

Effects of Ether Solvents on the Reactivity of Transient Silenes

William J. Leigh* and Xiaojing Li

Department of Chemistry, McMaster University, 1280 Main Street West,
Hamilton, Ontario, Canada L8S 4M1

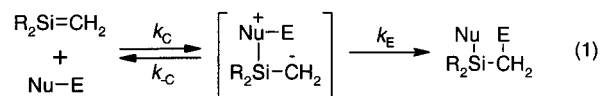
Received July 10, 2001

Absolute rate constants and Arrhenius parameters have been determined for reaction of two transient silenes, 1,1-diphenylsilene (**2a**) and 1,1-bis(4-trifluoromethylphenyl)silene (**2e**), with methanol, *tert*-butanol, acetic acid, acetone, and methoxytrimethylsilane in tetrahydrofuran (THF) solution over the 0–60 °C temperature range. The results are compared to previously reported data for the same reactions in hydrocarbon and/or acetonitrile solution. In the latter solvents, **2e** is significantly more reactive than **2a** toward all of these reagents, and in most cases the Arrhenius activation energies for reaction are negative, a result of the common stepwise mechanism by which these reactions proceed. In contrast, the reactivities of both silenes are reduced in THF solution, their relative reactivities are reversed, and positive Arrhenius activation energies for reaction are obtained in every case. The UV absorption spectra of the two silenes in THF at various temperatures between 0 and 60 °C show that this is due mainly to the effects of complexation of the silenes with the ether solvent, the equilibrium constant for which enters the expression for the observed overall second-order rate constant for reaction. The positive activation energies result from the effect of temperature on the equilibrium constant for solvent complexation, which increases with decreasing temperature and accordingly reduces the concentration of free silene present in solution. For nonacidic nucleophiles like acetone, this leads to particularly large reductions in the overall rate constant for reaction. The effects are smaller with more acidic reagents, consistent with competing addition via initial protonation of the solvent complex. Weak complexation appears to be present even in acetonitrile, which partially accounts for the reduced reactivity of the silenes in this solvent relative to that in hexane.

Introduction

Simple silene derivatives are highly reactive molecules that undergo strongly exothermic reactions with themselves (via 2+2-dimerization) or with added nucleophiles (via 1,2-addition), with bimolecular rate constants that approach the encounter- or diffusion-controlled limit in the gas phase or in solution.¹ The Arrhenius activation energies for these reactions are typically negative due to the strong overall reaction exothermicities and the stepwise nature of the reaction mechanisms. For example, the reaction of silene (H₂-Si=CH₂, **1**) with water is calculated to be on the order of 83 kcal/mol exothermic at the HF/6-31G* level of theory,^{2,3} and experimental studies of several simple transient silene derivatives have shown that the reactions with water and aliphatic alcohols proceed by a stepwise mechanism involving rate-controlling proton transfer within an initially formed Lewis acid–base complex between the silene and the nucleophile.^{4–13} In

fact, kinetic studies of the addition of other common nucleophilic reagents (Nu–E) to transient silenes, such as alkoxysilanes (Nu–E = RO–SiR'₃),¹⁴ acetic acid (Nu–E = AcO–H),⁹ acetone (Nu–E = CH₃COCH₂–H),¹⁵ and *n*-butylamine (Nu–E = *n*-BuNH–H),^{12,16} have shown this mechanism to be a general one for most Nu–E additions to silenes. The general mechanistic scheme is shown in eq 1, while eq 2 gives the expression



for the overall second-order rate constant that is dictated by this mechanism, assuming the steady-state

(1) Morkin, T. L.; Owens, T. R.; Leigh, W. J. In *The Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley and Sons: New York, 2001; Vol. 3, pp 949–1026.

(2) Nagase, S.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1983**, 363.

(3) Nagase, S.; Kudo, T.; Ito, K. In *Applied Quantum Chemistry*; Smith, V. H., Jr., Schaefer, H. F., Morokuma, K., Eds.; D. Reidel: Dordrecht, 1986; pp 249–267.

(4) Wiberg, N. *J. Organomet. Chem.* **1984**, 273, 141.

(5) Wiberg, N.; Preiner, G.; Wagner, G.; Kopf, H. *Z. Naturforsch. [B]* **1987**, 42B, 1062.

(6) Kira, M.; Maruyama, T.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, 113, 3986.

(7) Sluggett, G. W.; Leigh, W. J. *J. Am. Chem. Soc.* **1992**, 114, 1195.

(8) Leigh, W. J.; Bradaric, C. J.; Kerst, C.; Banisch, J. H. *Organometallics* **1996**, 15, 2246.

(9) Bradaric, C. J.; Leigh, W. J. *Can. J. Chem.* **1997**, 75, 1393.

(10) Leigh, W. J.; Sluggett, G. W. *J. Am. Chem. Soc.* **1994**, 116, 10468.

(11) Leigh, W. J.; Boukherroub, R.; Kerst, C. *J. Am. Chem. Soc.* **1998**, 120, 9504.

(12) Leigh, W. J. *Pure Appl. Chem.* **1999**, 71, 453.

(13) Morkin, T. L.; Leigh, W. J. *Acc. Chem. Res.* **2001**, 34, 129.

(14) Leigh, W. J.; Bradaric, C. J.; Morkin, T. L.; Li, X. *Organometallics* **2001**, 20, 932.

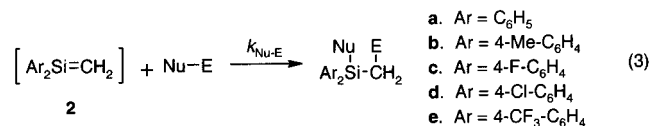
(15) Bradaric, C. J.; Leigh, W. J. *Organometallics* **1998**, 17, 645.

(16) Leigh, W. J., Li, X., Harrington, C., Toltl, N. P. To be published.

approximation holds for the zwitterionic intermediate. Reactions via mechanisms of this type exhibit negative activation energies over the temperature range where $k_{-C} > k_E$ and positive activation energies over the range where $k_E > k_{-C}$.^{9,15}

$$k_{\text{Nu-E}} = k_C [k_E / (k_E + k_{-C})] \quad (2)$$

The effects of substituent and solvent on the absolute rate constants for these reactions have been studied in detail in the case of 1,1-diphenylsilene (**2a**) and the four ring-substituted derivatives **2b–e** (eq 3).^{9,12–15} All five



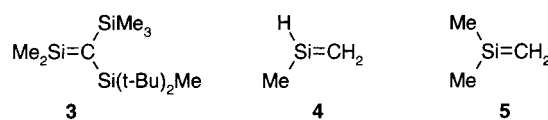
- a. Ar = C₆H₅
- b. Ar = 4-Me-C₆H₄
- c. Ar = 4-F-C₆H₄
- d. Ar = 4-Cl-C₆H₄
- e. Ar = 4-CF₃-C₆H₄

reactions exhibit positive Hammett ρ -values in hydrocarbon (isooctane or hexane) and acetonitrile (MeCN) solution, verifying early theoretical predictions that the reactivity of the Si=C bond with nucleophiles should be enhanced by inductive electron-withdrawing substituents at silicon.¹⁷

With the exception of methoxytrimethylsilane addition, the overall rate constants for reaction ($k_{\text{Nu-E}}$) are slightly smaller in acetonitrile compared to hydrocarbon solvents, and the overall activation energy is invariably shifted to more positive values.^{9,12–15} The origins of these effects are difficult to sort out completely, but the effect on the Arrhenius activation energy is consistent with the complex partitioning ratio ($= k_E / (k_{-C} + k_E)$ in eq 2) being somewhat higher in the more polar solvent.^{9,12–15} This should produce a rate *enhancement* in MeCN compared to hydrocarbon solvents, which would be expected to be complemented by an increase in k_C due to stabilization of the zwitterionic intermediate. The overall *decrease* in $k_{\text{Nu-E}}$ that is generally observed has thus been ascribed to the effects of weak complexation of the free silene by the weakly basic acetonitrile. This would have the effect of decreasing the overall rate constant by decreasing the concentration of free silene present in solution, assuming that the reactivity of the complexed species is considerably lower than that of the free silene toward nucleophilic addition.

