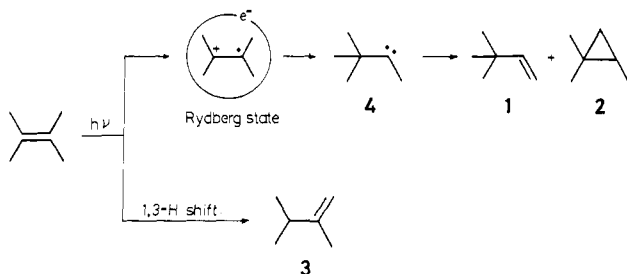


Table II. Fluorescence Intensity and Relative Ratio of Photolysis Products upon Excitation at 185-229 nm in Neat (Fluorescence) or 10 mM Solution (Photolysis) of 2,3-Dimethyl-2-butene

exc wave-length, nm	fluorescence		product ratio "carbene"/"1,3-shift" ^c
	quantum yield ^a	rel int ^b	
185	1.5×10^{-4}	$\equiv 1$	0.36 ($\equiv 1$)
214	2.7×10^{-4}	2.2	0.78 (2.2)
229	3.5×10^{-4}	3.5	5.9 (16)

^aReference 5. ^bThis work. ^cReferences 3 and 12.

Scheme I. Photochemistry of 2,3-Dimethyl-2-butene in Solution



citation light and the different phase employed, the maximum of fluorescence excitation spectrum shows good agreement with the absorption maximum of the R-N transition band for each alkene, although a somewhat larger difference is seen with 2-methyl-2-butene.¹¹ Furthermore, the relative intensity of the fluorescence from 2,3-dimethyl-2-butene excited at 185, 214, and 229 nm

(11) The different phases employed in the measurements of absorption and fluorescence excitation spectra would be responsible for the difference in both maxima, although the Rydberg transitions typically shift to shorter wavelengths with considerable broadening of the bandwidth in going from vapor to condensed phase.

coincides nicely with the relative quantum yield reported,⁵ as shown in Table II. These results provide further evidence in support of the assignment that the emissive state is a $\pi, R(3s)$ Rydberg state rather than a π, π^* excited state.

From the photochemical point of view, the present result is crucial in identifying the excited state involved in the photoreaction of 2,3-dimethyl-2-butene.^{2,3} As shown in Scheme I, the direct irradiation of 2,3-dimethyl-2-butene in solution phase gives three major photoproducts, 1-3. The combined yield of rearrangement products 1 and 2, which are derived from a carbene 4, increases with increasing excitation wavelength from 185 to 214 and then to 229 nm, whereas the yield of 1,3-hydrogen-shift-derived product 3 decreases compensatorily.^{3,12} As a result, a dramatic change in the relative ratio of "carbene" to "1,3-shift", i.e., $(1 + 2)/3$, is observed as shown in the last column of Table II. It is noted that the relative fluorescence yield is in good agreement with the relative product ratio $(1 + 2)/3$. This coincidence reinforces the reaction mechanism proposed by Kropp² and Inoue et al.³ that the carbene 4 arises from the $\pi, R(3s)$ Rydberg state, in which the cation-radical-like electronic configuration around the molecular core¹³ promotes the alkyl shift to the cation center.

Acknowledgment. This work was performed mostly at the Ultraviolet Synchrotron Orbital Radiation Facility (UVSOR), the Institute for Molecular Science (joint studies program No. 62-B901). We are grateful for the technical support of Drs. M. Watanabe, K. Fukui, and T. Kasuga of the UVSOR. We also appreciate the helpful discussion with Prof. F. Hirayama of Miyazaki Medical College.

Registry No. *trans*-2-Octene, 13389-42-9; *trans*-cyclooctene, 931-89-5; 2-methyl-2-butene, 513-35-9; 2,3-dimethyl-2-butene, 563-79-1.

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Determination of the β -Silicon Effect from a Mass Spectrometric Study of the Association of Trimethylsilylium with Alkenes

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Abstract: A mass spectrometer equipped with a high-pressure ion source and pulsed electron beam has been used to study the association of alkenes with trimethylsilylium: $\text{Me}_3\text{Si}^+ + \text{alkene} \rightleftharpoons \text{Me}_3\text{Si-alkene}^+$ (7). The equilibrium constants for reaction 7 have been measured for a series of alkenes over a range of temperatures, and from the resulting van't Hoff plots the following $-\Delta H_7^\circ$ (kcal mol⁻¹) and $-\Delta S_7^\circ$ (in brackets; cal K⁻¹ mol⁻¹) values are obtained: ethene, 23.6 ± 0.3 (38.5 ± 0.8); propene, 30.6 ± 0.4 (42.5 ± 0.8); *trans*-2-butene, 30.9 ± 0.6 (41.5 ± 1.5); isobutene, 36.5 ± 1.1 (42.7 ± 2.1); 2-methyl-2-butene, 38.2 ± 0.5 (48.0 ± 1.1); cyclohexene, 32.9 ± 1.0 (45.6 ± 2.1); styrene, 36.6 ± 0.7 (42.4 ± 1.4). The β -silicon effect, defined as the stabilization energy resulting from a silicon atom in a position β to a carbenium carbon, is given by ΔH° for the isodesmic reaction $\text{Me}_3\text{Si-X}^+ + \text{XH}_2 \rightleftharpoons \text{Me}_3\text{SiXH} + \text{XH}^+$ (X = alkene). $\Delta H_f^\circ(\text{Me}_3\text{SiX}^+)$ is obtained from ΔH_7° using $\Delta H_f^\circ(\text{Me}_3\text{Si}^+) = 141$ kcal mol⁻¹; $\Delta H_f^\circ(\text{Me}_3\text{SiXH})$ is estimated. The stabilization energies (kcal mol⁻¹) are the following: X = ethene, 48.2; propene, 38.4; *trans*-2-butene, 38.2; isobutene, 28.1; 2-methyl-2-butene, 28.8; 2,3-dimethyl-2-butene, 25.8; styrene, 21.8. These values are grouped according to the number of substituents α to the carbenium carbon in classically drawn structures and are consistent with the theoretically predicted large hyperconjugative interaction between the Si-C σ -bond and the formally empty p orbital on the carbenium carbon.

Organosilicon compounds are finding increasing use in synthetic organic chemistry,¹ but unfortunately the basic thermochemical information required to predict the mechanistic properties of organosilicon molecules is very sparse and what little there is

should be treated very critically.² Quantitative information is required regarding the effects on the kinetics and thermochemistry of reactions caused by the introduction of silicon-containing substituents into organic molecules. One aspect of organosilicon

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chemistry that has long been known is the remarkable increase in rates engendered in solvolytic reactions by the presence of a silyl group in a position β to the site of a proposed carbenium ion intermediate (the so-called β -silicon effect).³ New examples of such solvolytic rate enhancement attributable to this effect continue to be cited.⁴ It is only recently however that theoretical calculations have provided quantitative support for the phenomenon.^{5,6} The calculations apply only to gas-phase ions whereas all the experimental data are for the liquid phase in which large solvent effects, not accounted for in the calculations, are usually present. It is therefore essential that the calculations be complemented by gas-phase experimental work.

