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Efficient Isomerization of $Si(C_2H_5)H_2^+$ to $Si(CH_3)_2H^+$ by Collisional Activation in the Gas Phase

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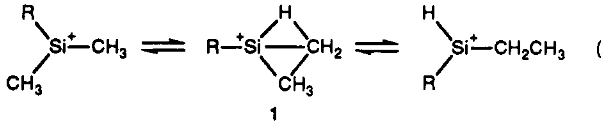
Summary: Efficient isomerization of $Si(C_2H_5)H_2^+$ to the thermodynamically more stable $Si(CH_3)_2H^+$ ion in the gas phase by using Fourier transform mass spectrometry (FTMS) is described. This isomerization is induced by collisional activation with structures of the $SiC_2H_7^+$ ions probed by specific ion molecule reactions with ethene-d_4 and methanol. The isomerization is proposed to proceed by a concerted 1,2-hydrogen/1,2-methyl migration (dyotropic rearrangement).

Cationic organosilane ions are highly reactive species in the gas phase and often undergo interesting rearrangements.[1-3] For example, Groenewold and Gross[4] observed that $Si(CH_3)_3^+$ yields predominant elimination of C_2H_4 upon collision-activated dissociation (CAD)[5] using a sector mass spectrometer (process 1). Recently, we studied the

$$Si(CH_3)_3^+ \xrightarrow{CAD} Si(CH_3)H_2^+ + C_2H_4 \qquad (1)$$

mechanism of ethene elimination for dissociation of $Si(CH_3)_3^+$ by using Fourier transform mass spectrometry (FTMS)[6] combined with isotopic exchange reactions and CAD.[7] We found that elimination of C_2H_4 is the lowest energy pathway for decomposition of both $Si(CH_3)_3^+$ and $Si(C_2H_5)(CH_3)H^+$. Furthermore, CAD of the isotopolog $Si(^{13}C_2H_5)(CH_3)H^+$, by using an "off-resonance" electric field pulse,[8] yields ethene elimination with a statistical distribution of the carbon isotope.[7] This result suggests that activated $Si(CH_3)_3^+$ and $Si(C_2H_5)(CH_3)H^+$ interconvert prior to ethene elimination, presumably by a concerted 1,2-hydrogen/1,2-methyl migration (dyotropic rearrangement)[9] (process 2). We envision that dyotropic rearrangement (process 2) involves a thermally allowed $[\sigma_s^2 + \sigma_a^2]$ process.[7] Decomposition of $Si(CH_3)_2H^+$ is believed to proceed by an analogous mechanism (cf. process 2) with conversion to $Si(C_2H_5)H_2^+$ preceding dissociation.[7] $Si(CH_3)_2H^+$ and $Si(CH_3)_3^+$ are estimated to be 27 and 20 kcal/mol, respectively, more stable than the corresponding ethyl isomers.[10] In principle, it should be possible to convert the less stable ethylsilylenium isomer to the more stable methylsilylenium species by careful activation, provided the barrier for isomerization is less than the energy required for decomposition.[12] In this communication, we report efficient isomerization of $Si(C_2H_5)H_2^+$ to $Si(CH_3)_2H^+$ by collisional activation by using an "off-resonance" electric field pulse.[8] The two $SiC_2H_7^+$ isomers were distinguished by reaction with ethene-d_4 and methanol.[13]



(2)

Experiments were performed by using a modified Nicolet FTMS-1000 Fourier transform mass spectrometer.[6,14] $Si(CH_3)_2H^+$, $Si(C_2H_5)H_2^+$, $Si(CH_3)_3^+$, and $Si(C_2H_5)(CH_3)H^+$ were generated by electron impact ionization (−20 eV beam voltage) of the corresponding hydroorganosilane. Precursor organosilanes were admitted into the vacuum chamber via a pulsed solenoid inlet valve,[15] in order to minimize complicating side reactions with background silane.[1,2] A static argon pressure of 1 × 10^{-5} Torr was maintained throughout these experiments and serves as the target for collisional activation and serves to facilitate ion thermalization prior to reaction with a neutral reagent. Ions are collisionally activated by using a sustained (500 ms) "off-resonance" electric field pulse. A consequence of "off-resonance" irradiation is that an irradiated ion undergoes acceleration–deceleration cycles throughout the duration of the pulse[8] with the kinetics energy given by

$$E_{tr,max} = \{(E_{Rf})^2 e^2/[2m(\omega - \omega_c)^2]\} \sin^2[(\omega - \omega_c)t/2] \qquad (3)$$

where E_{Rf} is the electric field amplitude, e is the electric charge, t is the duration of the electric field pulse, m is the mass of the ion, ω (rad/s) is the excitation frequency, and ω_c is the natural cyclotron frequency of the ion.[16] This method of excitation allows irradiated ions to maintain a

