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Formation of Adduct Ions of $Si^+(^2P)$ with Benzene and Naphthalene and Their Reactions in the Gas Phase: Graphitic Surface Chemistry in the Gas Phase

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Abstract: Results of laboratory measurements are presented for the capture of ground-state atomic silicon ions by benzene and naphthalene molecules in the gas phase and for the kinetics of the reactions of the resulting adduct ions Si^+·benzene and Si^+·naphthalene with the molecules D_2, CO, N_2, O_2, H_2O, NH_3, C_2H_2, and C_4H_2 at 296 ± 2 K. The addition of these aromatic molecules to Si^+ is seen to modify significantly the reactions of the atomic silicon ion. A wide range in reactivity is observed with both aromatic adduct ions and, while some common features are apparent in this chemistry, significant differences in reactivity also are seen, particularly for the reactions with C_2H_2 and C_4H_2. The reactions occurring in the presence of benzene appear to involve a π complex in which the atomic silicon ion is poised above the aromatic ring ready for reaction with an incoming molecule. In contrast, the reactions occurring in the presence of naphthalene seem to proceed with a neutral silicon atom perched above the (charged) aromatic surface. The intermediates for both types of reaction appear to undergo multistep transformations before separation into products. A case is made for the importance of reactions of adducts of Si^+ with benzene, naphthalene, and larger PAH molecules and analogous adducts with other atomic ions in the synthesis of molecules in interstellar and circumstellar environments, both when benzene and the PAH molecules exist as free molecules and when they are embedded in surfaces of hydrogenated amorphous carbon (HAC) or exist dehydrogenated in larger hexagonal lattices such as graphite or fullerene molecules.

Introduction

Neutral and positively charged polycyclic aromatic hydrocarbon (PAH) molecules, either completely or partially hydrogenated, recently have been invoked to account for both observed infrared emission features in nebulae[1] and observed diffuse interstellar absorption bands.[2] A very recent proposal suggests that these aromatic molecules are two- to five-ring PAH species, including naphthalene, anthracene, and tetracene, and that benzene may also be observable in these environments.[3] The PAH species are proposed to exist embedded in hydrogenated amorphous carbon (HAC) grains and as free molecules. Even though the evidence is still circumstantial, the presence of PAH species in the interstellar medium is now generally accepted and has stimulated considerable interest in the physical and chemical consequences of that presence. For example, Omont has proposed that PAH molecules may be a major sink in the interstellar medium for atomic metal and silicon cations because these atomic ions do not recombine efficiently with electrons and do not react with hydrogen.[4] There appears to be little previous terrestrial evidence for addition reactions of such atomic ions with PAH molecules and no information about the chemistry of the resulting adduct ions. We were intrigued by the prospect of observing such attachment in our selected-ion flow tube (SIFT) mass spectrometer and, given the considerable versatility of this instrument, by the prospect of being able to characterize the kinetics of chemical reactions of the resulting adduct ions and so even to mimic the surface chemistry which might occur on larger hexagonal lattices such as graphite, the end member of the PAH series, and even on fullerene molecules such as C_{60}.

Here we report laboratory observations that provide evidence for the occurrence of the efficient gas-phase attachment of Si^+ to naphthalene, the simplest PAH molecule, and benzene, a possible precursor of naphthalene in interstellar environments. The observation of these adduct ions raises questions about the influence of these aromatic molecules on the intrinsic reactivity of atomic silicon ions and on the formation of product ions and molecules. We have already reported elsewhere our extensive studies of the chemistry initiated by bare atomic silicon ions with interstellar and other molecules.[5] In this study we have taken laboratory measurements that explore how this chemistry is modified by the presence of naphthalene and benzene. We believe the results to be of fundamental chemical significance and also to have implications for the role of polycyclic aromatic hydrocarbon molecules in promoting graphitic "surface" reactions of Si^+ and other atomic ions in interstellar environments, both in the gas phase and on the surfaces of interstellar grains of HAC or graphite or on the surfaces of fullerene molecules.[6]

We note that atomic silicon has an ionization energy (8.152 eV) lower than that of benzene (9.247 eV) but just higher than that of naphthalene (8.14 eV). This means that we can expect differences in the distribution of the charge in the adduct ions of the two aromatic molecules and so also differences in chemical reactivity. For example, the charge should remain localized on the silicon atom in the adduct with benzene, as in $Si^+\cdots C_6H_6$, while it should be transferred to the naphthalene molecule in the adduct with naphthalene, as in $Si\cdots C_{10}H_8^+$. One might then, perhaps naively, expect the benzene adduct to react more like an atomic silicon ion and the naphthalene adduct to react more like a neutral silicon atom. In these mechanisms, the aromatic component of the adduct ions serves as a carbonaceous substratum or "surface" (which, in the limit of large PAH's, would resemble solid graphite), above which transpires the reaction between the atomic silicon ion or the neutral atom with the incoming molecule. We shall see how these expectations are born out by the experimental results.