The latter assumption is supported by the further reduction in rate that has been observed for the reactions of these and other reactive silenes in THF solution, which is much less polar than acetonitrile but is a significantly stronger Lewis base, particularly toward silicon electrophiles.^{8,10,18} That THF complexes readily with silenes is well known, as a result of the early report by Wiberg and co-workers of the isolation and crystal structure determination of the THF complex of silene **3**.¹⁹ This silene is kinetically stabilized by the bulky di-*tert*-butylmethylsilyl substituents at carbon, but can otherwise be expected to be a highly polar (and hence intrinsically strongly electrophilic) silene.^{20,21} An even

more dramatic example of the stabilizing effect of ether solvents on reactive silenes is provided by a recent report by Auner and co-workers of the NMR spectra of silene (**1**), 1-methylsilene (**4**), and 1,1-dimethylsilene (**5**) in dimethyl ether-*d*₆ solution at -100 °C.²² All three of these silenes are known to dimerize to the corresponding 1,3-disilacyclobutane at close to the encounter- or diffusion-controlled rates in the gas or inert condensed phases over wide ranges in temperature,^{23–25} and the rate constant for dimerization of **5** is known to be temperature-independent over the 25–300 °C range.^{24,26,27} The fact that these silenes are stable toward dimerization in (fluid) ether solution at temperatures as high as -100 °C is thus quite remarkable, and suggests that solvent complexation not only reduces their normally considerable reactivity but also fundamentally alters the form of the temperature dependences of their characteristic reactions.



In this paper, we report a study of the temperature dependences of the absolute rate constants for reaction of 1,1-diphenylsilene (**2a**) and 1,1-bis(4-trifluoromethylphenyl)silene (**2e**) with an extensive series of nucleophiles in THF solution, which was initiated in an attempt to explore the effects of complexing solvents on silene reaction kinetics in detail. UV absorption spectra of the two silenes have been measured as a function of temperature in this solvent and in MeCN solution, to obtain discrete evidence for solvent complexation and to investigate the manner in which it varies with temperature and silene electrophilicity. Absolute rate constants for reaction of **2a,e** with methanol (MeOH), *tert*-butanol (*t*-BuOH), acetic acid (AcOH), acetone, and methoxytrimethylsilane (MeOTMS) have then been determined over the 0–60 °C temperature range, and the results are compared to previously published kinetic data for these systems in hydrocarbon and acetonitrile solution.^{9,12–15} Finally, kinetic deuterium isotope effects have been measured in the cases of methanol and acetic acid addition, in an effort to address the possibility that complexing solvents might also alter the mechanisms for reaction compared to those in noncomplexing solvents.

Results and Discussion

Solvent and Temperature Effects on the UV Absorption Spectra and Lifetimes of 2a,e. Silenes **2a,e** were generated and detected by laser flash photolysis of air-saturated solutions of the corresponding

(22) Auner, N.; Grobe, J.; Muller, T.; Rathmann, H. W. *Organometallics* **2000**, *19*, 3476.

(23) Maier, G.; Mihm, G.; Reisenauer, H. P. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 597.

(24) Brix, Th.; Arthur, N. L.; Potzinger, P. *J. Phys. Chem.* **1989**, *93*, 8193.

(25) Vatsa, R. K.; Kumar, A.; Naik, P. D.; Upadhyaya, H. P.; Pavanaja, U. B.; Saini, R. D.; Mittal, J. P.; Pola, J. *Chem. Phys. Lett.* **1996**, *255*, 129.

(26) Guse'nikov, L. E.; Konobeyevsky, K. S.; Vdovin, V. M.; Nametkin, N. S. *Dokl. Akad. Nauk. SSSR (Engl. transl.)* **1977**, *235*, 791.

(27) Bastian, E.; Potzinger, P.; Ritter, A.; Schuchmann, H.-P.; von Sonntag, C.; Weddle, G. *Ber. Bunsen-Ges. Phys. Chem.* **1980**, *84*, 56.

(17) Apeloig, Y.; Karni, M. *J. Am. Chem. Soc.* **1984**, *106*, 6676.

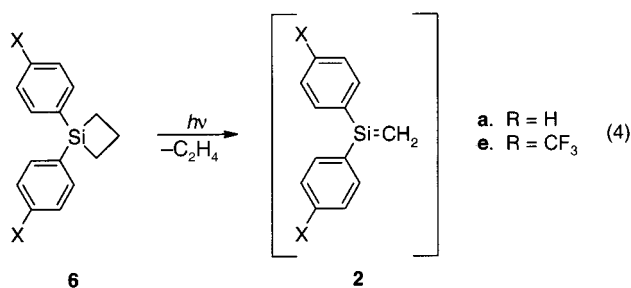
(18) Leigh, W. J.; Sluggett, G. W. *Organometallics* **1994**, *13*, 269.

(19) Wiberg, N.; Wagner, G.; Muller, G.; Riede, J. *J. Organomet. Chem.* **1984**, *271*, 381.

(20) Leigh, W. J.; Kerst, C.; Boukherroub, R.; Morkin, T. L.; Jenkins, S.; Sung, K.; Tidwell, T. T. *J. Am. Chem. Soc.* **1999**, *121*, 4744.

(21) Morkin, T. L.; Leigh, W. J.; Tidwell, T. T.; Allen, A. D. *Organometallics* **2001**, *20*, 5707.

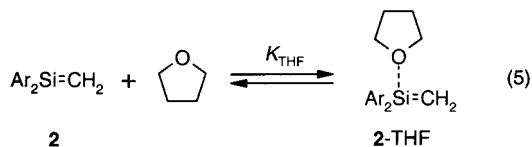
1,1-diarylsilacyclobutanes **6a,e** (eq 4), as previously



described.^{9,14,15} In dry hexane or acetonitrile solution at 23 °C, **2a,e** exhibit essentially identical UV spectra ($\lambda_{\text{max}} = 325 \text{ nm}$) and decay with mixed first- and second-order kinetics.⁹ The lifetimes are typically no greater than 1–4 μs in dry acetonitrile (MeCN), with that of **2e** being significantly shorter than **2a** owing to its higher sensitivity toward trace amounts of water in the solvents.

The two silenes also decay with mixed first- and second-order kinetics in THF solution at 25 °C, but the lifetimes are significantly longer, the sensitivity to extraneous moisture is reduced, and the absorption spectra are very different from those observed in hexane or MeCN. For example, silene **2a** exhibits a lifetime $\tau \approx 4 \mu\text{s}$ and a spectrum that is much broader than in hexane or MeCN, tailing out to well past 400 nm.⁸ In contrast, that of **2e** ($\tau \approx 10 \mu\text{s}$) remains sharp and well-defined, but the absorption maximum is shifted (from its value of 325 nm in hexane or acetonitrile) to $\lambda_{\text{max}} = 375 \text{ nm}$.

UV spectra of the two silenes in dry THF solution were measured at several temperatures over the 0–60 °C range; examples of spectra recorded at 1 and 58 °C are shown in Figure 1. The spectrum of **2a** in THF is strongly temperature dependent. At 58 °C it consists of a single, broad absorption band ($\lambda_{\text{max}} = 325 \text{ nm}$), assignable to the free silene on the basis of the similarities in spectral width and position to that of **2a** in hexane solution.⁸ In contrast, spectra recorded at 30 °C and below are much broader due to enhanced absorption in the 370–420 nm range. At the lowest temperature studied (1 °C; Figure 1a), the spectrum exhibits a well-defined maximum at 350 nm, superimposed on an additional absorption extending below 280 nm. We assign this spectrum to the complex of **2a** with the ether solvent. At each temperature studied, transient decays recorded at various wavelengths throughout the 280–420 nm range exhibited identical decay kinetics, with lifetimes in the 4–6 μs range. This indicates that the free silene and its solvent complex are in rapid equilibrium with one another (as defined by eq 5) and



interconvert rapidly relative to dimerization or reaction with trace impurities in the solvent. The same behavior is observed in the presence of reagents that cause a reduction in lifetime owing to reaction with the silene (vide infra).

