The Ei Reaction of Substituted *threo*- and *erythro*-1-Phenylethyl Phenyl Sulfoxides

Toshiaki Yoshimura,* Eiichi Tsukurimichi, Yukihiko Iizuka, Hironobu Mizuno, Hiroshi Isaji, and Choichiro Shimasaki
Department of Industrial Chemistry, Faculty of Engineering, Toyama University, Gofuku, Toyama 930
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Substituted (*RS,SR*)-1-phenylethyl phenyl sulfoxides (threo) ($XC_6H_4S(O)CH(CH_3)C_6H_4Y$) and some substituted (*RR,SS*)-sulfoxides (erythro) were prepared and kinetic investigation for the thermal decomposition was carried out at 80.0, 90.0, and 100.0 °C in dioxane. Hammett plots for *threo*-$XC_6H_4S(O)CH(CH_3)C_6H_5$ gave positive ρ-values (ρ_X=0.60—0.64 at three temperatures), while those for *threo*- and *erythro*-$C_6H_5S(O)CH(CH_3)C_6H_4Y$ showed V-shape lines with bottoms at the *m*-OCH_3 substituent though the effects of the substituents are small. Meanwhile, large kinetic isotope effects for *threo*- and *erythro*-$C_6H_5S(O)CH(CD_3)C_6H_4Y$ (Y=H, *p*-OMe, *m*-Cl) (k_H/k_D=4—6) were observed at all temperatures. The activation energies were in the range of 104—121 kJ mol^{-1} for all sulfoxides, while the activation entropies were relatively large (7—−37 J K^{-1} mol^{-1}) and were correlated with Hammett σ-values to give small negative trend. Reactions of all erythro-isomers examined were 2—3 times faster than those of the corresponding threo-isomers. From these results, it is suggested that the pyrolysis of 1-arylethyl aryl sulfoxides proceeds via a concerted mechanism in which the transition state is variable from an E1-like to a conjugated one. In the latter transition state, conjugation of the phenyl group bearing the electron-withdrawing substituent with the developing π-bond electron acidifies the β-proton.

Thermolysis of sulfoxides bearing at least one β-hydrogen atom has been shown to proceed via an intramolecular cis elimination[1] affording olefins[2-8] and sulfenic acids which are dimerized to thiosulfinic S-esters or can be trapped by activated olefins.[9-16] Cram et al.[1] prposed a radical mechanism based on the observation of loss of stereospecificity for the pyrolysis of 1,2-diphenyl-1-propyl phenyl sulfoxides at high temperatures. However, no evidence suggesting the radical mechanism has been reported ever since. Though the Ei-reaction of sulfoxides is generally regarded as a concerted process, some kinetic investigations using aryl propyl sulfoxides[17] or aryl *t*-butyl sulfoxides[8] reveal that electron-withdrawing substituents on the phenyl ring accelerate the reaction suggesting the polarization of the carbon-sulfur bond and development of partially negative charge on the sulfinyl group in the transition state. From these results, development of partially positive charge on the α-carbon atom, i.e., E1-like mechanism, has been assumed. However, we recently proposed a carbanion-like mechanism for the pyrolysis of 2-phenylethyl phenyl sulfoxide which showed positive trends for Hammett substituent effects on both phenyl groups (ρ_X=0.76 for $XC_6H_4S(O)CH_2CH_2Ph$, ρ_Y=0.32 for $PhS(O)CH_2CH_2C_6H_4Y$). These results reveal that partial charge on the α-carbon atom in the transition state cannot be determined without an examination of the substituent effect on the α-position.

Meanwhile, Oae et al. reported the mechanistic investigation of Ei-reaction of sulfilimines which have isoelectronic structure to the sulfoxides. They suggested cis-concerted E1-like mechanism.[18-21]

In order to clarify the transition state of the Ei-reaction of sulfoxides and to compare with that of sulfilimines, kinetic investigation of the thermolysis of substituted *threo*- and *erythro*-1-phenylethyl phenyl sulfoxides was carried out.

Results

Preparation of Substituted 1-Phenylethyl Phenyl Sulfoxides and Their Diastereoisomer. The substituted *threo*- and *erythro*-1-phenylethyl phenyl sulfoxides were prepared from the corresponding sulfides by oxidation with hydrogen peroxide in acetic acid. The mixture of threo- and erythro-isomers obtained were separated by fractional crystallization and repeated column chromatography. The *threo*- and *erythro*-sulfoxides obtained were tentatively assigned as follows. ^1H NMR chemical shifts of methine protons of the sulfoxides were plotted against Hammett σ-values as shown in Fig. 1.

Apparently, two series of methine signals were observed. The higher field one could be assigned as that of threo isomer by comparing with that of 1-phenylethyl phenyl and 1-phenylethyl *p*-tolyl sulfoxides whose absolute configurations[22,23] are known. A similar series of ^1H NMR methine signals of 1-phenylethyl (*p*-substituted phenyl) sulfoxides and their lanthanoid-induced shifts, solvent effects, and assignments of their absolute configurations were reported.[24,25]

Upon heating the sulfoxides in carbon tetrachloride at 100 °C for 15—20 min, formation of the substituted styrenes were observed by NMR and liquid chromatography. If the reaction should be accompanied by a possible threo-erythro isomerization due to a pyramidal inversion[30] on sulfur atom or a homolytic cleavage like in the racemization of benzyl *p*-tolyl sulfoxide at 135—165 °C,[31] the kinetic behavior should be complicated. But the NMR spectra showed no contamination of the threo-erythro isomerization, also sug-

gesting that the radical mechanism is unlikely.

Kinetics. The reaction was followed by measuring the decreasing peak area of the sulfoxide in liquid chromatography using diphenyl ether, diphenyl sulfide or methyl phenyl sulfide as an internal standard. The process of the reactions was found to follow good first-order kinetics and the rate constants had no dependence on initial concentration of the sulfoxides. The results obtained are listed in Table 1 and Hammett substituent effects are compiled in Table 2.

