

ON THE FORMATION OF $C_2H_5O_2^+$ IONS HAVING THE STRUCTURE OF HYDROXY-PROTONATED ACETIC ACID

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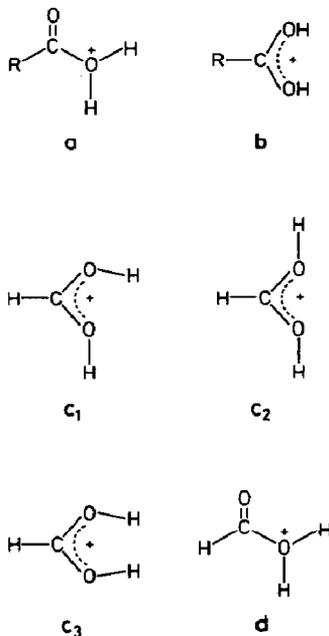
ABSTRACT

Experiments are reported which are best explained in terms of the formation of the long-sought hydroxy-protonated acetic acid, $CH_3C(O)OH_2^+$. This $C_2H_5O_2^+$ species, generated upon dissociative ionization of 2,4-dihydroxy-2-methylpentane (consecutive losses of CH_3 and C_3H_6), is characterized by a unique collisional activation mass spectrum and an extraordinarily small kinetic energy release for the unimolecular loss of H_2O ($T_{0.5} < 0.15$ kJ mol⁻¹). The latter observation is in good agreement with the results of semi-empirical molecular orbital calculations.

INTRODUCTION

The question as to whether hydroxy-protonated carboxylic acids (a) exist in addition to their well-known carbonyl-protonated isomers (b) has been studied in great detail over the last years both experimentally and theoretically [1–9]. Using spectroscopic methods, Hogeveen [1] demonstrated for formic acid (R = H) that, in solution, the most stable form of the protonated molecule is that having the *cis/trans* conformation c_1 . This conclusion is in line with *ab initio* calculations [2,3] which indicate that the conformational isomers *cis/cis* (c_2) and *trans/trans* (c_3) as well as the hydroxy-protonated

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formic acid isomer **d** are less stable by 25, 29 and 105 kJ mol^{-1} , respectively.

For $\text{R} = \text{CH}_3$, protonated acetic acid, it was also shown that **b**-type ions are significantly more stable than **a**-type ions [5–8(a)]. In the gas phase, **b**-type ions can conveniently be generated by either direct protonation of the ($\text{C}=\text{O}$) group under chemical ionization (CI) conditions [6] or dissociative ionization of aliphatic carboxylic acids [8a,9]. The latter decompose via a double hydrogen transfer to ions **b**, as shown by a combined field ionization kinetics and collisional activation (CA) study of deuterium-labelled isotopomers, and these conclusions are supported by molecular orbital (MO) calculations [8,9]. The experimental evidence for the existence of **a**-type ions as stable species in the work of Harrison and co-workers [5,7] on ionized aliphatic esters is of particular interest. From their detailed investigation they make the following conclusions.

(1) The gaseous protonated acids generated via a double hydrogen migration from the ester molecular ions, which further fragment in the first field-free region (1.FFR) of a mass spectrometer by loss of H_2O , yield acylium type ions, $\text{R}-\overset{+}{\text{C}}=\text{O}$, only.

(2) The composite metastable peaks observed in the foregoing water loss are best explained by assuming that both ions **a** and **b** ($\text{R} = \text{CH}_3$) are generated in the primary dissociation route. The major contribution to metastable peak intensities is the loss of H_2O from **b**-type ions which is characterized by a large kinetic energy release [i.e. T (most probable) for $\text{R} = \text{CH}_3$ is 44 kJ mol^{-1}]. This may be due to a rate-determining isomeriza-

tion **b** → **a**, followed by loss of H₂O. The much smaller energy release [e.g. R = CH₃, $T(\text{most probable}) = 1.9 \text{ kJ mol}^{-1}$] associated with the narrow component (see Fig. 1) is believed to correspond to the loss of water via direct bond cleavage [10–12] from hydroxy-protonated ions **a**.

