Precise Determination of Stabilities of Primary, Secondary, and Tertiary Silicenium Ions from Kinetics and Equilibria of Hydride-Transfer Reactions in the Gas Phase. A Quantitative Comparison of the Stabilities of Silicenium and Carbonium Ions in the Gas Phase

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Abstract: Fourier transform ion cyclotron resonance spectroscopy has been used to examine kinetics and equilibria of hydride-transfer reactions of methyl-substituted silanes with various hydrocarbons having well-established gas-phase hydride affinities. The derived hydride affinities, $D(R_3Si^+–H^-)$, for the silicenium ions $SiMeH_2^+$, $SiMe_2H^+$, and $SiMe_3^+$ are 245.9, 230.1, and 220.5 kcal/mol, respectively, to be compared with the values of 270.5, 251.5, and 233.6 kcal/mol for the corresponding carbonium ions. This indicates that the silicenium ions are significantly more stable than the corresponding carbonium ions in the gas phase with H^- as a reference base.

Carbonium ions are well-established reactive intermediates and their properties have been extensively studied both in solution[1] and in the gas phase.[2] In contrast, exhaustive experimental attempts to generate even detectable concentrations of silicenium ions (R_3Si^+) in solution, under conditions where analogous carbonium ions are long-lived, have been unsuccessful.[3] The factors responsible for the apparently exceedingly low stability of silicenium ions in solution as compared with their carbon analogues have been debated as the "silicenium ion question".[3b] Much of the progress in this field is fairly recent. Lambert et al.[4] reported preparation of two persistent silicenium ions (i,e,, $(i\text{-PrS})_3Si^+$ and Ph_3Si^+) by the Corey method[5] involving hydride transfer from the silane to the trityl cation (Ph_3C^+). Barton and co-workers[6] proposed cyclopropylsilicenium ions as possible reaction intermediates in reactions of a variety of (chloromethyl)vinylsilanes with $AlCl_3$. Eaborn et al.[7] provided evidence for the formation of methoxy-bridged silicon-containing cations in the alcoholysis of organosilicon halides and the detection of methyl-bridged species. Evidence has been presented by Apeloig et al.[8] for the solvolytic generation of the silicenium ion via 1,2-methyl migration in a solvolytically produced α-silyl carbonium ion. The transient formation of silicenium ions, which may be modified by interactions with solvent, has been suggested by Chojnowski et al.[9] in the hydride-transfer reaction of organosilyl hydrides with carbonium ions having various complex counterions in CH_2Cl_2. The synthesis of cyclic silyl ethers from acyclic precursors has been accomplished by Chen and Barton[10] via catalytic, in situ, formation of transient silicenium ions. Most recently, Lambert et al.[11] demonstrated that the ionic triphenylsilyl perchlorate form is favored at low concentrations in polar solvents of low nucleophilicity but that association occurs at the high concentrations, which had been used by Prakash et al.[12] in their ^{29}Si and ^{35}Cl NMR spectroscopic study of triphenylsilyl perchlorate. This recent progress in the solvolytic generation of silicenium ions calls for a reconsideration of silicenium ions as viable reaction intermediates and draws attention to the relative stabilities of carbonium and silicenium ions both in solution and in the gas phase.

Studies of the positive ion chemistry of methylsilanes utilizing ion cyclotron resonance techniques[13] have provided information regarding the relative stabilities of methyl-substituted silicenium ions in the absence of complicating solvation phenomena.[14,15] The ion stability order (determined by the energetics of binding H^- as a reference base), $CH_3^+ < CMeH_2^+ < SiH_3^+ < CMe_2H^+ < SiMeH_2^+ < CMe_3^+ < SiMe_2H^+ < SiMe_3^+$, has been determined from investigations of hydride-, chloride-, and fluoride-exchange reactions between substituted carbonium and silicenium ions[14,15] and from photoionization mass spectrometric studies of silanes in our laboratory.[16] Results obtained through bracketing techniques are less reliable and precise than those obtained through equilibria measurements because of numerous possible complications.[17] Also, the interpretation of photoionization thresholds requires detailed considerations of both the dynamics and energetics of photofragmentation processes to obtain accurate heats

(1) *Carbonium Ions*; Olah, G. A.; Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1976.
(2) *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vols. 1 and 2; 1984; Vol. 3.
(3) (a) Sommer, L. H. *Stereochemistry, Mechanisms, and Silicon*; McGraw-Hill: New York, 1965, and earlier references therein. (b) Corriu, R. J. P.; Henner, M. *J. Organomet. Chem.* **1974**, *74*, 1, and references therein. (c) Bickart, P.; Llort, F. M.; Mislow, K. *Ibid.* **1976**, *116*, C1. (d) Cowley, A. H.; Cushner, M. C.; Riley, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 624, and references therein.
(4) (a) Lambert, J. B.; McConnell, J. A.; Schulz, W. J., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 2482. (b) Lambert, J. B.; Schulz, W. J., Jr. *Ibid.* **1983**, *105*, 1671.
(5) Corey, J. Y. *J. Am. Chem. Soc.* **1975**, *97*, 3237.
(6) Robinson, L. R.; Burns, G. T.; Barton, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 3935.
(7) (a) Eaborn, C.; Lickiss, P. D.; Najim, S. T.; Romanelli, M. N. *J. Chem. Soc., Chem. Commun.* **1985**, 1754. (b) Dhaher, S. M.; Eaborn, C.; Smith, J. D. *J. Chem. Soc., Chem. Commun.* **1987**, 1183, and earlier references therein.
(8) Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1987**, *109*, 272.
(9) Chojnowski, J.; Fortuniak, W.; Stańczyk, W. *J. Am. Chem. Soc.* **1987**, *109*, 7776.
(10) Chen, Y.-L.; Barton, T. J. *Organometallics* **1987**, *6*, 2590.
(11) Lambert, J. B.; Schulz, W. J., Jr.; McConnell, J. A.; Schilf, W. *J. Am. Chem. Soc.* **1988**, *110*, 2201.
(12) Prakash, G. K. S.; Keyaniyan, S.; Aniszfeld, R.; Heiliger, L.; Olah, G. A.; Stevens, R. C.; Choi, H.-K.; Bau, R. *J. Am. Chem. Soc.* **1987**, *109*, 5123.
(13) For reviews of ion cyclotron resonance spectroscopy, see: (a) Beauchamp, J. L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 527. (b) Lehman, T. A.; Bursey, M. M. *Ion Cyclotron Resonance Spectrometry*; Wiley: New York, 1976. (c) Marshall, A. G. *Acc. Chem. Res.* **1985**, *18*, 316, and references therein.
(14) (a) Murphy, M. K. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1977. (b) Corderman, R. R.; Murphy, M. K.; Beauchamp, J. L., unpublished results. Corderman, R. R. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1977.
(15) Eyler, J. R.; Silverman, G.; Battiste, M. A. *Organometallics* **1982**, *1*, 477.
(16) Corderman, R. R.; Shin, S. K.; Beauchamp. J. L., to be submitted for publication in *J. Am. Chem. Soc.* In addition, the silylene cation (e.g. SiR_2^+, R = H and CH_3) stability order was included.
(17) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

