen. This causes a deviation to an E1-like or a carbanion-like mechanism in the five-membered cyclic transition state. Likely, a partial positive charge develops at the α-carbon atom in the E1-like transition state, while a partial negative charge develops at the β-carbon atom in the carbanion-like transition state, although the development of any charge is small because of the concerted nature of the cyclic transition state. The present positive Hammett ρ-values for X-substituents are consistent with an E1-like mechanism and are larger than that for the pyrolysis of substituted phenyl propyl sulfoxides ($\rho = 0.51$),[9] *threo*-1-phenylethyl substituted phenyl sulfoxides ($\rho = 0.60\sim0.64$),[12] and *t*-butyl substituted phenyl sulfoxides ($\rho = 0.695$).[8] These pyrolyses proceed via an E1-like mechanism. The magnitude of the ρ-values may be related to the degree of stretch of the C—S bond in the transition state. The "looseness" of the transition state reflects an increase

in the activation entropy. As discussed a the previous article,[12] the looseness of the transition state in the Ei-reaction of sulfoxides is attributed to the extension of the C—S bond and the progress of the proton transfer, although the latter contribution is small due to the cancellation of the contribution of looseness of the C—H bond by that of development of the O—H bond formation. Therefore, the large activation entropy may be related to looseness of the C—S bond in the transition state and thus to the E1-like mechanism to give a large positive Hammett ρ-value. In fact, the pyrolysis of *threo*-1-phenylethyl aryl sulfoxides [12] shows a larger activation entropy ($\Delta S^{\ddagger} = -6$ $JK^{-1}mol^{-1}$) and a larger positive ρ-value ($\rho = 0.60 \sim 0.64$) than aryl propyl sulfoxide ($\Delta S^{\ddagger} = -63$ $JK^{-1}mol^{-1}$, $\rho = 0.51$).[9] Pyrolyses of aryl *t*-butyl and aryl 1-methylcyclohexyl sulfoxides also reveal a large ρ-value ($\rho =$ 0.695,[8] $\rho = 0.865$[22]). Though there is no activation data for the pyrolysis of aryl *t*-butyl sulfoxides, the reaction of the sulfoxides can be assumed to have a large activation entropy from the fact that the data for di-*t*-butyl sulfoxide and 1-methylcyclohexyl phenyl sulfoxide give a large activation entropy ($\Delta S^{\ddagger} = -21 \sim +34$ $JK^{-1}mol^{-1}$,[22] $\Delta S^{\ddagger} = -1.7$ $JK^{-1}mol^{-1}$ [22]). However, in spite of the large ρ-values for the pyrolysis of **2a** ($\rho = 0.76$) and **2b** ($\rho =$ 0.80), the activation entropy is not very large, i.e., the value is between that of 1-phenylethyl phenyl sulfoxide and propyl phenyl sulfoxide or ethyl phenyl sulfoxide. This must be the result of an α-oxygen heteroatom effect.

Table II indicates that the enhancement effect of α-chloro atom is smaller than that of α-phenyl or α-acetoxy group. There are two factors concerning the effect of the heteroatom on the sulfoxides. One is the effect of electronegativity, which resists the heterolytic cleavage of the C_α—S bond in the transition state. The other is the effect of a lone pair of electrons, which deviates the transition state to the E1-like one by a resonance stabilization with the partially positive α-carbon or with the developing C—C π-bond involving lowering C_α—S σ^* orbital, thereby assisting the C_α—S bond cleavage but resisting the C—H bond scission. The present results suggest that the electronegativity of α-heteroatoms diminishes the rate enhancement effect. The data indicate that the acceleration of the pyrolysis by α-heteroatoms is due mainly to the conjugation of partially positive α-carbon atom with the lone-pair electrons on the α-heteroatom in the transition state, changing the reaction mechanism of the sulfoxides into a nearly E1-like one as shown in Figure 3. In general, conjugation is more effective than electronegativity, as can be seen from the fact that the methoxy group substituted on the α-carbon atom accelerates solvolysis[23,24] very much. In the present system using α-acetoxy group, the rate-enhancing effect by the conjugation is also more effective than the electronegativity effect, though it is not so much with the methoxy group. As a result, the lone pair of electrons on the oxygen atom operates to loosen the C—S bond in the transition state, but the electronegativity of the oxygen atom resists the development of the positive charge on the α-carbon atom to suppresses the stretch of the C—S bond, giving the middle extent of the activation entropy. Why were

