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The Energetics and Dynamics of Free Radicals, Ions, and Clusters

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

Tomas Baer, Principal Investigator
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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. Molecules (or free radicals) are prepared in a molecular beam so that they are translationally and vibrationally cold. The translational temperature is calculated from the measured time of flight (TOF) peak width, while the vibrational temperature is determined from the shift in the dissociation onset. Free radicals are produced by pyrolysis in the nozzle. 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 has been used to measure the dissociation rates of cold and warm butene ions. The analysis of this reaction has established the role of angular momentum in dissociation reactions.

Summary of Major Results:

The analysis of broad and narrow TOF peaks

The new molecular beam chamber has been operating for about two 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. The ability to distinguish "cold" and "warm" samples has permitted us to distinguish two types of processes. In one we can determine whether a given cluster ion was produced from the corresponding sized neutral cluster, or whether it was formed by dissociative ionization. That is:

$$(AB)_n + h\nu \dashrightarrow (AB)_n^+ + e^- \quad (1)$$

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

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. Figure 1 shows this very dramatically for the case of the methylchloride dimers where we see both processes taking place. Reactions (1) and (2) are associated with the narrow and broad peaks, respectively.

More recently, we have found that this same approach permits us to establish the parentage of ions in free radical studies. This is particularly important when dealing with pyrolysis products in which a mixture of free radicals, parent molecules, and other fragments are produced. Upon ionization, it is often difficult to determine whether a given ion comes from reaction 3 or 4.

$$A\cdot + h\nu \dashrightarrow A^+ + e^- \qquad (3)$$

$$AB + h\nu \dashrightarrow A^+ + B\cdot + e^- \qquad (4)$$

In these two reactions, the dot indicates a free radical. The corresponding ion is, of course a closed shell specie. The point is that the two processes can be distinguished on the basis of the TOF peak widths. Figure 2 shows the PEPICO mass spectrum obtained from the pyrolysis products of 1-propyl nitrite. The spectrum consists of numerous peaks, some of them narrow and some of them broad. We can thus readily distinguish the fragments obtained by direct ionization (reaction 3) from those formed by dissociative ionization (reaction 4). The various mass peaks are identified. Of particular interest is the observation of cold $C_2H_5^+$ signal which, because of its narrow TOF distribution, can be assigned to the direct ionization of cold $C_2H_5\cdot$ free radicals which were produced in the pyrolysis nozzle. This result also demonstrates that it is possible to cool free radicals in a supersonic expansion.

Mass 28 is an unknown species. It is not ethylene because at the photon energy of 10.2 eV, ethylene cannot be ionized. On the other hand, it could be H_2CN, CNH_2, or HCNH none of whose IP's are known, but are probably below 10.2 eV. It is interesting that the ionic heats of formation of the latter two are known, but the neutral IP's are not. Thus, a measurement of the IP would establish the neutral heat of formation. Among the other peaks in the mass spectrum of Figure 2 are several broad peaks, one of which is mass 59. We assign this to the alkoxide ion, $C_3H_7O^+$, which is formed predominantly by dissociative ionization of the parent propyl nitrite. A small narrow peak appears to be due to directly ionized alkoxy free radical. It is interesting that we can change the relative intensities of the various peaks by changing source conditions. This property will be utilized in further studies on this very rich system.

The dissociation dynamics of cold and warm butene ions

The butene ion dissociates at low energies to three products:

$$\dashrightarrow C_4H_7^+ + H \qquad (5)$$

$$C_4H_8 + h\nu \quad \dashrightarrow C_3H_5^+ + CH_3 \qquad (6)$$

$$\dashrightarrow C_3H_4^+ + CH_4 \qquad (6)$$

Reactions 5 and 6 appear to be simple bond breaking reactions which should have not reverse activation barrier, while the loss of CH_4 requires an H atom transfer, which we have largely confirmed via *ab initio* calculations. We have measured the dissociation rates for all three channels starting with both cold and warm butene molecules. 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) and normal RRKM 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 contradicts earlier findings which suggested that the centrifugal barrier is the main bottle neck. 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.

The ionization of ethylene dimers

In publication 113 we showed that acetylene dimer ions were produced exclusively from acetylene trimer neutrals by dissociative ionization. Similarly, the tetramer neutrals ionized dissociatively to $C_6H_6^+ + C_2H_2$. Furthermore, we showed conclusively that the ion did not have the benzene structure. The ethylene clusters behaved somewhat similarly, except that in this case, the dimer ion produced from the trimer neutral formed the butene ion structure. We established this in the following manner.

C_4H_8 (trans-butene) + $h\nu$ ----> $C_4H_8^+$ + e^- --> products

$[C_2H_4]_3$ + $h\nu$ ----> $C_4H_8^+$ + C_2H_4 + e^-
|
|-----> butene ion dissociation products

The $C_4H_8^+$ ions produced upon ionization of the ethylene clusters have precisely the same dissociation rates and branching ratios as the butene ions. This establishes that these ions isomerize, but only in a dissociative ionization process. From the measured ionic dissociation rates, we were able to determine the binding energy of the neutral dimers. The value of 300 cm^{-1} is the first experimental binding energy for the ethylene dimer.

