

An Estimation of the π -Bond Energy of 1-Methyl-1-Phenyl-2-Neopentylsilene

Myong Euy Lee* and Paul R. Jones†

Department of Chemistry, Yonsei University, Kangwondo 222-701

†Department of Chemistry, University of North Texas, Denton, Texas 76203, U. S. A.

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The *E*- and *Z*- isomers of 1-methyl-1-phenyl-2-neopentylsilene, generated by the sealed tube thermolyses of their anthracene adducts are stereospecifically trapped by trimethylmethoxysilane to give diastereomeric adducts. The temperature dependence of the ratio of the two diastereomers obtained when the silene formed from the pure *E*- or *Z*-anthracene adduct was trapped at higher temperatures permitted the determination of an activation energy for the silene isomerization. The activation energies for the *E*- to *Z*- and *Z*- to *E*-silene isomerization are 45 ± 6 and 20 ± 4 kcal mol⁻¹, respectively. The significance of these values is discussed.

Introduction

There is considerable interest in the chemistry of silicon-carbon double bonds, but little quantitative information on the stability and stereochemistry of these important intermediates.¹⁻³ We recently reported the unambiguous evidence that 1-methyl-1-phenyl-2-neopentylsilene is configurationally stable at temperatures below 300°C.⁴ Above this temperature *cis-trans* isomerization began to occur at a measurable rate, which allowed us to obtain the first experimental determination of the activation energy for a silene *E*- to *Z*-isomerization of 43 ± 6 kcal/mole.⁵ We now wish to report the measurement of the more significant activation energy for the configurational isomerization of a silene obtained by carefully controlled thermolyses at a series of temperatures with the pure *E*- and *Z*-silene precursors, respectively.

Results and Discussion

When isomerically pure *E*- or *Z*-2-methyl-2-phenyl-3-neopentyl[5,6:7,8]dibenzo-2-silabicyclo[2.2.2]octadiene (*E*-2 or *Z*-2)⁶ was subjected to sealed tube thermolysis at temperatures above 300°C in the presence of excess trimethylmethoxysilane as the silene trapping agent two separable diastereomeric adducts (*D*-1 and *D*-2) of *E*-1 and *Z*-1 were obtained, respectively. The kinetic scheme for the silene *cis-trans* isomerization in the presence of a large excess of trimethylmethoxysilane, is shown in Figure 1 in which it is assumed that the *E*-anthracene adduct, *E*-2 gives rise to *E*-silene and *Z*-anthracene adduct, *Z*-2 gives rise to *Z*-silene.⁴

With regard to Figure 1, the rates of the formation of *D*-1 and *D*-2 are:

$$d[D-1]/dt = k_3[T][E-I] \quad (1)$$

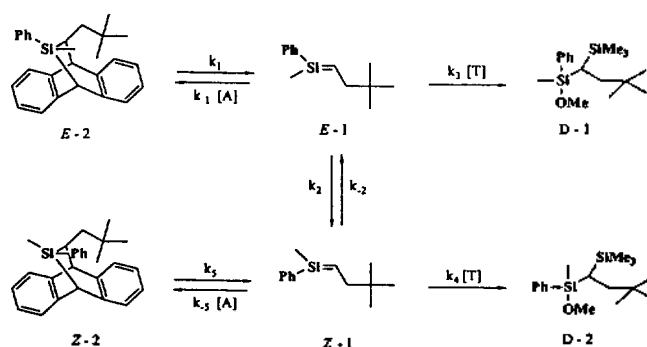
$$d[D-2]/dt = k_4[T][Z-I] \quad (2)$$

where $[T]$ is the concentration of trimethylmethoxysilane.

Integrating the equations from $t=0$ to $t=t$ gives:

$$[D-1] = k_3[T][E-I]t \quad (3)$$

$$[D-2] = k_4[T][Z-I]t \quad (4)$$



[A]; [Anthracene], [T]; [Trimethylmethoxysilane]

Figure 1. Kinetic scheme for silene *cis-trans* isomerization.