Effects of X-substituents for the threo-isomer gave positive ρ-values suggesting that departure of leaving group is important in the transition state. However, both the electron-withdrawing and -releasing Y-substituents were found to accelerate the reaction to give concave curves in which a series of substituents from the p-OCH_3 to m-OCH_3 groups gave negative ρ-values, while the m-OCH_3 to p-NO_2 groups afforded

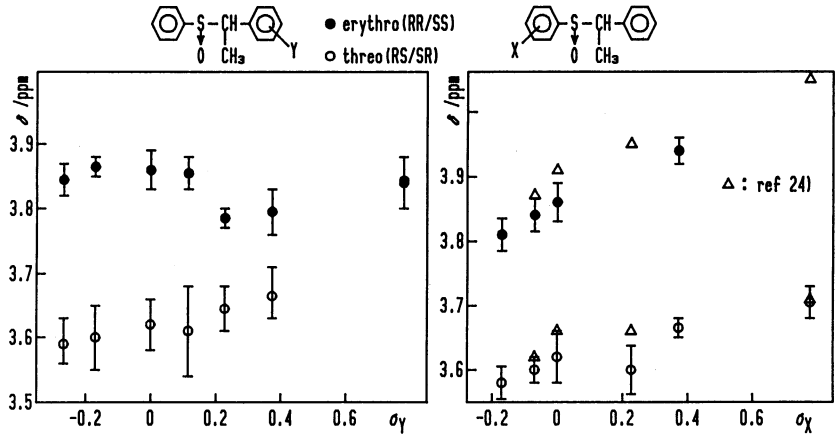


Fig. 1. Dependence of ^{1}H NMR methine signals of *threo*- and *erythro*-1-arylethyl aryl sulfoxides on Hammett σ-values.

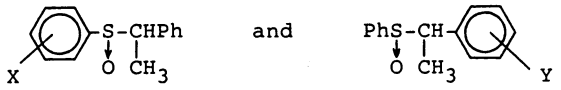
Table 1. The Kinetic Data for Pyrolysis of Substituted 1-Phenylethyl Phenyl Sulfoxides in Dioxane

XC_6H_4-S-CHC_6H_4Y
↓ |
O $CH_3(CD_3)$

Sulfoxides			Rate constants[a]			Activation parameters		
X	Y	Isomer	$k\times10^5$ / s^{-1}			ln A	E_a / kJ mol^{-1}	ΔS^* / J K^{-1} mol^{-1}
			80.0 °C	90.0 °C	100.0 °C			
H	*p*-OMe	th[b]	6.92 ±0.07	22.4 ±0.4	57.7 ±0.8	30.1±1.8	116±5	−5±15
H	*p*-OMe	er[c]	18.1 ±0.9	55.2 ±0.9	137 ±4	29.2±1.6	111±5	−12±13
H	*p*-OMe	th(β-d_3)[d]	1.60 ±0.06	4.91±0.12	13.2 ±0.2	28.4±0.8	116±2	−19±6
H	*p*-Me	th	6.04 ±0.02	18.5 ±0.5	48.7 ±0.6	29.3±1.0	114±3	−12±8
H	*p*-Me	th(β-d_3)	1.20 ±0.04	3.65±0.23	9.77±0.44	27.8±0.7	115±2	−24±6
H	H	th	5.15 ±0.18	14.5 ±0.4	43.5 ±1.6	29.9±1.3	117±4	−6±11
H	H	er	10.2 ±0.5	30.4 ±0.6	83.9 ±3.0	30.1±0.2	115±1	−4±2
H	H	th(β-d_3)	1.00 ±0.02	2.92±0.05	9.12±0.14	29.7±1.3	121±4	−8±11
H	H	er(β-d_3)	2.30 ±0.05	6.12±0.07	17.9 ±0.2	27.6±1.6	112±5	−26±13
H	*m*-OMe	th	4.98 ±0.18	15.8 ±0.6	40.2 ±1.1	29.1±1.7	114±5	−13±14
H	*m*-OMe	er	12.8 ±1.8	35.6 ±0.4	96.0 ±1.4	28.6±0.3	110±1	−17±2
H	*p*-Cl	th	5.47 ±0.22	14.7 ±0.6	43.1 ±1.0	28.7±1.5	113±5	−17±13
H	*p*-Br	th	4.40 ±0.16	13.1 ±0.2	34.9 ±1.1	28.6±0.6	113±2	−17±5
H	*m*-Cl	th	5.21 ±0.10	15.1 ±0.5	39.9 ±0.8	28.1±0.4	112±1	−21±3
H	*m*-Cl	er	15.0 ±0.3	42.4 ±0.9	104 ±3	27.4±0.9	106±3	−27±8
H	*m*-Cl	th(β-d_3)	0.858±0.008	2.53±0.09	7.09±0.36	27.7±0.1	116±1	−24±1
H	*p*-NO_2	th	6.97 ±0.33	19.3 ±0.9	47.5 ±4.5	26.3±0.7	105±2	−37±6
H	*p*-NO_2	er	20.6 ±1.1	49.4 ±2.0	138 ±5	26.9±2.2	104±6	−31±18
p-Me	H	th	4.21 ±0.05	12.2 ±0.2	34.1 ±1.4	29.0±0.2	115±1	−14±2
m-Me	H	th	4.91 ±0.05	13.2 ±0.4	37.5 ±0.5	28.0±1.2	111±4	−22±10
p-Cl	H	th	6.05 ±0.22	15.2 ±0.4	46.6 ±1.6	28.3±2.7	112±8	−20±22
m-Cl	H	th	6.61 ±0.34	20.2 ±0.6	53.5 ±2.8	29.4±0.9	115±3	−10±7
p-NO_2	H	th	17.5 ±0.3	47.3 ±1.1	151 ±2	31.5±2.4	118±7	7±20

a) The rate constants and activation parameters were calculated by the least-squares method and the errors are standard deviations. b) Threo-isomer. c) Erythro-isomer. d) β-Deuterated sulfoxide.