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[10] $\Delta H_f(Si(CH_3)H_2^+)$ = 204 kcal/mol, $\Delta H_f(Si(CH_3)_2H^+)$ = 172 kcal/mol, and $\Delta H_f(Si(CH_3)_3^+)$ = 147 kcal/mol, from: Shin, S. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 900. $\Delta H_f(Si(C_2H_5)H_2^+)$ and $\Delta H_f(Si(C_2H_5)(CH_3)H^+)$ are estimated to be 199 and 167 kcal/mol, respectively. These are estimated by using the known ΔH_f values of the corresponding methylsilylenium ion and assumed energy increments for replacing methyl with ethyl.[11]

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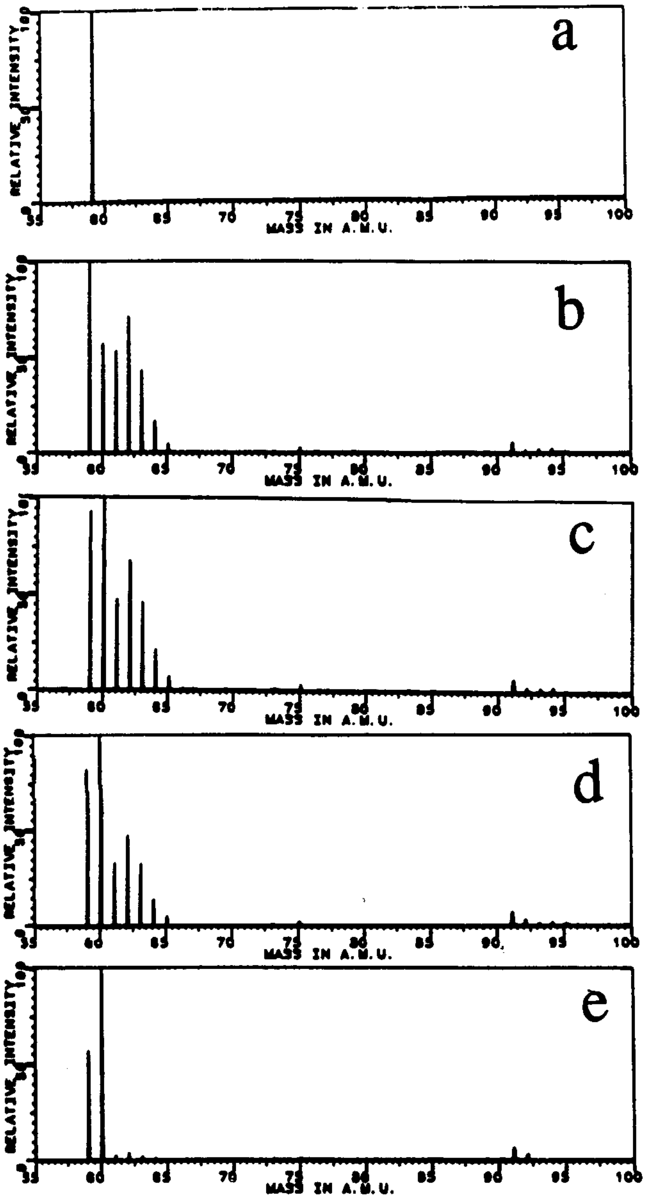

Figure 1. Mass spectra obtained for reaction of $Si(C_2H_5)H_2^+$ with 1.8×10^{-8} Torr of ethene-d_4 following application of an "off-resonance" electric field pulse for inducing rearrangement to $Si(CH_3)_2H^+$ (1×10^{-5} Torr of Ar as target). The duration of the electric field pulse is 500 ms with a 1.02-V amplitude. The maximum kinetic energy obtained by the ion is calculated directly from eq 3 and is varied by controlling $\Delta\omega$($\Delta\omega = |\omega - \omega_c|$): (a) isolation of $Si(C_2H_5)H_2^+$ where a 500-ms delay follows isolation with reisolation after this 500-ms trap; (b) same conditions as (a) except a 5-s trap follows the final isolation; (c) same conditions as (b) except $Si(C_2H_5)H_2^+$ is irradiated during the initial 500-ms trap with an electric field pulse with $\Delta\omega$ = 3.1 kHz corresponding to $E_{tr,max}$ of 0.86 eV; (d) same conditions as (c) except $\Delta\omega$ = 2.8 kHz ($E_{tr,max}$ = 1.1 eV); (e) same conditions as (c) except $\Delta\omega$ = 1.8 kHz ($E_{tr,max}$ = 2.6 eV).

