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Reactions of Methyl Cations with Ethylsilanes[1]

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Abstract: The gas-phase reactions of CH_3^+ with $(C_2H_5)_nSiH_{4-n}$ (n = 1, 2, 3, 4) 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^+. The major reactions are charge transfer, hydride ion transfer, and ethide ion ($C_2H_5^-$) transfer from the silane to CH_3^+. A rather surprising result is that, except for the case of $C_2H_5SiH_3$, ethide ion transfer is the predominant process. Isotopic labeling of the reactant ions shows only minor (<10%) incorporation of the label into the ionic products which is interpreted to mean that the major part of the reactions are either direct processes or proceed through complexes that do not involve pentavalent silicon.

Introduction

Recently[2] we reported the results of a study of the gas-phase reaction of CH_3^+ ions with the methylsilanes, $(CH_3)_nSiH_{4-n}$, when n = 1, 2, 3, 4. A very surprising feature of these results was the always important and sometimes dominant contribution to the total reaction by methide ion (CH_3^-) transfer from the silane to the attacking CH_3^+ ion. The cross sections for the methide ion transfer are comparable to those of the expected hydride ion transfer process in the case of $(CH_3)_2SiH_2$ and are larger than those for hydride ion transfer when $(CH_3)_3SiH$ and $(CH_3)_4Si$ are the targets of the reactant CH_3^+ ions. In order to investigate whether this unexpected alkyl anion abstraction from alkylsilanes might be a general reaction and not one limited to the methylsilanes, we have studied the reactions of gaseous CH_3^+ ions with the ethylsilanes, $(C_2H_5)_nSiH_{4-n}$, when n = 1, 2, 3, 4. This paper is a report of our findings.

Experimental Section

1. Apparatus and Techniques. The experiments were carried out in an ion-beam-target gas apparatus that has been described previously.[2] Briefly it consists of a modified plasma ion source (Colutron Corp.) for ion formation, a Wien velocity filter for reactant-ion selection, a collision chamber for reaction of the mass-selected ions with the target molecules, and a quadrupole mass filter for analysis of the ionic products. Electrostatic lenses are used to focus the ion beam into the Wien filter, to decelerate the reactant ions to energies in the range of 0.5-5 eV before they enter the collision chamber, and to focus the ionic products into the quadrupole mass filter for analysis.

We have examined further the question of internal energy in the CH_3^+ ions produced in the plasma source by measurement of the energy threshold for the known[2-4] endothermic reaction

$$CH_3^+ + (CH_3)_3SiH \rightarrow CH_3SiH^+ + CH_4 + C_2H_5 \qquad (1)$$

On the basis of available thermochemical data[3,4] the standard enthalpy change of (1) is $\Delta H°$ = 1.5 ± 0.3 eV. We find experimentally a threshold energy of 1.6 ± 0.2 eV in the center-of-mass system which is in excellent agreement with the thermochemical values for the endothermicity. This agreement strongly suggests that internal excitation energy in the CH_3^+ ions is at most 0.4 eV and is probably smaller.

Absolute cross sections for the reactions of CH_3^+ ions with the various ethylsilanes were determined at 1 eV laboratory energy by direct comparison with the process[5,6]

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

the cross section of which we have redetermined to be σ_2 (1 eV, lab) = 54 ± 2 Å^2. The measured cross sections were extrapolated to the limit of zero pressure in the collision chamber in order to eliminate the influence of further reactions of product ions. Pressures in the collision chamber were measured with a capacitance monometer and were varied from 0.5 to 2.0 × 10^{-3} Torr. We believe that the cross sections measured at 1 eV laboratory energy of CH_3^+ are accurate to within ±15%.

The form of dependence of relative cross section, i.e.

$$\sigma_{rel} = i_{product}/i_{CH_3^+}P$$

where the i's are currents and P is the pressure, on the kinetic energy of CH_3^+ was used to classify the reactions as exothermic or endothermic. The cross sections of endothermic reactions increase from zero at the energy threshold to a broad maximum, while the cross sections for exothermic processes usually decrease monotonically with increasing energy. All ion intensities were corrected for the naturally occurring isotopes of silicon and carbon, namely, ^{29}Si = 4.7%, ^{30}Si = 3.1%, and ^{13}C = 1.1%.

