Ion–Molecule Reactions in Monosilane–Benzene Mixtures. Long-Lived Collision Complexes[1]

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Abstract: The principal ion–molecule reactions of SiH_4–C_6H_6 mixtures have been identified and the reaction cross sections measured as functions of ion kinetic energy and of neutral molecule density. SiH_3^+, SiH^+, and Si^+ form energy-rich collision complexes with C_6H_6 that are observed directly at the detector of a tandem mass spectrometer. It is shown that these energy-rich collision complexes have mean lifetimes of about 8 μs. The complexes can be collisionally stabilized by increasing the pressure so that the abundances of the simple adduct ions approach 60–70% of the total ionic product. The addition of SiH_3^+ to C_6H_6 appears to follow a mechanism that is completely analogous to that proposed for the addition of carbonium ions to aromatics. Deuterium labeling studies show that the $SiC_6H_7^+$ formed in this reaction is better described by a benzyl-type structure, $C_6H_5SiH_2^+$, than by a seven-membered ring analogous to the tropylium ion. SiH_2^+ does not form a complex with C_6H_6 of sufficient lifetime for it to reach the detector, but undergoes principally exothermic charge transfer. Ions derived from C_6H_6 do not react extensively with SiH_4, but the principal reaction of all such ions is to abstract an H^- ion to form SiH_3^+.

On the basis of a previous study in this laboratory of ion-molecule reactions in SiH_4–C_6H_6 mixtures, it was reported[2] that internally excited $C_6H_6^+$ ions underwent a number of reactions with SiH_4, but that reactions of Si^+, SiH^+, SiH_2^+, and SiH_3^+ with C_6H_6 could not be detected. This previous study[2] was conducted in a mass spectrometer at ion-source pressures below 5×10^{-3} Torr, with reaction identification relying principally on the measurement of appearance potentials of the product ions. Since more recent reports[3-6] of ion-molecule reactions in similar systems have demonstrated the inadequacy of such apparatus and techniques for the study of complex systems involving more than one neutral reactant, a reinvestigation of the SiH_4–C_6H_6 was felt to be warranted. Accordingly, we have carried out a new study using tandem mass spectrometric techniques which avoid many of the ambiguities inherent in the previous work.[2]

The present results are in qualitative agreement with the earlier study[2] only with regard to the identification of the major products of ionized SiH_4–C_6H_6 mixtures. The earlier conclusions that Si-containing ions are unreactive toward C_6H_6 and that all ion–molecule reactions between SiH_4 and C_6H_6 are to be attributed solely to reaction of internally excited $C_6H_6^+$ ions with SiH_4 are incorrect. This paper constitutes a report of our reinvestigation of ion–molecule reactions in this system.

Experimental Section

The chemical reactions taking place when ions derived from electron impact on C_6H_6 collide with SiH_4 and ions from SiH_4 collide with C_6H_6 were studied in a tandem mass spectrometer. This apparatus, which has been described previously,[5] consists of two quadrupole mass filters mounted in an "in-line" configuration and separated from each other by a collision chamber and ion lenses. It permits the injection of mass-selected ions, having kinetic energies variable down to about 1 eV, into a collision chamber containing the reactant molecule. Product ions scattered in the forward direction are collected with an acceptance angle of ~10° and mass analyzed. Ion intensity measurements were made with a Bendix Model 4700 continuous-dynode electron multiplier.

The energy of the ionizing electron beam in the ion source was 85 eV and the trap currents used were in the range of 10–20 μA. The pressure of target gas in the collision chamber was measured with a CGS Barocel capacitance manometer. The reactant ion beam entering the collision chamber was found by retarding field measurements to have an energy spread of about 1 eV (full width at half-maximum).
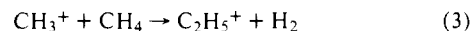
Reaction cross sections were calculated from the relationship given in the equation

$$\sigma = \gamma I_s / I_p n l \qquad (1)$$

in which I_p and I_s are the multiplier currents due to primary and secondary ions, respectively, n is the number density of gas molecules in the collision chamber, l is the length of the collision chamber (1.0 cm), and γ is an instrumental calibration factor which takes into account different detection efficiencies of primary and secondary ions. For reactions in which very little momentum may be transferred from the primary ions to the product ions, such as exothermic hydride ion transfer,[7] γ (at 1 eV) was determined from the reaction ($\sigma = 47 \pm 14$ Å^2)[3,4]

$$CH_3^+ + SiH_4 \rightarrow SiH_3^+ + CH_4 \qquad (2)$$
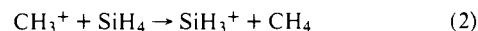
to be 1.4. For endoergic reactions and those of sufficient complexity to require that considerable momentum be transferred to product ions, γ was determined from the reaction ($\sigma = 33 \pm 4$ Å^2)[8-12]

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 \qquad (3)$$

to be 1.2. We believe the reaction cross sections reported to be accurate to within ±30%.

