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Theoretical Study of Silylene Insertion into N–H, O–H, F–H, P–H, S–H, and Cl–H Bonds

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Abstract: The potential energy surfaces for the insertion reactions of silylene into NH_3, H_2O, HF, PH_3, H_2S, and HCl have been characterized in detail by using ab initio molecular orbital theory, including electron correlation and zero-point corrections. All the interactions involve the initial formation of a donor–acceptor complex followed by a proton shift via an unsymmetrical high-energy transition state. The binding energies of the complexes as well as the rearrangement barriers for the hydrogen migration of these complexes to give the normal valent compounds have been calculated in all cases. The complex between SiH_2 and NH_3 exists in a deep minimum with a high barrier for rearrangement (38 kcal/mol) and is predicted to be a suitable candidate for spectroscopic observation. The silylene complex with PH_3 also involves a fairly deep minimum, but the overall insertion barrier is small. The interaction between SiH_2 and H_2O, widely studied experimentally, involves a complex with a fairly high rearrangement barrier (22 kcal/mol). The interactions with H_2S, HF, and HCl are fairly weak with lower calculated rearrangement barriers (13, 10, and 8 kcal/mol, respectively). Detailed comparison is made between the structure and bonding of the silylene addition complexes with those of their carbon analogues. Significant differences, particularly in the multiple bond character of the central bond, are found.

Electron-deficient reactive intermediates like carbenes,[1] nitrenes,[2] and vinylidenes[3] have long been the subject of intense experimental and theoretical investigation. The structures and reactivity of the corresponding divalent silicon species, silylenes, are gaining increasing attention in recent years.[4] Thus, gas-phase and matrix-isolation spectroscopic studies have resulted in the structural characterization of the parent silylene, SiH_2, as well as numerous derivatives,[5,6] while the study of the chemical reactivity of silylenes has led to the synthesis of several organic and inorganic molecules.[4,7]

A recurring theme in the above studies is the degree to which silylenes resemble carbenes. Both similarities and differences have been noted. For example, silylenes, like carbenes, readily undergo insertion into a variety of σ bonds.[4] Although the reactions are formally similar, detailed examination has revealed significant differences in the mechanisms of silylene and carbene insertion.[8] While carbene insertion reactions are generally thought to occur in a single step without activation, Weber and his associates have proposed that the insertion of dimethylsilylene into O–H bonds occurs in a two-step process, involving a zwitterionic intermediate.[8]

High-level theoretical calculations have confirmed the proposed differences in the mechanisms of carbene and silylene insertion reactions.[9,10] The prototypical reaction between singlet carbene and H_2O to yield CH_3OH is calculated to have no barrier.[11-13] On the other hand, our previous investigation of the insertion of singlet SiH_2 into the O–H bonds of H_2O and H_3SiOH indicated the formation of an initial complex between the silylene and the oxygen base, followed by a rearrangement to the stable silanol and disilyl ether, respectively.[9] The calculated rearrangement barriers were large enough to suggest that the intermediate complexes may be spectroscopically observable. A complex of this nature involving hydroxysilylene and H_2O, formed in the reaction of silicon atoms with excess water, has indeed been observed recently with the aid of infrared spectroscopy by Margrave and his co-workers.[6]

In order to examine the generality of the above results, we have now undertaken a systematic investigation of the insertion reactions of the parent silylene into six first- and second-row halides (eq 1) at sophisticated levels of theory. Since the ground state of SiH_2 is known to be a singlet,[4] only the singlet surface was considered. All the reactions involve the initial formation of a donor–acceptor complex (which can formally be viewed as a zwitterionic structure though the calculations do not reveal significant charge separation), followed by a 1,2-hydrogen shift. The theoretical methods employed here have been shown to be reliable for such reactions.[14]

$$SiH_2 + XH_n \rightarrow H_2Si - XH_n \rightarrow H_3Si - XH_{n-1} \qquad (1)$$

$$X = N, P, O, S, F, Cl$$

$$n = 3, 3, 2, 2, 1, 1$$

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Experimentally, silylene insertions into N–H, O–H, F–H, P–H, S–H, and Cl–H bonds have all been observed.[4,13,15-18] However, with the exception of the studies of Weber et al. involving O–H bonds,[8] few mechanistic details are available. The present calculations provide comprehensive energetic information on the insertion potential energy surface for all the reactions.

The energetics involving the donor–acceptor complexes are of particular interest. As is well-known, divalent Sn and Pb salts readily form adducts with donor solvents like water, acetone, pyridine, etc.[19] The calculated complexation energies for the different intermediates in eq 1 quantify the ability of divalent silicon to form such adducts.

The thermodynamic stability of a complex does not assure its experimental observation. The structure should also be separated from the more stable normal valent product by a sizable barrier. The calculated rearrangement barriers indicate the most favorable candidates for experimental study.

We have also compared the structure and bonding of the silylene addition complexes with those of their carbon analogues, the ylides. Significant differences, particularly in the multiple bond character of the central bond, are found.

Theoretical Methods

The geometries for all the stationary points were completely optimized at the Hartree–Fock level with the 6-31G* basis set[20] (split-valence plus d-type polarization functions on heavy atoms). This level of theory is denoted by HF/6-31G*. Previous experience[12] has shown that reoptimization of the geometries with the inclusion of electron correlation effects might change some of the geometrical parameters significantly, especially those parameters involving small force constants. However, since the potential energy surface is extremely flat for such parameters, the error introduced in the calculation of the relative energies of the different species involved by the use of these HF/6-31G* geometries is usually very small, ≈1 kcal/mol. Some of the interesting geometrical parameters are listed in Table I along with the symmetry constraints under which the optimizations were performed. Complete geometry specifications are available as supplementary material.

