Metastable Decomposition of $C_3H_6O^{+\cdot}$ Ions

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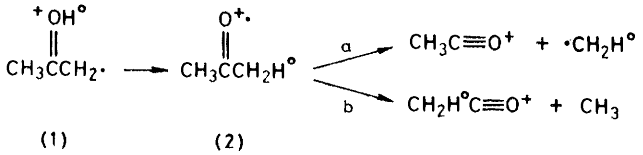
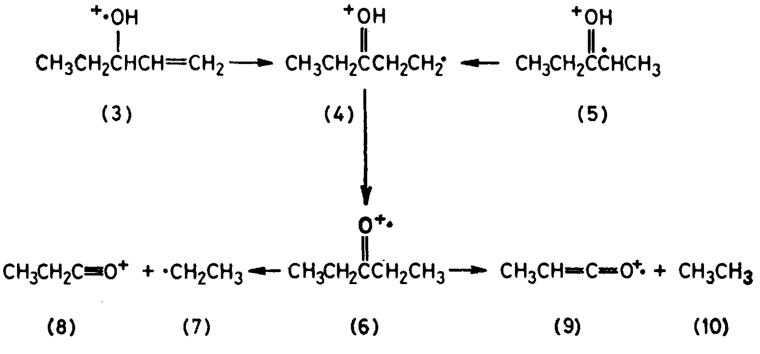
The metastable enol isomer (1) of the acetone ion probably ketonizes and then loses methyl in the mass spectrometer. We report here that ionized acetone (2) loses methane instead of methyl upon metastable decomposition. The metastable losses of methyl and methane starting from (1) and (2) differ in relative rate by >10^4, apparently due to excess internal energy in the keto-ions generated by isomerization. $C_3H_6O^{+\cdot}$ ions with the oxygen on the first carbon lose a hydrogen atom rather than methyl or methane. Thus, metastable $C_3H_6O^{+\cdot}$ ions with the oxygen on the first carbon do not rearrange to their isomers with the oxygen on the second carbon, in contrast to $C_4H_8O^{+\cdot}$ ions.

THE metastable decompositions of simple carbonyl-containing ions and their isomers are preceded by a variety of rearrangements,[1-5] some of which are not completely understood. We are characterizing the metastable decompositions of such ions to determine the extent to which general mechanisms for the reactions of related metastable ions can be defined.



SCHEME 1

While metastable decompositions of $C_3H_6O^{+\cdot}$ ions with the oxygen on the middle carbon have been studied,[1,6,7] reactions of the isomeric ions with the oxygen on the first carbon have not been reported. The enol form of the acetone ion appears to decompose according to Scheme 1.[1,7] This mechanism is supported by the decomposition patterns of labelled ions, isotope effects, identical appearance energies for the two methyl losses, and very similar dependences of the rates of the two methyl losses on ion internal energy.[1] There appears to be an energy barrier between (1) and (2) such that ions formed by (1) ⟶ (2) contain substantially more energy than they need to decompose,[1,7] so the first step of Scheme 1 should be slow and the second step very rapid. A problem with accepting Scheme 1 is that step b occurs at 0.72 times the rate of a, instead of at the same rate. The unequal rates have been attributed to non-randomization of energy following (1) ⟶ (2).[1] Others[6] have favoured a concerted hydrogen transfer and loss of methyl from (1) based on their failure to observe metastable decompositions of (2), and different energy releases in the collision-induced decompositions of (1) and (2). However, the ions from the two sources undergoing collision differ in structure, since unimolecular decomposition following (1) ⟶ (2) is probably too rapid for an appreciable concentration of acetone ions to build up. Hence the differences in the collision-induced decompositions of (1) and (2) do not rule out the mechanism in Scheme 1. The differences in internal energy between the acetone ions formed by direct ionization and by (1) ⟶ (2) could give substantially different reactions of those ions, since other examples of differing reaction patterns of the same ions formed by direct ionization and by isomerization due to resulting internal energy differences have since been reported.[8-10] Metastable $C_5H_{10}O^{+\cdot}$ ions with the oxygen on the middle carbon all decompose from the pentan-3-one structure (Scheme 2).[4] However, directly ionized pentan-3-one loses ethane at least 100 times as often as it loses ethyl, while the other three $C_5H_{10}O^{+\cdot}$ ions with the oxygen on the middle carbon all lose ethyl *ca.* 50 times as often as they lose ethane. This reactivity difference has been attributed to internal energy differences between isomerized and non-isomerized pentan-3-one ions.[5]



SCHEME 2

The $C_3H_6O^{+\cdot}$ metastable decompositions remain of interest because of the uncertainties regarding the dynamics of decomposition of (1). The observations on the $C_5H_{10}O^{+\bullet}$ ions [4] led us determine whether metastable (2) loses methane even though loss of methyl appears to follow (1) ⟶ (2), and the conclusion that non-ether metastable $C_4H_8O^{+\bullet}$ ions decompose largely by common mechanisms caused us to compare the decompositions of metastable $C_3H_6O^{+\bullet}$ ions with the oxygen on the first and second carbons.