2. Materials. SiH_4 was purchased from the Matheson Co. while $(C_2H_5)_2SiH_2$, $(C_2H_5)_3SiH$, and $(C_2H_5)_4Si$ were purchased from Penninsular Chemresearch. $C_2H_5SiH_3$ was prepared by the reduction of $C_2H_5SiCl_3$ (Peninsular Chemresearch) with $LiAlH_4$ (Alfa Inorganics). CH_4, CD_3H, and $^{13}CH_4$, which were used in the ion source to produce the CH_3^+, CD_3^+, and $^{13}CH_3^+$ reactant ions, were obtained from Phillips Petroleum Co., Merck Sharp and Dohme, and Stohler Isotopes, respectively. All gases and liquids were subjected to freeze-pump-thaw cycles on a high-vacuum line prior to use.

Results and Discussion

1. Exothermic Reactions. The reactions of CH_3^+ ions with ethylsilanes are somewhat more complex but similar to the reactions of CH_3^+ with the methylsilanes.[2] Thus for $C_2H_5SiH_3$, $(C_2H_5)_2SiH_2$, and $(C_2H_5)_3SiH$, we find as major reactions (1) hydride ion transfer from the silane to the CH_3^+ ion; (2) ethide ion transfer from the silane to the CH_3^+ ion; (3) a more complex process in which the attacking CH_3^+ moiety is incorporated into the ionic product. As in the case of

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Table I. Major Reactions of CH_3^+ with Ethylsilanes at 1 eV (Laboratory)

reaction no.	reaction	$\Delta H°$, kcal	σ, Å^2	10^9k, cm^3/s
3	$CH_3^+ + C_2H_5SiH_3 \rightarrow C_2H_5SiH_3^+ + CH_3$		4.9	0.18
4	$CH_3^+ + C_2H_5SiH_3 \rightarrow C_2H_5SiH_2^+ + CH_4$		80	2.8
5	$CH_3^+ + C_2H_5SiH_3 \rightarrow CH_3SiH_2^+ + C_2H_6$	-57^a	11	0.39
6	$CH_3^+ + C_2H_5SiH_3 \rightarrow SiH_3^+ + C_3H_8$	-38^a	22	0.79
7	$CH_3^+ + (C_2H_5)_2SiH_2 \rightarrow (C_2H_5)_2SiH_2^+ + CH_3$	+1	42	1.5
8	$CH_3^+ + (C_2H_5)_2SiH_2 \rightarrow (C_2H_5)_2SiH^+ + CH_4$		22	0.79
9	$CH_3^+ + (C_2H_5)_2SiH_2 \rightarrow C_2H_5SiH_2^+ + C_3H_8$		87	3.1
10	$CH_3^+ (C_2H_5)_3SiH \rightarrow (C_2H_5)_3SiH^+ + CH_3$	−8	35	1.3
11	$CH_3^+ + (C_2H_5)_3SiH \rightarrow (C_2H_5)_3Si^+ + CH_4$	−90	3.9	0.14
12	$CH_3^+ + (C_2H_5)_3SiH \rightarrow (C_2H_5)_2SiH^+ + C_3H_8$		74	2.7
13	$CH_3^+ + (C_2H_5)_3SiH \rightarrow (C_2H_5)_2Si^+ + CH_4 + C_2H_5$	−7	14	0.50
14	$CH_3^+ + (C_2H_5)_3SiH \rightarrow C_2H_5SiH_2^+ + CH_4 + 2C_2H_4$		17	0.61
15	$CH_3^+ + (C_2H_5)_4Si \rightarrow (C_2H_5)_4Si^+ + CH_3$	−22	10	0.36
16	$CH_3^+ + (C_2H_5)_4Si \rightarrow (C_2H_5)_3Si^+ + C_3H_8$	−80	91	3.3
17	$CH_3^+ + (C_2H_5)_4Si \rightarrow (C_2H_5)_2SiH^+ + C_3H_8 + C_2H_4$		11	0.39

[a] Estimated using the bond energy scheme of Allen[7] with the data of Potzinger, Ritter, and Krause[3] to calculate $\Delta H_f°$ ($C_2H_5SiH_3$).

