A Theoretical Study of Some Reactions of HCSi⁻

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Abstract: The ions HCSi⁻ and H₂CSiH⁻ produced in recent flowing afterglow experiments are characterized structurally. Reactivity of the former ion with four molecules (CO_2, OCS, CS_2, SO_2) is examined. Three of these species react in a sequence of intermediates of cyclic followed by acyclic structures, before reaching the final products.

Introduction

Recent experiments by Damrauer and DePuy[1] have produced silaacetylide anion, of composition HCSi⁻ (m/z = 41), along with about 20 other anions, including one of composition H₃CSi⁻ (m/z = 43). The ions were produced by electron bombardment of methylsilane in a tandem flowing afterglow apparatus. Virtually all possible breakup products of methylsilane are observed,[2] for example, SiH$_x^-$ (x = 0–3) and SiCH$_x^-$ (x = 0–5). Some recombination products are also seen, such as Si₂H$_x$ (x = 0–3). After mass selection of any one of the ions produced in the initial bombardment, that species may be reacted with various small molecules injected into the flow tube. Such reactivity experiments, using small molecules such as CO_2, OCS, CS_2, SO_2, MeI, MeOH, and H₂S, have been carried out with the m/z species 41 and 43.[3] A description of the apparatus and of similar experiments involving silaformyl anion (HSiO⁻) is available,[3a] as is a similar study[3b] of reactions of H₃Si⁻ and (CH₃)₃Si⁻.

The present paper considers two questions raised by these experiments: What is the structure of the m/z species 41 and 43? How do the four species CO_2, OCS, CS_2, and SO_2 react with the m/z = 41 ion silaacetylide? Of the four reactants considered here, only three are known to lead to reaction.[1] CO_2 reacts with HCSi⁻ to yield an ion of composition HCCO⁻, OCS reacts to yield HCCS⁻, and SO_2 reacts to yield HCSO⁻. CS_2 apparently does not react.[2]

Computational Method

Standard quantum chemical techniques can be applied to the present problem. All of the reactions that will be considered here are symmetry allowed, so closed-shell SCF wave functions (RHF) are used to locate transition states as well as equilibrium geometries. Electron correlation contributions to energetics are obtained with use of second-order perturbation theory (MP2).[4]

Anions such as those considered here are formed by adding an electron to a half-filled valence orbital. Alternatively, the ions may be thought of as formed by deprotonation of neutral closed-shell species. It is thus apparent that these anions are not as diffuse as those formed by adding an electron to a closed-shell species like water. Therefore, all structures reported for the present ions are located with use of the 6-31G* basis.[5] Experience[6] shows reliable structures may be obtained for this type of anion without the use of diffuse functions. All structures are verified as either minima or transition states by analytic computation of the energy Hessian, which has either zero or one imaginary frequency, respectively. All structures and frequencies reported below were obtained at this RHF/6-31G* level.

The final energies are obtained with diffuse functions[7] added to all atoms and polarizations functions added to hydrogen.[5] Thus the final energies are obtained from calculations with double-ζ plus polarization plus diffuse basis sets and may be summarized as MP2/6-31++G**//RHF/6-31G*, where the // means "at the geometry of". These energies are corrected to include zero-point corrections obtained at the RHF/6-31G* level, and thus correspond to the enthalpy difference at absolute zero, Δ$H°$(0). Unless otherwise mentioned, all energies reported in this paper are at this level.

In a few instances we have tested the effect of electron correlation at higher levels, up to fourth-order perturbation theory. These MP4/6-31++G**//RHF/6-31G* results are quite time consuming. As will be shown, the MP4 results are similar enough to the MP2 values that the latter are deemed appropriate.

The majority of the calculations were performed with use of GAMESS,[8] while some of the preliminary Hessian runs and the MP4 calculations were performed with use of GAUSSIAN86.[9]

Structures of the m/z = 41 and 43 Ions

These two ions were chosen from the twenty produced by electron bombardment for a study of their chemistry,[1] because the most plausible structures for them involve silicon–carbon triple and double bonds, respectively. While silicon–carbon double bonds are well-known,[10] the triple bond is characterized only theoretically.[10] The question of their structure is easily resolved computationally.

