J. Am. Chem. Soc. **1986**, *108*, 2541–2546 2541

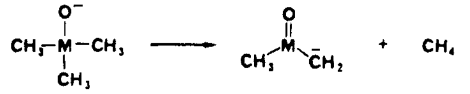
Dimethylsilanone Enolate Anion: Competitive Fragmentation and Electron Autodetachment of Vibrationally Excited Siloxide Anions in the Gas Phase

William Tumas, Karen E. Salomon, and John I. Brauman*

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. *Received September 6, 1985*

Abstract: Infrared multiple photon photochemical studies of gas-phase siloxide anions trapped in an ion cyclotron resonance spectrometer are reported. Upon CO_2 laser irradiation, trimethylsiloxide anion, **1**, and dimethylsiloxide anion, **3**, eliminate methane and molecular hydrogen, respectively, resulting in the production of dimethylsilanone enolate anion, the silicon-containing analogue of acetone enolate anion. These fragmentation reactions are analogous to the unimolecular decompositions of gas-phase alkoxide anions which react via a stepwise mechanism involving initial heterolytic cleavage to an intermediate anion–ketone complex and a subsequent proton-transfer reaction within the ion–molecule complex. Extension of this mechanism to the siloxide systems suggests that dimethylsilanone is an intermediate in the decomposition. In contrast to the alkoxides, vibrationally excited siloxide anions also undergo electron loss (vibrationally induced electron detachment, VED). The use of both high-power pulsed and low-power continuous-wave (CW) CO_2 lasers provides access to both available reaction channels and aids in the elucidation of the primary photochemical events. For **1**, pulsed laser activation results in both methane elimination and VED, while activation with the CW laser leads to electron loss exclusively. Products resulting from both fragmentation and electron detachment are observed for **3** activated by either laser. A significant contribution from secondary photochemistry was found in the pulsed laser-induced reactions of **3**. The observation of direct photochemical branching between fragmentation (H_2 elimination) and electron detachment (VED) in the CW laser photolysis of **3** provides an estimate of 62 kcal/mol as an upper limit for the silicon–oxygen π bond energy in dimethylsilanone.

Infrared multiple photon (IRMP) photochemistry,[1] a highly useful method for molecular activation, offers the opportunity for generating new, interesting, and very reactive species under well-controlled conditions. This paper describes the IR photochemical generation of the enolate anion of dimethylsilanone, the silicon analogue of acetone enolate ion, in the gas phase. This work constitutes an extension of our continuing efforts to probe gas phase ion unimolecular decompositions through IRMP photochemical studies in an ion cyclotron resonance (ICR) spectrometer. The present study was motivated by our studies on *tert*-butoxide anion (eq 1, M = C), (and other alkoxide anions)



$$(CH_3)_3MO^- \longrightarrow CH_3M(=O)CH_2^- + CH_4 \qquad (1)$$

which eliminates methane (alkanes) to produce acetone enolate ion upon irradiation with a CO_2 laser.[2,3] Methane elimination from trimethylsiloxide anion, **1** (M = Si) (or alkane elimination from homologous systems), should result in the production of dimethylsilanone enolate, **2** (eq 1, M = Si).

While this work was in progress, Squires et al. reported[4] the generation of **2** by collision-induced decomposition of trimethylsiloxide anion (**1**) in an ICR spectrometer. In their preliminary report, these authors also describe an investigation of several ion–molecule reactions of this enolate ion.

Herein we report the results of an investigation of the CO_2 laser photochemistry of trimethylsiloxide anion, **1**, and the related dimethylsiloxide anion in the gas phase. The nature of the IRMP photochemical technique enables us to explore the lowest energy reaction channel as well as higher energy pathways. In addition to the elimination reaction forming **2** (eq 1, M = Si), we report the existence of another reaction channel, vibrationally induced electron detachment,[6,7] which is evidently of lower energy but has not been previously observed. The results of this study are compared to our previous results on the analogous unimolecular decompositions of the closely related alkoxide anions[8] and have some implications concerning the strength of the silicon–oxygen double bond.

Compounds containing multiple bonds involving silicon have recently attracted considerable experimental and theoretical interest.[9] Most of the experimental work in this area has centered on the generation and characterization of multiple bonded neutral species. These investigations use a variety of methods including pyrolytic, photochemical, and low-temperature matrix techniques.[10] There is a rich literature on the theoretical and experimental aspects of compounds containing silicon–carbon multiple bonds.[11] Silanones, silicon-containing ketone analogues ($R_2Si{=}O$), have been implicated as transient intermediates in a variety of thermal and photochemical reactions. Dimethylsilanone produced from dimethylsilylene, Me_2Si, and N_2O has been characterized by its infrared spectrum in a recent low-temperature matrix study.[13] Withnall and Andrews have reported spectroscopic evidence for matrix isolated $H_2Si{=}O$, the parent silanone.[14] This field continues to expand at a rapid pace as more reports on the generation of novel silicon compounds and their characterization by both experimental and theoretical methodology appear in the literature.

---

(1) (a) Schultz, P. A.; Sudbo, A. S.; Kranovich, D. J.; Kwok, H. S.; Shen, Y. R.; Lee, Y. T. *Ann. Rev. Phys. Chem.* **1977**, *23*, 321. (b) Golden, D. M.; Rossi, M. J.; Baldwin, A. C.; Barker, J. R. *Acc. Chem. Res.* **1981**, *14*, 56.

(2) Tumas, W.; Foster, R. F.; Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1983**, *105*, 7464.

(3) Tumas, W.; Foster, R. F.; Pellerite, M. J.; Brauman, J. I., submitted for publication.

(4) Froelicher, S. W.; Freiser, B. S.; Squires, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 6863.

(5) Cody, R. B.; Burnier, R. C.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 96.

