

“Gas Phase Ion Thermochemistry through Imaging Photoelectron Photoion Coincidence Mass Spectrometry”

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Impact

Having the opportunity to conduct research with undergraduate students in a small liberal arts college setting is an enjoyable and rewarding experience that I highly value as a teacher and mentor. To have the ability to do this work, in part, at a world class research facility in another country has a lasting impact on my research students. With the funding from the American Chemical Society Petroleum Research Fund, five Hiram College undergraduates have traveled to the Paul Scherrer Institute to conduct experiments at the vacuum ultraviolet beamline (VUV) of the Swiss Light Source (SLS) this year. Four other students have been financially supported for 10-week summer research programs at Hiram College. The students who have been supported by this grant have continued their education in numerous graduate programs in the areas of physical chemistry, polymer chemistry, and organic chemistry. Several others have transitioned from academia to research positions in numerous industries. Students are introduced to data collection methods, numerical analysis, and computational methods that they are not exposed to in the classroom.

One of the most important aspects of the project is that students spend about one week working at the lab in Switzerland. For almost all students supported by this grant, it is the first time they have travelled abroad. I believe this type of experience is a critical component in their education and adds a significant component to their liberal arts education. Students are also able to routinely present our work at regional, national and international meetings.

The grant has had a very significant impact on my career as a teacher and advisor. The financial support has allowed me to incorporate computational chemistry into the physical chemistry the department curriculum. Our lab is currently planning a collaborative project, with two other Hiram College chemistry faculty, which will integrate this work into the general, organic and inorganic curriculum within our Chemistry program.

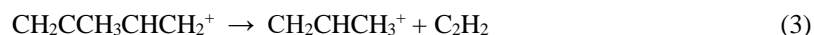
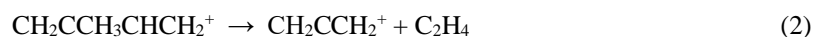
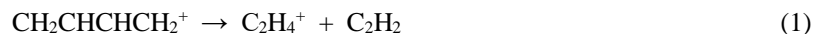
The Experiment

The double imaging photoelectron photoion coincidence (*i*²PEPICO) apparatus at the vacuum ultraviolet (VUV) beamline of the Swiss Light Source (SLS), with close to 1 meV energy resolution, the ability to suppress hot electrons, the capability to image electrons and ions, and the available software for modeling complex dissociation reactions is ideally suited for the obtaining accurate thermochemistry for gas phase species. This experiment generates energy selected ions by measuring the ions in coincidence with zero energy electrons. The electrons and ions provide the start and stop signals, respectively to generate an ion time of flight spectrum, from which we obtain dynamical information such as dissociation rates and energies for fragmentation products. Over this reporting period we have published our results on Cr(CO)₆ and are in the process of finalizing the manuscript on a series of methylbutanes. Our group recently conducted experiments at the SLS on a series of dienes including butadiene, isoprene, 2,3-dimethyl 1,3-butadiene, 1,3-pentadiene and 2,4-hexadiene. Preliminary and published results are described below.

Research Progress***Butadiene Series***

Numerous cationic unimolecular dissociation reactions proceed to products without a reverse barrier and resulting investigations using the *i*²PEPICO technique have produced some of the most accurate thermochemical data available to date. However, some fragmentation reactions involve rearrangements of the molecular structure during the course of fragmentation. Recent examples of such reactions are HCl loss in ethylchloride and CH₄ loss in acetone. One of our aims in this project is to continue our investigation in these reactions to test the application of current statistical theories in current modeling capabilities in more complex systems than previously studied. The butadiene series studied recently at the SLS will allow us to further test and develop theories related to hydrogen transfer reactions and obtain new, accurate thermochemistry for a variety of neutral and ionic species.

Dissociative photoionization processes in both butadiene (1) and isoprene (2,3) involve the loss of a closed-shell alkene or alkyl as illustrated below.



