

also not as high and the associated kinetic energy release (3.2 eV) is larger.

**Ar<sub>2</sub><sup>2+</sup> Dication.** The calculated stability of the argon dimer dication **9**, like that of the hydrogen fluoride dimer dication **4**, is sensitive to the introduction of electron correlation into the calculations. At the Hartree-Fock level, **9** is predicted to be unbound, but at the UMP2 level, a barrier of 65 kJ mol<sup>-1</sup> impedes its fragmentation. However, more sophisticated correlation treatments reduce this barrier until, at the level of fourth-order perturbation theory (RMP4), it disappears altogether. However, at this level, it appears that the potential curve is rather flat for 2 < r < 3 Å, and this plateau may be detectable in collision experiments. The simple ACDCP model<sup>10</sup> for the fragmentation of a diatomic dication predicts that the transition-structure bond length in the case of Ar<sub>2</sub><sup>2+</sup> is 2.24 Å, which is similar to that (2.159 Å) of the UMP2/6-31G(d) structure **17**.

### Concluding Remarks

Many of the important results of this paper are summarized in Table VI, and it is useful to note some of the features of dicationic structure and stability that are revealed in this table.

(1) The dimer dications (A<sub>2</sub><sup>2+</sup>) are more tightly bound than corresponding (hemibonded) monocations (A<sub>2</sub><sup>•+</sup>) in the sense of exhibiting shorter equilibrium A-A bond lengths, but the dissociation barriers are generally smaller (and in some cases close to zero) for the dications.

(2) Transition-structure bond lengths and the associated barriers for the symmetric fragmentations and deprotonations of the dimer dications H<sub>n</sub>XXH<sub>n</sub><sup>2+</sup> are largest when X is a group V element, and both quantities decrease from left to right across the periodic table. This is in accord with the qualitative predictions of the ACDCP model (vide supra) but contrasts with the pattern of hemibond strengths in the related H<sub>n</sub>XXH<sub>n</sub><sup>•+</sup> systems,<sup>2</sup> which are greatest when X is from group VII.

(3) The hydrazinium and diphosphonium dications (**2** and **6**, respectively) should form very stable salts. Three of the remaining dimer dications (H<sub>2</sub>OOH<sub>2</sub><sup>2+</sup>, H<sub>2</sub>SSH<sub>2</sub><sup>2+</sup>, and HClClH<sup>2+</sup>) may be experimentally observable under certain (nonequilibrium, low-temperature, or short-time-scale) conditions. The other dimer dications (HFFH<sup>2+</sup>, Ne<sub>2</sub><sup>2+</sup>, and Ar<sub>2</sub><sup>2+</sup>) appear to be unstable.

(4) The equilibrium structures of the dimer dications are comparable to those in their isoelectronic, isostructural, neutral analogues. For example, the geometries of He<sub>2</sub><sup>2+</sup> (**1**) and H<sub>3</sub>NNH<sub>3</sub><sup>2+</sup> (**2**) are very similar to those of the hydrogen and ethane molecules, respectively.

(5) The value of the Δ parameter for a dicationic fragmentation is a very useful indicator of the dissociation behavior. Thus, (a) a small Δ value (less than ~2-3 eV) indicates that the associated transition structure will be late and, in such cases, Δ constitutes a reliable measure of the consequent kinetic energy release; (b) for fragmentations with larger Δ values, the transition structures occur earlier along the reaction coordinate, and the resulting kinetic energy releases are larger, though bounded above by Δ; and (c) if the Δ value for a fragmentation is large (greater than ~15 eV), the barrier inhibiting the fragmentation is likely to be small or nonexistent. A notable exception is the extraordinary He<sub>2</sub><sup>2+</sup> dication **1**.

**Acknowledgment.** We gratefully acknowledge a generous allocation of time on the Fujitsu FACOM VP-100 of the Australian National University Supercomputer Facility.

**Supplementary Material Available:** Calculated total energies, zero-point vibrational energies, and ⟨S<sup>2</sup>⟩ values of the dimeric dications, their deprotonated and dehydrogenated forms, and relevant transition structures (Table VII) and of fragment neutrals, monocations, and dications (Table VIII) (4 pages). Ordering information is given on any current masthead page.

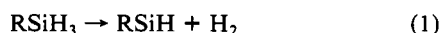
## A Theoretical Investigation of the Primary Dissociation Paths of Ethynylsilane

J. J. W. McDouall, H. B. Schlegel, and J. S. Francisco\*

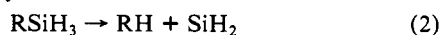
Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. Received July 5, 1988

**Abstract:** Various mechanisms leading to the dissociation of ethynylsilane have been investigated by ab initio molecular orbital methods. Geometries corresponding to the reactant, transition states, and products have all been optimized at the HF/3-21G and HF/6-31G\* levels of theory. Heats of reaction and barrier heights have been obtained at the MP4SDTQ/6-31G\* level. Zero-point energy corrections and harmonic vibrational frequencies have been computed at the HF/3-21G level. These results have been used to calculate unimolecular dissociation rate constants by RRKM theory. This information is then used to reexamine the mechanisms of dissociation for ethynylsilane from previous experimental shock-tube and stirred-flow studies.

