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Thermochemistry and Unimolecular Reactions of Ionized Acetic Acid and Its Enol in the Gas Phase

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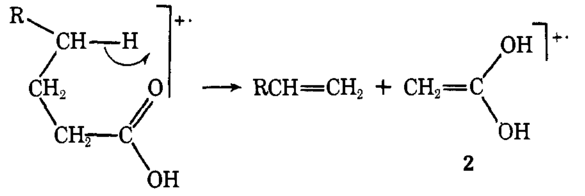
Abstract: The heats of formation of the molecular ion of acetic acid (**1**) and its tautomer $[CH_2{=}C(OH)_2]^{+\cdot}$ (**2**) have been obtained from ionization and appearance energies measured with energy selected electrons. The enolic ion, **2**, has $\Delta H_f = 120 \pm 1$ kcal mol^{-1} and is 22 ± 2 kcal mol^{-1} more stable than its ketonic tautomer, **1**. A detailed examination of metastable peak shapes for the losses of $OH^\cdot$ and H_2O from **1** and **2** and appropriate deuterium-labeled analogues led to the following conclusions. The loss of $OH^\cdot$ from **1** takes place at the thermochemical threshold for production of $[CH_3CO]^+$, but $OH^\cdot$ loss from the enolic ion, **2**, takes place at an appreciably higher energy. This excess energy may be ascribed to that required for a concerted 1,3 hydrogen shift, again to yield the acetyl cation. Some interconversion of **1** and **2** does take place among ions having sufficient energy to fragment in the microsecond time frame but this process is slow relative to the fragmentation reactions. Loss of H_2O from **1** must yield $[CH_2CO]^{+\cdot}$ as daughter ion but at an energy ca. 0.6 eV (15 kcal mol^{-1}) above the thermochemical threshold. Loss of H_2O from **2** requires a larger energy (possibly ca. 1.2 eV) but again generating the ketene molecular ion. The chief significance of these results is to show the importance of keto and enol forms of ionized acetic acid as reacting configurations for fragmentation reactions and that the two tautomers are not in equilibrium in these gas-phase systems.

Introduction

The thermochemistry and gas-phase unimolecular reactions of the simple tautomeric molecular ions, acetaldehyde and vinyl alcohol, have recently been described.[2] It was found that the ionized enol was 15 kcal mol^{-1} more stable than the acetaldehyde molecular ion (ΔH_f = 196 kcal mol^{-1}) and that the two ions could be easily identified from the shapes of the metastable peaks associated with the loss of a hydrogen atom.

The present work continues the examination of keto-enol cations and describes observations made on the molecular ion of acetic acid and its enolic form.

Previous experiments have shown that ionized acetic acid (**1**) generates important metastable peaks in its mass spectrum, corresponding to loss of $OH^\cdot$ and H_2O.[3-5] Similar metastable peaks appear in the mass spectrum of the enol[3-5] (**2**) which can unequivocally be generated by loss of an olefin from ionized butanoic acid (or a homologue) via a McLafferty rearrangement.[6]



The heat of formation, ΔH_f, of **1**, 142 kcal mol^{-1}, is well established (see Table I). ΔH_f(**2**) has recently been estimated to be 144 kcal mol^{-1},[5] making the keto form apparently more stable than its tautomer.

Activation energies for the losses of $OH^\cdot$ and H_2O from **1** and **2** have also been estimated[4,5] and a lower limit of 195 kcal mol^{-1} has been set for the interconversion of **1** and **2**. The metastable peak abundance ratios for losses of hydroxyl and water from the unlabeled[3] and deuterium-labeled tautomers[4,5] have been studied and it was concluded[5] that **2** undergoes a rate-determining 1,3-hydrogen shift to yield **1** prior to loss of $OH^\cdot$. It was also concluded that **1** and **2** eliminate H_2O *without* interconversion but yielding ionized ketene in each case.[5] Collisional activation (CA) mass spectra have been used[4] to show that **2** ions of low internal energy do not readily isomerize to **1**, and that ionized ketene is produced by loss of H_2O from both tautomers.[5]

The purpose of the present investigation was firmly to establish the heat of formation of the enol **2**, to measure the activation energies for the losses of $OH^\cdot$ and H_2O from **1** and **2**, and to examine in detail the shapes of the corresponding metastable peaks. It was hoped that the metastable peak shapes would unequivocally show whether **1** and **2** fragment independently by OH loss or whether the rate-determining isomerization referred to above governed the metastable fragmentations of **2**.

