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An ab initio study of the thermal decomposition of dichlorosilane

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Abstract

The reactants, products and transition states for the two lowest channels of the thermal decomposition of dichlorosilane were optimized at the MP2/6-311 + G(2df,2p) and QCISD/6-311 + G(2df,2p) levels of theory. Corrections to the energy were calculated at the QCISD(T)/6-311G(2df,2p) and MP2/6-311 + + G(3df,3pd) levels of theory and were used to estimated the QCISD(T)/6-311 + + G(3df,3pd) energies. The barrier for the $SiH_2Cl_2 \rightarrow SiHCl + HCl$ decomposition channel is found to be 1.9 kcal/mol lower than for $SiH_2Cl_2 \rightarrow SiCl_2 + H_2$.

1. Introduction

The gas-phase thermal decomposition of dichlorosilane is an important first step in chemical vapor deposition of silicon from SiH_2Cl_2. Some of the possible pathways are:

$$\begin{array}{llll} SiH_2Cl_2 & \rightarrow & SiCl_2 + H_2, & \Delta H^{\ddagger} = 76\ \mathrm{kcal/mol}, \\ & \rightarrow & SiHCl + HCl, & = 74\ \mathrm{kcal/mol}; \\ & \rightarrow & SiHCl_2 + H, & \geq 92\ \mathrm{kcal/mol}; \\ & \rightarrow & SiH_2Cl + Cl, & \geq 111\ \mathrm{kcal/mol}; \\ & \rightarrow & SiH_2 + Cl_2, & \geq 140\ \mathrm{kcal/mol}, \end{array}$$

where the barrier heights have been calculated previously [1] at the G2 level of theory [2]. The lower bounds on the barriers for the last three reactions are based on the heats of reaction, for which there is good agreement between theory and experiment [3,4]. However, there is some uncertainty in the relative rates of the two most likely pathways for unimolecular decomposition of dichlorosilane, $SiH_2Cl_2 \rightarrow SiHCl + HCl$ and $SiH_2Cl_2 \rightarrow SiCl_2 + H_2$. Kruppa, Shin and Beauchamp [5] found $SiCl_2$ and HCl to be the major products from heterogeneous vacuum flash pyrolysis of SiH_2Cl_2. An IR multiphoton dissociation study by Sausa and Ronn [6] gave only $SiCl_2$ and H_2 as products. Ring, O'Neal and co-workers [7], using both static pyrolysis and a single-pulse shock-tube method, determined the products of thermal decomposition to be $SiCl_2$ and H_2. Ho, Breiland and Carr [8] found that excimer laser photolysis for SiH_2Cl_2 produced SiHCl. A previous theoretical study by Su and Schlegel [1] predicted the barrier for thermal decomposition into SiHCl + HCl to be 2 kcal/mol lower than for $SiCl_2 + H_2$. The structures and energetics of these transition states can be quite sensitive to the level of theory and the size of the basis set [4]. Therefore, we have re-examined the thermal decomposition of dichlorosilane at higher levels of theory and compared the rates for the two lowest channels.

2. Computational method

Ab initio MO calculations were performed with the GAUSSIAN 94 programs [9]. Geometries were

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Table 1
Energies [a] and partition functions at 600°C

Structure	Total energy [b]	Zero-point energy [c]	Thermal correction [c]	Partition function [c]
SiH_2Cl_2	−1209.7812883	0.020784	0.0200570	1.25×10^{16}
SiHCl–HCl (TS)	−1209.6684375	0.015453	0.0201400	4.06×10^{16}
$SiCl_2$–H_2 (TS)	−1209.6653680	0.016405	0.0194860	1.24×10^{16}
SiHCl	−749.3573656	0.007834	0.0117060	2.87×10^{14}
$SiCl_2$	−1208.5638039	0.002841	0.0141610	1.37×10^{15}
HCl	−460.3230669	0.006854	0.0070190	7.13×10^{9}
H_2	−1.1628694	0.010135	0.0069280	8.06×10^{6}

