Proton Affinity and Heat of Formation of Silylene

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Using the techniques of Fourier transform ion cyclotron resonance spectroscopy, we determined the proton affinity of silylene to be 201 \pm 3 kcal-mol⁻¹ from a study of the kinetics and thermochemistry of proton transfer from SiH₃⁺ to a series of n-donor bases with well-established gas-phase base strengths. This value leads to $\Delta H_{f}^{\circ}_{298}(SiH_2) = 69 \pm 3 \text{ kcal-mol}^{-1}$, which is 11 kcal-mol⁻¹ higher than the previously accepted value (Walsh, R. Acc. Chem. Res. 1981, 14, 246-252), but in excellent agreement with the recent theoretically recommended value of 68.1 kcal-mol⁻¹ (Ho, P.; Coltrin, M. E.; Binkely, J. S.; Melius, C.F. J. Phys. Chem. 1985, 89, 4647-4654).

The thermochemical properties of the reactive molecule silylene are of fundamental interest in organometallic chemistry and also of importance in understanding the process of silicon chemical vapor deposition (CVD).¹ Although the heat of formation of silvlene has been studied experimentally, there is considerable discrepancy among the various published values. For example, the value of $\Delta H_1^{\circ}_{298}$ (SiH₂) = 58 kcal·mol⁻¹ recommended by Walsh² (based on pyrolysis measurements of silane species)³ is considerably below the more questionable value of 81 kcal·mol⁻¹ obtained from the mass spectrometric study of silylarsine by Saalfeld and McDowell.⁴ However, the higher value is supported by arguments offered by Robertson et al.⁵ in their recent studies of silane pyrolysis. Ho et al.⁶ obtained a heat of formation of SiH₂ of 68.1 kcal-mol⁻¹ by ab initio calculation at the MP4/6-31G** level. This is corroborated by the value of 67.9 kcal·mol⁻¹ estimated from the most recent theoretical calculation (MP4SPTQ/6-31G* level) reported by Luke et al.⁷

To more firmly define an experimental value for the heat of formation of silvlene, we have used the techniques of Fourier transform ion cyclotron resonance spectroscopy⁸ to examine proton-transfer reactions of SiH₃⁺ (reaction 1) with a series of

$$\mathrm{SiH}_3^+ + \mathrm{B} \to \mathrm{SiH}_2 + \mathrm{BH}^+ \tag{1}$$

n-donor bases B with known gas-phase basicities^{9,10} (proton affinities). The proton affinity of SiH₂ determined in this fashion yields $\Delta H_{f}^{\circ}(SiH_{2})$ with the use of eq 2. This experimental

$$\Delta H_{\rm f}^{\circ}({\rm SiH}_2) = {\rm PA}({\rm SiH}_2) + \Delta H_{\rm f}^{\circ}({\rm SiH}_3^+) - \Delta H_{\rm f}^{\circ}({\rm H}^+)$$
(2)

methodology has successfully yielded heats of formation of halocarbenes¹¹ and other reactive molecules¹² in previous studies.

Silane ionized by electron impact with an electron energy of 14 eV provides a convenient source of SiH_3^+ ions. The most abundant primary ions are SiH_2^+ and SiH_3^+ ,¹³ the former being converted to the latter by reaction 3 ($k = 6.2 \times 10^{-10} \text{ cm}^3$. molecule⁻¹ s⁻¹).¹⁴ The symmetrical hydride-transfer reaction of

$$\operatorname{SiH}_2^+ + \operatorname{SiH}_4 \to \operatorname{SiH}_3^+ + \operatorname{SiH}_3 \tag{3}$$

 SiH_3^+ with silane is also very fast.¹⁴ The silyl cation reacts very slowly with silane to yield Si₂H₅^{+,15} Various oxygen-, nitrogen-, and sulfur-containing n-donor bases were chosen as neutral reactants, covering a range of base strengths and expected reactivities. The Fourier transform ICR spectrometer used in these studies comprises a 1-in. cubic cell¹⁶ in a 15-in. electromagnet (operated typically at 1 T) with an Ionspec FTMS-2000 data system. Pressures were measured with a Schulz-Phelps ion gauge calibrated against an MKS Baratron (Model 390 HA-0001) capacitance manometer. Experiments were carried out with 1:1 SiH₄-B mixtures with a total pressure in the range $(1-2) \times 10^{-6}$ torr and an electron energy of 14 eV. Although other reactions are noted below, this study focused on the proton-transfer reaction of SiH_3^+ with the neutral bases. Ion ejection pulses were used to remove all ions except SiH_3^+ from the ICR cell shortly after

the electron beam pulse.¹⁷ The results are summarized in Table T.