The complete set of harmonic force constants was also evaluated[21] for each stationary point. These can then be used to characterize the nature of the stationary point, a minimum being characterized by all positive eigenvalues of the force constant matrix and a transition state being characterized by one (and only one) negative eigenvalue. More than one negative eigenvalue of the force constant matrix signifies a higher order saddle point, and lowering the symmetry in such cases usually leads to a nearby transition state. The number of negative eigenvalues for each stationary point is listed under the title Hessian index in Table I. The force constants were also used to compute harmonic vibrational frequencies and corresponding zero-point vibrational energies.

Electron correlation effects were included by means of Moller–Plesset perturbation theory[22] by using the HF/6-31G* geometries. The calculations were performed in two stages. In the first stage, fourth-order Moller–Plesset perturbation (MP4) theory calculations in the space of single, double, and quadruple (SDQ) substitutions[22b] were performed with the larger 6-31G** basis[20] (including p-type polarization functions on H). In the next stage, the effect of triple (T) substitutions[22c] on the correlation energy was computed, again using fourth-order theory but only with the smaller 6-31G* basis set. Such effects of triple substitutions have been previously shown to be important for similar reactions involving first-row elements, especially for the calculation of activation barriers. The various correlation energy contributions are listed in Table II along with the zero-point energy corrections. All of these effects are used to calculate the final relative energies listed in the last column of Table II.

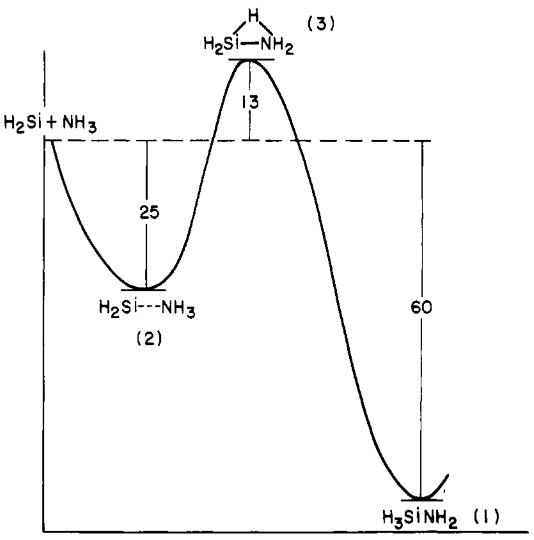

Figure 1. Energy profile for the insertion reaction of silylene into NH_3 (kcal/mol).

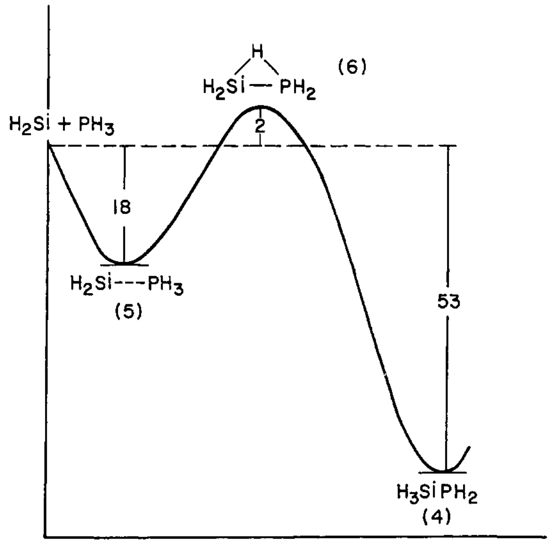

Figure 2. Energy profile for the insertion reaction of silylene into PH_3 (kcal/mol).

Results and Discussion

The results are divided into three sections, discussing the silylene insertion into NH_3 and PH_3, H_2O and H_2S, and HF and HCl, respectively. In each case, we point out the essential features of the reaction of a first-row hydride, along with the modifications that result in the reaction involving the second-row analogue. The results are also compared with available theoretical results on the corresponding carbene reactions. In the final section, the molecular and electronic structures of the silylene addition complexes are compared with those of ylides.

Insertion into N–H and P–H Bonds. The calculated reaction profiles for silylene insertion into NH_3 and PH_3 are shown in Figures 1 and 2, respectively. The interaction between the empty p orbital in singlet SiH_2 and the lone pair in NH_3 leads to the adduct **2**, which has the largest binding energy (25 kcal/mol) of all the complexes considered in this study. This interaction energy is quite similar to that calculated for the analogous complex

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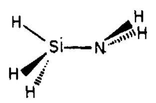
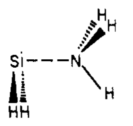
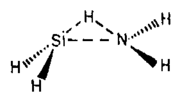


1 (C_s)



2 (C_s)



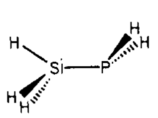
3 (C_1)

involving singlet CH_2 and NH_3 (28 kcal/mol).[13] The nature of the interaction holding **2** together is evident from its geometry in which the SiH_2 unit is virtually orthogonal to the Si–N axis. The donor–acceptor interaction leads to a calculated Si–N bond length of 2.09 Å, considerably longer than the single bond length of 1.72 Å calculated for silylamine. Evaluation of the analytical force constants and vibrational frequencies shows that both **1** and **2** are local minima on the potential energy surface.

