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Experimental and Theoretical Characterization of Isomeric Adduct Ions of $Si^{\cdot+}$ and Benzene and Their Neutral Counterparts

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Abstract: Results of gas-phase experiments and theoretical investigations are reported which provide evidence for the stability of the π-complex $Si^{\cdot+}$–C_6H_6 and the C–H insertion complex $C_6H_5SiH^{\cdot+}$. Theory also predicts the stability of the ring-insertion complex for which the experiments could not provide unambiguous experimental evidence. The π-complex and C–H insertion complex are distinguished with neutralization–reionization (NR) mass spectrometry experiments at 8 keV which also provide evidence for the stability of the corresponding neutral molecules. The $[C_6,H_6,Si]^{\cdot+}$ cations were generated either by electron-impact ionization of phenylsilane or a mixture of benzene and $Si(CH_3)_4$ at 70 eV, or by charge reversal of an anion produced from a mixture of phenylsilane and N_2O. At the MP2/6-31G**//UHF/3-21G* level, ab initio MO calculations predict the stability order for the cations as π-complex > C–H insertion complex > ring-insertion complex and the order for the corresponding neutral species as C_6H_5SiH > ring-insertion complex > π Si–C_6H_6.

Introduction

The recent experimental results obtained for the chemistry of $Si^{\cdot+}$ in the absence and presence of benzene and naphthalene as reported by Bohme et al.[1,2] point to the exciting prospect of investigating the chemistry of atomic ions (or neutrals) poised above neutral (or ionized) benzene or other aromatic substrates and so to mimic "graphitic" surface chemistry in the gas phase. For example, these researchers have found that the ^2P ground state of the atomic silicon ion reacts rapidly with benzene in helium buffer gas at 0.35 Torr and 296 ± 2 K to form the adduct ion $SiC_6H_6^{\cdot+}$, $k = (1.5 \pm 0.5) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1},[2,3] and that this adduct ion reacts with molecules in a manner consistent with a π-structure for the adduct ion in which the $Si^{\cdot+}$ is available above the benzene ring for interaction with incoming molecules.[2] No other evidence for the π-structure was available in these experiments. The structures, stabilities, and reactivities of atomic ion and neutral adducts with benzene have now also become of more general interest.[4] Here we report results of a detailed theoretical and experimental investigation of various possible isomeric structures of the adduct of $Si^{\cdot+}$ and benzene and their neutral counterparts. Ab initio MO calculations were performed at the MP2/6-31G**//UHF/3-21G* level, and the experiments were performed with combined collisional activation and neutralization–reionization mass spectrometry which has been shown previously to be well-suited for structural investigations of ions and their neutral counterparts in the gas phase.[5] There have been no previous *structural* investigations of these species other than the indirect reactivity study reported by Bohme et al.[2] Observation of the C–H insertion isomer has not been reported before. There has been no report concerning the stability of the neutral van der Waals molecule Si–C_6H_6, and until recently, evidence for the stability of neutral phenylsilylene has been only indirect and based on end-product studies of the photolysis of phenylsilane, $C_6H_5SiH_3$.[6] A broad absorption feature at ca. 500 nm now has been attributed to C_6H_5SiH in a recent study of the gas-phase insertion reactions of phenylsilylene with Si–H bonds.[7]

Experimental Section

The experiments were performed with a substantially modified ZAB-HF mass spectrometer which has been described in detail previously.[8] The facility is a four-sector mass spectrometer with BEBE configuration, where B denotes a magnetic and E denotes an electric sector. Positive $[Si,C_6,H_6]^{\cdot+}$ ions were generated by the ionization of a mixture of tetramethylsilane and benzene with 70-eV electrons under chemical ionization (CI) conditions (>5 × 10^{-4} Torr) or directly by the electron-impact ionization of phenylsilane under electron-impact ionization (EI) conditions. Measurements at high resolution, $m/\Delta m$ > 4000, indicated the absence of $C_8H_{10}^{\cdot+}$ which lies very close in mass. Negative $[Si,C_6,H_6]^{\cdot-}$ ions were generated from a mixture of phenylsilane as a precursor and N_2O as an electron-moderating gas and as a source gas for $O^{\cdot-}$ under CI conditions.[8a,c] The ion-source conditions were as follows: ion trap current, 100 μA; emission current in chemical ionization mode, 500 μA; ion-source temperature, 200 °C; mass resolution, $m/\Delta m$ = 1500 (10% valley definition).

