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研究论文

HO_2自由基与NO_2反应通道的理论研究

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摘要 应用密度泛函理论DFT/B3LYP对HO_2＋NO_2反应进行了研究, 在B3LYP/6-311G**和CCSD(T)/6-311G**水平上计算了HO_2自由基与NO_2分子反应的单重态和三重态反应势能面, 计算结果表明, 单重态反应势能面中的直接氢抽提反应机理是此反应的主要反应通道, 即HO_2自由基的氢原子转移到NO_2分子的氮原子上形成产物P_1 (HNO_2＋$^3O_2$), 另一个可能的反应通道是单重态反应势能面上HO_2中的端位氧原子进攻NO_2分子中的氮原子形成中间体**1** ($HOONO_2$), 接着中间体**1** ($HOONO_2$)经过氢转移形成产物P_2 (*trans*-HONO＋$^3O_2$), 以上两个反应通道都是放热反应通道, 分别放热90.14和132.52 kJ•mol^{-1}.

关键词 密度泛函理论 势能面 HO_2＋NO_2 反应通道

分类号

Theoretical Study on the Reaction of HO_2 Radical with NO_2 by Density Functional Theory Method

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Abstract Using the density functional theory (DFT/B3LYP) method, the reaction of HO_2 radical with NO_2 was studied. The potential energy surfaces (PES) of the HO_2＋NO_2 reaction were calculated at B3LYP/6-311G** and CCSD (T)/6-311G** (single-point) levels of the theory. It is shown that the direct H-extrusion reaction mechanism is the main reaction channel on the singlet PES for the title reaction, namely, a direct H-shift from the HO_2 radical to the N atom of the NO_2 molecule to form the product P_1 (HNO_2＋$^3O_2$). Another favorable reaction channel on the singlet PES involves that the end O atom of the HO_2 radical attacks on the N atom of the NO_2 molecule, forming the isomer **1** ($HOONO_2$), then H-shift follows, producing P_2 (*trans*-HONO＋$^3O_2$). Both of the reaction channels mentioned above are exothermic with the energy of 90.14 and 132.52 kJ•mol^{-1}, re-spectively.

Key words DFT potential energy surface HO_2＋NO_2 reaction channel

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