

特定能態二氯丙烷離子的解離動態學：
門檻光電子光離子同現質譜和量子理論計算

學生：王智祥

指導教授：江素玉博士

國立交通大學應用化學所碩士班

摘 要

本論文利用門檻光電子光離子同現質譜技術，研究 1,3 二氯丙烷和 2,2 二氯丙烷的光游離解離動態學。我們由 1,3 二氯丙烷在光能量範圍 10.8-12.0 eV 的同現質譜得到 $C_3H_5Cl^+$ 和 $C_3H_5^+$ 的初現能分別是 ≤ 10.79 和 11.77 ± 0.03 eV，與形成 $c-C_3H_5Cl^+ + HCl$ 和 $CH_2CHCH_2^+ + HCl + Cl$ 的 G3B3 預測反應能量 10.62 和 11.77 eV 一致。我們也預測 1,3 二氯丙烷離子(6, C_1) 在形成 $c-C_3H_5Cl^+ + HCl$ 時，會經過一個五圓環的過渡態，形成五圓環的過渡態無需能障的結果和實驗觀察到釋放的動能近似統計分佈的結果相吻合。相反地，我們由 2,2 二氯丙烷的同現質譜中並沒有觀測到 2,2 二氯丙烷離子，而且 2,2 二氯丙烷離子解離形成 $CH_3CClCH_3^+ + Cl$ 釋放出大量的動能，搭配我們使用理論計算 2,2 二氯丙烷離子解離形成 $CH_3CClCH_3^+ + Cl$ 所需的能障 10.74 eV (G3B3) 比實驗觀測到的游離能 10.78 eV 低，推測 2,2 二氯丙烷被光游離後，由於結構不穩定，馬上就碎裂掉 Cl 並且釋放出大量的動能。結合同現實驗和 G3B3 理論計算的結果，我們討論 1,3 二氯丙烷離子和 2,2 二氯丙烷離子的解離產物與釋放動能的差異性和可能的解離機制。

Dissociation of energy-selected $C_3H_6Cl_2^+$ isomers : threshold photoelectron
photoion coincidence experiments and quantum-chemical calculations

Student : Chih-Shiang Wang

Advisor : Dr. Su-Yu Chiang

Institute of Applied Chemistry
National Chiao Tung University

ABSTRACT

The dissociative photoionization of 1,3- $C_3H_6Cl_2$ and 2,2- $C_3H_6Cl_2$ were investigated with threshold photoelectron-photoion coincidence (TPEPICO) technique and theoretical calculations. For 1,3- $C_3H_6Cl_2$, fragment ions $C_3H_5Cl^+$ and $C_3H_5^+$ were observed in the coincidence spectra in a region 10.8–12.0 eV; their appearance energies ≤ 10.79 and 11.77 ± 0.03 eV agree with the predicted G3B3 reaction energies 10.62 and 11.77 eV for formation of $c-C_3H_5Cl^+ + HCl$ and $CH_2CHCH_2^+ + HCl + Cl$, respectively. A predicted dissociation mechanism from 1,3- $C_3H_6Cl_2^+$ ($6, C_1$) via a five-membered ring transition state for formation $c-C_3H_5Cl^+ + HCl$ supports an observation of a statistical energy distribution upon dissociation. In contrast, 2,2- $C_3H_6Cl_2^+$ was absent and dissociation of 2,2- $C_3H_6Cl_2^+$ to form $CH_3CClCH_3^+ + Cl$ with substantial releases of kinetic energies was observed. A predicted G3B3 reaction energy 10.74 eV for formation of $CH_3CClCH_3^+ + Cl$ smaller than the ionization energy 10.78 eV for 2,2- $C_3H_6Cl_2$ and lack of parent ion 2,2- $C_3H_6Cl_2^+$ is probably due to an unstable 2,2- $C_3H_6Cl_2^+$ which dissociates into $CH_3CClCH_3^+ + Cl$ with large kinetic energies released. We discuss the differences in the dissociation products and releases of kinetic energies upon dissociation between 1,3- $C_3H_6Cl_2^+$ and 2,2- $C_3H_6Cl_2^+$ based on experimental results and G3B3 calculations