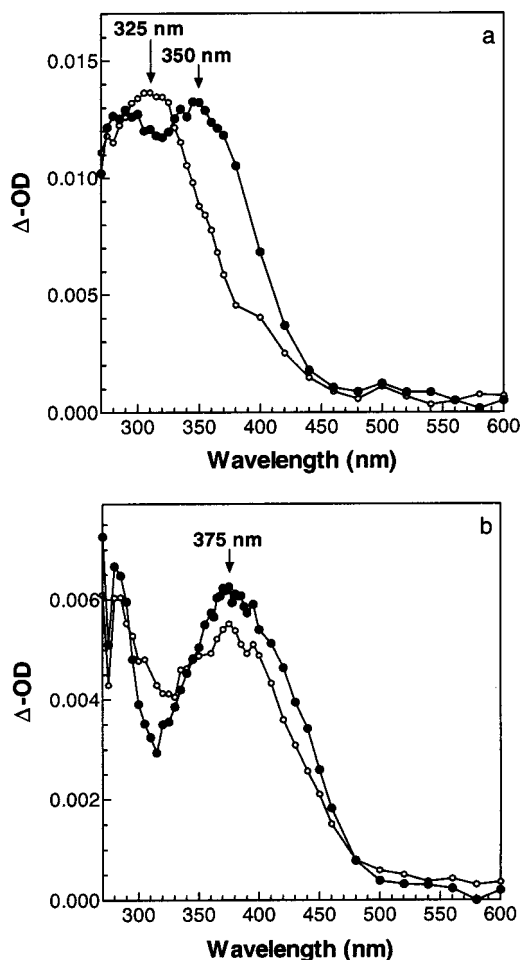


Figure 1. Transient UV absorption spectra of (a) 1,1-diphenylsilene (**2a**) and (b) 1,1-bis(4-trifluoromethylphenyl)silene (**2e**) in air-saturated THF solution at 1 °C (●) and 58 °C (○). The spectra were recorded 100–200 ns after the laser pulse.

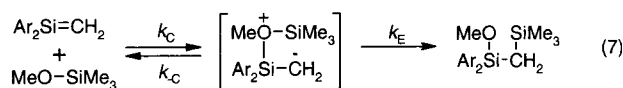
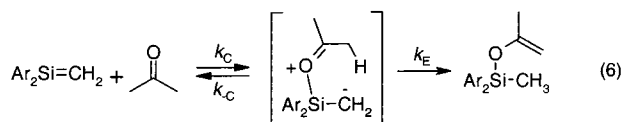
The variations in the spectra of **2a** with temperature indicate that the extent of complexation varies quite significantly over the 0–58 °C temperature range, with the free silene dominating the equilibrium at 58 °C and the complexed form dominating at 1 °C, assuming similar extinction coefficients for the two species. In contrast, the spectrum of **2e** varies only slightly over the same temperature range, consisting of a single absorption band with $\lambda_{\text{max}} = 375 \text{ nm}$ at all temperatures examined (see Figure 1b). On the basis of the behavior of **2a** as described above and the spectrum of **2e** in hexane solution ($\lambda_{\text{max}} = 325 \text{ nm}$), we assign the 375 nm absorption to the THF complex of **2e**. The high-temperature spectrum shows increased absorption at 325 nm compared to that recorded at low temperature, suggesting a somewhat higher equilibrium concentration of the free silene at the higher temperature, as would be expected based on the behavior of **2a**. Nevertheless, the spectra suggest that **2e** remains strongly complexed over the entire temperature range examined.

As was observed for **2a**, transient decays recorded for **2e** at various wavelengths throughout the 280–420 nm range exhibited identical decay kinetics, but the lifetimes were significantly longer ($\tau > 10 \mu\text{s}$) than those observed for **2a** under the same conditions. This was true at all temperatures throughout the 0–58 °C range.

This contrasts the behavior of these two silenes in hexane or MeCN, where **2e** is the shorter-lived of the two,⁸ and indicates that **2e** enjoys significantly greater stabilization than **2a** in the ether solvent. This suggests that the reactions responsible for the decay of the silenes under these conditions (presumably, competing dimerization and reaction with trace amounts of water) occur mainly via the free silenes, and the solvent complexes are relatively unreactive. The lifetimes of both silenes were observed to decrease with increasing temperature in THF solution, opposite to their behavior in hexane or acetonitrile, where a very modest increase in lifetime with increasing temperature is observed.⁸ This is also consistent with silene decay occurring mainly due to reaction of the free silenes, whose concentrations relative to those of the (much less reactive) solvent complexes increase as the temperature is raised.

Spectra were also recorded in acetonitrile solution as a function of temperature (see Supporting Information). No shifts in absorption maximum are observed over the -3 to 60 °C range in either case, although the spectrum of **2e** at -3 °C is broadened slightly on the long-wavelength side of the maximum compared to spectra recorded at room temperature and above. We thus conclude that complexation also occurs in MeCN solution, at least for **2e**. However, it is considerably weaker than in THF solution, consistent with the relative basicities of the two solvents.²⁸ As expected, no variation whatsoever is observed in the UV spectra of either **2a** or **2e** in hexane solution over the 0 – 60 °C temperature range.

Solvent and Temperature Effects on the Reactions of **2a,e with MeOTMS and Acetone.** We begin by examining the effects of THF complexation on the reactions of **2a,e** with acetone and MeOTMS, since these are the systems for which solvent effects on the absolute rate constants and Arrhenius parameters have been previously studied in greatest detail.^{14,15} These two reactions respond similarly to variation of the aryl substituents; for example, Hammett ρ -values of ca. $+1.5$ and $+0.9$ have been reported for reaction of **2a–e** with acetone and MeOTMS, respectively, in hydrocarbon solution.^{14,15} However, they respond differently to changes in solvent; reaction of **2a,e** with acetone is slower in MeCN than in hydrocarbon solution,¹⁵ while the opposite is true for reaction with MeOTMS.¹⁴ The proposed mechanisms for the two reactions in noncomplexing solvents are shown in eqs 6 and 7.¹⁵



Addition of either reagent to the THF solutions of **2a** and **2e** resulted in a shortening of their lifetimes and a change to clean pseudo-first-order decay kinetics. For both silenes, lifetimes measured in the presence of

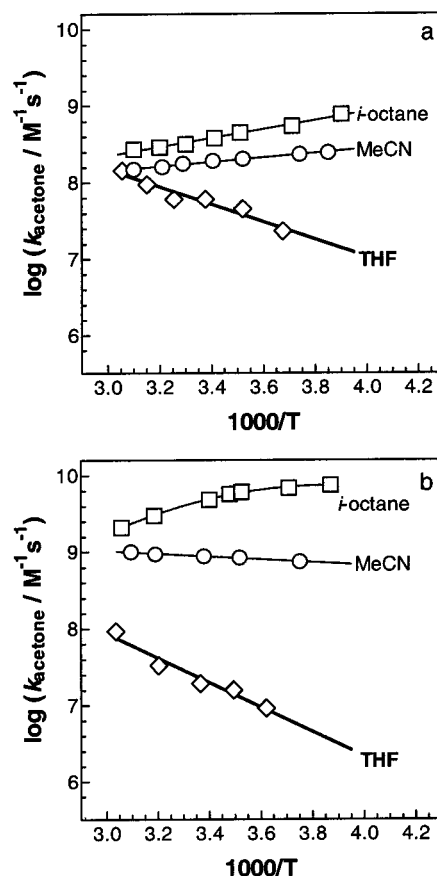


Figure 2. Arrhenius plots for reaction of **2a** (a) and **2e** (b) with acetone in isooctane (□), acetonitrile (○), and THF solution (◇). The isooctane and acetonitrile data are from ref 15.

added acetone or MeOTMS at several monitoring wavelengths throughout the 300 – 400 nm range were identical within experimental error, indicating that the solvent complexation equilibrium remains fast relative to reaction with added nucleophile. The transient decay rates (k_{decay}) increased in direct proportion to the concentration of added reagent, which allows the second-order rate constants for reaction ($k_{\text{Nu-E}}$) to be obtained in straightforward fashion from plots of k_{decay} vs $[\text{Nu-E}]$ according to eq 8. Rate constants were determined in this manner at several temperatures between 0 and 60 °C, and the resulting Arrhenius plots are shown in Figures 2 and 3. For comparison, the previously reported kinetic data for reaction of the two silenes in hydrocarbon and MeCN solution over a similar temperature range are also shown in Figures 2 and 3.^{14,15} The corresponding Arrhenius parameters and interpolated values of the absolute rate constants at 25 °C are listed in Table 1. It should be noted that the Arrhenius parameters reported in the table for the reaction of **2b** in isooctane were calculated by linear least-squares analysis of the reported (nonlinear) $\log k$ vs T^{-1} data,¹⁵ in order to give an estimate of the average values of E_a and $\log(A/M^{-1} s^{-1})$ over the 0 – 60 °C temperature range for qualitative comparison to the data in the other solvents.

$$k_{\text{decay}} = k_0 + k_{\text{Nu-E}}[\text{Nu-E}] \quad (8)$$

As the data in Figures 2 and 3 show, the reactivities of **2a,e** are altered quite dramatically in THF compared

(28) Izutsu, K. *Acid–base dissociation constants in dipolar aprotic solvents*. IUPAC Chemical Data Series #35; Blackwell Scientific Publications: Oxford, 1990; pp 17–35.

