

Arrhenius Parameters for the Addition of Nucleophiles to the Silicon–Carbon Double Bond of 1,1-Diphenylsilene

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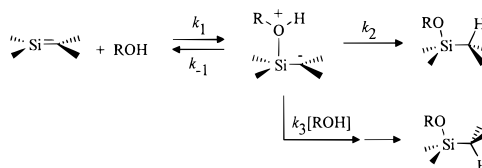
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Silenes are involved as reactive intermediates in a wide variety of thermal and photochemical reactions in organosilicon chemistry^{1–10} and are most commonly trapped as the addition product(s) with alcohols. The mechanism of this reaction is of considerable fundamental importance and has been the subject of numerous studies over the past few years.^{5,11–17} Wiberg proposed a mechanism involving initial nucleophilic attack at silicon, to yield a σ -bonded complex which collapses to (alkoxysilane) product by proton transfer from oxygen to carbon.⁵ Various product^{15,16b,17} and kinetic^{16,17} studies have lent support to the general features of this mechanism but have allowed it to be refined considerably. In particular, kinetic data suggest that for water and aliphatic alcohols, proton transfer is rate determining and is preceded by fast, reversible formation of the silene–alcohol complex (see Scheme 1). Both product and kinetic studies support the view that the complex collapses to product by two competing pathways, one involving intracomplex proton transfer and one involving a second molecule of alcohol. The relative rate constants for the two pathways depend on both the silene and the alcohol; the fact that both occur can lead to product distributions which vary with alcohol concentration,^{15,16b,17} and/or a quadratic dependence of the pseudo-first-order rate constant for silene consumption on alcohol concentration.¹⁶

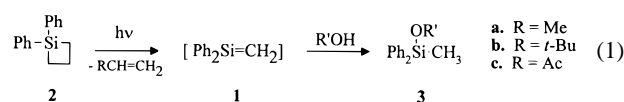
All the experimental and theoretical¹³ data reported to date are consistent with the involvement of silene–alcohol complexes in the reaction. There is as yet no direct proof of their existence, however, although spectroscopic and X-ray crystallographic evidence has been reported of the formation of related complexes between silenes and ethers.^{17,18} In this paper, we report additional (though still indirect) evidence for the involvement of such complexes in the addition of alcohols to silenes, in the form of the temperature dependences of the addition of

Scheme 1



methanol, *tert*-butyl alcohol, and acetic acid to 1,1-diphenylsilene (**1**) in acetonitrile solution.

Laser (248 nm) flash photolysis of continuously flowing, air-saturated¹⁹ solutions of 1,1-diphenylsilacyclobutane (**2**; 0.0071 M) in dry acetonitrile allows ready detection of the characteristic UV absorption spectrum of **1** ($\lambda_{\text{max}} = 325 \text{ nm}$; $\tau \sim 3 \mu\text{s}$),¹⁷ which decays with mixed first- and second-order kinetics in carefully dried solvent. Addition of methanol, *tert*-butyl alcohol, or acetic acid results in the expected shortening of the lifetime of the silene and a change to clean pseudo-first-order decay kinetics, due to reaction of the silene to form the corresponding alkoxysilane **3** (eq 1).¹⁷



Bimolecular rate constants for reaction of **1** with added ROH (k_{ROH}) were obtained from plots of the silene decay rate constant (k_{decay}) versus ROH concentration according to eq 2, where k_{d}° is the pseudo-first-order rate constant for decay of **1** in the absence of added ROH. Such plots were linear over the 0–0.01 M alcohol concentration range throughout a temperature range of -20 to $55 \text{ }^{\circ}\text{C}$; typical examples are shown in Figure 1 for quenching by MeOH at -17 and $55 \text{ }^{\circ}\text{C}$. The linearity in the plots indicates that over these concentration ranges, the addition of all three reagents to **1** proceeds essentially exclusively by a mechanism which is first-order in nucleophile; competition from a mechanism involving two molecules of ROH would be revealed by positive curvature.¹⁶

Arrhenius plots for MeOH, *t*-BuOH, and HOAc are shown in Figure 2. Table 1 lists the corresponding Arrhenius activation energies (E_{a}) and pre-exponential factors ($\log A$), along with activation entropies (ΔS^{\ddagger}) and rate constants at 296 K which were calculated or interpolated from the data.²⁰ The addition of both methanol and *tert*-butyl alcohol to **1** are characterized by negative Arrhenius activation energies and strongly negative entropies of activation.

$$k_{\text{decay}} = k_{\text{d}}^{\circ} + k_{\text{ROH}}[\text{ROH}] \quad (2)$$

Negative activation energies have been reported for a large number of bimolecular reactions—usually of reactive intermediates—in the gas phase and in solution. Examples include singlet carbene reactions with alkenes^{21–24} and halocarbons,²⁵

(19) Air-saturated solutions were employed for convenience and because the presence of oxygen has no detectable effect on either the lifetime of **1** or the course of its reaction with alcohols and acetic acid.¹⁷

(20) Quenching experiments employed the highest quality anhydrous reagents available from Aldrich Chemical Co. The rate constants determined for *tert*-butyl alcohol quenching are smaller by a factor of ~ 2 than those reported previously,¹⁷ which we believe is due to the better quality reagents employed in the present work. Water quenches silene **1** with a rate constant of ca. $8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in acetonitrile.¹⁷

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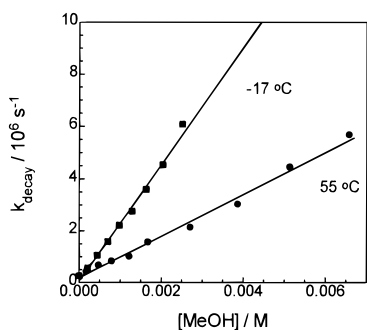


Figure 1. Plots of k_{decay} versus methanol concentration, from laser flash photolysis of air-saturated, 0.0071 M solutions of **2** in dry acetonitrile at -17.2 ± 0.2 (■) and $+55.0 \pm 0.2$ °C (●).