Monosilane was purchased from the J. T. Baker Chemical Co. It was subjected to several freeze-pump-thaw cycles, stored, and checked mass spectrometrically for satisfactory purity before use. Monosilane-d_4 was prepared from silicon tetrachloride (Peninsular Chem-Research, Inc.) by reduction with an excess of lithium aluminum deuteride.[13] It too was checked mass spectrometrically for satisfactory purity before use. The benzene used was Baker Analyzed Reagent, spectrophotometric grade. Except for degassing by freeze-pump-thaw cycles on the vacuum line it was used as received.

Results

Cross sections for formation of the various product ions in collisions of Si^+, SiH^+, SiH_2^+, and SiH_3^+ (at 1 eV of kinetic energy in the laboratory frame of reference) with C_6H_6 at ambient temperature (20 °C) are shown in Table I. Similarly, cross sections for formation of product ions in collisions of 1-eV $C_4H_2^+$, $C_4H_3^+$, $C_4H_4^+$, $C_6H_5^+$, and $C_6H_6^+$ ions with SiH_4 are shown in Table II. The cross sections in these tables have been corrected for the naturally occurring isotopes of ^{13}C (1.1%), ^{29}Si (4.7%), and ^{30}Si (3.1%).

It is apparent from Tables I and II that the major ionic products of ionized SiH_4–C_6H_6 mixtures that do not appear in the respective ionized pure compounds are those having m/e values in the range of 105–109, i.e., $SiC_6H_x^+$ ($x = 5$–9). This observation is in agreement with the previous report.[2] However, the product ions in the 105–109 m/e range are formed by reactions of Si-containing ions with C_6H_6 and this fact is a direct contradiction of the earlier reaction identification.[2] It must be

Table I. Reactions of Silicon-Containing Ions[a] with C_6H_6[b]

Reactant ion	Cross section in Å² for formation of product ion of m/e								
	78	79	81	83	105	106	107	108	109
Si^+	4.6				3.8	7.4			
SiH^+	14	2.2	3.6		6.6	1.4	6.7		
SiH_2^+	75	6.0			2.6	33	18		
SiH_3^+	8.0	1.5	2.8	1.0			8.6		18

[a] Reactant-ion energy of 1.0 eV in the laboratory frame of reference. [b] Collision chamber pressure of 1.0×10^{-3} Torr.

Table II. Reactions of Ions Derived from C_6H_6[a] with SiH_4[b]

Reactant ion	Cross section in Å² for formation of product ion of m/e											
	31	33	39	42	43	52	53	54	55	56	57	67
$C_4H_2^+$	8.9			1.6	2.0		2.8	3.9	6.5	2.2	0.2	3.4
$C_4H_3^+$	5.6	0.6			1.1			0.1	2.3		2.1	0.2
$C_4H_4^+$	1.4			0.6	1.2				1.2	2.3	0.5	0.5
$C_6H_5^+$	9.6				0.3							
$C_6H_6^+$	3.8		0.2			0.5						

[a] Reactant-ion energy of 1.0 eV in the laboratory frame of reference. [b] Collision chamber pressure of 1.0×10^{-3} Torr.

Table III. Reactions of Deuterated Si Ions[a] with C_6H_6[b]

Reactant ion	Cross section in Å² for formation of product ion of m/e										
	78	79	80	105	106	107	108	109	110	111	112
SiD^+	c	c		3.9	4.8	2.7	5.5				
SiD_2^+	c	c	1.6	1.1	12	17	23	17			
SiD_3^+	9.2	2.8	1.6			1.1	3.2	26	6.3	5.2	27

[a] Reactant-ion energy of 1.0 eV in the laboratory frame of reference. [b] Collision chamber pressure of 1.0×10^{-3} Torr. [c] Not measured.

concluded that the reaction identification of the earlier study[2] was incorrect and represents another example[3-6] of the unreliability of product-ion appearance potentials for the identification of ion–molecule reactions in systems containing two or more neutral reactants.

The most striking feature of the results shown in Table I is the detection of the ions of m/e 106, 107, and 109 in collisions of Si^+, SiH^+, and SiH_3^+, respectively, with C_6H_6. Since these ions represent $SiC_6H_6^+$, $SiC_6H_7^+$, and $SiC_6H_9^+$, respectively, they are simply adducts containing all the atoms of the colliding particles. Such direct detection of collision adducts or complexes is rare in beam studies, there being to our knowledge only two prior reports in the literature.[5,14] In addition to adduct formation, charge exchange to yield $C_6H_6^+$ (m/e 78) is another probable reaction of Si-containing ions with C_6H_6.

Significantly less reaction occurs when ions derived from C_6H_6 are injected into SiH_4 (Table II). The predominance of SiH_3^+ (m/e 31) as a product ion in these collisions is as expected, though, on the basis of previous reports of the tendency of SiH_4 toward H^- transfer to attacking positive ions.[3,4,15]
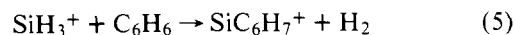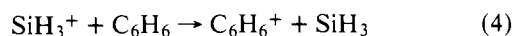
Table III shows the cross sections for formation of various product ions in collisions of SiD^+, SiD_2^+, and SiD_3^+ ions with C_6H_6. As with the data in Tables I and II these cross sections have been corrected for the naturally occurring isotopes of carbon and silicon. In calculating these corrected cross sections from the primary data it has been assumed that the fraction of total reaction of a given SiD_x^+ ion that yields products in the range of m/e 105–112 is the same as that for the corresponding SiH_x^+ ion. While this assumption is surely a reasonable one, its use must result in a greater uncertainty being assigned to the cross sections in Table III as compared with the cross sections in Tables I and II. A conservative estimate is that the cross sections in Table III are accurate with ±50%.

