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研究论文

Cl原子与CH_2SH自由基反应机理及电子密度拓扑研究

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摘要 采用MP2(Full)/6-311G(d,p)和B3LYP/6-311G(d,p)找到了反应Cl＋CH_2SH→HCl＋CH_2S的两个可能的反应通道, 得到了各反应通道的反应物、中间体、过渡态和产物的优化构型、谐振频率. 对反应进程中若干关键点进行了电子密度拓扑分析, 讨论了反应进程中键的断裂、生成和化学键的变化规律, 找到了该反应的结构过渡区(结构过渡态)和能量过渡态, 发现了反应热与结构过渡区之间的关系.

关键词 自由基反应 能量过渡态 结构过渡态 结构过渡区 电子密度拓扑分析

分类号

Reaction Mechanisms and Topological Studies of Electron Density on the Reaction of CH_2SH Radical and Cl Atom

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Abstract Two possible reaction channels for the reaction of CH_2SH＋Cl have been studied at the MP2(Full)/6-311G(d,p) and B3LYP/6-311G(d,p) levels. Geometries of the reactants, intermediates, transition states and products were optimized and IRC calculations were carried out. The computed results show that the reaction proceeds through the addition of a Cl atom to CH_2SH by either Cl—C or Cl—S combination to form initial intermediates. The cleavage and formation of the chemical bonds in the reaction pathways have been discussed by the topological analysis of electronic density. The “energy transition state” and the “structure transition state” in both channels of the studied reaction have been found. The calculated results suggest the relationship between the reaction enthalpy and the “structure transition region”.

Key words radical reaction energy transition state structure transition state structure transition region topological analysis of electronic density

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