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研究论文

BrO与CH_3SH反应机理的量子化学及拓扑研究

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摘要 利用密度泛函和电子密度拓扑分析方法对BrO与CH_3SH反应的微观机理进行了理论研究. 在B3LYP/6-311G (d, p)水平上对反应势能面上的各驻点进行几何构型的全优化;
振动分析和IRC计算证实了中间体和过渡态的真实性和相互连接关系; 计算得到了各反应通道的活化能,
并进行了零点能校正. 计算结果表明: 该反应存在7个反应通道,
其中生成CH_3S＋HOBr和CH_3SO＋HBr的通道为主要反应通道. 通过对反应过程中部分驻点的电子密度拓扑分析,
首次发现了接近平面的四元环状过渡态, 从而拓展了原来对环状结构过渡态定义的适用范围.

关键词 反应机理 电子密度拓扑分析 结构过渡态

分类号

Quantum Chemical and Topological Study on the Reaction Mechanism of BrO with CH_3SH

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Abstract The reaction mechanism of BrO with CH_3SH has been investigated by density function theory (DFT) and electronic density topological analysis method. Geometries of the stationary points on the potential energy surface have been optimized at B3LYP/6-311g (d, p) level. Vibration analysis and intrinsic reaction coordinate (IRC) calculation at the same level have been applied to validate the connection of the stationary points. The reaction barriers with zero point energy correction have also been calculated. The calculated results show that there are seven pathways on the reaction surface of BrO with CH_3SH, and those in the formations of CH_3S＋HOBr and CH_3SO＋HBr are dominant. The non-planar four-member-ring structure transition state (STS), which was firstly found in this paper, extended the concept of ring STS.

Key words reaction mechanism topological analysis of electronic density structure transition state

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