Table 2. Hammett ρ-Values (vs. σ) for Pyrolysis of 1-(Substituted phenyl)ethyl Phenyl Sulfoxides and 1-Phenylethyl (Substituted phenyl) Sulfoxides in Dioxane



Temp °C	ρ_X(threo)	ρ_{Y1}(threo)[a]	ρ_{Y2}(threo)[a]	ρ_{Y1}(erythro)	ρ_{Y2}(erythro)
80.0	0.61(0.96)	−0.38(0.98)[b]	0.24(0.86)	−0.49(0.75)	0.31(0.99)
90.0	0.60(0.96)	−0.43(0.88)	0.19(0.78)	−0.58(0.85)	0.21(0.99)
100.0	0.64(0.95)	−0.39(0.97)	0.13(0.68)	−0.47(0.84)	0.24(0.98)

a) ρ_{Y1}, *p*-OMe≈*m*-OMe; ρ_{Y2}, *m*-OMe≈*p*-NO_2. b) The numbers in the parentheses are correlation coefficients.

Table 3. Isotope Effects for 1-Arylethyl-2,2,2-d_3 Phenyl Sulfoxides

X	Y	Isomer	Isotope effects (k_H/k_D)			$E_{aD}-E_{aH}$	A_H/A_D
			80.0 °C	90.0 °C	100 °C	kJ mol^{-1}	
H	*p*-OMe	th	4.33±0.17	4.56±0.14	4.37±0.09	0±7	5.5
H	H	th	5.15±0.21	4.97±0.16	4.77±0.19	4±8	1.2
H	H	er	4.43±0.24	4.97±0.11	4.69±0.18	3±6	12
H	*m*-Cl	th	6.07±0.13	5.97±0.29	5.63±0.31	4±2	1.49

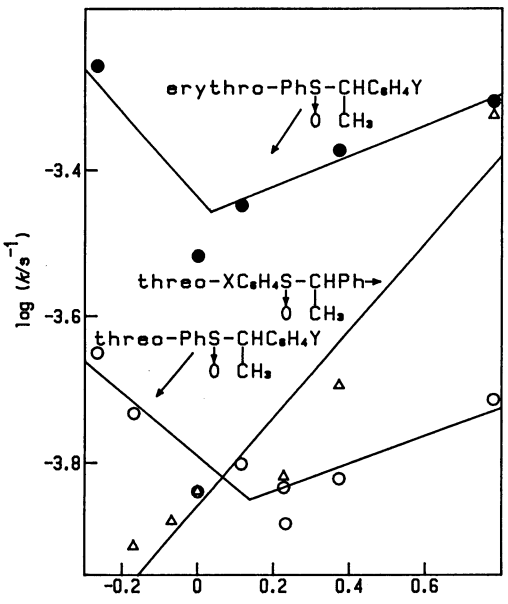


Fig. 2. Hammett plots for the rates of pyrolysis of *threo*- and *erythro*-1-arylethyl aryl sulfoxides at 90.0 °C in dioxane.

positive ρ-values for both the threo- and erythro-isomers as the example at 90.0 °C shown in Fig. 2. Though some Hammett correlations are not very good and the reflecting point is not clear, all of the correlations for different temperatures and different isomers have the same tendencies. The bottoms of the Hammett plots for Y-substituent effects for the threo-isomers seem to be deviated to a positive side at all temperatures unlike the erythro-isomers whose bottom positions are not clear due to only a few measured points. The Hammett plots for the threo- and the erythro-isomers gave the separated parallel lines suggesting that the present assignments of the isomers are valid, especially for 1-(*p*-nitrophenyl)ethyl phenyl sulfoxides ^{1}H NMR methine signals of which cannot be distinguished the isomers.

Large kinetic isotope effects using β,β,β-d_3 sulfoxides were observed as shown in Table 3 for both the *erythro*- and the *threo*-sulfoxides bearing both the electron-withdrawing and -releasing Y-substituents (*p*-OCH_3, *p*-CH_3, H, *m*-Cl), suggesting an involvement of a proton transfer from the β-carbon to the oxygen and no radical cleavage of the C-S bond in the transition state, since the free radical mechanism involving the rate-determining C-S bond cleavage is not in accord with the large kinetic isotope effect. These results 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.

Activation parameters were calculated for all the sulfoxides (Table 1). The activation entropies are all in the range of 7 to −37 J K^{-1} mol^{-1}. These values are of positively deviated compared to those for primary alkyl aryl sulfoxides (phenyl propyl sulfoxide −63 J K^{-1} mol^{-1},[17] 2-phenylethyl phenyl sulfoxide −45 J K^{-1} mol^{-1}.[26] The activation entropies correlate with the Hammett σ-values giving a negative correlation for Y-substituents as shown in Fig. 3, though the correlation for X-substituents is not clear. Namely, the activation entropy for the reaction of the sulfoxide having more electron-withdrawing Y-substituent is more negative.

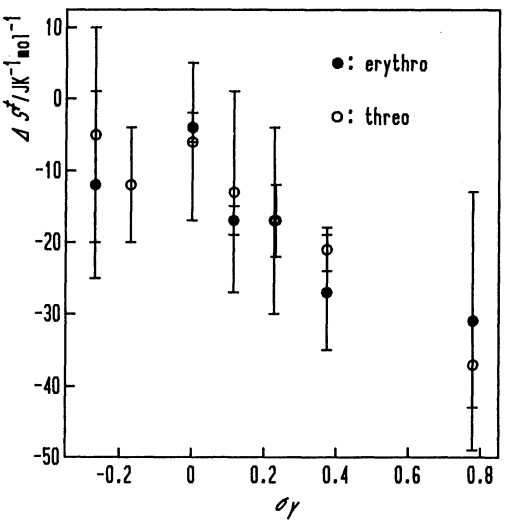


Fig. 3. Dependence of activation entropies on Hammett σ-values for the pyrolysis of *threo*- and *erythro*-1-arylethyl phenyl sulfoxides.