[a] In atomic units. [b] Estimated QCISDT/6-311++G(3df,3pd) with ZPE.
[c] Scaled MP2/6-31G(d,p).

optimized at both MP2 and QCISD levels of theory with the 6-311+G(2df,2p) basis set. Triples corrections to the QCISD/6-311+G(2df,2p) energies were estimated using QCISD(T)/6-311G(2df,2p) calculations at the QCISD/6-311+G(2df,2p) optimized geometry. Additional basis set effects were estimated using MP2/6-311++G(3df,3pd) and MP2/6-311+G(2df,2p) energies computed at the QCISD/6-311+G(2df,2p) geometry. Zero-point corrections were computed using previous frequency calculations [1] at the MP2/6-31G(d,p) level and 0.9646 as a scaling factor [10]. Thermal corrections and partition functions were computed using a scaling factor of 0.9427 recommended for fundamental frequencies [10].

3. Results and discussion

Total energies, harmonic zero-point energies, thermal corrections and partition functions at 600°C appear in Table 1. The calculated heats of reaction and barrier heights for decomposition of SiH_2Cl_2 are given in Table 2. The values are within 4 kcal/mol of previous calculations ($\Delta H_r = 67$ kcal/mol, barrier = 74 kcal/mol for decomposition into SiHCl + HCl and $\Delta H_r = 36$ kcal/mol, barrier = 76 kcal/mol for decomposition into $SiCl_2$ and H_2) [1]. Harmonic frequencies of all species are reported in previous papers [1,3].

3.1. Structures

The geometries of SiH_2Cl_2, the decomposition products SiHCl and $SiCl_2$, and the corresponding transition states are shown in Fig. 1. For the reactants and products, optimization at the higher levels of theory changes the geometries slightly. Bond lengths (Å) differ from previous MP2/6-31G(d,p) calculations [1] by 0.005 to 0.010 Å. Bond angles differ by ≈ 0.5°. The differences in the transition states for thermal decomposition are somewhat larger, with bond lengths changing by ≈ 0.01–0.04 Å and angles changing by 0.5–1.5°. However, the difference in MP2/6-31G(d,p) and QCISD/6-311+G

Table 2
Thermal decomposition barriers of SiH_2Cl_2 [a]

Reaction	QCISD/6-311+G(2df,2p)		Est. QCISDT(T)/6-311++G(3df,3pd)	
	ΔH_r (298)	barrier	ΔH_r (298)	barrier
$SiH_2Cl_2 \rightarrow SiHCl + HCl$	64.7	74.3	64.7	70.8
$SiH_2Cl_2 \rightarrow SiCl_2 + H_2$	34.1	76.2	36.1	72.7

[a] In kcal/mol.

