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THE ENERGETICS AND DYNAMICS OF FREE RADICALS, IONS, AND CLUSTERS

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SUMMARY OF RESULTS FROM 1991-1993

The structure and energetics of free radicals, ions, and clusters have been investigated by photoelectron photoion coincidence (PEPICO) and analyzed with the aid of *ab initio* molecular orbital and statistical theory (RRKM) calculations. The two major themes are the quantitative analysis of unimolecular reactions with no adjustable parameters, and the study of cluster ion dissociation processes. Molecules (or free radicals) were prepared in a molecular beam so that they are translationally and vibrationally cold. The translational temperature was calculated from the measured time of flight (TOF) peak width, while the vibrational temperature was determined from the shift in the dissociation onset. Free radicals are produced by pyrolysis in the nozzle, and subsequent cooling of the free radicals is demonstrated. Ion dissociation rates in the range from 10^4 to 10^7 sec^{-1} are measured from the asymmetric TOF distribution. This method was used to measure the dissociation rates of a number of cold and warm ions, among them HCl (DCl) loss from $C_2H_5Cl^+$ ($C_2D_5Cl^+$), a reaction that proceeds via tunneling. The analysis of the butene ion dissociation provided information about the role of angular momentum in dissociation reactions. The dissociative ionization of ethylene clusters demonstrated that ethylene dimer ions rearranged to butene ions prior to dissociation. Finally, a new value for the t-butyl ion heat of formation, which corrects a 15 kJ/mol error in the previous value, was obtained from the 0 K breakdown diagram of t-butyl iodide.

The PEPICO Experiment

The photoelectron photoion coincidence experiment is a method for energy selecting ions and investigating their subsequent unimolecular or bi-molecular reaction rates. By collecting ions in coincidence with energy selected electrons (in practice zero energy electrons), ions are energy selected. A seeded and skimmed molecular sample beam is ionized by vacuum UV radiation generated by a continuous hydrogen discharge and dispersed by a 1 meter normal incidence monochromator. As shown in Figure 1, ions and electrons are extracted in opposite directions by a 20 V/cm field. The electrons gained 12 volts before they enter the threshold electron energy analyzer, which consists of a 10 cm field-free drift region terminated by a 3 mm diameter aperture concentric to the flight axis. While threshold electrons pass readily through this aperture, energetic electrons drift off-axis and are thus discriminated. A hemispherical electrostatic sector analyzer placed after the drift region serves to further discriminate against initially hot electrons as well as to reduce the signal of stray electrons. After traversing the first field region, the ions enter a second

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acceleration region with a 387 V/cm field and are detected after passing through a field free 25 cm drift region.

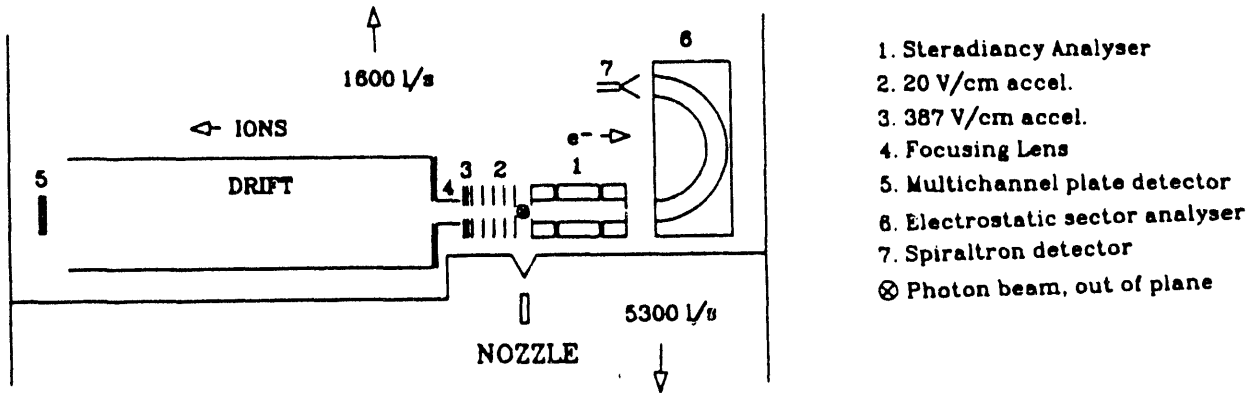

Figure 1. The molecular beam PEPICO apparatus. The drift tube is 25 cm long.

