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Ion-Molecule Reactions in Methylsilane¹

by

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Abstract

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Positive ion-molecule reactions in methylsilane have been investigated by tandem and high pressure mass spectrometry. Reaction identification and rate constants for exothermic bimolecular reactions of all primary ions have been obtained for reactant ion energies of 1.0 eV in the center of mass system. A number of endothermic reactions have been observed. The dominant mode of reaction is that involving the transfer of an H⁻ species, giving CH₃SiH₂⁺ product. It is concluded that, in general, the methyl group does not play an active role in the ionic chemistry of methylsilane, in that there appears to be no scrambling of H atoms bound to the carbon and silicon atoms, and in that H⁻ or H abstraction comes exclusively from the silicon end of the molecule. High pressure mass spectra, up to 0.3 torr, reveal a number of termolecular association reactions, the rate constants of which have been measured.

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Introduction

Following the rather extensive study of the ion-molecule chemistry of hydrocarbons in the past decade,² hydrides of Group IV elements other than carbon have attracted interest in recent years. To date, ion-molecule reactions in monosilane³⁻⁶, disilane,⁷ monogermane,⁸ and a few mixtures of monosilane and simple organic compounds⁹⁻¹² have received extensive study; simple alkylsilanes^{13,14} have received less extensive examination.

A previous study of positive ion-molecule reactions in methylsilane¹³ performed in this laboratory reported a number of reactions of the CH_3SiH^+ ion and their rate constants, along with considerable thermochemical information concerning the ions formed by electron impact on methylsilane. This study was carried out in a single source mass spectrometer and was limited to source pressures below 6×10^{-3} torr. Later studies of several ion-molecule reaction systems^{4,10,11,12} using ion-cyclotron resonance and high pressure and tandem mass spectrometry have shown that the low pressure, single source experiments may be quite incomplete in describing the ion-molecule chemistry of systems containing more than one or two possible reactant ions and neutral reactant molecules. In general the ion-molecule chemistry of the silanes has been much more complex than our earlier studies indicated. Accordingly we have undertaken further studies of the methylsilane system with the intention of presenting a complete picture of the ion-molecule chemistry of methylsilane. The effect of the addition of an alkyl group, and the similarities to the ion-molecule chemistry of monosilane are of interest to the general behavior of Group IV hydrides.

Experimental

The tandem mass spectrometer used in this study has been described previously.^{3,6} The apparatus permits injection of mass selected ions having kinetic energies variable down to about 1 eV, with energy spread of about 1 eV, into a collision chamber containing the neutral target gas. Products scattered into the forward direction are collected with an acceptance angle of $\sim 10^\circ$. The collision chamber pressure in all experiments was 1.0×10^{-3} torr, as measured with a CGS Barocel capacitance manometer. Collection efficiency of the analyzer was found to be mass dependent over the rather large range of masses involved in this study, and corrections were made for this in the calculation of relative cross sections and rate constants.

Measurements of ionic abundance as a function of source pressure were carried out in modified Nuclide Associates 12-90G sector field mass spectrometer which has been described previously.³ Pressures in the ion source were measured with a Granville-Phillips capacitance manometer which had been calibrated with a McLeod gauge. The calibration was checked by observing the pressure dependent formation of CH_5^+ in methane. The known specific reaction rate¹⁵ indicated that our pressure readings are accurate to within $\pm 10\%$. The ionizing electron energy was 100 eV, and all experiments were carried out with a repeller field of 6.25 V/cm, which lead to free drift ion exit energy of 1.9 eV. The temperature of the ion source was about 100°C in all experiments.

Methylsilane (CH_3SiH_3) obtained from the PCR Co., was fractionated on the vacuum line and checked mass spectrometrically for satisfactory purity. Methylsilane- d_3 , (CH_3SiD_3), was synthesized by the reduction of CH_3SiCl_3 , obtained from Alfa Inorganics, by LiAlD_4 in di-n-butyl ether solution.¹⁶ The product was purified in the same manner as

methylsilane.

All data were corrected for the presence of Si^{29} and Si^{30} isotopes and all data presented represent only ions containing the major Si^{28} isotope. No corrections for C^{13} isotopes were not made.

Results and Discussion

Electron impact ionization of methylsilane yields nine ions with abundances greater than 3%, all of which can be considered as possible reactant ions. The earlier studies of Potzinger and Lampe¹³ indicated that only the major CH_3SiH^+ ion, and to a small extent the minor SiH_2^+ ions were reactive in this system. All observed product ions were attributed to reactions of these two ions. We have found this to be an incomplete description of the ion-molecule chemistry of this system, and, indeed, all primary ions are found to react with methylsilane. The bimolecular reactions of various primary ions will be discussed in detail followed by an analysis of reactions occurring at elevated pressures in the single source instrument.

