Stabilization Energies for α- and β-Silyl Substituents on Vinyl Cations determined using Mass Spectrometric Techniques†

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Vinyl cation stabilization energies in the gas phase of 29.5 kcal mol⁻¹‡ for an α-trimethylsilyl substituent and 43.5 kcal mol⁻¹ for a β-trimethylsilyl substituent relative to hydrogen are obtained from measurement of the appearance energies for metastable peaks for loss of I· from ionized $Me_3Si–CI=CH_2$ and (E)-$Me_3Si–CH=CHI$ respectively.

The unusual reactivity of α- and β-silyl compounds in solvolysis and other reactions has been recognized and studied for many years[1] and the subject of silyl substituted carbocations has recently been reviewed.[2] The stabilities of α- and β-silyl carbenium ions and silicenium ions are of interest because the first two species are reactive intermediates when organosilicon compounds are used in synthesis[3] while the latter are well known in the gas phase[4] but are only rarely claimed to be intermediates in solution.[5] Recently, the structures and thermochemistry of the gas phase alkyl cations, in particular the $C_5H_{13}Si^+$ isomers, have been investigated by mass spectrometric techniques[6] and by *ab initio* calculations.[7]

We report here the experimentally determined vinyl cation stabilization energies of 29.5 kcal mol⁻¹‡ for an α-trimethylsilyl substituent and 43.5 kcal mol⁻¹ for a β-trimethylsilyl substituent relative to hydrogen. In order to minimize rearrangements which are known to be facile for silyl containing carbenium ions in the gas phase[4,6] we selected precursor molecules 1–4 for our investigation of $C_5H_{11}Si^+$ ions. The m/z 99 $C_5H_{11}Si^+$ ions derived therefrom by dissociative electron impact ionization were characterized by their metastable ion (MI), collisional activation (CA), and neutralization–reionization (NR) mass spectra.§

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† *Note added in proof*: a report of the first persistent β-silyl-substituted vinyl cation has appeared.[21]

‡ 1 kcal = 4.184 kJ.

§ Using a VG Analytical ZAB-R mass spectrometer of BE_1E_2 geometry (B = magnet, E = electric sector).[9] Oxygen was used as the target gas for CA experiments.[10] In NR experiments cyclopropane was used as the reducing agent[11] and the neutral species were reionized by collision with oxygen.

Experimentally all four isomers: the silicenium ions 1a and 4a, the α-trimethylsilyl vinyl cation 2a and the β-trimethylsilyl vinyl cation 3a, have been identified as stable species in the gas phase. The spectra from ion 4a, which have been previously investigated,[12] are quite distinct from those of the other isomers. In particular, we conclude on the basis of the MI, CA[13] and NR mass spectra (Fig. 1) that at the thermochemical threshold the loss of an iodine radical from the molecular ions of 2 and 3 generates the α- and β-silyl substituted vinyl cations 2a and 3a, respectively.