(6) Meyer, F. K.; Jasinski, J. M.; Rosenfeld, R. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1982**, *104*, 663.

(7) Foster, R. F.; Tumas, W.; Brauman, J. I. *J. Chem. Phys.* **1983**, *79*, 4644.

(8) (a) Tumas, W.; Foster, R. F.; Brauman, J. I. *J. Am. Chem. Soc.* **1984**, *106*, 4053. (b) Tumas, W.; Foster, R. F.; Brauman, J. I., manuscript in preparation. (c) Tumas, W. Ph.D. Thesis, Stanford University, 1985.

(9) (a) Coleman, B.; Jones, M., Jr. *Rev. Chem. Intermed.* **1981**, *4*, 297. (b) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529.

(10) (a) Chapman, O. L.; Chang, C. C.; Kolc, J.; Jung, M. E.; Lowe, J. A.; Barton, T. J.; Tumey, M. L. *J. Am. Chem. Soc.* **1976**, *98*, 7844. (b) Chedekel, M. P.; Skoglund, M.; Kreeger, R. L.; Schechter, H. *J. Am. Chem. Soc.* **1976**, *98*, 7846. (c) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y. *J. Am. Chem. Soc.* **1982**, *104*, 5667. (d) Arrington, C. A.; Klingesmith, K. A.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1984**, *106*, 525.

(11) This area has been recently reviewed: Schaeffer, H. F., III. *Acc. Chem. Res.* **1982**, *15*, 283.

(12) (a) Hussmann, G.; Wulff, W. D.; Barton, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 1263 and references within. (b) Soysa, H. S. D.; Okinoshina, H.; Weber, W. P. *J. Organomet. Chem.* **1977**, *133*, C17.

(13) Arrington, C. A.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 6176.

(14) Withnall, R.; Andrews, L. *J. Am. Chem. Soc.* **1985**, *107*, 2567.

0002-7863/86/1508-2541\$01.50/0

Experimental Section

All experiments were performed on a pulsed ion cyclotron resonance spectrometer modified for IRMP photochemical experiments. This apparatus and the optical configuration along with the general procedure for IRMP photochemical studies of gas-phase ions have been described in detail elsewhere.[15] The light sources used in these experiments consist of a commercial high-power pulsed CO_2 laser (Lumonics TEA-103-2) which has been described previously[15] and a home built low-power continuous-wave (CW) CO_2 laser. In all cases, the occurrence of IR driven vibrationally induced electron detachment was verified by chemical trapping experiments by using low pressures of CCl_4 which efficiently scavenges photoelectrons to produce chloride ion.[6,7] For these experiments pulsed electron ejection (applied to the trapping plates of the cell) was employed.

All materials were obtained from commercial sources and used without further purification: nitrogen trifluoride (Ozark Mahoning), hexamethyldisiloxane (Petrarch), 1,1,3,3-tetramethylsiloxane (Petrarch), dimethylsilane (Petrarch), and carbon tetrachloride (Alrich). Dimethylsilane was subjected to bulb-to-bulb distillation at −78 °C to remove any chlorine containing impurities. All samples were degassed by several freeze–pump–thaw cycles on the ICR foreline prior to use. Total operating pressures were in the range of 1 to 5 × 10^{-6} torr.

Results

Trimethylsiloxide Anion. Trimethylsiloxide anion, $(CH_3)_3SiO^-$ (**1**), was formed via the bimolecular reaction of fluoride ion (generated by electron impact on nitrogen trifluoride) with hexamethyldisiloxane[16] (eq 2 and 3). This reaction was complete

$$NF_3 + e^- \rightarrow F^- + NF_2 \qquad (2)$$

$$F^- + (CH_3)_3SiOSi(CH_3)_3 \rightarrow \underset{\mathbf{1}}{(CH_3)_3SiO^-} + (CH_3)_3SiF \qquad (3)$$

within several hundred milliseconds, after which, no ions other than **1** could be detected in the negative ion mass spectrum. This siloxide anion was found to undergo extensive decomposition (>50%) when irradiated with a single pulse from the pulsed CO_2 TEA laser, *R*(24)/9.6 *μ* line. The time dependence of the ion intensity demonstrates that this photochemical decomposition is truly unimolecular (i.e., occurs on a submillisecond time scale). Furthermore, the ion signal did not recover after the laser pulse indicating that the reactant ion is not regenerated by any ion–molecule reactions of the products. Accompanying this photodecrease was the appearance of a small ion signal at *m*/*e* = 73 which corresponds to the overall elimination of methane from **1**. By analogy to the methane elimination observed for *tert*-butoxide anion[2,3] (to produce acetone enolate anion), we suggest that the structure of this ion at *m*/*e* = 73 can be assigned as the enolate of dimethylsilanone.[4] The amount of this photoproduct generated was considerably less than the amount of **1** decomposed and accounted for only 5–10% of the total photodecrease of **1**. Since no other ions could be detected after firing the laser, we suspected that **1** must also undergo vibrationally induced electron detachment (VED). Chemical-trapping experiments using CCl_4, which efficiently captures electrons to produce chloride ion,[6,7] revealed that VED was indeed the dominant reaction pathway. A photoincrease in the chloride ion signal was observed upon pulsed-laser photolysis, Figure 1. Double resonance experiments[17] confirm that **1** is the precursor for both photoproducts, enolate **2** and photoelectrons (eq 4).

