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Computational Study of the Proton-Transfer Chemistry of the Silaacetylide Anion

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Summary: Reactions involving two [H,C,Si]$^-$ anions with the protonated neutral analogues (HSiCH, H_2CSi, and H_2SiC) have been studied. Calculations through fourth-order perturbation theory (MP4) suggest possible routes for single-proton transfer between the silaacetylide [HCSi]$^-$ anion and neutral species. Various important reaction paths for proton-transfer reactions and internal rearrangements of ion−molecule complexes are discussed. Accurate estimates of the acidity of HSiCH and H_2SiC are presented and discussed in light of earlier experimental studies.

Introduction

The silaacetylide anion [HCSi]$^-$ was prepared in early tandem flowing afterglow selected ion flow tube (FA-SIFT) experiments.[1] Both experimental and computational studies indicate that the connectivity of this anion is that shown above.[1] Reactivity studies of [HCSi]$^-$ with CO_2, COS, and SO_2 found reactivity patterns that are characteristic of other low-valent silicon-containing anions.[2] Measurement of the basicity of [HCSi]$^-$ using the bracketing method gave a ΔH_{acid} value of 360 ± 3 kcal/mol for the acidity of the parent compound. The parent was assumed to be H_2CSi on the basis of computational studies establishing it as the most stable [H_2,C,Si] isomer.[3−6] Related computational work has been carried out on the reaction chemistry of [HCSi]$^-$.[7] The experimental reaction studies combined with these computational studies have provided further insight into the chemistry of the silaacetylide ion by probing the potential energy surface (PES) and its numerous low-lying transition states and minima in detail. The present computational paper considers an aspect of previous work that is not fully understood, namely, the details of the proton-transfer reactions of [HCSi]$^-$.

Computatonal Methods

The reactions were initially probed using the restricted Hartree−Fock (RHF) method with the 6-31++G(d,p) basis set.[8−12] The structures were determined by optimizing the geometry using analytical gradient methods. The RHF structures were then refined using Møller−Plesset second-order perturbation theory (MP2)[13] with the same basis set (6-31++G(d,p)).

The identification of stationary points as minima or saddle points was determined by calculation and diagonalization of the Hessian force-constant matrix (matrix of energy second derivatives). Transition states were determined at both the RHF and MP2/6-31++G(d,p) levels of theory.

Once the transition states were located, minimum energy reaction paths connecting reactants with products. The intrinsic reaction coordinates (IRC) were calculated using the Gonzalez−Schlegel second-order method[14,15] normally using a step size of 0.3 amu$^{1/2}$ bohr; steps as small as 0.01 amu$^{1/2}$ bohr were used in regions close to minima intrinsic reaction path (IRP) calculations were carried out at both the RHF and MP2/6-31++G(d,p) levels of theory.

Using the MP2/6-31++G(d,p) stationary points, advanced levels of theory were employed to obtain more reliable energies: fourth-order perturbation theory (MP4) and single and doubles coupled-cluster theory with triple excitations estimated perturbatively (CCSD(T)).[16] The MP4 calculations were carried out using the 6-311++G(d,p) basis,[8−12] and the CCSD(T) calculations were performed with the 6-311++G^{2df,2pd} basis set.[8−12] The notation A//B indicates that an energy is calculated by method A using a geometry optimized by method B.

Ion−molecule complexes were located by positioning neutral species 3−5 Å away from an anion and allowing full geometry optimization. Variations in orientation of the ion with respect to the neutral substrate resulted in different complexes from the same reactants. Minima, as well as first- and second-order saddle points, were located using this technique. The second-order saddle points were used to locate minima or first-order saddle points by following the IRP's associated with the imaginary frequencies.

Reaction energies in the following discussions are reported relative to the energy of HCSi$^-$ + H_2CSi, the lowest energy anion−neutral reaction studied at the CCSD(T)/6-311++G(2df,2pd) level of theory.

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Table 1. MP2/6-31++G(d,p), MP4/6-311++G(d,p), and CCSD(T)/6-311++G(2df,2pd) Relative Energies (in kcal/mol) of the Reactants[a]

reactant	MP2//MP2	MP4//MP2	CCSD(T)//MP2	ZPE
$HCSi^-$	0[b]	0[c]	0[d]	8
$HSiC^-$	+59	+52	+59	5
H_2CSi	0[e]	0[f]	0[g]	14
HCSiH	+39	+37	+38	13
H_2SiC	+97	+89	+88	10

[a] ZPE is the MP2/6-31++G(d,p) harmonic zero-point energy. [b] Relative to −327.525 56 Hartree. [c] Relative to −327.576 45 Hartree. [d] Relative to −327.620 74 Hartree. [e] Relative to −328.094 96 Hartree. [f] Relative to −328.151 15 Hartree. [g] Relative to −328.196 17 Hartree.

