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Registry No. Cytochrome b_5, 9035-39-6; heme, 14875-96-8.

Communications to the Editor

The Reaction of Dimethylsilylene with Carbon Monoxide in Low-Temperature Matrices

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The gas-phase reaction of methylene with carbon monoxide to form ketene has been studied for both singlet and triplet methylene.[1] Calculated potential energy surfaces suggest that the barrier for addition of singlet methylene to carbon monoxide is low (less than 1 kcal/mol) or nonexistent.[2] We expect the corresponding reaction of dimethylsilylene to have a similar low barrier. In this communication we report evidence for a reaction of dimethylsilylene with carbon monoxide resulting in the formation of a species in which the CO is bonded to the silicon atom.

Dimethylsilylene, $(CH_3)_2Si$, has a singlet ground state with an empty p orbital and a lone pair in an sp^2 hybrid orbital. The 1-2 hydrogen migration which occurs so readily in the corresponding alkylcarbenes[3] has a calculated barrier of about 170 kJ/mol[4] and occurs in low-temperature matrices for dimethylsilylene only upon photoexcitation, so that this form of divalent silicon can be readily generated and trapped in low-temperature matrices.[5] Bimolecular reactions of dimethylsilylene with small reactant molecules can be conveniently followed in low-temperature matrices and can be used to produce reactive species which have structures not normally found in silicon-containing compounds.[6]

Most of the experiments were conducted in solid argon by using conventional low-temperature matrix techniques with an Air Products closed cycle helium refrigerator operated at temperatures between 15 and 40 K. Infrared spectra were recorded on a Perkin Elmer 983-G spectrophotometer and UV–vis spectra on a Perkin Elmer 552 spectrophotometer. Gas mixtures of CO in Ar were passed over crystalline dodecamethylcyclohexasilane, **1**, and deposited on a CsI window. Spectra were recorded before and after irradiation with either a low-pressure or medium-pressure mercury lamp. Additional experiments were carried out with **1** dissolved in 3-methylpentane glasses at 77 K in a quartz dewar. Carbon monoxide was obtained from Matheson, isotopically labeled CO from MSD Isotopes, and **1** and dimethyldiazidosilane, **2**, from Petrarch Chemicals.

Figure 1 displays infrared spectra of **1** in a matrix of Ar with 2% CO before and after irradiation. The intense product band appearing at 1962 cm^{-1} is assigned as the CO stretch of carbon monoxide that has formed an adduct with dimethylsilylene. This infrared band only appears when both **1** and CO are present and have been irradiated. The band increases following warming of the irradiated matrix to 40 K to allow migration of CO and to a lesser extent dimethylsilylene. In addition there is a change in the relative intensities of the overlapping features within the band presumably attributable to the annealing of different sites within the argon lattice and the possible influence of neighboring molecules on vibrational frequencies. The 1962-cm^{-1} band also appears when dimethyldiazidosilane, **2**, is irradiated in the presence of CO. Dimethylsilylene has been shown to be formed by photolysis of **2**.[7]

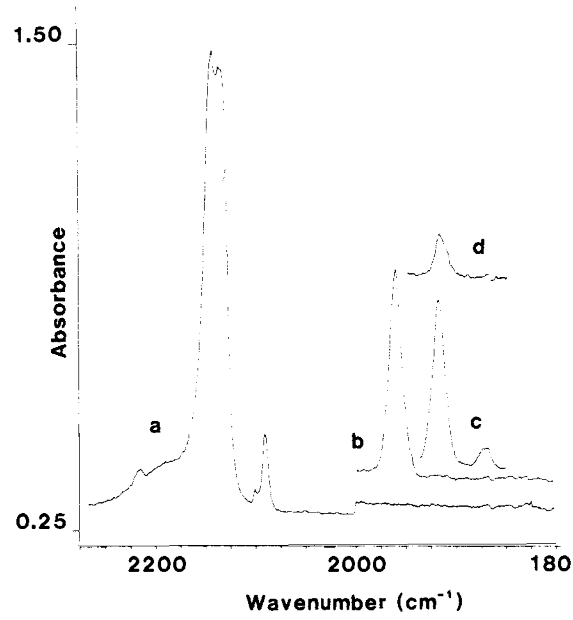

Figure 1. Infrared spectra of **1** in solid argon with 2% CO: (a) before irradiation, (b) after irradiation with $^{12}C^{16}O$, (c) after irradiation with $^{13}C^{16}O$, and (d) after irradiation with $^{12}C^{18}O$.

Table I. Experimental and Calculated Wavenumbers (cm^{-1}) for the CO Stretch

species	exptl wavenumber (isotope shift)	AM1[a] (shift)	MNDO[a] (shift)	3-21G[b]
$(CH_3)_2Si^{12}C^{16}O$	1962	2208	2310	2351
$(CH_3)_2Si^{13}C^{16}O$	1918	2156	2255	
	(44)	(52)	(55)	
$(CH_3)_2Si^{12}C^{18}O$	1915	2162	2262	
	(47)	(46)	(48)	
$^{12}C^{16}O$	2149[c]	2267	2382	2316

[a] Calculated wavenumber using AM1 or MNDO Hamiltonian in MOPAC4.[8a] [b] Calculated wavenumber using GAUSSIAN 86 with 3-21G basis set.[8b] [c] In argon matrix: Davies, J. B.; Hallam, H. E. *J. Chem. Soc., Faraday Trans. II* **1972**, *68*, 509.

