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Reactions of Methyl Cations with Methylsilanes[1]

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Abstract: The gas-phase reactions of CH_3^+ with $(CH_3)_{4-n}SiH_n$ (n = 0, 1, 2, 3) have been studied in a tandem mass spectrometric apparatus. Reaction cross sections at 1-eV kinetic energy in the laboratory system have been determined by direct comparison with the known cross section for hydride ion transfer from SiH_4 to CH_3^+. Relative cross sections have been determined as a function of kinetic energy in the range of 1–10 eV in order to determine whether reactions were endothermic or exothermic. The major reactions are hydride and methide (CH_3^-) transfer from the silane to CH_3^+, with methide transfer becoming dominant for $(CH_3)_3SiH$ and $(CH_3)_4Si$. Isotopic studies show only very minor incorporation of ^{13}C atoms and D atoms in the ionic products when CH_3^+ reactant ions are replaced by $^{13}CH_3$ and CD_3^+. This is interpreted as indicating that the reactions do not proceed through pentavalent collision complexes but rather are of the direct type.

Introduction

Standard enthalpies of formation of gaseous ions,[2-4] determined for the most part from electron-impact appearance potentials, indicate that siliconium ions are thermodynamically more stable with respect to their constitutive elements than are the corresponding carbonium ions. Thus, for example, the standard enthalpy changes for hydride ion transfer from silane and the methylsilanes to methyl-substituted carbonium ions, i.e.

$$(CH_3)_nCH_{3-n}^+ + (CH_3)_mSiH_{4-m} \rightarrow (CH_3)_nCH_{4-n} + (CH_3)_mSiH_{3-m}^+ \qquad (1)$$

are as shown in Figure 1 for m, n = 0, 1, 2, 3. As seen in this figure, all reactions are exothermic, i.e., energetically feasible, with the exception of $(CH_3)_2CH^+$ and $(CH_3)_3C^+$ reacting with SiH_4 and CH_3SiH_3. It is to be expected, therefore, that gaseous carbonium ions will usually react rapidly with silanes that contain a silicon–hydrogen bond to produce siliconium ions. Moreover, the simplicity of hydride transfer suggests that it should be a major pathway for the reaction to take. However, with the exception of the reactions of gaseous CH_3^+ ions with SiH_4,[5,6] there do not seem to have been any investigations of the reactions of alkyl ions with alkylsilanes.

Studies of organosilicon chemistry in solution[7,8] have not detected the presence of siliconium ions, i.e., $\geqslant Si^+$ of sp^2 hybridization, in systems in which they had been expected on the basis of analogy with carbonium ion chemistry. Instead, it appears that in solution most reactions at silicon centers involve pentavalent silicon intermediates of sp^{3}d hybridization. This tendency of silicon to use the accessible 3d orbitals to expand its valence shell, at least in solution, suggests that ion–molecule

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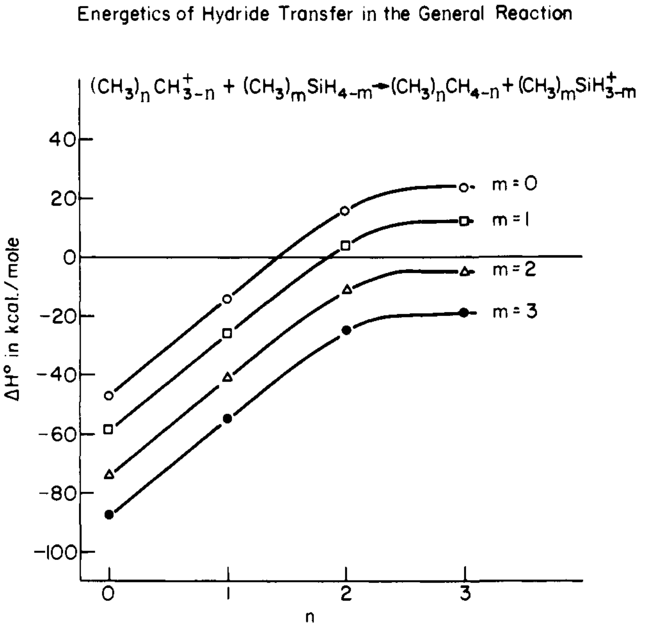


Figure 1. Standard enthalpy changes for hydride transfer from methylsilanes to methyl carbocations.

reactions that form trivalent siliconium ions as products might have a tendency to proceed through pentavalent intermediate collision complexes.

To investigate this possibility we have carried out a study of the reactions of CH_3^+, $^{13}CH_3^+$, and CD_3^+ ions with methyl- and ethylsilanes. This paper is a report of the results of that study.

Experimental Section

The experiments were carried out in a tandem mass spectrometric apparatus recently constructed in our laboratory. A schematic diagram of the apparatus is shown in Figure 2. The ion source is a commercial plasma source from Colutron Corp.[9] that has been modified by replacing the boron nitride block with a quartz sleeve and by mounting the anode into the heat sink that is supplied with the source. The water-cooled heat sink surrounding the quartz sleeve is thus floated at the anode potential which is usually about +200 V with respect to ground. The cathode-anode voltage and current of the arc discharge in the source depend somewhat on the gas but usually are about 40 V and 0.3 A, respectively. The current of ions leaving the source is typically 10^{-7}–10^{-6} A. The ions emerging from the source are accelerated and focused by an einzel lens into a Wien velocity filter[10-12] that is 3 in. in length and that was also obtained from the Colutron Corp. The velocity filter is usually operated with electric fields of 30–40 V/cm and magnetic fields of 500–1200 G.