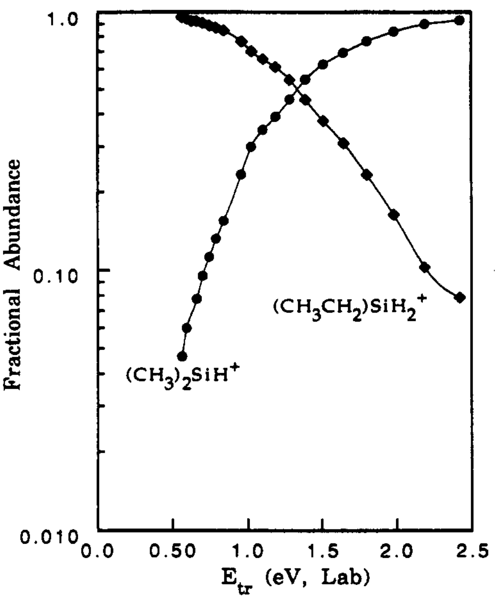

Figure 2. Variation of the fractional abundance of $Si(C_2H_5)H_2^+$ and $Si(CH_3)_2H^+$ isomers as a function of the maximum ion kinetic energy (laboratory frame, from eq 3) for "off-resonance" irradiation for collisional activation (500-ms pulse, 1.02-V amplitude). The isomers were distinguished by reaction with ethene-d_4. The distribution of the two isomers was determined by assuming that the m/z 60/61 ratio due to the $Si(C_2H_5)H_2^+$ isomer is fixed (Figure 1b). This allowed the amount of m/z 60 due to the $Si(CH_3)_2H^+$ isomer to be calculated.

low maximum translation energy throughout the irradiation period. Hence, ions can be slowly activated by numerous low-energy collisions with argon. This activation technique is analogous to infrared multiphoton dissociation (IRMPD) for elucidating the lowest energy pathway for ion dissociation.[17] The "off-resonance" irradiation is employed here, *not to dissociate ions* but, rather, to *tickle* ions in order to investigate low-energy isomerization.

Reaction with either ethene-d_4 or methanol readily distinguishes silylenium ion structural isomers.[13] For example, $Si(CH_3)_2H^+$ yields exclusively one H/D exchange with ethene-d_4,[18] whereas $Si(C_2H_5)H_2^+$ yields seven H/D exchanges. With methanol, $Si(CH_3)_2H^+$ gives competitive CH_4/H_2 eliminations and $Si(C_2H_5)H_2^+$ yields competitive C_2H_6/H_2 eliminations. Figure 1b illustrates the mass spectrum obtained for reaction of $Si(C_2H_5)H_2^+$ with ethene-d_4 and is characteristic of the multiple H/D exchange observed for $Si(C_2H_5)H_2^+$. In parts c–e of Figure 1, $Si(C_2H_5)H_2^+$ was first submitted to numerous low-energy collisions by using an "off-resonance" irradiation pulse and then allowed to react with C_2D_4. As the kinetic energy of irradiated $Si(C_2H_5)H_2^+$ is increased (Figure 1c–e), the spectra evolve to yield predominantly a single H/D exchange indicative of $Si(CH_3)_2H^+$.[18] There is a small amount (<10%) of ion dissociation observed at the highest collision energy. Similar isomerization results are observed by using CH_3OH as a probe of ion structure.[13] These results clearly indicate that $Si(C_2H_5)H_2^+$ is *efficiently* (ca. 90%) isomerized to the thermodynamically more stable $Si(CH_3)_2H^+$ ion.[10] Figure 2 illustrates the fractional abundance of the two isomeric forms of $SiC_2H_7^+$ versus collision energy. In contrast to the efficient isomerization of $Si(C_2H_5)H_2^+$, only a small amount (ca. 5%) of $Si(C_2H_5)(CH_3)H^+$ was isomerized to $Si(CH_3)_3^+$ by using "off-resonance" irradiation for collisional activation. Apparently, the energy required to convert $Si(C_2H_5)(CH_3)H^+$ to $Si(CH_3)_3^+$ is only slightly less than that required for ethene

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elimination; consequently, ions with sufficient energy for isomerization can also readily decompose.

The transition state for interconversion of $Si(C_2H_5)(R)H^+$ and $Si(CH_3)_2(R)^+$, 1, is highly ordered and, consequently, should have a significant barrier. This barrier, however, must be less than the energy required for ethene elimination from $Si(C_2H_5)H_2^+$ (ca. 51 kcal/mol).[10,19] The inefficient isomerization of $Si(C_2H_5)(CH_3)H^+$ may be explained by invoking a slightly (5–10 kcal/mol) higher barrier for conversion to $Si(CH_3)_3^+$ where the transition state 1 would be more constrained due to the additional methyl group. In this case, the barrier may approach the energy required for ethene extrusion from $Si(C_2H_5)(CH_3)H^+$ (ca. 50 kcal/mol)[10,19] and, consequently, ethene elimination from isomerized $SiC_3H_9^+$ would be highly probable.

The above results represent the first example of *efficient* ion isomerization without subsequent dissociation by using collisional activation in the gas phase.[12] The results for $Si(C_2H_5)H_2^+$ provide compelling evidence for rearrangement to $Si(CH_3)_2H^+$. Although ethene elimination dominated over isomerization of activated $Si(C_2H_5)(CH_3)H^+$, the results for $Si(C_2H_5)H_2^+$ provide additional support for ethene elimination from CAD of $Si(CH_3)_3^+$ involving prior rearrangment to $Si(C_2H_5)(CH_3)H^+$, as suggested by labeling studies.[7]

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