

## The uncatalyzed hydrosilation reaction

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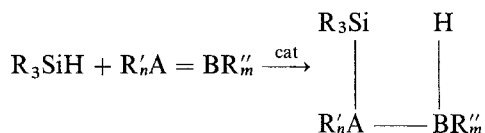
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**Summary.** The reactions of ethylene with silane, chlorosilane, fluorosilane, and dichlorosilane, and of propylene with silane are considered using *ab initio* electronic structure calculations. At both the MP2 and MP4 levels of theory with both DZP and TZP quality basis sets, the energy barriers for all reactions are found to be in excess of 50 kcal/mol.

**Key words:** Hydrosilation reaction – Catalyst

### Introduction

The hydrosilation reaction, which can be written in the general form



is a particularly important process for the production of new bonds to silicon (e.g., new Si–C bonds). Because the hydrosilation reaction is so important in the synthesis of a variety of organosilicon compounds, this reaction has been the subject of a recent review [1] and is of increasing interest to theoreticians [2]. As written above, A and B can be C, Si, O, or a metal atom, and a catalyst (e.g., TiCl<sub>2</sub>) is generally required for the reaction to proceed. Both A and B will be carbon atoms in this study, so  $n = m = 2$ .

There are several questions regarding the mechanism of the hydrosilation reaction. The analogous organic reaction would be the alkylation of alkenes. This reaction is usually carried out in an acidic environment to induce a carbonium ion mechanism. The other mechanism for addition to the double bond of an alkene, a free radical mechanism usually induced by peroxide, would result in polymerization.

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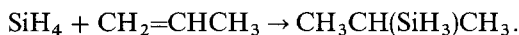
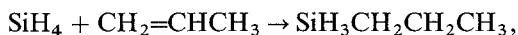
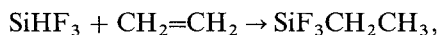
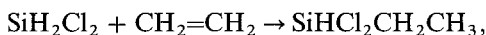
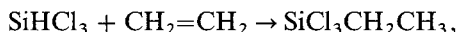
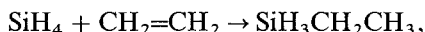
In this paper, the gas-phase hydrosilation reaction is studied in the absence of a catalyst, in order to determine the baseline energetics (thermodynamics and kinetics) without the catalyst present. This will provide a set of reference calculations against which subsequent studies including catalysts may be compared. This will also facilitate the evaluation of the effects of various reactant substituents R in the absence of the catalyst, thereby separating these two effects (substituent vs. catalyst).

In most of the reactions included in this study, the reacting alkene will be ethylene ( $R' = R'' = H$ ), although in one reaction the alkene is propylene, i.e.,  $R' = CH_3$ . Silane,  $SiH_4$ , and the substituted silanes,  $SiHF_3$ ,  $SiHCl_3$ , and  $SiH_2Cl_2$ , are all used as reactants in this study.

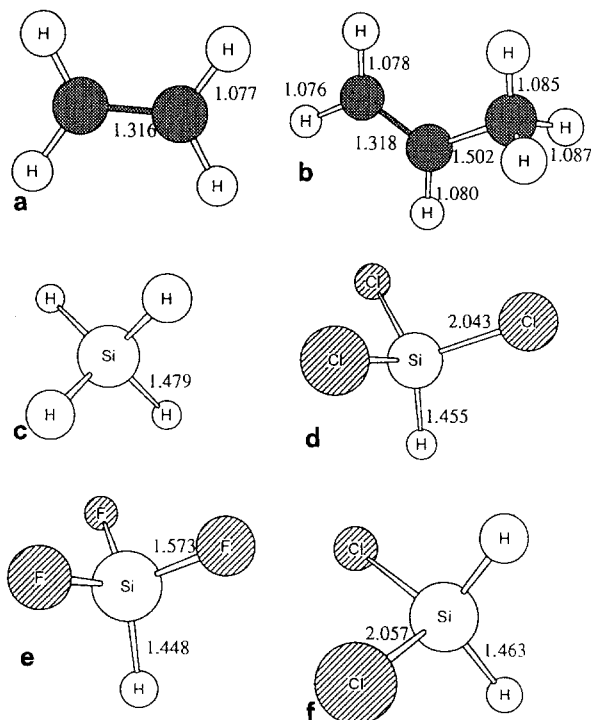
There has been one previous theoretical study related to the uncatalyzed hydrosilation reaction. Fransisco and Schlegel [3], in an analysis of the photodissociation dynamics of ethylsilane, investigated the reverse of the parent hydrosilation reaction with  $R = R' = R'' = H$ . Their results will be compared with ours below.