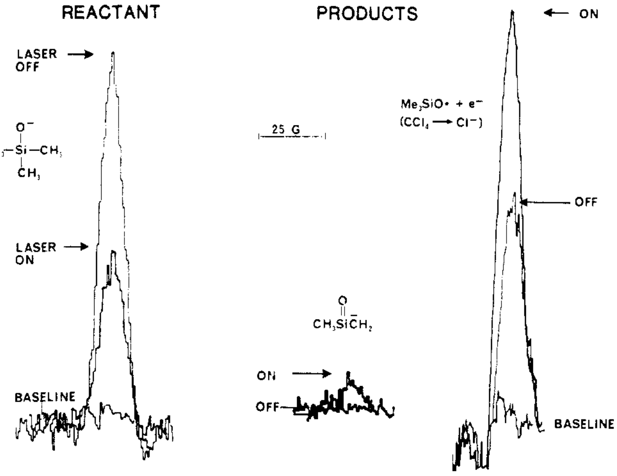
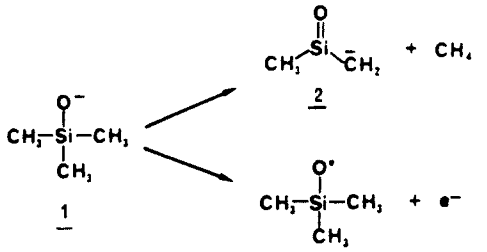
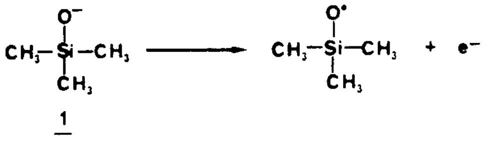


Figure 1. Magnetic field sweep of the reactant trimethylsiloxide anion, **1**, and photoproduct ion (dimethylsilanone enolate ion, **2**, and chloride ion) signal intensities in the absence (OFF) and presence (ON) of pulsed CO_2 laser irradiation. The increase in the chloride ion signal is due to the production of photoelectrons.



$$\underset{\mathbf{1}}{(CH_3)_3SiO^-} \rightarrow \underset{\mathbf{2}}{CH_3Si(=O)CH_2^-} + CH_4; \quad \underset{\mathbf{1}}{(CH_3)_3SiO^-} \rightarrow (CH_3)_3SiO^\bullet + e^- \qquad (4)$$

The low-power continuous-wave (CW) CO_2 laser photochemistry of **1** was also investigated. Irradiation with the output of the CW laser[18] results in significant decomposition. Electron detachment (demonstrated by trapping the photochemically generated electrons with CCl_4) was the only observable reaction pathway (eq 5). No other photoproduct ions could be detected.



$$\underset{\mathbf{1}}{(CH_3)_3SiO^-} \longrightarrow (CH_3)_3SiO^\bullet + e^- \qquad (5)$$

Dimethylsiloxide Anion. The silicon analogue of isopropoxide anion, **3**, was generated from the series of reactions illustrated below. Hydroxide ion was formed by electron impact on a mixture (ca. 1:9) of N_2O and butane (eq 6 and 7). Dimethylsiloxide

$$N_2O + e^- \rightarrow O^{-\cdot} + N_2 \qquad (6)$$

$$O^{-\cdot} + C_4H_{10} \rightarrow OH^- + C_4H_9 \qquad (7)$$

anion[19] was then prepared from the reaction of this ion with dimethylsilane (eq 8), a reaction which has been reported by

$$OH^- + (CH_3)_2SiH_2 \rightarrow \underset{\mathbf{3}}{H(CH_3)_2SiO^-} + H_2 \qquad (8)$$

DePuy and co-workers[20] for a variety of silanes.[21] A small amount

---

(15) Jasinski, J. M.; Rosenfeld, R. N.; Meyer, F. K.; Brauman, J. I. *J. Am. Chem. Soc.* **1982**, *104*, 652. The temporal energy profile of the laser pulse consisted of a 150–200 ns spike followed by a 3 *μ*s tail, each containing roughly half the pulse energy. The laser output also exhibited the characteristic high intensity spikes (separated by 20 ns) due to longitudinal mode beating. Ions were irradiated with one pulse at a fluence of 1–2 J/cm^2, corresponding to a mean laser intensity of ca. 10^{26} photons cm^{-2} s^{-1}. For a typical cross section for absorption of an infrared photon of ca. 10^{-19} cm^2, the pumping rate constant is calculated to be 10^7 s^{-1}. Since this rate is greater than typical reaction rates at threshold, ions activated by pulsed CO_2 lasers generally decompose at energies considerably higher than the reaction thresholds.

(16) DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J.; Sullivan, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 5012.

(17) Double resonance ejection of suspected precursor ions before the firing of the laser while observing the product ion intensities was used to verify all photochemical and thermal reaction pathways: Anders, L. R.; Beauchamp, J. L.; Dunbar, R. C.; Baldeschwieler, J. D. *J. Chem. Phys.* **1968**, *45*, 111.

(18) Ions were irradiated with ca. 20 W cm^{-2} for 150 ms; R(20)/9.6 *μ*, 1079 cm^{-1}.

(19) Photochemical experiments carried out by preparing **3** from the reaction of fluoride ion with 1,1,3,3-tetramethylsiloxane, analogous to the reaction used to prepare trimethylsiloxide (eq 3), were complicated by the production of three other ions (at approximate *m*/*e* values of 93, 147, 163–165). The structure and origin of these ions are not known; however, the most likely structure for the ion at *m*/*e* = 93 is the fluorodimethylsiloxide anion. Because this reaction sequence did not prove to be a viable source for **3**, no effort was made to elucidate this manifold of reaction pathways. These various ion–molecule reactions must, however, arise from reactions involving the Si–H bond since no ions other than **1** were observed from fluoride ion and hexamethyldisiloxane (eq 3). The poor trapping times of **3** under these conditions also suggest that it undergoes sequential ion–molecule reactions.

(20) DePuy, C. H.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1984**, *106*, 4051.

