Structure of Gaseous $C_2H_4O_2^{+\cdot}$ Ions formed by McLafferty Rearrangement from Aliphatic Acids

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Collisional activation spectra and deuterium labelling show that the $C_2H_4O_2^{+\cdot}$ ion formed by McLafferty rearrangement in aliphatic acids does not isomerise to the acetic acid molecular ion.

THE structure of fragment ions generated by unimolecular decay of excited molecular ions in a mass spectrometer is usually inferred from the mechanism by which they are formed, for which metastable transitions and isotopic labelling are the most powerful tools of elucidation. Thus, in straight chain aliphatic acids a McLafferty rearrangement leads to abundant $C_2H_4O_2^{+\cdot}$ ions (m/e 60) which according to the mechanism of formation should have the enolic structure (1).[1] Such an ion structure assignment does not, however, take the

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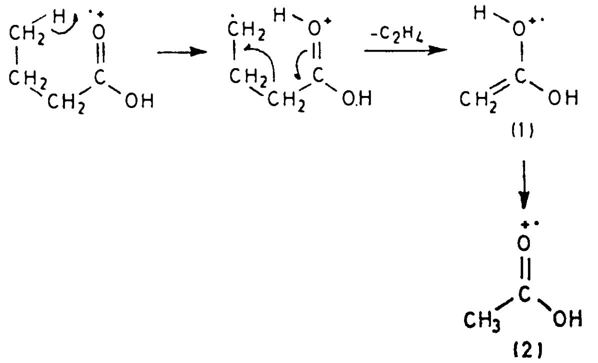
[1] (*a*) G. P. Happ and D. W. Stewart, *J. Amer. Chem. Soc.*, 1952, **74**, 4404; (*b*) N. C. Roe, *Rev. Trav. chim.*, 1965, **84**, 413; (*c*) R. B. Fairweather and F. W. McLafferty, *Org. Mass Spectrometry*, 1969, **2**, 755; (*d*) J. S. Smith and F. W. McLafferty, *ibid.*, 1971, **5**, 483.

possibility of isomerisation into account. Thus, an isomerisation of (1) to the acetic acid molecular ion (2) might be expected * (Scheme 1). Such isomerisation can only be detected when more direct methods for ion structure determination are used.



Scheme 1

In this paper we report the application of collisional activation (c.a.)[2] and metastable ion studies to this problem. With both techniques ions with a similar lifetime (*ca.* 10^{-5} s), but different internal energy, are sampled. Metastable ion studies give information on the structure of decomposing ions with a narrow range of internal energies just above the threshold for decomposition. The situation is more complex with the c.a. technique. Although only the non-decomposing ions with internal energies up to the lowest threshold for decomposition are reaching the collision region, the finally decomposing ions are highly excited with a broad range of internal energies. Thus, isomerisation may occur before or after collision.

Table 1

Collisional activation spectra of $C_2H_4O_2^{+\cdot}$ ions [a, b]

m/e	Butanoic acid	Pentanoic acid	Hexanoic acid	Decanoic acid	Tetradecanoic acid	Methoxyacetic acid	Acetic acid
13	0.1	0.1	0.1	0.1	0.1	0.1	0.1
14	1.0	1.0	0.8	0.8	1.1	0.7	0.2
15	1.0	1.0	0.8	0.8	1.1	0.8	0.7
16	0.1	0.1	0.1	0.1	0.1	0.1	0.2
17	0.1	0.1	0.1	0.1	0.1	0.1	0.1
18	0.2	0.2	0.1	0.1	0.1	0.1	
26	0.5	0.6	0.5	0.6	0.7	0.6	0.2
29	7.1	7.4	6.9	7.9	8.4	7.5	2.1
31	5.6	5.5	5.5	6.2	6.4	6.1	0.8
42	51	49	51	47	46	48	3.9
43	11	11	10	11	11	11	60
45	19	21	20	21	21	21	32
46	3.6	3.4	3.6	3.8	3.6	3.7	

[a] Abundance relative to the sum of all fragments. [b] C.a. spectra from $C_2H_4O_2^{+\cdot}$ precursors generated at 12—13 eV (nominal) were identical with the above spectra except for the low energy process *m/e* 42 the abundance of which decreased slightly. This demonstrates that decomposition occurs only from one structure and not from a mixture of structures.

RESULTS AND DISCUSSION

The c.a. spectra of $C_2H_4O_2^{+\cdot}$ ions formed by McLafferty rearrangement from five straight chain aliphatic acids (C_4, C_5, C_6, C_{10}, and C_{14}) as well as from methoxyacetic acid are contrasted with that of the acetic acid molecular ion in Table 1. While the relative abundances and the peak widths (kinetic energy release) † observed in the c.a. spectra for the ions formed by McLafferty rearrangement are almost identical, considerable differences are observed when compared to the acetic acid molecular ion demonstrating that no or only minor isomerisation (<10%) of (1) to (2) can have occurred within a lifetime of 10^{-5} s before collision induced fragmentation.