(3) The protonated acids generated at low internal energies are ions **b** (R = CH₃) whose experimental heat of formation is 315 kJ mol⁻¹ [6]. Ion **a** is estimated to be ~ 100 kJ mol⁻¹ (R = CH₃) less stable. This difference in stability qualitatively agrees with the results of our semi-empirical MO calculations [8].

In this communication, we report experiments which, we believe, are best interpreted by assuming that the long-sought hydroxy-protonated acetic acid ion **a** (R = CH₃) indeed exists as a stable gas-phase ion.

EXPERIMENTAL

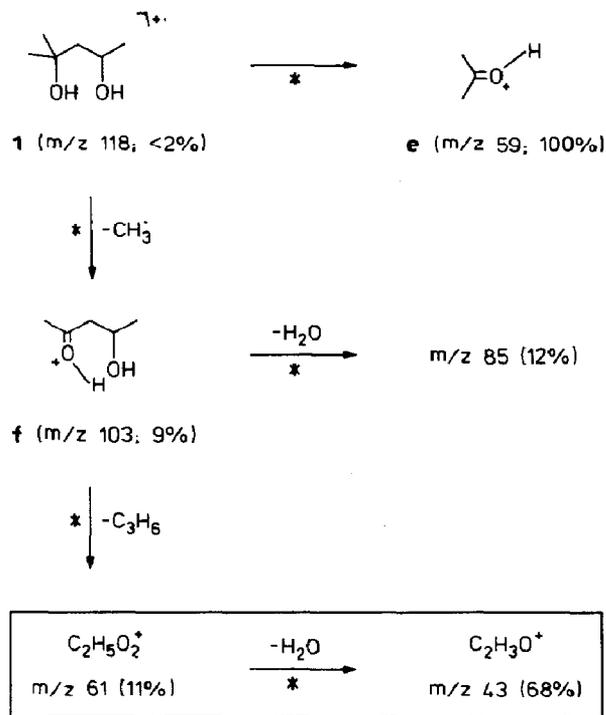
2,4-Dihydroxy-2-methylpentane (**1**) and its isotopomer [5,5,5-D₃]-**1** were prepared by the following standard laboratory procedure. HOCl addition to *i*-butylene [20] gave a 40% yield of 1-chloro-2-methylpropanol-2 which was transformed in 68% yield to the corresponding 3-hydroxy-3-methylbutyronitrile. Reaction of the latter with trimethyl chlorosilane [21] gave an 85% yield of the corresponding silyl ether, which was reacted [22] with either CH₃MgI or CD₃MgI, followed by LiAlH₄-reduction and cleavage of the silyl ether with (*n*-C₄H₉)₄NF [23] to eventually give **1** and [5,5,5-D₃]-**1**.

CA and MI mass spectra were measured as described elsewhere [24] using a VG ZAB-2F mass spectrometer in Utrecht.

DISCUSSION AND RESULTS

The molecular ion of 2,4-dihydroxy-2-methylpentane (**1**) undergoes, among other reactions, the processes depicted in Scheme 1 (relative intensities of the ion source generated ions are expressed as % base peak). Investigation of the two D-labelled isotopomers of **1** [(5,5,5-D₃)-**1** and (OD)₂-**1**] shows that (1) the methyl loss from **1** involves specifically the isopropyl group, and (2) the hydrogens involved in the water elimination from both ion **f** (m/z 103) and m/z 61, are exclusively those of the hydroxyl groups in the intact molecule.

