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RADIATION CHEMISTRY AND MASS SPECTROMETRY
OF SILANES AND GERMANES

Progress Report

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Preface

Our continuing study of the radiation chemistry of silane and germane systems may as in the past be subdivided into three types of investigation as follows:

- A. Gamma-ray radiolyses of silanes and germanes and of mixtures of these substances with organic compounds, free radical scavengers and ion scavengers.
- B. Mass-spectrometric studies of the ionic reactions occurring when the systems in (A) are subjected to electron impact. This type of study affords an examination of the pure ionic reaction component of a radiolysis.
- C. Mass-spectrometric studies of the silyl and germyl radical reactions characteristic of gamma-ray radiolyses of the systems in (A) and free of the ionic component. Initiation of the reactions in this phase of the project is by photosensitization.

This annual progress report describes the work done from June 1, 1972 to May 31, 1972. In those cases where complete descriptions are contained in papers that have appeared in the scientific literature reference is made but only abstracts are presented herewith. The remainder of the report consists of descriptions of studies just now completed or currently in progress.

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ION-MOLECULE REACTIONS MONOGERMANE

J. K. Northrup and F. W. Lampe, J. Phys. Chem. 77, 30-35 (1973).

Abstract

Ion-molecule reactions occurring in ionized monogermane have been studied by high-pressure mass spectrometry at pressures up to 0.2 torr. The reactions found are as follows:

Rate constants for the reactions observed have been determined.

ION-MOLECULE REACTIONS IN MONOSILANE-METHANE MIXTURES

In a previous study² of ion-molecule reactions in monosilane-methane mixtures we reported the occurrence of a large number of reactions of SiH_2^+ with CH_4 and of CH_3^+ and CH_4^+ with SiH_4 in which product ions containing the Si-C bond were formed. This study was limited to ion-source pressures below 5 microns and reaction identification was made principally on the basis of the appearance potentials of the product ions. A subsequent study³ of the electron-impact ionization and dissociation of methylsilane showed that several of the ion-molecule reactions reported² were quite endothermic and, therefore, very improbable under the experimental conditions obtaining. Accordingly, we initiated a further investigation of the monosilane-methane system employing considerably higher ion-source pressures and tandem mass spectrometry. During the course of this investigation, an ion-cyclotron-resonance study by Stewart, Henis and Gaspar⁴ confirmed the incorrectness of some of the reaction identifications made in the previous report.² The results of our present investigation, reported herewith, are generally in agreement with those of the Stewart, Henis and Gaspar.⁴ In addition, we have observed a large number of reactions in the monosilane-methane system not reported by them.

EXPERIMENTAL

Measurements of the dependence of ionic abundances on ion-source pressure up to about 0.25 torr were carried out in a Nuclide Associates 12-90G sector-field mass spectrometer, an instrument which has been described previously.^{2,5-8} The energy of the ionizing

electron beam was 100 eV, the trap current was very small and not measured, and the ion-accelerating voltage was 2500V. In all experiments the repeller field was 6.25 V/cm leading to an ion-exit energy of 2.1 eV. The temperature of the ion-source was 70° in all experiments.

Ion-source pressures in the Nuclide mass spectrometer were measured by a McCleod gauge that was connected via 5/16 in. diameter tubing to the ion-source. The pressure-dependent formation of CH_5^+ , which occurs in $\text{CH}_4^+ - \text{CH}_4$ collisions with a known specific reaction rate,⁹⁻¹² indicated the pressure readings to be accurate to within $\pm 10\%$.

The tandem mass spectrometer, which consists of two quadrupole mass filters separated by a collision chamber and ion lenses, has been described previously.⁵ All experiments described in this work were carried out with the mass filters mounted in the in-line configuration. Relative reaction cross-sections were measured for reactant ion-energies in the range of 1-6 eV in the laboratory systems.

Monosilane was purchased from the J. T. Baker Chemical Co. and was also prepared in the laboratory by the action of lithium aluminum hydride on silicon tetrachloride in di-n-butylether solution. Research Grade methane, stated to have a purity of 99.54%, was obtained from the Phillips Petroleum Company. All gases were fractionated on a vacuum line and checked mass spectrometrically for satisfactory purity before use.

RESULTS AND DISCUSSION

1. Pressure-Variation Studies

The dependence on pressure of the intensities of the most abundant ions in a 10% SiH₄-90% CH₄ mixture is shown in Figures 1-5, while Figures 6-8 depict analogous data for a 12% CH₄-88% SiH₄ mixture. In all figures the ion-intensities are reported as per cent of total ionization and refer to the ²⁸Si isotope, the necessary corrections for the naturally occurring isotopes (²⁸Si-92.2%; ²⁹Si-4.7%; ³⁰Si-3.1%) having been made.

Inspection of Figures 1-8 indicates that the monosilane-methane system is a very complex one with regard to ion-molecule reactions. This complexity precludes, from pressure-variation studies alone, a complete elucidation of the reactions occurring and would appear to account for the failure of the earlier low-pressure investigation² to identify correctly all the processes. Nonetheless some general conclusions may be drawn from the behavior shown in Figures 1-8 which are of supplementary value to the specific reaction identification by tandem mass spectrometry, discussed in a later section.

A. Primary Ions

A comparison of the intensity-pressure behavior of the primary ions of methane (i.e. C⁺, CH⁺, CH₂⁺, CH₃⁺, and CH₄⁺) in the methane-rich mixture with that in the monosilane-rich mixture demonstrates that all primary ions of methane react with monosilane. Comparison in the two mixtures can be made for CH₄⁺ (m/e 16) by reference to Figures 2 and 7. The data for the other primary ions are not shown for the monosilane rich mixture, but their intensity-pressure

behavior is similar to that of the other primary ions. Figures 1 and 2 depict the behavior in the methane-rich mixture.

An analogous comparison of the pressure dependence of the intensity of SiH_2^+ (m/e 30) in the two mixtures (Figures 1 and 6) indicates that SiH_2^+ is formed by reactions of primary ions of methane with monosilane and confirms that it is consumed not only by known reactions with monosilane^{5,13,14} but also by reactions with methane.⁴ The large increase with pressure in the intensity of SiH_3^+ (m/e 31) to an abundance near 50% of the total ionization in the methane-rich mixture suggests that SiH_3^+ is probably the most significant product of reactions of methane primary ions with monosilane. Furthermore, the very magnitude of this increase in SiH_3^+ intensity indicates that the major secondary ions of methane namely CH_5^+ and/or C_2H_5^+ are also involved. In the methane-rich mixture (Figure 2) the abundance of SiH_3^+ falls off from the maximum, with increasing pressure, much more slowly than is the case in the monosilane-rich mixture (Figure 6), indicating that SiH_3^+ reacts much more slowly, with methane than with monosilane. The intensity-pressure behavior of SiH^+ (m/e 29) is completely obscured in the methane-rich mixture by formation of C_2H_5^+ (m/e 29) via the well-known reaction of CH_3^+ with methane.¹⁵ To a lesser, but still significant, extent the intensity of Si^+ (m/e 28) in the methane-rich mixture suffers from interferences from C_2H_4^+ (m/e 28), which is formed by reaction of CH_2^+ with methane.¹⁶

B. Secondary Ions of Methane

The formation of CH_5^+ via the well-known reaction of CH_4^+ with methane¹⁷ is shown in Figures 3 and 7. In the methane-rich mixture the abundance of CH_5^+ rises to a maximum of 22.5% of total

ionization at a source pressure of ~ 0.025 torr and then decreases with further increase in pressure. Since CH_5^+ is unreactive towards methane¹⁸ up to ion-source pressures of at least 2 torr and, in pure methane, attains an abundance-plateau of $\sim 48\%$, we interpret the maximum and subsequent decrease of CH_5^+ -abundance shown in Figure 3 as indicating that CH_5^+ undergoes reaction with monosilane. This is in agreement with the recent report of Stewart, Henis, and Gaspar.⁴ Very little formation of CH_5^+ , relative to the depletion of CH_4^+ , occurs in the monosilane-rich mixture, as may be seen in Figure 7. This can only mean, in agreement with our early report,² with the recent ion-cyclotron-resonance study⁴ and with our present conclusion based on the behavior of primary ions, that CH_4^+ reacts with monosilane.

C_2H_3^+ (m/e 27) is a minor secondary ion in ionized pure methane¹⁷ that reacts further with methane to produce C_3H_5^+ (m/e 41). Its intensity-pressure behavior (Figure 3) in the methane-rich mixture is identical to that in pure methane.¹⁸ In the monosilane-rich mixture the intensity of C_2H_3^+ was too low to be of significance. This is in accord with the observation in Section 1A that CH_2^+ (the precursor to C_2H_3^+) reacts with monosilane.

