Notes

Theoretical Study of Addition Reactions of SiX_2 to Acetylene ($X = H, CH_3$, t-Bu, Cl, F)

Gyusung Chung[†] and Mark S. Gordon*

Department of Chemistry, Iowa State University, Ames, Iowa 50011

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Summary: The addition reaction of SiX_2 ($X = H$, CH_3, t-Bu, F, and Cl) to acetylene is considered using ab initio calculations. Second-order perturbation theory (MP2) and coupled cluster CCSD(T) calculations confirm there is no barrier for SiH_2, $Si(CH_3)_2$, and $Si(t\text{-}Bu)_2$ additions, while electronegative substituents such as F and Cl have nonzero barriers. It is concluded that electronegativity is more important than steric effects in determining barrier heights for these reactions. The CCSD(T)/6-31+G barriers for SiF_2 and $SiCl_2$ additions are computed to be about 24 and 8 kcal/mol, respectively.*

Introduction

The formation of highly strained small ring molecules using carbenes has long been of great interest.[1,2] In particular, the addition of silylene (SiH_2) to multiple bonds has been an important topic of theoretical as well as experimental studies.[3−13] According to the experimental studies by Walsh et al.,[4−9] the addition reaction of SiH_2 ($^1A_1$) into a π bond of ethylene or acetylene in the gas phase proceeds with no barrier. The result of previous theoretical studies[10,11] are consistent with the experiments. However, a recent theoretical study[13] has shown that the additions of SiF_2 and $SiCl_2$ to ethylene have nonzero barriers. The prediction that the barrier for SiF_2 addition is much larger than that for $SiCl_2$ suggests the barrier height is related to the electronegativity of the substituted atoms. More recently, it has been reported, based on experiment, that the addition of $Si(CH_3)_2$ to ethylene also proceeds with no barrier.[9] The addition pathway on the singlet potential energy surface appears to be concerted. In this paper, the addition reaction pathways for the insertion of SiX_2 ($X = H$, CH_3, t-Bu, Cl, and F) into the triple bond of acetylene are examined.

Computational Methods

Optimized geometries for the stationary points were obtained using second-order perturbation theory (MP2)[14] with the 6-31+G* basis set. The MP2/6-31+G* Hessians (matrix of energy second derivatives) were calculated in order to verify whether the stationary points are local minima or saddle points. Minimum energy pathways connecting the reactants and products were confirmed using the intrinsic reaction coordinate (IRC) method with the Gonzalez−Schlegel second-order algorithm.[15] To achieve more reliable energetics, CCSD(T) single-point energy corrections were obtained with the 6-31+G* basis set. All RHF and MP2 calculations in this study were performed using the GAMESS electronic structure program.[16] The Gaussian 94 program[17] was used for the CCSD(T) calculations.

Results and Discussion

Molecular Structures. The MP2/6-31+G* geometric parameters of the final products for the addition reactions of SiX_2 ($X = H$, CH_3, t-Bu, F, and Cl) to the acetylene triple bond are summarized in Table 1. All products except for $X =$ t-Bu have C_{2v} symmetry. The MP2/6-31+G* Hessian calculations show that all of these stationary points are local minima. There is little variation in the three-membered ring for $X = H$, CH_3, and t-Bu. The Si−C bond lengths for $X = F$ and Cl are somewhat shorter than those of the others, while the C−C bond lengths are longer. This suggests stronger

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[†] Permanent address: Department of Chemistry, Konyang University, Chungnam 320-711, Korea.

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Table 1. MP2/6-31+G* Geometric Parameters for Final Products ($SiX_2C_2H_2$)[a]

X	R(Si−C)	R(C−C)	R(C−H)	R(Si-X)	∠(CCH)	∠(XSIX)
H	1.826	1.346	1.086	1.486	136.1	111.6
CH_3	1.826	1.354	1.088	1.882	134.4	111.3
t-Bu	1.834	1.352	1.088	1.917	134.5	118.4
Cl	1.789	1.368	1.087	2.044	134.2	107.6
F	1.775	1.380	1.087	1.619	132.6	103.5

[a] Bond lengths in Å, angles in deg.

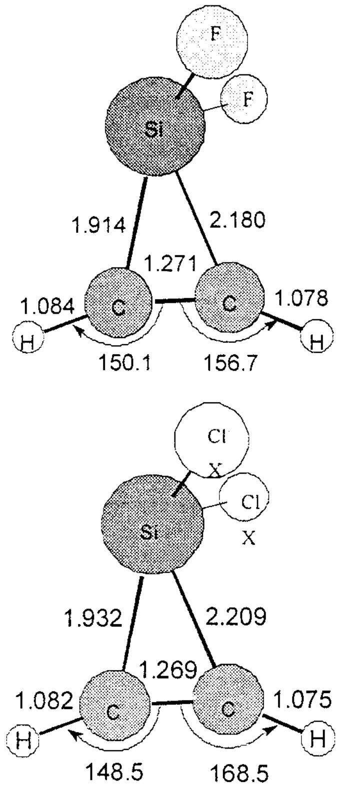


Figure 1. Molecular structures for transition states of $SiF_2C_2H_2$ and $SiCl_2C_2H_2$ molecules.

Si−C bonds perhaps due to the more positive Si when halogens are attached.