Since the ions entering the velocity filter have been accelerated to a fixed energy (~200 eV), the velocity filter acts also as a mass filter and permits selection of a desired reactant ion. After emerging from the velocity filter the ions move at constant energy (~200 eV) for a distance of 50 cm, during which time the mass separation process is achieved. A typical mass spectrum obtained from neo-C_5H_{12} at a pressure of 0.5 Torr in the ion source is shown in Figure 3 and indicates the type of ions obtainable with the plasma source and the resolution of the velocity filter. After leaving the velocity filter the ions are decelerated by a retardation lens[12] to energies in the range of 0.5–5 eV and then enter a collision chamber containing the neutral reactant at pressures in the range of 2–20 × 10^{-4} Torr. The current of CH_3^+ ions injected into the collision chamber was typically 10^{-10} A at 2 eV and above. The current decreased with energy below 2 eV. Product ions are extracted from the collision chamber, mass analyzed with a quadrupole mass filter, and detected by a continuous dynode electron multiplier. The multiplier is mounted off the axis of the instrument in order to avoid detection of any energetic neutrals. A typical potential profile used for the reactions of 2-eV ions is as follows: source filament, +170 V; anode, +210 V; velocity filter, ground; collision chamber, +208 V; quadrupole mass filter, +200 V; dynode surface of multiplier, −2000 V.

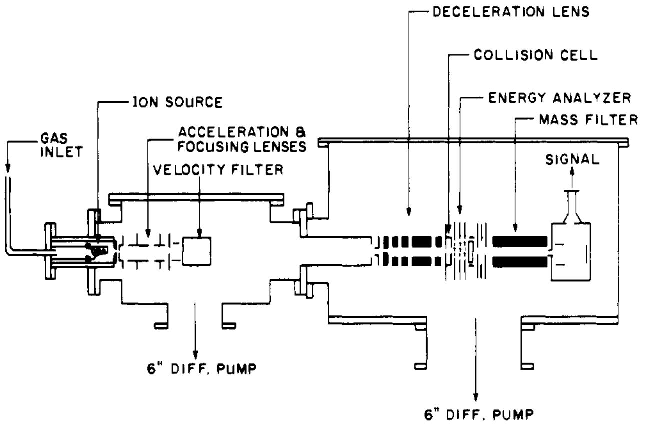


Figure 2. Schematic diagram of the tandem mass spectrometer.

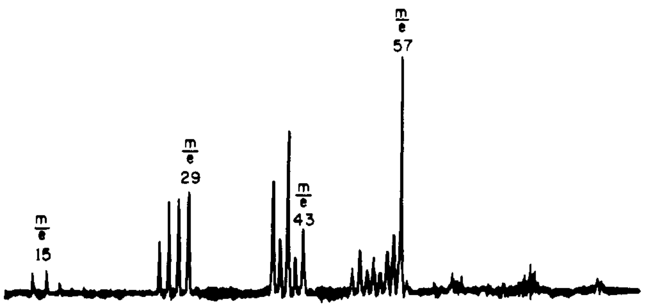


Figure 3. Mass spectrum of neopentane from modified colutron source as determined by Wien velocity filter. Acceleration potential = 200 V.

Cross sections for the reactions of CH_3^+ ions with the various alkylsilanes were determined at each energy by direct comparison with the process

$$CH_3^+ + SiH_4 \rightarrow CH_4 + SiH_3^+ \qquad (2)$$

the cross section of which has been previously measured.[5,6] In order to eliminate the influence of further collision reactions of the product ions, all reaction cross sections were extrapolated to the limit of zero pressure in the collision chamber. Pressures in the collision chamber were measured with a capacitance manometer. We believe the cross sections for the reactions to be accurate to within +30%.

As described previously,[6] the shapes of cross section vs. energy curves were used to differentiate between exothermic and endothermic reactions; the cross sections of endothermic reactions generally rise from zero at an energy threshold to a broad maximum several electron volts above threshold, while the cross sections for exothermic reactions decrease for all values of ion kinetic energy. This procedure can be misleading if the reactant ions are internally excited because a reaction that is endothermic for reactant ions in the ground state may then appear as exothermic. Since we are using a source that has not been used extensively in studies of the reactions of molecular ions, we have considered very carefully the question of internal excitation in the CH_3^+ reactant ions. Typical excitation functions for an exothermic and an endothermic reaction observed in the system CH_3^+ + $(CH_3)_3SiH$ are shown in Figure 4. Our data show energy thresholds, such as in Figure 4, for all clearly identifiable reactions of CH_3^+ with the methylsilanes that are indicated by the known thermochemistry[3] to be endothermic. From consideration of the endothermicities of the reactions that exhibit thresholds, we conclude that the internal excitation in the reactant CH_3^+ ions is not greater than 0.5 eV.

SiH_4 was purchased from the Matheson Co. while CH_3SiH_3, $(CH_3)_2SiH_2$, $(CH_3)_3SiH$, and $(CH_3)_4Si$ were obtained from Peninsular Chemresearch. CH_4, CD_3H, and $^{13}CH_4$, which were used to produce CH_3^+, CD_3^+, and $^{13}CH_3^+$ reactant ions, were obtained from Phillips Petroleum Co., Merck Sharpe and Dohme, and Stohler Isotopes, respectively. All gases were subjected to freeze-pump-thaw cycles on a high-vacuum line prior to use.