Tandem Mass Spectrometric Studies:

Reaction identification and the dependence of reaction cross section on ion energy in the range 0.5-5 eV C.M. were carried out in the tandem mass spectrometer. Heats of formation of many of the species involved are not known, but the shape of the cross section curves as a function of energy in general allows one to determine whether a reaction is exo- or endothermic.¹⁷ Exothermic bimolecular reactions observed for the various primary ions with methylsilane are listed in Table 1. Specific reaction rates for the reactions in Table I were obtained by measuring relative cross-sections for all reactions at 1.0 eV (C.M.) and comparing these to cross section obtained for reaction (36).

for which the specific reaction rate has been measured.³ The values obtained were checked relative to the formation rates of $(\text{CH}_3)_2\text{SiH}^+$ and $(\text{CH}_3)_2\text{Si}_2\text{H}_2^+$, represented by reactions (5) and (10), and to the total reaction rate of CH_3SiH^+ in the Nuclide mass spectrometer. Rate constants calculated by the two different methods were found to agree within experimental error. Although the collision energy obtaining in the Nuclide mass spectrometer is generally quite a bit lower than the 1.0 eV used in the tandem machine, phenomenological rate constants should be quite insensitive to ion-kinetic energy, as predicted by the polarization theory of ion-molecule reactions.² The good agreement between the two greatly different methods of measuring rate constants attests to the validity of this assumption and to the overall internal consistency of this work. Standard enthalpy changes were calculated using existing thermochemical information.^{18,19} The neutral products of all reactions have been written arbitrarily to yield products that give the greatest exothermicity, or require the least amount of rearrangement. In the last column of Table I are listed the results of Potzinger and Lampe¹³ for reactions observed in both studies. The agreement between this work and the earlier results is quite good. It is seen from the table that the earlier study, while giving reliable rate constants, was very incomplete with regard to reaction identification. Endothermic reactions observed in the range 0.5-5 eV are listed in Table II. Phenomenological rate constants cannot be calculated in the manner used for the exothermic reactions, because the polarization theory does not predict the behavior of cross sections of endothermic reaction. Relative cross sections at 1.0 eV (C.M.) collision energy are listed and may be compared with the relative cross-sections listed

in Table I.

a) $\text{CH}_3\text{SiH}_2^+$: This ion comprises about 24% the total ions produced by impact of 100 eV electrons on methylsilane. We write structure of the ion as such on the basis that the dissociation energy of Si-H bonds are generally lower than the corresponding C-H bonds.²⁰ In the mass spectrum of CH_3SiD_3 the peak at m/e 47, corresponding to $\text{CH}_3\text{SiD}_2^+$ is about ten times as large as the peak at m/e 48, corresponding to $\text{CH}_2\text{SiD}_3^+$, thus we conclude that $\text{CH}_3\text{SiH}_2^+$ is the most probable structure of this ion.

When $\text{CH}_3\text{SiH}_2^+$ is injected into methylsilane we observe two reactions to occur, namely reactions (1) and (2) shown in Table I. Reaction (1) involves the transfer of an H^- ion and yields products identical to the reactants. We were able to observe this reaction in the tandem mass spectrometer by using CH_3SiD_3 as the target gas. The corresponding reaction of the SiH_3^+ ion in monosilane has been shown⁶ to proceed predominantly via a direct H^- stripping type reaction. This same process in methylsilane should lead to products at m/e 47, $\text{CH}_3\text{SiD}_2^+$, and m/e 48, $\text{CH}_2\text{SiD}_3^+$ if the H^- is stripped from the silicon or carbon end of the molecule, respectively. We observe that the bulk of the product lies at m/e 47 with only a very small amount of m/e 48. The virtual absence of m/e 48 in the product spectrum indicates that the hydride which is transferred comes exclusively from the silicon end of the molecule. This fact is undoubtedly due to the hydridic nature of the Si-H bonds²⁰ and is consistent with the observation that H^- transfer is by far the dominant mode of reaction in other silane systems.

Reaction (2) was observed to occur with much smaller cross-section than the H^- transfer reaction. Potzinger and Lampe¹³ observed $(CH_3)_2Si_2H_3^+$ as a product ion but were unable to identify correctly its precursor, presumably because $CH_3SiH_2^+$ is also a product ion from other reactions, a fact which masked its reactivity in the low pressure single source instrument.

b) CH_3SiH^+ : Potzinger and Lampe observed this ion to be reactive in CH_3SiH_3 and our measurements are in good agreement with their's for reactions (3)-(10). This is the major primary ion in methylsilane, comprising about 34% of the 100 eV mass spectrum, and to a large extent its reactions characterize the overall ion-molecule chemistry of the system. Again the net hydride transfer reaction (3) proceeds with large cross section. In monosilane it was pointed out⁶ that the analogous reaction, (37),

proceeds through a variety of mechanisms, including H^- transfer, H atom transfer and an intermediate complex. The details of the dynamics of reaction (3) will be treated in a following paper, but it should be noted that again when CH_3SiD_3 is used as a target gas, only trace amounts of $CH_2SiD_3^+$ are observed, indicating that the hydrogens bound to the carbon atom are not involved in the reaction.

In the case of reactions (4) and (5) there is some ambiguity about the identity of the products. An m/e value of 58 can be assigned to either $(CH_3)_2Si^+$ or $Si_2H_2^+$ and m/e 59 can be either $(CH_3)_2SiH^+$ or $Si_2H_3^+$. As noted by Potzinger and Lampe¹³, however, reactions leading to $Si_2H_2^+$ and $Si_2H_3^+$ have enthalpy changes of -1 and +7 kcal respectively, while reactions (4) and (5) as written are highly

