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Novel Hydrogen/Methyl Exchange between $SiH_x(CH_3)_{3-x}^+$ (x = 1–3) and Propene in the Gas Phase

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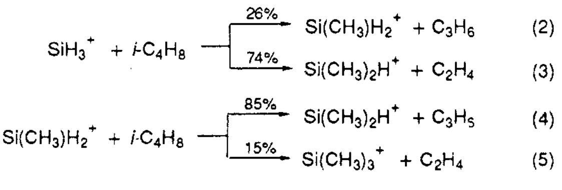
Summary: A novel H/CH_3 exchange reaction involving $SiH_x(CH_3)_{3-x}^+$ (x = 1–3) with propene and 2-methylpropene in the gas phase using Fourier transform mass spectrometry is described. The mechanism of this exchange process was investigated by using specific isotopic labeling. The facility of the exchange suggests small barriers for this reaction.

There is increasing interest in silicenium ions as reactive intermediates;[1-8] however, they have proven elusive and only recently were directly observed in solution.[1] The difficulty in observing these ions in solution is open to debate; however, their high reactivity with Lewis bases is certainly an important contributing factor.[1] Gas-phase ion techniques[9] are uniquely suited for probing the chemistry of silicenium ions since their high reactivity presents no complications. In this report we wish to describe a novel H/CH_3 exchange reaction between $SiH_x(CH_3)_{3-x}^+$ (x = 1–3) and propene (process 1) in the gas phase.

$$SiH_x(CH_3)_{3-x}^+ + C_3H_6 \rightarrow SiH_{x-1}(CH_3)_{4-x}^+ + C_2H_4 \qquad (1)$$
$$x = 1\text{–}3$$

All experiments were performed by using a Nicolet FTMS-1000 Fourier transform mass spectrometer[10] equipped with a 5.08-cm cubic trapping cell and a 3.0-T superconducting magnet.[11] Methylsilicenium ions were generated by electron impact on appropriate methylsilane precursors. For example, SiH_3^+ was formed from SiH_4, $Si(CH_3)H_2^+$ from $Si(CH_3)H_3$, etc. The precursor silanes were introduced into the vacuum chamber through a pulsed solenoid inlet valve[12] in order to prevent complicating side reactions with background silane.[13] A static argon pressure of 1×10^{-5} Torr was employed throughout these experiments in order to facilitate thermalization of the ions prior to reaction with selected olefins. In addition, argon was also employed as the collision gas for collisional activation (CA).[14,15] Pressures of the reactant olefins were on the order of $(2\text{–}4) \times 10^{-8}$ Torr.[16]

The hydrogen/methyl exchange reaction, process 1, occurs exclusively for reaction of the $SiH_x(CH_3)_{3-x}^+$ (x = 1–3) ions with propene. Rate constants for these reactions are summarized in Table I along with reaction efficiencies and exothermicities. Isobutene reacts in an analogous fashion, however, in addition to simple hydrogen/methyl exchange, processes 2 and 4, the double exchange, processes 3 and 5, also occur. The double-exchange reaction dominates for SiH_3^+ whereas the single exchange dominates for $SiH_2(CH_3)^+$ (reactions 2–5). The branching ratios for reactions 2–5 were determined by continuous ejection of the intermediate single exchange ion products in reactions 2 and 4.[10] Decomposition of the products of reactions 1–5 upon CA yielded indentical product distributions and energy dependence as that for authentic methylsilicenium ions; hence, the products of these reactions are assigned as methylsilicenium ions.



$$SiH_3^+ + i\text{-}C_4H_8 \xrightarrow{26\%} Si(CH_3)H_2^+ + C_3H_6 \qquad (2)$$
$$SiH_3^+ + i\text{-}C_4H_8 \xrightarrow{74\%} Si(CH_3)_2H^+ + C_2H_4 \qquad (3)$$
$$Si(CH_3)H_2^+ + i\text{-}C_4H_8 \xrightarrow{85\%} Si(CH_3)_2H^+ + C_3H_5 \qquad (4)$$
$$Si(CH_3)H_2^+ + i\text{-}C_4H_8 \xrightarrow{15\%} Si(CH_3)_3^+ + C_2H_4 \qquad (5)$$