Table 4. Solvent Effect on Pyrolysis of *threo*-1-Phenylethyl Phenyl Sulfoxide at 90.0 °C

Solvent	Dielectric constant	Rate constant $k\times10^5$ / s^{-1}	Relative rates
Dioxane	2.21	14.5 ±0.4	1
DMSO	48.9	7.48±0.09	0.52
Acetonitrile	37.5	5.59±0.25	0.39
Ethanol	24.3	2.31±0.09	0.16

Pyrolysis of the sulfoxide in other solvents was carried out as shown in Table 4. The pyrolysis was not much affected by the solvent change, the rates of pyrolysis are not correlated to the dielectric constants, and the relative rates are very similar to those for the pyrolysis of 2-phenylethyl phenyl sulfoxide[26] and sulfilimines[19] suggesting that the transition state of the reaction is not ionic but concerted one like other sulfoxides and sulfilimines. Namely, the more solvation in the starting state by a dipole-dipole interaction between sulfoxides and dipolar aprotic solvents or by a hydrogen bonding to the sulfoxide oxygen than in the transition state causes the reduction of the reaction rate as described in the previous paper.[26]

Discussion

Though Ei-reaction of sulfoxides are generally recognized as a concerted process, a balance of extent of the C-S bond cleavage and the proton migration from the β-carbon to the oxygen causes the deviation to an E1-like or a carbanion-like mechanism in the five-membered cyclic transition state. Namely, in the E1-like mechanism the departure of leaving group progresses more than the proton abstraction developing a partially positive charge at the α-carbon while in the carbanion-like mechanism the reverse relation develops a partially negative charge at the β-carbon in the transition state.

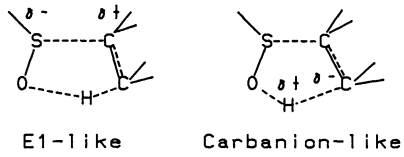


Fig. 4. E1-like and carbanion-like cyclic transition states.

However, unlike E2-reactions the development of charge at the α- or β-carbon should be small, because the stretching of the C-S bond can lead to an enhancement of both the basicity of the oxygen atom and the acidity of the β-proton which would facilitate the proton transfer resulting a neutralization of the positive charge at the α-carbon atom, similarly the progress of the proton transfer would promote the C-S bond cleavage neutralizing the negative charge at the β-carbon. In fact, relative yields of 1-butene to the 2-butene are nearly equal to those on the statistical basis of the numbers of the β-hydrogens in the pyrolysis of ethyl *s*-butyl and propyl *s*-butyl sulfoxides,[4] suggesting that the orientation of elimination has no tendency of Saytzeff or Hofmann rule. Nevertheless, examinations of a Hammett substituent effect have shown to some extent the development of the partial charge in the transition state of the pyrolysis of sulfoxides.[8,17,26] In many variations of Hammett σ-values, use of the usual σ-values for the correlations is considered to be enough to examine such small charge distributions in the concerted transition state, and has been done in these literatures.

Hammett Substituent Effect. The positive Hammett ρ-values for X-substituents appears to be consistent with an E1-like mechanism. Various examples of ρ-values for the pyrolysis of other alkyl aryl sulfoxides and sulfilimines are compiled in Table 5. The effects of X-substituents generally show a positive trend for both sulfoxides and sulfilimines except for 2-cyanoethyl phenyl sulfoxide.[26] However, the pyrolysis proceeding via a carbanion-like mechanism for 2-cyanoethyl phenyl and aryl 2-phenylethyl sulfoxides shows negative or small positive ρ-values. The posi-

Table 5. Representative Hammett ρ-Values of Pyrolysis of Sulfoxides and Sulfilimines

Substrate	Solvent	Temp / °C	ρx	Ref.
$XC_6H_4S(O)CH_2CH_2CH_3$	PhOPh	170—180	0.51	17
$XC_6H_4S(O)C(CH_3)_3$	$PhCH_3$	101.3	0.695	8
$XC_6H_4S(O)CH_2CH_2Ph$	Dioxane	120.0	0.33	26
$XC_6H_4S(O)CH_2CH_2CN$	Dioxane	100.0	−0.49	26
$XC_6H_4S(NTs)CH_2CH_3$	Benzene	80.3	0.90	20
$XC_6H_4S(NTs)CH(CH_3)Ph$	Benzene	25.0	0.90	19

tive trend for the pyrolysis of aryl 2-phenylethyl sulfoxides via even a carbanion-like mechanism is attributed to the substituent effect on the *S*-phenyl group being more susceptible to C-S bond cleavage than proton abstraction.[26] Therefore, from the examination of only the substituent effect on the *S*-phenyl group the mechanism can not be clarified. The substituent effect on the α-phenyl group showed negative Hammett ρ-values from the *p*-OCH_3 group to the *m*-OCH_3 group suggesting apparently development of partially positive charge on the α-position in the transition state, i.e., an E1-like mechanism. However, the ρ-values turned from negative to positive from the *m*-OCH_3 group to the *p*-NO_2 group to give V-shaped Hammett plots. A similar Hammett substituent effect is known in the nucleophilic substitution at substituted benzyl chlorides by trimethylamine which is interpreted in a change of the transition state from S_N1-like to S_N2-like.[29] The present results can also be explained in the same way. Namely, the transition state of the elimination presumably varies from E1-like in the case of the sulfoxides bearing electron-releasing Y-substituents into a conjugated system as shown in Fig. 5 in the case of electron-withdrawing groups.

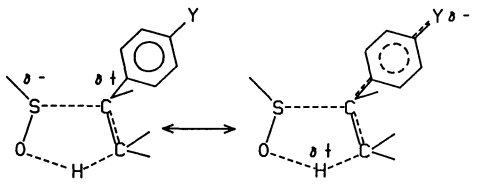


Fig. 5. Conjugated transition state of the pyrolysis of 1-(electron-withdrawing group-substituted phenyl)-ethyl phenyl sulfoxides.