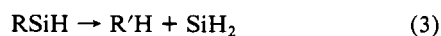
It has become generally accepted that the predominant dissociation process in alkyl-, alkenyl-, and arylsilanes is the formation of hydrogen via



with alkanes (or alkenes) formed from minor channels for primary dissociation pathways



or secondary reaction from the substituted silylene formed in reaction 1.



It is the minor and secondary channels that are responsible for the production of SiH<sub>2</sub>, an intermediate acknowledged to be important in the formation of amorphous silicon thin films. Results from numerous shock-tube and photodissociation studies<sup>1-10</sup> of

(1) Ring, M. A.; O'Neal, H. E.; Rickburn, S. F.; Sawrey, B. A. *Organometallics* **1983**, *2*, 1891.

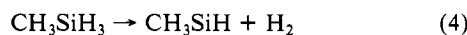
(2) Sawrey, B. A.; O'Neal, H. E.; Ring, M. A.; Coffey, D., Jr. *Int. J. Chem. Kinet.* **1984**, *16*, 31.

(3) Sawrey, B. A.; O'Neal, H. E.; Ring, M. A.; Coffey, D., Jr. *Int. J. Chem. Kinet.* **1984**, *16*, 801.

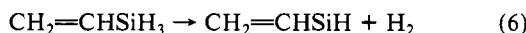
(4) Rickburn, S. F.; Ring, M. A.; O'Neal, H. E. *Int. J. Chem. Kinet.* **1984**, *16*, 1371.

a variety of organosilanes support the general claim that reaction 1 is the predominant primary dissociation process. In a series of ab initio molecular orbital studies, we have examined the relative importance of primary dissociation pathways for the simplest alkyl- and alkenylsilanes.<sup>11,12</sup>

Both experimental and theoretical studies support the claim that 1,1 H<sub>2</sub> elimination predominates the primary dissociation process of small alkylsilanes such as methylsilane<sup>5-7,13,14</sup> and ethylsilane.<sup>1,4,11</sup>



Studies on vinylsilane,<sup>1,9,12</sup> the simplest alkenylsilane, reveal that the predominant dissociation leads to the formation of hydrogen via



However, theoretical studies<sup>12</sup> have predicted 1,2 silyl shifts to be competitive with reaction 6. The simplest alkynylsilane is ethynylsilane; its major dissociation product is acetylene as shown from shock-tube and stirred-flow studies.<sup>15,16</sup> The dominant mechanism of dissociation has been suggested to involve 1,1 hydrogen elimination.



In this work we have investigated primary reaction pathways for ethynylsilane to determine if the 1,1 hydrogen elimination is also predominant over all other processes.

Computational Methods

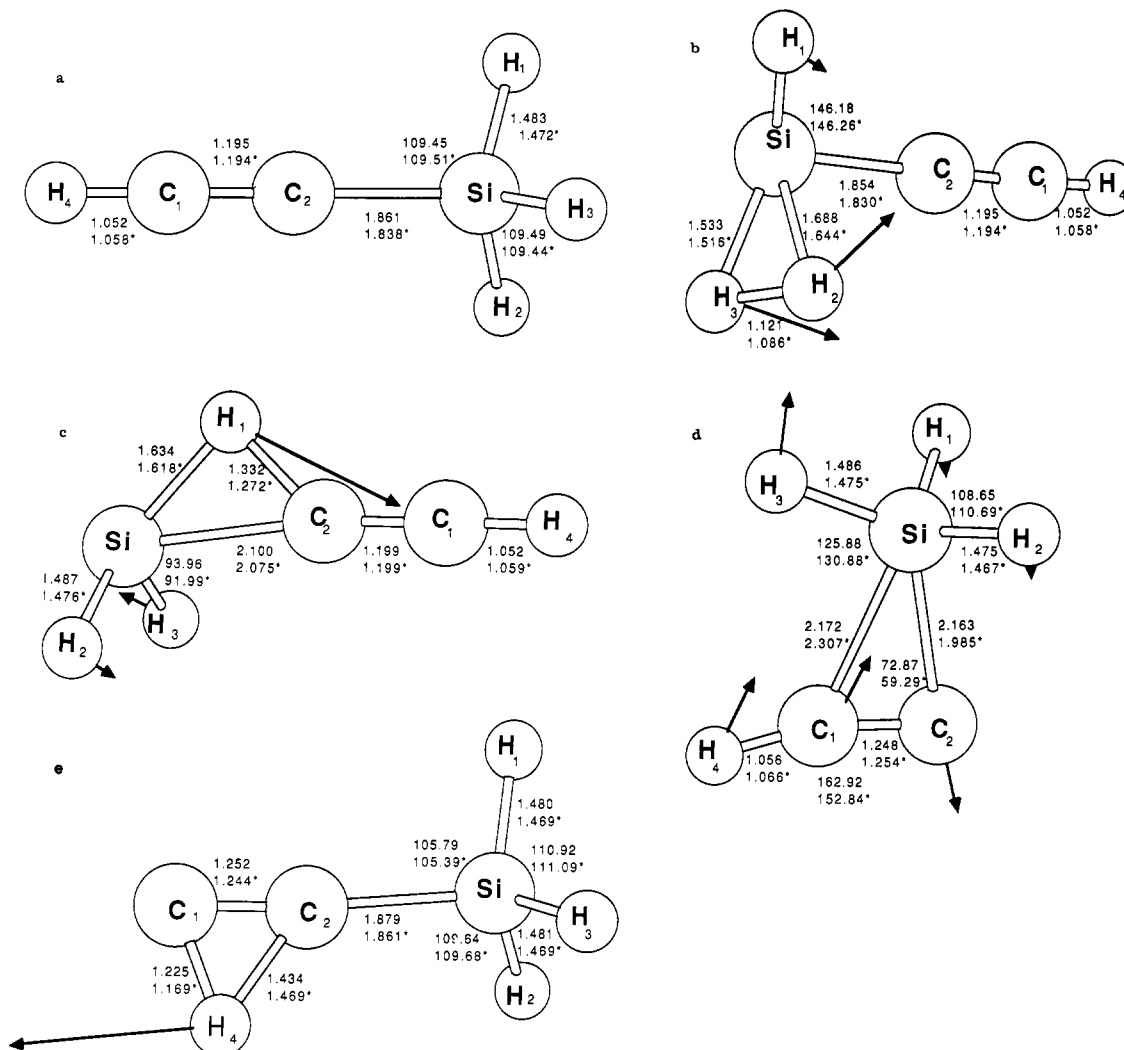
All calculations were performed with the GAUSSIAN 86 suite of programs<sup>17</sup> using split-valence (3-21G)<sup>18</sup> and polarized (6-31G\*)<sup>19</sup> basis sets. All equilibrium and transition-state geometries were fully optimized at the Hartree-Fock level using analytical gradient methods.<sup>20</sup> The effects of electron correlation were estimated by Møller-Plesset perturbation theory to fourth order<sup>21</sup> (including all single, double, triple, and quadruple excitations, frozen-core approximation). Harmonic vibrational frequencies were obtained from analytical second derivatives<sup>22</sup> calculated