The electron and ion signals served as start and stop pulses for measuring the ion time of flight (TOF) spectra. Parent and daughter ions from rapidly dissociating parent ions have symmetric TOF distributions. However, parent ions which dissociate in the course of acceleration in the first acceleration region, result in daughter TOF distributions which are asymmetrically broadened. The dissociation rates are extracted from these TOF distributions.[1] Of equal interest is the extraction of the kinetic energy of the dissociating fragments. This energy release leads to a symmetric broadening of the TOF peak. The use of molecular beams results in extremely narrow TOF distributions so that as little as 3 meV of kinetic energy can be readily detected.

The analysis of broad and narrow TOF peaks

The new molecular beam chamber has been operating for about three years now. The valuable features in this experiment are the ability to produce vibrationally and translationally cold molecules whose temperatures can be readily determined by the PEPICO experiment.[2] The ability to distinguish "cold" and "warm" samples has permitted us to determine whether a given cluster ion was produced from the corresponding neutral cluster, or whether it was formed by dissociative ionization of a higher order cluster.

$$(AB)_n + h\nu \text{ ---> } (AB)_n^+ + e^- \quad (1)$$

$$(AB)_{n+m} + h\nu \text{ ---> } (AB)_n^+ + (AB)_m + e^- \quad (2)$$

The difference in the two processes is evident in the peak widths because a dissociative ionization event results in the release of translational energy which shows up as broadened TOF peak widths. Figures 2 through 4 show this very dramatically for several different clusters. In the case of acetylene, the monomer peak is exceedingly narrow, while the dimer and trimer peaks are broad with no hint of a narrow component.[3,4] In the case of methanol (with the MCA set to a much larger time per channel), we see a narrow methanol dimer ion peak and a much broader protonated methanol dimer ion peak.[3] The former is a result

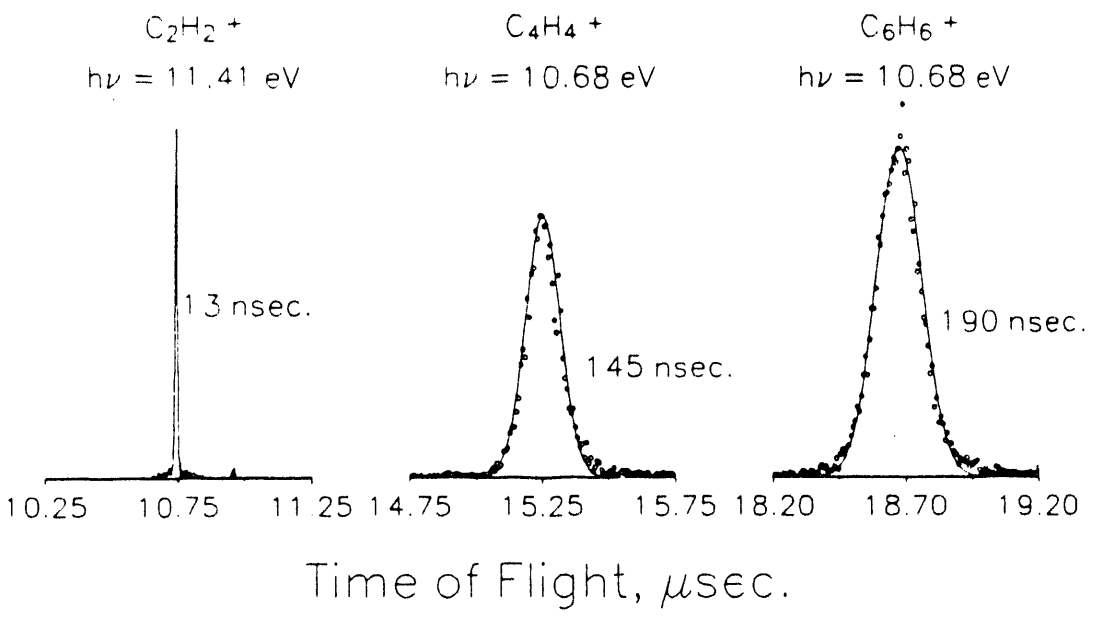

Figure 2. The PEPICO TOF distribution of acetylene (at its IP) and cluster ions produced at the indicated photon energies. The broad "dimer" and "trimer" ion peaks are a result of dissociative photoionization. At no pressure or photon energy were reproducible narrow components observed. Taken from reference 3.