### Computational methods

*Ab initio* electronic structure calculations were used to characterize five uncatalyzed hydrosilation reactions:



The structures and energies of equilibrium points (minima on the potential energy surface (PES)), corresponding to the reactants and products, and transition states (saddle points on the PES), were determined using the restricted Hartree-Fock (RHF) method in the electronic structure program GAMESS [4]. All stationary points were characterized by calculating the analytic hessian (matrix of energy second derivatives) and diagonalizing it to obtain the harmonic normal modes and corresponding frequencies. Minima and transition states on the PES have zero and one imaginary frequencies, respectively. The calculated frequencies are also used to obtain harmonic vibrational zero-point energies, which must be added to convert energy differences to 0 K enthalpy differences. Three different basis sets were used in this study. Preliminary geometries were obtained with the 3-21G [5] basis set. These geometries were then refined using the 6-31G(d) [6] and 6-311G(d,p) [7] basis sets. Energies were corrected for electron correlation effects by using second-order perturbation theory (MP2) [8] with the two larger basis sets, 6-31G(d) and 6-311G(d,p), and the structures obtained with these two basis sets. Full fourth-order perturbation theory (MP4SDTQ) energies were calculated with the 6-31G(d) basis at the RHF/6-31G(d) structures. Such energies are denoted

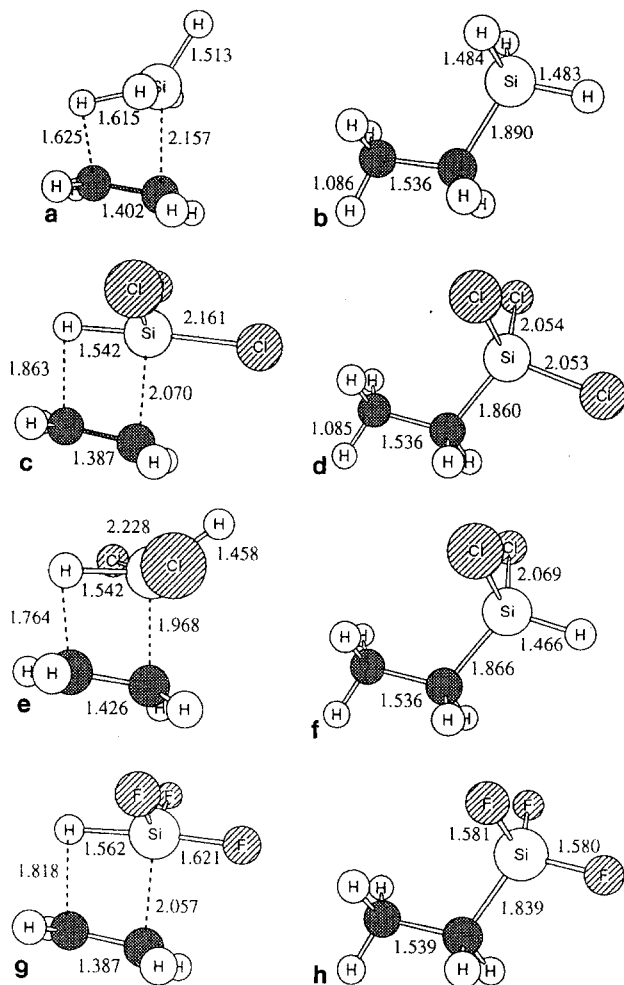


**Fig. 1 a-f.** Structures of the reactants of the hydrosilation reactions considered in this study. All structures are minima at the RHF level using the 6-311(d,p) basis set. **a** ethylene, **b** propylene, **c** silane, **d** trichlorosilane, **e** trifluorosilane, **f** dichlorosilane

MP4/6-31G(d)//RHF/6-31G(d). The GAMESS program was used for all calculations except the MP4 calculations, for which GAUSSIAN-92 [9] was used.

