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**Threshold Photoelectron Photoion Coincidence (TPEPICO) Studies:
The Road to ± 0.1 kJ/mol Thermochemistry**

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Program Scope

The threshold photoelectron photoion coincidence (TPEPICO) technique is utilized to investigate the dissociation dynamics and thermochemistry of energy selected medium to large organic molecular ions. The reactions include parallel and consecutive steps that are modeled with the statistical theory in order to extract dissociation onsets for multiple dissociation paths. These studies are carried out with the aid of molecular orbital calculations of both ions and the transition states connecting the ion structure to their products. The results of these investigations yield accurate heats of formation of ions, free radicals, and stable molecules. In addition, they provide information about the potential energy surface that governs the dissociation process. Isomerization reactions prior to dissociation are readily inferred from the TPEPICO data.

The Laboratory Based TPEPICO Experiment

The threshold photoelectron photoion coincidence (TPEPICO) experiment built with DOE funds in the 1970's and continuously modified and improved in Chapel Hill was sold to Prof. Balint Sztaray at the University of the Pacific in 2011, upon the retirement of the PI in the summer of 2011. (It continues to produce excellent data there, and has been further improved by the replacement of its data collection system.

One of the chief accomplishments of the PI during the past 10 years has been the construction of an imaging PEPICO (iPEPICO) experiment at the Swiss synchrotron light source (SLS), where a former post doc, Andras Bodi, is now the beamline scientist in charge of the VUV beamline. This user facility is state of the art and unequalled in signal strength, and energy resolution (1 meV). It has attracted users from around the globe, including some DOE supported groups in the USA. Because of the high photon flux, we have implemented the first multi-start multi-stop coincidence scheme using a master clock as the time base. Nearly all of the PI's publications since 2010 have been based on data collected at this facility.

Major Accomplishments and Recent Results

Discovery of barriers to H loss in simple ionic dissociation reactions.

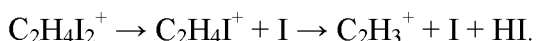
In the last progress report, we highlighted the observation of a barrier to H loss from the formic acid ion. These results were published in collaboration with a DOE supported theorist, John Stanton, of the University of Texas. Such barriers had not been observed before in part because they are not large, but more importantly because no experiments were sufficiently precise to measure them. In addition, they were not expected because the strong ion-neutral interaction

potential between the ion and the neutral leaving group results in barrier-less dissociations for all simply hemolytic bond breaking steps in ionic reactions. The barrier was discovered through the use of both normal and deuterated formic acid samples, whose isotope effect clearly indicated a barrier. In addition, data collected at the Swiss Light Source synchrotron demonstrated that this dissociation was slow (in the microsecond time scale), which was consistent with a mechanism that involved tunneling through a barrier. High level QM calculations by Stanton confirmed that even though the $\text{H} \cdots \text{C}(\text{O})\text{OH}^+$ dissociation involved simple H-C bond break, the geometry change in the remaining HOCO^+ ion was sufficiently large to involve a barrier of about 15 kJ/mol, which matched precisely the experimental barrier derived by assuming an Eckart barrier.

More recently, we investigated another H loss reaction, this time from the ethanol ion, $\text{CH}_3\text{CH}_2\text{OH}^+$, which loses the H atom exclusively from the CH_2 group. This was established by the use of multiply deuterated ethanol samples, including $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CD}_3\text{CH}_2\text{OH}$, $\text{CH}_3\text{CD}_2\text{OH}$, $\text{CH}_3\text{CH}_2\text{OD}$, and $\text{CD}_3\text{CD}_2\text{OH}$. The data were collected by a UNC undergraduate student, Daniel Brannock, who carried out measurements, first at the University of the Pacific (where our old laboratory based experiment is running) as well as at the Swiss Light Source. The results were published by Andras Bodi, M. Daniel Brannock, Balint Sztaray, and Tomas Baer, Tunneling in H loss from energy selected ethanol ions, *Phys.Chem.Chem.Phys.*, 14 16047-16054 (2012). As with the formic acid, these data also showed that this simple H-C bond break is associated with a substantial barrier of 150 meV (14 kJ/mol), which causes the dissociation at threshold to be slow due to tunneling.

Dimensionality of translational energy release in the dissociation of polyatomic ions.

Threshold photoelectron photoion coincidence (TPEPICO) has been used to study the sequential photodissociation reaction of internal energy selected 1,2-diiodoethane cations:



In the first I-loss reaction, the excess energy is partitioned between the internal energy of the fragment ion $\text{C}_2\text{H}_4\text{I}^+$ and the translational energy. The breakdown diagram of $\text{C}_2\text{H}_4\text{I}^+$ to C_2H_3^+ , i.e., the fractional ion abundances below and above the second dissociation barrier as a function of the photon energy, yields the internal energy distribution of the first daughter, whereas the time-of-flight peak widths yield the released translational energy in the laboratory frame directly. Both methods indicate that the kinetic energy release in the I-loss step is inconsistent with the phase space theory (PST) predicted two translational degrees of freedom, but is well-described assuming only one translational degree of freedom. Reaction path calculations partly confirm this and show that the reaction coordinate changes character in the dissociation, and it is, thus, highly anisotropic. For comparison, data for the dissociative photoionization of 1,3-diiodopropane are also presented and discussed. Here, the reaction coordinate is expected to be more isotropic, and indeed the two degrees of freedom assumption holds. Characterizing kinetic energy release distributions beyond PST is crucial in deriving accurate dissociative photoionization onset energies in sequential reactions. On the basis of both experimental and theoretical grounds, we also suggest a significant revision of the 298 K heat of formation of 1,2- $\text{C}_2\text{H}_4\text{I}_2(\text{g})$ to 64.5 ± 2.5 kJ mol⁻¹ and that of $\text{CH}_2\text{I}_2(\text{g})$ to 113.5 ± 2 kJ mol⁻¹ at 298 K.

This work was carried out in both Chapel Hill and at the Swiss Light Source. It was published by: Tomas Baer, S. Hunter Walker, Nicholas S. Shuman, and Andras Bodi, One- and two-

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