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研究论文

全氟烷基磺酸酯C—O键断裂的同面S_N2反应

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摘要 用密度泛函理论研究了$CF_3SO_3CF_2CF_3+F^-$的碳氧键断裂反应的机理. 首先, 用DFT方法优化了反应物、中间体、过渡态、产物的平衡构型, 分析了碳氧键断裂反应的势能面变化. 发现在S_N2反应机理中, 除了S—O断裂S_N2反应外, 引起C—O键断裂的同面进攻也是一个可能的反应途径. 理论计算表明, 最终反应的产物是受热力学控制的, S—O键的断裂绝对地优于C—O的断裂. 因此, C—O断裂的同面机理虽然是可能的, 但却难以被实验观察到. 本文还讨论了端基 —F_3在同面S_N2反应中的邻位效应, 以及基组对这个效应的影响.

关键词 反应机理 DFT方法 全氟磺酸酯 同面S_N2反应

分类号

Front-Side S_N2 Reaction, $CF_3SO_3CF_2CF_3+F^-$, Leading to the C—O Cleavage

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Abstract The front-side S_N2 reaction, $CF_3SO_3CF_2CF_3+F^-$, leading to the C—O cleavage was studied using DFT. The reactant complex, transition state, product complex and products, including their vibration frequencies, were optimized and calculated at B3LYP/6-311G** level. The potential energy surface for the front-side S_N2 reaction was investigated, showing that the front-side S_N2 mechanism is possible. However, as shown by computation, the products are thermodynamically controlled, and the S—O cleavage is predominates over the C—O cleavage. As a result, it is difficult for the products resulting from the C—O cleavage to be detected experimentally. Meanwhile, the neighboring effect of the —CF_3 group on the front-side S_N2 mechanism was found.

Key words reaction mechanism DFT method perfluorosulfonate the front-side S_N2 reaction

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