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Stabilization of Vinyl Cations by β-Silicon: A Quantitative Mass Spectrometric Study

Wan Zhang,[†] John A. Stone,*,[†] Michael A. Brook,[‡] and Graham A. McGibbon[‡]

Contribution from the Chemistry Department, Queen's University, Kingston, Ontario, Canada K7L 3N6, and McMaster University, Hamilton, Ontario, Canada L8S 4M1

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Abstract: The stabilization afforded a vinyl cation by a β-$(CH_3)_3Si$ substituent has been determined by measuring in a high-pressure mass spectrometer the thermodynamic data for the association of three alkynes (RCCR′) with $(CH_3)_3Si^+$ and with the proton. The measured $-\Delta H°$ (kcal mol^{-1}) and $-\Delta S°$ (in parentheses, cal K^{-1} mol^{-1}) values for the reaction $(CH_3)_3Si^+ + RCCR' \rightleftarrows (CH_3)_3Si{\cdot}C(R)CR'^+$ are as follows: 1-hexyne (R = H, R′ = *n*-C_4H_9) 25.9 ± 1.5 (19.1 ± 0.2), 2-hexyne (R = CH_3, R′ = *n*-C_3H_7) 28.8 ± 1.4 (25.5 ± 0.3), and phenylacetylene (R = H, R′ = C_6H_5) 28.2 ± 2.8 (16.5 ± 0.4). By comparison the values for 1-hexene which forms an alkyl cation are 38.2 ± 0.5 kcal mol^{-1} (48.2 ± 0.1 cal K^{-1} mol^{-1}). The deduced stabilizations (*A*) for all the substituents (R, R′ and $(CH_3)_3Si$) obtained from the isodesmic reaction $(CH_3)_3Si{\cdot}C(R)CR'^+ + CH_2CH_2 \rightarrow (CH_3)_3Si{\cdot}C(R)C(H)R' + CH_2CH^+$ are (kcal mol^{-1}) as follows: 1-hexyne 55, 2-hexyne 58, and phenylacetylene 58. The deduced stabilization for the $(CH_3)_3Si^+$ adduct of 1-hexene relative to the ethyl cation is 60 kcal mol^{-1}. The measured proton affinities are (kcal mol^{-1}) as follows: 1-hexyne 194.5 ± 0.5, 2-hexyne 195.8 ± 0.2, phenylacetylene 198.6 ± 0.2, and 1-hexene 194.0 ± 0.5. The stabilizations (*B*) due to R and R′ in the vinyl cations $RC(H){=}CR'^+$ produced by protonaton are calculated from the isodesmic reactions $RC(H)CR'^+ + CH_2CH_2 \rightarrow RC(H)C(H)R' + CH_2CH^+$ and are (kcal mol^{-1}) as follows: 1-hexyne 44, 2-hexyne 46, and phenylacetylene 50. The comparable value for the alkyl cation from the protonation of 1-hexene is 34 kcal mol^{-1}. The stabilizations of the vinyl cations $RC(H){=}CR'^+$ due to the presence of a β-$(CH_3)_3Si$ ($A - B$) are (kcal mol^{-1}) as follows: 1-hexyne 11, 2-hexyne 12, and phenylacetylene 9. For the alkyl cation formed from 1-hexene, the value is 26 kcal mol^{-1}. The stabilization of a vinyl cation by an α-alkyl or α-aryl substituent is subtantially greater than that afforded by the same substituent in an alkyl cation. The total stabilization afforded by both an α-alkyl or α-aryl substituent and a β-$(CH_3)_3Si$ substituent appears to be approximately the same in both alkyl and vinyl cations and hence the β-silicon effect is considerably smaller for the vinyl cation.

Introduction

The increased stability of a carbenium ion due to the presence of a silicon in a position β to the carbon bearing the formal charge is known as the β-silicon effect. Solvolysis studies, in which the transition state of the rate determining step involves significant charge separation, have provided much information regarding the effect.[1] High-level *ab initio* calculations[2,3] and gas-phase experiments[4,5] have quantified the effect for saturated carbenium ions for which both theoretical[3] and experimental[5] results show that the magnitude of the stabilization, i.e. the electron demand on the hyperconjugating C-Si bond, decreases when the carbenium center is stabilized by the presence of electron-donating α substituents. For example, the stabilization energy of 48 kcal mol^{-1} in $(CH_3)_3SiCH_2CH_2+$ determined by experiment was found to decrease by 10 kcal mol^{-1} when an α-methyl substituent was present and was decreased by a further 10 kcal mol^{-1} when there was a second α-methyl substituent.[5] (All stabilization energies are relative to hydrogen as substituent.) These decreases are consistent with the *ab initio* values of 16.4 and 5.8 kcal mol^{-1} respectively for the first and second methyl groups.[3]

In spite of the intense interest in the possible existence of silyl-substituted carbocations, especially those of the type R_3Si^+, and although they are readily prepared and studied in the gas phase, attempts to observe them in solution have until recently been failures. No β-silyl-substituted saturated carbocations have so far been positively identified in the liquid phase,[6] even though as fully-formed or incipient species they are invoked as being present on solvolysis reaction coordinates. The first persistent β-silyl-substituted carbocation to be observed in solution was a vinyl cation. ^{13}C NMR identified $((CH_3)_3Si)_2C{=}C^+C(H)(Si(CH_3)_3)_2$ as the stable product resulting from protonation of $((CH_3)_3Si)_2C{=}C{=}C(Si(CH_3)_3)_2$ in HSO_3F/SbF_5 at 143−173 K.[7] The hyperconjugational origin and the resulting strong dependence of the effect on dihedral angle have been substantiated in later NMR studies of stable β-silyl-substituted vinyl cations.[8−10]

There has been only one report of a gas-phase quantitative study of the stabilization of a vinyl cation by a β silicon.[11] $(CH_3)_3SiCH{=}CH^+$, produced by electron impact ionization of $(CH_3)_3SiCH{=}C(H)I$, was shown by neutralization−reionization mass spectrometry to be stable on a microsecond time scale and also to be differentiable from its similarly stable isomer $(CH_3)_3SiC^+{=}CH$ which was formed by ionization of $(CH_3)_3$-

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[†] Queen's University.

[‡] McMaster University.

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(1) For a comprehensive review see: Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677.

(2) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496.

(3) Ibrahim, M. R.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 819.

(4) Hajdasz, D.; Squires, R. *J. Chem. Soc., Chem. Commun.* **1988**, 1212.

(5) Li, X.; Stone, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 55869.

(6) Olsson, L.; Cremer, D. *Chem. Phys. Lett.* **1993**, *215*, 433.

(7) Siehl, H-U.; Kaufmann, F-P.; Apeloig, Y.; Brande, V.; Danovich, D.; Berndt, A.; Stamatis, N. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1479.

(8) Prakesh, G. K. S.; Reddy, V. P.; Rasul, G.; Casanova, J.; Olah, G. A. *J. Am. Chem. Soc.* **1992**, *114*, 3076.