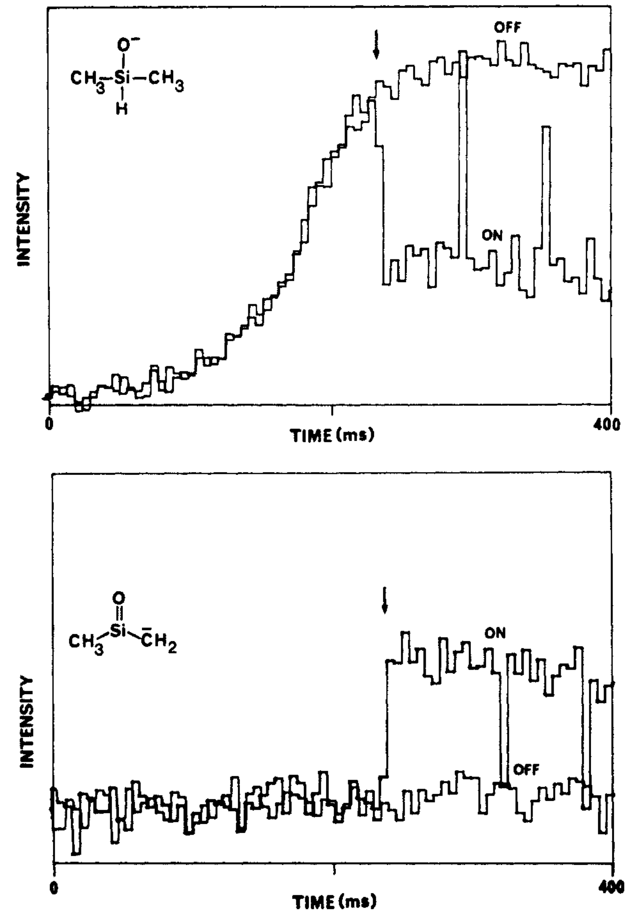


Figure 2. Time dependence of dimethylsiloxide anion, 3 (upper traces), and the photoproduct dimethylsilanone enolate anion, 2 (lower traces), with (ON) and without (OFF) pulsed IR laser irradiation. The arrow indicates the time at which the laser is fired. The large spikes after this arrow are due to laser misfires.

(ca. 5%) of an ion at $m/e = 59$ was also produced. This ion is likely deprotonated dimethylsilane resulting from competitive proton transfer to hydroxide ion.[22]

IRMP activation of **3** with the output of either the pulsed or CW CO_2 laser resulted in significant decomposition. In contrast to **1**, pulsed laser photolysis of dimethylsiloxide resulted in efficient elimination of molecular hydrogen to produce dimethylsilanone enolate **2** (up to 50–60%), Figure 2.

No evidence was found for any methane elimination which would result in the formation of the silicon analogue of acetaldehyde enolate, $^{-}CH_2Si(O)H$ ($m/e = 59$); the small ion signal at $m/e = 59$ which accompanies the initial formation of **3** did not change upon laser irradiation.[22] The amount of **2** produced did not quantitatively account for the amount of **3** decomposed. A CCl_4 experiment revealed that electrons were also generated photochemically.

Electron detachment (demonstrated by using CCl_4) was the dominant reaction pathway observed upon irradiation with the CW laser,[23] but a small amount (≤10%) of **2** was also produced, Figure 3.

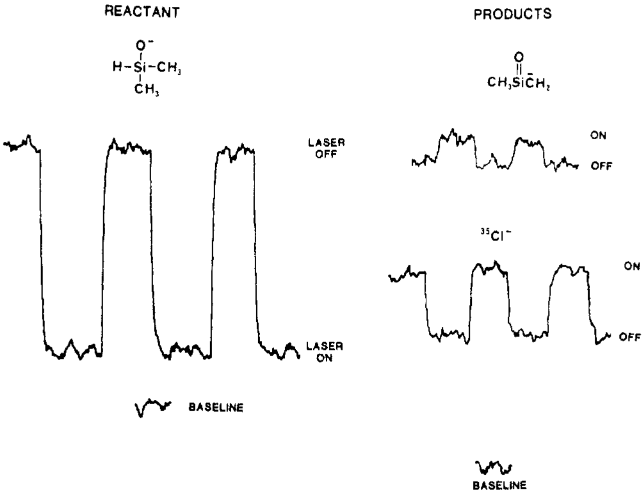


Figure 3. Signal intensities of dimethylsiloxide anion, **3** (REACTANT), and dimethylsilanone enolate ion, **2**, and chloride ion (PRODUCTS) in the presence (ON) and absence (OFF) of CW CO_2 laser irradiation. The photodecreases in the siloxide signal correspond to increases in the photoproduct signals.

On the basis of our studies involving the determination of a rate for electron detachment from acetone enolate anion[24] (and some inference of its energy dependence), direct branching of **3** with both pulsed and CW lasers would not be expected. Our work on acetone enolate anion suggested that its electron detachment is quite slow near the autodetachment threshold and that the rate of the fragmentation reaction increases much more rapidly with increasing internal energy than does the detachment rate. By analogy, electron detachment from **3** would also be quite slow near the autodetachment threshold. If the observed products in the CW laser photolysis of **3** result from direct branching of vibrationally activated **3**, then the fragmentation and autodetachment channels must be fairly close in energy.[25] In IRMP activation, reaction occurs when the microcannonical rate constant for decomposition becomes comparable to the pumping rate constant. The pulsed laser has a much higher pumping rate constant and thus decomposition occurs from energy levels which are higher than those accessed by the CW laser;[15] under these conditions fragmentation might well exceed electron detachment. Thus we expected little, if any, detectable reaction through the detachment channel in the pulsed-laser photolyses. Since we observed reaction through both channels for both lasers, we searched for secondary photochemical reactions; i.e., whether the observed photoelectrons were a primary photoproduct or were a result of the primary photoproduct **2** absorbing more infrared photons and undergoing subsequent electron detachment. The importance of secondary photochemistry in CW laser experiments can be readily determined with use of double resonance techniques[16] by selective ejection of a primary photoproduct suspected of subsequent photochemistry and observation of the other photoproduct ions. When the double resonance oscillator was tuned to eject **2** during the CW laser irradiation period, the chloride ion increase was unaffected. Thus, we are able to rule out secondary photochemistry of the silanone enolate, **2**, as the source of the photoelectrons in the CW laser experiments; the photoelectrons are evidently primary photoproducts. The time dependence of the ion abundances also suggests that secondary photochemistry is not important.