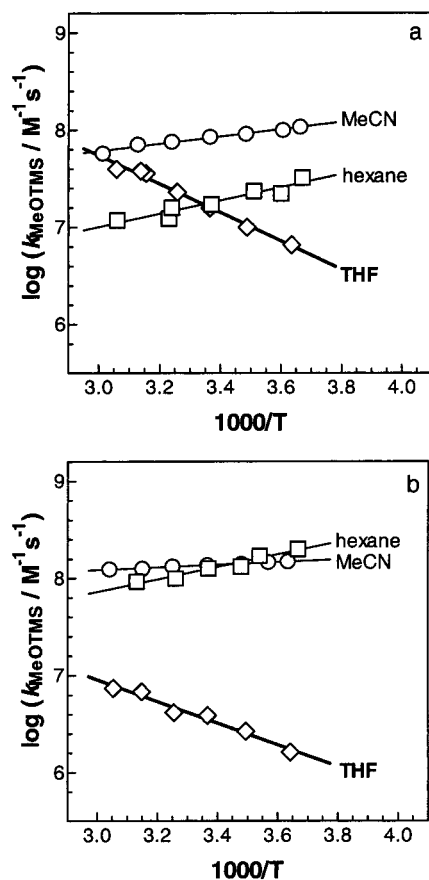


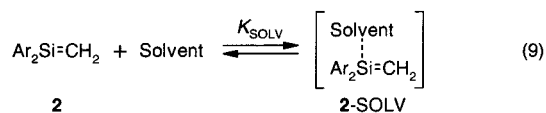
Figure 3. Arrhenius plots for reaction of **2a** (a) and **2b** (b) with MeOTMS in hexane (□), acetonitrile (○), and THF solution (◇). The hexane and acetonitrile data are from ref 14.

to hydrocarbon or acetonitrile solvents. In all cases, the Arrhenius activation energies take on strongly positive values in THF solution, and there is a clear inversion in the relative reactivities of the two silenes compared to what they are in the noncomplexing and weakly complexing solvents.

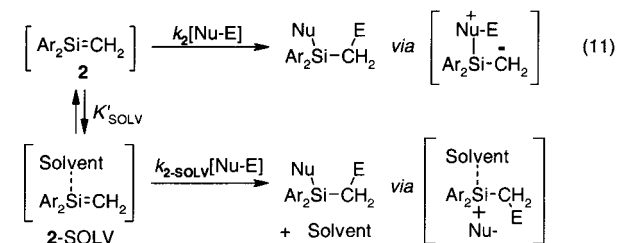
Qualitatively, the effects of solvent complexation on the rate constants for nucleophilic addition reactions of silenes can be thought of as arising from the fact that complexation reduces the concentration of free silene available for reaction by converting some portion of the total to a species of substantially lower electrophilicity (i.e., the solvent complex), hence reducing the overall rate constants for reaction with nucleophilic reagents compared to their values in a noncomplexing solvent. The activation energy shifts to more positive values because the equilibrium constant for solvent complexation decreases (and hence raises the concentration of free silene) with increasing temperature.

A more quantitative understanding can be obtained by considering the expression for the overall rate constant for reaction in the situation where the free silene is involved in a fast (Lewis) acid–base equilibrium with the solvent (eq 9), characterized by the equilibrium constant K_{SOLV} (eq 10). The general situation is one in which the free and complexed species are both reactive toward an added reagent (Nu–E), as defined by eq 11. If the solvent complexation equilibrium is fast relative to reaction of either species with Nu–E, then the overall rate constant for reaction in the

complexing solvent ($k_{\text{Nu–E}}^{\text{SOLV}}$) is given by the equivalent expressions of eqs 12 and 13, where F_2 and $F_{2-\text{SOLV}}$ are the fractional concentrations of free and complexed silene, and k_2 and $k_{2-\text{SOLV}}$ are the individual rate constants for reaction of the two species with Nu–E.²⁹ It is important to note that under the conditions where eqs 12 and 13 are valid, the value of $k_{\text{Nu–E}}^{\text{SOLV}}$ that is obtained experimentally does not depend on which species (i.e., the free silene, its complex, or some undefined mixture of the two) is actually being monitored in the kinetic experiment. That this holds in the present cases is indicated by the fact that the transient decay rate constants (k_{decay}) measured in the presence of added Nu–E are independent of monitoring wavelength.



$$K'_{\text{SOLV}} = K_{\text{SOLV}}[\text{Solvent}] = [\text{2-SOLV}] / [\text{2}] \quad (10)$$



$$k_{\text{Nu-E}}^{\text{SOLV}} = F_2 k_2 + F_{2-\text{SOLV}} k_{2-\text{SOLV}} \quad (12)$$

$$k_{\text{Nu-E}}^{\text{SOLV}} = \frac{1}{(1 + K'_{\text{SOLV}})} k_2 + \frac{K'_{\text{SOLV}}}{(1 + K'_{\text{SOLV}})} k_{2-\text{SOLV}} \quad (13)$$

As is suggested in eq 11, the free and complexed silenes can be expected to react in fundamentally different ways with Nu–E: the free silene via initial nucleophilic attack, and the complexed silene via initial electrophilic attack.³⁰ Thus, particularly weak Bronsted or Lewis acids such as acetone and MeOTMS can be expected to react via the free silene only, in which case eq 13 reduces to the limiting expression of eq 14. If the mechanism for reaction of the free silene with Nu–E in the complexing solvent is identical to that in noncomplexing solvents, then k_2 can be expected to be of a magnitude similar to that of $k_{\text{Nu–E}}$ in a noncomplexing solvent of similar bulk polarity. Thus to a first approximation, the overall rate constant for reaction in the complexing solvent will be reduced from its value in a noncomplexing solvent, to an extent determined solely by the magnitude of K_{SOLV} .

$$k_{\text{Nu-E}}^{\text{SOLV}} \sim F_2 \cdot k_2 = \frac{1}{(1 + K'_{\text{SOLV}})} \cdot k_2 \quad (k_2 \gg k_{2-\text{SOLV}} K'_{\text{SOLV}}) \quad (14)$$

Since for a given silene K_{SOLV} increases (and F_2 decreases) with decreasing temperature (vide supra), then it follows that the overall activation energy for

(29) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1995; pp 15–45.

(30) Wiberg, N.; Kopf, H. *J. Organomet. Chem.* **1986**, *315*, 9.

Table 1. Arrhenius Parameters and Interpolated Second-Order Rate Constants (at 25 °C) for Reaction of 1,1-Diphenylsilene (2a) and 1,1-Bis(4-Trifluoromethylphenyl)silene (2e) with Acetone and Methoxytrimethylsilane (MeOTMS) in Hydrocarbon, MeCN, and THF Solution^a

	2a			2e		
	hydrocarbon	MeCN	THF	hydrocarbon	MeCN	THF
acetone ^b						
$k_{25}^{25C}/10^7 \text{ M}^{-1} \text{ s}^{-1}$	35.8 ± 3.2	17.9 ± 1.8	5.9 ± 0.9	450 ± 30	88.5 ± 9.0	2.3 ± 0.3
E_a (kcal/mol)	-2.6 ± 0.3	-1.3 ± 0.1	+5.2 ± 0.7	-3.1 ± 0.9 ^c	+0.8 ± 0.1	+7.3 ± 0.9
$\log(A/M^{-1} \text{ s}^{-1})$	6.6 ± 0.2	7.3 ± 0.1	11.6 ± 0.5	7.3 ± 0.6 ^c	9.6 ± 0.1	12.8 ± 0.6
MeOTMS ^d						
$k_{25}^{25C}/10^7 \text{ M}^{-1} \text{ s}^{-1}$	1.7 ± 0.1	8.2 ± 0.7	1.7 ± 0.2	12.2 ± 0.8	13.6 ± 0.9	0.36 ± 0.08
E_a (kcal/mol)	-3.1 ± 0.4	-1.7 ± 0.3	+6.7 ± 0.3	-3.0 ± 0.3	-0.6 ± 0.1	+5.1 ± 0.4
$\log(A/M^{-1} \text{ s}^{-1})$	5.0 ± 0.3	6.6 ± 0.2	12.1 ± 0.3	5.9 ± 0.3	7.7 ± 0.1	10.3 ± 0.3

^a Errors reported as $\pm 2\sigma$. Rate constants are the interpolated values calculated from the best fits of $\log k$ vs T^{-1} data. ^b Hydrocarbon (isooctane) and MeCN data are from ref 15. ^c Values calculated by linear least-squares analysis of the nonlinear $\log k$ vs T^{-1} data. ^d Hydrocarbon (hexane) and MeCN data are from ref 14.