C_2H_4^+ (m/e 28) is also a minor secondary ion in ionized pure methane that arises from reaction of CH_2^+ with methane; it differs from C_2H_3^+ in that it is much less reactive with methane.¹⁷ Interpretation of the intensity-pressure behavior of m/e 28 in the methane-rich mixture (Figure 1) is complicated by interference with Si^+ , a primary ion of monosilane, and unfortunately neither the contributions of C_2H_4^+ and Si^+ to the intensity of m/e 28 are negligible above 0.01 torr. The fall-off of m/e 28 with increasing pressure above the intensity maximum, seen in Figure 1, is significantly

faster than is observed in pure methane,¹⁸ suggesting that $C_2H_4^+$ reacts with monosilane or Si^+ reacts with methane or both. In the monosilane-rich mixture the contribution of $C_2H_4^+$ to m/e 28 is negligible.

$C_2H_5^+$ (m/e 29) is a major secondary ion of methane. The similarity of the dependence of m/e 29 intensity on pressure in the methane-rich mixture, shown in Figure 2, to the analogous dependence for CH_5^+ (Figure 3) indicates that interferences at m/e 29 from SiH^+ are not serious. Comparison of Figures 2 and 3 shows that with increasing pressure the fall-off from the maximum of the $C_2H_5^+$ intensity is not as sharp as in the case of CH_5^+ . Since both ions are unreactive towards methane, this indicates that CH_5^+ reacts more rapidly with monosilane than does $C_2H_5^+$. The contribution of $C_2H_5^+$ (a secondary ion) to m/e 29 in the monosilane-rich mixture appears to be negligible, as would be expected since its primary-ion precursor, CH_3^+ , reacts with monosilane.

C. Secondary Ions of Monosilane

The pressure dependence of the intensities of $Si_2H_2^+$ (m/e 58), $Si_2H_3^+$ (m/e 59), $Si_2H_4^+$ (m/e 60) and $Si_2H_5^+$ (m/e 61) in the methane-rich mixture, shown in Figure 5, confirms our conclusion that the primary ions of methane are reacting with monosilane to produce SiH_2^+ and SiH_3^+ and, moreover, extends it to include Si^+ and SiH^+ . The initial upward curvature in the intensity-pressure plots of all these monosilane secondary ions indicates that the intensities of their precursors (namely all the primary monosilane ions) are initially increasing; this can be seen in Figures 1 and 2 for the cases of SiH_2^+ (m/e 30) and SiH_3^+ (m/e 31), respectively. Mass

interferences at m/e 28 and m/e 29 from secondary ions of methane preclude an analogous direct demonstration of the increases in intensity of Si^+ and SiH^+ . As may be seen in Figures 6-8, this upward curvature is not perceptible in the monosilane-rich mixture, with the exception of the formation curve for Si_2H_5^+ (m/e 61). This is as expected, since the primary ions of methane are present in very low abundance and do not produce any increases in the intensities of the precursor ions of Si_2H_2^+ , Si_2H_3^+ and Si_2H_4^+ , namely Si^+ , SiH^+ and SiH_2^+ , respectively.^{5,14} On the other hand, Si_2H_5^+ (m/e 61) is formed by reaction of SiH_3^+ (m/e 31) with monosilane^{5,14} and the intensity of this latter ion does increase initially in the monosilane-rich mixture (Figure 6) just as in pure monosilane.^{5,13,14} We may, therefore, state the general conclusion that all primary ions of monosilane (Si^+ , SiH^+ , SiH_2^+ and SiH_3^+) are formed by reaction of the primary ions and the secondary ions of methane with monosilane.

The behavior of m/e 61 warrants some additional comment. In pure monosilane m/e 61 is clearly Si_2H_5^+ and is produced in much lower abundance than Si_2H_4^+ (m/e 60), Si_2H_3^+ (m/e 59) and Si_2H_2^+ (m/e 58). In the monosilane-rich mixture the relative intensities of these ions (Figures 6-8) are very similar to those in pure monosilane. However, in the methane-rich mixture m/e 61 is produced in considerably greater abundance than are the ions of m/e 58-60. This is not because of any increased abundance of SiH_3^+ (m/e 31), the precursor of Si_2H_5^+ , in the methane-rich mixture, as may be seen by comparing Figures 2 and 6. Hence we conclude that the ion of m/e 61 in the methane-rich mixture is not uniquely Si_2H_5^+ but includes SiC_2H_9^+ . Most probably this latter ion is a tertiary ion

arising by a third-order association reaction between $C_2H_5^+$ and SiH_4 . In the monosilane-rich mixture formation of $C_2H_5^+$ would be negligible, since CH_3^+ , the precursor ion, reacts with the monosilane and hence the enhanced intensity noted in the methane-rich mixture would not be observed.

$Si_2H_7^+$ (m/e 63) is a secondary ion of monosilane, in that it is formed by a reaction between a primary ion SiH_3^+ and monosilane, even though, as shown previously,⁵ the reaction is a third-order association process. High abundances of $Si_2H_7^+$ are observed in both mixtures, as may be seen by reference to Figures 3 and 6. That this is true in the methane-rich mixture must mean that SiH_3^+ is quite unreactive with methane because such reactions would obviously not lead to $Si_2H_7^+$.

As may be seen in Figure 5, the intensities of the major secondary ions of monosilane (with the exception of $Si_2H_7^+$ and possibly of $Si_2H_5^+$) attain plateaus at the higher pressures in the methane-rich mixture. This suggests that at least $Si_2H_2^+$, $Si_2H_3^+$, $Si_2H_4^+$, do not react significantly with methane. On the other hand, it is known that these secondary ions do react efficiently with monosilane⁵ and this is born out by the occurrence of maxima in the intensity-pressure plots for the monosilane-rich mixture (Figures 6-8). $Si_2H_7^+$ reacts with monosilane⁵ and so exhibits an intensity maximum in its pressure dependence in the monosilane-rich mixture (Figure 6); however, in the methane-rich mixture the intensity is still rising at the highest pressure studied (Figure 3), due to the unreactivity of SiH_3^+ with methane, and no qualitative conclusion concerning the reactivity of $Si_2H_7^+$ with methane may be drawn.

D. Mixed Secondary Ions

Some of the secondary ions formed by reactions of primary ions of one constituent of the mixture with molecules of the other contain both carbon and silicon atoms. Thus in both mixtures we observe the formation of SiCH^+ (m/e 41), SiCH_2^+ (m/e 42), SiCH_3^+ (m/e 43), SiCH_4^+ (m/e 44) and SiCH_5^+ (m/e 45), formation curves of the latter three, which are the most abundant, being shown in Figures 3, 4 and 8. Significant amounts of SiCH_7^+ (m/e 47) are observed in the methane-rich mixture (Figure 4) but the abundance in the monosilane-rich mixture is smaller by an order of magnitude.

As shown in Figure 4 the intensity-pressure curve of SiCH_3^+ (m/e 43) in the methane-rich mixture is initially concave downward and may still be rising slowly at the highest pressures studied. Such behavior means that the ionic precursors are methane primary ions, that react with monosilane to form SiCH_3^+ with large enough reaction cross-sections for the reaction to be significant in the methane-rich mixture, and/or monosilane ions that are only minor products (i.e. Si^+ , SiH^+) of reactions of the less-intense primary ions of methane (i.e. C^+ , CH^+ , CH_2^+) with monosilane. The absence of a maximum, at least up to 0.22 torr indicates that SiCH_3^+ is unreactive with methane. Although not shown graphically, in the monosilane-rich mixture the initial shape of the intensity-pressure curve for SiCH_3^+ is unchanged but a clear maximum as observed, suggesting that SiCH_3^+ ions do react with monosilane.

The intensity-pressure curve of SiCH_4^+ (m/e 44) in the methane-rich mixture (Figure 4) is clearly concave upward at low pressures suggesting that the major precursor ions are monosilane ions that

are major products of the reactions of primary methane ions with monosilane. The maximum indicates that SiCH_4^+ reacts efficiently with methane. In accord with this conclusion the intensity-pressure curve of SiCH_4^+ in the monosilane-rich mixture (not shown) is not concave upward and this is because the formation of monosilane ions via reaction of methane primary ions with monosilane is in this mixture negligible compared to the formation of monosilane ions by electron impact. A maximum at low pressures is observed for the monosilane-rich mixture also and this fact suggests SiCH_4^+ reacts efficiently with monosilane.

The intensity-pressure curves of SiCH_5^+ (m/e 45) for the methane-rich mixture and the monosilane-rich mixture are shown in Figures 3 and 8, respectively. In the methane-rich system the curve is clearly concave upward at low pressures and attains a plateau, while in the monosilane-rich mixture the curve is not concave upward at low pressures and passes through a maximum at about 0.035 torr. For the reasons given in the preceding paragraph this behavior points to the major precursor ions being monosilane ions that are major products of the reactions of methane primaries with monosilane. It also suggests that SiCH_5^+ is unreactive towards methane but reacts efficiently with monosilane.

As may be seen in Figure 4, in the methane-rich mixture the initial slope of the intensity-pressure curve of SiCH_4^+ (m/e 44) is greater than that of SiCH_3^+ (m/e 43). The reversal of the relative magnitudes of the slopes in the monosilane-rich mixture is most easily explained if SiCH_3^+ arises principally from reactions of primary ions of methane, that in the methane-rich mixture react predominantly with methane, and SiCH_4^+ arises principally from

monosilane primary ions that in the monosilane-rich mixture react predominantly with methane.

