Ab initio Mechanistic Comparison of Addition of Hydrogen Chloride to Silaethene and Ethene

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The addition of HCl to silaethene proceeds, with a small overall barrier, *via* the formation of a complex and a two-centred transition state; this differs significantly from the analogous reaction of ethene.

Although in recent years much progress has been made in the generation and characterization of silicon–carbon doubly bonded intermediates,[1] very little quantitative information on the kinetic and mechanistic aspects of the reaction of these important intermediates is available. In a recent communication, Davidson *et al.*[2] reported kinetic parameters for the gas-phase addition of hydrogen halides and oxygen to 1,1-dimethylsilaethene.[3] We now report *ab initio* mechanistic calculations of the addition of hydrogen chloride to silaethene, and compare these with the analogous reaction of ethene.

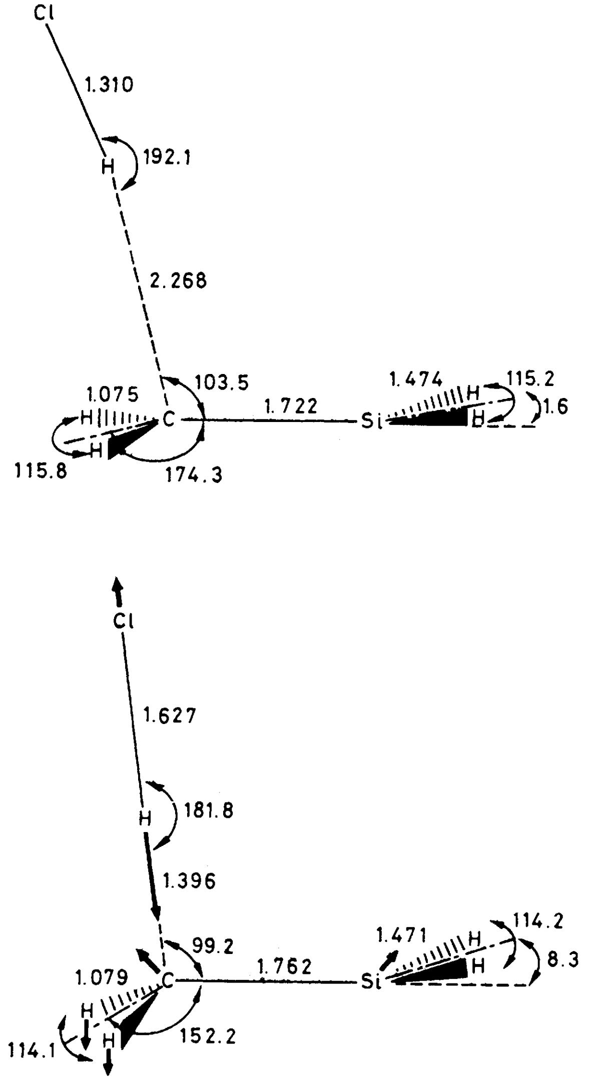

Figure 1. 3-21G SCF optimised geometries of a complex (upper) and a transition state (lower) for the addition of hydrogen chloride to silaethene, in Ångstroms and degrees. The total energies are calculated to be −785.17722 and −785.16550 Hartree, respectively [1 Hartree = 4.359814(24) × 10^{-18} J]. The arrows indicate the displacement vector of the reaction co-ordinate (the normal co-ordinate corresponding to the imaginary vibration) at the transition state.

The stationary points on the potential energy surface of the title reaction were carefully determined by the 3-21G SCF method[4] and the analytic energy gradient technique[5] and were then identified as the equilibrium or the transition state (saddle point) by calculating normal vibrational frequencies. Upon going from the reactants, HCl + $H_2Si{=}CH_2$, to the product, $H_3Si{-}CH_2Cl$, two stationary points were calculated which were found to be an intermediate complex and a transition state. As Figure 1 shows, a complex forms in a fairly early stage of the reaction and is held together by a stabilization energy of 15.9 kJ mol^{-1}. A transition state, which resembles the complex in structure, was calculated to be 30.8 kJ mol^{-1} more unstable than the complex.

Comparing this with the reaction of HCl with ethene, the following similarities and differences are worth mentioning. A Mulliken population analysis† reveals that HCl adds to both silaethene and ethene in an electrophilic way. The reaction of silaethene is calculated to be 340.5 kJ mol^{-1} exothermic while the reaction of ethene is 98.3 kJ mol^{-1} exothermic. Reflecting this large difference in exothermicity, the former reaction gives rise to a considerably looser transition state than does the latter reaction. A most interesting finding is that the reaction of silaethene involves a two-centre-like transition state, while, as noted in the previous STO-3G[6] and MNDO[7] calculations, the reaction of ethene proceeds *via* a cyclic four-centre-like transition state (Figure 2).

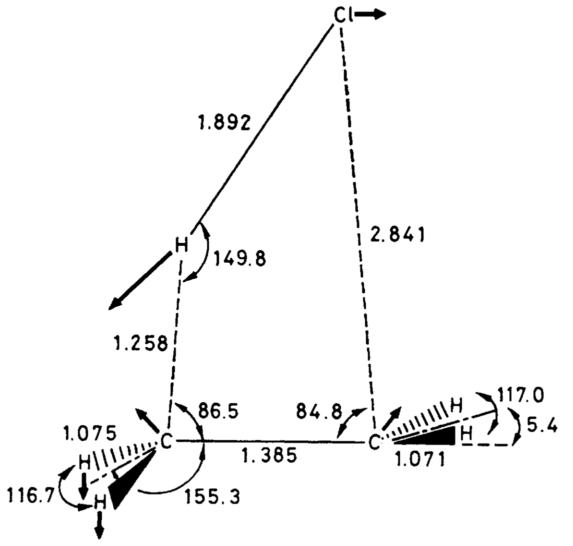

Figure 2. 3-21G SCF optimised geometry of a transition state for the addition of hydrogen chloride to ethene, in Ångstroms and degrees. The calculated total energy is −535.41294 Hartree. The arrows indicate the displacement vector of the reaction co-ordinate.

As might be expected from the characteristic frontier orbitals of molecules containing doubly bonded group 4B metals,[8] an overall barrier of 14.8 kJ mol^{-1} calculated for the reaction of silaethene is far smaller than the barrier of 151.0 kJ mol^{-1} calculated for the reaction of ethene, indicating the very high reactivity of a silicon–carbon double bond. The barrier height calculated for the reaction of silaethene seems to be in reasonable agreement with a 10 ± 7 kJ mol^{-1} activation energy observed recently by Davidson *et al.*[2] for the reaction of 1,1-dimethylsilaethene with HCl.

All computations were carried out at the Computer Center of the Institute for Molecular Science, using the computer centre library program (IMSPAK).

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† Since care may need to be exercised for the absolute values of charge densities from Mulliken population analyses, the interpretation is meant to be rather qualitative.