(9) Siehl, H-U.; Kaufmann, F-P.; Hori, K. *J. Am. Chem. Soc.* **1992**, *114*, 3076.

(10) Siehl, H-U.; Kaufmann, F-P. *J. Am. Chem. Soc.* **1992**, *114*, 4937.

(11) McGibbon, G. A.; Brook, M. A.; Terlouw, J. K. *J. Chem. Soc., Chem. Commun.* **1992**, 360.

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SiC(I)=CH$_2$. The appearance energy of $(CH_3)_3SiCH{=}CH^+$ yielded an enthalpy of formation of 181 kcal mol^{-1} leading to a calculated β-silicon stabilization energy of 44 kcal mol^{-1}. *Ab initio* calculations had predicted a value which was about $^3/_4$ that for a saturated carbenium ion (38.5 and 28.6 kcal mol^{-1} for $H_3SiCH_2CH_2^+$ and $H_3SiCH{=}CH^+$, respectively).[2] The different relative values of theory and experiment were ascribed to the difference between SiH$_3$ and Si(CH$_3$)$_3$ as substituent since an *ab initio* 3−21G basis set calculation had shown that the trimethylsilyl group was the more stabilizing in the α position by 10.8 kcal mol^{-1}.[12]

In this paper we report on the quantitative determinations of the stabilization enthalpies of vinyl cations in the gas phase due to the presence of a $(CH_3)_3Si$ group in a position β to the carbon carrying the formally empty p-orbital. The results, which were obtained through measurement of the $(CH_3)_3Si^+$ affinities of selected alkynes, show significant reductions in stabilization enthalpies compared with those found for saturated carbenium ions. As discussed later, it was found necessary to use higher alkynes than acetylene; two C$_6$ alkynes, 1-hexyne and 2-hexyne, and phenylacetylene were chosen for their ready availability and ease of use. The $(CH_3)_3Si^+$ affinity of 1-hexene was also determined in order to compare the stabilization enthalpy afforded a vinyl cation with that of a saturated analogue.

Experimental Section

The high-pressure mass spectrometer (HPMS) with pulsed electron beam and associated ion counting system has been described previously in detail.[13−15] Premixed samples consisting of >99 mol % methane, ~0.1 mol % sulfur hexafluoride as electron capture reagent,[16] very small amounts of tetramethylsilane (TMS), and an alkene or alkyne were passed from a heated 5-L glass reservoir via a heated metering valve and a heated glass tube to the ion source. The latter was operated at 3−5 Torr at temperatures between 450 and 620 K.

The methane was Matheson Purity Grade (>99.99%), the phenylacetylene was from MTM Research Chemicals, and all other chemicals were from the Aldrich Chemical Company; all were used without further purification.

Results

$(CH_3)_3Si^+$ is formed by the dissociative protonation of TMS by the methane reagent ions CH_5^+ and $C_2H_5^+$.[17]

$$CH_5^+\ (C_2H_5^+) + (CH_3)_4Si \rightleftarrows CH_4 + (CH_3)_3Si^+ + CH_4\ (C_2H_4) \quad (1)$$

$(CH_3)_3Si^+$ associates with many gas-phase bases M in equilibrium reactions:

$$(CH_3)_3Si^+ + M \rightleftarrows (CH_3)_3Si{\cdot}M^+ \quad (2)$$

In this work M is either 1-hexene or an alkyne. The association of $(CH_3)_3Si^+$ with 1-hexene is shown in the time-resolved normalized ion intensities of Figure 1. The major initial ion *m/z* 73 ($(CH_3)_3Si^+$) rapidly forms the association ion *m/z* 157 ($(CH_3)_3Si{\cdot}C_6H_{12}^+$) and the ratio of their intensities becomes constant after ~0.4 ms. This signifies that the equilibrium of eq 3 has been attained and the equilibrium constant may be computed from the constant ion intensity ratio and the known pressure of 1-hexene in the source (eq 4). The standard pressure is 760 Torr.

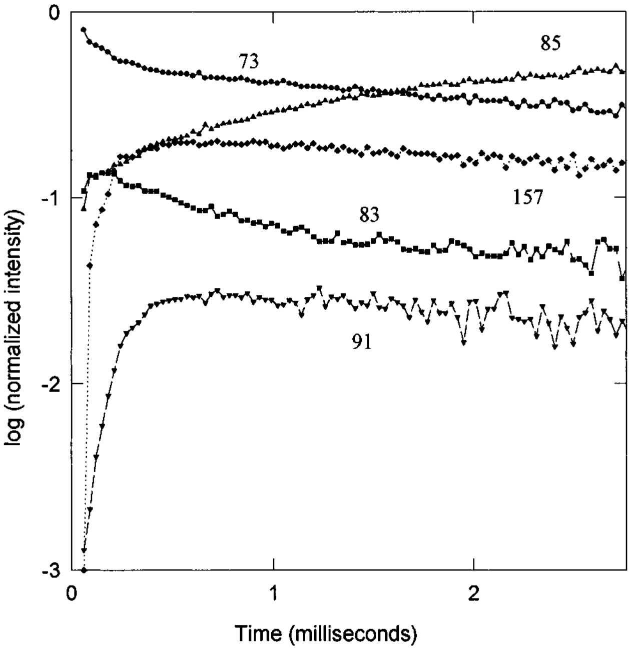

Figure 1. Normalized ion intensities as a function of ion source residence time for a CH$_4$/TMS/1-hexene mixture (99.13/0.52/0.35) at 561 K and 4.0 Torr.

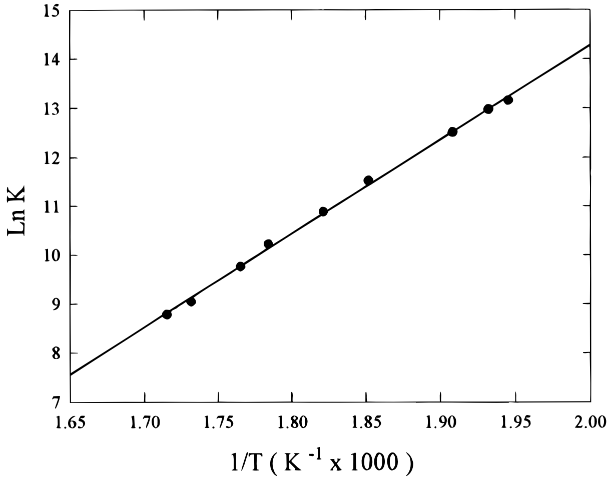

Figure 2. Van't Hoff plot for the equilibrium $(CH_3)Si^+$ + 1-hexene ⇄ $(CH_3)Si{\cdot}(1\text{-hexene})^+$.

$$(CH_3)_3Si^+ + C_6H_{12} \rightleftarrows (CH_3)_3Si{\cdot}C_6H_{12}^+ \quad (3)$$

$$K = \frac{i_{(CH_3)_3Si\cdot C_6H_{12}^+}}{i_{(CH_3)_3Si^+}}\frac{P^\circ}{P_{C_6H_{12}}} = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

The usual checks were made to prove that indeed equilibrium had been attained. The computed equilibrium constant for the reaction was found to be independent of ion source pressure for a given sample and of alkene concentration in different samples. The equilibrium constant was measured at different temperatures; the results are shown in the van't Hoff plot of Figure 2 and the standard enthalpy and entropy changes, obtained from the slope and intercept respectively, are presented in Table 1. To be noted in Figure 1 is the very low intensity at all times of *m/z* 91, the $(CH_3)_3Si^+$ adduct with adventitious

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[12] Apeloig, Y.; Stanger, A. *J. Org. Chem.* **1982**, *47*, 1462; **1983**, *48*, 5413.

