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Far-UV laser flash photolysis in solution. A study of the chemistry of 1,1-dimethylsilene in hydrocarbon solvents

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Abstract

The far-UV (193 nm) laser flash photolysis of nitrogen-saturated isooctane solutions of 1,1-dimethylsiletane allows the direct detection of 1,1-dimethylsilene as a transient species, which (at low laser intensities) decays with pseudo-first-order kinetics ($\tau \sim 10$ μs) and exhibits a UV absorption spectrum with $\lambda_{max} \sim 255$ nm. Characteristic rapid quenching is observed for the silene with methanol ($k_{MeOH} = (4.9 \pm 0.2) \times 10^9$ M^{-1} s^{-1}), tert-butanol ($k_{BuOH} = (1.8 \pm 0.1) \times 10^9$ M^{-1} s^{-1}) and oxygen ($k_{O_2} = (2.0 \pm 0.5) \times 10^8$ M^{-1} s^{-1}). The Arrhenius activation parameters for the reaction with methanol have been determined to be $E_a = -2.6 \pm 0.6$ kcal mol^{-1} and log $A = 7.7 \pm 0.3$. © 1997 Elsevier Science S.A.

Keywords: 1,1-Dimethylsilene; Far-UV laser flash photolysis; Hydrocarbon solvent; 1,1-Dimethylsiletane

1. Introduction

We have recently found that, with only minor modifications to the experimental design, it is possible to employ a 193 nm (ArF) excimer laser as an excitation source for laser flash photolysis experiments in non-aqueous solvents [1], thus considerably broadening the scope of this already powerful method for the study of photochemically generated reactive intermediates in solution. With the far-UV technique, it is possible to generate and detect transient species from precursors which do not absorb at the more conventional pulsed laser wavelengths, and to determine absolute rate constants for their reactions with alcohols and oxygen.

There have been numerous reports over the past 15 years of the direct detection of silene reactive intermediates in solid matrices at low temperature [2–10], in solution [11–17] and in the gas phase [18,19], and there is now a reasonable amount of kinetic data for several of their more common reactions, such as dimerization and nucleophilic addition of alcohols, carboxylic acids and ketones. Studies of silene reactivity in the gas phase have concentrated on simple alkyl-substituted derivatives, because of precursor volatility considerations, whereas those in solution have been confined to more highly conjugated derivatives whose precursors absorb significantly at wavelengths in the mid-UV. There have been no time-resolved studies of simple alkyl-substituted silenes in solution, which may allow correlations with gas phase data or with solution phase data for more highly substituted derivatives.

In this work, we have employed these methods to study the chemistry of 1,1-dimethylsilene (**2**) in hydrocarbon solution, using 1,1-dimethylsiletane (**1**) as the precursor (Eq. (1)). Compound **1** is a well-known thermal and photochemical precursor to **2** [18,20], and its pyrolysis or photolysis has been employed previously for kinetic and spectroscopic studies of **1** in the gas phase [18,21–23] and in solid matrices at low temperature [5,10]. In addition, Steinmetz and Bai [24] have shown that far-UV (185 nm) irradiation of 1,1-dimethylsiletane derivatives in solution leads to the formation of the corresponding silenes in high yield, on the basis of steady state trapping studies.

We report the UV absorption spectrum of **2** in hydrocarbon solution at room temperature, together with the absolute rate constants for reaction with aliphatic alcohols and oxygen. The deuterium kinetic isotope effects on the reaction with alcohols and the Arrhenius parameters for the addition of methanol (MeOH) have also been determined. These data allow a comparison of the reactivity of **2** with that of more highly substituted transient silenes under similar conditions.

1 **2** **3**

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2. Results and discussion

Direct irradiation of deoxygenated 0.01 M solutions of **1** in isooctane-containing MeOH or tert-butanol (t-BuOH) (0.1 M) leads to the formation of ethylene and the corresponding alkoxysilane (**3**; see Eq. (1)) as the only detectable products between 5% and 20% conversion. The alkoxysilanes were identified by gas chromatography (GC) co-injections with authentic samples.

