化学学报 2001 59 (5): 696-700 ISSN: 0567-7351 CN: 31-1320/06

吡啶光氯化反应过渡态和反应途径的量子化学研究

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收稿日期 修回日期 网络版发布日期 接受日期

摘要 用量子化学B3LYP方法在3---21G*水平上优化吡啶光氯化反应加成取代反应机理生成邻、间、对位氯代吡啶不同反应途径的过渡态并对反应热和活化能进行了计算，对邻位反应途径进行了IRC反应路解析，计算结果表明邻位反应途径过渡态的能量最低，为－704.830027a.u.,生成2－氯吡啶所需的活化能最低，为114.60kJ/mol。光氯化反应主要产物为2－氯吡啶，与实验结果一致。IRC反应路径显示在反应过程中C(2)---H(7)键的断裂和C(2)-----Cl(8)键的生成是协同但不是同步的。

关键词 吡啶 光氯化 过渡态理论 从头计算法 反应机理

分类号 0641

Quantum -chenical study of transtion states and reaction pathways of photochemical chlornation of pyridine

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Abstract The mechanism od photochemical chlorination of pyridine has been investigated using density functional theory (DFT) at the B3LYP/3--- 21G* level. The transition states for three possible reaction paths are obtained and verified by vibration analysis. IRC calculation is carried out for formation of 2-chloropyridine. By comparing the calculated barriers, it is found that the acitvation energy for formation of 2- chloropyridine is 114.60kJ/MOL, which is the lowest among the three reaction pathways. Therefore, the main product should be 2-chloropyridine. This is in agreement with the experimental result. The IRC calculation shows that the breaking of C(2)-----H(7) and the forming of C(2)---Cl(8) are concerted but not synchronous.

Key words PYRIDINE TRANSITION STATE THEORY AB INITIO CALCULATION REACTION MECHANISM

DOI:

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