中文摘要

我們使用高層級的初始法（*Ab initio*）去研究 cyanomethylene radical（HCCN）與 NO 的反應機構與動力學分析。我們使用 B3LYP/6-311++G(3df,2p) 做結構最佳化，單點能量則使用 CCSD(T)/aug-cc-PVQZ//B3LYP/6-311++G(3df,2p) 去計算。我們預測並計算所有的結構去找出最適當的路徑，在我們的所有路徑當中，以產生 **P1**（HCN + NCO）與 **P3**（HCNO + CN）兩種產物為主要路徑。

經由 Fukui functions 以及硬軟酸鹼理論（HSAB）可以去合理地解釋我們所計算出來的結果。所預測的速率常數(k_{total})於 760 torr Ar pressure 下可以從方程式中得到：當溫度介於 298–3000 K 時 $k_{total} = 1.40 \times 10^{-7} T^{-2.01} \exp(3.15 \text{ kcal mol}^{-1}/RT)$，單位為 $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$。

除此之外，在實驗上有觀察到在 18 與 30 torr 下，關於 HCCN+NO 預測之速率常數可以提供我們作進一步比較我們可以利用不同的溫度與壓力之條件計算其速率常數並列在表中，可以作為未來燃燒化學的應用。

關鍵字：初始法、Fukui functions、硬軟酸鹼理論。

Abstract

High level *ab initio* calculations have been performed to study the mechanism and kinetics of the reaction of the cyanomethylene radical (HCCN) with the NO. The species involved have been optimized at the B3LYP/6-311++G(3df,2p) level and their corresponding single-point energies are improved by the CCSD(T)/aug-cc-PVQZ// B3LYP/6-311++G(3df,2p) approach. From the calculated potential energy surface, we have predicted that that the favorable pathways for the formation of several isomers of an HCCN−NO complex.

Formations of HCN + NCO (**P1**) and HCNO + CN (**P3**) are also probable, although these two pathways require little thermal activation. To rationalize the scenario of our calculated results, we also employ the Fukui functions and HSAB theory to seek the possible clues.

The predicted total rate coefficient, k_{total}, at He pressure 760 torr can be represented with an equation: $k_{total} = 1.40 \times 10^{-7}\ T^{-2.01}\ \exp(3.15\ \text{kcal mol}^{-1}/RT)$ at T = 298–3000 K, in units of $\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$. The predicted total rate coefficients at some available conditions (18 and 30 torr) are in good agreement with experimental observation. In addition, the rate constants for key individual product channels are provided in different temperature and pressure conditions.

Key word：*ab initio*、Fukui functions、HSAB theory.