As reported by Lampe et al.,¹⁸ SiH₃⁺ reacts sequentially with D_2O to yield a protonated silanone (H_2SiOD^+), $HSi(OD)_2^+$, and $Si(OD)_3^+$. The primary reaction products with CD₂OD are $H_2SiOCD_3^+$, H_2SiOD^+ , and a deuteride-transfer product CD_3OD^+ . The protonated silanone was also observed as a major product in the reaction of SiH_3^+ with CH_3CHO and $(CD_3)_2CO$. In the reaction of SiH_3^+ with aliphatic nitriles, the formation of $RCNSiH^+$ (R = CH₃, c-C₃H₅) is predominant, with hydrogen being eliminated from the silicon center.¹⁹ SiH₃⁺ reacts with CH₃OCH₃ exclusively via a hydride-transfer reaction. Hydride

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(7) The reaction enthalpy at 0 K for $SiH_4 + CH_2(^3B_1) \rightarrow CH_4 + SiH_2(^1A_1)$ is estimated to be -51.9 kcal-mol⁻¹ from Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M.-B.; Apeloig, Y.; Chandrasekhar, J.; Schleyer, P. v. R. J. Am. Chem. Soc. 1986, 108, 260–269. It is assumed that the enthalpy of this reaction at 298 K is nearly the same as that at O K by an ideal gas approximation. This value of the enthalpy of reaction and the heat of for-mation of silane (8.2 kcal·mol⁻¹; ref 2), methane (-17.9 kcal·mol⁻¹; Pedley, J. B.; Rylance, J. Sussex N. P. L. Computer Analyzed Thermochemical Data: Organic and Organometallic Company and pitter information and a Disservery and Construction of the Company and Statistics of Sussex: Sussex, England, 1977) and methylene (93.7 kcal·mol⁻¹; Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. J. Phys. Chem. Ref. Data Suppl. 1977, 6.) leads to $\Delta H_1^{\circ}{}_{298}(SiH_2) = 67.9 \text{ kcal·mol}^{-1}$. (8) Marshall, A. G. Acc. Chem. Res. 1985, 18, 316–322, and references

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[†]Contribution No. 7377.

TABLE I: Observed Reactions and Rate Constants for the Reaction	ctions
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$SiH_3^+ + B \rightarrow products$						
B	PA ^a	products	prod distr ^o	k_{total}^{c}	k_{ADO}^{a}	
D_2O	166.5 ^e	$H_2SiOD^+ + HD$	1.0	2.1 ± 0.2	19.7	
CD ₃ OD	181.9 ^e	$H_2SiOCD_3^+ + HD$	0.44	6.4 ± 0.7	16.5	
		$CD_2OD^+ + SiH_3D$	0.38			
		$H_2SiOD^+ + CD_3H$	0.18			
CH3CHO	186.6	$H_2SiOH^+ + C_2H_4$	1.0	9.9 ± 0.8	21.4	
CH ₃ CN	188.4	$CH_3CNSiH^+ + H_2$	>0.99	15.5 ± 1.5	29.3	
$(CH_3)_2O$	192.1	$CH_3OCH_2^+ + SiH_4$	1.00	5.4 ± 0.5	14.7	
c-C ₃ H ₅ CN	195.4	$C_3H_5CNSiH^+ + H_2$	0.65	22.8 ± 2.2	22.8	
		$C_3H_4SiH_2^+$ + HCN	0.22			
		$C_3H_5^+$ + SiH ₃ CN	0.13			
(CD ₃) ₂ CO	196.7 ^e	$H_2SiOD^+ + C_3H_6$	0.80	20.7 ± 1.1	21.5	
		$CD_3CO^+ + SiH_3CD_3$	0.20			
$(C_2D_5)_2O$	200.2^{e}	$C_2D_5OC_2D_4^+ + SiH_3D$	f	15.2 ± 1.6	15.3	
		$C_2D_5OCD_2^+ + SiH_3CD_3$				
		$C_2D_5OSiH_2^+ + CD_3CD_2H$				
		$C_2D_5OH_2^+ + HSiCD_2CD_3$				
(CH ₃) ₂ S	200.6	$CH_3SCH_2^+ + SiH_4$	0.86	17.2 ± 1.5	15.8	
		$HSSiH_3^+ + C_2H_5$	0.14			
(C ₂ H ₅) ₂ CO	201.4	$(C_2H_5)_2COH^+ + SiH_2$	0.56	14.4 ± 1.3	20.3	
		$H_2SiOH^+ + C_4H_{10}$	0.24			
		$(C_{1}H_{9})$,COSiH ₁ ⁺	0.20			
(<i>n</i> -Pr) ₂ O	202.3	$(C_{3}H_{7})_{2}OH^{+} + SiH_{2}$	0.42	15.0 ± 1.4	17.5	
		$C_3H_7^+ + H_3SiOC_3H_7$	0.44			
		$C_3H_7OC_3H_6^+ + SiH_3D$	0.07			
		$C_3H_7OH_2^+ + HSiC_3H_7$	0.07			
NH ₃	204	$NH_4^+ + SiH_2$	0.74	6.0 ± 0.5	17.6	
		$H_{siNH_{s}}^{+} + H_{s}$	0.26			