Table I. Rate Constants, Reactions Efficiencies, and Exothermicities for Reaction of $SiH_x(CH_3)_{3-x}$ (x = 1–3) with Selected Olefins

reactant ion	neutral reactant	k_{obsd}[a]	efficiency[b]	$-\Delta H_{rxn}$[c]
SiH_3^+	propene	1.39 (0.4)	0.97	23.3
	2-methylpropene	1.65 (0.5)	1.02	22.0
$Si(CH_3)H_2^+$	propene	1.33 (0.4)	1.02	24.4
	2-methylpropene	1.43 (0.4)	1.02	23.0
$Si(CH_3)_2H^+$	propene	0.83 (0.23)	0.68	17.4
	2-methylpropene	1.07 (0.29)	0.79	16.1
$Si(CH_3)_2D^+$	ethene	0.52 (0.16)[d]	0.47 (0.71)[e]	

[a] Observed bimolecular rate coefficient for disappearance of reactant ion in units of 10^{-9} cm^3 molecule^{-1} s^{-1} with uncertainties in parentheses. Neutral pressures were measured by using a Bayard–Alpert ionization gauge that was calibrated for ethene by monitoring the following proton abstraction reaction $ND_3^+ + C_2H_4 \rightarrow ND_3H^+ + C_2H_3$ that has a reported rate constant of 1.3 ± 20% X 10^{-9} cm^3 molecule^{-1} s^{-1}.[25] Propene and 2-methylpropene pressures were measured by using the above calibration along with corrections for ionization gauge efficiencies.[26] [b] Overall reaction efficiency = k(obsd/k(ado).[27] [c] In kcal/mol and calculated by using the thermochemical information found in ref 28. These calculations are for a single exchange and assume ethene and propene are the neutral products. [d] Rate constant of symmetric H/D exchange. [e] Reaction efficiency in parentheses is corrected for the $^2/_3$ statistical factor.

The H/CH_3 exchange process was investigated in detail for $Si(CH_3)_2H^+$ with propene, process 1, by using specific isotopic labeling. Propene-2-^{13}C reacts with $Si(CH_3)_2H^+$ yielding *no* incorporation of label into the trimethyl-

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(16) Pressure measured by using a Bayard–Alpert type ionization gauge and corrected for ionization efficiencies. See Table I for a description.

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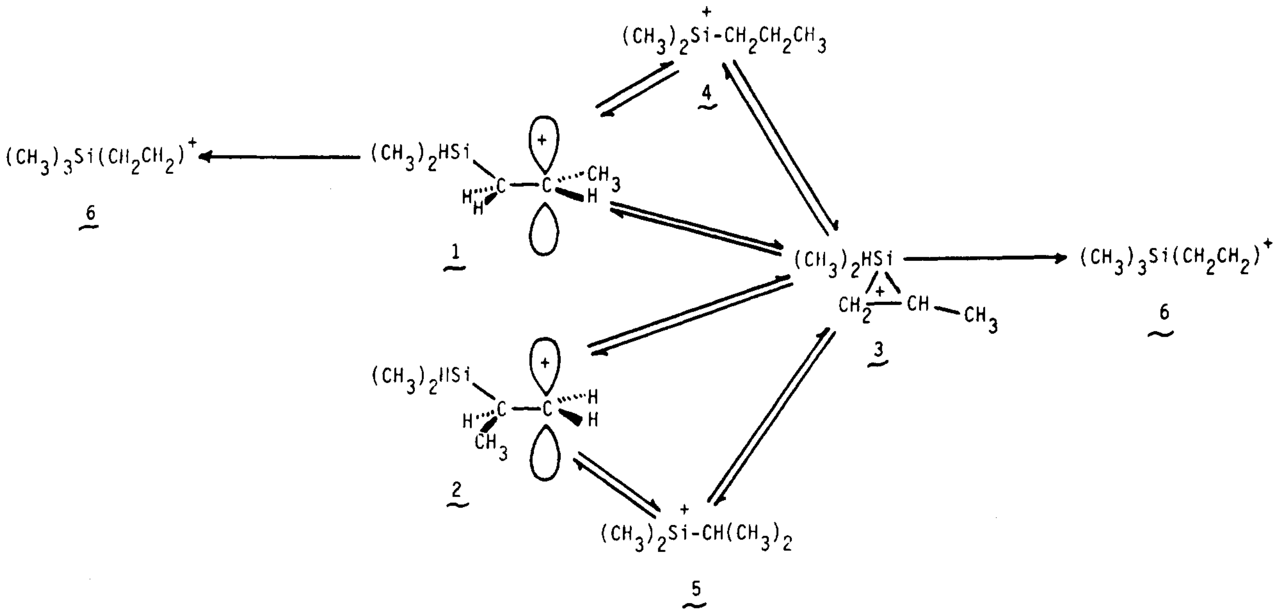
Scheme I



