化学学报 2007 65 (6): 509—516 ISSN: 0567-7351 CN: 31-1320/06

研究论文

气相中Cu^+和Zn^+与SCO反应的理论研究

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收稿日期 2006-4-15 修回日期 2006-9-14 网络版发布日期 2007-3-16 接受日期 2006-11-9

摘要 为更清晰地揭示M^+与SCO基元反应的机理, 采用密度泛函B3LYP方法, 在6-311＋＋G**基组水平上研究了Cu^+＋SCO和Zn^+＋SCO反应体系. 对反应势能面上各驻点的几何构型进行了全优化, 用频率分析方法和内禀反应坐标(IRC)方法对过渡态进行了验证. 在Cu^+与SCO的反应中, 对影响反应机理和反应速率的势能面交叉现象进行了讨论, 运用Hammond假设和Yoshizawa等的内禀反应坐标垂直激发的计算方法找到了势能面交叉点. 计算结果表明, C—S和C—O键的活化都是通过插入消去机理, 但C—S键的活化在能量上更占优势. 计算确认了标题反应的主通道, 所有的计算结果与实验吻合.

关键词 过渡金属离子 反应机理 密度泛函理论

分类号

Theoretical Study of the Reaction of Cu^+ and Zn^+ with SCO in Gas Phase

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Abstract In order to elucidate the mechanism of reaction M^+＋SCO, the reactions of Cu^+＋SCO and Zn^+＋SCO have been investigated at the B3LYP level of density functional theory with the standard 6-311＋＋G** basis set. The geometries for reactants, transition states and products were completely optimized. All the transition states were verified by the vibrational analysis and the intrinsic reaction coordinate calculations. For the reaction of Cu^+＋SCO, the involved potential energy curve-crossing dramatically affected reaction mechanism, and the reaction rate has been discussed detailedly, the crossing point are localized by means of the Hammond postulate and the intrinsic reaction coordinate approach. The results show that the reaction took insertion-elimination mechanism both along the C—S and C—O bond activation branches, but the C—S bond activation is much more favorable than the C—O bond activation in energy. The main reaction channel was detected for the title reaction. All theoretical results are in line with early experiments.

Key words transition-metal ion reaction mechanism density functional theory

DOI:

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