Moreover the fragmentation pattern also clearly reflects the different structures. The CH_3CO^+ ion (*m/e* 43) is, as expected, much more abundant in the c.a. spectrum of acetic acid and the $CH_2CO^{+\cdot}$ ion (*m/e* 42) more intense in the spectrum of the McLafferty rearrangement product. The relative abundances of CH_3^+ *versus* $CH_2^{+\cdot}$ and $C(OH)_2^{+\cdot}$ *versus* CO_2H^+ also reflect the different structures.

This conclusion is reinforced by a study of the metastable ions ‡ in conjunction with deuterium labelling. (Note, however, that metastable ions do not necessarily give the same information as the c.a. spectra as ions of different internal energies are sampled as outlined above). Table 2 contrasts the metastable peaks from $C_2H_4O_2^{+\cdot}$ (1), $C_2H_3DO_2^{+\cdot}$ (1a), $C_2H_2D_2O_2^{+\cdot}$ (1b), and $C_2HD_3O_2^{+\cdot}$ (1c) generated by McLafferty rearrangement from butanoic acid, butanoic [^{2}H]acid, [2,2-$^2H_2$]butanoic acid, and [2,2-$^2H_2$]butanoic [^{2}H]acid. The two metastable peaks observed for the unlabelled ion (1) correspond to the loss of water (*m/e* 42) and a hydroxyl radical (*m/e* 43). An isomerisation of the $C_2H_4O_2^{+\cdot}$ ions prior to decomposition would lead to a randomization of

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* An isomerisation of an ion A^+ to a distinct structure B^+ is only expected if there exists a possibility of deactivation of B^+, *e.g.* by radiation. If there is no such mechanism for unimolecular energy release isomerisation will always lead to a mixture of rapidly exchanging ions A^+ and B^+ prior to decomposition, even if decomposition occurs predominantly or exclusively from B^+. For the sake of simplicity we shall speak in the following always of an isomerisation of (1) to (2) keeping the above statement in mind.

† The kinetic energy release data have not been included in Table 1.

‡ A discussion of the metastable peaks instead of the collision induced fragments is preferred as the former are better resolved than the latter.

[2] F. W. McLafferty, R. Kornfeld, W. F. Haddon, K. Levsen, I. Sakai, P. F. Bente, S.-C. Tsai, and H. D. R. Schüddemagge, *J. Amer. Chem. Soc.*, 1973, **95**, 3886.

the hydrogen atoms. Such randomization prior to water loss should give rise to peaks at *m*/*e* 42—44 for the ion (1b) and to peaks at *m*/*e* 43 and 44 for the ion (1c). Table 2 reveals that no such hydrogen randomization is observed, demonstrating that there is no isomerisation of (1) prior to water loss.

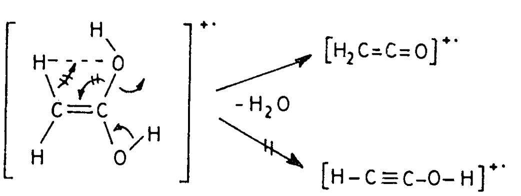
TABLE 2

Metastable transitions from $C_2H_4O_2^{+\cdot}$,[a] $C_2H_3DO_2^{+\cdot}$,[b] $C_2H_2D_2O_2^{+\cdot}$,[c] and $C_2HD_3O_2^{+\cdot}$,[d] relative abundance [e]

m/*e*	$C_2H_4O_2^{+\cdot}$ (1)	$C_2H_3DO_2^{+\cdot}$ (1a)	$C_2H_2D_2O_2^{+\cdot}$ (1b)	$C_2HD_3O_2^{+\cdot}$ (1c)
42	73	71		
43	27	21		
44		8	73	67
45			27	24
46				9

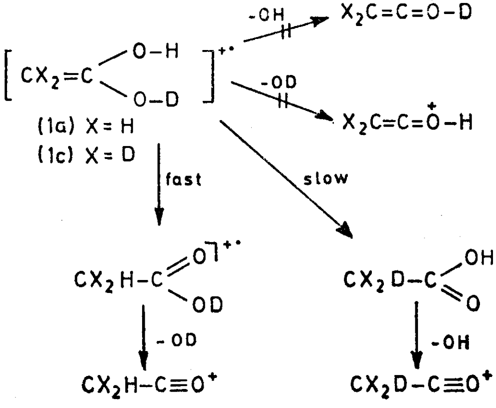
[a] Generated from butanoic acid. [b] Generated from butanoic [^{2}H]acid. [c] Generated from [2,2-$^2H_2$]butanoic acid. [d] Generated from [2,2-^{2}H]butanoic [^{2}H]acid. [e] Abundances relative to the sum of all peaks.

