ION-MOLECULE REACTIONS IN MONOSILANE-ETHYLENE MIXTURES¹

by

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MASTERAbstract

The reactions of Si^+ , SiH^+ , SiH_2^+ and SiH_3^+ with C_2H_4 and the reactions of C_2H_2^+ , C_2H_3^+ and C_2H_4^+ with SiH_4 have been studied by tandem and high-pressure mass spectrometry. Phenomenological rate constants have been measured at a reactant ion kinetic energy of 1.4 eV in the laboratory system and reaction cross-sections have been studied over the range of 0.4 to 3.0 eV in the center-of-mass system. A persistent or "sticky" complex SiC_2H_7^+ is observed in collisions of SiH_3^+ with C_2H_4 with a cross-section that decreases to zero at a center-of-mass energy of 1.3 eV. Formation of this complex in bimolecular reactions is confirmed in the high-pressure mass spectrometric studies. It further is shown that at higher pressures the complex SiC_2H_7^+ successively adds two more molecules of C_2H_4 and it is suggested that all these adducts have the ultimate form of alkylsiliconium ions, namely $\text{C}_2\text{H}_5\text{SiH}_2^+$, $(\text{C}_2\text{H}_5)_2\text{SiH}^+$, and $(\text{C}_2\text{H}_5)_3\text{Si}^+$.

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Introduction

A previous study² of ion-molecule reactions in the $\text{SiH}_4\text{-C}_2\text{H}_4$ system was carried out at pressures below 5×10^{-3} torr in a single source mass spectrometer system, relying principally on appearance potential measurements of product ions for reaction identification. In-as-much as more recent reports³⁻⁵ of ion-molecule reactions in similar systems have demonstrated that the application of such techniques to complex systems involving more than one neutral reactant leads to a very incomplete picture of the ionic chemistry of the system, a reinvestigation of the $\text{SiH}_4\text{-C}_2\text{H}_4$ system was felt to be warranted. Accordingly we have conducted studies of the ion-molecule reactions in this system using both tandem mass spectrometry and high-pressure mass spectrometry up to about 0.3 torr. This paper constitutes a report of our findings.

Experimental

The tandem mass spectrometer, which has been described previously,⁶ consists of two quadrupole mass filters, separated by a collision chamber and ion lenses, mounted in an "in-line" configuration. It permits the injection of mass-selected reactant ions, having kinetic energies variable down to about 1 eV, into the collision chamber containing the reactant molecule and mass-analysis of the product ions emerging from the collision chamber. Retarding field measurements show the energy spread of the reactant ion beam to be generally about 1 eV, but dependent on the cleanliness (past history) of the ion-source.

Relative cross-sections of the various ion-molecule reactions were studied as a function of collision energy in the range of 0.4-3 eV. As described previously^{4,7}, the shapes of the cross-

section versus energy curves were used to differentiate between exothermic and endothermic processes. Phenomenological rate constants and cross-sections of the various reactions were determined by direct comparison of relative cross-sections for 1.4 eV (LAB) reactant ions with the cross-sections for reactions (1) and (2), viz.

the rate constants of which have been previously determined.⁴ Collision chamber pressures of the order of 1×10^{-3} torr and ionization chamber pressures of the order of $1-5 \times 10^{-3}$ torr were used.

The high-pressure-mass-spectrometric experiments were carried out in a Nuclide Associates 12-90G sector-field mass spectrometer⁶. In these experiments the ionic abundances in a mixture containing 10% C_2H_4 were measured over the pressure range of 0.02 - 0.3 torr. The energy of the ionizing electron beam was 100 eV, the trap current was very small and not measured, and the ion-accelerating potential was 2500 V. In all experiments the ion-exit energy from the source was 1.9 eV and the ion-source temperature was 100°C. Ion-source pressures were measured with a Granville-Phillips capacitance manometer that was calibrated against a McCleod gauge, which in turn was checked by measurement of the known pressure-dependent formation of CH_5^+ in CH_4 . We estimate our source pressure to be accurate to $\pm 10\%$.

Monosilane, purchased from the Matheson Company, was purified by fractionation on a vacuum line prior to use. The ethylene was Phillips Research Grade and was used as received.

