thermodynamics for copper and oxygen in condensed matrices (Table I) confirm that O^{2-} is a strong reducing agent that will transfer electrons to Cu^{3+} and Cu^{2+} ions (strong oxidizing agents) to give copper atoms and O^{--} ions. A recent analysis¹⁸ of the interactions of oxo oxygen with transition-metal ions demonstrates that the reducing propensity of oxo ion (O^{2-}) is enhanced by covalent bond formation between the unpaired electron of the O^{--} product with the unpaired d-electrons of the reduced metal [e.g., $Cu^0(d^{10}s)$]; the reduction potential shifts more negative by 1.0 V per 23.1 kcal of covalent bond energy. Hence, the reaction between O^{2-} and Cu^+ is favored by 6.1 V (140 kcal).

$$Cu^+ + O^{2-} \rightarrow Cu^0 - O^-$$

 $\Delta E_{reac} \ge 2.9 + (73/23.1) = 6.1 V (140 \text{ kcal exothermic}) (1)$

Given the formula $(Ba_2YCu_3O_7)$ and the electronic properties of the constituent elements (Table I), the Ba and Y atoms will transfer their valence electrons to the O atoms

$$[2Ba^{0} + Y^{0}] + 7O \rightarrow [2Ba^{2+} + Y^{3+}]^{7+} + 7O^{-}$$
(2)

The three Cu^0 atoms (d¹⁰s valence shell) possess an unpaired electron that will couple with three O⁻⁻ ions (s²p⁵ valence shell) via covalent bond formation to give three diamagnetic Cu⁰-O⁻ groups (d¹⁰s-p⁵s²).

$$\begin{array}{ccc} 3Cu^{0} + 3O^{\bullet-} \rightarrow 3Cu^{0} - O^{-}(s^{2}d^{9} - p^{5}s^{2}) \\ d^{10}s & s^{2}p^{5} \end{array}$$
(3)

Two of these, under the influence of the four remaining $O^{\bullet-}$ ions, will have their $d^{10}s$ valence shell hybridized to d^9sp to accommodate the formation of two additional covalent copper- $O^{\bullet-}$ bonds per Cu^0-O^-

$$2Cu^{0}-O^{-} + 4O^{-} \rightarrow 2Cu^{0}(-O^{-})_{3}^{3-}[d^{9}sp \equiv (p^{5}s^{2})]$$
(4)
diamagnetic

[This is equivalent to the addition of two $O^{\bullet-}$ ions to a C=O (s²p² carbon) to give

$$0 = 0 = 0 = (sp^3 carbon)]$$

Thus the chemical reactivities of the elements in $Ba_2YCu_3O_7$ will result in a family of ionic groups via electron transfer and covalent-bond formation.

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$$[Ba_2YCu_3O_7] \rightarrow [2Ba^{2+}, Y^{3+}]^{7+}[2Cu^0(-O^-)_3^{3-}, Cu^0-O^-]^{7-}$$
 (5)

Two possible arrangements of these ions would be ordered arrays with an alternating copper-oxygen chain in one dimension.



-, covalent bond; ---, ionic bond; ---, semi-ionic bond

Such arrangements have two classes of copper atoms and four classes of $O^{\bullet-}$ ions, which is in accord with the neutron-diffraction structure for Ba₂YCu₃O₇ (recently confirmed by X-ray diffraction).¹⁹

The electronegativity difference $(\chi_O - \chi_{Cu})$ for the gas-phase Cu^0-O^{\bullet} molecule (1.0–1.5 units, Table I) indicates that the bonding is 30–40% ionic. However, the electronegativity of O^{•-} should be about 0.7 unit less than for O, which means that the Cu^0-O^{-} bond is less than 15% ionic, and that the charge density at the copper is less than +0.1. The gas-phase covalent bond energy is estimated (Table I) to be 73 kcal for Cu^0-O^{-} and represents the dominate interatomic force within the $Ba_2YCu_3O_7$ superconductor.

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Production of Si(¹D₂) from Electronically Excited SiH₂

C. M. Van Zoeren, J. W. Thoman, Jr.,[†] J. I. Steinfeld,*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

and M. W. Rainbird

School of Science, Griffith University, Nathan, Brisbane, Queensland 4111, Australia (Received: October 22, 1987)

Si(¹D₂) has been detected by atomic laser-induced fluorescence following photoexcitation of SiH₂ into high bending vibrational levels of the \tilde{A}^1B_1 state. The Si(¹D₂) + H₂ channel appears to open between $v_2' = 6$ and 7, establishing $\Delta H_1^{\circ}(SiH_2) = 65.4 \pm 1.6$ kcal mol⁻¹. SiH₂ appears to dissociate preferentially from high rotational levels of the \tilde{A} , $v_2' > 6$ states.