The m/z = 41 ion is silaacetylide anion, HC≡Si⁻. This linear arrangement, with the hydrogen attached at the carbon end, is the only stable molecule on the triatomic surface. The linear structure with the H at the Si end is a second-order transition state, with a doubly degenerate imaginary frequency of 501i cm⁻¹ and an energy 59 kcal/mol above the minimum. All nonlinear trial structures optimize to the linear minimum. The computed bond distances for the minimum are R(CH) = 1.071 and R(CSi) = 1.622 Å. This may be compared to typical experimental CSi single-bond (1.87 Å) and CSi double-bond (1.70 Å) distances.[11] The computed frequency for the CSi stretch is 1245 cm⁻¹, which may be compared to computed stretching frequencies for the CSi single bond (736 cm⁻¹) and CSi double bond (1080 cm⁻¹).[11] On the basis of both bond length and stretching frequency, we feel silaacetylide ion is best represented as a triple bond.

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(7) Standard diffuse exponents were used: H (s = 0.0360), C (l = 0.0438), O (l = 0.0845), Si (l = 0.0331), and S (l = 0.0405), where l means an sp shell. See: Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. R. *J. Comput. Chem.* **1983**, *4*, 294–301. See footnote 13 of: Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265–3269.

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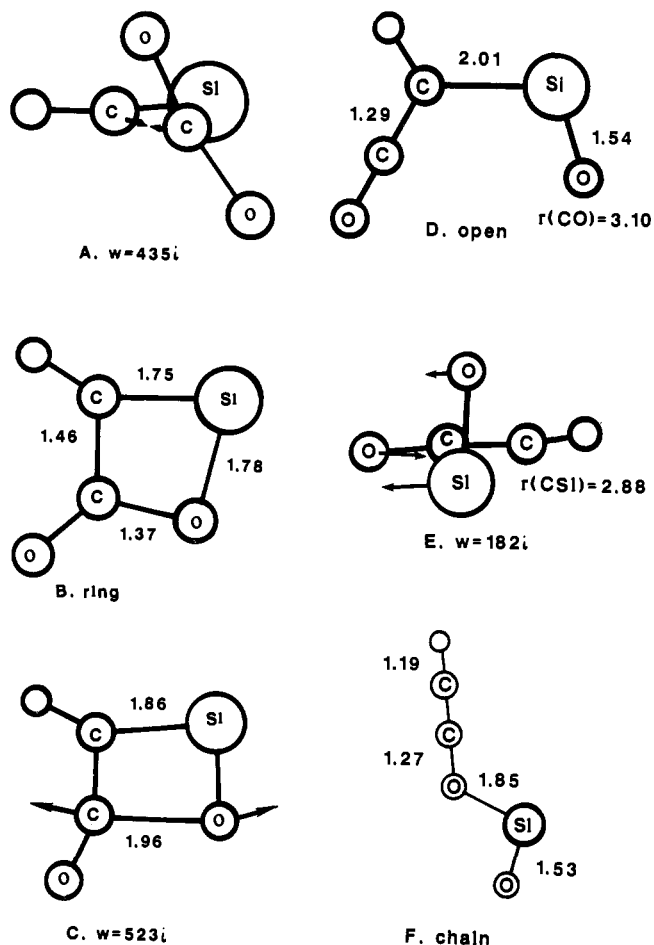
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Figure 1. Structures at stationary points for the CO_2 reaction. Bond distances in angstroms, angles in degrees, transition frequencies in wavenumbers.