All the qualitative conclusions concerning secondary ion formation discussed above are consistent with the work of Stewart, Henis, and Gaspar⁴ and with our tandem mass spectrometric work to be discussed in a subsequent section. It was also mentioned that significant amounts of SiCH_7^+ (m/e 47) are observed in the methane-rich mixture but mean lesser amounts in the silane-rich mixture. This ion is not formed in bimolecular processes involving primary ions from methane with monosilane or primary ions of monosilane with methane since no ion at m/e 47 was detected in any of the tandem mass spectrometric experiments. We think it most likely that SiCH_7^+ arises from a third-body stabilized association of SiH_3^+ with methane. If true, we would not expect to observe much SiCH_7^+ in the monosilane-rich mixture because SiH_3^+ reacts reasonably efficiently with monosilane to form Si_2H_5^+ and Si_2H_7^+ .

E. Tertiary Ions

In both mixtures Si_2CH_9^+ (m/e 77) is found in significant amounts (Figure 4 shows the formation curve in the methane-rich mixture) and the shapes of the intensity-pressure plots suggest that the ion is formed via a termolecular association reaction between a secondary ion and a neutral molecule. The only secondary ion of correct stoichiometry and of sufficient intensity in both mixtures to account for Si_2CH_9^+ is Si_2H_5^+ . We therefore believe that Si_2CH_9^+ is formed via a third-body stabilized association of Si_2H_5^+ with methane.

Tertiary ions containing two carbon atoms and one silicon atom are obscured by mass interferences with the more intense

secondary ions characteristic of pure monosilane and clear-cut identification of such ions is precluded. As already mentioned, however, the relative intensities of m/e 61 (Si_2H_5^+ and SiC_2H_9^+) in the two mixtures lead us to conclude that SiC_2H_9^+ is formed as a tertiary ion.

The tertiary ions characteristic of pure monosilane⁵, Si_3H_x^+ ($x=4-9$) are observed in both mixtures and the quarternary ions characteristic of pure monosilane are observed in the monosilane-rich mixture. We do not, however, consider these further, since that is outside the scope of this paper.

2. Tandem Mass-Spectrometric Studies

In order to identify the individual reactions that make up the complex chemical conversion depicted in Figures 1-8, we have used the tandem quadrupole mass spectrometer⁵, in the in-line configuration, to study the reactions of all the primary ions of methane with monosilane and of monosilane with methane. Relative reaction cross-sections, computed from the ratio of the secondary-ion intensity to the product of primary-ion intensity and target gas pressure were measured for reactant ion energies in the range of 1-6 eV in the laboratory system.

In Table I are shown relative cross-sections at 1 eV (Lab) reactant-ion energy for reactions of all the primary ions of methane and monosilane with the other molecule. As mentioned earlier, the ion-exit energy obtaining in the pressure study with the single mass spectrometer was 2.1 eV, so the cross-sections shown in Table I should correspond reasonably closely to the reaction conditions pertinent to Figures 1-8 and to the discussion in the preceding section.

Correction of the cross-section of $m/e\ 17 \rightarrow m/e\ 31$ in Table I for the isotopic contribution from $^{13}\text{CH}_4^+$ has been made. The other cross-sections in Table I have not been corrected for isotopic contributions. With the exceptions of processes $m/e\ 13 \rightarrow m/e\ 43$, $m/e\ 14 \rightarrow 30$, and $m/e\ 31 \rightarrow m/e\ 45$, these isotopic corrections to the cross-sections in Table I are all less than 5% and the corrections were not deemed necessary. For the three reactions noted, however, corrections due to isotopic contributions were made in the subsequent computation of reaction rate constants.

The data in Table I identify clearly the reactant ion, the reactant molecule, and the product ion. For a complete reaction identification one needs also to know the neutral product(s). Thermochemical considerations are of considerable value in choosing among the various stoichiometrically possible sets of neutral products of a reaction, particularly if one knows if the reaction producing the given ion is exothermic or endothermic. When plotted as a function of reactant-ion energy the cross-sections of endothermic reactions generally rise from zero at the energy threshold to a broad maximum several eV above the threshold.²⁰⁻²⁴ On the other hand, the cross-section of exothermic ion-molecule reactions generally decrease for all values of the reactant ion-energy.^{19,20,25-28} Exceptions to this general behavior are exothermic reactions in which symmetry and spin properties of the molecular orbitals involved prevent the reaction from occurring on the lowest potential energy surfaces.^{29,30} In such cases, as exemplified by the formation of NO^+ from O^+-N_2 collisions,²⁹⁻³¹ exothermic reaction cross-sections may show the threshold and broad maximum in their dependence on reactant-ion energy that is

characteristic of endothermic processes. However, endothermic reactions will not exhibit typical exothermic behavior. Therefore, while remaining alert to exceptions of the sort discussed, we use the general shape of the dependence of reaction cross-section on relative kinetic energy of reactants as an indication of the sign of the reaction enthalpy change. Figures 9-14 show the dependence of reaction cross-sections (in arbitrary units) on the reactant-ion energy in the center-of-mass system for laboratory kinetic energies in the range of 1-6 eV.

As shown in Table I, injection of 1 eV (laboratory energy) C^+ ions, produced by the impact of 100 eV electrons on methane, into monosilane produces ions at m/e 28-31, 41 and 42, which in this system can be only Si^+ , SiH^+ , SiH_2^+ , SiH_3^+ , SiCH^+ , and SiCH_2^+ , respectively. The dependence of the cross-sections on relative kinetic energy, shown in Figures 9b, 10a, 10b, 11, 14a, and 14b indicate that all processes are exothermic.

Energetic considerations^{3,32} show that Si^+ may be formed only in processes involving complex formation or ionic dissociation subsequent to H_2^+ transfer from SiH_4 to C^+ . Since H_2^- transfer is a very dominant process, as will be seen, in the reactions of methane primary ions with monosilane, we conclude that (1) is the process producing Si^+ , viz.

In the case of formation of SiH^+ , the thermochemical data available indicate that only a complex formation followed by dissociation to SiH^+ and CH_3 is exothermic. However, this reaction is so highly

exothermic that one must expect that SiH^+ so formed would be prone to dissociate rapidly. Formation of SiH^+ by dissociative H^- transfer and dissociative H_2^- transfer is indicated to be endothermic by 11 and 15 kcal/mole, respectively. We believe that the combined uncertainties in the enthalpies of formation^{3,32} of SiH^+ , CH_2 , CH , and SiH_4 coupled with the possibility of excited states of C^+ being present in the reactant beam are sufficient for an exothermic reaction to be occurring by dissociative H^- or even H_2^- transfer. Accordingly, we rather arbitrarily choose between the two and ascribe SiH^+ formation to the dissociative H^- transfer shown in (2), viz.

Thermochemical considerations show very convincingly that SiH_2^+ and SiH_3^+ can be formed in C^+ - SiH_4 collisions only by H_2^- transfer and H^- transfer, respectively. In the case of the SiCH^+ and SiCH_2^+ ions, enthalpies of formation are not known and we ascribe their formation to reactions of lowest enthalpy change possible. Thus we write for the remainder of the reactions of C^+ with SiH_4 , (3)-(6), viz.

Neither of the earlier reports of ion-molecule reactions in monosilane-methane mixtures^{2,4} reported the occurrence of reactions of C^+ .

When CH^+ ions react with monosilane, the product ions observed are: Si^+ , SiH^+ , SiH_2^+ , SiH_3^+ , SiCH_2^+ and SiCH_3^+ . All reactions producing these ions appear to be exothermic, as shown in Figures 9b, 10, 11, 13a, and 14a. Of the possible reactions producing Si^+ , only: (1) complex formation, followed by dissociation to the neutral products $\text{CH}_4 + \text{H}$; and (2) dissociative H_2^- transfer, leading to the neutral products $\text{CH}_3 + \text{H}_2$, are feasible. We choose the latter and write (7), viz.

Thermochemical considerations indicate that SiH^+ may be formed by either dissociative H^- transfer or dissociative H_2^- transfer, while SiH_2^+ formation in an exothermic process is possible only by H_2^- transfer and SiH_3^+ must be formed in an H^- transfer process. The neutral products formed along with SiCH_2^+ have to be 3H or $\text{H}_2 + \text{H}$ and, since the enthalpy of formation of SiCH_2^+ is not known, we cannot choose except arbitrarily. Formation of SiCH_3^+ is exothermic^{3,32} whether the neutral products are H_2 or 2H , and again we can here make only an arbitrary choice. In view of the above discussion the reactions identified are shown by (8)-(12)

Of the above reactions observed to occur in collisions of CH^+ with monosilane, only (11) has been reported⁴ previously. The ion-cyclotron-resonance study⁴ reported (11) to be exothermic which is in accord with the behavior shown in Figure 14b.