The conjugation with electron-withdrawing groups is advantageous for the elimination, because it acidifies the β-proton effectively, assists the C-H bond cleavage, and stabilizes the transition state. Meanwhile, the conjugation with electron-releasing substituents interferes the development of C-C π-bond formation, instead, stabilizes the partially positive charge at the α-carbon, assisting the extension of the C-S bond to increase the basicity of the sulfoxide oxygen which also accelerates the elimination. Figure 2 shows that the position of 1-phenylethyl phenyl sulfoxide is on the negative line suggesting that the transition state of its Ei is E1-like.

Activation Parameters. Activation parameters for pyrolysis of sulfoxides are usually in the range of 106—125 kJ mol^{-1} for activation enthalpies and −71—+30 J K^{-1} mol^{-1} for activation entropies.[1,4,8,17,26] The activation entropy of the slowest type of such simple sulfoxides as phenyl propyl is large negative (−63 J K^{-1} mol^{-1})[17] suggesting that the transition state is more rigid than the starting state due mainly to a cyclization. However, the present system shows a nearly zero activation entropy which is presumably a result of a relatively large contribution of the extension of the C-S bond in the cyclic transition state compared to the small contribution of the progress of the proton transfer according to the following reason. The contribution of extent of the proton transfer to the activation entropy is probably small, because the contribution of looseness of the C-H bond is canceled by that of development of the O-H bond formation. Therefore the increase of the activation entropy to the positive direction in the present system is mainly based on the contribution of the looseness of the C-S bond in the transition state. In the case of the pyrolysis via a carbanion-type transition state such as that of 2-phenylethyl phenyl sulfoxide, the C-S bond is not so loose as compared with the progress of the proton transfer resulting a relatively large negative activation entropy.[26] Therefore, the positively deviated activation entropy for the present system is consistent with the E1-like mechanism. The fact that the plot of activation entropies for Y-substituents vs. Hammett σ-values gave the negative trend is probably due to the increase of an E1-like character by electron-releasing substituents.

Isotope Effect. Kinetic isotope effects for the Ei-reaction of β-deuterated sulfoxides, sulfilimines, and tertiary amine oxides are usually small (k_H/k_D=2—3.5)[19,20,27] due to the cyclic transition state. However, the present system shows relatively large kinetic isotope effects. Meanwhile, Kwart et al. reported a usual magnitude of kinetic isotope effect for the thermolysis of heptyl-2-*d* phenyl sulfoxide (k_H/k_D=2.3—3.1)[27,28] and a relatively large effect for *t*-butyl-d_9 ethyl sulfoxide (k_H/k_D=3.3—6).[11] They examined a temperature dependence of k_H/k_D to result that the activation energy difference and the frequency factor ratio between hydrogen and deuterium for the cis-elimination of heptyl phenyl sulfoxide ($E_{a_D}-E_{a_H}$=4.81 kJ mol^{-1} A_H/A_D=0.76)[27] are in the range of zero-point energy controlled isotope effect ($E_{a_D}-E_{a_H}<5.9$ kJ mol^{-1}, $0.6<A_H/A_D<1.4$),[28] but those for *t*-butyl ethyl sulfoxide ($E_{a_D}-E_{a_H}$=13 kJ mol^{-1}, A_H/A_D=0.07) are out of that range suggesting the incursion of hydrogen tunneling.[11] The temperature dependences of the isotope effects for the present system were examined as shown in Table 3. Though it is difficult to discuss about the involvement of the tunnel effect from the data for only one sample because of unavoidable large errors in the differences of the activation parameters measured in the narrow temperature range, in total view of data for all samples, the parameter differences do not seem to be deviated so much from the range of the zero-point energy differences. Though the ratios of the frequency factors are scattered, the values do not fit to tunneling since smaller values ($0<A_H/A_D \ll 1$) can be expected for the tunnel effect.[28] Assuming the isotope effect to be controlled by a zero point energy, the large kinetic isotope effects for the present system (the

isotope effects are larger than that for heptyl phenyl sulfoxide[27] even though the values are extrapolated to the same temperatures) should be explained by a change of the structure of the transition state. In general, a maximum magnitude of the hydrogen-deuterium isotope effect controlled by a zero-point energy is known to be ca. 8 for linear hydrogen transfer reactions.[28] Therefore, small isotope effects for Ei reactions have been attributed to their non-linearity. The relatively large activation entropies for the present system are the result of the C-S bond loosened transition state which allows the linear hydrogen transfer to show the large isotope effect.

The substituent effect on the magnitude of the isotope effects is also interesting. There might be two geometric factors in the transition state to affect the isotope effect. One is the linearity of the hydrogen transfer as described above. The C-S bond in the transition state might be more loosened for the sulfoxide having more electron-releasing Y-substituent as discussed in the activation parameters section expecting the more linear hydrogen transfer and larger isotope effect. The other factor is a symmetry of the hydrogen transfer which shows a maximum primary isotope effect. In view of that the hydrogen transfer is performed by a low basic sulfoxide oxygen, the position of the hydrogen atom in the transition state is considered to be nearer to the starting state. In this situation, the more acidic β-proton the sulfoxide has, the more symmetric hydrogen transfer can be expected. Contrary to the former factor, the more electron-withdrawing Y-substituent will show the larger isotope effect. The present results show that the latter effect could be more important than the former in the substituent effect on the kinetic isotope effects.

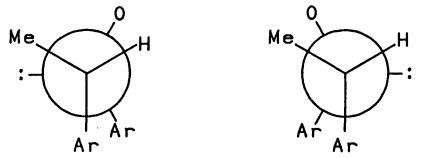
Reactivity of Isomers. The ratios of pyrolytic rates of threo-erythro-isomers (k_{er}/k_{th}) are listed in Table 6. The pyrolysis of erythro-isomers is 2—3 times faster than that of threo-isomers for all substituents and at all three temperatures.

