

Reaction Kinetics, Quantum Yields, and Product Studies for the Dimerization of a Stabilized Silene

S. Zhang and R. T. Conlin*

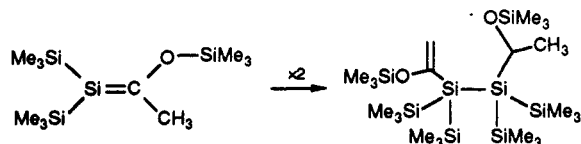
Center for Organometallic Research and Education, Department of Chemistry, University of North Texas, Denton, Texas 76203

P. F. McGarry and J. C. Scaiano*

Department of Chemistry, University of Ottawa, Ottawa, Canada K1N 6N5

Received September 30, 1991

Summary: 1,1-Bis(trimethylsilyl)-2-methyl-2-(trimethylsilyloxy)silene (**1**) dimerizes in a head to head fashion to give the acyclic disilane **3**. The bimolecular rate constant, $2k_1$, at 293 K was $1.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. The temperature dependence of this rate constant yielded $\log A/\text{s}^{-1} = 7 \pm 1$ and $E_a = 0.2 \pm 0.1 \text{ kcal mol}^{-1}$. Rates of reaction with molecular oxygen and 2,3-dimethylbutadiene were also measured.



In the past decade, two milestones in organosilicon chemistry, the syntheses of structures containing stable silicon-carbon and silicon-silicon π bonds, were reported.^{1,2} Both achievements encouraged successful syntheses of a variety of new structures^{3,4} as well as prompted theoretical exploration⁵ of further possibilities for bonding to silicon. Kinetic and mechanistic descriptions of these novel processes, guided largely by thermochemistry, theory, and intuition provide additional insight into the elementary steps of reactions for electron-deficient silicon. Herein we

(1) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K.; Poon, Y. C.; Chang, Y.-M.; Wong-Ng, W. J. *Am. Chem. Soc.* 1982, 104, 5667.

(2) West, R.; Fink, M. J.; Michl, J. *Science* 1981, 214, 1343.

(3) For example, consider the recent variety of structures containing portions of a disilirane ring [$E = (X)$ in ESi_2]: (a) (Si) Masamune, S.; Hanzawa, Y.; Murakami, S.; Baily, T.; Blount, J. F. *J. Am. Chem. Soc.* 1982, 104, 1150. (b) (C) Masamune, S.; Murakami, S.; Tobita, H.; Williams, D. *J. Am. Chem. Soc.* 1983, 105, 1776. See ref 3f for a more comprehensive list. (c) ($\text{C}=\text{CR}_2$) Ishikawa, M.; Sugisawa, H.; Kumada, M.; Higuchi, T.; Matsui, K.; Hirotsu, J. *Organometallics* 1983, 2, 174. (d) (O) Yokelson, H. B.; Millevoite, A. J.; Gillette, G. R.; West, R. *J. Am. Chem. Soc.* 1987, 109, 6865. (e) (N) Gillette, G. R.; West, R. *Organomet. Chem.* 1990, 394, 45. (f) (S) West, R.; DeYoung, D.; Haller, K. J. *J. Am. Chem. Soc.* 1985, 107, 4942. (g) (Se, Te) Tan, R. P.-K.; Gillette, G. R.; Powell, D. R.; West, R. *Organometallics* 1991, 10, 546. (h) (Pt) Pham, E. K.; West, R. *J. Am. Chem. Soc.* 1989, 111, 7667. (i) (Mo, W) Berry, D. H.; Chey, J. H.; Ziplin, H. S.; Carroll, P. J. *J. Am. Chem. Soc.* 1990, 112, 452. Silirane ring [$E = (X)$ in ECSi]: (j) (N) Brook, A. G.; Saxena, A. K.; Kong, Y. K.; Sawyer, J. F. XXII Organosilicon Symposium, Philadelphia, PA, April, 1989. C-substituted siliranes: 2-alkylidene-siliranes: (k) Saso, H.; Ando, W.; Ueno, K. *Tetrahedron* 1989, 45, 1929. 2-Vinylsiliranes: (l) Zhang, S.; Conlin, R. T. *J. Am. Chem. Soc.* 1991, 113, 4272.

