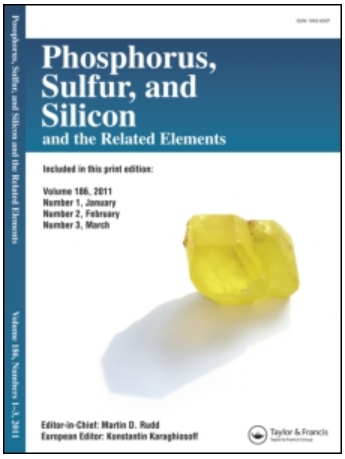

Phosphorus, Sulfur, and Silicon and the Related Elements

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PRYROLYSIS OF α-ACYL SUBSTITUTED ETHYL PHENYL SULFOXIDE

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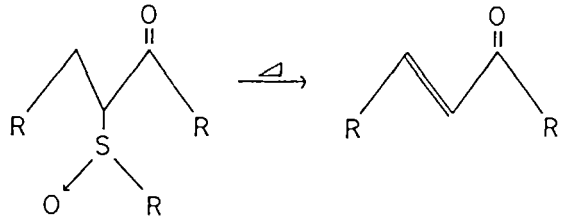
The effect of pyrolysis of the acyl group substituted on α-position carbon in S-ethyl group of ethyl phenyl sulfoxide was investigated by using two kinds of substrates, 1-ethoxycarbonylethyl phenyl sulfoxide (**1**) and 1-ethoxycarbonyl-1-methylethyl phenyl sulfoxide (**2**) together with 2-methoxycarbonylethyl phenyl sulfoxide (**4**). The rate of pyrolysis of (**1**) was found to be about 740 ~ 890 times faster than that of ethyl phenyl sulfoxide (**5**), while (**2**) was 5700 times faster. The rate enhancement effect on α-ethoxycarbonyl group was larger than that on β-methoxycarbonyl group. Large deuterium kinetic isotope effect ($k_H/k_D = 5.5$ for $PhS(O)C(CD_3)_2CO_2Et$ (**3**)) was observed. Activation energy for (**2**) is about 110 kJ/mol, which is just about the same as that of (**5**) (108 kJ/mol), while activation entropy lies in ca. 1 $Jdeg^{-1}mol^{-1}$. Hammett plot for substituted (**2**) gave $\rho = 0.69$. These kinetic results reveal that the pyrolysis of the sulfoxides proceeds via a loose transition state involving advanced C—S bond cleavage. The remarkably large rate enhancement by α-carbonyl group might be due mainly to the conjugation of that group and developing double bond acidifying the β-proton in the transition state.

Key words: Pryolysis; elimination; mechanism; isotope effect; kinetics; sulfoxide,

INTRODUCTION

The kinetic study for the pyrolysis of such sulfoxides as dialkyl, alkyl aryl, or cyclic has been made already.[1–3,5] Some of the sulfoxides undergo pyrolysis rapidly even at considerably low temperatures.[4,6,12] We observed that sulfoxides bearing a carbonyl group at α-carbon in S-ethyl group of ethyl phenyl sulfoxide decompose facile to get the corresponding α,β-unsaturated carbonyl compounds. In general, α,β-unsaturated carbonyl compounds have been known as a starting material for the elaboration of complex structural organic compounds.[7–11] A convenient method to get the α,β-unsaturated carbonyl compounds is thus to pyrolyze α-carbonyl substituted sulfoxides, as shown in Scheme 1, since the sulfoxides can also be readily prepared in good yields from the corresponding carbonyl compounds and disulfides.[12] However, the investigation that what is the role playing of the carbonyl group for the facile decomposition of the sulfoxides has not yet been made kinetically, in spite of the favorable method to get the α,β-unsaturated carbonyl compounds.