Results and Discussion

Reactions of Methyl Ions with Methylsilanes. Collisions of

Table I. Major Exothermic Reactions of CH_3^+ with Methylsilanes[a]

reaction no.	reaction	$\Delta H°$, kcal/mol	σ, Å^2	$k \times 10^9$, cm^3 s
3	$CH_3^+ + CH_3SiH_3 \rightarrow SiH_3^+ + C_2H_6$	−37	15	0.54
4	$CH_3^+ + CH_3SiH_3 \rightarrow CH_3SiH_2^+ + CH_4$	−59	62	2.2
5	$CH_3^+ + (CH_3)_2SiH_2 \rightarrow SiH_3^+ + C_3H_8$	−28	8	0.29
6	$CH_3^+ + (CH_3)_2SiH_2 \rightarrow CH_3SiH_2^+ + C_2H_6$	−48	42	1.5
7	$CH_3^+ + (CH_3)_2SiH_2 \rightarrow (CH_3)_2SiH^+ + CH_4$	−74	59	2.1
8	$CH_3^+ + (CH_3)_3SiH \rightarrow CH_3SiH_2^+ + C_3H_8$	−39	19	0.68
9	$CH_3^+ + (CH_3)_3SiH \rightarrow (CH_3)_2SiH^+ + C_2H_6$	−64	66	2.4
10	$CH_3^+ + (CH_3)_3SiH \rightarrow (CH_3)_3Si^+ + CH_4$	−88	30	1.1
11	$CH_3^+ + (CH_3)_4Si \rightarrow (CH_3)_2SiH^+ + C_3H_8$	−55	19	0.67
12	$CH_3^+ + (CH_3)_4Si \rightarrow (CH_3)_3Si^+ + C_2H_6$	−78	73	2.7
13	$CH_3^+ + (CH_3)_4Si \rightarrow (CH_3)_4Si^+ + CH_3$	−7	32	1.2

[a] Ion energy = 1 eV (lab).

Table II. Major Endothermic Reactions of CH_3^+ with Methylsilanes at 1 eV Ion Energy

reaction no.	reaction	ΔH, kcal/mol	σ, Å^2
14	$CH_3^+ + CH_3SiH_3 \rightarrow CH_3Si^+ + CH_4 + H_2$	2	2.4
15	$CH_3^+ + (CH_3)_2SiH_2 \rightarrow CH_3SiH^+ + CH_3 + CH_4$	29	1.7
16	$CH_3^+ + (CH_3)_2SiH_2 \rightarrow (CH_3)_2Si^+ + CH_3 + H_2$	20	3.2
17	$CH_3^+ + (CH_3)_2SiH_2 \rightarrow (CH_3)_2SiH_2^+ + CH_3$	10	0.6
18	$CH_3^+ + (CH_3)_3SiH \rightarrow (CH_3)_2Si^+ + CH_3 + CH_4$	15	7.7
19	$CH_3^+ + (CH_3)_3SiH \rightarrow (CH_3)_3SiH^+ + CH_3$	1	14.8

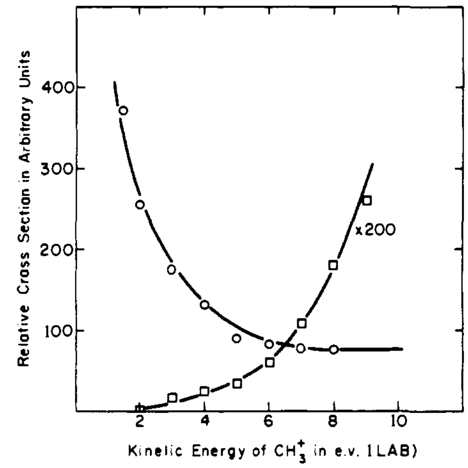


Figure 4. Energy dependence of reaction cross sections for exothermic and endothermic reactions: ○, reaction 8, Table I: □, $CH_3^+ + (CH_3)_3SiH \rightarrow CH_3SiH^+ + CH_4 + C_2H_5$.

CH_3^+ ions with methylsilanes initiate a rather simple set of chemical processes as may be seen from the mass spectrum of ionic products of the $CH_3^+ + (CH_3)_2SiH_2$ system shown in Figure 5. It may be seen in this figure that there are three principal products: (1) $(CH_3)_2SiH^+$ (*m/e* 59), which formally represents a hydride ion abstraction reaction; (2) $CH_3SiH_2^+$ (*m/e* 45), which formally represents a methide ion abstraction process; (3) SiH_3^+ (*m/e* 31), which must arise from a more complex process that may be a unimolecular decomposition that occurs subsequent to hydride ion abstraction. These type processes appear to be common to all the reactions of methylsilanes with CH_3^+ ions.

The major reactions (i.e., 10% or more of total reaction) of CH_3^+ with the methylsilanes that were found to be exothermic on the basis of the dependence of cross sections on ion kinetic energy are shown in Table I. Also shown in Table I are the standard enthalpy changes calculated from available thermochemical data,[2,3] the reaction cross sections measured at 1-eV ion energy in the laboratory frame of reference, and phenomenological rate constants computed from the cross sections and the ionic velocity. In all cases the electrically neutral products are written such as to yield the maximum exothermicity for the process. It is to be seen from Table I that hydride abstraction from target molecules containing Si-H bonds is a major process in all cases, a fact that is consistent with previous studies of the reactions of CH_3^+ with SiH_4. One may note from the case of $(CH_3)_4Si$, however, that hydride abstraction does not play a major role in the absence of Si-H bonds in the target molecule.

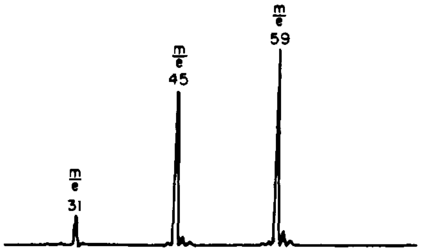


Figure 5. Product ion mass spectrum in the reaction of CH_3^+ ions with $(CH_3)_2SiH_2$.