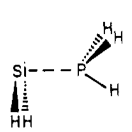
The rearrangement of **2** to **1** with a C_s symmetry constraint involves a cyclic transition state (not shown) in which a proton simultaneously interacts with two electron pairs. This pathway is clearly unfavorable, being formally similar to a 1,2-hydrogen shift in the ethyl anion, also involving a repulsive four-electron interaction in the transition state.[23] The introduction of heteroatoms in the present system could lead to sufficient perturbation, invalidating the above analogy. For example, the transition state in the corresponding carbene reaction is calculated to preserve a plane of symmetry.[13] A similar C_s transition structure for the $SiH_2 + NH_3$ system, however, is calculated to have two negative eigenvalues of the force constant matrix. The true transition state for the rearrangement is calculated to be the unsymmetrical structure **3**, with the hydrogens twisted about 10–15° away from the C_s structure, although the torsional potential is relatively flat.

The transition state **3** is calculated (Table II) to be 13 kcal/mol higher in energy than the separated $SiH_2 + NH_3$. The overall activation energy for the formation of silylamine from SiH_2 and NH_3 is thus highly significant, in marked contrast to the analogous carbene reaction which has no overall activation barrier. More importantly, **3** is calculated to be 38 kcal/mol higher in energy than **2**, indicating that **2** exists in a deep minimum and might have a significant lifetime to be an observable species spectroscopically.

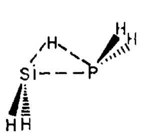
The present calculations reveal two striking differences between carbene and silylene insertion into N–H bonds. Although the reaction paths are initially similar, the intermediate carbene complex exists only as a shallow minimum. On the other hand, the silylene complex requires a significant barrier for rearrangement. Secondly, the overall exothermicity of the reaction of SiH_2 and NH_3 to form silylamine (60 kcal/mol) is considerably less than the computed value of 101 kcal/mol for the carbene-insertion reaction.[13]



4 (C_s)



5 (C_s)



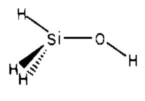
6 (C_s)

The reaction of SiH_2 with PH_3 seems to differ significantly from that with NH_3. The complexation energy of the intermediate **5** is quite large (18 kcal/mol, Table II), although the value is smaller than that calculated for **2**. The coordination at silicon is again strongly pyramidal in **5**. The Si–P bond length of 2.40 Å is also longer than that calculated for $H_3Si–PH_2$ (2.27 Å). However, two transition-state structures have been detected on this surface. The higher of the two has a twisted C_1 symmetry (not shown) and appears to connect **4** and **5**, with a large (37 kcal/mol) barrier for the 1,2-shift. The lower energy transition state, **6**, is only 2 kcal/mol above the separated reactants (silylene and phosphine), leading to the smallest overall activation barrier of all the insertion reactions considered in this study, and the insertion process should be fairly facile. Experimentally, insertion of SiF_2 into PH_3 had indeed been observed.[17b] The addition complex **5** exists in a fairly deep minimum (20 kcal/mol) and may have significant lifetime for experimental detection. Analysis of the reaction path[26] from the saddle point **6** leads in the forward direction to silylphosphine and in the reverse direction appears to lead to the separated reactants when the symmetry is restricted to C_s. However, the Si–P distance is already large in **6**, and there is a small a'' frequency at the saddle point which turns imaginary along this reaction path. Thus, as the two fragments separate, the system might distort into C_1 symmetry and fall into the well of the complex.

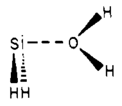
A detailed comparison of carbene and silylene insertion into PH_3 is not possible at present, since high-level theoretical results are not available for the former reaction. However, the reaction profile up to the formation of methylenephosphorane, the ylide structure analogous to **5**, has been calculated at the Hartree–Fock level.[24] The structure of the ylide is quite different from that of **5**, the carbon atom having nearly a planar coordination with a flat inversion potential (vide infra). However, the reaction between CH_2 and PH_3 is calculated to proceed initially with a configuration similar to **5** in order to maximize the interaction between the phosphine lone pair and the empty p orbital on the carbene. At short P–C distances, a CH_2 rocking mode leads to the optimum ylide geometry with a trigonal carbon.[24] A similar rocking of the SiH_2 group does not occur in the case of the silylene insertion reaction.

Insertion into O–H and S–H Bonds. Insertion of dimethylsilylene into O–H bonds of water, alcohols, oxetanes, and epoxides has been the basis of detailed mechanistic studies by Weber and associates.[8] The unusual solvent effects on the insertion reactions of dimethylsilylene into O–H bonds (not observed for the corresponding carbene insertion reactions) support the interpretation in terms of the participation of zwitterionic intermediates.

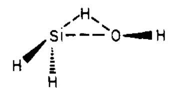
In a previous study,[9] we have reported results of our investigations on the insertion of silylene into H_2O and SiH_3OH. Now we have performed geometry optimizations for all the stationary points involved with the larger 6-31G* basis. Some of the geometrical parameters change appreciably (compared to the earlier 3-21G* structures), but the final relative energies do not differ significantly. The interaction complex **8** between SiH_2 and H_2O has the C_1 structure as shown, with an oxygen lone pair directed along the empty p orbital on silicon. The silicon lone pair is nearly orthogonal to the second oxygen lone pair. Our previous optimization[9] with the smaller 3-21G* basis had yielded a C_s structure with planar coordination around oxygen. It was pointed out[9] that this was probably due to the deficiency of not including d functions on oxygen. Our current studies with the 6-31G* basis confirm the earlier expectations of a pyramidal structure around oxygen, the hydrogens making an angle of about 50° with the plane formed by Si–O and the H–Si–H bisector. The Si–O bond length, 2.13 Å, is considerably longer than the previous 3-21G* value[9] (1.96 Å). The calculated complexation energy (13 kcal/mol) is, however, very similar to our previous value[9] (12 kcal/mol).