Table 2. Arrhenius Parameters and Absolute Second-Order Rate Constants (25 °C) for Reaction of MeOH(D), *t*-BuOH, and AcOH(D) with 1,1-Diphenylsilene (2a) and 1,1-Bis(4-Trifluoromethylphenyl)silene (2e) in MeCN and THF Solution^a

reagent	solvent	2a			2e		
		$k_{\text{Nu-E}}^{25C}/10^7 \text{ M}^{-1} \text{ s}^{-1}$	E_a (kcal/mol)	$\log(A/M^{-1} \text{ s}^{-1})$	$k_{\text{Nu-E}}^{25C}/10^7 \text{ M}^{-1} \text{ s}^{-1}$	E_a (kcal/mol)	$\log(A/M^{-1} \text{ s}^{-1})$
MeOH	MeCN ^b	122 ± 12	-2.5 ± 0.2	7.3 ± 0.2	220 ± 20	-0.8 ± 0.5 ^c	8.7 ± 0.4 ^c
	THF	59.6 ± 4.2	+0.33 ± 0.24	9.0 ± 0.2	11.9 ± 2.0	+1.2 ± 0.8	8.9 ± 0.6
MeOD	MeCN ^b	65 ± 12	-3.2 ± 0.3	6.5 ± 0.2	<i>d</i>	<i>d</i>	<i>d</i>
	THF	22.2 ± 2.5	+0.78 ± 0.64	8.9 ± 0.4	4.6 ± 0.5	+4.9 ± 0.2	11.3 ± 0.1
<i>t</i> -BuOH	MeCN	21.4 ± 2.5 ^b	-0.38 ± 0.09 ^b	8.1 ± 0.1 ^b	74.8 ± 5.2	+1.0 ± 0.7 ^c	9.5 ± 0.5 ^c
	THF	4.3 ± 1.5	+1.0 ± 0.7	8.4 ± 0.5	0.86 ± 0.22	+5.0 ± 0.9	10.6 ± 0.7
AcOH	MeCN ^b	148 ± 11	+1.9 ± 0.2	10.5 ± 0.2	242 ± 30	+3.5 ± 0.5	12.0 ± 0.4
	THF	38.2 ± 1.6	+3.1 ± 0.6	10.9 ± 0.4	39.6 ± 2.3	+4.2 ± 0.3	11.7 ± 0.2
AcOD	THF				33.8 ± 1.5	+4.7 ± 0.5	12.0 ± 0.4

^a Errors reported as $\pm 2\sigma$. Rate constants are the interpolated values calculated from the best fits of $\log k$ vs T^{-1} data. ^b Data from ref 9. ^c Values calculated by linear least-squares analysis of the nonlinear $\log k$ vs T^{-1} data. ^d Not determined.

reaction will be shifted to more positive values in the complexing solvent relative to a noncomplexing one. The greater the variation in the equilibrium constant with temperature and the milder the intrinsic temperature dependence of the reaction rate, the greater will be the effect on the temperature dependence of the overall (observed) rate constant compared to its value in a noncomplexing solvent. For a given solvent, the magnitude of the effect can also be expected to increase as the electrophilicity of the silene (and hence K_{SOLV}) increases, which explains the inversion in the relative reactivities of **2a** and **2e** in THF compared to hydrocarbon or acetonitrile solution. Equations 12 and 13 indicate that the effects of solvent complexation on the overall rate constants, activation energies, and relative reactivities of silenes of different intrinsic electrophilicities should be maximized when the limiting condition leading to eq 14 applies; smaller differences can be expected for nucleophilic reagents which react via both the free and complexed forms of the silene. Even in the limiting situation where the kinetics are simplest, the observed activation parameters are complicated functions of the solvent-complexation equilibria and the activation parameters associated with product formation from the free silene. Presumably, it is this complexity that leads to preexponential factors that approach or slightly exceed that for diffusion (ca. $10^{12} \text{ M}^{-1} \text{ s}^{-1}$ in THF) in some of the cases in Table 1 (and Table 2; vide infra).

The reaction with acetone is one that involves addition of a relatively basic substrate and transfer of a

relatively nonacidic proton, presumably with minimal assistance from the solvent in the proton-transfer step. Of all the reactions studied in this work, this one displays the greatest variation in rate constant as a function of solvent: in the case of **2e**, almost 3 orders of magnitude at the low end of the temperature range studied. It also exhibits much larger positive shifts in E_a with increasing solvent basicity and more pronounced effects on the relative reactivities of the two silenes compared to those observed with more acidic nucleophiles (vide supra). This reaction comes the closest to defining the maximum effects of solvent complexation on the reactivities of these two silenes and serves as a convenient model on which to base the interpretation of our results for the other nucleophilic reagents studied here.

Figure 4 shows plots of $\log(k_{\text{NuE}}^{\text{THF}}/k_{\text{NuE}}^{\text{i-oct}})$ versus inverse temperature for reaction of the two silenes with acetone in THF solution. If bulk solvent polarity effects play a relatively small role in controlling the kinetics of acetone addition (i.e., k_2 in eqs 12–14 is approximately equal to $k_{\text{NuE}}^{\text{i-oct}}$ for the two silenes), then this plot should roughly define the variations in the fractional concentrations of free silene (F_2) with inverse temperature for **2a,e** in the complexing solvent. The results indicate that F_{2a} and F_{2e} vary from ~ 0.05 to ~ 0.6 and ~ 0.001 to ~ 0.04 , respectively, over the 1–60 °C temperature range, which is qualitatively consistent with the results of the UV study discussed earlier (Figure 1), assuming similar extinction coefficients for the absorptions due to the free and complexed forms of

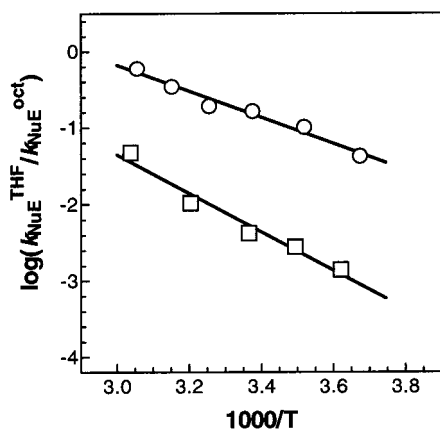
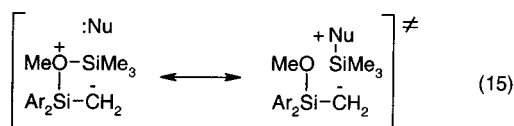


Figure 4. Plots of $(k_{\text{Nu-E}}^{\text{THF}}/k_{\text{Nu-E}}^{\text{i-oct}})$ vs T^{-1} for reaction of **2a** (○) and **2e** (□) with acetone in THF, calculated using the experimental values for $k_{\text{Nu-E}}^{\text{THF}}$ and $k_{\text{Nu-E}}^{\text{i-oct}}$ values that were calculated at the appropriate temperatures by linear or nonlinear least-squares analyses of the isoctane data shown in Figure 1.

the silenes in THF solution. The corresponding results for MeCN (not shown) appear to overestimate the extent of solvent complexation in this case (judging from the results of the UV study), but this is not surprising given the much larger difference in bulk solvent polarity between MeCN and isoctane.

