greater than the lower limit set by the present experiments. A similar calculation for Eu^+ using D(Eu–O) = 114.5 ± 4.0 kcal/mol, IP(EuO) = 6.48 ± 0.1 eV, and IP(Eu) = 5.68 ± 0.1 eV, yield an EuO^+ bond dissociation energy of 96.1 ± 5.2 kcal/mol, explaining why no EuO^+ product was seen due to background oxygen in the system.

Conclusion

The results presented show that those lanthanide cations which, of necessity, must involve the f electrons in bonding, are unable to activate the C–H or C–C bonds of saturated hydrocarbons. This supports the contention that bonds formed utilizing the f electrons are inherently weak. On the other hand, where two non-f valence electrons are available for use in bonding, the metal ion is very reactive. Gd^+, with a ground state derived from the $4f^7 5d^1 6s^1$ configuration, exhibits reactivity similar to that of the group 3 transition metal cations. Product distributions are fairly similar to Sc^+, although more multiple dehydrogenation products are seen for Gd^+. As with Sc^+, Gd^+ is capable of forming two strong σ bonds to carbon and hydrogen. An estimate of the sum of the two bonds in GdH_2^+ is 120 ± 5 kcal/mol. $Gd(CH_3)(H)^+$ is produced in the reaction with propane indicating that the sum of the bonds is around 125 kcal/mol. Although the reactions yielding $Gd(C_2H_6)^+$ yield an estimate of 115 kcal/mol for the sum of the bond energies, it is also likely to be over 120 kcal/mol.

By looking at the electronic states of the other lanthanide cations, one can try to make predictions of reactivity. Ce^+ and Lu^+ are the other two ions with two non-f valence electrons; however, Lu^+ has a closed-shell $f^{14}s^2$ configuration. An $f^{14}d^1s^1$ configuration which would be necessary for bonding is at over 1.5 eV. Ce^+ has two 5d electrons, like La^+, and should be quite reactive in its ground state. The other lanthanide cations only have one non-f valence electron. Except for Tb^+, which has a state at approximately 0.4 eV with a $4f^8 5d^1 6s^1$ configuration, the reactive excited states are fairly high in energy and it can be expected that these ions will all be unreactive.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant No. CHE84-07857) for partial support of this work.

Registry No. Eu^+, 15065-79-9; Pr^+, 20193-53-7; Gd^+, 19180-89-3; CH_4, 74-82-8; C_2H_6, 74-84-0; C_3H_8, 74-98-6; n-C_4H_{10}, 106-97-8; i-C_4H_{10}, 75-28-5; n-C_5H_{12}, 109-66-0; i-C_5H_{12}, 78-78-4; *neo*-C_5H_{12}, 463-82-1; n-C_6H_{14}, 110-54-3; propane-*2,2*-d_2, 2875-95-8; 2-methylpropane-*2*-d_1, 20717-74-2; n-butane-*1,1,1,4,4,4*-d_6, 13183-67-0; cyclopropane, 75-19-4; cyclobutane, 287-23-0; cyclopentane, 287-92-3; cyclohexane, 110-82-7; ethene, 74-85-1; propene, 115-07-1; 1-butene, 106-98-9; 1-pentene, 109-67-1; 1-hexene, 592-41-6; cyclohexene, 110-83-8; nitric oxide, 10102-43-9; formaldehyde, 50-00-0; acetaldehyde, 75-07-0; acetone, 67-64-1.

Thermochemistry of Silaethylene and Methylsilylene from Experiment and Theory

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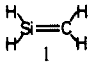
Abstract: Fourier transform ion cyclotron resonance spectroscopy has been used to examine the deprotonation energetics of the methylsilyl cation, $CH_3SiD_2^+$, to yield silaethylene and methylsilylene proton affinities of 205 ± 3 and 215 ± 4 kcal/mol, respectively. These values, combined with the known heat of formation of methylsilyl cation, yield $\Delta H_f{}^\circ{}_{298}(CH_2SiH_2)$ = 43 ± 3 kcal/mol and $\Delta H_f{}^\circ{}_{298}(CH_3SiH)$ = 53 ± 4 kcal/mol. These results are corroborated by ab initio generalized valence bond–configuration interaction calculations which indicate that silaethylene is more stable than methylsilylene by 11.6 kcal/mol, in excellent agreement with the experimental difference (10 ± 3 kcal/mol). The adiabatic ionization potential of methylsilylene is calculated to be 8.22 eV, which is lower than the value of 8.85 eV determined for silaethylene using photoelectron spectroscopy.

The reactivities, structures, and thermochemistry of Si–C double-bonded compounds,[1] silaethylenes, and divalent silicon compounds, silylenes,[2] have been the subject of extensive study, ever since dimethylsilaethylene was first suggested as a reactive intermediate in the pyrolysis of 1,1-dimethylsilacyclobutane.[3] Silaethylene (**1**) and its isomer methylsilylene (**2**) have been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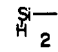
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isolated in an argon matrix[4] and spectroscopically characterized.[5,6] The interconversion of these two reactive species has been examined to elucidate the isomerization energetics.[5,7] However, no experimental determinations of the heats of formation of these

Table I. Theoretical Predictions of the Relative Stabilities of Silaethylene and Methylsilylene

year	method[a]	ΔE($SiHCH_3$ – SiH_2CH_2) (kcal/mol)	ref
1978	CI/STO-3G//HF/STO-4G	−6.8	*b*
1980	MP2/6-31G*//HF/4-31G	2.1	*c*
1980	CI/DZ+d//HF/DZ	−0.4	*d*
1981	CI(pseudo-pot)/DZ+d	3.5	*e*
1982	CI/DZ+P//HF/DZ+P + Davidson correction	1.7	*f*
1982	CEPA/extended (p+d) //HF/extended (d)	0.6	*g*
1984	CI/6-31G*//HF/6-31G* + Davidson correction	−3.4	*h*
1987	CC-CI/VDZ+P//MP2/6-31G** + zero-point-energy correction	11.6	*i*

[a] Calculational level for total energy/basis sets//calculational level for geometry optimization/basis sets; for example, CI/STO-3G//HF/STO-4G represents the CI level energy calculation with STO-3G basis sets and the HF/STO-4G optimized geometry. For details, see references. [b] Reference a. [c] Reference 8b. [d] Reference 8c. [e] Reference 8d. [f] Reference 1d. [g] Reference 8e. [h] Reference 8f. [i] This work.