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Table I. Optimized Geometries of Reactant, Transition States, and Products

	[CCH(SiH <sub>3</sub> ) <sup>†</sup> ]						[CCH(SiH <sub>3</sub> ) <sup>†</sup> ]						[CCH(SiH <sub>3</sub> ) <sup>†</sup> ]						[CCH(SiH <sub>3</sub> ) <sup>†</sup> ]						[CCH(SiH <sub>3</sub> ) <sup>†</sup> ]						[CCH(SiH <sub>3</sub> ) <sup>†</sup> ]																	
	HCCSiH <sub>3</sub> <sup>a</sup>		1,2 silyl <sup>b</sup>		1,2 hydrogen <sup>c</sup>		:CCH(SiH <sub>3</sub> ) <sup>c</sup>		[HCCSiH + H <sub>2</sub> ] <sup>a</sup>		HCCSiH + H <sub>2</sub> <sup>a</sup>		[C <sub>2</sub> H <sub>2</sub> + SiH <sub>2</sub> ] <sup>a</sup>		C≡CSiH <sub>3</sub> <sup>a</sup>		HC≡C + SiH <sub>3</sub> <sup>a</sup>		HCCSiH <sub>2</sub>																													
	3-	6-	3-	6-	3-	6-	3-	6-	3-	6-	3-	6-	3-	6-	3-	6-	3-	6-	3-	6-	3-	6-	3-	6-	3-	6-	3-	6-	3-	6-	3-	6-	3-	6-	3-	6-												
R(H <sub>2</sub> H <sub>3</sub> ) <sup>d</sup>	1.195	1.194	1.248	1.254	1.252	1.244	1.285	1.284	1.121	1.086	1.188	1.185	1.199	1.199	1.233	1.228	1.224	1.215	1.205	1.202																												
R(C <sub>2</sub> )	1.052	1.058	1.056	1.066	1.225	1.169			1.195	1.194	1.051	1.057	1.199	1.199	1.233	1.228	1.224	1.215	1.205	1.202																												
R(C <sub>1</sub> H <sub>4</sub> )	1.861	1.838	2.172	2.307	1.879	1.861	1.914	1.890	1.052	1.058	1.052	1.057	1.052	1.052	1.863	1.839	1.053	1.058	1.052	1.058																												
R(SiC <sub>2</sub> )	1.483	1.472	1.475	1.467	1.480	1.469	1.481	1.470	1.882	1.848	1.882	1.848	2.100	2.075	1.863	1.839	1.487	1.476	1.476	1.476																												
R(SiH)	1.483	1.472	1.475	1.467	1.481	1.469	1.483	1.472	1.528	1.506	1.531	1.509	1.487	1.476	1.483	1.472	1.487	1.476	1.476	1.476																												
R(SiH <sub>2</sub> )	1.483	1.472	1.475	1.467	1.481	1.469	1.483	1.472	1.688	1.644	1.531	1.509	1.487	1.476	1.483	1.472	1.487	1.476	1.476	1.476																												
R(SiH <sub>3</sub> )	1.483	1.472	1.475	1.467	1.481	1.469	1.483	1.472	0.735	0.730	1.531	1.509	1.487	1.476	1.483	1.472	1.487	1.476	1.476	1.476																												
R(C <sub>2</sub> H <sub>4</sub> )			2.163	1.985	1.434	1.469	1.076	1.078																																								
R(C <sub>2</sub> H <sub>1</sub> )			109.49	109.44	108.65	110.69	111.09	109.98	111.97	109.86	93.80	93.32	1.332	1.272																																		
H <sub>2</sub> SiH <sub>2</sub>	109.45	109.51	100.94	97.84	105.79	105.39	109.72	109.52	94.88	95.30																																						
H <sub>2</sub> SiC	109.45	109.51	100.94	97.84	105.79	105.39	109.72	109.52	146.18	146.26																																						
H <sub>2</sub> SiC <sub>2</sub>	109.45	109.51	100.94	97.84	105.79	105.39	109.72	109.52	112.27	111.87																																						
H <sub>3</sub> SiC <sub>2</sub>	109.45	109.51	100.94	97.84	105.79	105.39	109.72	109.52	93.65	93.85																																						
C <sub>2</sub> C <sub>2</sub> Si	180.00	180.00	172.87	59.29	177.06	174.60	116.65	114.11	177.28	174.88																																						
H <sub>4</sub> C <sub>2</sub> C <sub>2</sub>	180.00	180.00	162.92	152.84	53.76	50.21	123.85	123.86	179.86	179.76																																						
H <sub>4</sub> C <sub>2</sub> C <sub>1</sub>									179.88	179.76																																						