Collisional activation[9] used to characterize the positive ions leaving the source was achieved by mass-selecting the 8-keV ion beam by means of combined magnetic and electric sectors and colliding the ion beam with He gas in the collision chamber located in the third field-free region (He, 80% transmittance, T). Ionic products were recorded by scanning B(2). In the neutralization–reionization mass spectrometry (NRMS) experiments[10] the 8-keV beam of positive ions was neutralized with xenon (80%

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[3] An energy-rich $SiC_6H_6^{\cdot+}$ complex was first reported by Allen and Lampe to be formed in the collision of $Si^{\cdot+}$ (not state-selected) with C_6H_6 at center-of-mass energies of 0.7–7 eV. Decomposition of this complex was seen to lead to $C_6H_6^{\cdot+}$ and $SiC_6H_5^+$, and the complex could be stabilized by collision at ca. 5 × 10^{-3} Torr of benzene to form the adduct ion $SiC_6H_6^{\cdot+}$. The formation of the adduct could be attributed predominantly to the stabilization of the benzene complexes of the ground-state $Si^{\cdot+}(^2P)$ ions in the $Si^{\cdot+}$ beam. (a) Allen, W. N.; Lampe, F. W. *J. Chem. Phys.* **1976**, *65*, 3378. (b) Allen, W. N.; Lampe, F. W. *J. Am. Chem. Soc.* **1977**, *99*, 2943.

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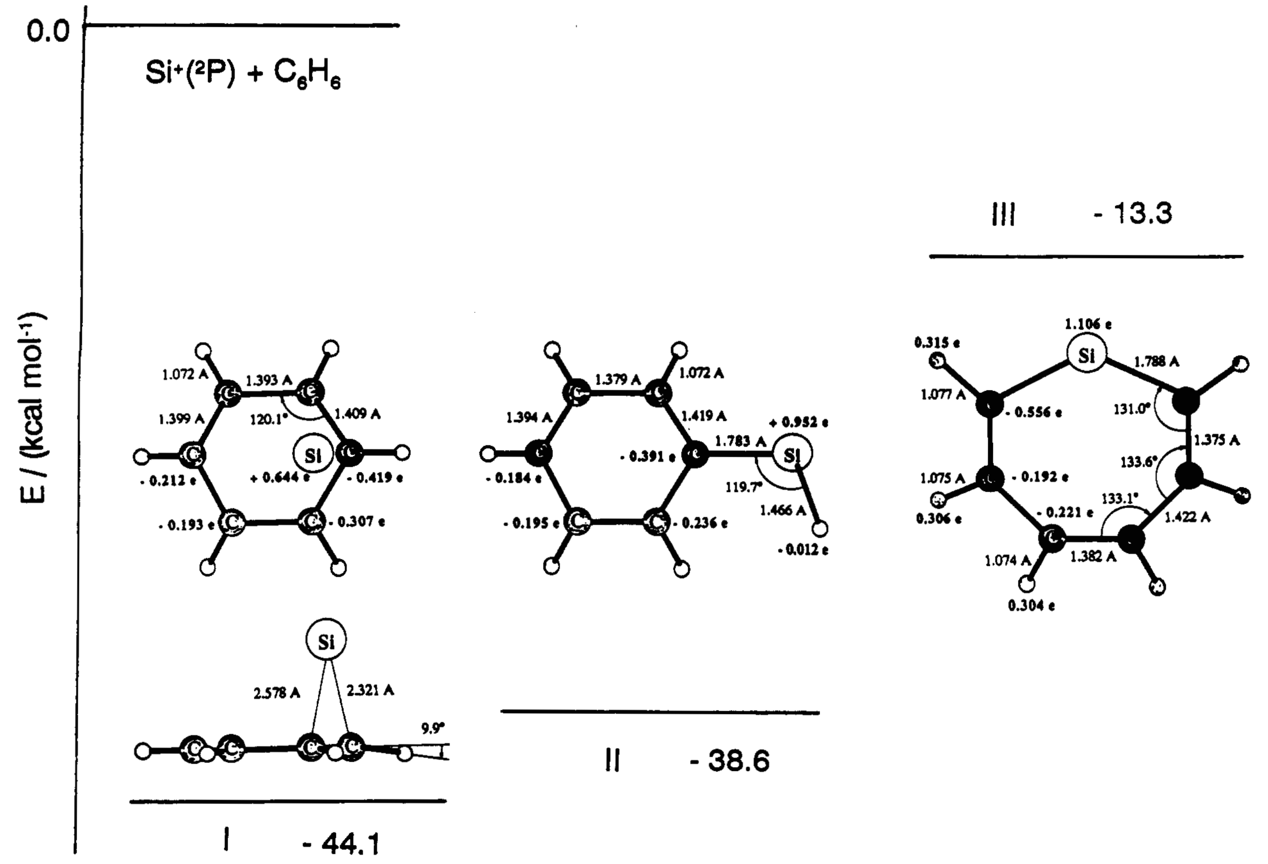

