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The reactions between negative hydrogen ions and silane

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Contracted CI-calculations have been performed in order to find out the mechanisms of the reactions involved when negative hydrogen ions react with silane. There were initially severe problems to find a balanced basis set to describe the reactions including correlation, particularly for the choice of diffuse functions. Finally, in agreement with earlier calculations, SiH_5^- was found to be more stable than SiH_4+H^- by 21 kcal/mol but less stable than SiH_3^- and H_2 by 6 kcal/mol. A barrier in the S_N2 reaction $SiH_4+H^- \rightarrow SiH_5^-$ has previously been predicted by calculations, which was not confirmed by the present CI calculations. The lack of a barrier is in agreement with experimental evidence. Contrary to what is expected from the orbital symmetry rules, which predict two allowed pathways, SiH_5^- does not dissociate easily to the lower lying $SiH_3^- + H_2$. A barrier of 57 kcal/mol, which was very difficult to locate, was finally found. In order to explain the experimental observation of SiH_3^- and the lack of observation of SiH_5^- a different mechanism for the reaction $SiH_4+H^- \rightarrow SiH_3^- + H_2$ is suggested. For a direct proton transfer a barrier of less than 10 kcal/mol is predicted.

Key words: Silane—negative hydrogen ions—reactions with silane

1. Introduction

The nature of the bonding in pentacoordinated silicon, phosphorus and chlorine compounds is of fundamental chemical importance. There have consequently been enumerable studies every year, theoretical and experimental, of these types of compounds ever since the beginning of the century [1]. The reader is referred to Ref. [2] for further references on this very large subject. The simplest possible of these pentacoordinated compounds are SiH_5^- and PH_5. Due to their importance as model compounds, during the last ten years there have been several very accurate *ab initio* studies of these molecules. The first such studies of PH_5 were at the SCF-level [3, 4]. Somewhat later Keil and Kutzelnigg [5] made a calculation where a large fraction of the valence correlation energy was accounted for using the CEPA-method. PH_5 was shown to be stable with respect to PH_3+2H by 64 kcal/mol, but unstable with respect to PH_3+H_2 by 38 kcal/mol. In a more recent study [6] a force field for PH_5 was also given and additional information, showing that the molecule is in a local minimum and that in principle it should be possible to observe it, if the lifetime is sufficiently long.

The first studies of SiH_5^- were by Wilhite and Spialter [7], by Keil and Ahlrichs [8] and by Baybutt [9]. In the most accurate of these studies [8] the relative energies of some isomers on the SiH_5^- potential surface were determined using the CEPA-method. It was found that SiH_5^- is more stable than SiH_4+H^- by 20.3 kcal/mol but less stable than $SiH_3^-+H_2$ by 6.3 kcal/mol. In Ref. [7] a reaction path for the S_N2 reaction,

$$H^-+SiH_4\rightarrow SiH_5^-\rightarrow SiH_4+H^- \qquad (1)$$

was determined using the CNDO/2 method. SCF-calculations, using rather large basis sets, were then performed along this path. SiH_5^- was found more stable than SiH_4+H^- by 16.9 kcal/mol, using this method, but a barrier for its formation of 8.6 kcal/mol was also found.

With the purpose of experimentally testing the earlier theoretical predictions, the gas-phase kinetics of the reaction of H^- with SiH_4, among other reactions, was determined using the flowing afterglow technique [10]. Although SiH_5^- is not directly observed in these experiments, the results are in accord with a lower energy for this intermediate than for H^-+SiH_4, but do not corroborate the prediction of a large reaction barrier for the H^--attack made in Ref. [7]. Reaction (1) was further observed to compete with the proton transfer reaction,

$$H^-+SiH_4\rightarrow SiH_3^-+H_2. \qquad (2)$$

Channel (1) is, however, preferred by at least 4 to 1 over channel (2).