Although different cross-sections are observed (Table I), reaction of CH_2^+ with SiH_4 produces the same product ions as when CH^+ is the reactant ion, namely Si^+ , SiH^+ , SiH_2^+ , SiH_3^+ , SiCH_2^+ and SiCH_3^+ . All reactions are exothermic (or thermoneutral) as shown in Figures 9b, 10, 11, 13a, 14a. Thermochemical considerations^{3,32} then lead to the conclusion that Si^+ must be formed by dissociative H_2^- transfer, SiH^+ must be formed by either dissociative H_2^- or dissociative H^- transfer (or both), SiH_2^+ must be formed by H_2^- transfer, and SiH_3^+ must be formed by H^- transfer. Thus for formation of the product ions of m/e 28-31, we have the processes shown in (13)-(16), viz.

The only exothermic reaction yielding SiCH_3^+ must produce $\text{H}_2 + \text{H}$ as the neutral products. In the case of SiCH_2^+ , we cannot compute enthalpy changes but we write for the reaction the neutral products that give the smallest ΔH . Thus we have the reactions shown in (17) and (18).

Only (18), of the reactions observed between CH_2^+ and SiH_4 , has been reported previously⁴.

Table I shows that 1-eV- CH_3^+ ions react with monosilane to produce only three product ions, namely SiH_3^+ , SiCH_3^+ , and SiCH_5^+ . All reactions are exothermic, as may be seen by reference to Figures 9a, 12a, and 13b. Thermochemical considerations show that SiH_3^+ must be formed in an H^- transfer, as shown by (19), viz.

Reactions (20) and (21), which describe the observed formation

of SiCH_3^+ and SiCH_5^+ have enthalpy changes of +4 and -48 kcal., respectively when reported^{3,32} enthalpies of formation are used. Since the combined uncertainties in the enthalpies of formation^{3,32} of SiH_4 and SiCH_3^+ exceed 4 kcal, and we do observe exothermic behavior of the cross-section as a function of kinetic energy, we believe that the actual enthalpy change for (20) is zero or less. It is noteworthy that SiH_2^+ , SiH^+ , and Si^+ are not observed in CH_3^+ - SiH_4 collisions at these energies, since their formation would be endothermic by +47, +22 and +84 kcal/mole respectively.

Reaction (19) was reported by Stewart, Henis and Gaspar⁴. These latter authors also reported that (20) was observed as an endothermic reaction. Reaction (21) was not reported but the tandem mass spectrometric experiment shows clearly that this exothermic reaction occurs. Beggs and Lampe² reported the occurrence of (20).

When CH_4^+ ions collide with SiH_4 , the ionic products, as shown in Table I, are SiH_2^+ , SiH_3^+ , SiCH_4^+ , and SiCH_5^+ . All processes producing these ions, moreover, are exothermic as may be seen in Figures 9a, 10a, and 12. Thermochemical computations then show that the reactions responsible for formation of these product ions must be those shown by (22) - (25), viz.

Reaction (22) cannot be H^- transfer from SiH_4 followed by dissociation of SiH_3^+ to SiH_2^+ and H , because it would then be 85 kcal. endothermic. It must be as written and is best pictured as an H_2^- transfer to CH_4^+ with dissociation of the CH_6 neutral intermediate to CH_4 and H_2 . Reaction (23) is clearly an H^- transfer and although we have written the neutral products as $\text{CH}_3 + \text{H}_2$, we cannot distinguish them from $\text{CH}_4 + \text{H}$.

Reactions (23)-(25) were also reported by Stewart, Henis and Gaspar⁴ in their ion-cyclotron-resonance study and (24) and (25) were reported by Beggs and Lampe² in their low-pressure mass spectrometric study.

In agreement with observations from ion-cyclotron-resonance investigations⁴, Table I shows that only one product ion is produced in collisions of CH_5^+ with SiH_4 , namely SiH_3^+ . The process is exothermic as may be seen in Figure 9a, and therefore must be written as shown in (26), viz.

Although the proton affinity of monosilane is about 30 kcal/mole greater than that of methane³³, the mechanism involved in (26) cannot be to any great extent a protonation of SiH_4 followed by dissociation as shown in (26a) and (26b), viz.

The reason for this conclusion is that if (26a) and (26b) were operative, appreciable amounts of SiH_5^+ would have to have been observed in the high-pressure mass-spectrometric studies of the methane-rich mixtures, due to the stabilization process (26c), viz.

Since only minute amounts of SiH_5^+ were observed in any of the high-pressure studies, we conclude that (26a)-(26c) cannot be the mechanism responsible for (26). The only reasonable alternative left is direct H^- transfer from SiH_4 ; this conclusion is in agreement with recent ion-cyclotron-resonance studies of CD_4 - SiH_4 mixtures.³⁴

When 1 eV Si^+ ions react with methane, the only ion observed as a product is the SiCH_3^+ ion, as may be seen in Table I. The reaction involved can be only that shown in (27), viz.

The dependence of the reaction cross-section on relative kinetic energy indicates the reaction to be an endothermic process with a threshold below 0.4 eV. (9 kcal/mole). The enthalpy change of the reaction for ground state Si^+ ions,^{32,35} is +48 kcal, which is in accord with the qualitative observation of an endothermic process but not with the indicated location of the threshold energy. However, it is probable that the Si^+ beam, produced by the impact of 100 eV electrons on SiH_4 , contains significant numbers of excited ions. It is, therefore, plausible that it is the reaction of excited ions that yield the low threshold value.

Although not shown in Table I because it does not occur at 1 eV reactant ion energy (Laboratory), the reaction shown in (28), viz.

occurs as an endothermic process. This may be seen in Figure 14a. The apparent threshold of 0.5 eV cannot be used to check for the presence of excited states of Si^+ in the beam because the enthalpy of formation of SiCH_2^+ is not known.

Neither reaction of Si^+ has been reported before.

Table I shows that SiH^+ ions react with methane to yield two product ions, namely SiCH_3^+ and SiCH_4^+ . The behavior of the reaction cross-sections with relative kinetic energy shown in 12b and 13a indicate both reactions to be exothermic. Therefore, for the formation of SiCH_3^+ , we must have the reaction given in (29), viz.

and stoichiometry demands that the reaction producing SiCH_4^+ be that shown in (30), namely,

However, available thermochemical data^{3,32,35} indicate that, while (29) is exothermic by 18 kcal., (30) should be endothermic by 26 kcal. We can only suggest that either a considerable fraction of the SiH^+ beam is in excited states or that the heat of formation of SiCH_4^+ , determined by electron impact on SiH_3CH_3 ,³ is grossly in error. In view of a similar need to invoke the presence of excited states in the reactant ion beam in order to explain the low threshold observed for the endothermic reaction (27), and in view of the likelihood of this occurrence when using 100 eV electrons, we prefer the first suggestion. Of course, because of the fact that the energy-spread of our ion beam is about 1 eV, we cannot rule out the possibility that, at energies lower than we could obtain experimentally, a maximum in the cross-section could occur and endothermic behavior would thus be exhibited. However, the cross-section observed is quite large for an endothermic process and this fact, coupled with the disparity of the curve

shown in Figure 12b with the curves typical of endothermic reactions²⁰⁻²⁴, leads us to conclude that the actual process producing SiCH_4^+ from SiH^+ under our conditions is exothermic; and this in turn most likely demands the participation of excited states of SiH^+ .

Although (29) was reported by Stewart, Henis, and Gaspar⁴, these authors did not report the occurrence of (30).

Two product ions appear when SiH_2^+ ions are injected into methane, namely SiCH_4^+ and SiCH_5^+ , products which were also reported by Stewart, Henis and Gaspar.⁴ The reactions producing these products can hardly be anything except what is shown in (31) and (32), viz.

Available thermochemical data^{3,32,35} show (31) to be thermoneutral while (32) is endothermic by 8 kcal.; the dependence of the cross-sections on relative kinetic energy, shown in Figure 12, indicates both reactions to be exothermic. Since the combined uncertainties in the reported enthalpies of formation^{3,35} of SiCH_5^+ and SiH_2^+ exceed 8 kcal/mole, we feel it most probable that (32) is actually exothermic even for ground state ions. This is confirmed by the observation of both (31) and (32) by Gaspar, Henis and Stewart⁴ even at low electron-impact energies. Reaction (31) was also reported by Beggs and Lampe.²

When ions of m/e 31 from monosilane are injected into methane a small product ion peak at m/e 45 is observed. While the major fraction of these product ions (0.7) is due to the interfering reactions of the minor isotopic constituents of the m/e 31 beam, viz.

extensive examination of the isotopic contributions as a function of energy lead us to conclude that (33) does indeed occur as an exothermic process, although with very small cross-section. This is contrary to the conclusion of Stewart, Henis and Gaspar,⁴ who

reported that (29') and (31') account for all of the m/e 45 produced when m/e 31 impinges on methane.

3. Discussion of High-Pressure Mass Spectra of Mixtures

The detailed information in Table I concerning the origin of secondary ions and the relative cross-sections of the various reaction affords now a more detailed understanding of the complex pressure-dependent mass spectra shown in Figures 1-8.