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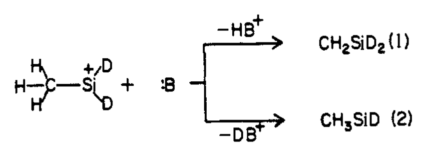
0002-7863/88/1510-0024$01.50/0

Scheme I



reactive isomers have been reported. There have been numerous theoretical studies[8] of the relative stabilities of silaethylene and methylsilylene, resulting in values of $\Delta E = E(\mathbf{2}) - E(\mathbf{1})$ which range from –6.8 to 3.5 kcal/mol (note that a positive value of this quantity indicates that **1** is more stable than **2**).

Herein, we report the deprotonation energetics of methylsilyl cation using Fourier transform mass spectrometry to estimate the heats of formation of silaethylene and methylsilylene. Our previously reported[9] results for silylene using this experimental methodology are in excellent agreement with both a theoretical recommendation[10] and the recent experiments of Berkowitz et al.[11] and Boo et al.[12] The current consensus is that the heat of formation of silylene is 69 ± 3 kcal/mol. This revision in the heat of formation of silylene from the previously accepted value[13] of 58 kcal/mol leads to some changes in the *estimated* heats of formation of methyl-substituted silylenes.[14]

Previously suggested values[13] of heats of formation of silaethylene (39 ± 5 kcal/mol) and methysilylene (42 kcal/mol)[14] yield a 3-kcal/mol differences, in agreement with some previous theoretical calculations ($\Delta E = -6.8$ to 3.5 kcal/mol), as indicated in Table I. For example, an MP2 calculation by Gordon[8b] leads to $\Delta E = 2.1$ kcal/mol. Schaefer's[1d] CI calculation with Davidson's correction yields 1.7 kcal/mol and a CI calculation by Malrieu[8d] leads to 3.5 kcal/mol. On the other hand, the most recent CI (Nagase[8f]) leads to –3.4 kcal/mol and CEPA[8e] leads to 0.6 kcal/mol. *However, the recent revision*[14] *of the heat of formation of methylsilylene (53 kcal/mol) leads to* $\Delta E = 14.6$ *kcal/mol*, which is substantially larger than what appear to be the "best" theoretical calculations.

To resolve some of the conflicts apparent in the results discussed above and more firmly define the values of the heats of formation of silaethylene and methylsilylene, we have studied the kinetics and thermochemistry of the proton- and deuteron-transfer reactions of $CH_3SiD_2^+$ with various n-donor bases of well-established gas-phase basicities.[15,16] Using this methodology, Hehre and co-workers[17] have previously studied the onsets of proton and deuteron abstraction from $(CH_3)_2SiD^+$ by various n-donor bases and found that the proton transfer has the lower threshold than the deuteron transfer. As shown in Scheme I, transfer of the carbon-bound proton from $CH_3SiD_2^+$ to the base yields silaethylene, and transfer of the silicon bound deuteron produces methylsilylene as the neutral products. The proton affinities of silaethylene and methylsilylene determined in this fashion yield the heats of formation of the two isomers with the use of eq 1.

$$\Delta H_f{}^\circ{}_{298}(CH_2SiD_2 \text{ or } CH_3SiD) = PA(CH_2SiD_2 \text{ or } CH_3SiD) + \Delta H_f{}^\circ{}_{298}(CH_3SiD_2^+) - \Delta H_f{}^\circ{}_{298}(H^+ \text{ or } D^+) \quad (1)$$

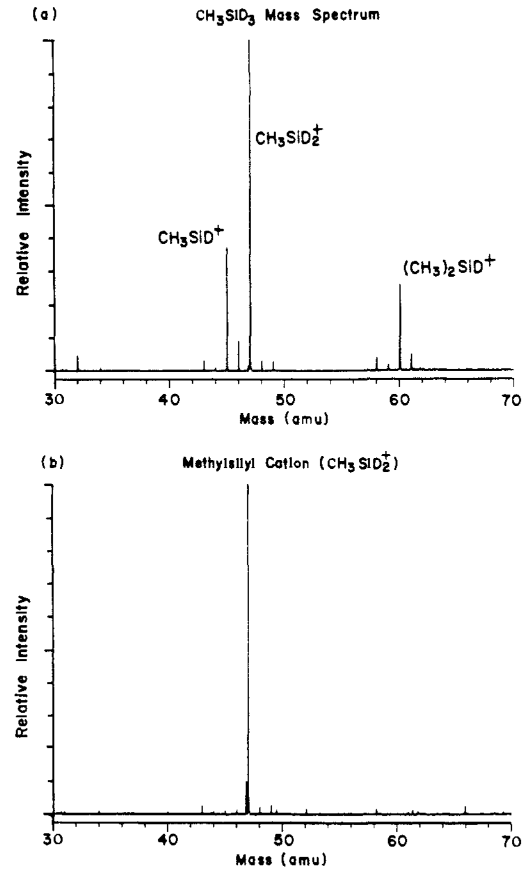


Figure 1. (a) Mass spectrum of CH_3SiD_3 with 15-eV electron energy at 1.2×10^{-6} torr and 30-ms delay before ion detection. (b) Mass spectrum of $CH_3SiD_2^+$ shortly after a series of ion ejection pulses. Even though the ion ejections are incomplete because of the use of low rf levels to avoid excitation of the isolated reactant ion, the conditions suffice for an examination of the deprotonation kinetics.

In addition, we have performed ab initio calculations to reexamine the relative stabilities of the two isomers and to estimate the rotational barrier in silaethylene.