<sup>a</sup> See Figure 1a for atom numbering. <sup>b</sup> See Figure 1d for atom numbering. <sup>c</sup> See Figure 1e for atom numbering. <sup>d</sup> Bond lengths in angstroms. <sup>e</sup> Bond angles in degrees.

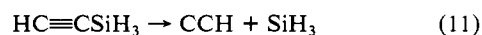
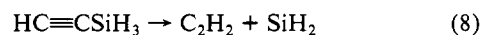


**Figure 1.** Reactants and transition states for the dissociation of ethynylsilane (HF/3-21G-optimized geometry, no superscript; HF/6-31G\*-optimized, asterisk; see Table I for the complete list of geometrical parameters).

at the HF/3-21G//HF/3-21G level. Finally, unimolecular rate constants were obtained by RRKM theory<sup>23</sup> using the HF/3-21G unscaled harmonic frequencies and the MP4SDTQ/6-31G\*//HF/6-31G\* estimates of the reaction barrier corrected for zero-point energy.

### Results and Discussion

In addition to reaction 7 mentioned above, our study of the primary dissociation pathways of ethynylsilane includes the following pathways:



The optimized geometries and transition states for reactions 7–12 are summarized in Table I, and the transition-state structures obtained for reaction 7–9 are displayed in Figure 1. The structural features for ethynylsilane calculated at the HF/6-31G\* level are in good agreement with values derived from microwave data<sup>24,25</sup> (CC = 1.826 ± 0.003 Å, CSi = 1.207 ± 0.006 Å, and SiH = 1.455 ± 0.002 Å).

**Table II.** Vibrational Frequencies<sup>a</sup>

reactant: HC≡CSiH <sub>3</sub>	transition structures			
	1,2 silyl	[CCH(SiH <sub>3</sub> )] <sup>‡</sup> 1,2 hydrogen	[C <sub>2</sub> H <sub>2</sub> + SiH <sub>2</sub> ] <sup>‡</sup>	[HCCSiH + H <sub>2</sub> ] <sup>‡</sup>
332 E	349i a'	1179i a'	1447i	1727i
655 A <sub>1</sub>	188 a''	100 a''	303	327
742 E	501 a'	296 a''	328	366
980 E	663 a'	347 a'	489	617
1007 A <sub>1</sub>	682 a''	625 a'	698	666
1026 E	801 a''	735 a''	818	755
2299 E	952 a'	746 a''	840	851
2310 A <sub>1</sub>	1004 a'	988 a'	964	945
2338 A <sub>1</sub>	1025 a'	1007 a''	976	1000
3651 A <sub>1</sub>	1034 a''	1036 a'	981	1110
	1971 a'	2056 a'	1730	1548
	2284 a'	2311 a''	2263	2153
	2341 a'	2319 a'	2272	2319
	2346 a''	2323 a'	2282	2330
	3585 a'	2354 a'	3645	3652

<sup>a</sup>Harmonic vibrational frequencies in reciprocal centimeters calculated at the HF/3-21G level.

If viewed from the reverse direction, the 1,1 hydrogen elimination reaction 7 is a ethynylsilylene insertion into hydrogen. This reaction takes place via a three-centered transition state as shown in Figure 1b. As discussed above, these reactions are considered prototypical of reactions involving organosilane decompositions. The major structural features of the transition state include the approach of H<sub>2</sub> roughly parallel to the RSiH plane and bisecting the RSiH angle accompanied by a lengthening of the H<sub>2</sub> bond;

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Table III. Total Energies<sup>a</sup>

compd	HF/3-21G	HF/6-31G*	MP2/6-31G*	MP3/6-31G*	MP4SDQ/ 6-31G*	MP4SDTQ/ 6-31G*
HC≡CSiH <sub>3</sub>	-364.96521	-366.91528	-367.23762	-367.25833	-367.26667	-367.28100
C <sub>2</sub> H <sub>2</sub> + SiH <sub>2</sub>	-364.88025	-366.81760	-367.13169	-367.15919	-367.16904	-367.18106
HCCSiH + H <sub>2</sub>	-364.89407	-366.82273	-367.15112	-367.17528	-367.18518	-367.19887
CCH(SiH <sub>3</sub> )	-364.90284	-366.85859	-367.16117	-367.19197	-367.20084	-367.21299
H + CCSIH <sub>3</sub>	-364.79928	-366.74840	-367.01229	-367.03909	-367.05077	-367.06004
SiH <sub>3</sub> + CCH	-364.81260	-366.75621	-367.01562	-367.04677	-367.05904	-367.06768
HCCSiH <sub>2</sub> + H	-364.85591	-366.79803	-367.09887	-367.11908	-367.12793	-367.14164
[CCH(SiH <sub>3</sub> )]* (1,2 silyl)	-364.88815	-366.85259	-367.16844	-367.19463	-367.20270	-367.21716
[CCH(SiH <sub>3</sub> )]* (1,2 hydrogen)	-364.86352	-366.83467	-367.15201	-367.17674	-367.18652	-367.20090
[C <sub>2</sub> H <sub>2</sub> + SiH <sub>2</sub> ]*	-364.82309	-366.76318	-367.11138	-367.13105	-367.14002	-367.15801
[HCCSiH + H <sub>2</sub> ]*	-364.83797	-366.78174	-367.12509	-367.14867	-367.15739	-367.17328