^a All proton affinity values from ref 10. In units of kcal-mol⁻¹. ^b Product distribution normalized to unity for reactant ions. ^c In units of 10^{-10} cm³-molecule⁻¹·s⁻¹. ^d Ion-polar molecule collision rate constant obtained by using the average-dipole-orientation theory: Su, T.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 347-416. ^c Proton affinity of the deuterated molecule is slightly lower. ^f The reaction sequence is too complicated to get a product distribution. Double resonance experiments indicate that nearly all of the secondary product ions undergo proton transfer to the neutral diethyl ether.

transfer and more complex processes occur in the reaction with $C_2D_5OC_2D_5$. With $(CH_3)_2S$, hydride-transfer is also a dominant reaction channel. Although a small amount of $(CH_3)_2SH^+$ is observed in this system, ion ejection experiments confirm that it results from a complex sequence of reactions and it is not a direct proton-transfer product involving SiH_3⁺. The above molecules all have proton affinities below 200.6 ± 3 kcal·mol^{-1,20} With stronger bases, proton transfer is an important reaction channel. For example, the predominant reaction (~56% of the product distribution) of SiH_3⁺ with 3-pentanone is a proton transfer, with a rate constant of 8.0×10^{-10} cm³·molecule⁻¹ s⁻¹. In the case of (*n*-Pr)₂O and NH₃, proton transfer also occurs predominantly.

There are several factors²¹ contributing to the uncertainty in deriving of a value of $\Delta H_f^{\circ}(\text{SiH}_2)$ from these experiments. These include (i) the near impossibility of pinpointing from such experiments (in which other fast reactions compete with proton transfer) the precise transition point at which proton transfer from SiH₃⁺ is thermoneutral; (2) the difficulties associated with the assignment of absolute values to the proton affinity scale,¹⁰ and (3) the uncertainties in the heat of formation of SiH₃^{+,22} The results shown in Figure 1 strongly suggest that PA((CH₃)₂S) < PA(SiH₂) < PA((C₂H₅)₂CO). Using a value of 204 ± 3 kcal·mol⁻¹ for PA(NH₃) leads to a value for PA(SiH₂) of 201 ± 3 kcal·mol⁻¹. Using a value of 234.1 kcal·mol⁻¹ for $\Delta H_f^{\circ}(\text{SiH}_2)^{23}$ in eq 2 yields $\Delta H_f^{\circ}(\text{SiH}_2)$



Figure 1. Variation with base strength of the reaction efficiency (defined as the ratio of the rate constant to the calculated collision rate) for proton transfer from SiH_3^+ to various n-donor bases. Base strengths (proton affinities) are given relative to NH_3 [PA(NH₃) = 204 ± 3 kcal·mol⁻¹].