Experimental Section

All experiments were performed with a selected-ion flow tube (SIFT) apparatus described previously.[7] Ground-state $Si^+(^2P)$ ions were gen-

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Table I. Kinetic Data Obtained for Reactions of $SiC_6H_6^+$ and $SiC_{10}H_8^+$ at 296 ± 2 K in Helium Buffer Gas at 0.35 Torr

	$SiC_6H_6^+$			$SiC_{10}H_8^+$		
	reaction	B.R.[b]	k[c]	reaction	B.R.[b]	k[c]
D_2	no reaction		<0.003	no reaction		<0.0035
CO	no reaction		<0.0009	no reaction		<0.0031
N_2	no reaction		<0.002	no reaction		<0.004
O_2	$C_6H_6^+ + SiO_2$	0.9	0.03	$C_{10}H_8^+ + SiO_2$	1.0	0.0037
	$C_6H_6O^+ + SiO$	0.1				
H_2O	$SiC_6H_6^+{\cdot}H_2O$	0.4[a]	2.0	$C_{10}H_8^+ + SiOH_2$	1.0	0.055
	$C_6H_6^+ + SiOH_2$	0.35[a]				
	$C_6H_7^+ + SiOH$	0.25[a]				
NH_3	$SiC_6H_6^+{\cdot}NH_3$	1.0	3.9	$SiC_{10}H_8^+{\cdot}NH_3$	1.0	4.1
C_2H_2	$SiC_6H_6^+{\cdot}C_2H_2$	0.6	0.6	$C_{10}H_8^+ + SiC_2H_2$	0.9	0.63
	$SiC_8H_7^+ + H$	0.4		$SiC_{10}H_8^+{\cdot}C_2H_2$	0.1	
C_4H_2	$SiC_4H_2^+ + C_6H_6$	>0.3	7.0	$C_{10}H_8^+ + SiC_4H_2$	1.0	10
	$SiC_6H_6^+{\cdot}C_4H_2$	<0.7				

[a] Product distribution from the completely deuterated reaction. [b] B.R. is the branching ratio with an estimated accuracy of ±30%. [c] The rate constant is given in units of 10^{-10} cm^3 molecule^{-1} s^{-1} and has an estimated accuracy of ±30%.

Table II. Kinetic Data Obtained for Reactions of $Si^+(^2P)$ at 296 ± 2 K in Helium Buffer Gas at 0.35 Torr

Reactant	Products	B.R.	k[a]
H_2	none		<0.002
D_2	none		<0.001
CO	none		<0.0002
O_2	SiO_2^+		<0.001
H_2O	$SiOH^+ + H$		2.3
NH_3	$SiNH_2^+ + H$		6.4
C_2H_2	$SiC_2H^+ + H$	0.7	3.5
	$SiC_2H_2^+$	0.3	
C_4H_2	$C_4H^+ + SiH$		16

[a] The rate constant is given in units of 10^{-10} cm^3 molecule^{-1} s^{-1} and has an estimated accuracy of ±30%.

erated from a 2–3% mixture of $Si(CH_3)_4$ in deuterium by electron impact at 50–100 eV, mass selected with a quadrupole mass filter, and injected into a flowing helium buffer at 0.35 Torr and 296 ± 2 K. The deuterium was added to scavenge metastable $Si^+(^4P)$ ions in the ion source with reaction 1. One or more neutral reagents were added downstream.

$$Si^+(^4P) + D_2 \rightarrow DSi^+ + D \qquad (1)$$

Reactant and product ions were monitored still further downstream with a second quadrupole mass filter as a function of the added neutral reagent. Established methods of analysis were used to derive rate constants and product distributions from these observations.[7a,8]

The helium buffer gas and the reagent gases D_2, CO, N_2, O_2, NH_3, and C_2H_2 were of high purity (99.5 mol %). H_2O and D_2O (minimum 99.8 atom % D), C_6H_6 (99.9 mol %), and C_6D_6 (minimum 99.6 atom % D) were used as the vapors of their liquids. To remove traces of water vapor, the helium buffer gas was passed through zeolite traps (a 50:50 mixture of Union Carbide molecule sieves 4A and 13X) cooled to liquid nitrogen temperature. The reagent gases were used without further purification. Diacetylene was prepared by the alkaline hydrolysis of 1,4-dichlorobut-2-yne and stored at dry ice temperature to avoid polymerization.[9] Previous experiments with H_3^+ as the "chemical ionization" reagent indicated a purity for the gas produced in this manner of greater than 99%.

Results

Formation of Adduct Ions. When either benzene or naphthalene vapor was introduced into the flow tube upstream of the reaction region, adduct ions were observed to be formed rapidly according to reactions 2 and 3. Some charge transfer was seen to compete with adduct formation in the case of naphthalene. The branching ratio for (3a):(3b) is approximately 7:1. The apparent bimolecular

$$Si^+ + C_6H_6 \rightarrow SiC_6H_6^+ \qquad (2)$$

$$Si^+ + C_{10}H_8 \rightarrow SiC_{10}H_8^+ \qquad (3a)$$

$$\rightarrow C_{10}H_8^+ + Si \qquad (3b)$$

rate constant for the addition reaction 2 was found to be (1.5 ± 0.5) × 10^{-9} cm^3 molecule^{-1} s^{-1} at 0.345 Torr of helium. The rate constant for reaction 3 was not measured due to the low vapor pressure of naphthalene.