0002-7863/89/1511-0900$01.50/0

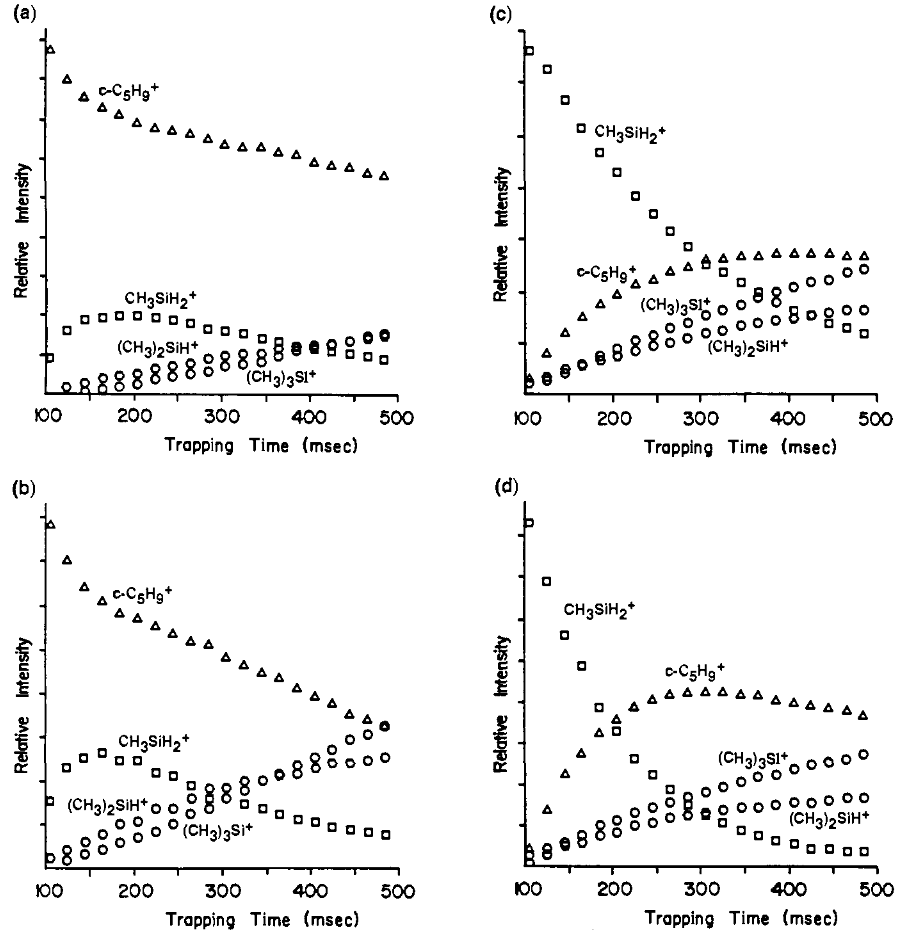

Figure 1. Temporal variations of reactant and product ion abundances starting with either the c-$C_5H_9^+$ ion (a,b) or the $CH_3SiH_2^+$ ion (c,d) in the hydride-transfer reaction 2 and the subsequent side reactions: (a) P(c-C_5H_{10}) = 2.0×10^{-7} Torr and $P(CH_3SiH_3)$ = 3.1×10^{-7} Torr; (b) P(c-C_5H_{10}) = 2.0×10^{-7} Torr and $P(CH_3SiH_3)$ = 6.2×10^{-7} Torr; (c) P(c-C_5H_{10}) = 2.0×10^{-7} Torr and $P(CH_3SiH_3)$ = 3.1×10^{-7} Torr; (d) P(c-C_5H_{10}) = 4.0×10^{-7} Torr and $P(CH_3SiH_3)$ = 3.1×10^{-7} Torr.

of formation of the fragments ions.[18,19] Measurement of ion–molecule reaction equilibria is a proven experimental methodology for the determination of accurate thermochemical properties of various carbonium ions.[20,21] In particular, hydride-transfer equilibria[20] directly provide precise *relative* hydride affinities. Reference hydride affinity values are provided by accurate heats of formation available for numerous carbonium ions, obtained from the known heats of formation and ionization potentials of the corresponding radicals, in addition to the well-established homolytic C–H bond dissociation energies of the corresponding alkanes.[23]

Fourier transform ion cyclotron resonance spectroscopy[13c] has been used in the present work to examine kinetics and equilibria of hydride-transfer reactions of methylsilanes with various hydrocarbons having well-established gas-phase hydride affinities.[22] Hydride affinities of primary, secondary, and tertiary silicenium ions obtained from these experiments permit a precise determination of gas-phase stabilities of the silicenium ions. These values serve to compare the stabilities of silicenium and carbonium ions in the gas phase. The derived heats of formation for the silicenium ions combined with heats of formation for silylenes[24] allow estimation of proton affinities for silylenes and silaethylenes,[24,25] which can be compared with their carbon analogues.[17]

Because of the interest in thermal decomposition processes of silanes, we discuss several pyrolysis mechanisms in the Appendix, using reaction enthalpies estimated from heats of formation of silanes, silylenes, and silaethylenes, and the available Arrhenius parameters for various thermal decomposition processes.

Experimental Section

Experimental techniques associated with ICR spectroscopy,[13] and in particular Fourier transform ion cyclotron resonance spectroscopy,[13c] have been previously described in detail. Experiments were performed with an Ion Spec FT-ICR data system in conjunction with a 1-in. cubic trapping cell[26] built by Bio-Med Tech[27] situated between the poles of a Varian 15-in. electromagnet maintained at 2 T. Where available, chemicals were obtained commercially in high purity and used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensable gases. CH_3SiH_3 was prepared by reducing CH_3SiCl_3 with $LiAlH_4$.[28] Pressures were measured with a Schulz–Phelps ion gauge[29] calibrated

(18) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, Supplement 1.

(19) (a) Chupka, W. A.; Berkowitz, J. *J. Chem. Phys.* **1967**, *47*, 2921. (b) Chupka, W. A. *Ibid.* **1971**, *54*, 1936. (c) Chupka, W. A. *Ibid.* **1959**, *30*, 191. (d) Rosenstock, H. M.; Larkins, J. T.; Walker, J. A. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *11*, 309.

(20) (a) Aue, D. H.; Bowers, M. T. *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Chapter 9. (b) McMahon, T. B.; Kebarle, P. *J. Am. Chem. Soc.* **1985**, *107*, 2612. (c) McMahon, T. B.; Blint, R. J.; Ridge, D. P.; Beauchamp, J. L. *Ibid.* **1972**, *94*, 8934. (d) Blint, R. J.; McMahon, T. J.; Beauchamp, J. L. *Ibid.* **1974**, *96*, 1269.

(21) (a) Sharma, R. B.; Sen Sharma, D. K.; Hiraoka, K.; Kebarle, P. *J. Am. Chem. Soc.* **1985**, *107*, 3747, and references therein. (b) Sen Sharma, D. K.; Meza de Höjer, S.; Kebarle, P. *Ibid.* **1985**, *107*, 3757. (c) Solomon, J. J.; Field, F. H. *Ibid.* **1976**, *98*, 1567. (d) Meot-Ner, M. *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Chapter 6.

(22) See Table II and discussion section.

(23) See Table III.

(24) (a) Shin, S. K.; Beauchamp, J. L. *J. Phys. Chem.* **1986**, *90*, 1507. (b) Shin, S. K.; Irikura, K. K.; Beauchamp, J. L.; Goddard, W. A., III *J. Am. Chem. Soc.* **1988**, *110*, 24.

(25) (a) Pau, C. F.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1983**, *105*, 16. (b) Pietro, W. J.; Pollack, S. K.; Hehre, W. J. *Ibid.* **1979**, *101*, 7126.

(26) Comisarow, M. B. *Int. J. Mass. Spectrom. Ion Phys.* **1981**, *37*, 251.

(27) Bio-Med Tech, 2001 E. Galbreth, Pasadena, CA 91104.

(28) Gaspar, P. P.; Levy, C. A.; Adair, G. M. *Inorg. Chem.* **1970**, *9*, 1272.

Table I. Thermochemical Data from Kinetics and Equilibira of Hydride-Transfer Reactions: $R^+ + (CH_3)_nSiH_{4-n} \rightleftharpoons (CH_3)_nSiH_{3-n}^+ + RH$

R^+	$(CH_3)_nSiH_{3-n}^+$	k_f^a	k_r^a	K	$\Delta G_{298}°$, kcal/mol	$\Delta S°$, eu	$\Delta H°$, kcal/mol
$c\text{-}C_5H_9^+$	$CH_3SiH_2^+$	1.4	5.4	0.28	0.8	−0.6	0.6
$t\text{-}C_4H_9^+$	$(CH_3)_2SiH^+$	6.0	0.036	167	−3.0	1.4	−2.6
$p\text{-}CH_3C_6H_4CH_2^+$	$(CH_3)_2SiH^+$	2.6	1.1	2.4	−0.5	0.8	−0.3
$C_6H_5C(CH_3)_2^+$	$(CH_3)_3Si^+$	0.41	0.56	0.74	0.2	3.0	1.1

[a] Units 10^{-10} cm^3 molecule^{-1} s^{-1}.

against an MKS Baratron (Model 390 HA-0001) capacitance manometer. The principal errors in the rate constants (estimated to be ±20%) arise from uncertainties in pressure measurements.[30] Mixtures of methylsilanes and hydrocarbons were used with a total pressure in the range $1\text{-}5 \times 10^{-6}$ Torr. Ionization was by electron impact at 15–25 eV. The reaction temperature in the ICR cell is assumed to be 298 K.

