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Time-Dependent Metastable Fragmentations. The $\dot{C}H_2OH$ Loss from Methyl Acetate Ions

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The metastable ion intensity for the loss of $\dot{C}H_2OH$ from ionized methyl acetate has been measured as a function of the ion-source residence time up to 100 μs by means of the ion-trapping technique. The decay of the metastable ion intensity was adequately interpreted by the use of a prior isomerization mechanism on the basis of RRKM calculations. It was suggested that the intermediate precursor for the generation of CH_3CO^+ and $\dot{C}H_2OH$ from ionized methyl acetate is not a hydrogen-bridged complex structure, $CH_3CO\text{-}H\text{-}OCH_2^{+\cdot}$, but a distonic ion structure, $CH_3\overset{+}{C}(OH)O\dot{C}H_2$.

The unimolecular gas-phase chemistry of ionized methyl acetate has been the subject of a number of studies.[1-6]

$$CH_3COOCH_3^{+\cdot} \rightarrow CH_3CO^+ + COH_3^{\cdot} \qquad (1)$$

This interest has been directed toward determining what configuration is a reacting precursor in the complexity of isomerization/dissociation paths, and also the structure of the neutral product, $COH_3^{\cdot}$. A variety of experimental techniques[1-3] have suggested that the structure of the neutral product is a hydroxymethyl $\dot{C}H_2OH$ radical rather than the methoxyl $CH_3\dot{O}$ which would be expected from a simple bond cleavage. However, recent studies[3,4] have shown that the neutral product is a mixture of these radicals. Moreover, the rearrangement of the $CH_3\dot{O}$ radical into $\dot{C}H_2OH$ is a possible process. Thus, the structure of the neutral product is still an unresolved question.

Extensive labeling experiments[3,5] on methyl acetate and its enol isomer have led to the proposal that the distonic ion $CH_3\overset{+}{C}(OH)O\dot{C}H_2$, in which the charge and radical site are separated by more than one atom, is the key intermediate. This intermediate accounts for the considerable, but incomplete, loss of the positional identity of H and D atoms in the labeled isomers. Moreover, ^{18}O-labeling and collisional activation experiments by Burgers et al.[5] have led to the similar conclusion that the distonic ion is the intermediate precursor for Reaction (1). However, their time-resolved mass spectra of ionized methyl acetate indicated that the isomerization of methyl acetate ions into other isomers is a rate-determining step in a microsecond time-frame. On the other hand, ab initio calculations at a sufficiently high level of theory were used for resolving the ionized methyl acetate problem of a multistep isomerization/dissociation pattern.[6] The theoretical analysis showed that the hydrogen-bridged radical ion/dipole complex, $CH_3CO\text{-}H\text{-}OCH_2^{+\cdot}$, is probably a precursor ion decomposing to the observed $CH_3CO^+ + \dot{C}H_2OH$.

There is, therefore, an unsettled problem regarding the isomerization/dissociation paths of ionized methyl acetate. The apparent activation energy (appearance energy—ionization energy) is as small as ca. 0.7 eV; RRKM theory predicts a minimum rate of ca. 10^7 s^{-1}. Thus, such a rate yields no metastable peak for the dissociation of ionized methyl acetate. One way of accounting for the unusual characteristics of Reaction (1) is to assume a mechanism in which the reaction path involves isomerization to a more stable structure prior to dissociation. This idea of a prior isomerization has been applied by Baer to explain the complex dissociation of several molecular ions.[7] We have investigated which isomer serves as the intermediate precursor by assuming a prior isomerization mechanism, based on RRKM calculations, so as to explain the experimental time-resolved metastable fragmentation. The decay of metastable ions is principally dependent on the rate vs. energy curve; thus, it is affected by the reaction mechanism.

Experimental

The ion-trapping technique has been described in detail elsewhere.[8] Briefly, the space charge formed by a continuous 5 eV electron beam was used to trap the 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 to remove ions for mass analysis. The ionizing pulse was applied to the filament at 0.5 ms intervals. The delay time was successively varied at 3.6-μs steps. These pulse-sequence and data-acquisition systems were both computer-controlled. The measurement of the metastable-ion intensities was performed with a home-made tandem-type mass spectrometer. The temperature of the ion source was 423 K. The ion-source pressure was kept at 2×10^{-6} Torr (1 Torr≈133.322 Pa). A collision-induced reaction in the field-free region was negligible, because the pressure was maintained at less than 5×10^{-7} Torr.

