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Mass Spectral Study of Ionized-Hydroxyacetone Dissociation

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Synopsis. The ionization and appearance energies of hydroxyacetone (CH_3COCH_2OH) were obtained. The metastable dissociation of ionized hydroxyacetone involves the loss of a hydrogen atom and CHO. The results of the metastable-ion intensity and collisional activation indicate that the hydroxyacetone ion does not isomerize to the enol tautomers prior to dissociation.

The unimolecular gas-phase chemistry of ions containing oxygen atoms, such as $C_3H_6O_2^{+\cdot}$ isomers,[1–7] is usually complex in a multistep isomerization/dissociation pattern. Interest has been directed toward determining the configuration of the reacting precusor or the key intermediate. Recently, distonic ions in which the charge and radical sites are separated and/or the ion-dipole complexes have been shown to be the reacting precursor from collisional activation (CA) experiments and theoretical calculations. For instance, in an *ab initio* calculation of ionized methyl acetate,[4] a hydrogen-bridged radical ion/dipole complex, $[CH_3CO\text{-}H\text{-}OCH_2]^{+\cdot}$, is probably a precursor ion which decomposes to the observed $CH_3CO^{+} + \cdot CH_2OH$. In the case of ionized propanoic acid, a deuterium-labeling experiment[5] and metastable ion fragmentation[7] indicated that a water-loss reaction involves isomerization to an enol form prior to dissociation. The enol form was found to be ca. 1 eV more stable than the corresponding keto form.

Some of the $C_3H_6O_2^{+\cdot}$ isomers show metastable dissociation, although the activation energy is less than 1 eV. Observation of a metastable ion requires a rate in the $10^5\,s^{-1}$ range. However, the predicted RRKM rate is much greater than $10^7\,s^{-1}$. One explanation for this problem is that the reaction involves isomerization to an energetically stable isomer prior to dissociation. The dissociation of this isomer is a rate-determining step.

The dissociation of ionized hydroxyacetone is within the same category mentioned 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. It is thus possible for the keto ion to isomerize to two kinds of ions (enol-1 or enol-2) by transferring a different hydrogen atom. In this paper interest is focused on the participation of the enol forms shown below as the reacting precursor in the metastable dissociation of ionized hydroxyacetone:

$[CH_3\text{-}CO\text{-}CH_2OH]^{+\cdot}$ $[CH_2\text{=}C(OH)\text{-}CH_2OH]^{+\cdot}$
keto enol-1

$[CH_3\text{-}C(OH)\text{=}CHOH]^{+\cdot}$
enol-2

Experimental

The metastable-ion intensities and the CA spectra were measured with a home-made tandem-type mass spectrometer. The CA spectra were measured at a 30% decrease in the main beam intensity by increasing the He gas pressure in the collision cell. The time-dependent appearance energies (*AE*) were measured by an ion-storage technique, which is the same as that described in detail by Herod and Harrison.[8] The enol-1 and enol-2 ions were generated by a McLafferty rearrangement from $(CH_3)_2CH(CH_2)_2COCH_2OH$ (HyMH) and $CH_3(CH_2)_2CH(OH)COCH_3$ (HyH). These precursors were prepared according to the procedure of Stansburg and Proops,[9] and of Baldwin et al.[10]

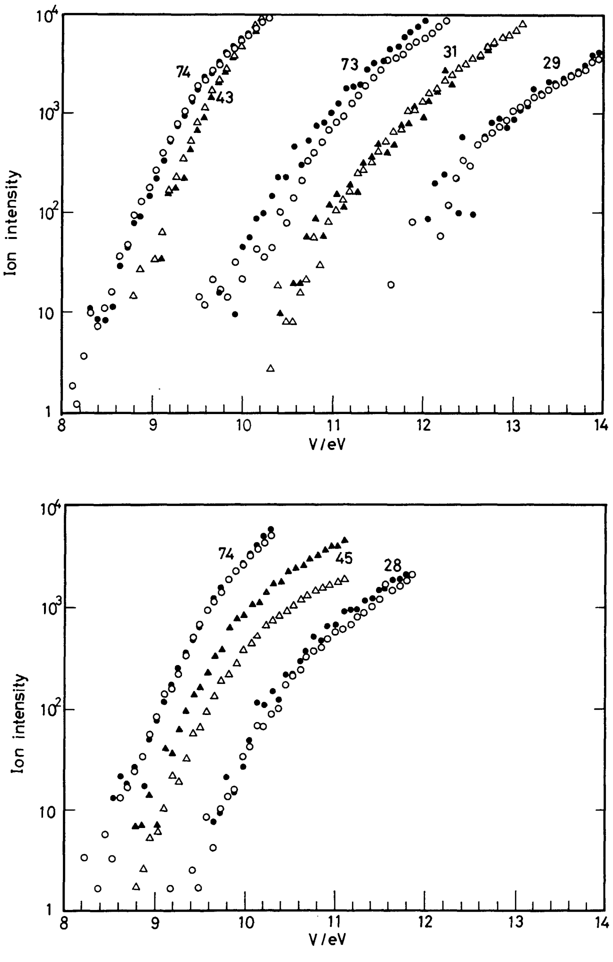

Fig. 1. The semi-log plots of the ion intensity vs. the nominal electron energy, *V* for hydroxyacetone; the storage times of $t=0$ (open mark) and 900 μs (closed mark).