exothermic. Furthermore, when CH_3SiD_3 is used as target gas no ion above m/e 60 is observed, where if Si_2H_3^+ were formed, products at $m/e = 61$ and 62 (Si_2HD_2^+ and Si_2D_3^+) would be expected. The large rate constant for reaction (5), probably reflecting the high stability of the $(\text{CH}_3)_2\text{SiH}^+$ ion, is interesting and somewhat suggestive of a direct mechanism for this reaction. It can be seen in Tables I and II that reaction proceeding presumably through a direct mechanism, namely H^- transfer or H atom transfer reactions, generally have rate constants between 5 and 10 times larger than reactions involving a complex formation. The magnitude of the rate of reaction (5) suggests that this may proceed through a direct CH_3 group transfer. Isotopic distribution of the product ions obtained when CH_3SiD_3 is used as a target gas support this conjecture. If, indeed, the hydrogens attached to the carbon are not reactive and reaction 5 proceeds through a randomized complex, then products should be observed at masses 59, $(\text{CH}_3)_2\text{SiH}^+$, and 60 $(\text{CH}_3)_2\text{SiD}^+$, in the ratio 1:3 respectively. Fig. 1 shows the observed isotopic products as a function of collision energy. The fact that the product containing hydrogen, $(\text{CH}_3)_2\text{SiH}$ is by far the most abundant in the energy range 1.5 + 5.2 eV, suggests that this reaction involves a more or less direct transfer of CH_3 from the target to the projectile ion. The inversion of product contributions at low energies, is likely due to transition to a mechanism more complex in nature. This type of complex to direct mechanism transition has been observed fairly often in ion-molecule reactions.^{21,22}

Reactions (6)-(8) are observed to be exothermic reactions that presumably proceed through a complex type of mechanism. The neutral products of these reactions are written rather arbitrarily, as either the ones giving greatest exothermicity or requiring the least

rearrangement of atoms. The cross sections for reactions (6)-(8) exhibit unusual behavior as shown in Fig. 2. The initial decrease in cross section at low energies is normal behavior for exothermic reactions, however, particularly for reactions (6) and (8) the cross section goes through a minimum at about 1 eV C.M. energy and then rises to a broad maximum at about 2.2-2.5 eV. This type of behavior is usually indicative of the onset of an endothermic channel for the production involved. We suspect that this behavior is due to the dissociation of neutral products. The neutral products of reaction (6) have been written as $\text{CH}_3^+ 2\text{H}_2$ but, energetically $\text{CH}_4 + \text{H}_2 + \text{H}$ are just as plausible. The dissociation of whatever set neutral molecular products are involved, e.g.

may account for the rise in the cross section of reaction (6). Both processes require about 4 eV energy. Since the heat of formation of CH_3Si_2^+ is not known we cannot predict a threshold for these processes, but in any case, the apparent threshold of about 1 eV, evident from Fig. 2(a) is almost surely too low. Lack of further information concerning possible internal excitation of the reactant ion, and of the energetics of the species involved, preclude further speculation about this reaction. Similar considerations obtain for the behavior with energy of the cross-section of reaction (8). Reaction (7) exhibits more typical exothermic behavior as shown in Fig. 2b. The slight leveling off of cross section at about 1.5 eV may be indicative of some alternative process taking place, but we haven't enough information to speculate further.

Reactions (9) and (10) are observed as exothermic reactions most probably involving the liberation of hydrogen molecules as neutral products. Measured rate constants for these reactions are in reasonably good agreement with those reported by Potzinger and Lampe. These reactions appear to be analogous to those of the SiH_2^+ ion reported in monosilane,^(3,4) namely (40) and (41),

the products of which are the major 2 silicon atom products of reaction of SiH_2^+ . It is of interest here to observe the effect of addition of an alkyl group to the molecule. If the methyl group plays an active role in the chemistry of methylsilane, then one would expect that there would be scrambling of the H atoms bond to the carbon and silicon atoms and that H atoms from both should appear among the neutral fragments. The extent of methyl group participation in reactions (9) and (10) can be determined from isotopic labeling of the methylsilane. Tables III and IV give the expected isotopic distribution of product ions of reactions (9) and (10) using CH_3SiD_2 as target gas, assuming, first, that the methylgroups are intimately involved in the complex, that hydrogen atoms are completely scrambled and that dissociation of the complex is completely statistical; and secondly, that the methyl groups are not involved in the chemistry of the complex and the liberated hydrogen comes exclusively from the silicon atoms. The observed isotope distribution for reaction (9), shown in Table III is in excellent agreement with the second prediction, while the distribution for reaction (10), shown in Table IV while not as clear, is considerably closer to the second prediction. These observations, together with those for reactions (1) and (3) offer

convincing evidence that the methyl group acts as a more or less inert unit and does not play a major role in the chemistry of the system. The reactions involving a complex, namely (6)-(10) then appear as the general type reaction

where X is either CH_3 or H and $y+2z+\omega = 6$. Considered in this fashion, the reactions of the CH_3SiH^+ ion in methyl silane are very similar to those of SiH_2^+ in monosilane.

c) CH_3Si^+ , CH_2Si^+ , CHSi^+ : These ions are all relatively minor primary ions comprising 11.2, 5.5 and 3.0%, respectively, of the primary mass spectrum. Reactions of these ions observed to be exothermic are listed in Table I. While the cross section of (11), exhibits exothermic behavior, we calculate from existing thermochemical data it to be endothermic by 30 kcal. This contradiction is perhaps due to internal excitation of the CH_3Si^+ primary ion. The large rate constant is indicative of a direct mechanism which could be either H atom or H_2^- transfer. The reactions of CH_2Si^+ and CHSi^+ are of relatively minor importance and will not be treated in detail, however, it is significant to note that the two endothermic reactions of CHSi^+ , namely (30) and (31), proceed with rather large cross sections at 1.0 eV. Based on previous observations we suspect that these are direct H atom and H^- transfer reactions, and even though they exhibit clearly endothermic behavior, the direct nature of the reaction results in a large cross section.