7 (C_s)



8 (C_1)



9 (C_1)

The transition state **9** for the rearrangement of the complex **8** to silanol **7** again has C_1 symmetry, thus avoiding a potential

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Table I. HF/6-31G* Energies and Structural Information[a]

structure[b]	point group	bond lengths, Å			HF/6-31G*, hartrees	Hessian Index[e]
		Si–A[c]	Si–H[d]	A–H[d]		
H_3Si-NH_2 (**1**)	C_s	1.724	1.482		−346.283 94	0
$H_2Si\cdots NH_3$ (**2**)	C_s	2.089		1.004	−346.226 03	0
$H_2Si(H)NH_2$ (**3**)	C_1	1.900	1.614	1.376	−346.136 29	1
H_3Si-PH_2 (**4**)	C_s	2.267	1.476		−632.534 97	0
$H_2Si\cdots PH_3$ (**5**)	C_s	2.404		1.394	−632.473 03	0
$H_2Si(H)PH_2$ (**6**)	C_s	2.618	1.535	1.830	−632.416 60	1
H_3Si-OH (**7**)	C_s	1.648	1.469		−366.130 40	0
$H_2Si\cdots OH_2$ (**8**)	C_1	2.129		0.951	−366.034 92	0
$H_2Si(H)OH$ (**9**)	C_1	1.874	1.620	1.271	−365.969 85	1
H_3Si-SH (**10**)	C_s	2.151	1.470		−688.770 72	0
$H_2Si\cdots SH_2$ (**11**)	C_1	2.606		1.325	−688.680 29	0
$H_2Si(H)SH$ (**12**)	C_1	2.530	1.626	1.636	−688.633 99	1
H_3Si-F (**13**)	C_{3v}	1.594	1.470		−390.148 40	0
$H_2Si\cdots FH$ (**14**)	C_s	2.378		0.917	−390.013 51	0
$H_2Si(H)F$ (**15**)	C_s	1.883	1.650	1.162	−389.973 44	1
$H_2Si\cdots HF$ (**16**)	C_{2v}	3.703	2.787	0.916	−390.008 44	0
H_3Si-Cl (**17**)	C_{3v}	2.067	1.468		−750.183 41	0
$H_2Si\cdots ClH$ (**18**)	C_s	3.125		1.267	−750.063 29	0
$H_2Si(H)Cl$ (**19**)	C_s	2.621	1.686	1.525	−750.030 81	1
$H_2Si\cdots HCl$ (**20**)	C_{2v}	4.305	3.034	1.271	−750.063 20	0

[a] Not all structural parameters are listed. The structures were, however, completely optimized within the given symmetry constraint. The complete structural information is available as supplementary material. [b] (H) denotes position intermediate between nonhydrogen atoms. [c] The other heavy atom in the molecule is denoted by A. [d] Bond lengths between the heavy atoms and the migrating hydrogen. Only bonded and partially bonded distances are shown. [e] The number of negative eigenvalues of the matrix of energy second derivatives.

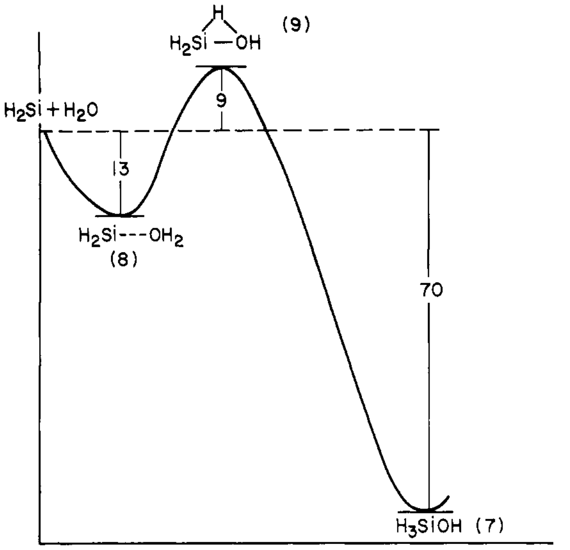
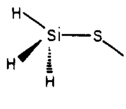


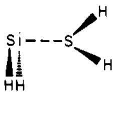
Figure 3. Energy profile for the insertion reaction of silylene into H_2O (kcal/mol).

four-electron destabilizing interaction in the more symmetrical C_s structure. The Si–O bond length of 1.87 Å is again intermediate between the values in **7** and **8**. The overall calculated activation barrier, 9 kcal/mol (Figure 3), is slightly smaller than our previous value[9] but is still significant. The calculated barrier from the complex **8** is 22 kcal/mol, indicating that **8** might have a sufficient lifetime for spectroscopic observation. The experimental observation of the complex involving hydroxysilylene and H_2O is particularly significant in this context.[6]

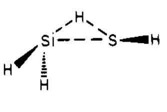
The insertion of SiH_2 into H_2S shows essentially the same features as above but with uniformly reduced energy differences (Figure 4). The addition complex **11** has a geometry similar to **8**, but the complexation energy is smaller, 9 kcal/mol. This is also reflected in the calculated Si–S bond length, 2.61 Å, considerably longer than in silanethiol, **10** (2.15 Å). The transition state with an intermediate Si–S bond length of 2.53 Å has a C_1 structure similar to **9**. The overall activation barrier is only 5 kcal/mol. The barrier for the hydrogen shift in the complex is also quite small, 13 kcal/mol.



