000-3416-14

ION-MOLECULE REACTIONS IN MONOSILANE-ACETYLENE MIXTURES¹

by

T. M. Mayer^a and F. W. Lampe*

Davey Laboratory
Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

MASTER

Abstract

The reactions of Si^+ , SiH^+ , SiH_2^+ , and SiH_3^+ with C_2H_2 and the reactions of C_2H_2^+ with SiH_4 have been studied as a function of collision energy in the range of 0.3 to 2.5 eV in the center-of-mass system by tandem mass spectrometry. Phenomenological rate constants have been measured in the low-energy region of 0.3 to 0.9 eV in which the polarization theory cross-section dependence on energy of the form $\alpha \sigma E^{-1/2}$ seems to be reasonably valid. High-pressure mass spectrometry in the range of 0.04 - 0.3 torr for a mixture containing 10% of acetylene indicates that acetylene has a striking effect on the ionic chemistry of monosilane. Above 0.05 torr, the principal reaction of acetylene with ions derived from monosilane appears to be that of simple association, leading to ionic polymerization of acetylene.

a) Present Address: Hahn-Meitner Institut für Kernforschung
Bereich Strahlenchemie
1 Berlin 39
GERMANY

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

247

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Introduction

In a previous study of ion-molecule reactions in monosilane-acetylene mixtures² rate constants were reported for a number of reactions of $C_2H_2^+$ with SiH_4 and of SiH_2^+ with C_2H_2 . In this investigation, which was carried out in a single-source mass spectrometer, reaction identification was made principally on the basis of appearance potential measurements of product ions and rate constants were determined by the pulse technique³⁻⁵ for ion-source pressures below 0.006 torr. In view of the fact that application of the same apparatus and technique to the monosilane-methane system⁶ has been shown by ion-cyclotron resonance studies⁷, tandem mass spectrometry⁸, and high-pressure mass spectrometry⁸ to have yielded incomplete and/or misleading results, a reinvestigation of this system was felt to be desirable. Accordingly we have carried out a tandem mass spectrometric study of ion-molecule reactions in the monosilane-acetylene system. Our results are in qualitative accord with the earlier report² but we have identified a number of additional secondary processes in this system not reported earlier and have measured phenomenological rate constants or cross-sections for them. In addition, a limited high-pressure mass spectrometric study (up to 0.3 torr) was carried out in order to define the fates of the major secondary ion products in this system.

Experimental

The tandem mass spectrometer used in these studies permits the injection of mass-selected reactant ions, having kinetic energies variable down to about 1 eV, into a collision chamber containing the neutral reactant molecule. The apparatus, which has been described

previously⁹, consists of two quadrupole mass filters separated by the collision chamber and ion lenses, and mounted in the "in-line" configuration. Retarding field measurements indicate that the energy spread of the reactant ion beam entering the collision chamber is about 1 eV.

In addition to identification of the reactions of Si^+ , SiH^+ , SiH_2^+ and SiH_3^+ with C_2H_2 and of C_2H_2^+ with SiH_4 , the various relative reaction cross-sections were studied as a function of collision energy in the range 0.4 - 3 eV. As described previously^{8,10} the shapes of the cross-section versus energy curves were used to differentiate between exothermic and endothermic processes. Since our major interest in this system, pertains to the effect of acetylene on the radiolysis of monosilane¹¹ and therefore is concerned with monosilane-rich mixtures, we did not study reactions of the low-abundant C_2H^+ with SiH_4 .

Phenomenological rate constants were determined by direct comparison of relative reaction cross-section for 1.4 eV ions (laboratory system) with the cross-sections for reactions (1) and (2), viz.

whose rate constants had been determined previously⁸. Collision chamber pressures of the order of 10^{-3} torr and ionization chamber pressures in the range of $1-5 \times 10^{-3}$ torr were employed.

Measurements of the dependence of ionic abundances on ion-source pressures in the range of 0.04 to 0.03 torr for a 90% - 10% SiH_4 - C_2H_2 mixtures were carried out in a Nuclide Associates 12-90G sector-field mass spectrometer, an instrument that has been described previously.⁹ 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 2500 v. In all experiments the ion-exit energy was 1.9 eV. The ion-source temperature was 100°C.