The ratio of the products at a given time is obtained by dividing equation 3 by equation 4.

$$\frac{[D-1]}{[D-2]} = \frac{k_3[E-I]}{k_4[Z-I]} \quad (5)$$

Application of the steady state approximation to $[Z-I]$ in a thermolysis using *E*-II as the silene precursor gives:

$$[Z-I] = (k_2[E-I] + k_5[Z-2]) / (k_4[T] + k_{-5}[A] + k_{-2}) \quad (6)$$

where $[A]$ is the concentration of anthracene. Substitution of equation 6 in equation 5 gives:

$$\frac{[D-1]}{[D-2]} = \frac{k_3[E-I] \times (k_4[T] + k_{-2} + k_{-5}[A])}{k_4(k_2[E-I] + k_5[Z-2])} \quad (7)$$

Assuming that $k_5[Z-2] \ll k_2[E-I]$, equation 8 can be obtained.

$$\frac{[D-2]}{[D-1]} = \frac{(k_{-5}[A] + k_2)}{k_4 k_2 + k_3 k_2 [T]} \quad (8)$$

Starting with *Z*-2 as the precursor of silene in Figure 1, a similar derivation gives:

$$\frac{[D-2]}{[D-1]} = \frac{(k_2 k_4 + k_4 k_{-1}[A])}{k_3 k_{-2} + k_4 k_{-2} [T]} \quad (9)$$

where it is assumed that $k_1[E-2] \ll k_{-2}[Z-I]$

Table 1. D-2/D-1 Ratios for Sealed Tube Thermolysis of Z-2

Z-2	10 mins.				D-2+D-1
	Cyclohexane, Me ₃ SiOMe, C ₁₆ H ₃₄				
[T], M	D-2/D-1				
	633.1 K	651.9 K	660.2 K	672.1 K	
0.7562	7.75	5.78	4.46	2.66	
1.2898	8.51	6.11	4.65	2.82	
1.7851	8.79	6.52	5.02	3.19	
2.1673	9.38	6.61	5.21	3.26	
R ^a	0.986	0.987	0.990	0.977	

^aCorrelation coefficient for ratios vs. concentration of trap

Table 2. D-2/D-1 Ratios for Sealed Tube Thermolysis of E-2

E-2	10 mins.				D-2+D-1
	Cyclohexane, Me ₃ SiOMe, C ₁₆ H ₃₄				
[T], M	D-1/D-2				
	633.1 K	651.9 K	660.2 K	672.1 K	
1.0238	11.24	9.27	6.90	4.23	
1.7146	14.96	10.28	7.89	4.64	
2.3171	16.52	11.29	8.51	5.04	
2.8822	19.65	11.54	8.75	5.26	
R	0.992	0.981	0.976	0.996	

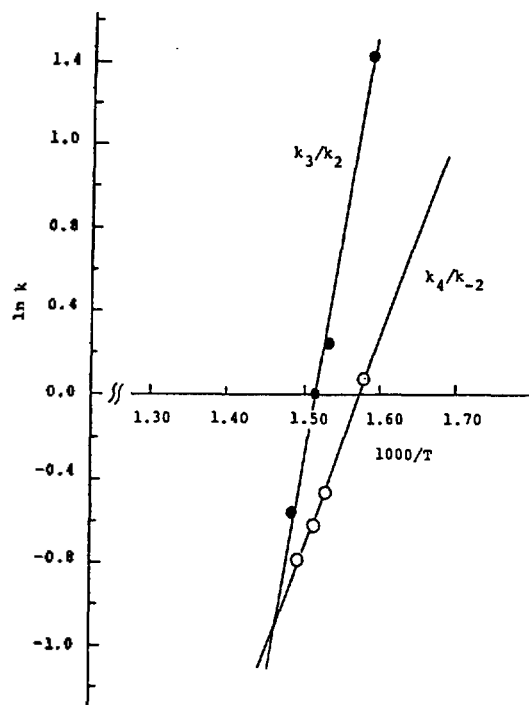
An experiment to justify the assumptions that $k_1[E-2] \ll k_{-2}[Z-1]$ or that $k_3[Z-2] \ll k_2[E-1]$, was carried out, which gave the time dependence of the percent decomposition of starting material (E-2) at 344°C. A plot of $\ln [E-2]_0/[E-2]_t$ vs time gave a straight line (correlation coefficient, 0.998) with a zero intercept between 0 and 90 mins. and the rest of the plot gave a curve, indicating that the disappearance of E-2 is no longer first order. The rate constant, k_1 , $1.50 \times 10^{-4} \text{ sec}^{-1}$, was calculated from the slope of the linear portion using a least squares program. The rate constant, k_1 is negligibly small when compared with k_{-2} , $1.3 \times 10^5 \text{ sec}^{-1}$, given in Table 4. If the concentration of E-2 were enough higher than that of Z-1 to compensate for the difference between the rate constants, k_1 and k_{-2} , the assumption, $k_1[E-2] \ll k_{-2}[Z-1]$ could not be applied. But this is not likely in experiments starting with Z-2 conducted to low percent decomposition in which no E-2 is initially present.