Some years earlier than these mentioned theoretical and experimental studies, the concerted fragmentation reaction $PR_5\rightarrow PR_3+R_2$ was discussed by Hoffmann et al. [2]. Conservation of molecular orbital symmetry showed that this reaction had two allowed pathways and one forbidden. The allowed reactions occur when the removed R-groups both come from equatorial or axial positions of PR_5. The equatorial-axial departure of R_2 is forbidden. These results were used in Ref. [8], where it was concluded that since there are two symmetry allowed dissociation paths for $SiH_5^-\rightarrow SiH_3^-+H_2$, and the products have lower energy, one should expect no, or at most a small barrier for dissociation. Besides explaining why SiH_5^- has not been observed experimentally, these arguments would further fully explain the mechanisms of the reactions studied experimentally in Ref. [10]. SiH_5^- was not directly observed in (1), and SiH_3^- in (2) would simply be formed by immediate dissociation of SiH_5^-.

The present SCF and contracted CI calculations were performed to test the orbital symmetry arguments given in Ref. [2] and to further clarify the mechanisms of the reactions studied experimentally in Ref. [10]. The results show that the S_N2 reaction (1) proceeds without a barrier contrary to what was found in Ref. [7], and that SiH_5^- does not easily dissociate into $SiH_3^- + H_2$, which is contrary to what is expected from the symmetry allowedness of this reaction. From the geometry and barrier height of the concerted dissociation reaction, it is not even clear that different transition states exist for the three different dissociation paths discussed in Ref. [2]. In order to explain the observation of SiH_3^- in the experiments [10], a different reaction mechanism is suggested involving a direct proton abstraction. The technical details of the calculations are presented in Sect. 2, and the results in Sect. 3.

2. Details of calculations

The design of a basis set capable of describing correlation effects for negative ions is not always an easy problem. For SiH_5^- this turned out to be extremely difficult. Reasonable and fairly large basis sets gave, for example, only 10% of the correct correlation effect for the S_N2 reaction (1), and severely exaggerated the correlation effect in reaction (2). The details of the basis set investigation and the methods used are given in this section.

For the S_N2-reaction, see Fig. 1, a $12s, 9p$-basis [11] contracted to $6s, 5p$ for silicon (contraction $6, 2, 4 \times 1$; $5, 4 \times 1$) and a $5s$-set [12] contracted to $3s$ for hydrogen, were used as a starting point. It is well known that for the description of the negative hydrogen ion a diffuse s-function is needed at the SCF-level. An s-function with exponent 0.03 was therefore added, but only to the axial hydrogens, which become ionic at large distance. It was shown in Ref. [8] that diffuse functions are not needed to describe SiH_5^- and therefore additional diffuse functions were not added. Two sets of d-functions with exponents 0.7 and 0.2, basically the same as in Ref. [8], were used on silicon. For the equatorial hydrogens a p-function with exponent 0.4 was used, which was found optimal for SiH_4 [8]. For the axial hydrogens a p-exponent of 0.2 was used instead, which is the optimal value for H^- [8]. For the energy difference between SiH_5^- and $SiH_4 + H^-$ this basis set gave 11.2 kcal/mol at the SCF-level, in reasonable agreement with