silicenium product ion. Ethene-d_4 yields exclusively one H/D exchange with $Si(CH_3)_2H^+$, process 6, with no exchange observed for either $Si(CH_3)_2D^+$ or $Si(CH_3)_3{}^+$, indicating that the methyl hydrogens are not involved in the exchange process. The above exchange presumably proceeds by reversible ethene insertion/β-hydrogen elimination (process 7).[17-19] The competition between H/D exchange (process 7) and H/CH_3 exchange (process 1) was investigated by monitoring the reaction of $Si(CH_3)_2D^+$ with propene (reactions 8–10) and reaction of $Si(CH_3)_2H^+$ with propene-*2*-d_1 (reactions 11–13) and propene-*3,3,3*-d_3 (reactions 14–18).

$$Si(CH_3)_2H^+ + C_2D_4 \rightarrow Si(CH_3)_2D^+ + C_2HD_3 \quad (6)$$

$$(CH_2CH_2)Si(CH_3)_2H^+ \rightleftharpoons (CH_3CH_2)Si(CH_3)_2{}^+ \quad (7)$$

$$Si(CH_3)_2D^+ + CH_2CHCH_3 \xrightarrow{18\%} Si(CH_3)_2H^+ + C_3H_5D \quad (8)$$
$$\xrightarrow{53\%} Si(CH_3)_3{}^+ + C_2H_3D \quad (9)$$
$$\xrightarrow{29\%} Si(CH_3)_2CH_2D^+ + C_2H_4 \quad (10)$$

$$Si(CH_3)_2H^+ + CH_2CDCH_3 \xrightarrow{16\%} Si(CH_3)_2D^+ + C_3H_6 \quad (11)$$
$$\xrightarrow{56\%} Si(CH_3)_3{}^+ + C_2H_3D \quad (12)$$
$$\xrightarrow{28\%} Si(CH_3)_2CH_2D^+ + C_2H_4 \quad (13)$$

$$Si(CH_3)_2H^+ + CH_2CHCD_3 \xrightarrow{1\%} Si(CH_3)_2D^+ + C_3H_4D_2 \quad (14)$$
$$\xrightarrow{27\%} Si(CH_3)_3{}^+ + C_2HD_3 \quad (15)$$
$$\xrightarrow{3\%} Si(CH_3)_2CH_2D^+ + C_2H_2D_2 \quad (16)$$
$$\xrightarrow{11\%} Si(CH_3)_2CHD_2{}^+ + C_2H_3D \quad (17)$$
$$\xrightarrow{58\%} Si(CH_3)_2CD_3{}^+ + C_2H_4 \quad (18)$$

A proposed mechanism for the above H/CH_3 exchange involving $Si(CH_3)_2H^+$ and propene is presented in Scheme I. Initially, olefin coordination yields tetrahedral species, 1 or 2, with stabilization due to hyperconjugation of the developing p orbital on the carbenium carbon and the bisected C–Si σ-bonding orbital.[20-22] The carbenium ions 1 and 2 may collpase yielding pentavalent silacyclopropane 3 or 3 may be generated directly upon interaction of propene with the dimethylsilicenium ion.[20-22] Ab initio calculations predict that the silacyclopropane configuration is only slightly (~4 kcal/mol) less stable than the corresponding carbenium species for interaction of propene with the SiH_3 group.[21b] Some differences are expected when the $Si(CH_3)_2H$ group is substituted for the SiH_3 group; however, intermediates 1 and 3 should still have similar thermo stability. Reversible olefin insertion/β-hydrogen migration interconverts intermediates 1–5, rendering all propene hydrogens exchangeable with the lone Si–H hydrogen atom.[17-19] Competitive with this reversible hydrogen atom migration is an *irreversible* H/CH_3 exchange, presumably involving either intermediates 1 or 3. In either case this exchange may proceed by synchronous methyl migration to the silicon atom and Si–H hydrogen atom migration to the vacated carbon atom of the nascent olefin generating 6. Alternatively, this exchange may involve sequential methyl/hydrogen migrations.[20a] Elimination of ethene completes the process. The binding energy of propene to the silicenium ion provides the driving force for these rearrangements (~20 kcal/mol).[23]

Careful examination of the isotopic distribution for reactions 8–18 yields additional insights on reaction mechanism and dynamics. Reaction of $Si(CH_3)_2D^+$ with propene and $Si(CH_3)_2H^+$ with propene-*2*-d_1 yields strikingly similar isotopic distributions. Of particular interest is the fraction of the symmetric H/D exchange product (processes 8 and 11). In contrast, reaction of $Si(CH_3)_2H^+$ with propene-*3,3,3*-d_3 yields only a trace (1%) of simple H/D exchange (process 14) despite the higher fraction of reactant deuterium. These results can be rationalized by in-