No experiment was carried out to get the rate constant, k_3 for the decomposition of Z-2. This rate constant might be expected to be larger than k_1 for the decomposition of E-2 because of steric effects. The actual decomposition of Z-2 in comparable experiments was only about 15% faster than that of E-2. Based on this, k_3 may be estimated to be $1.73 \times 10^{-4} \text{ sec}^{-1}$, which is negligible when compared with k_2 , $5.8 \times 10^4 \text{ sec}^{-1}$, given in Table 4. Therefore, the assumption, $k_3[Z-2] \ll k_2[E-1]$ is also justified in experiments starting with E-2 conducted to low percent decomposition in which no Z-2 is initially present. With these assumptions justified, equations 8 and 9 predict that the ratio of diastereomers should be a linear function of the concentration of

Table 3. Values of k_4/k_{-2} and k_3/k_2

Temp. K	633.1	651.9	660.2	672.1
k_4/k_{-2}^a	1.09	0.62	0.55	0.46
k_3/k_2^b	4.34	1.27	1.01	0.57

Correlation coefficient: ^a0.993, ^b0.984

**Figure 2.** Arrhenius plots of $\ln(k_4/k_{-2})$ and $\ln(k_3/k_2)$ vs $1000/T$.**Table 4.** Arrhenius Parameters for Silene Isomerization

	E_a , kcal mol ⁻¹	$\log_{10} A$	k (645 K), sec ⁻¹
E-1→Z-1	45±6	19.8±1.0	5.8×10 ⁴
Z-1→E-1	20±4	11.8±0.7	1.3×10 ⁶

trimethylmethoxysilane at a given temperature.

For this reason, kinetic experiments were designed based on the previous work⁵ with the exception that both using E-2 and Z-2 were carried out simultaneously with short reaction time, 10 mins. to minimize the reverse reactions, k_{-1} and k_{-5} , in Figure 1. The ratios of D-2 to D-1 for the sealed tube thermolysis of Z-2 are given in Table 1. The ratios of D-1 to D-2 for the thermolysis of E-2 are given in Table 2.

The plots of the data in Table 1 and 2 give the values of k_4/k_{-2} and k_3/k_2 from the slopes (Table 3). Linear least squares fits of the Arrhenius plots for the values of $\ln(k_4/k_{-2})$ and $\ln(k_3/k_2)$ vs temperature, Figure 2, gave intercepts and slopes, which were used to calculate the Arrhenius parameters for k_{-2} and k_2 respectively.

$$\ln(k_4/k_{-2}) = (-14.91 + 1.51) + (9465 + 989)/T \quad (10)$$

$$\ln(k_3/k_2) = (-33.41 + 2.37) + (22038 + 1552)/T \quad (11)$$

The Arrhenius parameters for the silene isomerization in

Table 5. Isomerization Rate Constants vs. Temperature^a

Temp. K	$k_2 \times 10^{-4}/\text{sec}$	$k_{-2} \times 10^{-4}/\text{sec}$
633.1	1.39	5.54
651.9	4.91	10.10
660.2	6.29	11.49
672.1	11.42	14.03

