UNIMOLECULAR REACTION DYNAMICS OF WELL CHARACTERIZED IONIC REACTIONS

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FINAL REPORT

SUMMARY OF RESULTS FROM 1993-1997

The dissociation dynamics of well characterized and energy selected ions have been investigated by photoelectron photoion coincidence (PEPICO) spectrometry. A number of ions have been found which dissociate in competition with isomerization and which thus lead to multi-component decay rates. The dissociation dynamics on such complex potential energy surfaces are common for many free radical reactions, including some of importance to combustion processes. Individual reaction rates for isomerization and dissociation have been extracted from the data. In addition, all rates have been successfully modeled with the RRKM theory in combination with *ab initio* molecular orbital calculations. The dissociation dynamics of a dimer ion system has been studied on the UNC PEPICO apparatus as well as at the Chemical Dynamics Beam line of the ALS. This proof of principle experiment shows that it is possible to investigate such systems and to determine the heats of formation of free radicals by this approach. Finally, a dissociation involving a loose transition state with no exit barrier has been successfully modeled with a simplified version of the variational transition state theory (VTST). The aim of all of these studies is to develop protocols for modeling moderately complex unimolecular reactions with simple models.

The PEPICO Experiment

The photoelectron photoion coincidence experiment is a method for energy selecting ions and investigating their subsequent unimolecular or bimolecular reaction rates.¹⁻³ Ions are energy selected by collecting them in coincidence with energy selected electrons (in practice zero energy electrons). A seeded and skimmed molecular sample beam is ionized by vacuum UV radiation generated by a continuous hydrogen discharge lamp and dispersed by a 1 meter monochromator. At the Advance Light Source, the experiment is the same, except that the light is produced by an undulator and dispersed with a 6 m monochromator.⁴ As shown in Figure 1, ions and electrons are extracted in opposite directions by a small electric field (10-20 V/cm). The electrons are energy selected by a combination of a steradiancy analyzer⁵⁻⁷ and a hemispherical energy analyzer. The ions are accelerated by a two stage acceleration field with a 25 cm drift region. At the end of the drift region, it is possible to slow or speed up the ions in order to distinguish ions that have decayed in the drift region. The electrons and ions provide the start and stop inputs to a time to pulse height converter whose output goes to a 4096 channel multichannel pulse height

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analyzer. The resolution is typically 2.5 ns/channel. This is sufficient for the narrowest peaks of parent ions which have a width, for the case of m/z 28 ions, of 12 ns full width at half maximum.

Figure 1 TPEPICO apparatus at UNC. A cw H_2 discharge lamp dispersed by a 1 m monochromator provides the source of photons.

The experimental data consist of ion time of flight (TOF) distributions. These contain a wealth of information. For instance, if a molecule in the molecular beam is ionized without dissociating, it will appear as a very narrow parent ion peak. If that same ion is formed from the background gas in the chamber, the peak will be broad and have a width characteristic of the 298 K Maxwell Boltzmann distribution. Thus it is simple to distinguish the 20% of the peak that is due to background gas,⁸ and thus to subtract its contribution from the data. In a similar manner, product ion peaks can be distinguished from parent ion peaks because the former are broadened due to the release of translational energy in the dissociation process. This is particularly important in the analysis of dimer ions which can be produced from the photoionization of the dimer and from dissociative photoionization of trimers.⁹⁻¹²

A critical part of the data analysis is the determination of the internal energy content of molecules in the molecular beam. Even though they are translationally (and probably rotationally) cold they need not be vibrationally cold. By measuring the shift in the observed dissociation onset for room temperature and molecular beam sample, we determine directly the amount of internal energy removed in the molecular beam.¹³ In general, we have found that the cooling of the vibrational modes of molecules in cw molecular beams is not complete. Typical vibrational temperatures achieved are about 200 K.¹⁴ In some cases, complete cooling has been noted.^{13,15}