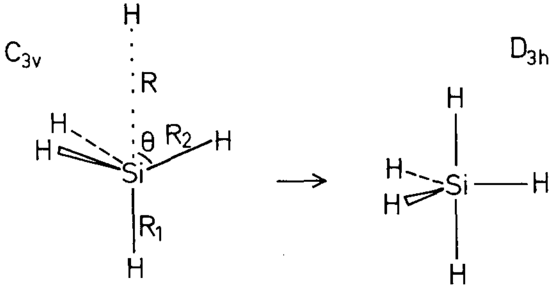

Fig. 1. Geometries for the S_N2 reaction $H^- + SiH_4 \rightarrow SiH_5^-$

13.8 kcal/mol obtained in Ref. [8], where a very large basis set including *f*-functions was used. On the CI-level the present basis set performed very poorly, however. An energy difference of 12.0 kcal/mol was obtained with a total correlation effect of only 0.8 kcal/mol. This should be compared to 20.3 kcal/mol with a correlation effect of 6.5 kcal/mol obtained in Ref. [8]. The initial guess that this large discrepancy was due to the lack of *f*-functions in our basis set turned out not to be true. Ahlrichs [13] recalculated the energy difference using the same basis set without *f*-functions and obtained nearly the same result. The only other plausible explanation was that the use of the *p*-exponent 0.2 for the axial hydrogens, rather than a larger value, causes the problem, which also turned out to be the case. Further experimentation with the basis set indicated that the use of the two *d*-exponents on silicon rather than one is not necessary. To further reduce computation time the $12s, 9p$-basis was changed to a $10s, 6p$-set [14] contracted to $6s, 4p$. The final basis set used for the S_N2 reaction is consequently $6s, 4p, 1d$ with *d*-exponent 0.5 for silicon, $3s, 1p$ with *p*-exponent 0.4 for the equatorial hydrogens and $4s, 1p$ with a diffuse *s*-exponent of 0.03 and the same *p*-exponent 0.4 for the axial hydrogens. This basis set gave an SCF-energy difference of 13.7 kcal/mol and a CI-value of 20.7 kcal/mol in excellent agreement with 13.8 kcal/mol and 20.3 kcal/mol obtained in the much larger calculations in Ref. [8].

The above described basis set cannot be used for the calculation of the dissociation of SiH_5^- into $SiH_3^- + H_2$, see Fig. 2. It was shown in Ref. [8] that in order to describe SiH_3^- diffuse functions are needed on silicon in contrast to the case of

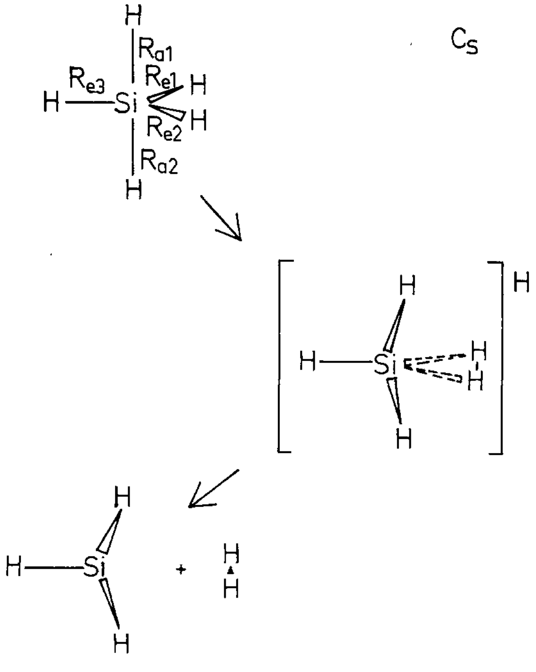

Fig. 2. Geometries for the dissociation reaction $S_iH_5^- \rightarrow [SiH_5^-]^{\#}_{diss} \rightarrow SiH_3^- + H_2$

SiH_5^-. A balanced description of the dissociation is therefore not obtained without diffuse functions. One set of s-functions and one set of p-functions were therefore added on silicon, both with exponents 0.03, in the study of the dissociation. The diffuse s-function on the axial hydrogens could on the other hand be removed. Apart from these changes the same basis set was used for the two reactions. The investigation of the dissociation reaction was done mainly at the SCF-level, where this basis set works very well. For the energy difference between SiH_5^- and $SiH_3^- + H_2$ the SCF-value is 6.1 kcal/mol, compared to the value 5.6 kcal/mol obtained in Ref. [8]. For obtaining a balanced description at the CI-level two sets of d-functions, the other set more diffuse with exponent 0.15, are needed. Without this extra d-function a CI-value of 2.0 kcal/mol is found compared to 6.3 kcal/mol from Ref. [8]. It is consequently clear that even in situations where only very small correlation effects are found, artificial effects can easily be introduced if the basis set is not very well balanced.

For the finally studied direct abstraction reaction, see Fig. 3, the same silicon basis was used as for the dissociation reaction. For the two hydrogens directly involved in the abstraction the diffuse s-function 0.03 had to be added again, however.