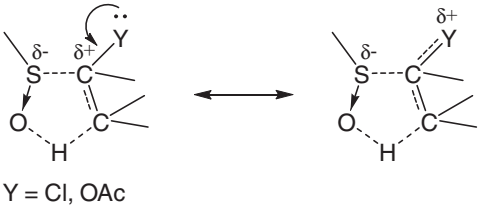


Figure 3 α-Heteroatom effect on the transition state of the pyrolysis of sulfoxides.

the large ρ-values obtained for the reaction of **2**? The substituent effect relates to an increase in electron density of the *S*-phenyl group, which is a result of balance of positive contribution by C—S bond stretch and negative contribution by O—H bond formation. The conjugation of partially positive α-carbon with the lone-electron pair of the α-heteroatom in turn diminishes the acidity of the β-CH protons to resist the C—H bond cleavage and thus O—H bond formation unlike that with the α-phenyl group,[12] which involves both electron-attracting and -releasing conjugation with the developing π-bond. Therefore, the increasing electron density on the *S*-phenyl group is larger than other sulfoxides such as propyl aryl sulfoxides[9] or 1-phenylethyl phenyl sulfoxides[12] in the transition state and thus gives the larger ρ-values.

On the other hand, as shown in Table II, the pyrolysis rates of β-halogen substituted ethyl phenyl sulfoxides are very similar to that of ethyl phenyl sulfoxide, but that of β-methoxyethyl phenyl sulfoxide is considerably slower. Both activation enthalpies and entropies are larger than those of ethyl phenyl sulfoxide. The electronegative β-heteroatoms acidify the β-proton, but the lone pair of electrons repulses the developing C—C π-electrons to reduce the rates. Therefore, it is necessary to stretch the C—S bond using high energy in the transition state deviating to an E1-like mechanism.

EXPERIMENTAL

Measurement

The IR spectra were determined on a Jasco 810 spectrometer, and the ^{1}H NMR spectra were obtained on a Hitachi R-24B spectrometer in $CDCl_3$ or CCl_4 using TMS as an internal standard. The HPLC analyses were carried out with a Jasco Familic-100N apparatus with UV monitor UVIDEC-100II using silica gel (SS-10) and styrene-divinylbenzene copolymer (HP-01) columns (CH_3CN/H_2O, hexane/THF as eluents). The peak area was measured by a Takeda-Riken TR-2217 integrator. The mass spectra were taken with JEOL JMS-D300 mass spectrometer.

Procedures and Materials

All the reactions were monitored by TLC (Merck, silica gel 60 GF), and the reaction mixtures were separated by column chromatography using Merck silica gel 60 or Wako activated alumina (200 mesh). The products obtained were identified by IR, ^{1}H NMR, GLPC, MS, and elemental analyses. All the melting points are uncorrected. 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 Company, Inc., and were further purified by usual methods.

Preparation of 1-Chloroethyl Phenyl Sulfoxide (1)

1-Chloroethyl phenyl sulfoxide was prepared by treating ethyl phenyl sulfoxide (2.8 g, 15 mmol) with sulfuryl chloride (2.8 g, 2.1 mmol)[15] in dichloromethane (100 mL) at 0°C for 3 h. The reaction mixture was neutralized with sodium bicarbonate solution and extracted with dichloromethane. After removal of the solvent, the crude sulfoxide was purified through silica gel column chromatography using chloroform as an eluent; 62% yield. No stereoisomer was formed in the preparation of (**1**). ^{1}H NMR ($CDCl_3$):

$\delta = 7.35-7.70$ (5 H, m, C_6H_5), 4.50−4.82 (1 H, q, J = 6 Hz, CH), 1.55 (3 H, d, J = 6 Hz, CH_3). IR (neat) : 1045 cm^{-1} (S=O).