Recently, Hajdasz and Squires⁷ used a flowing afterglow triple quadrupole apparatus to study the properties of the association complex formed by Me_3Si^+ (trimethylsilylium) and ethene. They obtained by the bracketing technique a proton affinity (PA) of 199 ± 2 kcal/mol for $\text{Me}_3\text{SiCH}=\text{CH}_2$ and from this estimated that the ethyl cation is stabilized by 39 kcal/mol when an H is replaced by Me_3Si . This value is in excellent agreement with a calculated value of 38 kcal/mol.⁵ In this paper we report an approach that involves the direct determination, using high-pressure mass spectrometry, of the binding energy of Me_3Si^+ to a variety of alkenes. From this data the enthalpy of formation of $\text{Me}_3\text{Si-alkene}^+$ can be obtained, which allows the calculation of the β -silicon effect in these ions. The data demonstrate both the magnitude of the effect and its attenuation with increasing methyl substitution α to the carbenium carbon.

Experimental Section

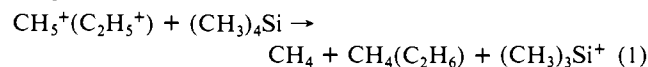
The high-pressure mass spectrometer with pulsed electron beam and data collection system has been described previously in detail.⁸ Gaseous samples are premixed in a 5-L glass vessel from which they are fed to the ion source via a heated variable leak. The field free ion source is operable at pressures of 2–5 Torr and temperatures of 300–600 K. In the pulsed electron beam mode the 2-kV electron beam is switched on for a period of 50 μs , during and after which the resulting ions disappear from the ion source either by diffusion to the walls or entrained in the buffer gas leaving the source through the 1×0.03 mm² ion exit and electron entrance slits. The pulse is not repeated until all ions from the previous pulse have disappeared from the source. At 600 K the repetition rate is ~ 200 Hz while at 300 K, when the half-life of the ions is much longer, it may be as low as 50 Hz. Reactions between ions and neutrals occur during the ion residence times, and qualitative and quantitative information regarding these reactions is obtained from the temporal profiles of ions of all m/z values that exit the source. Data resulting from 1000–5000 electron beam pulses are usually sufficient to accumulate an acceptable number of counts for each ion in the multichannel analyzer, which follows the ion-counting equipment.

Metastable spectra and collision-assisted dissociation (CAD) spectra, using helium as the collision gas in the second field-free region, were obtained with a ZAB-2FQ instrument.

Methane (better than 99.99% pure) and ethene, propene, *trans*-2-butene, and isobutene (all CP grade) were from Matheson. Tetramethylsilane (TMS; Merck, Sharpe and Dohme), styrene, cyclohexene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene (Aldrich) were dried with 3- \AA molecular sieves prior to use.

Results

Me_3Si^+ is the only initial silicon-containing ion observed following the reaction of the methane reagent ions (mainly CH_5^+ and C_2H_5^+) with TMS in CH_4/TMS (99.5/0.5) mixtures at any temperature.⁹



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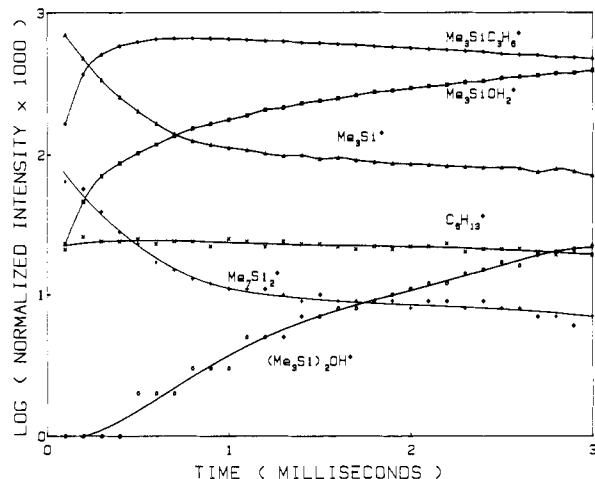
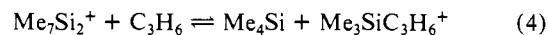


Figure 1. Normalized ion intensities as functions of time after a 50- μs pulse of ionizing electrons for a methane/TMS/propene ($1/1.1 \times 10^{-3}/1.5 \times 10^{-4}$) mixture at 413 K (3.6 Torr). The methane reagent ions (CH_5^+ and C_2H_5^+) disappear within 50 μs of the end of the electron beam pulse and are not shown.

In this system Me_3Si^+ associates reversibly with TMS, giving Me_7Si_2^+ ($\Delta H^\circ = -22.3$ kcal/mol¹⁰), and with adventitious water, giving protonated trimethylsilanol ($\text{Me}_3\text{SiOH}_2^+$, $\Delta H^\circ = -30.1$ kcal/mol¹¹). Displacement from these complexes of TMS or H_2O occurs when a stronger nucleophile is present. If the concentration of the latter is small, then these competitive reactions, especially that with water, may complicate the delineation of the kinetic pathways involving the reaction of Me_3Si^+ with the added nucleophile.

Figure 1 shows a typical plot of the normalized ion yields as functions of time, in this case for a propene/TMS/ CH_4 mixture. Me_3Si^+ and Me_7Si_2^+ are in equilibrium throughout the whole observation period as demonstrated by the constancy of the ratio of their ion currents. They both decay in parallel on the logarithmic plot as the $\text{Me}_3\text{Si-propene}^+$ complex is formed. A time of 1 ms after the electron pulse the intensities of all three ions decay in parallel, showing their interrelationship via the following equilibria:



At long reaction time the yield of $\text{Me}_3\text{SiOH}_2^+$ builds up but at a rate that is sufficiently low due to the low concentration of adventitious water that the equilibria of the faster reactions 2–4 are not disturbed and equilibrium is not attained by reaction 5.



A small yield of m/z 163 appears at long reaction time. This is protonated hexamethyldisiloxane, which we believe, but have never proved, is formed in reaction 6. m/z 85, $\text{C}_6\text{H}_{13}^+$, is unreactive



and presumably arises from the association of protonated propene (C_3H_7^+) with propene. C_3H_7^+ is probably formed by protonation of propene by the methane reagent ions since Me_3Si^+ is too weak a gas-phase acid to protonate propene.¹²

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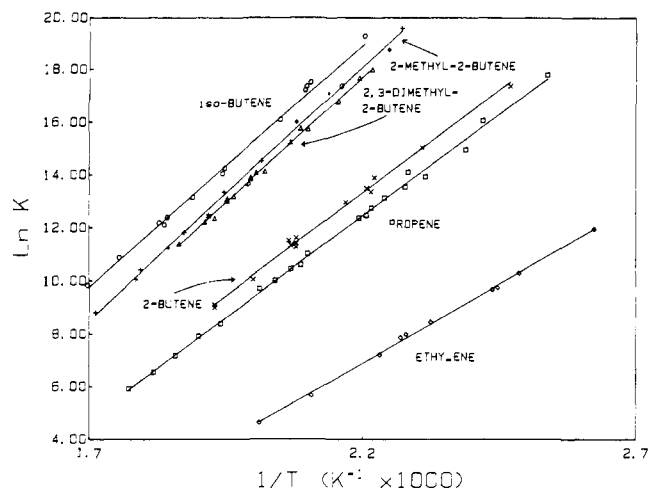


Figure 2. van't Hoff plots for the equilibria $\text{Me}_3\text{Si}^+ + \text{alkene} \rightleftharpoons \text{Me}_3\text{Si-alkene}^+$.