## Results and discussion

The structures of the reactants for the hydrosilation reaction are shown in Fig. 1. The two alkenes considered in this study, ethylene and propylene, are shown in Fig. 1a and b and silane and the three substituted silanes are shown in Fig. 1c-f. The structures of the transition states and products for the four uncatalyzed reactions involving ethylene, obtained with the 6-311G(d,p) basis, are shown in Fig. 2. All of these transition states and products have  $C_s$  symmetry. The products all have very similar structures, the only significant difference being that the bonds to the halogen atoms are of course longer than those to the hydrogen atoms. The transition states for the four ethylene reactions are also quite similar. One noticeable difference is that, in the transition states involving the trihalogenated silanes, the out-of-plane halogens are in an equatorial orientation and the in-plane halogen is axial and nearly collinear with the reacting Si-H bond. On the other hand, in the transition states involving silane and dichlorosilane, the out-of-plane silane substituents are axial and the in-plane substituent atom, which for these two reactions is a hydrogen atom, has an equatorial orientation.



**Fig. 2 a-h.** Structures of the transition states and products of the uncatalyzed hydrosilation reactions involving ethylene, all at the RHF level using the 6-311(d,p) basis set. **a** transition state leading to ethylsilane, **b** ethylsilane equilibrium geometry, **c** transition state leading to ethyltrichlorosilane, **d** ethyltrichlorosilane equilibrium geometry, **e** transition state leading to ethyldichlorosilane, **f** ethyldichlorosilane equilibrium geometry, **g** transition state leading to ethyltrifluorosilane, **h** ethyltrifluorosilane equilibrium geometry

The relative energies for these uncatalyzed reactions are listed in Table 1, and the total energies at both the MP4/6-31G(d) and MP2/6-31G(d,p) levels of theory are listed in Table 2. All of the reactions have a barrier of over 50 kcal/mol, and all are exothermic by 25–40 kcal/mol. At the highest levels of theory (MP4 and MP2) the barrier heights for the reactions of interest are nearly independent of both the nature of the silane and the nature of the substrate. The barrier for the reaction involving  $\text{SiH}_2\text{Cl}_2$  is the most distinguishable, as it is consistently 2–4 kcal/mol lower than the others. The substituents on the silane have a small but discernible effect on the heat of reaction, with the three substituted silanes having a greater

Table 1. Heats of reaction and barrier heights for the uncatalyzed hydrosilation reaction in kcal/mol.  $\Delta E$  indicates the energy change, while  $\Delta H$  is obtained by correcting for zero-point vibrational energy in the harmonic approximation.  $\Delta E^\ddagger$  and  $\Delta H^\ddagger$  are the corresponding quantities for the reaction barrier