Isomerization and Dissociation in Competition

Most dissociation reactions so far studied (ionic and neutral) exhibit single exponential decay dynamics. This is the case if the dissociation proceeds from a single well in the potential energy surface. Several isomeric structures may intervene, but if the barriers to isomerization are low compared to the barrier for dissociation, all the isomers are in equilibrium so that the ensemble of wells acts as a single well. However, if the barriers are large and the second well is deep, then reaction proceeds via separate rates from the two wells, and the resulting decay rate will exhibit two-component decay. Each additional well adds another component to the decay

rate. Such wells are common among free radical decomposition or in hydrocarbon flame mechanisms. For instance, the addition of acetylene to $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}\cdot$ yields chemically activated $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}\cdot$, which isomerizes to cyclohexadienyl before decomposing to benzene and $\text{H}\cdot$.¹⁶ whose energies are within 15 kcal/mol. The reason is that there are often a number of low energy wells [e.g. the free radical $\text{C}_3\text{H}_3\text{O}$ has several isomers ($\text{CH}_2\text{CHC}=\text{O}\cdot$, $\text{CH}_3\text{C}=\text{C}=\text{O}\cdot$, and $\text{CH}_2=\text{CCH}=\text{O}\cdot$) that are within 15 kcal/mol.].¹⁷ In addition, isomerization barriers in free radicals tend to be lower than they are in closed shell species.

The butadiene ion dissociation

The butadiene ion at low energies dissociates by the loss of CH_3 and the formation of cyclopropenyl cation $\text{c-C}_3\text{H}_3^+$. Although this reaction is not a simple bond cleavage reaction and involves the participation of a high energy well, the dissociation dynamics can nevertheless be successfully modeled with a single exponential decay.

Figure 2 shows some of the product C_3H_3^+ ion TOF distributions and their fit to a single exponential decay. The mechanism for this reaction was determined with the aid of *ab initio* MO calculations (MP2/UHF6-31G* level) and RRKM statistical theory fit to the measured decay rates. A full analysis was only possible by taking into account the thermal energy distribution of the butadiene ions at 200 K (the molecular beam vibrational temperature). This paper has been accepted for publication in the Journal of Physical Chemistry.¹⁸

Figure 2. C_3H_3^+ product ion TOF distribution (points) with a single exponential fit (solid line).

The pentene ion dissociation¹⁹

Figures 3 shows the TOF distribution for various isomers of $\text{C}_5\text{H}_{10}^+$ ions at the same total energy above the dissociation limit for production of C_3H_6^+ and C_4H_7^+ ions. Immediately apparent is the two-component decays of the cyclopentane and 1-pentene ions. The sharp fragment ion peaks is a result of a fast dissociation, while the broad asymmetric peaks to the right are due to the slow rate. The slow decay rate is the same for all the isomers. The other interesting aspect is that the 6 isomers investigated fall into 3 groups. The cyclopentane and 1-pentene isomers have identical TOF distributions, the 2-pentene ion is in a group by itself which has much reduced fast components, while all the branched isomers dissociate only with slow rate constants.

Figure 4 shows a potential energy surface which is consistent with the TOF distributions of Figure 3 and also makes chemical sense. That is, the C_4H_7^+ product ions can only be produced from the 2-pentene ion structure while the ethylene loss channel must go through the 1-pentene ion well. By solving the five differential equations for the three isomers and two products, it is possible to obtain an expression for the slowest of the three dissociation rates. The two fast decay rates are both faster than we can measure. The slow rate constant is given by:

$$k_{slow} = \frac{1}{2}(k_3f + k_4 + k_5 + k_6) - \frac{1}{2}\sqrt{(k_3f + k_4 + k_5 + k_6)^2 - 4k_5k_6 - 4k_3k_5f} \quad (1)$$

where $f = k_1/(k_1 + k_2)$. In addition to the slow rate constant, which we can measure, there are three

Figure 3 Product ion TOF distributions for various $C_5H_{10}^+$ isomers.

Figure 4. A 3-well Potential energy surface for the dissociation of $C_5H_{10}^+$ isomers.

expressions for ratios of rate constants which can be equated to ratios of peak areas (e.g. fast C_2H_4 loss from 2-pentene ion to total area). Finally, the ratios of k_2/k_3 and k_4/k_5 can be expressed in terms of ratios of density of states of the wells A and B, and B and C, respectively. Since the energies of the three pentene isomers are known experimentally, and the vibrational frequencies are determined by *ab initio* MO calculations, it is possible to determine these densities of states with considerable accuracy.

Figure 5. Measured rate constants for the two dissociation and four isomerization rates. The solid lines are RRKM calculated rates with *ab initio* vibrational frequencies. The six adjustable parameters for the RRKM calculations were the isomerization TS energies and frequencies and the dissociation TS frequencies.

