

The Chemistry of Monovalent Silicon Cation SiH^+ : Reactions with Small Molecules.

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The most common reactions of singlet silylene, including additions, insertions, and rearrangements, involve the concerted formation of two bonds. What reactions do we expect for a species that differs from a silylene by the presence of two degenerate LUMOs and a positive charge, as is the case for the four-valence-electron, monovalent silicon cation SiH^+ ? This species has the opportunity to form one, two, or three new bonds in a single reactive collision. To investigate these possibilities and uncover the fundamental properties of the monovalent silicon species, we designed and carried out detailed experimental and theoretical studies of the gas-phase reactivity of SiH^+ .

All experiments were carried out with a modified ThermoFinnigan quadrupole ion trap mass spectrometer. The monovalent silicon cation, SiH^+ , was generated by electron ionization of silane. Unwanted ions were ejected from the ion trap, and the desired ion was mass selected for further studies. The neutral reagent was introduced via a fine capillary column to control its flow into the trap as a part of the background helium gas flow. Ion-molecule reactions were examined after isolation and “thermalization” of the reactant ions by collisions with helium. The PolarisQ’s Xcalibur software was used for parameter controls and data acquisition. Density functional theory was used to gain insight on the reactions and interpret the results.

We investigated reactions of ground singlet monovalent silicon cation, SiH^+ , with amines, alkynes, alkenes, and aromatic compounds by using both a modified quadrupole ion trap and supported the experimental results with density functional theory (DFT). The major conclusions are as follows:

(1) In contrast to carbene and silylene additions, a π -complex intermediate is formed between SiH^+ and the unsaturated alkynes and alkenes; the SiH^+ cycloadditions occur in a concerted, asynchronous manner. The product ion of C_2HSi^+ formed in the reaction of SiH^+ with acetylene is the silicon acetylide cation, whose chemical reactivity we also investigated. Theoretical studies show that addition is much more favored over insertion in the reaction of SiH^+ with acetylene, and this is consistent with isotopic labeling results.

(2) The product ions of $\text{C}_2\text{H}_3\text{Si}^+$ formed in the reaction of SiH^+ with ethylene are predicted to be three non interconverting isomers by DFT, which is consistent with the experimental studies. The silicon analog of the cyclopropenylum ion is not the global minimum on the $\text{C}_2\text{H}_3\text{Si}^+$ energy surface, which is due to its low resonance (10.2 kcal/mol) and high strain energies (53.7 kcal/mol) as calculated at the B3LYP/6-31G* level. DFT studies suggest that the addition pathway is favored over other processes.

(3) The product ion of $C_6H_7Si^+$ formed in the reaction of SiH^+ with benzene is the silatropylium ion, which is consistent with its reactivity and fragmentation patterns. DFT predicts that a π -complex intermediate is formed first between SiH^+ and the benzene ring, which could easily rearrange to the silatropylium ion via a low energy barrier (Figure 1). The lack of reactivity with cycloheptatriene is consistent with the high-energy barrier requirement in the hydride transfer reaction (Figure 2), although the silatropylium ion has a higher hydride affinity (calculated) than that of the tropylium ion.

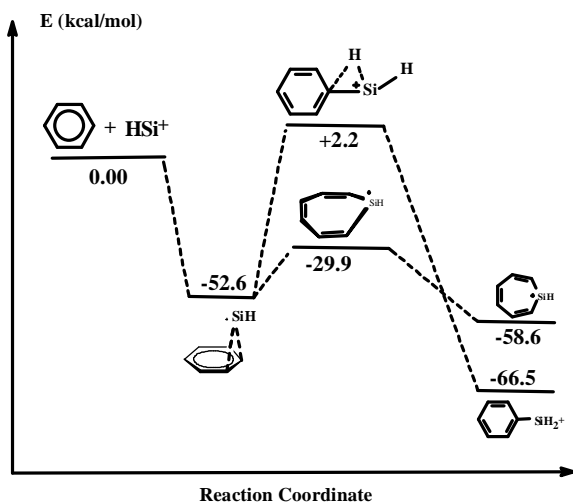


Figure 1. Reaction coordinate between SiH^+ and benzene.

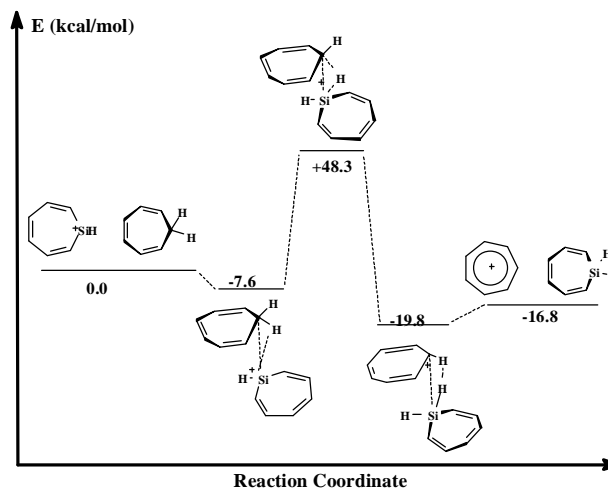
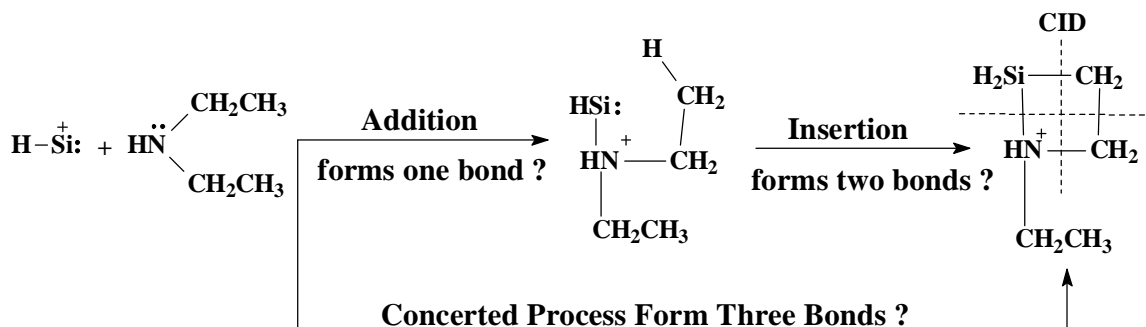


Figure 2. Hydride transfer reaction between silatropylium ion and c-C7H8.

(4) The structure of the ion $C_4H_{12}NSi^+$ (m/z 102) formed in the reaction of SiH^+ with diethylamine is likely to be a four-membered ring. The CID of m/z 102 gives three fragment ions: $C_2H_8NSi^+$ with loss of C_2H_4 , $C_3H_8N^+$ with loss of $CSiH_4$, and $C_4H_{10}N^+$ with loss of SiH_2 . The formation of the four-membered ring structure most likely occurs by a two-step process: formation of a silylene intermediate by a Lewis acid/Lewis base reaction followed by intramolecular insertion of the silylene into a methyl C-H bond. Three bonds are formed in a single reactive encounter, but the stepwise process is more likely than the concerted reaction.



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