Results and Discussion

1. Nature of the Elementary Reactions. The ion-molecule reactions in the $\text{SiH}_4\text{-C}_2\text{H}_4$ system found to be exothermic on the basis of the dependence of reaction cross-section on collision energy are shown in Table I. Also shown in Table I are standard enthalpy changes calculated from thermochemical data⁸⁻¹⁰ and phenomenological rate constants determined at 1.4 eV ion-kinetic energy in the laboratory system. For comparison, the rate constants reported previously² are shown in the last column of the table. In all cases except one, namely reaction (20), the neutral products are written arbitrarily as those that lead to maximum exothermicity. Reactions exhibiting rate constants below 10^{-11} cm^3/sec are not shown in the table.

Before proceeding to a discussion of the individual elementary reactions shown in Table I, we must first make the general observation that only qualitative agreement with the previous results of Beggs and Lampe² is obtained, and that only for the cases of what would be the major reactant ions in an equimolar mixture, namely SiH_2^+ , C_2H_2^+ and C_2H_4^+ . This is not surprising when one considers the complexity of this system, with respect to ion-molecule reactions, and the fact that Beggs and Lampe² used a single-source mass spectrometer at pressures below 5×10^{-3} torr with almost complete reliance on appearance potentials and energetics for reaction identification. The comparison makes it clear that these more primitive techniques are quite inadequate for a quantitative study of a system containing two components when both are more complex than diatomic molecules, and we must conclude that our present results supercede those of the earlier report of Beggs and Lampe.²

Secondly, we may point out once again the pre-eminence of hydride ion transfer processes leading to formation of SiH_3^+ , a phenomenon that has proven to be quite general when gaseous systems containing SiH_4 are subjected to the passage of ionizing radiation.

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

(a) $\text{SiH}_3^+ + \text{C}_2\text{H}_4$. When SiH_3^+ ions are injected into the collision chamber containing C_2H_4 , SiC_2H_5^+ and SiC_2H_7^+ ions are formed via reactions (3) and (4) shown in Table I. In addition, very small amounts of SiC_2H_3^+ are also observed. Neither of the rate constants of (3) and (4) are particularly large and so we must conclude that most of the Langevin encounters of this pair ($k_L = 1.25 \times 10^{-9} \text{ cm}^3/\text{sec}$) revert to the original reactants. Nonetheless, these reactions are of considerable interest because in ionized mixtures containing a large excess of SiH_4 , the predominance of hydride ion transfer from SiH_4 insures that the SiH_3^+ ion will be the major ion leading to chemical conversion of the mixture.

The observation of (4) is of considerable interest in that the product of this reaction represents a persistent collision complex that contains all the atoms of the reactants. The observation of such persistent or "sticky" collision complexes is rather rare in ion-molecule reaction studies. The cross-section of (4) decreases rapidly with increasing collision energy, as shown in Figure 1, becoming apparently zero at a relative collision energy of 1.3 eV. Previous observations of persistent complexes¹¹⁻¹³ have been made in single-source mass spectrometers and mostly, but not always, have been made on systems having more vibrational degrees of freedom than SiC_2H_7^+ .

Many complexes of this sort have been observed as a result of stabilizing collisions taking place before the complex can decompose and it may be argued that the SiC_2H_7^+ we have observed is the product of such a third-order process. However, if we make this assumption we immediately run into a number of contradictions: (1) The magnitude of the third-order rate constant necessary to produce this product in the amounts observed in the high-pressure experiments would require that the lifetime of the complex be of the order of 5×10^{-5} sec, which is appreciably larger than the ion residence time in the collision chamber and is of the order of magnitude of the total flight time in the tandem instrument, i.e., it would be observed as a bimolecular product; (2) For a stabilization rate constant of about 10^{-10} $\text{cm}^3/\text{mole-sec}$, at 0.001 torr pressure the mean distance travelled by the complex between collisions is on the order of 50 cm which is considerably more than the 2.0 cm total path length of the collision cell; (3) To the best of our knowledge, no other collision complexes of this nature have been observed in tandem mass spectrometers under similar conditions of collision cell pressure and total flight time.