The effects of pressure and reactant-ion energy on the distributions of major products of collisions of Si-containing ions with C_6H_6 are shown in Figures 1–4. Reaction cross sections as functions of the energy of the reactant ions are shown in Figure 5. In view of the significantly lower reaction probabilities, detailed measurements of the pressure and energy dependencies of the reactions of ions derived from C_6H_6 with SiH_4 were not carried out. A few measurements of the energy dependence of the cross section for hydride transfer from SiH_4 to $C_6H_6^+$ showed typical exothermic behavior.[4,16]

Discussion

A. Nature of the Elementary Reactions. While some of the general features of the results have been remarked upon earlier, in this section we discuss the nature of the individual elementary reactions that take place when Si-containing ions collide with benzene.

1. SiH_3^+ + C_6H_6. As shown in Table I the major products of the reaction of SiH_3^+ ions of 1-eV kinetic energy with C_6H_6 are ions having m/e values of 78, 107, and 109, and the processes involved are clearly those shown by the reactions

$$SiH_3^+ + C_6H_6 \rightarrow C_6H_6^+ + SiH_3 \qquad (4)$$

$$SiH_3^+ + C_6H_6 \rightarrow SiC_6H_7^+ + H_2 \qquad (5)$$

$$SiH_3^+ + C_6H_6 \rightarrow SiC_6H_9^+ \qquad (6)$$

respectively. The charge-transfer reaction (eq 4) is endothermic[17,18] for ground-state ions by 19 kcal. As shown by Figures 1b and 5a the energy dependence of the cross section of eq 4 is in accord with the process being endothermic. The absence of an energy threshold for $C_6H_6^+$ formation in Figure 1b is to be attributed to contributions from the fast exothermic charge
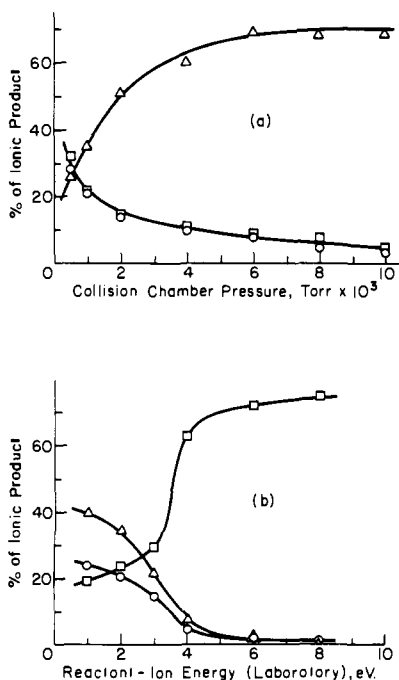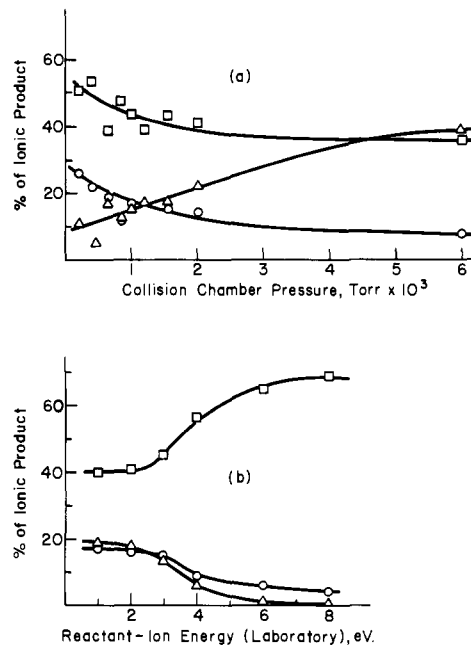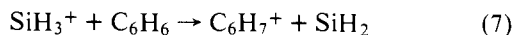
Figure 1. $SiH_3^+ + C_6H_6$ reaction. Dependence of major product distribution on (a) collision chamber pressure and (b) kinetic energy of reactant ions: □ $C_6H_6^+$; ⊙ $SiC_6H_7^+$; △ $SiC_6H_9^+$.
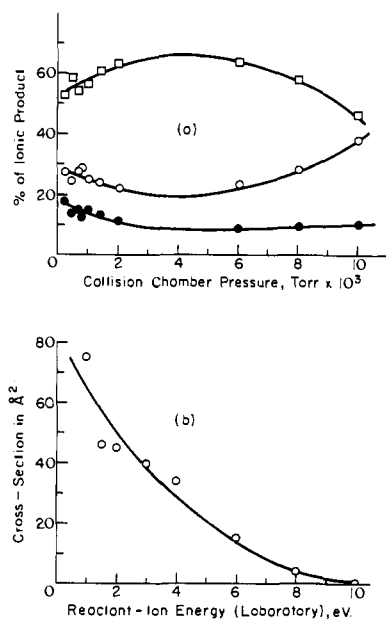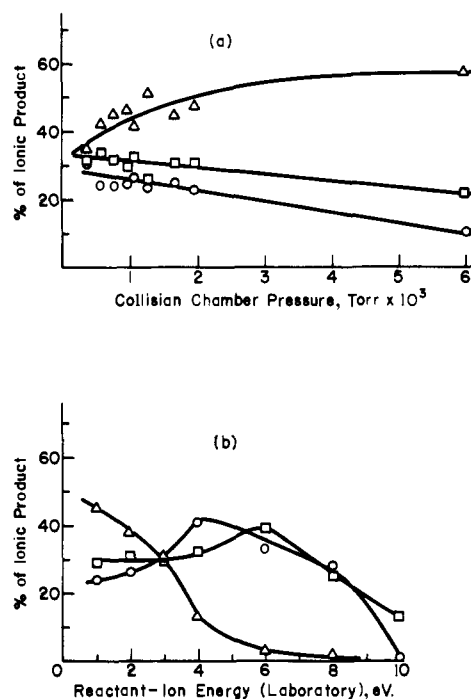