Ion-source pressures in the Nuclide mass spectrometer were measured with a Granville-Phillips capacitance monometer that had been calibrated using a McCleod gauge. The calibration was checked by observation of CH_5^+ formation in methane. We estimate our source pressures to be accurate to $\pm 10\%$.

Monosilane, purchased from the Matheson Company, was purified by fractionation on a vacuum line prior to use. Research grade acetylene, also purchased from the Matheson Company, was used as received.

Results and Discussion

1. Nature of the Elementary Reactions.

The ion-molecule reactions found to be exothermic on the basis of the dependence of reaction cross-section on kinetic energy are tabulated in Table I. Also shown in Table I are standard enthalpy changes, calculated from available thermochemical data,^{12,13} and phenomenological rate constants determined at 1.4 eV ion-kinetic energy in the laboratory system. For comparison the rate constants reported previously are shown in the last column of Table I. With the exception of reaction (3), the neutral products are written arbitrarily as those that yield the maximum exothermicity.

One may note immediately from Table I, that the most rapid of all reactions with monosilane is hydride ion abstraction leading to formation of SiH_3^+ ; the predominance of this process in the reactions of positive ions with silanes^{8,9,14} is undoubtedly due

to the hydridic character of hydrogen in the Si-H bond.^{15,16} Recent studies in this laboratory¹⁷ have shown that the process of transfer of the hydride ion from SiH_4 occurs with very little if any momentum transfer from the reactant ion to the product SiH_3^+ . In other words the SiH_3^+ species acts as a spectator to the pick-up of its bound H^- by the reactant ion.

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

a) $\text{C}_2\text{H}_2^+ + \text{SiH}_4$. When C_2H_2^+ ions are injected into SiH_4 , reactions 3-11 (Table I) are observed as exothermic processes in that the cross-sections decrease with increasing collision energy over the entire range studied. With the exception of reaction 4 the calculated enthalpy changes for 3-7 are in agreement with the experimental conclusion that the reactions are exothermic processes. Enthalpies of formation are not available for the SiC_2H_x^+ ions. Thermochemical calculations using available data^{12,13} indicate reaction 4 to be endothermic by 8 kcal/mole, in contradiction to our experimental observations. This contradiction is undoubtedly due to the value $\Delta H_f^\circ (\text{SiH}^+) = 308$ kcal/mole¹² being too high. This value was determined from the appearance potential of SiH^+ from SiH_4 and processes involving the breakage of so many bonds are notorious for yielding high values. In fact, Potzinger and Lampe¹² state that the ionization-efficiency curve for SiH^+ from SiH_4 showed a long tail indicating processes involving excess energy. Therefore, we believe 4 to be, in fact, exothermic or thermoneutral which places an upper limit of 300 kcal/mole on the standard enthalpy of formation of SiH^+ .

The rate constants obtained in this work for the reactions of $C_2H_2^+$ with SiH_4 are in qualitative agreement with those of Beggs and Lampe² for reactions 5, 7, 9 -11 but are in general smaller by a factor of 3-4. Our rate constants for reaction 8 cannot be considered to be in even qualitative agreement since it is smaller by a factor of thirty than that reported by Beggs and Lampe². Moreover, the fastest of all the reactions of $C_2H_2^+$ with SiH_4 , namely formation of SiH_3^+ , could not be observed with the single-source technique of Beggs and Lampe², since SiH_3^+ is a reactant ion as well as a product ion in this system. Since the rate constants of Beggs and Lampe² refer to thermal energy ions and in this work were determined at a center-of-mass energy of 0.77 eV, it is conceivable that the former values could be correct. However, we do not think so because normally the phenomenological rate constants at low energies are not very sensitive to collision energy; secondly, the total reaction rate constant of $C_2H_2^+$ with SiH_4 obtained by Beggs and Lampe², when increased by the contribution of reaction 6, which they could not observe, is far in excess of the Langevin polarization theory rate constant¹⁸ for this reactant pair of $14.4 \times 10^{-10} \text{ cm}^3/\text{sec}$. On the other hand the total reaction rate constant for $C_2H_2^+$ with SiH_4 determined in this work is 17.9×10^{-10} , a much more plausible result, especially when one considers that the major process, reaction 6, most probably occurs by a direct stripping process¹⁷ which, while governed by the long range polarization r^{-5} attractive force, may not require an orbiting complex.