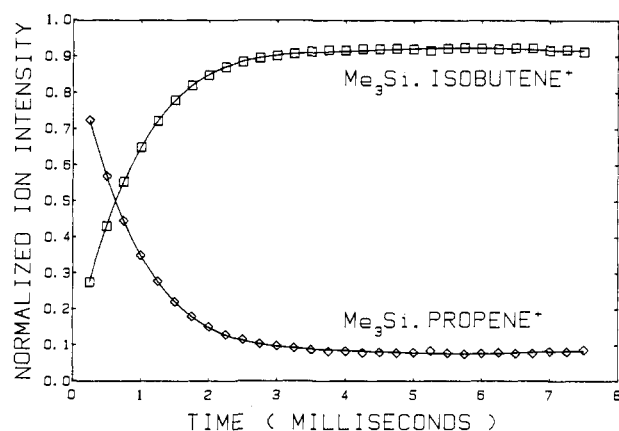


Figure 3. Normalized ion intensities as functions of time after a 50- μs ionizing pulse of electrons for the Me_3Si^+ -transfer reaction: $\text{Me}_3\text{Si-propene}^+ + \text{isobutene} \rightleftharpoons \text{Me}_3\text{Si-isobutene}^+ + \text{propene}$. Sample composition: methane/TMS/propene/isobutene (99.5/0.5/0.016/0.000027) at 461 K (4.5 Torr).

Table I. Thermodynamic Data for the Equilibrium $\text{Me}_3\text{Si}^+ + \text{Alkene} \rightarrow \text{Me}_3\text{Si-alkene}^+$ Obtained from the van't Hoff Plots of Figure 2

alkene	$-\Delta H^\circ$ ^a	$-\Delta S^\circ$ ^{b,c}	ΔH_f° ^d ($\text{Me}_3\text{Si-alkene}^+$) ^{a,d}
ethene	23.6 ± 0.3	38.5 ± 0.8 (42)	130.0
propene	30.6 ± 0.4	42.5 ± 0.8 (43)	115.2
<i>trans</i> -2-butene	30.9 ± 0.6	41.5 ± 1.3	107.4
isobutene	36.5 ± 1.1	42.7 ± 2.1 (44)	100.5
2-methyl-2-butene	38.2 ± 0.5	48.0 ± 1.1 (47)	92.8
2,3-dimethyl-2-butene	37.9 ± 0.5	48.1 ± 1.1 (48)	86.8
cyclohexene	32.9 ± 1.0	45.6 ± 2.1	106.9
styrene	36.6 ± 0.7	42.4 ± 1.4	139.75

^aIn kcal mol⁻¹. ^bIn cal K⁻¹ mol⁻¹. ^cFigures in brackets are calculated entropy changes at 300 K taking into account changes in translational and external rotational entropy and the free rotation of the Me_3Si group in the adduct. Details of the calculations are in ref 28. ^dAbsolute values may be in error by up to 10 kcal mol⁻¹ due to the uncertainty in $\Delta H_f^\circ(\text{Me}_3\text{Si}^+)$, which is taken as 141 kcal mol⁻¹ (see text). Relative values are probably better than ± 5 kcal mol⁻¹.

K_3 , the equilibrium constant for reaction 3, is obtained from the ratio of ion intensities of $\text{Me}_3\text{SiC}_3\text{H}_6^+$ and Me_3Si^+ when equilibrium has been attained and from the known partial pressure of propene in the ion source. The standard state P° is 760 Torr.

$$K_3 = i_{\text{Me}_3\text{SiC}_3\text{H}_6^+} / i_{\text{Me}_3\text{Si}^+} (P_{\text{C}_3\text{H}_6} / P^\circ)$$

The values of K are independent of ion-source pressure over the accessible range of 1.5–5.0 Torr. The van't Hoff plots shown in Figure 2 were each obtained over several days with samples containing different alkene concentrations. The alkenes studied

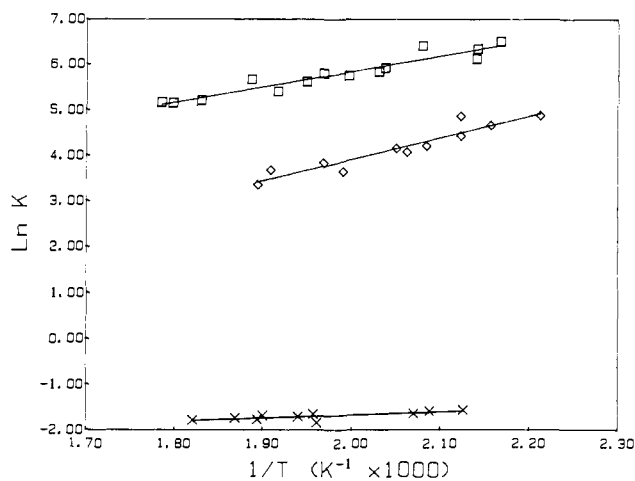


Figure 4. van't Hoff plots for Me_3Si^+ -transfer equilibria between pairs of olefins: \square , $\text{Me}_3\text{Si-propene}^+ + \text{isobutene} \rightleftharpoons \text{Me}_3\text{Si-isobutene}^+ + \text{propene}$; \diamond , $\text{Me}_3\text{Si-propene}^+ + 2,3\text{-dimethylbutene} \rightleftharpoons \text{Me}_3\text{Si-2,3-dimethylbutene}^+ + \text{propene}$; \times , $\text{Me}_3\text{Si-isobutene}^+ + 2,3\text{-dimethylbutene} \rightleftharpoons \text{Me}_3\text{Si-2,3-dimethylbutene}^+ + \text{isobutene}$.

STANDARD ENTHALPY AND ENTROPY CHANGES FOR THE EQUILIBRIA:

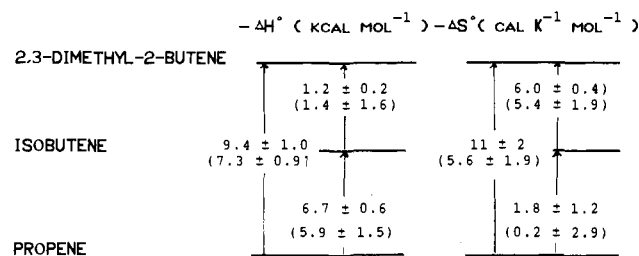
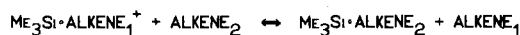


Figure 5. Changes in standard enthalpies and entropies obtained from the van't Hoff plots in Figure 4. The numbers in parentheses are those obtained from the appropriate data in Table I.