	HF/3-21G	HF/6-31G(d)	MP2/6-31G(d)	MP4/6-31G(d)	HF/6-311G(d,p)	MP2/6-311G(d,p)
<b>C<sub>2</sub>H<sub>4</sub> + SiH<sub>4</sub></b>						
$\Delta E$	-33.7	-28.7	-34.2	-32.1	-26.4	-34.2
$\Delta H$	-28.5	-23.7	-29.2	-27.1	-21.4	-29.1
$\Delta E^\ddagger$	76.2	73.6	57.3	57.9	74.8	53.6
$\Delta H^\ddagger$	78.1	76.0	59.7	60.3	77.2	56.0
<b>C<sub>2</sub>H<sub>4</sub> + SiH<sub>2</sub>Cl<sub>2</sub></b>						
$\Delta E$	-41.8	-32.5	-39.7	-37.5	-30.5	-39.4
$\Delta H$	-37.3	-28.2	-35.4	-33.2	-26.2	-35.2
$\Delta E^\ddagger$	50.6	63.8	54.0	54.3	63.6	51.0
$\Delta H^\ddagger$	51.6	65.4	55.7	56.0	65.3	52.7
<b>C<sub>2</sub>H<sub>4</sub> + SiHCl<sub>3</sub></b>						
$\Delta E$	-45.3	-33.4	-41.3	-39.0	-31.5	-41.2
$\Delta H$	-40.9	-29.3	-37.2	-34.9	-27.4	-37.1
$\Delta E^\ddagger$	54.3	66.6	56.0	56.6	67.6	54.5
$\Delta H^\ddagger$	55.2	68.1	57.5	58.1	69.1	56.1
<b>C<sub>2</sub>H<sub>4</sub> + SiHF<sub>3</sub></b>						
$\Delta E$	-48.3	-34.7	-40.6	-39.1	-32.7	-39.4
$\Delta H$	-44.2	-30.7	-36.6	-35.2	-28.8	-35.5
$\Delta E^\ddagger$	63.4	67.0	58.3	57.7	64.8	55.9
$\Delta H^\ddagger$	64.0	68.3	59.6	59.0	66.1	57.2
<b>C<sub>3</sub>H<sub>6</sub> + SiH<sub>4</sub> → 1-silylpropane</b>						
$\Delta E$	-31.6	-25.8	-31.7	-29.7	-23.7	-31.9
$\Delta H$	-26.4	-20.8	-26.7	-24.8	-18.7	-26.9
$\Delta E^\ddagger$	83.6	76.8	69.6	69.8	77.3	66.2
$\Delta H^\ddagger$	83.9	77.7	70.5	70.7	78.1	67.0
<b>C<sub>3</sub>H<sub>6</sub> + SiH<sub>4</sub> → 2-silylpropane</b>						
$\Delta E$	-30.6	-23.8	-30.9	-28.9	-21.6	-31.2
$\Delta H$	-25.6	-19.0	-26.1	-24.1	-16.8	-26.4
$\Delta E^\ddagger$	88.6	82.2	70.5	71.4	81.8	65.2
$\Delta H^\ddagger$	89.0	83.4	71.7	72.6	83.0	66.3

**Table 2.** Total energies (hrees) of reactants, products, and transition states at highest levels of theory. The label t.s. indicates that this listing is the energy of the transition state leading to the given compound

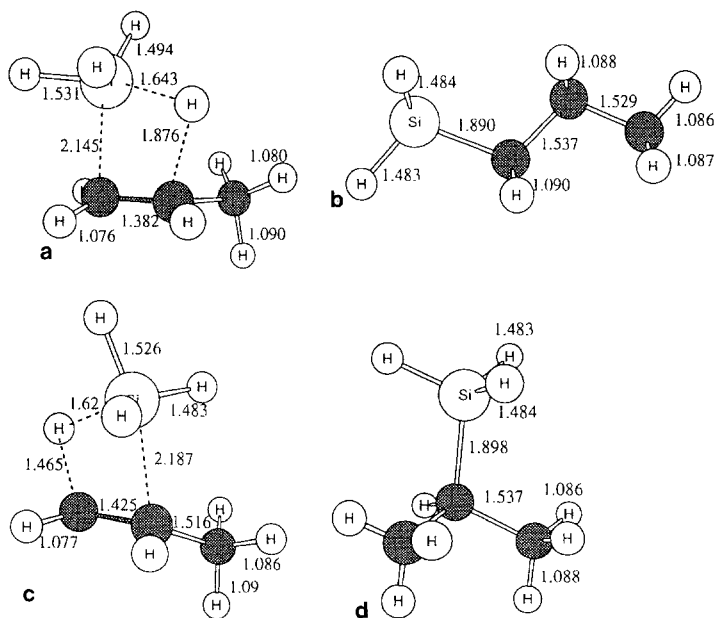
Compound	MP4/6-31G(d)	MP2/6-311G(d,p)
Ethylene	- 78.3187	- 78.3466
Silane	- 291.3324	- 291.3725
Ethylsilane t.s.	- 369.5588	- 369.6337
Ethylsilane	- 369.7023	- 369.7736
Trichlorosilane	- 1668.6158	- 1668.7052
Ethyltrichlorosilane t.s.	- 1746.8443	- 1746.9649
Ethyltrichlorosilane	- 1746.9967	- 1747.1175
Trifluorosilane	- 588.6323	- 588.8344
Ethyltrifluorosilane t.s.	- 666.8590	- 667.0920
Ethyltrifluorosilane	- 667.0133	- 667.2439
Dichlorosilane	- 1209.5203	- 1209.5937
Ethylchlorosilane t.s.	- 1287.7524	- 1287.8591
Ethylchlorosilane	- 1287.8987	- 1288.0032
Propylene	- 117.5044	- 117.5473
1-Silylpropane t.s.	- 408.7255	- 408.8144
1-Silylpropane	- 408.8841	- 408.9707
2-Silylpropane t.s.	- 408.7229	- 408.8160
2-Silylpropane	- 408.8828	- 408.9695

