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Time-Dependent Metastable Fragmentations. The H_2O Loss from Ethyl Acetate Ions

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Synopsis. The metastable transitions for $CH_3COOC_2H_5^+ \rightarrow C_4H_6O^+ + H_2O$ have been measured as a function of the ion lifetime of 0—200 μs by using trapped ion mass spectrometry (TIMS). The experimental data were well explained by tunneling corrections to the prior isomerization rate.

The H_2O loss from ionized ethyl acetate is the lowest energy process, only 0.3 eV higher than the ionization energy. This reaction has a strong metastable peak in a μs time-frame. The reaction mechanism for H_2O loss has been of much interest and has been studied by labeling experiments[1] and by means of the collisional activation spectra[2] for a daughter ion of $C_4H_6O^+$. These results previously reported suggest that all hydrogen atoms and both oxygen atoms participate in the complex reaction mechanism. The photoion-photoelectron coincidence(PIPECO) study by Baer and his co-workers[3] has provided close measurements of the dissociation rate as a function of the photon energy for the rate range of 10^5—10^6 s^{-1}. Moreover, the time-dependent kinetic energy releases have been measured for ion lifetimes up to 20 μs by means of double-focusing mass spectrometry[4] and by means of TIMS.[5] However, there is still an unresolved question as to the ethyl-acetate dissociation near the threshold.

The present paper will report on the slow metastable fragmentations of less than 10^5 s^{-1}, which have not previously been observed for an ethyl acetate system. The metastable intensities for H_2O loss were measured as a function of the ion-source-residence time by means of TIMS. The longest lifetime of 200 μs corresponds to the average rate of ca. 5×10^3 s^{-1}.

Experimental

The ion-trapping technique has been described in detail elsewhere.[6] Briefly, the space charge formed by a continuous 5-eV electron beam was used to trap ions produced when a negative pulse was applied to a filament. At a known delay time after the ionizing pulse, a positive pulse, 4 μs in duration and 5 eV in height, was applied to a repeller electrode in order to remove ions for mass analysis. The delay time was successively varied with a 3.7-μs step. The ionizing pulse was applied to the filament at a 0.5-ms interval. These pulse-sequence and data-acquisition systems were both computer-controlled.

The metastable parent ions, which are selected by the first magnet, decompose in the second-field-free region. The product ions are analyzed by the use of the second magnet. Several hours of data accumulation were statistically needed for the measurement. The temperature of the ion source was 423 K. The ion-accelerating voltage was 1.5 kV. The ion-source pressure was kept at 2×10^{-6} Torr (1 Torr=133.322 Pa). The collision-induced reaction in the field-free region was negligible, because the pressure was less than 1×10^{-6} Torr.

Results and Discussion

Figure 1 shows the metastable-to-main-beam intensity ratio at the electron-impact energy of 40 eV. This metastable decay, of course, reflects the rate constant, and its intensity at the ion-residence time of t is proportional to:[7]

$$m^*(t) \propto \int_0^\infty p(E)\,[\exp(-t_1 k(E)) - \exp(-t_2 k(E))]\,dE.$$

Here, $p(E)$ is the internal energy distribution, t_1 and t_2 are the time windows in the experiment ($t_1 = 6.5 + t$ and $t_2 = 11.7 + t$ μs), and $k(E)$ is the unimolecular rate constant. The photoelectron spectrum for ethyl acetate[8] was assumed to represent $p(E)$.

The PIPECO experimental rates previously reported by Baer and his co-workers[3] are shown in Fig. 2. The RRKM calculation has given a rate 100 times larger than the measured rates. This is mainly because of the low activation energy, that is, the low state density for the reactant. They therefore concluded that the parent ethyl acetate ion rearranges to a more stable structure prior to dissociation. The energy of its isomer, 0.62 eV lower than the ionization energy of ethyl acetate, was determined as a parameter, so that the RRKM rates agreed with the measured rates. Such a prior isomerization mechanism provides a rate-energy curve which is truncated at the threshold (Fig. 2). As may be seen in

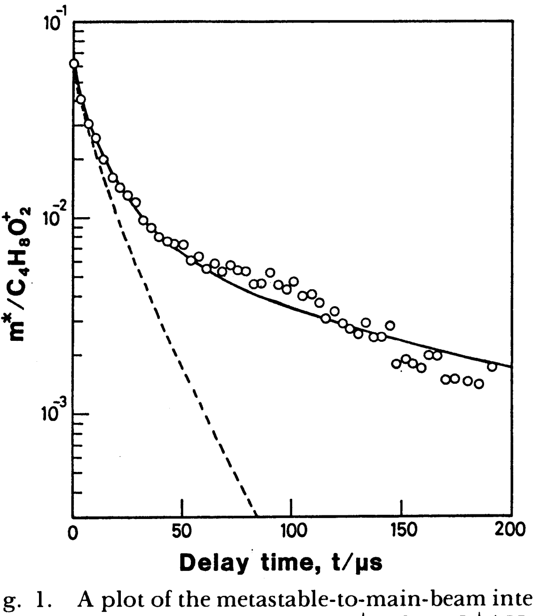

Fig. 1. A plot of the metastable-to-main-beam intensity ratios for $CH_3COOC_2H_5^+ \rightarrow C_4H_6O^+ + H_2O$ against the delay time: experiment(○) and calculated with the prior isomerization rate model, ---- and with the tunneling correction, ——.