Results and Discussion

Figure 1 shows semi-log plots of the ion intensity vs. the nominal electron energy at ion-storage times of t=0 and 900 μs. These curves were measured with a constant detection sensitivity. The efficiency of ion storage decreases with an increase in the storage time. Thus, the intensity curves for t=900 μs were corrected using the parent ion intensity. The distribution of electron energy was estimated to be ca. 1 eV at the full width of half maximum. The *AE*s were determined by comparing the ion intensity with the reference intensity of a known critical energy at a sensitivity of 10^2. In Fig. 2, the ionization energy (*IE*) of hydroxyacetone was estimated using CH_3OH and CH_3CN as the energy of calibration; their *IEs* are 10.85 and 12.19 eV, respectively.[11] The results of *IE*/*AE* are listed in Table 1.

A shift in the ion-intensity curve with the storage time was observed for m/z 73 and 45 ion. This is a so-called kinetic shift, which increases as the rising slope of the rate vs. energy curve decreases. Ions of m/z 73 and 45 are significant metastable peaks for hydroxyacetone. This is therefore consistent with observations of the kinetic shift. However, a question arises concerning m/z 43: its observed *AE* was almost equal to that of m/z 45. If this is correct, it seems that the dissociations for m/z 43 and 45 are not competitive, since m/z 43 is not metastable. Such nonstatistical behavior is often explained by the formation of two different electronic states during the initial ionization process: one of these states dissociates rapidly, while the other dissociates via an electronic predissociation, though there is no supporting evidence.

Shown in Fig. 3 is an energy diagram constructed from recently published energetic information[11] and the heat of formation, ΔH_f, for the keto and enol ions.

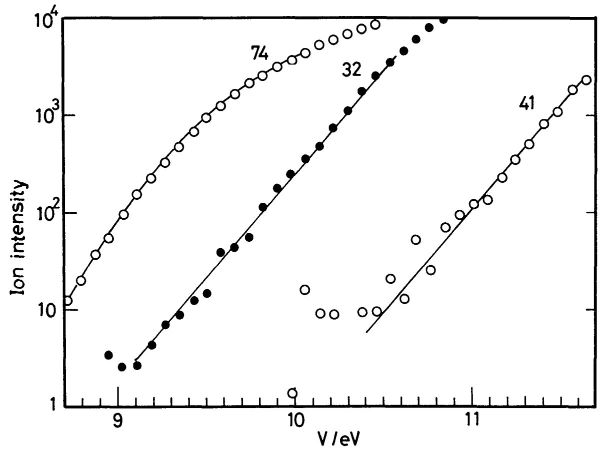

Fig. 2. The semi-log plots of the ion intensity of hydroxyacetone (74), methanol (32), and acetonitrile (41).

Table 1. Ionization and Appearance Energies in the Mass Spectra of Hydroxyacetone

Ions		*AE*/eV	
m/z		t=0 μs	t=900 μs
74	$CH_3COCH_2OH^+$	10.0±0.1	
73	$C_3H_5O_2^+$	11.8	11.6
45	$C_2H_5O^+$	10.5	10.3
43	CH_3CO^+	10.3	10.3
31	CH_3O^+	12.4	12.4
29	$C_2H_5^+$ CHO^+	13.7	13.7
28	$C_2H_4^+$ CO^+	11.3[b]	11.3
74→45*[a]		10.5	

a) The *AE* for the metastable ion was obtained from the procedure of Burgers and Holmes[15] using ethyl acetate as a reference standard. b) For example, *IE*s for N_2 and CO are 15.58 and 14.01 eV, respectively.[11]

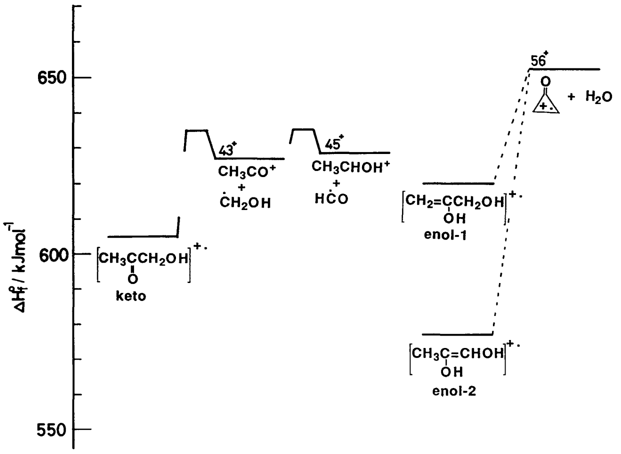

Fig. 3. A potential energy diagram of ionized hydroxyacetone and its enol isomers.