d) SiH_3^+ , SiH_2^+ , SiH^+ , Si^+ : The reactions of these minor ions are listed in Tables I and II as reactions (19)-(26), (32)-(35), and again are dominated by the reactions involving transfer of H^- or H_2^- . Of

particular interest here are the reactions of the Si^+ ion. Reaction (25), an H^- transfer reaction, which from available thermochemical data we calculate to be endothermic by 10 kcal for ground state reactants, is observed to have a cross section that shows exothermic behavior in the low energy region, with a subsequent rise in cross-section beginning at about 1 eV, C.M. as shown in Fig. 3a. The shape of the cross section curve is indicative of superimposed exo- and endothermic processes. An extrapolation of the onset of the endothermic process is in good agreement with the calculated endothermicity of the reaction. The superimposed exothermic process giving a decreasing cross section at low energies is undoubtedly due to reactions of an electronically excited state of the Si^+ ion. The first excited state of the Si^+ ion ($3p^2 4p$) lies 5.4 eV above the ground state²³ and could easily supply the needed energy. Independent measurements in this laboratory⁽²⁴⁾ have indicated that as much as 25% of the Si^+ ions formed by 100 eV electron impact on monosilane are formed in electronically excited states. Assuming a similar situation obtaining in methylsilane, this could easily account for the observed exothermic behavior of reaction (25). Reaction (35) in Table II is calculated to be endothermic by 30 kcal/mole for ground state reactants. The cross section as a function of collision energy is shown in Fig. 2b, and displays typical endothermic behavior. Despite the endothermic shape of its dependence on energy, the cross section has a fairly high value even at the lowest energies we can measure. The fact that this reaction has an onset well below the calculated onset of 1.30 eV, in the center-of-mass system, is a further indication of internal excitation of the Si^+ ion. The magnitude of the cross section is indicative of a direct reaction.

High Pressure Studies:

Single-source mass-spectrometric studies of methylsilane are in general agreement with the tandem mass-spectrometric results with regard to the total reaction rates of the primary ions. However, the secondary ion spectra is so complex that unambiguous reaction assignments and calculation of rate constants from the single-source data can be made ^{for} only a few reactions. The principal advantage of the high-pressure mass spectra is the possibility of observing higher order reactions not observable in the tandem machine. The high-pressure studies are more likely to give a closer view of the overall ionic chemistry of the system in a situation where multiple collisions are possible, such as in gas-phase radiolysis situations. Thus in addition to the bimolecular processes observed in the tandem studies we have observed a great number of tertiary and higher order product ions.

The percentage ion abundances of the major primary ions; $\text{CH}_3\text{SiH}_2^+$, CH_3SiH^+ , CH_3Si^+ , are shown in Fig. 4 as a function of source pressure. The CH_3SiH^+ ion, the major reactant ion observed by Potzinger and Lampe,¹³ and by us in the present tandem studies, is seen to react very rapidly. The decay rate constant measured from the initial slope of the decay of CH_3SiH^+ is calculated to be $20.0 (\pm 3) \times 10^{-10} \text{ cm}^3/\text{sec}$, in good agreement with the total rate constant for reaction of CH_3SiH^+ in Table I, and also with that of Potzinger and Lampe. The $\text{CH}_3\text{SiH}_2^+$ and CH_3Si^+ show an initial rise in abundance indicating that they are formed as products, consistent with reactions (3), (15)-(18), (19), (20), (23), (25), (33). Above about 0.01 torr their decreasing abundance indicates further reactions of these ions.

Reactions leading to formation of $\text{CH}_3\text{SiH}_2^+$ from Table I indicate

that $\text{CH}_3\text{SiH}_2^+$ should reach a maximum abundance of between 45-50% of the total ions present. As seen in Fig. 3, however, the $\text{CH}_3\text{SiH}_2^+$ abundance peaks at about 0.01 torr with a value of 40%. Further reactions of this ion prevent it from reaching its peak abundance. The only bimolecular reaction observed in the tandem machine that depletes $\text{CH}_3\text{SiH}_2^+$ is reaction (2). As shown in Fig. 5 this product, $(\text{CH}_3)_2\text{Si}_2\text{H}_3^+$ rises rapidly and reaches a maximum of about 10%. This is clearly not sufficient to explain the total depletion of $\text{CH}_3\text{SiH}_2^+$. Similar to the situation for SiH_3^+ in monosilane,³ we conclude that $\text{CH}_3\text{SiH}_2^+$ undergoes a third-order reaction leading to the ion at mass 91, $(\text{CH}_3)_2\text{Si}_2\text{H}_5^+$, which is the major product ion in the spectrum, viz.

The $(\text{CH}_3)_2\text{Si}_2\text{H}_5^+$ ion, shown in Fig. 5, is seen to have a pressure dependence consistent with a third order formation process; it reaches a maximum abundance of about 40% and appears to be unreactive toward CH_3SiH_3 up to 0.25 torr. It can be seen from the abundances of $\text{CH}_3\text{SiH}_2^+$, $(\text{CH}_3)_2\text{Si}_2\text{H}_3^+$, and $(\text{CH}_3)_2\text{Si}_2\text{H}_5^+$ that in the region of 0.01 - 0.04 torr, where further reactions are negligible, that the sum of the abundances of these three ions is constant, satisfying the stoichiometric requirements of the proposed reaction scheme.