The data for reaction of **2a,e** with MeOTMS indicate that while the activation energies follow the same trend with solvent as those for acetone addition (Table 1), the effect of complexing solvents on the reaction kinetics is more complicated. For example, reaction of **2a** in the weakly complexing solvent MeCN is accelerated relative to hexane, while in THF solution reaction in the high temperature range is actually faster than in hexane. This is only partly due to a simple bulk polarity effect, since the rate constant for reaction of **2a** with MeOTMS in 1,2-dichloroethane, a noncomplexing solvent of slightly higher dielectric constant than THF,³¹ is only ca.1.5 times larger than in hexane at 60 °C, and the difference decreases at lower temperatures.¹⁴

We speculate that, in this case, complexing solvents have two opposing effects on the reaction kinetics; a rate-decelerating effect due to silene–solvent complexation, and a rate-accelerating effect due to solvent assistance in the product-forming (electrophile-transfer) step of the reaction. The latter can be understood in terms of eq 15, which depicts resonance structures for



the transition state for the product-forming step in a nucleophilic solvent (:Nu). These resonance structures suggest that while the importance of solvent assistance to trimethylsilyl transfer should depend on the nucleophilicity or Lewis basicity of the solvent, it should probably not vary appreciably with substitution on the silene. Since complexation of a given solvent with the

free silene *does* vary appreciably with substituent, the *relative* importance of the two effects should vary with silene electrophilicity. Thus, solvent assistance effects are proportionately greater than solvent complexation effects in the case of the less electrophilic derivative **2a**, particularly at high temperatures, where the solvent complexation equilibrium favors the free silene. The opposite is true in the case of **2e**, which results in smaller differences in reaction kinetics in MeCN compared to hexane and much larger reductions in reactivity in THF compared to the other solvents.

Solvent and Temperature Effects on the Reactions of 2a,e with Alcohols and Acetic Acid. Plots of k_{decay} versus concentration for quenching of **2a,e** by MeOH, *t*-BuOH, and AcOH are linear in MeCN solution throughout the 0–60 °C temperature range,⁹ consistent with the simple 1,2-addition mechanism of eq 1 being the dominant one over the range of concentrations that can be studied by nanosecond flash photolysis techniques. Absolute rate constants have been reported by us previously for reaction of **2a** with the three reagents in hexane, MeCN, and THF at a single temperature (23 °C) and follow the same general trend as that noted above for reaction of **2a** with acetone; i.e., reaction is fastest in hexane and slowest in THF.⁸ However, the temperature dependences of these reactions have not been studied in hydrocarbon solvents, so we do not have sufficient data to comment on the specific role that solvent complexation effects play in determining the temperature dependences in acetonitrile. We can only assume that they will be similar to those discussed above for the addition of acetone and in any event should be relatively weak.

Unlike the case in acetonitrile solution, plots of k_{decay} vs [ROH] for reaction of the two alcohols with **2a,e** generally exhibit mild curvature in THF, particularly at low temperatures. For example, Figure 5 shows a series of plots of k_{decay} vs [ROH] for quenching of **2a,e** by MeOH at 3 °C and at 54 °C. Such behavior is indicative of reaction by two competing mechanisms, one involving a single molecule of alcohol in the rate-determining step and one involving two. In cases where the plots were curved, the data were analyzed according to the quadratic expression of eq 16, where k_{ROL} and $k_{2\text{ROL}}$ are the second- and third-order rate coefficients corresponding to reaction with one and two molecules of alcohol, respectively. Figure 6 shows the Arrhenius plots for the second-order rate constants (k_{ROL}) for reaction of **2a,e** with MeOH, MeOD, and *t*-BuOH in THF solution. The corresponding data for reaction of **2a,e** with the protiated alcohols in acetonitrile, of which all but those for reaction of **2e** with *t*-BuOH in MeCN have been reported previously,⁹ are included for comparison. Table 2 lists the Arrhenius parameters obtained from these experiments, along with values of the second-order rate constants at 25 °C that were interpolated from the Arrhenius plots. As before, linear regression analyses have been applied to the nonlinear $\log k$ vs T^{-1} data reported previously for reaction of **2e** with MeOH and *t*-BuOH in acetonitrile,¹⁵ to provide estimates of the average Arrhenius parameters over the temperature ranges examined.

$$k_{\text{decay}} = k_0 + k_{\text{ROL}}[\text{ROL}] + k_{2\text{ROL}}[\text{ROL}]^2 \quad (16)$$

(31) *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, 1995; pp 6–241.

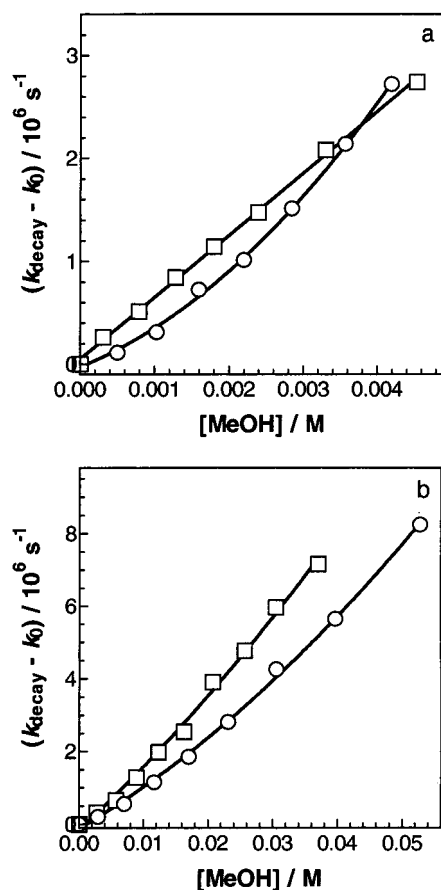


Figure 5. Plots of $(k_{\text{decay}} - k_0)$ vs $[\text{MeOH}]$ for (a) **2a** and (b) **2e** in air-saturated THF solution at 3 °C (O) and at 54 °C (□). The solid lines represent the least-squares fit of the data; those for reaction of **2a** at 54 °C were analyzed according to eq 8, while the others were analyzed according to eq 16.

The differences between MeCN and THF are smaller than those observed for the addition of acetone. However, the trends are the same: significant reductions in reactivity are observed, the activation energies are shifted to more positive values, and the relative reactivities of the two silenes are reversed in THF compared to MeCN. Moreover, the kinetic isotope effects on the reaction with methanol are larger in THF; the data afford $k_{\text{H}}/k_{\text{D}}$ values of 2.5 ± 0.2 and 2.4 ± 0.3 at 23 °C for **2a** and **2e**, respectively, which should be compared to the corresponding values of 1.9 ± 0.1 and 1.0 ± 0.1 reported by us previously for reaction of the two silenes in MeCN at the same temperature.⁹ Together with the quadratic dependences of k_{decay} vs $[\text{ROH}]$ that are observed at the lower temperatures, the data suggest a significant change in the mechanism of alcohol addition in THF solution compared to that in noncomplexing or weakly complexing solvents. All things considered, the THF data are rather difficult to interpret, but are consistent with the involvement of at least three competing reaction mechanisms that vary in relative importance depending on the silene and the temperature. The positive temperature dependences and inversion in the relative reactivities of **2a** and **2e** suggest that the dominant mechanism involves addition of ROH to the free silene, presumably via the same sequence of events as are involved in noncomplexing or weakly complexing solvents. However, the smaller changes in rate constant

