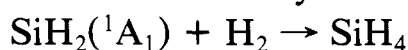


An ab Initio Study of the Insertion Reaction

Alexander Sax[†] and Gottfried Olbrich^{*†}

Contribution from the Institut für Theoretische Chemie der Universität Graz, Graz, Austria, and the Max-Planck-Institut für Strahlenchemie, Mülheim a. d. Ruhr, West Germany.

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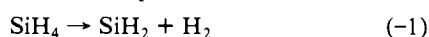
Abstract: A two-dimensional potential energy surface for the insertion reaction of singlet silylene ($\text{SiH}_2\ ^1\text{A}_1$) into the H_2 molecule to form SiH_4 was calculated, using basis sets of at least double-quality and CI techniques. From the analysis of the structural changes it is deduced that this reaction proceeds similarly to the analogous reaction of singlet methylene. However, in contrast to the latter, an activation energy of 6.3 kcal/mol at 600 K is evaluated for the reaction of SiH_2 with H_2 . This apparent difference between SiH_2 and CH_2 is traced to the different ordering of their respective lowest lying states. From the energy values of the potential energy surface $\Delta H_{298}^\ddagger = 62.2$ kcal/mol for singlet silylene is deduced, and, further, an activation energy of 60.2 kcal/mol for the thermal decomposition of monosilane at 600 K is calculated.

I. Introduction

It is now well established that silylenes are formed as reactive intermediates in many decomposition reactions of silanes.¹ In spite of the increasing number of experimental investigations on the reactions of silylenes,^{1a} only relatively few theoretical studies are concerned with the insertion reaction of silylene into single²⁻⁷ and double⁸ bonds. The reaction



may be regarded as a prototype for the insertion reaction of silylenes into nonpolar single bonds.⁹ A further important aspect of reaction 1 comes from the fact that it is the reverse of the primary step in the thermal decomposition reaction of silane^{1a,10}



Therefore, a theoretical investigation of reaction 1 may contribute to the understanding of reaction mechanisms in thermal silane chemistry.

Reaction 1 is the analogue to the insertion of singlet methylene into H_2 which has been investigated very extensively.^{11,12} In the case of the latter reaction it was well established experimentally that at least one of the two lowest electronic states of CH_2 reacts with H_2 without any activation energy.¹³ Theoretical investigations by Kollmar and Staemmler¹¹ and Bauschlicher et al.^{12a,b} revealed that the reaction of $^1\text{A}_1$ CH_2 with H_2 indeed proceeds without an energy barrier, whereas the reaction of $^3\text{B}_1$ CH_2 with H_2 may be regarded as a prototype for H abstraction by carbene exhibiting a barrier of about 10.8 kcal/mol.^{12c,d} Furthermore, as an example of a carbene insertion into double bonds, we may mention the work of Zurawski and Kutzelnigg,¹⁴ who calculated potential energy curves for the addition of singlet methylene to ethylene to form cyclopropane. This reaction also proceeds without activation energy.¹³ A result common to all these theoretical studies is that the reaction proceeds without any barrier only if a highly unsymmetrical geometry is maintained along the reaction coordinate.

The insertion of silylene into H_2 could not be observed until now¹ and no direct experimental evidence for the existence of an activation energy is available. However, John and Purnell¹⁵ from copyrolysis studies of Si_2H_6 and H_2 deduced a lower bound to the activation energy of 5.5 kcal/mol for this reaction. A number of theoretical investigations of insertion reactions of silylene appeared quite recently. From SCF calculations together with Møller-Plesset second-order (MP2) perturbation corrections Gordon² found a transition state for the reaction $\text{SiH}_2 + \text{H}_2$ lying 8.6 kcal/mol above the energy of the reactants. This value does not include zero-point energy (ZPE) corrections. Grev and Schaefer³ (GS) report on two-configuration SCF (TCSCF)

calculations for the transition state of the same reaction. At the TCSCF optimized geometries electron correlation was taken into account by configuration interaction including all single and double excitations (CISD). They achieve an activation energy of 6.7 kcal/mol, including ZPE at the highest level of theory. After submission of our manuscript two further studies appeared, dealing with the insertion of SiH_2 into H_2 . Gordon and Gano⁴ (GG) performed MCSCF calculations including 20 configurations and arrived at a barrier height of 16.2 kcal/mol. Inclusion of correlation via CISD reduced the barrier to 8.4 kcal/mol, whereas from MP3 calculations 5.2 kcal/mol were deduced. All these values are without ZPE corrections, however. Sosa and Schlegel⁵ (SS), at the MP4 level of theory and including ZPE corrections, found an activation energy of 12.2 kcal/mol. From SCF calculations for the reaction of silylene with ethylene Anwari and Gordon⁸ concluded that this reaction proceeds without an activation energy.

However, no explanation has been advanced so far for the existence of the activation energy in reaction 1 in contrast to the analogous methylene insertion for which no activation energy is observed. To the best of our knowledge, no studies were concerned yet with the reaction of $^3\text{B}_1$ SiH_2 and H_2 .¹⁶ Bell and co-workers,¹⁷

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^{*} Max-Planck-Institut für Strahlenchemie.