Although other reactions are noted below, this study focused on the hydride-transfer equilibria between methylsilanes and various hydrocarbons. Methylsilanes ionized by electron impact are convenient sources of silicenium ions.[24,31,32] Various carbonium ions are generated by either electron impact ionization or hydride-transfer reactions.

Ion ejection pulses were used to remove all species except selected silicenium or carbonium ions from the ICR cell.[33] Translational excitation of the reactant ion was minimized by using the lowest possible radio frequency fields. The temporal variations of reactant and product ion abundances starting from either the carbonium ion R^+ or the silicenium ion $(CH_3)_nSiH_{3-n}^+$ ion (n = 1–3) in the hydride-transfer reaction 1 were recorded and used to calculate forward and reverse rate constants

$$R^+ + (CH_3)_nSiH_{4-n} \rightleftharpoons (CH_3)_nSiH_{3-n}^+ + RH \qquad (1)$$

and equilibrium constant therefrom. The occurrence of side reactions consuming the reactant or product ions in the reaction mixtures used for the measurements of hydride-transfer equilibria is unavoidable and complicates the measurements. However, the reaction rate constants from the separate forward and reverse hydride-transfer reactions made it possible to calculate the precise equilibrium constants. For example, the temporal variations of reactant and product ion abundances in the hydride-transfer reaction of $c\text{-}C_5H_9^+$ with methylsilane (forward process 2) and $CH_3SiH_2^+$ with cyclopentane (the reverse of process 2) are shown

$$c\text{-}C_5H_9^+ + CH_3SiH_3 \rightleftharpoons CH_3SiH_2^+ + c\text{-}C_5H_{10} \qquad (2)$$

$$CH_3SiH_2^+ + CH_3SiH_3 \rightarrow (CH_3)_2SiH^+ + SiH_4 \qquad (3)$$

in Figure 1 with the subsequent reaction products. Since the partial pressures of the reactant neutrals are kept constant during the experiment, we used the general solution for the first-order series and parallel reaction schemes to analyze the experimental data.[34]

Results and Discussion

Reactions. Reaction rates and equilibrium constants for the hydride-transfer process 1 are summarized in Table I with other thermochemical properties.

$CH_3SiH_2^+$ reacts with cyclopentane to yield $c\text{-}C_5H_9^+$ with a rate constant of 5.4×10^{-10} cm^3 molecule^{-1} s^{-1} and undergoes sequential reactions with CH_3SiH_3 to produce $(CH_3)_2SiH^+$ and $(CH_3)_3Si^+$. $c\text{-}C_5H_9^+$ generated from the hydride-transfer reaction of $C_3H_7^+$ with cyclopentane reacts with CH_3SiH_3 via exclusive hydride transfer with a rate constant of 1.4×10^{-10} cm^3 molecule^{-1} s^{-1}.

The reactions of $(CH_3)_2SiH^+$ in the 1:10 $(CH_3)_2SiH_2$–isobutane mixtures produce $t\text{-}C_4H_9^+$ and $(CH_3)_3Si^+$ with rate constants of 3.6×10^{-12} and 2.0×10^{-10} cm^3 molecule^{-1} s^{-1}, respectively. The reverse reaction of $t\text{-}C_4H_9^+$ with $(CH_3)_2SiH_2$ is exclusively via hydride transfer with a rate constant of 6.0×10^{-10} cm^3 molecule^{-1} s^{-1}. Since the hydride-transfer reaction of $t\text{-}C_4H_9^+$ with $(CH_3)_2SiH_2$ is estimated to be exothermic by 2.6 kcal/mol,[35] $p\text{-}CH_3C_6H_4CH_2^+$, the hydride affinity of which is 3.2 kcal/mol lower than that of $t\text{-}C_4H_9^+$,[35] is used to observe the near-thermoneutral hydride-transfer reaction with $(CH_3)_2SiH_2$. In the reactions of $(CH_3)_2SiH^+$ with p-xylene–$(CH_3)_2SiH_2$ mixtures, the desired hydride-transfer product $p\text{-}CH_3C_6H_4CH_2^+$ ($k = 1.1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) and $(CH_3)_3Si^+$ were observed. $(CH_3)_3Si^+$ reacted further to yield a p-xylene–$Si(CH_3)_3^+$ adduct. The predominant reaction of $p\text{-}CH_3C_6H_4CH_2^+$, generated from the electron impact ionization of p-xylene, with $(CH_3)_2SiH_2$ is hydride transfer ($k = 2.6 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}).

Finally, $(CH_3)_3Si^+$ reacts with cumene to give rise to a hydride-transfer product $C_6H_5C(CH_3)_2^+$ ($k = 5.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) and a cumene–$Si(CH_3)_3^+$ adduct. The occurrence of hydride transfer is predominant ($k = 4.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) in the reaction of $C_6H_5C(CH_3)_2^+$, isolated after long reaction time delay from the $(CH_3)_3Si^+$–cumene reaction products, with $(CH_3)_3SiH$. This hydride-transfer reaction was confirmed by the reaction of $C_6H_5C(CH_3)_2^+$, generated from the electron impact ionization of $C_6H_5C(CH_3)_3$, with $(CH_3)_3SiH$. In the reactions of silicenium ions with the substituted benzenes, there are no indications of problems associated with either the electron-transfer or the proton transfer reactions, which are known to complicate hydride-transfer equilibria measurements in studies of the corresponding carbonium ions.[21a]

Hydride Affinities and Heats of Formation of Silicenium Ions. Equilibrium constants for the hydride-transfer reactions are obtained from the calculated forward and reverse rate constants. The $\Delta G_{298}°$ values given in Table I for the hydride-transfer reactions are derived from equilibrium constants and estimated to have uncertainties of less than 0.5 kcal/mol arising from errors in the rate constants. Using the $\Delta S°$ values estimated on the basis of symmetry numbers[36] leads to the $\Delta H°$ values given in Table I. For the reaction 2 of $c\text{-}C_5H_9^+$ with CH_3SiH_3, the $\Delta S°$ value is estimated by combining the experimental $\Delta S°$ value for the reaction 4[21a] with the evaluated $\Delta S°$ value for the reaction 5 based on symmetry numbers (σ). For the substituted benzyl ions, apart

$$c\text{-}C_5H_9^+ + C_3H_8 \rightleftharpoons s\text{-}C_3H_7^+ + c\text{-}C_5H_{10} \quad \Delta S° = -1.4 \qquad (4)$$

$$\underset{\sigma = 18}{s\text{-}C_3H_7^+} + \underset{9}{CH_3SiH_3} \rightleftharpoons \underset{6}{CH_3SiH_2^+} + \underset{18}{C_3H_8} \quad \Delta S° = \underset{0.8}{R \ln (^3/_2)} \qquad (5)$$

$$c\text{-}C_5H_9^+ + CH_3SiH_3 \rightleftharpoons CH_3SiH_2^+ + c\text{-}C_5H_{10} \quad \Delta S° = -0.6(\text{eu}) \qquad (2)$$

from symmetry numbers, it is also assumed that a loss of entropy due to restricted internal rotations in the benzyl cation is 3 eu.[21a] Uncertainties of the $\Delta H°$ values coming from those of the $\Delta G°$ values and $\Delta S°$ estimates, which may be in error by as much as 3 eu,[21a] are expected to be ~1 kcal/mol.