Laser flash photolysis of continuously flowing, deoxygenated 0.0025 M isooctane solutions of **1** ($\epsilon_{193} = 800 \pm 30$ M^{-1} cm^{-1}) with pulses from an ArF excimer laser (193 nm, 12 ns, approximately 20 mJ) produces a transient species which exhibits an absorption maximum at 255 nm, and decays with mixed pseudo-first-order and second-order kinetics. The decay kinetics change to clean first order when the laser intensity is reduced with neutral density filters or when small amounts of MeOH are added to the solution (e.g. $\tau \sim 1.7$ μs when [MeOH] = 1.1×10^{-4} M). Fig. 1 shows a typical decay trace and time-resolved absorption spectrum, obtained from a solution of **1** containing 3.8×10^{-4} M MeOH. The spectrum was recorded over a 150 ns time window starting about 120 ns after the laser pulse, and did not change significantly (except in intensity) throughout the decay. The apparent shoulder in the spectrum represents normal noise and is not significant.

Plots of the pseudo-first-order rate constant for the decay of the transient (k_{decay}) vs. the MeOH concentration according to Eq. (2) are linear. The slope of the plot affords k_q, the bimolecular rate constant for quenching of the transient by the added quencher. Quenching by MeOD, *t*-BuOH and *t*-BuOD is slower than that by MeOH, but the plots of k_q vs. [Q] show similar degrees of linearity over the concentration ranges studied. Fig. 2 shows typical plots of this type for quenching of the transient by MeOH and MeOD. On the basis of the high reactivity of the transient towards alcohols, the comparison of the UV absorption spectrum (Fig. 1) with literature data [5] and the products of the steady state irradiation of **1** in the presence of MeOH and t-BuOH, we assign the transient species observed in these experiments as 1,1-dimethylsilene (**2**). Table 1 lists the absolute rate constants for the reaction of **2** with MeOH, t-BuOH, oxygen (see below) and the deuterated isotopomers of the two alcohols in isooctane solution at 23 °C.

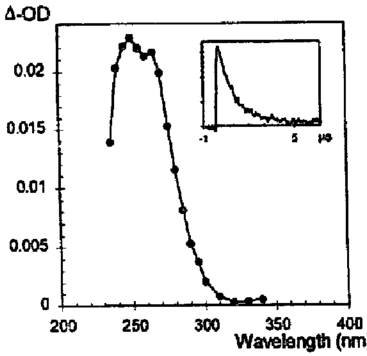


Fig. 1. Time-resolved UV absorption spectrum, recorded by far-UV (193 nm) laser flash photolysis of a deoxygenated 0.0025 M solution of 1,1-dimethylsiletane (**1**) in isooctane containing 3.8×10^{-4} M methanol at 23 °C. Inset: decay trace recorded at a monitoring wavelength of 270 nm; the spectrum was recorded over a time window of 0.12–0.27 μs after the laser pulse.

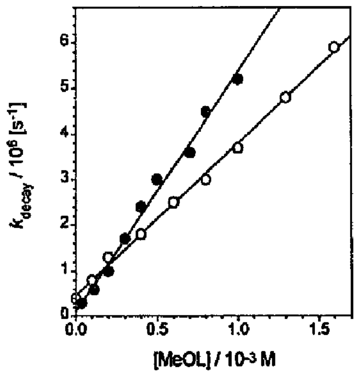


Fig. 2. Plots of k_{decay} vs. [MeOL] (L ≡ H (●) or D (○)) for the quenching of 1,1-dimethylsilene (**2**) in deoxygenated isooctane solution at 23 °C.

Table 1

Bimolecular rate constants for the reaction of 1,1-dimethylsilene (**2**) with MeOH(D), t-BuOH(D) and oxygen in isooctane solution at 23 °C[a]

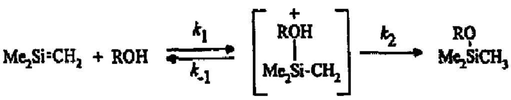
Quencher	k_q (10^9 M^{-1} s^{-1})
MeOH	4.9 ± 0.2
MeOD	3.3 ± 0.1
t-BuOH	1.8 ± 0.1
t-BuOD	1.11 ± 0.05
O_2	0.20 ± 0.05

[a] Errors are listed as twice the standard deviation from least-squares analysis of k_{decay} vs. concentration data according to Eq. (2).

$$k_{decay} = k_0 + k_q[Q] \tag{2}$$

Silene **2** is the most reactive silene studied by us so far in solution, reacting at nearly the diffusion-controlled rate with MeOH in isooctane. It exhibits a typical reduction in reactivity towards the more sterically hindered alcohol t-BuOH, and deuterium isotope effects are observed which can conclusively be identified as primary for both alcohols. These trends in reactivity with alkyl and isotopic substitution on the alcohol are similar to those reported previously for a number of other reactive silenes in solution [1,15,17,25].

