Transition State and Barrier Height for the Silanediyl Insertion Reaction $SiH_2 + H_2 \rightarrow SiH_4$

Roger S. Grev and Henry F. Schaefer III*

Department of Chemistry, University of California, Berkeley, California 94720, U.S.A.

The potential energy hypersurface for the title reaction has been investigated *via a priori* quantum mechanical methods, leading to acceptable agreement with the experimental activation energy.

Insertion of singlet carbenes into alkanes generally proceeds without an activation energy.[1] The simplest model for this family of reactions, $CH_2 + H_2 \rightarrow CH_4$, has been shown theoretically[2,3] and experimentally[1] to proceed without a barrier. However the prototype silanediyl plus hydrogen reaction (1) appears to have an activation energy. From the copyrolysis of disilane and hydrogen, John and Purnell[4] inferred a 23 ± 4 kJ mol^{-1} barrier for the model silanediyl insertion.

$$SiH_2 + H_2 \rightarrow SiH_4 \qquad (1)$$

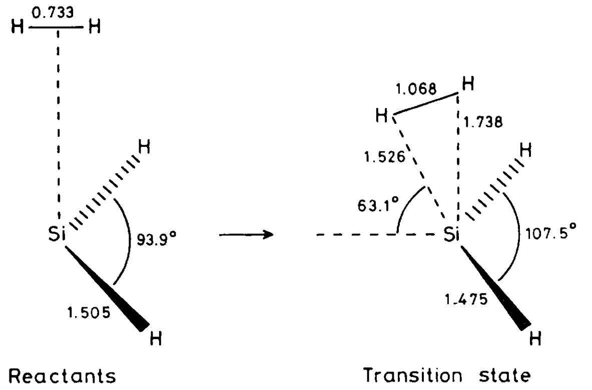

Figure 1. Stationary point geometries predicted at the (DZ+P) TCSCF level of theory. The bond lengths are in Å.

In a recent communication, Gordon[5] located the transition state for reaction (1) using the single-configuration SCF method in conjunction with a 3-21G basis set. Using the larger 6-31G* basis the predicted barrier is 78 kJ mol^{-1} and this was reduced to 36 kJ mol^{-1} when second order perturbation theory was appended. Meadows has shown[6] that a single configuration description of SiH_2 can be inadequate, so we have re-examined reaction (1) using a two-configuration SCF procedure. In addition, a significantly larger double zeta plus polarization (DZ+P) basis set[7] was used throughout this research. Finally, electron correlation was treated *via* configuration interaction (CISD) including all single and double excitations relative to both reference configurations.† Two configuration (TC) SCF stationary points were precisely located using analytic gradient techniques.[8]

The TCSCF wave function for $SiH_2 + H_2$ is of the general form $C_1\,1a'^2 2a'^2 3a'^2 4a'^2 1a''^2 5a'^2 6a'^2 2a''^2 7a'^2 + C_2\,1a'^2 2a'^2 3a'^2 4a'^2 1a''^2 5a'^2 6a'^2 2a''^2 8a'^2$. These are the two most important configurations for the SiH_2 diradical itself, and in addition are the two configurations required to describe qualitatively the least motion (Woodward–Hoffmann forbidden) pathway[2] for reaction (1).

The reactant and transition state geometries are shown in Figure 1. The bond angle and distances of the SiH_2 fragment in the transition state have shifted significantly towards those of the tetrahedral product SiH_4 [$\theta = 109.47°$, R(Si–H) = 1.480 Å].[9] Yet the location of the H_2 fragment relative to SiH_2 (sideways approach) and its remaining short bond distance (compared to an H–H separation of 2.417 Å in SiH_4) preclude any definite conclusion about this insertion reaction being an exception to Hammond's postulate, that the transition state for an exothermic reaction should resemble the reactants.[10]

The single imaginary vibrational frequency, corresponding to motion over the energy barrier, has the value 1241 i cm^{-1}. The activated complex incorporates 6057 cm^{-1} of zero point vibrational energy in the eight bound vibrational degrees of freedom, while the reactants' zero point energy is 5088 cm^{-1}. Typically, harmonic vibrational frequencies predicted using (DZ+P) basis sets with SCF wave functions are 10% higher than the observed fundamentals.[11] Thus we estimate the zero point vibrational correction to the barrier height to be 10.4 kJ mol^{-1}. Gordon's transition state would therefore have an activation energy of 46 kJ mol^{-1}, compared to his reported[5] classical barrier, 36 kJ mol^{-1}.

Table 1. Zero-point corrected[a] barrier heights for the reaction $SiH_2 + H_2 \rightarrow SiH_4$. All results were obtained using the TCSCF optimized stationary point geometries.

Method	Activation energy/kJ mol^{-1}
Single configuration SCF	74.6
Two-configuration SCF	54.5
CISD/TCSCF	29.9
CISD/1 reference	34.2
CISD/1 reference + Davidson	27.9
Experiment[b]	23.0 ± 4

[a] TCSCF vibrational frequencies are 2203, 1131, and 2181 cm^{-1} (SiH_2); 4657 cm^{-1} (H_2); and 2341, 2337, 2211, 1378, 1117, 1071, 841, 818, and 1241 $i\,cm^{-1}$ (transition state). [b] Ref. 4.

Table 1 shows the predicted activation energies for several levels of theory. All results reported were determined at the TCSCF optimized geometries. The TCSCF result of 54.5 kJ mol^{-1} is 20.1 kJ mol^{-1} below the SCF value, yet still lies 31.5 kJ mol^{-1} above the experimental result.[4] The barrier lowering in TCSCF reflects the fact that the second configuration for $SiH_2 + H_2$ has coefficient −0.178, while for the transition state this coefficient is larger, −0.204. Including correlation effects the CISD treatment relative to the TCSCF reference function lowers the activation energy to 29.9 kJ mol^{-1}, in quite good agreement with experiment. Also reported are the results of CI with all single and double excitations with respect to the single reference SCF (3831 configurations). The effects of quadruple excitations may then be included in an approximate manner using the Davidson correction.[12] These results are very similar to the CISD/TCSCF values, as one might expect.

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† The occupied core orbitals resembling 1s, 2s, 2p Si were deleted from the CI procedure, as were the virtual orbital counterparts for this (DZ+P) basis set. A total of 7272 $^1A'$ configurations were thus included.