The total rate equation for $\text{CH}_3\text{SiH}_2^+$ formation and reaction can be written as

$$\frac{dX_{\text{CH}_3\text{SiH}_2^+}}{dt} = \sum_i k_i X_i [\text{M}] - k_2 X_{\text{CH}_3\text{SiH}_2^+} [\text{M}] - k_{43} X_{\text{CH}_3\text{SiH}_2^+} [\text{M}]^2 \quad (44)$$

where X is the % abundance of the various ions, [M] is the number density of methylsilane. Above about 0.01 torr the processes leading to formation of $\text{CH}_3\text{SiH}_2^+$, indicated by the first term in equation (44)

can be ignored, as the abundances of the primary ions, X_i , have been nearly totally depleted. Then the equation becomes,

$$-\frac{dX_{\text{CH}_3\text{SiH}_2^+}}{dt} = k_2 X_{\text{CH}_3\text{SiH}_2^+} [M] + k_{43} X_{\text{CH}_3\text{SiH}_2^+} [M]^2 \quad (45)$$

and with simple integration:

$$\ln X_{\text{CH}_3\text{SiH}_2^+}^0 - \ln X_{\text{CH}_3\text{SiH}_2^+} = [k_2 [M] + k_{43} [M]^2] \tau \quad (46)$$

where $X_{\text{CH}_3\text{SiH}_2^+}^0$ is the maximum abundance of $\text{CH}_3\text{SiH}_2^+$ and τ is the residence time in the ion source. A plot of $1/[M] \ln X^0/X$ vs $[M]$ should then be linear in pressure regions where $\text{CH}_3\text{SiH}_2^+$ is no longer formed and permit calculation of k_{43} . Figure 7 shows this plot and the rate constant calculated from this treatment is given in Table V. The residence time used in the calculation is the residence time of the free drift on the $\text{CH}_3\text{SiH}_2^+$ in the repeller field. This quantity is expected to be quite uncertain. At pressures below 0.05 torr it is expected that diffusion effects will not lengthen the residence time a great deal, but the path length of the ion in the source is not well known. Since $\text{CH}_3\text{SiH}_2^+$ is formed as a product ion, the assumption that the path length is the distance between the electron beam and the exit slit is not valid. However, the uncertainties in path length and diffusion effects tend to offset one another. As a result we feel the residence time is uncertain to at least 50% leading to a large uncertainty assigned to k_{43} .

The third order formation of $(\text{CH}_3)_2\text{Si}_2\text{H}_5^+$ can be viewed as the collisional stabilization of an energetic complex formed by the association of $\text{CH}_3\text{SiH}_2^+$ and CH_3SiH_3 , and thus the overall process of

reaction of $\text{CH}_3\text{SiH}_2^+$ may be described by:

Assuming this mechanism we can then write the rate constants for reactions (2) and (43) as

$$k_2 = \frac{k_a k_d}{k_{-a} + k_a + k_s [\text{M}]} = 0.3 \times 10^{-10} \text{ cm}^3/\text{mole-sec} \quad (50)$$

$$k_{43} = \frac{k_a k_s}{k_{-a} + k_d + k_s [\text{M}]} = 5.2 \times 10^{-25} \text{ cm}^6/\text{molecule-sec} \quad (51)$$

Thus the ratio k_s/k_a can be gotten from k_{43}/k_2 , or

$$\frac{k_{43}}{k_2} = \frac{k_s}{k_d} = 17.3 \times 10^{-15} \text{ cm}^3/\text{molecule} \quad (52)$$

The same ratio can be obtained from a plot of $X_{(\text{CH}_3)_2\text{Si}_2\text{H}_5^+} / X_{(\text{CH}_3)_2\text{Si}_2\text{H}_3^+}$ vs $[\text{M}]$ from the pressure data. The slope of this line gives directly the ratio k_s/k_d . The value derived from this plot is $4.0 \times 10^{-15} \text{ cm}^3/\text{molecule}$. The agreement is satisfactory considering the large error limits on k_{43} and the fact that k_2 was obtained in a completely different apparatus. We may estimate the mean lifetime of the complex involved in the collisional stabilization model, represented by $1/k_{-a} + k_d$. If we assume k_a and k_s to be of the order of magnitude of the polarization theory rate constant,¹ namely $\sim 1 \times 10^{-9} \text{ cm}^3/\text{molecule-sec}$, then from equation (51)

$$\tau^* \approx \frac{1}{k_{-a} + k_d} = \frac{k_{43}}{k_a k_s} \approx 5 \times 10^{-7} \text{ sec} \quad (53)$$

The magnitude of the rate constants k_2 , k_{43} demand that $k_{-a} \gg k_d$ so that the mean lifetime of the complex with respect to decomposition to original reactants is of the order of 5×10^{-7} sec. This time is a great deal longer than the few rotational periods usually assumed to be necessary to obtain randomization of energy within the complex.²² We can thus conclude that this and similar reactions in methylsilane proceed through a randomized complex mechanism. The lifetime of the complex is short enough to preclude its observation in the tandem mass spectrometer, where multiple collisions are quite infrequent, and indeed it was not observed.

Other condensation reactions similar to reaction (43) are observed at elevated pressures in methylsilane. From stoichiometric considerations alone it can be inferred that the two additional condensation-type reactions (54) and (55), take place.

The abundances of these ions are shown in Figs. 5, 6. Similar treatment as that performed on reaction (43), shown in Fig. 7 yields third order rate constants for these two reactions that are listed in Table V. The residence times were taken to be the free drift residence times of the $(\text{CH}_3)_2\text{SiH}^+$ and $(\text{CH}_3)_2\text{Si}_2\text{H}_3^+$ ions. Again these are unlikely to be very accurate, but for lack of information concerning the mobility of these ions in the gas and unspecified path length, a better estimate cannot be made.

