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Reactions of $SiCl_2$ and SiHCl with H and Cl Atoms

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Calculations have been carried out for the reaction of $SiCl_2$ and SiHCl with H and Cl atoms. In each case, the stationary point geometries and harmonic frequencies were characterized using CASSCF/derivative methods and the cc-pVDZ basis set. Accurate energetics were obtained by combining the CCSD(T) results using the aug-cc-pVTZ basis set with an extrapolation to the basis set limit using the aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets at the MP2 level. The geometries, energetics, and harmonic frequencies were used to obtain rate constants using conventional transition state theory or a Gorin-like model. In each case, we find direct abstraction pathways compete with an addition elimination pathway. In the case of SiClH + H, the two direct pathways are H abstraction which is barrierless and Cl abstraction with a barrier of 13.5 kcal/mol, whereas the addition elimination process has a barrrier of 26.9 kcal/mol. In the case of $SiCl_2$ + H, the direct pathway is Cl abstraction with a barrier of 16.4 kcal/mol, whereas the addition elimination pathway has a barrier of 29.6 kcal/mol. In the case of SiClH + Cl, the direct pathway is H abstraction which is barrierless and the addition elimination pathway has a barrier of 2.0 kcal/mol.

I. Introduction

As part of a project to create a reliable database in microelectronic processing, calculations of gas-phase reaction rates have been carried out for use in modeling thermal chemical vapor deposition (CVD) reactors. We are investigating the thermal decomposition of silane, chlorosilane, dichlorosilane, and trichlosilane with H_2 as an additional feed gas. In a previous paper,[1] we reported on the important reaction pathways and reaction rate coefficients for the thermal decomposition of silane and Cl substituted silane. We found that the major decomposition products are $SiH_2 + H_2$ for silane, SiH_2 + HCl and SiClH + H_2 for $SiClH_3$, $SiCl_2 + H_2$ and SiClH + HCl for $SiCl_2H_2$, and $SiCl_2$ + HCl for $SiCl_3H$. In this paper, we consider the reactions of the silylenes SiHCl and $SiCl_2$ with H and Cl atoms. These secondary reactions are expected to be important in the thermal decomposition of dichlorosilane/H_2, which is a system of interest to the reactor modelers. The reactivities of SiH and SiH_2 have been reviewed by Jasinski, Becerra, and Walsh[2]. Becerra and Walsh[3] discuss the reactivities of substituted silylenes including SiHCl and $SiCl_2$. However, we have not found published rate constants for the reactions considered in this paper.

The details of the calculations are described in section II. Section III discusses the results obtained, and the conclusions are given in section IV.

II. Computational Details

The geometries and harmonic frequencies for all the stationary points (minima or saddle points) were determined using the complete active space self-consistent field (CASSCF)/derivative method with the correlation consistent polarized valence double-ζ (cc-pVDZ) basis sets.[4] In these calculations, all of the bond pairs plus the open-shell orbital were included in the active space e.g., for $SiClH_2$ this consists of 7 electrons distributed over 7 orbitals. The energetics were obtained using the coupled cluster single and double excitation with perturbational estimate of triple excitations (CCSD(T)) method using the augmented cc-pVTZ basis set (aug-cc-pVTZ) and extrapolated to the complete basis set (CBS) limit using the Moller−Plesset second-order perturbation theory method (MP2) with the aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets[5] as described below. (The CCSD(T) and MP2 calculations made use of the closed shell methods[6] for singlet states and open shell methods[7] for cases with open-shells.) Here, the Ne core electrons are frozen for Si and Cl. The calculations were done in the nonrelativistic limit. The MP2 results were extrapolated to the basis set limit using the Martin−Schwartz three-point extrapolation.[8] The results of the MP2 extrapolation were combined with CCSD(T) results obtained with the aug-cc-pVTZ basis set to obtain an estimate of the CCSD(T) results in the limit of a complete basis set. The basis for this was described by Ricca and Bauschlicher,[9] who noticed that for bond strengths the ratio D_e(CCSD(T))/D_e(MP2) was constant for a series of correlation consistent basis sets. Thus, for barrier heights and other relative energy quantities, the value in the limit of a complete basis set was obtained as the following

$$(\Delta E\ (\text{aug-cc-pVTZ/CCSD(T)})/\Delta E(\text{aug-cc-pVTZ/MP2})) \times \Delta E\ (\text{CBS/MP2}) \quad (1)$$

where ΔE (aug-cc-pVTZ/CCSD(T) and ΔE(aug-cc-pVTZ/MP2) are the values obtained with the aug-cc-pVTZ basis set for CCSD(T) amd MP2, respectively, and ΔE (CBS/MP2) is the MP2 value extrapolated to the complete basis set limit.

