Infrared Spectroscopic Evidence for Silicon–Oxygen Double Bonds: Methyl- and Dimethylsilanones in Solid Argon

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Silanone and silanoic and silicic acid molecules, each containing a silicon–oxygen double bond, have recently been formed in this laboratory by mercury-arc irradiation of argon matrices containing SiH_4 and O_3.[1,2] In view of the current interest in silicon-containing double bonds,[3-9] we have extended this method to the methylsilanes. Infrared spectra recorded after irradiation of argon matrices containing $MeSiH_3$ and O_3 provide the first evidence for methylsilanone $Me(H)SiO$, and irradiation of similar Me_2SiH_2 and O_3 samples produce dimethylsilanone Me_2SiO, which has previously been formed in argon matrices by using a more complicated synthetic route.[8]

The cryogenic apparatus,[10] ozone preparation,[11] and high-pressure mercury-arc lamp[12] have been described previously. $MeSiH_3$, Me_2SiH_2, or Me_3SiH (Petrarch Systems) and O_3 diluted in argon were codeposited on a CsI window (14–17 K) through two separate spray-on lines at equal rates of 1–2 mmol h^{-1} for 10 h. Deuterated silanes were prepared by $LiAlD_4$ reduction of the chlorides in ether solution. Spectra were recorded on a Perkin-Elmer 983 spectrophotometer; the frequency accuracy of band locations is ±0.2 cm^{-1}.

After full (220–1000 nm) high-pressure mercury-arc irradiation of argon matrices containing Me_2SiH_2 and $^{16}O_3$, a new band appeared at 1209.6 cm^{-1} (labeled D, Figure 1a) which shifted to 1174.4 cm^{-1} with $^{18}O_3$ (Figure 1b) and showed no deuterium shift when Me_2SiD_2 was employed. Similar experiments with Me_3SiH and $^{16}O_3$ gave CH_4 and a sharp new product band at 1208.7 cm^{-1}, which was displaced to 1173.5 cm^{-1} with the $^{18}O_3$ reagent. The isotopic shift of 35.2 cm^{-1} in this frequency region is indicative of a $Si=O$ stretch and the absence of a deuterium shift is consistent with assignment of the D bands to dimethylsilanone, $Me_2Si=O$. The production of Me_2SiO by full-arc irradiation of Me_2SiH_2 or Me_3SiH and O_3 is analogous to the formation of silanone, H_2SiO, with SiH_4 and O_3 as precursors.[1,2] Arrington et al.[8] reported the $Si=O$ stretching fundamental of Me_2SiO at 1204 cm^{-1} in solid argon; the small discrepancy is easily accounted for by the sensitivity of this fundamental to other photochemical byproduct molecules in its environment. More important is the agreement in the ^{18}O shift (35 cm^{-1}) for this fundamental. The shoulders to higher wavenumbers of the major product bands in Figure 1 are presumed to be due to the same species in a slightly different matrix environment.

Similarly full-arc irradiation of argon matrices containing the methylsilane, $MeSiH_3$, precursor and $^{16}O_3$ gave a new band at 1207.6 cm^{-1} (labeled M, Figure 1c), a smaller yield of the 1201.7-cm^{-1} silanone band (labeled B),[1,2] and methane at 1303.7 cm^{-1}. The M band shifted to 1170.6 cm^{-1} with $^{18}O_3$ (Figure 1d)