RESULTS

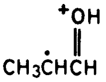
The relative intensities of peaks representing the metastable decompositions of $C_3H_6O^{+\bullet}$ ions with oxygen on the second carbon are given in Table 1. As reported previously,[1] the enol ion loses methyl, but it also loses methane 0.7% as often as it loses methyl. In contrast, the only significant unimolecular decomposition of the metastable acetone ion is loss of methane. A peak representing loss of methyl from (2) was observed, but its appearance energy matched that of (2), indicating that the process was predominantly collision-induced. The appearance energy for the loss of methane from (2) was 53 ± 12 kJ mol^{-1} higher than that for (2) itself, demonstrating that that process is unimolecular. The energy released in this loss of methane was 0.36 ± 0.03 kJ mol^{-1}, while the energy released in the loss of methyl starting from (1) was 5.8 ± 0.9 kJ mol^{-1}. The latter value compares reasonably with a previously reported value of *ca.* 4.6 kJ mol^{-1}.[6]

TABLE 1

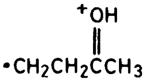
Intensities of peaks representing loss of methyl and methane from $C_3H_6O^{+\bullet}$ ions

Ion	$-CH_3$	$-CH_4$
(2)	9.3 [a]	100
(1) [b]	100	0.7

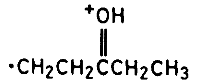
[a] >90% collision-induced. [b] Obtained from heptan-2-one.


$CH_3\overset{\bullet}{C}H\overset{\overset{+}{O}H}{\overset{\|}{C}}H$

(11)

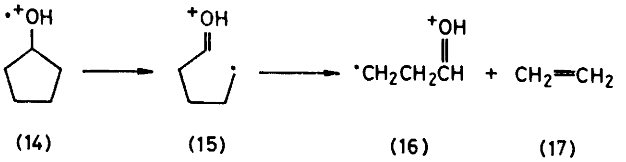

$\bullet CH_2CH_2\overset{\overset{+}{O}H}{\overset{\|}{C}}CH_3$

(12)


$\bullet CH_2CH_2\overset{\overset{+}{O}H}{\overset{\|}{C}}CH_2CH_3$

(13)

The relative intensities of the peaks representing decomposition of metastable $C_3(H,D)_6O^{+\bullet}$ ions with the oxygen on the first carbon are given in Table 2. All the metastable $C_3H_6O^{+\bullet}$ ions with the oxygen on the first carbon lose only a hydrogen atom, while some loss of deuterium takes place from all $C_3(H,D)_6O^{+\bullet}$ ions examined. Propanal and allyl alcohol ions were obtained by ionization of the corresponding molecules. Species (11) was obtained by the McLafferty rearrangement of ionized 2-methylpentanal, while an attempt was made to obtain (16) from cyclopentanol according to Scheme 3. Appearance energy measurements indicate that this reaction may give (16).[11] However, species (12) and (13) appear to be produced in reactions analogous to Scheme 3.[3,4]



SCHEME 3

DISCUSSION

Decompositions of (1) *and* (2)—The reactions of these two ions differ drastically in that (1) loses methyl almost exclusively, while (2) loses predominantly methane. This might be taken as evidence that (1) and (2) do not decompose from the same structure. However ionized pentan-3-one loses only ethane upon metastable decomposition, while $C_5H_{10}O^{+\bullet}$ ions which isomerize to the pentan-3-one structure prior to metastable decomposition lose ethyl *ca.* 50 times as often as they lose ethane.[4] We think it highly unlikely that hydrogen rearrangement from the oxygen to C-1 (Scheme 2) and C–C bond cleavage on either side of the carbonyl group could be concerted in $C_5H_{10}O^{+\bullet}$ ions since the bonds between the carbons do not need to be altered during the hydrogen transfer, and C–C bond cleavage in concert with hydrogen transfer would considerably raise the activation energy for the overall decomposition. The conclusion that the decomposition of (1) is stepwise is made more reasonable, although not proven, by the similarity of the metastable decompositions of the keto