[13] Stone, J. A.; Splinter, D. E. *Can. J. Chem.* **1981**, *59*, 1779.

[14] Li, X.; Stone, J. A. *Can. J. Chem.* **1988**, *66*, 1288.

[15] Zhang, W.; Beglinger, Ch.; Stone, J. A. *J. Phys. Chem.* **1995**, *99*, 11673.

[16] Kebarle, P. In *Techniques for the Study of Ion−Molecule Reactions*; Wiley: New York, 1988.

[17] Wojtyniak, A. C. M.; Stone, J. A. *Int. J. Mass Spectrom. Ion Processes* **1986**, *74*, 59.

Table 1. Thermodynamic Data for the Association Reaction $(CH_3)_3Si^+ + M \rightleftarrows (CH_3)_3Si{\cdot}M^+$

M	$-\Delta H^\circ$ [a]	$-\Delta S^\circ$ [b]	$\Delta H_f^\circ((CH_3)_3Si{\cdot}M^+)$[a]
1-hexyne	25.9 ± 1.5	19.1 ± 0.2	144.1
2-hexyne	28.8 ± 1.4	25.5 ± 0.3	138.2
phenylacetylene	28.2 ± 2.8	16.5 ± 0.4	185.8
1-hexene	38.2 ± 0.5	48.2 ± 0.1	92.8

[a] kcal mol^{-1}. [b] cal K^{-1} mol^{-1}.

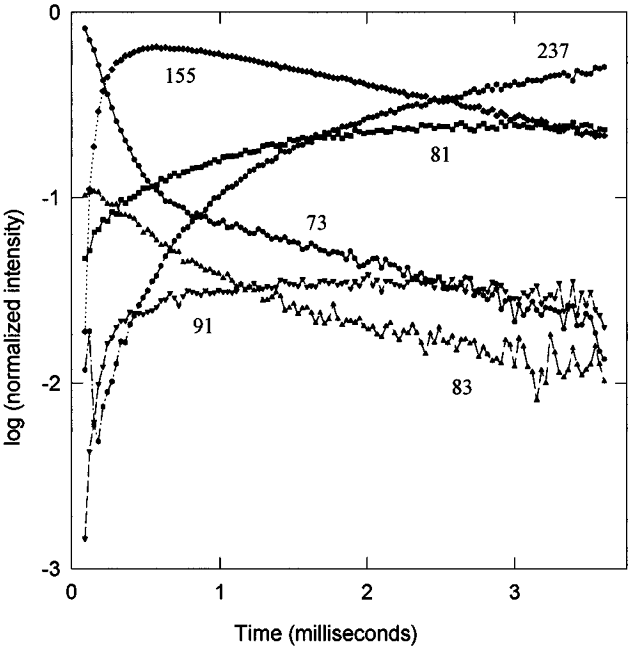

Figure 3. Normalized ion intensities as a function of ion source residence time for a CH_4/TMS/2-hexyne mixture (99.96/0.03/0.01) at 492 K and 3.5 Torr.

water, which is protonated trimethylsilanol.[18] The alkene has a higher basicity toward $(CH_3)_3Si^+$ than does water. The decline in the intensities of *m/z* 73 and 157 is matched by an increase in the intensity of *m/z* 85, protonated 1-hexene, due to a slow and slightly endoergic proton transfer to 1-hexene from *m/z* 157.

The mass spectrum of a CH_4/TMS/alkyne mixture was different in two main respects from that of a CH_4/TMS/alkene mixture. The M + 1 peak was much smaller and peaks at $M_n + 1$ ($n = 1, 2, ...$) and at $(CH_3)_3Si{\cdot}M_n^+$ ($n = 1,2, ...$) showed that gas-phase polymerization was occurring. It was therefore found necessary to work with very small amounts of alkyne to minimize polymerization and this also necessitated the use of very small amounts of TMS. Figure 3 shows the time-resolved ion intensities for a CH_4/TMS/2-hexyne mixture. The adduct ion, $(CH_3)_3Si{\cdot}C_6H_{10}^+$, is *m/z* 155. There is a constant value of i_{155}/i_{73} after ~0.7 ms suggesting the attainment of equilibrium. This was confirmed in the manner described above for 1-hexene. The equilibrium constants, determined over a range of temperatures, are shown in the van't Hoff plot of Figure 4 as are data for the association of $(CH_3)_3Si^+$ with the isomeric 1-hexyne. The thermodynamic data derived from the two linear plots are given in Table 1.

In Figure 3 both $(CH_3)_3SiC_6H_{10}^+$ and $(CH_3)_3Si^+$ decrease in parallel to be superceded by *m/z* 81 and 237. The former is $(M - 1)^+$ and the latter is $(CH_3)_3Si{\cdot}M_2^+$ which is the result of cationic polymerization as mentioned above. The origin of *m/z* 81 was not investigated; it could possibly result from the slow thermal decomposition of *m/z* 155 by loss of $(CH_3)_3SiH$.

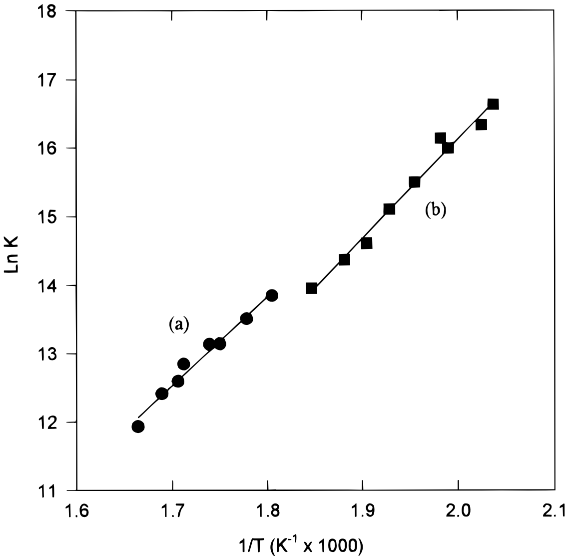

Figure 4. Van't Hoff plots for the equilibrium $(CH_3)_3Si^+$ + 1-hexyne $\rightleftarrows$ $(CH_3)_3Si{\cdot}$(1-hexene)$^+$ (●) and for the equilibrium $(CH_3)Si^+$ + 2-hexyne $\rightleftarrows$ $(CH_3)_3Si{\cdot}$(2-hexyne)$^+$ (■).

$$(CH_3)_3Si{\cdot}C_6H_{10}^{\ +} \rightarrow (CH_3)_3SiH + C_6H_9^{\ +} \qquad (5)$$

Phenylacetylene readily forms an association ion but no equilibrium could be attained between it and $(CH_3)_3Si^+$ since at long reaction time all the latter ions had disappeared, i.e. the basicity of this compound toward $(CH_3)_3Si^+$ is greater than that of either of the other two hexynes or of 1-hexene. Competitive $(CH_3)_3Si^+$ transfer between very low concentrations of phenylacetylene and larger concentrations of 2-hexyne was investigated.