Results and Discussion

Ionic Heats of Formation. The electron impact ionization

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Table I. Heats of Formation of $[C_2H_4O_2]^{+\cdot}$ Ions

compd	ΔH_f, kcal mol^{-1}	AE $[C_2H_4O_2^{+\cdot}]$, eV	ΔH_f $[C_2H_4O_2^{+\cdot}]$, kcal mol^{-1}
CH_3COOH	-103.3^{9}	10.70^{7}	143
		10.63^{8}	142
		10.66^{a}	142
$CH_3CH_2CH_2COOH$	-112.8^{b}	10.60^{a}	119
$CH_3(CH_2)_3COOH$	-117.2^{9}	10.56^{a}	121
$CH_3(CH_2)_4COOH$	-122.7^{9}	10.52^{a}	120^{c}
$CH_3(CH_2)_5COOH$	-127.7^{9}	10.54^{a}	121^{c}

[a] Electron impact values, this work; all ±0.05 eV. [b] In the absence of a "selected value" in ref 9 ΔH_f for the neutral acid was calculated by additivity;[10] a correction of +1 kcal applied to the result because the additivity method gave ΔH_f values approximately 1 kcal mol^{-1} below the "selected values" for acids in ref 9. [c] Calculated assuming that but-1-ene and pent-1-ene are the respective neutral olefins.

(IE) and appearance energies (AE) obtained using energy-selected electrons are shown in Table I together with the heats of formation of the neutral precursor molecules. Heats of formation of the ions were calculated from the relationships IE = $\Delta H_f[C_2H_4O_2]^{+\cdot} - \Delta H_f[C_2H_4O_2]$ and AE = $\Delta H_f[C_2H_4O_2]^{+\cdot} - \Delta H_f$[precursor acid] + ΔH_f[olefin]. It is clear that the enol of ionized acetic acid has $\Delta H_f = 120 \pm 1$ kcal mol^{-1} and is thus the more stable tautomer by 22 kcal mol^{-1}, with a probable error of ±2 kcal mol^{-1}, a stabilization energy significantly greater than that for ionized vinyl alcohol vs. acetaldehyde,[2b] 15 kcal mol^{-1}.

The metastable peaks for the olefin losses from the ionized acids were of the same Gaussian type. Energy releases from half-height widths of the metastable peaks were 3 and 9 meV for butanoic and pentanoic acids, respectively. For hexanoic and heptanoic acids no metastable peaks were observed for the fragmentations m/z 116 → 60 and 130 → 60, respectively. The very small energy releases permit us to conclude that the reactions involve no significant reverse activation energy.

The AE for loss of OH$^\cdot$ from **1** was measured as 11.54 ± 0.05 eV (11.45 ± 0.15[11]); the calculated AE for (CH_3CO^+ + OH$^\cdot$) is 11.43 eV [$\Delta H_f[CH_3COOH] = -103.3$, $\Delta H_f[OH^\cdot] = 9.3$, $\Delta H_f[CH_3CO]^+ = 151$ kcal mol^{-1}][11] and thus the daughter ion at threshold is undoubtedly $[CH_3CO]^+$. The AE for m/z 42 (H_2O loss) proved impossible to measure because the ion abundance asymptotically approached zero at ca. 9.7 eV, and must arise from a trace impurity, possibly neutral ketene. Measurements of the AE for m/z 42 and 43 from homologues of acetic acid proved similarly unreliable; furthermore, the composition of the daughter ions could not be ascertained with the quadrupole mass analyzer (e.g., m/z 43 = CH_3CO^+ or $C_3H_7^+$) (see Experimental Section).