It is quite clear from Table I that by far the predominant reaction of all methane primary ions with monosilane is hydride abstraction to produce SiH_3^+ . Since this is also the principal process in pure monosilane,^{5,13,14} the rapid growth and large abundance of SiH_3^+ in both the methane-rich and the monosilane-

rich mixtures is explained.

The maximum in the abundance of SiH_2^+ (m/e 30) in the methane-rich mixture and the absence of this maximum in the monosilane rich mixture is also now understood. In the methane-rich mixture (Figure 1) the primary ions of methane are sufficiently intense that a net formation of SiH_2^+ by reactions (3), (9), (15) and (22) occurs with increasing pressure until sufficient depletion of methane primary ion intensity has taken place for the loss processes, namely reactions (31), (32) and those characteristic of pure monosilane to balance the formation. At balance, of course, a maximum is observed (0.013 torr) and as the pressure is further increased the abundance of SiH_2^+ decreases. The maximum in the abundance of SiH_2 is not observed in the monosilane-rich mixtures because the methane primary ion intensities are not sufficiently high at low pressures to contribute significantly to SiH_2^+ intensity.

A similar argument applies to the maximum in Si^+ (m/e 28), shown in Figure 1, as Si^+ is produced in the methane-rich mixtures by reactions (1), (7), and (13) and react by (27), (28) and the reactions characteristics of this ion in pure monosilane. Probably a similar behavior is exhibited by SiH^+ (m/e 29) but interference from C_2H_5^+ (m/e 29) is too great for this to be observed. A maximum is obtained in the (m/e 29) curve (Figure 2) but this is probably due principally to the process

a reaction known to occur.³⁶

The reactivity of CH_5^+ with monosilane, indicated by the maximum in the abundance of m/e 17), shown in Figure 3, is attributed to (26). The rather insignificant production of CH_5^+

in the monosilane-rich mixture (Figure 7) is clearly due to the reactions of CH_4^+ with monosilane, namely reactions (22-25). Similarly the absence of C_2H_3^+ (m/e 27) formation in the monosilane-rich system was attributed earlier to competitive reaction precursor ion CH_2^+ with monosilane, and it is now clear from Table I that the pertinent reactions are (13)-(16).

It was remarked earlier that the formation curves for the secondary ions of monosilane, namely Si_2H_2^+ (m/e 58), Si_2H_3^+ (m/e 59), Si_2H_4^+ (m/e 60) and Si_2H_5^+ (m/e 61), all show an initial upward curvature with increasing pressure in the methane-rich mixture (Figure 5) but only Si_2H_5^+ (m/e 61) shows this in the monosilane-rich mixture (Figure 8). This is now understandable, since in the former mixture all the precursor ions to these secondary products, namely Si^+ , SiH^+ , SiH_2^+ , and SiH_3^+ , are produced in significant amounts by reactions (1)-(4), (7)-(10), (13)-(16), (19), (22), (23), (26), and (34). In the monosilane-rich mixture only SiH_3^+ (m/e 31), a precursor⁵ to Si_2H_5^+ , shows a net increase (Figure 6) and this is due to reactions characteristic of pure monosilane.^{5,13,14}

The pressure dependence of the intensities of the secondary ions containing carbon and silicon, shown in Figures 3 and 4 is explained in a general way by the data in Table I for product ions (m/e 41-45) and by reactions (5), (6), (11), (12), (17), (18), (20), (21), (24) and (25). It was mentioned earlier that the intensity-pressure curve for SiCH_3^+ (m/e 43) exhibited a downward curvature (Figure 4) while both of the curves for SiCH_4^+ (m/e 44) and SiCH_5^+ (m/e 45) (Figures 4 and 3, respectively) showed initial upward curvature. These details may now be understood on the basis of the relative cross-sections and reactions shown by Table I. Thus, in

the initial stages of the plots shown in Figures 4 and 5, it may be shown that 60% of the formation of SiCH_3^+ is due to the precursors CH^+ , CH_2^+ , and CH_3^+ and since the intensities of these major precursors to SiCH_3^+ decrease continuously with increasing pressure (Figures 1 and 2), a downward curvature is observed. On the other hand 89% of SiCH_4^+ is due to the precursor ions SiH^+ and SiH_2^+ , ions whose intensities at first increase with pressure (Figure 1) due to reactions (2), (3), (8), (9), (14), (15), and (22). Because there is an initial increase in intensity of the precursors to SiCH_4^+ , the intensity-pressure curve shows an initial upward curvature. In a similar way the fact that 53% of the initial formation of SiCH_5^+ is due to the precursors SiH_2^+ and SiH_3^+ explains the initial upward curvature of the intensity-pressure curve of SiCH_5^+ . In particular, for SiCH_5^+ , the upward curvature extends over a wide pressure region, since one of the precursor ions is SiH_3^+ and the intensity of this ion grows from ~4% to about 44% in the same pressure region.

The upward curvature in the intensity-pressure dependence of SiCH_4^+ and SiCH_5^+ is not detectable in the monosilane-rich mixture because of the amount of formation of monosilane primary ions by reactions of methane primaries with monosilane is not sufficient to result in a net formation of monosilane primaries.

4. Reaction Rate Constants of Cross-Reactions

It has been remarked earlier that since the cross-sections shown in Table I refer to a reactant ion-energy of 1 eV, these relative cross-sections should also be representative of the

situation in the single mass spectrometer pressure studies in which the ion-exit energy was 2.1 eV. Making the assumption that this is true we may evaluate rate constants for the reactions using the intensity-pressure data of Figures 1-8 and the relative cross-sections of Table I.

Thus consider the initial slope of an intensity-pressure curve for SiCH_4^+ (m/e 44). Since the precursor ions are known to be CH_4^+ (m/e 16), SiH^+ (m/e 29), and SiH_2^+ (m/e 30) it is easily shown that this initial slope is given by

$$\left(\frac{dX_{44}}{dn}\right)_{p=0} = L[X_{16}^0 \sigma_{16} \gamma_{\text{SiH}_4} + X_{29}^0 \sigma_{29} \gamma_{\text{CH}_4} + X_{30}^0 \sigma_{30} \gamma_{\text{CH}_4}] \quad (35)$$

where L is the travel distance of the ions in the source, X_i^0 is the zero-pressure limit of the percentage of the ion of $m/e = i$, σ_i is the reaction cross-section for reaction of ion of $m/e = i$ to form SiCH_4^+ , and γ_i is the mole fraction of neutral substance i . Since the initial slopes and X_i^0 - values may be measured, γ_i is known, and the relative cross-sections σ_{29}/σ_{16} and σ_{30}/σ_{16} are known from Table I, we evaluate directly the quantity $\sigma_{16}L$. We obtain rate constants by the general relationship

$$k_i t_i = \sigma_i L \quad (36)$$

when k_i is the rate constant corresponding to the cross-section σ_i and t_i is the residence time of the reactant ion in the source. Since we deal only with slopes in the limit of zero pressure, the residence time t_i is well-defined. Knowing any one absolute cross-section or rate constant we may use the data in Table I

and equation (36) to evaluate the rate constants of all secondary reactions observed.

We have evaluated all the rate constants using the pressure data in the manner described for: (1) the formation of SiH_3^+ in the methane-rich mixture; (2) the formation of SiCH_4^+ in both mixtures; (3) the formation of SiCH_5^+ in both mixtures. From these data we obtained, for example, a value of $14.9 \pm 3.2 \times 10^{-10} \text{ cm}^3/\text{sec}$ for reaction (23), the hydride abstraction from monosilane by CH_4^+ . To compare this result with an independent measurement in the tandem mass spectrometer we measured the cross-section for reaction (23) relative to that for the well-known reaction, viz.

by simply interchanging methane and monosilane in the collision chamber. Taking the accepted value⁹⁻¹² of $12.0 \times 10^{-10} \text{ cm}^3/\text{sec}$ for the rate constant of (37), we obtain $k_{23} = 13.3 \pm 1.0 \times 10^{-10}$, a value in excellent agreement with the average obtained from Table I and the pressure data.

Rate constants for all reactions observed are collected in Table II, where the uncertainties indicated are average deviations from the average. Also shown in Table I are the enthalpy changes for the reactions and the rate constants reported by Stewart, Henis and Gaspar in their ion-cyclotron resonance study⁴ and by Beggs and Lampe² in their low-pressure mass spectrometric study. Although we have observed many more reactions than Stewart, Henis and Gaspar,⁴ where it is possible to compare, the agreement is generally quite good. This is particularly true for the major process, which

is clearly H^- transfer from monosilane with formation of SiH_3^+ . The agreement with the low-pressure studies of Beggs and Lampe² is quite poor, which no doubt is a result of the complete inadequacy of low-pressure, single mass spectrometer studies (using appearance potentials for reactant identification) as a method for the detailed elucidation of such a complex system of ion-molecule reactions.