Since there is no evidence for transition states on the MP2 potential surfaces for the addition of SiH_2, $Si(CH_3)_2$, and $Si(t\text{-}Bu)_2$ (see below), the transition state structures reported here are for addition of $SiCl_2$ and SiF_2. The MP2/6-31+G* transition state structures for these two additions are illustrated in Figure 1. Note that these two transition states have C_s symmetry. According to the MP2/6-31+G* Hessian calculations, the imaginary frequencies for the $SiCl_2$ and SiF_2 additions are 370.6i and 569.7i cm^{-1}, respectively. The Si−C bond lengths and the CCH bond angles of these transition states are moderately sensitive to the substituent. The $SiCl_2$ transition state is somewhat earlier than that for SiF_2, as is clear from the longer Si−C bond distance and the slightly shorter C−C bond. In addition, the CCH bond angle on the Cl_2 side is larger (greater asymmetry) than in the SiF_2 transition state. This may be due to steric repulsion from the bulky chlorines.

Reaction Path and Energetics. For X = H, CH_3, and t-Bu, the RHF/6-31+G* reaction barriers for the concerted mechanism are computed to be less than 5 kcal/mol. MP2/6-31+G* saddle point searches for these species found no evidence for the existence of transition states for these three reactions. CCSD(T) single-point calculations on the RHF reaction paths confirm zero barriers for X = H, CH_3, and t-Bu. This suggests that steric hindrance is not the deciding factor in determining the barrier heights of these reactions.

Table 2. Energetics for SiX_2 + Acetylene in kcal/mol

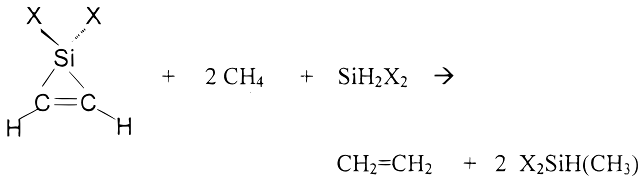
calculational level	F		Cl		H	CH_3	t-Bu
	E_b	ΔH	E_b	ΔH	ΔH	ΔH	ΔH
RHF/6-31+G*	30.9	−56.2	19.9	−47.7	−45.3	−46.8	−48.8
MP2/6-31+G*	19.9	−25.5	5.2	−38.4	−53.9	−54.2	−57.5
CCSD(T)/6-31+G*	23.9	−22.0	8.2	−36.7	−51.2	−49.7	

The energetics for the addition reactions are summarized in Table 2. As can be seen in this table, the barrier height correlates with the electronegativity of the substituent on Si. The MP2 calculation lowers the RHF barrier height for X = F and Cl by more than 10 kcal/mol. The coupled cluster results differ only slightly from the MP2 energetics. At the best level of theory, CCSD(T)/6-31+G*//MP2/6-31+G*, the computed barrier heights for X = Cl and F are 8.2 and 23.9 kcal/mol, respectively. Since the size of the Cl atom is close to that of a methyl group, it can be conjectured that the zero barrier for X = CH_3 is caused by its relatively low electronegativity. Note also that the calculated barrier heights generally follow the Hammond postulate: The reaction exothermicities for H and the alkyl groups are similar to each other and about 15 kcal/mol greater than that for Cl. Likewise, the exothermicity for X = Cl is nearly 15 kcal/mol greater than that for X = F. This follows the reverse trend for stabilization of the divalent silicon, with the more electronegative (and lone pair-containing) halogens being more effective in this regard. It is also possible that the weakened C=C bond in the products for X = F, Cl (see Table 1) decreases the exothermicities for the SiF_2 and $SiCl_2$ reactions. One expects increased barrier heights as the reaction exothermicity decreases.

According to the previous theoretical study[12] for insertion of SiX_2 into ethylene, the barrier heights for X = Cl and F are 5.2 and 19.3 kcal/mol at the MP4/6-311G(d,p) level, respectively. These values for ethylene are not largely different from those of acetylene. So the barrier height is not particularly dependent on the number of π bonds in the substrate molecule.

Calculations have also been performed to determine the reaction barriers for addition of SiHCl and SiHF to acetylene. There appear to be no corresponding transition states on the MP2 potential energy surface, while the RHF calculations predict only small reaction barriers (<4 kcal/mol) for these two addition reactions. So, just one electronegative substituent is not enough to create a barrier for the addition reaction. It is important to note in this regard that the CCSD(T)/6-31+G* exothermicities for the reactions of SiHF and SiHCl are 44.1 and 43.7 kcal/mol, respectively. These are about 7 kcal/mol larger in magnitude than that for $SiCl_2$ and about 6 kcal/mol smaller than that for $SiMe_2$ (Table 2). Once again this is consistent with the Hammond postulate.

As noted above, the predicted relative exothermicities may be partially explained in terms of the relative stabilities of the silylenes. Strain in the product silacyclopropenes may also play a role. One can estimate the ring strain of the product molecules using the following isodesmic reaction.



The MP2/6-31+G* optimizations for the above species show that the ring strains for X = F, Cl, (H, F), (H, Cl), H, CH_3, and t-Bu are 49.4, 46.2, 41.0, 40.9, 38.6, 38.1, and 35.8 kcal/mol, respectively. This trend is consistent with the predicted exothermicity. Since, as noted above, the relative barrier heights are driven by the reaction exothermicities, it appears that the sizes of the barriers for these addition reactions are determined by the relative stabilities of the divalent silicon on one hand and the “ring strain” on the other hand. Both of these factors preferentially stabilize the reactants for highly electronegative substituents.

Conclusions

The reaction barrier and energetics of addition reactions of SiX_2 to acetylene for X = H, CH_3, t-Bu, Cl, and F on the singlet energy hypersurface have been investigated with ab initio calculations. It is confirmed that there is no barrier for the three additions of SiH_2, $Si(CH_3)_2$, and $Si(t\text{-}Bu)_2$, while the additions of SiF_2 and $SiCl_2$ have barriers of about 24 and 8 kcal/mol, respectively, at the best level of theory. It is suggested that the electronegatvity of X is more important than steric hindrance in determining the barrier heights for these reactions and that the relative barrier heights are driven by the relative exothermicities.

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