The normalized intensities of the two ions shown in Figure 5 suggest the attainment of

$$(CH_3)_3Si{\cdot}C_6H_{10}^{\ +} + C_6H_5C{\equiv}CH \rightleftarrows$$
$$(CH_3)_3Si{\cdot}C(H)C{\equiv}C_6H_5^{\ +} + C_6H_{10} \qquad (6)$$

equilibrium, however the limited conditions of composition and source pressure over which this system could be studied precluded the changing of sample composition to any significant extent and hence denied the employment of the usual tests for the attainment of equilibrium. The data shown in the van't Hoff plot of Figure 6 were however obtained with five different samples. The absolute enthalpy and entropy of binding of $(CH_3)_3Si^+$ to phenylacetylene shown in Table 1 are obtained with reference to the values for 2-hexyne in the same table.

The proton affinities of the two hexynes and of 1-hexene were determined by equilibrium proton transfer experiments at constant temperature using *m*-xylene as reference base. The samples fed into the ion source comprised ~98.5 mol % methane and an excess of benzene relative to the amounts of the two bases of interest. Protonation of the bases was then by transfer from protonated benzene rather than by transfer in the more highly exothermic reactions with the methane reagent ions CH_5^+ and $C_2H_5^+$. The value for each compound was obtained with data from 3−6 different mixture compositions at a single temperature of ~600 K. A typical set of data showing the approach to equilibrium and its attainment after ~0.3 ms is presented in Figure 7 for the equilibrium proton transfer between *m*-xylene and 1-hexyne. The use of protonated benzene as a reagent ion was not possible for phenylacetylene since the vinyl cation formed added to benzene in a fast irreversible reaction. For the same reason neither *m*-xylene nor any other aromatic

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(18) Stone, J. A.; Wojtyniak, A. C. M.; Wytenburg, W. *Can. J. Chem.* **1986**, *64*, 575.

(19) Li, X.; Stone, J. A. Unpublished result.

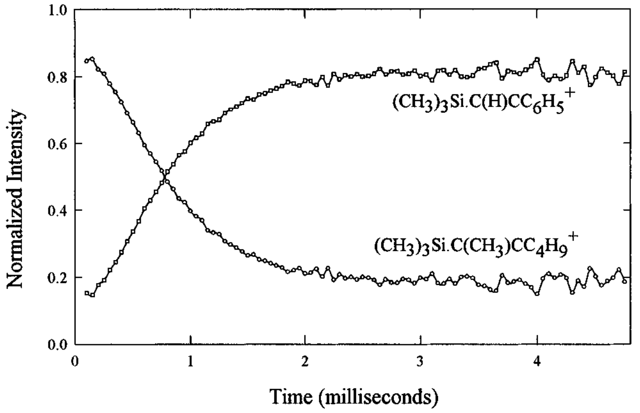

Figure 5. Normalized ion intensities as functions of ion source residence time for the $(CH_3)_3Si^+$ transfer equilibrium reaction $CH_3)_3$-$Si{\cdot}$(2-hexyne)$^+$ + phenylacetylene ⇄ $(CH_3)_3Si{\cdot}$(phenylacetylene)$^+$ + 2-hexyne in a CH_4/TMS/2-hexyne/phenylacetylene (99.87/0.11/0.019/0.0017) mixture at 535 K and 4.1 Torr.

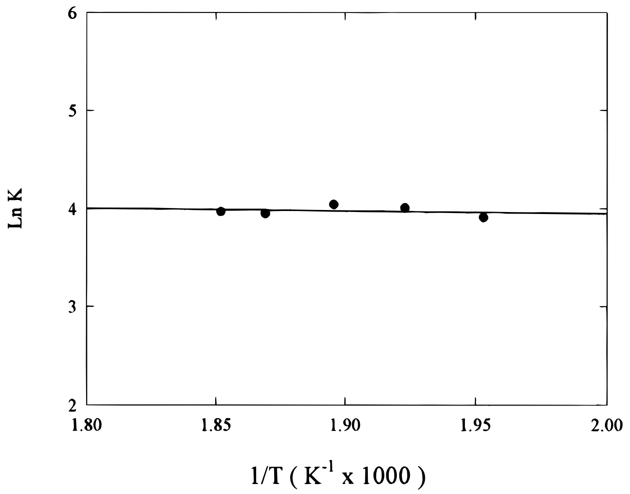

Figure 6. Van't Hoff plot for the equilibrium $CH_3)_3Si{\cdot}$(2-hexyne)$^+$ + phenylacetylene ⇄ $(CH_3)_3Si{\cdot}$(phenylacetylene)$^+$ + 2-hexyne.

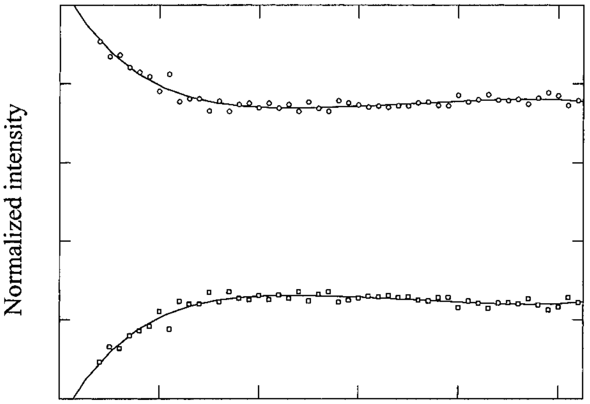

Figure 7. Normalized ion intensities as functions of ion source residence time for the proton transfer equilibrium *m*-xylene$\cdot H^+$ + 1-hexyne ⇄ *m*-xylene + 1-hexyne$\cdot H^+$ in a CH_4/C_6H/*m*-xylene/1-hexyne (99.8/0.2/0.0054/0.12) mixture at 610 K and 3.8 Torr.

hydrocarbon was a suitable reference base. Methylacetate, which was unreactive toward the phenylvinyl cation, was the reference base used. The results of these measurements are shown in Table 2. At a referee's suggestion, methylacetate was also used as a reference base for some of the other compounds. The proton affinities obtained for 1-hexene and 1-hexyne with the use of this reference base, which are also shown in Table 2, are in excellent agreement with those obtained with reference to *m*-xylene.