It is of interest to investigate the effect of the α-acyl group in the sulfoxides. Thus, 1-ethoxycarbonylethyl phenyl sulfoxide(1), 1-ethoxycarbonyl-1-methylethyl phenyl sulfoxide (**2**) and 1-ethoxycarbonyl-1-(methyl-d_3)ethyl-2,2,2-d_3 phenyl



SCHEME 1 Pyrolysis of sulfoxide.

sulfoxide (**3**) were prepared and subjected to the pyrolysis together with 2-methoxycarbonylethyl phenyl sulfoxide (**4**). This paper describes the detailed account for the large rate enhancement effect of α-acyl group on the pyrolysis of (**1**) and (**2**).

RESULTS AND DISCUSSION

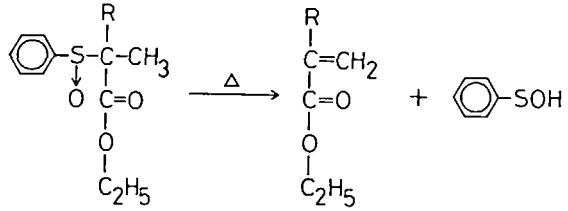
Preparation of Sulfoxides

The sulfoxide (**2**) and its derivatives were prepared by oxidation of the corresponding sulfides prepared according to the method described by Trost *et al.*[12]

Two diastereomeric isomers are possible for the substrate (**1**).[15] Each isomer was isolated by means of column chromatography. One isomer was not contaminated with another from observation of NMR signals of methine (—CH—) at higher field (a) for one isomer and lower one (b) for another.

Reaction Products

The pyrolysis was carried out by heating a solution of the sulfoxide in dioxane in a thermostat adjusted in the range ±0.1°C of the desired temperature. The products resulted were identified mainly by comparing the retention times of the corresponding olefins and the authentic samples by means of GLC. Thus, under



(1) R=H

(2) R=CH_3

SCHEME 2 Pyrolysis products of sulfoxides.

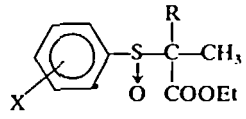
the reaction conditions, the products yielded from the substrates (1) and (2) were found to be ethyl acrylate and ethyl methacrylate, respectively. Other product containing sulfur was mainly diphenyl disulfide which is the second product from sulfenic acid (this unstable acid affords rapidly diphenyl disulfide[16]).

Kinetics

The rates of the pyrolysis of sulfoxides (1), (2), (3) and (4) were measured by following the increase of the GLC peak due to olefin produced. Each pyrolysis rate was all correlated in fine manner with first-order kinetic equation ($\gamma = 0.999$). The rate constants obtained at 90°C are listed in Table I together with the substituent effect (70°C) of substrate (2), and their relative rates are summarized in Table II.

TABLE I

Rate constants of pyrolysis of 1-ethoxycarbonyl-1-(substituted ethyl) substituted phenyl sulfoxide and 1-ethoxycarbonyl-1-methyl-d_3-ethyl-2, 2, 2-d_3 phenyl sulfoxide in dioxane



	Sulfoxide X	Sulfoxide R	Reaction temperature (±0.1°C)	Rate constant[a] (10^4 k/s^{-1})	
(1)	H	H[a]	90.0	5.63 ± 0.31[b,c]	
	H	H[b]	90.0	4.64 ± 0.24	
	H	CH_3	90.0	36.1 ± 0.6	
	H	CH_3	80.0	12.5 ± 0.3	
	H	CH_3	70.0	4.78 ± 0.08	
(2)	H	CH_3	60.0	1.31 ± 0.03	
	p-OCH_3	CH_3	70.0	2.39 ± 0.03	
	p-CH_3	CH_3	70.0	3.59 ± 0.07	($\rho = 0.69$)
	H	CH_3	70.0	4.78 ± 0.08	($\gamma = 0.97$)
	p-Cl	CH_3	70.0	5.90 ± 0.10	
	m-Cl	CH_3	70.0	7.34 ± 0.09	
(3)	Ph—S(O)—C(CD_3)(CD_3)—COOEt		90.0	6.55 ± 0.17 $k_H/k_D = 5.5$	
(4)	Ph—S(O)—$CH_2CH_2COOCH_3$		100.0	4.77 ± 0.04	
			110.0	12.0 ± 0.1	
			120.0	27.8 ± 0.2	

[a] Rate constants were calculated by the least squares method.
[b] Errors are standard deviations.
[c] (a) and (b) in Table are diastereomers which are observed by means of ^{1}H NMR signal of methine of higher field (a) and lower (b).