Figure 1. Calculated geometries, charge distributions, and energies (kcal mol^{-1} relative to Si$^{\bullet+}$ and C_6H_6) for isomers of $[H_6,C_6,Si]^{\bullet+}$.

T) in the first of two differentially-pumped collision cells located in the field-free region between E(1) and B(2). Unreacted ions were deflected away from the beam of neutral species by applying a voltage of 1000 V on the deflector electrode. Subsequent reionization occurred in the second collision cell by collision with oxygen (70% T). The resulting mass spectra were recorded by scanning B(2). The experimentally-determined minimum lifetime *t* (equal to the transit time between the two collision cells) is of the order of a microsecond.

Charge reversal (CR) experiments[9b,c,11] with negative ions were performed by colliding the beam of mass-selected anions with O_2 (80% T) also in the second collision cell and recording the positively-charged ions, along with concomitant ionic fragments, by scanning B(2). In the neutralization–reionization ($^-NR^+$) experiments the negative ion beam was neutralized by collisions with O_2 (60% T), the remaining anions were deflected, and the neutrals were reionized by collision with O_2.

In all experiments signal-averaging techniques were used to improve the signal to noise (S/N) ratio. The data were accumulated by on-line processes using an AMD-Intectra computer system DP 10.

Theoretical Section

The lack of previous theoretical studies of ions with composition $[H_6,C_6,Si]^{\bullet+}$ prompted us to perform thorough ab initio MO calculations which will be reported in detail elsewhere.[12] Here we report only the structural features, charge distributions, and energies of the three isomers which are pertinent to the interpretation of the experimental results.

All molecular orbital calculations were performed with the GAUSSIAN 88 program package,[13] in which the open shell systems are treated in the unrestricted Hartree–Fock (UHF) formalism.[14] The geometries were fully optimized (irrespective of all restrictions arising from symmetry) using analytical gradient techniques. All stationary points have been characterized to correspond to local minima or transition structures by having zero or one, and only one, negative eigenvalue in the analytically-computed Hessian force-constant matrix. The structures were optimized with the polarized 3-21G* set,[15] and the same basis set was used for the computation of the zero-point vibrational energy (ZPVE) from the harmonic frequency. The ZPVE was scaled by a factor of 0.89 in order to account for the systematic overestimation of normal frequencies by Hartree–Fock calculations.[16] The effect of electron correlation was taken into account with second-order Møller–Plesset perturbation theory (MP2)[17] at the 3-21G* geometry. This level of calculation has been denoted as MP2/6-31G**//UHF/3-21G*.

Theoretical Results

Figure 1 provides details of the calculated geometrical features, the charge distributions and relative energies (kcal mol^{-1}), total energies of the ionic π-complex, and the Si–H insertion complex and the ring-insertion complex which corresponds to minima on the global potential energy surface. Attempts to approach a σ structure by changing the C–Si–H angle did not lead to a stationary point, whereas a transition state for the rotation around the C–Si axis was found with an imaginary frequency of 314 cm^{-1}.

