Time-Resolved Dissociation of Ionized Propanoic Acid

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The appearance energies of $C_3H_5O_2^+$, $C_3H_5O^+$, $C_3H_4O^+$, $C_3H_3O^+$, CHO_2^+, and $C_2H_5^+$ from propanoic acid were obtained. The kinetic shifts were observed for the formation of $C_3H_5O_2^+$, $C_3H_5O^+$, and $C_3H_4O^+$. The dissociation of ionized propanoic acid is metastable for the loss of a hydrogen atom and water. The results of the metastable-ion-intensity ratios, collisional activation mass spectra and kinetic-energy releases indicate that the propanoic acid ion isomerizes to a more stable enol tautomer prior to dissociation.

The structures of the ions formed in a mass spectrometer are of fundamental interest. One of the approaches for obtaining ion structural information is a precise determination of the heats of formation for ions in the gas phase. For this reason, the development of experimental techniques using an energy-selected electron and photon beam enabled us to measure the appearance energies and ionization energies with uncertainties of less than 0.05 eV. More precise heats of formation have been obtained from low-temperature photoionization experiments. These can lead to reliable 0 K critical energies, provided that a sample cooled by the appropriate methods, such as a supersonic beam, is available. In most cases, these are not always practicable because of problems of sample condensation and reduced sample pressure. The other origin to yield the uncertainty is a kinetic shift, i.e., an energy in excess of the critical energy required to drive the dissociation at a rate sufficient to be observed on the μs time scale. Thus, the kinetic shift can be obtained from the time-resolved experiments.

The reaction mechanism for the dissociation of ions containing oxygen atoms such as ethyl acetate,[1] butanoic acid,[2] methyl acetate,[3] and their isomers is usually complex in a multistep isomerization/dissociation pattern. Moreover, the dissociation shows strong metastable peaks in the mass spectra, although the activation energy is less than 1 eV.[4] In such case, the predicted rates on the basis of RRKM theory are much greater than 10^7 s^{-1}, while the measured rates are in the 10^5 s^{-1} range. For this explanation, one has proposed that the reaction involves isomerization into sufficiently stable isomers or ion-dipole complexes[5] prior to dissociation. In addition, tunneling through a potential barrier[6] and participation of an anharmonic interaction potential[7] have been studied for the origin of the slow dissociation. The dissociation of propanoic acid cations is the same class in a reaction system as stated above.

Generally, the ionized enol form is more stable than the keto form, while for the neutral keto and enol form the thermodynamic stability is in reverse order. In the cases of ionized methyl acetate[8] and acetic acid,[9] the enol forms are ca. 1 eV more stable than the corresponding carbonyl forms of ions. In the metastable dissociation of ionized propanoic acid, the major processes are the hydrogen atom and water-loss reactions. The deuterium-labeling experiment[10] indicated that these reactions involve isomerization to the enol forms prior to dissociation. It is complicated to determine the energy barrier of isomerization to the enol forms. Occasionally, the barrier is above the critical energy of dissociation. This is the case in rate-determining isomerization. The classic example of this situation was first described by Hvistendahl and Williams[11] in a study of the isomeric oxonium ions $CH_3CH_2O{=}CH_2^+$ and $CH_3CH{=}OCH_3^+$. However, according to the labeling experiment[10] the enol form is likely to be a product structure. Thus, the energy barrier of isomerization seems to be lower than the dissociation limit.

In this paper we reexamine the reaction mechanism of propanoic acid ions concerning the keto–enol isomerization followed by dissociation with particular application to the time-resolved experiments.

Experimental

The ion-storage technique is the same as that described in detail by Herod and Harrison.[12] Briefly, the space charge formed by a continuous 5 eV electron beam is used to store ions produced when a negative ionizing pulse is applied to a filament. At a known delay time after the ionizing pulse, a positive pulse is applied to a repeller electrode in order to remove ions for mass analysis. The ionizing pulse is applied to the filament at a 1-ms interval. These pulse-sequence and data-acquisition systems are both computer-controlled. The metastable intensities and collisional activation (CA) spectra were measured with a home-made tandem-type mass spectrometer. The temperature of the ion source was 423 K. The CA spectra were measured at a 30% decrease in the main beam intensity by increasing the He gas pressure in a collision cell.