It is interesting to contrast the linear geometry found for HCSi⁻ with computations on the neutral parent silaacetylene. These studies[12] have found a trans-bent configuration, with a CSi bond length of 1.635 Å. Our finding of a single linear minimum for the anion is in agreement with earlier work, which did not include vibrational characterization of HCSi⁻ structures.[13]

The $m/z = 43$ ion is best thought of as a deprotonated form of silaethene, $H_2C\text{=}SiH_2$. In this case, two minima are found on the potential surface, corresponding to removing a proton from either the C or Si end of silaethene. Both deprotonated structures are planar. Deprotonation at Si gives a species with a bond length of 1.751 Å and a CSi stretch at 945 cm⁻¹. Deprotonation at C leads to an isomer of higher energy, by some 35 kcal/mol, but with a shorter bond length of 1.719 Å. Comparing these distances with those quoted two paragraphs above shows both ions are best described as containing doubly bonded C=Si. We have located the saddle point for hydrogen 1,2-migration connecting these isomers. It has an energy of 71 kcal/mol relative to the more stable $H_2C\text{=}SiH^-$ and is decidedly nonplanar. The migrating H is approximately perpendicular to the remaining four atoms, the CSi bond length is 1.87 Å, and the transition frequency is 654i cm⁻¹.

The transition state for the migration occurs at a geometry that seems to have a bridging hydrogen and occurs at a high energy. We have carried out FORS-type MCSCF calculations[14] on the

minima and the transition state, using six active electrons in five orbitals. For example, for $H_2C\text{=}SiH^-$, the active orbitals would be the π and π^*, the Si lone pair, and the CH σ and σ^* orbitals. The MCSCF/6-31G* barrier is 65 kcal/mol, at an essentially unchanged bridged structure, with an isomerization energy of 34.5 to HC=SiH₂⁻. The results are essentially identical with the HF+MP2 results presented in the preceding paragraph.

Note that there are two more possible isomers for the $m/z = 43$ species, namely $H_3C\text{—}Si^-$ and $C\text{—}SiH_3^-$. Both of these are triplet ground states (e^2 configurations) and have been considered before.[14] The geometries have been reoptimized at the UHF level here, so that their energies might be compared to the doubly bonded structures discussed above. At the HF level, triplet $H_3C\text{—}Si^-$ lies just below singlet $H_2C\text{=}SiH^-$, but MP2 level calculations reverse this. This result is not surprising: closed-shell singlets typically have more correlation energy than triplets do. At the highest level we consider here, UMP2/6-31++G**, singlet $H_2C\text{=}SiH^-$ is the most stable $m/z = 43$ isomer, by 10 kcal/mol relative to triplet $H_3C\text{-}Si^-$, by 35 kcal/mol relative to singlet HC=SiH₂⁻, and by 69 kcal/mol relative to triplet C-SiH₃⁻. We have not considered isomerizations to the two triplets, as the two doubly bonded structures are on singlet surfaces.

At first glance, it might seem odd that either the only or the most stable isomer of these species is one bearing negative charge at Si. However, knowing that the gas-phase acidities (energy for deprotonation) of silane and methane are 374 ± 2.7 and 416.6 ± 1.0 kcal/mol[16] readily rationalizes the present results: It is easier to deprotonate at the Si end of the molecule.

Reactions of HCSi⁻

The four reactants with HCSi⁻ considered here are CO_2, OCS, CS_2, and SO_2. These four were chosen for their small size and apparent range of reactivity patterns. Three of the four are known to react, while CS_2 apparently does not.[2] We note that one of the possible reaction channels of OCS is unprobed. The observed ion products can be rationalized by four-membered ring structures.
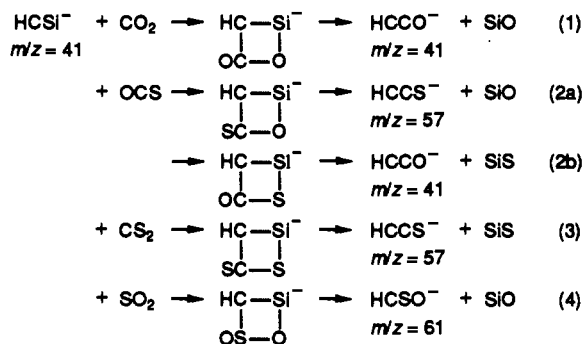
Note that the product ion HCCO⁻ coincidentally has the same mass as the reactant, HCSi⁻. However, reaction 1 with CO_2 has been proved to occur, as using labeled ¹³CO_2 leads to labeled HC¹³CO⁻ at $m/z = 42$.[1] The corresponding labeling experiment for reaction 2b has not been done; however, reaction 2a is known to occur. Reaction 3 is not observed, while reaction 4 does occur.