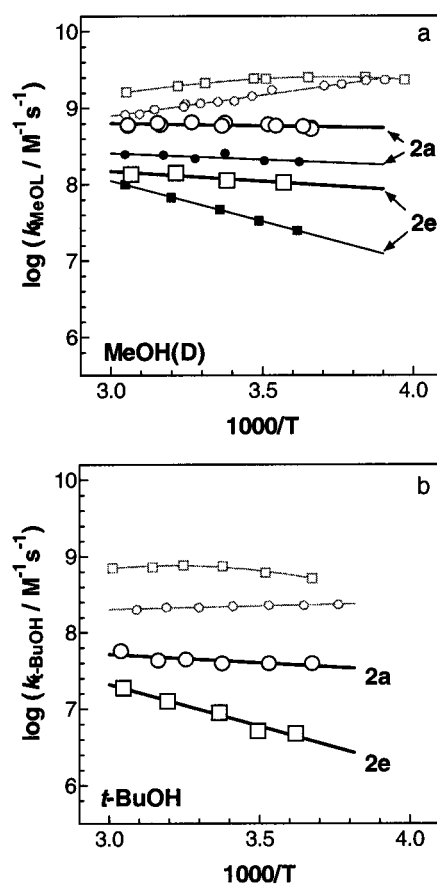
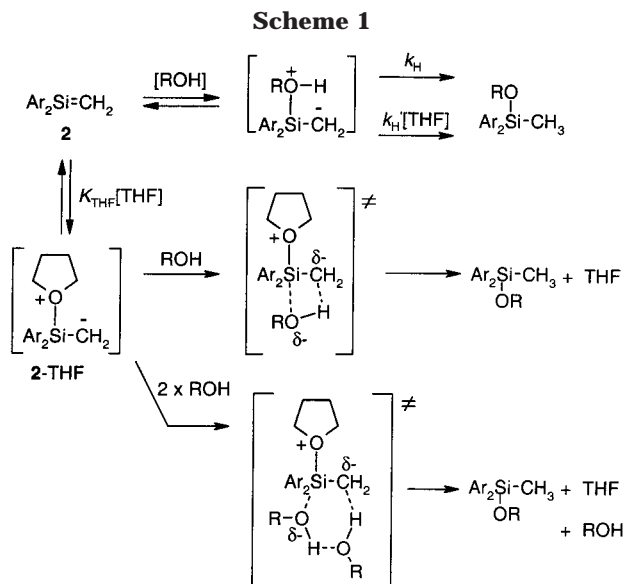


Figure 6. Arrhenius plots of the second-order rate constants (k_{ROL}) for reaction of **2a** (O) and **2e** (□) with alcohols in air-saturated THF solution: (a) MeOH (open symbols) and MeOD (closed symbols); (b) $t\text{-BuOH}$. The lighter colored data are the corresponding data for reaction of **2a** (O) and **2e** (□) with the protiated alcohols in MeCN solution (ref 9 and this work).

and activation energy compared to those for acetone addition suggest that a component of the reaction with alcohols involves reaction with the *complexed* silene. This component has the effect of accelerating the rate of reaction compared to what would be expected in the limit where only the free silene reacts, and results in a smaller apparent activation energy because its contribution to the overall reaction rate increases as the fractional concentration of complexed silene ($F_{2\text{-SOLV}}$ in eq 12) increases with decreasing temperature.

As mentioned above, the reaction of MeOH with **2a,e** in MeCN solution is thought to proceed by the simple [1,2]-addition mechanism of eq 1 in the millimolar concentration regime. A second (termolecular) pathway, involving two molecules of alcohol in the product-forming step of the reaction, is known to compete with the bimolecular pathway in the cases of less electrophilic silenes and/or at higher bulk alcohol concentrations.^{6–10} Evidence that this second pathway occurs as well in the addition of MeOH to **2a** in MeCN at decimolar alcohol concentrations has been reported previously⁸ and has been proposed to involve catalyzed proton transfer in the silene–alcohol complex, with the second alcohol molecule acting as a general base.¹⁰ In THF solution, the solvent can serve the role of general base in this process. This leads to enhancements in the second-order rate constants for addition of MeOH in THF relative to



those in MeCN solution, with silenes that do not complex appreciably with THF for one reason or another.¹⁰ However, the presence of this additional proton-transfer pathway cannot account on its own for the relatively small positive activation energies and the larger kinetic isotope effects that are observed for the addition of ROH to **2a,e** in THF solution, if both the simple [1,2]-addition and THF-catalyzed pathways proceed via the free silene. Similarly, the reaction pathway responsible for the second-order dependences of k_{decay} on [ROH] that are observed at low temperatures cannot involve the free silene either, since only a first-order dependence is observed in the reaction kinetics in MeCN or hexane solution.⁹

We conclude that while reaction of the alcohols with **2a,e** in THF probably occurs mainly via the free silenes, there are two additional pathways involving reaction of the complexed species that become particularly important at low temperatures (where $F_{2-\text{SOLV}}$ is highest). These are tentatively formulated in Scheme 1 along with the conventional reaction pathways involving the free silene. The mechanisms involving the complexed silene are proposed to proceed via initial protonation of the complex, either as a discrete step or in concert with nucleophilic attack, to explain the sizable primary kinetic isotope effects on the second-order rate constants. It should be noted that the pathway involving protonation of the complex by a single molecule of alcohol is analogous to the mechanism originally proposed by Kira and co-workers for the termolecular reaction of silenes with alcohols, which leads to the formation of the anti-addition product in cyclic silenes.⁶ It is interesting that the isotope effect on the second-order rate constant for reaction of **2a** with MeOH is as large as ca. 2.5 in THF and does not vary with temperature, given that the activation energy for MeOH addition is close to zero. However, the isotope effect on the reaction of MeOH with the free silene is known to increase with increasing temperature (from ca. 1.7 at 0 °C to ca. 2.3 at 60 °C in MeCN⁹), while that on the reaction with the complex (if it indeed proceeds via initial protonation) should decrease. Thus, the net isotope effect remains roughly constant as the relative contributions from reaction via the free and complexed

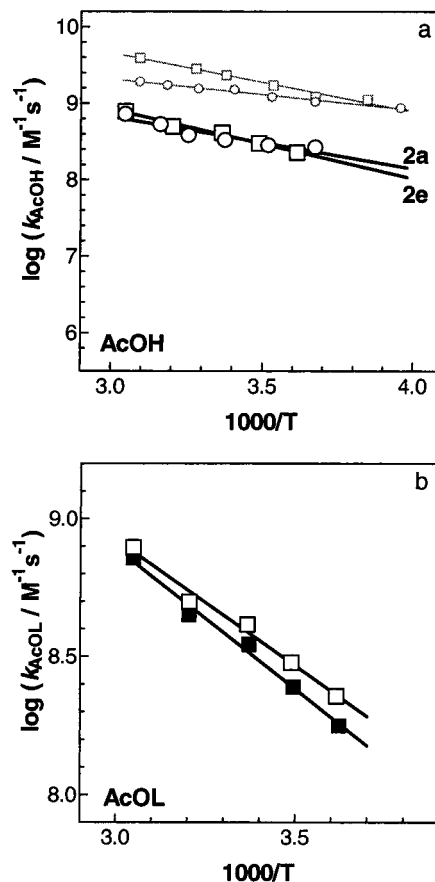


Figure 7. Arrhenius plots of the second-order rate constants for reaction of **2a** (○) and **2e** (□) with (a) AcOH and (b) AcOL in air-saturated THF solution (open symbols: L = H; filled symbols: L = D). The lighter colored data in (a) are the corresponding data for reaction of **2a,e** with AcOH in MeCN solution (ref 9).

silenes change with temperature. This conclusion is supported by the behavior of **2e**, whose KIE increases quite dramatically with decreasing temperature (from ~1.3 at 58 °C to ~4 at 0 °C); presumably, the relatively small KIE at the high temperature limit mostly reflects that on the reaction with the free silene, which is negligible.⁹

The temperature dependence exhibited by the pathway involving two molecules of alcohol is highly variable, depending on the silene and the alcohol, and in any event the rate constants are poorly reproducible. Arrhenius plots (see Supporting Information) afforded activation energies of $E_a = (-16.4 \pm 4.6)$, $(+0.1 \pm 0.7)$, and (-4.8 ± 1.4) kcal/mol for reaction of **2a** and **2e** with MeOH and of **2e** with *t*-BuOH, respectively. No third-order component could be detected in the quenching of **2a** with *t*-BuOH over the -1 to 54 °C temperature range. Isotopic substitution had no significant effect on the values of the third-order rate constants for reaction with MeOH, within the error limits of the analyses.