TABLE II

Relative rates for pyrolysis of sulfoxides at 90°C in dioxane

	Sulfoxide	Rate constants (k/s^{-1})	Relative rate
(5)	Ph—S(O)—CH_2CH_3	6.29×10^{-7}[a]	1
(4)	Ph—S(O)—CH_2CH_2COOMe	1.85×10^{-4}[a]	294
(1)	Ph—S(O)—CH(COOEt)—CH_3 (a)[b]	5.63×10^{-4}	895
	(b)	4.64×10^{-4}	738
(2)	Ph—S(O)—$C(CH_3)_2$(COOEt)	3.61×10^{-3}	5740
	Ph—S(O)—CH(Ph)—CH_3 (threo)	1.45×10^{-4}[c]	231
	(erythro)	3.04×10^{-4}	483
	Ph—S(O)—CH_2CH_2Ph	5.35×10^{-6}[a,d]	8.5

[a] The rate constants were calculated by Arrhenius equation from the data at other temperatures.
[b] (a) and (b) are the same as those in Table I.
[c] Ref. 17
[d] Ref. 20

As shown in Table II, very large rate enhancement by ethoxycarbonyl group was observed, that is 890 and 5700 times for the substrates (1) and (2), respectively, in comparison with the ethyl phenyl sulfoxide (5) as a reference substrate. The rate acceleration by β-methoxycarbonyl group is also large but less than by α-ethoxycarbonyl. Recently, we observed similar large acceleration by α-phenyl group on ethyl phenyl sulfoxide[17] but not β-phenyl group so much.[20]

In order to clarify what contributes to such large rate accelerations, primary kinetic isotope effect for (3) to (2) was examined. A large deuterium kinetic isotope effect ($k_H/k_D = 5.5$) was observed suggesting that the transfer of β-proton take part in the rate determining step. This magnitude of isotope effect is relatively large in spite of the reaction process through cyclic transition state (e.g. $k_H/k_D = 2 \sim 3$ for heptyl phenyl sulfoxide.[19] The large effect is probably due to involvement of more linear proton transfer in the transition state.

Activation parameters calculated from the Arrhenius equation and those of other related sulfoxides are summarized in Table III. Activation energy for (2) (about 110 kJ/mol) is about the same as that for the reference sulfoxide (5), while the activation entropy for (2) is larger than that for the sulfoxide (5) suggesting that C_α—S bond is substantially loose in the transition state. The looseness probably makes possible nearly linear proton transfer. Further, in order to determine charge distribution at the transition state, substituent effect on the phenyl group of the pyrolysis of (2) was examined. Hammett plot vs. σ gave a positive ρ-value ($\rho = 0.69$ $\gamma = 0.97$) which is similar to that for phenyl t-butyl sulfoxide ($\rho = 0.695$).[2] Though mechanism of Ei-reaction of sulfoxide is usually considered to be concerted process and charge distribution of the transition state is small because of the small Hammett ρ-values (usually $\rho < 1$) on S-phenyl group, there should be some deviation of the transition state from ideal concerted

TABLE III

Activation parameters for pyrolysis of 1-ethoxycarbonyl-1-methylethyl phenyl sulfoxide and other related sulfoxides at 90°C

	Sulfoxide	Ea kJ/mol	$\Delta S^{\neq a}$ J. K^{-1}. mol^{-1}
(5)	Ph—S(O)—CH_2—CH_3	108 ± 7	−75 ± 16
	Ph—S(O)—CH(Ph)—CH_3 (threo)	117	−6[b]
	Ph—S(O)—CH(Ph)—CH_3 (erythro)	115	−4
	Ph—S(O)—CH_2CH_2Ph	113	−45[c]
(4)	Ph—S(O)—$CH_2CH_2COOCH_3$	108 ± 1	−30 ± 3
(2)	Ph—S(O)—$C(CH_3)_2$(COOEt)	110 ± 4	1 ± 10

