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研究论文

烯丙位化学键均裂离解能及其取代基效应

王毅敏，周畅，傅尧，刘磊，郭庆祥*

(中国科学技术大学化学系 合肥 230026)

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摘要 使用复合从头算方法系统地获得了一批精确的烯丙位化学键的均裂裂解能(BDE). 取代基效应的研究表明, C—H与Si—H的BDE表现出差的Hammett关系, 而N—H, O—H, P—H与S—H的BDE表现出好的Hammett关系. 进一步分析表明烯丙位BDE受共轭效应比诱导/场效应的影响更为明显. 并且还讨论了BDE的基态效应和自由基效应, 其结果与最近报道的有关苄位BDE的结果基本一致.

关键词 键能 G3 CBS-Q 取代基效应

分类号

Homolytic Bond Dissociation Energies of Allylic Compounds and Related Substituent Effects

WANG Yi-Min,ZHOU Chang,FU Yao,LIU Lei,GUO Qing-Xiang*

(*Department of Chemistry, University of Science and Technology of China, Hefei 230026*)

Abstract Reliable bond dissociation energies (BDE) of various allylic compounds were obtained using compound methods. It was found that the C—H and Si—H BDE data display poor Hammett relationships, whereas the N—H, O—H, P—H and S—H BDE ones exhibit good Hammett relationships. It was also found that the resonance effect was more important than the inductive/field effect on the allylic BDE. In addition, the ground state and radical state effects on BDE were analyzed. All the results in the present study are in good agreement with our recent results about the benzylic BDE.

Key words bond dissociation energy G3 CBS-Q substituent effect

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通讯作者 郭庆祥 qxguo@ustc.edu.cn