10 (C_s)



11 (C_1)



12 (C_1)

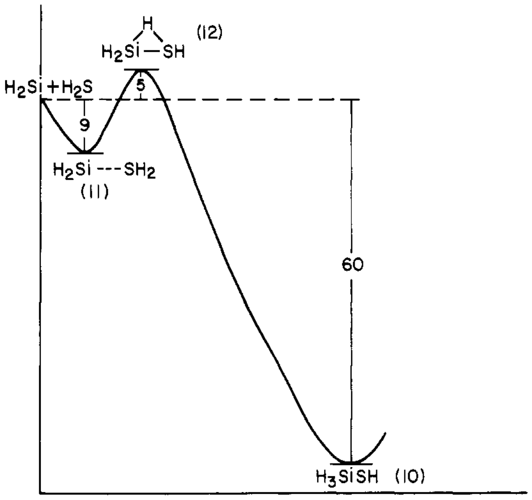
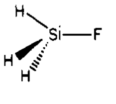
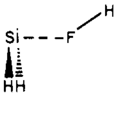


Figure 4. Energy profile for the insertion reaction of silylene into H_2S (kcal/mol).

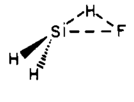
Insertion into F–H and Cl–H Bonds. The insertion of SiH_2 into HF has a large thermodynamic driving force in view of the strength of the Si–F bond (calculated exothermicity = 84 kcal/mol, Table II, Figure 5). Since the reaction is indicated to be readily observable (calculated activation barrier is only 3 kcal/mol), experimental detection of the intermediate formed during the reaction is unlikely. The adduct formed by the interaction of a fluorine lone pair with the LUMO of the silylene involves only a weak bond (r_{Si-F} = 2.38 Å compared to 1.59 Å in H_3SiF, **13**), with a complexation energy of only 7 kcal/mol. This is not surprising since the analogous carbene complex involving HF as a σ donor has been shown not to be a minimum at similar theoretical levels.[13] Although **14** is calculated to be



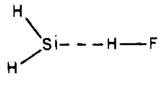
13 (C_{3v})



14 (C_s)



15 (C_s)



16 (C_{2v})

Table II. Total and Relative Energies[a] for Stationary Points

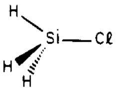
structure[b]	HF[c]	$\epsilon^{(2)}$ [c]	$\epsilon^{(3)}$ [c]	$\epsilon_{SDQ}^{(4)}$ [c]	$\epsilon_T^{(4)}$ [d]	E(vib)[d]	E(rel)
$H_2Si + NH_3$	-346.19816	-268.15	-31.01	-6.68	-3.20	31.1	0.0
H_3Si-NH_2 (**1**)	-346.29646	-275.98	-25.01	-5.09	-4.57	33.8	-60.0
$H_2Si \cdots NH_3$ (**2**)	-346.23920	-278.02	-28.08	-5.72	-4.51	36.3	-25.1
$H_2Si(H)NH_2$ (**3**)	-346.15207	-298.50	-22.78	-6.18	-7.40	31.6	+13.2
$H_2Si + PH_3$	-632.45680	-205.11	-39.60	-8.40	-2.86	24.3	0.0
H_3Si-PH_2 (**4**)	-632.54362	-214.99	-35.52	-5.98	-4.24	28.7	-53.1
$H_2Si \cdots PH_3$ (**5**)	-632.48203	-217.60	-36.89	-6.47	-4.50	28.6	-17.5
$H_2Si(H)PH_2$ (**6**)	-632.42777	-235.59	-36.67	-6.18	-6.66	26.6	+2.2
$H_2Si + OH_2$	-366.02620	-276.54	-24.67	-6.92	-2.71	22.3	0.0
H_3Si-OH (**7**)	-366.14188	-284.36	-17.78	-6.33	-4.37	25.9	-70.2
$H_2Si \cdots OH_2$ (**8**)	-366.05041	-284.34	-21.91	-6.67	-3.85	26.5	-13.3
$H_2Si(H)OH$ (**9**)	-365.98502	-309.21	-14.63	-8.44	-7.46	23.3	+8.7
$H_2Si + SH_2$	-688.67766	-215.80	-36.99	-6.99	-3.11	18.2	0.0
H_3Si-SH (**10**)	-688.77903	-224.11	-31.94	-4.64	-4.55	23.1	-60.2
$H_2Si \cdots SH_2$ (**11**)	-688.69031	-224.39	-35.34	-5.92	-4.19	22.0	-8.6
$H_2Si(H)SH$ (**12**)	-688.64687	-244.64	-32.07	-4.94	-7.35	20.1	+4.8
$H_2Si + FH$	-390.01418	-263.71	-20.02	-7.32	-2.77	14.1	0.0
H_3Si-F (**13**)	-390.15284	-271.34	-13.05	-7.68	-4.55	18.6	-84.3
$H_2Si \cdots FH$ (**14**)	-390.02494	-269.13	-18.13	-7.65	-3.50	16.8	-7.0
$H_2Si(H)F$ (**15**)	-389.98211	-294.99	-10.34	-10.43	-7.59	15.2	+2.7
$H_2Si \cdots HF$ (**16**)	-390.01984	-264.58	-19.61	-7.07	-2.90	15.8	-2.1
$H_2Si + ClH$	-750.06884	-219.98	-33.40	-5.72	-2.88	12.5	0.0
H_3Si-Cl (**17**)	-750.18774	-225.33	-28.10	-3.65	-4.16	17.8	-68.8
$H_2Si \cdots ClH$ (**18**)	-750.07224	-222.83	-32.94	-5.42	-3.20	14.3	-1.8
$H_2Si(H)Cl$ (**19**)	-750.04155	-241.75	-28.80	-4.50	-6.54	13.6	+5.9
$H_2Si \cdots HCl$ (**20**)	-750.07251	-220.94	-33.03	-5.44	-3.01	13.7	-1.4

[a] Total energies in hartrees, correlation energies in millihartrees, vibrational and relative energies in kcal/mol. [b] (H) denotes position intermediate between non-hydrogen atoms. [c] Obtained with the 6-31G** basis. [d] Obtained with the 6-31G* basis.