Discussion

The thermodynamic data obtained for the association of $(CH_3)_3Si^+$ with 1-hexene shown in Table 1 are in excellent accord with earlier studies of the association reactions of $(CH_3)_3Si^+$ with methyl-substituted ethenes.[5] In particular, the enthalpy of association is very large, so large in fact that without the accompanying very substantial decrease in entropy the basicity would have been too large for equilibrium to have been observed and for thermodynamic data to have been obtained within the temperature range of our HPMS. The large $-\Delta S°$ value can be rationalized, as for the methyl-substituted ethenes,[5] as due to the large loss in translational entropy (37 cal K^{-1} mol^{-1}) plus a restriction of rotation about the C−Si bond due to its hyperconjugative interaction. The enthalpies of association of $(CH_3)_3Si^+$ with the acetylenes are very different from those for the ethenes. They are all significantly smaller than that of 1-hexene and in fact are smaller than those of any of the alkenes except ethylene. In addition, the $-\Delta S°$ values for the acetylenes are only about one-half those for the alkenes. Considering that for all the association reactions the decrease in translational entropy is 37 cal K^{-1} mol^{-1}, a very large *increase* (~20 cal K^{-1} mol^{-1}) in the entropy associated with internal degrees of freedom must have occurred. At the moment we cannot account for this large value, nor for the very large difference between the entropy change for the alkynes compared with the alkenes. It is to be noted that there is an extremely small $-\Delta S°$ value for the association of $(CH_3)_3Si^+$ with phenylacetylene. The resulting relatively large $-\Delta G°$ value is the reason why the association reaction could not be studied directly but had to be determined relative to the value for 2-hexyne.

It would have been preferable to include in this study thermodynamic data for the association of $(CH_3)_3Si^+$ with the lowest alkyne, acetylene. However, we had previously found that this was not possible with the HPMS.[19] Essentially no signal (<0.1% total ionization) was observed at *m*/*z* 99, the value for the ion $(CH_3)_3Si{\cdot}C_2H_2^+$. The major product was due to the association of $(CH_3)_3Si^+$ with adventitious water. It was found to be impossible to reduce the water level to a sufficiently low value for a successful determination. Acetylene is obviously much less basic toward $(CH_3)_3Si^+$ than is water which has a standard enthalpy of association of −30.1 kcal mol^{-1} and an entropy of −27.2 cal K^{-1} mol^{-1}.[18] The value of the enthalpy of association for acetylene will certainly be lower than that for any of the substituted acetylenes since we find that the value for any base invariably increases with alkyl substitution at the basic site. In addition, since we also invariably find a correlation between the enthalpy and the entropy of association of $(CH_3)_3Si^+$ with gas-phase bases, the latter will also be smaller, i.e. less negative than for the alkynes for which data have been obtained. The basicity of acetylene toward $(CH_3)_3Si^+$ must be very low indeed, consistent with our being unable to observe the adduct ion. The basicities of the acetylenes, taken as a group, toward $(CH_3)_3Si^+$ are the lowest of any series of compounds studied in this laboratory, lower even than those of the aromatics.

The addition of a proton to an alkyne RC≡CR′ at either of the vinyl carbons must initially produce a vinyl cation of the form $HC(R){=}CR'^+$ and likewise the addition of $(CH_3)_3Si^+$ will initially produce a silicon-substituted vinyl cation of the form $(CH_3)_3SiC(R){=}CR'^+$. The first part of this statement requires no justification. The evidence for the second part is that (a) the ions produced by both the proton and $(CH_3)_3Si^+$ behave in the same manner at long reaction times, i.e. take part in gas-phase cationic polymerization, (b) by analogy with the reactions of $(CH_3)_3Si^+$ with alkenes,[5] the production of a covalent Si−C bond is expected, (c) collision-assisted dissociation of the ions results in the formation of $(CH_3)_2SiH^+$ as well as the major loss of the alkyne showing that $(CH_3)_3Si{\cdot}M^+$ is not simply an electrostatically-bound complex, and (d) the derived thermodynamic data for β-silicon stabilization are consistent with such an assumption of covalent bond formation.

The vinyl cation $(CH_3)_3SiC(R){=}CR'^+$ has an α-substituent R′ and two β-substituents $(CH_3)_3Si$ and R. For 1-hexyne and phenylacetylene, R = H and R′ is C_4H_9 and C_6H_5, respectively. For 2-hexyne, R = CH_3 and R′ = C_3H_7. The assumptions made in these assignments are that no rearrangement occurs and that the addition of $(CH_3)_3Si^+$ to an alkyne will be according to the Markownikow rule, i.e. the sole or larger alkyl or phenyl group will be in the position α to the carbon having the formally vacant orbital. Apeloig and Stanger[12] found that for the vinyl cation at both the STO-3G and the 3−21G level an α-H_3C is more stabilizing than an α-H_3Si but that at both levels $(CH_3)_3Si$ is more stabilizing than H_3C- by 11−15 kcal mol^{-1}. This suggests that the silicon should preferentially be in the α-position. However, an Si−C bond in the β-position is much more effective than a C−C bond in stabilizing by hyperconjugation[2] and the net result is expected to be that the silicon will occupy the β-position. An even more definitive argument for this being the case can be made for the adduct of phenylacetylene. If the aromatic ring is in the α-position then the formally empty $2p(C^+)$ orbital is in the same plane as the ring p orbitals which allows for charge delocalization and significant stabilization.

The stabilization of the positive charge in $(CH_3)_3SiC(R){=}CR'^+$ by all substituents ($(CH_3)_3Si$, R, and R′) may be obtained from the enthalpy changes for the isodesmic reaction of eq 7 while the isodesmic reaction of eq 8 gives the stabilization of the positive charge due to the β-R and the α-R′ in $HC(R){=}CR'^+$. It is assumed that the stabilizations due to the substituents are additive and hence the difference between the two values, $\Delta H_7° - \Delta H_8°$, gives the stabilization due to the β-silyl group in $(CH_3)_3SiC(R){=}CR'^+$. For comparison purposes, the stabilization afforded an ethyl cation such as is formed by the protonation of 1-hexene is obtainable from the two isodesmic reactions of eqs 9 and 10.

$$(CH_3)SiC(R){=}CR'^+ + CH_2{=}CH_2 \rightarrow (CH_3)SiC(R){=}C(H)R' + CH_2{=}CH^+ \quad (7)$$

$$RC(H){=}CR'^+ + CH_2{=}CH_2 \rightarrow RC(H){=}C(H)R' + CH_2{=}CH^+ \quad (8)$$

$$(CH_3)_3SiCH_2C(H)R'^+ + CH_3CH_3 \rightarrow (CH_3)_3SiCH_2CH_2R' + CH_3CH_2^+ \quad (9)$$

$$CH_3CHR'^+ + CH_3CH_3 \rightarrow CH_3CH_2R' + CH_3CH_2^+ \quad (10)$$

In order to calculate these stabilization enthalpies, the enthalpies of formation of both the ions and neutrals are required. Those for the formation of the silicon-containing ions are obtained from the measured $(CH_3)_3Si^+$ affinities and those for the non-silicon-containing ions are obtained from proton affinity values. The enthalpies of formation of the silicon-containing neutral molecules have not been experimentally determined and must be estimated.