Results and Discussion

The production of CH_3CO^+ was the predominant process in the metastable fragmentation of ionized methyl acetate. Figure 1 shows the metastable-to-main-beam intensity ratio against the delay time at the

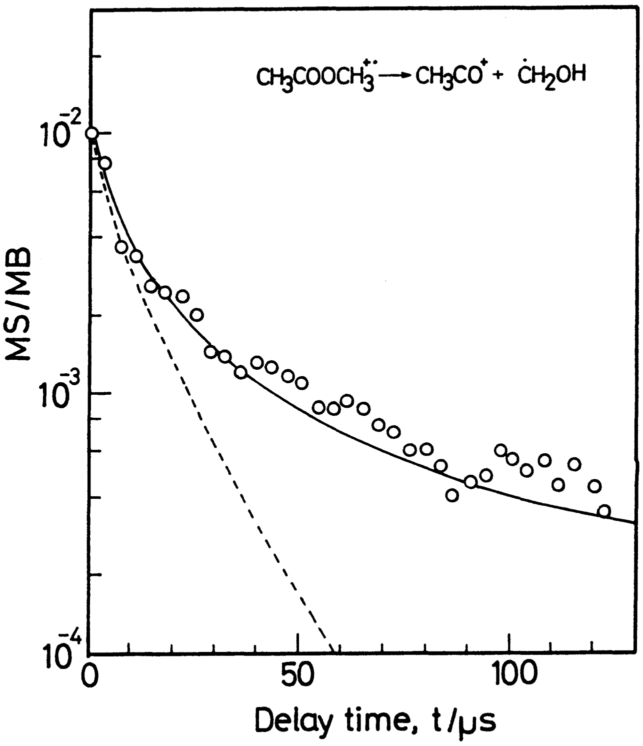

Fig. 1. A plot of the metastable to main beam intensity ratios, MS/MB, vs. the delay time for CH_3CO^+ from ionized methyl acetate: experiment (○) and calculated with the distonic precursor model (——), and the hydrogen-bridged complex model (----).

electron-impact energy of 40 eV. The metastable-ion intensity at the delay time of t is given by:[9]

$$m^{*}(t) \propto \int_0^{\infty} f(E)\,w(E)\,\mathrm{d}E.$$

Here, $f(E)$ is the internal energy distribution, $w(E)=\exp(-t_1 k(E))-\exp(-t_2 k(E))$ is the time window in the present experiment ($t_1=6.5+t$ and $t_2=11.7+t$ µs), and $k(E)$ is the unimolecular rate constant. According to the threshold behavior of ionization,[10] $f(E)$ was approximated by the photoelectron spectrum of methyl acetate.[11]

The lowest energy path for ionized methyl acetate to CH_3CO^+ and $\dot{C}H_2OH$ was obtained by Heinrich et al.[6] using a high level of ab initio calculations. In the first step, methyl acetate ions isomerize into the distonic ion $CH_3\overset{+}{C}(OH)O\dot{C}H_2$, followed by rearrangement to the hydrogen-bridged complex, $CH_3CO\text{-}H\text{-}OCH_2^{+\cdot}$. Along their potential energy profile and the previous result[3] regarding barrier height (Fig. 2), we suppose two prior isomerization models for calculating $k(E)$ by the use of the RRKM theory: the distonic ion and the hydrogen-bridged complex serve as precursor ions, whose activation energies of E_0 for the generation of $CH_3CO^+ + \dot{C}H_2OH$ are assumed to be 1.27 and 0.64 eV respectively. The RRKM calculation was carried out by a direct counting method of the state and sum densities.[12]

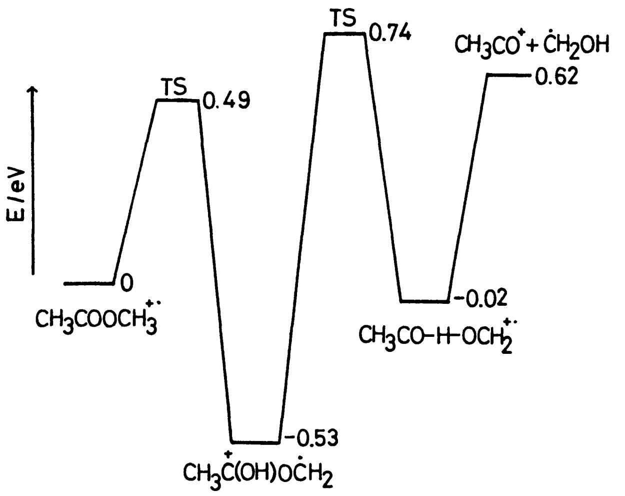

Fig. 2. A potential energy diagram of ionized methyl acetate and its isomers for the prior isomerization. This indicates a part of results previously determined from ab initio calculation by Heinrich et al.[6]