<sup>a</sup> Total energies in au; 1 au = 627.51 kcal/mol.

Table IV. Relative Energies<sup>a</sup>

reaction system	HF/ 3-21G	HF/ 6-31G*	MP2/ 6-31G*	MP3/ 6-31G*	MP4SDQ/ 6-31G*	MP4SDTQ/ 6-31G*	ZPE/ 3-21G	best theor est MP4SDTQ/ 6-31G* + ZPE
HC≡CSiH <sub>3</sub> → C <sub>2</sub> H <sub>2</sub> + SiH <sub>2</sub>	53.3	61.3	66.5	62.2	61.3	62.7	-9.8	52.9
HC≡CSiH <sub>3</sub> → [C <sub>2</sub> H <sub>2</sub> + SiH <sub>2</sub> ]*	89.2	95.4	79.2	79.9	79.5	77.2	-3.0	74.2
HC≡CSiH <sub>3</sub> → HCCSiH + H <sub>2</sub>	44.6	58.1	54.3	52.1	51.1	51.5	-5.5	46.0
HC≡CSiH <sub>3</sub> → [HCCSiH + H <sub>2</sub> ]*	79.8	83.8	70.6	68.8	68.6	67.6	-3.0	64.6
HC≡CSiH <sub>3</sub> → CCH(SiH <sub>3</sub> )	39.1	35.6	48.0	41.6	41.3	42.7	-1.9	40.8
HC≡CSiH <sub>3</sub> → [CCH(SiH <sub>3</sub> )]* (1,2 silyl)	48.3	39.3	43.4	40.0	40.1	40.1	-1.9	38.2
HC≡CSiH <sub>3</sub> → [CCH(SiH <sub>3</sub> )]* (1,2 hydrogen)	63.8	50.6	53.7	51.2	50.3	50.3	-4.9	45.4
HC≡CSiH <sub>3</sub> → H + CCSIH <sub>3</sub>	104.1	104.7	141.3	137.6	137.6	138.6	-8.8	129.8
HC≡CSiH <sub>3</sub> → SiH <sub>3</sub> + CCH	95.8	99.8	139.3	132.8	130.3	133.9	-6.4	127.5
HC≡CSiH <sub>3</sub> → HCCSiH <sub>2</sub> + H	68.6	73.6	87.1	87.4	87.1	87.4	-7.0	80.4

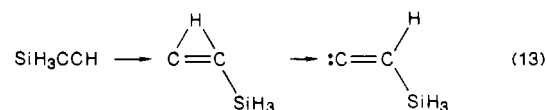
<sup>a</sup> Zero-point energies and relative energies in kilocalories per mole.

this is similar to that observed in the addition of silylene,<sup>26</sup> methylsilylene,<sup>13</sup> ethylsilylene,<sup>11</sup> and vinylsilylene<sup>12</sup> to H<sub>2</sub>. The vibrational frequencies for this transition structure are characterized by one imaginary frequency as shown in Table II. The transition vector (normal mode associated with the imaginary frequency) consists mainly of the H<sub>2</sub> stretching mode coupled to H<sub>2</sub> translation and rotation and is compatible with the changes in the geometry that occur during the reaction. Furthermore, the imaginary frequency is quite large (1727i cm<sup>-1</sup>) and is consistent with a narrow barrier.

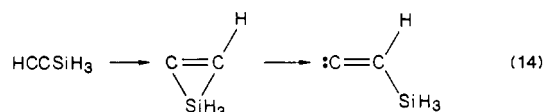
The total and relative energies for reaction 7 are given in Tables III and IV. At the MP4/6-31G\* level, including zero-point energy correction, the transition state for the 1,1 hydrogen elimination reaction lies 64.6 kcal/mol above the ethynylsilane equilibrium structure. This agrees well with the experimental activation energy (61.2 ± 5.2 kcal/mol) measured in shock-tube studies.<sup>15</sup> The barrier for the reverse process (-7) is quite small relative to the other barriers, 18.6 kcal/mol, and is consistent with experimental studies on methylsilane,<sup>5-7</sup> ethylsilane,<sup>1,4</sup> and vinylsilane.<sup>1,9</sup>