In the case of butanoic acid the differences between the AE for the metastable peaks for the fragmentations (1) m/z 60 → 43, (2) m/z 60 → 42, and that for (3) m/z 88 → 60 were measured. The results were in satisfactory agreement with the similar observation of Levsen and Schwarz,[4] AE(1) − AE(3) = 1.6 ± 0.2 eV (37 ± 5 kcal mol^{-1}) (1.7 ± 0.2 eV)[4] and AE(2) − AE(3) = 1.9 ± 0.2 eV (44 ± 5 kcal mol^{-1}) (1.9 ± 0.2 eV).[4] The difference AE(2) − AE(1) was also measured for acetic, pentanoic, and heptanoic acids and in each case AE(2) was ≤0.2 eV (≤5 kcal mol^{-1}) greater than AE(1). The thermochemical results are summarized in Figure 1, which shows the threshold energies for the above processes. Thus OH$^\cdot$ and H_2O loss from the $[C_2H_4O_2]^{+\cdot}$ tautomers have common *threshold* energies. These results are in marked disagreement with those of Schwarz et al.,[5] who reported no AE values for any of the reactions discussed above and presented an energy diagram showing $\Delta H_f[CH_2C(OH)_2]^{+\cdot} \simeq 144$ kcal mol^{-1}. However, the activation energies shown by Schwarz et al. for OH$^\cdot$ and H_2O loss from **2**, 51 and 48 kcal mol^{-1}, respectively (2.2 and 2.1 eV), are moderately compatible with the present results and the earlier observations of Levsen and Schwarz.[4] The results thus far indicate either that **1** can be produced directly by loss of C_2H_4 from ionized butanoic acid or that **2** can convert to **1** at energies comparable with the thresholds for the ionic fragmentations.

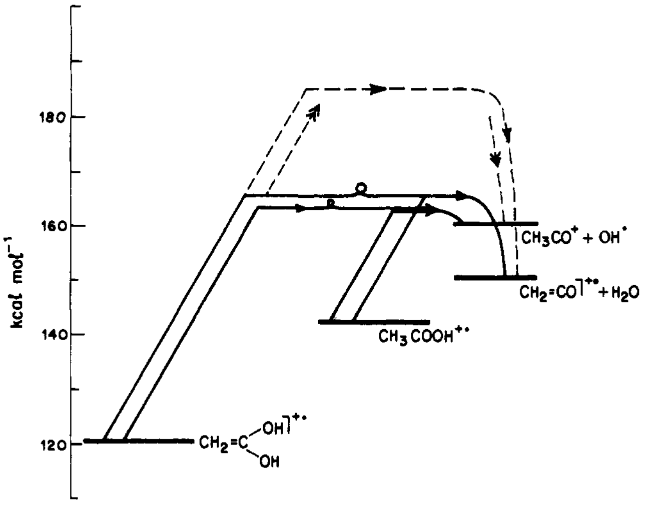


Figure 1. Energy diagram for the ketonic and enolic forms of $[C_2H_4O_2]^{+\cdot}$ ions, showing the minimum energies for their fragmentation by loss of OH$^\cdot$ and H_2O. The energy level for OH$^\cdot$ loss from $[CH_2{=}C(OH)_2]^{+\cdot}$ could not be estimated.