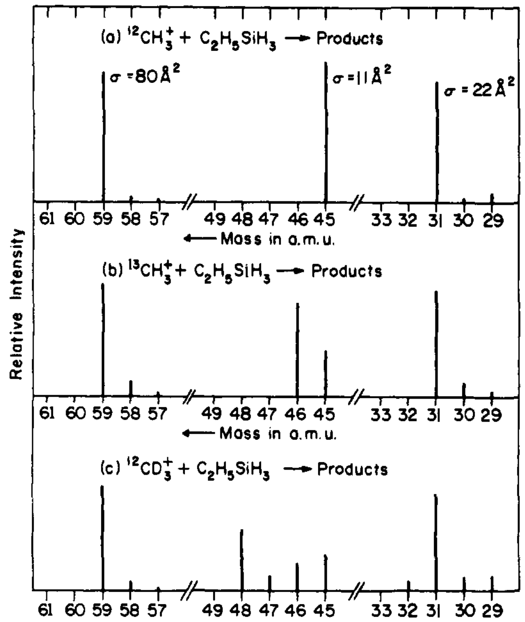


Figure 1. Effect of reactant ion labeling on the mass spectrum of the products of the CH_3^+-$C_2H_5SiH_3$ reaction: (a) $^{12}CH_3^+$; (b) $^{13}CH_3^+$; (c) $^{12}CD_3^+$.

$(CH_3)_4Si$, H^- transfer from $(C_2H_5)_4Si$ is not a significant process. Exothermic charge transfer reactions are observed for all of the ethylsilanes. This is in contrast with the observation for the methylsilanes and is undoubtedly a consequence of the fact that the ionization potentials of the ethylsilanes are lower than those of the corresponding methylsilanes by about 0.5 eV.[3]

The major reactions of CH_3^+ with ethylsilanes are shown in Table I. With the exception of reactions 3 and 11, all reactions in this table account for more than 7% of the total reaction and all were observed to be exothermic on the basis of the dependence of cross sections on CH_3^+ ion kinetic energy. Also shown in Table I are the standard enthalpy changes calculated from available thermochemical data,[3,4] the reaction cross sections for CH_3^+ ions with 1 eV of kinetic energy in the laboratory frame of reference, and phenomenological rate constants calculated from the cross sections and the ion velocity. As mentioned in a previous section, we believe that the cross sections are uncertain to ±15%.

In general, the enthalpy changes calculated from thermochemical data are in agreement with our conclusions as to the sign of $\Delta H°$ based on the dependence of cross section on ion kinetic energy. The exceptions are the charge transfers to $C_2H_5SiH_3$ and $(C_2H_5)_2SiH_2$, namely, reactions 3 and 7 in Table I. The uncertainty in the calculated value of $\Delta H°$ for (7) is at least 5 kcal/mol,[3,4] so that our observation that (7) is exothermic is not necessarily inconsistent with thermochemical data. Neither the ionization potential nor the standard enthalpy of formation of $C_2H_5SiH_3$ is available so that $\Delta H°$ for (3) could not be calculated. Nonetheless, the trend of $\Delta H°$ through the series of charge transfers in Table I and including charge transfer to SiH_4 suggests that (3) is endothermic by about 12 kcal/mol. The considerable uncertainty in this estimated value of $\Delta H°$ and the fact that CH_3^+ may contain up to 0.4 eV of internal energy may well account for the exothermic dependence of the cross section of (3) on reactant ion energy.

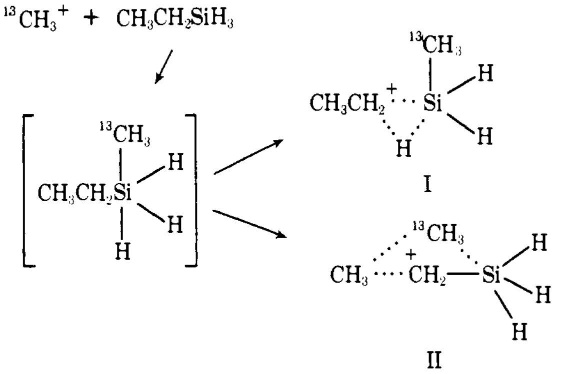
In the remainder of this section we discuss the details of the various processes shown in Table I.