Figure 2. $SiH_2^+ + C_6H_6$ reaction. (a) Dependence of major product distribution of collision chamber pressure: □ $C_6H_6^+$; ⊙ $SiC_6H_6^+$; ● $SiC_6H_7^+$. (b) Dependence of charge exchange cross section (eq 11) on kinetic energy of reactant ions.

Figure 3. $SiH^+ + C_6H_6$ reaction. Dependence of major product distribution on (a) collision chamber pressure and (b) kinetic energy of reactant ions: □ $C_6H_6^+$; ⊙ $SiC_6H_5^+$; △ $SiC_6H_7^+$.
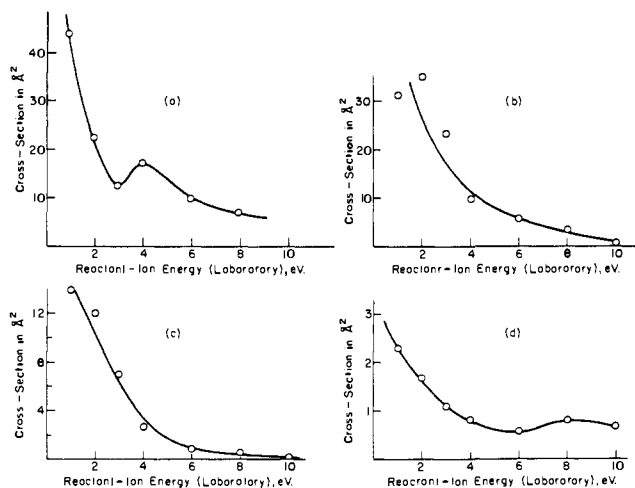

Figure 4. $Si^+ + C_6H_6$ reaction. Dependence of major product distribution on (a) collision chamber pressure and (b) kinetic energy of reactant ions: □ $C_6H_6^+$; ⊙ $SiC_6H_5^+$; △ $SiC_6H_6^+$.

transfer from $^{29}SiH_2^+$ (for which corrections below 1 eV could not be made) and to the presence of internally excited SiH_3^+ in the beam. On the basis of the energy dependence of the respective reaction cross sections, reactions 5 and 6 are exothermic processes.

Minor products of the reaction are ions with m/e values of 79, 81, and 83, as may be seen in Table I. On the basis of the appearance of m/e 80 when SiD_3^+ is substituted for SiH_3^+ (Table III) we conclude that m/e 79 is $C_6H_7^+$ formed by the proton-transfer reaction depicted by the reaction

$$SiH_3^+ + C_6H_6 \rightarrow C_6H_7^+ + SiH_2 \qquad (7)$$

The dependence of the cross section of eq 7 on kinetic energy is consistent with available thermochemical data[17-21] that indicate eq 7 to be about thermoneutral. The formation of the products having m/e 81 and 83 are best described by the reactions

$$SiH_3^+ + C_6H_6 \rightarrow SiC_4H_5^+ + C_2H_4 \qquad (8)$$

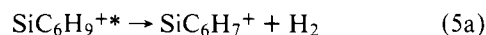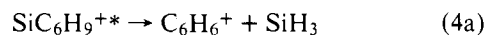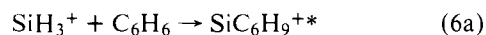$$SiH_3^+ + C_6H_6 \rightarrow SiC_4H_7^+ + C_2H_2 \qquad (9)$$

respectively. The dependence of the cross sections on kinetic energy indicate that reactions 8 and 9 are both exothermic processes.

Figure 5. Dependence of reaction cross sections on kinetic energy of reactant ions: (a) $SiH_3^+ + C_6H_6 \rightarrow$ products; (b) $SiH^+ + C_6H_6 \rightarrow$ products; (c) $Si^+ + C_6H_6 \rightarrow$ products; (d) $C_6H_6^+ + SiH_4 \rightarrow SiH_3^+ + C_6H_7$.