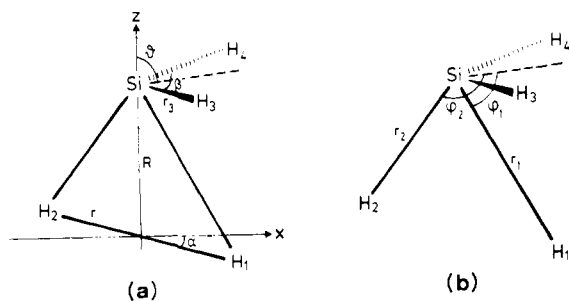


Figure 1. Coordinate system and numbering scheme for the atoms. (a) Parameters optimized in the calculation of the (R, θ) surface are r , r_3 , α , β . (b) Geometry of the transition state; internal coordinates used in Figures 3 and 4 are indicated.

with the help of symmetry arguments, conjectured that the insertion of silylene into H_2 could proceed via the triplet state of SiH_2 , and they estimated the activation energy for this reaction to be at least as large as the singlet-triplet excitation energy of silylene, i.e., about 18.6 kcal/mol.¹⁸

In this study we present the results of extensive CI calculations for a potential energy surface of the insertion reaction of $^1A_1 \text{SiH}_2$ into $^1\Sigma_g \text{H}_2$. These calculations were undertaken to confirm the experimental activation energy by quantum chemical methods and, possibly, to derive an explanation for the existence of this activation barrier in contrast to the reaction of methylene. The paper is organized as follows: Section II describes the technical details of the computations; in the next section, after the presentation of the potential energy surface, the structural changes along the reaction surface are analyzed. Thereafter, the energetics of the calculated reaction are evaluated and compared to experimental results where possible. The results are discussed in section V, and in connection with the general model of Shaik¹⁹ for the construction of potential energy curves, a proposal is made for the mechanism of silylene insertion reactions.

II. Computational Approach

The system $\text{SiH}_2 + \text{H}_2$ has nine internal degrees of freedom of which six were considered explicitly in this study. These six geometrical parameters and the coordinate system used, which is closely related to that of Bauschlicher et al.,^{12b} are depicted in Figure 1. The distance R between the silicon atom on the positive z axis and the midpoint of the H-H distance at the origin of the coordinate system served as a measure for the reaction coordinate.

As is well known, the insertion of $^1A_1 \text{XH}_2$ ($X = \text{C}, \text{Si}, \dots$) into H_2 is forbidden in the Woodward-Hoffmann sense if a least-motion path maintaining C_{2v} is followed.¹² For the methylene insertion, it was found^{11,12} that symmetry reduction from C_{2v} to C_s permits the reaction to occur without an energy barrier. The angle θ between the z axis and the bisector of the H-Si-H angle of the SiH_3 group is, therefore, the main geometrical parameter that describes the preference of the system to adopt C_s symmetry instead of C_{2v} symmetry. The bond distance of the H_2 molecule is designated by r . The angle α allows for different distances between the Si atom and the hydrogens; this was found to be of lesser importance in the case of the methylene insertion,¹¹ but it proved to be essential in the case of silylene. It should be stressed that any nonzero value of α led to a symmetry lowering from C_{2v} to C_s , irrespective of the value of θ . Therefore, only for $\theta = 0$ and $\alpha = 0$ does the system have the higher C_{2v} symmetry. The Si-H bond lengths of the SiH_2 moiety were held equal and are designated by r_3 , while β is the H-Si-H bond angle.

To exhibit the most characteristic features of the potential energy surface we represented it as a function of R and the angle θ . At every point of the grid the energy was minimized with

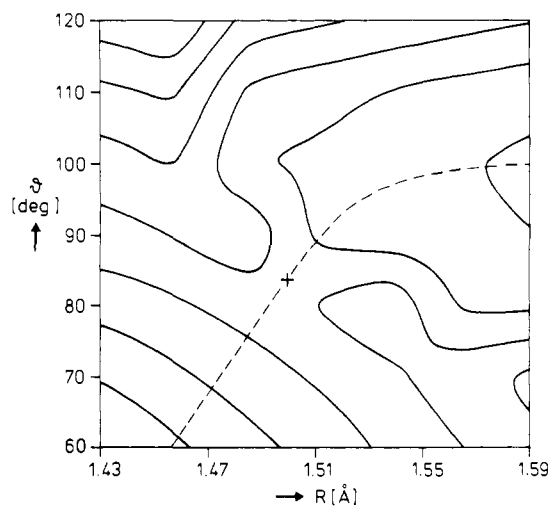


Figure 2. Contour diagram of the potential energy surface. The difference between adjacent contour lines is 3 kcal/mol; the saddle point is marked by (+), and the dashed line indicates the minimum energy path.

respect to the other four parameters by employing a Newton-Raphson-type procedure.²⁰ All calculations, and these included all geometry optimizations, were performed at the CI level of theory with use of the MRD-CI method.²¹ In the CI part of the calculations all single and double replacements with respect to at least two reference configurations were generated and energy selection²¹ was employed. For these rather extensive calculations, the pseudopotential method of Durand and Barthelat²² was adopted to perform the SCF calculations on which the CI was based. Three different kinds of basis sets were employed: For the geometry calculations, a $(4s/4p)$ basis set with a contraction scheme $(22/22)$ ²³ at the Si atom and a (31) set at the H atoms was used.²⁴ This basis set—denoted as basis A—is of double- ζ quality for the valence electrons. The selection criterion in the CI was 20 μ hartree, resulting in secular problems of dimension 400 on the average. Basis B consisted of basis A augmented by a d set on the Si atom with an exponent 0.45 and p sets on the hydrogens with exponents 0.8 and served for the final calculation of the potential energy surface; the selection threshold was 10 μ hartree, leading to CI dimensions of about 2500. In a final set of all-electron calculations for the potential curve along the minimum energy path, at the Si atom, a $(12s8p)$ basis was used contracted to $[6s4p]$ according to McLean and Chandler,²⁵ together with a $(5s/3s)$ basis set at the H atom.²⁴ A d set at silicon and p sets on the hydrogens were added, both with an exponent of 0.4; the low value for the exponents of the p functions was chosen to account for the hydride character of the H atoms in Si-H bonds. In this set of calculations, the reference space was individually optimized at each point, the selection threshold was again 10 μ hartree, leading to similar dimensions of CI as with basis B, and extrapolation to zero threshold²¹ was performed.