There are three published values of the proton affinity of the reference base, m-xylene, which may be used in deriving the proton affinities of the alkynes, viz 192.2 kcal mol^{-1} from the newly proposed, extensive proton affinity scale of Szuljeko and McMahon,[20] 195.9 kcal mol^{-1} from a standard database of evaluated proton affinities,[21] and 196.2 kcal mol^{-1} by Jennings and co-workers.[22] The first and third values were obtained using HPMS. The last value, corrected to the new scale proposed by Szuljeko and McMahon, is 193.2 kcal mol^{-1}. The latest value of 192.2 kcal mol^{-1} together with a $\Delta S_{1/2}°$ value for m-xylene of 7.3 cal K^{-1} mol^{-1} ($(CH_3)_2C_6H_4 \rightarrow (CH_3)_2C_6H_4{\cdot}H^+$)[20] and $\Delta S_{1/2}° = 0$ for the hexynes and 1-hexene were used in computing their proton affinities. Surprisingly the evaluated proton affinity of 195.9 kcal mol^{-1},[21] together with $\Delta S_{1/2}° = 1.3$ cal K^{-1} mol^{-1} for m-xylene which, as is usual for most single-temperature proton affinity measurements, takes into account only the changes in external rotational symmetry numbers, yields almost identical (within 0.1 kcal mol^{-1}) proton affinity values for the hexynes and 1-hexene. The proton affinity of methylacetate (193.7 kcal mol^{-1}) together with its experimentally determined $\Delta S_{1/2}°$ of 4 cal K^{-1} mol^{-1}, both values from ref 20, yields a proton affinity of phenylacetylene of 198.6 ± 0.5 kcal mol^{-1}. (The entropy change for this computation also includes a contribution of 1.37 J K^{-1} mol^{-1} for the loss of symmetry when phenylacetylene is protonated.) This proton affinity is in reasonable agreement with the value of 200.2 kcal mol^{-1} obtained by a bracketing technique and an assumed entropy change in which only the change in rotational symmetry is considered.[23] The proton affinities obtained in this work are shown in Table 2. The derived enthalpies of formation of the protonated molecules are given in Table 3.

The enthalpies of formation of the $(CH_3)_3Si^+$ adducts were obtained from the enthalpy change for eq 1.

$$\Delta H_f°((CH_3)_3Si{\cdot}M^+) = \Delta H_1° - \Delta H_f°((CH_3)_3Si^+) - \Delta H_f°(M) \quad (11)$$

The latest value of 145 kcal mol^{-1} taken for $\Delta H_f°((CH_3)_3Si^+)$[24] is in excellent agreement with an earlier value of 147 ± 3 kcal mol^{-1} from the same laboratory.[25] It is 4 kcal mol^{-1} larger than the value used in interpreting data from this laboratory on the stabilization of saturated carbenium ions by a β-silicon substituent.[5] Any discussion in this paper of thermodynamic data derived in the latter study will incorporate this changed value. The derived enthalpies of formation of $(CH_3)_3Si{\cdot}M^+$ are in Table 1.

There are no tabulated standard enthalpies of formation for the neutral silicon-containing molecules which appear in eqs 7 and 9. The thermochemistry of tetraalkylsilanes now appears to be satisfactory, the enthalpies of formation from the bomb calorimetric results of Voronkov and co-workers[26] being in excellent accord with group additivity estimates,[27] the differences for the different alkyl groups are consistent with those for analogous hydrocarbons, and the value for $(CH_3)_4Si$ is in

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(20) Suljeko, J. E.; McMahon, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 7839; and private communication.

(21) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1934**, *13*, 695.

(22) Fernandez, M. T.; Jennings, K. R.; Mason, R. S. *J. Chem. Soc., Faraday Trans. 2*, **1989**, *85*, 1813.

(23) Marcuzzi, F.; Modena, G.; Paradisi, C. *J. Org. Chem.* **1985**, *50*, 4973.

(24) Shin, S. K.; Corderman, R. R.; Beauchamp, J. L. *Int. J. Mass Spectrom. Ion Processes* **1990**, *101*, 257.

(25) Shin, S. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1989,** *111*, 900.

(26) Voronkov, M. G.; Baryshok, V. P.; Klyuchnikov, V. A.; Danilova, T. F.; Pepekin, V. I.; Korchagina, A. N.; Khudobin, Yu. I. *J. Organomet. Chem.* **1988**, *345*, 27.

(27) Walsh, R. In *The Chemistry of Organic Silicon Compounds*; Patai, S.; Rappoport, Z., Eds.; Wiley: New York, 1989; p 371.

Table 2. Proton Affinity Determinations for the Reaction $BH^+ + M \rightleftarrows B + MH^+$

M	B	*T* (K)	$\Delta G°$ [a]	$\Delta S°$ [b]	$\Delta H°$ [a]	PA[a]
1-hexyne	*m*-xylene	610	2.1 ± 0.2	−7.3[c]	−2.5	194.7[d]
1-hexyne	methylacetate	574	2.9 ± 0.2	−4.0[c]	0.6	194.4[e]
2-hexyne	*m*-xylene	603	1.0 ± 0.2	−7.3[c]	−3.6	195.8[d]
phenylacetylene	methylacetate	588	−2.2 ± 0.2	−2.4[f]	−3.6	198.6[e]
1-hexene	*m*-xylene	580	2.3 ± 0.1	−7.3[c]	−2.1	194.3[d]
1-hexene	methylacetate	573	3.7 ± 0.1	−4.0[c]	1.4	193.6[e]

[a] kcal mol^{-1}. [b] cal K^{-1} mol^{-1}. [c] Reference 21. [d] Referenced to PA(*m*-xylene) = 192.2 kcal mol^{-1}. [e] Referenced to PA(methylacetate) = 193.7 kcal mol^{-1}. [f] See text.

Table 3. Stabilization of Cations $R(H)C{=}CR'^+$ According to Isodesmic Reaction Eq 8 and of Cations $H_3C{-}C(H)R'^+$ According to Eq 10

R	R′	$\Delta H_f°(R(H)C{=}CR'^+)$[a]	$\Delta H_f°(R(H)C{=}C(H)R')$[a]	ΔH_{stab}[a]
H	*n*-C_4H_9	200.2	−10.0	44.2
CH_3	*n*-C_3H_7	196.0	−11.4(z)	46.2
H	C_6H_5	240.1	35.3	49.6
R	**R′**	$\Delta H_f°(H_3CC(H)R'^+)$[a]	$\Delta H_f°(H_3CC(R')H_2)$[a]	
H	C_4H_9	161.7	−39.9	34.1
H	C_6H_5	199	7.0	43.6

[a] kcal mol^{-1}.