In the case of reaction (54), it can be shown from the ion abundance curve in Fig. 4 that above 0.03 torr the disappearance of $(\text{CH}_3)_2\text{SiH}^+$ is clearly due to a bimolecular process, while the formation of $(\text{CH}_3)_3\text{Si}_2\text{H}_4^+$ is clearly due to a termolecular process. This indicates to us that $(\text{CH}_3)_2\text{Si}_2\text{H}_8^+$ is being depleted, in addition to reaction (54), by a bimolecular reaction which is not immediately evident in the spectra. In view of the fact that all other mono-silicon ions readily undergo a hydride transfer reaction with methylsilane, it is tempting to postulate that the bimolecular process depleting $(\text{CH}_3)_2\text{SiH}^+$ is the H^- transfer reaction (56). However, the most recent thermochemical data¹⁹ indicate (56) to be endothermic

by 16 kcal. At present we simply do not know the identity of the other product(s) of this bimolecular depletion of $(\text{CH}_3)_2\text{SiH}^+$.

It should be noted that the third order rate constants for $\text{CH}_3\text{SiH}_2^+$ and $(\text{CH}_3)_2\text{SiH}^+$ are about an order of magnitude higher than those observed for similar reactions in monosilane³ and monogermane.⁸ The fact that the ratio k_s/k_d calculated for reaction 43 is nearly the same as that observed for the analogous reaction in monosilane leads us to the conclusion that k_{-a} , the rate of decomposition back to reactants is about an order of magnitude slower in reaction (43). This is undoubtedly due to the greater ability of the complex to distribute the internal excitation among its many degrees of internal freedom (42 for $(\text{CH}_3)_2\text{Si}_2\text{H}_5^+$ compared to 24 for Si_2H_7^+ and Ge_2H_7^+) thus giving the complex a longer lifetime.

As indicated in Figs. 5,6, the products of these condensation reactions appear to be unreactive up to 0.3 torr, as shown by their constant abundance with increasing pressure. These three ions account for 68% of the total ion current at 0.2 torr. At pressures up to 0.5 torr we have observed many smaller product ions ranging up to m/e 225, presumably containing at least 5 silicon atoms. Because of the complexity of the spectra it is impossible to extract a detailed reaction scheme, but the general appearance of the spectra seems to indicate an ionic polymerization chain, most probably proceeding through the general type of reactions:

Above about 0.3 torr the spectra became further obscured by reactions with residual water in the mass spectrometer, such that at 0.5 torr these water containing ions account for at least 46% of the total ions present. This tendency to react with even very small amounts of water in the mass spectrometer at high pressures has also been noted to occur in monosilane³⁷ and methane²⁵.

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References

1. U. S. Atomic Energy Commission Document No. C00-3416-15.
2. Recent reviews include: J. H. Futrell and T. O. Tiernan, "Fundamental Processes in Radiation Chemistry", P. Ausloos, Ed., Interscience Publishers, New York 1968; P. Ausloos, S. G. Lias, "Ion-Molecule Reactions", J. L. Franklin, Ed., Plenum Press, New York 1972.
3. T-Y. Yu, T. M. H. Cheng, V. Kempter, F. W. Lampe, J. Phys. Chem. 76, 3321 (1972).
4. J. M. S. Henis, G. W. Stewart, M. K. Tripodi, P. P. Gaspar, J. Chem. Phys. 57, 389 (1972).
5. J. M. S. Henis, G. W. Stewart, P. P. Gaspar, J. Chem. Phys. 58, 3639 (1973).
6. T. M. Mayer, F. W. Lampe, J. Phys. Chem. (Submitted).
7. T-Y. Yu, T. M. H. Cheng, F. W. Lampe, J. Phys. Chem. (In Press).
8. J. K. Northrup, F. W. Lampe, J. Phys. Chem. 77, 30 (1973).
9. D. P. Beggs, F. W. Lampe, J. Phys. Chem. 73, 4194 (1969); 73, 3307 (1969); 73, 3315 (1969).
10. T-Y. Yu, T. M. H. Cheng, F. W. Lampe, J. Phys. Chem. 77, 2587, (1973).
11. G. W. Stewart, J. M. S. Henis, P. P. Gaspar, J. Chem. Phys. 57, 1990 (1972); 57, 2247 (1972).
12. T. M. Mayer, F. W. Lampe, J. Phys. Chem. (Submitted).
13. P. Potzinger, F. W. Lampe, J. Phys. Chem. 74, 587 (1970).
14. P. Potzinger, F. W. Lampe, J. Phys. Chem. 75, 13 (1971).
15. M. J. Henchman, "Ion-Molecule Reactions", J. L. Franklin, Ed, Plenum Press, New York (1972).
16. E. A. Finholt, A. C. Bond, K. E. Wilzbach, H. I. Schlesinger, J. Amer. Chem. Soc. 69, 2692 (1947).
17. T. M. H. Cheng, F. W. Lampe, Chem. Phys. Lett. 19, 532 (1973).
18. J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Drexel, F. H. Field, Nat. Bur. Stand. Ref. Data Ser., Nat. Bur. Stand., No. 26, June, 1969.
19. P. Potzinger, F. W. Lampe, J. Phys. Chem. 73, 3912 (1969), 74, 719 (1970).

20. "Volatile Silicon Compounds", E. A. V. Ebsworth, Pergamon Press, London 1963, p. 16-17,
21. A. Henglein, International School of Physics, "Enrico Fermi", XLIV Course, Ch. Schlier, Ed. 1969.
22. Z. Herman, R. Wolfgang, "Ion Molecule Reactions", J. L. Franklin, Ed. Plenum Press, New York, 1972.
23. "Atomic Energy Levels", Vol. 1., C. E. Moore, Ed., USNBS Circular No. 467 (1949).
24. W. N. Allen, F. W. Lampe, unpublished results.
25. M. Vestal, private communication, 1973.