III. The Potential Energy Surface and Structural Changes

From preliminary calculations, it was concluded that the transition state of the reaction should be located at R values below 1.6 Å and at a value for θ of about 90°. Therefore, a grid was generated by varying R from 1.429 to 1.588 Å in steps of 0.026 Å and for θ between 60 and 120° in steps of 10°. At every point of that grid, the geometry was optimized as described in the last section, and finally, the energy surface was calculated by using

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Table I Geometries and Energies along the Minimum Energy Path of the Reaction^a

R	θ	$r(\text{Si-H})$	$r(\text{H-H})$	β	α	E
52.92		1.5175	0.7415	92.04	0.00	-291.297 182
5.292	100	1.5175	0.7415	92.04	0.00	-291.297 209
2.646	100	1.5575	0.7694	93.34	-19.83	-291.298 279
2.117	100	1.5497	0.7798	94.35	-15.16	-291.299 301
1.799	100	1.5379	0.8014	96.37	-12.42	-291.300 664
1.693	100	1.5328	0.8236	97.36	-10.80	-291.299 850
1.588	100	1.5254	0.8573	98.76	-8.94	-291.296 172
1.535	100	1.5224	0.8917	100.06	-8.16	-291.292 879
1.508	90	1.5098	0.9895	104.46	-9.25	-291.290 927
1.498	83	1.4942	1.9744	118.44	-16.15	-291.289 325
1.482	80	1.4933	1.9651	119.26	-15.15	-291.292 187
1.455	60	1.4899	1.9411	122.45	-11.56	-291.304 243
1.429	40	1.4885	1.9623	120.48	-7.40	-291.318 421
1.376	0	1.4891	2.0107	116.64	0.00	-291.340 371
1.270	0	1.4905	2.0744	115.14	0.00	-291.358 704
1.164	0	1.4943	2.2529	112.11	0.00	-291.383 088
0.863	0	1.4986	2.4472	109.47	0.00	-291.389 954

^a Atomic distances are in Å, angles are in deg and the energies are in hartrees (1 hartree 627.524 kcal/mol = 2623.1 kJ/mol).

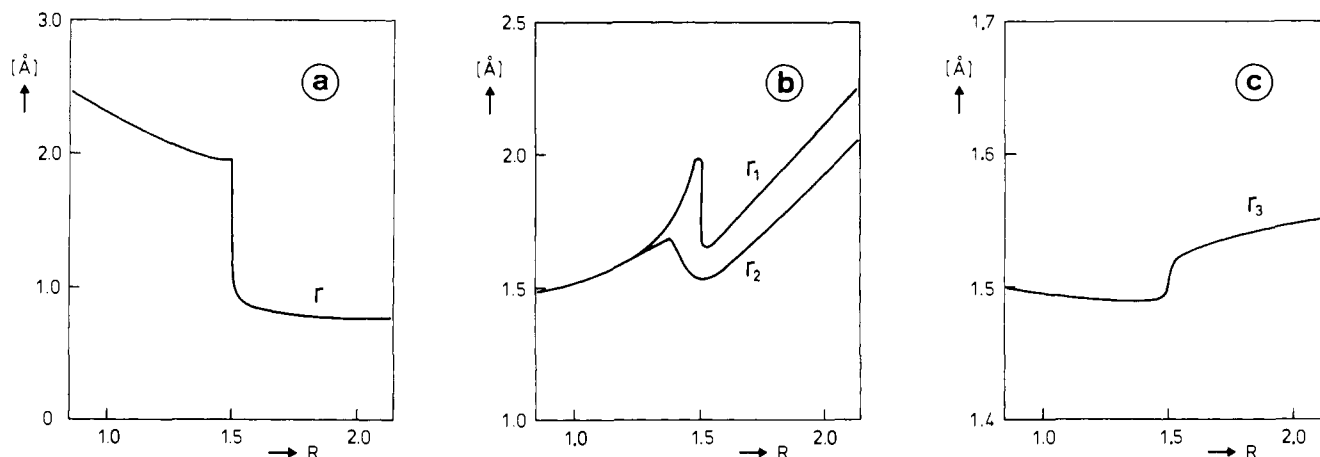


Figure 3. Variation of different atomic distances along the reaction coordinate; (a) H-H distance of the hydrogen molecule, (b) Si-H distances of the new bonds, (c) Si-H distance of the silyl group.

basis B. A contour plot of this energy surface obtained by two-dimensional spline interpolation²⁶ is given in Figure 2.

Further investigations of the reaction surface for values of R larger than 1.588 Å led to a single minimum with respect to θ at the value of $\theta = 100^\circ$. The path along this minimum forms the entrance valley of the reaction, the last part of which can be seen in the upper right hand corner of Figure 2. Similar calculations for fixed values of R below 1.429 Å always resulted in a minimum at $\theta = 0^\circ$. Thus, below $R = 1.429$ Å the least-motion path and the minimum-energy path coincide.

On the potential energy surface as a function of R and the angle θ shown in Figure 2, one can clearly distinguish the following regions: (i) a valley for large R and $\theta \approx 100^\circ$ corresponding to the reactants, (ii) the region leading to silane for $R < 1.482$ Å and $\theta < 70^\circ$, both separated by (iii) a saddle point at $R = 1.498$ Å and $\theta = 83^\circ$. The occurrence of a saddle point implies the existence of an activation energy along the reaction coordinate. Therefore, it follows from the present study also that the insertion of singlet silylene into the H-H single bond exhibits an activation barrier in contrast to the analogous reaction of singlet methylene. Furthermore, the region of the transition state turns out to be relatively flat, in the sense that only a minor amount of energy is necessary to pass from the educt to the product side along trajectories which avoid the saddle point. It follows that the system is highly nonrigid in the region of the transition state with respect to the coordinates chosen. A discussion of this transition state will be postponed to the next section.