Table II. CAD Spectra of $\text{Me}_3\text{Si-alkene}^+$ Complexes Taken with Helium as the Collision Gas and 5% Attenuation of the Main Beam

neutral loss	relative abundance		
	propene	2-methyl-2-butene	2,3-dimethyl-2-butene
CH_3	0.007	0.004	0.004
CH_4	0.014	0.009	0.004
C_2H_5	0.008	0.006	0.018
C_2H_6	0.013	0.027	
C_3H_6	0.921	0.004	
C_3H_7	0.037	0.003	
C_4H_9		0.004	0.013
$\text{C}_4\text{H}_9 + \text{H}_2$			0.006
C_5H_{10}		0.934	
$\text{C}_5\text{H}_{11} + \text{H}_2$			0.012
C_6H_{12}			0.926

were ethene (E), propene (P), *trans*-2-butene (TB), isobutene (IB), 2-methyl-2-butene (MB), 2,3-dimethylbutene (DMB), cyclohexene (CY), and styrene (ST). The thermodynamic data obtained from the van't Hoff plots of Figure 2 are given in Table I.

Competitive Me_3Si^+ transfer between pairs of nonisomeric alkenes can be studied in certain cases. The temperature range over which such an equilibrium transfer can be observed for any one pair is severely limited in most cases by the relatively large difference in enthalpy of binding of Me_3Si^+ to the individual members of the alkene pair. Figure 3 illustrates typical time-

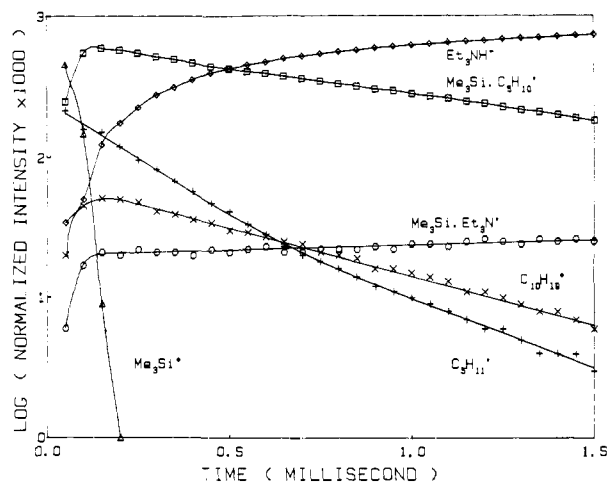


Figure 6. Normalized ion intensities as functions of time after a 50- μ s ionizing pulse of electrons for the system methane/TMS/2-methyl-2-butene/triethylamine (99.8/0.18/9.2 $\times 10^{-4}$ /2.9 $\times 10^{-5}$) at 400 K (3.7 Torr).

resolved normalized ion currents for a pair of $\text{Me}_3\text{Si-alkene}^+$ complexes while Figure 4 shows the van't Hoff plots for the three pairs studied. The thermodynamic data obtained from these plots are in Figure 5.

The pure metastable spectra of the $\text{Me}_3\text{Si-alkene}^+$ complexes of P, MB, and DMB from decompositions in the second field-free region of the ZAB-2FQ show only one peak, Me_3Si^+ , resulting from the loss of alkene. The CAD spectra taken with 5% attenuation of the main beam for the same $\text{Me}_3\text{Si-alkene}^+$ complexes contain more ions than the metastable spectra; however, the normalized CAD spectra in Table II show that loss of alkene is by far the predominant decomposition mode.

The alkenes in $\text{Me}_3\text{Si-E}^+$, $\text{Me}_3\text{Si-P}^+$, $\text{Me}_3\text{Si-CY}^+$, and $\text{Me}_3\text{Si-TB}^+$ are readily displaced by adventitious water to give $\text{Me}_3\text{Si-OH}_2^+$. Since the water concentration in the ion source was unknown and since free Me_3Si^+ was always present in significant quantities in equilibrium with $\text{Me}_3\text{Si-alkene}^+$ in these samples, it was not possible to determine whether $\text{Me}_3\text{Si-OH}_2^+$ was formed via alkene displacement from $\text{Me}_3\text{Si-alkene}^+$ by water or via the reaction of free Me_3Si^+ with water. Other oxygen bases, B, such as methanol, ethanol, and diethyl ether also decrease the $\text{Me}_3\text{Si-alkene}^+$ yields and in fact can decrease the yields of all the $\text{Me}_3\text{Si-alkene}^+$ complexes, not just those noted above. The products of such reactions are $\text{Me}_3\text{Si-B}^+$. The measured rate constant for the disappearance of $\text{Me}_3\text{Si-DMB}^+$ by reaction with EtOH is $3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ at 613 K. No proton transfer from $\text{Me}_3\text{Si-DMB}^+$ to ethanol is observed, which is as expected since $\text{PA}(\text{EtOH}) = 188 \text{ kcal mol}^{-1}$ is less than $\text{PA}(\text{DMB}) = 199 \text{ kcal mol}^{-1}$. In addition no proton transfer is observed from $\text{Me}_3\text{Si-DMB}^+$ to DMB. In the presence of added water the yield of DMBH^+ very slowly increases at the expense of $\text{Me}_3\text{Si-DMB}^+$. This is attributable to the slow displacement of DMB^+ by H_2O followed by proton transfer from the resulting $\text{Me}_3\text{Si-OH}_2^+$ ($\text{PA}(\text{Me}_3\text{SiOH}) = 191 \text{ kcal mol}^{-1}$).

The strong base NEt_3 (triethylamine, $\text{PA} = 232 \text{ kcal mol}^{-1}$) was examined as a potential acceptor of protons from $\text{Me}_3\text{Si-alkene}^+$. Figure 6 shows the time-resolved normalized ion intensities for a MB/ Et_3N / Me_3Si / CH_4 mixture. Et_3N reduces the yield of $\text{Me}_3\text{Si-alkene}^+$ for all alkenes; the major product of the reaction for TB and higher alkenes is Et_3NH^+ together with smaller amounts of $\text{Me}_3\text{Si-Et}_3\text{N}^+$. The yield of the latter ion however increases only while free Me_3Si^+ is present. As seen in Figure 6, after Me_3Si^+ has disappeared the $\text{Me}_3\text{Si-Et}_3\text{N}^+$ yield remains constant. The binding energy of Et_3N to Me_3Si^+ has not been measured, and we cannot measure it directly by generating a van't Hoff plot like those in Figure 3 because the temperature range required to study the association equilibrium is above that attainable with our instrument. Competitive Me_3Si^+ -transfer experiments suggest a value above 50 kcal/mol. Conditions under