Table 4. Stabilization of Vinyl Cations $(CH_3)_3SiC(R){=}CR'^+$ According to Isodesmic Eq 7 and of Alkyl Cations $(CH_3)_3SiC(H)H{-}C(H)R'^+$ According to Isodesmic Eq 9

R	R′	$\Delta H_f°((CH_3)_3SiC(R){=}CR'^+)$	$\Delta H_f°((CH_3)_3SiC(R){=}C(H)R')$	ΔH_{stab}	*β*-silicon stabilization
H	*n*-C_4H_9	148.1	−51.4	54.9	11
CH_3	n-C_3H_7	142.2	−54.4	57.8	12
H	C_6H_5	189.8	−6.2	58.4	9

R′	$\Delta H_f°((CH_3)_3SiC(H)H{-}C(H)R'^+)$	$\Delta H_f°((CH_3)_3SiC(H)H{-}C(H)HR'$	ΔH_{stab}	*β*-silicon stabilization
n-C_4H_9	96.8	−78.6	60.3	26
C_6H_5	143.7[a]	−31.7	60.3	17

Units kcal mol^{-1}. [a] Data from Reference 5 corrected to $\Delta H_f°((CH_3)_3Si^+)$ = 145 kcal mol^{-1}.

excellent agreement with the value obtained by Steele.[28] Unfortunately for the present purposes, although Voronkov and co-workers' results for the enthalpies of formation of $(CH_2{=}CH)_4Si$ (−19.6 ± 1.2 kcal mol^{-1}), $(CH_3)_4Si$ (−54.7 ± 0.3 kcal mol^{-1}), and $(CH_3)_3SiCH{=}CH_2$ (−45.6 ± 1.2 kcal mol^{-1}) are internally consistent, the results for the the two vinyl silanes are questionable. They imply that in replacing a $CH_3{-}Si$ of $(CH_3)_4Si$ by $CH_2{=}CH{-}Si$ the enthalpy of formation is increased by only 9.1 kcal mol^{-1}, whereas the value in a hydrocarbon is 25 kcal mol^{-1}. In addition, Walsh[27] has cited the anomolously high enthalpy of hydrogenation for $(CH_3)_3SiCH{=}CH_2$ that is computable from Voronkov's data. Because of such problems, the value that will be used in this paper for $\Delta H_f°((CH_3)_3SiCH{=}CH_2)$ is −29 kcal mol^{-1}, the value estimated using the above 25 kcal mol^{-1}. This is also the estimated value in a standard compilation of ion energetics.[29] The estimated values of the enthalpies of formation of the compounds $(CH_3)_3SiC(R){=}C(H)R'$ shown in Table 4 were obtained by assuming group additivity, that is that the changes which occur on substituting R and R′ for H in $(CH_3)_3SiCH{=}CH_2$ are the same as those for their substitution in ethylene.

The stabilizations of the vinyl cation by R and R′ obtained from the isodesmic reaction, eq 8, are presented in Table 3 and those for stabilization by $(CH_3)_3Si$, R, and R′ according to the isodesmic reaction eq 7 are in Table 4. Also shown in both tables are data for stabilization of the ethyl cation by the same or similar substituents.

Protonation of 1-hexene, ethenylbenzene, 1-hexyne, 2-hexyne, and phenylacetylene produces respectively the ions $CH_3C^+(H)C_4H_9$, $CH_3C^+(H)C_6H_5$, $CH_2{=}C^+C_4H_9$, $CH_3C(H){=}C^+C_4H_9$ and $CH_2{=}C^+C_6H_5$. Table 3 shows that the same α-substituent is more effective at stabilizing the charge on the vinyl cation than on the ethyl cation. The difference is 6 kcal mol^{-1} when protonated ethenylbenzene is compared with protonated phenylacetylene and 10 kcal mol^{-1} when protonated 1-hexene is compared with protonated 1-hexyne. The presence of a *β*-CH_3 substituent as well as the α-C_3H_7 group in protonated 2-hexyne increases the stabilization over that for the single α-C_4H_9 substituent in protonated 1-hexyne by only 2 kcal mol^{-1}. If the plausible assumption is made that there will be little difference in stabilization between the *n*-C_3H_7 and the *n*-C_4H_9 substituent then a *β*-CH_3 and by extension a *β*-alkyl group probably has little stabilizing ability. This is in line with theoretical calculation[2] and with for example the identical values of the proton affinities of propyne and 2-butyne.[21] An α-phenyl substituent is more stabilizing than an α-alkyl group in both alkyl and vinyl ions by 6−8 kcal mol^{-1}.

The presence of $(CH_3)_3Si$ as an additional substituent is further stabilizing as seen in the fifth column of Table 4. Remarkably, this total stabilization due to all substituents is not very different for both vinyl and ethyl cations. In particular, the stabilizations of the phenyl-containing ions differ by only 2 kcal mol^{-1}. This means that the more stabilizing the alkyl group in the α-position, the less is the electron demand via hyperconjugation from the *β*-silyl group and the less the stabilization that is attributable to the *β*-silicon effect. The values for the latter quantity, obtained by subtracting the stabilization enthalpies of Table 3 from those in Table 4, are shown in the last column of Table 4. Of course this assignment is, as mentioned previously, arbitrary in that the stabilizing effects of the α- and *β*-substituents are assumed to be separate and additive and

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(28) Steele, W. V. *J. Chem. Thermodyn.* **1983**, *15*, 595.

(29) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. No. 1.

priority is given to the α-substituents in assessing the stabilizing abilities. Since the ethyl cation is less stabilized by an α-alkyl substituent than the vinyl cation it has the greater potential for further stabilization by the *β*-silyl group; indeed, the effect is more than twice as great with an alkyl substituent for the ethyl cation as for the vinyl cation. For example, for the *n*-C_4H_9 group, the effect is 26 kcal mol^{-1} for the alkyl cation and 11 kcal mol^{-1} for the vinyl cation. With an α-phenyl group, which is significantly more stabilizing particularly for the ethyl cation than an α-alkyl group, the difference is not as great, 17 kcal mol^{-1} vs 9 kcal mol^{-1}.

The stabilization energy attributable to a *β*-$(CH_3)_3Si$ group on the vinyl cation with no α-substituent was found experimentally to be 43.5 kcal mol^{-1} and the stabilization due to an α-$(CH_3)_3Si$ group was 28.5 kcal mol^{-1}.[11] The latter number appears to be much too low. The stabilization afforded by a CH_3 group, taking $\Delta H_f°(CH_3C^+{=}CH_2)$ as 231 kcal mol^{-1},[29] is 27 kcal mol^{-1}, and since $(CH_3)_3Si$ has been calculated to be 15.3 kcal mol^{-1} more stabilizing than methyl as an α-substituent,[12] a value of about 40 kcal mol^{-1} would appear to be more appropriate.