The direct observation of $SiC_6H_9^+$ (m/e 109) at the detector is of major interest because it means that this adduct, or complex, of the reactants survives the 2×10^{-5}-s flight from the collision chamber. As shown in Figure 1a, increasing the pressure of C_6H_6 in the collision chamber for 1-eV SiH_3^+ ions increases the abundance of the $SiC_6H_9^+$ ion to 70% of the total product. Clearly this pressure effect is to be attributed to collisional stabilization of the energy-rich adducts, or complexes, initially formed. In the absence of such stabilization the $SiC_6H_9^+$ ions must contain all the energy of reaction and the relative kinetic energy of reactants as internal energy, and an appreciable fraction decomposes during the flight to the detector. The data in Figure 1a suggest (and it has been confirmed in a number of other pressure dependence studies of this system) that in the extrapolated limit of zero pressure, i.e., no collisional stabilization, an appreciable fraction of the energy-rich complexes reaches the detector and therefore has lifetimes in excess of 2×10^{-5} s. The increase in relative abundance of $SiC_6H_9^+$ due to pressure stabilization is accompanied by a concomitant decrease in the other ionic products, as shown in Figure 1a for $C_6H_6^+$ (m/e 107).
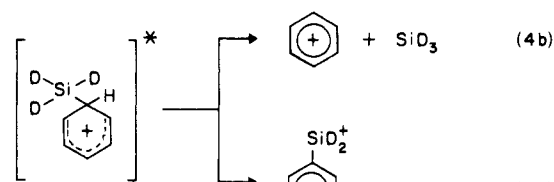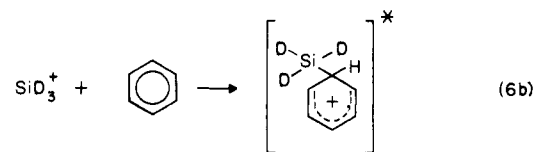
The effect on product distribution of increasing the relative kinetic energy of the reactants (i.e., internal energy of the adduct) for a C_6H_6 pressure of 1.0×10^{-3} Torr is shown in Figure 1b. In accord with the conclusion that $SiC_6H_9^+$ (m/e 109) is an energy-rich complex, the abundance of this ionic product falls rapidly with increasing energy. The relative abundance of the decomposition product $SiC_6H_7^+$ (m/e 107) falls less rapidly, while the relative abundance of $C_6H_6^+$ (m/e 78) increases sharply to over 70% of the product. This behavior is completely consistent with the following mechanistic scheme,

$$SiH_3^+ + C_6H_6 \rightarrow SiC_6H_9^{+*} \qquad (6a)$$

$$SiC_6H_9^{+*} \rightarrow C_6H_6^+ + SiH_3 \qquad (4a)$$

$$SiC_6H_9^{+*} \rightarrow SiC_6H_7^+ + H_2 \qquad (5a)$$

$$SiC_6H_9^{+*} + C_6H_6 \rightarrow SiC_6H_9^+ + C_6H_6 \qquad (10)$$

in which all ions shown, including both energy-rich and collisionally stabilized $SiC_6H_9^+$ ions, are registered at the detector. Other ionic products not shown in Figure 1 also arise from unimolecular decomposition of $SiC_6H_9^{+*}$.

Further insight into the reaction mechanism can be obtained by considering the product distribution of the reaction of SiD_3^+ ions with C_6H_6. These data, in terms of cross sections, are

shown in Table III for 1.0-eV SiD_3^+ ions and 1.0×10^{-3} Torr of C_6H_6. The ion at m/e 80 is accounted for entirely by $C_6H_6D^+$ formed by the D^+ transfer process analogous to reaction 7. This means that the benzene ion product (m/e 78 and 79) is comprised of 77% $C_6H_6^+$ and 23% $C_6H_5D^+$, respectively. The ionic product formed by loss of molecular hydrogen from the energy-rich complex, i.e., the ionic product of reaction 5, appears in this case at m/e 108, 109, and 110, corresponding to loss of D_2, HD, and H_2. Neglecting any possible contribution to m/e 110 by loss of a D atom, the data in Table III indicate that at least 73% of the product appears at m/e 109, i.e., corresponds to loss of HD from the energy-rich complex. These facts suggest that the SiD_3^+ ion retains to a very large extent its chemical identity in the complex and, further, that very little exchange of deuterium with the hydrogen atoms of the benzene ring takes place. Simple rupture of the Si–C bond leads to charge transfer (eq 4), while a 1,2-molecular hydrogen elimination forms the phenylsilyl ion. The reaction therefore appears to occur in a completely analogous manner to the classical addition of carbonium ions to aromatics,[22] and the mechanism proposed for major product formation is shown by eq 6b, 4b, and 5b. The energy-rich adduct is thus indicated to be a dienyl-type cation[22] characteristic of such ionic additions in liquid-phase organic chemistry. The benzyl-type structure of the product ion of reaction 5b has been previously proposed in studies of the electron-impact ionization of phenylsilane.[23]

$$SiD_3^+ + \text{(benzene)} \rightarrow \left[\begin{array}{c} D\text{-Si-D} \\ D \quad H \\ (+) \end{array} \right]^* \qquad (6b)$$

$$\left[\begin{array}{c} D\text{-Si-D} \\ D \quad H \\ (+) \end{array} \right]^* \rightarrow \text{(benzene)}^+ + SiD_3 \qquad (4b)$$