The m/z 61 (C₂H₅O₂⁺) product ion generated from **1**, has the following characteristic features. (1) Its collisional activation mass spectrum mainly consists of a signal at m/z 43, C₂H₃O⁺, (> 96%) which is due to the loss of H₂O. The remaining 4% of the total fragment ion current accounts for the signals given in Table 1. Essentially the same CA mass spectrum was obtained for the m/z 61 ions generated in the first field-free region from m/z 103 ions losing neutral C₃H₆. This CA mass spectrum differs greatly



Scheme 1

from that of carbonyl-protonated acetic acid, generated by dissociative ionization of ethyl and *n*-propyl acetate, alkanolic acids and gas-phase protonation of acetic acid (**b**, R = CH₃). The CA data for **b**-type ions, generated upon protonation of acetic acid, are also given in Table 1. This leaves little doubt that the C₂H₅O₂⁺ ions from **1** do not have the structure of carbonyl-protonated acetic acid. Rather, the predominant water loss and its specificity from the (OD)₂-**1** and (5,5,5-D₃)-**1** isotopomers suggests that we are dealing with ions of structure (C₂H₃O)-(OH₂)⁺, possibly **a**-type ions, CH₃C(O)OH₂⁺. In view of this observation and the proposal by Middlemiss and Harrison [7] that **a**-type ions are co-generated with **b**-type ions in a slow reaction * of the acetate molecular ions, we have examined the CA mass spectrum of the metastably dissociating molecular ions of *n*-propylacetate (**3**) (M⁺ → C₂H₅O₂⁺, i.e. m/z 36,48). However, the CA mass spectrum measured at both the peak centre of the simple Gaussian metastable peak and its high and low mass sides is not really different from that of the source-gener-

* The co-generation of a thermochemically unfavoured product (e.g. **a**) at longer reaction times seems unlikely: with increasing lifetime (decreasing internal energy), the formation of the most stable species is usually favoured. For a case in which internal energy (lifetime) differences of a precursor ion are sufficient to even determine which stereoisomeric product is generated, see ref. 13.

TABLE 1

CA mass spectra of m/z 61, $C_2H_5O_2^+$ ions

m/z , daughter ion	$(CH_3)_2C(OH)CH_2CH(OH)CH_3$	CH_3COOH/CH_4
60	3	320
46	0.3	60
45	2	320
44	1	43
43	1000	1000
42	35	220
41	9	50
40	1	13
33	1.5	
31	1.5	19
30	0.5	16
29	7	145
28	3	30
27	1	7
26	2	16
25	1	10
19	3	2
18	6	7
17	0.5	6
16		7
15	5.5	81
14	3.5	50
13	1.5	19
12	0.3	6

ated, carbonyl-protonated acetic acid ions. Thus, the CA mass spectra of both ion source and first field-free region-generated $C_2H_5O_2^+$ ions derived from *n*-propylacetate do not yield evidence for the existence of a-type ions.

Assuming that the m/z 61 ions derived from **1** are a-type ions, another discrepancy arises with the work of Harrison and co-workers: the kinetic energy release associated with H_2O loss from m/z 61 in ionized **1** is extraordinarily small ($T_{0.5} < 0.15$ kJ mol⁻¹), and the peak is, as demonstrated in Fig. 1, substantially narrower than the narrow components of the composite metastable peaks for H_2O losses from the m/z 61 ions generated from ethyl acetate (**2**) and *n*-propyl acetate (**3**), respectively*. Further, the

* A referee suggested that the discrepancy between our work and that of Harrison and co-workers is perhaps due to the fact that Harrison's experiments were performed on an MS 902 instrument and the T values obtained refer to ions decomposing in the first field-free region; these ions may have a small excess energy compared with the ions decomposing in the second FFR of the ZAB-2F. We doubt this because we do not find any significant change in the T values (Fig. 1) when the reactions are studied in either the first or second FFR.