= 69 ± 3 kcal·mol⁻¹. This is 11 kcal·mol⁻¹ higher than the previously accepted value (58 kcal·mol⁻¹),² but in good agreement with the recent theoretical value (68.1 kcal·mol⁻¹) recommended by Ho et al.⁶ With this value and $\Delta H_{\rm f}^{0}_{298}({\rm SiH}_{4})$ = 8.2 kcal· mol⁻¹,^{2.6} the enthalpy of the decomposition reaction 4 is 60.8 ±

$$SiH_4 \rightarrow SiH_2 + H_2$$
 (4)

3 kcal·mol⁻¹ at 298 K, which is close to the activation energy (59.5 kcal·mol⁻¹) for silane pyrolysis obtained by Newman et al.²⁴ This

⁽²⁰⁾ $PA((CH_3)_2S) = 200.6 \pm 3 \text{ kcal-mol}^{-1}$; with $\Delta H_1^{\circ}_{298}(SiH_2) = 58 \text{ kcal-mol}^{-1}$, the expected proton affinity of silylene is 189.6 kcal-mol}^{-1}.

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result strongly favors silvlene chemistry, as opposed to silvl radical chemistry, as the primary decomposition reaction in silane pyrolysis. Using a similar approach, Hehre et al.¹² have determined the proton affinity of dimethylsilylene to be 232 kcal-mol⁻¹. The effect of methyl substitution (31 kcal·mol⁻¹) is close to that observed in comparing H_2S to $(CH_3)_2S$ (30.4 kcal·mol⁻¹). Combining the known heat of formation²⁵ $\Delta H_{f}^{\circ}_{298}(\text{SiH}_{2}^{+}) = 276.3 \text{ kcal·mol}^{-1}$ with the heat of formation of SiH₂ derived in this study yields an adiabatic ionization potential of 8.99 eV for SiH₂. This is in excellent agreement with the value 8.98 eV predicted by ab initio

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calculation at the MRD-CI level.26

The results of the present study signal another triumph for high-quality ab initio calculations as a reliable approach to predicting the thermochemical properties of reaction intermediates. With the necessary blessing granted by experimental certification, some changes in the estimated thermochemistry of processes involving silvlene are recommended. Related studies of substituted silylenes are in progress in our laboratory.

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FEATURE ARTICLE

Some Comments on Multicomponent Diffusion: Negative Main Term Diffusion Coefficients, Second Law Constraints, Solvent Choices, and Reference Frame Transformations

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We discuss some interesting aspects of multicomponent diffusion in liquids. These include the existence of a negative main term diffusion coefficient; the utility of taking different components as the solvent; the change-of-solvent transformation for Fick's law coefficients and Onsager coefficients; the validity of the Onsager reciprocal relations on changing solvents; and the calculation of partial molar volumes from diffusion data. For this, we first survey previous work on the irreversible thermodynamic basis for macroscopic diffusion; the importance of reference frames and transformations among them; and second law conditions on the volume-fixed diffusion coefficient matrix. Certain diffusion descriptions in other reference frames do not preserve these second law conditions.

I. Introduction

Diffusion is one of the major transport processes in liquids. Such processes, especially in multicomponent systems, are increasingly recognized as significant in the earth sciences, biology, nuclear waste isolation, and chemical engineering. Unfortunately, multicomponent diffusion is more complicated than is often realized. For example, a ternary system (two solutes in a solvent) has four diffusion coefficients, not just two. The cross terms can be large and be positive or negative, thus having a substantial effect on flows of matter.

The experimental investigation of liquid diffusion in binary systems began with Graham³ in 1850 and its theoretical description

began with Fick⁴ in 1855. However, the possibility of cross terms in multicomponent systems was not even suggested until 1932 by Onsager and Fuoss.⁵ The experimental verification of their existence by Gosting and collaborators^{6,7} was as recent as 1955, a century after Fick. Precision experimental work did not begin until the late 1940's, following the design and construction of optical interferometers. Experimental matters are nicely described by Dunlop et al.8 and Tyrrell and Harris.9

Among the complications of multicomponent liquid diffusion is the issue of reference frames. The one closest to most exper-

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