In light of these arguments we think it most unlikely that the SiC_2H_7^+ observed is the result of a third-order process, but indeed is the result of a bimolecular process giving a very long-lived complex.

A loosely bound collision complex in which the reactants retain essentially their original identities, i.e. $\text{C}_2\text{H}_4 \cdot \text{SiH}_3^+$, could not be expected¹⁴ to have a sufficient lifetime, relative to reversion to free reactants, to be detected in our system. In the absence of stabilizing collisions the reversion of a complex to reactants is always energetically feasible. However, if a chemical transformation

takes place leading to a complex whose dissociation to reactants is hindered mechanistically, sufficient lifetime for detection ($\sim 10^{-5}$ seconds in our apparatus) may well result. With this in mind we suggest that the formation of SiC_2H_7^+ as a persistent complex occurs via a concerted proton transfer and addition of $:\text{SiH}_2$ to the π -electron system of C_2H_4 , as shown by (29), viz.

In both the cyclic structure and linear structure it is the loss of the SiH_3^+ moiety that provides the proposed mechanistic hindrance towards dissociation to reactants that is necessary for the observation of SiC_2H_7^+ some 10^{-5} seconds after its formation. Of course, we do not know whether the cyclic structure or the linear structure is the correct description of the persistent complex. We write the cyclic structure as a possible intermediate in view of reports¹⁵⁻¹⁷ that singlet silylene radicals, (ground spin-state) react with unsaturates in a fashion analogous to that of singlet methylene. The position of protonation of the cyclic structure is assumed in view of recent calculations by Hariharan, Radom, Pople, and Schleyer,¹⁸ showing that corner-protonated cyclopropane is the most stable form of a protonated cyclopropane ring. Evidence for the linear structure in (29) comes from high-pressure mass spectrometric experiments, to be presented in a subsequent section, that indicate the rapid successive addition of three ethylene molecules to SiH_3^+ , forming presumably the stable $(\text{C}_2\text{H}_5)_3\text{Si}^+$ cation.

Regardless of whether the persistent complex is better represented by the cyclic structure or the linear one, the protonation and addition must be concerted since simple proton transfer from

SiH_3^+ to C_2H_4 is endothermic by 32 kcal/mole.^{9,10,19}

b) $\text{SiH}_2^+ + \text{C}_2\text{H}_4$. Reactions 5-8, shown in Table I, are observed to occur when SiH_2^+ ions are injected in C_2H_4 . The dependence of reaction cross-section on collision energy clearly shows that all reactions are exothermic, yet thermochemical calculations^{9,10} indicate that (5) should be endothermic by 14 kcal. These thermochemical calculations assume that SiCH_3^+ produced by the reaction of SiH_3^+ with C_2H_4 is the same species as one obtains from electron impact on CH_3SiH_3 , an assumption that may not be valid. Alternatively, it is possible that a significant fraction of the SiH_2^+ ions, formed by impact of 100 eV electrons on SiH_4 , contain sufficient internal energy to overcome the endothermicity. We cannot choose between the two alternatives on the basis of our data, but because the rate constant obtained is so large (and this is not typical of endothermic processes) we favor the idea that the SiCH_3^+ ion produced here is more stable than that formed by electron impact on CH_3SiH_3 and that the reaction observed is exothermic for ground-state reactants. We may note that the reaction is very efficient, some 85% of the Langevin encounters leading to products.

c) $\text{SiH}^+ + \text{C}_2\text{H}_4$. When SiH^+ ions react with C_2H_4 , SiC_2H_3^+ ions are formed in the exothermic process shown as reaction (9) in Table I; the reaction proceeds with a Langevin efficiency of ~20%. An endothermic process forming SiC_2H_2^+ is observed at higher energies, with the threshold of the reaction being of the order of 1 eV-center-of-mass.

d) $\text{Si}^+ + \text{C}_2\text{H}_4$. Si^+ ions react exothermically with C_2H_4 to form SiC_2H_3^+ as shown by (10) in Table I. The reaction has a very low efficiency with only ~5% of the Langevin encounters leading to

reaction products. In addition to (10), an apparently endothermic process with a threshold between 0.8 and 1.0 eV, center-of-mass, produces SiC_2H_2^+ .