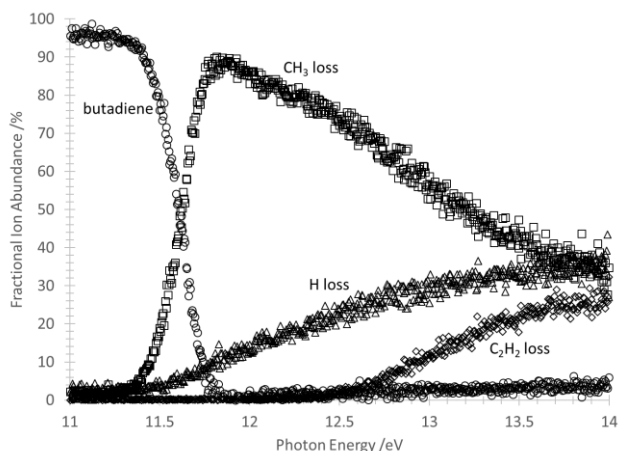
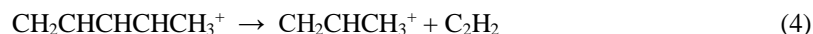


Figure 1: Breakdown curve of butadiene from 11 - 14 eV. The open circles are butadiene, the squares are the methyl loss reaction, the triangles are the hydrogen loss reaction and the diamonds are the hydrogen transfer reaction leading to the loss of acetylene.

hydrogen transfer yielding the propene radical cation and acetylene. Because the heats of formation of propene and acetylene and the ionization energy of propene are well known, the thermochemistry obtained from this ion cycle can be compared to that of the reactions involving simple bond cleavage. These results allow us to determine ion energetics and thermochemistry in two ways which provides a unique opportunity to assess the 1-D model in ionic reactions.



Chromium hexacarbonyl, $\text{Cr}(\text{CO})_6$ – published in *Int. Jour. Mass Spec.* 2019 438: 63-71

The fragmentation processes of internal energy selected chromium hexacarbonyl cations, $\text{Cr}(\text{CO})_6^+$, were investigated by imaging photoelectron photoion coincidence (iPEPICO) spectroscopy at the vacuum ultraviolet (VUV) beamline of the Swiss Light Source (SLS). In the 9.3 to 21.5 eV photon energy range, $\text{Cr}(\text{CO})_6^+$ dissociates by six sequential carbonyl ligand losses. The fragment ion fractional abundances along with the time-of-flight mass spectra for the first three metastable CO-loss channels were modeled using a statistical approach. Between 12 and 16 eV, the statistical model overestimates the degree of fragmentation, which is explained by enhanced kinetic energy release in impulsive CO loss on repulsive electronic states of the parent ion $\text{Cr}(\text{CO})_6^+$, as confirmed by TD-DFT calculations. This is the first reported example for an embedded non-statistical unimolecular dissociation regime, bracketed by statistical regimes at low and at high energies. The statistical model was employed to derive 0 K appearance energies for $\text{Cr}(\text{CO})_n^+$ ($n = 0-5$). The measured Cr–CO bond dissociation energies in $[(\text{CO})_n\text{Cr}-\text{CO}]^+$ ($n = 0-5$), and the enthalpies of formation of the chromium carbonyl ion series were also determined.

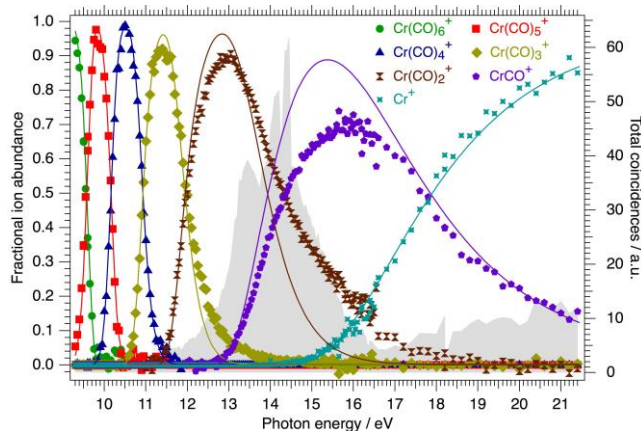


Figure 2: Breakdown curve of chromium hexacarbonyl showing six consecutive CO loss reactions from 9.3 – 21.5 eV.

Conclusions

Our lab has continued to make progress on determining accurate thermochemical and kinetic quantities for neutral and ionic species in the gas phase using the i²PEPICO apparatus at the VUV beamline of the SLS. Undergraduate students have an active role in the collection and analysis of the data.