Table III. Rate Constants for the Reaction of Et_3N^+ with $\text{Me}_3\text{Si-alkene}^+$

alkene	T, K	k , $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
propene	449	6×10^{-10}
isobutene	448	3×10^{-10}
2-methyl-2-butene	401	3×10^{-10}
2,3-dimethyl-2-butene	404	8×10^{-11}

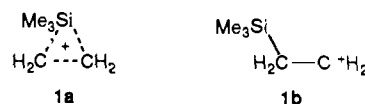
which measurable equilibria occur were not obtained in these competition experiments because, in addition to the formation of the adduct $\text{Me}_3\text{Si-Et}_3\text{N}^+$, the reaction of Me_3Si^+ with Et_3N also produces an ion at m/z 100, which we presume to be $\text{Et}_3\text{NC}_2\text{H}_4^+$. This ion disappears to give $\text{Me}_3\text{Si-Et}_3\text{N}^+$, probably by reaction with TMS. Rate constants are determined for the decay of $\text{Me}_3\text{Si-alkene}^+$ in the presence of Et_3N from the slopes of the linear portions of the decay curves at long reaction time. For propene a correction is made for the reaction of $\text{Me}_3\text{Si-P}^+$ with adventitious water using data for the system in the absence of Et_3N . The results are presented in Table III.

The weaker Brønsted bases Me_2NH ($\text{PA} = 221 \text{ kcal/mol}$) and MeNH_2 ($\text{PA} = 214 \text{ kcal/mol}$) were examined as potential proton acceptors, but they were found to react with $\text{Me}_3\text{Si-DMB}^+$ mainly by Me_3Si^+ transfer. The major product with MeNH_2 is not the expected $\text{Me}_3\text{Si-MeNH}_2^+$ but m/z 102, which corresponds to an ion formed by loss of H_2 from the adduct.

Discussion

The exclusive loss of alkene in the metastable spectra, the near exclusive loss of alkene in the CAD spectra, and the observation of competitive Me_3Si^+ -transfer equilibria, taken collectively, constitute convincing proof that the Me_3Si group remains inviolate in the $\text{Me}_3\text{Si-alkene}^+$ complexes. This absence of rearrangement by transfer or methyl from Me_3Si to the carbenium carbon with charge localization on silicon is in agreement with calculation,⁶ which shows an energy barrier of 42 kcal/mol^{-1} to any type of rearrangement whatsoever in the $\text{Me}_3\text{Si-E}^+$ complex. This is also in accord with results from a flow-type study⁷ of the association of Me_3Si^+ with C_2H_4 and C_2D_4 . Analysis of the resulting $\text{Me}_3\text{Si-E}^+$ complexes by triple quadrupole CAD showed that decomposition was only by loss of ethylene, and there was no evidence for scrambling of hydrogens between Me_3Si and the ethene prior to the loss of ethene.

Ab initio MO calculations for $\text{Me}_3\text{Si-E}^+$ show the bridged structure, **1a**, is more stable than the open structure, **1b** (geometry



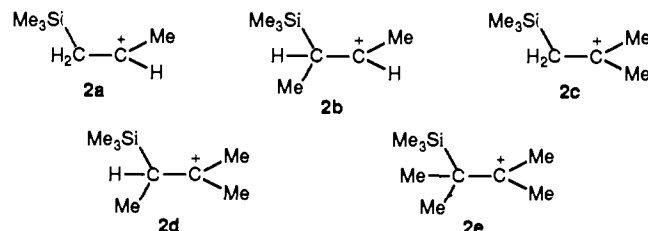
optimized but not given), which is not at a minimum on the potential energy surface.⁶ This is in agreement with the nonobservation of proton transfer from $\text{Me}_3\text{Si-E}^+$ to such strong Brønsted bases as tertiary amines.⁷ We were unable to confirm this observation in our apparatus because, at the relatively low temperatures required to observe $\text{Me}_3\text{Si-E}^+$ in good yield, the added base can also be protonated by the ever present $\text{Me}_3\text{Si-OH}_2^+$. Both $\text{Me}_3\text{Si-Et}_3\text{N}^+$ and Et_3NH^+ are formed when a small amount of Et_3N is present in a P/TMS/ CH_4 mixture. $\text{Me}_3\text{Si-Et}_3\text{N}^+$ may be formed in this system by direct association of the free Me_3Si^+ with the amine, and some, if not all of the Et_3NH^+ may arise via $\text{Me}_3\text{Si-OH}_2^+$ as an intermediate. The rate constant in Table III for $\text{Me}_3\text{Si-P}^+ + \text{Et}_3\text{N}$ is therefore an upper limit for proton transfer. There is no problem in confirming proton transfer from $\text{Me}_3\text{Si-IB}^+$ and $\text{Me}_3\text{Si-MB}^+$ to Et_3N since the higher binding energies of these complexes allow study at higher temperatures than for $\text{Me}_3\text{Si-P}^+$ when the problems posed by adventitious water are considerably diminished. Figure 6 shows that $\text{Me}_3\text{Si-MB}^+$ reacts with Et_3N by proton transfer only. The rate constant of $3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ compared with an ADO collision rate constant of $1.1 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ shows that transfer occurs once every four collisions between Et_3N and $\text{Me}_3\text{Si-MB}^+$. Proton transfer from $\text{Me}_3\text{Si-DMB}^+$ to Et_3N is much slower, presumably

because only the less acidic methyl hydrogens are available, although the intervention of $\text{Me}_3\text{SiOH}_2^+$ cannot be entirely ruled out.

It is logical, but not proved, that the proton transferred from $\text{Me}_3\text{Si-alkene}^+$ to Et_3N is from the alkene group. Therefore, despite the fact that Et_3N has a higher enthalpy of binding to Me_3Si^+ than other bases such as esters, ethers, aromatics, etc., proton transfer rather than Me_3Si^+ transfer occurs for the Me_3Si^+ adducts IB, MB, and DMB. This must be simply a function of the very high proton affinity of Et_3N ($232 \text{ kcal mol}^{-1}$) although it is admittedly not much higher than that of Me_2NH ($221 \text{ kcal mol}^{-1}$) for which Me_3Si^+ transfer is the major reaction.

The absolute enthalpies of binding of Me_3Si^+ to the alkenes shown in Table I are confirmed by the data from the equilibrium Me_3Si^+ -transfer studies (Figure 5). The measured differences for the pairs P/IB and IB/DMB are the same, within experimental error, as those computed from the absolute values in Table I. The two values for the much larger change for P/DMB are not as close but are still within the range of experimental uncertainty. An enthalpy change of $\sim 10 \text{ kcal/mol}$ for an ion-transfer equilibrium is usually difficult to measure with good precision by high-pressure mass spectrometry.