a. $CH_3^+ + C_2H_5SiH_3$. Reactions 3-6, shown in Table I, are the predominant processes that occur when CH_3^+ ions with 1 eV of kinetic energy collide with $C_2H_5SiH_3$. Although $\Delta H_3°$ and $\Delta H_4°$ could not be calculated, owing to lack of thermochemical data on ions derived from $C_2H_5SiH_3$, analogy with the case of CH_3SiH_3 strongly suggests that (3) and (4) must be as written in order for them to be exothermic. It is possible that the product ion of (5) is $SiH_3CH_2^+$ and not $CH_3SiH_2^+$; however, experience in mass spectrometric studies of organosilicon compounds has indicated that the charge invariably resides on the Si atom. The neutral product(s) of (5) could just as well be $C_2H_4 + H_2$ without conflicting with the fact that the reaction is observed to be exothermic. Similarly the neutral product(s) of (6) may well be $C_3H_6 + H_2$ or $C_2H_4 + CH_4$.

As expected,[2] the principal elementary reaction is that of hydride ion transfer, namely, (4), to form the monoethylsiliconium ion. Analogous to the case of the CH_3^+-CH_3SiH_3 reaction,[2] the transfer of a $C_2H_5^-$ ion, as shown by (6), to form SiH_3^+ is also a major process. In addition, the transfer of methide ion, (5), which has no analogy in the reactions of methylsilanes with CH_3^+, occurs to a significant extent.

The effect of replacement of $^{12}CH_3^+$ by $^{13}CH_3^+$ and $^{12}CD_3^+$ on the product ion spectra of the CH_3^+-$C_2H_5SiH_3$ reaction is shown in Figure 1. There is no significant change in the product ion spectra in the mass 57-61 amu region, which suggests that charge transfer and hydride ion transfer occur mainly by direct processes[8,9] and do not involve a pentavalent Si intermediate complex. In writing (4) we have assumed that abstraction of the hydride ion by CH_3^+ always occurs at the silicon atom. We have shown[9,10] this to be true in the case of attack by $CH_3SiH_2^+$ and SiH_2^+ on CH_3SiD_3. The assumption that it is true also in the case of attack by CH_3^+ is supported by the fact that hydride transfer is not observed to be a significant process in the reactions of CH_3^+ with $(CH_3)_4Si$[2] or $(C_2H_5)_4Si$, namely, with silanes containing no Si-H bonds.

In the 45-48-amu region of the product ion spectra a significant change is observed when $^{12}CH_3^+$ is replaced by $^{13}CH_3^+$ and $^{12}CD_3^+$. With $^{13}CH_3^+$ reactant ions the product ion originally observed only at 45 amu is observed at 45 and 46 amu in an approximately 1:2 ratio. In the case of CD_3^+, product ions are observed in the range of 45-48 amu. The overall reaction involves the transfer of a methide ion from ethylsilane and these facts suggest that the reaction proceeds via an intermediate complex$[(C_2H_5)(CH_3)SiH_3]^+$ that gives rise to reactions via two transition states (I and II) as shown in (18) and (19) for $^{13}CH_3^+$. Dissociation of I along the reaction coordinate leads directly to the products $^{13}CH_3SiH_2^+$ and C_2H_6 while II dissociates along the reaction coordinate to $SiH_3CH_2^+$ and $^{13}CH_3CH_3$. It may be that the ion detected at 45 amu in the reaction of $^{13}CH_3^+$ is $SiH_3CH_2^+$, but we think that it is more likely that this ion rapidly rearranges to the more stable $CH_3SiH_2^+$. The relative intensities of products at 45 and 46 amu indicate that the formation of transition state I from the complex is twice as probable as that of transition state II.


(18)

(19)

I

II

In the case of $^{12}CD_3^+$ reactant ions the major product is observed at 48 amu with a relative intensity nearly twice as great as that of the ionic product at 45 amu. This result is in accord with the mechanistic conclusions drawn from the studies with $^{13}CH_3^+$, although some H-D scrambling in the complex leading to ionic products at 46 and 47 amu somewhat complicates the matter.