In general, it is much more difficult to ascertain the intervention of secondary photochemistry in pulsed laser experiments. The relative time scales of the laser pulse (a few μs) and ion ejection (at least several ms) preclude the use of double resonance methodology. For an incoherent pumping scheme, provided that the ions decompose during the laser pulse, an increase in laser

---

(21) At a total pressure of ca. 4 × 10^{-6} torr and a partial pressure of dimethylsilane of ca. 1 × 10^{-6}, the reaction went to completion in several hundred milliseconds.

(22) There are actually two reasonable structures for this ion at $m/e = 59$. In addition to dimethylsilyl anion, it is possible that this ion corresponds to the silicon analogue of acetaldehyde enolate, although we believe that this is less likely, since no dimethylsilanone enolate (from H_2 elimination) is formed without laser irradiation.

(23) R(20)/9.6 μ (1079 cm^{-1}) with irradiation times of a few hundred milliseconds at 15–30 W cm^{-2}.

(24) Upon pulsed CO_2 laser irradiation, acetone enolate anion undergoes competitive methane elimination (to produce deprotonated ketene, HC_2O^-) and electron detachment: ref 7.

(25) A typical pumping rate for CW laser activation is only 10–100 s^{-1}. This rate is much less than typical reaction rates even at threshold, thus ions activated by low-power CW CO_2 lasers must decompose at energies very close to threshold.

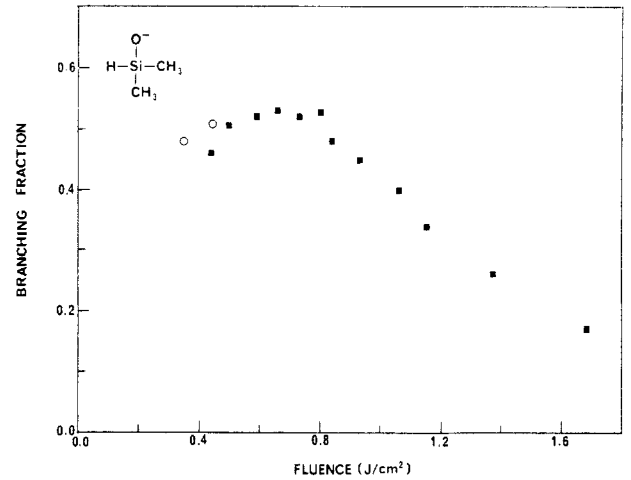
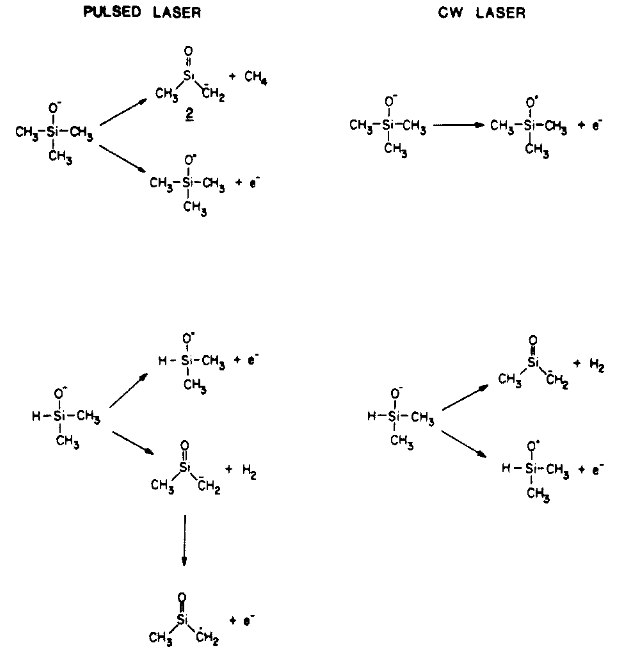


Figure 4. Fluence dependence of the branching fraction for the pulsed-laser photodecomposition of dimethylsiloxide anion, 3. The branching fraction is defined as the yield of dimethylsilanone enolate anion, 2, divided by the total photodissociation yield. The open circles correspond to irradiation with the higher intensity short pulse (150–200 ns duration) produced by taking the nitrogen out of the laser gas mixture.

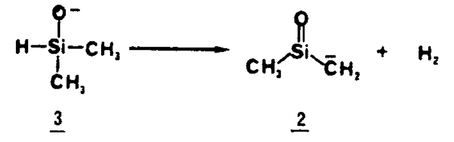
fluence (at constant laser pulse duration) should result in the formation of product ions earlier in the pulse. Therefore, one would expect more secondary photochemistry at higher fluences, where the primary product ions should be subjected to more photons for a longer time.[26] The fluence dependence of the branching fraction for dimethylsiloxide, **3** (i.e., the amount of enolate **2** produced relative to the amount of siloxide decomposed: [**2**]/[**3** decomposed]), is strongly indicative of secondary photochemistry. At low fluences, this branching fraction is relatively independent of fluence; at higher fluences this ratio decreases monotonically with fluence, Figure 4. These results provide strong evidence that a significant fraction of the photoelectrons from the pulsed-laser photolysis of dimethylsiloxide is the result of secondary photochemical reactions of the primary product, dimethylsilanone enolate. In contrast to acetone enolate, however, it appears that some electron loss competes with bond cleavage in both the CW and the pulsed experiments.