Table II. Relative Abundances of Metastable Peaks[a] for the Losses of Hydroxyl and Water from Ionized Acetic Acid and Its Enol

	neutral fragment			
$[ion]^{+\cdot}$	OH$^\cdot$	OD$^\cdot$	H_2O	HDO
CH_3COOH	69 (45) 92,[5] 88,[3], 87[12] 78[b]		31 (55) 8,[5] 12,[3] 13[12] 22[b]	
CH_3COOD	5 (10) 4[12] 2[b]	70 (52) 91,[5] 81[12] 70[b]		25 (38) 9,[5] 15[12] 28[b]
CD_3COOH	94 (88) 95,[5] 94[12]	4 (8)		2 (4) 5,[5] 6[12]
$CH_2{=}C(OH)_2$[c]	28 (19) 32,[5] 25[12]		72 (81) 68,[5] 75[12]	
$CH_2{=}C(OH)(OD)$[c]	8 (5.5) 9,[5] 9[12]	19 (14) 22,[5] 18[12]		73 (80.5) 65,[5] 73[12]

[a] Measured with a Kratos-A.E.I. MS902S mass spectrometer under conditions of good energy resolution.[15] Peak heights are presented above; peak *areas* are in parentheses. All peaks were observed at the same acceleration potential, 7100 V, to ensure that fragmentations were compared at identical times after ionization. [b] Measured with a V.G. Micromass ZAB-2f mass spectrometer. [c] Generated from butanoic acid and butanoic acid-*O-d*.

Metastable Peak Studies. The relative abundances of the metastable peaks for the losses of OH$^\cdot$, OD$^\cdot$, H_2O, and HDO from unlabeled and D_2O-exchanged acetic[3,5,12] and butanoic[4,5,12] acid molecular ions have been reported previously. These together with the present results are shown in Table II. Agreement between the various observations is poor in the case of acetic acid but good for butanoic acid.

Previous results[5] indicated no appreciable isotope effects for the fragmentations of labeled acetic acids. The present results, however, indicate a significant deuterium isotope effect acting against the elimination of HDO from CD_3COOH, where the deuterium atom is that which has to be transferred (from methyl to hydroxyl) prior to HDO loss (see Table II). In agreement with the earlier work[5,12] enolic ions generated

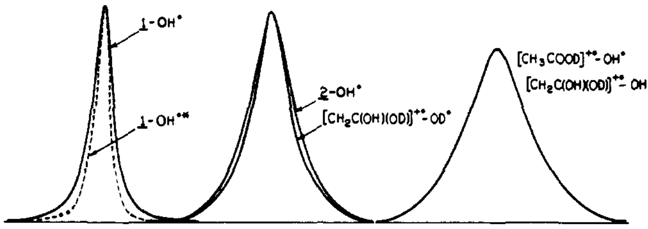


Figure 2. Metastable peak shapes for hydroxyl loss from $[C_2H_4O_2]^{+\cdot}$ ions. (The peak widths are drawn to a common scale but the peak heights are arbitrary.) * The inner (broken line) peak for **1** − OH is that observed at longer ion lifetimes (see text).

Table III. Kinetic Energy Releases in the Metastable Losses of Hydroxyl and Water from $[C_2H_4O_2]^{+\cdot}$ and $[C_2H_3DO_2]^{+\cdot}$ Ions

	kinetic energy release ($T_{0.5}$), meV neutral fragment			
$[\text{ion}]^{+\cdot}$	$OH^\cdot$	$OD^\cdot$	H_2O	HDO
CH_3COOH	4.2 ± 0.1[a]		28[a]	
	13[b]		30[b]	
	2.3 ± 0.1[c]		27[c]	
CH_3COOD	41 ± 4[a]	4.6 ± 0.2[a]		29[a]
CD_3COOH	3.6 ± 0.2			
$CH_2{=}C(OH)_2$	21[a]		63[a]	
	95[b]		260[b]	
$CH_2{=}C(OH)(OD)$	40[a]	16[a]		70[a]

[a] Measured with a Kratos-A.E.I. MS902S mass spectrometer under conditions of good energy resolution.[15] Main beam width (7100 V) ca. 3 V. Except where indicated, all values ±1 meV. [b] Values from ref 5, reported as "average energy releases". [c] Measured with a V.G. Micromass ZAB-2f mass spectrometer.