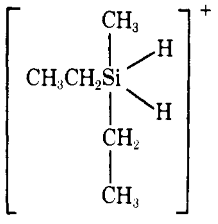
The formation of SiH_3^+ (31 amu) occurs via (6) (cf. Table I) and, of course, substitution of $^{13}CH_3^+$ for $^{12}CH_3^+$ effects no change in the intensity of this ionic product. The use of $^{12}CD_3^+$ as reactant produces a small but significant current of SiH_2D^+ (32 amu) ions as shown in Figure 1. This indicates that the reaction proceeds to a minor extent, at least, through some intermediate with sufficient lifetime to permit a small amount of H-D exchange. However, the small intensity at 32 amu suggests that by far the major part of the reaction occurs via a direct abstraction of $C_2H_5^-$ from the neutral molecule or via an intermediate complex of a form such that very little H-D exchange between carbon and silicon can occur. This would imply that the intermediate complex is not one involving pentavalent silicon.

The small intensities observed at 29 and 30 amu are due mainly to $C_2H_5^+$ ions, although SiH_2^+ may make a small contribution to the very low intensity at 30 amu.

b. $CH_3^+ + (C_2H_5)_2SiH_2$. As seen in Table I, there are three major reactions that take place when CH_3^+ ions with 1 eV of kinetic energy are injected in $(C_2H_5)_2SiH_2$, namely, charge transfer (7), H^- ion transfer (8), and $C_2H_5^-$ ion transfer (9). It is surprising that the $C_2H_5^-$ abstraction process is the most probable reaction, being observed to occur with a very large reaction cross section of 87 Å^2. As mentioned earlier the charge-transfer process is observed to be exothermic even though available enthalpies of formation[2,3] lead one to conclude that the process is slightly endothermic. Enthalpy changes for (8) and (9) could not be calculated because the enthalpies of formation of $(C_2H_5)_2SiH^+$ and $C_2H_5SiH_2^+$ have not been measured.

The effect of replacement of $^{12}CH_3^+$ reactant ions by $^{13}CH_3^+$ and $^{12}CD_3^+$ on the major product ion spectra is to be seen in Figure 2. There are no significant differences in the spectra obtained with $^{12}CH_3^+$ and $^{13}CH_3^+$ as reactant ions. With $^{12}CD_3^+$ reactant ions an increase in the relative intensity at 86 and 58 amu is observed, but we think that this is to be attributed to the fact that the CD_3^+ experiments, which were run some 8 months prior to the $^{12}CH_3^+$ and $^{12}CH_3^+$ experiments, involved somewhat higher kinetic energy ions. In any event very little change is observed in the pattern at 87-89 and 59-60 amu. The conclusion we draw from these results is that all three reactions, namely, (7)-(9), occur via a direct process or through a loose intermediate complex that does not involve pentavalent silicon that would result from a binding of the incoming ion to the silicon atom.

The formation of pentavalent silicon complexes to some extent, however, is indicated by the effect of labeling of the reactant ions on the product ion mass spectra of the minor products of the reaction, namely, $C_2H_5(CH_3)SiH^+$ or $(CH_3)_3Si^+$ at 73 amu, $CH_3SiH_2^+$ at 45 amu, and SiH_3^+ at 31 amu. The results show equal probabilities for retention and nonretention of the incoming CH_3^+ in the formation of $C_2H_5(CH_3)SiH^+$ and a 3:2 preference for retention of the reactant ion in the formation of $CH_3SiH_2^+$. Significant deuteration of SiH_3^+ occurs when CD_3^+ is the reactant ion. These facts are most easily explained by the assumption of a pentavalent silicon intermediate complex of the form i, but the amount of reaction that proceeds through such an intermediate is at most 8% of the total reaction.