Experimental Section

Experimental techniques associated with ICR spectroscopy,[18] and in particular Fourier transform mass spectrometry,[19] have been previously described in detail. Experiments were performed with an Ion Spec-2000 Fourier transform mass spectrometer equipped with a 1-in. cubic trapping cell[20] built by Bio-Med Tech[21] situated between the poles of a Varian 15-in. electromagnet maintained at 1 T. Chemicals were obtained commercially in high purity and used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensable gases. CH_3SiD_3 and CH_3SiH_3 were prepared by reducing CH_3SiCl_3 with $LiAlD_4$ and $LiAlH_4$.[22] Pressures were measured with a Schulz-Phelps ion gauge[23] cali-

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Table II. Observed Reactions and Rate Constants for the Reactions $CH_3SiD_2^+ + B \rightarrow$ Products

B	PA^a	products	prod distr^b	k_{total}^a	k_{ADO}^a
$(CH_3)_2S$	200.6	$CH_3SCH_2^+ + CH_3SiD_2H$	1.0	11.2	19.3
NH_3	204.0	$CH_3SiDNH_2^+ + HD$	1.0	5.4	18.3
CH_3CONH_2	206.2	$CH_3CONH_3^+ + CH_2SiD_2$	0.75	18.7	18.5
		$CH_3SiDNH_2^+ + CH_3COD$	0.15		
		$CH_3SiDNHCOCH_3^+ + HD$	0.05		
		$CH_3SiD_2NH_2COCH_3^+$	0.05		
$C_6H_5NH_2$	210.5	$C_6H_5^+ + CH_3SiD_2NH_2$	0.40	26.2	18.1
		$C_6H_5NH_3^+ + CH_2SiD_2$	0.20		
		$CH_3SiDNHC_6H_5^+ + HD$	0.20		
		$CH_3SiD_2NH_2C_6H_5^+$	0.20		
CH_3NH_2	214.1	$CH_3NH_3^+ + CH_2SiD_2$	0.30	12.0	15.9
		$CH_2NH_2^+ + CH_3SiD_2H$	0.30		
		$CH_3SiDNHCH_3^+ + HD$	0.30		
		$CH_3SiDNH_2^+ + CH_3D$	0.05		
		$CH_3SiD_2NH_2CH_3^+$	0.05		
$C_6H_5CH_2NH_2$	216.8	$C_6H_5CH_2^+ + CH_3SiD_2NH_2$	0.55	2.8	17.8
		$C_6H_5CH_2NH_3^+ + CH_2SiD_2$	0.30		
		$C_6H_5CHNH_2^+ + CH_3SiD_2H$	0.10		
		$C_6H_5CH_2NH_2D^+ + SiDCH_3$	0.05^e		
$C_2H_5NH_2$	217.0	$C_2H_5NH_3^+ + CH_2SiD_2$	0.40	16.0	15.6
		$C_2H_4NH_2^+ + CH_3SiD_2H$	0.20		
		$CH_3SiDNHC_2H_5^+ + HD$	0.20		
		$C_2H_5NH_2D^+ + SiDCH_3$	0.14^e		
		$CH_3SiDNH_2^+ + C_2H_5D$	0.03		
		$CH_3SiD_2NH_2C_2H_5^+$	0.03		
$(CH_3)_2NH$	220.6	$(CH_3)(CH_2)NH^+ + CH_3SiD_2H$	0.55	20.5	14.7
		$(CH_3)_2NH_2^+ + CH_2SiD_2$	0.20		
		$(CH_3)_2NHD^+ + SiDCH_3$	0.20^e		
		$(CH_3)_2NSiDCH_3^+ + HD$	0.05		

[a] All proton affinity values from ref 16. In units of kcal/mol. [b] Product distribution normalized to unity for reactant ion. [c] In units of 10^{-10} cm^3 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. [e] Corrected for ^{13}C natural abundance.

brated 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.[24] Approximately 1:1 mixtures of methylsilane and base were used with a total pressure in the range $1 \sim 5 \times 10^{-6}$ torr. Ionization was by electron impact at 15 eV.

Although other reactions are noted below, this study focused on the proton- and deuteron-transfer reactions of $CH_3SiD_2^+$ with the neutral bases. Methylsilane ionized by electron impact is a convenient source of $CH_3SiD_2^+$ ions.[25,26] The most abundant primary ion is CH_3SiD^+, which is converted to $CH_3SiD_2^+$ by reaction 2 with a rate constant of 5.3×10^{-10} cm^3 molecule^{-1} s^{-1}.

$$CH_3SiD^+ + CH_3SiD_3 \rightarrow CH_3SiD_2^+ + CH_3SiD_2 \qquad (2)$$

Ion ejection pulses were used to remove all ions except $CH_3SiD_2^+$ from the ICR cell shortly after the electron beam pulse.[27] We used as low rf levels as possible to avoid thermal excitation of the reactant ion. Figure 1 shows a spectrum of $CH_3SiD_2^+$ ion just after a series of ejection pulses. The temporal variations of reactant and product ion abundances were recorded and used to calculate rate constants directly. As an example, Figure 2 shows the temporal variations of the reactant $CH_3SiD_2^+$ ion and the product $CH_3CONH_3^+$ ion in the reaction involving carbon-bound proton transfer from methylsilyl cation to acetamide.

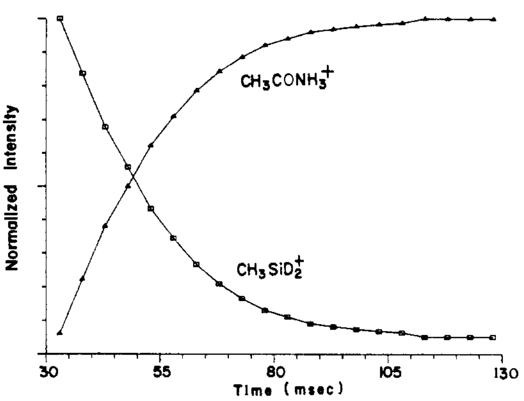

Figure 2. Temporal variation of methylsilyl cation and protonated acetamide ion in the proton-transfer reaction from methylsilyl cation to acetamide; $P(CH_3SiD_3) = 1.2 \times 10^{-6}$ torr, $P(CH_3CONH_2) = 9.5 \times 10^{-7}$ torr, and 15 eV electron energy.

Results and Discussion

Reactions of Methylsilyl Cation. Product distributions and rate constants for the reaction of $CH_3SiD_2^+$ with various n-donor bases are summarized in Table II. $CH_3SiD_2^+$ reacts with CH_3SiD_3 to yield $CH_3SiD_2^+$ by symmetrical deuteride transfer[28] with a rate constant of 6.4×10^{-10} cm^3 molecule^{-1} s^{-1} and $(CH_3)_2SiD^+$ with a rate constant of 1.6×10^{-10} cm^3 molecule^{-1} s^{-1}. The major reaction with $(CH_3)_2S$ yields the hydride transfer product $CH_3SCH_2^+$. In the reaction of $CH_3SiD_2^+$ with NH_3, the formation of $CH_3SiDNH_2^+$ with loss of HD is predominant, in contrast to the facile proton-transfer reaction[9] of SiH_3^+ with NH_3.[29] With CH_3CONH_2, the dominant reaction is H^+ transfer from $CH_3SiD_2^+$ to yield silaethylene as the neutral product ($k = 1.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}). There is no evidence that hydrogen and deuterium scrambling occurs either in the formation of the reactant ion or during the course of the reaction with acetamide.[30] Proton transfer in addition to more complex processes are observed with $C_6H_5NH_2$ as the neutral base. In the case of CH_3NH_2, proton-transfer, hydride-transfer, and Si-N

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(30) If scrambling occurs in the $CH_3SiD_2^+$ ion, the ratio of BD^+ to BH^+ could be 0.4 instead of 0.0 at the onset of proton-transfer reaction.