For the CI-calculations performed here the contracted CI-method was used, which is described elsewhere [15]. All calculations are done at the one reference state level since one configuration strongly dominates everywhere. Davidson's correction [16] is added to the CI-energy to account for unlinked cluster effects.

The location of the saddle point for the direct abstraction reaction (Fig. 3) was no problem and very simple methods could be used. A few calculations were first performed to locate the area of the saddle point. A grid was then set up in three internal coordinates and the energy was fitted to a second degree polynomial. From this polynomial a Hessian was calculated and a first saddle point was obtained. The energy was calculated in the new point, a new polynomial fitted and a new saddle point obtained etc. until convergence. This procedure, however, does not work at all for the location of the transition state for dissociation of SiH_5^- (Fig. 2). The situation is here much more complicated as practically all degrees of freedom are strongly coupled. A sophisticated and rather expensive procedure, described in detail in another paper [17], had to be used instead. In

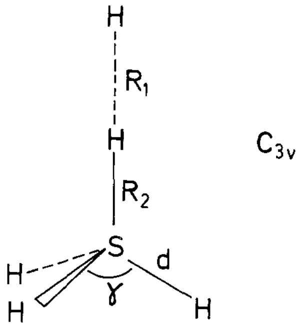

Fig. 3. Geometry for the abstraction reaction $SiH_4 + H^- \rightarrow [SiH_5^-]^{\#}_{ab} \rightarrow SiH_3^- + H_2$

this method the area of the saddle point is located in energy-optimizations on successively approaching hyper-spheres [18]. When the correct area is reached an exact Hessian matrix is calculated numerically from the analytically obtained gradients [19] in close-lying points. With this Hessian the Newton–Raphson procedure is used to obtain a better guess of the saddle point. It was then found important to update the Hessian for the new point before continuing the procedure [20, 21]. It was not enough to keep the same Hessian and just calculate new gradients in the new point. Nor was it enough to start the updating procedure by a reasonable guess of a diagonal Hessian matrix, as is normally done when locating local minima with gradient methods. The finally located saddle point is in an area where the energy changes very little upon rather large coordinate changes. At the point where the procedure was stopped the energy is therefore well determined, but the geometry may still change substantially.

3. Results

The results for the three reactions given in Figs. 1–3 are presented in this section with one sub-section for each reaction. The details of the calculations were given in the preceding section and the results are discussed and compared in the next section.

3.1. *The S_N2-reaction*

In the earlier investigation of the reaction path for the S_N2 reaction [7] a barrier was found of 8.6 kcal/mol at a distance of 6.6 a.u. between the silicon and the hydride ion. This result is not in line with what was observed experimentally [10]. In order to definitely find out, if there is a barrier or not, a careful geometry optimization of the reaction path was undertaken. Keeping C_{3v}-symmetry the geometry was fully optimized at the SCF-level for eight different values of the reaction coordinate, which was taken to be the silicon - hydride ion distance. In these optimized points the energy was also calculated at the contracted CI-level and Davidson's correction was added. The results are given in Table 1 and plotted in Fig. 4. As can be seen, there is no trace of a barrier in these calculations. The barrier obtained in Ref. [7] must have been an artefact of the way the geometry was optimized, which was done only at the CNDO/2-level. The coordinates along the reaction path given in Table 1 show no region of dramatic changes, which would indicate an electron jump. The initially diffuse electron on the hydride ion is slowly spread out over the whole SiH_5^- molecule. The distance to the equatorial hydrogens shows an initial small decrease before increasing to its equilibrium value, while the other two coordinates increase monotonically all the way. The difference between this reaction and the S_N2-reaction involving carbon is nearly total. In that case a large barrier of 55 kcal/mol was obtained with consequently also much longer axial distances [22]. The difference between carbon and silicon in this respect is usually explained by the lower lying *d*-orbitals in silicon. Another explanation is found in the very strong three center four electron bond formed by the lone pair in SiH_3^- and the axial hydrogens. Since