Calculations were carried out using either GAMESS[17] or Gaussian 92/DFT,[18] with their respective built-in basis sets.

Results and Discussion

1. Reactants. The relative energies of H_2CSi, HCSiH, H_2SiC, $HCSi^-$, and $HSiC^-$ at various levels of theory are presented in Table 1 (relative to $HCSi^-$ for the anions and H_2CSi for the neutrals). These data as well as the MP2/6-31++G(d,p) geometries are consistent with previous computations establishing $HCSi^-$ and H_2CSi as the most stable species on their respective potential energy surfaces.[3,7]

Thus, H_2CSi lies 88 kcal/mol below H_2SiC and 38 kcal/mol below HCSiH at the CCSD(T)/6-311++G(2df,2pd)//MP2/6-31++G(d,p) level of theory. H_2CSi has C_{2v} symmetry, with a C−Si bond length of 172 pm (a typical C−Si single bond length is ∼180 pm). Although silaacetylene, HSiCH, is not a stationary structure on the RHF/6-31++G(d,p) potential energy surface, it exists as a minimum with a Si−C bond distance of 163 pm at the MP2/6-31++G(d,p) level of theory. Unlike acetylene, however, HSiCH has a nonlinear trans geometry. Unlike HSiOH, no cis isomer can be found.[19]

The far less stable $HSiC^-$ isomer is a second-order saddle point (two imaginary vibrational frequencies) at the RHF/6-31++G(d,p) level of theory. At the MP2/6-31++G(d,p) level of theory, it exists as a stable, albeit high-energy, minimum. Both $HSiC^-$ and $HCSi^-$ are linear. Calculations at the CCSD(T) level of theory suggest that $HSiC^-$ probably does not exist, since the barrier to hydrogen transfer is ∼0. Ion−molecule studies suggest that the nucleophilic center of reactivity of $HCSi^-$ is at carbon ($HC^-{=}Si$).[1]

2. Gas-Phase Enthalpies of Acidity. FA-SIFT experiments using bracketing techniques have established that $\Delta H_{acid} = 360 \pm 3$ kcal/mol for the conjugate acid of $HCSi^-$.[1] Since the most energetically accessible conjugate acid is H_2CSi, the computed $\Delta H_{acid} = 355$ kcal/mol (CCSD(T)) leading to $HCSi^-$ is the most relevant entry in Table 2 (several other computed ΔH_{acid} values at different theoretical levels are presented). Comparison of the experimental and computational results for $H_2CSi \rightarrow H^+ + HCSi^-$ show a reasonable correspondence. Thus, the computational studies of the proton-transfer dynamics reported in the next section are important in evaluating the possible pathways for this reaction.

Table 2. Computed ΔH_{acid} Values (in kcal/mol at 298.15 K) at Various Levels of Theory

reaction	MP2//MP2	MP4//MP2	CCSD(T)//MP2
$HSiCH \rightarrow HCSi^-$	314	319	318
$H_2SiC \rightarrow HSiC^-$	315	319	327
$H_2CSi \rightarrow HCSi^-$	351	355	355
$HSiCH \rightarrow HSiC^-$	370	368	373

Table 3. Combined Relative Energies (in kcal/mol) of Anions and Neutral Combinations, Including MP2/6-31++G(d,p) Zero-Point Energy Corrections, at MP2/6-31++G(d,p), MP4/6-311++G(d,p), and CCSD(T)/6-311++G^{2Df,2pd} Levels of Theory

reactants	MP2//MP2	MP4//MP2	CCSD(T)//MP2
$HCSi^- + H_2CSi$	0[a]	0[b]	0[c]
$HCSi^- + HCSiH$	+38	+36	+37

[a] Relative to −655.620 53 Hartree. [b] Relative to −655.727 60 Hartree. [c] Relative to −655.816 91 Hartree.