e) $\text{C}_2\text{H}_4^+ + \text{SiH}_4$. Reactions 11-17 are observed as exothermic processes when C_2H_4^+ ions are injected into SiH_4 . The total reaction of C_2H_4^+ with SiH_4 is very rapid with ~100% of the calculated Langevin encounters leading to products. The predominant processes, namely some 94% of the total, involve the transfer of H, H_2^- , and H^- from SiH_4 , as shown by (11)-(13). This is quite typical of the reactions of hydrocarbon ions with silanes.^{4,5,7}

The ion, C_2H_5^+ , formed in (11), has the same m/e as SiH^+ but we choose C_2H_5^+ as the actual product observed at this m/e, since formation of SiH^+ would be endothermic by at least 70 kcal. Uncertainties in the standard enthalpies of formation of SiH_3 and SiH_2^+ could explain the fact that thermochemical computations indicate (11) to be endothermic by 8 kcal. Moreover, it is very possible for C_2H_4^+ to contain sufficient internal energy for (11) to be exothermic, if one does not consider the uncertainties in the thermochemical data. Uncertainties in the thermochemical data may easily account for the calculated endothermicity of (12) and (13).

The near-thermoneutral nature of (11)-(13), coupled with the large reaction rate constants and strong evidence of exothermicity from the dependence of cross-section on energy lead one immediately to the conclusion that the neutral products must be as written for any other set makes the ion formation very endothermic. This in turn leads to the mechanistic conclusion that (11)-(13) involve simple transfer from SiH_4 to C_2H_4^+ of H, H_2^- and H^- , respectively.

d) $\underline{C_2H_3^+} + SiH_4$. The only significant reactions of $C_2H_3^+$ with SiH_4 are those involving hydride ion transfer to form SiH_3^+ , as shown by (18) and proton transfer to form SiH_5^+ as shown by (19). That SiH_3^+ is not a dissociation product of SiH_5^+ , but rather is formed in a completely different reaction channel, has been demonstrated in other systems by deuterium-labelling experiments.^{4,20,21} In this system the reaction sequence consisting of (19) followed by (30), viz.

is endothermic by 16 kcal/mole, and would hence not be expected to yield SiH_3^+ with a rate constant as large as that shown in Table I.

e) $\underline{C_2H_2^+} + SiH_4$. The reaction of $C_2H_2^+$ with SiH_4 is described by (20) - (27) shown in Table I. The magnitude of the rate constants indicate a very efficient reaction with some 80% of the Langevin encounters leading to products. Again the system is dominated by H^- and H_2^- transfer leading to formation of SiH_3^+ and SiH_2^+ , respectively as shown by (22) and (23). The considerable uncertainty⁸ in the standard enthalpy of formation of SiH^+ is sufficient to account for the endothermicity of 8 kcal indicated by thermochemical calculations.

It is possible that the product of (20) is not Si^+ but rather $C_2H_4^+$, as these species have the same m/e. To produce $C_2H_4^+$ in an exothermic reaction would require a H_2 transfer process and since we have not often observed such processes but have often observed Si^+ formation in the reaction of hydrocarbon ions with SiH_4 , we favor (20).

With a few exceptions the rate constants for reaction of $C_2H_2^+$ with SiH_4 shown in Table I agree within experimental error with those determined previously for reactions of $C_2H_2^+$ formed by electron impact on acetylene.⁵ The few exceptions can easily be rationalized by the

possibility of greatly differing amounts of internal excitation contained in ions formed by electron impact on the two different molecules.

2. High-Pressure Mass Spectra

The abundances of the major ions in a mixture of SiH_4 and C_2H_4 containing 10% C_2H_4 as a function of ion-source pressure are shown in Figure 2. To fully appreciate the implication of the results shown in Figure 2 one must first note the major features of such a plot for pure SiH_4 .^{6,22}

In pure SiH_4 ,⁶ the abundance of SiH_3^+ increases with increasing source pressure until at 0.06 torr it passes through a maximum of about 50% of the total ionization. At pressures higher than 0.06 torr, Si_2H_7^+ , which is formed by termolecular association of SiH_3^+ with SiH_4 , increases in abundance and attains a maximum at 0.19 torr that represents about 35% of the total ionization. The SiH_2^+ abundance simply decays to very small values while Si_2H_4^+ , Si_2H_3^+ , and Si_2H_2^+ are the major secondary ions formed in bimolecular processes.