TABLE :

RELATIVE CROSS-SECTIONS^{a,c} FOR SECONDARY ION FORMATION

Reactant Ion (m/e)	Major Reactant Ion	Reactant Molecule	Relative Cross-Section for Formation of Secondary Ion at Given m/e								
			28	29	30	31	41	42	43	44	45
12	$^{12}\text{C}^+$ (100%)	SiH_4	5.2	7.8	13.0	54.6	2.7 ^b	7.1 ^b	-	-	-
13	$^{12}\text{CH}^+$ (> 99%)	SiH_4	5.0	9.8	9.1	42.5	-	18.6	13.4	-	-
14	$^{12}\text{CH}_2^+$ (> 99%)	SiH_4	2.3	7.3	2.3	47.2	-	2.5	15.1	-	-
15	$^{12}\text{CH}_3^+$ (> 99%)	SiH_4	-	-	-	52.5	-	-	1.7	-	1.6
16	$^{12}\text{CH}_4^+$ (99%)	SiH_4	-	-	10.9	35.2	-	-	-	1.0	1.5
17	$^{12}\text{CH}_5^+$ (74%)	SiH_4	-	-	-	49.5	-	-	-	-	-
28	$^{28}\text{Si}^+$ (100%)	CH_4	-	-	-	-	-	-	2.5	-	-
29	$^{28}\text{SiH}^+$ (96%)	CH_4	-	-	-	-	-	-	6.7	10.4	-
30	$^{28}\text{SiH}_2^+$ (98%)	CH_4	-	-	-	-	-	-	-	4.4	2.6
31	$^{28}\text{SiH}_3^+$ (94%)	CH_4	-	-	-	-	-	-	-	-	0.5

a) Reactant Ion-Energy of 1 eV (Laboratory) unless otherwise indicated.

b) Reactant Ion-Energy of 1.5 eV (Laboratory).

c) To convert to units of $\text{\AA}^2$ the data in table should be multiplied by 1.2.

TABLE 11

CROSS-REACTIONS IN MONOSILANE-METHANE MIXTURES

REACTION	ΔH (kcal.)	$10^{10} k \text{ in cm}^3/\text{sec}$		
		Ref. 2	Ref. 4	This Work
$C^+ + SiH_4 \rightarrow Si^+ + CH_2 + H_2$	-48	-	-	2.5 ± 0.5
$C^+ + SiH_4 \rightarrow SiH^+ + CH_2 + H$	+15	-	-	3.7 ± 0.7
$C^+ + SiH_4 \rightarrow SiH_2^+ + CH_2$	-63	-	-	6.3 ± 1.2
$C^+ + SiH_4 \rightarrow SiH_3^+ + CH$	-58	-	-	26.4 ± 5.3
$C^+ + SiH_4 \rightarrow SiCH^+ + H_2 + H$	<0	-	-	1.3 ± 0.2
$C^+ + SiH_4 \rightarrow SiCH_2^+ + H_2$	<0	-	-	3.4 ± 0.7
$CH^+ + SiH_4 \rightarrow Si^+ + CH_3 + H_2$	-77	-	-	2.3 ± 0.5
$CH^+ + SiH_4 \rightarrow SiH^+ + CH_3 + H$	-14	-	-	4.6 ± 0.9
$CH^+ + SiH_4 \rightarrow SiH_2^+ + CH_3$	-92	-	-	4.2 ± 0.7
$CH^+ + SiH_4 \rightarrow SiH_3^+ + CH_2$	-74	-	-	19.7 ± 3.9
$CH^+ + SiH_4 \rightarrow SiCH_2^+ + H_2 + H$	<0	-	1.56 ± 0.4	8.6 ± 1.7
$CH^+ + SiH_4 \rightarrow SiCH_3^+ + H_2$	-135	-	-	6.2 ± 1.2
$CH_2^+ + SiH_4 \rightarrow Si^+ + CH_4 + H_2$	-62	-	-	1.0 ± 0.2
$CH_2^+ + SiH_4 \rightarrow SiH^+ + CH_3 + H_2$	0	-	-	3.3 ± 0.7
$CH_2^+ + SiH_4 \rightarrow SiH_2^+ + CH_4$	-77	-	-	1.0 ± 0.2
$CH_2^+ + SiH_4 \rightarrow SiH_3^+ + CH_3$	-69	-	-	21.6 ± 45
$CH_2^+ + SiH_4 \rightarrow SiCH_2^+ + 2H_2$	<0	-	-	1.1 ± 0.3
$CH_2^+ + SiH_4 \rightarrow SiCH_3^+ + H_2 + H$	-17	-	2.91 ± 0.53	6.9 ± 1.4

TABLE II (Continued)

REACTION	ΔH (kcal.)	10^{10} k in cm ³ /sec		
		Ref. 2	Ref. 4	This Work
$\text{CH}_3^+ + \text{SiH}_4 \rightarrow \text{SiH}_3^+ + \text{CH}_4$	-47	-	11.1±1.8	22.5±4.5
$\text{CH}_3^+ + \text{SiH}_4 \rightarrow \text{SiCH}_3^+ + 2\text{H}_2$	+4	0.12	- ^a	0.73±0.15
$\text{CH}_3^+ + \text{SiH}_4 \rightarrow \text{SiCH}_5^+ + \text{H}_2$	-48	-	-	0.69±0.14
$\text{CH}_4^+ + \text{SiH}_4 \rightarrow \text{SiH}_2^+ + \text{CH}_4 + \text{H}_2$	-18	-	-	4.6±1.1
$\text{CH}_4^+ + \text{SiH}_4 \rightarrow \text{SiH}_3^+ + \text{CH}_3 + \text{H}_2$	-10	-	25±10	14.7±3.0
$\text{CH}_4^+ + \text{SiH}_4 \rightarrow \text{SiCH}_4^+ + 2\text{H}_2$	-18	7.47	0.35±0.23	0.42±0.08
$\text{CH}_4^+ + \text{SiH}_4 \rightarrow \text{SiCH}_5^+ + \text{H}_2 + \text{H}$	-10	2.20	0.30±0.18	0.63±0.12
$\text{CH}_5^+ + \text{SiH}_4 \rightarrow \text{SiH}_3^+ + \text{CH}_4 + \text{H}_2$	-8	-	17.8±2.5	19.9±4.0
$\text{Si}^+ + \text{CH}_4 \rightarrow \text{SiCH}_3^+ + \text{H}$	+48	-	-	0.77±0.15
$\text{SiH}^+ + \text{CH}_4 \rightarrow \text{SiCH}_3^+ + \text{H}_2$	-18	-	0.82±0.28	2.1±0.4
$\text{SiH}^+ + \text{CH}_4 \rightarrow \text{SiCH}_4^+ + \text{H}$	+26	-	-	3.5±0.8
$\text{SiH}_2^+ + \text{CH}_4 \rightarrow \text{SiCH}_4^+ + \text{H}_2$	0	-	3.07±0.61	1.3±0.3
$\text{SiH}_2^+ + \text{CH}_4 \rightarrow \text{SiCH}_5^+ + \text{H}$	+8	0.18	0.52±0.15	0.80±0.17
$\text{SiH}_3^+ + \text{CH}_4 \rightarrow \text{SiCH}_5^+ + \text{H}_2$	-1	-	-	0.05±0.03

(a) Reported as endothermic reaction with no rate constant or cross-section given.

REFERENCES

1. U. S. ATOMIC Energy Commission Document No. COO-3416-8
2. D. P. Beggs and F. W. Lampe, J. Phys. Chem. 73, 4194 (1969).
3. P. Potzinger and F. W. Lampe, J. Phys. Chem. 74, 587 (1970).
4. G. W. Stewart, J. M. S. Henis, and P. P. Gaspar, J. Chem. Phys. 57, 1990 (1972).
5. Tung-Yang Yu, T. M. H. Cheng, V. Kempter, and F. W. Lampe, J. Phys. Chem. 76, 3321 (1972).
6. P. Potzinger and F. W. Lampe, J. Phys. Chem. 74, 719 (1970).
7. J. J. DeCorpo and F. W. Lampe, J. Phys. Chem. 74, 3939 (1970).
8. P. Potzinger and F. W. Lampe, J. Phys. Chem. 75, 13 (1971).
9. V. L. Tal'roze and E. L. Frankevich, Zh. Fiz. Khim. 34, 2709 (1960).
10. C. W. Hand and H. von Weyssenhoff, Can. J. Chem. 42, 195 (1964).
11. J. L. Franklin, Y. Wada, P. Natalis, and P. M. Hierl, J. Phys. Chem. 70, 2353 (1966).
12. S. K. Gupta, E. G. Jones, A. G. Harrison, and J. J. Myher, Can. J. Chem. 45, 3107 (1967).
13. G. G. Hess and F. W. Lampe, J. Chem. Phys. 44, 2257 (1966).
14. J. M. S. Henis, G. W. Stewart, M. K. Tripodi, and P. P. Gaspar, J. Chem. Phys. 57, 389 (1972).
15. D. O. Schissler and D. P. Stevenson, J. Chem. Phys. 24, 926 (1956).
16. S. Wexler and N. Jesse, J. Am. Chem. Soc. 84, 3425 (1962).
17. V. L. Tal'roze and A. K. Lyubimova, Dokl. Akad. Nauk SSSR 86, 909 (1952).
18. F. H. Field and M. S. B. Munson, J. Am. Chem. Soc. 87, 3289 (1965).
19. G. Gioumousis and D. P. Stevenson, J. Chem. Phys. 29, 294 (1958).
20. C. F. Giese and W. B. Maier, J. Chem. Phys. 39, 197 (1963).
21. W. B. Maier, J. Chem. Phys. 46, 4991 (1967).
22. J. D. Martin and T. L. Bailey, J. Chem. Phys. 49, 1977 (1968).