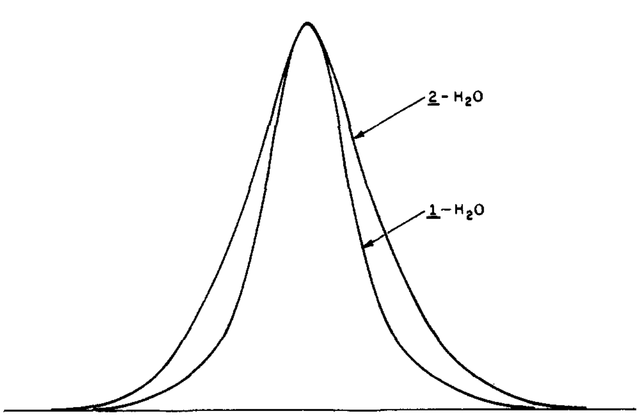


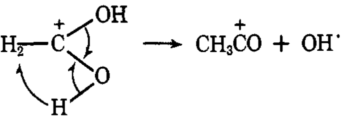
Figure 3. Metastable peak shapes for water elimination from $[C_2H_4O_2]^{+\cdot}$ ions. (The peak widths are drawn to a common scale but the peak heights are arbitrary.)

from butanoic acid-*O-d* lose more OD than OH but the abundances of hydroxyl vs. water loss processes are isotope independent. The present observations are in keeping with the reaction mechanisms proposed (see below).

The metastable peak shapes were also measured under conditions of good energy resolution; the peak shapes were not of simple Gaussian form and so peaks for $OH^\cdot$ and H_2O losses will be discussed separately.

Metastable Peaks for Hydroxyl Loss. The metastable peaks for loss of $OH^\cdot$ from $[C_2H_4O_2]^{+\cdot}$ ions produced from acetic and butanoic acids are shown in Figure 2, which also includes the metastable peaks for loss of $OD^\cdot$ and $OH^\cdot$ from m/z 61 generated from butanoic acid-*O-d* and for $OH^\cdot$ loss from acetic acid-*O-d*. The latter peak is of low abundance (see Table II) but note that a signal of similar breadth can clearly be seen at the foot of the peak for $OH^\cdot$ loss from **1**. The kinetic energy releases corresponding to the half-height widths of these peaks are given in Table III.

We propose that these metastable peaks are composite signals, made up from a common pair of components, a narrow Gaussian peak resulting from the threshold loss of $OH^\cdot$ from ions of structure **1** and a broad component corresponding to $OH^\cdot$ loss from **2**. Composite metastable peaks are generated when an ion fragments via two pathways having similar rate constants but involving different potential surfaces, e.g., a single fragmenting ion structure yielding two isomeric daughter ions or a pair of reacting configurations of the fragmenting ion yielding a single daughter ion.[13,14] Such reactions are unlikely to have activation energies differing by more than ~1 eV. If acetyl cations are generated directly from **2**, then the larger energy release results from this fragmentation having a significantly higher activation energy than that for the ketonic ion. The magnitude of this activation energy cannot be directly measured. The concomitant 1,3 hydrogen shift may, as was proposed by Schwarz et al.,[5] be responsible for the energy requirement:



The proportion of narrow Gaussian component in the peak for loss of $OD^\cdot$ from **2** (produced from butanoic acid-*O-d*) is clearly greater than that in the peak for **2** − $OH^\cdot$ (see Figure 2). Proportionate summation of the peaks for $OH^\cdot$ and $OD^\cdot$ loss from deuterated **2** reproduces the peak for loss of $OH^\cdot$ from unlabeled **2**. It must be noted that the peak for loss of $OH^\cdot$ from deuterated **1** and **2** also probably contains both components because its profile differs considerably from that of a typical Gaussian-type metastable peak; e.g., the ratio of the peak width at 10% of its height to that at half height, 2.55, is significantly greater than that most commonly observed in Gaussian-type metastable peaks, 1.8 → 2.1. This observation is also therefore compatible with the metastable peak being composite.

