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Abstract

The additions of SiFz and Sic12 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 kcallmol are predicted for the fluoro- and chlorosilylenes, respectively. These results are interepreted in terms of the net energetics, ring strain, and orbital properties.

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

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Summary: The additions of SiF$_2$ and SiCl$_2$ 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 SiH$_2$ 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 interepreted in terms of the net energetics, ring strain, and orbital properties.
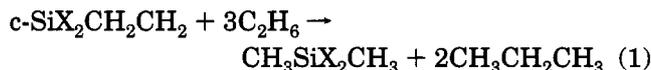
Introduction

Previous calculations on the addition of SiH$_2$ to the C=C bond of ethylene[1] and the C≡C bond of acetylene[2] have shown that both reactions proceed with no barrier. On the other hand, replacement of the H ligand with F results in the introduction of a nonzero barrier to addition of SiF$_2$ to acetylene,[2] due to the stabilization of the silylene leading to decreased exothermicity. Continuing experimental interest in silylene insertions into ethylene[3] has prompted us to investigate the effect of substituents, particularly F and Cl, on the additions of SiX$_2$ species to the C=C bond of ethylene, using reliable electronic structure calculations.

Computational Methods

Geometries of minima and transition states were optimized at the MP2(FULL) level of theory,[4] using the 6-31G(d) basis set.[5] The stationary points located in this manner were verified as minima or transition states by calculating and diagonalizing the matrix of energy second derivatives (hessian) to determine the number of imaginary frequencies (0 for minima, 1 for transition states). Vibrational zero point corrections were obtained at this level of theory. Final energetics were then

determined using full fourth order perturbation theory (MP4[6]) with the 6-311G(d,p) basis set.[7]

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.[8] For the substituted siliranes of interest here, the appropriate homodesmic reactions are

$$c\text{-SiX}_2\text{CH}_2\text{CH}_2 + 3\text{C}_2\text{H}_6 \rightarrow$$
$$\text{CH}_3\text{SiX}_2\text{CH}_3 + 2\text{CH}_3\text{CH}_2\text{CH}_3 \quad (1)$$

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.[9]

Results and Discussion

A. Geometries. The MP2/6-31G(d) structures of the reactants, products and transition states for the SiF$_2$ and SiCl$_2$ addition reactions are shown in Figure 1. Note that although the reactants SiX$_2$ and cyclic products all have C_{2v} symmetry, the transition states are distorted into C_s 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[10] and is discussed further below. The imaginary frequencies for the SiF$_2$ and SiCl$_2$ insertions are 529i and 312i cm^{-1}, respectively.

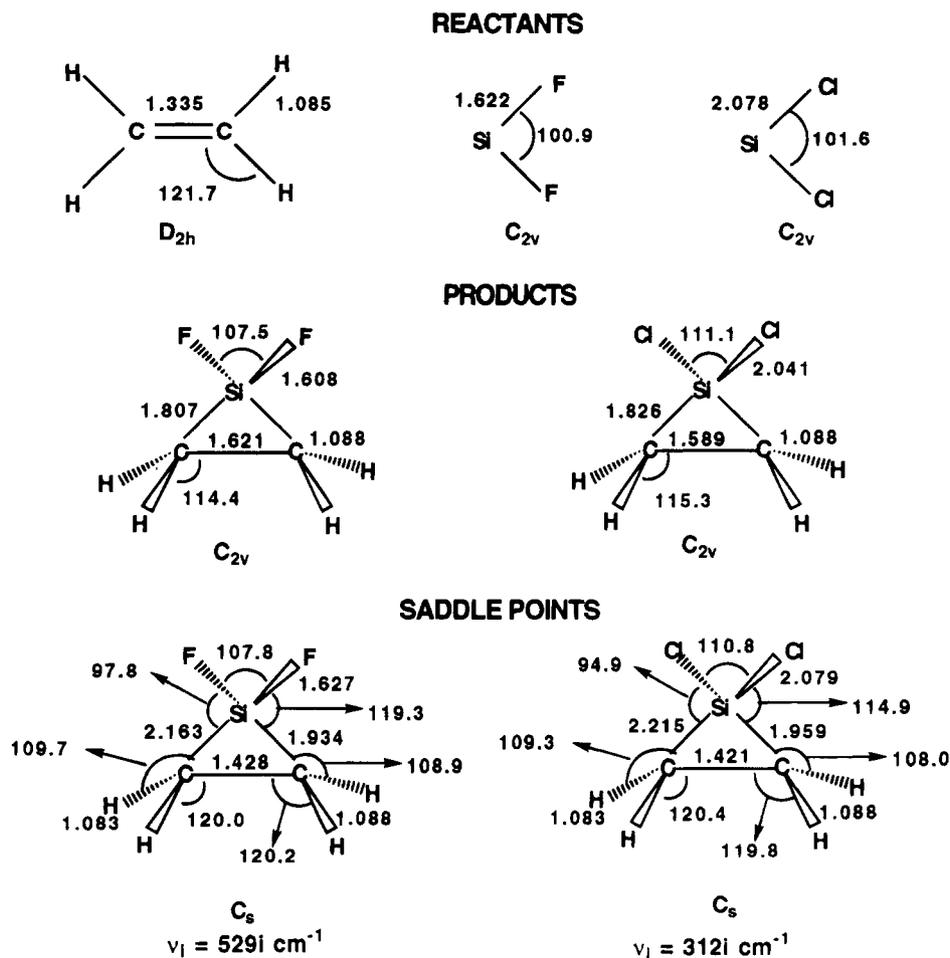[®] Abstract published in *Advance ACS Abstracts,* December 15, 1994.