^aWith assumption of $k_3=k_4$, $\ln k_3=2.303 \log_{10}A-E_a/RT$, where $\log_{10}A=5.3$, $E_a=6300 \text{ Jmol}^{-1}$, and $R=8.3142 \text{ Jmol}^{-1}\text{K}^{-1}$ ⁷

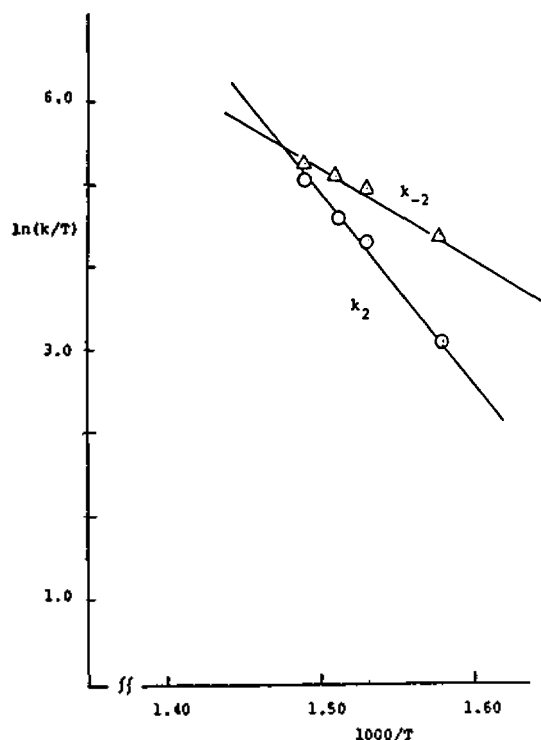
**Figure 3.** Eyring plots of $\ln(k_2/T)$ and $\ln(k_{-2}/T)$ vs $1000/T$.

Table 4 were obtained using Davidson's kinetic parameters⁷ and equations 10 or 11.

As shown in Table 4, the activation energy for the isomerization of *E*- to *Z*-I, 45 kcal mol^{-1} , is consistent with the previous measurement within the range of error.⁵ The lower activation energy, 20 kcal mol^{-1} for the isomerization of *Z*- to *E*-I as compared to the *E*- to *Z*-I isomerization is unusual when compared with activation energy differences between *E*- and *Z*-isomers in substituted ethylenes, $1.0\text{--}10.0 \text{ kcal mol}^{-1}$ ⁸

One anticipates that, in the absence of significant steric or electronic effects, the major contributor to the activation energy for the *trans-cis* isomerization of an olefin is the π bond energy. The large difference in activation energies for *E*- and *Z*-I might be a direct consequence of steric hindrance, for which the bulky substituents, phenyl and neopentyl, in the *Z*-isomer would lead to a destabilization of the planar or twisted ground state. It is reasonable that going from *E*-I to the transition state requires the input of steric strain energy, whereas going from *Z*-I to the transition state, steric strain is relieved. If this is the case, our measured activation energies include an important steric component. The value of $45 \pm 6 \text{ kcal mol}^{-1}$ obtained for the isomerization of *E*-

Table 6. Activation Parameters for Silene Isomerization

	ΔS^\ddagger , cal mol ⁻¹ K ⁻¹	ΔH^\ddagger , kcal mol ⁻¹	ΔG^\ddagger , kcal mol ⁻¹
<i>E</i> -I→ <i>Z</i> -I	29.0 ± 6.1	44.0 ± 6.0	25.0 ± 6.2
<i>Z</i> -I→ <i>E</i> -I	-8.1 ± 3.3	19.0 ± 4.0	24.3 ± 4.0

^a $\ln(k/T) = (\ln(k_B/h) + \Delta S^\ddagger/R) - \Delta H^\ddagger/RT$, ^b $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$

to *Z*-I represents a maximum value for the silicon-carbon π bond energy in 1-methyl-1-phenyl-2-neopentylsilene, while the value of $20 \pm 4 \text{ kcal mol}^{-1}$ obtained for the isomerization of *Z*-I to *E*-I represents a minimum value for the Si-C π bond energy.