We turn our attention now to a discussion of the geometric parameters; in that context it has already been mentioned that

the relaxation of the restriction $\alpha = 0$ proved to be essential, especially in the region of the transition state, thus allowing for different distances between the Si atom and the H atoms of the hydrogen molecule. In the following we shall designate the path of minimum energy on the potential surface (see Figure 2) from the reactants to the product SiH_4 as the reaction path. In order to get an intuitive representation for the variation of the geometry along the reaction path, we transformed the parameters R , θ , r , and α given in Table I into the more instructive parameters r_1 , r_2 , φ_1 , and φ_2 (see Figure 1b); Figures 3 and 4 display these parameters as functions of the reaction coordinate R along the reaction path. In Figure 3a, the variation of the H-H distance of the hydrogen is shown, and the sudden rupture of the bond at $R = 1.498$ Å is clearly indicated. The different behavior of the two new Si-H bonds being formed in the reaction can be seen in Figures 3b and 4a. As long as the H_2 molecule approaches the SiH_2 molecule in the entrance valley, i.e., $R > 1.498$ Å, both bond lengths and bond angles exhibit a parallel trend. The difference between r_1 and r_2 is about 0.12 Å, whereas the angles φ_1 and φ_2 vary only slowly. In this region, the H-H bond is nearly parallel to the plane of the SiH_2 molecule. This can be explained by assuming an attractive interaction between the empty π MO of silylene and the occupied MO of H_2 . Repulsive interactions, on the other hand, between the silylene lone pair and the σ electrons of the H-H bond are minimized in this geometrical arrangement. This was called the electrophilic phase of the reaction in the case of the methylene insertion.¹¹

At $R = 1.498$ Å, the parameters exhibit a sudden change. Both atomic distances increase, but r_1 increases considerably more than r_2 , so that at the saddle point the difference reaches 0.45 Å. For $R < 1.455$ Å, both Si-H bonds decrease, but r_2 attains the final value earlier than r_1 . The angles φ_1 and φ_2 undergo a similar rapid

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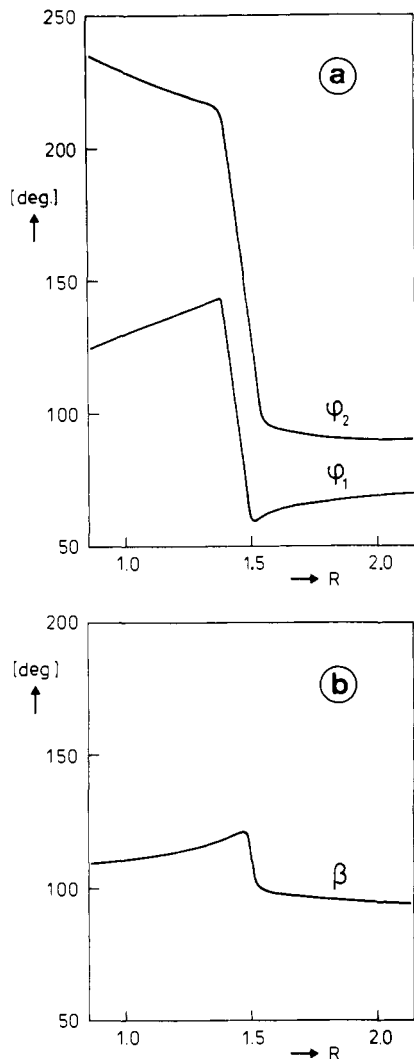


Figure 4. Variation of angles along the reaction coordinate: (a) angles between the plane of the SiH₂ group and the new bonds, (b) bond angle in the silyl group.

Table II. Geometry Parameters at the Saddle Point in Comparison to Data from the Literature^a

	this work	reference			
		3	2	4	5
$r(\text{Si}-\text{H}_1)$	2.001	1.738	1.691	1.751	1.637
$r(\text{Si}-\text{H}_2)$	1.548	1.526	1.547	1.557	1.519
$r(\text{Si}-\text{H}_3)$	1.494	1.475	1.484		1.473
$r(\text{H}_1-\text{H}_2)$	1.974	1.068	1.103		1.092
$\angle(\text{H}_3\text{SiH}_4)$	118.4	107.5	112.5		111.6
θ	83.0	79.7	71.0		75.9
R	1.498	1.546	1.527		1.482

^a Atomic distances are in angstroms, angles are in degrees.

variation in the region of $1.429 \leq R \leq 1.498$ and, subsequently, change more slowly to their final values.