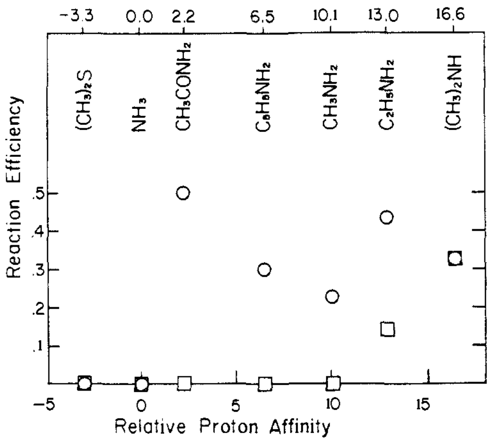


Figure 3. Variation with base strength of the reaction efficiency (defined as the ratio of the rate constant to the calculated collision rate) for proton and deuteron transfer from $CH_3SiD_2^+$ to various n-donor bases: ○, proton transfer; □, deuteron transfer. Base strengths (proton affinities) are given relative to NH_3 [PA(NH_3) = 204 ± 3 kcal/mol].

bond-formation processes are all important channels. Although a small amount of $CH_3NH_2D^+$ is observed in this system, double resonance experiments indicate that it is not a direct silicon-bound deuteron-transfer product involving $CH_3SiD_2^+$ but rather a higher order product of a complex sequence of reactions. $CH_3SiD_2^+$ undergoes proton, deuteron, hydride transfer, and more complex sequences of reactions with $C_6H_5CH_2NH_2$. The predominant reaction of $CH_3SiD_2^+$ with $C_2H_5NH_2$ is proton transfer ($k = 6.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}), but ion ejection experiments confirm that direct deuteron transfer also occurs ($k = 2.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}). In addition, hydride transfer and Si–N bond formation processes occur in this system. In the reaction of $CH_3SiD_2^+$ with $(CH_3)_2NH$, the ratio of the reaction efficiency of deuteron transfer to proton transfer increases by a factor of 3 relative to $C_2H_5NH_2$. Hydride transfer from $(CH_3)_2NH$ to $CH_3SiD_2^+$ is dominant and Si–N bond formation processes are also observed.

Proton Affinity and Heat of Formation. Several factors[31] in these experiments contribute to the uncertainty in derived heats of formation of silaethylene and methylsilylene. These include (i) the near impossibility of pinpointing (in the presence of fast, competing reactions) the precise base strength for which proton or deuteron transfer from $CH_3SiD_2^+$ is thermoneutral, (ii) the difficulties associated with the assignment of absolute values to the proton affinity scale,[16] and (iii) the uncertainty in the heat of formation of the $CH_3SiD_2^+$ ion.[32]

The results shown in Figure 3 strongly suggest that PA(NH_3) < PA (CH_2SiD_2) < PA(CH_3CONH_2) and PA(CH_3NH_2) < PA(CH_3SiD) < PA($C_2H_5NH_2$). These values indicate that silaethylene is 10 ± 3 kcal/mol more stable than methylsilylene. Choosing a value of 204 ± 3 kcal/mol for PA(NH_3)[16] leads to values for PA(CH_2SiD_2) and PA(CH_3SiD) of 205 ± 3 and 215 ± 4 kcal/mol, respectively. Using a value of 204 ± 1 kcal/mol for $\Delta H_f{}^\circ{}_{298}(CH_3SiD_2^+)$[32] and 365.7 kcal/mol for $\Delta H_f{}^\circ{}_{298}(H^+)$[33] in eq 1 yields $\Delta H_f{}^\circ{}_{298}(CH_2SiD_2)$ = 43 ± 3 kcal/mol, and $\Delta H_f{}^\circ{}_{298}(CH_3SiD)$ = 53 ± 4 kcal/mol. The value for the heat of formation of silaethylene is slightly higher than the previously accepted value[13] (with a reduced uncertainty), but that of methylsilylene is somewhat higher than the previous estimate of 42 kcal/mol.[14] The heat of formation of dimethylsilylene may be estimated by assuming a constant CH_3 for H replacement energy in silylenes.[34] Assuming a methyl-substituent effect of 16 ± 5 kcal/mol, which is the difference between the heats of formation of silylene (69 ± 3 kcal/mol) and methylsilylene (53 ± 4 kcal/mol), yields a heat of formation of 37 ± 6 kcal/mol for dimethylsiylene, which is significantly higher than Walsh's recent estimate[35] of 26 ± 2 kcal/mol. These results are summarized in Table III.

Table III. Thermochemical Data Used in Text (kcal/mol)

molecule	$\Delta H_f{}^\circ{}_{298}$	ref	molecule	$\Delta H_f{}^\circ{}_{298}$	ref
SiH_4	8.2	*a*	SiH_2Me_2	−23	*a*
SiH_3	47.6	*b*	$SiHMe_2$	14.3	*a*
SiH_2	69 ± 3	*c*	$SiMe_2$	26 ± 2, 37 ± 6	*d*, *e*
SiH_3Me	−7	*a*	$SiMe_4$	−55.4	*a*
SiH_2Me	30.5	*a*	$CH_3SiH_2^+$	204 ± 1	*f*
SiHMe	53 ± 4	*g*	SiH_2CH_2	43 ± 3	*g*