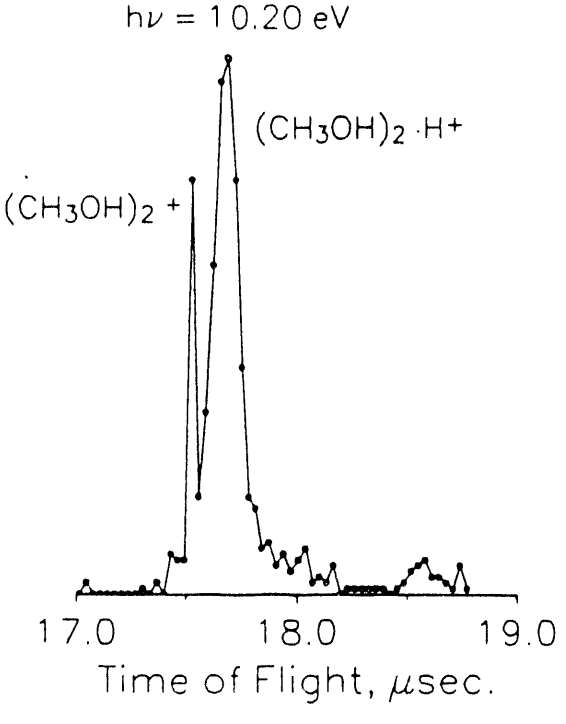

Figure 3. The PEPICO TOF distribution obtained from a seeded methanol beam. The narrow peak is due to photoionization of neutral methanol dimers. Taken from reference 3.

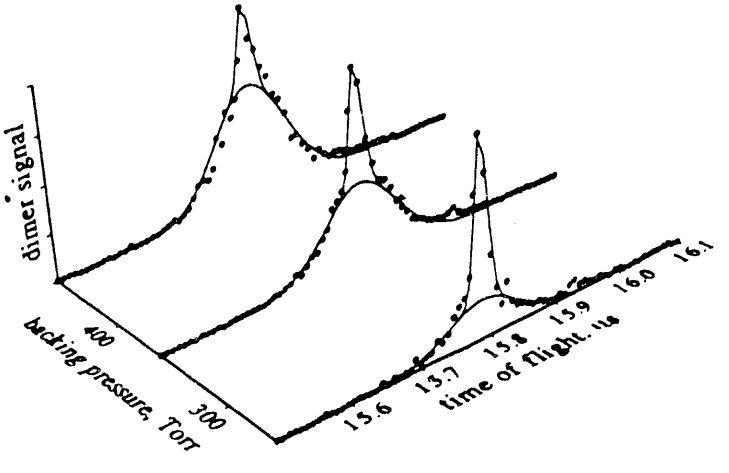

Figure 4. The PEPICO TOF distribution obtained with a seeded (10%) ethylene beam as a function of the total pressure. The narrow and broad peaks have widths of 17 and 125 ns, respectively. From reference 5.

of neutral dimer ionization, while the latter results from an internal proton transfer reaction upon dissociative ionization of a methanol trimer. In the case of the ethylene clusters, the narrow peak is again a result of neutral dimer ionization, while the broad peak results from dissociative ionization of trimers (or possibly higher order clusters). By changing the backing pressure, it is possible to vary the fraction of clusters in the beam and thus to suppress the higher order cluster reactions.[5] The important feature of our experiment is that the narrow TOF distribution provides a very clear signature of the non-dissociative photoionization process.

The dissociation dynamics of cold propanol ions

The propanol ion dissociation rates have been difficult to interpret in terms of simple RRKM theory because the low activation energy and the slow rates are incompatible with a simple statistical model. We have thus repeated previous experiments[6] with cold samples which permitted us to measure not only the H_2O loss rates but also the H loss rate.[7] In addition, we have carried out extensive *ab initio* molecular orbital calculations on the molecular ion and transition state structures and vibrational frequencies.[8] In the process, we discovered a much lower energy propanol ion structure in which the electron hole moves from the oxygen atom to the C-O sigma bond. This became evident only at the 6-32G**/MP2 level of calculations. With this lower energy structure, the activation energy increases so that standard RRKM analysis fits the measured rates rather well. These conclusions were tested by measuring and calculating the rates for deuterated samples as well. The latter calculation were done with no adjustable parameters and fit the data perfectly.