In 1982, Kobayashi et al.[25] reported that there is some attractive interaction between *S*-phenyl and α-phenyl group (CH-π interaction) in the conformation of both *threo*- and *erythro*-1-phenylethyl aryl sulfoxides, and the most stable conformers are as shown in Fig. 6 for the threo- and the erythro-isomers, respectively. The most stable conformer of the erythro-isomer in the starting state is advantageous for the Ei-reaction compared to that of the threo-isomer since the sulfoxide oxygen and the methyl group is close. Assuming the phenyl-phenyl attractive interaction still remained in the transition state for the erythro-isomer, the activation free energy for the threo-isomer would be larger than that for the erythro-isomer because of an unavoidable breaking of the interaction for the threo-isomer. Thus the pyrolysis results in the faster elimination for the erythro-isomers. Inspection of the data in the Table 6 reveals that there are similar tendencies between k_{er}/k_{th} and σ-values of Y-substituents at all temperatures, though

Table 6. The Ratios of Pyrolysis Rates of Erythro-Threo Isomers (k_{er}/k_{th}) of 1-Arylethyl Phenyl Sulfoxides in Dioxane

Ph-S-CHC$_6$H$_4$Y
↓ |
O CH$_3$

Y	80.0 °C	90.0 °C	100.0 °C
p-OMe	2.62	2.46	2.37
H	1.98	2.07	1.93
H(β-d$_3$)	2.30	2.10	1.96
m-OMe	2.57	2.25	2.39
m-Cl	2.88	2.81	2.61
p-NO$_2$	2.96	2.56	2.91



threo(RS/SR) erythro(RR/SS)

Fig. 6. The most favorable conformations of *threo*- and *erythro*-1-arylethyl aryl sulfoxides.

Table 7. Effects of the Phenyl Group on the α -and β-Positions of Ethyl Phenyl Sulfoxide and Sulfilimine

	Solvent	Temp °C	$k\times10^5$ s^{-1}	Rel rate	Ref.
PhS(O)CH$_2$CH$_3$	Dioxane	100	0.165	1	
PhS(O)CHCH$_3$ threo	Dioxane	100	43.5	264	
Ph erythro	Dioxane	100	83.9	508	
PhS(O)CH$_2$CH$_2$Ph	Dioxane	100	1.41	12.8[a]	26
PhS(NTs)CH$_2$CH$_3$	Benzene	80.3	1.08	1	19,20
PhS(NTs)CHCH$_3$	Benzene			10^3	19
Ph					
PhS(NTs)CH$_2$CH$_2$Ph	Benzene			1.5[a]	19

a) Corrected with number of β-hydrogens.

the data are scattered. The tendencies that both the electron-withdrawing and -releasing substituents enlarge the ratios (k_{er}/k_{th}) are similar to those for log k vs. σ. Though the reason for this observation is not clear, it might be explained by the stronger CH-π interaction for the more polar sulfoxides.

Effect of the α-Phenyl Group on the Rate of the Pyrolysis. The pyrolysis of *threo*- and *erythro*-1-phenylethyl phenyl sulfoxides was found to be 264 and 508 times faster than that of ethyl phenyl sulfoxide at 100 °C in dioxane. The effects of the phenyl substituent on the α- and β-positions of ethyl phenyl sulfoxide and sulfilimine are compared in Table 7. Introduction of a phenyl group at the α-position results in much more acceleration than that at the β-position suggesting that the C-S bond cleavage is more important than the proton transfer in the transition state of pyrolysis for both sulfoxides and sulfilimines.

Conclusion

From these results the following conclusion can be obtained. The large β-hydrogen kinetic isotope effect rules out a radical pair mechanism and an ionic mechanism is also ruled out because of the small solvent effect and the relatively small Hammett substituent effects. The reaction mechanism is thus considered to be a concerted process through a five-membered cyclic transition state. The large activation entropies reveal a C-S bond loosened transition state to make possible to more linear proton transfer and to give the large hydrogen kinetic isotope effect compared to primary alkyl sulfoxides. The V-shaped Hammett plot for the rates and the negative trend for the substituent effect for the activation entropies on the 1-phenyl group indicate that the transition state changes as follows. Electron-releasing substituents on the 1-phenyl group change the transition state to a C-S bond loosened E1-like type, while electron-withdrawing ones change that to C-S bond not so stretched conjugated type in which the acidity of the β-proton is increased. These results suggest that the transition state is on a broad potential energy surface. The higher reactivity of erythro-isomers than threo-isomers can be attributed to a 1-phenyl-*S*-phenyl attractive interaction (CH-π interaction)[25] of the sulfoxide in both the ground and the transition states. The larger enhancement by a 1-phenyl group on the rate of pyrolysis of ethyl phenyl sulfoxide than that by a 2-phenyl group suggests that the Ei-reaction of sulfoxides essentially tend to take an E1-like transition state.

Experimental

General. All melting points were uncorrected. IR spectra were taken on a JASCO IRA-1 spectrometer. NMR spectra were recorded with a Hitachi R-24B spectrometer (60 MHz) using TMS as an internal standard.

Preparation of 1-Arylethyl Aryl Sulfoxides. All sulfoxides were prepared by oxidation of the corresponding 1-arylethyl aryl sulfides with hydrogen peroxide in acetic acid at room temperature. Most of the threo-isomers were obtained by repeated recrystallization from ether, ether-hexane, or methanol except for 1-phenylethyl phenyl, 1-(*m*-methoxyphenyl)ethyl phenyl, and 1-(*m*-chlorophenyl)ethyl phenyl sulfoxides, instead the erythro-isomers of which were isolated by recrystallization. The threo-isomers of the latter three sulfoxides and other erythro-isomers were obtained by repeated silica-gel column chromatography using chloroform or ether-hexane (3 : 1) as an eluent. The sulfoxides thus obtained have the following physical properties.

$XC_6H_4S(O)CH(CH_3)C_6H_4Y$: X,Y, Threo or Erythro: H, *p*-MeO, Threo: Mp 92 °C (from ether-hexane); IR (KBr) 1051 cm^{-1} (S-O); ^1H NMR (CCl_4) δ=1.52 (3H, d, J=7 Hz, CH_3), 3.59 (1H, q, J=7 Hz, CH), 3.73 (3H, s, OCH_3), 6.5—7.1 (4H, AB, J=9 Hz, Ar), 7.1—7.5 (5H, s-like, Ph). Found: C, 69.59; H, 6.19%. Calcd for $C_{15}H_{16}O_2S$: C, 69.20, H, 6.19%.