As shown in Figure 2 the addition of 10% of C_2H_4 has a large effect on this system. The maximum in SiH_3^+ , which is a result of hydride-transfer reactions, must lie in this system below 0.02 torr, (Figure 2a) a fact that reflects the much more rapid reaction of SiH_3^+ with C_2H_4 , as shown by (3) and (4) in Table I, as compared with the termolecular association with SiH_4 that is the sole depletion channel in pure SiH_4 . Consistent with this is the fact that, as shown in Figure 2b, m/e 59 comprising SiC_2H_7^+ and Si_2H_3^+ exhibits a larger initial slope (bimolecular rate constant) than Si_2H_4^+ (m/e 60), whereas in pure SiH_4 , the ratio of initial slopes

is $i_{59}/i_{60} = 0.41$.²² Correction of the initial slope of m/e 59 (Figure 2b) for formation of Si_2H_3^+ and use of the known rate constant for formation of Si_2H_4^+ leads to a bimolecular rate constant of 1.6×10^{-10} for formation of SiC_2H_7^+ via (4). Considering the lower average energy of reactant ions in the high-pressure studies as compared with the tandem studies (0.7 eV vs. 1.4 eV) and the strong dependence of the cross-section of (4) on energy, one must consider this agreement as satisfactory. The product of the competing reaction of SiH_3^+ , namely Si_2H_7^+ , attains a maximum abundance of only 5% in the mixture as opposed to 35% in pure SiH_4 , again underscoring the rapidity of (4) relative to termolecular association.

Comparison of Figures 2b and 2c shows that with increasing pressure the maximum and the subsequent decay of SiC_2H_7^+ is accompanied by formation of $\text{SiC}_4\text{H}_{11}^+$ and $\text{SiC}_6\text{H}_{15}^+$, produced by the processes shown as (31) and (32), viz.

As shown in Figure 3 the species SiC_2H_7^+ , $\text{SiC}_4\text{H}_{11}^+$, and $\text{SiC}_6\text{H}_{15}^+$ become, successively, the most abundant species in the system and completely dominate the m/e patterns in their respective mass groups, which is an expected feature of alkylsiliconium ions. An ion of m/e 143, which could be $\text{SiC}_8\text{H}_{19}^+$, is observed at the higher pressures but this ion never becomes the dominating one in its mass group as do the former three species; moreover, there are essentially no ions of m/e less than 143. We believe, therefore, that the ultimate ion products of (4), (31) and (32) are ethyl siliconium ions formed by the sequence shown below, which may proceed via protonated cyclic

intermediates:

Such a sequence would be expected to stop at the triethylsiliconium ion, since further addition of ethylene would destroy the siliconium ion center leading to a less stable ionic species. This mechanism receives some additional support from the observation that ethylsilane and diethylsilane are formed via non-free-radical processes in the radiolysis of SiH_4 - C_2H_4 mixtures.²²