The dissociation dynamics of cold and warm butene ions

The butene ion dissociates at low energies to three products:

$$C_4H_8 + h\nu \quad \text{----->} \quad C_4H_7^+ + H \qquad (5)$$

$$\text{----->} \quad C_3H_5^+ + CH_3 \qquad (6)$$

$$\text{----->} \quad C_3H_4^+ + CH_4 \qquad (6)$$

Reactions 5 and 6 appear to be simple bond breaking reactions which should have no reverse activation barrier, while the loss of CH_4 requires an H atom transfer, whose transition state we have determined by *ab initio* calculations. Figure 5 shows the potential energy surface. We have measured the dissociation rates for all three channels (Figure 6) starting with both cold and warm butene molecules.[9] The former is rotationally cold, even when considerable vibrational energy is deposited into the ion by the photoionization process. On the other hand, the warm sample begins with its thermal distribution of rotational energy which remains largely intact upon ionization. The comparison of the warm and cold rates thus permit us to determine the effect of the rotational energy. Our modeling of these rates with variational transition state theory (VTST)[10-13] and normal RRKM[14] theory shows that the transition state is best described as the vibrator type and that the rotational effect is primarily associated with the barriers close in. This conclusion thus

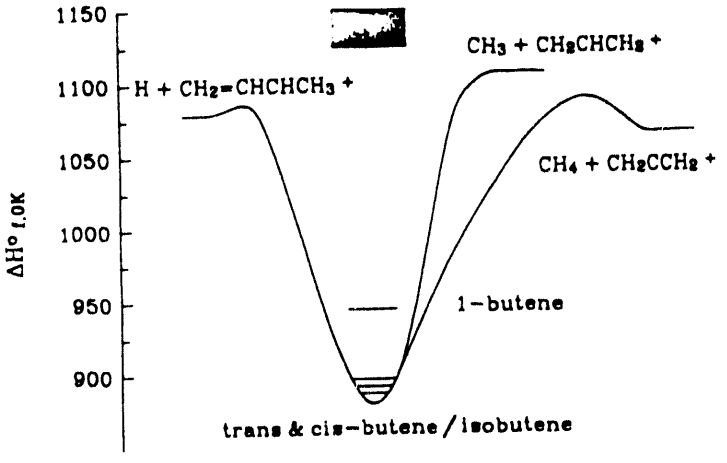

Figure 5: Potential energy diagram for the butene ion dissociation reactions. The energy is based on the 0 Kelvin heat of formation scale. The molecular ion well consists of several $C_4H_8^+$ isomers which contribute to the total density of states. Reverse barrier heights for the H and CH_4 loss channels are those obtained from the RRKM analysis of this study. The shaded region is the energy range in which rate data were collected. From reference 9.

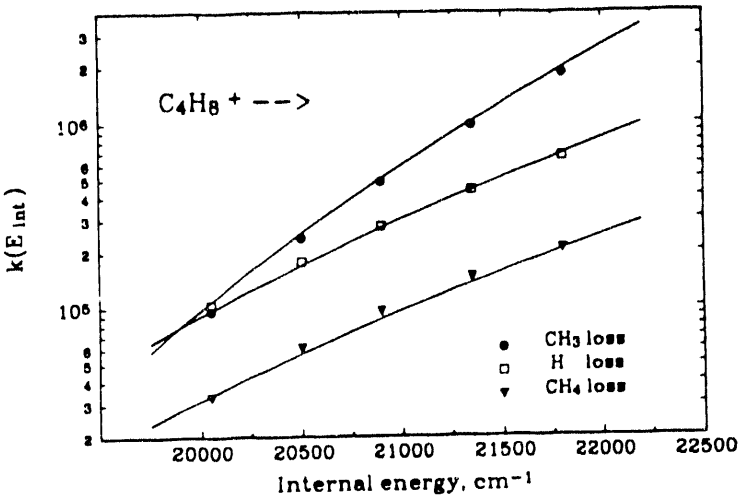

Figure 6: Microcanonical rate constats for the three dissociation channels of energy selected butene ions. The points are the experimentally measured rates, while the solid lines are the RRKM calculated rates using vibrational frequencies obtained from our *ab initio* calculations. The assumed activation energies for the H, CH_3, and CH_4 loss channels RRKM calculations were 16,220, 17,470, 16,890 cm^{-1} respectively. The CH_3 loss rate was obtained with the VTST. From reference 9.