Supporting evidence for the direct involvement of silene-THF complexes in the reaction with alcohols is provided by the data for addition of acetic acid to **2a,e**. Plots of k_{decay} vs [AcOH] are strictly linear for both silenes over the 0–60 °C temperature range in THF and so were analyzed according to eq 8. Figure 7a shows Arrhenius plots for quenching of **2a,e** by AcOH in THF and MeCN. Reaction of the two silenes with AcOD

proved to be slightly slower than with AcOH at 23 °C, the data affording k_H/k_D values of 1.05 ± 0.05 and 1.18 ± 0.05 for **2a** and **2e**, respectively. Absolute rate constants were measured for the latter compound over the 0–60 °C range in THF and are shown as Arrhenius plots in Figure 7b along with the corresponding data for reaction with AcOH. The Arrhenius parameters calculated from these data are summarized along with those for the alcohols in Table 2.

As Figure 7a shows, the addition of acetic acid is the only reaction whose kinetics are *not* altered substantially in THF solution compared to MeCN; the absolute rate constants are a factor of only 3–8 times slower in THF, and the normal inversion in the reactivities of the two silenes is not observed. These trends are consistent with a proportionately greater contribution to reaction from the complexed forms of the silenes, as might be expected considering the substantially higher acidity of the carboxylic acid compared to the alcohols. Small but significant deuterium isotope effects are observed, and they are larger for the more highly complexed of the two silenes (**2e**), as would again be expected for this mechanism. In contrast, isotope effects on the rate constants for addition of acetic acid to **2a,e** in acetonitrile solution are barely detectable and do not differ significantly from one another.⁹ This has been explained in terms of a stepwise, ene-addition reaction mechanism analogous to that shown in eq 6 for the addition of acetone, but with the rate constant for the product-forming (proton-transfer) step being considerably faster than that for reversion of the complex to starting materials. In fact, this mechanism was proposed primarily on the basis of the differences between the Arrhenius activation energies for addition of AcOH to **2a,e** in acetonitrile solution.⁹ We now know that **2e** complexes weakly with acetonitrile at temperatures below 25 °C, so the difference in activation energy compared to **2a** might be better explained in terms of solvent complexation effects rather than a stepwise mechanism initiated by nucleophilic attack at silicon. The reaction of acetic acid with these silenes may well be a concerted process.

Summary and Conclusions

The spectroscopic and kinetic data reported here verify that Lewis-basic solvents complex readily with reactive silenes at ambient temperatures, to an extent that depends on the basicity of the solvent, the electrophilicity of the silene, and the temperature. The effects of complexing solvents on silene reactivity vary enormously depending on the reaction and its specific characteristics. Several examples of nucleophile–electrophile (“Nu–E”) addition reactions have been studied in this work. In noncomplexing solvents, these are all thought to proceed by reversible nucleophilic attack at silicon, followed by transfer of the electrophilic group to carbon, and they all exhibit Arrhenius activation energies that are negative or only slightly positive in value.

With all but the most acidic of nucleophilic reagents, our results indicate that reaction of the free silene is substantially faster than that of the complexed form. Thus, the complex generally acts mainly as a spectator, supplying the free silene to reaction via a rapid pre-

equilibrium. The superposition of the temperature dependence of the equilibrium between free and complexed silene on the intrinsic temperature dependence of the reaction results in a shift of the observed activation parameters to more positive values in complexing relative to noncomplexing solvents. The effect increases with the Lewis basicity of the solvent and with the intrinsic electrophilicity of the silene. The most dramatic example of this effect is provided by the ene-addition of acetone, a reaction that involves a relatively basic, nonacidic nucleophile. In this case, rate decelerations of up to ~3 orders of magnitude are observed at ~0 °C in THF relative to isooctane solution, and the apparent activation energy and preexponential factor are higher by 9–11 kcal/mol and ca. $10^5 \text{ M}^{-1} \text{ s}^{-1}$, respectively. The effect is larger for the more electrophilic of the two silenes studied, resulting in an inversion of their relative reactivities in THF compared to isooctane solution. Silene dimerization can be expected to be affected similarly.

Secondary effects can act to accentuate or reduce the net effects of complexing solvents on silene reaction kinetics. The smallest net effects are observed for acetic acid addition, for which it is proposed that reaction occurs via both the free silene (by initial nucleophilic attack) and the solvent complex (by initial protonation). The competition between these two mechanisms has the effect of counterbalancing the normal rate-retarding effect of solvent complexation on the reaction kinetics, since as the equilibrium concentrations of free and complexed silene change with temperature, so too do the relative contributions of the two mechanisms to the overall rate constant for reaction. Relatively small net effects are also observed for alcohol additions, although they are somewhat larger than those exhibited by acetic acid addition. Presumably, this is because of the lower proton acidities of the alcohols compared to AcOH, and so reaction via the complexed silene is proportionately slower. In these cases, the reaction pathway involving the complexed silene is revealed by significantly larger kinetic deuterium isotope effects on the second-order rate constants for methanol addition in THF compared to those in acetonitrile and by the observation of mixed first- and second-order dependences of the silene decay rates on alcohol concentration. The second-order dependence on [ROH] increases in importance with decreasing temperature and is proposed to be due to a mechanism in which two molecules of alcohol are involved in the rate-determining step for protonation of the silene–THF complex.

Methoxytrimethylsilane addition exhibits kinetic variations that are unlike the others in a number of ways. In this case, reaction occurs only via the free silene, so the increases in activation energy in THF compared to hexane or acetonitrile are large and similar in magnitude to those observed for acetone addition. However, with 1,1-diphenylsilene (**2a**), the less electrophilic of the two silenes studied, the high-temperature rate constants are actually faster in THF and MeCN than in hexane solution. This is not a simple bulk solvent polarity effect, but is proposed to result from assistance from the solvent in the electrophile-transfer step of the reaction.

Experimental Section

Acetonitrile (Caledon Reagent) was refluxed over calcium hydride (Fisher) for several days, distilled under dry nitrogen, and then cycled three times through a 1 in. \times 6 in. column of neutral alumina (Aldrich) which had been activated by heating under vacuum (ca. 0.05 Torr) at 320° C for 10 h with periodic shaking. Tetrahydrofuran (Caledon Reagent) was refluxed over molten potassium in a nitrogen atmosphere and distilled. Methoxytrimethylsilane was synthesized by reaction of methanol with excess hexamethyldisilazane and purified by distillation (bp 56–58 °C).³² Methanol, *tert*-butanol, acetone, and glacial acetic acid were of the highest quality available from Aldrich Chemical Co. and were used as received. Methanol-*Od* and acetic acid-*Od* were also used as received from Aldrich. The 1,1-diarylsilacyclobutanes (**6a,e**) were prepared according to the published methods.⁹

Nanosecond laser flash photolysis experiments employed the pulses (248 nm; 15–20 ns; 70–120 mJ) from a Lambda Physik Compex 100 excimer laser, filled with F₂/Kr/Ne mixtures, and either the home-built detection system described previously^{9,33} or a Luzchem Research mLFP-111 laser flash photolysis system. Solutions were prepared at concentrations such that the absorbance at the excitation wavelength (248 nm) was ca.

(32) Schrock, R. R.; Sancho, J.; Pederson, S. F. *Inorg. Synth.* **1989**, *26*, 44.

(33) Leigh, W. J.; Workentin, M. S.; Andrew, D. *J. Photochem. Photobiol. A: Chem.* **1991**, *57*, 97.

0.7 (0.003–0.004 M) and were flowed continuously through a 7 \times 7 or 3 \times 7 Suprasil flow cell connected to a calibrated 100 mL reservoir. Solution temperatures were measured with a Teflon-coated copper/constantan thermocouple that was inserted directly into the flow cell. Reagents were added directly to the reservoir by microliter syringe as aliquots of standard solutions. Rate constants were calculated by linear or non-linear least-squares analysis of decay rate-concentration data (6–10 points) that spanned at least a factor of 5 (usually more than 1 order of magnitude) in the transient decay rate. Errors are quoted as twice the standard deviation obtained from the least-squares analysis in each case.

Acknowledgment. We wish to thank the Natural Sciences and Engineering Research Council of Canada for financial support. This paper is dedicated to our good friend Professor Ossie Tee, on the occasion of his retirement from Concordia University.

Supporting Information Available: Transient UV absorption spectra at ~0, 23, and ~55 °C for silenes **2a,e** in acetonitrile and hexane solution, tables of absolute rate constants for reaction of **2a,e** with acetone, MeOTMS, MeOH-(D), *t*-BuOH, and AcOH(D) in THF at various temperatures, and Arrhenius plots of the third-order rate constants for reaction of **2a,e** with MeOH and *t*-BuOH (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM0106175