The naphthalene adduct ion was observed to be completely unreactive toward benzene, $k < 6 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Not even trace amounts of the Si^+·benzene adduct ion which might arise from a ligand-switching reaction were observed to be formed. Nor was there any formation of the adduct Si^+·naphthalene·benzene which might correspond to a benzene/naphthalene sandwich ion of atomic silicon. The benzene adduct ion of Si^+ was also found to be quite unreactive toward benzene, $k < 10^{-12}$ cm^3 molecule^{-1} s^{-1}, but in this case formation of trace amounts of an ion with a mass consistent with $Si^+{\cdot}(C_6H_6)_2$ were observed to be formed.

Reactions of Adduct Ions. When the adduct ions Si^+·benzene or Si^+·naphthalene were established as dominant ions upstream of the flow tube, additions of neutral reactant molecules into the reaction region led to the reactions for which the measured rate constants, products, and product distributions are summarized in Table I. Individual reactions are discussed below. Comparisons are made with the reactivities of Si^+ measured in the absence of benzene or naphthalene which are summarized in Table II and which have been reported earlier.[5] In writing the (unobserved) neutral products in Tables I and II, the most exothermic channel or, when the thermodynamic information was insufficient, the channel assumed to be the most exothermic is given. Thermochemical information was derived from the compilation of Lias et al.,[10] unless indicated otherwise.

D_2, CO, and N_2. As was the case with atomic silicon ions,[5] both $SiC_6H_6^+$ and $SiC_{10}H_8^+$ were found to be unreactive with D_2, CO, and N_2. This result is not surprising since there are no bimolecular exothermic channels with the atomic silicon ion, and it is unlikely that possible endothermic product ions would bind sufficiently more strongly to the two aromatic molecules than the reacting atomic silicon ion so as to overcome the endothermicity.

O_2. Under SIFT conditions in the absence of benzene and naphthalene atomic silicon ions only add molecular oxygen to form SiO_2^+.[5d] In this study we have observed that addition of naphthalene to the atomic silicon ion *increases* the rate of reaction by more than a factor of 3 and forms ionized naphthalene as the only ionic product as shown in reaction 4. The neutral product is likely to be SiO_2 rather than Si + O_2 or SiO + O. Of these three options,

$$SiC_{10}H_8^+ + O_2 \rightarrow C_{10}H_8^+ + (SiO_2) \qquad (4)$$

formation of SiO_2 is the most exothermic with a standard enthalpy of reaction of (−180 ± 9) + $D(Si^+{-}C_{10}H_8)$ kcal mol^{-1}. Formation of SiO + O is 109 ± 10 kcal mol^{-1} more endothermic, while

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formation of Si + O_2 requires an additional 181 ± 10 kcal mol^{-1}. Addition of benzene to the atomic silicon ion, rather than naphthalene, enhances the rate by more than a factor of 30 and leads to the formation of two product ions, $C_6H_6^+$ and what could be the phenol cation, $C_6H_5OH^+$. The two channels are shown in reaction 5. Available thermochemical information indicates exothermicities of (157 ± 9) − $D(Si^+{-}C_6H_6)$ and (168 ± 3) − $D(Si^+{-}C_6H_6)$ kcal mol^{-1} for these two channels, respectively, when the neutral products are taken to be SiO_2 and SiO and $C_6H_6O^+$ is taken to be the phenol cation. The neutral product in reaction 5b must be SiO since the homolytic dissociation of this molecule requires 192 ± 2 kcal mol^{-1}. As was the case with the analogous naphthalene reaction, the neutral product of reaction 5a is almost certainly SiO_2. As already indicated, dissociation into Si + O_2 requires 181 ± 10 kcal mol^{-1}. This is more than is available from the reaction. Dissociation into SiO + O requires 109 ± 10 kcal mol^{-1}, which is also probably not available from this reaction.

$$SiC_6H_6^+ + O_2 \rightarrow C_6H_6^+ + (SiO_2) \qquad (5a)$$

$$\rightarrow C_6H_6O^+ + SiO \qquad (5b)$$

H_2O. The intrinsic reaction of H_2O with Si^+ leads exclusively to H atom elimination with the formation of $SiOH^+$ (and not $HSiO^+$).[5a] In this case addition of a naphthalene molecule to Si^+ *reduces* the reaction rate by about a factor of 40, but again the product ion changes and again it is ionized naphthalene as shown in reaction 6. The nature of the neutral product is not known, but the formation of either silanone, H_2SiO, or hydroxysilylene, HSiOH, might be expected to be preferred over the formation of their dissociation fragments, SiO + H_2 or SiOH + H, for example. Quantum-mechanical stabilities estimated by CID+Q with use of the 6-31G** basis set[11] indicate stabilities relative to H_2SiO (in kcal mol^{-1}) of −2.22 for H_2 + SiO, −4.15 for *trans*-HSiOH, and −3.60 for *cis*-HSiOH. Of these possible neutral products *trans*-HSiOH would then be most stable. The formation of *trans*-HSiOH has an overall exothermicity given by −75 + $D(Si^+{-}C_{10}H_8)$ kcal mol^{-1}. The benzene adduct ion reacts with H_2O at a rate about equal to that of its reaction with the atomic ion and so about 40 times faster than the naphthalene adduct ion. Also, three product channels are observed in this case as shown in reaction 7. The product distribution indicated in reaction 7 was determined from the completely deuterated version of the reaction, viz. the reaction of $SiC_6D_6^+$ with D_2O, which showed a rate constant of 2.0×10^{-10} cm^3 $molecule^{-1}$ s^{-1}. Formation of trans-HSiOH in reaction 7b is exothermic by −50 + $D(Si^+{-}C_6H_6)$ kcal mol^{-1} while formation of SiOH in reaction 7c is exothermic by −66 + $D(Si^+{-}C_6H_6)$ kcal mol^{-1} and 39 kcal mol^{-1} more exothermic than the formation of the dissociation products SiO + H. The secondary reaction 8 of the water adduct of the benzene adduct of Si^+ was also observed. Again, the product distribution was derived from the completely deuterated analogue. Possible neutral products are silanoic acid, HSi(O)OH, and the dihydroxy radical $HSi(OH)_2^{\bullet}$ for reactions 8a and 8b, respectively, but the relative exothermicities for other connectivities or for the formation of neutral fragments are not known.