3. Proton-Transfer Reactions. Additional interest in the details of the proton-transfer reactions derives from recent studies of Gronert on a series of proton-transfer identity reactions, $AH_n + {}^-A'H_{n-1} \rightarrow {}^-AH_{n-1} + A'H_n$, of the second- and third-row elements (CH_4, NH_3, H_2O, HF, SiH_4, PH_3, H_2S, and HCl) at several computational levels.[20] Such proton transfers are dramatically different, depending on the nature of A. Thus, the barrier to proton transfer for second- and third-row elements decreases as the electronegativity of A increases, and the double-well potential of $[CH_3\cdots H\cdots CH_3]^-$ with a significant barrier “monotonically” transforms with increasing electronegativity until a single-well potential with a stable, symmetric intermediate for $[F\cdots H\cdots F]^-$ is obtained. Gronert also observed that third-row elements experience higher barriers to proton transfer when compared with second-row analogues of similar acidity.

Although all of the proton-transfer reaction combinations between the anions $HCSi^-$ and $HSiC^-$ and the neutral molecules H_2CSi, HCSiH, and H_2SiC have been studied, only $HCSi^-$, H_2CSi, and HCSiH, the lower energy species on the $[H_2,C,Si]/[H,C,Si]^-$ PES, are considered here (reactions 1−3).

$$HCSi^- + H_2CSi \rightarrow H_2CSi + HCSi^- \quad \Delta H^\circ = 0 \text{ kcal/mol} \quad (1)$$

$$HCSi^- + HSiCH \rightarrow HSiCH + HCSi^- \quad \Delta H^\circ = 0 \text{ kcal/mol} \quad (2)$$

$$HCSi^- + HSiCH \rightarrow H_2CSi + HCSi^- \quad \Delta H^\circ = -37 \text{ kcal/mol} \quad (3)$$

The CCSDT/6-311++G(2df,2pd)//MP2/6-31++G(d,p) ΔH° values (in kcal/mol, including MP2/6-31++G(d,p) zero-point energy correc-

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Table 4. Reaction Species and Relative Energies[a] (in kcal/mol) for Reactions 1−3

reacn 1	reacn 2	reacn 3	reacn 3
$H_2CSi + HCSi^-$ (0)	$HCSiH + HCSi^-$ (36)	$HCSiH + HCSi^-$ (36)	$HCSiH + HCSi^-$ (36)
complex **1** (−59)	complex **2** (−53)	complex **3** (−45)	complex **3** (−45)
TS1-1 (10)	$HCSiH + HCSi^-$ (36)	**TS3-4** (−9)	**TS3-5** (18)
complex **1** (−59)		complex **4** (−66)	complex **5** (−48)
$H_2CSi + HCSi^-$ (0)		$H_2CSi + HCSi^-$ (0)	$H_2CSi + HCSi^-$ (0)

[a] Relative to $H_2CSi + HCSi^-$ at the CCSD(T)/6-311++G(2df,2pd) levels of theory.

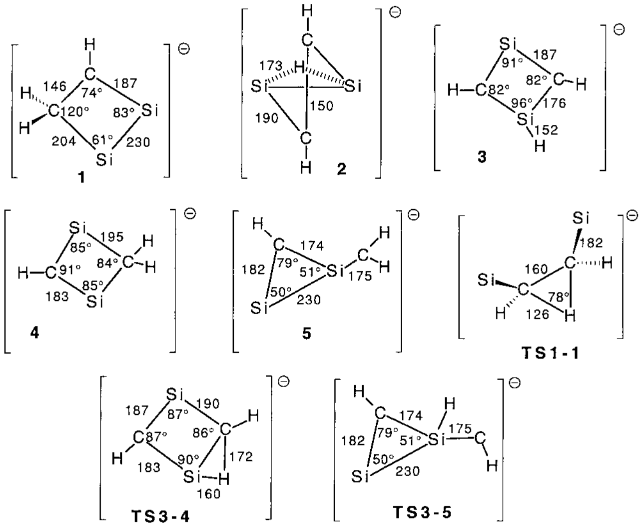

Figure 1.

tions) are listed to the right of each reaction. Table 3 gives the relative energies of these combinations of anions and neutrals studied at the different levels of theory. Table 4 summarizes the pathways discovered for reactions 1−3.

Examination of reaction 1 has revealed only one proton-transfer pathway. It involves the formation of a four-membered disilane complex (**1**; Figure 1) whose energy is 59 kcal/mol below the entrance channel energy. Considerable lengthening of the C−Si bonds in both $HCSi^-$ and H_2CSi accompany complex formation. Proton transfer occurs through a symmetric three-membered transition state (**TS1-1**), which is characterized by a mirror plane bisecting two equivalent HCSi fragments that has a hydrogen atom bridging the two carbon atoms. The formation of transition state **TS1-1** requires fission of the Si−Si bond of **1** as well as movement of a hydrogen atom to the bridging position. Accompanying this is a shortening of the Si−C bond distances. Critical to an examination of this reaction is the 10 kcal/mol barrier that would significantly limit the rate of such a proton transfer.