We have then a total of 6 data points for the 6 rate constants and can thus **determine from the data all six rate constants**. These experimentally determined rate constants are shown in Figure 5. The solid lines are calculated RRKM rate constants in which only 6 parameters were varied. Generally, a total of two parameters (E_0 and $\Delta S^\ddagger$) are needed for each $k(E)$ plot. Since we obtained k_2 in terms of k_3 and k_4 in terms of k_5 , a total of four $k(E)$ curves were modeled with six variable parameters. The excellent fit shows that the potential energy surface is qualitatively correct. An important point is that all this was done with relatively modest calculational efforts.

It is rather unusual that a reaction system provides this much information. For example, consider the fast component peaks for the 2-pentene in Figure 3. If the ISO_{BC} barrier in Figure 4 had been just slightly lower, k_4 would have been much larger than k_6 so that the fast component would not have been evident.

Other multi-component decay reactions

Since discovering the pentene ion dissociation, we have found five other reactions that proceed via two or more component decay rates. The results and analysis of the dissociation of trimethyl borate ions has already been published.²⁰ In this case, both the slow and the fast decay rates were sufficiently slow to be measurable. Again, all six decay rates were obtained and modeled with the RRKM statistical theory.

Other reactions that exhibit multi-component decay are a series of $\text{C}_3\text{H}_6\text{O}_2$ organic esters and their isomers, including methyl acetate,²⁰ ethyl formate, and acetol. The methyl acetate data are fully analyzed and a paper has been submitted. In this case, we have only three experimental observables and six isomerization and dissociation rate constants. As a result, it was not possible to determine the rate constants experimentally. However, the combination of *ab initio* MO calculations from which we obtain the vibrational frequencies, and RRKM calculations established limits on isomerization barriers and energies of stable isomers.

Figure 6. The TOF distributions of three $\text{C}_3\text{H}_6\text{O}_2^+$ isomers. The two-component dissociation rates are a result of competition between dissociation and isomerization to a lower energy structure.

Some sample data for ethyl formate, acetol, and methyl acetate are shown in Figure 6. It is interesting that these three ions produce completely different products. Not unexpectedly, the acetol ion ($\text{CH}_3\text{COCH}_2\text{OH}$) loses $\text{CH}_2\text{OH}\cdot$ via a fast rate, whereas the methyl acetate ion loses mostly $\text{CH}_3\text{O}\cdot$ via both fast and slow rates. Among other channels, the ethyl formate ion loses H_2O , a reaction it has in common with ethyl acetate. The dissociation rates of acetol ions will be difficult to determine just from the experimental results because we have only two experimental parameters, the slow rate constant associated with $\text{CHO}\cdot$ loss, and the ratio of $\text{CH}_2\text{OH}\cdot$ to $\text{CHO}\cdot$ loss. On the other hand, the ethyl formate ion dissociation looks very promising. We will have nearly sufficient information to determine the rate constants for the following mechanism:

Here, we have four experimental observables: k_{slow} , fast HCOOH loss area/ Total area; slow HCOOH loss area/total slow area; and slow H_2O loss area/total slow area. Thus with just one RRKM calculation of one of the rates, we will be able to extract all five rate constants. This work will begin within the next month.

The dissociation of a cluster ion

A major portion of the previous proposal was devoted to the determination of free radical heats of formation through the dissociative ionization of dimers. The basic idea involves the following reaction:

If A were isopropyl alcohol and BH were ethylene, then the products would be $\text{I-C}_3\text{H}_7\text{OH}_2^+ + \text{C}_2\text{H}_3\cdot$. Since the heat of formation of protonated isopropyl alcohol is known,^{21,22} the heat of formation of the $\text{C}_2\text{H}_3\cdot$ radical can be determined. These reactions tend to proceed with no reverse activation energy and thus can potentially yield accurate onsets. While the idea was good in principle, it has been difficult to execute for two reasons. In the case of H-bonded dimers such as $(\text{H}_2\text{O})_2$ the ions are difficult to produce as stable dimer ions because the dissociative ionization of the trimer ions or protonated dimer ions dominate the signal. Evidently, the Franck-Condon factors for producing the dimer ion are very small due to the very different neutral and ion geometries. In the case of non-H-bonded systems and heteroclusters such as (cyclopentanone-isopentane) it has been difficult to observe any cluster signal under our relatively mild expansion conditions. A solution for these problems will be discussed in the proposed research section.