[a] The activation parameters were calculated by the least squares method using Arrhenius equation, and errors are standard deviations.
[b] Reference 17.
[c] Reference 20.

one. A transition state of Ei-reaction which involves development of even a small positive charge at α-carbon like that for t-butyl phenyl sulfoxide[2] or phenyl propyl sulfoxide[21] or the sulfoxide with α-carbocation-stabilizing substituents[17] is considered to be E1-like type. Meanwhile, we recently reported Ei-reaction via a carbanion-like transition state[20] in which sulfoxides with electron-withdrawing groups at β-carbon are involved and small ρ-value for S-phenyl group and large negative activation entropy were observed. The electron-withdrawing substituents at β-carbon assist the β-proton abstraction, but not C_α—S bond cleavage remaining the activation entropy large negative. Therefore, the pyrolysis of (4) is considered to proceed via a similar carbanion-like transition state. These deviations of transition states are considered not to be so large enough to reduce the deuterium primary isotope effect, since the substituent effects are small. Present results are similar to those of other E1-like type sulfoxides in the pyrolysis. However, in these systems E1-like mechanism is generally unfavorable, because the α-carbonyl group destabilizes positive charge of α-carbon. In any event, only from the deviation of the transition state, the effect of the large rate enhancement of the pyrolysis can not be explained, since the charge distribution at the transition state is essentially small. Meanwhile, the products, α,β-unsaturated carbonyl compounds are conjugated system which can contribute to the stabilization of the transition state as shown in Figure 1.

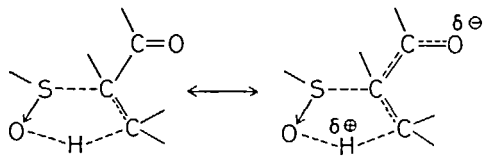


FIGURE 1 Conjugated transition state of pyrolysis of α-carbonyl substituted sulfoxide.

Namely, the conjugation of carbonyl group and developing double bond will increase the β-proton acidity and assist C_α—S bond cleavage by supplement of electron into the C_α—S antibonding σ^* orbital, reflecting the large activation entropy and similar ρ-value to those for the other reaction systems which proceed via E1 like type transition state.

The conclusion can be drawn as follows. The α-carbonyl group in the sulfoxide may very accelerate the rate by the conjugation with developing double bond so as to assist both C_α—S bond cleavage and β-proton abstraction resulting loose transition state within the range of concerted process. Thus, in the present system the resonance structure at the transition state should play an important role for the rate acceleration in the pyrolysis.

The authors are grateful to Professor Shigeru Oae of Okayama University of Science, and Professor Naomichi Furukawa, the University of Tsukuba, for their helpful discussions.

EXPERIMENTAL

General The IR spectra were obtained on JASCO-810 spectrometer and the NMR spectra were obtained on a HITACHI R-24 spectrometer in $CDCl_3$ or CCl_4 using TMS as an internal standard. The GLC analyses were carried out with a HITACHI 163 Gaschromatograph (column: SE-30, carrier gas: N_2). The peak area was measured by a YANAKO Integrator System-1100. Mass spectra were taken with JEOL-JMS-D300 mass spectrometer. The HPLC analyses were carried out with a JASCO FAMILIC-100N and UVIDEC-100 SYSTEM apparatus by using silica gel(SS-10) column (hexane/THF = 5/2 as eluent), and the peak area was measured by a TAKEDA-RIKEN TR-2217 integrater.

All reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Co. Ltd., or Aldrich Chemical Co. Ltd. The reagents and solvents used were further purified by usual methods. All the sulfoxides obtained were identified by IR, NMR, GC-MS and elemental analyses. Elemental analyses were carried out by Chemical Analysis Center in Toyama Medical and Pharmaceutical University. The computations were performed on the NEC 9801-F computer.