Table 1. The S_N2 reaction path, distances in a.u. and energies in kcal/mol

	R	R_1	R_2	θ	ΔE_{SCF} [a]	ΔE_{CI} [b]	ΔE_{CEPA} [c]
SiH_4+H^-	∞	2.792	2.792	70.5	0	0	0
	7.8	2.820	2.784	73.0	−2.07	−2.57	−2.51
	6.6	2.838	2.780	73.9	−2.76	−3.77	−3.70
	5.5	2.870	2.778	76.2	−3.26	−5.27	−5.27
	4.5	2.931	2.788	81.2	−4.46	−8.35	−8.60
	4.0	2.973	2.805	84.5	−6.84	−12.05	−12.42
	3.5	3.032	2.840	87.8	−11.11	−17.57	−18.07
SiH_5^-	3.073	3.073	2.872	90.0	−13.68	−20.71	−21.08

[a] Relative $E_\infty = -291.6351$.
[b] Relative $E_\infty = -291.7987$.
[c] Relative $E_\infty = -291.8140$

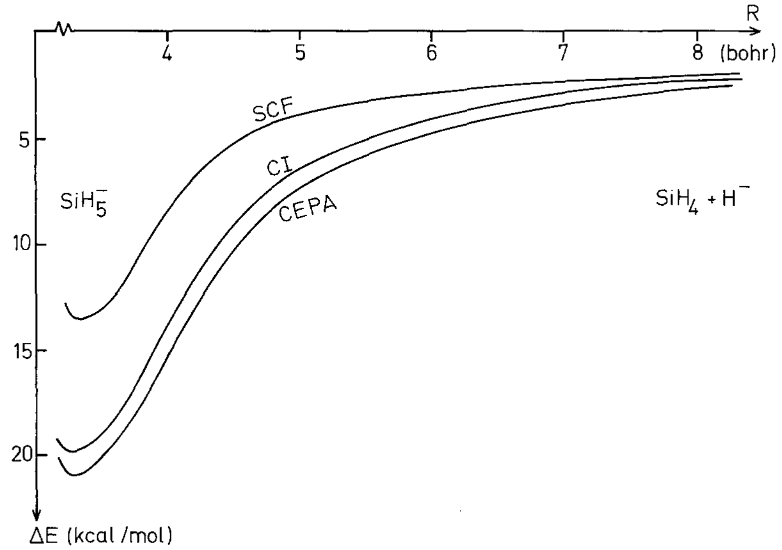

Fig. 4. Potential energy curve for the S_N2 reaction

this type of bonding requires a large charge transfer it is stronger the lower the ionization potential is. SiH_3^- has a very low ionization potential, which also explains the higher stability of SiH_5^- compared to PH_5 [8].

3.2. The dissociation reaction

The concerted dissociation of H_2 from SiH_5^- is the most complicated of the three different reactions considered here. This type of reaction has earlier been discussed by Hoffman et al. [2] and the arguments given there will first be briefly reviewed here. The outer molecular orbitals of SiH_5^- are shown schematically in Fig. 5. The simplest way to describe the bonding in SiH_5^- is to consider it as composed