Preparation of 1-Acetoxyethyl Aryl Sulfoxides (2a) and (2b)

Sulfoxides (**2**) were prepared by oxidation of the corresponding sulfides, which were prepared by the Pummerer reaction.[16] A typical example is as follows:

Preparation of 1-acetoxyethyl phenyl sulfides. Ethyl phenyl sulfoxide (19.8 g, 0.13 mol) dissolved in acetic anhydride was heated under reflux for 3 h. The reaction mixture was then poured into ice water and neutralized with sodium bicarbonate. The organic layer was extracted with chloroform and dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated, and the residue was distilled under reduced pressure to give 1-acetoxyethyl phenyl sulfide as colorless oil in 7.7% yield (bp 92−100°C/1 mmHg) together with phenyl vinyl sulfide as a major product. The 1-acetoxyethyl phenyl sulfide obtained was further purified by silica gel column chromatography using benzene as an eluent. Substituent: *p*-OCH_3; yield 28.6%, bp 103−113°C/2 mm Hg. *p*-CH_3; yield 1.2%, bp 102–103°C/2 mm Hg. *p*-Cl; yield 2.5%, bp 108−122°C/1 mm Hg. *p*-Br; yield 11%, bp 130−135°C/1 mm Hg. *m*-Cl; yield 9.1%.

Oxidation of 1-acetoxyethyl phenyl sulfide. To a stirred solution of 1-acetoxyethyl phenyl sulfide (2.1 g, 10 mmol) in dichloromethane (5 mL), *m*-chloroperbenzoic acid (*m*-CPBA) (2 g, 12 mmol) in dichloromethane (10 mL) was added dropwise with cooling. After the mixture was stirred at 0°C for 2 h, dimethyl sulfide was added to decompose the unreacted *m*-CPBA, and the solution was poured into cold aqueous sodium bicarbonate. The organic layer was extracted with chloroform, washed with water, and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was separated by silica gel column chromatography using ether:hexane (1:1) as an eluent. The sulfoxides thus obtained have the following physical properties. Elemental analyses of the oily sulfoxides (X: *p*-OCH_3, *p*-CH_3, H) were made after oxidation to the corresponding sulfones with *m*-CPBA.

p-OCH_3, Isomer (**a**): oil. ^{1}H NMR (CCl_4); $\delta = 7.41$ and 6.89 (4 H, AB, $J_{AB} = 8$ Hz, C_6H_4), 5.26 (1 H, q, J = 6 Hz, CH), 3.76 (3 H, s, OCH_3), 2.08 (3 H, s, OAc), 1.24 (3 H, d, J = 6 Hz, CH_3). IR (neat); 1745 (C=O), 1250 (−O−CH_3), 1210 (C−O−C), 1045 cm^{-1} (S=O). Sulfone, mp 51−53°C. Anal. Found; C, 50.93, H, 5.27%. Calcd for $C_{11}H_{14}O_5S$; C, 51.15, H, 5.46%.

Isomer (**b**): oil. ^{1}H NMR (CCl_4); $\delta = 7.39$ and 6.91 (4 H, AB, $J_{AB} = 9$ Hz, C_6H_4), 5.55 (1 H, q, J = 6 Hz, CH), 3.77 (3 H, s, OCH_3), 1.96 (3 H, s, OAc), 1.28 (3 H, d, J = 6 Hz, CH_3). IR (neat); 1750 (C=O), 1250 (−O−CH_3), 1205 (C−O−C), 1045 cm^{-1} (S=O).

p-CH_3, Isomer (a): oil. ^{1}H NMR ($CDCl_3$); $\delta = 7.45$ and 7.25 (4 H, AB, $J_{AB} = 8$ Hz, C_6H_4), 5.47 (1 H, q, J = 6 Hz, CH), 2.39 (3 H, s, CH_3), 2.10 (3 H, s, OAc), 1.34 (3 H, d, J = 6 Hz, CH_3). IR (neat); 1745 (C=O), 1210 (C−O−C), 1050 cm^{-1} (S=O). Sulfone, mp 67.5−69.0°C. Anal. Found; C, 54.81, H, 5.87%. Calcd for $C_{11}H_{14}O_4S$; C, 54.53, H, 5.82%.

Isomer (**b**): oil. ^{1}H NMR ($CDCl_3$); $\delta = 7.44$ and 7.26 (4 H, AB, $J_{AB} = 8$ Hz, C_6H_4), 5.68 (1 H, q, J = 6 Hz, CH), 2.39 (3 H, s, CH_3), 1.99 (3 H, s, OAc), 1.40 (3 H, d, J = 6 Hz, CH_3), IR (neat); 1750 (C=O), 1205 (C−O−C), 1045 cm^{-1} (S=O).