$$\rightarrow \text{(phenyl)}SiD_2^+ + HD \qquad (5b)$$

Recent evidence[24-29] showing the existence of silicon–carbon π bonds in compounds of the type $(CH_3)_2Si=CHR$ raises the possibility that the structure of the $SiC_6H_7^+$ might be analogous to that of the tropylium ion,[30,31] i.e.,
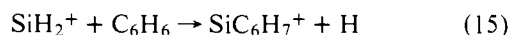
(tropylium-type structure with Si)
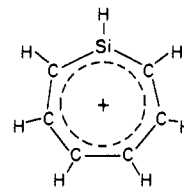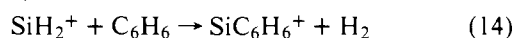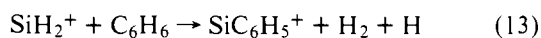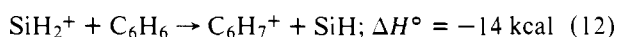
However, the formation of such a structure from the $SiC_6H_6D_3^{+*}$ formed in reaction 6b would be expected to lead to extensive scrambling and nearly statistical loss of hydrogen and deuterium, as was observed in studies of the formation of $C_7H_5D_2^+$ and $C_7H_4D_3^+$ ions by electron-impact ionization of $C_6H_5CD_3$.[32,33] The predominance of $C_6H_6^+$ formation in reaction 4b and of $SiC_6H_5D_2^+$ formation in reaction 5b strongly suggests that such scrambling does not occur. We conclude, therefore, that $SiC_6H_4^+$ ions are better described by the benzyl-type structure, as shown in eq 5b, and as suggested earlier.[23]

2. $SiH_2^+ + C_6H_6$. The major reaction of 1-eV SiH_2^+ ions with C_6H_6 is charge transfer, a reaction that is exothermic for

ground-state ions and that for 1-eV ions proceeds with a very large cross section (Table I). Other major products formed with large cross sections are $SiC_6H_7^+$ (m/e 107) and $SiC_6H_6^+$ (m/e 106), while $SiC_6H_5^+$ (m/e 105) and $C_6H_7^+$ (m/e 79) arise from considerably less probable processes. It is noteworthy that no product corresponding to an adduct of the reactants was detected until the pressure of C_6H_6 in the collision chamber exceeded 6×10^{-3} Torr (i.e., only collisionally stabilized ions of m/e 108 are detected). This means no energy-rich collision complexes, i.e., $SiC_6H_8^{+*}$, have sufficiently long lifetimes to reach the detector and this is probably a consequence of the existence of the exothermic charge-transfer channel. As already discussed an exothermic charge-transfer channel does not exist for collisions of SiH_3^+ with C_6H_6, nor for collisions of SiH^+ and Si^+ and in all three of these systems energy-rich collision complexes are observed.

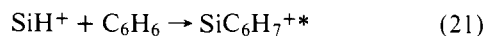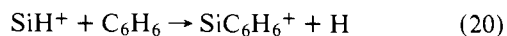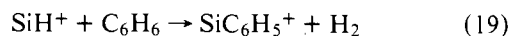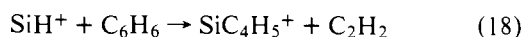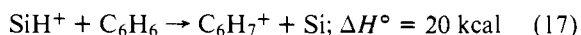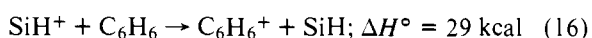The reactions observed in this system for 1-eV ions and the enthalpy changes of the reactions, calculated where possible, for ground-state ions[17,19-21,34] are shown by

$$SiH_2^+ + C_6H_6 \rightarrow C_6H_6^+ + SiH_2; \Delta H° = -11 \text{ kcal} \quad (11)$$

$$SiH_2^+ + C_6H_6 \rightarrow C_6H_7^+ + SiH; \Delta H° = -14 \text{ kcal} \quad (12)$$

$$SiH_2^+ + C_6H_6 \rightarrow SiC_6H_5^+ + H_2 + H \quad (13)$$

$$SiH_2^+ + C_6H_6 \rightarrow SiC_6H_6^+ + H_2 \quad (14)$$

$$SiH_2^+ + C_6H_6 \rightarrow SiC_6H_7^+ + H \quad (15)$$
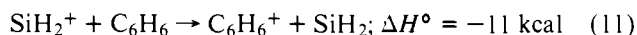
The dependence of the product distribution of this reaction on pressure is shown in Figure 2a and the dependence of the charge-transfer cross section on the kinetic energy of SiH_2^+ is shown in Figure 2b. The cross section of reaction 11 is seen to exhibit exothermic behavior which is in accord with the calculation from thermochemical data[16-20] of $\Delta H° = -11$ kcal. Detailed studies of the energy dependencies of the cross sections for reactions 12–15 were not carried out, but the magnitudes of the cross sections at 1 eV (Table 1) suggest strongly that these reactions are also exothermic. Indeed, thermochemical data[17-21,34] confirm that reaction 12 is exothermic.