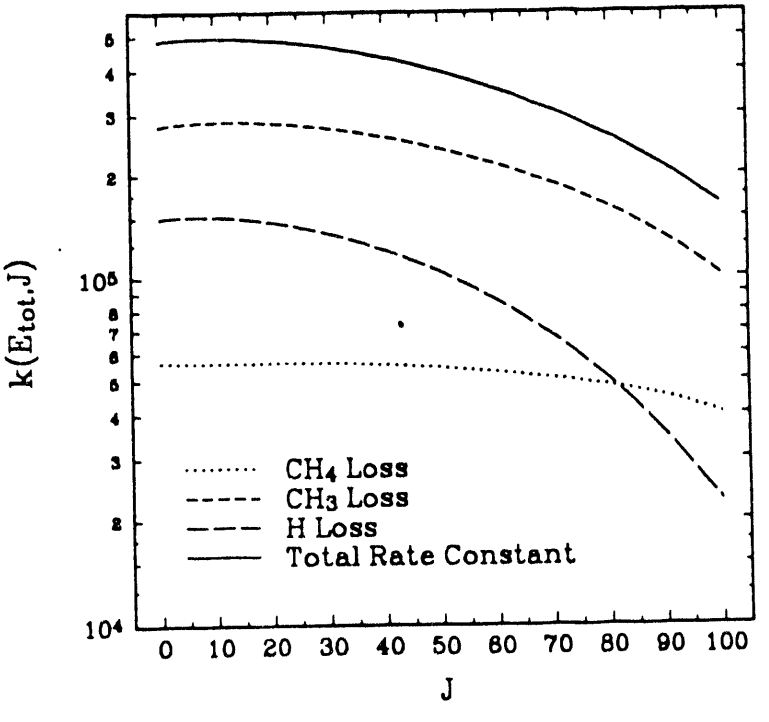

Figure 7: RRKM dissociation rate contants for a fixed rovibrational energy of E_{tot} = 21,000 cm^{-1} as a function of the rotational quantum number J. The transition state structures of all three channels are of the vibrator type from the analysis of the molecular beam data with J=0. Due to the large rotational constant of the H loss transition state, the rate constants for this channel fall off more sharply with J than the other two channels. Taken from reference 9.

contradicts earlier findings which suggested that the centrifugal barrier is the main bottle neck,[15-18] and supports the conclusion of Bowers and co-workers that the transition state has switched to the high energy limit.[19,20]

This finding has considerable practical significance. The practice of determining dissociation energies by RRKM modeling of the dissociation rates will give only an upper limit for reactions with no barriers. This is because the effective E_0 being located close in, is less than the dissociation energy. It is only through a variational treatment that the true dissociation energy can be found. In the case of our butene ion analysis, the effective E_0 was a full 11 kJ/mol below the dissociation limit. This is the first example of this effect for a system in which the dissociation limits are known. Previous analysis were on systems in which the dissociation limit is not known so that the variational (or transition state switching) analysis could not be independently confirmed. Among those studies are those of benzene [21] and butadiene. [20,22]

The role of angular momentum is shown in Figure 7 in which the rate for all three reactions are plotted as a function of J, while keeping the total energy (E_v+E_r) constant. The measured decrease of the rate could be modeled by taking into account the rotational energy at the transition state, which affects the activation energy. The assumptions about K-mixing had very little effect on the rates. The important conclusion here is that a thorough knowledge of the transition state structure is necessary to model rotational effects, and that the question of K-mixing is of secondary importance. We thus feel that previous conclusions about K-mixing in the benzene ion dissociation in which the transition state structure was completely ignored, are premature. [23,24]

The photoionization of ethylene dimers

Early photoionization studies of ethylene clusters suggested that these dimer ions dissociate by first rearranging to the butene ion structure.[25] However, that conclusion was based only on the similarity in the branching ratios for H, CH_3 and CH_4 loss between the $(C_2H_4)_2^+$ and the $C_4H_8^+$ systems. With our measured rates for the dissociation of cold butene ions, we were in an excellent position to test this hypothesis by measuring the rates of dimer ion dissociation. Because the rates are a strong function of the activation energy, it gives a direct measure of the well depth. In addition, new *ab initio* MO calculations on the ethylene dimer ion have provided valuable information about the shape of the potential energy surface and the barrier to isomerization.[26] Figure 8 shows the potential energy surface(s) for the ethylene trimers, dimers, and monomers.