Two systems that did work so far are the methanol and dimethylamine systems:

The methanol work did not really lead to any new conclusions and so we have not published this. However, the diethylamine results have been accepted for publication by the Journal of Physical Chemistry. Because the dimer ion well is so deep, the dissociation rates are in the 10^6 sec^{-1} range and could thus be measured by TPEPICO. The fragmentation rate constant data obtained from the experiment were modeled with variational RRKM theory using potential energies and vibrational frequencies from *ab initio* molecular orbital calculations at the MP2/6-31G* level. The results are consistent with the fragmentation of the diethylamine dimer ion into protonated diethylamine and the $\cdot\text{CH}_2\text{N}(\text{H})\text{CH}_3$ radical. This was supported by *ab initio* calculations in which the dimer ion was found to consist of a N-H-C hydrogen bonded complex between the above two products (see Figure 7). Our calculated structure for the neutral dimer

Figure 7. Calculated Structures for the neutral and ionic dimers of dimethyl amine. These structures were optimized with an MP2/6-31G* basis set.

agreed very well with a recent microwave study for this dimer.²³ The RRKM/VTST fit to the experimental $k(E)$ vs E data for the ion gave a dimethylamine dimer ion $\Delta_f H^\circ_0$ of $655 \pm 11 \text{ kJ mol}^{-1}$ and thus a dimer ion binding energy of $147 \pm 16 \text{ kJ mol}^{-1}$. The neutral dimethylamine dimer was calculated to be an N-H-N hydrogen bonded dimer with a 0K binding energy of 13 kJ mol^{-1} . The resulting neutral dimer adiabatic ionization energy is $6.8 \pm 0.2 \text{ eV}$. This is the first good value for this IP. A previous measurement of the PES yielded just a vertical IP of $8.3 \pm 0.15 \text{ eV}$.²⁴

Of particular interest is that the dissociation rate constants, $k(E)$ were modeled with the VTST²⁵⁻²⁷ because the dimer ion structure was an ion-radical complex which dissociated without a barrier to yield the protonated dimethyl amine. By calculating the vibrational frequencies as a function of the reaction coordinate, it was possible to fit the transitional vibrational frequencies to the following equation:

$$v^\ddagger(R) = v(R_{eq}) e^{-a(R-R_{eq})} \quad (5)$$

The "a" parameter in the exponential that best fit the calculated frequencies turned out to be $0.08 \text{ \AA}^{-1}$. This is considerably smaller than the usual values for this parameter which ranges between 1 and $2 \text{ \AA}^{-1}$ for neutral reactions such as the dissociation of ethane to two methyl radicals.²⁸ However, it is similar to one determined by Hase for the case of $\text{Li}^+ - \text{H}_2\text{O}$ dissociation

($0.10 \text{ \AA}^{-1}$).²⁹ This is an important result because if we can find values of a for various classes of reactions, it will be possible to carry out VTST calculations without the need for high level *ab initio* calculations. Clearly, ionic reactions have lower a values than neutral reactions because of the much longer range interactions due to the ion-induced dipole forces.

Other Studies

We have carried out other studies that will not be described in detail. These include measuring the vibrational temperature of molecules generated in a cw molecular beam and relating these temperatures to the backing gas pressure and nozzle temperature.¹⁴ The results could not be readily correlated with the standard Schwartz, Slawski, Herzfeld³⁰ theory of vibrational energy transfer in which the molecule's lowest vibrational frequency is assumed to be the dominant bottle neck. Instead, our results were more consistent with a model in which combinations of vibrations combined to transfer small chunks of energy from the vibrational manifold to the translational degrees of freedom, as proposed recently by Barker.³¹

Another study of some interest is the measurement of the ClSO^+ ion heat of formation.³² This was done by measuring the dissociative photoionization onset of Cl_2SO . By measuring the translational energy released as a function of the excess energy, it was possible to establish that the Cl loss reaction does not involve a reverse activation energy. Thus the onset can be used to establish, for the first time, a heat of formation of the ClSO^+ ion at both 0 and 298K.

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