Tests of the MP2 extrapolation have been made by Dunning and Peterson.[10] They studied convergence of MP2 and MP3 extrapolation of CCSD(T) results for a series of diatomic molecules formed from first row atoms. They found the MP3 extrapolation was more accurate than the MP2 extrapolation. However, for AB molecules MP2 extrapolation of aug-cc-pVTZ results leads to an average error in D_e of 0.72 kcal/mol. It is probable that D_e is a more difficult quantity to compute than barrier heights. Thus, their work suggests that our extrapolation should be accurate to well within 1 kcal/mol.

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TABLE 1: $SiCl_2 + H \rightarrow SiCl + HCl$, CCSD(T) Plus MP2 Extrapolation[a]

structure	CBS[b] from MP2
$SiCl_2 + H$	0.0
$SiCl_2H$	−52.2
SiCl + HCl	−2.8
SiCl−HCl SP	29.6
$SiCl_2$−H abs SP	16.4

[a] Relative energies in kcal/mol. [b] CBS estimate obtained by combining the CCSD(T) results with the aug-cc-pVTZ basis set with the results of the MP2 extrapolation.

TABLE 2: SiClH + H → Products, CCSD(T) Plus MP2 Extrapolation[a,b]

structure	CBS[c] from MP2
SiClH + H	0.0
$SiClH_2$	−63.9
HSiCl−H SP	13.5
ClSiH−H SP	−0.4
SiCl−H_2 SP1	−4.3
SiCl−H_2 SP2	26.9
SiCl−H_2 SP3	−3.4
SiCl + H_2	−32.8
SiH + HCl	−2.8

[a] Relative energies in kcal/mol. [b] The notation SP denotes a saddle point. [c] CBS estimate obtained by combining the CCSD(T) results with the aug-cc-pVTZ basis set with the results of the MP2 extrapolation.

TABLE 3: SiClH + Cl → SiCl + HCl, CCSD(T) Plus MP2 Extrapolation[a]

structure	CBS[b] from MP2
SiClH + Cl	0.0
$SiCl_2H$	−79.6
SiClH−Cl SP	−13.6
SiCl−HCl SP	2.0
SiCl + HCl	−30.4
SiH + Cl_2	47.4

[a] Relative energies in kcal/mol. [b] CBS estimate obtained by combining the CCSD(T) results with the aug-cc-pVTZ basis set with the results of the MP2 extrapolation.

The CCSD(T) method used here is a single reference based method, but this method has been shown to deal with all but the most severe near-degeneracy effects. In a recent paper,[11] we showed that for the decomposition of dimethylaluminum hydride CCSD(T) gave results in good agreement with the multireference internally contracted CI method.[12]

For the reactions with barriers (i.e., those with well-defined saddle points), rate coefficients as a function of temperature were obtained using conventional transition state theory. For reactions without barriers a Gorin-like model[13] was used.

The CASSCF/derivative calculations were carried out using DALTON,[14] the CCSD(T) calculations were carried out using MOLPRO,[15] and the MP2 calculations were done using Gaussian94.[16] The transition state theory calculations were carried out using POLYRATE.[17]

III. Discussion

Table 1 gives energetics for the reaction of $SiCl_2$ with H atom. (Note that in the text and figures a saddle point is denoted by SP.) Here, the energetics are obtained by combining the CCSD(T) results with the results of the MP2 extrapolation to the basis set limit using eq 1. (The same approach is used for Tables 2 and 3.) The energetics and structures of the stationary points are also shown in Figure 1. There are two pathways from $SiCl_2$ + H. The pathway denoted by SiCl2−H abs SP is a H abstraction of Cl leading to SiCl + HCl. This process has a barrier of 16.4 kcal/mol. The second pathway is addition of H atom to $SiCl_2$ leading to $SiCl_2H$ with no barrier. The $SiCl_2H$ molecule is bound by 52.2 kcal/mol with respect to $SiCl_2$ + H. The pathway denoted by SiCl−HCl SP has a barrier of 32.4 kcal/mol with respect to SiCl + HCl. The main features of the PES are a direct abstraction pathway in competition with an addition elimination pathway.

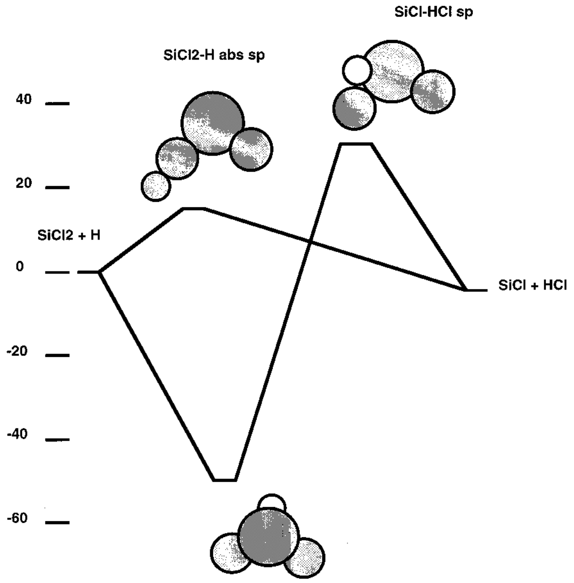

Figure 1. Energetics, pathways, and structures for $SiCl_2$ + H → products. Energies in kcal/mol. Large dark circles are Si atom, smaller dark circles are Cl atom, and small light circles are H atom. The same conventions are used for the remaining figures.

