

Ab initio方法研究CH₃+OCIO反应的可能通道

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摘要 利用abinitio方法研究了CH₃+OCIO反应的三个可能通道,首次应用UMP2(full)/6-31G(d,p)方法得到各反应物、产物、中间物及过渡态的优化构型和谐振频率;然后采用G2MP2理论计算各通道反应焓变和势垒高度。理论计算表明产物通道CH₃+OCIO是最可能发生的途径,反应放热为443.80kJ·mol⁻¹。可能的反应过程为:CH₃和OCIO自由基先经无垒过程生成了一个富能中间物,继而通过较低的势垒解离成HOCl+H₂CO。

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Ab initio calculation on the mechanism for the reaction CH₃+OCIO

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Abstract The three possible production channels for the reaction CH₃+OCIO are studied by ab initio calculations. Geometries of the reactants, products, intermediates and transition states are optimized at the UMP2(full)/6-31G (d, p) level. The corresponding vibrational frequencies are calculated at the same level. Based on the total energies calculated at the G2MP2 level, the reaction heats and activation barriers are obtained. The computation results show that the production channel HOCl+H₂CO is the most feasible pathway, which is exothermic by 443.80 kJ·mol⁻¹. It suggests that an activated intermediate is first formed through a barrierless process in this reaction, and the intermediate will dissociate to HOCl+H₂CO via a fivecenter transition state.

Key words [AB INITIO CALCULATION](#) [METHANE](#) [FREE RADICALS](#) [REACTION MECHANISM](#) [TRANSITION STATE THEORY](#)

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