In view of the above discussion we believe that our present results supercede those of Beggs and Lampe² and demonstrate once again^{4,8} the inadequacy of low-pressure, single-source mass spectrometric techniques for detailed studies of ion-molecule reactions in systems containing more than one neutral reactant.

(b) $\text{Si}^+ + \text{C}_2\text{H}_2$. The only product ion observed when Si^+ ions were injected into the collision chamber containing C_2H_2 was SiC_2H^+ . The reaction is exothermic, as indicated by the dependence of cross-section on collision energy and has a phenomenological rate constant of $1.8 \pm 0.7 \times 10^{-10} \text{ cm}^3/\text{sec}$. Comparison with the Langevin orbiting rate constant for this reactant pair indicates a reaction efficiency of 0.15 per orbiting encounter. Beggs and Lampe² were unable to observe this reaction in their apparatus.

(c) $\text{SiH}^+ + \text{C}_2\text{H}_2$. Two product ions are observed when 1.4 eV SiH^+ ions react with C_2H_2 , namely SiC_2H^+ and SiC_2H_2^+ . Both reactions are exothermic since all cross-sections decrease with increasing collision energy. The total phenomenological rate constant for this reactant pair of 3.2×10^{-10} as compared with the Langevin orbiting value indicates a reaction efficiency of 0.28 for orbiting collisions.

The dependence of total cross-section for reactions of SiH^+ with C_2H_2 on collision energy is shown in Figure 1a. The adherence to an $E^{-1/2}$ dependence, which is required by the polarization theory¹⁸, is seen to be reasonably good in the low-energy region of 0.3 to 0.9 eV (center-of-mass) and the line through the origin is drawn with reference to the observed cross-sections in this energy range. Deviations from the $E^{-1/2}$ dependence are expected at collision energies above about 1 eV, partly because above this energy an endothermic channel for formation of SiC_2H^+ appears to open and partly because the polarization theory itself has no meaning above energies for which the orbiting cross-section becomes smaller than the gas-kinetic cross-section¹⁹. The reasonable assumption of a value of 4 Å for the gas-kinetic collision diameter of SiH^+ and C_2H_2 would suggest 1 eV as the collision energy for which the two cross-sections become equal. The dependence of cross-section on collision energy

shown in Figure 1a is typical of the reactions investigated in this work and supports our assumption that in the low-energy region of ~ 0.3 to 0.9 eV, the phenomenological rate constants should be approximately independent of energy.

In Figure 1b is shown the relative contributions of the two channels of reaction of SiH^+ with C_2H_2 as a function of collision energy. The increase in relative abundance of the SiC_2H^+ product above 1.2 eV is due to an increase in the actual cross-section for SiC_2H^+ formation which is probably the result of the opening of the endothermic channel depicted by (20), viz.

Neither of the reactions of SiH^+ with C_2H_2 could be detected in the apparatus used by Beggs and Lampe².

(d) $\text{SiH}_2^+ + \text{C}_2\text{H}_2$. Collision of SiH_2^+ with C_2H_2 produces SiC_2H^+ , SiC_2H_2^+ , and SiC_2H_3^+ ions by reactions 15-17 shown in Table I. All reactions exhibit exothermic behavior in the dependence of cross-section on collision energy. Comparison of the rate constant for product formation with the polarization theory¹⁸ indicates a reaction efficiency of 0.37 per orbiting encounter. The cross-section of reaction 15 goes through a minimum at 1.2 eV collision energy, similar to that of reaction 13. The most probable explanation for this behavior is the opening of the endothermic channel shown by (21), viz.

Reaction 17 was reported by Beggs and Lampe² to occur with a rate constant in qualitative agreement with that obtained in this work; if one assumes the rate constants in the two investigations

to be the same for reaction 5, one obtains values for 17 that are in excellent agreement.

(e) $\text{SiH}_3^+ + \text{C}_2\text{H}_2$. Collision of SiH_3^+ with C_2H_2 results in the formation of SiC_2H^+ and SiC_2H_3^+ by reactions 18 and 19 shown in Table I. Both reactions are quite slow, the total rate constant indicating a reaction-efficiency of only about 0.03 per orbiting encounter. Such behavior is quite typical of second-order reactions of SiH_3^+ with hydrocarbons^{7,8,20} and probably reflects the rather high stability of SiH_3^+ . Beggs and Lampe² were not able to observe any reactions of SiH_3^+ in their apparatus. The cross-section dependence on energy indicates both 18 and 19 to be exothermic.