Another adjustable parameter is the set of vibrational frequencies for the reactant and transition states. Their vibrational frequencies are obtained by a vibrational analysis[13] for the assumed geometries and approximate simple-valence force fields (Appendix 1). For the distonic precursor model, the H atom of the OH bond migrates to another oxygen, and at the same time the bond order of $C\text{-}OCH_2$ decreases by 0.5. The hydrogen-bridged precursor model is described as a simple $C\text{-}HOCH_2$ bond cleavage for the H bridged bond. The bond orders of the hydrogen-bridged C-H and H-O bonds are assumed to be 0.5 in the reactant state. In both cases, the bond cleavage for the O-H stretching mode is employed as the reaction coordinate for the transition state; its bond order was taken as $n=0.1$. The vibrational frequencies obtained from the vibrational analysis are given in Appendix 2. The activation entropy, ΔS^{*}, is calculated from the set of vibrational frequencies for the reactant and transition state, and it is related to the Arrhenius preexponential factor.

The experimental results are well reproduced by the distonic-ion model (Fig. 1). The activation entropy is $\Delta S^{*}_{1000}=4.0$ e.u. (cal/mol/deg) if we adopt $T=1000$ K. This seems a reasonable value for the "tight" transition model, which involves a four-center cyclic moiety. For example, the loss of a halogen atom from a halobenzene ion proceeds via a simple bond cleavage and a "loose" transition state. Its activation entropy is known to be $\Delta S^{*}_{1000}=7-10$ e.u.[14] As may be seen in Fig. 3, the rate constants obtained by the prior isomerization models are metastably slow ($\leqq 10^5\ s^{-1}$), but if the isomerization of methyl acetate ions is a rate-determining step, its rate is much greater than those obtained by the prior isomerization models. This is mainly because the distonic-ion model exhibits a high activation energy and because the hydrogen-bridged

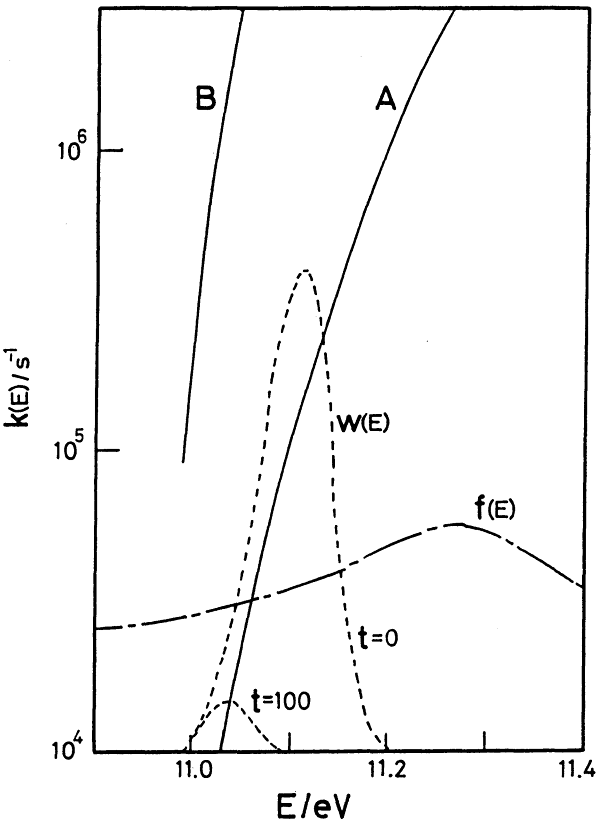

Fig. 3. The dissociation rate, $k(E)$, vs. energy, E; the rates derived from the distonic precursor model (A) and the hydrogen-bridged complex model B). $w(E)$ indicates the metastable time windows at $t=0$ and 100 μs. $f(E)$ represents the internal energy distribution. $w(E)$ and $f(E)$ are plotted on a linear scale.