For the thermal unimolecular *Z*, *E* isomerizations, noram preexponential factors of the Arrhenius equation, $\log_{10}A$, are in the range of $12\text{--}13$ ^{9,10} As shown in Table 4, the *A* factor for the isomerization of *Z*- to *E*-I is in good agreement with expected value, while the *A* factor for the isomerization of *E*- to *Z*-I is higher than usual values. Unfortunately, the reason for this is not clear. It will be discussed later.

The rate constant, k_3 at different temperatures could be evaluated using Davidson's parameters for the reaction of dimethylsilene with trimethylmethoxysilane.⁷ Assuming that $k_3=k_4$, the isomerization rate constants, k_2 and k_{-2} , were calculated from the data given in Table 3. The values, k_2 and k_{-2} obtained are summarized in Table 5.

Eyring plots, Figure 3, of $\ln(k_2/T)$ vs $1/T$ and of $\ln(k_{-2}/T)$ vs $1/T$ using the data given in Table 5 gave the values of ΔH^\ddagger from the slopes, and ΔS^\ddagger from the intercepts, as given in Table 6. For the thermal unimolecular *Z*, *E* isomerizations one should expect small positive entropies of activation.¹¹ The entropies of activation, ΔS^\ddagger for the isomerization of *E*- to *Z*-I and *Z*- to *E*-I are higher and lower, respectively, than the values expected based on steric effects, $0\text{--}10 \text{ cal mol}^{-1} \text{K}^{-1}$.^{10,11} The difference in ΔS^\ddagger between the isomerization of *E*- to *Z*-I and *Z*- to *E*-I, $37 \text{ cal mol}^{-1}\text{K}^{-1}$, seems to be unusual. One must understand that the values of ΔS^\ddagger and $\log_{10}A$ are derived from the intercepts of Eyring and Arrhenius equation, respectively, which means that both values are obtained from the same original source. The free energy of activation, ΔG^\ddagger is calculated using the value of the entropy of activation. It is reasonable that if the value of $\log_{10}A$ were unusual, the values, ΔS^\ddagger and ΔG^\ddagger could be unusual. But the measurement of these parameters under the extremely high pressure involved, in our systems has not, to our knowledge, been done prior to this work.

A possible reason for these unusual Arrhenius and activation parameters is the assumption that the activation energies and *A* factors for the trapping reaction of both of *E*- and *Z*-I with trimethylmethoxysilane are the same, E_a , $1.5 \text{ kcal mol}^{-1}$ and $\log_{10}A$, 5.3 , respectively.⁷ If k_4 were greater than k_3 , the rate constant, k_{-2} for the isomerization of *Z*- to *E*-I would be greater than k_2 obtained, which allows a greater $\log_{10}A$ and ΔS^\ddagger than values given in Tables 4 and 6. Consequently, the differences in $\log_{10}A$ and ΔS^\ddagger between the isomerization of *E*- to *Z*- and *Z*- to *E*-I would be decreased. If the rate constants, k_3 and k_4 for the reaction of both *E*- and *Z*-I with trimethylmethoxysilane were smaller than those for the reaction of the dimethylsilene with trimethylmethoxysilane which were used, which is likely because of steric effects, the values of $\log_{10}A$ and ΔS^\ddagger would also be

Table 7. Values of Intercepts^a, *m* and *n*

Temp. K	633.1	651.9	660.2	672.1
<i>m</i> ^b	6.97	5.33	4.01	2.29
<i>n</i> ^c	6.98	8.07	6.01	3.67
<i>m</i> ⁻¹	0.14	0.19	0.25	0.44

^aThe plots of the data given in Tables 1 and 2, ^b $(k_2k_4 + k_3k_{-1}[A])/k_2k_{-2}$, ^c $(k_{-3}k_3 + k_5k_{-5}[A])/k_2k_4$

decreased.