The experimental TOF distributions of the dimer ion dissociation are shown in Figure 9.[5] These results were obtained with several backing pressures (see Figure 4) to insure that the reaction investigated was:

$$[C_2H_4]_2 + h\nu \longrightarrow (C_2H_4)_2^+ + e^-$$
$$\hookrightarrow \text{butene ion products}$$

and not sequential reactions from higher order clusters. The TOF distributions of Figure 9 are nearly indistinguishable from those of the butene ion. All three dissociation channels are evident in the same ratio.

The smooth lines through the data in Figure 9 are calculated TOF distributions using the measured butene ion rates and a calculated binding energy of the ethylene neutral

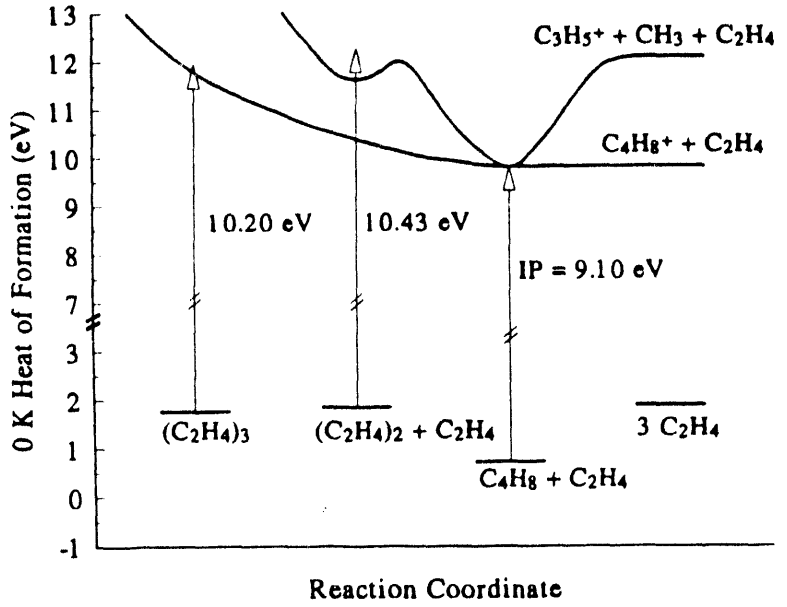

Figure 8. The potential energy diagram for the ethylene trimer, dimer, and monomer systems. The energy scale is absed on the 0 K heat of formation of 3 C_2H_4. The isomerization barrier is taken from reference 26 and the neutral dimer energy from reference 27. Figure taken from reference 5.

