

过渡金属离子与烷烃反应机理的理论研究: 镍离子与丙烷反应 中甲烷的还原消除机理

张冬菊, 刘成卜

山东大学理论化学研究所, 济南(250100)

收稿日期 修回日期 网络版发布日期 接受日期

摘要 用量子化学方法在B3LYP/6-311++g(3df,3pd)水平上研究了Ni⁺与C₃H₈的反应, 获得了[Ni,C₃H₈]⁺基态(双重态)势能面上CH₄还原消除的详细机理。结果表明: 该势能面上CH₄消除反应经历两个基元步骤: Ni⁺首先通过C—C活化过渡态形成插入型中间体, 然后分别过不同的H-转移鞍点异构化为产物型中间体, 并继而解离生成CH₄, 这些结果与以前从实验推测的反应机理明显不同。计算表明: 对于该势能面上的甲烷消除反应, 能量最有利的反应通道是Ni⁺+C₃H₈→Ni(C₂H₄)⁺+CH₄, 计算的反应热为127.85kJ/mol, 与实验结果(106.13kJ/mol)符合较好。

关键词 [烷烃](#) [反应机理](#) [丙烷](#) [甲烷](#) [镍离子](#)

分类号 [0641](#)

Theoretical studies of the mechanism and energetics for the reaction of transition metal ions with alkanes: Methane elimination mechanism in the reaction of Ni⁺ (2^D) with propane

Zhang Dongju, Liu Chengbu

Shandong Univ, Inst Theoret Chem, Jinan(250100)

Abstract The reaction of Ni⁺ with propane has been studied extensively using density functional theory. The detailed information regarding the mechanism and energetics of CH₄ elimination on the potential energy surface of [Ni, C₃, H₈]⁺ has been obtained at B3LYP/6-311++g(3df, 3pd) level of theory. The present study indicates that the CH₄ elimination in the reaction of Ni⁺ with propane undergoes two elementary steps, namely, the initial C—C bond activation in propane mediated by Ni⁺ and the subsequent isomerization of the inserted intermediate. Ni⁺ inserting into the initial primary C—H bond cannot result in the elimination of CH₄, which is in contrast to the early postulated mechanism. After the C—C inserted species are formed on the potential energy surface, three reaction channels are open, which result in the elimination of CH₄. The relative energy of the energetically most favored transition state is found to be 9.18kJ/mol above the entrance channel. The heat of reaction for Ni⁺+C₃H₈ → Ni(C₂H₄)⁺+CH₄ is calculated to be 127.85kJ/mol. This result is in good agreement with the experimental finding, a value of 106.13kJ/mol.

Key words [ALKANE](#) [REACTION MECHANISM](#) [PROPANE](#) [METHANE](#) [NICKEL ION](#)

DOI:

通讯作者

扩展功能

本文信息

▶ [Supporting info](#)

▶ [PDF\(0KB\)](#)

▶ [HTML全文\(0KB\)](#)

▶ [参考文献](#)

服务与反馈

▶ [把本文推荐给朋友](#)

▶ [加入我的书架](#)

▶ [加入引用管理器](#)

▶ [复制索引](#)

▶ [Email Alert](#)

▶ [文章反馈](#)

▶ [浏览反馈信息](#)

相关信息

▶ [本刊中 包含“烷烃”的 相关文章](#)

▶ 本文作者相关文章

· [张冬菊](#)

· [刘成卜](#)