Figures 3c and 4b show the changes of the geometrical parameters in the SiH₂ fragment. The bond length r_3 contracts to 1.494 Å and β widens to 118° at the saddle point. The geometry of the SiH₂ moiety at this point is very similar to that of triplet silylene.¹⁸ From a comparison of parts b and c of Figure 3 it is deduced that at the saddle point three of the four Si-H bonds are very similar, viz., the Si-H distances in the silylene group and r_2 , whereas r_1 is considerably longer. The explicit geometrical parameters at the saddle point are displayed in Table II, together with corresponding values from the literature. One finds that atom H₂ is already firmly bound to the Si atom, but atom H₁ is not. The structure of the transition state may be roughly described as a complex formed by a distorted SiH₃ radical and a loosely

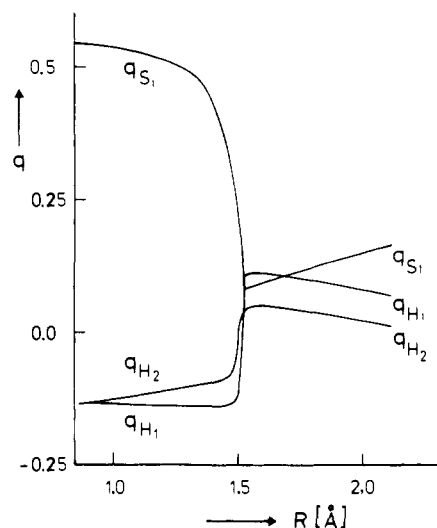


Figure 5. Variation of the gross atomic charges at the Si atom and the H atoms of the hydrogen molecule.

bonded H atom. Figure 1b actually corresponds to this geometry at the saddle point. Comparing our values in Table II to previous results, the following differences emerge: the elongation of the H-H distance is more pronounced, the H-Si-H bond angle of the SiH₂ moiety is considerably larger, and, with exception of the 6-31G* results of SS, our saddle point occurs at a shorter R value. Thus, our saddle point structure corresponds rather to a late transition state. These differences could be due to different quality of basis sets, geometry optimization at different levels of sophistication (CI vs. SCF or MCSCF), or different methods for the saddle point search (numerical vs. analytical gradient methods).

The formation of the first new Si-H bond is the second phase of the reaction, which has been termed the nucleophilic phase.^{11a} In the third phase, i.e., for R less than 1.498 Å, an "inversion of the umbrella" takes place, similar to an S_N2 reaction, during which the second new Si-H bond is formed. These findings may be summarized by the statement that the insertion of SiH₂ into H₂ occurs via a highly unsymmetrical two-step mechanism.

The conclusions drawn from the variation of the geometry along the reaction path are corroborated by the results of a population analysis given in Figure 5. The net charge at the Si atom decreases gradually during the approach before the transition state; parallel to this, the positive charges at the hydrogen atoms increase. This variation of the charge distribution supports the notion of an electrophilic phase of the reaction, electrophilic with respect to the Si atom. At the transition state, the charge at silicon switches immediately to a large positive value whereas the hydrogen atoms become negative after the new Si-H bonds are formed. Accordingly, the charge distribution corresponds to the nucleophilic phase of the reaction.^{11a} The overlap populations (not shown explicitly) are in complete agreement with this behavior of the system; the overlap population between the hydrogen atoms changes from positive to negative values at the transition state and, at the same time, becomes positive between the hydrogens and the silicon atom.

IV. The Energetics of the Reaction

Whereas the potential energy surface of Figure 2 is confined to the immediate region around the saddle point, the potential energy curve shown in Figure 6 includes the entire reaction coordinate and represents a cut through the surface. This potential curve was calculated by employing basis C and the reference space for the CI was carefully optimized at every point calculated. The potential energy surface exhibits a shallow minimum corresponding to a small decrease in energy of about 2 kcal/mol between the educts and the transition state; this may be attributed to the bonding interaction between the reactants during this phase of the reaction. A similar finding has already been reported for the reactions of methylene with H₂^{11,12} and ethylene¹⁴ and for SiH₂

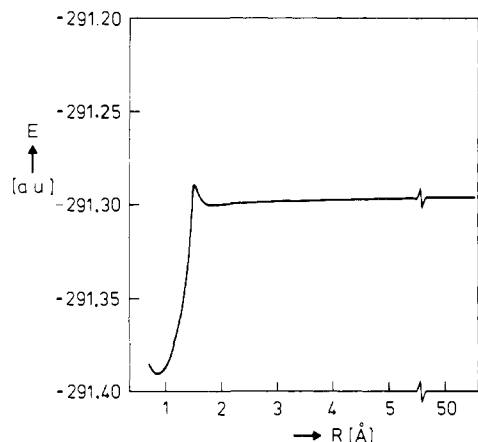


Figure 6. Reaction profile along the minimum energy path.

Table III. Vibrational Frequencies for SiH₄, SiH₂, and the Transition State (in cm⁻¹) and Zero-Point Energies ε₀ (in kcal/mol)

	SiH ₄		SiH ₂		H ₂ SiH ₂ calcd
	calcd	exptl ^a	calcd	exptl ^b	
ν ₁	2258	2187	2163	2032	2254
ν ₂	1051	978	1102	1008	2047
ν ₃	2243	2183	2146	2022	990
ν ₄	1013	910			780
ν ₅					672
ν ₆					670i
ν ₇					2284
ν ₈					1044
ν ₉					817
ε ₀	20.2	19.2	7.7	7.2	15.6

^a Reference 26. ^b Reference 27.

+ H₂.⁵ After passing this very flat minimum around $R = 1.799$ Å, the energy increases until the transition state is reached.

An unambiguous test for the occurrence of a transition state is the existence of exactly one negative force constant and, consequently, one imaginary frequency. In this context, a force calculation²⁷ was performed at the saddle point which we located at the potential surface. The basis used in these calculations was the MIDI-3* basis set by Sakai and co-workers.²⁸ To assess the quality of the results, similar calculations were performed for SiH₄ and SiH₂. In Table III, the computed frequencies are displayed together with experimental values for SiH₄²⁹ and SiH₂.³⁰ From a comparison between the calculated and experimental frequencies, it is deduced that the former are too high by at most 10%. The zero-point energies evaluated from these values are in error by about 5%; the absolute values are 1 kcal/mol for SiH₄ and 0.5 kcal/mol in the case of SiH₂.