$$SiC_{10}H_8^+ + H_2O \rightarrow C_{10}H_8^+ + (SiOH_2) \qquad (6)$$

$$SiC_6H_6^+ + H_2O \xrightarrow{0.4} SiC_6H_6^+{\cdot}H_2O \qquad (7a)$$

$$\xrightarrow{0.35} C_6H_6^+ + (SiOH_2) \qquad (7b)$$

$$\xrightarrow{0.25} C_6H_7^+ + SiOH \qquad (7c)$$

$$SiC_6H_6^+{\cdot}H_2O + H_2O \xrightarrow{0.6} C_6H_8^+ + (SiH_2O_2) \qquad (8a)$$

$$\xrightarrow{0.4} C_6H_7^+ + (SiH_3O_2) \qquad (8b)$$

NH_3. Ground-state atomic silicon ions react with ammonia to give only the bimolecular products $SiNH_2^+$ + H. In sharp contrast, only the adduct ions were observed in the reactions of ammonia with the adduct ions of Si^+ with benzene and naphthalene as indicated in reactions 9 and 10. These reactions are presumably termolecular at the conditions maintained in the SIFT with He acting as the stabilizing gas. Ammonia efficiently bonds to both adduct ions with essentially equal rates.

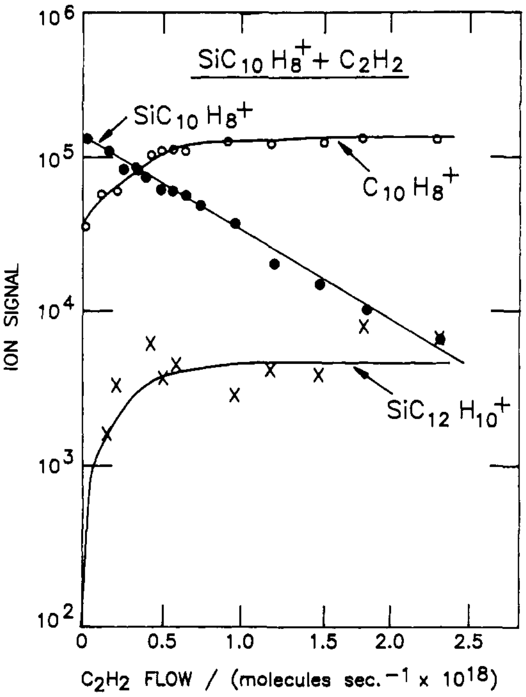

Figure 1. The observed variations of ion signals recorded for the addition of acetylene into the reaction region of the SIFT apparatus in which $SiC_{10}H_8^+$ has been established as the dominant ion in helium buffer gas. P = 0.35 Torr, $\bar{v}$ = 7.0×10^3 cm s^{-1}, L = 46 cm, and T = 295 K. Naphthalene vapor is added upstream to convert Si^+ to $SiC_{10}H_8^+$. The Si^+ is derived from the ion source in which tetramethylsilane undergoes electron impact at 78 eV in the presence of added deuterium (3%).

$$SiC_6H_6^+ + NH_3 \rightarrow SiC_6H_6^+{\cdot}NH_3 \qquad (9)$$

$$SiC_{10}H_8^+ + NH_3 \rightarrow SiC_{10}H_8^+{\cdot}NH_3 \qquad (10)$$

In the subsequent reactions of these adduct ions with ammonia there is again a switch in the molecularity (as was partly the case with H_2O). Both of the ammonia adduct ions react rapidly with ammonia to form $Si(NH_3)_2^+$ according to the interesting bimolecular reactions 11 and 12.

$$SiC_6H_6^+{\cdot}NH_3 + NH_3 \rightarrow Si(NH_3)_2^+ + C_6H_6 \qquad (11)$$

$$SiC_{10}H_8^+{\cdot}NH_3 + NH_3 \rightarrow Si(NH_3)_2^+ + C_{10}H_8 \qquad (12)$$

C_2H_2, C_4H_2. The adducts of Si^+ with benzene and naphthalene show a different mode of reactivity toward acetylene and diacetylene. In the case of naphthalene, these two molecules both release $C_{10}H_8^+$ from $SiC_{10}H_8^+$ as shown in reactions 13 and 14. With acetylene some adduct formation (10%) is also observed.