The calculations reported here find a similar pattern for all four reactions. All reactions initially proceed via a very stable four-membered ring. An internal barrier (lower than the isolated reactants) separates the four-membered rings from an open form. This open form is obtained by opening the bottom side of the ring and also has a longer CSi distance than the initial ring. The SiX neutral fragment can now dissociate without barrier to the observed (or unobserved) products indicated. Alternatively, the open forms can rearrange to chain forms, with a zigzag shape, such as HCCO-SiO. These chain forms can also dissociate neutral SiX without barrier to arrive at the products. All four overall reactions are found to be exothermic, and each will be discussed below. The reaction with CO_2 is discussed in the greatest detail.

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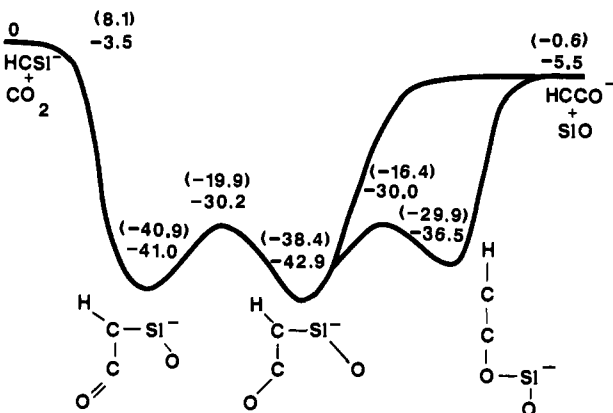
Figure 2. Schematic potential energy surface for the CO_2 reaction. MP2/6-31++G** energies relative to the reactants are given in kilocalories per mole, with RHF energies at the same level in parentheses.

Reaction with CO_2. Structures for species involved in the CO_2 reaction are shown in Figure 1, with a schematic potential energy surface shown in Figure 2. At the SCF level, there is a small barrier to the formation of the four-membered ring. This barrier disappears with inclusion of electron correlation at the MP2 level. The structure at this reaction bottleneck is shown in Figure 1A and shows that the CC bond forms well before the SiO bond. The attack of CO_2 is nonplanar, with a twist angle of about 55° between the CO_2 and HCSi⁻ planes.

The planar ring (Figure 1B) that is formed has a short CSi bond distance of 1.753 Å, almost as short as a double bond. The negative charge in this molecule sits mainly in a doubly occupied p_π orbital on carbon, where it has moved from the Si atom of the reactant HCSi⁻. The silicon in the ring is a silylene species, with a lone-pair orbital in plane and a vacant p_π orbital. Of course, with filled and vacant p_π orbitals on adjacent C and Si atoms, partial delocalization occurs. The resulting partial π bond is responsible for the short CSi bond distance. The rest of the bonding in the ring is conventional. The ring is very stable compared to the reactants, lying 41 kcal/mol below them.

Concerted cleavage of the ring to form the observed product ion HCCO⁻ and the inferred neutral cofragment SiO does not occur. Instead, the ring opens the CO bond initially, passing over a barrier (Figure 1C) that lies 30 kcal/mol below the reactants. This transition state leads to an "open form" (Figure 1D), which has a nonbonded CO distance of 3.10 Å and an unusually long CSi distance of 2.01 Å. Despite its appearance, this open form is actually slightly more stable than the ring, lying at 43 kcal/mol below the reactants.

At this point the SiO fragment can dissociate by simple detachment. The energy rises as the SiO fragment leaves, to form the products HCCO⁻ and SiO at an energy 5.5 kcal/mol below the initial reactants. Calculations at various fixed values of r(CSi) out to $R = 4.0$ Å, with optimization of all other geometry parameters, show that the dissociation proceeds via a barrierless, uphill climb.

