化学学报 1997 55 (11): 1047-1055 ISSN: 0567-7351 CN: 31-1320/06

乙酰胆碱水解反应的从头算研究

张昌军,湛昌国

华中师范大学化学系

收稿日期 修回日期 网络版发布日期 接受日期

摘要 本文对乙酰胆碱水解反应历程进行了从头算分子轨道研究。首先, 我们在RHF/6-31G级别上研究了乙酰胆碱的水解反应的势能面, 找到了反应过程中的两个过渡态和连接这两个过渡态的中间体。然后进行了RHF/6-31G**级别上的单点能量计算。优化结果表明在两个过渡态中都包含有四元环状结构, 而且, 两个过渡态的四元环中存在着不同的分子内氢键。计算结果还表明,乙酰胆碱最终分解成胆碱和乙酸盐部分时, 酯键的断裂发生在羰基碳和酯基氧之间。最后, 进一步考虑溶剂化效应, 我们还运用量子Onsager模型, 在RHF/6-31G**级别上对整个水解反应的反应物、产物、中间体和过渡态分别进行了从头算自洽反应场能量计算, 求出了包含溶剂化效应在内的反应的能垒及总反应热。

关键词 反应机理 水解 乙酰胆碱 从头计算法 势能面 过渡态

分类号 0641

Ab initio study of the hydrolysis of acetylcholine

ZHANG CHANGJUN,ZHAN CHANGGUO

Abstract Ab initio molecular orbital method has been empolyed, in this paper, to study the mechanism of the hydrolysis of acetylcholine. First of all, the optential energy surface of the reaction system has been investigated at HF/6-31G level, and two transition states and and intermediate linking the two transition states have been found. The optimized geometries have been used to perform further single point energy calculatios at RHF/6-31G** level. It has been shown that there existed different intramolecular hydrogen bonding in two four-center cycles of the two transition states, and that during the hydrolysis of acetylcholine, the fission took places at the bond between the carbonyl carbon and the ester oxygen. Finally, the self-consistent-reaction-field (SCRF) procedure based on the Quantum Onsager model has been applied to the energy calculations on all the reactions, transition states, intermediate and products at the RHF/6-31G** level in order to work out the energy barriers and the total reaction heat involving the solvent effect.

Key words REACTION MECHANISM HYDROLYSIS ACETYLCHOLINE AB INITIO CALCULATION POTENTIAL ENERGY SURFACES TRANSITION STATE

DOI:

通讯作者