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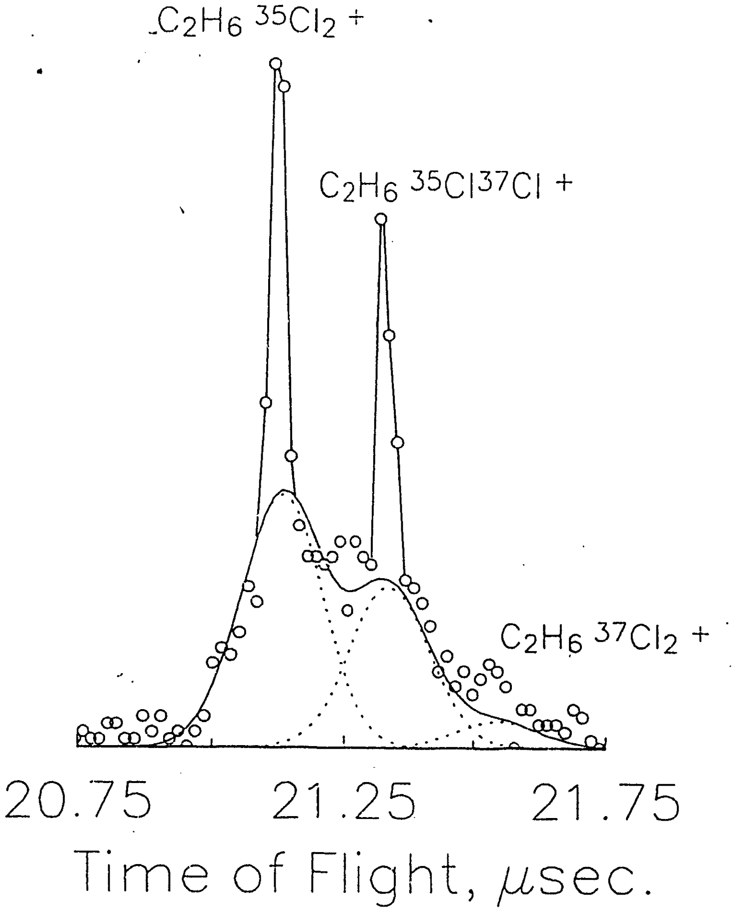

Fig. 1 PEPICO TOF distribution of methylchloride dimer ions. The sharp peaks arise from neutral dimers; the broad peaks from neutral trimers.

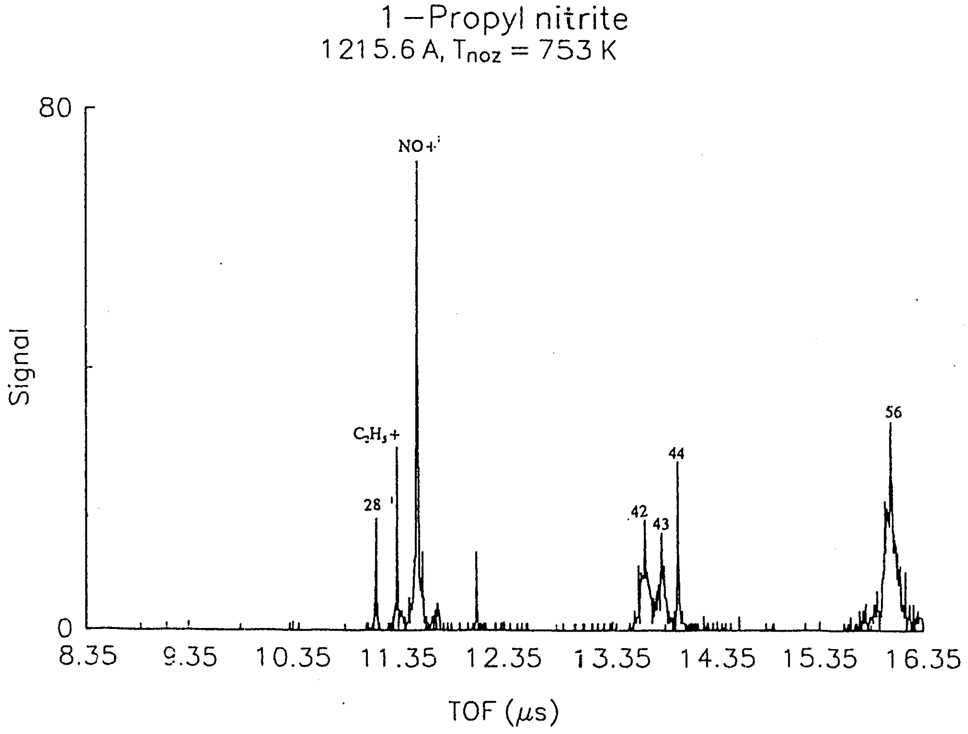

Fig. 2 PEPICO TOF distribution for pyrolysis products of 1-propyl nitrite.

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