The identity reaction (2) charts the interaction between the lower energy anion, $HCSi^-$, and the relatively high energy neutral, HCSiH. It is a barrierless proton transfer and occurs through complex **2**, a structure containing a hydrogen atom bridging two silicon atoms. Complex **2** has C_{2v} symmetry with a mirror plane bisecting the two silicon atoms and including the three hydrogen and two carbon atoms. The symmetry of this complex shows clearly that the bridging hydrogen can transfer to either silicon atom, yielding two equivalent sets of products.

The most exothermic of eqs 1−3 also involves the reaction of $HCSi^-$ and HCSiH but results in the more stable products $HCSi^-$ and H_2CSi (eq 3). This reaction proceeds from reactants 36 kcal/mol above the MP4 reference reactants to form the four-membered, 1,3-disilacyclobutyl complex **3**, which is 45 kcal/mol below that reference. These computations suggest that a proton in complex **3** is transferred from the silicon through transition state **TS3-4** to a carbon atom to form complex **4**. The barrier to complex **4** is 36 kcal/mol but is far below the entrance channel energy. Complex **4** also is a 1,3-disilacyclobutyl anion but differs from **3** in that it has its hydrogen atoms attached to carbon. Complex **4** then can dissociate to products through a barrierless exit channel. Complex **3** has another, slightly higher energy, pathway to the exit channel $HCSi^-$ plus H_2CSi products. Here **TS3-5** has an unusual 1,2-disilacyclopropyl structure, which is reached by a complex rearrangement involving the scission of two Si−C bonds and the formation of one Si−Si bond. It is through **TS3−5** that a hydrogen transfer occurs from the ring SiH to the exocyclic CH. The resulting complex **5** continues to products by ring fragmentation.

Another feature of complex **4** that has been examined is its ring inversion, in which **TS4-4** with C_{2v} symmetry connects the two mirror images of complex **2**. This barrier is 5 kcal/mol above **4**.

Complexes **2**−**4** are among the lower energy complexes located relative to the MP4 reference species. As lower energy minima on the $[H_3,C_2,Si_2]^-$ potential energy surface, it is quite likely that such species could be observed experimentally. Each of these complexes is characterized by having a greater number of stronger C−H than of weaker Si−H bonds.

Conclusions

The silaacetylide anion has a rich chemistry.[1] Several stable, low-energy anion−neutral complexes on the $[H_3,Si_2,C_2]^-$ potential energy surface have been found in these computations. These species are complexes between the lower energy anion $HCSi^-$ and H_2CS and HCSiH. The key findings of these computations are as follows.

(1) Only a trans isomer of HCSiH can be found.

(2) The computed gas-phase acidity of H_2CSi is close to the experimental acidity reported for the conjugate acid of $HCSi^-$.

(3) Proton-transfer reactions between $HCSi^-$ and both H_2CSi and HCSiH lead to several ion−dipole complexes (Table 4 and Figure 1), which have energies sufficiently lower than the separated reactants so that these reactions can be driven to products.

(4) Protonation of $HCSi^-$ does not give triply bonded $HC{\equiv}SiH$.

(5) The barrier to proton transfer in the most energy favorable reaction, $HCSi^- + H_2CSi$, is slightly higher

than the separated reactants and, consquently, should retard its rate.

Taken together, these computational results are consistent with the preliminary experimental studies; however, they also provide some insight into the proton-transfer dynamics.

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Additions and Corrections

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Xinjian Lei, Maoyu Shang, and Thomas P. Fehlner*: Reactions of the Cobaltaborane 2,4-$\{(\eta^5\text{-}C_5Me_5)Co\}_2B_3H_7$ with Metal Fragments. Synthesis and Characterization of *nido*-1-$\{(\eta^5\text{-}C_5Me_5)Co\}$-2-$\{(CO)_3Fe\}$-$B_3H_7$ and *arachno*-$\{(\eta^5\text{-}C_5Me_5)(CO)CoB_3H_7$.

Page 1560. The cluster 2-(Cp*Os)-3-$\{(PPh_3)_2(CO)Rh\}$-B_3H_7 should be 2-(Cp*Ir)-3-$\{(PPh_3)_2(CO)Os\}B_3H_7$. We thank Prof. Lawrence Barton for bringing this error to our attention.

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