The unexpected phenomenon to be seen in Table I is the important role played by the apparent methyl anion (methide ion) abstraction from the methylsilanes. Indeed, methide ion abstraction is of almost equal importance to hydride ion abstraction in $(CH_3)_2SiH_2$, which has equal numbers of methyl groups and hydrogen atoms, but becomes of significantly greater importance than hydride abstraction in $(CH_3)_3SiH$ and $(CH_3)_4Si$.

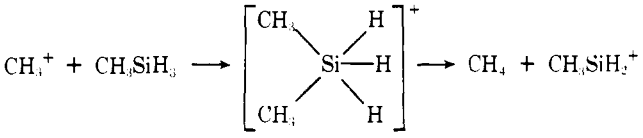
The reactions observed to be endothermic, on the basis of the dependence of cross section of energy, are shown in Table II. Also shown in Table II are the standard enthalpy changes calculated from available thermochemical data[2,3] and the cross sections of the reaction at 1 eV ion kinetic energy.

In general the enthalpy changes calculated from thermochemical data are in agreement with our observation of the dependence of cross section on energy. The observation of charge transfer from CH_3^+ to $(CH_3)_2SiH_2$ and $(CH_3)_3SiH$ (reactions 18 and 20 in Table II) as endothermic processes suggests that there is very little excitation energy in the reactant CH_3^+ ions. Charge transfer to $(CH_3)_4Si$ (reaction 13, Table I) is, however, observed to be exothermic, as predicted from thermochemical data. On the other hand, the observation of reaction 15 (Table II) at 1-eV energy suggests that excitation energy up to 0.5 eV may be present in the CH_3^+ ions. We are uncertain as to the reasons for this apparent contradiction but we think contributing factors may be uncertainty in the standard enthalpy of formation of CH_3SiH^+ and uncertainty in the actual kinetic energy of the ion in the experiment.

In the remainder of this section we discuss the details of the various reactions that occur when the reactant pairs are brought together.

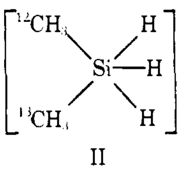
A. CH_3^+ + CH_3SiH_3. According to Table I, reactions 3 and 4 are the major exothermic reactions that occur when CH_3^+ ions having a kinetic energy of 1 eV collide with CH_3SiH_3. The products of (3) and (4) were identified by the ionic masses of 31 and 45 amu, respectively. It is possible that the ion with *m/e* 45 amu could be $SiH_3CH_2^+$ but past experience[5,6,13-16] demonstrating the prevalence of H^- transfer from Si-H bonds to attacking positive ions tends to rule out this possibility. More specifically, it has been shown[16,17] that D^- ion abstraction from the silicon atom in CH_3SiD_3 by $CH_3SiH_2^+$ and SiH_3^+ occurs readily, but there is virtually no transfer of an H^- species from carbon to these attacking ions. We assume that this will also be true when CH_3^+ is the reactant ion. As will be seen later, the absence of significant H^- transfer from $(CH_3)_4Si$ to CH_3^+ supports this assumption. In both reactions, (3) and (4), the neutral products are taken to be those that lead to the highest exothermicity. In reaction 4, CH_4 must be the neutral product for the reaction to be exothermic; however, in reaction 3 the neutral products could be C_2H_4 + H_2 and the reaction would still be exothermic, but in this case by only 4 kcal/mol.

Reaction 4 represents overall a simple hydride transfer and it is of interest to inquire into the mechanism of the process. If the transfer proceeds through a pentavalent-Si intermediate complex such as I, then replacement of CH_3^+ by the isotopic

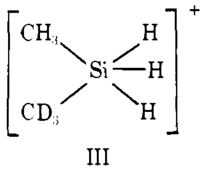


I

species $^{13}CH_3^+$ and CD_3^+ would result in the intermediates II and III, respectively. The product ions arising from the



II



III

breakup of II would be expected to yield equal amounts of $^{12}CH_3SiH_2^+$ (*m/e* 45) and $^{13}CH_3SiH_2^+$ (*m/e* 46). However, only a very slight increase of *m/e* 46 was observed when $^{12}CH_3^+$ was replaced by $^{13}CH_3^+$, the ratio of the current of $^{13}CH_3SiH_2^+$ to that of $^{12}CH_3SiH_2^+$ being of the order of 0.06. Similarly, the formation and decomposition of III would be expected to yield equal amounts of $^{12}CH_3SiH_2^+$ (*m/e* 45) and $CD_3SiH_2^+$ (*m/e* 48), but the observed current ratio I_{48}/I_{45} was 0.05. It is, therefore, apparent that the contribution of a pentacovalent Si intermediate such as I, in which the methyl groups are equivalent, is at most 6%. On the basis of these results, and earlier kinematic studies[16] of hydride transfer from CH_3SiH_3 to $CH_3SiH_2^+$ ions, we suggest that the predominant mechanism of (4) is a direct[18] one not involving a long-lived intermediate complex. However, we cannot rule out the possibility that the reaction proceeds through an intermediate complex in which the methyl groups are nonequivalent.

In the case of reaction 3 (cf. Table I), there was no significant change in the product mass spectra in the 31-33-amu range when CD_3^+ was substituted for CH_3^+. This fact indicates that exchange of hydrogen and deuterium between carbon and silicon does not occur, as might be expected if an intermediate complex such as III is playing a significant role in the reaction. The fact that reaction 3 is observed to be exothermic rules out the occurrence of dissociative charge transfer or of dissociation of $CH_3SiH_2^+$ subsequent to hydride transfer. The evidence suggests to us that (3) is occurring via a direct CH_3^- (methide) transfer from CH_3SiH_3 to CH_3^+ to form C_2H_6, which may contain sufficient internal energy to dissociate to C_2H_4 + H_2.

