Theoretical Study of the Addition of SiF$_2$ and SiCl$_2$ to Ethylene

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Abstract
The additions of SiF₂ and SiCl₂ to ethylene have been studied using fourth order perturbation theory and the 6-31 1 Wd,p) basis set at geometries determined with second order perturbation theory. In contrast with earlier calculations on the analogous SiHz addition, found to proceed with no barrier, barrier heights of 18.4 and 4.5 kcal/mol are predicted for the fluoro- and chlorosilylenes, respectively. These results are interpreted in terms of the net energetics, ring strain, and orbital properties.

Disciplines
Chemistry

Comments
Theoretical Study of the Addition of SiF2 and SiCl2 to Ethylene

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Summary: The additions of SiF2 and SiCl2 to ethylene have been studied using fourth order perturbation theory and the 6-311G(d,p) basis set at geometries determined with second order perturbation theory. In contrast with earlier calculations on the analogous SiHz addition, determined using full fourth order perturbation theory (MP4) with the 6-311G(d,p) basis set. Since the product of each reaction is a three-membered ring, it is of interest to determine the relative strain on these rings. A consistent method for assessing ring strain is to determine the energy for a series of "homodesmic" reactions, defined as reactions that preserve the number of each type of chemical group upon proceeding from reactants to products. For the substituted silylides of interest here, the appropriate homodesmic reactions are

\[
c-SiX_2CH_2CH_2 + 3C_2H_4 \rightarrow \text{CH}_3\text{SiX}_2\text{CH}_3 + 2\text{CH}_3\text{CH}_2\text{CH}_3 \tag{1}\n\]

The energetics for these homodesmic reactions have also been determined at the MP4/6-311G(d,p)/MP2/6-31G(d)-level of theory. The calculations reported here were performed using GAUSSIAN92.

Results and Discussion

A. Geometries. The MP2/6-31G(d) structures of the reactants, products and transition states for the SiF2 and SiCl2 addition reactions are shown in Figure 1. Note that although the reactants SiX2 and cyclic products all have C2v symmetry, the transition states are distorted into C1 symmetry. For both reactions, the SiC bond distances in the transition states are ~1.9 and 2.2 Å. This distortion is consistent with the structures of other transition states and is discussed further below. The imaginary frequencies for the SiF2 and SiCl2 insertions are 529i and 312i cm\(^{-1}\), respectively.


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Table 1. Energetics for $\text{SiX}_2 + \text{H}_2\text{C}==\text{CH}_2$ \(^{\text{a,c}}\)

<table>
<thead>
<tr>
<th></th>
<th>$\text{X} = \text{F}$</th>
<th></th>
<th>$\text{X} = \text{Cl}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E$</td>
<td>19.3</td>
<td>$\Delta E$</td>
<td>16.7</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>19.0</td>
<td>$\Delta H$</td>
<td>18.1</td>
</tr>
<tr>
<td>$E_b$</td>
<td>19.0</td>
<td>$E_b$</td>
<td>18.1</td>
</tr>
<tr>
<td>$E_a$</td>
<td>19.0</td>
<td>$E_a$</td>
<td>18.1</td>
</tr>
</tbody>
</table>

\(^{\text{c}}\) All geometries and vibrational frequencies were determined using MP2/6-31G(d). \(^{\text{a}}\) Energies are given in kcal/mol. \(^{\text{b}}\) $\Delta E$ and $\Delta H$ give the net reaction energy and enthalpy, respectively; $E_b$ and $E_a$ refer to the classical barrier height and the activation energy, respectively. $\Delta H$ and $E_b$ include harmonic zero point vibrational energy (ZPE) corrections. \(^{\text{d}}\) A and B refer to the basis sets 6-31G(d) and 6-311G(d,p), respectively.

B. Energetics. The energetics for the two addition reactions are summarized in Table 1. For comparison, both MP2 and MP4 results are listed for the 6-31G(d) and 6-311G(d,p) basis sets. First, consider the overall reaction thermodynamics. For both reactions ($\text{X} = \text{F, Cl}$), improving the basis set increases the exothermicity by several kcal/mol, while improving the level of theory from MP2 to MP4 has the opposite effect. At all levels of theory, the addition of $\text{SiCl}_2$ is predicted to be 4–6 kcal/mol more exothermic than the $\text{SiF}_2$ addition, with the difference at the highest level of theory, MP4/6-311G(d,p), being 6.4 kcal/mol when vibrational zero point corrections (ZPE) are included. To facilitate a direct comparison with the unsubstituted reaction, the exothermicity has been recalculated for $\text{X} = \text{H}$ using MP4/6-311G(d,p) with MP2 geometries and ZPE corrections. The exothermicity for the addition of $\text{SiH}_2$ to ethylene is 40.7 kcal/mol, much larger than the values of 20.4 and 14.0 kcal/mol for $\text{X} = \text{F}$ and $\text{F}$, respectively.

The calculated barrier heights for the two reactions, as well as the previous calculation of a zero barrier for $\text{X} = \text{H}$, are consistent with the predicted thermodynamics, given the Hammond Postulate: the barrier for the $\text{SiCl}_2$ addition is found to be rather smaller than that for the $\text{SiF}_2$ addition. Once again, improving the basis set and the level of theory have opposite effects on the predicted barrier heights, with basis set improvement lowering the barriers and increasing the level of theory raising the predicted barrier. The MP4/6-311G(d,p) classical barrier heights are 19.3 and 5.2 kcal/mol for X = F, Cl, respectively. These are lowered to 18.4 and 4.5 kcal/mol, respectively, when ZPE are included. The strain energies calculated at the same level of theory using reaction (1) are also consistent with this picture. These strain energies are predicted to be 45.8, 55.0, and 59.9 kcal/mol for $\text{X} = \text{H}$, Cl, and F, respectively. These are in the same order as the calculated exothermicities and barrier heights and clearly suggest that substitution of electronegative substituents at the apical position in siliranes destabilize the ring.

Further insight regarding the relative barrier heights may be obtained by considering the nature of the

\(^{\text{(1)}}\) The strain energy calculated for the parent silirane, before correction for ZPE, is 43.6 kcal/mol. This is quite similar to the predicted ring strain predicted earlier for this molecule using lower levels of theory (e.g., Gordon, M. S. J. Am. Chem. Soc., 1980, 102, 7419; illustrating the stability of energetics predicted for homodesmic reactions.)
Since the substrate (ethylene) is the same for the two reactions of interest, the source of the difference in barrier heights clearly lies in the \textit{SiX}_2 wave functions, in particular, the lone pair (HOMO) and empty p orbital (LUMO) on Si. The energies of LUMO in \textit{SiF}_2 and \textit{SiCl}_2 are 0.032 and 0.003 hartree, respectively. The lower energy of this empty p orbital when \( X = \text{Cl} \) facilitates the interaction in the electrophilic phase of the reaction. Similarly, the energies of HOMO in \textit{SiF}_2 and \textit{SiCl}_2 are \(-0.410\) and \(-0.379\) hartree, respectively, so the higher lone pair energy when \( X = \text{Cl} \) serves to facilitate the nucleophilic step for this system. The net effect, therefore, is to preferentially stabilize the transition state for \( X = \text{Cl} \), relative to that for \( X = \text{F} \).

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