

硝基甲烷热解机理的量子化学研究

肖鹤鸣,江明

华东工学院化学系

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摘要 用ab initio和NMDO两种方法,对CH₃NO₂沿C-N键断裂的热解反应过程进行了较细致的计算研究。所得势能曲线(E-Rc-n)彼此一致,并与Kaufman等[1]的近期结果相符。将各单点下所得正则离域化处理,发现当C和N原子间的距离Rc-n=1.6-1.8Å时,定域成键σc-n-MO从能级较低的五的个占有MO跃升为HOMO(即第16个MO)。考察占有末占有前沿轨道 能级和位相,可推在CH₃NO₂热解的初拾阶段,通过分子重排成C-O键的可能性较小。其热解引发步骤可能是生成CH₃和NO₂双自由基。

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Quantum-chemical studies of thermal decomposition mechanism of nitromethane

XIAO HEMING,JIANG MING

Abstract The thermal decomposition mechanism of CH₃NO₂ has been studied by ab initio and MNDO methods. The potential-energy curves obtained with both methods are qual. consistent with each other. The canonical delocalized MO's given using ab initio calculation for CH₃NO₂ in its ground electronic state and at each point along the decomposition pathway are localized. The bonding localized sC-N-MO energy drastically increases and the sC-N-MO moves correspondently from the 5th to 16th-MO when the C-N distance changes from 1.6 to 1.8 Å. According to the energy level and the phase of the FMO, HOMO, and LUMO, the formation of C-O bond by rearranging to CH₃ONO is less likely to be the first step in the decomposition of CH₃NO₂. It is more likely that CH₃NO₂ decompose into radicals (.CH₃+.NO₂) initially.

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