At CH_3^+ ion energies of 1 eV, small amounts of the product CH_3Si^+ (*m/e* 43) are observed, corresponding to reaction 14 in Table II. The form of the variation of cross section with energy shows this reaction to be endothermic, in agreement with existing thermochemical data.[2,3]

Simple charge transfer to form $CH_3SiH_3^+$ (*m/e* 46) is observed but the large corrections to the total ion current at *m/e* 46 due to the isotope $CH_3{}^{29}SiH_2^+$ precluded an experimental determination of the sign of $\Delta H°$ for the process. The available thermochemical data[2,3] indicate charge transfer to be endothermic by 19 kcal/mol.

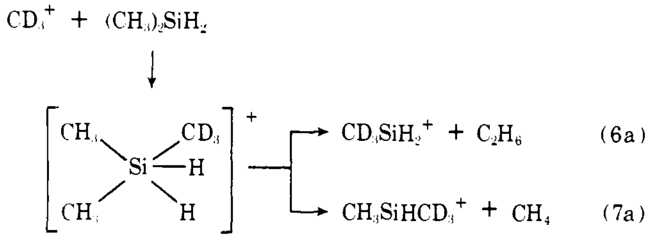
B. CH_3^+ + $(CH_3)_2SiH_2$. As may be seen in Table I, the predominant exothermic reactions in this system are the hydride transfer (reaction 7) to form $(CH_3)_2SiH^+$ and the methide transfer (reaction 6) to form $CH_3SiH_2^+$. As was true for the analogous reactions in the CH_3SiH_3 case, energetic considerations require that reaction 7 be as written but reaction 6 would also be exothermic if the neutral products were C_2H_4 + H_2. A rather surprising result is that in this system the cross sections for hydride transfer and for methide transfer are comparable. Also exothermic, but of smaller cross section, is the formation of SiH_3^+ via reaction 5 (cf. Table I). In this case the neutral products could also be C_2H_4 + CH_4 and still meet the exothermicity requirement.

When CH_3^+ is replaced by CD_3^+ the only changes observed in the product ion mass spectra are the appearances of small ion currents at *m/e* values of 32, 33, 34, 48, and 62 amu. In the case of substitution of $^{13}CH_3^+$ for CH_3^+ the major changes observed are slight enhancements of the ion-current ratios i_{46}/i_{47} and i_{60}/i_{61}; in this case no effect on the intensities in the 31-34-amu range is observed.

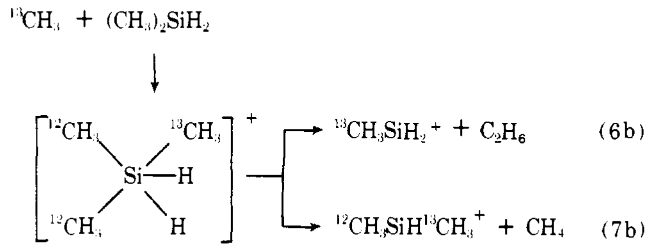
The appearance of product ions at *m/e* 48 and 62 in the case of CD_3^+-$(CH_3)_2SiH_2$ collisions indicates the formation of $CD_3SiH_2^+$ and $CD_3SiHCH_3^+$ in reactions 6 and 7, respectively. Similarly, the enhancement of the ion-current ratios i_{46}/i_{47} and i_{60}/i_{61} when $^{13}CH_3^+$ is the reactant ion, while not as definitive because of interferences from the ^{29}Si isotope, suggests the formation of $^{13}CH_3SiH_2^+$ and $^{13}CH_3SiHCH_3^+$ as products of reactions 6 and 7, respectively. We think that these product ions most likely arise from the breakup of intermediate complexes of the form IV and V, i.e., eq 6 and 7. It thus seems apparent that a part of both hydride transfer and methide transfer proceeds through a mechanism involving a pentavalent persistent intermediate with equivalent methyl groups. However, the intensities of the product ions are such as to indicate that not more than 5% of the total hydride and methide transfers occurs via this intermediate complex. The predominant fractions of both reactions appear to occur by direct transfers, or by loose complexes involving nonequivalent methyl groups, a finding not surprising for hydride ions, perhaps, but not expected for the more complex methide ions.

The ions with *m/e* values in the range of 32-34 that are observed when CD_3^+ replaces CH_3^+ are attributed to SiH_2D^+, $SiHD_2^+$, and SiD_3^+. The intensities of these deuterated ions are far below the expectations from silyl ion formation via statistical breakup of IV. Thus, there is no indication of randomization of hydrogen and deuterium in the processes forming silyl ions.

