Dissociation of Chlorobenzene on a Double Dimer Cluster Model of the Si(100) Surface

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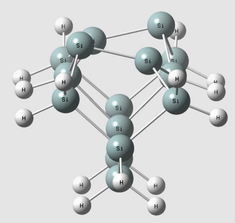
Abstract

The adsorption and dissociation of chlorobenzene on Si(100) surface was modeled using density functional theory. A double dimer cluster was used to represent the (100) face of silicon. Initial adsorption occurs by breaking one double bond on the phenyl ring and forming two new carbon-silicon bonds with the dimer cluster. For further dissociation to occur, the system must undergo a spin crossing process from the singlet electronic configuration to a higher energy triplet state. After this spin crossing event, the carbon-chorine bond is broken and a new silicon-chloride bond is formed. This cleavage is followed by an additional cleavage of the bond between one of the two carbons attaching the ring to the silicon dimer. This restores the aromaticity of the phenyl ring, and results in a lower energy product. The final product is a dissociation product with chlorine and a phenyl ring attached directly to the (100) surface of silicon.

Introduction

The adsorption and dissociation mechanism of organic compounds on the (100) surface of silicon is important for the development of "molecular wires", chemical sensors, and other electronics[1,2,3]. In this work, we use a double dimer cluster to model the Si(100) surface. We follow the reaction of chlorobenzene with this cluster, and discuss the feasibility of this pathway.



Computational Details

• Calculations were performed using the B3LYP hybrid density functional method along with the 6-31G(d) basis set.

• Geometry optimizations where done using Gaussian 09 software.

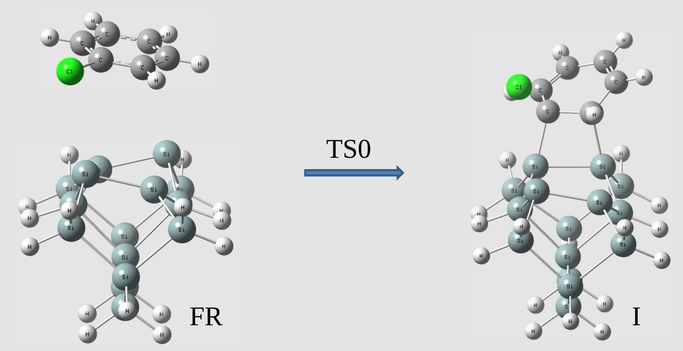
• Minimum energy crossing points were located using a Fortran program developed by Harvey[4] based on an algorithm by Bearpark[5].

• GAMESS (US) was used to calculate the spin orbit coupling constants.

• The same 6-31G(d) basis set used in the geometry calculations was used for the SOC calculations.

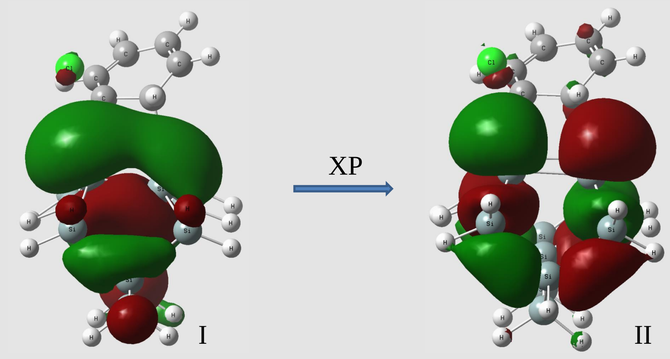
Initial Adsorption

The chlorobenzene breaks a double bond and forms two new bonds with the dimer in a Diels-Alder type reaction.

