化学学报 2007 65 (2): 129～134 ISSN: 0567-7351 CN: 31-1320/06

研究论文

环丙酮光解离和热异构机理的从头算研究

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收稿日期 2005-12-22 修回日期 2006-6-7 网络版发布日期 2007-1-12 接受日期 2006-9-20

摘要 运用精确的量子化学计算方法CASSCF, B3LYP和MP2, 结合cc-pVDZ基组, 优化了环丙酮的基态和激发态势能面上的驻点结构, 计算了它们的相对能量. 在此基础上, 深入探讨了环丙酮光解离反应的机理. 在292～365 nm波长的光的激发下, 环丙酮被激发至S_1态, 最可能的初始过程是α C—C键断裂. 我们的理论研究发现, 在α C—C键断裂途径上, 存在基态和第一激发势能面的交叉点, 它在随后的反应过程中起着重要作用. 一方面可形成单态双自由基中间体, 然后发生另一个C—C键的断裂, 生成基态产物一氧化碳和乙烯. 另一方面, 经过S_1/S_0交叉点可以回到热的基态. 在这种情况下, 体系具有足够的能量, 克服基态途径上的势垒, 生成同样的基态产物乙烯和一氧化碳. 此外, 还对环丙酮基态异构化反应进行了理论研究.

关键词 环丙酮 从头计算 光解离 异构化 交叉点

分类号

Ab initio Study on Mechanisms of Photodissociation and Thermal Isomerization of Cyclopropanone

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Abstract In the present work, the potential energy profiles, governing the dissociation of cyclopropanone to $CO+C_2H_4$ in the S_0, S_1 and T_1 states, have been determined using complete active space self-consistent field (CASSCF), density functional theory (DFT), and the second-order Moller-Plesset perturbation theory (MP2) in conjugation with the correlation-consistent atomic natural orbital basis set, cc-pVDZ. Upon photoexcitation in the range of 292～365 nm, the initial process was determined to be the α C—C bond cleavage after the cyclopropanone was excited to the S_1 state. Our research found that the S_1/S_0 intersection point played an important role in the subsequent processes. On one hand, the singlet diradical is produced as an intermediate, which is followed by formation of CO and $CH_2=CH_2$ in the S_0 state. On the other hand, the "hot" parent molecule can be formed through the S_1/S_0 intersection point, which has enough internal energies to overcome the barrier on the pathway to CO and $CH_2=CH_2$. Besides, the isomerization reactions of cyclopropanone in the ground state were investigated in this work.

Key words cyclopropanone *ab initio* calculation photodissociation isomerization conical intersection

DOI:

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