The metastable peaks for the loss of $OH^\cdot$ and H_2O from **1** were also measured at longer times using a V.G. Micromass ZAB-2f mass spectrometer (relative time scales of the observations, MS902S first field-free region, ca. 2 μs, ZAB-2f mass analyzed ion kinetic energy spectrum, ca. 10 μs[16]). The $T_{0.5}$ value for H_2O loss decreased slightly (Table III) but the $OH^\cdot$ loss peak had a significantly narrower profile at the longer times (Figure 2), a further indication of the composite nature of the metastable peak. It is noteworthy that the relative abundances of the two components in this peak are markedly dependent upon the precursor ion. Observations on such $C_2H_4O_2^{+\cdot}$ ions generated from a variety of homologous aliphatic acids will be reported elsewhere.

Metastable Peaks for Water Elimination. The metastable peaks for loss of H_2O from **1** and **2** are shown in Figure 3. Deuterium substitution does not significantly alter the peak shapes. The peak for loss of H_2O from the molecular ion of acetic acid has a very broad base, similar to that for loss of H_2O from **2**. It is possible that both forms of the $[C_2H_4O_2]^{+\cdot}$ ion again are contributing to these metastable peaks, although the distinction is not so clearly discernible as in the case of hydroxyl loss. The metastable peak from **1** showing the smaller energy release must correspond to the process yielding $[\text{ketene}]^{+\cdot}$ as daughter ion. The magnitude of the energy release ($T_{0.5}$ = 28 meV) is compatible with the fragmentation not taking place at the minimum for $[CH_2CO]^{+\cdot}$ formation but having a reverse activation energy, the magnitude of which is ~0.6 eV (15 kcal mol^{-1}). It is noteworthy that in this molecular elimination the reverse activation energy is not largely converted into translational energy of the products; i.e., the reaction between $[CH_2CO]^{+\cdot}$ and H_2O is favored by vibrational energy of the reactants rather than their relative translational energies. The fragmenting ion in this reaction is assumed to have the acetic acid structure; the larger energy release process may then be ascribed to decomposition of the enolic ion, **2**. If the ratio of the energy releases approximately corresponds to the ratio of the internal energies of the fragmenting ions (and assuming that the same daughter ion is being produced), then the threshold for the higher energy process lies at the 185 ± 5 kcal mol^{-1} level in Figure 1. It is not unlikely that an alternative daughter ion structure is being produced. (Note that $\Delta H_f[CH{\equiv}COH]^{+\cdot} \simeq 242$ kcal mol^{-1}, assuming that substitution of $H^\cdot$ by $OH^\cdot$ reduces ΔH_f by ca. 75 kcal mol^{-1}; taking $\Delta H_f\,[C_2H_4]^{+\cdot} = 256$ kcal mol^{-1},[11] $\Delta H_f[CH_2CHOH]^{+\cdot} = 181$ kcal mol^{-1},[2] $\Delta H_f[C_2H_2]^{+\cdot} = 317$ kcal mol^{-1}.[11])