A possible mechanism to describe reaction 5 is that of hy-



IV



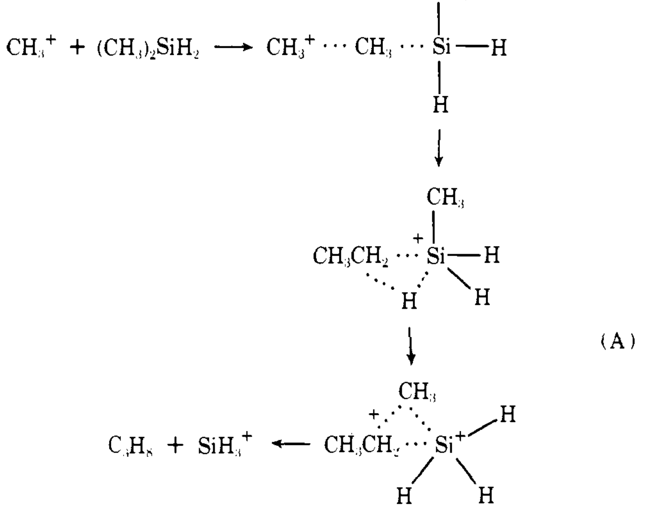
V

dride transfer followed by breakup of internally excited $(CH_3)_2SiH^+$ ions, i.e., eq 7. With hydride transfer (7) being

$$CH_3^+ + (CH_3)_2SiH_2 \longrightarrow (CH_3)_2SiH^{+*} + CH_4 \qquad (7)$$
$$\hookrightarrow SiH_3^+ + C_2H_4 \qquad (5)$$

(7)

predominantly a direct process, the result would be that very little of the silyl ion product would contain deuterium when CD_3^+ ions are substituted for CH_3^+ ions. However, an alternative to this mechanism is the formation and decomposition of an intermediate complex involving nonequivalent methyl groups. Such a scheme (A) is depicted below.[19] On the basis



(A)

of the present information, we are unable to distinguish between these alternatives. The fact that the analogous overall process is observed in the reaction of CH_3^+ with $(CH_3)_4Si$ and H^- transfer is virtually absent in that case tends to support scheme A.

Reactions 15-17, which form CH_3SiH^+, $(CH_3)_2Si^+$, and $(CH_3)_2SiH_2^+$ ions as products, respectively, are observed as endothermic processes in the collisions of CH_3^+ ions with $(CH_3)_2SiH_2$. The enthalpy changes calculated from thermochemical data are in agreement with our experimental conclusions that these processes are endothermic. Reaction 17 is a simple charge-transfer process, the detection of which is apparent only after subtraction of the isotopic contribution of $(CH_3)_2{}^{29}SiH^+$ to the total ion current at *m/e* 60. This isotopic correction was much less severe in this system than in the CH_3SiH_3 case with the result that reaction 17 could be shown to be endothermic.

Reactions 15 and 16 can be easily visualized as occurring by charge transfer followed by unimolecular breakdown of the parent molecular ion, i.e., eq 15-17. Being observed as endothermic reactions, energy available for these reactions must come from the relative kinetic energy of the system and from any internal excitation in the CH_3^+ reactant ions.

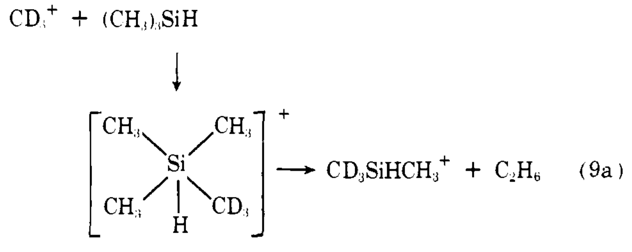
$$CH_3^+ + (CH_3)_2SiH_2 \longrightarrow (CH_3)_2SiH_2^{+*} + CH_3 \qquad (17)$$
$$\hookrightarrow CH_3SiH^+ + CH_4 \qquad (15)$$
$$\hookrightarrow (CH_3)_2Si^+ + H_2 \qquad (16)$$

Alternatively, reaction 15 could be pictured as dissociative hydride transfer in which internally excited $(CH_3)_2SiH^+$ ions lose CH_3, i.e., eq 7 and 15. We are unable to distinguish between these two possibilities for (15).

$$CH_3^+ + (CH_3)_2SiH_2 \longrightarrow (CH_3)_2SiH^{+*} + CH_4 \qquad (7)$$
$$\hookrightarrow CH_3SiH^+ + CH_3 \qquad (15)$$

C. CH_3^+ + $(CH_3)_3SiH$. According to the data in Table I, the dominant reactions of this collision pair are methide transfer to form $(CH_3)_2SiH^+$ (reaction 9), a more complicated process that produces $CH_3SiH_2^+$ (reaction 8), and hydride transfer to form $(CH_3)_3Si^+$ (reaction 10). That hydride transfer to yield the very stable $(CH_3)_3Si^+$ should not be the most probable of these three processes is unexpected but continues the trend observed with CH_3SiH_3 and $(CH_3)_2SiH_2$. Thus the fraction of total reaction that is hydride transfer in collisions of CH_3^+ with methylsilanes decreases as the number of Si-H bonds decreases. In Table I, reaction 10 must be as written to be endothermic but the neutral products of reaction 8 could be C_3H_6 + H_2 or C_2H_4 + CH_4 while those of reaction 9 could be C_2H_4 + H_2. The calculated enthalpy changes are in agreement with our experimental determination of the sign of $\Delta H°$.

Substitution of $^{13}CH_3^+$ for CH_3^+ does not cause any discernible change in the product ion mass spectrum. Substitution of CD_3^+ for CH_3^+ yields essentially the same mass pattern of products with the only change being the appearance of very low currents of ions having *m/e* values of 48 and 62 amu. The intensity of *m/e* 62, i.e., $(CD_3)SiHCH_3^+$, is about 1% of that of the $(CH_3)_2SiH^+$ ion. This suggests that only a few percent, at most, of reaction 9 proceeds through a pentavalent Si intermediate complex, VI, in which the methyl groups have become equivalent. Thus just as in the case of CH_3SiH_3 and $(CH_3)_2SiH_2$, methide transfer from the methylsilane to CH_3^+ appears to be predominantly a direct process or one involving a complex with nonequivalent methyl groups.