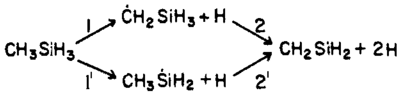
[a] Reference 13. [b] We use the average values of 46.4, 47.9, and 48.5 kcal/mol for $\Delta H_f{}^\circ{}_{298}(SiH_3)$. The value of 46.4 kcal/mol is derived from $D(H_3Si–H)$ = 90.3 kcal/mol (ref 13). The value of 47.9 kcal/mol is derived from $D(H_3Si–H)$ = 91.8 kcal/mol, which is estimated from the gas-phase acidity, $D(H_3Si^-–H^+)$ = 372.2 kcal/mol (Bartmess, J. E. In *Sturcture/Reactivity and Thermochemistry of Ions* (NATO ASI Series); Ausloos, P., Lias, S. G., Eds; D. Reidel: Dordrecht, 1987; pp 367–380), combined with EA(SiH_3) = 33.2 kcal/mol (Reed, K. J.; Brauman, J. I. *J. Chem. Phys.* **1974**, *61*, 4380) and $\Delta H_f{}^\circ{}_{298}(H^+)$ = 365.7 kcal/mol (ref 33). The value of 48.5 kcal/mol is taken from ref 12 and yields $D(H_3Si–H)$ = 92.4 kcal/mol. [c] References 9, 10, 11, and 12. [d] Reference 42. [e] Derived; see text. [f] Reference 32. [g] This work.

Table IV. Adiabatic Ionization Potentials for Silylenes

molecule	$\Delta H_f{}^\circ{}_{298}$(M) (kcal/mol)	$\Delta H_f{}^\circ{}_{298}$(M$^+$) (kcal/mol)	IP(M) (eV)
SiH_2	69 ± 3[a]	274.1[b]	8.89, 9.02[c]
SiHMe	53 ± 4[a]	242.6[b]	8.22
$SiMe_2$	37 ± 6[a]	211.3[b]	7.56

[a] See Table III. [b] The photoionization mass spectrometric study of Corderman and Beauchamp (Corderman, R. R. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1977). [c] Reference 11.

Scheme II



Using the above heats of formation of silylenes, combined with the known heats of formation of their molecular ions in Table IV, leads to the adiabatic ionization potentials of 8.89, 8.22, and 7.56 eV for SiH_2, $SiHCH_3$, and $Si(CH_3)_2$, respectively. The calculated adiabatic ionization potential of 8.22 eV for methylsilylene is 0.63 eV lower than the experimental value of 8.85 eV determined for silaethylene using photoelectron spectroscopy by Bock and coworkers.[5b] The value for the ionization potential of silaethylene, combined with its heat of formation, yields 247 ± 4 kcal/mol for the heat of formation of silaethylene molecular ion, which is only slightly higher than that (242.6 kcal/mol) of methylsilylene molecular ion. Interestingly, CH_3SiD^+ is the most abundant primary ion produced by the electron impact ionization of CH_3SiD_3 with 15 eV electron energy, even though the heat of formation of $CH_2SiD_2^+$ is only slightly higher than that of CH_3SiD^+. The absence of the $CH_2SiD_2^+$ ion may be attributed either to a higher activation energy for 1,2-hydrogen loss or to a kinetic shift or to both. It is well known that the analogous $C_2H_4^+$ ion formation from ethane occurs with an excess energy of 0.22 eV.[36]

The strength of the π-bond energy of silaethylene is an important index of its reactivity. A useful definition of the π-bond

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(31) Ausloos, P.; Lias, S. G. *J. Am. Chem. Soc.* **1978**, *100*, 4594.

(32) We use $\Delta H_f{}^\circ{}_{298}(CH_3SiD_2^+)$ = 204 ± 1 kcal/mol determined from the kinetics and equilibrium studies of the hydride transfer reaction: $c\text{-}C_5H_9^+ + CH_3SiH_3 \rightleftharpoons c\text{-}C_5H_{10} + CH_3SiH_2^+$ (Shin, S. K.; Beauchamp, J. L., manuscript in preparation). This is significantly lower than the previous value of 213 ± 3 kcal/mol determined by Potzinger and Lampe using electron impact ionization (ref 25).

(33) $\Delta H_f{}^\circ{}_{298}(H)$ = 52.1 kcal/mol and IP(H) = 13.598 eV from: Moore, C. E. *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* **1970**, No. 34. We used the stationary electron convention (ref 16).

(34) The methyl substituent effect of 16 kcal/mol is identical with the previous estimate (ref 13) based on the heats of formation of SiH_4 and $SiMe_4$.

(35) Baggott, J. E.; Blitz, M. A.; Frey, H. M.; Lightfoot, P. D.; Walsh, R. *Chem. Phys. Lett.* **1987**, *135*, 39.

(36) (a) Chupka, W. A.; Berkowitz, J. *J. Chem. Phys.* **1967**, *47*, 2921. (b) Stockbauer, R. *Ibid.* **1973**, *58*, 3800.

Table V. Calculated Energy Differences between $^1A_1$ SiH_2CH_2 and $^1A'$ $SiHCH_3$[a]

	$^1A_1$ SiH_2CH_2		$^1A'$ $SiHCH_3$		
level	total energy[b] (hartrees)	CI lowering[c] (kcal/mol)	total energy[b] (hartrees)	CI lowering[c] (kcal/mol)	$\Delta E(SiHCH_3 - SiH_2CH_2)$ (kcal/mol)
HF	−328.97724 (1/1)	0.0	−328.98401 (1/1)	0.0	−4.2
GVB(2/4)-PP	−329.01285 (4/4)	−22.3	−329.01467 (4/4)	−19.2	−1.1
GVB-RCI(4)	−329.02412 (9/10)	−29.4	−329.01467 (6/6)	−19.2	5.9
RCI(4)*D_π	−329.03423 (813/1033)	−35.8	−329.03087 (1421/1837)	−29.4	2.1
RCI(4)*D_σ	−329.03810 (853/1093)	−38.2	−329.02571 (979/979)	−26.2	7.8
RCI(4)*[D_σ+D_π]	−329.04805 (1657/2116)	−44.4	−329.04150 (2394/2810)	−36.1	4.1
RCI(4)*D_{GVB}	−329.05799 (2233/3268)	−50.7	−329.04802 (3902/5750)	−40.2	6.3
RCI(4)*S_{val}	−329.05849 (657/1154)	−51.0	−329.03774 (776/994)	−33.7	13.0
RCI(4)*[D_π+S_{val}]	−329.06482 (1425/2129)	−55.0	−329.05095 (2075/2671)	−42.0	8.7
RCI(4)*[D_σ+S_{val}]	−329.06879 (1405/2109)	−57.4	−329.04844 (1647/1865)	−40.4	12.8
DC-CI[d]	−329.07491 (2173/3084)	−61.3	−329.06144 (2946/3542)	−48.6	8.5
CC-CI[e]	−329.08441 (2749/4236)	−67.2	−329.06780 (4454/6482)	−52.6	10.4
zero-point-energy[f] (kcal/mol)	26.8		28.0		1.2