REFERENCES (Continued)

23. P. S. Wilson, R. W. Rozett, and W. S. Koski, J. Chem. Phys. 52, 5321 (1970).
24. E. Lindemann, L. C. Frees, R. W. Rozett, and W. S. Koski, J. Chem. Phys. 56, 1003 (1972).
25. W. B. Maier, Planet. Space Sci 16, 477 (1968).
26. J. Sayers and D. Smith, Discussion Faraday Soc. 37, 167 (1964).
27. T. F. Moran and L. Friedman, J. Chem. Phys. 45, 3837 (1966).
28. C. F. Giese and W. B. Maier, J. Chem. Phys. 39, 739 (1963).
29. J. J. Kaugman and W. S. Koski, J. Chem. Phys. 50, 1942 (1969).
30. A. Pipano and J. J. Kaugman, J. Chem. Phys. 56, 5258 (1972).
31. C. F. Giese, Adv. Chem. Series 58, 20 (1966).
32. J. L. Franklin, J. G. Dilland, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, NSRDS-NBS26 National Bureau of Standards, June 1969.
33. T. M. H. Cheng and F. W. Lampe, Chem. Phys. Letts. (IN PRESS).
34. G. W. Stewart, J. M. S. Henis and P. P. Gaspar, J. Chem. Phys. 57, 2247 (1972).
35. P. Potzinger and F. W. Lampe, J. Phys. Chem. 73, 3912 (1969).
36. T. M. H. Cheng and F. W. Lampe, Unpublished results.

- Figure 1: Dependence of Primary Ion Abundance on Source Pressure in Methane-rich Mixture.
m/e 12; m/e 13; m/e 14; m/e 28; m/e 30.
- Figure 2: Dependence of Primary Ion Abundance on Source Pressure in Methane-rich Mixture.
m/e 15; m/e 16; m/e 29; m/e 31.
- Figure 3: Dependence of Secondary Ion Abundance on Source Pressure in Methane-rich Mixture.
m/e 17; m/e 27; m/e 45; m/e 63.
- Figure 4: Dependence of Secondary and Tertiary Ion Abundance on Source Pressure in Methane-rich Mixture.
m/e 43; m/e 44; m/e 47; m/e 77.
- Figure 5: Dependence of Secondary Ion Abundance on Source Pressure in Methane-rich Mixture.
m/e 58; m/e 59; m/e 60; m/e 61.
- Figure 6: Dependence of Primary and Secondary Ion Abundance on Source Pressure in Monosilane-rich Mixture.
m/e 29; m/e 30; m/e 31; m/e 60; m/e 63.
- Figure 7: Dependence of Primary and Secondary Ion Abundance on Source Pressure in Monosilane-rich Mixture.
m/e 16; m/e 17; m/e 28; m/e 59.
- Figure 8: Dependence of Secondary Ion Abundance on Source Pressure in Monosilane-rich Mixture.
m/e 45 (Abundance x 10); m/e 58; m/e 61.

Figure Captions (continued)

Figure 9: Dependence of Relative Reaction Cross-Section for Hydride Transfer from Monosilane on Center-of-Mass Energy.

- (a) Reactant Ions: CH_3^+ ; CH_4^+ ; CH_5^+ .
 (b) Reactant Ions: C^+ ; CH^+ ; CH_2^+ .

Figure 10: (a): Dependence of Relative Reaction Cross-Section for SiH_2^+ Formation from Monosilane on Center-of-Mass Energy. Reactant Ions: C^+ ; CH^+ ; CH_2^+ ; CH_4^+ .

- (b): Dependence of Relative Reaction Cross-Section for SiH^+ Formation from Monosilane on Center-of-Mass Energy. Reactant Ions: C^+ ; CH^+ ; CH_2^+ .

Figure 11: Dependence of Relative Reaction Cross-Section for Si^+ Formation from Monosilane on Center-of-Mass Energy. Reactant Ions: C^+ ; CH^+ ; CH_2^+ .

Figure 12: (a): Dependence of Relative Reaction Cross-Section for SiCH_5^+ Formation on Center-of-Mass Energy. Reactant Ions: CH_3^+ ; CH_4^+ ; SiH_2^+ .

- (b): Dependence of Relative Reaction Cross-Section for SiCH_4^+ Formation on Center-of-Mass Energy.. Reactant Ions: CH_4^+ ; SiH^+ ; SiH_2^+ .

Figure 13: Dependence of Relative Reaction Cross-Section for SiCH_3^+ Formation on Center-of-Mass Energy.

- (a) Reactant Ions: CH^+ ; CH_2^+ ; SiH^+ .
 (b) Reactant Ions: CH_3^+ ; CH_4^+ ; Si^+ .

Figure Captions (continued)

- Figure 14: (a): Dependence of Relative Reaction Cross-Section for SiCH_2^+ Formation on Center-of-Mass Energy.
Reactant Ions: $\square \text{C}^+$; $\bigcirc \text{CH}^+$; $\odot \text{CH}_2^+$; $\blacksquare \text{Si}^+$.
- (b): Dependence of Relative Reaction Cross-Section for SiCH^+ Formation on Center-of-Mass Energy.
Reactant Ions: $\square \text{C}^+$; $\bigcirc \text{CH}^+$.

Fig. 1

Fig. 2.

Fig. 3

44
% TOTAL IONIZATION

3
2.5
2
1.5
1
0.5

0.02 0.04 0.06 0.08 0.10 0.12 0.14 0.16 0.18 0.20 0.22

ION - SOURCE PRESSURE IN TORR

% TOTAL IONIZATION

Fig. 5

Fig. 6

Fig. 7

5
4
3
2
1
0

Fig. 8

RELATIVE REACTION CROSS-SECTION

Fig. 9

CENTER-OF-MASS ENERGY IN eV

Fig. 10

Fig. 11

RELATIVE REACTION CROSS SECTION

Fig. 12

Fig. 13

RELATIVE REACTIVE CROSS-SECTION

Fig. 14

CENTER-OF-MASS ENERGY IN eV

ION-MOLECULE REACTIONS IN DISILANE

High-pressure, mass-spectrometric studies of ion-molecule reactions in disilane have been carried out in the Nuclide magnetic deflection mass spectrometer. Reaction identification studies using tandem mass spectrometry have not yet been carried out but in the remainder of this section we report our results to date on this very complex system of ion-molecule reactions.

The ion fractions of primary ions and reaction product ions from ionized disilane as a function of ion-source pressure are shown in Figures 1-11. The highest source pressure obtaining in this study was 215 microns; this is only about one-half of the maximum pressure reached in the study of monosilane, although the pressures in the gas handling equipment were almost the same as in the monosilane study, and the same valve setting was used. Such a dependence of source pressure on molecular weight has been reported by Field and Munson (1).

The primary ion spectrum of disilane has been reported by Potzinger and Lampe (2). In this study it has been found all primary ions are reactive toward disilane molecules with all disilane ions but one showing the same characteristics of exponential decay with increasing pressure. The only exception is the Si_2H_5^+ ion which shows the same behavior with pressure as does SiH_3^+ ; i.e., its ion fraction increases with increasing pressure, reaches a maximum at about 8 microns and then decreases. Thus, Si_2H_5^+ is a primary reactant ion as well as a secondary product. The

Si_2H_7^+ ion is formed in this system at very low pressures and is also reactive; it has a broader peak than does SiH_3^+ , and diminishes to almost zero at about 50 microns.

Semilogarithmic plots of the ion fractions of primary ions m/e 28-31, 56-60, and 62 versus source pressure show good linear relationships with increasing pressure. If $t=1.73 \times 10^{-6}$ for m/e 56-62, the total decay constants of these primary ions listed in Table I are obtained.

It is interesting to note in Table I that the total decay constants for these primary ions are almost 4-5 times higher than for the primary ions in monosilane. When the pressure reaches about 100 microns in the ion source, the total ion fractions of the primary ions is only about 0.01 of the total ion currents. It is thus indicated that all the primary ions have reacted with disilane molecules in very rapid reactions.

Table I

Total Decay Constants for the Primary Ions in Disilane

Primary Ion	$k \frac{\text{cm}^3}{\text{molecule-sec}} \times 10^9$	Primary Ion	$k \frac{\text{cm}^3}{\text{molecule-sec}} \times 10^9$
Si^+	2.4	Si_2H^+	1.9
SiH^+	2.9	Si_2H_2^+	1.2
SiH_2^+	3.0	Si_2H_3^+	1.2
SiH_3^+	2.7	Si_2H_4^+	1.2
Si_2^+	2.1	Si_2H_6^+	1.8

The ion fraction curve of Si_2H_3^+ is somewhat peculiar in that it reaches a minimum at 35 microns then rises again and forms a plateau. Since the rate constant for its decay is large (1.2×10^{-9}) as determined in the lower pressure region, it is felt that the subsequent rising part may be the contribution from an unknown impurity.