Figure Captions

- Figure 1: Isotopic distribution of products of reaction (5) using CH_3SiD_3 as target.
- Figure 2: Relative cross-sections as a function of collision energy: a) reaction (6); b) reaction (7); c) reaction (8).
- Figure 3: Relative cross-sections as a function of collision energy: a) reaction (25); b) reaction (35).
- Figure 4: Major primary ion abundances as a function of source pressure.
- Figure 5: Major product ion abundances as a function of source pressure.
- Figure 6: Major product ion abundances as a function of source pressure.
- Figure 7: Termolecular decay of (a) $\text{CH}_3\text{SiH}_2^+$; (b) $(\text{CH}_3)_2\text{SiH}^+$; (c) $(\text{CH}_3)_2\text{Si}_2\text{H}_3^+$.

Table I. Exothermic Bimolecular Reactions in CH_3SiH_3

Reaction No.	Reaction	Product m/e	ΔH° kcal/mole	σ^*	$k \times 10^{10} \text{ cm}^3/\text{sec}$ This Work	$k \times 10^{10} \text{ cm}^3/\text{sec}$ Ref. 13
1	$\text{CH}_3\text{SiH}_2^+ + \text{CH}_3\text{SiH}_3$					
	$\rightarrow \text{CH}_3\text{SiH}_2^+ + \text{CH}_3\text{SiH}_3$	45	0			
2	$\rightarrow (\text{CH}_3)_2\text{Si}_2\text{H}_3^+ + \text{H}_2$	89		1.14	.30 $\pm$.1	
	$\text{CH}_3\text{SiH}^+ + \text{CH}_3\text{SiH}_3$					
3	$\rightarrow \text{CH}_3\text{SiH}_2^+ + \text{CH}_3\text{SiH}_2$	45	-1	46	9.9 $\pm$ 2	6.4
4	$\rightarrow (\text{CH}_3)_2\text{Si}^+ + \text{SiH}_4$	58	-26	3.7	.74 $\pm$.2	0.44
5	$\rightarrow (\text{CH}_3)_2\text{SiH}^+ + \text{SiH}_3$	59	-26	40	8.6 $\pm$ 2	3.8
6	$\rightarrow \text{CH}_3\text{Si}_2^+ + \text{CH}_3 + 2\text{H}_2$	71		1.5	.33 $\pm$.1	0.42
7	$\rightarrow \text{CH}_3\text{Si}_2\text{H}_2^+ + \text{CH}_3 + \text{H}_2$	73		4.0	.90 $\pm$ 2	1.0
8	$\rightarrow \text{CH}_3\text{Si}_2\text{H}_3^+ + \text{CH}_4$	74		3.2	.70 $\pm$.4	0.46
9	$\rightarrow (\text{CH}_3)_2\text{Si}_2^+ + 2\text{H}_2$	86		4.8	1.1 $\pm$.3	0.46
10	$\rightarrow (\text{CH}_3)_2\text{Si}_2\text{H}_2^+ + \text{H}_2$	88		10.2	2.2 $\pm$.6	0.92
	$\rightarrow$ Total Product Production				24.5 $\pm$ 6	17.2

Table 1 Continued

Reaction No.	Reaction	Product m/e	ΔH° kcal/mole	σ^*	$k \times 10^{10} \text{ cm}^3/\text{sec}$ This Work	$k \times 10^{10} \text{ cm}^3/\text{sec}$ Ref.
11	$\text{CH}_3\text{Si}^+ + \text{CH}_3\text{SiH}_3$					
	$\rightarrow \text{CH}_3\text{SiH}^+ + \text{CH}_3\text{SiH}_2$	44	+30	54	10.8±3	
12	$\rightarrow \text{CH}_3\text{Si}_2\text{CH}_2^+ + 2\text{H}_2$	85		1.6	.32±.1	
13	$\rightarrow (\text{CH}_3)_2\text{Si}_2^+ + \text{H}_2 + \text{H}$	86		2.4	.51±.1	
14	$\rightarrow (\text{CH}_3)_2\text{Si}_2\text{H}^+ + \text{H}_2$	87		3.0	.64±.1	
15	$\rightarrow (\text{CH}_3)_2\text{Si}_2\text{H}_2^+ + \text{H}$	88		1.3	.28±.05	
16	$\text{CH}_2\text{Si}^+ + \text{CH}_3\text{SiH}_3$					
	$\rightarrow \text{CH}_3\text{Si}^+ + \text{CH}_3\text{SiH}_2$	43		2.7	.60±.2	
17	$\rightarrow \text{CH}_3\text{Si}_2\text{H}_2^+ + \text{CH}_3$	73		5.0	1.1±.2	
18	$\text{CHSi}^+ + \text{CH}_3\text{SiH}_3$					
	$\rightarrow \text{CH}_3\text{Si}^+ + \text{CH}_3\text{SiH}$	43		8.8	1.9±.3	
19	$\text{SiH}_3^+ + \text{CH}_3\text{SiH}_3$					
	$\rightarrow \text{CH}_3\text{SiH}_2^+ + \text{SiH}_4$	45	-11	17.5	3.6±.7	
20	$\text{SiH}_2^+ + \text{CH}_3\text{SiH}_3$					
	$\rightarrow \text{CH}_3\text{SiH}^+ + \text{SiH}_4$	44	-12	3.3	.84±.1	
21	$\rightarrow \text{CH}_3\text{SiH}_2^+ + \text{SiH}_3$	45	-11	26.5	6.9±1	