The reactions shown in Figure 2 are all Woodward–Hoffmann allowed. It is possible to draw reasonable, closed-shell Lewis structures for all species involved, showing all 13 valence pairs. Each has three a″ (π) symmetry orbitals, so that the transformations are in fact allowed. Furthermore, it is possible to add "electron pushing arrows" to show how the orbitals rearrange during these reactions:
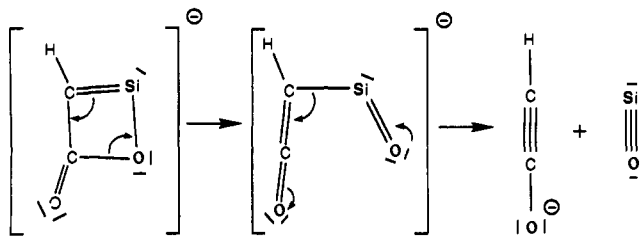

Since even the open form is a closed-shell species (that is, opening the CO bond does not yield a diradical), triplet states are at relatively high energy. The vertical excitation energy from the open form to a ³A″ state is 45 kcal/mol (calculated qualitatively with restricted open-shell SCF, ROHF/6-31++G**). This is somewhat above the reactants HCSi⁻ and CO_2. Surprisingly, although the reactants also possess exactly three a″ orbitals when arranged in a coplanar geometry, the bottleneck in the entrance channel occurs at a geometry with no symmetry, as discussed above.

As an alternative to direct detachment, the SiO fragment can undergo a 1,3-migration via Figure 1E to a chain structure shown in Figure 1F. The zigzag-shaped "chain form" represents the third quite stable reaction intermediate, at 37 kcal/mol below the reactants. To understand the open and chain structures, one must examine the electronic structure of the HCCO⁻ product. This ion is linear (consider isoelectronic HCCF), and possesses alternating Mulliken charges: H, +0.12; C, –0.62; C, +0.28; O, –0.78. It is thus apparent that the positive Si end of SiO would prefer to attach to the first C, as in the open form, or at the O, as in the chain form. The transition state connecting the planar open and chain structures must of necessity bring the Si atom near the middle C. In this configuration, there would be an unfavorable overlap of the Si$^{\delta+}$O$^{\delta-}$ dipole with the HCCO⁻, so the transition state shown in Figure 1E actually contains a SiO rotated nearly perpendicular to the HCCO.

The chain structure closely resembles the final products. The HCCO portion has a nearly linear geometry and bond lengths near those of the isolated ion. The SiO also has nearly the same length as the free diatom. Note that the OSi cross-link distance in the chain is 1.85 Å, shorter than the CSi bond in the open form (Figure 1D) but still significantly longer than a normal OSi single bond (1.63 Å).[11] It is not surprising that SiO dissociates in a uphill climb to the observed products.

We note that there are two additional minima on this surface that are not shown in Figure 2. Both the open and chain conformations possess rotational minima where the O is cis rather than trans to the hydrogen atom. These rotamers are 1.0 kcal/mol below and 0.7 kcal/mol above the trans-type conformations shown in Figures 1, parts D and E, respectively. Thus, the cis rotamer of Figure 1D is the lowest energy structure found on the surface, at 44 kcal/mol below HCSi⁻ and CO_2. The barriers to rotation from trans to cis are moderate, 4.0 and 6.2 kcal/mol for Figure 1, parts D and F, respectively. This means there is free rotation of the SiO groups within the approximately 10 kcal/mol deep relative minima for the closed and chain forms.

Finally, we note that CO_2 can react to form a different four-membered ring

$$\begin{array}{ccc} HC & - & Si^- \\ | & & | \\ O & - & C - O \end{array}$$
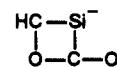
lying 4 kcal/mol above the reactants, with a barrier through a planar transition state of 9.5 kcal/mol to its formation. Because of its high energy, and because it does not appear to be related to the observed ionic product HCCO⁻, this type of ring is not considered for the other reactions.

Reaction with OCS. This reactant is interesting because it can form a ring with HCSi⁻ in two orientations (reactions 2a and 2b). The energetics for this reaction are summarized in Figure 3. Note first of all that the more exothermic channel leading to HCCS⁻ is the one which is observed experimentally. The other channel has not been definitively ruled in or out, as the mass labeling needed to prove or disprove the formation of HCCO⁻ has not been done. However, this second channel is more than twice as exothermic as the production of HCCO⁻ in the CO_2 reaction. The driving force for the preferred channel is presumably formation of the very stable SiO bond compared to the SiS diatom.