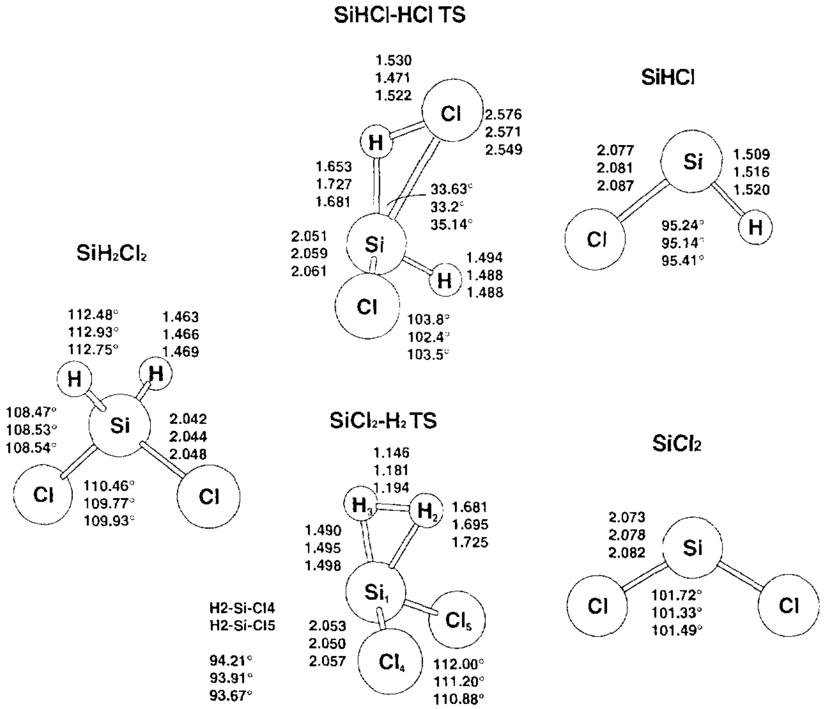

Fig. 1. Optimized geometries of dichlorosilane, transition states and decomposition products. Bond lengths are in Å. Values for the different levels of theory are listed in the following order; MP2/6-31G(d,p), MP2/6-311 + G(2df,2p) and QCISD/6-311 + G(2df,2p).

(2df,2p) geometries results in only −0.098 and 0.057 kcal/mol changes in the barrier heights of HCl and H_2 elimination computed at the MP2/6-311 + + G(3df,3pd) level. Thus, the geometries used in the previous study were probably sufficiently accurate.

3.2. Energetics

The QCISD(T)/6-311 + + G(3df,3pd) energy is estimated by:

$$\begin{aligned}\text{Est. QCISD(T)/6-311} &+ +\text{G(3df,3pd)}\\ &= \text{QCISD/6-311} + \text{G(2df,2p)}\\ &\quad + \text{QCISD(T)/6-311G(2df,2p)}\\ &\quad - \text{QCISD/6-311G(2df,2p)}\\ &\quad + \text{MP2/6-311} + + \text{G(3df,3pd)}\\ &\quad - \text{MP2/6-311} + \text{G(2df,2p)}.\end{aligned}$$

Similar additivity approximations are made in the G2 method [2] and are found to be sufficiently accurate [11]. At the QCISD/6-311 + G(2df,2p) level, the barrier for HCl elimination is 1.8 kcal/mol lower than that for H_2 elimination. Individually, the triples and the basis set corrections give barrier height differences of 1.2 and 2.6 kcal/mol. With both corrections, the HCl elimination barrier is lower by 1.9 kcal/mol.

Transition state theory [12] was used to estimate the decomposition rates of both the forward and reverse reactions. The high-pressure unimolecular rate constants, activation energies and pre-exponential factors at 600°C for $SiH_2Cl_2 \rightarrow SiHCl + HCl$, $SiH_2Cl_2 \rightarrow SiCl_2 + H_2$ and the reverse reactions are

Table 3
Rate constants at 600°C from transition state theory [a]

Reaction	k (s^{-1})	log A	E_a (kcal/mol)
$SiH_2Cl_2 \rightarrow SiHCl + HCl$	4.5×10^{-4}	14.83	72.6
$SiH_2Cl_2 \rightarrow SiCl_2 + H_2$	2.2×10^{-5}	13.9	74.1
	k(l mol^{-1} s^{-1})		
$SiHCl + HCl \rightarrow SiH_2Cl_2$	6.9	3.38	10.2
$SiCl_2 + H_2 \rightarrow SiH_2Cl_2$	1.4×10^{-6}	3.95	39.2

[a] Calculated with reaction path degeneracies of 4, 2, 2 and 4, respectively.