A direct comparison cannot be made between the results in Table 3 for the effect of a *β*-silicon in α-substituted vinyl cations obtained in this work and the value of 43.5 kcal mol^{-1} obtained by Terlouw and co-workers for the unsubstituted ion.[11] We previously found that the stabilization by a *β*-silicon in the ethyl cation decreased by 10 kcal mol^{-1} for each α-methyl substituent ($-CH_2^+ > -CH(CH_3)^+ > -C(CH_3)_3^+$).[5] On the basis of the vinyl cations in Table 3 having only one (but larger) alkyl substituent we would place a lower limit of 20 kcal mol^{-1} on the *β*-silicon effect for the unsubstituted vinyl cation. A value of 43.5 kcal mol^{-1} would appear to be too high, in fact it is as large as the 44 kcal mol^{-1} that we measured for the saturated ion $(CH_3)_3SiCH_2CH_2^+$.[5] *Ab initio* calculations suggest that the value for the vinyl cation should be about 25% less than that for the ethyl cation.[2] Some insight can be gained from a computed enthalpy of association of $(CH_3)_3Si^+$ with C_2H_2. The value derived according to eq 11 from $\Delta H_f°((CH_3)_3Si{\cdot}CH{=}CH^+) = 181$ kcal mol^{-1} in ref 11 is -18 kcal mol^{-1}. This is certainly a reasonable value in terms of our inability to observe any significant signal due to this ion in the presence of the more strongly basic adventitious water. Another method of obtaining data to determine the stabilization due to the *β*-silicon in $(CH_3)_3Si{\cdot}CH{=}CH^+$ is clearly desirable.

There are two questions which may legitimately be posed regarding the identity of the ions formed and studied in this work. The first is whether a covalently bound complex is produced upon the addition of $(CH_3)_3Si^+$ to an alkyne. This assumption was justified earlier in this paper. The second question pertains to the possibility that ions with the isomeric allyl rather than the vinyl structure are formed by protonation of alkynes or by $(CH_3)_3Si^+$ addition to alkynes. Information from studies on the isomeric allyl and vinyl forms of C_3H_5+ would suggest that this is not the case. Collision assisted dissociation studies have shown that the non-decomposing allyl and 2-propenyl ions do not interconvert[30] even though the latter is less stable by 11 kcal mol^{-1}.[31] There is a computed energy barrier for this interconversion of 18 kcal mol^{-1}.[32] Evidence for a slow, collision-induced rearrangement of the 2-butenyl cation to the the 1-methylallyl cation has been obtained in an ion cyclotron resonance study of the protonation of 2-butyne.[33] However, the measured proton affinity of this compound to yield the 2-butenyl cation, 188 kcal mol^{-1}, is consistent with the values of ~195 kcal mol^{-1} obtained for the hexynes in this work when allowance is made for an increased stabilization due to a larger α-alkyl substituent. The computed enthalpy of formation of the 2-butenyl cation is 213 ± 2 kcal mol^{-1}. By analogy we also expect $(CH_3)_3Si^+$ to produce a substituted vinyl cation with, as argued earlier, the silicon in the *β*-position where it has the most favorable, planar, geometry with the formally vacant p-orbital.[12]

It has been assumed that protonation of 2-hexyne forms $C_3H_7C^+{=}C(H)CH_3$ and not $C_3H_7C(H){=}C^+CH_3$, i.e. that stabilization of the charge is more efficient with an α-propyl than with an α-methyl group. This assumes that the inductive effect of an α-alkyl substituent is more important than the hyperconjugative effect in stabilizing the charge. This is consistent with the calculation which suggests that since the cation center is an sp carbon, stabilization by induction is more important than stabilization by hyperconjugation for an α-methyl.[2] The high-pressure mass spectrometer does not provide a means of ion identification other than the mass to charge ratio and hence cannot resolve this question. It is to be noted that both ions have both α- and *β*-stabilization by alkyl groups but with a different mix of inductive and hyperconjugative stabilizations.

Siehl[34] has convincingly demonstrated from the para-carbon NMR chemical shift data for 1-mesityl substituted vinyl cations that in solution a *β*-silyl group is superior to either a *β*-alkyl or *β*-hydrogen in delocalizing charge. No quantitative data were obtained, but the results are in accord with the observations made in this study that has demonstrated the substantial stabilizing influence of such groups in vinyl cations, although the magnitude is not as great as that observed and computed for alkyl cations.

Conclusion

The data presented in this paper show that the further stabilization of the vinyl cation which already has a stabilizing α-alkyl or aryl substituent is significantly less than that for the ethyl cation with the same α-substituent. However, the stabilization of the vinyl cation by an α-alkyl or aryl substituent is significantly greater than that for the ethyl cation. The *total* stabilization due to the same pair of α-alkyl or α-aryl and *β*-trimethylsilyl substituents is only slightly greater for the ethyl than for the vinyl cation. The relative values for the two types of cation are in line with theoretical predictions for *β*-silyl stabilization of the unsubstituted vinyl and ethyl cations which predict the greater effect in the ethyl cation.[2] The weak stabilization of the already strongly α-stabilized vinyl cation is in accord with the finding of a "surprisingly weak" stabilization of a carbocation by a *β*-trimethylsilyl group in the condensed phase.[35] The acid-catalyzed conversion of phenylacetylene to acetophenone has as its rate determining step an initial protonation to give the α-substituted vinyl cation $C_6H_5CCH_2^+$. The presence of a *β*-trimethylsilyl substituent increases the rate by only a factor of 300 in contrast to the factors of up to 10^{12} that have been reported for accelerations of solvolysis reactions due to the presence of the same substituent in a saturated substrate.[36]

From the above it follows that a vinyl cation with a destabilizing (electron-withdrawing) α-substituent will be sta-

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(30) Bowen, R. D.; Williams, D. H.; Schwarz, H.; Wesdemiotis, C. *J. Am. Chem. Soc.* **1979**, *101*, 4681.

(31) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649.

(32) Radom, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 6531.

(33) Lias, S. G.; Ausloos, P. *Int. J. Mass Spectrom. Ion Processes*. **1987**, *81*, 165.

(34) Siehl, H-U. *Pure Appl. Chem.* **1995**, *67*, 769.

(35) Kresge, J.; Tobin, J. B. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 721.

(36) Lambert, J. B.; Wang, G.; Finzel, R. B.; Teramura, D. H. *J. Am. Chem. Soc.* **1987**, *111*, 7838.

bilized to a significantly greater extent by a β-silyl substituent than will be one with a stabilizing (electron-donating) alkyl or aryl group. *Ab initio* calculations show that trifluoromethyl and cyano substituents destabilize vinyl cations when in the α-position,[37] and it is therefore predicted that the β-silicon effect will be very large for these ions. It is doubtful that gas-phase data for such systems can be obtained by the HPMS method since the affinities for $(CH_3)_3Si^+$ of molecules such as $HC{\equiv}CCF_3$ are expected to be even lower than that of acetylene.

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[37] Apeloig, Y.; Biton, R.; Zuilhof, H.; Lodder, G. *Tetrahedron Lett.* **1994**, *35*, 265.