(4) Metal stabilized silylenes: (a) (Cr) Zybill, C.; Muller, G. *Angew. Chem., Int. Ed. Engl.* 1987, 26, 583. (b) (Rh) Straus, D. A.; Grumbine, S. D.; Tilley, T. D. *J. Am. Chem. Soc.* 1990, 112, 2673. (c) (Fe, Mn) Corriu, R.; Lanneau, G.; Priou, C. *Angew. Chem., Int. Ed. Engl.* 1991, 30, 1130. (d) (Cr) Probst, R.; Leis, C.; Gamper, S.; Herdweck, E.; Zybill, C.; Auner, N. *Angew. Chem., Int. Ed. Engl.* 1991, 30, 1132. (e) (Os) Woo, K. L.; Smith, D. A.; Young, V. G. *Organometallics* 1991, 11, 3977.

(5) (a) Gordon, M. S. In *Molecular Structure and Energetics*; Liebman, J. F.; Greenberg, A., Eds.; VCH: New York, 1986; Vol. 1, p 101. (b) Grev, R. S.; Schaefer, H. F. *J. Am. Chem. Soc.* 1989, 111, 5687. (c) Trinquier, G. *J. Am. Chem. Soc.* 1990, 112, 2130. (d) Maxka, J.; Apeloig, Y. *J. Chem. Soc., Chem. Commun.* 1990, 737.

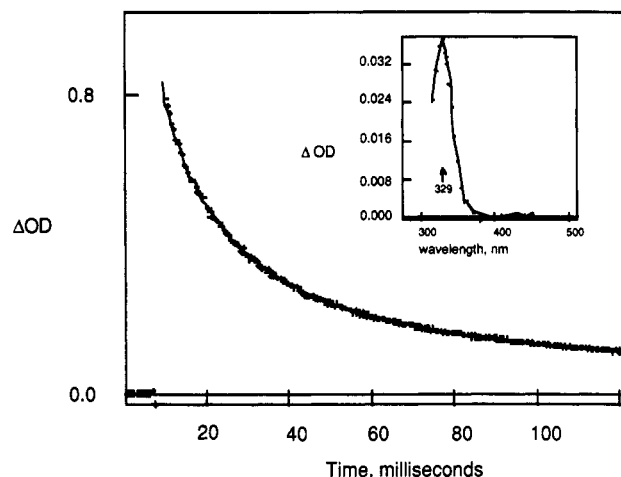
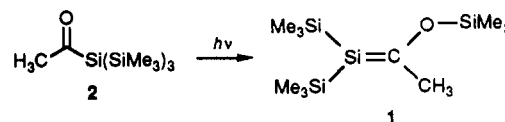


Figure 1. Transient trace obtained in the conventional flash photolysis of **2** at room temperature. The insert is the transient absorption spectrum of the silene recorded 200 ns after the laser pulse ($\lambda = 308 \text{ nm}$, excimer laser).

Table I. Temperature Dependence of $2k_1$ Measured by Conventional Flash Photolysis

$2k_1 \times 10^7 \text{ (M}^{-1} \text{ s}^{-1})$	$T \text{ (K)}$	$2k_1 \times 10^7 \text{ (M}^{-1} \text{ s}^{-1})$	$T \text{ (K)}$
1.30	272.3	1.33	296.2
1.27	273.2	1.34	307.4
1.33	279.6	1.32	317.3
1.27	279.8	1.34	325.4
1.28	286.1	1.40	332.6
1.29	287.6		

report rate constants for head to head dimerization of and for reaction of oxygen and 2,3-dimethylbutadiene with the transient 1,1-bis(trimethylsilyl)-2,2-ethyl(trimethylsilyloxy)silene (**1**).⁶



Laser flash photolysis^{7,8} of solutions containing (acetyl)tris(trimethylsilyl)silane (**2**) (10^{-4} M , cyclohexane) at 299.8 K quickly gave rise to an intensely absorbing transient. A point by point spectrum, collected 200 ns after the laser pulse, displayed a λ_{max} at 330 nm (see insert of Figure 1). The same species was also observed by Hg lamp photolysis in a 3-methylpentane matrix at 77 K and is readily assigned to silene **1**.⁹ The silene signal did not

(6) Brook, A. G.; Harris, J. W.; Lennon, J.; El Shiekh, M. *J. Am. Chem. Soc.* 1979, 101, 83.