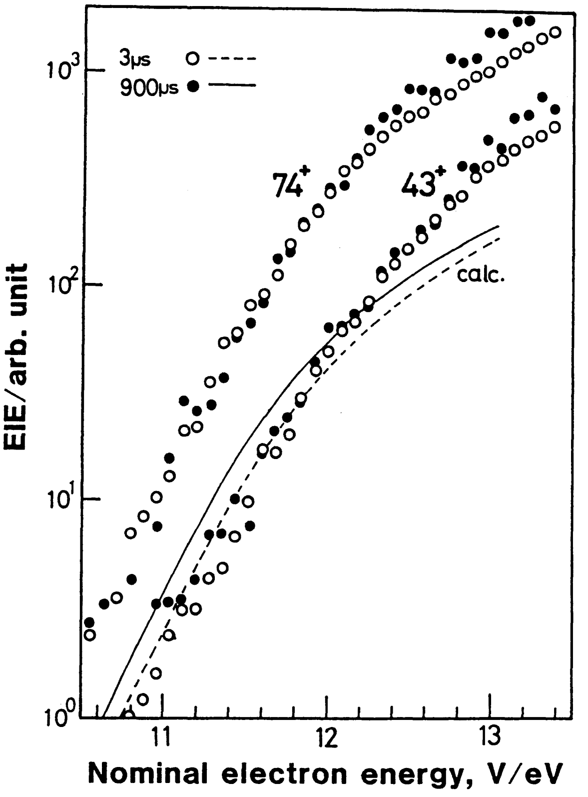

Fig. 4. The time-dependent electron ionization efficiency (EIE) curve vs. nominal electron energy, V, for methyl acetate ion (74^+) and CH_3CO^+ (43^+): experiment (○, ●) and calculated (----, ——) at the ion-source-residence time of $t=3$ and 900 μs.

complex model has a loose structure, e.g., small vibrational frequencies, in spite of the low activation energy. The prior isomerization models cause the higher state density of the reactant state at the threshold energy. The decay of metastable ions depends upon the two adjustable parameters of E_0 and ΔS^*. However, from actual calculations, the decay was found to be much more dependent on E_0 than ΔS^*. The activation entropy increases with the decrease in the bond order of the reaction coordinate.

The "kinetic shift," which is called the excess energy required to produce a detectable dissociation, usually in several μs, is attributable to a slope of $k(E)$ vs. the energy; a steeply-rising slope gives a less kinetic shift. In order to determine the kinetic shift, the time-dependent electron ionization efficiency (EIE) curves were measured for $t=3$ and 900 μs; they are shown on a semilogarithmic plot in Fig. 4. The EIE curves for the parent ion were used for normalization. There is no shift observed in the time-resolved EIEs of the CH_3CO^+ fragments. It can be reproduced, within the limits of experimental error, by use of the distonic-ion model. Naturally, the EIE shift decreases with the steepness of the $k(E)$ vs. energy plot. The energy distribution of electron impact should be considered for the EIE calculation.[9] Its distribution, as estimated from the second derivative of the helium EIE curve,[15] was found to be 0.8 eV at a half-maximum. Because of the poor energy resolution, the most significant result is not the EIE curve itself, but only its shift. The appearance energy of 10.9±0.1 eV obtained from the EIE difference near the threshold agrees with the previous result.[16]

In a system of ionized methyl acetate, the prior isomerization mechanism was examined in order to explain the present results of time-resolved metastable fragmentations and EIEs. It is suggested that the distonic structure among several isomers is the plausible precursor decomposing metastably to CH_3CO^+ + $\dot{C}H_2OH$.

Appendix

1. The geometry of the reactant state is most conveniently specified in terms of the bond orders and bond angles. The reacting bond length for the transition state is modified from the standard length, r_0, and adjusted by Pauling's expression, $r=r_0-0.31$ n (n), where n is the bond order. The stretching and angle bending force constants for the transition state are modified by $F_r=nF_r^0$ and $F_a=g(\theta)n_in_jF_a^0$, where F^0 is the standard force constant, n_i and n_j are the bond orders in the bending mode, and $g(\theta)=1.39+1.17\cos(\theta)$ is the hybridization factor for the bond angle θ. The torsional and

out-of-plain bending force constants are not modified from the reactant force constants. For a simple bond cleavage, the force constant for the stretching mode of the reacting bond in the reaction coordinate is negative. This provides an imaginary frequency because of a negative curvature at barrier.

2. The following vibrational frequencies (cm^{-1}) for the reactant and the transition state were obtained by means of vibrational analysis using a simple vibrational force field; they were used in the RRKM calculations.

1) Distonic-ion model($\Delta S^{\ddagger}_{1000}$=4.0 e.u.)

3750	3080	3080	3080	3000	2960	1530	1520	1480	1380
1260	1150	1130	1080	1010	960	900	800	630	560
480	430	360	240	230	200	100			

3080	3080	3080	3000	2960	1530	1520	1480	1380	1250
1140	1130	1080	970	900	800	630	560	470	440
260	240	220	200	180	100				

2) Hydrogen-bridged complex model($\Delta S^{\ddagger}_{1000}$=2.0 e.u.)

3290	3090	3080	3070	3010	2960	2010	1990	1760	1620
1530	1510	1320	1230	1070	980	820	680	520	500
380	290	260	230	190	100	50			

3090	3080	3070	3010	2960	2550	1990	1800	1730	1610
1530	1500	1230	1060	940	820	650	500	480	360
350	260	230	110	100	20				

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