It is noteworthy that if our kinetic scheme were correct, the intercepts given in Table 7 should depend on a concentration of anthracene based on equations 12 and 13. The data of intercepts given in Table 7 support this statement,

$$m = k_2k_4/k_2k_{-2} + (k_3k_{-1}/k_2k_{-2})[A] \quad (12)$$

$$n = k_{-3}k_3/k_2k_4 + (k_5k_{-5}/k_2k_4)[A] \quad (13)$$

because if $k_3k_{-1}[A]$ and $k_5k_{-5}[A]$ were negligible, there should be an inverse relationship between intercepts, *m* and *n* of plots of *D*-1/*D*-2 and *D*-2/*D*-1 vs $[\text{Me}_3\text{SiOMe}]$, respectively, which is not true, as can be seen in Table 7.

Experiments which could be performed using different concentrations of anthracene in the presence of fixed amount of trimethylmethoxysilane can be designed based on equations 12 and 13. The rate constants, k_3 and k_4 which might be obtained from these studies could eliminate the dependency on Davidson's parameters, thus allowing determination of more accurate kinetic parameters for the isomerizations of *E*- to *Z*-I and *Z*- to *E*-I.

In conclusion, the first experimentally-measured activation energies, 45 ± 6 and 20 ± 4 kcal mol⁻¹ for the configurational isomerization of *E*- to *Z*-I and *Z*- to *E*-I, respectively, represent a maximum and a minimum value for the silicon-carbon *pi* bond energy in the 1-methyl-1-phenyl-2-neopentylsilene. If the increase of steric strain in going to the transition state for the *E*- to *Z*-I isomerization equals the loss of steric strain in reaching the transition state for the *Z*- to *E*-I isomerization, then the silicon-carbon double bond energy can be estimated to be 33 ± 5 kcal mol⁻¹, which is strikingly close to recently reported estimates for the Si=C bond energy of 39, 37, 28, or 23 kcal mol⁻¹.^{12,13}

Experimental

Materials and equipments. All reactions and manipulations were carried out under a dry atmosphere of nitrogen or argon, and all solvents were dried and distilled prior to use. Precursors, *E*-2 and *Z*-2 were synthesized by method previously reported.⁶ All thermolysis reactions were carried out in Pyrex tubes, 6.3 mm (OD) × 150 mm with thick wall (1.2 mm), using a thermolysis tube holder which was made of asbestos plate with eight holes. The thermolysis bath was a stirred, thermostated, molten salt bath (eutectic mixture, 40% NaNO₂, 7% NaNO₃ and KNO₃, mp. 142°C) which was well insulated by an Aqua-Cel (diatomite, Johns-Manville Co.). Temperature was controlled using a "Thermotrol" proportional controller (GCA No. 1253A) with a platinum sensing element (GCA No. 805-506). Temperature was measured *via*

a Chromel-Alumel thermocouple in coordination with a "Millivolt Potentiometer" (Leeds and Northrup No. 8691) within error, 0.5°C. In order to get accurate measurement of temperature within error, $\pm 0.1^\circ\text{C}$, an Iron-Constantan thermocouple in coordination with a No. 7552 potentiometer (K-2) (Leeds and Northrup Co.) which was connected to Galvanometer and standard cell, was used.

General procedure for the vacuum sealed tube thermolysis experiments. In typical experiments weighed amounts of trimethylmethoxysilane were combined with weighed quantities of a stock solution of the silene precursor *E*-2 (or *Z*-2) and hexadecane(internal standard) in cyclohexane as the solvent. The samples were degassed and sealed in heavy-walled pyrex tubes under vacuum. The set of five or four samples containing different amounts of the trap were then introduced simultaneously into a molten salt bath. The reaction temperature were constant to $\pm 0.1^\circ\text{C}$.

When the thermolysis tubes were taken out from the molten salt bath after the reaction times indicated, all the reaction mixtures were in the gaseous state. After cooling to room temperature, there were a light yellow liquid phase and a white precipitate which was identified to be anthracene.

Reactants and thermolysates, which have been previously characterized,^{4,6} were analyzed using an internal standard method with a Perkin-Elmer Sigma-3 FID gas chromatograph, a Hewlett-Packard 3390A recording integrator and a 25 m fused silica capillary column with a methylphenylsilicone, SE-54 stationary phase. The data given in Tables are the averages of a minimum of three measurements on separate samples.