$$SiC_{10}H_8^+ + C_2H_2 \xrightarrow{0.9} C_{10}H_8^+ + (SiC_2H_2) \qquad (13a)$$

$$\xrightarrow{0.1} SiC_{10}H_8^+{\cdot}C_2H_2 \qquad (13b)$$

$$SiC_{10}H_8^+ + C_4H_2 \rightarrow C_{10}H_8^+ + (SiC_4H_2) \qquad (14)$$

Figure 1 shows data obtained for the reaction of the naphthalene adduct of Si^+ with acetylene. Release of $C_{10}H_8^+$ was also the dominant feature of the reactions of the naphthalene adduct ion with O_2 and H_2O so that one might expect a common mechanism for the reactions with these four molecules. For example, one might suspect that naphthalene receives the charge already during the initial interaction as the adduct is formed, as in $Si{\cdots}C_{10}H_8^+$, so that the reactions of this adduct might resemble reactions with

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neutral atomic silicon. In any case, the observations clearly show that naphthalene addition to the atomic silicon ion dramatically alters the mode of reaction with the molecules C_2H_2, C_4H_2, O_2, and H_2O. In contrast, the reaction of acetylene with the benzene adduct $SiC_6H_6^+$ resembles that observed with Si^+ in that adduct formation and H atom elimination are the observed products as shown in reaction 15, but it is more than 5 times slower. Also, and quite remarkably so, the product distribution is almost the

$$SiC_6H_6^+ + C_2H_2 \xrightarrow{0.6} SiC_6H_6^+{\cdot}C_2H_2 \qquad (15a)$$

$$\xrightarrow{0.4} SiC_8H_7^+ + H \qquad (15b)$$

same. Diacetylene, on the other hand, reacts quite differently in the presence and absence of benzene. The bare atomic silicon ion reacts with diacetylene simply by hydride transfer. With the benzene adduct of Si^+ diacetylene reacts to displace the benzene molecule from $SiC_6H_6^+$ to form $SiC_4H_2^+$ as shown in reaction 16. Because of the mass coincidence of $SiC_4H_2^+$ and $C_6H_6^+$, confirmation of this result was required with experiments involving $SiC_6D_6^+$. An ion with a mass corresponding to that of the adduct ion, $SiC_6H_6^+{\cdot}C_4H_2$, was also observed but an unambiguous identification could not be made because of the mass coincidence with the adduct ion, $SiC_4H_2^+{\cdot}C_6H_6$, which could be formed from the clustering reaction 17 with the benzene added upstream of the reaction region to form the benzene adduct ion with Si^+. Also, it should be noted that both the $SiC_4H_2^+$ and the $SiC_{10}H_8^+$ product ions were observed to add two additional molecules of diacetylene in sequential addition reactions.

$$SiC_6H_6^+ + C_4H_2 \xrightarrow{>0.3} SiC_4H_2^+ + C_6H_6 \qquad (16a)$$

$$\xrightarrow{<0.7} SiC_6H_6^+{\cdot}C_4H_2 \qquad (16b)$$

$$SiC_4H_2^+ + C_6H_6 \rightarrow SiC_{10}H_8^+ \qquad (17)$$

Discussion

The results of the SIFT experiments reported here clearly establish that ground-state atomic silicon ions are effectively captured by benzene and naphthalene molecules in the gas phase in helium buffer gas at 0.35 Torr and 296 K, presumably by termolecular collisional association. The contribution of bimolecular radiative association was not established. For the further reactions of the silicon adduct ions, the comparison with our earlier results for the reactions involving the bare atomic silicon ion vividly demonstrates the influence of addition of benzene and naphthalene on the intrinsic reactivity of Si^+. Both rate enhancement and rate depression are observed as well as changes in the mode of reaction. The largest rate enhancement, by a factor of more than 30, was observed with benzene in the reaction with O_2. The largest rate depression, by a factor of more than 40, was recorded with naphthalene in the reaction with H_2O. For both of these reactions a complete change in the nature of the products occurs.

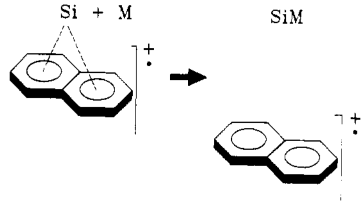
The structures of the adduct ions of Si^+ with benzene and naphthalene are not known from our experiments, nor are there calculations available, to our knowledge, which might provide some insight into these structures. However, several of the reaction features observed in the experimental study reported here allow some inferences to be made about these structures. Let us first consider the adduct ion of Si^+ with benzene. Possible isomers of the benzene adduct ion with Si^+ include the π complex in which Si^+ sits above the benzene ring, an ipso form in which Si^+ is σ bonded to a carbon atom, and a form involving the insertion of Si^+ into a C–H bond of benzene. A number of the experimental observations, taken together, appear to favor the π complex structure: (1) No proton transfer was observed, not even with ammonia which is a very strong base. (2) A switching reaction is observed in which a diacetylene molecule displaces a benzene molecule. The observation of switching with diacetylene and the failure to observe switching with acetylene would suggest that $D(Si^+{-}C_4H_2) > D(Si^+{-}C_6H_6) < D(Si^+{-}C_2H_2) = 43.7$ kcal mol^{-1}.[5e] (3) The reaction of the benzene adduct ion with acetylene mimics that observed for the free Si^+ ion in that it leads to similar reaction products, H atom elimination, and formation of an adduct ion, with a similar branching ratio, 4/6 as opposed to 7/3.[5e]

Also, it may be argued that further support for the assignment of the π structure comes simply from the ability to explain the observed reaction products in terms of reactions involving such a complex. Consider the reaction with oxygen, for example, which may be viewed to proceed in the following steps: (1) First, the oxygen molecule interacts with the Si^+ sitting above the benzene ring to form the chemically bonded ion SiO_2^+. (2) Then charge transfer occurs between SiO_2^+ and benzene which is exothermic by about 2.2 eV,[12] and the products separate to yield the $C_6H_6^+$ ion which is observed. (3) Some O-atom insertion into the C–H bond of $C_6H_6^+$ occurs after the charge transfer has happened and as the products separate to yield the $C_6H_6O^+$ ion which is observed and which presumably is the phenol cation $C_6H_5OH^+$.