Results and Discussion

Figure 1 displays semi-log plots of the electron ionization efficiency (EIE) curves at ion-storage times of t=0 and 900 µs. The EIE measurements were performed with a constant detection sensitivity. The efficiency of the ion storage decreases with an increase in the storage time. For this correction, EIE curves for t=900 µs were normalized using the EIE curve of parent ions. The electron impact energy was not mono-energetic; its resolution, as estimated from the second derivative of a helium EIE curve, was ca. 1 eV at the full width of half maximum. Because of the poor energy resolution, the AE values were determined by comparing the EIEs with the reference EIE curve of a known critical energy. Unfortunately, since the EIE curves are not parallel, the AEs were obtained from semi-log plots at an EIE intensity of 10^1, which is sufficiently statistical. For Fig. 1, the ionization energy (IE) of propanoic acid was used as the energy reference; IE=10.41 eV.[9] The AE results are listed in Table 1. The metastable ion yields are shown in Fig. 2 with the metastable dissociation of ethyl acetate, $CH_3COOC_2H_5^+ \rightarrow C_4H_6O^+ + H_2O$. The AEs of metastable ions were determined in the same manner using ethyl acetate as the reference, whose AE=10.31 eV has been obtained from the photoion–photoelectron coincidence experiments.[13] Another convenient procedure for the AE determination has been described by Burgers and Holmes.[14] On the basis of this procedure, we obtained the same AE values within experimental

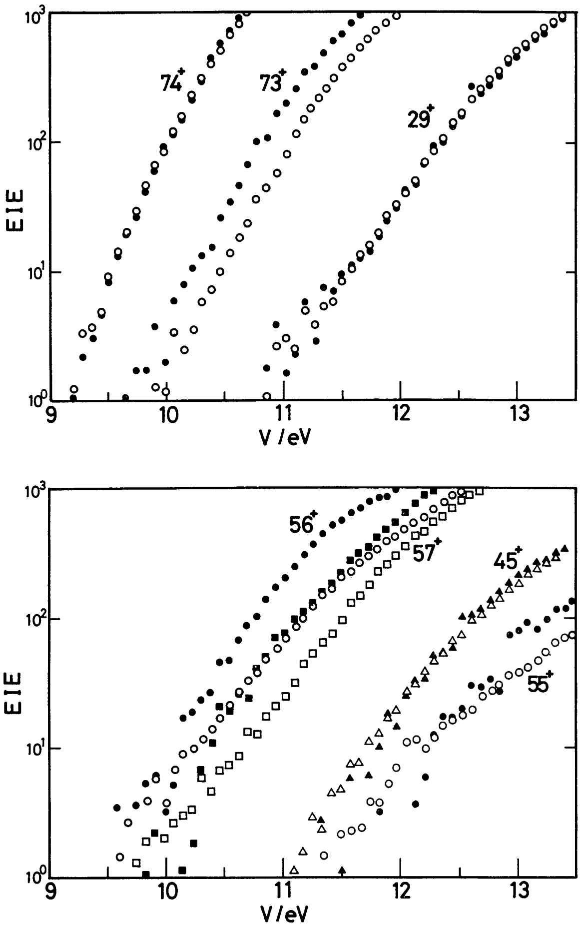

Fig. 1. The semi-log plots of the electron ionization efficiency (EIE) vs. nominal electron energy, V for propanoic acid; the storage times of t=0 (open mark) and 900 µs (closed mark).

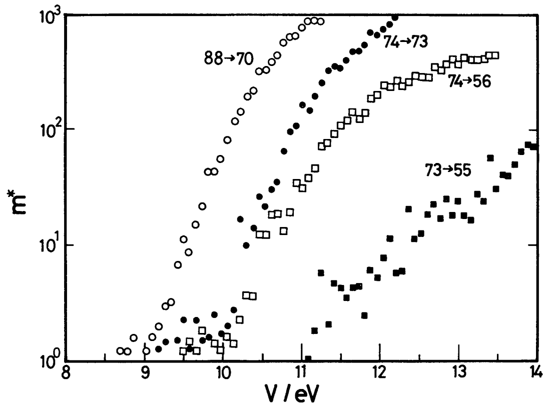

Fig. 2. The semi-log plots of the metastable ion yield, m^* vs. nominal electron energy; 74→73 and 74→56 indicate the hydrogen atom and water loss from propanoic acid ions, respectively, and 73→55 does the water loss from the m/z 73 fragment. The metastable dissociation of ethyl acetate, $CH_3COOC_2H_5^+ \rightarrow C_4H_6O^+ + H_2O$(88→70) is used as an energy reference.