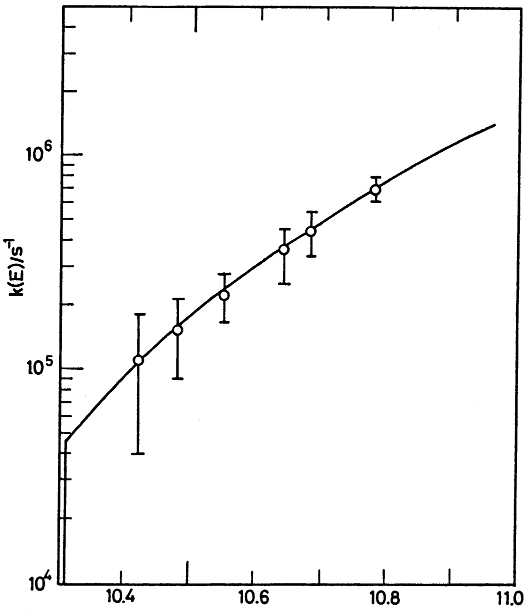

Fig. 2. The dissociation rate $k(E)$ vs. photon energy: the PIPECO experimental rate,[3] (○) and the RRKM rate arising from the prior isomerization mechanism(——).

Fig. 1, this rate model fails to fit the experimental data. The reason for this failure is probably because the model provides no rate less than 10^4 s^{-1}. From the actual calculation it was found that a decrease in the metastable decay is dependent on the slope of $k(E)$ vs. E, especially in the range of 10^3—10^5 s^{-1}.[7]

In this study, the tunneling effect was examined to explain the slow fragmentations. Tunneling corrections to unimolecular rate constants have previously been investigated for neutral reactions by Miller and his co-workers.[9] Moreover, applications to metastable transitions have been reported for methane,[10] methanol,[11] and phenol[12] cations. These experiments have usually been carried out to observe the temperature dependence on the ratios of the metastable-to-main-beam intensity or on kinetic energy releases. For example, Klots predicted that the metastable intensity, if tunneling through a centrifugal barrier occurs, increases as a square of the temperature.[10]

The probability of tunneling is generally favored for the case of one-step hydrogen-bond cleavage. The H_2O loss of the ethyl acetate cation probably involves a hydrogen migration to a oxygen atom prior to dissociation. On the basis of a Miller modification with the generalized Eckart potential,[8] the tunneling probabilities were calculated, and they are shown in Fig. 3. For the calculation, the activation barrier of 0.92 eV was obtained from the PIPECO results;[3] the reverse barrier was assumed to be 0.5 eV, for the product structure of $C_4H_6O^+$ was not well defined. The probability depends strongly upon an imaginary frequency. Here, the imaginary frequency of 2300 cm^{-1} was taken from Ref. 6. The rate below the threshold was obtained by multiplying the rate at the threshold by the tunneling probability. The tunneling correction to the prior isomerization rate is very satisfactory for the experimental metastable decay in Fig. 1. It may be concluded that the decrease in the metastable intensity with the ion lifetime beyond 20 μs arises from tunneling through a potential barrier. This conclusion is supported by the good agreement between the experimental data and the results of calculation by taking the tunneling effect into account. In other words, this indicates that the hydrogen-atom migration is a rate-determining step for slow fragmentations. However, such consideration has not been definitely confirmed by direct observation. It has been well known that a OH or H_2O loss which involves hydrogen-atom migration is generally a complex mechanism.

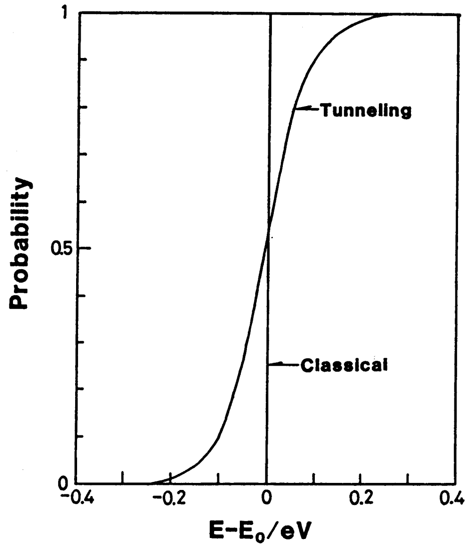

Fig. 3. Tunneling probability near threshold energy, E_0.

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