An important result, also given in Table III, is that only one imaginary frequency occurs. We take this as a confirmation for the structure of the transition state located by our calculational procedure. The shape of the reaction coordinate connected with this imaginary frequency is displayed in Figure 7. The nuclear displacements clearly point in those directions which ultimately lead to the formation of tetrahedral SiH₄. When one compares the frequencies of the transition state from Table III with those reported by GS³ and SS,⁵ some differences in the low-frequency modes as well as in the imaginary frequency are encountered. These differences may be due to the different bonding situation at the respective saddle points.

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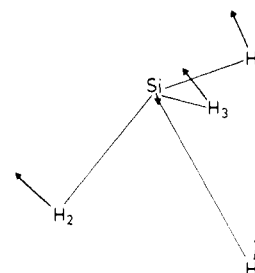


Figure 7. The reaction coordinate at the saddle point derived from the force calculation.

Table IV. Barrier Heights, Zero-Point Energy Corrections (ε₀), and Activation Energies (in kcal/mol) for the Reaction SiH₂ + H₂ → SiH₄

level of theory	basis	ref	barrier height	ε ₀	activation energy
MRD-CI	TZ+P	this work	4.9	1.4	6.3
CISD/TCSCF	DZ+P	3	4.7	2.5	7.1
CISD/SCF	DZ+P	3	5.7	2.5	8.2
CISD/SCF ^a	DZ+P	3	4.2	2.5	6.7
MCSCF	6-31G*	4	16.2		
CISD/MCSCF	6-31G*	4	8.4		
MP3/MCSCF	6-31G*	4	5.2		
MP2/SCF	6-31G*	5	8.4	3.1	11.5
MP3/SCF	6-31G*	5	8.4	3.1	11.5
MP4/SCF	6-31G*	5	9.1	3.1	12.2
exptl		15			5.5 ± 1.0

^a with Davidson correction.

We are now in a position to estimate the activation energies for both the insertion reaction 1 and the decomposition step -1 and to give a theoretical assessment of the heat of formation of singlet silylene. To this end, SiH₂ and H₂ were calculated together in their respective minimum geometries at an R value of 52.9 Å (see Table I, first entry). In a further set of calculations for SiH₄, the transition state, and the educts SiH₂ + H₂ the basis set convergence was tested. For these computations the [6s5p] triple-ζ basis for Si²⁵ and a [4s] set for H²⁴ together with two d and p sets on Si and H, respectively, were employed; here a change of less than 0.5 kcal/mol for the energy differences was encountered. From this result, we infer an error of at most 1 kcal/mol due to incompleteness of the basis and an overall error of 2 kcal/mol, including that of the zero-point corrections. In order to be compared with experimental data, the activation energies and the heat of formation must be evaluated for finite temperatures. To accomplish this, we use the following equation³¹ for the activation energy E_A derived from the expression for the rate constant as given by the transition state theory:³¹

$$E_A = \Delta\epsilon_0 + RT - \frac{d(\ln(Q^\ddagger/V))}{d(1/RT)} + \sum_{\text{react.}} \frac{d(\ln(Q_i/V))}{d(1/RT)}$$

$\Delta\epsilon_0$ denotes the energy difference between the zero-point energies of the reactants and the transition state. With the classical approximation for the translational and rotational partition function, the activation energy for reaction 1 may be written

$$E_A(1) = \Delta E - \frac{3}{2}RT + E_{\text{vib}}^\ddagger - E_{\text{vib}}(\text{SiH}_2) - E_{\text{vib}}(\text{H}_2)$$

Here, ΔE is the difference of the energies of the transition state and of the reactants which is 4.9 kcal/mol from the values in Table I, and E_{vib} denotes the zero-point energies together with the vibrational contributions from the partition functions. The latter were calculated within the harmonic approximation³¹ by using the frequencies of Table III. Evaluating all the temperature-dependent quantities at 600 K, we arrive at a value for the ac-

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tivation energy of 6.3 ± 2.0 kcal/mol. This is in satisfactory agreement with the lower bound of 5.5 ± 1.0 kcal/mol given by John and Purnell.¹⁵ In Table IV, barrier heights and activation energies which were calculated until now for the reaction $\text{SiH}_2 + \text{H}_2$ are collected. A critical examination of the data clearly reveals the importance of *both* post Hartree-Fock methods and flexible basis sets to arrive at reliable results which permit a sound comparison with experiment. These conditions are met as close as possible by the work of Grev and Schaefer³ and in the present study.

For the decomposition reaction of silane (-1) we have the expression

$$E_A = \Delta E + RT + E_{\text{vib}}^\ddagger - E_{\text{vib}}(\text{SiH}_4)$$

and we evaluate 60.2 ± 2.0 kcal/mol as the theoretical estimate at 600 K. This should be contrasted with the experimental value of 59.5 ± 0.5 kcal/mol given by Newman and co-workers¹⁰ from shock-tube measurements. Finally, to estimate the heat of formation of SiH_2 , we use the following expression for the enthalpy:

$$\begin{aligned} \Delta H^\circ_{298} &= \Delta U^\circ_{298} + RT \\ &= \Delta E + \frac{7}{2}RT + E_{\text{vib}}(\text{SiH}_2) + E_{\text{vib}}(\text{H}_2) - E_{\text{vib}}(\text{SiH}_4) \end{aligned}$$

Evaluating the temperature-dependent quantities for $T = 298$ K and using the experimental value for $\Delta H_f^\circ(\text{SiH}_4)$ of 8.2 ± 0.3 kcal/mol,³² we arrive at 62.6 ± 2.0 kcal/mol, again in satisfactory agreement with the experimental value of 58 kcal/mol.^{15,32}

V. Discussion

The results of the calculations presented in section IV for the reaction of singlet silylene with H_2 clearly indicate that this reaction actually exhibits a transition state for which we have deduced an activation energy of 6.3 kcal/mol. Furthermore, other thermochemical data evaluated from the calculations, viz., the activation energy of the primary decomposition step of SiH_4 and the heat of formation of silylene, are in satisfactory agreement with recent experimental results.