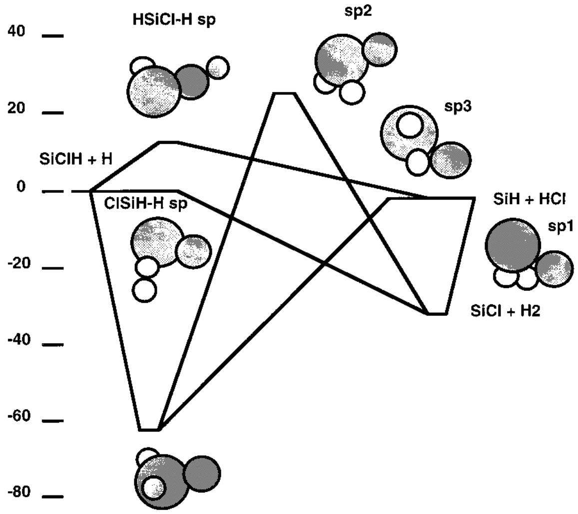

Figure 2. Energetics, pathways, and structures for SiClH + H → products. The reaction SiH + HCl → SiCl + H_2 is barrierless, but has a saddle point at the CASSCF level and this saddle point is shown as sp1.

From Figure 2 it is seen that there are three pathways from SiClH + H. The first is addition of H atom to the Si atom of SiClH. This pathway, which has no barrier, leads to SiH_2Cl. The other two pathways from the reactants are abstraction processes. HSiCl−H SP is H abstraction of a Cl leading to SiH + HCl. This pathway has a barrier of 13.5 kcal/mol. The pathway ClSiH−H SP is H abstraction of a H leading to SiCl + H_2. This pathway has no barrier. (The energy of the CASSCF saddle point is computed to be −0.4 kcal/mol with respect to the reactants, which means there is no barrier due to the

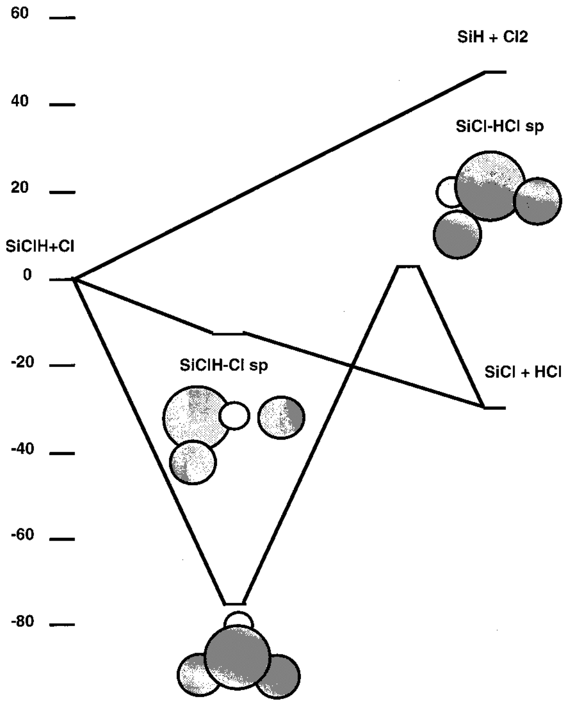

Figure 3. Energetics, pathways, and structures for SiClH + Cl → products

saddlepoint.) $SiClH_2$ is computed to be 63.9 kcal/mol below the SiClH + H reactants. There are two elimination pathways from this minimum to products. Both of these lead to silylidynes. SP2 leads to SiCl + H_2 and SP3 leads to SiH + HCl. Note that SP3 involves no barrier, whereas SP2 involves a 59.7 kcal/mol barrier (with respect to SiH + HCl). This result is consistent with our earlier work[1] in which we showed that substituting H with Cl greatly reduces the reactivity of silylenes and silylidynes for the series SiH_2, SiClH, $SiCl_2$, and SiH, SiCl in reaction with H_2. Finally, SP1 interconnects SiCl + H_2 with SiH + HCl. The main features of the potential energy surface (PES) are direct abstraction pathways leading to SiH + HCl and SiCl + H_2 and a competing addition elimination pathway which also leads to SiH + HCl and $SiCl_2$ + H_2.