It is interesting that reaction 2b is actually favored initially over reaction 2a. Thus, for the first two intermediates of these parallel reaction sequences (the ring and open conformations), placing the O atom exocyclic gives a lower energy.
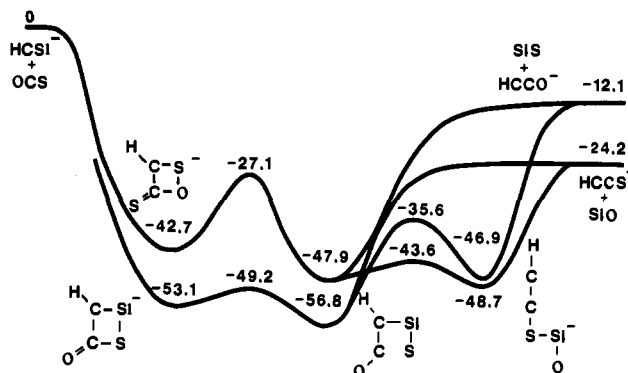
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Figure 3. Schematic potential energy surface for the OCS reaction. Numbers have the same meaning as in Figure 2.

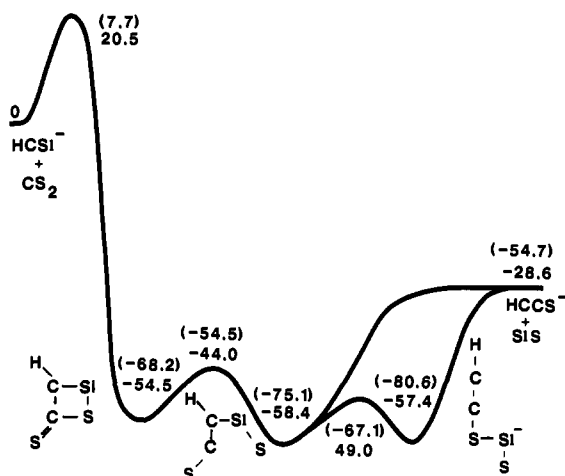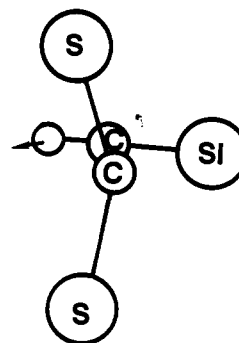**Figure 4.** Schematic potential energy surface for the CS_2 reaction. Numbers have the same meaning as in Figure 2.

W=147i

Figure 5. Transition state in the entrance channel of the reaction of CS_2 with HCSi⁻. The transition frequency is in wavenumbers.
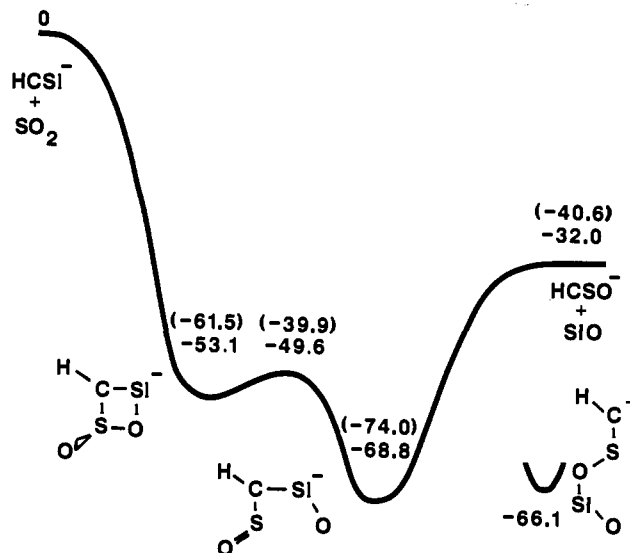

Figure 6. Schematic potential energy surface for the SO_2 reaction. Numbers have the same meaning as in Figure 2.