When all geometric parameters (including C–C bond lengths, for example) are treated as independent parameters, the Si$^{\bullet+}$ ion in the optimized structure of the Si$^{\bullet+}$–benzene π-complex (I in

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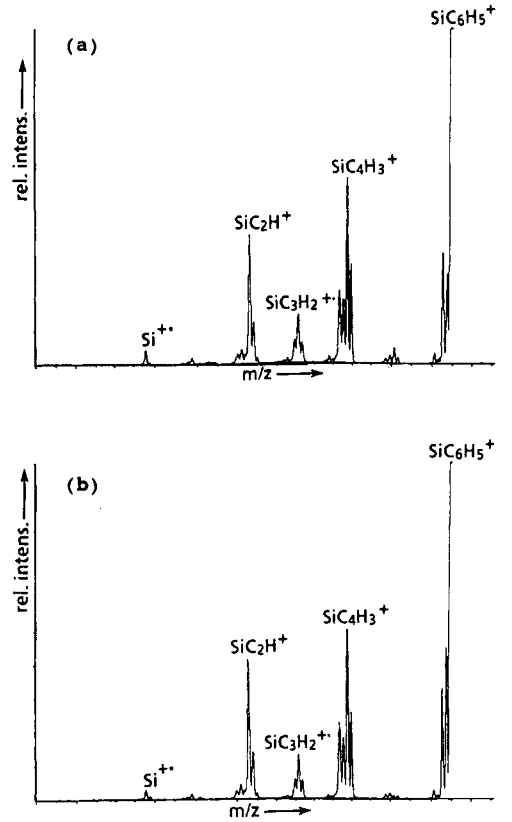

Figure 2. (a) CA mass spectrum (He, 80% T) of *m/z* 106 $[H_6,C_6,Si]^{\bullet+}$ generated under CI conditions by ion-molecule reactions in a mixture of $Si(CH_3)_4$ and C_6H_6. (b) CA mass spectrum (He, 80% T) of *m/z* 106 $[H_6,C_6,Si]^{\bullet+}$ generated from $C_6H_5SiH_3$ by electron-impact ionization at 70 eV.

Figure 1) is displaced from the C_6 axis, resulting in a lowering of the symmetry to C_s. This result is somewhat surprising in view of the SCF/DZ calculations reported by Bauschlicher and Partridge[18] for Mg^+–benzene which indicate that the C_{6v} structure is the global minimum. Our calculations predict that the C_{6v} structure of $Si^{\bullet+}$–benzene is a higher-order, degenerate transition structure which lies 9.8 kcal mol^{-1} higher in energy than the minimum (I). The structural parameters and the formal charges of the π-complex are given in Figure 1. We can report that the calculated separation between $Si^{\bullet+}$ and benzene (2.251 Å) is somewhat shorter than the 2.500-Å separation which results for the C_{6v} structure. The changes in the structure of benzene which result from the addition of $Si^{\bullet+}$ are not particularly pronounced. The C–C bonds are somewhat elongated because of the large coulombic repulsion and the perturbation of the π-system (the C–C bond distance in the isolated benzene molecule is calculated to be 1.386 Å). The C–H bond lengths do not change significantly. But it is noteworthy that a significant charge transfer occurs in the addition of $Si^{\bullet+}$ to benzene which reduces the charge on Si to 0.664 e. Those carbon atoms which participate in the interaction are somewhat more negative as in isolated benzene (q_c = 0.240 e). This perturbation of the π-system results in a slight bending of the corresponding H atoms out of the plane of the benzene molecule, away from the apical silicon atom.[19]

The bonding in the C–H insertion complex (II) given in Figure 1 shows a Si–C bond slightly shorter than a simple Si–C bond (1.849 Å in $HSiCH_3^+$, for example)[20] due to its partial π-character, while the Si–H bond length is similar to that in $SiH_4^{\bullet+}$ (1.477 Å).[21] It is important to note that structure II is planar with a C–Si–H angle of about 120°. The benzene skeleton shows a greater deformation than in structure I. The C_1–C_2 bond has increased significantly (Δr = 0.034 Å) while the C_2–C_3 bond has decreased in length. The positive charge lies almost completely on Si, and the carbon skeleton is only slightly polarized.