Ions with three silicon atoms are the first product ions to be seen in the mass spectrum of disilane; these ions are in the range $\text{Si}_3\text{H}_2^+ - \text{Si}_3\text{H}_7^+$ and include also Si_3H_9^+ . The ion fraction curves in Figures 4 and 5 show clearly that at low pressure these ions are secondary products, but that in the pressure region 10-20 microns, their intensities decrease because they are reactive toward disilane molecules and contribute to the overall polymerization.

Since the m/e value of the product ions in disilane are quite high, (from m/e 86-212) and the resolution of the second quadrupole in the tandem spectrometer is limited to about 120, no tandem mass spectrometric data were obtained. Early appearance potential measurement data show clearly that m/e 58 and 88 have the same onset potentials; also m/e 60 and 90 have the same appearance potentials. This suggests that the following general reaction is an important one in ionized disilane.

For the ions with four silicon atoms, Si_4H_8^+ ions are the most reactive ones, showing a maximum at about 25 microns. However, the rest of these ions, namely, Si_4H_3^+ , Si_4H_7^+ , Si_4H_9^+ ,

and $\text{Si}_4\text{H}_{11}^+$ show a more-or-less form of plateau at pressures above 40 microns. Si_5H_8^+ and $\text{Si}_5\text{H}_{10}^+$ ions are the most reactive of the ions with five silicon atoms. They show a maximum at about 60 microns while the rest of these ions, namely, Si_5H_6^+ , Si_5H_7^+ , $\text{Si}_5\text{H}_{11}^+$, and $\text{Si}_5\text{H}_{13}^+$ all reach a plateau at about 60 microns. The $\text{Si}_5\text{H}_{12}^+$ ion was absent and it is of interest to note that also absent were $\text{Si}_4\text{H}_{10}^+$ and Si_3H_8^+ ion. The reason for their absence is not clear but may be related to the absence of Si_2H_6^+ in the pure monosilane system.

It is of interest to note in the disilane system ions with six and seven silicon atoms are observed. For the ions with six or seven silicon atoms only $\text{Si}_6\text{H}_{10}^+$ ion is reactive showing a maximum at about 70 microns. The remainder of these ions all show a plateau, i.e., they are the end products of the polymerization in the pressure region being studied. Since no ions with six silicon atoms were observed in the investigation of monosilane system, these ions with six or seven silicon atoms may well have a branched silicon-silicon chain, which render them more stable.

References

1. F. H. Field and M. S. B. Munson, Paper presented at 11th ASTM Conference on Mass Spectrometry, San Francisco, California, May 1963.
2. P. Potzinger and F. W. Lampe, J. Phys. Chem. 73, 3912 (1969).

SiH₅⁺ AND THE PROTON AFFINITY OF MONOSILANE

T. M. H. Cheng and F. W. Lampe, Chem. Phys. Letts. 19, 532-534 (1973).

Abstract

Tandem mass spectrometric studies show that SiH₅⁺ is formed in the following bimolecular reactions:

The dependence of the cross-sections of the above reactions on kinetic energy indicates that (1)-(3) are exothermic while (4) is endothermic. It is thus possible to place the proton affinity of SiH₄ in the range 150-156 kcal/mole.

Figure 1. Primary Ion Fractions in Si_2H_6 as a Function of Source Pressure²(A).

Figure 2. Primary Ion Fractions in Si_2H_6 as a Function of Source Pressure²(B).

Figure 3. Primary Ion Fractions in Si_2H_6 as a Function of Source Pressure (C).

Figure 4. Three-Silicon-Atom Ion Fractions in Si_2H_6 as a Function of Source Pressure (A).

Figure 5. Three-Silicon-Atom Ion Fractions in Si_2H_6 as a Function of Source Pressure (B).

Figure 6. Four-Silicon-Atom Ion Fractions in Si_2H_6 as a Function of Source Pressure (A).

Figure 7. Four-Silicon-Atom Ion Fractions in Si_2H_6 as a Function of Source Pressure (B).

Figure 8. Five-Silicon-Atom Ion Fractions in Si_2H_6 as a Function of Source Pressure (A).

Figure 9. Five-Silicon-Atom Ion Fractions in Si_2H_6 as a Function of Source Pressure (B).

Figure 10. Six-Silicon-Atom Ion Fractions in Si_2H_6 as a Function of Source Pressure.

Figure 11., Seven-Silicon-Atom Ion Fractions in Si_2H_6 as a Function of Source Pressure.

REACTIONS OF TRIFLUOROMETHYL RADICALS

H. S. Tan and F. W. Lampe, J. Phys. Chem. 77, (1973)
IN PRESS.

In our studies of silyl radical reactions we plan to generate silyl radicals by the reaction

It was therefore appropriate, as a preliminary, to conduct studies of CF_3 -radicals with themselves and with nitric oxide.

Trifluoromethyl radicals, formed by the photolysis of hexafluoroazomethane, react with nitric oxide by successive addition to yield trifluoronitrosomethane and perfluorotrimethylhydroxylamine. Trifluoronitrosomethane is the sole product until the nitric oxide concentration has been reduced to very low levels, at which time the addition reaction to form perfluorotrimethylhydroxylamine can occur. After the trifluoronitrosomethane has been depleted the trifluoromethyl radicals can react with hexafluoroazomethane to yield perfluorotetramethylhydrazine and with each other to yield hexafluoroethane. Kinetic analysis of the data subsequent to depletion of nitric oxide permits evaluation of a lower limit to the specific reaction rate for the addition of trifluoromethyl radicals to trifluoronitrosomethane. The value found is: $k_8 \geq 9.7 \pm 0.7 \times 10^{-14} \text{ cm}^3\text{-molecule}^{-1}\text{sec}^{-1}$ at 56°C .

RADIOLYSIS OF MONOSILANE-NITRIC OXIDE MIXTURES

Photosensitized free-radical studies have shown that silyl radicals react with nitric oxide in the presence of monosilane to produce nitrous oxide and siloxanes. Moreover, the process appears to proceed by a free-radical chain that has no analog in carbon-radical chemistry.

We have initiated a radiolysis study of this process in which our first experiments have consisted of the gamma-ray irradiation of 100 torr samples of 90% monosilane and 10% nitric oxide. The dose rate was 1.3×10^{16} ev/cm³-hr and doses in the range of 0.78 - 9.4×10^{17} ev/cm³ were employed.

The mass spectrum of the mixtures irradiated to a dose of 9.4×10^{17} ev/cm³ from m/e 36 - m/e 139 is shown in Figure 1 where it is compared with the mass spectra of pure samples of Si₂H₆¹, SiH₃OSiH₃², SiH₃OSiH₂OSiH₃² and (SiH₃O)₃SiH². It is clear that the above four compounds account completely for the radiolysis product (other than H₂). It is also clear that we have here a very specific radiation chemical conversion, with over 90% of the reaction being accounted for by the stoichiometry:

Approximate analyses of N₂O formation, and NO consumption from the mass spectra indicate that at the lowest total doses G(N₂O) = 31 and G(-NO) = 62, which is in accord with essentially all of the reaction being described by (1). Quantitative analyses for the siloxanes have not yet been made but the observed mass spectra and the absence of products other than those described strongly suggests the following relationships.

$$G(\text{SiH}_3\text{OSiH}_3) \approx G(\text{N}_2\text{O})$$

$$G(\text{SiH}_3\text{OSiH}_2\text{OSiH}_3) \approx G[(\text{SiH}_3\text{O})_3\text{SiH}] \lesssim 0.1 G(\text{N}_2\text{O})$$

There is no question that NO and SiH_4 are being consumed in a chain reaction and the free-radical chain described in our previous mass-spectrometric studies³ is operative. We do not yet know if an ionic chain is operative but we are presently studying the ion-molecule reaction chemistry of SiH_4 -NO mixtures.

It is also of interest to note that Si_2H_6 is a significant product at all doses used. However, we know from our elementary reaction studies³ that the presence of NO completely inhibits the free-radical formation of Si_2H_6 . Thus in the radiolysis Si_2H_6 is formed in significant amounts by a non-radical process and, as we have described in our previous ion-molecule reaction investigations⁴, such processes most probably involve the Si_2H_7^+ ion.

Experiments are continuing in the radiation chemistry of this interesting system.

References

1. P. Potzinger and F. W. Lampe, J. Phys. Chem. 73, 3912 (1969).
2. T. Yoshioka, Ph. D. Thesis, University of Pennsylvania, Philadelphia, Pa. 1967.
3. E. Kamaratos and F. W. Lampe, J. Phys. Chem. 74, 2267 (1970).
4. T-Y. Yu, T. M. H. Cheng, V. Kempter, and F. W. Lampe, J. Phys. Chem. 76, 3321 (1972).

Product Mass Spectrum of Irradiated SiH_4 - NO Mixtures