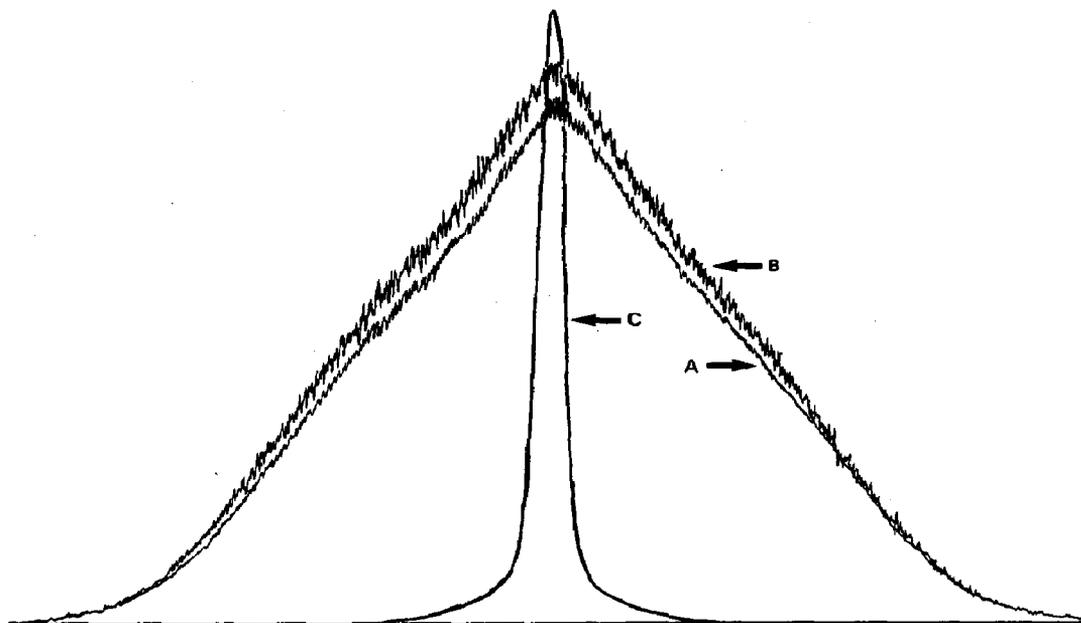


Fig. 1. Metastable peak shapes (ZAB-2F, second field-free region) for the loss of H_2O from $\text{C}_2\text{H}_5\text{O}_2^+$ (m/z 61), generated from (A) ethylacetate, (B) *n*-propylacetate, and (C) 2,4-dihydroxy-2-methylpentane.

facts that the loss of H_2O from m/z 61 in ionized **1** is strongly favoured for both its unimolecular and collision-induced dissociations and the associated kinetic energy release is very small point to a potential energy profile which is characterized by a small critical energy for both the forward and reverse reactions, i.e. m/z 61 \rightleftharpoons m/z 43 + H_2O . The eventually generated m/z 43 product ion corresponds to the acetyl ion [14] ($\text{CH}_3\text{C}^+=\text{O}$, **g**) as substantiated by its CA mass spectrum. Thus, the unusual features mentioned can only be accounted for by the structure of the precursor ion m/z 61.

Semi-empirical molecular orbital calculations (both MNDO [15] and MINDO/3 [16]) *, shows that only ion **h** (i.e. hydroxy-protonated acetic acid) has the required properties. Although this ion is thermochemically less stable than its isomeric form **b** ($\text{R} = \text{CH}_3$) [8], it is separated from the latter by a substantial barrier ($> 220 \text{ kJ mol}^{-1}$); however, in contrast to ion **b**, ion **h** can undergo a facile water loss to generate the most stable $\text{C}_2\text{H}_3\text{O}^+$ isomer, the acetyl ion **g** ($E_0 < 33 \text{ kJ mol}^{-1}$). The reverse process (i.e. H_2O addition to **g** to form **h**) also proceeds, at least according to the calculations, via quite a small barrier ($E_0^\ddagger < 7.5 \text{ kJ mol}^{-1}$) (see Fig. 2).

H_2O loss from any other conceivable, chemically reasonable $\text{C}_2\text{H}_5\text{O}_2^+$

* All species, including transition states, were fully geometry-optimized and rigorously characterized by appropriate methods. Details are available from the authors upon request.