The optimized geometry of isomer III shown in Figure 1, resulting from ring insertion, has been found to be planar with C_{2v} symmetry. The Si insertion gives rise to C–C–C bond angles >130°. The calculated C–Si–C out-of-plane deformation frequency is 183 cm^{-1}. The delocalization of the π-system has disappeared so that two different C–C bond lengths result. One of them (1.375 Å) is close to a typical C=C double bond while the other is significantly elongated from its value in unperturbed benzene. The Si–C bond lengths are slightly shorter than a simple single bond (1.849 Å).[20] The C–H bonds remain nearly unchanged as was the case for the other isomers. The positive charge which is located mainly on the silicon (1.106 e) is compensated by the negative charge of the neighboring carbon atoms. In contrast to the two previous isomers, the negative charge of the other four carbon atoms remains nearly the same and the charge on the H atoms has increased by ca. 0.07 e.

Experimental Results

The CA spectrum with helium of the ion at *m/z* 106 with the elemental composition $[H_6,C_6,Si]^{\bullet+}$ derived from a mixture of tetramethylsilane and benzene under CI conditions is shown in Figure 2a.

In order of decreasing intensity, the major peaks recorded in Figure 2a correspond to the following fragmentation reactions (the neutral fragment may or may not leave intact):

$$SiC_6H_6^{\bullet+} \rightarrow SiC_6H_5^+ + H^\bullet \quad (1)$$
$$\rightarrow SiC_4H_3^+ + C_2H_3^\bullet$$
$$\rightarrow SiC_2H^+ + C_4H_5^\bullet\ (C_4H_5^+ + SiC_2H^\bullet)$$
$$\rightarrow SiC_6H_3^+ + H_2 + H^\bullet$$
$$\rightarrow SiC_4H_4^{\bullet+} + C_2H_2$$
$$\rightarrow SiC_6H_4^{\bullet+} + H_2$$
$$\rightarrow SiC_4H^+ + C_2H_5^\bullet\ (C_6H_5^+ + SiH^\bullet)$$
$$\rightarrow SiC_4H_2^{\bullet+} + C_2H_4\ (C_6H_6^{\bullet+} + Si)$$
$$\rightarrow SiC_3H_2^{\bullet+} + C_3H_4\ (C_5H_4^{\bullet+} + SiCH_2)$$
$$\rightarrow Si^{\bullet+} + C_6H_6\ (C_2H_4^{\bullet+} + SiC_4H_4)$$

The CA spectrum obtained with helium for the ion at *m/z* 106 derived by electron impact from phenylsilane (Figure 2b) is essentially identical to that given in Figure 2a with only a slight enhancement in the relative intensity of the *m/z* 76 peak. Also it is interesting to note that the metastable decomposition of these two *m/z* 106 ions are similar and showed peaks at *m/z* 105, 80, 53, and 28 in addition to 105 which dominated the spectrum. Also, the "energy-rich" complex formed in the collision of $Si^{\bullet+}$ with C_6H_6 in the experiments of Lampe[3] at low collision energies was reported to dissociate into $SiC_6H_5^+$ (with loss of $H^\bullet$) and an ion at *m/z* 78 attributed to $C_6H_6^{\bullet+}$ but not resolved from $SiC_4H_2^{\bullet+}$. All these dissociation patterns are consistent with each other but do not seem to provide any significant structure-specific information. They do imply that the parent ions have similar structures either produced in the source directly or as a result of isomerization upon collisional activation.

The results of the neutralization–reionization experiments are much more telling. The NRMS spectra of the *m/z* 106 ion derived from the tetramethylsilane/benzene mixture under CI conditions and from phenylsilane by electron impact are shown in Figure 3, parts a and b, respectively.

It can be seen that the two NR mass spectra are practically identical which again indicates, as was the case with the CA

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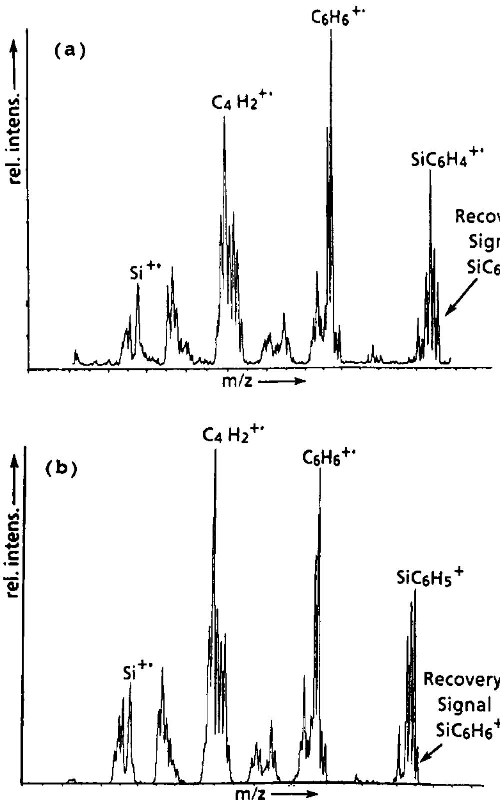

