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## 论文

### 锆苯与亲二烯体的Diels-Alder反应的理论研究

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#### 摘要:

采用密度泛函理论方法在B3LYP/6-311G(d,p)水平上研究了锆苯与一些亲二烯体的Diels-Alder反应的微观机理和势能剖面, 考察了取代基和苯溶剂对反应势能剖面的影响, 探讨了杂Diels-Alder反应中区域选择性的起源. 计算结果表明, 所研究反应均以协同的方式进行. 亲二烯体分子碳原子上的苯基取代基对杂Diels-Alder反应中2个新键形成的非同步性和活化能垒的影响与最终产物中苯基和锆原子间的相对位置有关, 锆苯分子中锆原子上的CCl<sub>3</sub>取代基在热力学和动力学上均有利于反应的进行. 苯溶剂对所研究反应的势能剖面影响较小. 实验观察到的杂Diels-Alder反应的区域选择性由动力学因素所控制.

关键词: 锆苯; 亲二烯体; Diels-Alder反应; 反应机理; 密度泛函理论

### Theoretical Study on the Diels-Alder Reactions Between Germabenzenes and Dienophiles

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#### Abstract:

Density functional theory(DFT) calculations, at the B3LYP/6-311G(d,p) level of theory, were performed to study the reaction mechanism and potential energy surface of the Diels-Alder reactions between germabenzenes and some dienophiles. The influences of substituents and benzene as a solvent on the potential energy surface of the hetero-Diels-Alder reactions were investigated and the origin of regioselectivity in the he-tero-Diels-Alder reactions was explored. Our calculation results show that all of studied reactions proceed in a concerted way. The influences of phenyl at C atom of dienophiles on the asynchronicity in the bond-formation process and activation barrier of reaction are closely related to the relative position of phenyl with respect to Ge atom in products. The CCl<sub>3</sub> group at Ge atom of germabenzene molecule is in favor of process of the hetero-Diels-Alder reactions and solvent effect is not crucial for the potential energy surfaces of the studied reactions. The present calculations reproduce the regioselectivity observed experimentally in hetero-Diels-Alder reactions, which indicates that the kinetic factor controls the reaction proceeding.

Keywords: Germabenzene; Dienophile; Diels-Alder reaction; Reaction mechanism; Density functional theory

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