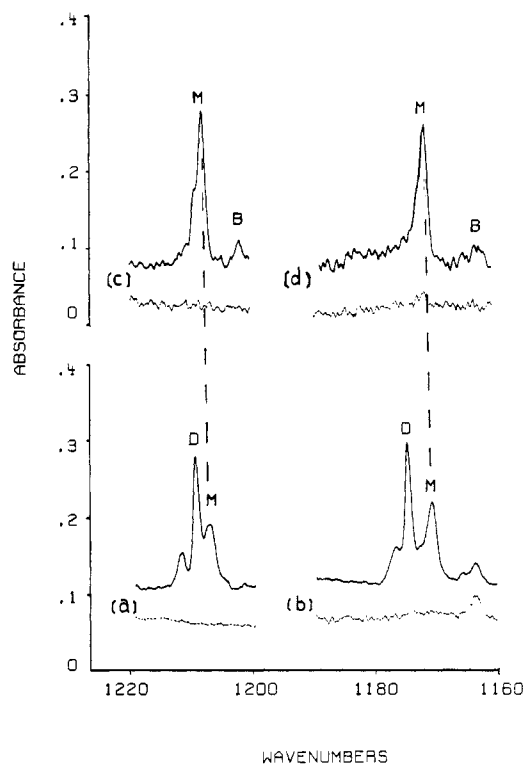

Figure 1. Infrared spectra in the 1160–1220-cm^{-1} region for methylsilane, ozone, argon matrix samples (1/1/400) at 12 K; dotted trace before photolysis and solid trace after full-arc photolysis (220–1000 nm) for 30 min: (a) $(CH_3)_2SiH_2$ and $^{16}O_3$; (b) $(CH_3)_2SiH_2$ and $^{18}O_3$; (c) CH_3SiH_3 and $^{16}O_3$; (d) CH_3SiH_3 and $^{18}O_3$.

and showed a small deuterium shift to 1202.3 cm^{-1} with CH_3SiD_3 as given in Table I. Note that the M bands were also produced from dimethylsilane along with a weak silanone band (Figure 1a). Scrambled $^{16,18}O_3$ gave doublets in all cases with components centered on $^{16}O_3$ and $^{18}O_3$ band locations. The isotopic data support assignment of the M band to the $Si=O$ stretching fundamental of $CH_3(H)SiO$, which is predicted in this spectral region, based on the observation of H_2SiO at 1202 cm^{-1}.[1,2] Other modes, expected to be weaker absorbers, were not detected in these experiments. Recent calculations suggest that methylsilanone is thermodynamically most stable of the possible H_4CSiO isomers.[9]

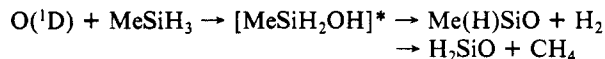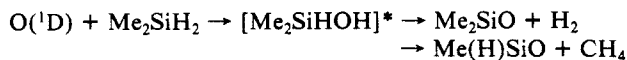Two analogous experiments were done with Me_4Si and ozone, and no silanone product bands were observed.

The mechanism of formation of these methylsilanones follows that discussed earlier for silanone from ozone photolysis.[1,2] Two possible mechanisms may be considered: (i) addition to form a five-centered intermediate and (ii) oxygen atom insertion into a Si–H bond. The failure to observe silanone products with Me_4Si and ozone photolysis indicates a preference for the latter insertion mechanism. Here oxygen atom insertion into the silane reagent produces an energized silanol, which eliminates H_2 or CH_4. It is noteworthy that the silanone (B) bands produced from SiH_4, $MeSiH_3$, and Me_2SiH_2 agree within experimental error as do the $Me(H)SiO$ bands (M) produced from $MeSiH_3$ and Me_2SiH_2, although Me_2SiO bands (D) produced from Me_2SiH_2 and Me_3SiH

Table I. $Si=O$ Fundamental Absorption Frequencies (cm^{-1}) of Major Silanones Produced in Silane/Ozone Photochemical Reactions in Solid Argon

species				
$H_2Si=O$ (B)[a]	$^{16}O,H$, 1202	$^{18}O,H$, 1162	$^{16}O,D$, 1189	$^{18}O,D$, 1147
$Me(H)Si=O$ (M)	$^{16}O,H$, 1207.6	$^{18}O,H$, 1170.6	$^{16}O,D_1$, 1202.3	$^{18}O,D_1$, 1165.4
$Me_2Si=O$ (D)	^{16}O, 1209.6	^{18}O, 1174.4		

[a] Reference 1.

differ by 0.9 cm^{-1}. Both H$_2$ and methane elimination reactions occur because Si–H and Si–C bond energies are nearly the same,[13] but Si–H bond cleavage is clearly favored in these experiments.

$$O(^1D) + Me_2SiH_2 \rightarrow [Me_2SiHOH]^* \rightarrow Me_2SiO + H_2$$
$$\rightarrow Me(H)SiO + CH_4$$

$$O(^1D) + Me_3SiH \rightarrow [Me_3SiOH]^* \rightarrow Me_2SiO + CH_4$$

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$$O(^1D) + MeSiH_3 \rightarrow [MeSiH_2OH]^* \rightarrow Me(H)SiO + H_2$$
$$\rightarrow H_2SiO + CH_4$$

The infrared spectra reveal another product that appears on visible irradiation of these samples, which may have the stoichiometry of the energized precursor to the silanones. Further work is in progress to identify this species.