The reaction products with water can be similarly understood in terms of sequential transformations within the intermediate complex. The water molecule interacts with the Si^+ attached to the benzene ring initially to form $Si^+{\cdots}OH_2$ and then $HSiOH^+$.[13] Apparently the further reaction to form $SiOH^+$ and H which is observed for the bare Si^+ ion is not sufficiently exothermic in the presence of benzene for these two products to leave the benzene molecule. If the intermediate $HSiOH^+$ then transfers a charge or a proton to the benzene molecule, the proposed neutral molecules HSiOH and SiOH and the observed ions $C_6H_6^+$ and $C_6H_7^+$ are produced, respectively. An analogous mechanism for the secondary reaction of the water adduct ion, $Si^+{\cdot}C_6H_6{\cdot}H_2O$, with another water molecule which was also observed would form the $H_2Si(OH)_2^+$ ion. This ion could lose a proton or H_2^+ in the reaction intermediate to leave the neutral molecules $HSi(OH)_2$ and $Si(OH)_2$, respectively, along with the protonated and hydrogenated benzene ions, $C_6H_7^+$ and $C_6H_8^+$.

Our measurements indicate that the chemistry of the $SiC_{10}H_8^+$ adduct ion (with the exception of its reaction with ammonia) is dominated by the elimination of ionized naphthalene in reactions of the type shown in (18). This observation, together with our observation of a small bimolecular charge-transfer channel competing with the formation of the adduct ion, strongly suggests that charge is transferred from Si^+ to naphthalene as the adduct is formed and that the adduct $SiC_{10}H_8^+$ is a π complex of a neutral silicon atom interacting with a positive naphthalene ion. The charge transfer to naphthalene is exothermic by only 0.01 eV, but if the charge resides mostly on the naphthalene, reaction 18 may be viewed as a "surface" reaction in the sense that a neutral Si atom would interact with the incoming molecule M while perched above the plane of the charged naphthalene molecule as is shown in reaction 19.[6] The identity of the neutral products of such a "surface" reaction of the naphthalene adduct is intriguing, particularly if SiM leaves as a bound molecule. We have postulated that SiO, SiO_2, SiOH, *trans*-HSiOH and c-SiC_2H_2 are the likely neutral products in the reactions of the Si^+ adduct ions with O_2, H_2O, and C_2H_2. SiO and SiO_2 are well-known as stable molecules in the gas phase. An argon matrix-isolation study of the reaction of silicon atoms with water has shown that the silicon atom inserts into the O–H bond to form the hydroxysilylene, HSiOH, molecule.[14] Also, HSiOH has been shown to be stable in the gas phase

$$SiC_{10}H_8^+ + M \rightarrow C_{10}H_8^+ + (SiM) \qquad (18)$$



(19)

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in a recent study by chemical-activation and neutralization–reionization mass spectrometry.[15] A comprehensive theoretical study by Kudo and Nagase[16] and other calculations[17] indicate that the *trans*-HSiOH is the most stable isomer of SiH_2O, 0.3 kcal mol^{-1} more stable than the cis isomer (with a barrier of 9.3 kcal mol^{-1} for conversion from trans to cis) and 2.4 kcal mol^{-1} more stable than silanone, H_2SiO (with a barrier of 63.2 kcal mol^{-1} for conversion into silanone). The gas-phase reaction of Si with acetylene has been attributed to efficient addition with formation of 3-silacyclopropenylidene[18] which is then also a plausible product of the gas-phase naphthalene "surface" reaction. Ab initio calculations have shown that 3-silacyclopropenylidene is the most stable isomer of SiC_2H_2 and that formation of the isomers vinylidenesilene, CH_2CSi, and silylenylacetylene, $HSiC_2H$, requires an additional 17 and 22 kcal mol^{-1} of energy, respectively.[19] These results suggest that the $SiC_{10}H_8{}^+{\cdot}C_2H_2$ adduct ion is most reasonably viewed as 3-silacyclopropenylidene attached to the "surface" of an ionized naphthalene molecule. Bimolecular channels for the reaction between the neutral Si atom and acetylene are likely to be endothermic: H atom abstraction is endothermic by 63 kcal mol^{-1}, but the energetics for H atom elimination with formation of SiC_2H are not known. Experimental support for the stability of c-SiC_2H_2 has come from recent measurements with neutralization–reionization mass spectrometry.[20] In analogy to the reaction with acetylene, the reaction with diacetylene can be expected to lead to a product molecule involving the cyclic attachment of Si to one of the triple bonds of diacetylene.