The reaction path for 8, 1,2-elimination of SiH<sub>2</sub>, passes through a three-center transition state involving two heavy atoms and a hydrogen. The SiH<sub>3</sub> group must break a SiH bond and form a new CH acetylenic bond, as shown in Figure 1c. For ethynylsilane, the transition state occurs later along the reaction path than for vinylsilane and ethylsilane; this is evident from the CH bond lengths: 1.272, 1.407, and 1.574 Å, respectively, at the HF/6-31G\* level. Viewed in the reverse direction, the reaction is the insertion of SiH<sub>2</sub> into the CH bond of acetylene and occurs early along the reaction coordinate. Calculated vibrational frequencies given in Table II for this transition structure reveal that this structure is a true first-order saddle point with one imaginary frequency. Computed barrier height for ethynylsilane dissociation to C<sub>2</sub>H<sub>2</sub> and SiH<sub>2</sub> is 74.2 kcal/mol at the MP4/6-31G\* with zero-point energy correction. The corresponding barriers for dissociation of ethylsilane to C<sub>2</sub>H<sub>6</sub> and SiH<sub>2</sub> and vinylsilane to C<sub>2</sub>H<sub>4</sub> and SiH<sub>2</sub> are 72.2 kcal/mol (MP4SDQ/6-31G\*)<sup>11</sup> and 68.7 kcal/mol (MP4SDTQ/6-31G\*),<sup>12</sup> respectively. Consequently, the calculated barrier for ethynylsilane 1,3-elimination of SiH<sub>2</sub> appears to be reasonable.

The isomerization reaction of ethynylsilane can take place via two different processes: a 1,2 hydrogen shift via

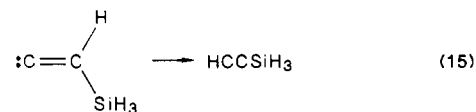


or 1,2 silyl shift via

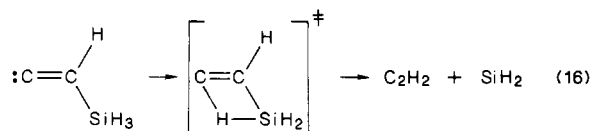


Both processes have been examined, and the geometries for the transition states are given in Table I. In the transition state for the 1,2 silyl shift, computed at the HF/3-21G level of theory, the SiH<sub>3</sub> group is 0.3 Å closer to the carbon containing the remaining hydrogen than to the other carbon, and the transition structure resembles the final product and is indicative of a late transition state. When polarization functions are added, the transition state shifts significantly toward the product, the ∠C<sub>1</sub>C<sub>2</sub>Si angle changes from 72.9° (3-21G) to 59.3° (6-31G\*).

For the back-reaction (15), there is a 9.2 kcal/mol barrier. At the HF/6-31G\* level this barrier decreases to 3.7 kcal/mol and disappears entirely when correlation is included at the MPn/6-31G\* level. To study this process further, we have optimized



the geometries of the reactant, the intermediate, and several points along the path connecting the two at the MP2/3-21G\* level. We have found no maximum or transition state but rather a smoothly increasing energy profile (i.e. no barrier to the back-reaction). This suggests that silylvinylidene, :CCH(SiH<sub>3</sub>) may be a transient species rather than a true intermediate. Nevertheless, it can undergo secondary reactions leading to dissociation. A 1,3 hydrogen shift leading to the elimination of silylene and the production of acetylene via is a good candidate for this secondary process and is consistent with the observation that acetylene is

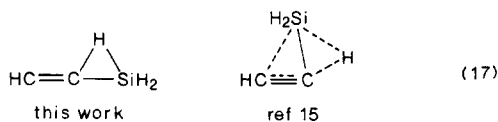


the major product. Preliminary calculations indicate that reaction 16 takes place via a four-center transition state involving a 1,3 hydrogen shift from the silyl group to the carbon lone pair; this reaction proceeds without a barrier at the HF/3-21G and HF/6-31G\* levels. The computed heat of reaction for silylvinylidene dissociation (16) into  $\text{C}_2\text{H}_2$  and  $\text{SiH}_2$  is 18.8 kcal/mol at the MP4SDTQ/6-31G\* level of theory (the details of the structure and energetics of this process will be elaborated in a forthcoming paper<sup>26</sup>). Consequently, the dissociation of ethynylsilane to observed products takes place in a two-step process through a transient species,  $\text{:CCH}(\text{SiH}_3)$  during the dissociation process. The net energetics is represented by summing up the heat of reactions 14 and 16, since no activation barriers are involved in either reaction. The net energy of activation is 57.0 kcal/mol for  $\text{HC}\equiv\text{CSiH}_3 \rightarrow [\text{:C}=\text{CH}(\text{SiH}_3)]^\ddagger \rightarrow \text{C}_2\text{H}_2 + \text{SiH}_2$ . This compares quite favorably with the activation energy of  $61.2 \pm 5.2$  kcal/mol obtained experimentally for the decomposition. Note that this route is 17.2 kcal/mol lower in energy than the direct 1,2  $\text{SiH}_2$  elimination route (8).

The 1,2 hydrogen shift reaction (13) can also take place and may be an important pathway at higher energies (see below). At the HF/3-21G, HF/6-31G\*, and MP4/6-31G\* levels this process is energetically less favored than the shift of the silyl group by 12.5, 8.3 and 7.4 kcal/mol, respectively. However, it should be noted that the 1,2 hydrogen shift is significantly lower in energy than the paths that lead to the elimination of molecular hydrogen (18.3 kcal/mol lower at MP4/6-31G\* with zero-point correction) or the elimination of silylene (27.9 kcal/mol lower). Hence, the formation of the silylvinylidene by either path is favored over 1,1  $\text{H}_2$  or 1,2  $\text{SiH}_2$  eliminations, reactions 7 and 8, respectively.