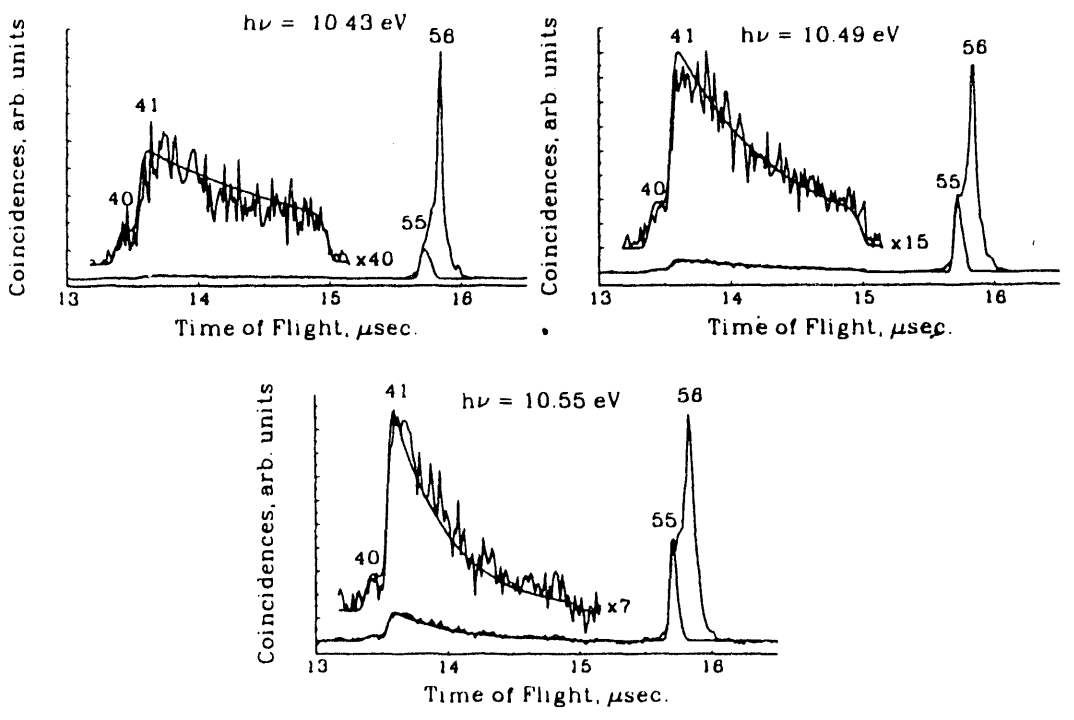

Figure 9. The PEPICO TOF distributions of the dimer ion dissociation products at three energies above the dissociation limits. The smooth lines are calculated TOF distributions in which the J=0 rate constants for the butene ion dissociation from reference 9 were used to fit the data. The excellent fit demonstrates that the dimer ion rearranges to the butene ion prior to dissociation. Taken from reference 5.

dimers of 374 cm^{-1}. The perfect fit not only demonstrates the isomerization of the dimer to the butene ion system, but also experimentally confirms the calculated neutral binding energy.[27]

The investigation of higher order clusters shows that the $(C_2H_4)_3$ trimer does not ionize to a trimer ion. All ionization leads to dissociation. Furthermore, the ethylene cluster ions dissociate by evaporating a single ethylene unit during which time the remaining ion is transformed into a stable ion. This means for the case of the trimer, the dissociative ionization product is the stable butene ion plus an ethylene monomer.

Dissociative ionization of acetylene clusters

Unlike the ethylene clusters, in which it was possible to prepare ethylene dimer ions from the ionization of neutral ethylene dimers, no narrow TOF peaks were found in the photoionization of acetylenc clusters (see Figure 2). This means that all acetylene clusters ionize exclusively by dissociative ionization. This results has been corroborated by our *ab initio* MO calculations which show that the trimer ion spontaneously dissociates by losing an acetylene monomer and forming a $C_4H_4^+$ ion.[4] Similarly, the tetramer neutrals ionized dissociatively to $C_6H_6^+ + C_2H_2$. Furthermore, on the basis of kinetic energy released, we showed conclusively that the ion did not have the benzene structure.

Determination of t-butyl ion heat of formation

In a recent paper,[28] we reported a new value [ΔH^o_{f0} = 734 kJ/mol] for the heat of formation of the t-butyl ion, obtained from the appearance energy of this ion from supersonically cooled t-butyl iodide. *ab initio* calculated vibrational frequencies of t-butyl iodide as well as the t-butyl radical, provided by Leo Radom, were used in the data analysis. The new value corrects a 15 kJ/mol error that has existed in the literature since 1979.[29,30] The proton affinity scale[31,32] now finally makes sense and experiments and *ab initio* calculations[33] finally agree. A new value for the t-butyl radical heat of formation [51.3 kJ/mol] also has been proposed during the past year.[34] Because of difficulties in measuring the adiabatic ionization potential, it is too early to say whether the two values are consistent.

Other Studies

As is evident from the list of publications, we have carried out many other studies during the past 3 years. Among the significant ones are paper # 99 in the list of publications in which we developed a method for measuring directly the average vibrational energy of molecules in a molecular beam. In paper # 103, we analyzed experimental rate data in terms of the tunneling corrected RRKM theory with an Eckart barrier. All vibrational frequencies of the ethyl chloride ion and the transition state were calculated by *ab initio* MO methods. In paper # 105, we measured for the first time the dissociation rate of an energy selected cluster ion. In paper # 116 we analyzed the measured rates of dimethylformamide dissociation with RRKM theory using molecular ion and transition state vibrational frequencies from *ab initio* calculations. The only adjustable parameter used was the energy of the transition state. Finally, in paper # 121 we present the results of a PEPICO free radical study in which our normal molecular beam nozzle was replaced with a quartz nozzle that was heated to 700 °C. Finally, several papers are being published jointly with colleagues in the US and in Europe

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