The hydride affinities for methyl-substituted silicenium ions are derived from the $\Delta H°$ values in Table I and the hydride affinities for the reference hydrocarbons with aid of relationship 6 for the reaction 1. The reaction of $p\text{-}CH_3C_6H_4CH_2^+$ with

$$D(\mathrm{Me}_nSiH_{3-n}^+\text{–}H^-) = D(R^+\text{–}H^-) + \Delta H°(1) \qquad (6)$$

$(CH_3)_2SiH_2$ provides the $\Delta H°$ value used to calculate the hydride affinity of $(CH_3)_2SiH^+$. The hydride affinity of 245.3 kcal/mol for $c\text{-}C_5H_9^+$ is obtained by combining the hydride affinity of $s\text{-}C_3H_7^+$ in Table II with the $\Delta H°$ value of −6.2 kcal/mol for the hydride-transfer reaction of $s\text{-}C_3H_7^+$ with cyclopentane,[21a] with an estimated error of ±1 kcal/mol. The value of 230.4 kcal/mol for $D(p\text{-}CH_3C_6H_4CH_2^+\text{–}H^-)$ is calculated by adding the relative chloride affinity[21a] of −6.5 kcal/mol for $p\text{-}CH_3C_6H_4CH_2^+$ with

(29) Schulz, G. J.; Phelps, A. V. *Rev. Sci. Instrum.* **1957**, *28*, 1051.
(30) Blint, R. J.; McMahon, T. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 1269.
(31) (a) Potzinger, P.; Lampe, F. W. *J. Phys. Chem.* **1970**, *74*, 587. (b) Mayer, T. M.; Lampe, F. W. *Ibid.* **1974**, *78*, 2422, 2429.
(32) Litzow, M. R.; Spalding, T. R. *Mass Spectrometry of Inorganic and Organometallic Compounds*; Elsevier: Amsterdam, The Netherlands, 1973.
(33) Cody, R. B.; Burnier, R. C.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 96.
(34) Frost, A. A.; Pearson, R. G. *Kinetics and Mechanism*; 2nd ed.; Wiley: New York, 1961.
(35) See Table II.

(36) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976; p 47.

Table II. Hydride Affinities and Heats of Formation Used in Text

R	$D(R^+-H^-)$,[a] kcal/mol	$\Delta H_f°_{298}(RH)$,[b] kcal/mol	$\Delta H_f°_{298}(R^+)$, kcal/mol
SiH_3	261.4[c]	8.2	234.9[c]
C_2H_5	270.5[d]	−20.24	215.6[d]
s-C_3H_7	251.5[d]	−24.83	192.0[d]
CH_3SiH_2	245.9[e]	−7.0	204 ± 1[e]
c-C_5H_9	245.3[f]	−18.44	191.9[g]
$C_6H_5CH_2$	236.9[h]	11.99	214.2[i]
t-C_4H_9	233.6[d]	−32.41	166.5[d]
p-$CH_3C_6H_4CH_2$	230.4[f]	4.31	200.0[g]
$(CH_3)_2SiH$	230.1[e]	−23.0	172 ± 2[e]
$(CH_3)_3Si$	220.5[e]	−39.0	147 ± 3[e]
$C_6H_5C(CH_3)_2$	219.4[f]	0.96	185.7[f]

[a] Accuracy of hydride affinities estimated as ±1 kcal/mol except ±2 kcal/mol for p-$CH_3C_6H_4CH_2^+$ and $(CH_3)_2SiH^+$ and ±3 kcal/mol for $C_6H_5C(CH_3)_2^+$ and $(CH_3)_3Si^+$. [b] Heats of formation for hydrocarbons from Cox and Pilcher[48] and those for methylsilanes from Walsh.[46] [c] Reference 16. [d] See Table III. [e] This work. [f] See text. [g] $\Delta H_f°_{298}(R^+) = D(R^+-H^-) + \Delta H_f°_{298}(RH) - \Delta H_f°_{298}(H^-)$; $\Delta H_f°_{298}(H^-) = 34.7$ kcal/mol. [h] From $\Delta H_f°_{298}(C_6H_5CH_2^+)$. [i] Derived from the $\Delta H°$ value of −0.5 kcal/mol for the chloride-transfer reaction of t-$C_4H_9^+$ with $C_6H_5CH_2Cl$ and heats of formation for t-$C_4H_9^+$ in Table II, C_4H_9Cl, and $C_6H_5CH_2Cl$ from Cox and Pilcher.[48]

respect to $C_6H_5CH_2^+$ to the hydride affinity of 236.9 kcal/mol for $C_6H_5CH_2^+$, assuming equality of the relative chloride and hydride affinities of $C_6H_5CH_2^+$ and p-$CH_3C_6H_4CH_2^+$,[37] and may be in error by 2 kcal/mol mainly due to uncertainties in this assumption. The hydride affinity for $C_6H_5C(CH_3)_2^+$ is evaluated from heats of formation of $C_6H_5C(CH_3)_2^+$ and cumene in Table II. Values of 207.0 and 27.0 kcal/mol for the proton affinity[17] and the heat of formation[38] of 2-methylstyrene, respectively, lead to a value of 185.7 kcal/mol for $\Delta H_f°_{298}(C_6H_5C(CH_3)_2^+)$. The calculated hydride affinity for $C_6H_5C(CH_3)_2^+$ is 219.4 kcal/mol and has an error estimate of ±3 kcal/mol due to uncertainties in the absolute proton affinity scales.[17]

The derived hydride affinities for the silicenium ions $SiMeH_2^+$, $SiMe_2H^+$, and $SiMe_3^+$ are 245.9, 230.1, and 220.5 kcal/mol, respectively, and listed in Table II. These values are significantly lower than the hydride affinities of 270.5, 251.5, and 233.6 kcal/mol in Table III for the analogous carbonium ions $C_2H_5^+$, s-$C_3H_7^+$, and t-$C_4H_9^+$, respectively, which indicates that *the silicenium ions are much more stable than the corresponding carbonium ions in the gas phase when* H^- *is used as a reference base.* Heats of formation for the silicenium ions in Table II are calculated from hydride affinities of silicenium ions and heats of formation of methylsilanes in Table II. The calculated heats of formation for silicenium ions are 204 ± 1, 172 ± 2, and 147 ± 3 kcal/mol for $SiMeH_2^+$, $SiMe_2H^+$, and $SiMe_3^+$, respectively. The heat of formation of $SiMe_3^+$ is in excellent agreement with a value of 145.0 kcal/mol derived from the photoionization mass spectrometric study of trimethylsilane in our laboratory[16] but slightly lower than the reported value of 150.5 kcal/mol estimated from the unimolecular decomposition of the $SiMe_3Br^+$ molecular ion using the photoelectron–photoion coincidence technique by Szepes and Baer.[39] Uncertainties of the derived hydride affinities and heats of formation for the silicenium ions mainly arise from those of reference hydride affinities for the corresponding carbonium ions used in the hydride-transfer equilibria measurements.

A Quantitative Comparison of the Stabilities of Silicenium and Carbonium Ions in the Gas Phase. A comparison of hydride affinities derived in this study for silicenium ions (Table II) with literature data for the analogous carbonium ions (Table III) is shown in Figure 2. Consider the hydride affinity data for the carbonium ions in Table III. In the series CH_3^+, $CMeH_2^+$, CMe_2H^+, and CMe_3^+, successive replacements of H in CH_3^+ by

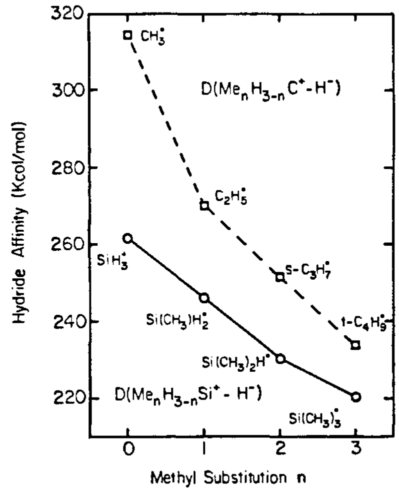

Figure 2. Hydride affinities of carbonium ions and silicenium ions.

a methyl group decrease the hydride affinity by 44.2, 19.0, and 17.9 kcal/mol, following in order. Since the incremental decrease in hydride affinity (ΔHA) directly reflects the difference between $D(R_2C^+-CH_3) - D(R_2HC-CH_3)$ (where R = H, CH_3) and $D(R_2C^+-H) - D(R_2HC-H)$,[40] this ΔHA is an index of an extra stabilization of the carbonium ions by methyl substitution. This extra stabilization effected by successive methyl substitution appears to be consistently smaller for silicenium ions than carbonium ions, presumably due to poorer spatial overlap of occupied substituent orbitals with an empty Si^+ 3p orbital relative to C^+ 2p orbital because of the greater size of Si 3p orbital and the longer Si–C bond. For example, the introduction of a first CH_3 on CH_3^+ in place of H decreases $D(C_2H_5^+-H^-)$ 44.2 kcal/mol below $D(CH_3^+-H^-)$ as compared with the 15.5 kcal/mol decrease in going from SiH_3^+ to $CH_3SiH_2^+$. This difference in methyl substituent effect between $C_2H_5^+$ and $CH_3SiH_2^+$ may result from extensive σ(C–H) participation[41] in $C_2H_5^+$, which favors a fully delocalized, two-electron, three-center nonclassical hydrogen-bridged ion. On the other hand, the C–H bonding electrons in $CH_3SiH_2^+$ are less effectively available to the empty Si^+ 3p orbital and favor a classical methylsilicenium ion. Both the nonclassical hydrogen-bridged $C_2H_5^+$[42] and the classical $CH_3SiH_2^+$[43] are found to lie at minima on their respective potential energy surfaces from theoretical calculations.