(7) Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* 1985, 107, 4395.

(8) Scaiano, J. C. *J. Am. Chem. Soc.* 1980, 102, 7747.

decay appreciably in the microsecond time domain. Conventional flash photolysis,¹⁰ however, allowed observation of the remarkably clean second-order decay kinetics for 1 on a millisecond time scale (Figure 1). This observation is consistent with the isolation of the acyclic, dimeric photoproduct 3.¹

Values of ϵ_{330} were measured by two different methods. In one, exhaustive photolysis of the matrix isolated 2 at three different concentrations, providing a value for ϵ_{330} for 1 = $6500 \pm 300 \text{ M}^{-1} \text{ cm}^{-1}$. In the other method, a time-resolved technique employing Aberchrome-540 as an actinometer was used.¹¹ In the latter case the laser flash photolysis experiment yielded the product, $\phi_{328(\text{silene})} \epsilon_{328(\text{silene})} = 9130 \text{ M}^{-1} \text{ cm}^{-1}$. The quantum yield for silene generation, ϕ_1 , was measured using conventional techniques with Aberchrome-540 as the actinometer. The production of the dimer 3 was monitored by capillary GC, and its quantum yield ($\phi_{\text{dimer}} = 0.335$) can be equated to $\phi_1/2$ which provided $\phi_1 = 0.670$ and therefore $\epsilon_{328} = 1.36 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. Combination of an intermediate value ($\epsilon \approx 9000 \text{ M}^{-1} \text{ cm}^{-1}$)¹² with the flash photolysis data at room temperature, 296.2 K, $k_{\text{obs}} = (2k_t \epsilon^{-1})$, allowed calculation of $2k_t$, the rate constant for dimerization at ambient temperature, 296.2 K, $1.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. This value is much slower than expected for a diffusion-controlled process in cyclohexane.

The temperature dependence of $2k_t$ was investigated from 272.3 to 332.6 K and exhibited very little change (Table I). An Arrhenius treatment of the data led to $\log(A/\text{M}^{-1} \text{ s}^{-1}) = 7 \pm 1$ and $E_a = 0.2 \pm 0.1 \text{ kcal mol}^{-1}$.¹³

These activation parameters suggest a highly ordered transition state requiring only small enthalpic changes for reaction. The Arrhenius parameters show features, low A and E_a , similar to those reported previously for dimerization of benzophenone oxide,¹⁴ a process in which the two

Table II. Product Yields for the Steady-State Photolysis of 2 in the Presence of DMB As Determined by GC Analysis^a

[DMB]	[3]	[4]	[5]
0.0	3.89	0.00	0.00
0.2	2.68	0.41	0.07
0.4	2.60	0.86	0.15
0.6	2.38	1.24	0.22
0.8	2.04	1.86	0.33

^a [DMB] in M and [3], [4], and [5] in mM.