Introduction

Silylene (SiH_2) has been implicated as an important intermediate in the formation of amorphous silicon thin films from chemical vapor deposition (CVD) of silane.¹ This species has also been postulated as a key intermediate in the infrared multiple-photon dissociation (IRMPD) of organosilanes.² In previous

[†]Present address: Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94550.

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publications, we have reported the spectroscopic detection of SiH_2 by laser-induced fluorescence (LIF) following IRMPD of alkyland phenylsilanes,³ observed a wide fluctuation in the fluorescence lifetimes of individual rovibronic levels of $SiH_2(\tilde{A}^1B_1)$,⁴ and interpreted these fluctuations in terms of quantum chaos in the background SiH₂($\tilde{a}^{3}B_{1}, \tilde{X}^{1}A_{1}$) levels.⁵ We have also measured the v_2' dependence of the SiH₂ Å state fluorescence lifetimes⁶ for $6 \le v_2' \le 10$. The behavior of these lifetimes suggests the opening of a new dissociation channel (to Si(${}^{1}D_{2}$) + H₂) at high v_{2}' levels, which permits us to establish the heat of formation of $SiH_2(g)$.

One expects the appearance of $Si(^{1}D_{2})$ following excitation of SiH_2 into \tilde{A} state levels (above the threshold for this channel). Spears and co-workers^{7,8} have detected ground-state $Si(3p^2 {}^{3}P_0)$ in glow discharges in silane using atomic fluorescence and have also observed excited Si($3p4s P_1^{\circ}$) atoms in emission following UV laser ablation of particles in the discharge. The observed emission was attributed to electron-impact excitation of metastable $Si(3p^2 D_2)$ present in the plasma, but the D_2 atoms have not been observed directly. In this Letter, we report the observation of $Si(^{1}D_{2})$ following photoexcitation of SiH_{2} and use the appearance spectrum of these species to improve the precision of the determination of $\Delta H_{\rm f}^{\rm o}({\rm SiH}_2)$.

Experimental Section

SiH₂ was produced by the IRMPD of *n*-butylsilane (Silar Industries), which was slowly flowed through the experimental chamber at pressure of 7 mTorr or less. The flow system has been described previously.³ A CO₂ TEA laser (Laser Science PRF-150s) was loosely focused at the center of the cell and provided pulses with a fluence at the focal point of 5 J cm⁻³ at the 10P(20)line (944 cm⁻¹) with a repetition rate of 20 Hz.

 $SiH_2 \tilde{A}^1B_1 \leftarrow \tilde{X}^1A_1$ vibronic bands were excited by a home-built, prism tuned, broad-band dye laser. This laser was pumped by an excimer laser (Lumonics 860-1) operating on XeF at 351 nm and provided 10-ns pulses of tunable light with a 2-4-nm bandwidth. The pulse energy of this laser depended strongly on the dye being used and on the position within the dye's gain envelope, typically attaining in excess of 5 mJ per pulse at the maximum. As both the SiH₂ fluorescence and the Si(${}^{1}D_{2}$) signals depend linearly on the power of this laser, both signals were normalized to same, employing a photodiode and a home-built sample and hold unit. SiH₂ LIF was imaged onto a photomultiplier tube (Hamamatsu R928), equipped with the appropriate colored glass filters (Schott and Corning).

Si(¹D₂) atoms were detected via LIF, exciting the ¹P₁° \leftarrow ¹D₂ transition at 288.158 nm and observing the ${}^{1}P_{1}^{\circ} \rightarrow {}^{1}S_{0}$ transition at 390.522 nm.^{9,10} Tunable UV light was generated by using the output of an excimer pumped dye laser (Lambda Physik EMG101E + FL2002) and a KD*P crystal. Pulses of 10 ns, 1-cm⁻¹ fwhm, and 40 μ J were obtained with this system. A band-pass filter, centered at 390 nm with a fwhm width of 10 nm (Corion), was used to select out the Si atom fluorescence, which was imaged onto a photomultiplier tube (Hamamatsu 1P28).