When SiD_2^+ ions of 1-eV kinetic energy collide with C_6H_6 the silicon-containing product ions are distributed over the m/e 105–109 range as shown in Table III. This rather broad distribution is in contrast to that observed in $SiD_3^+-C_6H_6$ collisions and suggests that appreciable exchange of hydrogen and deuterium atoms occur between the incoming SiD_2^+ and the benzene ring. However, the relative probabilities of formation of $SiC_6H_5D_2^+$ and $SiC_6H_6D^+$ ions by reaction 15 are not close to the 3:1 ratio predicted by randomization of H and D. These results are therefore also consistent with a benzyl-type structure for $SiC_6H_7^+$.

3. $SiH^+ + C_6H_6$. The data in Table I show that SiH^+ ions react with C_6H_6 to form ionic products having m/e values of 78, 79, 81, 105, 106, and 107. The respective reactions involved and, where possible, calculated enthalpy changes are shown in the reactions below.

$$SiH^+ + C_6H_6 \rightarrow C_6H_6^+ + SiH; \Delta H° = 29 \text{ kcal} \quad (16)$$

$$SiH^+ + C_6H_6 \rightarrow C_6H_7^+ + Si; \Delta H° = 20 \text{ kcal} \quad (17)$$

$$SiH^+ + C_6H_6 \rightarrow SiC_4H_5^+ + C_2H_2 \quad (18)$$

$$SiH^+ + C_6H_6 \rightarrow SiC_6H_5^+ + H_2 \quad (19)$$

$$SiH^+ + C_6H_6 \rightarrow SiC_6H_6^+ + H \quad (20)$$

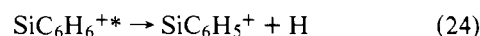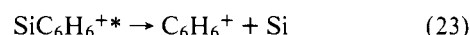$$SiH^+ + C_6H_6 \rightarrow SiC_6H_7^{+*} \quad (21)$$

As indicated by Table I and as confirmed by Figures 3a and 3b, energy-rich complexes with sufficient lifetime to be observed at the collector are formed in reaction 21. It is also to

be noted from the calculated enthalpy change and from the behavior of the cross section with energy (cf. Figures 3b and 5b) that the charge-transfer channel (eq 21) is endothermic. The amount of charge transfer that does occur below threshold, i.e., in the relative kinetic energy range of 0.73–1.5 eV (17–34 kcal/mol), must be attributed to the presence of internally excited SiH^+ ions in the reactant-ion beam. The presence of appreciable internal excitation in SiH^+ formed by electron impact on SiH_4 has been noted previously.[35,36] Reaction 17 is also endothermic and hence the extent of formation of $C_6H_7^+$ shown in Table I is also indicative of the presence of internally excited SiH^+ ions. The cross sections of reactions 18–21 exhibit the energy dependence that is typical of exothermic processes, as may be seen in Figures 3b and 5b for the specific cases of reactions 19 and 21.

If SiH^+ ions are replaced with 1-eV SiD^+ ions the ionic products containing six carbon atoms and one silicon atom are distributed as shown in Table III. This distribution suggests that the deuterium atom on the silicon is exchanged rather extensively with the ring hydrogens. In view of this complication and the absence of any classical organic chemical analogues we are unable to say more concerning the detailed mechanism.

4. $Si^+ + C_6H_6$. As shown in Table I the reaction of 1-eV Si^+ ions with C_6H_6 results in the formation of $C_6H_6^+$ (m/e 78), $SiC_6H_5^+$ (m/e 105), and $SiC_6H_6^{+*}$ (m/e 106). The pressure dependence and energy dependence of the distribution of these three products is shown in Figures 4a and 4b and the energy dependence of the total cross section is shown in Figure 5c. It is apparent from these figures that an energy-rich collision complex $SiC_6H_6^{+*}$, which has sufficient lifetime to be registered at the detector, is formed and that this energy-rich ion can be stabilized by collision so that at 6×10^{-3} Torr it counts for ~57% of the ionic product. Decomposition of this collision complex leads to the products $C_6H_6^+$ (m/e 78) and $SiC_6H_5^+$ (m/e 105). The suggested mechanism is depicted by the sequence of reactions 22–25, in which all ions shown are observed at the detector.

$$Si^+ + C_6H_6 \rightarrow SiC_6H_6^{+*} \quad (22)$$

$$SiC_6H_6^{+*} \rightarrow C_6H_6^+ + Si \quad (23)$$

$$SiC_6H_6^{+*} \rightarrow SiC_6H_5^+ + H \quad (24)$$

$$SiC_6H_6^{+*} + C_6H_6 \rightarrow SiC_6H_6^+ + C_6H_6 \quad (25)$$

We note again that in this system, in which an energy-rich collision complex is detected, the charge-transfer channel is endothermic by 24 kcal.[17] The appreciable amounts of $C_6H_6^+$ seen in Figure 4b and 5c at energies below the calculated threshold of 1.4 eV (laboratory) must be due to the presence of electronically excited Si^+ in the beam. This has been confirmed by ion-beam attenuation[37] experiments in CO_2 and by study of the endothermic reactions of Si^+ with D_2.[36] The results of these experiments lead to the conclusion that under our conditions the Si^+ ion beam consists of 62% Si^+ (^2P), which is the ground state, and 38% Si^+ (^4P) which lies 5.5 eV above the ground state.[38] Certainly the presence of this amount of excited state in the beam will account for the abundance of $C_6H_6^+$ at energies below the threshold for ground-state ions and for the shape of the cross section vs. energy curve. Further, it is tempting to interpret the apparent limiting abundance of pressure-stabilized collision complex of about 57%, seen in Figure 4a, as meaning that essentially all of the collision complexes of Si^+ (^2P) with C_6H_6 can be stabilized, but that very little of the collision complex of Si^+ (^4P) with C_6H_6, for which the charge-transfer channel is exothermic, can be stabilized at these pressures.