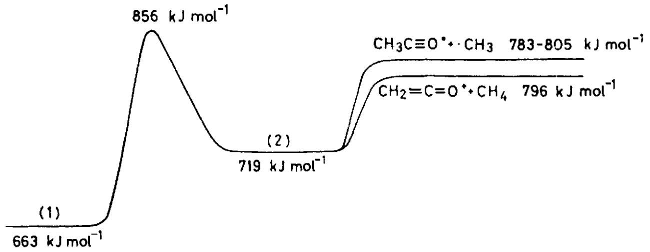
TABLE 2

The metastable decompositions of $C_3(H,D)_6O^{+\bullet}$ ions

Ion	Source	$-H$	$-D$	$\frac{\text{Obs. D/H}}{\text{Stat. D/H}}$
$CH_3CH_2CHO^{+\bullet}$	Propanal	100		
$CH_2{=}CHCH_2\overset{+}{O}\overset{\bullet}{H}$	Allyl alcohol	100		
$CH_2{=}CHCH_2\overset{+}{O}\overset{\bullet}{D}$	Allyl [^{2}H]alcohol	100	1.8	0.09
$\cdot CH_2CH_2CH({=}\overset{+}{O}H)$	Cyclopentanol	100		
$\cdot CH_2CH_2CH({=}\overset{+}{O}D)$	Cyclopentan[^{2}H]ol	100	3.2	0.16
$\cdot CH_2CH_2CD({=}\overset{+}{O}H)$	[1-$^2H_1$]Cyclopentanol	100	5.8	0.29
$\cdot CM_2CH_2CD({=}\overset{+}{O}D)$	[1-$^2H_1$]Cyclopentan[^{2}H]ol	100	12	0.24
$\cdot CH_2CD_2CH({=}\overset{+}{O}H)$	[2,2,5,5-$^2H_4$]Cyclopentanol	100	21	0.42
$CH_3\overset{\bullet}{C}DCH({=}\overset{+}{O}H)$	[2-$^2H_1$]-2-Methylpentanal	100	6.2	0.31
$\cdot CH_2CD_2CH({=}\overset{+}{O}D)$	[2,2,5,5-$^2H_4$]Cyclopentan[^{2}H]ol	100	48	0.48

and enol $C_3H_6O^{+\cdot}$ and $C_5H_{10}O^{+\cdot}$ ions. The change in the relative rates of methyl and methane loss by more than 10^4 between (1) and (2) observed here is the largest difference in metastable decomposition patterns *via* the same structure yet reported.

The Figure represents the energy surface for the metastable decompositions of $C_3H_6O^{+\cdot}$ ions with the oxygen on the middle carbon. It should take 120—142 kJ mol^{-1} to form $CH_3C{\equiv}O^+ + \cdot CH_3$ from (1) {based on ΔH_f ($\cdot CH_3$) 142 kJ mol^{-1} [12] ΔH_f ($CH_3C{\equiv}O^+$) 663 or 641 kJ mol^{-1} [13] and ΔH_f $[CH_3C(=\overset{+}{O}H)\dot{C}H_2]$ 663 kJ mol^{-1} [14]}. Published appearance energies indicate that *ca.* 193 kJ mol^{-1} is actually required.[1] Thus, if (1) isomerizes to (2) and then decomposes, the intermediate (2) contains *ca.* 51—73 kJ mol^{-1} more energy than it requires to decompose. (The same values indicate that 64—86 kJ mol^{-1} should be required to fragment (2) to $CH_3C{\equiv}O^+ + \cdot CH_3$ {ΔH_f $[CH_3C(=\overset{+}{O})\cdot CH_3]$ 719 kJ mol^{-1} [14]}; the observed value being 63 kJ mol^{-1}.[14]) The much greater energy release in the loss of methyl following (1) $\longrightarrow$ (2) than in the loss of methane from (2) supports the existence of an activation energy for (1) $\longrightarrow$ (2) substantially in excess of the energy required to subsequently decompose 2.[9,10]



Potential surface for the metastable decompositions of (1) and (2) based on published heats of formation and appearance energies as described in the text

$C_3H_6O^{+\cdot}$ ions with the oxygen on the middle carbon,[1] the enol isomer of the acetic acid ion,[5,15] most $C_4H_8O^{+\cdot}$ ions,[3] and $C_5H_{10}O^{+\cdot}$ ions with the oxygen on the middle carbon [4] all decompose predominantly or totally *via* their keto-isomers. However, ionized acetone and pentan-3-one both lose alkane molecules upon metastable decomposition, while ionized butan-2-one loses methyl and ethyl at least 20 times as often as it loses methane and ethane.[16]

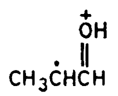
The Figure compares the heats of formation of the products of the decomposition of both (1) and (2). We utilize a published heat of formation [12] for $CH_2{=}C{=}O^+$ [871 kJ mol^{-1}, ΔH_f (CH_4) 75 kJ mol^{-1} [12]] based on photoelectron spectroscopy rather than the difference in appearance energies given in the Results section because the former value is likely to be more accurate. Whether the loss of methane or the loss of methyl from (2) is found to be energetically favoured depends on the value utilized for ΔH_f ($CH_3C{\equiv}O^+$). Therefore the value 663 kJ mol^{-1} for ΔH_f ($CH_3C{\equiv}O^+$),[13] which indicates that CH_4 loss is energetically favoured, is almost certainly more nearly correct.