Finally, looking at the relative energetics of the fragmentation processes in reactions 10–12, it can be seen that reaction 10 and 11 are high-energy processes compared with isomerization or elimination paths. The fragmentation process represented in (12) is significantly lower in energy than either (10) or (11). At the HF/3-21G level this process is only 3.5 kcal/mol higher in energy than the 1,2 hydrogen shift transition state (13) and may be competitive.

In summary, we have located the transition structures that account for the two elimination reactions proposed by Ring and co-workers.<sup>15,16</sup> The transition structure we have obtained for the direct  $\text{SiH}_2$  elimination, reaction 8, is very different from that postulated by Rogers et al.,<sup>15,16</sup> i.e. To investigate this further,



a geometry resembling the structure proposed by Rogers et al.<sup>15,16</sup> was taken as the starting point for a geometry optimization. The structure was fully optimized, and a frequency calculation showed this structure to be a second-order saddle point; that is to say, the potential energy hypersurface has 2 degrees of freedom with negative curvature. Since a true transition state may have only 1 degree of freedom with negative curvature, the structure proposed in ref 15 cannot be a transition state. One negative eigenvalue,  $-302 \text{ cm}^{-1}$ , corresponded almost solely to the transfer of the silyl group from  $\text{C}_1$  to  $\text{C}_2$ , while the other negative eigenvalue,  $-1757 \text{ cm}^{-1}$ , corresponded to the shift of the migrating hydrogen from Si to C. The energy of the second-order saddle point at the HF/3-21G level of theory is found to be 18 kcal/mol higher in energy than the transition state for the direct 1,2  $\text{SiH}_2$  elimination process (8) (depicted on the left-hand side of (17)). Hence, this gives a barrier of 107.2 kcal/mol. While the addition of correlation to this structure may be expected to reduce this by some 15 kcal/mol (by comparison with Table IV), it cannot be

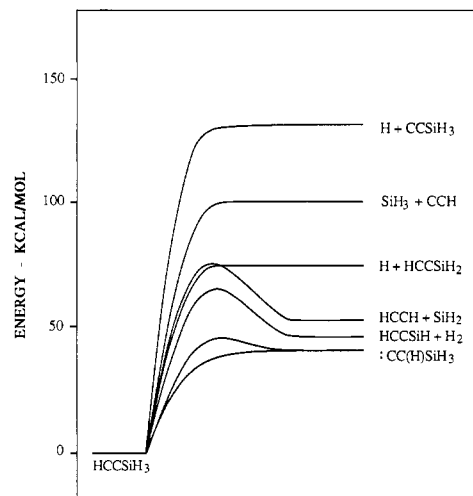


Figure 2. Summary of potential energy curves for primary dissociation pathways for ethynylsilane.

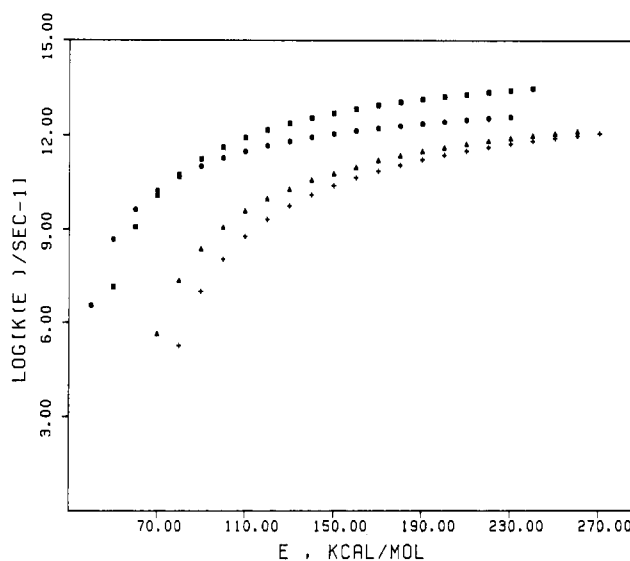


Figure 3. Unimolecular dissociation rates for primary molecular dissociation pathways of ethynylsilane as a function of energy: (●)  $\text{C}_2\text{HSiH}_3$  (1,2 silyl shift), (■)  $\text{C}_2\text{HSiH}_3$  (1,2 hydrogen shift), (▲)  $\text{C}_2\text{HSiH} + \text{H}_2$ , (+)  $\text{C}_2\text{H}_2 + \text{SiH}_2$ .

expected to overcome the difference in energy between the two structures depicted in (17) or in (9). Consequently, the isomerization leading to the silylvinylidene (reactions 9, 13, or 14 and subsequent  $\text{SiH}_2$  elimination (16) may be an energetically important process, which could predominate the primary dissociation surface for ethynylsilane. A summary of the potential energy surface for ethynylsilane is shown in Figure 2.