B. Phenomenological Rate Constants. It is not possible in beam experiments, such as described here, to obtain true re-

Table IV. Phenomenological Rate Constants[a] in SiH_4-C_6H_6 System for 1-eV Ions

Reaction	$k \times 10^{10}$, cm^3/s	$k \times 10^{10}$ (Langevin), cm^3/s
$Si^+ + C_6H_6 \rightarrow$ products	4.2	16.6
$SiH^+ + C_6H_6 \rightarrow$ products	8.9	16.4
$SiH_2^+ + C_6H_6 \rightarrow$ products	34	16.2
$SiH_3^+ + C_6H_6 \rightarrow$ products	10	16.0
$C_6H_5^+ + SiH_4 \rightarrow$ products	1.6	11.5
$C_6H_6^+ + SiH_4 \rightarrow$ products	0.7	11.5
$C_4H_2^+ + SiH_4 \rightarrow$ products	6.2	12.4
$C_4H_3^+ + SiH_4 \rightarrow$ products	2.3	12.3
$C_4H_4^+ + SiH_4 \rightarrow$ products	1.5	12.3

[a] Uncertainty in k is assumed to be ±30%, the same as in the cross sections.

action rate constants because the kinetic energy distributions of the two reactants are different. Nonetheless, from the viewpoint of the chemist it is useful to define a phenomenological rate constant in terms of the total reaction cross section as in the equation

$$k = \sigma V_r \qquad (26)$$

where σ is the experimental or phenomenological cross section for total reaction of a given ion and V_r is the relative velocity of reactants. The branching ratios, which are more sensitive to energy than are the total rate constants, may be obtained at the energy in question from the cross sections for formation of the individual products. Such phenomenological rate constants, as defined by eq 26, for the reactant pairs in this study are shown in Table IV. Also shown in Table IV are the rate constants for orbiting collisions according to the Langevin theory.[39] All the phenomenological rate constants are less than that predicted by Langevin theory with the exception of that for the reaction of SiH_2^+ with C_6H_6 and this exceeds the Langevin value by a factor of about 2. Over half of the total reaction of SiH_2^+ with C_6H_6 is simple electron exchange and reaction of SiH_2^+ with C_6H_6 is simple electron exchange and this strongly exothermic process that need not involve heavy-particle motion may well proceed by mechanisms other than Langevin orbiting collisions and complex formation.

C. Lifetimes of Energy-Rich Collision Complexes. It has been pointed out that energy-rich complexes of $SiC_6H_9^+$, $SiC_6H_7^+$, and $SiC_6H_6^+$ are registered directly at the detector. However, it is clear from Figures 1a, 3a, and 4a that some collisional stabilization does occur even at 10^{-3} Torr. The fractional contribution of the energy-rich complex to the total *observed* ionic product may be obtained as the intercept of an extrapolation of data such as in Figures 1a, 3a, and 4a to zero pressure. The limiting fraction of productions, which we denote by $F^0_{complex}$, clearly depends on the collision energy, or equivalently is a function of the natural lifetime, τ. If we assume that the fraction of collisions that do not revert back to reactants is given by the ratio of the experimental rate constant to the Langevin rate constant for orbiting (Table IV), it may be shown readily that the fraction $F^0_{complex}$ is given by the expression

$$F^0_{complex}(\tau) = \frac{e^{-t/\tau}}{k/k_L} \qquad (27)$$

In eq 27 τ is the lifetime of the energy-rich complex, t, the flight time to the detector is 2×10^{-5} s, k is the phenomenological rate constant, and k_L is the Langevin rate constant for orbiting collisions. Using eq 3, the data in Table IV, and extrapolated values of $F^0_{complex}$, we obtain lifetime estimates, of 8.2, 7.5, and

8.9 μs for $SiC_6H_6^{+*}$, $SiC_6H_7^{+*}$, and $SiC_6H_9^{+*}$, respectively. According to simple RRK theory,[40] the average lifetime of an energy-rich molecule with only one decomposition channel is given by

$$\tau \sim 10^{-13}(1) - (E_c/E))^{1-S} \qquad (28)$$

where S is the number of vibrational degress of freedom, E_c is the potential barrier separating the ground state of the energy-rich molecule from that of the product, and E is the total energy of the colliding reactants. The above experimental lifetimes of 8–9 μs are in accord with eq 28 if the ratio E_c/E is of the order of 0.4. This is certainly a reasonable number, but, unfortunately, the energetics of the system are not sufficiently well known at present to warrant more refined calculations using RRKM theory.[40]

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