The UV and visible beams were mixed with a 266-nm dichroic mirror (CVI) and focused with a 500-mm quartz lens into the



Figure 1. Si(${}^{1}D_{2}$) atomic fluorescence signal (upper panel) and SiH₂ Ã $\cdot \bar{\mathbf{X}}$ fluorescence signal (lower panel) vs SiH₂ excitation wavelength. Both have been normalized to broad-band dye laser excitation intensity. The Si atom signal between 520 and 540 nm arises from dissociation of SiH₂ in high-J states, as explained in the text; to the red of 540 nm, no $Si(^{1}D_{2})$ signal is detectable above the noise level.

chamber. The infrared beam was collinear and counterpropagating with respect to the others. Synchronization of these three lasers was achieved by using two delay generators; the first (analog, Evans Associates 4141-2) between the CO_2 and the broad-band dye laser and the second (digital, Berkeley Nucleonics) between the broad-band dye laser and the Si atom probe laser. The delay between the IR photolysis and visible SiH₂ probe laser was approximately 1 μ s, while the delay between the visible and the UV $Si(^{1}D_{2})$ probe was 250 ns.

 SiH_2 excitation and $Si(^1D_2)$ production spectra were simultaneously collected with two gated integrators (EG&G/PAR 165/166), and the SiH₂ LIF was further integrated with a boxcar averager (EG&G/PAR 162) and displayed on a strip-chart recorder. These two signal channels, and the output from the sample and hold, were collected on a laboratory computer (DEC MINC-11/03). The data were transmitted to a main frame computer (DEC VAX) for analysis and display.

Results

 $Si(^{1}D_{2})$ was detected by laser-induced atomic fluorescence at SiH_2 excitation wavelengths from 542 to below 445 nm. The appearance spectrum is shown in Figure 1, along with the SiH_2 fluorescence excitation spectrum in the same region for comparison. It is evident that $Si(^{1}D_{2})$ begins to appear at wavelengths somewhat to the red of the (050) band center near 515 nm, and the signal rises monotonically to the blue until the region of the (080) band center near 447 nm. At SiH_2 excitation wavelengths below 445 nm, $Si(^{1}D_{2})$ signal levels never exceeded those seen in the (080) region. Therefore, we consider the quantum yield for $Si(^{1}D_{2})$ production to have reached a maximum at $v_{2}' = 8$. Since the branching ratio to the other dissociation channel (viz., to Si(³P) $(+ H_2)^{11}$ is not known, we cannot assume unit quantum yield for $Si(^{1}D_{2})$ in this region.

By varying the delay between the SiH_2 excitation laser pulse and the 288.16-nm Si atom probe pulse, we determined that the decay time of the $Si(^{1}D_{2})$ atoms was on the order of several microseconds. The largest quenching rates for $Si(^{1}D_{2})$ reported by Husain and Norris¹² are approximately $(2-3) \times 10^{-10}$ cm³ s⁻¹ for hydrocarbon collision partners. At the pressures employed in the experiment, this would give a quenching half-time of approximately 10 μ s. Thus, the loss of Si(¹D₂) is not due to collisional quenching but primarily to diffusion of silicon atoms out of the small viewing region defined by the intersection of the three laser beams.

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Figure 2. Appearance spectrum for $Si({}^{1}D_{2})$ from SiH_{2} ($\tilde{A}{}^{1}B_{1}$) under the following conditions: open triangles, 100 mTorr of Ar and nominally zero delay between pulses; filled circles, 300 mTorr of Ar and 8- μ s delay between pulses. The arrows on the wavelength axis indicate the (070) and (060) band origin positions.

The experiments were repeated with argon as a buffer gas, to cool the $SiH_2(\tilde{X}^1A_1)$ rotational distribution prior to the excitation into the \tilde{A}^1B_1 state. Representative $Si(^1D_2)$ production spectra in the (060) and (070) regions are shown in Figure 2.

Discussion

The most striking feature about the $Si(^{1}D_{2})$ photoproduction spectrum shown in Figure 1 is that it does not follow the SiH₂ $A \leftarrow X$ fluorescence excitation spectrum, but instead increases monotonically to shorter wavelengths. While individual rovibronic transitions would not be resolved by the broad-band laser used to excite the SiH₂, the $(0v_20)$ vibrational band contours are clearly resolved and do not appear in the photoproduction spectrum. Thus, $Si(^{1}D_{2})$ photoproduction appears to contain disproportionately large contributions from high-J rovibronic levels of SiH₂. Previous measurements³ had shown that the SiH₂ formed by IRMPD of alkylsilanes is rotationally hot. We performed spectral simulations using the ASYROT program,¹³ using appropriate rotational constants¹⁴ and assuming a $T_{\rm rot}$ of 700 K, to verify that transitions into high-J levels of (070) occur at such long wavelengths. The simulations show the vibrational band centers, which include primarily low-J levels and closely spaced rotational transitions, and also many (070) \leftarrow (000) transitions arising from high-J" (5 to 10) levels extending to the red end of the wavelength region depicted in Figure 1. High-J levels of (060) which lie above the dissociation limit could also contribute to $Si(^{1}D_{2})$ production at the longer wavelengths.