Comparison of Proton Affinities of Silylene and Silaethylene with Their Carbon Analogues. The proton affinities of 201 ± 3, 215 ± 4, and 205 ± 3 kcal/mol for SiH_2, $SiHCH_3$, and $H_2C{=}SiH_2$, respectively, have been determined from the deprotonation energetics of SiH_3^+ and $CH_3SiD_2^+$ using Fourier transform ion cyclotron resonance spectroscopy[21] and used to calculate heats of formation of silylenes. Assuming a constant CH_3 for H replacement energy of 16 kcal/mol in silylenes yields a heat of formation of 37 kcal/mol for $Si(CH_3)_2$, which is significantly higher than Walsh's recent estimate[44] of 26 ± 2 kcal/mol. The experimental value of 232 ± 3 kcal/mol for $PA(Si(CH_3)_2)$ by Hehre and co-workers[25a] supports the higher value of the heat of formation for $Si(CH_3)_2$, which leads to the proton affinity of 231 kcal/mol from heats of formation data in Table IV using eq 7.

$$PA(R) = \Delta H_f°_{298}(R) + \Delta H_f°_{298}(H^+) - \Delta H_f°_{298}(RH^+) \quad (7)$$

The proton affinities for silaethylenes are derived from heats of

(37) Hayashibara, K.; Kruppa, G. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 5441.
(38) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279.
(39) Szepes, L.; Baer, T. *J. Am. Chem. Soc.* **1984**, *106*, 273.
(40) $D(R_2C^+-CH_3) - D(R_2HC-CH_3) - (D(R_2C^+-H) - D(R_2HC-H)) = \Delta H_f°_{298}(R_2(CH_3)CH) - \Delta H_f°_{298}(R_2(CH_3)C^+) - (\Delta H_f°_{298}(R_2CH_2) - \Delta H_f°_{298}(R_2HC^+)) = D(R_2HC^+-H^-) - D(R_2(CH_3)C^+-H^-) = \Delta HA$.
(41) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper & Row: New York, 1981.
(42) (a) Lischka, H.; Köhler, H. J. *J. Am. Chem. Soc.* **1978**, *100*, 5297. (b) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *Ibid.* **1981**, *103*, 5649.
(43) Hopkinson, A. C.; Lien, M. H. *J. Org. Chem.* **1981**, *46*, 998.
(44) (a) Baggott, J. E.; Blitz, M. A.; Frey, H. M.; Lightfoot, P. D.; Walsh, R. *Chem. Phys. Lett.* **1987**, *135*, 39. (b) Walsh, R. *Organometallics* **1988**, *7*, 75.

Table III. Thermochemical Data for Alkanes Used in Text

molecule (R)	$\Delta H_f°_{298}$(RH),[a] kcal/mol	$\Delta H_f°_{298}$(R), kcal/mol	D(R–H),[b] kcal/mol	IP(R), eV	$\Delta H_f°_{298}(R^+)$,[c] kcal/mol	$D(R^+–H^-)$,[d] kcal/mol
CH_3	−17.89	34.8[e]	104.8	9.842(S)[f]	261.8	314.4
$C(CH_3)H_2$	−20.24	28.4[g]	100.6	8.12[h]	215.6[i]	270.5
$C(CH_3)_2H$	−24.83	22.3[j]	99.2	7.36(PE)[k]	192.0	251.5
$C(CH_3)_3$	−32.41	12.0[l]	96.5	6.70(PE)[k]	166.5	233.6

[a] Reference 48. [b] $D(R–H) = \Delta H_f°_{298}(R) + \Delta H_f°_{298}(H) - \Delta H_f°_{298}(RH)$. [c] $\Delta H_f°_{298}(R^+) = \Delta H_f°_{298}(R) + IP(R)$. [d] $D(R^+–H^-) = \Delta H_f°_{298}(R^+) + \Delta H_f°_{298}(H^-) - \Delta H_f°_{298}(RH)$. [e] Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, supplement 2. [f] Herzberg, G.; Shoosmith, J. *Can. J. Phys.* **1956**, *34*, 523; S stands for spectroscopic measurement. [g] Brouard, M.; Lightfoot, P. D.; Pilling, M. J. *J. Phys. Chem.* **1986**, *90*, 445. [h] $IP(C_2H_5) = \Delta H_f°_{298}(C_2H_5^+) - \Delta H_f°_{298}(C_2H_5)$. The previously reported values for $IP(C_2H_5)$ are 8.39 eV detd. from Ne I photoelectron spectrum of ethyl radical generated by the pyrolysis of *n*-propyl nitrite (Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4067) and 8.26 eV measured from He I photoelectron spectrum of ethyl radical produced by the reaction of fluorine atoms with ethane (Dyke, J. M.; Ellis, A. R.; Keddar, N.; Morris, A. *J. Phys. Chem.* **1984**, *88*, 2565). [i] Reference 17. [j] Tsang, W. *J. Am. Chem. Soc.* **1985**, *107*, 2872. [k] Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4067. [l] Average value of $\Delta H_f°_{298}(t\text{-}C_4H_9)$ = 12.4 (ref *j*) and 11.6 kcal/mol: Russell, J. J.; Seetula, J. A.; Timonen, R. S.; Gutman, D.; Nava, D. F. *J. Am. Chem. Soc.* **1988**, *110*, 3084.

Table IV. Proton Affinities of Silylenes, Silaethylenes, and Their Carbon Analogues

M	$\Delta H_f°_{298}$(M), kcal/mol	$\Delta H_f°_{298}(MH^+)$,[a] kcal/mol	PA(M), kcal/mol	R	$\Delta H_f°_{298}$(R), kcal/mol	$\Delta H_f°_{298}(RH^+)$,[b] kcal/mol	PA(R),[c] kcal/mol
SiH_2	69 ± 3[d-f]	234.9[b]	201 ± 3[d]	CH_2	93.4[g]	262.1	197.0
$SiHCH_3$	53 ± 4[e]	204 ± 1	215 ± 3[e]	$CHCH_3$	85.8[h]	215.6	235.9
$Si(CH_3)_2$	37 ± 6[e]	172 ± 2	231[c]	$C(CH_3)_2$	76.6[h]	192.0	250.3
$H_2C{=}SiH_2$	43 ± 4[e]	204 ± 1	205 ± 3[e]	$H_2C{=}CH_2$	12.5[i]	215.6	162.6
$H_2C{=}SiHCH_3$	27[h]	172 ± 2	221[c]	$H_2C{=}CHCH_3$	4.9[i]	192.0	178.6
$H_2C{=}Si(CH_3)_2$	11[h]	147 ± 3	230[c]	$H_2C{=}C(CH_3)_2$	−4.3[i]	166.9	194.5