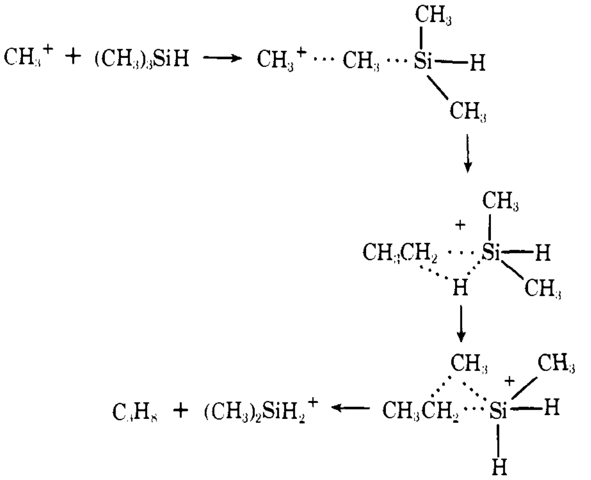
VI

As mentioned earlier, the cross section observed for hydride transfer is surprisingly small, amounting to only about 14% of the total reaction of CH_3^+ with $(CH_3)_3SiH$. As in the $(CH_3)_2SiH_2$ case, it is to be noted that the hydride transfer reaction (reaction 10) is very exothermic and therefore it may proceed by breakup of internally excited $(CH_3)_3Si^+$ that is formed by hydride transfer, i.e., eq 8 and 10. Such a mecha-

$$CH_3^+ + (CH_3)_3SiH \longrightarrow (CH_3)_3Si^{+*} + CH_4 \qquad (10)$$
$$\hookrightarrow CH_3SiH_2^+ + C_2H_4 \qquad (8)$$

nism for the major part of the formation of $CH_3SiH_2^+$ would explain why substitution of $^{13}CH_3^+$ for CH_3^+ produced no discernible effect on the mass pattern at $CH_3SiH_2^+$ (*m/e* 45) and substitution of CD_3^+ for CH_3^+ resulted in only very minor currents at *m/e* 48, i.e., $CD_3SiH_2^+$.

An alternative possibility, which receives some support from the fact that the overall process analogous to (8) is observed with $(CH_3)_4Si$ while H^- transfer is not observed, involves a complex with nonequivalent methyl groups, as shown in the scheme B.[19]



(B)

The formation of $(CH_3)_2Si^+$ and of $(CH_3)_3SiH^+$ via reactions 18 and 19, respectively (Table II), are observed as endothermic processes, in agreement with available thermochemical information.[2,3] Reaction 19 is a simple charge-transfer process and reaction 18 is most easily pictured as occurring by unimolecular breakup of internally excited product ions of reactions 10 (Table I) or 19 (Table II), i.e., eq 10 and 18 or 19 and 18. As in the case of reaction 15 in the CH_3^+-$(CH_3)_2SiH_2$ system, we are unable to distinguish between these two possibilities.

$$CH_3^+ + (CH_3)_3SiH \longrightarrow (CH_3)_3Si^{+*} + CH_4 \tag{10}$$

$$\hookrightarrow (CH_3)_2Si^+ + CH_3 \tag{18}$$

$$CH_3^+ + (CH_3)_3SiH \longrightarrow (CH_3)_3SiH^{+*} + CH_3 \tag{19}$$

$$\hookrightarrow (CH_3)_2Si^+ + CH_4 \tag{18}$$

D. CH_3^+ + $(CH_3)_4Si$. This system is quite different than those discussed so far in that there are no Si-H bonds present. One might, therefore, expect a drastic reduction in the extent of hydride transfer. Secondly, the ionization potential of $(CH_3)_4Si$ is lower than that of CH_3 radicals so that charge transfer would be exothermic[2,3] and would be expected to play a larger role than in the other collision systems investigated.

The above expectations are borne out by the data in Table I, where it may be seen that charge transfer (reaction 13) is observed to be a major exothermic process and there is no indication of a significant amount of hydride transfer. The major process is methide transfer (reaction 12) to yield the stable $(CH_3)_3Si^+$ product. The formation of $(CH_3)_2SiH^+$ ions also occurs by an exothermic process which we have written as reaction 11, although other neutral products could be formed, such as C_2H_4 + CH_4 or C_3H_6 + H_2, and still maintain exothermicity. Similarly the neutral products of reaction 12 could be C_2H_4 + H_2, but reaction 13 (charge transfer) must be as written.

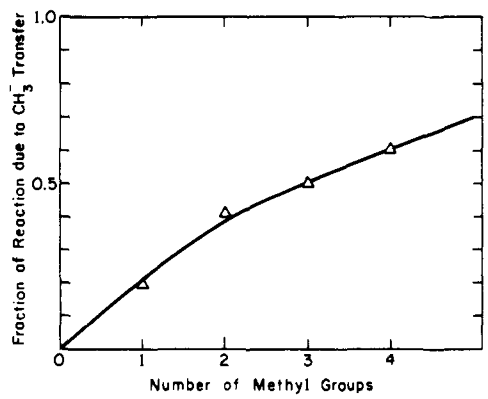
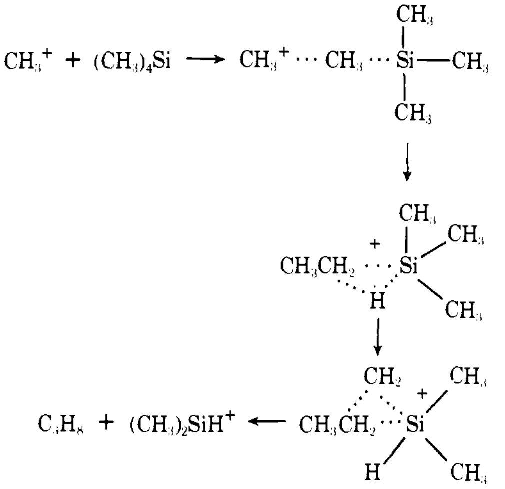


Figure 6. Fraction of methide ion transfer as a function of the number of methyl groups in the silane.