[a] See calculational details. [b] 1 hartree = 627.5096 kcal/mol. The number of spatial configurations/spin eigenfunctions associated with each calculation is given in parentheses under each total energy. [c] The CI lowering is the relative energy of CI calculation with respect to the HF level. [d] RCI(4)*[D_σ + D_π + S_{val}]. [e] RCI(4)*[D_{GVB}+S_{val}]. [f] Zero-point vibrational energies were calculated analytically at HF/6-31G** level with MP2/6-31G** optimized geometries and used without any corrections.

energy for silaethylene is the change in the bond strength of a C–H or Si–H bond, when the vicinal Si–H or C–H bond is broken.[37] From Scheme II, we see that D_1(C–H) + D_2(Si–H) = $D_{1'}$(Si–H) + $D_{2'}$(C–H), so that D_π(silaethylene) = D_1(C–H) − $D_{2'}$(C–H) = $D_{1'}$(Si–H) − D_2(Si–H). D_1(C–H) may be taken as 99 ± 2 kcal/mol,[38] and $D_{2'}$(C–H) is estimated to be 65 ± 3 kcal/mol using the values of heats of formation in Table III. These values of D_1(C–H) and $D_{2'}$(C–H) yield a π-bond energy of 34 ± 4 kcal/mol for silaethylene, compared with the value of 64.3 kcal/mol for ethylene.[39] This π-bond energy is less than the recent estimate[40a] of 41 ± 5 kcal/mol for D_π(dimethylsilaethylene).[40]

The stabilities of the divalent silylenes are associated with the Si lone-pair orbital containing substantial s character in the singlet ground state.[13] This divalent state stabilization energy (DSSE) may be operationally defined[13,40a] as the difference between the first and second dissociation energies, which is equal to the exothermicity of the disproportionation reaction:

$$2SiXYH \rightarrow SiXYH_2 + SiXY \qquad (3)$$

$$\Delta H = \Delta H_f{}^\circ{}_{298}(SiXYH_2) + \Delta H_f{}^\circ{}_{298}(SiXY) - 2\Delta H_f{}^\circ{}_{298}(SiXYH) = -[D(XYHSi\text{–}H) - D(XYSi\text{–}H)] = -DSSE(SiXY)$$

The DSSE values for SiH_2, $SiHCH_3$, and $Si(CH_3)_2$ are estimated to be 18 ± 3, 15 ± 4, and 15 ± 6 kcal/mol, respectively, from the heats of formation in Table III. These are significantly less than the previous estimates of 26 kcal/mol for SiH_2[40a] and 28 kcal/mol for $Si(CH_3)_2$.[35]

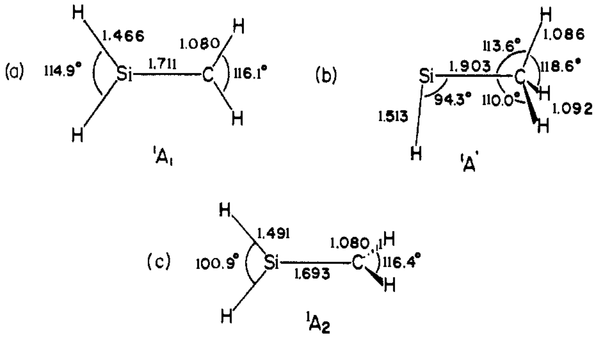

Figure 4. Optimum geometries at the MP2/6-31G** level for (a) silaethylene, (b) methylsilylene, and (c) 90° twisted silaethylene.

Theoretical Calculations

Geometry and Bonding. The calculated optimum geometries for CH_2SiH_2 ($^1A_1$), CH_3SiH ($^1A'$), and 90° twisted $\dot{C}H_2\dot{S}iH_2$ ($^1A_2$) are shown in Figure 4. The geometries for the ground-state silaethylene and methylsilylene compare well with the previous theoretical results. The Si=C bond length of 1.711 Å for silaethylene is in close agreement with a recent experimental value of 1.702 Å for $(Me)_2Si{=}C(SiMe_3)(SiMe(t\text{-}Bu)_2)$ by Wiberg and co-workers.[41] The lone pair on the Si is probably responsible for the Si–C bond length of 1.903 Å for methylsilylene being 0.036 Å longer than the prototype Si–C single bond length of 1.867 Å for SiH_3–CH_3.[42]

The generalized valence bond (GVB)[43] one-electron orbitals for the Si–C σ and π bonds in silaethylene, and for the Si–C σ

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[37] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976; p 67.

[38] $D(SiH_3CH_2\text{–}H)$ is estimated from $D(Me_3SiCH_2\text{–}H)$ = 99.2 kcal/mol (ref 13), $D(Me_3CCH_2\text{–}H)$ = 99.7 kcal/mol (ref 13), and $D(MeCH_2\text{–}H)$ = 100.6 kcal/mol (see ref 39).

[39] $\Delta H_f{}^\circ{}_{298}(C_2H_6)$ = −20.2 kcal/mol, $\Delta H_f{}^\circ{}_{298}(C_2H_4)$ = 12.5 kcal/mol (Wagman, D. D.; Schumm, R. H.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2), and $\Delta H_f{}^\circ{}_{298}(C_2H_5)$ = 28.3 kcal/mol (Doering, W. v. E. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5279) yield $D(C_2H_5\text{–}H)$ = 100.6 kcal/mol and $D(C_2H_4\text{–}H)$ = 36.3 kcal/mol. These values give D_π(ethylene) = 64.3 kcal/mol.

[40] (a) Walsh, R. *J. Phys. Chem.* **1986**, *90*, 389. (b) Gusel'nikov, L. E.; Nametkin, N. S. *J. Organomet. Chem.* **1979**, *169*, 155.

[41] Wiberg, N.; Wagner, G.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 229.