The CA spectra of m/z 99 ions generated from 1 and 2 are similar but not identical. The corresponding spectrum from precursor 3 shows characteristic differences in the m/z 57–59 region. This implies that 1a and 2a are both stable species
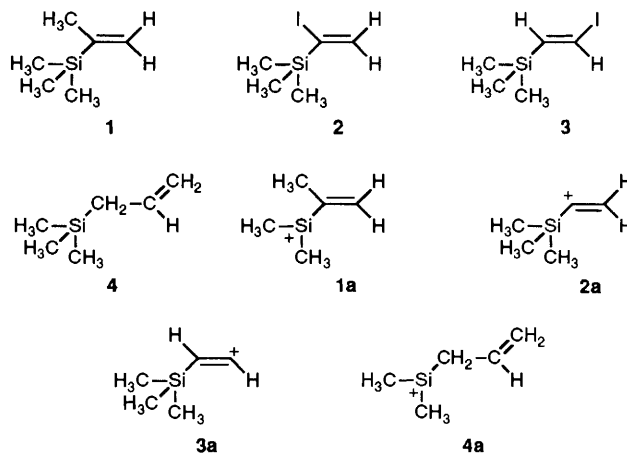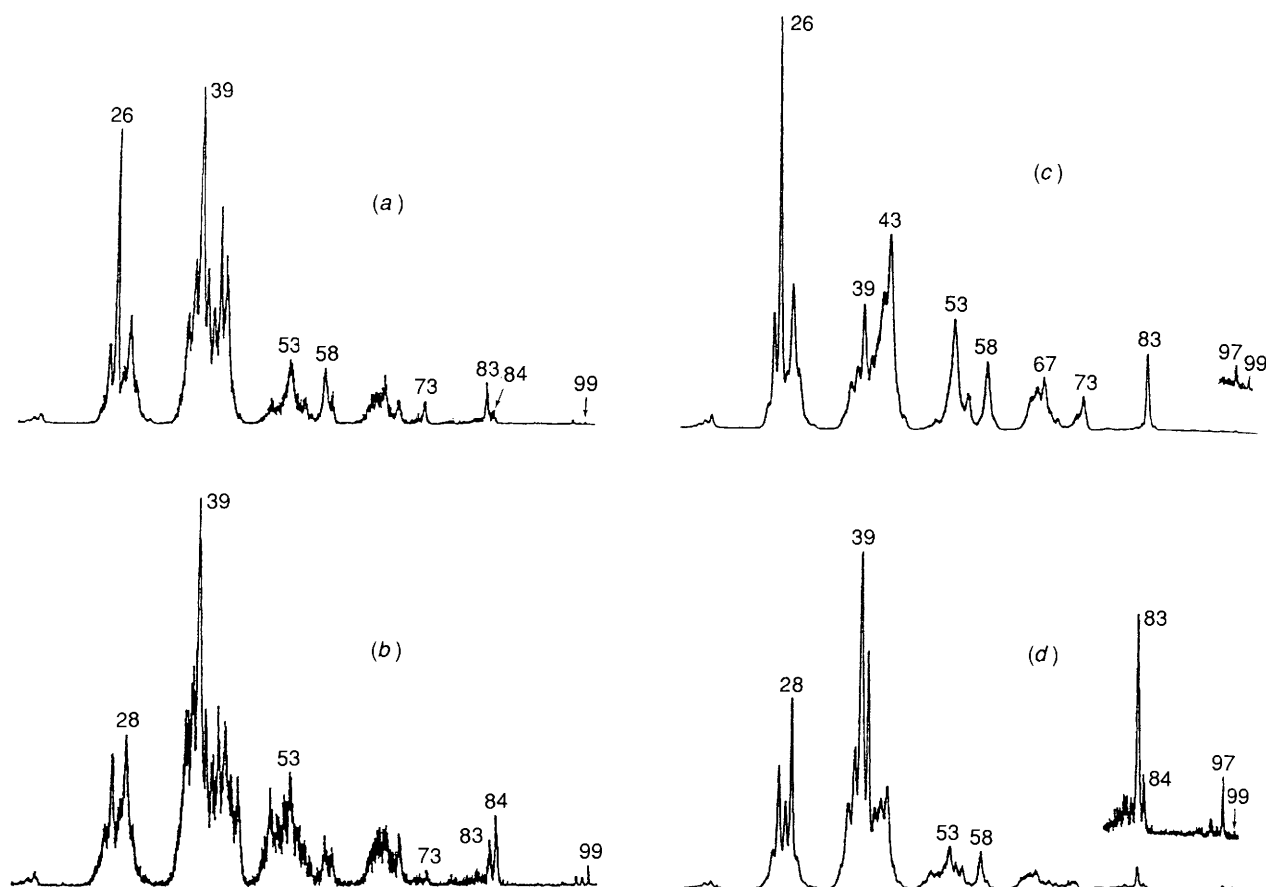
Fig. 1 NR mass spectra of $C_5H_{11}Si^+$ ions generated from (a) $Me_3Si-C(CH_3)=CH_2^{\cdot+}$, (b) from $Me_3Si-CI=CH_2^{\cdot+}$, (c) from (E)-$Me_3Si-CH=CHI^{\cdot+}$ and (d) from $Me_3Si-CH_2-CH=CH_2^{\cdot+}$
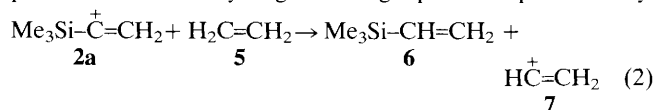
although there is probably a low barrier to their interconversion via a 1,2-methyl shift. This contrasts with the situation for the aliphatic species where the α-silyl cation lies in a shallow well or is not a minimum on the potential energy surface.[6b,c,e] Furthermore, a higher barrier to the 1,2-hydrogen shift must separate **2a** from **3a**, which is expected to lie in a deep potential well.

The NR mass spectra are of particular importance for two reasons. First, because they are more distinct than the CA mass spectra, they characterize the structures of isomers **1a–4a** better. In particular we note that the intensity of m/z 83 (loss of CH_4) is more than twice that of m/z 84 (loss of $^{\cdot}CH_3$) for **1a** but for **2a** the situation is reversed: m/z 84 is almost twice the intensity of m/z 83. Second, the appearance of peaks at m/z 99 in these spectra indicates that the corresponding α-trimethylsilyl and β-trimethylsilyl vinyl radicals ($C_5H_{11}Si^{\cdot}$) are stable species in the rarefied gas phase. The relative intensity of the 'survivor' ions was low for all four isomers with the highest signal being observed for **2a** (Fig. 1b) not **3a** (Fig. 1c). This observation, although consistent with theoretical calculations[6b,13] and experiments[14] performed on silyl substituted alkyl radicals, does not ensure that neutralized **2a** is more stable than neutralized **3a**. The survivor intensities do not directly reflect the relative stabilities of the corresponding radicals. This is because neutralization and reionization are vertical processes and when substantial geometry differences exist between the ionized and neutral species, very poor efficiencies are expected.[8d] Furthermore, while earlier theoretical investigations of the related $H_3Si-CH=CH^+$ ions considered only the open 'classical' structure[7a] more recent calculations[15] indicated that the bridged 'nonclassical' structure is more stable.