Metastable Decompositions of $C_3H_6O^{+\cdot}$ Ions with the Oxygen on the First Carbon.—These ions lose H· at least 100 more times often than they lose methyl or methane. Thus, in contrast to $C_4H_8O^{+\cdot}$ ions,[3] $C_3H_6O^{+\cdot}$ ions with the oxygen on the first carbon do not isomerize to ions with the oxygen in the second position, or *vice versa*.

The losses of deuterium from $C_3(H,D)_6O^{+\cdot}$ ions with the oxygen on the first carbon indicate that hydrogens initially on the oxygen, C-1, and C-2 are lost by these ions, while no results were obtained regarding the C-3 hydrogens. Of the positions examined, hydrogens are lost most readily from C-2 and least readily from the oxygen. Hydrogens on each of the carbons of allyl alcohol, but not the oxygen, are lost at similar rates at higher energies, probably indicating randomization of those hydrogens over the carbon atoms prior to H· loss.[17] The metastable propanoic acid ion and its enol isomer, which also decompose predominantly by loss of H·, form an almost equilibrated mixture of structures prior to decomposing.[18] Thus, the most likely reason that hydrogens are lost from all the $C_3H_6O^{+\cdot}$ ions with the oxygen on the first carbon, and apparently from all positions of those ions, is that those ions interconvert extensively prior to decomposing and lose H· by a common mechanism or mechanisms. At lower energies (18) isomerizes to (19), but (20) maintains its identity.[19] There are two reasonable products of the H· loss from $C_3H_6O^{+\cdot}$ ions, (8) and (21). Since metastable (22) decomposes to (8),[3] formation of the propanoyl ion might be expected upon the loss of H· from $C_3H_6O^{+\cdot}$ ions. However, the stronger relative loss of D· from (23) than from (24) might be interpreted as evidence for formation of (21).

$CH_2{=}CHCH_2\overset{+\cdot}{O}H$

(18)


$CH_3\dot{C}H\overset{\overset{+}{O}H}{\overset{\|}{C}}H$

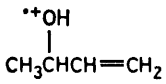
(19)

$CH_3CH_2CH\overset{+\cdot}{O}$

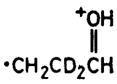
(20)

$CH_2{=}CHCH{=}\overset{+}{O}H$

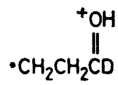
(21)


$CH_3\overset{\overset{+\cdot}{O}H}{\overset{|}{C}}HCH{=}CH_2$

(22)


$\cdot CH_2CD_2\overset{\overset{+}{O}H}{\overset{\|}{C}}H$

(23)


$\cdot CH_2CH_2\overset{\overset{+}{O}H}{\overset{\|}{C}}D$

(24)

EXPERIMENTAL

All measurements on (1) and (2) were made with a Kratos-AEI MS 50 mass spectrometer. Peak intensities and appearance energies were determined for decompositions occurring in the first field free region by lowering the electric sector voltage. Appearance-energy data were treated by 50 eV normalization of a semilog plot.[20] Energy releases were determined for decompositions in the second field free region from peak widths at half heights. The width of a normal spectrum peak multiplied by the mass of the product and divided by the mass of the precursor was subtracted from the metastable peak widths. The intensities of the decompositions of $C_3H_6O^{+\cdot}$ ions with the oxygen on the first carbon were determined in the first field free region of a DuPont 21–491 mass spectrometer by reducing the electric sector voltage. Peak intensities and peak widths were determined at an electron energy of 70 eV.

Heptan-2-one, propanal, cyclopentanol, allyl alcohol, and 2-methylpentanal were all obtained from Aldrich and used as received. Cyclopentan[^{2}H]ol (92% $^2H_1$) and allyl [^{2}H]-alcohol (60% $^2H_1$) were prepared by exchange with D_2O in the mass spectrometer inlet. [2-$^2H_1$]-2-Methylpentanal (50% $^2H_1$) was prepared by passing 2-methylpentanal through a g.l.c. column containing D_3PO_4. [1-$^2H_1$]Cyclopentanol (95% $^2H_1$) was prepared by reducing cyclopentanone with lithium aluminium deuteride. [2,2,5,5-$^2H_4$]-Cyclopentanol (81% $^2H_4$, 17% $^2H_3$) was prepared by exchanging cyclopentanone in DCl–D_3PO_4 and reducing the labelled ketone with lithium aluminium deuteride. All synthesized compounds were purified by g.l.c.

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