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研究论文

亚烷基卡宾及取代亚烷基卡宾与环氧乙烷反应的量子化学研究

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摘要 用量子化学的密度泛函理论(DFT)在6-311G(d,p)水平上对亚烷基卡宾及取代亚烷基卡宾与环氧乙烷的氧转移反应机理进行了系统的研究. 用IRC对过渡态进行了确认. 并用组态混合模型讨论了反应势垒($\Delta E^{\neq}$)与XYC＝C:的单-三态能量差ΔE_{ST}之间的关系, 结果表明, 取代基的电负性是控制反应的主要因素, 取代基的电负性越大, 取代基越多, π电子给予体越多, 单-三态能量差ΔE_{ST}就越小, 该反应的活化能就越小, 反应越容易发生. 同时还研究了该反应中环氧乙烷中C—O键的解离过程. 发现两个C—O键解离是一个不同步的协同过程.

关键词 亚烷基卡宾 从头算 密度泛函理论 过渡态

分类号

Quantum Chemistry Study on the Abstraction Reaction of Alkylidenecarbene and Its Substituted Species with Oxirane

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Abstract The mechanisms for the abstraction reactions of alkylidenecarbenes and its substituted species with oxirane have been characterized in detail by density functional theory. All the stationary points were determined at the B3LYP/6-311G(d,p) level of the theory. The transition states both to the reactant and the product directions in the reaction paths were examined by using the intrinsic reaction coordinate. A configuration mixing model based on the work of Pross and Shaik was used to rationalize the computational results. The results show that the electro negativity of the substituents played an important role to predict its activity for the abstraction reactions. The major conclusion was that the stronger the π-donation or the more electronegative the substituents, the smaller the ΔE_{ST} of XYC＝C: and the lower the activation en-ergy for the abstraction reactions. In other words, it is the electronic factors, rather than the steric ones, that play a decisive role in the chemistry of the alkylidenecarbene species.

Key words alkylidenecarbene *ab initio* density functional theory (DFT) transition state

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