The reaction of silenes with alcohols is thought to proceed by a mechanism involving reversible nucleophilic attack at silicon to form an alcohol–silene complex, which collapses to the product by proton transfer by competing unimolecular and bimolecular mechanisms (Eq. (3)). The intracomplex proton transfer results in a first-order dependence of k_{decay} on [ROH], while the extracomplex pathway involves a second molecule of alcohol and results in a quadratic [ROH] dependence [15,17] and variations in the stereochemistry or regiochemistry of addition at higher alcohol concentrations [15,25–27]. The excellent linearity in the plots of k_{decay} vs. [ROH] observed here for **2** indicate that the intracomplex proton transfer is too fast for the extracomplex pathway to compete at the low alcohol concentrations employed in our experiments. The reaction is also sufficiently rapid such that kinetic studies can be carried out using MeOH concentrations below that at which oligomerization of the alcohol becomes significant [28,29].



$$Me_2Si{=}CH_2 + ROH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \left[\begin{array}{c} \overset{+}{R O H} \\ | \\ Me_2\overset{-}{Si}\text{-}CH_2 \end{array} \right] \xrightarrow{k_2} \begin{array}{c} RO \\ | \\ Me_2SiCH_3 \end{array} \qquad (3)$$

Another consequence of pre-equilibrium complexation in the reaction of particularly reactive silenes with MeOH is the observation of apparent negative activation energies [1,16], and **2** also exhibits this behaviour. The bimolecular rate constants for the reaction of **2** with MeOH were determined at several temperatures between −10 and 44 °C, and found to decrease with increasing temperature over this range. Fig. 3 shows the Arrhenius plot, from which the values of $E_a = -2.6 \pm 0.6$ kcal mol^{-1} and $\log A = 7.7 \pm 0.3$ were obtained. The Arrhenius parameters are similar to those reported previously for the reaction of MeOH with 1,1-diphenylsilene (**4**) in acetonitrile [16] and 1,1-dimethyl-1,3-(1-sila)butadiene (**5**) in hexane solution [1]. These two silenes are only slightly less reactive than **2** towards alcohols in hydrocarbon solution, and exhibit similar deuterium kinetic isotope effects [1,16,25].

$Ph_2Si{=}CH_2$

4

5

Saturation of isooctane solutions of **1** with oxygen causes a substantial reduction in the lifetime of the absorption assigned to **2** ($\tau \sim 330$ ns) and the appearance of a new, long-lived transient species ($\tau \geq 10$ μs) which exhibits a similar UV absorption spectrum ($\lambda_{max} \sim 260$ nm) to that of the silene. The lifetime of the short-lived transient is shortened further on addition of MeOH to the solution, and so it can conclusively be identified as the silene. The lifetime of **2** under these conditions affords an estimate of $k_{O2} \sim 2 \times 10^8$ M^{-1} s^{-1} for the rate constant of reaction with oxygen. Laser flash photolysis of oxygen-saturated samples of pure isooctane or *n*-hexane leads to the formation of the same long-lived transient species as found in solutions containing **1**, indicating that it is a product of oxygen photolysis (probably peroxyl radical formed by hydrogen abstraction from the solvent) [30]. Steady state irradiation of an oxygen-saturated isooctane solution of **1** (185 nm) leads to the formation of at least a dozen products in comparable yields; the photolysis mixture is indistinguishable from that obtained when an oxygen-saturated isooctane solution without added **1** is photolysed under similar conditions.

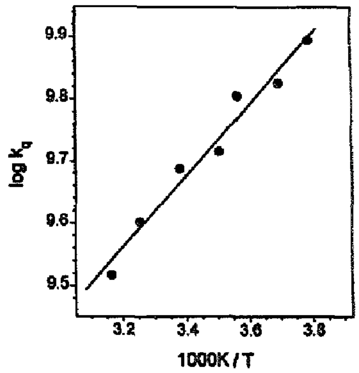


Fig. 3. Arrhenius plot for the quenching of 1,1-dimethylsilene (**2**) by methanol in deoxygenated isooctane solution.