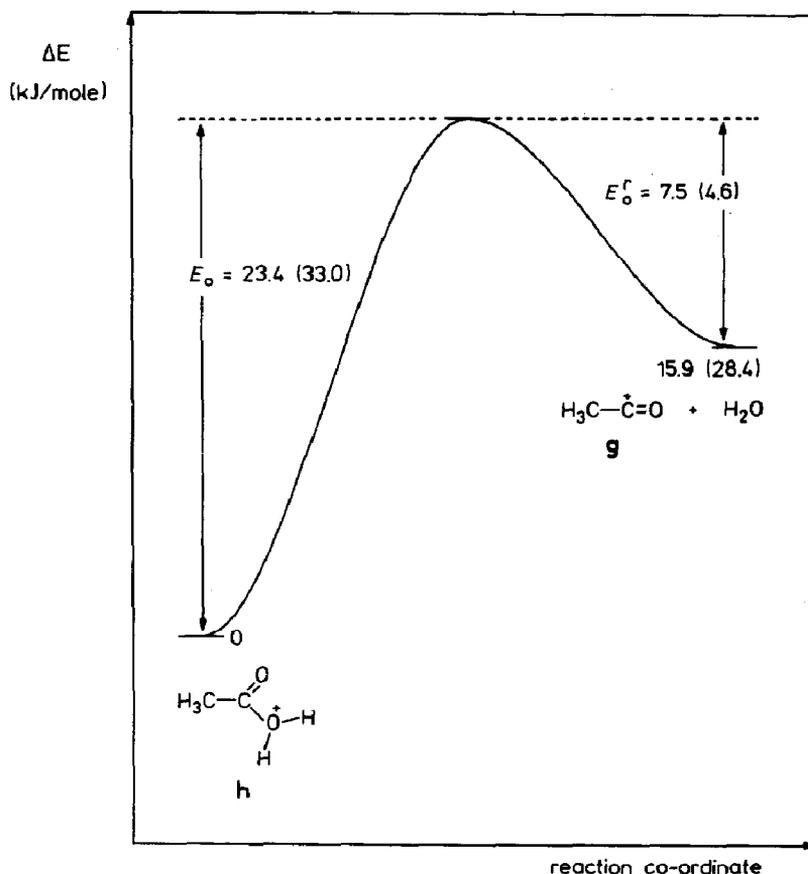
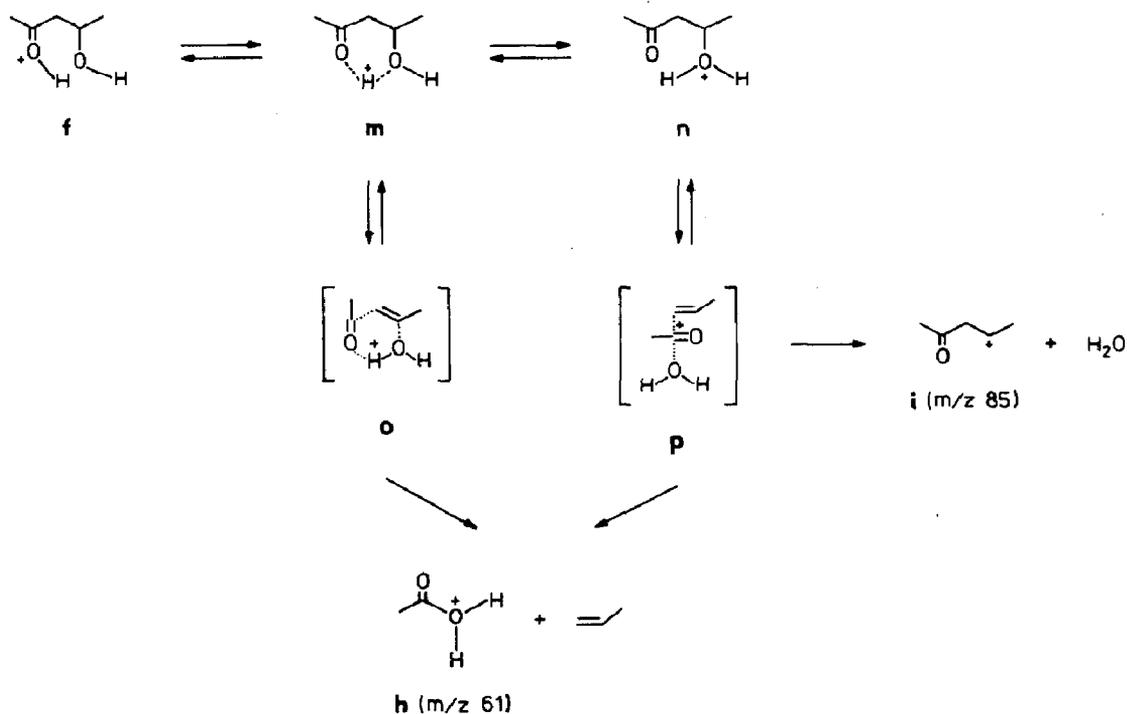