The observation that the high-J rotational states could account for the featurelessness of the $Si(^{1}D_{2})$ production spectrum prompted us to perform the buffer gas experiments with Ar shown in Figure 2. As we increased the pressure of the buffer gas and delay time between the IRMPD and the SiH₂ excitation laser pulses, two effects were observed. First, while total signal levels are decreased, $Si(^{1}D_{2})$ production remains relatively high near the (070) band center but falls to zero near the (060) band center. Second, structure in the region of the (070) band is appearing. The high-J'' states have rotationally relaxed, and therefore only the lower J'' states are populated. Under relaxed conditions, only low-J states give rise to the $Si(^{1}D_{2})$ production. That this structure appears only in a rotational partially cooled spectrum supports the assertion that high-J rovibronic levels contribute disproportionately to $Si(^{1}D_{2})$ production and that the (070) vibronic level lies above the dissociation limit. Indeed, spectral simulations assuming $T_{rot} = 300$ K indicate significantly less intensity in those rotational transitions to the red of 490 nm.

While it is conceivable that $Si(^{1}D_{2})$ photoproduction to the red of the (070) band could arise from hot-band excitation of excited

vibrational levels of SiH₂ produced in the photolysis, there are several reasons that this is unlikely. First, no features assignable to 2_1^n bands were observed in the SiH₂ excitation spectrum. Second, IRMPD is known to produce fragments possessing little excess vibrational energy. It is also possible that SiH₂* molecules with energies just below the Si(${}^{1}D_{2}$) + H₂ channel could be sufficiently energized in a collision to proceed to dissociate. This process has been termed "collisional release".¹⁵⁻¹⁸ If this were occurring, then addition of buffer gas might be expected to increase, rather than decrease, the Si(${}^{1}D_{2}$) yield at longer wavelength. No evidence for such a process was observed.

These results establish that the $Si(^{1}D_{2}) + H_{2}$ channel is coincident in energy with SiH₂ between $v_2' = 6$ and 7. Based on the behavior of the lifetimes in J' = 0 of various vibronic levels, it had previously been suggested⁶ that the $Si(^{1}D_{2}) + H_{2}$ channel was coincident in energy with SiH₂ between $v_2' = 7$ and 8. Based on the present results, it appears that this channel is energetically accessible at $v_2' = 7$ and above. Further consideration of the lifetime data indicates that, while the J' = 0 level and a few nearby (presumably low J) levels have relatively long lifetimes, most of the rovibronic levels in (070) have lifetimes characteristic of a predissociative state, less than 10 ns. In SiH₂(080), the J = 0rovibronic level lifetimes are significantly longer than those with higher J. These observations are consistent with other work involving photodissociation of bent triatomics.¹⁹ It is found that the rotational distribution of the diatomic after dissociation at room temperature is high, because the parent compound dissociates predominantly from states with $J' \neq 0$. The dissociation of $H_2CO(\tilde{A}^1A'', 2^{1}4^3)$ to H + HCO is also observed²⁰ to proceed through high rotational levels.

The appearance of Si(¹D₂) at the $v_2' = 7$ energy supports the theoretical prediction⁶ that there is essentially no additional barrier on the SiH₂($\tilde{A}^{1}B_{1}$) potential energy surface, other than the energy difference in going to Si(¹D₂) + H₂. Placing the dissociation level of SiH₂ to Si(¹D₂) + H₂ between $v_2' = 6$ and 7 gives the experimental heat of formation of SiH₂ as 65.4 ± 1.6 kcal mol⁻¹ by using the method described previously.⁶ The lower bound of possible values, 63.14 ± 0.96 kcal mol⁻¹, is fixed by noting that the $v_2' = 0$ level of SiH₂ can dissociate to Si(³P) + H₂, which lies 18.008 kcal mol⁻¹ below Si(¹D₂) + H₂. This value of $\Delta H_{f}^{\circ}_{298} \approx 65.4$ kcal mol⁻¹ for SiH₂ agrees very well with recent experimental²¹⁻²³ and theoretical estimates.²⁴⁻²⁶ In particular, it is in almost exact agreement with the lower of two possible values (65.6 ± 0.7 kcal mol⁻¹) obtained from photoionization mass spectrometry and with the value (65.3 ± 1.5 kcal mol⁻¹) obtained from RRKM calculations²⁷ and kinetic measurements.²⁸

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