H, Isomer (**a**): oil. ^{1}H NMR ($CDCl_3$); $\delta = 7.25-7.70$ (5 H, m, C_6H_5), 5.45 (1 H, q, J = 6 Hz, CH), 2.10 (3 H, s, OAc), 1.35 (3 H, d, J = 6 Hz, CH_3). (CCl_4); $\delta = 7.1-7.6$ (5 H, m, C_6H_5), 5.30 (1 H, q, J = 6 Hz, CH), 2.11 (3 H, s, OAc), 1.24 (3 H, d, J = 6 Hz, CH_3).

IR (neat); 1745 (C=O), 1210 (C−O−C), 1045 cm^{-1} (S=O). Sulfone, mp 52.5−54.0°C. Anal. Found; C, 52.85, H, 5.44%. Calcd for $C_{10}H_{12}O_4S$; C, 52.62, H, 5.30%.

Isomer (**b**): mp 66.5−67.5°C. ^1H NMR ($CDCl_3$); $\delta = 7.20-7.84$ (5 H, m, C_6H_5), 5.68 (1 H, q, J = 6 Hz, CH), 1.97 (3 H, s, OAc), 1.40 (3 H, d, J = 6 Hz, CH_3). (CCl_4); $\delta = 7.3-7.5$ (5 H, m, C_6H_5), 5.55 (1 H, q, J = 6 Hz, CH), 1.90 (3 H, s, OAc), 1.35 (3 H, d, J = 6 Hz, CH_3). IR (KBr); 1750 (C=O), 1205 (C−O−C), 1045 cm^{-1} (S=O). Sulfone, mp 52.5−54.0°C.

p-Cl, Isomer (**a**): mp 87.5−89.0°C. ^1H NMR (CCl_4); $\delta = 7.42$ (4 H, m, C_6H_4), 5.31 (1 H, q, J = 6 Hz, CH), 2.11 (3 H, s, OAc), 1.24 (3 H, d, J = 6 Hz, CH_3). IR (KBr); 1745 (C=O), 1205 (C−O−C), 1045 cm^{-1} (S=O). Anal. Found; C, 48.53, H, 4.45%. Calcd for $C_{10}H_{11}ClO_3S$; C, 48.68, H, 4.49%.

Isomer (**b**): oil. ^1H NMR (CCl_4); $\delta = 7.41$ (4 H, m, C_6H_4), 5.60 (1 H, q, J = 7 Hz, CH), 1.97 (3 H, s, OAc), 1.35 (3 H, d, J = 7 Hz, CH_3). IR (neat); 1745 (C=O), 1205 (C−O−C), 1045 cm^{-1} (S=O).

m-Cl, Isomer (**a**): oil. ^1H NMR (CCl_4); $\delta = 7.1-7.7$ (4 H, m, C_6H_4), 5.36 (1 H, q, J = 6 Hz, CH), 2.13 (3 H, s, OAc), 1.28 (3 H, d, J = 6 Hz, CH_3). IR (neat); 1750 (C=O), 1210 (C−O−C), 1050 cm^{-1} (S=O).

Isomer (**b**): oil. ^1H NMR (CCl_4); $\delta = 7.2-7.6$ (4 H, m, C_6H_4), 5.60 (1 H, q, J = 6 Hz, CH), 1.92 (3 H, s, OAc), 1.37 (3 H, d, J = 6 Hz, CH_3). IR (neat); 1755 (C=O), 1210 (C−O−C), 1050 cm^{-1} (S=O).

p-Br, Isomer (**a**): mp 115−116°C. ^1H NMR (CCl_4); $\delta = 7.53$ and 7.43 (4 H, AB, $J_{AB} = 8$ Hz, C_6H_4), 5.33 (1 H, q, J = 6 Hz, CH), 2.14 (3 H, s, OAc), 1.25 (3 H, d, J = 6 Hz, CH_3). IR (KBr); 1740 (C=O), 1210 (C−O−C), 1040 cm^{-1} (S=O). Anal. Found; C, 41.13, H, 3.78%. Calcd for $C_{10}H_{11}BrO_3S$; C, 41.25, H, 3.81%.

Isomer (**b**): mp 59.5−64.5°C. ^1H NMR (CCl_4); $\delta = 7.50$ and 7.33 (4 H, AB, $J_{AB} = 8$ Hz, C_6H_4), 5.58 (1 H, q, J = 6 Hz, CH), 1.92 (3 H, s, OAc), 1.32 (3 H, d, J = 6 Hz, CH_3). IR (KBr); 1755 (C=O), 1200 (C−O−C), 1050 cm^{-1} (S=O). Anal. Found; C, 41.38, H, 3.96%. Calcd for $C_{10}H_{11}BrO_3S$; C, 41.25, H, 3.81%.