H,*p*-MeO, Erythro: Mp 83—84 °C (from ether-hexane); IR (KBr) 1040 cm^{-1} (S-O); ^1H NMR (CCl_4) δ=1.49 (3H, d, J=7 Hz, CH_3), 3.82 (1H, q, J=7 Hz, CH), 3.69 (3H, s, OCH_3), 6.68 (4H, s-like, Ar), 6.9—7.4 (5H, s-like, Ph). Found: C, 69.39; H, 6.09%. Calcd for $C_{15}H_{16}O_2S$: C, 69.20; H, 6.19%.

H,*p*-Me, Threo: Mp 99—100 °C (ether-hexane); IR (KBr) 1051 cm^{-1} (S-O); ^1H NMR (CCl_4) δ=1.56 (3H, d, J=7 Hz, CH_3), 3.59 (1H, q, J=7 Hz, CH), 2.31 (3H, s, *p*-CH_3), 6.7—7.2 (4H, m, Ar), 7.2—7.5 (5H, s-like, Ph). Found: C, 73.72; H, 6.58%. Calcd for $C_{15}H_{16}OS$: C, 73.73; H, 6.60%.

H,H,Threo: Mp 67.5—68.5 °C (ether-hexane); IR (KBr) 1049 cm^{-1} (S-O); ^1H NMR (CCl_4) δ=1.59 (3H, d, J=7 Hz, CH_3), 3.66 (1H, q, J=7 Hz, CH), 6.7—7.5 (10H, m, Ph); ($CDCl_3$) δ=1.66 (3H, d, J=7 Hz, CH_3), 3.78 (1H, q, J=7 Hz, CH), 6.8—7.6 (10H, m, Ph).[22,25]

H,H, Erythro: Mp 111—112 °C (ether); IR (KBr) 1050 cm^{-1} (S-O); ^1H NMR (CCl_4) δ=1.55 (3H, d, J=7 Hz, CH_3), 3.88 (1H, q, J=7 Hz, CH), 6.7—7.4 (10H, m, Ph); ($CDCl_3$) δ=1.58 (3H, d, J=7 Hz, CH_3), 3.99 (1H, q, J=7 Hz, CH), 6.8—7.5 (10H Ph).[22,25]

H,*m*-OMe, Threo: Oil; IR (neat) 1046 cm^{-1} (S-O). ^1H NMR (CCl_4) δ=1.58 (3H, d, J=7 Hz, CH_3), 3.55 (1H, q, J=7 Hz, CH), 3.65 (3H, s, OCH_3), 6.3—7.3 (9H, m, Ar); ($CDCl_3$) δ=1.64 (3H, d, J=7 Hz, CH_3), 3.74 (1H, q, J=7 Hz, CH), 3.64 (3H, s, OCH_3), 6.4—7.5 (9H, m, Ar). Found: C, 68.59; H, 6.29%. Calcd for $C_{15}H_{16}O_2S$: C, 69.20; H, 6.19%.

H,*m*-OMe, Erythro: Mp 115 °C; IR (KBr) 1051 cm^{-1} (S-O); ^1H NMR (CCl_4) δ=1.53 (3H, d, J=7 Hz, CH_3), 3.85 (1H, q, J=7 Hz, CH), 3.65 (3H, s, OCH_3), 6.2—7.4 (9H, m, Ar); ($CDCl_3$) δ=1.56 (3H, d, J=7 Hz, CH_3), 4.00 (1H, q, J=7 Hz, CH), 3.66 (3H, s, OCH_3), 6.4—7.5 (9H, m, Ar). Found: C, 68.94; H, 6.36%. Calcd for $C_{15}H_{16}O_2S$: C, 69.20; H, 6.19%.

H,*p*-Cl, Threo: Mp 122.5 °C; IR (KBr) 1045 cm^{-1} (S-O); ^1H NMR (CCl_4) δ=1.49 (3H, d, J=7 Hz, CH_3), 3.63 (1H, q, J=7 Hz, CH), 6.7—7.7 (9H, m, Ar). Found: C, 63.78; H, 5.08%. Calcd for $C_{14}H_{13}ClOS$: C, 63.51; H, 4.95%.

H,*p*-Br, Threo: Mp 137.5 °C; IR (KBr) 1047 cm^{-1} (S-O); ^1H NMR (CCl_4) δ=1.45 (3H, d, J=7 Hz, CH_3), 3.61 (1H, q, J=7 Hz, CH), 6.7—7.7 (9H, m, Ar). Found: C, 54.46; H, 4.26%. Calcd for $C_{14}H_{13}BrOS$: C, 54.38; H, 4.24%.

H,*m*-Cl, Threo: Oil; IR (neat) 1049 cm^{-1} (S-O); ^1H NMR (CCl_4) δ=1.51 (3H, d, J=7 Hz, CH_3), 3.67 (1H, q, J=7 Hz, CH), 6.7—7.5 (9H, m, Ar). Found: C, 62.79; H, 5.29%.

Calcd for $C_{14}H_{13}ClOS$: C, 63.51; H, 4.95%.

H,*m*-Cl,Erythro: Mp 81.5 °C; IR (KBr) 1047 cm^{-1} (S-O); ^1H NMR (CCl_4) δ=1.56 (3H, d, J=7 Hz, CH_3), 3.79 (1H, q, J=7 Hz, CH), 6.6—7.4 (9H, m, Ar). Found: C, 63.28; H, 4.84%. Calcd for $C_{14}H_{13}ClOS$: C, 63.51; H, 4.95%.