A less favorable conclusion to be drawn from the discussion of the geometrical changes along the reaction coordinate and from the transformation of the electronic structure in Section III is that the reaction of SiH_2 with H_2 proceeds quite similarly to the analogous reaction of singlet methylene, but nothing alludes to the *source* of the activation energy. Kollmar^{11a} explains the mechanism of the methylene insertion with the aid of charge-transfer interactions as follows. In the first step, a charge transfer occurs from the occupied σ_g MO of H_2 to the unoccupied p_x MO of CH_2 (electrophilic step), followed by charge transfer in a second step from the σ lone pair of CH_2 into the antibonding σ_u MO of H_2 (nucleophilic step). It could be argued that the electrophilic step may be less likely for SiH_2 due to the smaller electronegativity of silicon as compared to carbon. But the charge distributions clearly indicate that this charge transfer does occur, and from the energies displayed in Table I, a stabilization of more than 2 kcal/mol between the educt geometry and the point $R = 1.799$ Å is evaluated. Therefore, the mechanism of Kollmar^{11a} does not explain the occurrence of an activation barrier in the case of the silylene insertion.

In the following, we attempt to provide a qualitative explanation for the source of the activation energy. This explanation will be based on the general conclusions which Shaik¹⁹ arrived at with the aid of the valence-bond configuration mixing (VBCM) model. Within this model, all possible configurations using the frontier orbitals of the individual reacting molecules are formed, and the wave functions along the reaction coordinate are analyzed in terms of these configurations. Shaik¹⁹ was able to show quite generally the following: (i) Whenever at least one of the reacting molecules is a closed-shell system, an avoided crossing occurs, the latter implying that an energy barrier may be anticipated. (ii) The electron pairs involved in the reaction must be decoupled in order to create unpaired electrons at the reaction centers, thus enabling the formation of the new bonds; as long as such a valence state

of the reacting system is not prepared, any adduct consists of a loose association complex only, in which the educts retain their individuality and which will not lead to the products.¹⁹

Applying these ideas to our problems, we observe that two electron pairs have to be decoupled to initiate the formation of the new Si-H bonds, viz., the lone pair at the silicon atom and the bonding pairs of the hydrogen molecule. Formally, such a decoupling is accomplished by a promotion to higher electronic states, and the lowest possible excitations in the two reacting molecules obviously are to the triplet states. On the basis of these considerations, we propose for the transition state of the insertion reaction of SiH_2 into H_2 that it may be composed of the respective triplet states of the reactants, these individual triplets being coupled to an overall singlet state. At first glance it might appear that the promotion to such a valence state requires too much energy. The following simple considerations, however, will indicate that such a promotion is indeed feasible. From thermochemical measurements,³² the formation of two Si-H bonds furnishes about 180 kcal/mol. At the transition state, the two new bonds are not formed completely, and the system contains about 56 kcal/mol of internal energy,¹⁰ thus leaving about 124 kcal/mol for the promotion energy. Although it is known that the singlet-triplet separation of SiH_2 amounts to about 19 kcal/mol,¹⁸ it is difficult to estimate this promotion energy for the H_2 part of the system. Nevertheless, this latter energy will be much smaller than the corresponding excitation energy at the equilibrium distance of H_2 , because in the region immediately before the transition state the H-H bond is already considerably elongated. As a plausible value, we take the bond-dissociation energy of H_2 of 104 kcal/mol leading to a total of 123 kcal/mol as an estimate for the promotion energy. Although such exact agreement of our estimate for the promotion energy with the above value of 124 kcal/mol is undoubtedly fortuitous, nevertheless, this rough calculation renders such a promotion plausible.

This concept of a valence state leads to the following qualitative explanation for the occurrence of an activation barrier in the insertion of singlet SiH_2 into H_2 , in contrast to the corresponding reaction of CH_2 . Under the assumption that the promotion to the valence state of the hydrogen molecule is nearly equal in both cases, there still remains the difference between methylene and silylene in the ordering of the lowest states: Note that for methylene, the triplet state (i.e., the ground state) is about 9 kcal/mol lower in energy than the singlet state, whereas for silylene, the triplet lies about 19 kcal/mol above the singlet ground state.¹⁸ Thus, the promotion to the valence state of the methylene insertion actually corresponds to a "de-excitation", in contrast to the silylene insertion where the valence state is reached by an "excitation". We conclude that the order of the singlet and triplet states as well as the amount of the singlet-triplet separation are responsible for the existence and for the height of the energy barrier.