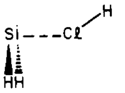
a true minimum, rearrangement to **13** requires a barrier of only 10 kcal/mol. The transition state for the hydrogen shift has C_s symmetry and a relatively short Si–F bond length (1.88 Å).

In the case of the SiH_2 + HF reaction an additional feature, previously observed for the analogous carbene reaction,[13] is seen. Silylene forms a loose complex **16** with HF where the σ lone pair on Si is involved in a hydrogen bond type of interaction. The structure has planar C_{2v} symmetry with a long Si–H distance, 2.79 Å. The complexation energy is only 2 kcal/mol, indicating that it is only a weak interaction. Analytical force constant evaluations show that this complex is indeed a local minimum. We have not, however, attempted to study the pathway for rearrangement of this structure to SiH_3F.

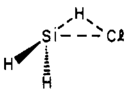
The calculated reaction profile of the insertion of SiH_2 into HCl is very similar to the previous case with the interactions being even weaker. The complex **18** where silylene is the acceptor has a binding energy of only 2 kcal/mol with a long Si–Cl bond, 3.13 Å (Si–Cl bond length of SiH_3Cl, **17**, is 2.07 Å). The rearrangement transition state, **19**, again has C_s symmetry with a fairly low overall barrier, 6 kcal/mol. More significantly, **18**, with a rearrangement barrier of only 8 kcal/mol, is the shallowest minimum of all the complexes studied in this paper (Figure 6).



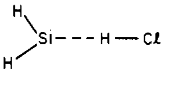
17(C_{3v})



18(C_s)



19(C_s)



20(C_{2v})

The hydrogen-bonded minimum **20** with SiH_2 acting as a σ donor is again calculated to be a minimum. The interaction Si–H bond length in **20**, 3.03 Å, is longer than that of the HF complex, and **20** has the smallest binding energy of all the complexes studied. Again, we did not attempt to calculate the rearrangement barrier for **20** going over to silyl chloride, **17**.

Comparison of the Addition Complexes of Silylene and Carbene. The nature of the addition complexes involving silicon is best understood by comparing the present results with the detailed studies available on the analogous carbene complexes, viz., the ylides. In view of their synthetic utility, ylides have attracted considerable attention.[25,27] While most of the experimental structural investigations have utilized highly stabilized derivatives,[25] theoretical calculations have been performed on model systems similar to those considered here.[27] The available structures, complexation energies, proton-transfer energies, and the barriers to the proton transfer provide a firm basis for comparison of ylides with their silicon analogues.

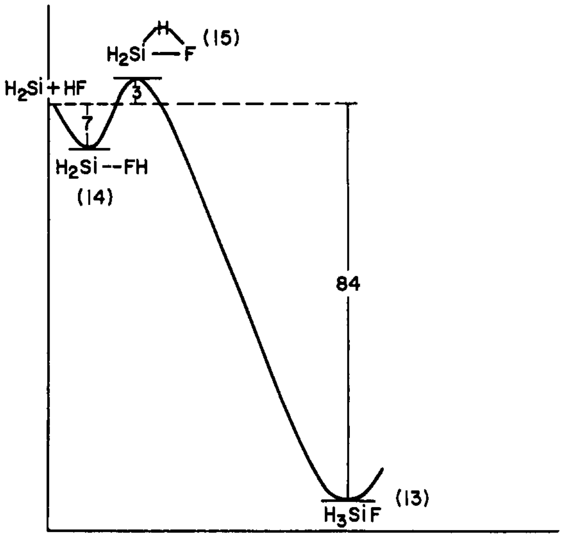


Figure 5. Energy profile for the insertion reaction of silylene into HF (kcal/mol).

A major conclusion from the study of carbene complexes is that second-row ylides differ significantly from their first-row coun-

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(27) (a) Absar, I.; Van Wazer, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 2382. (b) Whangbo, M. H.; Wolfe, S. *Can. J. Chem.* **1976**, *54*, 949. (c) Bernardi, F.; Schlegel, H. B.; Whangbo, M. H.; Wolfe, S. *J. Am. Chem. Soc.* **1977**, *99*, 5633. (d) Lischka, H. *Ibid.* **1977**, *99*, 353. (e) Strich, A. *Nouv. J. Chem.* **1979**, *3*, 105. (f) Graham, S. L.; Heathcock, C. H. *J. Am. Chem. Soc.* **1980**, *102*, 3713. (g) Eades, R. A.; Gassman, P. G.; Dixon, D. A. *Ibid.* **1981**, *103*, 1066.