Table 1. Appearance Energies in the Mass Spectra of Propanoic Acid

Ion		AE/eV		
			m/z	
		t=0 µs	t=900 µs	Ref.
74	$C_2H_5COOH^+$	10.4		10.41,[a] 10.53,[b] 10.51[c]
73	$C_3H_5O_2^+$	11.3±0.1	11.1	11.7[d]
57	$C_3H_5O^+$	11.5	11.2	12.2,[d] 11.00[c]
56	$C_3H_4O^+$	11.1	10.9	11.6,[d] ca. 10.5[c]
55	$C_3H_3O^+$	13.1	13.1	
45	CHO_2^+	12.6	12.6	12.8[d]
29	$C_2H_5^+$	12.4	12.4	12.9[d]
74→73*[e]		11.1 (11.0)[f]		
74→56*		11.2 (11.1)		
73→55*		13.1		

a) Ref. 9. b) Ref. 17. c) Photoionization mass spectrometry.[16] d) Normal electron impact mass spectrometry.[15] e) Metastable ions. f) Values in parentheses were obtained on the basis of the AE determination procedure of Burgers and Holmes.[14]

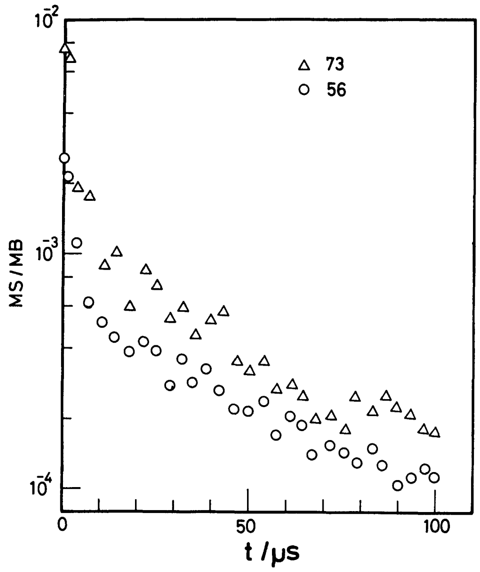

Fig. 3. Metastable-to-main-beam intensity ratios, MS/MB vs. the ion storage time, t at V=40 eV; $C_3H_5O_2^+$(73), $C_3H_4O^+$(56).

error.

Kinetic shifts were observed for m/z 73, 57, and 56 ions, becoming large since the slope of a rate vs. energy curve rises slowly. The AE values of m/z 57 and 45 are in fair agreement with those of the literature. It is noted that the AE of m/z 55 agrees with that for the metastable ion, 73→55. This indicates that the m/z 55 ions are formed by sequential dissociation. A question arises concerning the AEs for m/z 73 and 56. The EIE curve of m/z 56 exhibits a long tail, so that its AE is observed to be lower than for m/z 73. This is consistent with the previous results of normal electron impact mass spectrometry.[15] Moreover, the photoionization experiment[16] indicated that the AE of m/z 56 was very close to the ionization energy. This was also due to the long tailing. On the other hand, the AE values are in reverse order for measurements of metastable ions. In order to make this clear, the metastable ion intensities were measured as a function of the ion-storage time. As the storage time increased, the dissociation of ions the energy of which is much closer to the critical energy could be sampled. As can be seen in Fig. 3, the intensity of m/z 73 is always larger than that of m/z 56 over long storage times. This means that the dissociation rate of m/z 73 is greater than of m/z 56. In other words, the AE of m/z 73 is below that of m/z 56, supporting the AE reasult for metastable ion experiments. Taking into account the different AE estimation, we concluded that the AEs of m/z 73, 57, and 56 are 11.0±0.1, 11.2, and 11.1 eV, respectively.