[a] This work. [b] See Table III. [c] $PA(R) = \Delta H_f°_{298}(R) + \Delta H_f°_{298}(H^+) - \Delta H_f°_{298}(RH^+)$; $\Delta H_f°_{298}(H^+)$ = 365.7 kcal/mol.[17] [d] Shin and Beauchamp.[24a] [e] Shin et al.[24b] [f] $\Delta H_f°_{298}(SiH_2)$ = 69.0 ± 2 kcal/mol (Boo, B. H.; Armentrout, P. B. *J. Am. Chem. Soc.* **1987**, *109*, 3549), 65.4 or 68.4 kcal/mol (Berkowitz et al.[14]), 65.3 ± 1.5 kcal/mol,[44b] 64.6 kcal/mol (Jasinski, J. M.; Chu, J. O. *J. Chem. Phys.* **1988**, *88*, 1678), and 65.4 ± 1.6 kcal/mol (Van Zoeren, C. M.; Thoman, J. W., Jr.; Steinfeld, J. I.; Rainbird, M. W. *J. Phys. Chem.* **1988**, *92*, 9. [g] Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Supplementary 2. [h] See text. [i] Cox and Pilcher.[48]

formation of silaethylenes and the corresponding silicenium ions and listed in Table IV. The values of 27 and 11 kcal/mol for heats of formation of $H_2C{=}SiHCH_3$ and $H_2C{=}Si(CH_3)_2$, respectively, are estimated from heats of formation of methylene and silylenes in Table III by assuming a constant $D°(C{=}Si)$ of 119.4 kcal/mol for silaethylenes.[45] In addition, these values are 4 kcal/mol higher than Walsh's estimates[46] of 23 and 7 kcal/mol, respectively. These values lead to the proton affinities of 221 and 230 kcal/mol for $H_2C{=}SiHCH_3$ and $H_2C{=}Si(CH_3)_2$, respectively. The previous experimental values by Hehre and co-workers[25] are 204 ± 3 and 227 ± 3 kcal/mol, respectively. The experimental proton affinity[25b] for $H_2C{=}SiHCH_3$ may be in error, due to complications in identifying the onset of proton transfer, and detailed studies of deprotonation kinetics were unfortunately not reported. For the comparison of the proton affinities of silylenes and silaethylenes with their carbon analogues, the heats of formation and proton affinities for carbenes and ethylenes are included in Table III. Values of 85.8 and 76.6 kcal/mol for heats of formation of $CHCH_3$ and $C(CH_3)_2$, respectively, are evaluated from heats of formation of methylene and ethylenes in Table III by assuming a constant $D°(C{=}C)$ of 174.3 kcal/mol for ethylenes.[47] These values yield heats of formation of −2.7, −11.9, and −21.1 kcal/mol for $CH_3HC{=}CHCH_3$, $CH_3HC{=}C(CH_3)_2$, and $(CH_3)_2C{=}C(CH_3)_2$, respectively, using the above assumption, and are close to the accepted values[48] of −2.99, −10.12, and −16.42 kcal/mol, respectively. Uncertainties in the estimated heats of formation for $CHCH_3$ and $C(CH_3)_2$ may be as much as 2 kcal/mol. The calculated proton affinities for carbenes are 197.0, 235.9, and 250.3 kcal/mol for CH_2, $CHCH_3$, and $C(CH_3)_2$, respectively. Since these carbenes have triplet ground states,[49] the proton-transfer reactions of the singlet ground-state carbonium ions with bases to produce the triplet ground-state carbenes should be spin-forbidden and may not be observed. Instead, the spin-allowed proton-transfer reactions to yield the singlet excited-state carbenes would be observed and provide the singlet–triplet splittings of carbenes from the differences between the observed proton affinities of singlet carbenes and the estimated proton affinities of triplet carbenes. The calculated proton affinities of ethylenes from thermochemical data in Table III using eq 7 are 162.6, 178,6, and 194.5 kcal/mol for $H_2C{=}CH_2$, $H_2C{=}CH(CH_3)$, and $H_2C{=}C(CH_3)_2$, respectively. The values are ~40 kcal/mol lower than those of the corresponding silaethylenes.

Effects of Solvation and the Choice of Reference Base on the Relative Stabilities of Silicenium and Carbonium Ions. The hydride affinities for the silicenium ions are precisely determined from kinetics and equilibria of hydride-transfer reactions in the gas phase. It is experimentally confirmed that the silicenium ions are significantly more stable than the corresponding carbonium ions in the gas phase with hydride as a reference base. However, the relative stabilities between the silicenium and the carbonium ions are strongly dependent upon the reference bases. In addition to the hydride affinities of MR_3^+ (M = C or Si, R = H or CH_3), their gas-phase chloride and fluoride affinities are included in Table V with the calculated heat of solvation of MR_3^+ in CH_2Cl_2. For the comparison of the relative stabilities between the silicenium ions and their carbon analogues in the gas phase with those in solution, heats of solvation of the ions are estimated from the well-known Born[50] eq 8. This equation gives the electrical work

$$\Delta H_{sol}(M^+) = -\frac{1}{8\pi\epsilon_0}\frac{e^2}{r(M^+)}\left(1 - \frac{1}{\epsilon_r}\right) \quad (8)$$

involved in transferring an ion of radius r from a vacuum (ϵ_r = 1) to the solvent, the latter being regarded as a continuous dielectric of relative permittivity ϵ_r ($\epsilon_r(CH_2Cl_2)$ = 9.08).[51] Even

(45) $D°(C{=}Si) = \Delta H_f°_{298}(CH_2) + \Delta H_f°_{298}(SiH_2) - \Delta H_f°_{298}(H_2C{=}SiH_2)$.

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

(47) $D°(C{=}C) = 2\Delta H_f°_{298}(CH_2) - \Delta H_f°_{298}(H_2C{=}CH_2)$.

(48) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.
(49) Carter, E. A. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1987.
(50) (a) Born, M. *Z. Phys.* **1920**, *21*, 45. (b) Bethell, D.; Gold, V. *Carbonium Ions, An Introduction*; Academic Press: London, 1967; Chapter 5. (c) For more elaborate studies, see: Cournoyer, M. E.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1984**, *106*, 5104.
(51) Weast, R. C., Ed. *Handbook of Chemistry and Physics*, 63rd ed.; Chemical Rubber Co.: Cleveland, OH, 1982; p E-51.

Table V. Hydride, Chloride, Fluoride, and Hydroxide Affinities of MR_3^+ (M = C or Si, R = H or CH_3) and Their Heats of Solvation in CH_2Cl_2

molecule (M)	D(M–H),[a] kcal/mol	$D(M^+–H^-)$,[b] kcal/mol	D(M–Cl),[c] kcal/mol	$D(M^+–Cl^-)$,[b] kcal/mol	D(M–F), kcal/mol	$D(M^+–F^-)$,[b] kcal/mol	D(M–OH), kcal/mol	$D(M^+–OH^-)$,[b] kcal/mol	$r(M^+)$,[d] Å	$\Delta H_{sol}(M^+)$,[e] kcal/mol
CH_3	104.8	314.4	84.5	228.3	109.8[f]	258.3	92.1[g]	276.9	1.41	−104.8
SiH_3	91.5	261.4	110.6[h]	214.8	156.5[i]	265.4	127.9[j]	273.0	1.81	−81.6
$C(CH_3)_3$	96.5	233.6	84.8	156.1	110.6[k]	186.7	96.0[l]	208.3	2.41	−61.3
$Si(CH_3)_3$	90.3	220.5	112.9	177.3	156.5[m]	225.9	127.9[n]	233.5	2.75	−53.7

[a] From Table III and ref 16. [b] $D(M^+–X^-) = \Delta H_f°_{298}(M^+) + \Delta H_f°_{298}(X^-) - \Delta H_f°_{298}(MX)$. $\Delta H_f°_{298}(H^-) = 34.7$ kcal/mol, $\Delta H_f°_{298}(Cl^-) = -54.1$ kcal/mol, $\Delta H_f°_{298}(F^-) = -59.5$ kcal/mol, and $\Delta H_f°_{298}(OH^-) = -32.9$ kcal/mol. [c] From $\Delta H_f°_{298}$(MCl) in Cox and Pilcher,[48] $\Delta H_f°_{298}$(M) in Table III and ref 16, and $\Delta H_f°_{298}$(Cl) = 29.1 kcal/mol. [d] Calculated radii using the covalent radii for C (0.77 Å), Si (1.17 Å), and H (0.32 Å) from ref 36. [e] Calculated values using eq 8. [f] $\Delta H_f°_{298}(CH_3F) = -56 \pm 7$ kcal/mol from JANAF Table (1971). [g] $\Delta H_f°_{298}(CH_3OH) = -48.0$ kcal/mol and $\Delta H_f°_{298}$(OH) = 9.3 kcal/mol from JANAF Table (1982). [h] $\Delta H_f°_{298}(SiH_3Cl) = -33.9 \pm 2$ kcal/mol from JANAF Table (1982). [i] $\Delta H_f°_{298}(SiH_3F) = -90 \pm 5$ kcal/mol from JANAF Table (1978). [j] Assuming $D(SiH_3–OH) = D(Me_3Si–OH)$. [k] Assuming D(*i*-Pr–F) = D(*t*-Bu–F). $\Delta H_f°_{298}$(*i*-PrF) = -69.4 ± 0.4 kcal/mol from Cox and Pilcher.[48] [l] $\Delta H_f°_{298}$(*t*-BuOH) = -74.7 ± 0.2 kcal/mol from Cox and Pilcher.[48] [m] Assuming $D(Me_3Si–F) = D(H_3Si–F)$. [n] $\Delta H_f°_{298}(Me_3SiOH) = -119.4 \pm 0.9$ kcal/mol from Cox and Pilcher.[48]