3. Conclusions

1,1-Dimethylsilene (**2**), which has been detected here in solution for the first time, reacts with MeOH at nearly diffusion-controlled rates in isooctane solution at room temperature. The reaction exhibits a primary isotope effect and negative Arrhenius activation energy, consistent with a mechanism involving the formation of a silene–alcohol complex in a fast pre-equilibrium step, followed by proton transfer within the complex. Reaction with oxygen is also rapid, although the product(s) could not be determined, and kinetic studies are complicated by the formation of transient species due to oxygen photolysis.

The use of a 193 nm excimer laser for flash photolysis studies of reactive intermediates in solution is ideally suited to cases in which the required precursor has a low absorption above 240 nm. Studies of this type are restricted to a fairly limited range of solvents (water [31], hydrocarbons and fluorocarbons) and transient quenchers, because of the need to be transparent at the excitation wavelength. In spite of these limitations, the technique allows the study of a number of small reactive molecules which, so far, have been more commonly studied in the gas or solid phase. A number of examples of such systems in carbene, free radical and organosilicon chemistry are under investigation in our laboratory.

4. Experimental details

UV absorption spectra were recorded on a Perkin–Elmer Lambda 9 spectrometer with Ar-saturated solutions. GC analyses were carried out using a Hewlett-Packard 5890II gas chromatograph equipped with a conventional heated injector, a flame ionization detector, a Hewlett-Packard 3396A integrator and a DB1 megabore capillary column (15 m × 0.53

mm; Chromatographic Specialties, Inc.). GC/MS analyses were carried out on a Hewlett-Packard 5890II gas chromatograph equipped with an HP-5971A mass selective detector and a DB5 fused silica capillary column (30 m × 0.25 mm; Chromatographic Specialties, Inc.). Semi-preparative GC separations were carried out using a Varian 3300 gas chromatograph equipped with a thermal conductivity detector and a 3.8% UCW982 on 80/100 Supelcoport (24 ft × 0.25 in stainless steel) column.

2,2,4-Trimethylpentane (isooctane; BDH Omnisolv) exhibited an absorbance of less than 0.2 at 193 nm in a 3 mm cell, and was used without further purification. MeOH, MeOD, t-BuOH and t-BuOD were of the highest purity available and were used as received from Aldrich Chemical Co. Extra-dry oxygen was obtained from Vitalaire, Inc.

1,1-Dimethylsiletane (**1**) was prepared by the method of Auner and Grobe [32], and exhibited spectroscopic data and a boiling point (80 °C) similar to those reported. After distillation, it was isolated in better than 99% purity (as estimated by capillary GC analysis) after semi-preparative GC. Methoxytrimethylsilane and tert-butoxytrimethylsilane were prepared by the literature procedures [33].

Analytical-scale photolyses were carried out using a low pressure mercury lamp (185 + 254 nm; Osram HNS 10W/UOZ), with solutions contained in 5 mm quartz tubes. The solutions were bubbled prior to photolysis with a stream of dry argon (for alcohol trapping experiments) or oxygen, and sealed with rubber septa. In each case, the course of photolysis was monitored periodically by GC and/or GC/MS analysis.

Nanosecond laser flash photolysis experiments employed pulses (193 nm, approximately 15 ns, 20 mJ) from a Lumonics 510 excimer laser filled with an F_2–Ar–He mixture, and a microcomputer-controlled detection system [34]. Solutions were prepared at concentrations such that the absorbance at the excitation wavelength (193 nm) was approximately 0.6 (approximately 2.5×10^{-3} M), and were flowed continuously through a 3 mm × 7 mm Suprasil flow cell connected to a calibrated 100 ml reservoir. Dry nitrogen or oxygen was bubbled continuously through the reservoir throughout the experiments. Solution temperatures were controlled to within 0.1 °C with a constant-temperature circulating bath plumbed to a brass sample holder, and measured with a Teflon-coated copper/constantan thermocouple inserted directly into the flow cell. Quenchers were added directly to the reservoir by microlitre syringe as aliquots of standard solutions. Rate constants were calculated by linear least-squares analysis of decay rate–concentration data (six or more points) which spanned at least one 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.

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