The reactions of the Si^+ adduct ions with ammonia are unique in that they appear to proceed only by addition. We have shown previously that the bare Si^+ ion reacts with ammonia only by H atom elimination to form the silylene cation $:Si^+{-}NH_2$.[5b] The reaction is exothermic by only 20 kcal mol^{-1} which apparently is not sufficient to drive the reaction to completion when the ions are bound to benzene or naphthalene. The addition reactions which are observed instead have effective bimolecular rate constants which are only about 30% less than the rate constant of the bimolecular reaction of bare Si^+. The mechanisms invoked earlier for the reactions of the adduct ions lead to the expectations that the adduct ions with ammonia have the connectivities $HSiNH_2{}^+{\cdot}C_6H_6$ and $HSiNH_2{\cdot}C_{10}H_8{}^+$ and are formed by N–H bond insertion between ammonia and Si^+ above a benzene ring and between ammonia and Si above an ionized naphthalene "surface", respectively. The rapid bimolecular reactions of these adduct ions with another molecule of ammonia may then be viewed as reactions between $HSiNH_2{}^+$ and ammonia occurring above benzene and naphthalene, respectively, perhaps to form the covalently bound ion of diaminosilane, $H_2Si(NH_2)_2{}^+$. In the case of the reaction in the presence of naphthalene, this reaction would be preceded by the transfer of the charge on naphthalene to the $HSiNH_2$ molecule. It is interesting to note that benzene (B) and naphthalene (N) catalyze the formation of $Si(NH_3)_2{}^+$ according to the reaction sequence given in reactions 20–22

$$Si^+ + B,N \rightarrow SiB^+,SiN^+ \qquad (20)$$

$$SiB^+,SiN^+ + NH_3 \rightarrow SiB^+{\cdot}NH_3,SiN^+{\cdot}NH_3 \qquad (21)$$

$$\underline{SiB^+{\cdot}NH_3,SiN^+{\cdot}NH_3 + NH_3 \rightarrow Si(NH_3)_2{}^+ + B,N} \qquad (22)$$

$$Si^+ + 2\,NH_3 \rightarrow Si(NH_3)_2{}^+ \qquad (23)$$

which is written without any inferences being made about structure or mechanism. The sequential reactions of Si^+ with ammonia which occur in the absence of these aromatic molecules are given by reactions 24 and 25. They do not form an ion with the composition $Si(NH_3)_2{}^+$ but lead to protonated ammonia instead.

$$Si^+ + NH_3 \rightarrow SiNH_2{}^+ + H \qquad (24)$$

$$SiNH_2{}^+ + NH_3 \rightarrow NH_4{}^+ + SiNH \qquad (25)$$

Implications for Interstellar and Circumstellar Chemistry

The results of the SIFT experiments reported here clearly establish that gaseous benzene and naphthalene have a positive affinity for atomic silicon ions and that they can form adduct ions with Si^+ efficiently in the presence of a stabilizing gas. Under our SIFT conditions the adduct ions are likely to be formed predominantly by collisional stabilization in the helium bath gas. In interstellar and circumstellar environments in which gas densities are much lower, formation of similar adduct ions must occur largely by radiative association. The large rate constant measured for the capture of Si^+ by benzene implies a long lifetime for the intermediate complex against dissociation back to reactants and so opens radiative association as an avenue for the production of the $Si^+{\cdot}$benzene adduct at low gas densities. Charge transfer is likely to predominate in the reaction of Si^+ with naphthalene at low gas densities, but in this case the $SiC_{10}H_8{}^+$ adduct also may be formed by the radiative association of neutral silicon atoms with naphthalene cations. These observations suggest that Si^+ (or Si) is easily absorbed by PAH molecules (or ions) generally. They support the proposal by Omont[4] that absorption of this kind will contribute to the apparent depletion of gas-phase silicon in interstellar gas clouds and circumstellar envelopes.[21,22]

The non-reactivity of the $SiC_6H_6{}^+$ and $SiC_{10}H_8{}^+$ adduct ions toward D_2 and CO means that these adduct ions will persist in interstellar and circumstellar regions rich in H_2 and CO and be available for chemical reaction with other, less-abundant molecules. In this study we have characterized the reactions of these adduct ions with the molecules O_2, H_2O, NH_3, C_2H_2, and C_4H_2 and we have seen how these reactions may promote the synthesis of silicon-containing molecules such as SiO, SiO_2, SiOH, HSiOH, and the cyclic adducts of atomic silicon with acetylene and diacetylene. The rate constants for these reactions cover a large range in magnitude and the products, for the most part, are bimolecular. Because these reactions are largely bimolecular the rate constants are not expected to be strongly dependent on pressure. For those reactions in which bimolecular channels compete with adduct formation by collisional stabilization, the branching ratio will change with decreasing pressure in favor of the bimolecular channel, perhaps with no change in the total rate constant for reaction. It is difficult to know what to expect with regard to the temperature dependence of the rate constants. The reason for the very slow reactions of both adduct ions with O_2 and the very slow reaction of $SiC_{10}H_8{}^+$ with H_2O, for all of which $k < 6 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, may be a barrier in the potential surface so that k would decrease with decreasing temperature. The temperature dependence of the rate constants of the remaining reactions for which $k > 2 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} is also an open question, particularly since nothing is known about the potential surfaces for these reactions. Finally, the reactions with diacetylene proceed near the collision limit and so should be quite insensitive to changes in temperature. Clearly all those reactions with rate constants that decrease with decreasing temperature would be of less importance for the chemistry of interstellar gas clouds, in which the temperature is usually below 100 K, and for the chemistry in the cooler regions of circumstellar envelopes.