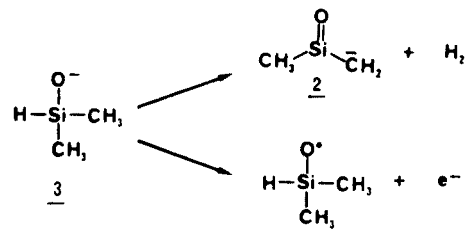
These results raise the possibility that some of the photoelectrons resulting from pulsed laser activation of trimethylsiloxide, **1**, may also be due to secondary photochemistry. The small photoproduct ion signal for this system, however, rendered a quantitative fluence study very difficult. Therefore, recognizing that there may be some secondary photochemical component,[27] we simply attach a larger uncertainty to the branching ratio observed in the pulsed laser studies of **1**.

Scheme I



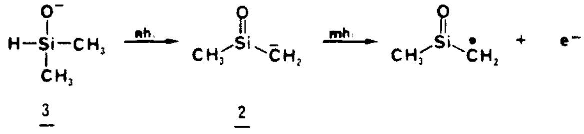
The following photochemical scheme (Scheme I) briefly summarized here is consistent with all of the above results as well as our previous studies on related systems.[3,8] Since the pulsed laser experiments are complicated by the intervention of secondary photochemistry, the branching ratios of the vibrationally excited siloxide anions cannot be determined exactly. According to this scheme, both photoproducts formed in the pulsed-laser photolysis of trimethylsiloxide anion (dimethylsilanone enolate (**2**) and photoelectrons) arise from primary photochemical reactions of the reactant ion (i.e., direct branching between methane elimination and electron detachment). Upon CW laser irradiation,


$$\mathrm{H{-}Si(O^-)(CH_3){-}CH_3} \longrightarrow \mathrm{CH_3Si(O)\bar{C}H_2} + \mathrm{H_2} \qquad (9)$$



(10)

trimethylsiloxide anion exclusively undergoes electron detachment. On the other hand, most of the photoelectrons observed for pulsed-laser activation of dimethylsiloxide, **3**, evidently result from subsequent photochemically-induced electron detachment of the primary photoproduct, dimethylsilanone enolate anion, during the laser pulse. That no evidence for secondary photochemistry could be found in the CW laser experiments on dimethylsiloxide anion strongly suggests that electron detachment and elimination of molecular hydrogen are competitive under these conditions with the former reaction predominating.


$$\underset{\mathbf{3}}{\mathrm{H{-}Si(O^-)(CH_3){-}CH_3}} \xrightarrow{nh} \underset{\mathbf{2}}{\mathrm{CH_3Si(O)\bar{C}H_2}} \xrightarrow{mh} \mathrm{CH_3Si(O)\dot{C}H_2} + e^- \qquad (11)$$

Discussion

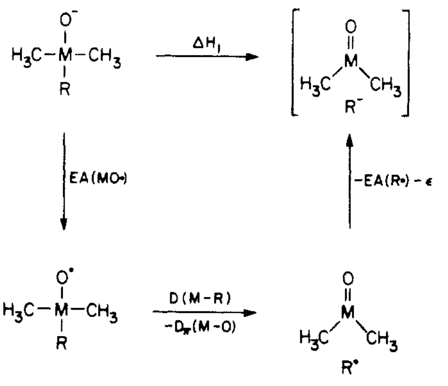
Two aspects of the IRMP photochemical reactivity of the siloxide ions **1** and **3** need to be considered: fragmentation (elimination of a neutral molecule) and vibrationally induced electron detachment (VED). The IRMP-induced elimination of methane and hydrogen from **1** and **3** is analogous to the previously reported reactions of the related alkoxide anions *tert*-butoxide[2,3] and isopropoxide,[8] respectively, for which the mechanism is well understood. Kinetic isotope effect studies revealed that methane elimination from *tert*-butoxide proceeds through a stepwise mechanism involving the intermediacy of an anion–ketone complex

---

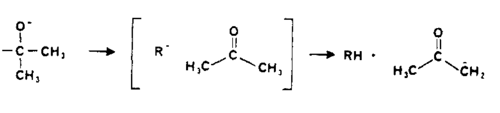
(26) Barfknecht, A. T.; Brauman, J. I., manuscript in preparation.

(27) An unpublished optical photodetachment study of acetone enolate anion generated by the IRMP-induced decomposition of several alkoxide anions reveals that the internal energy content of the enolate ion is greater when prepared from isopropoxide anion (H_2 elimination) than from *tert*-butoxide anion (methane elimination). The red shift of the threshold as well as the cross section for detachment near threshold is considerably larger for acetone enolate prepared via the former reaction. Although methane elimination from alkoxides has a greater critical energy than hydrogen elimination,[8] molecular hydrogen is apparently so inefficient at removing energy from the intermediate ion–molecule complex that this is compensated for. On the basis of these indications, we expect that secondary photochemical processes are more important for **3** than **1**, since, by analogy, it is very likely that the internal energy content of the silanone enolate, **2**, is higher, i.e., "hotter", when generated by H_2 elimination than methane elimination. Thus, it should be easier to activate this ion above its electron detachment threshold.

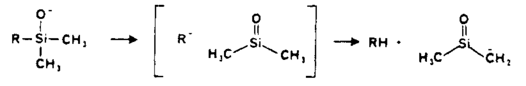
Scheme II



(R^{-}· acetone; here, R = CH_3) in which a subsequent proton transfer yields the observed products, acetone enolate ion and a hydrocarbon (RH). The initial cleavage was shown to be heterolytic by changing the R group and determining the relative leaving group propensities.[8] Of particular relevance to the present work, H_2 elimination was found to predominate over CH_4 elimination in isopropoxide ion.