Preparation of 1-Ethoxycarbonylethyl phenyl Sulfoxide (**1**).[13-15] To a stirred solution of 100 ml ethanol dissolved sodium metal (1.9 g, 83 mmol), thiophenol (11.6 g, 85 mmol) was added, and followed by dropwise addition of ethyl 2-chloropropanoate with stirring in an ice bath. Then precipitation of sodium chloride was observed in a short time. After mild heating, the solution was quenched with water. The organic layer was extracted with chloroform, washed with water and dried over magnesium sulfate. After removal of the solvent, the crude sulfide was distilled under reduced pressure to give colorless oil in 73% yield, bp: 113–116°C/5 mmHg. The sulfoxide (**1**) was prepared as follows. To a stirred solution of the sulfide (6.0 g, 29 mmol) in 30 ml of acetic acid was added dropwise hydrogen peroxide (3.0 g, 30 mmol) at 0°C. After an additional stirring at room temperature for a day, the solution was poured into ice-cold water, neutralized with sodium bicarbonate, extracted with chloroform, and dried over anhydrous sodium sulfate. After the solvent was evaporated, the oily material was separated through SiO_2-column chromatography (chloroform as eluent), sulfoxide was obtained in 52% yield. Diastereomers were separated by repeated column chromatography using ether-hexane (2:1) as eluent.

Isomer (a): NMR (CCl_4) $\delta = 7.36$ (5H, m, —C_6H_5), 4.01 (2H, q, —CH_2—), 3.43 (1H, q, —CH), 1.14 (3H, t, —CH_3), 1.42 (3H, d, —CH_3). IR (neat) 1060 (S=O), 1735 (C=O), 1215 cm^{-1} (C—O—C). Anal. Found: C, 57.41, H, 6.20. Calcd for $C_{11}H_{14}O_3S$: C, 58.38, H, 6.24.

Isomer (b): NMR(CCl_4) $\delta = 7.40$ (5H, s, —C_6H_5), 4.05 (2H, q, —CH_2—), 3.75 (1H, q, —CH), 1.31(3H, d, —CH—CH_3), 1.19(3H, t, CH_2—CH_3). IR (neat) 1060 cm^{-1} (S=O), 1735(C=O), 1220(C—O—C). Anal. Found: C, 57.18, H, 6.15. Calcd for $C_{11}H_{14}O_3S$: C, 58.38, H, 6.24.

2-Methoxycarbonylethyl phenyl sulfoxide[18] was also prepared by similar oxidation of the corresponding sulfide which was prepared by addition of thiophenol to methyl acrylate.

Preparation of 1-Ethoxycarbonyl-1-methylethyl substituted phenyl Sulfoxides (**2**). All the sulfoxides

were prepared by oxidation of the corresponding sulfides with m-CPBA in dichloromethane in good yields. A typical example is as follows.

Preparation of 1-ethoxycarbonyl-1-methylethyl substituted phenyl sulfides. The sulfides were prepared by the following method according to that reported by Trost *et al.*[12] To a stirred solution of diisopropylamine (1.5 g, 15 mmol) in 30 ml of dry THF at −60°C, n-butyllithium (22 mmol) was added. To this was added ethyl 2-methylpropanoate (1.7 g, 15 mmol) and then a solution of diaryl disulfide (3.3 g, 15 mmol) in dry THF (30 ml). The solution was allowed to warm to room temperature and then water was added. This solution was neutralized with aqueous acetic acid, and extracted with chloroform. The extracts were washed with water and dried over anhydrous sodium sulfate. After the solvent was evaporated, the residue was distilled under reduced pressure affording 1-ethoxycarbonyl-1-methylethyl aryl sulfide.

1-Ethoxycarbonyl-1-methylethyl substituted phenyl sulfide, substituent p-OCH_3: 84% yield; bp 142–145°C/3 mmHg; IR(neat) 1714(C=O), 1251 and 1141 cm^{-1} (C—O); NMR (CCl_4) $\delta = 1.21$ (3H, t, J = 7 Hz, CH_3), 1.36(6H, s, CH_3), 3.70(3H, s, OCH_3), 3.98(2H, q, J = 7 Hz, CH_2), 6.64 and 7.17 (4H, AB, J = 8 Hz, C_6H_4).

p-CH_3. 78% yield; bp 109–114°C/2.5 mmHg; IR(neat) 1715(C=O), 1251 and 1140 cm^{-1} (C—O); NMR (CCl_4) $\delta = 1.18$(3H, t, J = 7 Hz, CH_3), 1.38(6H, s, CH_3), 2.30(3H, s, $ArCH_3$), 3.99(2H, q, J = 7 Hz, CH_2), 6.95 and 7.16(4H, AB, J = 8 Hz, C_6H_4).