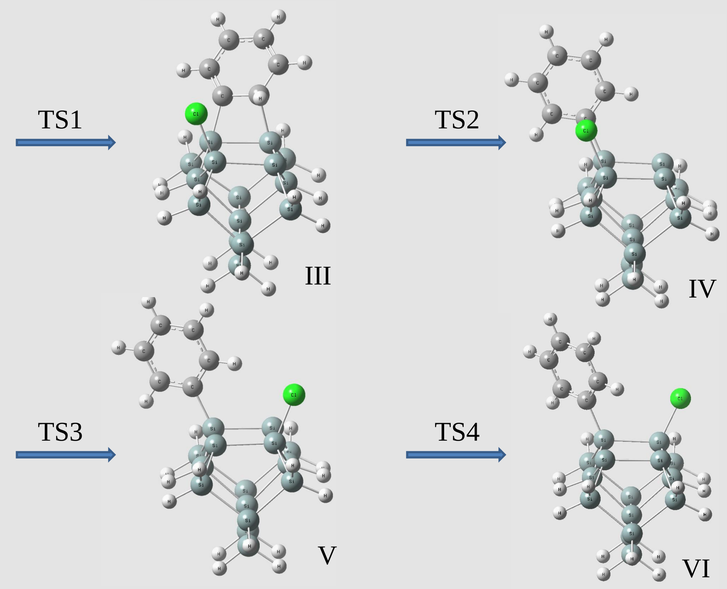


Spin Flip

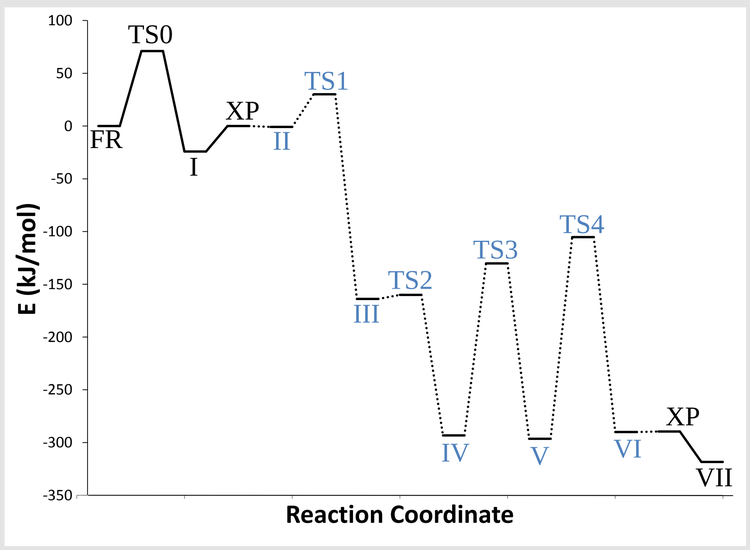
The surface must undergo a spin flipping process from the singlet ground state to the triplet state. This spin flipping process occurs at the minimum energy crossing point (XP). The highest occupied molecular orbital is shown for each state.



Further Dissociation



Energy Diagram



Conclusions

•Chlorobenzene adsorbs to the Si(100) surface by opening one of its double bonds in a Diels-Alder type reaction.

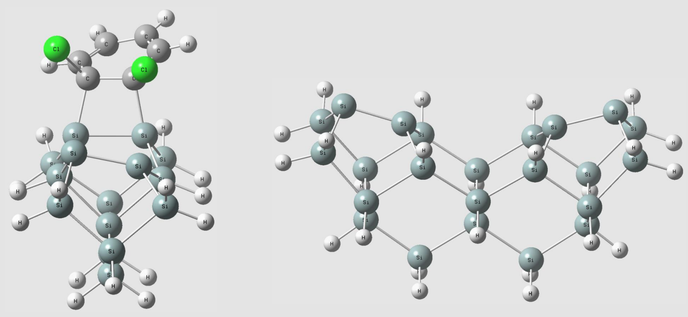
• For further dissociation of chlorobenzene to occur, the surface must undergo a spin flipping process.

• The chlorine may then attach to the surface and migrate to the lowest energy product, which is a dissociation product with chlorine and a phenyl ring attached directly to the (100) surface of silicon.

• Spin orbit coupling constants are currently being calculated.

Future Work

The next step in this work will be to model dichlorobenzene on the Si(100) surface. Another future goal of this work is to study the dissociation across dimer rows. Scanning tunneling microscopy evidence shows that chlorinated benzene will dissociate across dimer rows and well as along them[6].



References

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