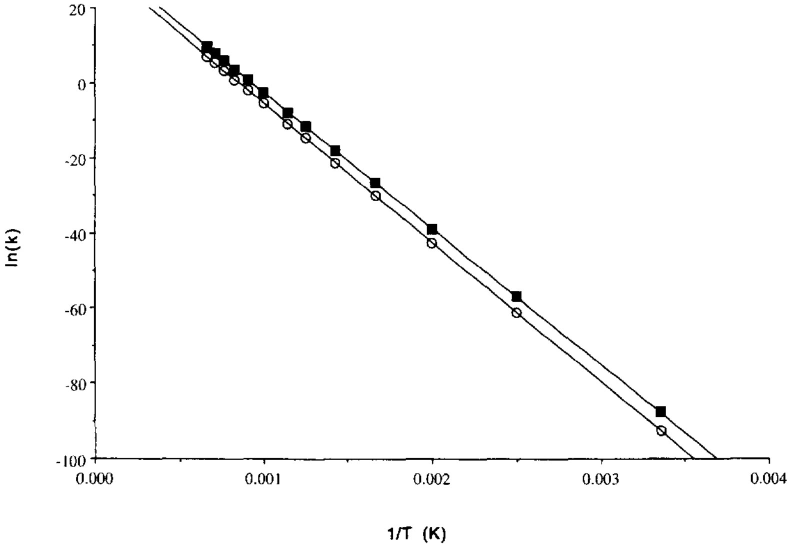

Fig. 2. ln(k) versus $1/T$ for the unimolecular decompositions of SiH_2Cl_2 to SiHCl + HCl and $SiCl_2 + H_2$ from 1500 K to 300 K. $SiH_2Cl_2 \rightarrow$ SiHCl + HCl is represented by solid squares, and $SiH_2Cl_2 \rightarrow SiCl_2 + H_2$ by open circles.

given in Table 3. Fig. 2 summarizes the behavior of the rate constants for the forward reactions in the range of 300 K to 1500 K. These values were calculated using the estimated QCISD(T)/6-311 + + G(3df,3dp) energies and the MP2/6-31G(d,p) frequencies.

Decomposition of SiH_2Cl_2 via HCl elimination, with the lower activation energy and larger A factor, is still predicted to be the preferred pathway in the high-pressure limit. Current calculations at 600°C predict HCl elimination to proceed 20 times faster than H_2 elimination, essentially the same as found at the lower level of theory [1]. For the temperature range covered by Fig. 2, HCl elimination is 14 to 120 times faster than H_2 elimination. For the reverse reactions, the barrier for SiHCl + HCl insertion is 31 kcal/mol lower than $SiCl_2 + H_2$ insertion, and the rate at 600°C is 5×10^6 greater.

The present work represents state-of-the-art molecular orbital calculations and consistently shows that the barrier for HCl elimination is lower than the barrier for H_2 elimination in the thermal decomposition of SiH_2Cl_2. However, very few of the experiments see HCl or SiHCl. A number of reasons might account for these differences. Many of the experiments were carried out in the low-pressure or fall-off regimes, whereas the present rates pertain to the high-pressure limit. Even in the high-pressure limit, one may need a more sophisticated method for calculating the rate constant than transition state theory. However, the use of variational, rather than conventional, transition state theory lowered the rate constants by only 2.9% and 4.5% respectively, for HCl and H_2 elimination at the MP2/6-31G(d,p) level of theory at 600°C. Finally, the products HCl and SiHCl are far more reactive than H_2 and $SiCl_2$. In some experiments, it is possible that these products are consumed in rapid secondary reactions, leaving only H_2 and $SiCl_2$ to be observed.

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Erratum

An ab initio study of the thermal decomposition of dichlorosilane

(Chem. Phys. Letters 265 (1997) 527) [1]

J.M. Wittbrodt, H.B. Schlegel

Due to a clerical error, the data for the bimolecular reactions in Table 3 should be as follows.

Table 3

Reaction	k (L mol^{-1} s^{-1})	log A	E_a (kcal/mol)
$SiHCl + HCl \rightarrow SiH_2Cl_2$	6.9×10^{-6}	−2.61	10.2
$SiCl_2 + H_2 \rightarrow SiH_2Cl_2$	3.5×10^{-13}	−2.64	39.2

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