If this concept of a valence state of the reactants bears any physical meaning, it should be possible to find structures along the reaction coordinate that can be attributed to triplet silylene and to triple H_2 . Obviously, one would expect these structures in the vicinity of the saddle point, and this is indeed the case. As mentioned above, the geometry of the SiH_2 fragment at the saddle point is very similar to that of triplet silylene, and the elongation of the H_2 molecule is in agreement with the repulsive character of the $^3\Sigma_u$ state of H_2 . Similar behavior was encountered in the studies of the singlet methylene insertion into H_2 ^{11,12} and ethylene¹⁴ and of singlet SiH_2 into ethylene.⁸ For the region along the reaction coordinate where the new bonds are formed, all authors report a maximal value for the H-C-H angle of methylene close to the angle in the triplet state. Moreover, Zurawski and Kutzelnigg¹⁴ report a contraction of the C-H bond; a similar contraction of the Si-H bond was encountered in our study as well (see Figure 3c). Such differences in the bond lengths of the singlet and triplet states are characteristic for the whole series XH_2 , X = C, Si, Ge, and Sn.³³

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VI. Concluding Remarks

The results of our study indicate that the structural aspects of the reaction of singlet silylene with H_2 are very similar to the analogous reaction of singlet methylene. The reaction proceeds in two steps: the first electrophilic step leads to the transition state with one Si-H bond almost formed, whereas in the second nucleophilic step the product SiH_4 is reached. On the basis of the VBCM model,¹⁹ it was assumed that for the formation of the transition state, the reactants must be promoted to a valence state which can be *formally* visualized as the two reactants in their respective triplet states coupled to a singlet. With this assumption, the existence of an activation energy in the silylene reaction in contrast to methylene could be explained. We want to stress that the notion of a triplet valence state should not mean that the reaction really proceeds via the triplet state as was conjectured by Bell and co-workers.¹⁷ Such a mechanism would imply a nonadiabatic reaction, including an intersystem crossing step and therefore, would render the reaction highly improbable. The results of our calculations, however, indicate the possibility of an adiabatic course of the reaction, together with a modest activation energy.

From our proposed reaction mechanism, further conclusions can be drawn concerning the reactions of singlet silylene with substrates other than hydrogen. We traced the activation energy to the promotion energy needed to form the transition state, and we may anticipate that in other systems less energy is necessary

for that process. This is probably the case in the reaction of silylene with silane to disilane, where the low activation energy of 3 ± 3 kcal/mol¹⁰ is estimated. For the addition of silylene to ethylene, one can safely assume that the promotion energy to a valence state of the ethylene will be much lower than that for hydrogen. Concomitantly, Anwari and Gordon,⁸ from their calculations for this reaction, find no activation energy. Finally, the reaction mechanism proposed above allows us to predict a higher activation energy for the reaction of GeH_2 with hydrogen since the singlet-triplet separation of this behavior analogue to SiH_2 is higher by about 4 kcal/mol.³⁴

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Registry No. SiH_2 , 13825-90-6; SiH_4 , 7803-62-5; H_2 , 1333-74-0.

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Spontaneous and Induced Homolysis of Bis(triphenylphosphine)octacarbonyldimanganese(*Mn-Mn*)

Anthony Poë* and Chandra V. Sekhar

Contribution from the J. Tuzo Wilson Laboratories, Erindale College, University of Toronto, Mississauga, Ontario, Canada L5L 1C6. Received June 1, 1984

Abstract: Kinetic studies show that the complex $Mn_2(CO)_8(PPh_3)_2$ reacts thermally by two paths with $C_2H_2Cl_4$, $C_{16}H_{33}I$, O_2 , NO , $P(OEt)_3$, and $P-n-Bu_3$ in decalin or cyclohexane. Reactions with CO or $P(OPh)_3$ proceed only by one of these paths. The two paths are of approximately equal importance and both show a very close fit to the same, rather complex, form of rate equation. The equation is quite inconsistent with any form of rate-determining dissociation, but it is consistent with two forms of reversible homolysis, one spontaneous and one induced. The latter involves initial, reversible formation of a reactive isomer of $Mn_2(CO)_8(PPh_3)_2$ which undergoes homolysis when attacked by a sufficiently reactive reagent. Both paths are therefore operative in reactions with the more reactive reagents, but reactions with CO and $P(OPh)_3$ proceed only via spontaneous homolysis because these reagents are evidently unable to induce homolysis of the reactive isomer of the complex. A possible structure for the reactive isomer is one formed by metal migration, i.e., it can be formulated as $(Ph_3P)(OC)_4Mn(\mu-CO)Mn(CO)_3(PPh_3)$ which contains a bridging CO ligand, no $Mn-Mn$ bond, and a vacant coordination site on one Mn atom. Attack at this site by suitably active reagents is postulated to lead to fragmentation. These results show that behavior previously thought to be uniquely indicative of spontaneous homolysis could also be explained by reversible homolysis induced by the reactant after isomerization of the complex. Rate constants are derived for halogen transfer from $C_2H_2Cl_4$ or $C_{16}H_{33}I$ to $\cdot Mn(CO)_4(PPh_3)$ and for nucleophilic displacement of PPh_3 from $\cdot Mn(CO)_4(PPh_3)$ by $P(OPh)_3$, $P(OEt)_3$, and CO .

Thermally induced homolysis of the metal-metal bonds in dinuclear metal carbonyls would, if it occurred, be a very useful phenomenon. It would allow activation enthalpies to be obtained for homolysis, and these would provide less ambiguous and more precise quantitative estimates of the strengths of the metal-metal bonds than are available by using other methods.¹ At first sight, the occurrence of initial homolysis should be demonstrable by kinetic methods. When the homolysis is reversible, reactions should change smoothly from being first order to half order in [complex] as the homolysis becomes more and more easily reversed.¹ This will generally be the case as the concentration of

the complex is increased. Such kinetic behavior has been observed for the thermal decomposition reactions of $Mn_2(CO)_{10}$,² $Re_2(CO)_{10}$,³ $Tc_2(CO)_{10}$,⁴ $MnRe(CO)_{10}$,² and $Mn_2(CO)_8[P(OPh)_3]_2$ ⁵ in the presence of oxygen, and it was proposed that initial reversible homolysis was indeed the dominant mechanism for decomposition reactions of these complexes, and for substitution and other reactions as well.

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