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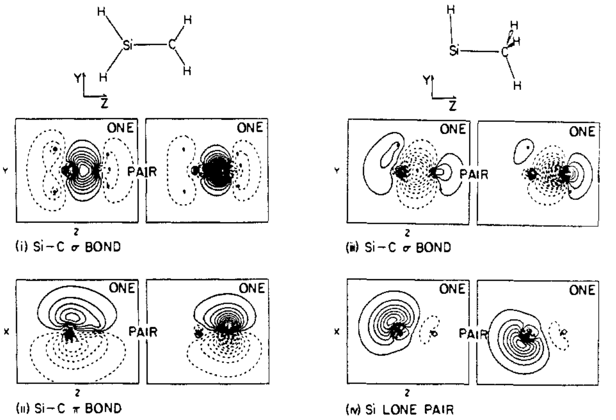

(i) Si–C σ BOND
(ii) Si–C σ BOND
(ii) Si–C π BOND
(iv) Si LONE PAIR

Figure 5. GVB orbitals for silaethylene (i and ii) and for methylsilylene (iii and iv): (i) Si–C σ bond; (ii) Si–C π bond; (iii) Si–C σ bond; (iv) Si lone-pair orbitals. Contours reflect regions of constant amplitude ranging from −1.0 to 1.0 au, with increments of 0.03 au.

and Si lone pair in methylsilylene, are shown in Figure 5. The nature of the Si=C bond in silaethylene is similar to that of the C=C bond in ethylene.[44] The Si–C σ and π bond pairs of silaethylene have overlaps of 0.85 and 0.61, respectively, which are close to the C–C σ and π overlaps of 0.88 and 0.65 in ethylene.[44] The overlaps are slightly lower in silaethylene than in ethylene due to the greater size of the Si 3p orbital relative to C 2p orbital [R(Si=C) = 1.711 Å vs. R(C=C) = 1.34 Å[45]]. The Si–C bond pair of methylsilylene has an overlap of 0.83, which is slightly lower than that of silaethylene because of the longer bond, and the Si lone pair has an overlap of 0.67 which is typical for lone pairs in SiH_2 ($^1A_1$) (0.67)[46] and CH_2 ($^1A_1$) (0.66).[46]

Relative Stabilities of Silaethylene and Methylsilylene and Rotational Barrier in Silaethylene. The energies of silaethylene and methylsilylene at various levels of theory are summarized in Table V. As electron correlation is included, ΔE changes from −4.2 kcal/mol (HF) to 10.4 kcal/mol (CC-CI). The subtle difference between HF and GVB(2/4)-PP (ΔE = −1.1 kcal/mol) is the higher correlation error in the HF Si–C π bond (because of the low overlap) with a differential correlation of 3.1 kcal/mol. Going from GVB(2/4)-PP to GVB-RCI(4) includes the additional spin coupling (more important for **1**) and also includes interpair correlations in the double bond leading to a differential effect of 7.0 kcal/mol and ΔE = 5.9 kcal/mol. Going to full correlation-consistent CI (CC-CI) leads to an additional differential of 4.5 kcal/mol (favoring the state with the largest correlation effect) and ΔE = 10.4 kcal/mol.

We calculate a zero-point-energy difference of 1.2 kcal/mol, in favor of silaethylene, leading to ΔE = 11.6 kcal/mol. This energy difference is significantly greater than the previous values but is in excellent agreement with our experimental result of 10 ± 3 kcal/mol.

The rotational barrier in silaethylene is calculated at various levels from the energy difference between the ground state $^1A_1$ CH_2SiH_2 and the 90° twisted biradical state $^1A_2$ $\dot{C}H_2\dot{S}iH_2$ (summarized in Table VI). The highest dissociation-consistent CI (DC-CI),[47] after correcting for the calculated zero-point-energy difference of −2.0 kcal/mol, yields the adiabatic rotational barrier of 59.9 kcal/mol, compared with the experimental value of 65 kcal/mol for ethylene.[48]

Table VI. Rotational Barrier in Silaethylene (kcal/mol)[a]

level	total energy (h)[b]		rotational barrier
	$^1A_1$ SiH_2CH_2	$^1A_2$ $\dot{S}iH_2\dot{C}H_2$	
HF	−328.97724 (1/1)	−328.91492 (1/1)	39.1
GVB(2/4)-PP	−329.01285 (4/4)	−328.92515 (2/2)	55.1
GVB-RCI(4)	−329.02412 (9/10)	−328.92716 (3/4)	61.0
RCI(4)*S_{val}	−329.05849 (657/1154)	−328.96542 (249/606)	58.4
RCI(4)*[D_σ+D_π]	−329.04805 (1657/2116)	−328.94306 (289/520)	65.8
DC-CI[c]	−329.07491 (2173/3084)	−328.97634 (503/1058)	61.9
zero-point-energy[d] (kcal/mol)	26.8	24.8	−2.0

[a] See calculational details. [b] 1 h = 1 hartree = 627.5096 kcal/mol. The number of spatial configurations/spin eigenfunctions associated with each calculation is given in parentheses under each total energy. [c] RCI(4)*[D_σ+D_π+S_{val}]. [d] Zero-point vibrational energies were calculated analytically at HF/6-31G** level with MP2/6-31G** optimized geometries and used without any corrections.

Summary

It is experimentally found that silaethylene is more stable than methylsilylene by 10 ± 3 kcal/mol. The correlation-consistent CI calculation, starting from the GVB(2/4) descriptions of the two isomers, yields an energy difference of 11.6 kcal/mol in favor of silaethylene. The effects of both electron correlation and zero-point-energy differences favor silaethylene. This result and our previously reported result for the parent silylene suggest that the lone-pair stabilization effects in (methyl-substituted) silylenes are significantly smaller than the previous expectations. The estimated π-bond energy and the calculated rotational barrier in silaethylene are 34 ± 4 and 59.9 kcal/mol, respectively, compared with the experimental values of 64.3 and 65 kcal/mol in ethylene, respectively. An experimental exploration of cis–trans isomerization in silaethylene is desired in order to determine the rotational barrier.

Calculational Details

Geometries and Vibrational Frequencies. The equilibrium geometries and harmonic vibrational frequencies were calculated using the GAUSSIAN 82 program.[49] All geometrical parameters were optimized at the MP2/6-31G** level (second-order Møller–Plesset perturbation theory[50] using the 6-31G** basis set[51]). MP2 theory incorporates the second-order perturbation corrections involving up to double excitations from the Hartree–Fock reference wave function. The 6-31G** basis set is of the split-valence quality and contains polarization functions on the hydrogen atoms as well as on the heavy atoms (Si and C). This level of theory has been shown to provide accurate equilibrium geometries.[52] Harmonic vibrational frequencies were calculated analytically at the HF/6-31G** level (Hartree–Fock theory[53] using the 6-31G** basis set) using the MP2/6-31G** geometries. These frequencies provide zero-point-energy corrections for de-

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(46) The overlaps of lone pairs in SiH_2 ($^1A_1$) and CH_2 ($^1A_1$) were obtained at GVB(1/2) level with VDZ + P basis sets and MP2/6-31G** optimized geometries.