The enthalpies of binding of ethene and substituted ethenes to Me_3Si^+ shown in Table I fall into three distinct groups according to the number and position of the methyl substituents. This is also illustrated by the groupings of the lines in Figure 2. The value of 23.6 kcal/mol for ethene is consistent with, but a little higher than, the measured threshold of $18.4 \pm 2.3 \text{ kcal/mol}$ for the collision-assisted dissociation of $\text{Me}_3\text{Si-E}^+$ into Me_3Si^+ and C_2H_4 .⁷ It is in excellent agreement with a calculated value of 23 kcal mol^{-1} .⁶ Ethene is the least strongly bound alkene. Roughly 7 kcal/mol more and equally strongly bound are propene and *trans*-2-butene, while the other methyl-substituted ethenes are still more strongly bound by another $6\text{--}8 \text{ kcal/mol}$. This grouping of values is consistent with a changeover from the bridged structure, **1a**, for ethylene toward the more classical structures **2a–2e** for the remainder.



The rationale for assigning these structures is as follows. Ab initio calculations suggest that an α -trimethylsilyl group is less effective at stabilizing a carbenium center than is an α -methyl group but is more stabilizing than hydrogen.¹³ A similar conclusion holds for α -silyl relative to α -methyl.⁵ The classical structures **2a–2e** are drawn with this in mind, with Markownikoff addition of Me_3Si^+ ensuring maximum stabilization of the resulting cation. We assume no ensuing rearrangement as argued earlier. There is an increase of $\sim 7 \text{ kcal/mol}$ for each extra methyl attached to the carbenium carbon but a β -methyl substituent has essentially no effect. This mirrors the roughly 17 kcal/mol increase in proton affinity per methyl on the carbenium carbon for the same alkenes that may be calculated when classical structures are assumed.¹⁴ Figure 7 shows that there is a good linear correlation between proton affinity and Me_3Si^+ affinity for all the alkenes studied. Such correlations for similar bases and the same Lewis acid are the rule rather than the exception.^{9,15} It is to be noted that both cyclohexene and styrene also fit the correlation line reasonably well. Styrene fits this correlation line much better than it fits the aromatic correlation line, which is shown for comparison,

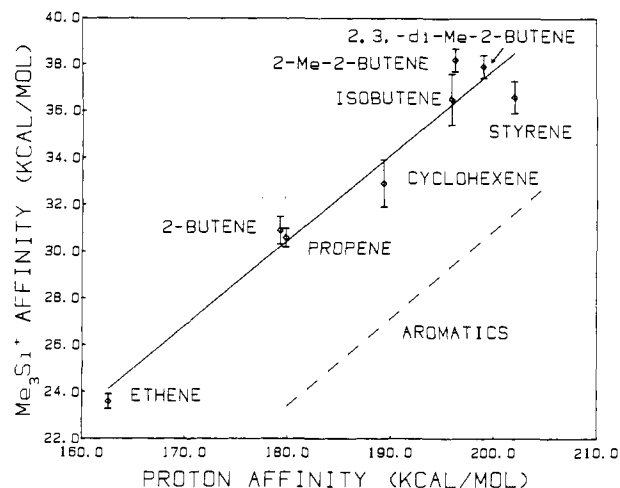


Figure 7. Correlation between the proton affinity and the binding energy of Me_3Si^+ to olefins. The broken line showing the correlation for aromatics is from ref 9.

and therefore Me_3Si^+ attaches to the alkene group rather than to the aromatic ring. This is also the preferred protonation site.^{16,17}

The enthalpy of formation of each of the $\text{Me}_3\text{Si-alkene}^+$ adducts can be computed from the measured enthalpy change for reaction 7.



The greatest uncertainty in these computations lies in the value of $\Delta H_f^\circ(\text{Me}_3\text{Si}^+)$. Walsh^{2a} has listed the published values for this quantity, recalculated according to his own assessment of the heats of formation of the neutral precursors. The original data were obtained by a variety of different experimental techniques. Without critical analysis of each technique he notes the high uncertainty in $\Delta H_f^\circ(\text{Me}_3\text{Si}^+)$ and suggests a value of $145.8 \pm 4.8 \text{ kcal/mol}$. This is actually very close to the mean of the eight values considered with, however, only one of the values falling below the mean. This lowest value of $141 \text{ kcal mol}^{-1}$ was obtained from the appearance energy of Me_3Si^+ in a photoionization study of $\text{Me}_4\text{Si}^{18}$ corrected for the most recent $\Delta H_f^\circ(\text{Me}_4\text{Si}) = -55.69 \text{ kcal mol}^{-1}$.¹⁹ It is much lower than a more recent value of $150.5 \text{ kcal mol}^{-1}$ obtained by the photoelectron-photoion coincidence (PEPICO) method.²⁰ We used this latest value to obtain $\text{PA}(\text{Me}_3\text{SiOH}) = 183.7 \text{ kcal mol}^{-1}$ from our measurement of $\Delta H^\circ = -30.1 \pm 1.9 \text{ kcal mol}^{-1}$ for $\text{Me}_3\text{Si}^+ + \text{H}_2\text{O} \rightarrow \text{Me}_3\text{SiOH}_2^+$.¹¹ Our later, direct equilibrium determination of $\text{PA}(\text{Et}_3\text{SiOH}) = 197.9 \pm 0.4 \text{ kcal mol}^{-1}$ ²¹ is inconsistent with the above value of $\text{PA}(\text{Me}_3\text{SiOH})$ since it would imply a very much greater change in proton affinity when Me is changed for Et in silanols than in alcohols. Assignment of a more normal 2 kcal mol^{-1} decrease in enthalpy of formation when ethyl is substituted for methyl suggests $\text{PA}(\text{Me}_3\text{SiOH}) \approx 192 \text{ kcal mol}^{-1}$ and hence a value of $140\text{--}145 \text{ kcal mol}^{-1}$ for $\Delta H_f^\circ(\text{Me}_3\text{Si}^+)$. In the calculations described below we have chosen to use the photoionization value of $\Delta H_f^\circ(\text{Me}_3\text{Si}^+) = 141 \text{ kcal mol}^{-1}$, but we agree with Walsh^{2a} that further determinations of this quantity are required.

The β -silicon effect is quantified as the stabilization afforded a carbenium center by a β -silicon relative to the stabilization afforded by a hydrogen at the same β -position. For example, the β -silicon effect in $\text{Me}_3\text{Si-P}^+$ (**2a**) is given by ΔH° for the isodesmic reaction 8, C_3H_7^+ being the isopropyl cation.