i

c. $CH_3^+ + (C_2H_5)_3SiH$. When 1-eV CH_3^+ ions react with $(C_2H_5)_3SiH$ five major reactions occur as shown in Table I. As in the case of $(C_2H_5)_2SiH_2$, the predominant process is the abstraction of $C_2H_5^-$ from the neutral molecule (12). Charge transfer (10) also occurs with a large cross section. The amount of hydride transfer (11) appears from the cross section for formation of $(C_2H_5)_3Si^+$ to be very small, namely, about 4 Å^2. However, we note that $(C_2H_5)_2Si^+$ (86 amu) and $C_2H_5SiH_2^+$ (59 amu) are formed with reasonably large cross sections. We note also that the exothermicity of hydride transfer is very large (90 kcal/mol) and, as will be seen, the intensities of the product ions at 59 and 86 amu are not affected by substitution of $^{13}CH_3^+$ or $^{12}CD_3^+$ for $^{12}CH_3^+$. We suggest, therefore, that these product ions are formed by dissociation of energy-rich $(C_2H_5)_3Si^+$ ions produced initially by H^- transfer, as shown below. If (13) and (14) do indeed occur by

$$CH_3^+ + (C_2H_5)_3SiH$$

$$\longrightarrow CH_4 + (C_2H_5)Si^{+*} \qquad (11)$$

$$\longrightarrow (C_2H_5)_2Si^+ + C_2H_5 \qquad (13)$$

$$\longrightarrow C_2H_5SiH_2^+ + 2C_2H_4 \qquad (14)$$

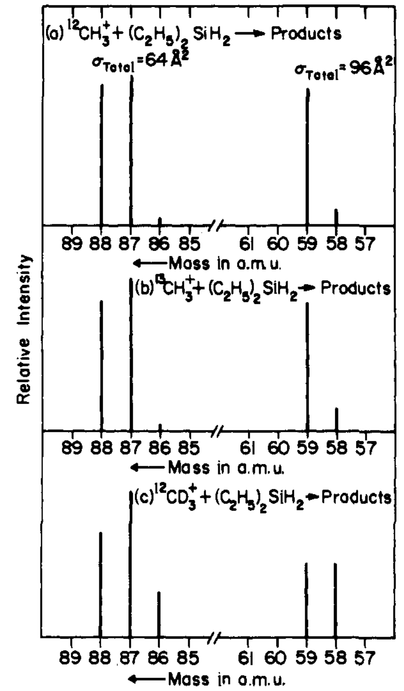


Figure 2. Effect of reactant ion labeling on the mass spectrum of the major products of the CH_3^+-$(C_2H_5)_2SiH_2$ reaction: (a) $^{12}CH_3^+$; (b) $^{13}CH_3^+$; (c) $^{12}CD_3^+$.

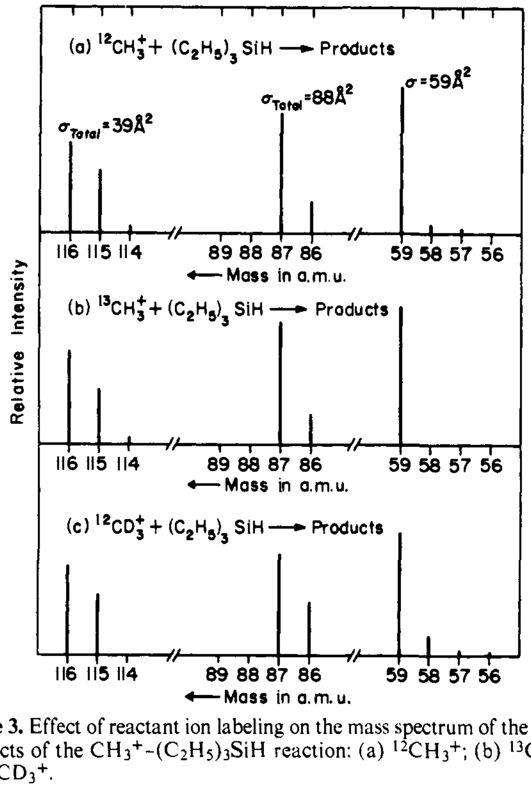


Figure 3. Effect of reactant ion labeling on the mass spectrum of the major products of the CH_3^+-$(C_2H_5)_3SiH$ reaction: (a) $^{12}CH_3^+$; (b) $^{13}CH_3^+$; (c) $^{12}CD_3^+$.

dissociation of internally excited $(C_2H_5)_3Si^+$, then the cross section for H^- transfer could be as high as 35 Å^2. This is still only about ½ of the cross section for the $C_2H_5^-$ transfer reaction.