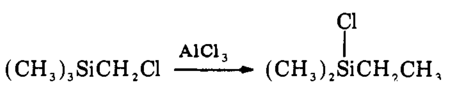
The replacement of CH_3^+ reactant ions by $^{13}CH_3^+$ and CD_3^+ results in almost undiscernible changes in the product ion mass spectra. Therefore, we must conclude that the exothermic product ions observed result from direct transfer reactions or from complexes involving nonequivalent methyl groups. Reactions 12 and 13 are easily pictured as direct transfers of a methide ion and an electron, respectively, and the resulting products, as demanded by the experimental facts, would not contain ^{13}C atoms or D atoms. Reaction 11 cannot, however, occur as the result of a dissociation of the product ions of reactions 12 and 13, because these overall processes would be endothermic. To be in accord with the experimental facts of exothermicity and no incorporation of ^{13}C atoms of D atoms when $^{13}CH_3^+$ and CD_3^+ are the reactant ions, we propose that reaction 11 occurs via the formation and decomposition of a complex involving nonequivalent methyl groups. This process, which is similar to (A) and (B) presented earlier, is shown as scheme C.[19]



(C)

E. Summary. As discussed for the individual collision pairs, the predominant reactions of CH_3^+ ions with methylsilanes are hydride abstraction and methide abstraction from the silane. The former reaction was expected to predominate in all systems investigated, on the basis of previous gas-phase studies and even of solution-phase results. The methide abstraction process, however, becomes the dominant reaction in the encounters of CH_3^+ with $(CH_3)_3SiH$ and $(CH_4)_4Si$ and is almost equally probable with hydride transfer in the case of the CH_3^+-$(CH_3)_2SiH_2$ system. Figure 6 shows a plot of the fraction of total reaction that is observed as methide transfer as a function of the number of Si-H bonds in the silane.

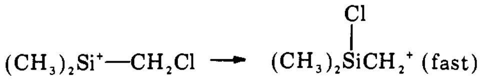
As in the case of hydride transfer, the ease of methide transfer is probably a result of the polarity of the carbon-silicon bond, which is usually taken as $^{\delta-}C$-$Si^{\delta+}$. The extent of methide transfer relative to hydride transfer is unexpected because of the disparity of sizes of the particles being transferred, yet the experimental facts clearly indicate the importance of the methide transfer. The consequences of such reactions do not appear to have been considered in discussions of organosilane reactions in solution.[7,8] It would seem possible that they play a role in the mechanisms of acid-catalyzed rearrangement reactions in silanes, such as[7,8,20-22] eq 20. Thus



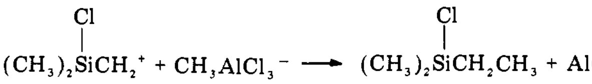
$$(CH_3)_3SiCH_2Cl \xrightarrow{AlCl_3} (CH_3)_2\overset{\displaystyle Cl}{\overset{|}{Si}}CH_2CH_3 \qquad (20)$$

with methide abstraction by the Lewis acid one could easily visualize the sequence of reactions shown by (21)-(23). Of

$$(CH_3)_3SiCH_2Cl + AlCl_3 \longrightarrow (CH_3)_2SiCH_2Cl^+ + CH_3AlCl_3^- \qquad (21)$$

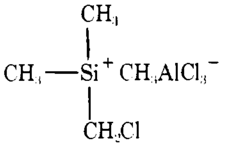


$$(CH_3)_2Si^+{-}CH_2Cl \longrightarrow (CH_3)_2\overset{\displaystyle Cl}{\overset{|}{Si}}CH_2^+ \text{ (fast)} \qquad (22)$$

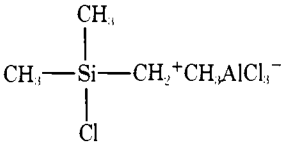


$$(CH_3)_2\overset{\displaystyle Cl}{\overset{|}{Si}}CH_2^+ + CH_3AlCl_3^- \longrightarrow (CH_3)_2\overset{\displaystyle Cl}{\overset{|}{Si}}CH_2CH_3 + AlCl_3 \qquad (23)$$

course, in solution free ions need not be present in (21)-(23) but rather only the ion pairs i and ii; however, the reaction may



i



ii

still be visualized as proceeding by methide ion abstraction. We do not claim that (21)-(23) is a more likely mechanism for (20) than the generally accepted one involving association of Cl^- with $AlCl_3$, but we do suggest that it is a reasonable possibility that warrants consideration. The failure to observe siliconium ions in the solution studies could then be attributed to the very fast migration of Cl^- to the positive silicon center.

The absence of significant changes in the product ion mass spectra when CH_3^+ is replaced by $^{13}CH_3^+$ and CD_3^+ leads us to conclude that in the gas phase, at least, the major reactions of CH_3^+ with $(CH_3)_{4-n}SiH_n$ (n = 0, 1, 2, 3, 4) do *not* proceed through pentavalent Si intermediate complexes. Instead, the reactions proceed mainly through either *direct* hydride and methide abstraction from the silane or via complexes involving nonequivalent methyl groups.

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