Table VI. Thermochemistry of Silane Thermal Decomposition

silanes	products	$\Delta H°$,[a] kcal/mol	log A[b]	E_a,[b] kcal/mol
SiH_4	$SiH_2 + H_2$	61	15.5[c]	59.6[c] (56.9)[d]
CH_3SiH_3	$H_2C{=}SiH_2 + H_2$	50		(96.3)[e]
	$SiH_2 + CH_4$	58	14.7[f]	66.7[f] (71.9)[e]
	$SiHCH_3 + H_2$	60	15.0[g]	63.2[g] (63.2)[e]
$(CH_3)_2SiH_2$	$H_2C{=}SiH_2 + CH_4$	48		
	$H_2C{=}SiHCH_3 + H_2$	50		
	$SiHCH_3 + CH_4$	58	14.8[h]	73.0[h]
	$Si(CH_3)_2 + H_2$	60	14.3[i]	68.0[i]
	$SiH_2 + C_2H_6$	72		
$(CH_3)_3SiH$	$H_2C{=}SiHCH_3 + CH_4$	48		
	$H_2C{=}Si(CH_3)_2 + H_2$	50		
	$Si(CH_3)_2 + CH_4$	58	(~14.8)[j]	(~80)[j]
	formation of CH_4		16.4[k]	76.5[k]
	formation of H_2		16.1[k]	80.3[k]
$(CH_3)_4Si$	$H_2C{=}Si(CH_3)_2 + CH_4$	48.5		
	$Si(CH_3)_2 + C_2H_6$	72		
	formation of CH_4		17.6[k]	84.8[k]

[a] The $\Delta H°$ values are esimated using heats of formation of silanes from Walsh,[46] silylenes and silaethylenes in Table III, and other thermochemical data from Cox and Pilcher.[48] [b] Experimental Arrhenius A factors and activation parameters; values in parenthesis are theor. results. [c] Newman et al.[56a] [d] Gordon et al.[56b] [e] Baldridge et al.[62] [f] Sawrey et al.[58a] [g] Neudorfl et al.[58b] [h] Rickborn et al.[59] [i] Neudorfl and Strausz.[57] [j] Estimated values, see text. [k] Baldwin et al.[60]

though this so-called "spherical ion in dielectric continuum" model is a crude approximation, it is useful in comparing the *relative* solvation effects between the silicenium ions and their carbon analogues. It is clear that the silicenium ions are less stable than the corresponding carbonium ions in the gas phase with F^- as a reference base. When Cl^- is used as a reference base in the gas phase, SiH_3^+ is more stable than CH_3^+ but $Si(CH_3)_3^+$ is less stable than $C(CH_3)_3^+$. Since the magnitude of heats of solvation is greater for the smaller ions, the nonspecific solvation effect favors the stabilization of the smaller carbonium ions than the corresponding silicenium ions. *As a result, the silicenium ions are significantly less stable than the analogous carbonium ions in CH_2Cl_2 solution with both Cl^- and F^- as reference bases,*[52] *and the hydride affinity differences between the silicenium ions and the analogous carbonium ions are greatly attenuated in solution.*[53]

The OH^- affinity data are included in Table V for the comparison of the effects of OH^- as a reference base with those of hydride and halides. This may explain the failure to detect the $Si(CH_3)_3^+$ ion under conditions developed for the stabilization of the carbonium ions.[54] Also, the result suggests that the earlier observation of hydrogen–halogen exchange of optically active R_3Si^*H with trityl halides by Sommer and Bauman[55] may occur via transient formation of silicenium ions by the hydride transfer from R_3Si^*H to Ph_3C^+ and carbonium ions by the chloride transfer from Ph_3CCl to R_3Si^+, which results in the complete racemization of silicon chlorides in CH_2Cl_2 solution. Further investigation of the kinetics of hydrogen–halogen exchange reactions both in the gas phase and in solution may give some information pertinent to the silicenium ion question as viable reaction intermediates.

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Appendix

Thermochemistry of Silane Thermal Decomposition. Thermal decomposition of silanes has been extensively studied to establish reliable thermochemistry of silicon containing compounds in the last two decades.[46,56–60] Recently, pyrolysis of silanes has been used to prepare thin silicon films for the fabrication of electric integrated circuits.[61] Understanding basic pyrolysis mechanisms, such as the lowest energy dissociation pathway and important reactive intermediates, under homogeneous or heterogeneous conditions is fundamental to developing mechanistic models for chemical vapor deposition film growth.[61] The newly derived heats of formation in Table III for some fundamental reactive intermediates, silylenes and silaethylenes,[24] can be used to evaluate reaction enthalpy changes for silane pyrolysis and may be helpful to elucidate pyrolysis mechanisms.

The $\Delta H°$ values for silane thermal decompositions involving silylenes or silaethylenes as products are listed in Table VI with previously reported Arrhenius parameters and available theoretical estimates for activation barriers.[56b,62] It is apparent in the pyrolysis of methylsilane[58] that three-center geminal elimination of molecular hydrogen forming methylsilylene is the lowest energy dissociation pathway. Although 1,2-elimination of hydrogen in the thermal decomposition of methylsilane is thermodynamically

(52) $D(R^+–X^-,s) = D(R^+–X^-) - \Delta H_{sol}(R^+) - \Delta H_{sol}(X^-) + \Delta H_{sol}(RX)$. $\delta(D) = D(R_3Si^+–X^-) - D(R_3C^+–X^-)$ and $\delta(D_s) = D(R_3Si^+–X^-,s) - D(R_3C^+–X^-,s)$. $\delta(D)$ and $\delta(D_s)$ are the X^- affinity differences between the silicenium and the carbonium ions in the gas phase and in solution, respectively. Assuming that $\Delta H_{sol}(R_3SiX) - \Delta H_{sol}(R_3CX)$ is considerably smaller than $\Delta H_{sol}(R_3Si^+) - \Delta H_{sol}(R_3C^+)$ leads to $\delta(D_s) = \delta(D) - (\Delta H_{sol}(R_3Si^+) - \Delta H_{sol}(R_3C^+))$. $\delta(D_s)$(R = H, X = H) = −29.8 kcal/mol, $\delta(D_s)$(R = CH_3, X = H) = −5.5 kcal/mol, $\delta(D_s)$(R = H, X = Cl) = 9.7 kcal/mol, $\delta(D_s)$(R = CH_3, X = Cl) = 28.8 kcal/mol, $\delta(D_s)$(R = H, X = F) = 30.3 kcal/mol, $\delta(D_s)$(R = CH_3, X = F) = 46.8 kcal/mol. $\delta(D_s)$(R = H, X = OH) = 19.3 kcal/mol, $\delta(D_s)$(R = CH_3, X = OH) = 32.8 kcal/mol. A positive value of $\delta(D_s)$ means that the silicenium ion is less stable than the corresponding carbonium ion in solution (CH_2Cl_2).

(53) $\delta(D)$(R = H, X = H) = −53.0 kcal/mol and $\delta(D_s)$(R = H, X = H) = −29.8 kcal/mol. $\delta(D)$(R = CH_3, X = H) = −13.1 kcal/mol and $\delta(D_s)$(R = CH_3, X = H) = −5.5 kcal/mol.