In principle, the adduct ion $(XPAH)^+$, where X is any atom, may be formed either by the capture of the atomic ion X^+ by the PAH molecule or by the capture of the neutral atom X by a positively charged PAH ion. We note here that the ionization

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energies (given in parentheses in eV) of the interstellar atoms S (10.360), Zn (9.394), Fe (7.870), and Mg (7.646) are all larger than that typical for the larger PAH molecules (7.0), as is the case for the relative ionization energy of Si and naphthalene. In conrast, the ionization energies of Ca (6.113) and Al (5.986) are both smaller, as is the case for the relative ionization energy of Si and benzene. The ions of Ca and Al are therefore likely to form $(XPAH)^+$ adduct ions in interstellar regions of low density in the manner analogous to that observed in our laboratory for Si^+ and benzene, viz. according to reaction 26, and the reactions

$$X^+ + PAH \rightarrow X^+{\cdot}PAH + h\nu \qquad (26)$$

of these adduct ions should mimic the behavior observed for Si^+·benzene adduct, e.g. form CaO/CaO_2 and AlO/AlO_2 from O_2 and AlOH and CaOH from H_2O. Because of the likelihood of charge transfer between the ions of the other atoms and PAH molecules, the corresponding adduct in this case must be formed by the radiative association of the neutral atom and the cation of the PAH molecule according to reaction 27. The reactions of these adduct ions should mimic those observed in this study for

$$X + PAH^+ \rightarrow X{\cdot}PAH^+ + h\nu \qquad (27)$$

$SiC_{10}H_8^+$, reactions of the type given in (28). The capture and chemistry of atomic ions other than Si^+ will be the subject of future studies in our laboratory.

$$XPAH^+ + M \rightarrow PAH^+ + (XM) \qquad (28)$$

Nothing is known about the spectroscopy of adduct ions of the type $(XPAH)^+$ so that a telescopic search for their presence in the interstellar or circumstellar gas is not yet possible. (Of course any ions, atomic or molecular, tied up in this fashion will also escape detection.) Finally we may note, by inference, that Si^+ and other atomic ions also should be captured in interstellar and circumstellar environments by PAH molecules embedded in grains of HAC and by larger hexagonal lattices such as graphite and fullerene molecules. Fullerene molecules such as C_{60} are thought to be ejected from stars into interstellar space.[23] (Alternatively the neutral atoms may be captured by the charged grains or fullerene molecules.) The chemistry which these atomic ions or atoms undergo above these surfaces with incoming molecules may well resemble that observed with small PAH molecules in the gas phase. In that case the study reported here for the chemistry of Si^+ in the presence of benzene and naphthalene should serve as an instructive prototype.

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C–H and C–C Bond Activations by Silicon. Thermochemistry and Mechanism of the Reaction of $Si^+(^2P)$ with Ethane

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Abstract: The reaction of ground-state silicon ion with ethane (-d_0, -*1,1,1*-d_3, and -d_6) is investigated by using guided ion beam techniques. Absolute reaction cross sections for all product ions are determined as a function of the relative collision energy. At thermal energies, Si^+–CH_3 accounts for 90% of all products. Exothermic dehydrogenation to form $SiC_2H_4^+$ and demethanation to form $SiCH_2^+$ are observed, but these processes are inefficient. When CH_3CD_3 is employed as the reactant neutral, all products are observed to incorporate hydrogen and deuterium atoms in near-statistical distributions at low energies. This suggests that the primary HSi^+–CH_2CD_3, CH_3CD_2–SiD^+, and CH_3–Si^+–CD_3 intermediates are rapidly interconverted via a cyclic $HDSi(CH_2CD_2)^+$ intermediate.

Introduction

The reactions of atomic silicon ion with alkanes are ideal systems for examining inter- and intramolecular C–H activations by reactive silicon species as well as determining the thermochemistry of organosilicon species. Previously, we investigated the reaction of ground-state silicon ion (^2P) with methane over a broad range of kinetic energies by using guided ion beam mass spectrometry.[1] A simple reaction mechanism was able to explain the variety of endothermic processes observed. In addition, thermochemical data for SiH and $SiCH_x^+$ (x = 1–3) species were extracted. Here, we continue these studies by evaluating the reaction of atomic silicon ion with ethane, which has been studied once before at thermal energies only.[2] The present study provides a detailed mechanism for this reaction, additional thermochemical data for organosilicon species such as $SiCH^+$, $SiCH_3^+$, $SiC_2H_3^+$, and $SiC_2H_5^+$, and insight into the ability of silicon to activate C–H versus C–C bonds.

Experimental Section

The guided ion beam apparatus has been described in detail elsewhere.[3] Silicon ions are produced as described below. The ions are extracted, accelerated, and focused into a 60° magnetic momentum analyzer where the ^{28}Si isotope is selected. The ions are then decelerated to a desired kinetic energy and focused into an octopole ion guide. Radio-frequency electric fields in the guide create a radial potential well that traps ions over the mass range examined. The velocity of the ions parallel to the axis of the guide is unchanged. The octopole passes through a static gas cell into which a reactant neutral gas is introduced. The pressure of the reactant gas is sufficiently low (~10^{-4} Torr) that multiple collisions are improbable. The product and unreacted beam ions are

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