(12)



(13)

Although we have not carried out a detailed study incorporating kinetic isotope effects or other probes into the mechanism of the siloxide anion fragmentation, this stepwise mechanism should pertain to these ions as well. Indeed, the observation of exclusive elimination of molecular hydrogen in preference to methane from dimethylsiloxide anion provides strong evidence that the same mechanistic scheme is operative. We therefore conclude that dimethylsilanone is a likely intermediate in the IRMP-induced reactions of the siloxide anions.

By analogy to the alkoxide anions,[3,8] the activation barrier for the fragmentation reaction is determined by the barrier of the rate-determining cleavage reaction in the first step. Thus the stability of the intermediate ion-molecule complex (relative to the reactant) determines the critical energy for the overall reaction. The activation barrier for this simple cleavage (i.e., the first step) can therefore be calculated to a good approximation from the heats of formation of the constituents of the intermediate, the heat of formation of the reactant, and the ion-molecule stabilization energy, ε, of the intermediate complex. Alkoxide anions undergo exclusive fragmentation and do not undergo vibrationally induced electron detachment,[3,8] whereas the siloxide anions react via both electron detachment and fragmentation. Within the same mechanistic framework, this contrasting reactivity suggests a significant difference in the relative stabilities of the respective intermediate ion-molecule complexes. For the alkoxide anions, the critical energy for the fragmentation channel, E_f (calculated from the heats of formation of the alkoxide, R^-, and acetone), is less than the threshold for electron detachment, E_d, for all leaving groups. For example, the threshold for methane elimination from *tert*-butoxide anion is ca. 40 kcal/mol, whereas the detachment threshold is 43 kcal/mol.[3] The fragmentation threshold is even lower for most of the other alkoxides.[8] A similar calculation cannot be carried out for the siloxide anions due to insufficient data on the heats of formation of dimethylsilanone and the siloxide ions. Nevertheless, consideration of the thermochemical cycle shown below (Scheme II) provides significant insight into the relative energetics of the two channels, RH elimination and electron detachment, for both systems.[38]

The critical energy, E_f, for the first step (a simple cleavage) is given by eq 14, while that for electron detachment, E_d, is just

$$E_f \approx \Delta H_1 = \mathrm{EA(MO\cdot)} + D(\mathrm{M{-}R}) - D_\pi(\mathrm{M{-}O}) - \mathrm{EA(R\cdot)} - \epsilon \tag{14}$$

$$E_d = \mathrm{EA(MO\cdot)} \tag{15}$$

$$\Delta E_c = D(\mathrm{M{-}R}) - D_\pi(\mathrm{M{-}O}) - \mathrm{EA(R\cdot)} - \epsilon \tag{16}$$

the electron affinity of $R(CH_3)_2M{-}O\cdot$, i.e., EA(MO)·). Here, $D°(M{-}R)$ is the M–R bond dissociation energy, $D_\pi°(M{=}O)$ is the strength of the M–O π bond (i.e., the contribution of the π bond to the M=O bond dissociation energy), EA(R·) is the electron affinity of the radical R·, and ε is the total ion-molecule interaction energy of the intermediate anion-neutral complex. The difference in critical energies for the two channels is given by eq 16. The available thermochemical data on silicon compounds has been tabulated in a recent review by Walsh.[29] The only unknown parameter required for calculation of ΔE_c for the silicon systems via eq 16 is the bond strength of the silicon-oxygen π bond. The Si–C and C–C bond dissociation energies[29,30] are similar (ca. 88 and 85 kcal/mol, respectively), so the origin of the different product distribution from trimethylsiloxide and *tert*-butoxide ions must lie in a difference in the strength[31] of the Si–O and C–O π bond, $D_\pi°(M{=}O)$. If the Si–O π bond energy were considerably less than the analogous C–O bond, then the critical energy for fragmentation of the siloxides would be greater than the electron detachment threshold, and reaction via both channels might be observable. There is a considerable amount of evidence in the literature that multiple bonds to silicon are considerably weaker than those to carbon. Most of this evidence stems from the many experimental and theoretical studies on silicon-carbon double bonds from which a best estimate of 39 ± 5 kcal/mol has been made for the Si–C π bond energy.[11,29] For comparison, the π bond energy of a typical carbon-carbon double bond is ca. 59 kcal/mol.[30] There is little thermochemical information for Si–O π bonds; however, the reported infrared stretching frequencies for single and double bonds appear to indicate a similar trend for M–O bonds (M = C, Si). The frequency of the C–O and Si–O stretches are similar; however, the stretching frequency is much larger for C=O (ca. 1600–1700 cm^{-1}) than for Si=O (ca. 1200 cm^{-1}).[32]

The above scheme also provides an explanation for the much more efficient production of dimethylsilanone enolate from the pulsed laser photolysis of dimethylsiloxide anion, **3**. The electron affinity of hydrogen atom is ca. 16 kcal/mol greater than the EA of methyl radical.[33] Since the bond energies[29] of Si–H (ca. 90 kcal/mol) and Si–C bonds are quite comparable, hydrogen elimination from **3** must be ca. 15 kcal/mol lower in energy (relative to the electron detachment channel) than methane elimination from **1**. Pulsed laser-induced hydrogen elimination from **3** appears to be a viable source of the silanone enolate ion because the productive fragmentation reaction is more favorable (relative to that for **1**) and can be much more competitive with electron detachment.

These photochemical results should provide an estimate of the silicon-oxygen π bond energy, $D_\pi°$ (Si=O), if ΔE_c and ε (from eq 16) could be determined. The CW laser photochemical result

---

(28) A more thorough discussion of these thermochemical considerations can be found in ref 3 and 8.

(29) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

(30) (a) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1983**, *33*, 493. (b) Benson, S. W. *Thermochemical Kinetics*; Wiley-Interscience: New York, 1976.