(54) Olah, G. A.; Mo, Y. K. *J. Am. Chem. Soc.* **1971**, *93*, 4942.
(55) Sommer, L. H.; Bauman, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 7076.
(56) (a) Newman, C. G.; O'Neal, H. E.; Ring, M. A.; Leska, F.; Shipley, N. *Int. J. Chem. Kinet.* **1979**, *11*, 1167. (b) Gordon, M. S.; Gano, D. R.; Binkley, J. S.; Frisch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 2191, and earlier references therein.
(57) Neudorfl, P.; Strausz, O. P. *J. Phys. Chem.* **1978**, *82*, 241.
(58) (a) Sawrey, B. A.; O'Neal, H. E.; Ring, M. A.; Coffey, D., Jr. *Int. J. Chem. Kinet.* **1984**, *16*, 31. (b) Neudorfl, P.; Lown, E. M.; Safarik, I.; Jodhan, A.; Strausz, O. P. *J. Am. Chem. Soc.* **1987**, *109*, 5780, and earlier references therein.
(59) Rickborn, S. F.; Rogers, D. S.; Ring, M. A.: O'Neal, H. E. *J. Phys. Chem.* **1986**, *90*, 408, and earlier references therein.
(60) Baldwin, A. C.; Davidson, I. M. T.; Reed, M. D. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 2171, and earlier references therein.
(61) Jasinski, J. M.; Meyerson, B. S.; Scott, B. A. *Annu. Rev. Phys. Chem.* **1987**, *38*, 109.
(62) Baldridge, K. K.; Boatz, J. A.; Koseki, S.; Gordon, M. S. *Annu. Rev. Phys. Chem.* **1987**, *38*, 211.

the most favorable process, theoretical studies by Gordon and co-workers[62] suggest that the 1,2-elimination process has a higher activation barrier than a 1,1-elimination process. As a result, the direct formation of silaethylenes in the pyrolysis of silanes under homogeneous conditions is unlikely. The ΔH° values for 1,1-elimination of hydrogen in the pyrolysis of SiH_4,[56] CH_3SiH_3,[57,58] and $(CH_3)_2SiH_2$[57,59] are almost identical, but the E_a values tend to increase by ~4.2 kcal/mol per methyl group with increasing methyl substitution in place of hydrogen. The E_a values for 1,1-elimination of methane in the pyrolysis of CH_3SiH_3 and $(CH_3)_2SiH_2$ are slightly higher than those for 1,1-elimination of hydrogen and increase as a result of methyl substitution by ~6.7 kcal/mol per methyl group. This may indicate that methyl substitution at the silicon center in silylenes raises the activation energy for insertion into H-H or C-H bonds by ~4.2 or ~6.7 kcal/mol, respectively.[59] The pyrolysis mechanism of trimethylsilane[60] has not been well established because of the complexity of the mechanism and the lack of experimental data for most of its steps. It will be of particular interest to see if the pyrolysis of trimethylsilane involves a 1,1-elimination process to form $Si(CH_3)_2$. For this process, estimates of Arrhenius parameters are ~14.8 and ~80 kcal/mol for log A and E_a by analogy with pyrolysis reactions of CH_3SiH_3 and $(CH_3)_2SiH_2$. In the pyrolysis of tetramethylsilane, Davidson and co-workers[60] concluded that the formation of methane at high temperature (955–1055 K) relates to a nonchain mechanism rate-determined by the Si–C bond rupture process with E_a of 84.8 kcal/mol, while at low temperature (840–950 K), a short-chain sequence probably operates. This may indicate that the molecular process involving 1,2-elimination of methane or 1,1-elimination of ethane in the pyrolysis of tetramethylsilane requires a higher activation energy than the Si–C bond rupture process.

A Study of the Thermal Decomposition and Dehydrochlorination of *N*-Chloroazetidine: Microwave Spectra of *N*-Chloromethylenimine, 1-Azetine, and 2-Azabutadiene

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Abstract: The microwave spectrum of *N*-chloromethylenimine and 1-azetine has been observed following pyrolysis and dehydrochlorination of *N*-chloroazetidine, respectively. In addition, pyrolysis of 1-azetine gives another unstable molecule, 2-azabutadiene. The rotational constants determined are A = 62434.90 (10), B = 6676.389 (13), and C = 6022.843 (11) MHz for *N*-chloromethylenimine, A = 62344.73 (11), B = 6531.700 (13), and C = 5904.017 (11) MHz for the ^{37}Cl species of *N*-chloromethylenimine, A = 13911.630 (24), B = 12713.799 (24), and C = 7254.990 (24) MHz for 1-azetine, and A = 47186.010 (23), B = 4886,5325 (27), and C = 4430.0673 (23) MHz for 2-azabutadiene. The dipole moments and nuclear quadrupole coupling constants have also been determined from analysis of the spectra. The molecular constants estimated by ab initio MO calculations have been found to be consistent with the experimental results.

We studied the pyrolysis of 2-methylaziridine (**1**; in Figure 1) in the gas phase by microwave spectroscopy[1] and found a new transient molecule *N*-methylvinylamine (**2**), which was unstable and easily rearranged to its tautomer *N*-methylethylidenimine (**3**). Recently, it has been found[2] that the pyrolysis of *N*-chloro-2-methylaziridine (**4**) gives unstable molecules, *N*-methylketenimine (**5**) and 2-methylazirine (**6**). Amatatsu et al.[3,4] studied the same reaction systems by infrared spectroscopy and identified similar reaction products as observed by us. These experimental results show that there exist more than two reaction pathways for 3-membered ring systems containing a chlorine atom. The ring cleavage is facile at elevated temperatures since a 3-membered ring molecule has a high ring strain. The resultant reactive intermediate is stabilized by hydrogen rearrangement. The dehydrohalogenation is another pathway and is as probable as the ring cleavage.

As for 4-membered ring systems, it is well-known[5] that azetidine (**7**) cleaves into ethylene and methylenimine (**8**). We have studied the pyrolysis of *N*-chloroazetidine (**9**) by microwave spectroscopy and found that the reaction is similar to that of azetidine. That is, the microwave spectrum of *N*-chloromethylenimine (**10**) was observed as one of the pyrolysis products.

Guillemin et al.[6] obtained 1-azetine (**11**) by dehydrochlorination of *N*-chloroazetidine. They obtained structural proof by such chemical procedures as reduction by $LiAlH_4$ and addition of HCN. Physical proofs were obtained by infrared, ^{1}H NMR, and ^{13}C NMR spectra. They also found that 2-azabutadiene (**12**) was produced by the flash vacuum photolysis of 1-azetine.

We obtained the microwave spectra of 1-azetine and 2-azabutadiene by a similar method, and the analysis of the spectra is presented together with that of *N*-chloromethylenimine.

The ab initio MO calculation was used as an aid to the analysis of spectra and the confirmation of the molecules. The results of ab initio MO calculations are also presented.

Experimental Section

A precursor sample, *N*-chloroazetidine, was prepared by passing azetidine through a U-tube containing NCS (*N*-chlorosuccinimide). The mixture containing azetidine and chloride was introduced into a 3-m X-band waveguide cell through a 4-mm i.d. quartz tube heated to about 600 °C, and the microwave spectrum of *N*-chloromethylenimine was observed. The spectrum of 1-azetine was obtained by passing *N*-chloroazetidine through a second U-tube, which contained *t*-BuOK (potassium tertiary butylate). This U-tube was heated to about 80 °C in order to maintain a high reaction efficiency. In order to observe the spectrum of 2-azabutadiene, the gas mixture emerging from the second U-tube was passed through the quartz tube heated to about 650 °C and introduced into the waveguide cell. A fast-flow method was adopted since

(1) Sugie, M.; Takeo, H.; Matsumura, C. *Chem. Phys. Lett.* **1985**, *113*, 140–144.
(2) Sugie, M.; Takeo, H.; Matsumura, C., to be submitted for publication.
(3) Amatatsu, Y.; Hamada, Y.; Tsuboi, M.; Sugie, M. *J. Mol. Spectrosc.* **1985**, *111*, 29–41.
(4) Amatatsu, Y.; Hamada, Y.; Tsuboi, M. *J. Mol. Spectrosc.* **1987**, *123*, 476–485.
(5) Rodler, M.; Bauder, A. *J. Mol. Struct.* **1983**, *97*, 47–52.
(6) Guillemin, J. C.; Denis, J. M.; Lablache-Combier, A. *J. Am. Chem. Soc.* **1981**, *103*, 468–469.

0002-7863/89/1511-0906$01.50/0