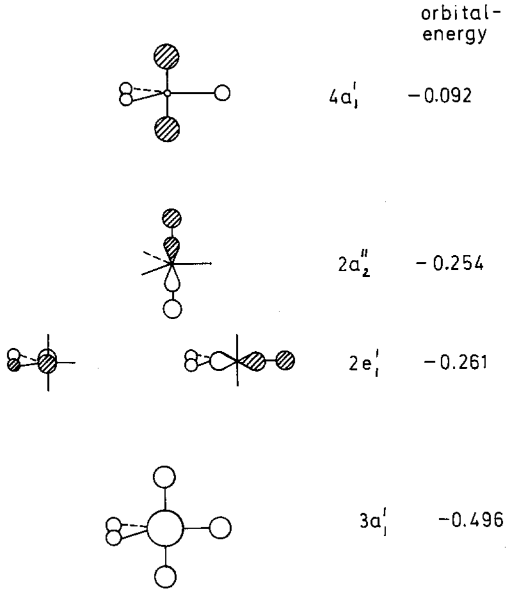

Fig. 5. SiH_5^- (D_{3h}) - valence orbitals

of a planar SiH_3^- and two axial hydrogens. The bonding in SiH_3^- is similar to that of ammonia with the three bonds in $3a_1'$ and $2e_1'$. The lone pair on SiH_3^- and the two axial hydrogen orbitals then combine to form three molecular orbitals. The lowest two of these, the bonding $2a_2''$ and the non-bonding $4a_1'$ are then occupied, while the antibonding combination is empty. This type of bonding usually requires a large charge transfer, which is best understood by looking at the formation of the molecule. If SiH_3^- is in a plane and H_2 is perpendicular to this plane with its midpoint in the plane and approaches, the silicon lone pair donates electrons into the antibonding orbital of H_2 to break it apart. Since only one bonding orbital is formed between SiH_3^- and the hydrogen atoms only part of the charge is donated back to silicon. The bonding is therefore quite ionic, silicon has a positive charge of +0.8 and the axial hydrogens a negative charge of −0.5. Since the SiH_3^- orbitals have their correspondence in SiH_5^-, and the two orbitals involved in the three center four electron bond, $2a_2''$ and $4a_1'$, have the same symmetry as the SiH_3^- lone pair and H_2-bond respectively, it is clear that the axial-axial concerted dissociation reaction is symmetry allowed. In Ref. [2] it is further shown in a similar way that the equatorial-equatorial dissociation is also allowed, whereas the axial-equatorial dissociation is forbidden. From these arguments one should therefore expect that SiH_5^- should dissociate rather easily into SiH_3^- and H_2.

The location of the transition state for the dissociation reaction turned out to be very complicated. The details of how the saddle point was finally found is described in Sect. 2 and in Ref. [17]. The initial idea was to try all the three different pathways discussed in Ref. [2] to find out which of the barriers is lowest, and in this way test the orbital symmetry arguments. Starting out with the most

Table 2. Geometries and energies for the reaction series $SiH_4+H^- \rightarrow SiH_5^- \rightarrow [SiH_5^-]^{\#}_{diss} \rightarrow SiH_3^- + H_2$

	R_{a1}	R_{a2}	R_{e1}	R_{e2}	R_{e3}	ΔE_{SCF} [a]	ΔE_{CI} [b]	ΔE_{CEPA} [c]
SiH_4+H^-	∞	2.792	2.792	2.792	2.792	0	0	0
SiH_5^-	3.073	3.073	2.872	2.872	2.872	−13.7	−20.7	−21.0
$[SiH_5^-]^{\#}_{diss}$	2.85	2.85	3.31	3.04	2.95	49.9	39.4	36.5
$SiH_3^-+H_2$	2.909	2.909	∞	∞	2.909	−7.7	−9.5	−9.9

[a] Relative $E(SiH_4+H^-) = -291.6471$.
[b] Relative $E(SiH_4+H^-) = -291.8171$.
[c] Relative $E(SiH_4+H^-) = -291.8328$.

probable allowed pathway, the equatorial-equatorial dissociation, it was soon realized that the potential energy surface was very complex. Searching over a wide region of the surface, the saddle point which was found is given in Table 2. This geometry was reached in the SCF-gradient calculations, with the only symmetry constraint being the equatorial plane as a plane of symmetry. The SCF-barrier is 64 kcal/mol. A contracted CI calculation in this point gave a lower barrier of 57 kcal/mol. With this height of the barrier and with the geometry given in Table 2, it is not clear that the three different pathways have different saddle points. Although the search for the saddle point started out by moving the equatorial hydrogens, the final axial hydrogen distances more resemble the initial equatorial distances, for example. Ideally, the minimal energy path from the saddle point should be followed to see which initial state is reached. This is, however, quite expensive and also in this case numerically uncertain since the potential energy surface is very flat in large regions, and this has not been done. A pathway to $SiH_3^-+H_2$ from SiH_4+H^- via SiH_5^- and this saddle point does further not seem so likely anymore, due to the high barrier. With this high barrier it is also interesting to consider a stepwise dissociation by the loss of one hydrogen, or hydride ion, at a time. The first step in this reaction would be the loss of a hydride ion, which is the same S_N2 reaction as discussed above. The energy required for this step is therefore 20 kcal/mol, much lower than the 57 kcal/mol needed for the concerted dissociation. In the next step the hydride ion would help a proton away from silane. This abstraction reaction is considered below.