Figure 3 shows the effect of reactant ion labeling on the major product ion mass spectra. No significant effect is to be seen on the product ion mass spectra of any of the major reactions of CH_3^+ with $(C_2H_5)_3SiH$. This is not a surprising result in the charge transfer (10) or H^- transfer (11) processes in which small particles are removed from the neutral molecule. It is surprising, in the case of transfer of a particle like $C_2H_5^-$ (12) from the $(C_2H_5)_3SiH$; however, it is consistent with the results found for the reactions of CH_3^+ with $C_2H_5SiH_3$ and $(C_2H_5)_2SiH_2$, as well as with our earlier findings of CH_3^- transfer in the reactions of CH_3^+ with the methylsilanes. The results suggest that all of these reactions proceed via a direct reaction or through an intermediate complex in which the incoming CH_3^+ ion is not bound to silicon.

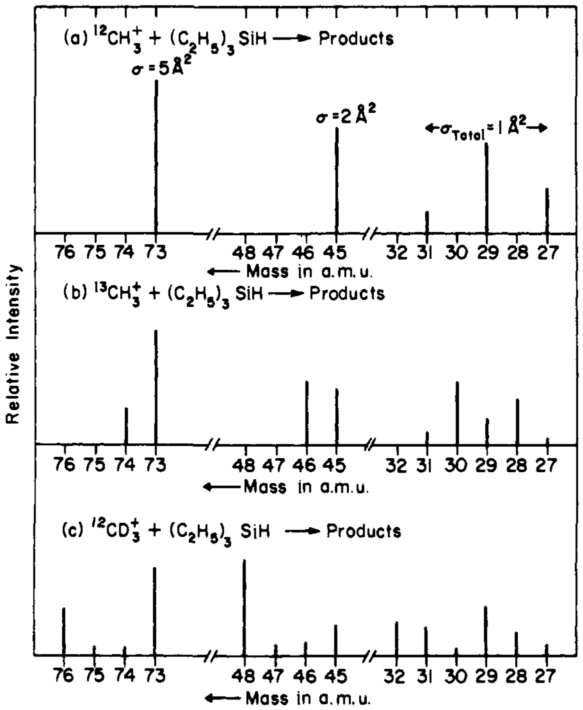


Figure 4. Effect of reactant ion labeling on the mass spectrum of the minor products of the CH_3^+-$(C_2H_5)_3SiH$ reaction: (a) $^{12}CH_3^+$; (b) $^{12}CH_3^+$; (c) $^{12}CD_3^+$.

The formation of $(C_2H_5)_2Si^+$ (86 amu) and $C_2H_5SiH_2^+$ (59 amu) would involve considerable atomic rearrangements if they were to proceed through an intermediate complex and one would expect in such a case that some retention of the ^{13}C or D labels would appear in the ionic product. The absence of such retention leads us to conclude that the most likely mechanism for the formation of these ions is ionic dissociation following direct H^- ion transfer.

A part of the total reaction most probably does proceed via a pentavalent silicon complex as may be seen from the effect of reactant ion labeling on the mass spectra of the minor products $C_2H_5(CH_3)SiH^+$ (73 amu), CH_3SiH_2 (45 amu), and SiH_3^+ (31 amu) as shown in Figure 4. Thus the product ion $C_2H_5(CH_3)SiH^+$ appears at 73 and 74 amu when $^{13}CH_3^+$ is the reactant ion and principally at 73 and 76 amu when $^{12}CD_3^+$ is the reactant ion. The product $CH_3SiH_2^+$ appears at both 45 and 46 amu with $^{13}CH_3^+$ and mostly at 45 and 48 amu when $^{12}CD_3^+$ is the reactant ion. Only very small amounts of SiH_3^+ (31 amu) were formed and the mass is shifted to 31 and 32 amu equally when $^{12}CD_3^+$ is used as the reactant ion. All these facts suggest that an intermediate of the form ii is taking part in the reaction. However, the amount of reaction so proceeding is at