exothermicity than the parent silane by 6–8 kcal/mol, at the MP2/6-311G(d,p) level of theory.

Correlation has a non-trivial effect on the predicted barrier heights, since the addition of MP2 corrections lowers the calculated barriers by 8–16 kcal/mol (Table 1). On the other hand, further improvement of the correlation from MP2 to MP4 has virtually no effect with the 6-31G(d) basis set, so it was deemed unnecessary to go beyond MP2 with the larger 6-311G(d,p) basis. The basis set itself does have a modest effect on the calculated barrier, lowering the barrier height by 2–4 kcal/mol upon going from 6-31G(d) to 6-311G(d,p) at the MP2 level of theory. With regard to the net reaction energetics, the use of MP2 increases the calculated *exothermicity* by 6–8 kcal/mol. The addition of MP4 corrections has a small (1–2 kcal/mol) moderating effect on this result. Since the larger basis set, 6-311G(d,p), has little effect on the predicted reaction enthalpies, the use of MP4 with this basis set is not necessary.

The reaction of silane with ethylene to form ethylsilane has previously been studied by Francisco and Schlegel, using MP4(SDQ)/6-31G(d) energies calculated with HF/3-21G geometries [3]. Their calculated exothermicity and activation barrier of 27.4 and 62.6 kcal/mol, respectively, are similar to the MP2/6-311G(d,p) values of 29.1 and 56.0 kcal/mol, respectively.

When propylene is substituted for ethylene in the hydrosilation reaction with silane as the attacking species, there are two possible products, 1-silylpropane and 2-silylpropane. The structures of these two products and of the transition states leading to them are shown in Fig. 3. While the products have  $C_s$  symmetry, the transition states do not. The products and the transition states resemble those for the reaction of  $\text{SiH}_4$  with ethylene to form ethylsilane. The transition state for 2-silylpropane has a smaller H–C distance for the transferring hydrogen than is found in the transition states leading to 1-silylpropane and ethylsilane, suggesting



**Fig. 3 a–d.** Structures of the transition states and products of the uncatalyzed hydrosilation reactions involving propylene and silane, all at the RHF level using the 6-311(d,p) basis set. **a** transition state leading to 1-silylpropane, **b** 1-silylpropane equilibrium geometry, **c** transition state leading to 2-silylpropane, **d** 2-silylpropane equilibrium geometry

that the new H–C bond is formed earlier in the reaction to produce 2-silylpropane than in the other two reactions. The transition state structures for the reactions leading to 1-silylpropane and ethylsilane imply that the new Si–C bond is formed before the new H–C bond.

The energetics for the hydrosilation reactions involving propylene and silane are also given in Table 1. The effects of basis set and correlation on the energetics of this reaction are the same as those noted earlier for the reactions of ethylene. Therefore, the conclusions for the propylene reactions will be based on the MP2/6-311G(d,p) results. The propylene reactions are less exothermic (by 2–10 kcal/mol) and have significantly higher barriers (by 9–13 kcal/mol) than the reactions involving ethylene. The energetics (overall exothermicities and barrier heights) for the formation of the two silylpropane isomers are almost identical: 26–27 kcal/mol for the exothermicity and 66–67 kcal/mol for the barrier height. The larger barriers when propene is the substrate may be explained by the steric hindrance of the additional methyl group. Repulsion from this group hinders the approach of the silane to the double bond.

The results presented in this paper illustrate the high energetic barriers that must be overcome in order for the hydrosilation reaction to proceed. As noted in the Introduction, these high barriers are overcome by the use of catalysts, such as divalent Ti. The effect of such catalysts on the energetic requirements discussed here will be considered in a subsequent paper.

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