Figure 3. (a) NR mass spectrum (Xe, 70% T; O_2, 70% T) of *m/z* 106 $[H_6,C_6,Si]^{\cdot+}$ generated as in Figure 2a. (b) NR mass spectrum (Xe, 70% T; O_2, 70% T) of *m/z* 106 $[H_6,C_6,Si]^{\cdot+}$ generated as in Figure 2b. The total contribution of the isotopic peaks $^{29}SiC_6H_5^+$ and $^{30}SiC_6H_4^+$ to the recovery signal of $^{28}SiC_6H_6^{\cdot+}$ is 6.4%.

spectra, that the same ion (or mixture of ions) is derived from these two different sources. The most striking features of the two NRMS spectra are the dominance of the peak at *m/z* 78 and the relatively small peak at *m/z* 105. (Both of these features are in sharp contrast to those obtained for the second isomer which will be described later.) These results are most consistent with a connectivity for the *m/z* 106 ion corresponding to the π-complex configuration. The *m/z* 78 ion almost certainly corresponds to $C_6H_6^{\cdot+}$ derived from the ionization of neutral C_6H_6 which would be formed in the neutralization of the π-complex if it dissociates into C_6H_6 and Si. In fact most of the peaks below *m/z* 78 can be attributed to the (dissociative) ionization of the neutral benzene (the NRMS spectrum of ionized benzene was taken separately for comparison), viz., the peaks at *m/z* 77–72, 63–59, 52–48, 39–36, 27–24, and 12. Superimposed on this benzene spectrum are strong features (in decreasing strength) at *m/z* 50, 53, 28, and 65 corresponding to $C_4H_2^{\cdot+}$, SiC_2H^+ ($C_4H_5^+$), $Si^{\cdot+}$ ($C_2H_4^{\cdot+}$), and SiC_3H^+ ($C_5H_5^+$), respectively.[22]

We can conclude from these spectra that the major portion of the *m/z* 106 ion has the connectivity of the π-complex and that it is formed under CI conditions probably by ionization and association reactions exemplified by the steps shown in eqs 2 and 3 and under EI conditions from $C_6H_5SiH_3$ by unimolecular re-

$$e + Si(CH_3)_4 \rightarrow Si^{\cdot+} + (C_4,H_{12}) \qquad (2)$$

$$Si^{\cdot+} + C_6H_6 \rightarrow Si^{\cdot+}\text{-}C_6H_6 \qquad (3)$$

arrangement (eqs 4 and 5).