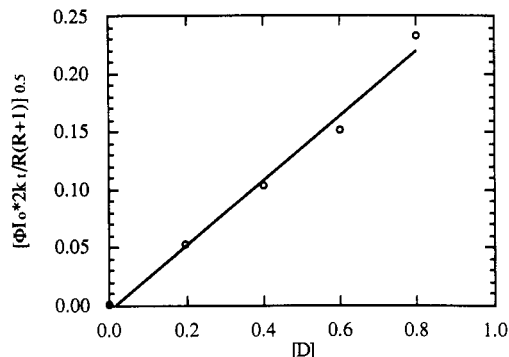
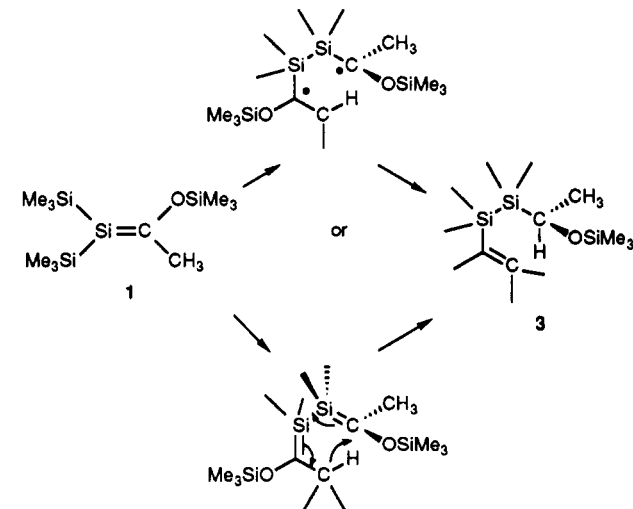


Figure 2. Plot according to eq 3. The slope, $k_t = 0.23 \text{ M}^{-1} \text{ s}^{-1}$.

fragments are highly oriented in a transition state leading to molecular oxygen and two benzophenone molecules. For the reaction reported here, formation of the final product from dimerization of 1, the acyclic disilane 3, requires either intramolecular disproportionation in a biradicaloid or a bimolecular "ene" reaction.^{1,15}



The bimolecular rate constant for quenching of 1 by O_2 in cyclohexane at 20.1 °C under pseudo-first-order conditions was $7.3 \pm 1.5 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$. This relatively slow rate value may reflect both the intrinsic stabilization¹⁶ of the silene by the 2-trimethylsilyloxy group and, additionally, a spin-imposed barrier for addition of triplet O_2 with the singlet ground state of 1 (see below). The final product of reaction was an involatile and polymeric oil whose IR spectrum indicated the presence of a strong and broad absorption centered at $\approx 1060 \text{ cm}^{-1}$, characteristic of sili-

(9) The possibility that a triplet state of 2 is the immediate precursor to silene 1 was investigated. A series of nanosecond flash photolysis experiments indicated that 1 was generated within the duration of the laser pulse (Moletron UV-24 nitrogen laser, 337 nm, 8-ns pulse duration, <9 mJ/pulse). Silene 1 was also generated from 2 by interaction with triplet sensitizers such as benzophenone and *p*-methoxyacetophenone. The quenching rate constants for these processes were 9.4×10^9 and 2.4×10^9 , respectively. Thus, a triplet precursor is a likely possibility but remains unproven. The role of reactive triplet states in the photolysis of acetyltrimethylsilane has been discussed previously. (a) Bourque, R. A.; Davis, P. D.; Dalton, J. C. *J. Am. Chem. Soc.* 1981, 103, 697. (b) Dalton, J. C.; Bourque, R. A. *J. Am. Chem. Soc.* 1981, 103, 699. (c) Dalton, J. C. In *Organic Photochemistry*; Padwa, A., Ed.; M. Dekker: New York, 1985; 7, p 149.

(10) The photolysis system was a PRA FP-1000 unit consisting of a cell (5 cm \times 2 cm), parallel with two quartz flash lamps (250–700 nm; 10- μ s pulse duration, 12 J/pulse at 2.5 kV); a 75-W Xe monitoring lamp; and a monochromator-photomultiplier detection system. Signals from the photomultiplier were captured with a Tektronix 2230 digital storage oscilloscope equipped with an RS-232 interface. Waveforms were transferred to a PDP 11-73 computer for kinetic analysis and storage. Generation of the silene occurred with the pulse of the Xe flash and was monitored at 330 nm.

(11) Wintgens, V.; Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* 1988, 110, 511.