Table I Continued

Reaction No.	Reaction	Product m/e	ΔH° kcal/mole	σ^*	$k \times 10^{10} \text{ cm}^3/\text{sec}$ This Work	$k \times 10^{10} \text{ cm}^3/\text{sec}$ Ref.
22	$\rightarrow \text{CH}_3\text{Si}_2\text{H}_3^+ + \text{H}_2$	74		2.0	.52 $\pm$.2	
23	$\text{SiH}^+ + \text{CH}_3\text{SiH}_3$					
	$\rightarrow \text{CH}_3\text{Si}^+ + \text{SiH}_4$	43	-22	14	3.6 $\pm$.7	
24	$\rightarrow \text{CH}_3\text{Si}_2\text{H}_2^+ + \text{H}_2$	73		36	9.5 $\pm$ 2	
25	$\text{Si}^+ + \text{CH}_3\text{SiH}_3$					
	$\rightarrow \text{CH}_3\text{SiH}_2^+ + \text{SiH}$	45	+10	14	3.8 $\pm$.8	
26	$\rightarrow \text{CH}_3\text{Si}_2\text{H}^+ + \text{H}_2$	72		23		

* relative cross section at 1.0 eV (C.M.)

Table II. Endothermic Bimolecular Reactions in CH_3SiH_3

Reaction No.	Reaction	Product m/e	ΔH° kcal/mole	relative cross-section σ at 1.0 eV C.M.
28	$\text{CH}_2\text{Si}^+ + \text{CH}_3\text{SiH}_3 \rightarrow \text{CH}_3\text{SiH}^+ + \text{CH}_3\text{SiH}$	44		4.0
29	$\rightarrow \text{CH}_3\text{Si}_2^+ + \text{CH}_3 + \text{H}_2$	71		4.4
30	$\text{CHSi}^+ + \text{CH}_3\text{SiH}_3 \rightarrow \text{CH}_2\text{Si}^+ + \text{CH}_3\text{SiH}_2$	42		51
31	$\rightarrow \text{CH}_3\text{SiH}_2^+ + \text{CH}_2\text{Si}$	45		17.5
32	$\text{SiH}_2^+ + \text{CH}_3\text{SiH}_3 \rightarrow \text{CH}_3\text{Si}_2\text{H}^+ + 2\text{H}_2$	72		2.4
33	$\text{SiH}^+ + \text{CH}_3\text{SiH}_3 \rightarrow \text{CH}_3\text{SiH}_2^+ + \text{SiH}_2$	45	+17	32.5
34	$\rightarrow \text{CH}_3\text{Si}_2^+ + 2\text{H}_2$	71		18
35	$\text{Si}^+ + \text{CH}_3\text{SiH}_3 \rightarrow \text{CH}_3\text{Si}^+ + \text{SiH}_3$	43	+30	66.5

Table III. Isotopic Distributions for Reaction (9) Using CH_3SiD_3 as Target

<u>m/e</u>	<u>Product Ion</u>	<u>Observed Intensity</u>	<u>Predicted Intensity Based on Scrambling of all H and D Atoms</u>	<u>Predicted Intensity Based on Scrambling Only of H and D Atoms Bound to Si</u>
86	$\text{Si}_2\text{C}_2\text{H}_6^+$	100	.83	100
87	$\text{Si}_2\text{C}_2\text{H}_5\text{D}^+$	-	5	-
88	$\text{Si}_2\text{C}_2\text{H}_4\text{D}_2^+$	-	75	-
89	$\text{Si}_2\text{C}_2\text{H}_3\text{D}_3^+$	-	100	-

Table IV. Isotopic Distributions for Reaction (10) Using CH_3SiD_3 as Target

<u>m/e</u>	<u>Product Ion</u>	<u>Observed Intensity</u>	<u>Predicted Intensity Based on Scrambling of All H and D Atoms</u>	<u>Predicted Intensity Based on Scrambling Only of H and D Atoms Bound to Si.</u>
89	$\text{Si}_2\text{C}_2\text{H}_7\text{D}^+$	69	14	100
90	$\text{Si}_2\text{C}_2\text{H}_6\text{D}_2^+$	100	49	100
91	$\text{Si}_2\text{C}_2\text{H}_5\text{D}_3^+$	25	100	-

Table V. Third Order Reactions in Methylsilane

<u>No.</u>	<u>Reaction</u>	<u>$k \times 10^{25} (\text{cm}^6/\text{molec}^2\text{-sec})$</u>
34	$\text{CH}_3\text{SiH}_2^+ + \text{CH}_3\text{SiH}_3 \xrightarrow{\text{M}} (\text{CH}_3)_2\text{Si}_2\text{H}_5^+$	5.2 ± 4
45	$(\text{CH}_3)_2\text{SiH}^+ + \text{CH}_3\text{SiH}_3 \xrightarrow{\text{M}} (\text{CH}_3)_3\text{Si}_2\text{H}_4^+$	1.8 ± 1
46	$(\text{CH}_3)_2\text{Si}_2\text{H}_3^+ + \text{CH}_3\text{SiH}_3 \xrightarrow{\text{M}} (\text{CH}_3)_3\text{Si}_3\text{H}_6^+$	$.59 \pm .4$

Fig. 1

Fig. 2

Reaction Cross Section, Arbitrary Units

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7