To further illustrate the dominance of reaction 14, we have performed RRKM calculations to determine energy-dependent unimolecular dissociation rates, in order to assess the relative importance of primary reactions 7, 8, 13, and 14 kinetically. The input parameters used were the frequencies for the reactant and transition states given in Table II, the reduced internal moments of inertia for the reactant and transition states are calculated from the optimized geometries of the HF/6-31G\* level of theory, and the critical energies for each pathway given in Table IV were obtained at the MP4/6-31G\*\*/HF/6-31G\* level. Our results are summarized in Figure 3. The salient point of these calculations is that the three-centered silyl shift mechanism (reaction 14) is seen to be a fast process at relatively low molecular energies. Consequently, in the low-energy range this process dominates, while at higher energies the 1,2 hydrogen shift mechanism (reaction 13) dominates. This behavior can be attributed to the fact

that, at higher molecular energies, the density of higher energy states accessed in the hydrogen shift process prevails over the silyl shift process. We also note that reactions 13 and 14 predominate the dissociation over all energies; rates for this process are estimated to be 2-4 orders of magnitude faster than that for the 1,1 H<sub>2</sub> elimination (reaction 7) and 1,2 SiH<sub>2</sub> elimination (reaction 8). Taking the rate into account, the dominant pathway for decomposition is expected to be isomerization of ethynylsilane via reaction 9 followed by elimination of SiH<sub>2</sub> via reaction 16.

### Conclusion

Primary dissociation pathways of ethynylsilane have been examined, and we find that pathways leading to the newly postulated species silylvinylidene, :CCH(SiH<sub>3</sub>), are preferred energetically and kinetically. Silylvinylidene is suggested to be a transient

species, which proceeds to dissociation, without barrier, to the products C<sub>2</sub>H<sub>2</sub> and SiH<sub>2</sub>. The net activation energy for the process is calculated to be 57.0 kcal/mol at the MP4SDTQ/6-31G\* level of theory and is in good agreement with experiment. Other pathways leading to the observed products have been discounted. We note that C<sub>2</sub>H<sub>4</sub> is a minor product of the decomposition studies of ethynylsilane.<sup>1</sup> No primary dissociation pathways of reasonable energy leading to C<sub>2</sub>H<sub>4</sub> could be found. Consequently, we conclude that C<sub>2</sub>H<sub>4</sub> results from secondary reactions.

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## Tetrazetidene: Ab Initio Calculations and Experimental Approach

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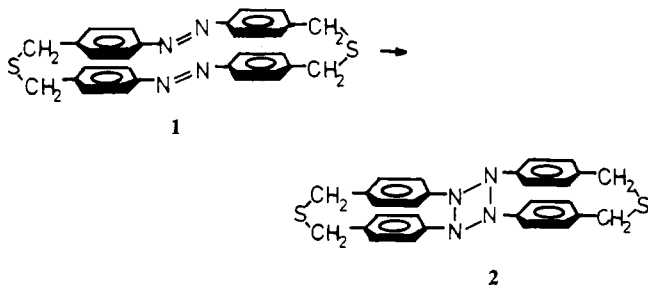
Contribution from the Institut für Organische Chemie, Universität Tübingen, 7400 Tübingen, West Germany, and FG Physikalische Chemie, Institut für Chemie, Universität Hohenheim, 7000 Stuttgart 70, West Germany. Received July 13, 1988

**Abstract:** The kinetic analysis of the photoreaction system of azobenzenophanes is presented. We find, besides the *cis* and *trans* forms, a transient species living for a few minutes. All experimental evidence we have is compatible with a tetrazetidene structure of this species. The molecular structures of five configurational isomers of the hitherto unknown parent tetrazetidene have been calculated by ab initio restricted Hartree-Fock self-consistent field molecular orbital gradient optimizations using STO-3G, 6-31G, and 6-31G\*\* basis sets. Geometries and total energies of the isomers with nonplanar, quadratic, and rectangular arrangements of the ring nitrogens are reported. The formation of tetrazetidene by approach to two *trans*-diazene molecules was simulated with optimization at all intermolecular separations *R* for a parallel [ $\pi^2s + \pi^2s$ ] ground-state reaction pathway. Although all isomers of tetrazetidene are energetically less stable than their diazene dissociation products, the tetrazetidene seems to be trapped kinetically by rather high energy barriers.

### 1. Introduction

The four-membered ring system built only of nitrogen atoms is one of the few simple structures in organic chemistry that has not yet been synthesized. Indeed, a search for tetrazetidene in CAS-Online produces only the registry no. 58674-00-3 and two references which, however, do not mention the structure.

In the course of our investigations of the thermal and photoisomerization of the azobenzenophane **1**,<sup>1</sup> we realize some peculiarities that find an easy explanation if the formation of a tetrazetidene species **2** is assumed.



As the experimental evidence for the formation of a tetrazetidene structure is still indirect, we have tried to gain firm ground by

employing ab initio restricted Hartree-Fock SCF MO calculations with analytical gradient optimization of possible molecular structure using STO-3G, 6-31G, and 6-31G\*\* basis sets. Of course we had to restrict ourselves to the parent tetrazetidene system. These calculations are the first ones for tetrazetidene, and they give a result surprising for the organic chemist in that tetrazetidene should be a kinetically stable molecule accessible in a photoreaction.

### 2. Theoretical Approach to Tetrazetidene Formation

**1. Ab Initio Calculations of the Molecular Structures and Stabilities for the Ground State of Configurational Isomers of Tetrazetidene.** To the best of our knowledge no ab initio calculations of the molecular system of tetrazetidene are reported in the literature. There are, however, many calculations known for hydrazine<sup>2-4</sup> (**8**) and *trans*- and *cis*-diazene<sup>4-9</sup> (**9**, **10**) which are

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