(12) The difference of a factor of 2 between the extinction coefficients probably reflects the uncertainties of the two methods employed. Thus, the matrix isolation approach is likely to provide low values if any side reactions convert 2 to any product other than 1 or if any 1 is further photoconverted during its synthesis. In contrast, the flash techniques can yield high values if ϕ_{dimer} is depressed as a result of side reactions, impurity quenching, or UV screening by products. An estimate of ϵ_{300} , ca. $9000 \text{ M}^{-1} \text{ cm}^{-1}$, is probably more realistic. This value compares reasonably well with reported values of moderately stable 1,1-bis(trimethylsilyl)-2-(trimethylsilyloxy)-2-alkylsilenes, see: Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* 1986, 25, 1.

(13) Experimental estimates of E_a , determined by mass spectrometry, for the gas-phase dimerization of 1,1-dimethylsilene suggest a very low barrier. Gusel'nikov, L. E.; Konobeyskii, K. S.; Vdovin, V. M.; Nametkin, N. S. *Dokl. Akad. Nauk SSSR* 1977, 235, 791. This is also consistent with calculations: Alrichs, R.; Heinzmann *J. Am. Chem. Soc.* 1977, 99, 7452.

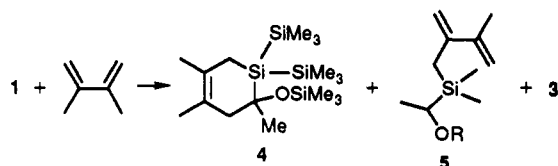
(14) Girard, M.; Griller, D. *J. Phys. Chem.* 1986, 90, 6801.

(15) Although mechanistic details of the silene "ene" reaction with allylic C-H bonds are unknown, this reaction is well-known to compete with silene cycloadditions to methyl substituted π bonds, see: Wiberg, N. *J. Organomet. Chem.* 1984, 273, 141. Atypical activation parameters have been observed for reactions passing through biradicaloid transition states, see: Johnston, L. J.; Scaiano, J. C. *Chem. Rev.* 1989, 89, 521.

(16) For a discussion of stabilization of silenes by the 2-silyloxy substituent, see: Apeloig, Y.; Karni, M. *J. Am. Chem. Soc.* 1984, 106, 6676.

con-oxygen bonds.¹⁷ Whether the cyclic dioxasiletane adduct is formed awaits further study.¹⁸

Attempts to monitor reaction rates of 1 with well-known trapping agents such as dienes¹⁹ led to unexpected results. The rate of decay of the 330-nm signal was unchanged by increasing concentrations of 2,3-dimethylbutadiene (DMB) up to 0.33 M, indicating that the rate of silene addition to the diene is much slower than silene dimerization under flash photolytic conditions. Thus, k_t must be $\ll 10^5 \text{ M}^{-1} \text{ s}^{-1}$. Continuous lamp ($\lambda_{\text{max}} = 350 \text{ nm}$, 20 m) photolysis of a cyclohexane solution of 2 (21.2 mM) and the diene (0.0, 0.2, 0.4, and 0.8 M) in a Rayonet-type reactor yielded products both from silene dimerization (3) and from reaction with DMB (4 and 5). Yields are summarized in Table II.



For this reaction the steady-state approximation (eq 1) may be used in combination with the expression relating the ratio of the rate constants to the ratio of products yields (eq 2) to arrive at eq 3. Thus, from a plot of the

$$d[1]/dt = 0 = \phi I_0 - 2k_t[1]^2 - k_r[1][\text{DMB}] \quad (1)$$

$$2k_t[1]^2/k_r[1][\text{DMB}] = R \quad R = [3]/([4] + [5]) \quad (2)$$

$$\sqrt{2k_t\phi I_0/R(R+1)} = k_r[\text{DMB}] \quad (3)$$

values of the left side of eq 3, which depends on the ratio of products, $R = [3]/([4] + [5])$, against the diene concentration, a straight line is obtained. The slope is to be equated to the composite rate constant, k_r , for the reaction of 1 with 2,3-DMB.

Interestingly, examination of eq 3 clearly reveals that low values of R (i.e. efficient diene trapping) can be expected only at low light intensities (I_0), thus explaining why addition products are observed from lamp irradiation but not in the flash irradiation and, also, the observation that the transient decays remain second order even in the presence high concentrations of the diene.