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voking rapid interconversion of intermediates **1**, **3**, and **4** with much slower interconversion of intermediates **2**, **3**, and **5**. This difference may simply reflect reduced thermal stability of the primary carbonium ion in **2** or may be a consequence of unfavorable steric factors for **2** and **5**. In any case, the interconversion of intermediates **1**, **3**, and **4** appears to dominate. Finally, the small amount of H/D scrambling for the H/CH_3 exchange products for reaction of $Si(CH_3)_2H^+$ with propene-*3,3,3*-d_3 (reactions 15 and 18), provides additional evidence that the irreversible migration of a methyl group to the silicon atom is occurring and that it is the key step in the process.

As can be seen in Table I the efficiency for the H/CH_3 exchange involving the dimethylsilicenium ion is less than that for either $Si(CH_3)H_2^+$ or SiH_3^+. This suggests that the transition state for the exchange involving the dimethylsilicenium species is more constrained or that there are unfavorable geometrical factors. Processes 3 and 5 are believed to proceed via sequential H/CH_3 exchanges where the initial exchange yields a propene–silicenium ion. The high abundance of the multiple exchange for SiH_3^+ with 2-methylpropene implies low barriers for this process. The small amount of the multiple exchange for $Si(CH_3)H_2^+$ suggests less favorable reaction dynamics for process 5, and this is consistent with the slightly less than unity reaction efficiency for exchange involving the dimethylsilicenium species with either propene or 2-methylpropene (Table I).[24]

The above results suggest that the gas-phase ion chemistry of organosilane fragment ions is quite complex with a number of interesting rearrangements accessible. We are currently investigating the dynamics of rearrangements involving a number of organosilane fragment ions that will aide in understanding reaction mechanisms. Detailed theoretical studies are required before these rearrangements can be fully characterized. Undoubtedly, these gas-phase results will provide new insights on organosilicenium transformations as important processes in solution-phase studies.

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Book Reviews

Chemical Reviews. Volume 88, Number 7, November 1988. Edited by J. Michl and J. A. Gladysz. American Chemical Society, Washington. 1988. 433 pp. $22.00.

A journal reviewing a review journal? This may seem unusual, but the November, 1988, issue of *Chemical Reviews* so closely resembles a volume of *Advances in Organometallic Chemistry* that it is worth drawing the attention of the readership of *Organometallics* to it. Editors Josef Michl and John Gladysz initiated thematic issues of *Chemical Reviews* in 1984, and this latest example is devoted to transition-metal organometallic chemistry. As stated in the Introduction, "the 17 articles in this issue provide an up-to-date perspective of many of the frontier research topics in transition-metal organometallic chemistry." All of the authors have made an effort to be comprehensive, putting their own (sometimes major) contributions in their proper relation to others' work. The articles range from 12 to 42 pages in length, with about 50 to over 350 references. They are organized around a property of the metal center, a ligand type, an application, or a reaction mechanism. A summary of topics and authors follows: nitrosyl complexes (Richter-Addo and Legzdins), carbonylation catalysis (Ojima), C–C bond formation through elimination reactions (Brown and Cooley), group 4 complexes of unsaturated hydrocarbons (Buchwald and Nielsen), η^2-acyls and η^2-iminoacyls (Durfee and Rothwell), alkyne cycloadditions (Schore), organometalloporphyrin chemistry (Guilard and Kadish), H_2 oxidative addition to iridium(I) complexes (Deutsch and Eisenberg), late metal hydroxides, alkoxides, and amides (Bryndza and Tam), 19-electron complexes (Astruc), 17-electron complexes (Baird), dinuclear early-transition-metal complexes (Messerle), pentadienyl complexes (Ernst), dihalocarbene complexes (Brothers and Roper), coordination chemistry of phosphorus–carbon multiple bonds (Nixon), (Cp)Fe chemistry relevant to CO and CO_2 fixation (Cutler, Hanna, and Vites), and complexes of weakly coordinating anions (Beck and Sünkel).

This reviewer vouches for the usefulness of this issue, having already used it to quickly find up-to-date information. Unlike most review volumes (even photoreproduced typescripts), there was a very short lag time between receipt and publication of the articles, with many references from 1987 and a few from 1988. The single-issue price of this issue is $22.00, about the same price as a photocopy. This is a bargain compared to most thematic monographs, so I suspect that many organometallic chemists will buy personal copies.

John P. Selegue, *University of Kentucky*