$$e + C_6H_5SiH_3 \rightarrow (C_6H_5SiH^{\cdot+})^* + H_2 + 2e \qquad (4)$$

$$(C_6H_5SiH^{\cdot+})^* \longrightarrow Si^{\cdot+}\text{-}C_6H_6 \qquad (5)$$

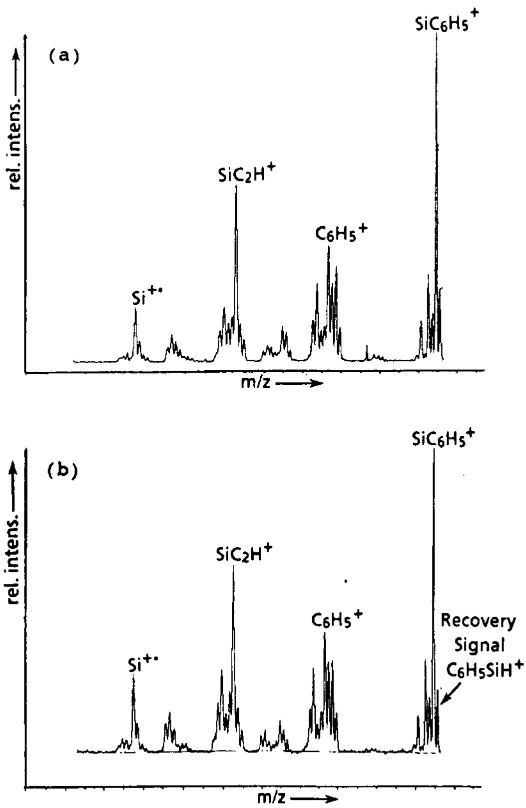

Figure 4. (a) CR spectrum (O_2, 80% T) of *m/z* 106 $[H_6,C_6,Si]^{\cdot-}$ generated under CI conditions by ion–molecule reactions in a mixture of phenylsilane and N_2O. (b) $^-NR^+$ spectrum (O_2, 70% T; O_2, 70% T) of *m/z* 106 $[H_6,C_6,Si]^{\cdot-}$ generated as in Figure 4a.

The observation of the recovery signal, although it is small, implies the occurrence of nearly vertical neutralization and ionization processes,[23] and so some retention of the connectivity and geometry of the initial *m/z* 106 ion. The neutral Si–C_6H_6 is a weakly-bound van der Waals molecule. The calculations indicate a binding energy of only a few kilocalories per mole and no significant geometric changes in the neutralization process.[12] The computed vertical ionization energy is 5.7 eV.

A possible contribution to the recovery signals and other features in the NR mass spectra in Figure 3 by another structure, such as the σ-bonded isomer, cannot be completely ruled out. However, if neutralization of this isomer produces a more survivable neutral, and if it were present in substantial amounts, it would probably lead to a larger recovery signal. Also it is less likely to dissociate upon neutralization to yield C_6H_6 in the relative abundance which was observed. Nevertheless, until an unambiguous source for the σ-bonded isomer becomes available, its contribution to the NR mass spectra in Figure 3 cannot be completely resolved.

Figure 4 shows the charge-reversal (CR) and the neutralization–reionization ($^-NR^+$) spectra of the anion at *m/z* 106, generated in the source from a mixture of phenylsilane and N_2O under CI conditions. On the basis of previous experience with similar systems, we are confident that the anion produced in this case corresponds to $C_6H_5SiH^{\cdot-}$ and that it is formed in the source by the following $H_2^{\cdot+}$ abstraction reaction (eq 6).

$$O^{\cdot-} + C_6H_5SiH_3 \rightarrow C_6H_5SiH^{\cdot-} + H_2O \qquad (6)$$

The CR and $^-NR^+$ spectra in Figure 4 are identical. They contain three strong features at *m/z* 105, 53, and 77 in contrast to the strong features in Figure 3 at *m/z* 50, 78, and 104. This result leaves no doubt about the formation of ionized and neutral isomers different from those derived from the positive ions.

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Furthermore, the interpretation of the spectra in Figure 4 favors the following identification of these isomers as ionized and neutral phenylsilylene, C_6H_5SiH.

In the charge-reversal spectrum, Figure 4a, the peak at m/z 105 corresponds to $H^•$ loss which is expected from the scission of the Si–H bond (which is weaker than the C–H bond). A m/z 77 peak, $C_6H_5^+$, would arise from the scission of the C–Si bond in $C_6H_5SiH^{•+}$ with charge transfer from the SiH unit to the phenyl ring (there is no simple cleavage which produces SiC_4H^+ which also has m/z 77). The large peak at m/z 53 can be accounted for by the formation of SiC_2H^+ + $C_4H_5^•$ or their charge-inversed counterparts. Again, such a dissociation follows from the $C_6H_5SiH^{•+}$ isomer II if the α C–C bond is broken which causes the localization of the double bonds so that the fragmentation of a C_2 unit connected to Si is favored. The strong $H^•$ loss and $SiH^•$ loss appear to be and should be specific to the C–H insertion isomer, C_6H_5SiH. SiC_2H^+, on the other hand, is also an expected fragment of the ionic ring-insertion isomer because of the conjugated nature of the ring, so that the presence of some of this isomer in the CR spectrum cannot be ruled out. Similar interpretations apply to the NRMS spectrum given in Figure 4b. Similar bond rupture is expected in the neutralization of the ion so that reionization establishes the same spectrum as that obtained by charge reversal.