(31) As mentioned above, methane elimination (fragmentation) has a lower activation barrier than electron detachment for *tert*-butoxide anion. For ε of ca. 10 kcal/mol, a critical energy of 35 kcal/mol is calculated for *tert*-butoxide (M = C) by using equation 14 with $D°(C{-}CH_3 = 82$, $D°(M{-}O) = 80$, and EA(MO·) = 43 (all values in kcal/mol).

(32) A brief discussion is given in ref 13. This treatment is, of course, not rigorous. Also: Michl, J., private communication.

(33) The electron affinities of methyl radical and hydrogen atom are 1.8 and 17.4 kcal/mol, respectively: Janousek, B. K.; Brauman, J. I. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2. Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 2556.

for **3**, where only a small amount of fragmentation (production of **2**) is observed, can be used to address this issue. In general, the rate for infrared photon absorption[25] from low-power CW lasers is less than reaction rates even near threshold. Hence, CW laser activation generally results in exclusive reaction via the lowest energy pathway.[34] The observation of competition between hydrogen elimination and electron detachment from dimethylsiloxide anion suggests that the thresholds for these two channels are quite close in energy. Taking ϵ as 10 kcal/mol[3,8,35] and ΔE_c as zero, the silicon–oxygen π bond energy can be estimated (from eq 16) to be ca. 62 kcal/mol. Because electron detachment may be very slow at its threshold, the threshold for hydrogen elimination might actually be a few infrared photons (3–9 kcal/mol) above the detachment threshold. Therefore, this estimate of the Si–O π bond energy should be considered an upper limit.[36] The uncertainty in this estimate is also controlled by the uncertainty in the ion–molecule interaction energy of the intermediate complex, ϵ.

Given that the threshold for methane elimination from trimethylsiloxide ion is ca. 20 kcal/mol higher than electron detachment, the results of this study indicate that the efficiency of electron autodetachment from the siloxide anion is evidently very similar to that from acetone enolate ion,[24] where the difference in the fragmentation and detachment critical energies is also ca. 20 kcal/mol. This comparable efficiency for these two systems is somewhat unexpected. One might expect that the necessary V–E coupling should be less efficient for the siloxide system because there is no apparent geometry where the anion and neutral potential energy surfaces should closely approach each other.[37] Obviously, such predictions on unrelated systems must be made cautiously, especially in view of the scarcity of rate information on vibrationally induced electron detachment of closed shell anions.

One final point that must be addressed is the apparent difference in reactivity of trimethylsiloxide ion under IRMP laser and collisional (CID) activation conditions. Our results and those of Squires et al.[4] might at first seem in conflict; no electron detachment was reported in the CID experiments. It is important, however, to realize that the internal energies of the reacting ions can be quite different for these two methods of activation. The observed reactivity of **1** strongly suggests that if higher internal energies are accessed in the CID experiment (quite likely), then the fragmentation reaction would be expected to predominate. Also Squires et al. make no mention of the efficiency (yield) of the CID reaction of **1**; it is possible that some electron detachment might have occurred and was not detected.

Conclusion

Infrared multiple photon activation of gas phase siloxide anions, trimethylsiloxide and dimethylsiloxide, results in the production of the enolate anion of dimethylsilanone, a process which is analogous to the unimolecular decomposition of alkoxide anions.[2,3,8] The pulsed-laser photochemistry of the siloxides is apparently complicated by a significant secondary photochemical component; however, we were able to establish the existence of a direct competition between the fragmentation reaction and vibrationally induced electron detachment. Extension of the stepwise fragmentation mechanism for alkoxide ions to the siloxide system suggests that dimethylsilanone is involved in an intermediate ion–molecule complex.

The results of this study have some interesting thermochemical implications. The observation of competing electron detachment and molecular hydrogen elimination in the CW laser photolysis of dimethylsiloxide anion coupled with mechanistic considerations permits an estimation of 62 kcal/mol as an upper limit for the silicon–oxygen π bond energy in dimethylsilanone.

Future work may lead to further characterization of the intrinsic properties of this enolate ion as well as the production of a variety of new unsaturated group 4 anions.

Acknowledgment. We are grateful to Dr. Robert F. Foster, Dr. Paul B. Comita, and Professor Josef Michl for helpful discussions and comments. We thank Jeffrey Marks for assistance with the CW CO_2 laser. This work was supported by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society. W.T. also gratefully acknowledges fellowship support from the National Science Foundation and the Fannie and John Hertz Foundation. The CW CO_2 laser was constructed with assistance of the San Francisco Laser Center, supported by the National Science Foundation (CHE79-16250).

Registry No. 1, 41866-81-3; **2**, 92641-69-5; **3**, 43641-64-1; $(CH_3)_3SiOSi(CH_3)_3$, 107-46-0; F^-, 16984-48-8; OH^-, 14280-30-9; dimethylsilane, 1111-74-6.

---

[34] Review: Thorne, L. R.; Wight, C. A.; Beauchamp, J. L. *Lect. Notes Chem.* **1982**, *31*, 43.

[35] This estimate for the ion–molecule stabilization energy, ϵ, is based on equilibrium studies of gaseous ion–molecule clusters: Kebarle, P. *Ann. Rev. Phys. Chem.* **1977**, *28*, 445.

[36] Recent calculations by Gordon suggest that the Si–O π bond is ca. 10 kcal/mol weaker than the C–O π bond: Gordon, M. S.; George, C. *J. Am. Chem. Soc.* **1984**, *106*, 609. Other pertinent calculations: Kudo, T.; Nagase, S. *J. Am. Chem. Soc.* **1985**, *107*, 2589. Jacquet, R.; Kutzelnigg, W.; Staemmler, V. *Theor. Chim. Acta* **1980**, *54*, 205. Kudo, T.; Nagase, S. *J. Phys. Chem.* **1984**, *88*, 2833.

[37] Simons, J. *J. Am. Chem. Soc.* **1981**, *103*, 3971.