The composite rate constant is the sum of the individual rate constants for the 2 + 4 cycloaddition producing 4 and the "ene" pathway producing 5. For these pathways the ratio of rates equals the ratio of the product yields in eq 4.

$$k_{\text{ene}}/k_{2+4} = [4][5] \quad k_r = k_{2+4} + k_{\text{ene}} \quad (4)$$

$$k_{2+4} = k_r/([4][5]^{-1} + 1)$$

Thus we find that $k_{\text{ene}} \approx 0.04 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{2+4} \approx 0.19 \text{ M}^{-1} \text{ s}^{-1}$. These rate constants are small and consistent with the results of the flash photolysis experiments.

Acknowledgment. R.T.C. gratefully acknowledges financial support from the R. A. Welch Foundation. J.C.S. acknowledges support from the National Science and Engineering Research Council of Canada.

OM910619X

(17) Bellamy, L. J. *Advances in Infrared Group Frequencies*; Chapman Hall: London, 1975.

(18) It has been suggested in ref 1 that reaction between the 1,1-bis(trimethylsilyl)-2-adamantylsilene and O_2 produced an unstable dioxasiletane that fragmented to a ketone and bis(trimethylsilyl)silanone, which subsequently cyclotrimerized.

(19) Brook, A. G.; Vorspohl, K.; Ford, R. R.; Hesse, M.; Chatterton, W. J. *Organometallics* 1987, 6, 2128.

Thermal Ring Closure in $\text{Mo}(\text{CO})_5\text{L}$ (L = bpy, dmbpy, dpbpy) Transients Generated by Pulsed Laser Flash Photolysis. Mechanistic Information from High-Pressure Effects

Kedika Bal Reddy, Rüdiger Hoffmann, Gabor Konya, Rudi van Eldik,*[†] and Edward M. Eyring*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Received January 28, 1992

Summary: The kinetics of the ring-closure reactions of $\text{Mo}(\text{CO})_5\text{L}$, produced during the laser flash photolysis of $\text{Mo}(\text{CO})_6$ and L where L = 2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (dmpby) and 4,4'-diphenyl-2,2'-bipyridine (dpbpy) were studied as a function of temperature and pressure. The values of the activation parameters ΔS^\ddagger and ΔV^\ddagger are small and negative for L = bpy and dmpby supporting an associative interchange mechanism (I_a) for CO extrusion. For L = dpbpy, ΔV^\ddagger is small and positive in line with a dissociative interchange mechanism (I_d). The results demonstrate a changeover in mechanism from I_a to I_d with increasing steric hindrance on the bidentate ligand L.

[†]Institute for Inorganic Chemistry, University of Witten/Herdecke, 5810 Witten, Germany.

There have been a number of pulsed laser flash photolysis studies of group VIb metal carbonyls in recent years.¹⁻⁸ Much attention has been focused on understanding the mechanistic behavior of coordinatively unsaturated intermediates produced after M-CO bond fission during photolysis because of the important applications of $\text{M}(\text{CO})_5\text{S}$ species in the area of systematic organometallic synthesis and the design of homogeneous catalysts.⁹⁻¹⁴ Application of high-pressure kinetic techniques

- (1) Lees, A. J.; Adamson, A. W. *Inorg. Chem.* 1981, 20, 4381.
- (2) Oishi, S. *Organometallics* 1988, 7, 1237.
- (3) Kalayanasundaram, K. *J. Phys. Chem.* 1988, 92, 2219.
- (4) Wang, Li; Zhu, X.; Spears, K. G. *J. Am. Chem. Soc.* 1988, 110, 8695.
- (5) Joly, A. G.; Nelson, K. A. *J. Phys. Chem.* 1989, 93, 2876.
- (6) Zhang, S.; Dobson, G. R. *Inorg. Chim. Acta* 1989, 165, 111.
- (7) Dobson, G. R.; Spradling, M. D. *Inorg. Chem.* 1990, 29, 880.
- (8) Zhang, S.; Dobson, G. R. *J. Coord. Chem.* 1990, 21, 155.