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TABLE I

EXOTHERMIC ION-MOLECULE REACTIONS IN SiH_4 - C_2H_4 MIXTURES

For 1.4 eV (LAB) REACTANT IONS

Reaction No.	Reaction	ΔH° kcal.	$k \times 10^{10}$ (cm^3/sec)	
			This Work	Reference 2
3	$\text{SiH}_3^+ + \text{C}_2\text{H}_4 \rightarrow \text{SiC}_2\text{H}_5^+ + \text{H}_2$	-	0.67 ± 0.20	Not detected
4	$\rightarrow \text{SiC}_2\text{H}_7^+$	-	0.78 ± 0.23	Not detected
5	$\text{SiH}_2^+ + \text{C}_2\text{H}_4 \rightarrow \text{SiCH}_3^+ + \text{CH}_3$	+14	4.8 ± 1.4	4.2 ± 1.1
6	$\rightarrow \text{SiC}_2\text{H}_3^+ + \text{H}_2 + \text{H}$	-	2.6 ± 0.8	0.3 ± 0.08
7	$\rightarrow \text{SiC}_2\text{H}_4^+ + \text{H}_2$	-	2.4 ± 0.8	0.2 ± 0.05
8	$\rightarrow \text{SiC}_2\text{H}_5^+ + \text{H}$	-	1.0 ± 0.3	Not detected
9	$\text{SiH}^+ + \text{C}_2\text{H}_4 \rightarrow \text{SiC}_2\text{H}_3^+ + \text{H}_2$	-	2.8 ± 0.8	Not detected
10	$\text{Si}^+ + \text{C}_2\text{H}_4 \rightarrow \text{SiC}_2\text{H}_3^+ + \text{H}$	-	0.74 ± 0.20	Not detected
11	$\text{C}_2\text{H}_4^+ + \text{SiH}_4 \rightarrow \text{C}_2\text{H}_5^+ + \text{SiH}_3$	+8	5.1 ± 1.5	Not detected
12	$\rightarrow \text{SiH}_2^+ + \text{C}_2\text{H}_6$	+1	2.0 ± 0.7	8.7 ± 2.2
13	$\rightarrow \text{SiH}_3^+ + \text{C}_2\text{H}_5$	+3	6.2 ± 2.0	Not detected
14	$\rightarrow \text{SiC}_2\text{H}_4^+ + 2\text{H}_2$	-	0.11 ± 0.03	0.7 ± 0.2
15	$\rightarrow \text{SiC}_2\text{H}_5^+ + \text{H}_2 + \text{H}$	-	0.11 ± 0.03	Not detected
16	$\rightarrow \text{SiC}_2\text{H}_6^+ + \text{H}_2$	-	0.24 ± 0.08	2.1 ± 0.5
17	$\rightarrow \text{SiC}_2\text{H}_7^+ + \text{H}$	-	0.33 ± 0.10	Not detected
18	$\text{C}_2\text{H}_3^+ + \text{SiH}_4 \rightarrow \text{SiH}_3^+ + \text{C}_2\text{H}_4$	-21	2.5 ± 0.8	Not detected
19	$\rightarrow \text{SiH}_5^+ + \text{C}_2\text{H}_2$	-1	0.34 ± 0.11	Not detected

Table I Continued...

Reaction No.	Reaction	ΔH° kcal.	$k \times 10^{10}$ (cm ³ /sec)	
			This Work	Reference 2
20	$C_2H_2^+ + SiH_4 \rightarrow Si^+ + C_2H_4 + H_2$	-15	0.69±0.15	Not detected
21	$\rightarrow SiH^+ + C_2H_5$	+8	0.46±0.14	Not detected
22	$\rightarrow SiH_2^+ + C_2H_4$	-30	1.7±0.5	14±4
23	$\rightarrow SiH_3^+ + C_2H_3$	-21	7.3±2.3	Not detected
24	$\rightarrow SiCH_3^+ + CH_3$	-16	0.22±0.07	2.1±0.5
25	$\rightarrow SiC_2H^+ + 2H_2 + H$	-	0.10±0.04	Not detected
26	$\rightarrow SiC_2H_3^+ + H_2 + H$	-	0.44±0.13	1.1±0.3
27	$\rightarrow SiC_2H_5^+ + H$	-	0.16±0.05	2.0±0.5

Figure Captions

Figure 1: Dependence of Cross-section for SiC_2H_7^+ Formation on Kinetic Energy of SiH_3^+ . Open and closed circles represent replicate experiments conducted two months apart.

Figure 2: Relative Abundances of Major Ions in a 90:10 $\text{SiH}_4:\text{C}_2\text{H}_4$ Mixture as a Function of Ion-source Pressure.
(a) Δ SiH_3^+ ; $\odot$ SiH_2^+ . (b) Δ Si_2H_4^+ ; $\odot$ SiC_2H_7^+ + Si_2H_3^+ .
(c) Δ $\text{SiC}_4\text{H}_{11}^+$; $\odot$ Si_2H_7^+ ; $\square$ $\text{SiC}_6\text{H}_{15}^+$.

Figure 3: Patterns of Selected Mass Groups as a Function of Ion-Source Pressure.

Fig. 1

Fig. 2

Fig. 3