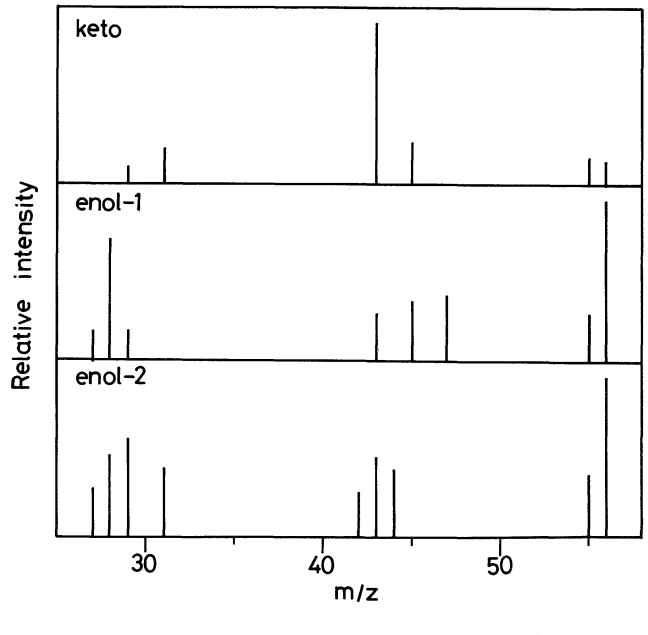

Fig. 4. Collisional activation spectra of ionized hydroxyacetone and its enol isomers.

Table 2. Metastable Ion Intensities and Kinetic Energy Releases for the Keto and Enol Forms

	Intensity ratio			
m/z	73	56	45	28
Keto (Hydroxyacetone)	1 (<10)[a]		9 (<10)	
Enol-1 (HyMH)	1 (<10)	0.5 (30±10)		
Enol-2 (HyH)		1 (<10)		0.09

a) The parentheses are $T_{0.5}$/meV.

These values were obtained from ΔH_f (neutral) estimated by the additivity rule[12] and measured *IE/AE*; the estimated values of ΔH_f (neutral) for hydroxyacetone, HyMH and HyH are −360, −459, and −446 kJ mol^{-1}, respectively. The *AE*s of enol-1 and enol-2 were 11.0 and 10.8 eV. The transition-state energies are those derived from the present *AE* measurements. The energy states of products were obtained assuming plausible ion structures, as shown in Fig. 3. Taking the estimation error into account, two enol forms are not so stable relative to the keto form. The activation energies relative to those of the enol isomers are still less than 1 eV. It is therefore difficult to explain the metastable rate based on isomerization prior to dissociation.

As can be seen in Fig. 4, the CA spectrum of the keto form is significantly different from the enol forms. Moreover, the results in Table 2 show that the metastable-ion intensities of hydroxyacetone are different from those of both enols. These results indicate that neither of the enols takes part in the metastable dissociation of ionized hydroxyacetone. The small kinetic energy release for m/z 45 is due to the low reverse activation energy (Fig. 3).

Finally, it is concluded that the hydroxyacetone ion does not isomerizes to the enol forms prior to dissociation. In addition, the previous results[1] concerning the metastable and CA spectra indicated that the hydroxyacetone ion was substantially different from the isomer structures produced from various esters, and $CH_3C(=OH^+)-CH_2O^\cdot$ from 2-acetoxy-2-methyloxirane. As a result, the keto form seems to be the precursor ion. Therefore, another reason for the slow metastable dissociation should be presented. The tunneling effect through a potential barrier[13] and participation of an anharmonic interaction potential[14] have been studied regarding the origin of slow dissociation. These mechanisms are, however, inadequate for an application to the present system. One possible mechanism for explaining such non-RRKM behavior is a slow predissociation due to an electronic spin-forbidden transition.

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References

1) C. Wesdemiotis, R. Csencsits, and F. W. McLafferty, *Org. Mass Spectrom.*, **20**, 98 (1985).

2) J. L. Holmes, C. E. C. A. Hop, and J. K. Terlouw, *Org. Mass Spectrom.*, **21**, 776 (1986).

3) P. C. Burgers, J. L. Holmes, C. E. C. A. Hop, and J. K. Terlouw, *Org. Mass Spectrom.*, **21**, 549 (1986).

4) N. Heinrich, J. Schmidt, H. Schwarz, and Y. Apeloig, *J. Am. Chem. Soc.*, **109**, 1317 (1987).

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

6) J. L. Holmes and F. P. Lossing, *J. Am. Chem. Soc.*, **102**, 1519 (1980).

7) R. Arakawa, *Bull. Chem. Soc. Jpn.*, **63**, 754 (1990).

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

9) H. A. Stansbury, Jr. and W. R. Proops, *J. Org. Chem.*, **27**, 279 (1962).

10) J. E. Baldwin, G. A. Hofle, and O. W. Lever, Jr., *J. Am. Chem. Soc.*, **96**, 7125 (1974).

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

12) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodger, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

13) J. H. Beynon, A. E. Fontaine, and G. R. Lester, *Int. J. Mass Spectrom. Ion Phys.*, **1**, 1 (1986); A. J. Illies, M. F. Jarrold, and M. T. Bowers, *J. Am. Chem. Soc.*, **104**, 3587 (1982).

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

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