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REACTANTS

PRODUCTS

SADDLE POINTS

Figure 1. Geometries with bond lengths (Å) and angles (deg). ν_i = Imaginary frequency.

Table 1. Energetics for SiX₂ + H₂C=CH₂$^{a-c}$

	X = F				X = Cl			
	ΔE	ΔH	E_b	E_a	ΔE	ΔH	E_b	E_a
MP2/A^d	−19.3	−16.7	19.0	18.1	−24.1	−21.7	4.1	3.4
MP4/A	−13.8	−11.2	21.0	20.9	−18.1	−15.7	7.3	6.6
MP2/B	−21.6	−19.0	17.6	16.7	−28.0	−25.6	2.3	1.6
MP4/B	−16.6	−14.0	19.3	18.4	−22.4	20.4	5.2	4.5

^{a} All geometries and vibrational frequencies were determined using MP2/ 6-31G(d). ^{b} Energies are given in kcal/mol. ^{c} ΔE and ΔH give the net reaction energy and enthalpy, respectively; E_b and E_a refer to the classical barrier height and the activation energy, respectively. ΔH and E_a include harmonic zero point vibrational energy (ZPE) corrections. ^{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 (X = 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 SiCl₂ is predicted to be 4−6 kcal/mol more exothermic than the SiF₂ 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 X = H using MP4/6-311G(d,p) with MP2 geometries and ZPE corrections. The exothermicity for the addition of SiH₂ to

ethylene is 40.7 kcal/mol, much larger than the values of 20.4 and 14.0 kcal/mol for X = Cl and F, respectively.

The calculated barrier heights for the two reactions, as well as the previous calculation of a zero barrier for X = H, are consistent with the predicted thermodynamics, given the Hammond Postulate: the barrier for the SiCl₂ addition is found to be rather smaller than that for the SiF₂ 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,[11] 55.0, and 59.9 kcal/mol for X = 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

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(11) 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.

interactions between SiX_2 and the substrate ethylene as the two approach each other during the reaction. Several authors[12–14] have discussed the two types of interactions that occur during carbene or silylene insertions: the *electrophilic* interaction between the empty p orbital on the carbene or silylene with the (in this case) π bond of the substrate, and the *nucleophilic* interaction of the carbene or silylene lone pair with the antibonding π orbital of the substrate. Examinations of the minimum energy paths for substrate H_2 reveal that the initial interaction is electrophilic in nature.[13] This is consistent with the distorted structure in the transition states, as well as with the need to avoid "symmetry forbidden" arrangements along the least motion path.[15] The optimal electrophilic interaction would occur if the SiX_2 plane were parallel to the CC bond, while the arrangement that maximizes the nucleophilic interaction is that of the final C_{2v} geometry of the ring. The distorted transition structure therefore suggests that the saddle point is part way between the two types of interaction.

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 SiX_2 wave functions, in particular, the lone pair (HOMO) and empty p orbital (LUMO) on Si. The energies of LUMO in SiF_2 and $SiCl_2$ are 0.032 and 0.003 hartree, respectively. The lower energy of this empty p orbital when X = Cl facilitates the interaction in the electrophilic phase of the reaction. Similarly, the energies of HOMO in SiF_2 and $SiCl_2$ are -0.410 and -0.379 hartree, respectively, so the higher lone pair energy when X = Cl serves to facilitate the nucleophilic step for this system. The net effect, therefore, is to preferentially stabilize the transition state for X = Cl, relative to that for X = F.

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