As for the CO_2 reaction, there is a transition state on the SCF surface leading to the S exocyclic ring (reaction 2a). The energy at this structure is reduced below the reactants when the second-order perturbation correction is included. At the bottleneck structure the two attacking molecules are even more twisted than in the CO_2 reaction, with a SiCCO dihedral of 79.2°. Again, the CC bond (2.36 Å) forms faster than the SiO bond (3.47 Å).

We were unable to locate a saddle point leading to the lower energy O exocyclic ring (reaction 2b). If the CC bond distance is fixed at 2.36 Å and the SiCCO dihedral varied in a full circle in steps of 10°, while optimizing all remaining geometric parameters, one obtains the potential for rotation about the CC bond. This rotational potential has two equivalent minima, at the SCF transition state just described ($\omega = \pm79.2°$). Relative maxima occur at ω(SiCCO) = 0° and 180°. Full geometry searches for both planar forms yield stationary points with *two* imaginary frequencies, one of which is rotation toward the 79° true transition state for reaction 2a.

The zero-point-corrected MP2 energies at these planar stationary points are 9.9 and 11.1 kcal/mol for $\omega = 0°$ and 180°, respectively, above the 79° true transition state. Since the true SCF saddle point lies 2 kcal/mol *below* the reactants (after inclusion of ZPE and MP2), these planar geometries are 8 and 9 kcal/mol above the reactants. Thus, all orientations between about 45° and 135° have energies not appreciably higher than the reactants. Presumably, a smaller angle attack will lead to the S exocyclic ring, while a larger angle attack leads to the O exocyclic ring.

Reaction with CS_2. CS_2 is not experimentally observed to react with HCSi⁻. The features of the potential energy surface are entirely analogous to the reactions of CO_2 and OCS, except for one crucial difference. Energetics for the ring, open, and chain minima are summarized in Figure 4. The CS_2 approaches the HCSi⁻ with both S's avoiding the Si end (Figure 5). This has

a small barrier at the RHF level, which *increases* to 20 kcal/mol with the inclusion of second-order perturbation theory. It is this initial barrier to the reaction that prevents this channel from being seen experimentally, in spite of its large overall exothermicity.

Reaction with SO_2. Seemingly, the reaction of SO_2 ought to be rather different than the three just considered. However, as Figure 6 reveals, there are more similarities than differences. Once again, ring, open, and chain conformers are found. The few differences are mainly quantitative: The entrance channel does not possess a barrier on the SCF surface. The ring form is nonplanar, as the exocyclic O which is "doubly bound" to sulfur is actually bonded by a dative bond (S lone pair to vacant O atom orbital). Thus, this oxygen's position is determined by the location of the S lone pair, and so is out of plane. The open and chain forms are still planar, however. Despite an extensive search, no transition state separating these open and chain forms could be found. The product fragment HCSO⁻ is cis bent, so that the open and chain conformers shown schematically in Figure 6 are also cis bent in this part of the molecule. While the experimentally observed product at $m/z = 61$ could be HSiS⁻, the calculations support the identification of this product as HCSO⁻ produced via the now familiar four-membered ring pathway.

MP4 vs MP2

In order to test the validity of using second-order perturbation theory to treat the present systems, the overall exothermicities of the four reactions were calculated with use of third- and fourth-order perturbation theory. The results are shown in Table I.

Table I. Reaction Exothermicities (kcal/mol)

	(1)	(2a)	(2b)	(3)	(4)
RHF/6-31G*	6.3	−30.0	−17.3	−54.5	−36.2
RHF/6-31++G**	−0.6	−30.3	−22.3	−53.4	−40.6
MP2/6-31++G**	−5.5	−24.2	−12.1	−27.3	−32.0
MP3/6-31++G**	−3.9	−25.7	−17.8	−37.8	−35.3
MP4/6-31++G**	−5.7	−23.2	−11.7	−26.6	−37.3

Generally speaking, the MP2 values reproduce the MP4 results very well (reaction 4 is the worst case). The quality of the basis affects only reactions 1 and 2b, while inclusion of electron correlation at the MP2 level can have a dramatic effect.