H,*p*-NO_2,Threo: Mp 119—120 °C (MeOH); IR (KBr) 1353, 1523 (NO_2) and 1048 cm^{-1} (S-O); ^1H NMR (CCl_4) δ=1.55 (3H, d, J=7 Hz, CH_3), 3.84 (1H, q, J=7 Hz, CH), 7.1—8.2 (9H, m, Ar); ($CDCl_3$) δ=1.64 (3H, d, J=7 Hz, CH_3), 3.99 (1H, q, J=7 Hz, CH), 7.1—8.3 (9H, m, Ar). Found: C, 61.17; H, 4.93; N, 5.22%. Calcd for $C_{14}H_{13}NO_3S$: C, 61.07; H, 4.76; N, 5.09%.

H,*p*-NO_2,Erythro: Mp 100 °C (ether); IR (KBr) 1322, 1490 (NO_2) and 1047 cm^{-1} (S-O); ^1H NMR (CCl_4) δ=1.73 (3H, d, J=7 Hz, CH_3), 3.82 (1H, q, J=7 Hz, CH), 6.8—8.1 (9H, m, Ar); ($CDCl_3$) δ=1.75 (3H, d, J=7 Hz, CH_3), 3.94 (1H, q, J=7 Hz, CH), 6.9—8.2 (9H, m, Ar). Found: C, 61.21; H, 4.88; N, 5.21%. Calcd for $C_{14}H_{13}NO_3S$: C, 61.07; H, 4.76; N, 5.09%.

***p*-Me,H,Threo:** Mp 136.8 °C; IR (KBr) 1052 cm^{-1} (S-O); ^1H NMR(CCl_4) δ=1.58 (3H, d, J=7 Hz, CH_3), 3.58 (1H, q, J=7 Hz, CH), 2.35 (3H, s, CH_3), 6.8—7.4 (9H, m, Ar); ($CDCl_3$) δ=1.64 (3H, d, J=7 Hz, CH_3), 3.73 (1H, q, J=7 Hz, CH), 2.30 (3H, s, CH_3), 6.8—7.4 (9H, m, Ar).[25] Found: C, 73.74; H, 6.50%. Calcd for $C_{15}H_{16}OS$: C, 73.73; H, 6.60%.

***m*-Me,H,Threo:** Mp 82.5 °C (from ether-hexane); IR (KBr) 1049 cm^{-1} (S-O); ^1H NMR (CCl_4) δ=1.56 (3H, d, J=7 Hz, CH_3), 3.59 (1H, q, J=7 Hz, CH), 2.27 (3H, s, CH_3), 6.8—7.3 (9H, m, Ar). Found: C, 73.52; H, 6.56%. Calcd for $C_{15}H_{16}OS$: C, 73.73; H, 6.60%.

***p*-Cl,H,Threo:** Mp 128.7 °C; IR (KBr) 1056 cm^{-1} (S-O); ^1H NMR (CCl_4) δ=1.60 (3H, d, J=7 Hz, CH_3), 3.61 (1H, q, J=7 Hz, CH), 6.7—7.4 (9H, m, Ar); ($CDCl_3$) δ=1.60 (3H, d, J=7 Hz, CH_3), 3.69 (1H, q, J=7 Hz, CH), 6.8—7.5 (9H, m, Ar). Found: C, 63.38; H, 4.87%. Calcd for $C_{14}H_{13}ClOS$: C, 63.51; H, 4.95%.

***m*-Cl,H,Threo:** Mp 73.5—74.5 °C (from ether-hexane); IR (KBr) 1052 cm^{-1} (S-O); ^1H NMR (CCl_4) δ=1.58 (3H, d, J=7 Hz, CH_3), 3.66 (1H, q, J=7 Hz, CH), 6.7—7.5 (9H, m, Ar). Found: C, 63.49; H, 5.07%. Calcd for $C_{14}H_{13}ClOS$: C, 63.51; H, 4.95%.

***p*-NO_2,H,Threo:** Mp 124—125.5 °C (methanol-ether); IR (KBr) 1338, 1522 (NO_2) and 1054 cm^{-1} (S-O); ^1H NMR (CCl_4) δ=1.68 (3H, d, J=7 Hz, CH_3), 3.68 (1H, q, J=7 Hz, CH), 6.8—8.3 (9H, m, Ar); ($CDCl_3$) δ=1.72 (3H, d, J=7 Hz, CH_3), 3.72 (1H, q, J=7 Hz, CH), 6.9—8.4 (9H, m, Ar). Found: C, 61.17; H, 4.78; N, 5.04%. Calcd for $C_{14}H_{13}NO_3S$: C, 61.07; H, 4.76; N, 5.09%.

Preparation of 1-(Substituted phenyl)ethyl-2,2,2-d_3 Phenyl Sulfoxides. To a stirred solution of methyl-d_3-magnesium iodide (0.06 mol) in dry ether (20 ml) was added dropwise substituted benzaldehyde (0.05 mol) in dry ether (20 ml). After usual work-up process, α-methyl-d_3-benzyl alcohol obtained was converted to the corresponding chloride which was then allowed to react with sodium benzenethiolate to give the corresponding sulfide-β,β,β-d_3 in ca. 85% yield. The obtained sulfide was oxidized with 35% H_2O_2 in acetic acid to afford the sulfoxide in ca. 67% yield.

Kinetics. Pyrolysis of the sulfoxides was carried out at 80.0±0.1 °C, 90.0±0.1 °C, and 100.0±0.1 °C in sealed capillary tubes, which contain 50 μl of 2.7 mmol dm^{-3} dioxane solution of each sulfoxide and 32 mmol dm^{-3} diphenyl ether or 5.4 mmol dm^{-3} diphenyl sulfide as an internal standard depending on the retention time of olefin formed in liquid chromatography. A sealed tube was taken out at several time intervals and was cooled in an ice bath to stop the reaction. The decreasing sulfoxide was followed by means of JASCO FAMILIC-100N liquid chromatograph with UV monitor UVIDEC 100II at 256 nm using TAKEDA RIKEN-TR-2217 Automatic Integrator. The rate of the reaction was found to fit nicely with a first-order rate equation and the rate constant was calculated by a least-squares method.

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