Reaction Mechanisms. Within the range of internal energies of ions decomposing in the microsecond time frame, a slow interconversion of ketonic and enolic ions can take place. This conclusion follows from the observation of the small, broad component in the metastable peak for $OH^\cdot$ loss from **1** and the common (broad) metastable peak for loss of $OH^\cdot$ from deuterium-exchanged **1** and **2**. (Although it is formally possible that **1** could be generated *directly* from butanoic acid, such a proposal is not warranted by the present observations.) This tautomeric rearrangement competes unfavorably with the fragmentation processes. The larger energy release process for $OH^\cdot$ loss can be ascribed to fragmentation of the enol ion. It is unlikely that the resulting daughter ion is $[CH_2COH]^+$, whose heat of formation is ca. 40 kcal mol^{-1} above that for $[CH_3CO]^+$ (assuming that $\Delta H_f[CH_2COH]^+ \simeq \Delta H_f[C_2H_3]^+$ (266 kcal mol^{-1} [11]) $- \Delta H_f[C_2H_4]^{+\cdot}$ (256 kcal mol^{-1} [11]) $+ \Delta H_f[CH_2CHOH]^{+\cdot}$ (181 kcal mol^{-1} [2]) $\simeq 192$ kcal mol^{-1}). Similarly, $[CH_2CHO]^+$ is an improbable daughter ion. Its heat of formation has been estimated by ourselves from AE *m/z* 43 from $CH_3OCH{=}CH_2 = 10.56 \pm 0.05$ eV; $\Delta H_f[CH_3OCH{=}CH_2] = -26.5$ kcal mol^{-1},[10] $\Delta H_f[CH_3^\cdot] = 34$ kcal mol^{-1},[11] whence $\Delta H_f[CH_2CHO]^{+\cdot} = 183$ kcal mol^{-1}. (Alternatively $\Delta H_f[CH_2CHO]^+ \simeq \Delta H_f[CH_3]^+$ (261 kcal mol^{-1} [11]) $- \Delta H_f\,[CH_4]^+$ (273 kcal mol^{-1} [11]) $+ \Delta H_f[CH_3CHO]^{+\cdot}$ (196 kcal mol^{-1} [2]) $\simeq 184$ kcal mol^{-1}.) Formation of these alternative daughter ions would require activation energies of ca. 41 and 33 kcal mol^{-1}, respectively, above the threshold for $[CH_3CO]^+$ production and it is very unlikely that these higher energy reactions could compete in the microsecond time frame with the low-energy pathway. The remaining possibility is that the larger energy release fragmentation is a concerted reaction as depicted above. The isotope effect noted above is in accord with such a mechanism with $OD^\cdot$ loss exceeding $OH^\cdot$ loss from $[CH_2C(OH)OD]^{+\cdot}$. These conclusions disagree with that of Schwarz et al.,[5] who proposed that the isomerization of **2** to **1** was the rate-determining process for $OH^\cdot$ loss from **2**. However, their conclusion was drawn from inadequate thermochemical data and without consideration of the metastable peak shapes.

The eliminations of water from **1** and **2** both involve 1,3 hydrogen shifts; that for **1** which proceeds via a hydrogen transfer from methyl to hydroxyl oxygen, confers a reverse activation energy of ca. 0.6 eV (15 kcal mol^{-1}) on the fragmentation. For **2**, a hydroxyl to hydroxyl hydrogen shift is required for $[CH_2CO]^{+\cdot}$ generation, and this involves an appreciably larger reverse activation energy, possibly twice as great as that for **1**. If the metastable peaks for water loss are indeed composite, then arguments similar to the above may apply to the concerted or stepwise nature of water-loss mechanisms vs. daughter-ion structures. The present results do not permit any firm conclusions other than that $[\text{ketene}]^{+\cdot}$ is the daughter ion produced at threshold.

An extended discussion of the thermochemistry of ketonic and enolic forms of ionized carbonyl compounds and their role in unimolecular ionic fragmentations has been published.[17]

Experimental Section

The electron impact ionization and appearance energies were measured with an apparatus comprising an electrostatic electron monochromator[18] together with a quadrupole mass analyzer and minicomputer data system[19] which has been described elsewhere.

Compounds were of research-grade purity. Deuteration of the acids was achieved by exchange with excess D_2O in the inlet system of the MS902S mass spectrometer. Metastable peak shapes and energy releases were measured under conditions of good energy resolution as described elsewhere.[15]

The difference in AEs of the metastable peaks (again arising from fragmentations taking place in the field-free region between the ion source and the electric sector of the MS902S mass spectrometer) was estimated by measuring the metastable peak abundances over the last 2 V above their thresholds and normalizing the curves to the relative abundance of the metastable peaks at (nominal) 20 eV. For these measurements the energy resolving slit was set to a width of 0.5 mm in order to improve sensitivity. All metastable peaks were observed at an accelerating voltage of 7100 V. Ion source focusing voltages were optimized for metastable peak observation at (nominal) 20 eV and were not adjusted when the electron energy was lowered. The reported AE differences represent the averaged difference between the AE curves over the three lowest readings (a voltage range of 0.4 V).

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