Individual experiments. 1. A stock solution was prepared with 0.3952 g of hexadecane, 1.9407 g of *E*-2, and 14.5252 g of cyclohexane within $\pm 0.069\%$ weighing error. With this stock solution, samples with a certain amount of trimethylmethoxysilane were prepared. From each sample, 110 μl was taken and then transferred into each of five thermolysis tubes. Each set containing one of each sample was submerged simultaneously in a molten salt bath at the various temperatures for exactly one hour.

2. A stock solution was prepared with 0.0319 g of hexadecane, 0.1179 g of *Z*-2, and 1.4268 g of cyclohexane within $\pm 0.49\%$ weighing error. A stock solution was also prepared with 0.2680 g of hexadecane, 0.8165 g of *E*-2, and 6.4167 g of cyclohexane within $\pm 0.066\%$ weighing error. With these stock solutions, eight samples with a certain amount of trimethylmethoxysilane were prepared. From each sample, 110 μl was taken and then transferred into each of four thermolysis tubes. A total of 32 sealed tubes were prepared from these samples. Each set of 8 sealed tubes (4 tubes from *Z*-2 stock solution, 4 tubes from *E*-2 stock solution) was submerged simultaneously in a molten salt bath at the indicated temperatures for exactly 10 minutes. The reaction temperatures were 359.9, 378.7, 387.0 and 398.9°C.

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A Mechanistic Study on Nucleophilic Substitution Reactions of Aryl Substituted Benzenesulfonates with Anionic Nucleophiles

Ik-Hwan Um*, Seok-Joo Lee, Jung-Joo Kim, and Dong-Sook Kwon

Department of Chemistry, Ewha Womans University, Seoul 120-750

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Second-order rate constants have been measured spectrophotometrically for the nucleophilic substitution reactions of aryl substituted benzenesulfonates (1, $X-C_6H_4SO_2-OC_6H_4-Y$) with aryloxides ($Z-C_6H_4O^-$) and ethoxide (EtO^-) in absolute ethanol at 25°C. The nucleophilicity of aryloxides increases with increasing electron donating ability of the substituent (Z) on aryloxides, and results in a good Hammett correlation with σ^- constant. The reactivity of 1 toward aryloxides and ethoxide shows also significant dependence on the electronic nature of the substituent X and Y . Large positive ρ_{OEt} values have been obtained for the reaction of 1 with phenoxide and ethoxide, indicating that the leaving group departure is little advanced at the transition-state of the rate-determining step. This has been further supported from the fact that σ^- constant gives extremely poor Hammett correlation, while σ^0 does reasonably good correlation for the reaction of 1 with ethoxide. Thus, the present sulfonyl-transfer reaction is proposed to proceed *via* a rate-determining attack of nucleophile to the sulfur atom of 1 followed by a fast leaving group departure.

Introduction

Since acyl-transfer reactions are known to be significantly important in chemistry and biochemistry, numerous studies have been performed in order to investigate the reaction mechanism.¹⁻³ However, detailed reaction mechanisms have not been fully understood.^{4,5} Two distinct reaction pathways have been suggested, *i.e.* one-step concerted and step-wise addition-elimination pathways.⁴⁻⁷ One-step mechanism has been known to proceed *via* a single transition-state in which bond formation by nucleophile occurs concertedly with leaving group departure.^{4,5} On the hand, step-wise mechanism has been suggested to proceed *via* formation of an addition intermediate.^{6,7}

The argument concerning reaction mechanisms is considered mainly on the basis of linear free energy relationships

(LFER),⁸ and the discrepancy seems to originate from lack of systematic studies. Therefore, we have performed a systematic study on LFER in order to investigate reaction mechanism. The reaction system chosen are the following nucleophilic substitution reactions of aryl substituted benzenesulfonates in absolute ethanol at 25.0°C. Unlike carboxylate esters, sulfonate esters have not been studied intensively. Furthermore, the systematic variation of substituents on the sulfonyl moiety, entering and leaving phenoxides in the present system would be considered to give us important informations concerning the reaction mechanism.

Experimental

Materials. The aryl substituted benzenesulfonates in the present study were easily prepared by a modification of the