H. 63% yield; bp 105–110°C/3.5 mmHg; IR (neat) 1713 (C=O), 1252 and 1142 cm^{-1} (C—O); NMR (CCl_4) $\delta = 1.16$(3H, t, J = 7 Hz, CH_3), 1.36(6H, s, CH_3), 4.00(2H, q, J = 7 Hz, CH_2), 7.0–7.5(5H, m, Ph).

p-Cl. 68% yield; bp 110–125°C/4 mmHg mp 47–48.5°C; IR (KBr) 1733(C=O), 1271 and 1161 cm^{-1} (C—O); NMR (CCl_4) $\delta = 1.20$(3H, t, J = 7 Hz, CH_3), 1.40(6H, s, CH_3), 4.01(2H, q, J = 7 Hz, CH_2), 7.22(4H, s, C_6H_4).

m-Cl. 70% yield; bp 105–109°C/2.5 mmHg; IR(neat) 1718 (C=O), 1258 and 1145 cm^{-1} (C—O); NMR (CCl_4) $\delta = 1.21$ (3H, t, J = 7 Hz, CH_3), 1.39(6H, s, CH_3), 3.98(2H, q, J = 7 Hz, CH_2), 7.23(4H, m, C_6H_4).

Oxidation of sulfide To a stirred solution of 1-ethoxycarbonyl-1-methylethyl phenyl sulfide (1.0 g, 4 mmol) in dichloromethane(10 ml) was added at 0°C m-CPBA (0.7 g, 4 mmol) in dichloromethane (10 ml). After the mixture was stirred at 0°C for 2 hrs, dimethyl sulfide was added, and then poured into cold water. Then the solution was extracted with chloroform, the extract was washed with sodium bicarbonate and then with water, and dried over anhydrous magnesium sulfate. After the solvent was removed in vacuo, the residue was separated through SiO_2-column chromatography(chloroform as an eluent). 1-Ethoxycarbonyl-1-methlethyl substituted phenyl sulfoxides were similarly obtained in 50–80% yields and the following properties were observed.

H. NMR (CCl_4) $\delta = 7.35$ (5H, s, —C_6H_5), 1.18 (3H, t, J = 7 Hz, —CH_2CH_3), 4.00(2H, q, J = 7 Hz, —CH_2—), 1.12 (3H, s, —CH_3), 1.50 (3H, s, —CH_3); IR(neat) 1038 (S=O), 1708(C=O), 1252 and 1140 cm^{-1}(C—O).

p-OCH_3. NMR(CCl_4) $\delta = 6.86$ and 7.32(4H, AB, J = 8 Hz, —C_6H_4—), 1.19(3H, t, J = 7 Hz, —CH_2—CH_3), 4.00(2H, q, J = 7 Hz, —CH_2—), 1.12 (3H, s, CH_3), 1.48 (3H, s, —CH_3), 3.79 (3H, s, —OCH_3); IR(neat) 1040 (S=O), 1710 (C=O), 1254 and 1141 cm^{-1} (C—O).

p-CH_3. mp 29–30°C; NMR(CCl_4) $\delta = 7.24$ and 7.38 (4H, AB, J = 9 Hz, —C_6H_4—), 1.19 (3H, t, J = 7 Hz, —CH_2—CH_3), 4.07 (2H, q, J = 7 Hz, —CH_2—), 1.26 (3H, s, —CH_3), 1.55 (3H, s, —CH_3), 2.38 (3H, s, C_6H_4—CH_3); IR(neat) 1041 (S=O), 1710(C=O), 1255 and 1143 cm^{-1} (C—O). anal. Found: C, 61.27; H, 6.93%. Calcd for $C_{13}H_{18}O_3S$: C, 61.39; H, 7.13%.