We have measured the appearance energies (AE) for metastable ions **2a** and **3a** with a Kratos AEI MS 902S mass spectrometer using a comparative method with diethyl ether as a standard.[16] The experimental values were 10.08 eV (232 kcal mol^{-1}) for the α-trimethylsilyl vinyl cation, **2a**, and 9.46 eV (218 kcal mol^{-1}) for the β-trimethylsilyl vinyl cation, **3a**. Using relevant thermochemical data[17] for species in eqn. (1)[18] and estimating[6c,19] the $\Delta H_f(3) = -11$ kcal mol^{-1} the measured $\Delta H_f(3a) = 181$ kcal mol^{-1}. If we assume that geminal interactions are negligible then $\Delta H_f(2) = -11$ kcal mol^{-1} also and making the appropriate substitutions in eqn. (1) leads to $\Delta H_f(2a) = 195$ kcal mol^{-1}.

$$\Delta H_f\,(3a) = \Delta H_f\,(3) + AE\,(3a) - \Delta H_f\,(I^{\cdot}) \qquad (1)$$

The isodesmic reaction (2)¶ allows us to ascertain the magnitude of stabilization that the α-trimethylsilyl group provides relative to hydrogen in the gas phase. Experimentally
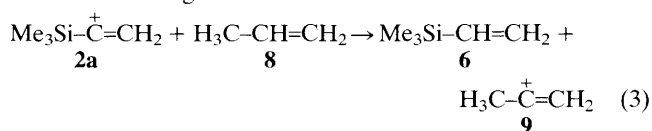
$$Me_3Si-\overset{+}{C}=CH_2 + H_2C=CH_2 \rightarrow Me_3Si-CH=CH_2 +$$
$$\mathbf{2a} \qquad\qquad \mathbf{5} \qquad\qquad\qquad \mathbf{6}$$
$$\overset{+}{HC}=CH_2 \qquad (2)$$
$$\mathbf{7}$$

the α-trimethylsilyl substituent stabilizes the vinyl cation by 29.5 kcal mol^{-1} relative to hydrogen. Using ion **3a** in place of **2a** in the above isodesmic reaction we find that the β-trimethylsilyl substituent provides a stabilization energy of 43.5 kcal mol^{-1} relative to hydrogen. Using isodesmic reaction (3)‖ the α-SiMe₃ group appears to be stabilizing by

¶ $\Delta H_f\,(5) = 12.5$ kcal mol^{-1}, $\Delta H_f\,(6) = -29$ kcal mol^{-1} and $\Delta H_f\,(7)$ = 266 kcal mol^{-1}; cf. ref. 17.

‖ $\Delta H_f\,(8) = 5$ kcal mol^{-1} and $\Delta H_f\,(9) = 231$ kcal mol^{-1}; cf. ref. 17.

only 2 kcal mol^{-1} relative to a methyl group. A value of *ca.* 9 kcal mol^{-1} was proposed from the results of *ab initio* MO calculations using a small basis set.[20]

$$Me_3Si\overset{+}{-}C=CH_2 + H_3C-CH=CH_2 \rightarrow Me_3Si-CH=CH_2 +$$
$$\mathbf{2a} \qquad\qquad \mathbf{8} \qquad\qquad\qquad \mathbf{6}$$
$$H_3C\overset{+}{-}C=CH_2 \quad (3)$$
$$\mathbf{9}$$

Results of *ab initio* MO calculations have not been reported for the β-SiMe$_3$ system and thus a direct comparison between theory and experiment is not possible. However, the stabilization energy of a β-SiH$_3$ substituent is available, 28.6 kcal mol^{-1},[7a] as is the stabilization energy of β-SiH$_3$ on alkyl cations, 38 kcal mol^{-1},[7a] which differs only slightly from the values obtained for β-SiMe$_3$ by experiment.[6c,d] These results seem to indicate that relative to β-SiH$_3$ the β-SiMe$_3$ group has a more pronounced stabilizing effect on a vinyl cation than on an alkyl cation. Finally, we note that *ab initio* calculations[20] predict the stabilization energy to be larger for the α-SiMe$_3$ group than the α-SiH$_3$ group on the vinyl cation by 15.5 kcal mol^{-1}. A similar stabilization effect for the β-silyl species would lead to a stabilization energy for β-SiMe$_3$ that is very close to our experimental value.

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