Table 3 and Figure 3 show results for the reaction of SiClH with a Cl atom. There are two pathways from SiClH + Cl. The first is an abstraction of H atom by Cl leading directly to SiCl + HCl in a barrierless process. The second is an H atom addition to $SiCl_2$ leading to $SiCl_2H$ which is bound by 79.6 kcal/mol with respect to the reactants. The main features of the PES are a direct abstraction pathway in competition with an addition elimination pathway.

Thermal rate coefficients in the high-pressure limit calculated using conventional transition state theory employing the POLYRATE program[17] are reported in Table 4. Input requirements are the geometries, harmonic frequencies, and the energetics of the reactants, products, and saddle points. For “loose” transition state cases, where there is no barrier, we employed a Gorin-like model,[13] where the data for the transition state is taken from the separated fragments of the reactant or product state. The rate coefficients for each reaction were calculated for 10 temperatures in the range from 300 to 2000 K and then fitted to an Arrhenius-like form

$$k(T) = A\,T^n \exp(-E_a/kT)$$

The values of A, n, and E_a for the reactions considered in this work are presented in Table 4. For the “tight” transition states (those with a well-defined saddle point) and for the endothermic direction of the loose transition state reactions, each calculated rate fits nicely to a pure Arrhenius form with $n = 0$, with an activation energy E_a that falls within a few kcal/mole of the saddle point barrier height, or the endothermicity for the latter cases. For the exothermic barrierless reactions, the fits resulted in nonzero values for n, and in a few cases, small negative activation energies.

TABLE 4: High-pressure TST Rate Coefficients $k(T) = A\,T^n \exp(-E_a/kT)$

reaction	A (sec^{-1} or cc $molecule^{-1}\ s^{-1}$)	E_a (kcal/mol)	n[b]
$SiCl_2H \rightarrow SiCl + HCl$	3.510×10^{13}	85.493	
$SiCl + HCl \rightarrow SiCl_2H$	4.193×10^{-12}	39.179	
$SiCl_2 + H \rightarrow SiCl + HCl$	4.068×10^{-10}	18.862	
$SiCl + HCl \rightarrow SiCl_2 + H$	1.053×10^{-10}	19.490	
$SiClH_2 \rightarrow SiCl + H_2$	3.975×10^{13}	92.894	
$SiCl + H_2 \rightarrow SiClH_2$	2.053×10^{-11}	62.885	
$SiClH_2 \rightarrow SiH + HCl$[a]	1.869×10^{14}	61.507	
$SiH + HCl \rightarrow SiClH_2$[a]	1.106×10^{-18}	−2.032	2.158
$SiClH + H \rightarrow SiCl + H_2$[a]	3.647×10^{-16}	−1.210	1.736
$SiCl + H_2 \rightarrow SiClH + H$[a]	6.681×10^{-10}	32.586	
$SiClH + H \rightarrow SiH + HCl$	1.404×10^{-10}	15.973	
$SiH + HCl \rightarrow SiClH + H$	8.414×10^{-11}	17.112	
$SiCl + H_2 \rightarrow SiH + HCl$[a]	3.149×10^{-11}	31.267	
$SiH + HCl \rightarrow SiCl + H_2$[a]	1.559×10^{-18}	−1.707	1.984

[a] Loose transition states, treated with Gorin-like model. [b] blank means $n = 0$

IV. Conclusions

Calculations have been carried out for the reaction of $SiCl_2$ and SiHCl with H and Cl atoms. In each case, the stationary point geometries and harmonic frequencies were characterized using CASSCF/derivative methods and the cc-pVDZ basis set. Accurate energetics were obtained by combining the CCSD(T) results using the aug-cc-pVTZ basis set with an extrapolation to the basis set limit using the aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets at the MP2 level. The geometries, energetics, and harmonic frequencies were used to obtain rate constants using conventional transition state theory or a Gorin-like model.

In each case, we find direct abstraction pathways compete with an addition elimination pathway. In the case of SiClH + H, the two direct pathways are H abstraction which is barrierless and Cl abstraction with a barrier of 13.5 kcal/mol, whereas the addition elimination process has a barrrier of 26.9 kcal/mol. In the case of $SiCl_2$ + H, the direct pathway is Cl abstraction with a barrier of 16.4 kcal/mol, whereas the addition elimination pathway has a barrier of 29.6 kcal/mol. In the case of SiClH + Cl, the direct pathway is H abstraction which is barrierless and the addition elimination pathway has a barrier of 2.0 kcal/mol.

These secondary reactions can convert $SiCl_2$ and SiHCl (the primary products of decomposition of dichlorosilane and trichlorosilane) to SiCl, and SiCl and SiH, respectively. This may be important because these species may have different reactivities with Si surface than the primary decomposition products.

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Supporting Information Available: Six tables of energetics from CCSD(T) and MP2 calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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