A small but clearly recognizable recovery signal is again observed. Nevertheless, its presence attests to the stability of neutral C_6H_5SiH for which some spectroscopic evidence also has been reported.[7] The theoretical investigation indicates a structure for the neutral very similar to that of the ion and an adiabatic ionization energy of 6.8 eV at 0 K.[12]

Conclusions

(1) Theory predicts that the lowest energy isomer thermodynamically accessible to the interaction of $Si^{•+}$ and benzene is the π-complex so that a π-structure is expected for the adduct formed in the thermal reaction of $Si^{•+}$ with benzene under both the CI conditions employed in this study and the SIFT experiments reported by Bohme et al.[2]

(2) Neutralization–reionization experiments provide evidence for the presence of at least two distinct isomers of the adduct of $Si^{•+}$ and benzene, the π-complex, and the C–H insertion isomer, and their neutral counterparts $Si–C_6H_6$ and C_6H_5SiH. Theory has provided structures, charge distributions, and energies for these two ionic and two neutral isomers, as well as for the neutral and ionized ring-insertion isomers, and predicts the stability order $Si^{•+}–C_6H_6 > C_6H_5SiH^{•+} >$ c-$SiC_6H_6^{•+}$ for the ions and $C_6H_5SiH >$ c-$SiC_6H_6 > Si–C_6H_6$ for the neutrals.

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Registry No. $C_6H_5SiH^{•-}$, 139313-00-1; $Si^{•+}$-C_6H_6, 139313-01-2; $C_6H_5SiH^{•+}$, 139313-02-3; c-$SiC_6H_6^{•+}$, 139313-03-4; C_6H_5SiH, 102389-83-3; c-SiC_6H_6, 139313-04-5; Si-C_6H_6, 139313-05-6; tetramethylsilane, 75-76-3; benzene, 71-43-2; phenylsilane, 694-53-1.

Nitrogen versus Fluorine Protonation of NF_3 in the Gas Phase. A Combined Mass Spectrometric and GAUSSIAN-1 ab Initio MO Study Reveals the Existence of Two Distinct Isomers F_3NH^+ and $F_2N–FH^+$

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Abstract: The potential energy surface of $[N,F_3,H]^+$ ions, generated by the gas-phase protonation of NF_3 using CH_5^+ and H_3^+, is probed by means of high-level GAUSSIAN-1 ab initio MO studies and mass-spectrometric techniques. The global minimum corresponds to the fluorine-protonated isomer $F_2N–FH^+$ (**1**). This ion/dipole complex is found to be 6.4 kcal mol^{-1} more stable than its nitrogen-protonated form F_3NH^+ (**2**). The barrier for the reaction $\mathbf{1} \rightarrow \mathbf{2}$ is significant (52.6 kcal mol^{-1}), thus preventing facile isomerization. Further, while the isomer $F_2N–FH^+$ has a low energy dissociation channel to produce NF_2^+ and HF, with a heat of reaction of <14.6 kcal mol^{-1}, the less stable isomer F_3NH^+ (**2**) is trapped in a deep potential well, which prevents both rapid isomerization and dissociation. The potential energy surface explains the distinctly different kinetic energy releases (KER's) associated with the reaction: $[N,F_3,H]^+ \rightarrow NF_2^+ + HF$. The loss of HF from the ion/dipole complex $F_2N–FH^+$ gives rise to a small KER ($T_{<0.5>}$ = 21 meV), while the same reaction of F_3NH^+ (**2**) is associated with a dished-top peak and a large KER ($T_{<0.5>}$ = 740 meV).

Introduction

The question of the protonation site of nitrogen fluoride, NF_3, has been recently addressed by Fisher and McMahon[1a] in the context of a study of the intriguing gas-phase ion chemistry of NF_3/CH_4 mixtures. In addition to the remarkable insertion of NF_2^+ into CH bonds of CH_4 to eventually generate $HCNH^+$, protonated NF_3 was formed, and the reactivity pattern in ion/molecule reactions was found to be consistent with the existence of fluorine-protonated isomer $F_2N–FH^+$ (**1**) rather than a nitrogen-protonated ion F_3NH^+ (**2**). Additional structural evidence

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