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Table IV. Thermodynamic Data^a for the Reaction $\text{Me}_3\text{Si}\cdot\text{X}^+ + \text{XH}_2 \rightarrow \text{Me}_3\text{Si}\cdot\text{XH} + \text{XH}^+$

$\text{Me}_3\text{Si}\cdot\text{X}^+$	Me_3SiXH	$-\Delta H_f^\circ(\text{Me}_3\text{SiXH})^b$	$-\Delta H_f^\circ(\text{XH}^+)^{c,d}$	$\Delta H^\circ{}^{d,e}$
1a or 1b	$\text{Me}_3\text{SiCH}_2\text{CH}_3$	57.4	215.6	48.2 (19.6) ^f
2a	$\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CH}_3$	62.4	191	38.4 (3)
2b	$\text{Me}_3\text{SiCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	67.4	183	38.2
2c	$\text{Me}_3\text{SiCH}_2\text{CH}(\text{CH}_3)_2$	69.5	166	28.1 (2)
2d	$\text{Me}_3\text{SiCH}(\text{CH}_3)\text{CH}(\text{CH}_3)_2$	74.2	159	28.8 (3)
2e	$\text{Me}_3\text{SiC}(\text{CH}_3)_2\text{CH}(\text{CH}_3)_2$	80.0	150	25.8
X = styrene	$\text{Me}_3\text{SiCH}_2\text{CH}_2\text{C}_6\text{H}_5$	30.3	199	21.8

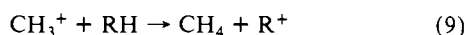
^aIn kcal mol⁻¹. ^bEstimated as described in text. ^cData from ref 14. ^dAbsolute values may be in error by 10 kcal mol⁻¹, relative errors by ± 5 kcal mol⁻¹. ^eNumbers in parentheses are for the analogous compounds with CH_3 instead of the Me_3Si group. ^fValue for the 2-propyl cation, which is calculated to have the bridged structure.²⁴ For the 1-propyl cation the value is 8.1 kcal/mol.⁵

Again the problem posed by the lack of thermodynamic information for organosilicon compounds leads to further uncertainties in the calculated data beyond that noted for $\Delta H_f^\circ(\text{Me}_3\text{Si}^+)$. An estimate of -57.4 kcal mol⁻¹ for $\Delta H_f^\circ(\text{Me}_3\text{SiEt})$ is obtained from $\Delta H_f^\circ(\text{Me}_3\text{Si}) = -55.4$ kcal mol⁻¹¹⁹ and $\Delta H_f^\circ(\text{Et}_4\text{Si}) = -63.4$ kcal mol⁻¹.²² The remainder of the enthalpies of formation of the neutral trimethylsilyl compounds shown in column 3 of Table IV were estimated by taking this value of $\Delta H_f^\circ(\text{Me}_3\text{SiEt})$ and assuming that the substitution of Me or C_6H_5 for H in the Et group changes ΔH_f° by the same amount as in the corresponding alkane; for example, the change from ethane to propane is assumed to be the same as that from Me_3SiEt to $\text{Me}_3\text{SiC}_3\text{H}_7$. Because of the total uncertainties in the enthalpies of formation of silicon-containing ions and molecules, the absolute values for the stabilization energies due to a β -silicon shown in the last column of Table IV are uncertain to at least ± 10 kcal/mol, but the relative values should be good to better than ± 5 kcal/mol. The values do fall into four groups and do present a consistent picture.

The value of 48.2 kcal/mol for the stabilization of the ethyl cation by a Me_3Si substituent is consistent with a theoretical value of 38 kcal mol⁻¹.⁵ Hajdasz and Squires⁷ obtained a value of 39 kcal mol⁻¹ from a measured $\text{PA}(\text{Me}_3\text{SiCH}_2=\text{CH}_2) = 199 \pm 2$ kcal mol⁻¹ and an estimated $\Delta H_f^\circ(\text{Me}_3\text{SiC}_2\text{H}_5) = -59$ kcal mol⁻¹. The 12 kcal mol⁻¹ discrepancy between our value and that of Hajdasz and Squires is in large part due to the 10 kcal mol⁻¹ difference in the assumed values for $\Delta H_f^\circ(\text{Me}_3\text{Si}^+)$.

Our initial discussion of the stabilizing effect of a β -silicon group will be in terms of the classical structures **1b** and **2a-2e**. The following observations may be made. The β -silicon effect is reduced by ca. 10 kcal mol⁻¹ by an α -methyl substituent on the carbenium carbon and by ca. 20 kcal mol⁻¹ when two such α -methyl substituents are present. Methyl substituents β to the carbenium carbon do not stabilize. Theoretical calculations show that maximum Si-C hyperconjugative stabilization of the carbenium center requires coplanarity of this bond and the formally vacant p orbital of the carbenium carbon,⁵ which then places any β -methyl substituent out of the plane of that orbital with little hyperconjugation possible. The data in Table IV are consistent with such a preference for Si-C rather than C-C hyperconjugative β -stabilization.

The effect of either a methyl or a phenyl substituent on the carbenium carbon is readily understood from its effect on the methyl cation. The stabilizing effects of methyl and phenyl substituents on CH_3^+ are computed from eq 9, where R^+ is the appropriate substituted CH_3^+ .²³ One, two, and three methyl



substituents stabilize, respectively, by 44, 63, and 81 kcal mol⁻¹ while a phenyl group stabilizes by 71 kcal mol⁻¹. Stabilization results from both polarization and inductive effects, the result being

a delocalization of positive charge away from the carbenium carbon. In the Me_3Si -alkene⁺ ions, hyperconjugation with the β -carbon-silicon bond is consequently reduced by α -methyl or phenyl substituents. The decline of the β -silicon effect shown in the last column of Table IV caused by methyl and phenyl substitution on the carbenium carbon is consistent with the order of increase in stabilization afforded by the type and number of α -substituents. Phenyl is significantly better than two methyl groups, but even with the considerable stabilization afforded by this substituent the β -silicon effect is still large. This latter statement still holds true even when an uncertainty of up to 10 kcal/mol is taken into account that may be present in the absolute values due to the above-noted uncertainties in the thermochemistry of silicon-containing neutrals and ions.

It is of interest to compare, where thermochemical information is available, the stabilization afforded by a β - Me_3Si with that afforded by a β -methyl, using isodesmic reactions analogous to eq 8. The data, shown in parentheses in column 5 of Table IV, demonstrate that only in the case of the ethyl cation does a β -methyl substituent significantly stabilize the ion; for any of the other ions a replacement of hydrogen at the β -position by methyl leads to no more than 3 kcal mol⁻¹ of stabilization, which is within the error limits of the data used in the calculations. This contrasts with the large, measureable β -silicon effect. These gas-phase studies substantiate the explanation of the remarkable properties of a β -silicon in significantly increasing the rates of liquid-phase reactions, which involve full or partial charge separation along the reaction coordinate.