Shown in Fig. 4 is an energy diagram constructed from recently published energetic information[17] and the heat of formation of ions obtained from a monoenergetic electron experiment.[9] The heat of formation for the keto and enol ion of propanoic acid is 5.68 and 4.55 eV, respectively.[9] The transition-state energies for dissociation are those derived from the present AE measurements; the heat of formation of the keto form plus the activation energy (=AE−IE). The ion structures of $CH_3CH{=}CO^+$(m/z 56), $C_2H_5CO^+$ (m/z 57), and $COOH^+$ (m/z 45) were employed for an energy estimation of the products. The reverse activation energy was assumed to be zero for the dissociation of 73^++H (Fig. 4), because the heat of formation for m/z 73 was not available. In the case of the prior isomerization, the enol form is a reacting precursor for m/z 73 and 56 formation. Their activation energies are so large that the minimum rates calculated from RRKM theory are as slow as 20 s^{-1}. If the transition state energy is not for the dissociation, but for the isomerization, rate-determining isomerization is a possible process. In such a case, because of the small activation energy, the predicted rates are much greater than the metastable dissociation range. Therefore, rate-determining isomerization may be ruled out.

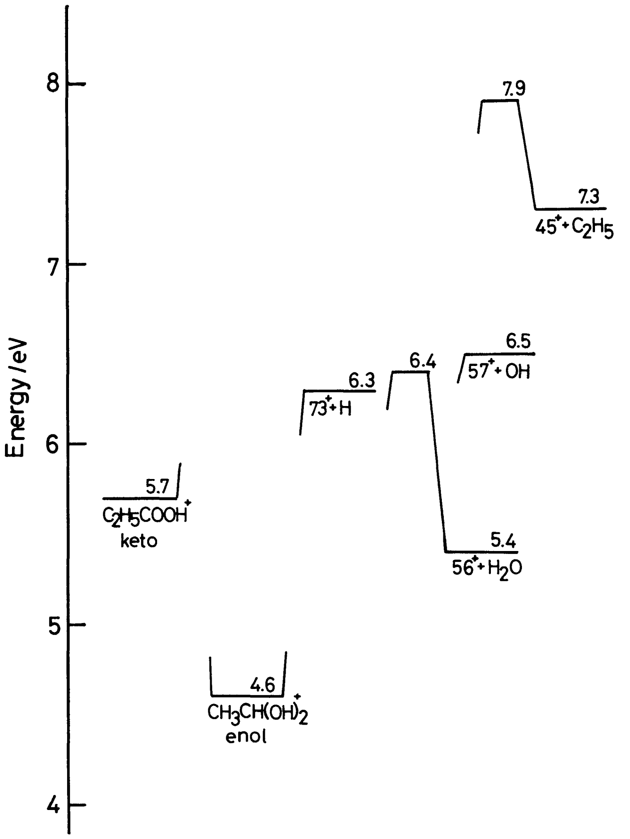

Fig. 4. A potential energy diagram of ionized propanoic acid and its isomer for the isomerization/dissociation path.

For the enol ion of m/z 74 generated by a McLafferty rearrangement from 2-methylbutanoic acid, the metastable dissociation and collisional activation (CA)

Table 3. Kinetic Energy Releases for the Keto and Enol Forms

t/μs	$T_{0.5}$/meV				
	Propanoic acid			2-Methylbutanoic acid	
	74→73	74→56	73→55	74→73	74→56
0	10±5	60±10	60±10	5	60±10
5	<10	60			
50	<10	30			

Table 2. Collisional Activation Spectra of the Keto and Enol Forms of $C_3H_6O_2^+$

t/μs	Relative aboundance				
	m/z				
	73	56	55	46	45
			Keto form		
0	1	0.36	0.18	0.07	0.16
4	1	0.37	0.21	0.06	0.15
20	1	0.41	0.17	0.06	0.17
50	1	0.36	0.20	0.06	0.17
			Enol form		
0	1	0.39	0.40	0.09	0.30

mass spectra were measured. The metastable-ion-intensity ratio of m/z 73 and 56 was 2.2. This was consistent with the ratio of 2.3 for propanoic acid. Also, as can be seen in Table 2, the CA spectra of the enol form were similar to those of propanoic acid. These indicate that the enol form is a reacting structure for the dissociation of the hydrogen and water loss. Its structure seems to be stable in a μs time scale, because the CA spectra are independent of the storage time, as shown in Table 2. The kinetic-energy releases indicated in Table 3 also show the same values for ionized propanoic acid and the enol ion form 2-methylbutanoic acid. Finally, it is concluded that ionized propanoic acid isomerizes to the more stable enol form prior to dissociation by the loss of hydrogen atom and water.