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termining relative stabilities and the rotational barrier in silaethylene.

GVB Wave Functions. The energies of the ground state of silaethylene and methylsilylene were calculated by using various levels of the generalized valence bond (GVB) plus configuration interaction (CI) method.[43,47]

For the $^1A_1$ state of silaethylene, the GVB(2/4) wave function corresponds to correlating the Si–C σ and Si–C π bonds, each with the natural orbitals, leading to four natural orbitals for the two correlation pairs.

For the $^1A'$ state of methylsilylene, the GVB(2/4) wave function correlates the Si–C σ bond with a second natural orbital and the Si nonbonding orbital with an empty Si $3p_x$ orbital.

For both cases, all other orbitals are doubly occupied and calculated self-consistently. To relax the simple valence bond (perfect pairing) spin coupling restriction, we allow all configurations arising from distributing the two electrons of each GVB pair between its two natural orbitals. This leads to the GVB-RCI(4) wave function which allows all spin couplings. To include various higher order correlation effects (beyond GVB), we use correlation-consistent CI (CC-CI), in which we start with GVB pairs of each RCI and allow all single and double excitations to all GVB, valence, and virtual orbitals [denoted as RCI(4)*D_{GVB}]. Since the correlated wave function may want orbitals with slightly different shapes, we also allow all single excitations from the valence orbitals of the GVB-RCI(4) configurations to all GVB, valence, and virtual orbitals. Thus the full CC-CI wave function is RCI(4)*[D_{GVB}+S_{val}].

Calculations carried out for the rotational barrier in silaethylene are such that the wave function at the equilibrium geometry of the Si=C double-bonded CH_2SiH_2 ($^1A_1$) dissociates correctly to the 90° twisted Si—C single-bonded $\dot{C}H_2\dot{S}iH_2$ ($^1A_2$), retaining the same level of electron correlation. In addition, we allow the 90° twisted singlet biradical state to relax to its equilibrium geometry, thus obtaining the adiabatic rotational barrier.

The GVB(2/4), GVB-RCI(4), and RCI(4)*S_{val} wave functions for CH_2SiH_2 ($^1A_1$) dissociate correctly to the GVB(1/2) (which corresponds to correlating the Si–C σ bond with its natural orbital), GVB-RCI(2), and RCI(2)*S_{val} wave functions for $\dot{C}H_2\dot{S}iH_2$ ($^1A_2$), respectively. The RCI(4)*[D_σ+D_π] wave function dissociates to RCI(2)*[D_σ+S_{open}] (single excitation from singlet open-shell orbitals in the RCI wave function to all virtual orbitals in addition to all single and double excitations from σ GVB pair of each RCI to all GVB, valence, and virtual orbitals) wave functions. The full DC-CI [designated as RCI(4)*[D_σ+D_π+S_{val}]] wave function dissociates to RCI(2)*[D_σ+S_{val}] wave function.

GVB Basis Sets. All atoms were described with valence double-ζ (VDZ) basis sets[54] which may be described as Si(11s7p/4s3p), C(9s5p/3s2p), and H(4s/2s). In addition, one set of p-polarization functions (exponent $\alpha = 1.0$) was added to the H basis set. Sets of d-polarization functions centered on Si ($\alpha = 0.42$) and C ($\alpha = 0.62$) (exponents optimized for CH_2SiH_2 at the HF level) were added to the valence double-ζ basis sets for Si and C.

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Registry No. **1**, 51067-84-6; **2**, 55544-30-4; CH_3SiD_3, 1066-43-9; $(CH_3)_2S$, 75-18-3; NH_3, 7664-41-7; CH_3CONH_2, 60-35-5; $C_6H_5NH_2$, 62-53-3; CH_3NH_2, 74-89-5; $C_6H_5CH_2NH_2$, 100-46-9; $C_2H_5NH_2$, 75-04-7; $(CH_3)_2NH$, 124-40-3; SiH_2, 13825-90-6; $SiMe_2$, 6376-86-9.

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Experimental Determination of Internal Energy Barriers in the Gas-Phase Aromatic Alkylation by Dimethylchloronium Ions

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Abstract: The temperature and pressure dependence of the substrate selectivity of the alkylation of mesitylene (M) and *p*-xylene (X) by radiolytically formed $CH_3ClCH_3^+$ ions have been investigated in CH_3Cl gas at pressures between 50 and 760 Torr in the range 40–140 °C. The Arrhenius plot of the empirical k_M/k_X ratio measured at 760 Torr is linear over the entire temperature range investigated, and its slope corresponds to a difference of 2.2 ± 0.2 kcal mol^{-1} between the activation energy for the $CH_3ClCH_3^+$ methylation of *p*-xylene and mesitylene. A pressure-dependence study of the same competition reactions carried out at 100 °C points to 300 Torr as the pressure limit, below which the correspondence between the phenomenological Arrhenius-plot slope and the actual activation-barrier difference is not any longer warranted. This conclusion is further corroborated by a comparison of the present results with those derived for the same reactions from reactant ion monitoring (RIM) "high-pressure" mass spectrometry at 0.5–1.2 Torr. The large discrepancy observed is interpreted as evidence that above 300 Torr the activation mechanism of the $CH_3ClCH_3^+$ methylation of arenes, a typical ion–molecule process, is essentially thermal and that, below this limit, coexistence of both thermal and electrostatic activation mechanisms as well as incomplete equilibration of the internal energy of the reactants make Arrhenius plots hardly a measure of the activation barriers involved in the gas-phase aromatic alkylations.

Ion–molecule reactions are normally investigated in the gas phase with different mass spectrometric methods, whose common feature is the low operating pressure (≤5 Torr). Under such conditions, the relevant kinetics are dominated by long-range ion–dipole attractive forces and found to fit Brauman's double-well energy surface model, involving an internal energy barrier E^*_0 at the transition state (curve a in Figure 1a).[1] Magnera and

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