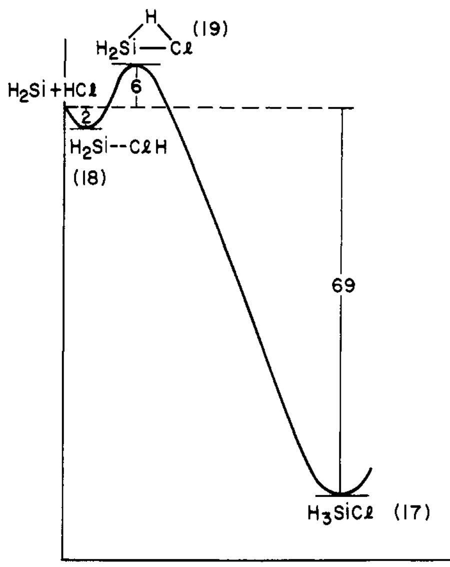

Figure 6. Energy profile for the insertion reaction of silylene into HCl (kcal/mol).

terparts in structure and stability. Experimentally, the $^-$C–X$^+$ bond lengths in ylides are consistently longer than C–X bonds in the stable tautomeric form when X is a first-row group.[25] The opposite is true for structures involving second-row elements.[25] Theoretical calculations on model ylides yield the same result. Thus, C–N and C–O bonds are longer in ylides than in CH_3NH_2 and CH_3OH, respectively. On the other hand, C–P and C–S bonds are shorter in CH_2PH_3 and CH_2SH_2 than in CH_3PH_2 and CH_3SH, respectively.[27] Therefore, first-row ylides are generally thought of as complexes between $^1CH_2$ and neutral bases, while multiple bond character is attributed to second-row ylides. *All* of the zwitterionic structures involving silicon considered in this study are similar to first-row ylides. At the calculated HF/6-31G* level, the Si–X bond length in the silylene addition complex is always longer than that in the more stable tautomer (Table I). Furthermore, the SiH_2 group in all these complexes is consistently aligned for maximizing the interaction between the vacant p orbital of silylene and the donor orbital of the base. Although geometry optimization with larger basis sets and electron correlation effects may change the calculated bond lengths somewhat, the qualitative features are not likely to change. A remarkable parallel to the calculated silylene addition complex structures is provided by the nature of the complex between triphenylphosphine and $GeCl_2$ which has a strongly pyramidal germanium center.[28] While a similar coordination is found in the calculated structures of ammonium and oxonium ylides, phosphonium and sulfonium ylides have nearly planar coordination around carbon.[27]

The calculated interaction energies for the zwitterionic structures of Si and C reveal the same trends. The complexation energies of SiH_2 with NH_3 and OH_2 are similar to those of $^1CH_2$. However, the complexation energies with PH_3 differ substantially. The value calculated for the interaction between $^1CH_2$ and PH_3 (36 kcal/mol, after zero-point corrections)[24] indicates a much stronger bond in the ylide than that between Si and P in **5** (complexation energy = 18 kcal/mol). It is evident that the nature of bonding in the first- and second-row addition complexes of silicon does not differ appreciably.

As a criterion of hypervalency in ylides, Eades et al.[27g] have examined proton-transfer energies, i.e., the energy differences between the addition complexes and the stable tautomers. The rearrangement process is visualized as deprotonating a C–H bond and protonating the heteroatom. Since the former energy should be fairly constant, the proton-transfer energy should parallel the proton affinities of the heteroatomic bases. Deviations from the expected values, noted for P and S ylides, were attributed to additional stabilizing effects like hypervalency in the ylides.[27g] In the silicon systems, the calculated proton-transfer energies of 35, 36, 52, 57, 67, and 77 kcal/mol for **2**, **5**, **11**, **8**, **18**, and **14**, respectively, qualitatively follow the trends in the proton affinities of $NH_3 > PH_3 > SH_2 > OH_2 > ClH > FH$.[29] This simple-minded analysis does not reveal any unusual stability for the second-row complexes. The large increase in the proton-transfer energies along the series $H_2Si–XH_3$, $H_2Si–XH_2$, and $H_2Si–XH$ is just a reflection of the increased destabilization of the addition complexes with increasing number of lone pairs as well as of the increased strength of the Si–X bond in the normal valent tautomers as X becomes more electronegative. The same trends within first- and second-row complexes were observed with carbene complexes also.[27g]

The differences in the bonding of first- and second-row ylides have been discussed repeatedly.[25,27] The lone pair on the carbon of a first-row ylide is highly destabilized. When an adjacent second-row atom is present, d_π–p_π bonding or donation into low-lying σ^* orbitals is possible. Second-row complexes thus have considerable multiple-bond character. As is well-known, silicon differs from carbon in preferring to retain its atomic configuration ($3s^2\ 3p^2$) in its bonding instead of forming multiple bonds.[4] The nearly equal stability calculated for silaethylene and methylsilylene provides a dramatic illustration.[30] In all the silylene addition complex structures considered in this study, silicon is essentially unhybridized with bond angles close to 90°, in spite of being tricoordinate. The lone pair on silicon has considerable s character and is relatively stabilized. There is little evidence for multiple-bond formation in these complexes even when second-row groups are present, since silicon does not gain much from the resulting rehybridization.

The reluctance of Si to rehybridize is also the reason for the significant barriers to hydrogen migration in these complexes. The rearrangement necessitates considerable electronic reorganization since the bonding in the addition complexes and in the stable tautomers differs considerably. However, the corresponding rehybridization is quite efficient with carbon derivatives, due to the smaller s–p gap associated with carbon.[4] Therefore, the first-row ylides, if at all they are true minima, readily rearrange to the more stable tautomeric forms.

