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研究论文

NO_2气相硝化金刚烷的计算研究

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摘要 运用密度泛函理论(DFT)和半经验MO-PM3方法研究了NO_2气相硝化金刚烷反应机理. 计算结果表明, NO_2不能直接取代金刚烷H; 在B3LYP/6-311＋＋G(3df,2pd)//B3LYP/6-31G* 较高水平下, 对三个可能机理的反应势垒(E_a)的精确计算表明, 该反应的决速步骤为NO_2中O和N进攻1-H的竞争过程, 且1-硝基金刚烷为主要产物. NO_2中O进攻1-H决速反应过程中, 分子几何、原子自然电荷及IR光谱变化表明, C—H键的断裂和N—H键的形成是一个协同过程; 参与新键形成和旧键断裂原子C(1), H(11), O(28), O(29)和N(27)的原子自然电荷及与其相关的键长、键角有明显的变化. 反应过程中体系偶极矩的变化表明, 极性溶剂能降低反应势垒, 有利于反应的进行.

关键词 金刚烷 密度泛函理论 硝化机理 反应势垒
分类号

Computational Studies on the Nitration of Adamantane with NO_2

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Abstract The density functional theory (DFT) and semi-empirical MO-PM3 methods were employed to study the reaction mechanism of the nitration of adamantane with NO_2. The calculated results showed that the H atom in adamantane can not be directly substituted with NO_2. By comparing the potential barriers E_a of the three possible reaction mechanisms at the B3LYP/6-311＋＋G(3df,2pd)//B3LYP/6-31G* level, it was found that the process of N to attack H competed with that of O to attack H during the crucial step, and 1-nitroadamantane was considered to be the main product. In addition, the changes of molecular geometry, atomic natural charge and IR spectra of the reaction system during the crucial step of O to attack H showed that the rupture of C—H bond and the formation of O—H bond were concerted stepwise. Obvious changes of atomic natural charge happened to atoms C(1), H(11), O(28), O(29) and N(27). The bond lengths and bond angles related to these atoms were also varied greatly. The dipole moment changes predicted that polar solvent could decrease reaction potential barrier E_a to facilitate the reaction.

Key words adamantane density functional theory nitration mechanism potential barrier

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