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硅烯及取代硅烯与饱和键插入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水平上对硅烯及其取代物与甲烷的C-H键进行插入反应的势能面进行了系统地研究。用IRC方法对过渡态进行了验证。并用组态混合模型讨论了反应势垒(△E^≠)和反应热(△H)与SiXY的单-三态激发能△Est的关系。我们发现，硅烯SiXY的△Est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电子给予越强，SiXY的△Est就越大，插入反应的活化能就越大，放热就越小。

关键词 硅烯 插入反应 密度泛涵理论 过渡态理论 甲烷 激发态

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Quantum chemistry study on the insertion reaction of silylene and its substituted species to saturated bond

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Abstract The potential energy surfaces for the insertion of silylene into C-H bond of methane were studied using density functional theory (DFT). All the stationary points were determined at the BELYP/6-311G level of the theory. The transition state both to the reactant and the product direction in the reaction paths was examined by using the intrinsic reaction coordinate (IRC). A configuration mixing model has been used to explain the barrie height and the reaction enthalpy. The results show that the single-triplet splitting △Est of the SiXY species plays an mportant role to predict its activity for the insertion reactions. The major conclusion is as follows: the more strong the π-donation is or the more electronegative the substituents are the larger the △Est of SiXY, the higher the activation energy, and the smaller the exothermicity for the insertion of SiXY into saturated C-H bonds will be. In other words, it is the electronic factors, rather than the steric factors, that play a decisive role in determinning the chemical reactivity of the silylene species.

Key words SILYLENE INSERTION REACTION TRANSITION STATE THEORY METHANE EXCITED STATE

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