Conclusions

The addition complexes formed between SiH_2 and NH_3, PH_3, H_2O, H_2S, HF, and HCl have been studied. The rearrangement barriers obtained for the hydrogen migration of these complexes to give the normal valent compounds have been calculated in all cases. The complex between SiH_2 and NH_3 exists in a deep minimum with a high barrier for rearrangement (38 kcal/mol). This addition complex is predicted to be a suitable candidate for spectroscopic observation. The complex between SiH_2 and PH_3 also exists in a fairly deep minimum (18 kcal/mol), but the overall activation energy for the insertion reaction is small. The complex formed between SiH_2 and H_2O again exists in a fairly deep minimum, the rearrangement barrier being fairly significant (22 kcal/mol). This interaction has already been widely studied in experimental studies. The interaction between SiH_2 and H_2S is weaker still with a smaller barrier for rearrangement (13 kcal/mol). In the case of both HF and HCl the interaction is extremely weak with very low rearrangement barriers (<10 kcal/mol). Both HF and HCl give loosely bound hydrogen-bonded complexes. Detailed comparison is made between the structure and bonding of the silylene addition complexes with those of their carbene analogues, the ylides. Significant differences, particularly in the multiple-bond character of the central bond, are found.

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Registry No. SiH_2, 13825-90-6; NH_3, 7664-41-7; H_2O, 7732-18-5; HF, 7664-39-3; PH_3, 7803-51-2; H_2S, 7783-06-4; HCl, 7647-01-0.

Supplementary Material Available: Listing of complete 6-31G* geometry specifications (7 pages). Ordering information is given on any current masthead page.

Experimental Determination of the Bond Density of Molecular Hydrogen in Momentum-Space by Binary (e,2e) Spectroscopy

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Contribution from the Department of Chemistry, The University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6. *Received October 3, 1983*

Abstract: The spherically averaged bond density of molecular hydrogen in momentum-space has been derived by using the momentum distribution of the H_2 $1\sigma_g$ orbital determined by binary (e,2e) spectroscopy and the exact solution of the Schrodinger equation for the 1s orbital of the H atom. Theoretical bond densities calculated by using different quality wave functions ranging from minimal basis set to extended Hartree–Fock are given for comparison. In addition, the orbital momentum moments of the H_2 $1\sigma_g$ orbital are estimated from the measured orbital momentum distribution (Leung, K. T.; Brion, C. E. *Chem. Phys.* **1983**, *82*, 113.) and are found to be in good agreement with those calculated by using theoretical wave functions. Moreover, the dependence of the bond density on the quality of the wave function is discussed by using density difference maps in both position and momentum-space. The formation of the σ bond in momentum-space is also examined topographically in the critical range of internuclear separation between 2 and 1 a_0. The bonding picture in momentum-space complements traditional position-space bonding concepts and further extends present understanding of momentum-space chemistry.

I. Introduction

The ground-state electronic wave function of molecular hydrogen has been the subject of many experimental investigations including binary (e,2e) spectroscopy[1,2] and Compton scattering.[3] Compton scattering experiments in general sample the momentum density due to all the electrons of the target. Binary (e,2e) spectroscopy[4] on the other hand, samples selectively the momentum density of individual orbitals and provides a direct and sensitive experimental evaluation of molecular orbital wave functions. In the case of H_2, the total momentum density is to a very good approximation that of the $1\sigma_g$ orbital. The generally good agreement of the momentum distribution of molecular hydrogen observed by the two different techniques has been demonstrated in our recent study using binary (e,2e) spectroscopy.[2] The ground-state wave function of H_2 has also been investigated by many elaborate theoretical ab initio calculations, and H_2 is also the simplest test molecule for configurational interaction methods. Moreover, the hydrogen molecule involves the simplest (covalent) chemical bond and is thus suitable for the most fundamental studies of chemical binding and electronic structural properties. Earlier works by Berlin,[5] Roux et al.,[6] and Bader et al.[7,8] involved position (charge) density difference (bond density) maps and the force concept. Other works by Bader and Preston[9] and by Feinberg et al.[10,11] examined the behavior of the kinetic and potential energy upon bond formation and the role of the Virial theorem in bond formation.

The bond density in either position or momentum space is defined in the present study to be the density difference between the molecular density ($\rho_{H_2 1\sigma_g}$) and the density due to independent atoms (the independent atom model density, ρ_{IAM}) at positions corresponding to the molecular nuclear geometry, i.e.

$$\Delta\rho = 2\rho_{H_2 1\sigma_g} - \rho_{IAM} \qquad (1a)$$

$$\rho_{IAM} = \rho_{H1s} + \rho_{H1s} \qquad (1b)$$

both at R, where R is the internuclear separation and ρ denotes the single electron density. It is possible to obtain the "experimental" (spherically averaged) momentum-space bond density using the experimental momentum distributions of the H_2 $1\sigma_g$ orbital and either the experimental or the exact theoretical momentum distribution of the 1s orbital for the H atom. The momentum distribution for the 1s orbital of atomic hydrogen has been determined recently in an elegant experiment by Lohmann and Weigold[12] using binary (e,2e) spectroscopy. The measured result is found to reproduce the square of the exact solution of the Schrodinger equation in momentum-space. The only difficulty involved in obtaining the bond density is the normalization of the measured spherically averaged momentum density of H_2 $1\sigma_g$ because the noncoplanar symmetric (e,2e) experiment in most cases measures only relative cross sections.[4] In the present study, this problem is solved by employing a numerical procedure. The "experimental" momentum-space bond density thus obtained is compared with theoretical calculations by using H_2 wave functions of different quality including extended Hartree–Fock (Ext-HF),[13]

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