We have performed one MP4 calculation on the ring form of reaction 1. This ring lies −40.9, −41.0, −46.6, and −44.9 kcal/mol below the reactants at the RHF, MP2, MP3, and MP4 levels with the diffuse basis set. The MP4 calculation required 17 cpu days on a Celerity minicomputer, and thus consistent application of MP4 to the present problem is prohibitive. Fortunately, MP2 is shown to give fairly reliable agreement with the full MP4 tests that were done.

Conclusions

The reactions of HCSi⁻ involve the initial formation of stable four-membered rings, of the type proposed by Damrauer, DePuy, Barlow, and Gronert.[1] However, these do not undergo synchronous cleavage to the observed products; instead, they open at one side leading to two different acyclic forms. Either of these can break a second bond, leading to the experimentally observed products.

Ab Initio Studies on the Hydrogen-Bonded Complexes between Hydrogen Fluoride and Hydroxylamine

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Abstract: The minimum-energy geometries for the complexes between hydrogen fluoride and hydroxylamine (HF)₁H₂NOH and (HF)₂H₂NOH were studied at the Hartree–Fock level and also at the second-order level in many-body perturbation theory (MBPT(2)) in order to estimate the effects of electronic correlation. The novel ring structures observed recently for these hydrogen-bonded complexes were confirmed. The 1:1 complex contains a loosely bound ring structure with a strong N–HF bond and weak long HF–HO bond. An association enthalpy of about −6 to −9 kcal/mol is predicted. For the 1:2 complex, a second HF molecule is inserted into the ring between the first HF moiety and the HO group. This complex exhibits three strong hydrogen bonds and a correspondingly larger association enthalpy of approximately −17 to −19 kcal/mol. The harmonic vibrational analysis at the MBPT(2) level supports most of the assumptions made in the analysis of the FTIR studies.

Introduction

Of the weak interactions, hydrogen bonding is the strongest. It is important in a wide variety of natural phenomena from the formation of interstellar clouds to determining the conformation and properties of biological compounds. Studies on isolated hydrogen-bonded complexes can provide new information on how hydrogen bonding affects the properties of molecular complexes. With the development of new theoretical and experimental methods, increasingly larger and more complex systems are being studied. One such example is the (HF)ₙ–H₂NOH complexes.

The hydrogen fluoride–hydroxylamine complexes represent a particularly interesting and difficult problem. Recently Lascola and Andrews have identified such complexes and proposed that they have cyclic structures.[1] They opted to use argon matrix isolation FTIR spectroscopy at temperatures of 12–25 K. This was dictated by the instability of hydroxylamine, which dissociates to water and ammonia. The possible presence of such dissociation products made the analysis of the FTIR data particularly difficult. Both HF and H₂NOH are capable of forming strong hydrogen bonds. Hydroxylamine has two electron-rich basic sites, the

nitrogen and oxygen. Some suspicion exists that the basicity of the nitrogen may be sufficiently reduced by the oxygen that the latter might become the preferred site of hydrogen atom attachment. The identification of the primary binding site was one of the major concerns of Lascola and Andrews.

The FTIR spectra indicated that both of the complexes (HF)₁NH₂OH (the 1:1 complex) and (HF)₂NH₂OH (the 1:2 complex) are stable. Both were of a cyclic nature. The primary binding site for HF attachment was the more basic nitrogen atom. However, for the 1:1 complex, the F atom formed a long secondary hydrogen bond with the hydroxyl hydrogen as indicated by the perturbation to the OH stretching and NOH bending motions. The large blue shift to the NH₂ wagging mode and the nature of the perturbation to the HF stretching vibration indicate that the nitrogen is the primary binding site, not the oxygen. Isotopic substitution on both monomers supports these conclusions as well as the cyclic geometry of the 1:1 complex. The attachment of the second HF molecule is also of considerable interest. Lascola and Andrews speculate that the second HF molecule inserts into the ring to give a seven-member ring with the linkage –N--H–F--H–F--H–O–.[1] The evidence for this structure is however not

(1) Lascola, R.; Andrews, L. *J. Am. Chem. Soc.* **1987**, *109*, 4765.