P-Cl. NMR (CCl_4) $\delta = 7.32$ (4H, s, —C_6H_4—), 1.22(3H, t, J = 7 Hz, —CH_2—CH_3), 4.07 (2H, q, J = 7 Hz, —CH_2—), 1.11 (3H, s, —CH_3), 1.51 (3H, s, —CH_3); IR(neat) 1040(S=O), 1710(C=O), 1255 and 1141 cm^{-1} (C—O).

m-Cl. NMR (CCl_4) $\delta = 7.30$ (4H, s, —C_6H_4—), 1.21 (3H, t, J = 7 Hz, —CH_2—CH_3), 4.03 (2H, q, J =

7 Hz, $—CH_2—$), 1.53 (3H, s, $—CH_3$), 1.12 (3H, s, $—CH_3$); IR (neat) 1049 (S=O), 1719 (C=O), 1267 and 1151 cm^{-1} (C—O).

Preparation of 1-Ethoxycarbonyl-1-methyl-d_3-ethyl-2, 2, 2-d_3 phenyl Sulfoxide (3). To a stirred suspension of Magnesium metal (3 g, 0.12 mol) in 30 ml of dry ethyl ether under nitrogen atmosphere was added dropwise 2-bromopropane-1, 1, 1, 3, 3, 3-d_6 (13 g, 0.1 mol), and the solution was stirred at room temperature for 2 hrs. Then ethyl chloromethanoate (19 g, 0.2 mol) was added and the mixture was stirred for 2 hrs. Aqueous ammonium chloride solution was added and the solution was extracted with ether three times. The ether layer was dried over anhydrous magnesium sulfate and the solvent was evaporated. The product was fractionally distilled under ordinary pressure. Ethyl 2-(methyl-d_3)propanoate-3,3,3-d_3 obtained in 46% yield was used to prepare sulfide by the same method already described. Deuterium contents of 1-ethoxycarbonyl-1-methyl-d_3-ethyl-2, 2, 2-d_3 phenyl sulfoxide(3) obtained in 28% yield was about 100%, which was determined by integration of its H^1-NMR.

Kinetics. A pre-cooled solution of sulfoxide (9.0×10^{-2} mmol) in anhydrous dioxane (0.5 ml) containing 0.1 mmol of internal standard was prepared in 20 μl of sealed capillary tubes, which were immersed in silicon oil bath (±0.1°C) adjusted at a desired temperature. At appropriate time interval, the tubes were immersed in an ice bath to stop the reaction. The reaction rate was then determined by following the increase of olefin formed by means of GLC (column temp 30°C, Injection temp 50°C, for (1); column temp 50°C, injection temp 50°C for (2). The internal standard used was mesitylene for (1) or p-xylene for (2). Calibration curve Q_n/Q_0 vs. P_n/P_0 was taken, where, Q_n/Q_0 are molarity of authentic sample of ethyl acrylate or ethyl methacrylate and internal standard. On the other hand, P_n, P_0 are their peak area, respectively. The curves gave good straight lines under the experimental conditions. The rate constant of the pyrolysis was determined from the slope of plot of $\ln(A_\infty - A_0)/(A_\infty - A_t)$ vs. time, where A_0 is initial peak area of olefin (actually, A_0 was equal to zero suggesting that decomposition of the sulfoxide at injection temperature is negligible), A_∞ is the peak area of olefin at final time and A_t is the one at a particular time. A linear correlation was observed and so the kinetics is of first order.

Kinetics of pyrolysis of ethyl phenyl sulfoxide (5) was also carried out similarly, and the rate was determined by following the decrease of the sulfoxide by means of HPLC using p-toluenesulfonamide as an internal standard.

Activation parameters were computer calculated by the least-squares method using $\ln k$ vs. $1/T$. The Hammett ρ-value was computed by the least-squares method using σ-values and logarithms of the rate constants.

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