3.3. *The abstraction reaction*

Since the concerted dissociation reaction discussed in the preceding section has a rather high barrier, the question is whether there is another pathway with a lower barrier by which SiH_3^- could be formed. It should be recalled that SiH_3^- was observed as a product in the gas phase reaction and not SiH_5^- [10]. One other possible mechanism for formation of SiH_3^- is by means of direct abstraction according to Fig. 3. This process could also be called a proton transfer reaction. Keeping C_{3v}-symmetry all four coordinates were varied at the SCF-level to determine the saddle-point. Keeping two of these optimized coordinates fixed, the other two strongly coupled coordinates R_1 and R_2 were redetermined at the CI-level with and without Davidson's correction. The resulting coordinates and

Table 3. Geometries and energies for the abstraction reaction $SiH_4 + H^- \rightarrow [SiH_5^-]^{\neq}_{ab} \rightarrow SiH_3^- + H_2$. Distances in a.u. and energies in kcal/mol

	R_1	R_2	d	γ	ΔE_{SCF} [a]	ΔE_{CI} [b]	ΔE_{CEPA} [c]
$SiH_4 + H^-$	∞	2.792	2.792	109.5	0	0	0
$[SiH_5^-]^{\neq}_{ab}$	2.35	3.31	2.86	102.1	23.7	17.0	14.6
	2.63[d]	3.13[d]					
$SiH_3^- + H_2$	1.401	∞	2.909	96.7	−7.7	−9.5	−9.9

[a] Relative $E_{R_1=\infty} = -291.6471$.
[b] Relative $E_{R_1=\infty} = -291.8171$.
[c] Relative $E_{R_1=\infty} = -291.8328$.
[d] Optimized at the CI-level

energies are given in Table 3. The influence of correlation is rather large with changes in the coordinates of 0.2–0.4 a.u. and in the barrier height of nearly 10 kcal/mol down to a value of 15 kcal/mol. Removing the symmetry constraints, further geometry optimization at the CI-level and enlarging the basis set would probably further reduce this value and a true barrier height below 10 kcal/mol for the proton transfer is more realistic. This apparently rules out dissociation of $SiH_5^-(D_{3h})$ as the preferred pathway for reaction (2), since the transition state for that mechanism lies about 35 kcal/mol above $SiH_4 + H^-$.

4. Conclusions

Parts of the SiH_5^- potential energy surface have been investigated to predict the outcome of an attack by hydride ions on silane. Methods were SCF and SCF-gradient calculations for geometry determinations followed by contracted CI in all points of importance. Two modes of the hydride approach have been studied. The first one is the nucleophilic attack on the silicon atom to form $SiH_5^-(D_{3h})$ which was found to proceed smoothly without barrier with a binding energy of 21 kcal/mol. The second one is the attack on one of the hydrogen atoms resulting in a proton transfer and the departure of a hydrogen molecule to form $SiH_3^- + H_2$. This last system was, in agreement with earlier calculations, found to be the most stable of the different isomers, lying 6 kcal/mol lower than SiH_5^-. Its formation via the mentioned proton transfer occurs with a calculated barrier of 15 kcal/mol. To investigate whether this mechanism is preferred to the alternative pathway with $SiH_5^-(D_{3h})$ as an intermediate, calculations on the dissociation of the latter was performed. As the most proabable way for H_2 to depart the symmetry allowed removal of two equatorial hydrogens was chosen. Contrary to what has been expected this dissociation was found to occur with a rather high barrier of about 55 kcal/mol i.e. 35 kcal/mol above $SiH_4 + H^-$. This seems to rule out this mechanism and leave the proton transfer as the most probable way of realizing the reaction $SiH_4 + H^- \rightarrow SiH_3^- + H_2$.

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