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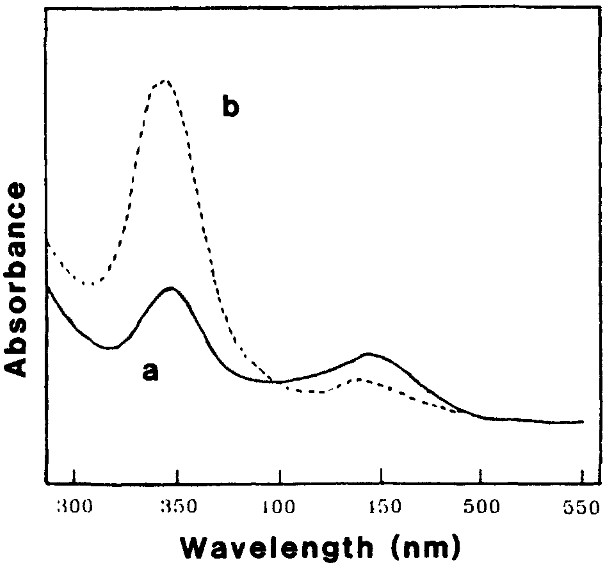

Figure 2. Ultraviolet spectra of **1** in solid nitrogen with 2% CO: (a) after irradiation at 20 K and (b) after warming to 40 K.

Carbon monoxide labeled with ^{13}C and separately with ^{18}O were reacted with dimethylsilylene and produced infrared bands with the expected shift in wavenumber. The isotopic shift data along with calculated wavenumbers are given in Table I. In addition to the 1962-cm^{-1} band one other weaker infrared band appears at 765 cm^{-1}. This band shows no shift with either ^{13}C or ^{18}O labeling of CO and appears to be a methyl rocking vibration.

A UV-vis band with maximum absorbance at 342 nm appears under the same reaction conditions that give rise to the 1962-cm^{-1} band. This band was observed in argon and nitrogen matrices as well as in a matrix of pure CO with **1**. See Figure 2. In inert matrices the characteristic 450-nm band of dimethylsilylene is present, but in pure CO the only band observed is that at 342 nm.

When **1** is dissolved in 3-methylpentane, frozen in liquid nitrogen, and irradiated, the matrix turns yellow, and the 450-nm band appears. With the addition of 300 Torr of CO to the sample cell before freezing irradiation of the glass results in a spectrum displaying both the 342- and 450-nm bands. As the glass remains at 77 K for several hours following irradiation the 342-nm band grows in intensity, while the 450-nm band diminishes—a result of the limited mobility of CO in the 3-methylpentane glass. Analysis of products of the 3-methylpentane glass reaction by GC-mass spectrometry gave no products attributable to a structure incorporating CO bonded with dimethylsilylene.

Our initial expectation was that the reaction product represented a Lewis acid-base adduct with the C lone pair of CO forming a coordinate covalent bond with the empty p orbital on silicon, which would assume a pyramidal geometry: $(CH_3)_2\ddot{Si}\leftarrow C\equiv O$. Formation of the ketene would formally require loss of one C–O π bond to form the Si–C π bond—a seemingly endothermic process. However MNDO/AM1 and ab initio calculations[8] give quite different structures for optimized geometries. Both AM1 and MNDO calculations have a minimum energy for the silaketene geometry. Calculated geometries have a Si–C bond length of 1.625 Å (MNDO) and 1.644 Å (AM1), clearly in the range of Si=C double bond lengths.[9] Ab initio calculations with a 3-21G basis set give a lowest energy structure which is pyramidal at Si with an Si–C bond length of 2.891 Å and a C–Si–CO angle of 89°, while the silaketene structure is 84 kJ/mol higher in energy than the pyramidal structure. The CO bond lengths are 1.185 Å (MNDO) and 1.125 Å (3-21G) for the adduct compared with 1.163 Å (MNDO), 1.129 Å (3-21G), and 1.128 Å (experimental) for CO. The data in Table I indicate that MNDO and AM1 predict a shift of the CO stretch to lower wavenumber than free CO, while the ab initio results give a shift to higher wavenumber. Although our experimental data would seem to be more consistent with the MNDO/AM1 results, which give a lower CO stretching wavenumber for the adduct than that of carbon monoxide, we cannot decide from experimental evidence alone what the structure of the adduct is. A silacyclopropanone structure is computed to lie higher in energy by both AM1 and ab initio calculations. A more complete computational study of the H_2SiCO system is being undertaken by Hamilton and Schaefer at the University of Georgia.

The possibility that the carbon monoxide bonds to dimethylsilylene through the oxygen rather than the carbon is unlikely on the basis of calculated energies. MNDO calculations give a barrier of about 8 kJ/mol for the oxygen attachment to give a product that is less stable than the ketene by about 200 kJ/mol. Ab initio calculations indicate a similar preference for bonding through the carbon.

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Registry No. 1, 4098-30-0; **2**, 4774-73-6; CO, 630-08-0; ^{13}CO, 1641-69-6; C^{18}O, 4906-87-0; $(CH_3)_2Si^{12}CO^{16}O$, 115591-59-8; $(CH_3)_2Si^{13}C^{16}O$, 115591-60-1; $(CH_3)_2Si^{12}C^{18}O$, 115591-61-2; H_2SiCO, 109284-39-1; $(CH_3)_2Si$, 6376-86-9.

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Ligand Field Transitions and the Origin of Zero Field Splitting in $[PPh_4][FeCl_4]$ and $[NEt_4][Fe(SR)_4]$ (R = 2,3,5,6-Me_4C_6H): A Model for the High-Spin Fe(III) Site in Rubredoxin

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Rubredoxin (Rb) is the simplest Fe–S center, containing an approximately D_{2d} distorted T_d Fe coordinated by four cysteines.[2] Geometric and electronic structure/function relationships for Rb have been investigated experimentally[2-17] and theoretically.[18-20]

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