(f) Endothermic Reactions. All of the reactions in Table I are observed to be exothermic, and the onset of the two endothermic processes (20) and (21) has already been mentioned. In addition to these latter reactions, (22) and (23), viz.,

where the state of aggregation of the products in parentheses is not known, were also observed as endothermic processes. The threshold of (22) lies above 1.1 eV and that of (23) above 1.4 eV, both energies being in the center-of-mass system.

2. High-Pressure Mass Spectra

The variation of abundance of the major product ions of Table I with ion-source pressure for an SiH_4 - C_2H_2 mixture containing 10% C_2H_2 is shown in Figures 2 and 3. Inspection of these figures and comparison with similar plots for pure SiH_4 demonstrate that the presence of 10%

of C_2H_2 has a major effect on the ionic chemistry of monosilane.

In pure monosilane the intensity of SiH_3^+ increases with pressure initially but passes through a maximum of about 50% of the total ionization at a source pressure of 0.06 torr. Subsequent to this maximum, $Si_2H_7^+$, which is formed by the termolecular association of SiH_3^+ with SiH_4 , increases with increasing pressure and attains a maximum at about 0.19 torr that represents about 35% of the total ionization. The major secondary ions in SiH_4 , typified by $Si_2H_4^+$, attain maxima in the range 0.10 - 0.15 torr, with $Si_2H_4^+$ reaching 19% of the total ionization.

This situation is drastically altered by the presence of 10% of acetylene as can be seen in Figure 2. Here one sees that the expected maximum in SiH_3^+ intensity must lie below 0.04 torr and that the maximum abundance of its' association product with monosilane, namely $Si_2H_7^+$, is less than 6%. Both effects are undoubtedly due to a very effective competition of C_2H_2 with SiH_4 for SiH_3^+ , even though SiH_4 is 9-fold more abundant. The bimolecular reactions of SiH_3^+ with C_2H_2 (Table I) and those of SiH_3^+ with SiH_4 ,⁹ while partially accounting for these facts, are not sufficient. Figure 3 shows that above 0.04 torr $SiC_2H_5^+$ appears in much greater abundance relative to SiC_2H^+ and $SiC_2H_3^+$ than expected from the bimolecular rate constants of Table I. It is thus indicated that SiH_3^+ undergoes rapid termolecular association with C_2H_2 as shown by (24), viz.

This association reaction could not be detected at the low pressures obtaining in the tandem experiments. The fact that the maximum in $SiC_2H_5^+$ occurs at higher pressures than do those for SiC_2H^+ and $SiC_2H_3^+$ is consistent with the formation of $SiC_2H_5^+$ from (24), since the SiH_3^+

is still very abundant at 0.10 torr,

In the $\text{SiH}_4\text{-C}_2\text{H}_2$ mixture the maximum abundance of Si_2H_4^+ (Figure 2) must be considerably lower than that in pure monosilane (19% of total ionization) and it is shifted from about 0.15 torr in the pure compound to a pressure of less than 0.04 torr. This is typical also of the behavior of Si_2H_2^+ and Si_2H_5^+ and indicates that these secondary ions of pure monosilane react rapidly with acetylene although the products of these reactions are at the moment somewhat obscure. Si_2H_3^+ appears to behave in the mixture identically to that in the pure compound, namely it appears to be quite unreactive, its abundance remaining essentially constant over the pressure range 0.04 to 0.3 torr.