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Additions and Corrections

Biomimetic Models for Cysteine Proteases. 2. Nucleophilic Thiolate-Containing Zwitterions Produced from Imidazole–Thiol Pairs. A Model for the Acylation Step in Papain-Mediated Hydrolyses [*J. Am. Chem. Soc.* **1985**, *107*, 4070–4072]. K. I. SKOREY and R. S. BROWN*

Page 4071, Table II: k_1 for **2b** and **3b** should be interchanged, e.g., **2b**, k_1 = 13.2 M^{-1} min^{-1}; **3b**, k_1 = 7.64 M^{-1} min^{-1}.

A Structural, Kinetic, and Thermodynamic Study of the Reversible Thermal C–H Activation/Reductive Elimination of Alkanes at Iridium [*J. Am. Chem. Soc.* **1986**, *108*, 1537]. J. MICHAEL BUCHANAN, JEFFREY M. STRYKER, and ROBERT G. BERGMAN*

An arithmetic error was made in the estimation of the combined iridium–cyclohexyl and iridium–hydrogen bond dissociation enthalpies in (C$_5$Me$_5$)(PMe$_3$)Ir(c-C$_6$H$_{11}$)(H) (**1**). The sum of these enthalpies, calculated correctly in Figure 6 but incorrectly in the text at the top of p 1545, is approximately 125 kcal/mol. The estimated lower limit for the combined iridium–phenyl and iridium–hydrogen bond dissociation enthalpies in (C$_5$Me$_5$)(PMe$_3$)-Ir(C$_6$H$_5$)(H) (**2**) is therefore 145 kcal/mol.

Gas Phase Nucleophilic Addition Reactions of Negative Ions with Transition Metal Carbonyls [*J. Am. Chem. Soc.* **1986**, *108*, 4368–4378]. KELLEY R. LANE, LARRY SALLANS, and ROBERT R. SQUIRES*

The caption for Figure 3 should read: Plot of Fe(CO)$_4$ binding energy vs. proton affinity for negative ions: $D[(CO)_4Fe–H^-]$ =

107.4 ± 6 kcal mol^{-1} (ref 54 and 32); $D[(CO)_4Fe–Cl^-]$ = 51.1 ± 6 kcal mol^{-1}, $D[(CO)_4Fe–Br^-]$ > 46.9 kcal mol^{-1}, $D[(CO)_4$-Fe–I$^-$] > 38.4 kcal mol^{-1} (ref 53).

Dehydrogenation of Isobutane by Oxygen-Deficient Cobalt/Oxygen Cluster Ions [*J. Am. Chem. Soc.* **1986**, *108*, 4659–4661]. R. B. FREAS* and J. E. CAMPANA*

Figure 1: Energies of structures should be the following: [M$_2$O$_2$]$^+$ (–17.55 eV), [M$_3$O$_3$]$^+$ (–27.74 eV), [M$_2$O]$^+$ (–0.56 eV), [M$_3$O$_2$]$^+$ (linear; –20.45 eV), (cyclic; –19.78 eV).

Figure 1 caption: (a) The corresponding linear structures were found to lie 0.9 and 1.69 eV in energy above the respective closed structures.

These models based on the correct value (a = 27.78) of one of the adjustable parameters in the potential energy function do not change the conclusions of the paper.

Donor–Acceptor Interaction and the Peculiar Structures of Dications [*J. Am. Chem. Soc.* **1986**, *108*, 5808–5817]. WOLFRAM KOCH, GERNOT FRENKING,* JURGEN GAUSS, and DIETER CREMER*

Page 5811: Equation 1 should read:

$$CH_2^{2+} + X \rightarrow CH_2X^{2+} + \Delta E_R \tag{1}$$
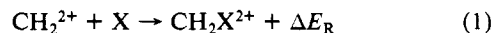
Page 5817: Reference 45 should read only: Koch, W.; Schwarz, H. *Chem. Phys. Lett.* **1985**, *113*, 145.