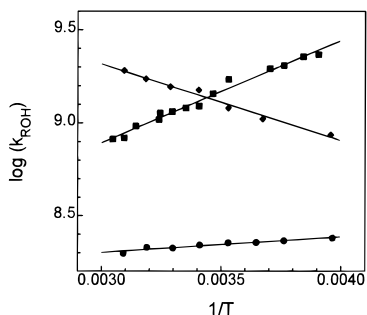


Figure 2. Arrhenius plots for quenching (k_{ROH}) of 1,1-diphenylsilene (**1**) by methanol (■), *tert*-butyl alcohol (●), and acetic acid (◆) in air-saturated, dry acetonitrile.

carbenium ion addition to alkenes,²⁶ reaction of silylenes with silanes^{27,28} and acetylenes,²⁹ cycloadditions of tetracyanoethylene³⁰ and singlet oxygen,³¹ and hydrogen abstraction reactions of methyl radicals;³² this list is by no means exhaustive. As well, a near-zero activation energy has been reported for the dimerization of a stabilized silene in solution.³³ There are two common mechanistic explanations for such behavior. One is that the reaction involves initial exothermic formation of a complex which undergoes competitive collapse to starting materials and product(s); the free energy barrier for the second, product-determining step is higher than those for either complex formation or its reverse, but the transition state for product

Table 1. Arrhenius Activation Energies (E_a), Pre-Exponential Factors ($\log A$), Entropies of Activation ($\Delta S^\ddagger_{296\text{K}}$), and Rate Constants (296 K) for the Addition of Methanol, *tert*-Butyl Alcohol, and Acetic Acid to 1,1-Diphenylsilene (**1**) in Acetonitrile Solution^a

ROH	$k_{\text{ROH}}/10^9 \text{ M}^{-1} \text{ s}^{-1} b$	$k_{\text{H}}/k_{\text{D}}$ (23 °C) ^c	$E_a/$ (kcal/mol)	$\log A/$ $\text{M}^{-1} \text{ s}^{-1}$	$\Delta S^\ddagger_{296\text{K}}/\text{eu}$
MeOH	1.26 ± 0.05	1.5 ± 0.1	-2.5 ± 0.2	7.3 ± 0.2	-27 ± 2
<i>t</i> -BuOH	0.22 ± 0.02	1.6 ± 0.1	-0.4 ± 0.1	8.1 ± 0.1	-24 ± 1
AcOH	1.44 ± 0.05	1.1 ± 0.1	$+1.9 \pm 0.2$	10.5 ± 0.2	-13 ± 2

^a Errors are quoted as twice the standard deviation from linear least-squares analysis of the data shown in Figure 2. The rate constants employed for calculation of activation parameters were corrected for thermal expansion of the solvent. ^b Interpolated from Arrhenius data. ^c Data from ref 17. The value for *t*-BuOH has been corrected from that originally reported.²⁰

formation is of enthalpy lower than that of the starting materials. The second is that the reaction proceeds concertedly, with the negative *apparent* activation energy resulting from the free energy of activation being dominated by a strongly negative entropic term (so that the rate of reaction *decreases* as the temperature increases).^{31,34} The stepwise mechanism is clearly the more consistent with the results of earlier theoretical,¹³ spectroscopic,^{17,18} kinetic,^{16,17} and product studies^{15,16b,17} of the reaction.

The suggestion that for addition of methanol and *tert*-butyl alcohol, the proton transfer step is slower than that for complex formation is consistent with the small but clearly primary deuterium kinetic isotope effects that these two alcohols exhibit in their reactions with **1**.¹⁷ The magnitudes of the Arrhenius activation energies indicate that the transition states for proton transfer within the two complexes are, respectively, *ca.* 2.5 and 0.4 kcal/mol lower in enthalpy than the starting materials and that the enthalpic barrier for proton transfer is lower than that for reversion to starting materials. Since the relative magnitudes of the kinetic isotope effects suggest that the activation enthalpies for intracomplex proton transfer are approximately the same for the two alcohols ($k_{\text{H}}/k_{\text{D}} = 1.6 \pm 0.1$ and 1.5 ± 0.1 for *tert*-butyl alcohol and methanol, respectively, at 23 °C),¹⁷ we tentatively conclude that structural changes in the alcohol have similar effects on the transition state enthalpy for intracomplex proton transfer as on the enthalpy of the silene–alcohol complex.

If the addition of HOAc also proceeds in stepwise fashion, then the small positive activation energy observed for this reaction can be identified as that for complexation (presumably at the carbonyl oxygen), which in this case proceeds to product faster than reverting to starting materials. That complex formation is rate determining is consistent with the $k_{\text{H}}/k_{\text{D}}$ value (indistinguishable from unity) reported previously for this substrate in acetonitrile at 23 °C,¹⁷ although the possibility of a concerted addition mechanism (with the very small kinetic isotope effect resulting simply from the fact that the reaction is strongly exergonic) cannot strictly be ruled out.

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