Fig. 2. Schematic potential energy profile for H_2O loss from hydroxy-protonated acetic acid (**h**). The numbers refer to relative energies (given in kJ mol^{-1}) and are calculated by MNDO and MINDO/3 (in parentheses), respectively.

structure, for example, ion **b** ($\text{R} = \text{CH}_3$) or the structures $\text{CH}_2\text{-O-CH}_2\text{OH}$ (**i**), $\text{CH}_3\text{-O-CH-OH}$ (**j**), $\text{CH}_3\text{-O(H)-CHO}$ (**k**), etc., is expected to require substantially larger critical energies [17]. In addition, the CA mass spectra of all other stable $\text{C}_2\text{H}_5\text{O}_2^+$ isomers that we have found so far (including **i** and **j**) [18] are characteristically different. The proton-bound complex $\text{CH}_3\text{-C=O...H}^+\text{...OH}$ (**1**) was also considered; **1** is calculated not to exist as a stable entity but, upon geometry optimization, it collapses spontaneously to **h**. The same applies to the addition of H_2O to $\text{CH}_3\text{-C=O}$, which is expected to have only a relatively small critical energy when the nucleophilic H_2O interacts directly with the electrophilic carbon centre of **g**, i.e. process $\text{g} + \text{H}_2\text{O} \rightarrow \text{h}$. Attempts to derive an experimental value for the energy requirements of the water loss from the $\text{C}_2\text{H}_5\text{O}_2^+$ ions from **1** by measurements of the appearance energy (AE) of the first FFR metastable transition $m/z\ 61 \rightarrow m/z\ 43$ failed; the process appeared to be very sensitive to collisions from residual gas. Considering the foregoing observations and



Scheme 2

arguments, we propose that ionized **1** produces a unique $C_2H_5O_2^+$ ion which, despite the discrepancies with the work of Harrison on ionized acetates, is best described as the hydroxy-protonated acetic acid ion **h**, $CH_3C(O)OH_2^+$. The question left to discuss concerns the genesis of **h** whose sole precursor is **f** (Scheme 1) (m/z 103 \rightarrow m/z 61). As already mentioned, the molecular ion of **1** expels a CH_3 radical from the isopropyl group, and we suggest that the carbonyl-protonated hydroxy ketone **f** thus obtained undergoes an intramolecular hydrogen migration ($f \rightleftharpoons m \rightleftharpoons n$) which eventually leads to the hydroxy-protonated ketone (**n**). In the rearrangement/dissociation step (loss of C_3H_6), the (otherwise departing) neutral C_3H_6 and H_2O are perhaps bound together via ion/dipole interaction with the "incipient" acetyl ion **g** (possibly involving hydrogen bonds). The actual dissociation may well take place from complexes of the general structures **o** or **p**, thereby generating C_3H_6 (propene?) and the H_2O -stabilized acetyl cation **h**. (This description of m/z 61 is more or less equivalent to the one in which **h** is referred to as hydroxy-protonated acetic acid.) It should be mentioned that there exist many precedences in the literature for this kind of ion/dipole interaction * [19].

* A referee pointed out that in addition to **o** and **p**, an H_2O -solvated ion **i** may serve as a precursor for **h** ions.

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