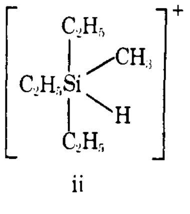


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Table II. Endothermic Reactions of CH_3^+ with Ethylsilanes at 1 eV (Laboratory)

reaction no.	reaction	$\Delta H°$, kcal	σ, Å^2
20	$CH_3^+ + C_2H_5SiH_3 \rightarrow C_2H_5SiH^+ + CH_3 + H_2$		0.6
21	$CH_3^+ + (C_2H_5)_4Si \rightarrow C_2H_5SiH^+ + C_4H_{10} + C_2H_4 + CH_3$		5.7
22	$CH_3^+ + (C_2H_5)_4Si \rightarrow CH_3SiH_2^+ + CH_3 + c\text{-}C_6H_{12} + CH_3$	+16	1.2
23	$CH_3^+ + (C_2H_5)_4Si \rightarrow SiH_3^+ + c\text{-}C_6H_{12} + C_2H_5 + CH_3$	+32	0.4
24	$CH_3^+ + (C_2H_5)_4Si \rightarrow C_2H_3^+ + (C_2H_5)_3SiCH_3 + H_2$	+25	0.4

most only 5% of the total reaction. The major part of the reaction is proceeding by direct reactions or via complexes in which the reactant ions do not bind to silicon.

d. CH_3^+ + $(C_2H_5)_4Si$. The major reactions of 1-eV CH_3^+ ions with $(C_2H_5)_4Si$ are seen in Table I to be charge transfer (15), $C_2H_5^-$ transfer (16), and a more complex rearrangement process (17) yielding $(C_2H_5)_2SiH^+$, with $C_2H_5^-$ transfer being by far the most probable. Hydride transfer is not observed as a significant process and this is consistent with our earlier findings[2] in the case of CH_3^+ ions reacting with $(CH_3)_4Si$.

Reactant ion labeling has no discernible effect on the major product ion mass spectra, suggesting that reactions 15-17 are direct or involve complexes in which the reactant ion is not bound to silicon. The absence of retention of the reactant ion label in (17) is most easily explained as a unimolecular dissociation of energy-rich $(C_2H_5)_3Si^+$ ions formed in the very exothermic $C_2H_5^-$ transfer (16).

Very little effect of reactant ion labeling on the minor products of the CH_3^+-$(C_2H_5)_4Si$ reaction was observed. This is in contrast with the other ethylsilanes and suggests that not only reaction 17 but the entire product ion spectra arises from breakdown of $(C_2H_5)_4Si^+$ and $(C_2H_5)_3Si^+$ formed with excess energy in the primary reactions of charge transfer and $C_2H_5^-$ transfer.

2. Endothermic Reactions. At 1-eV reactant ion energy only five endothermic reactions were observed and these are shown in Table II. The reactions are written with the neutral products chosen so as to represent the minimum endothermicity. Also shown in Table II are the cross sections at 1-eV energy in the laboratory system and, when possible, the standard enthalpy changes calculated from thermochemical data.

In view of the endothermic nature of these reactions, which requires use of the relative kinetic energy of the reactants in order to occur, and the extensive atomic rearrangement involved, it is probable that reactions 20-24 proceed through long-lived intermediate complexes. The cross sections, however, are so small that little useful information could be obtained by reactant ion labeling.

3. Conclusions. The predominant reactions of CH_3^+ with ethylsilanes are charge transfer, hydride ion transfer, and ethide ($C_2H_5^-$) ion transfer. Rather surprisingly, the ethide ion abstraction by CH_3^+ is the dominant process in all of the ethylsilanes except $C_2H_5SiH_3$, in which case hydride ion abstraction is the major process. Hydride transfer is not a significant process in these systems when Si-H bonds are absent.

The absence of significant changes in the major product ion mass spectra when $^{12}CH_3^+$ is replaced with $^{13}CH_3^+$ or $^{12}CD_3^+$ leads to the conclusion that in the gas phase the major reactions of CH_3^+ with $(C_2H_5)_nSiH_{4-n}$ ($n = 1, 2, 3, 4$) do *not* proceed via pentavalent Si intermediate complexes. Instead the reactions occur mainly as direct processes[8] or by way of intermediate complexes in which the reactant ion is not bound to silicon.

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