The calculations of the β -silicon effect from our results are based on the experimental values for the enthalpies of formation of $\text{Me}_3\text{Si}\cdot\text{X}^+$ and XH^+ (Table IV). We have taken the most stable form of XH^+ in each case. Thus, for example, when the stabilization is computed in $\text{Me}_3\text{Si}\cdot\text{P}^+$, the 2-propyl cation and not the 1-propyl cation is used. In this particular case the different isomeric structures are clearly defined and indeed calculation shows that the primary cation is not at a minimum on the potential energy surface.²⁴ The probable structures of other XH^+ may be divided into two groups. All may be regarded as protonated olefins, some of which are symmetrical with an equal number of methyl groups on both sides of the double bond (E, TB, DMB) while the others are nonsymmetrical (P, IB, MB, ST). Calculation shows that the protonated symmetrical olefins probably have the bridged structure as the most stable form; the protonated unsymmetrical olefins show no stable bridged structure.²⁵ Although no calculations have been performed, it would appear reasonable to suppose that since protonated ethylene and $\text{Me}_3\text{Si}\cdot\text{E}^+$ both have bridged structures, the structures of $\text{Me}_3\text{Si}\cdot\text{X}^+$ will also be bridged for symmetrical alkenes and nonbridged for nonsymmetrical ones. The stabilization energies computed are then comparisons of pairs of $\text{Me}_3\text{Si}\cdot\text{X}^+$ and XH^+ , which are either bridged structures or nonbridged structures. It is therefore a little surprising that the values obtained appear dependent only on the number and position of methyl substituents suggested by classical structures. One reason might be that there is little difference in energy between

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the classical and bridged structures for a given $\text{Me}_3\text{Si}\cdot\text{X}^+$. MO calculations suggest that this is the case for $\text{H}_3\text{Si}\cdot\text{C}_2\text{H}_4^+$.⁵ Another possibility might be that in comparing bridged with bridged and nonbridged with nonbridged a fortuitous cancellation of factors leaves only the methyl groups contributing to the stabilization energies. This then implies that two methyl substituents in, for example, the bridged $\text{Me}_3\text{Si}\cdot\text{TB}^+$ are equally as stabilizing as the single methyl in $\text{Me}_3\text{Si}\cdot\text{P}^+$. High-level MO calculations on these compounds would help in the elucidation of this topic. If bridged structures are present in $\text{Me}_3\text{Si}\cdot\text{X}^+$ ($\text{X} = \text{E}, \text{TB}, \text{MB}$), then the term β -silicon effect may not be the most appropriate. The silyl group in these ions has a considerable stabilizing influence, but it may not be in a position β to the carbenium carbon.

The entropy changes for the formation of $\text{Me}_3\text{Si}\text{-alkene}^+$ are unusually large; in fact, they are some of the largest that have been measured in the gas phase for bimolecular association reactions. Condensation reactions with covalent products usually have entropy changes in the range 30–40 cal/K·mol.²⁶ The significantly larger value of 49 ± 5 cal/K·mol was determined for the association of Me_3C^+ and benzene.²⁷ It was suggested that the large changes in translational entropy, because of the relatively massive particles involved, together with the considerable loss in external rotational freedom accounted for the majority of the decrease. Similar considerations should apply to the present case.

The calculated entropy changes shown in Table I are obtained by considering changes due to translation and external rotation. No changes in entropy due to vibration or internal rotation are considered with the exception that the Me_3Si group in the complex is assumed to behave as a classical free rotor. Moments of inertia are calculated assuming classical geometries for the complexes with $\text{C-Si} = 2.047 \text{ \AA}$ and a tetrahedral Si-C-C angle. Calculations are performed as described in ref 28. Because of the approximation employed, the excellent agreement between ex-

periment and calculation is obviously fortuitous, but the calculations do show that the large experimental entropy changes are consistent with expectations. In particular, there is no obvious evidence for a restriction of internal rotations of methyl groups in the complexes, which would lead to even larger decreases in entropy for the association reactions than are experimentally observed. It might be appropriate to point out here that if the entropy changes had not been so large, measurements of the temperature coefficients of the equilibrium constants for the more strongly bound alkenes would have been impossible at temperatures below 600 K.

Conclusion

The considerable stabilization afforded simple carbenium ions by a β -silicon has been quantified. Although the absolute values are somewhat uncertain due to uncertainties in the thermochemistry of silicon-containing species, especially Me_3Si^+ , the values obtained are consistent with previously published, calculated values. The results also show a consistent decrease of ~ 10 kcal/mol in the stabilization energy with each successive methyl group substituted on the carbenium carbon. The data show that even the very stable Me_3C^+ is stabilized by a further 28 kcal/mol by a Me_3Si substituent in the β -position in $\text{Me}_3\text{SiCH}_2\text{CMe}_2^+$.

MO calculations on $\text{Me}_3\text{Si}\text{-alkene}^+$ adducts such as those described in this study would be useful not only in helping elucidate the structures of the ions but also in providing insight into liquid-phase solvolytic experiments, which invariably involve molecules with substituents α to the proposed carbenium carbon. Solvent effects do attenuate the β -silicon effect in solution, but even increases in reaction rates of the order of 10^{10} observed for the extrusion of Me_3SiOH from 4-*tert*-butyl-2-trimethylcyclohexanol⁴ can be accommodated by the very large effect demonstrated by our data.

Acknowledgment. We thank the National Sciences and Engineering Research Council of Canada for financial support. The use of the ZAB-2FQ mass spectrometer at the Ontario Regional Ion Chemistry Laboratory, University of Toronto, is acknowledged. We thank Dr. A. B. Young for help and advice with the CAD studies.

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Substituent Effects on the Electron Affinities of Perfluorobenzenes $\text{C}_6\text{F}_5\text{X}$

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Abstract: The electron attachment free energy and enthalpy ΔG_a° and ΔH_a° corresponding to the reaction $\text{e}^- + \text{B} = \text{B}^-$ was determined by measuring electron-transfer equilibria, $\text{A}^- + \text{B} = \text{A} + \text{B}^-$, with a pulsed electron high-pressure mass spectrometer (PHPMS), involving compounds A whose attachment energies are known. Values were obtained for $\text{C}_6\text{F}_5\text{X}$ ($\text{X} = \text{F}, \text{Cl}, \text{C}_6\text{F}_5, \text{CF}_3, \text{COCH}_3, \text{CHO}, \text{CN}, \text{Br}, \text{I}, \text{NO}_2, \text{COC}_6\text{F}_5$). The substituent effects for the σ -acceptor/ π acceptor substituents were found to be very similar to those observed for the electron attachment energies of substituted nitrobenzenes: $\text{NO}_2\text{C}_6\text{H}_4\text{X}$. This correspondence shows that the extra electron in both systems enters a π^* -orbital. The substituent effects for the σ -acceptor/ π -donor substituents, $\text{X} = \text{Cl}, \text{Br}, \text{I}$, were found to be very much larger for the $\text{C}_6\text{F}_5\text{X}$, relative to the nitrobenzenes, and to increase greatly in the order $\text{F}, \text{Cl}, \text{Br}, \text{I}$. These results indicate that the extra electron enters a σ^* -orbital, which is localized on the C-X atoms.

Recent work^{1a} from this laboratory reported electron affinities of perfluorobenzene C_6F_6 and substituted perfluorobenzenes $\text{C}_6\text{F}_5\text{X}$ determined via gas-phase measurements of electron-transfer

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equilibria with a pulsed electron high-pressure mass spectrometer (PHPMS).^{1b} The electron affinity of C_6F_6 was found to be $\text{EA}(\text{C}_6\text{F}_6) = 0.52 \pm 0.1 \text{ eV}^{1a}$ and is thus some 1.7 eV higher than that of benzene, $\text{EA}(\text{C}_6\text{H}_6) = -1.15 \text{ eV}^{2}$. Since it is known that fluorine stabilizes σ -orbitals more than π -orbitals, it has been suggested³ that multiple fluorine substitution may lead to the singly

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