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References

1) J. L. Holmes, P. C. Burgers, and J. K. Terlouw, *Can. J. Chem.*, **59**, 1805 (1981).

2) C. E. Hudson, T. Lin, and D. J. McAdoo, *Org. Mass Spectrom.*, **22**, 311 (1987); J. J. Butler, M. L. F.-Monteiro, T. Baer, and J. R. Hass, *J. Phys. Chem.*, **86**, 747 (1982).

3) J. K. Terlouw, J. L. Holmes, and P. C. Burgers, *Int. J. Mass Spectrom. Ion Processes*, **66**, 239 (1985); C. Wesdemiotis, R. Csencsits, and F. W. McLafferty, *Org. Mass Spectrom.*, **20**, 98 (1985); H. Schwarz and C. Wesdemiotis, *Org. Mass Spectrom.*, **14**, 25 (1979); J. L. Holmes, C. E. C. A. Hop, and J. K. Terlouw, *Org. Mass Spectrom.*, **21**, 776 (1986).

4) P. C. Burgers, J. L. Holmes, C. E. C. A. Hop, and J. K. Terlouw, *Org. Mass Spectrom.*, **21**, 549 (1986); R. Arakawa, *Bull. Chem. Soc. Jpn.*, **61**, 569 (1988); H. Egsgaard and L. Carlsen, *Chem. Phys. Lett.*, **147**, 30 (1988); M. P. Irion, A. Selinger, A. W. Castelman, Jr., E. E. Ferguson, and K. G. Weil, *Chem. Phys. Lett.*, **147**, 33 (1988).

5) B. T. Golding and L. Radom, *J. Am. Chem. Soc.*, **98**, 6331 (1976); N. Heinrich, J. Schmidt, H. Schwarz, and Y. Apeloig, *J. Am. Chem. Soc.*, **109**, 1317 (1987).

6) J. H. Beynon, A. E. Fontaine, and G. R. Lester, *Int. J. Mass Spectrom. Ion Phys.*, **1**, 1 (1968); A. J. Illies, M. F. Jarrold, and M. T. Bowers, *J. Am. Chem. Soc.*, **104**, 3587 (1982).

7) J.-D. Shao, T. Baer, J. C. Morrow, and M. L. F. -Monteiro, *J. Chem. Phys.*, **87**, 5242 (1987).

8) J. L. Holmes and F. P. Lossing, *Org. Mass Spectrum.*, **14**, 512 (1979).

9) J. L. Holmes and F. P. Lossing, *J. Am. Chem. Soc.*, **102**, 1591 (1980).

10) D. J. McAdoo and D. N. Witiak, *Org. Mass Spectrom.*, **13**, 499 (1978).

11) G. Hvistendahl and D. H. Williams, *J. Am. Chem. Soc.*, **97**, 3097 (1975).

12) A. A. Herod and A. G. Harrison, *Int. J. Mass Spectrom. Ion Phys.*, **4**, 415 (1970).

13) L. F. -Monteiro, M. L. F. -Monteiro, J. J. Butler, and T. Baer, *J. Phys. Chem.*, **86**, 752 (1982).

14) P. C. Burgers and J. L. Holmes, *Org. Mass Spectrom.*, **17**, 123 (1982).

15) R. R. Bernecker and F. A. Long, *J. Phys. Chem.*, **65**, 1565 (1961).

16) J. C. Traeger, *Org. Mass Spectrom.*, **20**, 223 (1985).

17) S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, and W. G. Mallard, *J. Phys. Chem. Ref. Data*, **17**, Suppl. 1 (1988).