The major secondary organosilicon ions formed by the reactions in Table I and by (25) are also reactive in this system as shown by Figure 3. While we are not certain of the details of their fates, we believe that a major cause of their depletion as well as of Si_2H_5^+ and Si_2H_7^+ , is association with C_2H_2 . The basis of this contention is Figure 4 which shows the relative intensities of m/e 53-57, m/e 61 and m/e 63 as well as the relative intensities of ions with m/e increased by 26, respectively, for several pressures. The observed similarity of the patterns leads us to suggest that these secondary ions in question react primarily by association with acetylene. There is a suggestion in the spectra that at masses even higher this addition of successive units of C_2H_2 continues, analogously to the observed ionic polymerization of acetylene.²¹⁻²³

It has been reported^{II} that in the γ -ray radiolysis of monosilane at 0.5 atm pressure, the addition of acetylene results in an increase in $G(\text{H}_2)$, apparently from a value of 22.8 to 52.7. This is a rather startling effect since the radiolysis of acetylene²⁴ produces

very little hydrogen and the reactions of free radicals derived from SiH_4 would not be expected to produce hydrogen upon reaction with acetylene.²⁵⁻²⁷ We suggest that the striking effect of acetylene on $G(\text{H}_2)$ in the radiation chemistry¹¹ is associated with this very marked effect that acetylene has on the ionic chemistry of SiH_4 .

Acknowledgement: This work was supported by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-3416. We also wish to thank the National Science Foundation for providing funds to assist in the original purchase of the Nuclide Associates Mass Spectrometer.

TABLE I

EXOTHERMIC ION-MOLECULE REACTIONS IN $\text{SiH}_4\text{-C}_2\text{H}_2$ MIXTURES

Reaction No.	Reaction	$\Delta H^\circ, \text{kcal}$	$\times 10^{10} \text{ (cm}^3/\text{sec)}$	
			This Work	Reference 2
3	$\text{C}_2\text{H}_2^+ + \text{SiH}_4 \rightarrow \text{Si}^+ + \text{C}_2\text{H}_4 + \text{H}_2$	-15	1.1 ± 0.4	Not observed
4	$\rightarrow \text{SiH}^+ + \text{C}_2\text{H}_5$	+8	0.73 ± 0.30	Not observed
5	$\rightarrow \text{SiH}_2^+ + \text{C}_2\text{H}_4$	-30	4.1 ± 1.6	14 ± 4
6	$\rightarrow \text{SiH}_3^+ + \text{C}_2\text{H}_3$	-21	10 ± 4	Not observed
7	$\rightarrow \text{SiCH}_3^+ + \text{CH}_3$	-16	0.32 ± 0.13	1.1 ± 0.3
8	$\rightarrow \text{SiC}_2\text{H}^+ + 2\text{H}_2 + \text{H}$	-	0.10 ± 0.04	$3.0 \pm$
9	$\rightarrow \text{SiC}_2\text{H}_3^+ + \text{H}_2 + \text{H}$	-	0.49 ± 0.19	$3.5 \pm$
10	$\rightarrow \text{SiC}_2\text{H}_4^+ + \text{H}_2$	-	0.18 ± 0.07	$0.8 \pm$
11	$\rightarrow \text{SiC}_2\text{H}_5^+ + \text{H}$	-	0.89 ± 0.35	$2.6 \pm$
12	$\text{Si}^+ + \text{C}_2\text{H}_2 \rightarrow \text{SiC}_2\text{H}^+ + \text{H}$	-	1.8 ± 0.7	Not observed
13	$\text{SiH}^+ + \text{C}_2\text{H}_2 \rightarrow \text{SiC}_2\text{H}^+ + \text{H}_2$	-	1.5 ± 0.6	Not observed
14	$\rightarrow \text{SiC}_2\text{H}_2^+ + \text{H}$	-	1.7 ± 0.7	Not observed
15	$\text{SiH}_2^+ + \text{C}_2\text{H}_2 \rightarrow \text{SiC}_2\text{H}^+ + \text{H}_2 + \text{H}$	-	0.44 ± 0.17	Not observed
16	$\rightarrow \text{SiC}_2\text{H}_2^+ + \text{H}_2$	-	0.63 ± 0.25	Not observed
17	$\rightarrow \text{SiC}_2\text{H}_3^+ + \text{H}$	-	3.2 ± 1.2	11 ± 3
18	$\text{SiH}_3^+ + \text{C}_2\text{H}_2 \rightarrow \text{SiC}_2\text{H}^+ + 2\text{H}_2$	-	0.1 ± 0.04	Not observed
19	$\rightarrow \text{SiC}_2\text{H}_3^+ + \text{H}_2$	-	0.26 ± 0.10	Not observed