Preparation of 1-Acetoxyethyl-2,2,2-d_3 Phenyl Sulfoxide (2ad) and (2bd)

The deuterated acetic acid-2,2,2-d_3 (5.0 g, 79 mmol) was reduced with lithium aluminum hydride (7.0 g, 180 mmol) in dry ether by the usual method to give ethanol-2,2,2-d_3, yield 60%, bp 78−79°C. The deuterated alcohol was converted into the corresponding bromide in 48% yield by treatment with phosphorus tribromide. The ^1H NMR spectrum showed no signal due to methyl proton. Sulfoxides **2ad** and **2bd** were obtained by the method similar to that described in the preparation of **2a** and **2b**.

Ethyl-2,2,2-d_3 phenyl sulfide: bp 95−101°C/28 mmHg, yield 76%.

Ethyl-2,2,2-d_3 phenyl sulfoxide: bp 120−123°C/5 mmHg, yield 87%.

1-Acetoxyethyl-2,2,2-d_3 phenyl sulfide: Purified by silica gel column chromatography using benzene as an eluent, yield 17%.

1-Acetoxyethyl-2,2,2-d_3 phenyl sulfoxides (**2ad**) and (**2bd**): Purified by silica gel column chromatography using ether-hexane as an eluent, yield 55%.

Isomer (**2ad**): ^1H NMR ($CDCl_3$) $\delta = 7.2-7.7$ (5 H, m, C_6H_5), 5.52 (1 H, s, CH), 2.15 (3 H, s, OAc). IR (neat): 1748 (C=O), 1045 cm^{-1} (S=O).

Isomer (**2bd**): ^1H NMR ($CDCl_3$) $\delta = 7.36-7.80$ (5 H, m, C_6H_5), 5.75 (1 H, s, CH), 2.00 (3 H, s, OAc). IR (neat): 1748 (C=O), 1045 cm^{-1} (S=O).

Preparation of (2-Substituted Ethyl) Phenyl Sulfoxides (3, 4, 5)

2-Chloroethyl phenyl sulfoxide (**3**) [25] and 2-bromoethyl phenyl sulfoxide (**4**) were prepared by oxidation of the corresponding sulfides [17, 18] with hydrogen peroxide in acetic acid, and then treated with sodium methoxide to give 2-methoxyethyl phenyl sulfoxide (**5**).[19] **3**: mp 31−32°C. ^{1}H NMR ($CDCl_3$); $\delta = 7.50$ (5 H, s, C_6H_5), 3.00−4.04 (4 H, m, CH_2CH_2). IR (KBr); 1045 cm^{-1} (S=O). **4**: ^{1}H NMR ($CDCl_3$); $\delta = 7.50$ (5 H, s, C_6H_5), 3.10−4.14 (4 H, m, CH_2CH_2). IR (KBr); 1045 cm^{-1} (S=O). **5**: oil. ^{1}H NMR ($CDCl_3$); $\delta =$ 7.3−7.7 (5 H, s, C_6H_5), 3.4−4.0 (2 H, m, CH_2O), 3.30 (3 H, s,OCH_3), 2.8−3.1 (2 H, m, $C\underline{H}_2CH_2O$). IR (neat); 1040 cm^{-1} (S=O).

Kinetics

A pre-cooled solution of sulfoxide (7.0×10^{-2} mmol) and 0.10 mmol of an internal standard (diphenyl ether or diphenyl sulfide) in anhydrous dioxane was prepared in 10 μL of sealed capillary tubes, and the tubes were immersed in a constant temperature silicon oil bath ($\pm$ 0.1°C) at a desired temperature. At appropriate time intervals, the tubes were taken out and the pyrolysis was stopped in an ice bath. The reaction rate was then determined by following the decreasing peak area of the sulfoxide at 254 nm in HPLC measurement (column: HP−01, eluent: CH_3CN:H_2O = 5:2). The rate of the reaction was found to fit a first-order kinetics nicely, and the rate constant was calculated by the least-squares method.

Activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) were computer calculated by the least-squares method from the Arrhenius equation. The Hammett ρ-value was computed by the least-squares method using σ-values and logarithms of the rate constants.

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