Figure Captions

- Fig. 1: Kinetic Energy Dependence of Reactions of SiH^+ with C_2H_2 .
(a) Dependence of Total Cross-section on Center-of-Mass Energy.
(b) Contribution of the Two Reaction Channels to the total cross-section on Center-of-Mass Energy. ● SiC_2H^+ ;
□ SiC_2H_2^+ .
- Fig. 2: Pressure Dependence of Relative Intensities of Major Siliconium Ions in a 90% SiH_4 - 10% C_2H_2 Mixture: ○ SiH_3^+ ; ● SiH_2^+ ;
△ Si_2H_4^+ ; X Si_2H_7^+ .
- Fig. 3: Pressure Dependence of Relative Intensities of Major Organosilicon Ions in a 90% SiH_4 - 10% C_2H_2 Mixture;
△ SiC_2H^+ ; SiC_2H_3^+ ; SiC_2H_5^+ .
- Fig. 4: High pressure spectra of major ions in a SiH_4 -10% C_2H_2 mixture. Similarity of the ion intensity patterns for the mass regions 53-63, and 79-89 suggests reaction by association with an acetylene molecule.

References

1. U. S. Atomic Energy Commission Document No. COO-3416-14.
2. D. P. Beggs and F. W. Lampe, J. Phys. Chem. 73, 3307 (1969).
3. V. L. Tal'roze and E. L. Frankevich, Zhur. Fiz. Khim. 34, 2709 (1960).
4. C. W. Hand and H. von Weyssenhoff, Can. J. Chem. 42, 195 (1964).
5. G. G. Hess and F. W. Lampe, J. Chem. Phys. 44, 2257 (1966).
6. D. P. Beggs and F. W. Lampe, J. Phys. Chem. 73, 4194 (1969).
7. G. W. Stewart, J. M. S. Henis, and P. P. Gaspar, J. Chem. Phys. 57, 1990 (1972).
8. T. M. H. Cheng, Tung-Yang Yu, and F. W. Lampe, J. Phys. Chem. 77, 2587 (1973).
9. Tung-Yang Yu, T. M. H. Cheng, V. Kempter and F. W. Lampe, J. Phys. Chem. 76, 3321 (1972).
10. T. M. H. Cheng and F. W. Lampe, Chem. Phys. Letts. 19, 532 (1973).
11. W. Ando and S. Oae, Bull. Chem. Soc. Japan 35, 1540 (1962).
12. P. Potzinger and F. W. Lampe, J. Phys. Chem. 73, 3912 (1969); 74, 719 (1970).
13. J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Drexler, and F. H. Field, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand., No. 26 (June 1969).
14. T. M. H. Cheng and F. W. Lampe, J. Phys. Chem. 77, 2841 (1973).
15. A. G. MacDiarmid, Adv. in Inorg. and Radiochem. 3, 216 (1961).
16. E. A. V. Ebsworth, Volatile Silicon Compounds, Pergamon Press, London, 1963 p. 16.
17. T. M. Mayer and F. W. Lampe, J. Phys. Chem. (Submitted).
18. G. Gioumousis and D. P. Stevenson, J. Chem. Phys. 29, 294 (1958).
19. D. Hyatt and K. Lacmann, Z. Naturforsch. 23a, 2080 (1968).
20. D. P. Beggs and F. W. Lampe, J. Phys. Chem. 73, 3315 (1969).
21. M. S. B. Munson, J. Phys. Chem. 69, 572 (1965).
22. G. A. Derwish, A. Galli, A. Giardini-Guidoni, and G. G. Volpi, J. Am. Chem. Soc., 87, 1159 (1965).
23. J. H. Futrell and T. O. Tiernan, J. Phys. Chem. 72, 158 (1968).

References (Continued) -

24. S. C. Lind, D. C. Bardwell, and J. W. Perry, J. Am. Chem. Soc. 48, 1556 (1926).
25. D. G. White and E. G. Rochow, J. Am. Chem. Soc. 76, 3897 (1954).
26. G. Rabilloud, Bull. Soc. Chim. France, 2152 (1965).
27. J. F. Schmidt and F. W. Lampe, J. Phys. Chem. 73, 2706 (1969).

Fig. 2

Fig. 3

Fig. 3

Relative Abundance

Fig. 7