Furthermore, the deuterium labelling data suggest that from the two conceivable four centre reactions for the water elimination (Scheme 2) only the reaction leading to the ionised keten (and not to the ionised propargyl alcohol) is operating.



SCHEME 2

The situation is more complex for hydroxy-elimination. If the hydroxy-group is eliminated by direct cleavage from (1) and no isotope effect is operating then OH and OD should be lost from (1a and c) in equal proportions, while a complete randomization of all hydrogen atoms should lead to a ratio $[C_2(H,D)_4O_2^{+\cdot} - OH] : [C_2(H/D)_4O_2^{+\cdot} - OD] = 3 : 1$ for (1a) and 1 : 3 for (1c). The actual observed ratio is 1 : 2.6 for both (1a and c) which clearly rules out complete or partial randomization of the hydrogens, but suggests the presence of an isotope effect. No primary isotope effect should be found for the loss of the hydroxy-group from (1), while an isotope effect is expected for the rearrangement of (1) to (2) favouring the transfer of a hydrogen with subsequent loss of OD over the transfer of a deuterium with subsequent loss of OH (Scheme 3). In further support of this reasoning, identical intensity ratios are observed for the metastable transitions from (1) and (1b) proving that only OH and not OD is lost from (1b).* This observation does not contradict the above mechanism for hydroxy-elimination, but it clearly rules out any hydrogen randomization. Thus, we conclude that



SCHEME 3

hydroxy-loss from (1) proceeds *via* the acetic acid configuration in the transition state where α-cleavage favours the decomposition. Note that such a rearrangement during fragmentation is not identical with an isomerisation prior to fragmentation which should lead to a randomization of all hydrogens as long-living ions are sampled. It is indeed very unlikely that $C_2H_4O_2^{+\cdot}$ ions (1) isomerise to (2) prior to OH loss while no such isomerisation is observed prior to H_2O loss. As both decomposition processes have similar activation energies (see below) and thus $C_2H_4O_2^{+\cdot}$ ions decomposing *via* these two routes have a comparable energy content no difference in the isomerisation behaviour prior to these two processes is expected. Summarising, deuterium labelling supports the conclusion reached from the c.a. results that the enolic $C_2H_4O_2^{+\cdot}$ ions do not isomerise to a substantial amount to the acetic acid molecular ion although some decomposition processes proceed *via* a transition state with an acetic acid configuration.

This result is in agreement with the general observation[3] that heteroatom-containing molecular and fragment ions show little tendency to rearrange to isomeric structures. It has been concluded that isomerisation reactions in such heteroatom-containing ions are less prevalent because of the low activation energies for decomposition.[3] To test this assumption the activation energies for the loss of H_2O and OH † from $C_2H_4O_2^{+\cdot}$ (generated from the butanoic acid molecular ion) were determined by appearance potential measurements of the secondary decompositions. Metastable peaks were used for these appearance potential measurements (*i.e.* the processes *m*/*e* 88 ⟶ 60, 60 ⟶ 42, and 60 ⟶ 43) to reduce the kinetic shift ‡ and to allow an unambiguous assignment of the decomposition process. In contrast to the above mentioned earlier conclusion, relatively high activation energies ($E_{0(C_2H_4O_2^{+\cdot}-H_2O)}$ 1.9 ± 0.2,

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* The loss of OD leads to the same nominal mass as the loss of H_2O. The absence of OD loss from (1b) can therefore only be proved indirectly by comparing the metastable peaks from (1) and (1b).

† These are the processes of lowest activation energy recognizable by abundant metastable peaks.

‡ There may still be shifts of the appearance potentials due to the fact that competing and consecutive decompositions were studied.[4]

[3] N. A. Ucella, I. Howe, and D. H. Williams, *J. Chem. Soc.* (*B*), 1971, 1933.

[4] (*a*) A. G. Harrison, ' Topics in Organic Mass Spectrometry,' ed. A. L. Burlingame, Wiley–Interscience, New York, 1970; (*b*) D. H. Williams and I. Howe, ' Principles of Organic Mass Spectrometry,' McGraw-Hill, New York, 1971, ch. 4.

$E_{0(C_2H_4O_2^{+\cdot}-H_2O)}$ 1.7 ± 0.2 eV) were observed in this specific case. Thus the potential barrier for isomerisation must be considerably larger than 1.9 eV* corroborating earlier conclusions that the isomerisation barrier in heteroatom-containing ions is relatively high.[5]

EXPERIMENTAL

A Varian CH4B single focusing mass spectrometer, equipped with an additional electric sector following the magnetic sector, a collision chamber placed between magnetic and electric sectors close to the energy resolving slit and a differential pumping system, was used for all measurements (acceleration voltage 3 kV, electron energy 70 eV, electron beam 20 μA, source temperature 250°, gas inlet temperature 120°). For c.a. measurements the He pressure in the collision chamber was increased until the precursor ion intensity was reduced to one third of its original value due to scattering. C.a. spectra were recorded as reported previously.[2] All c.a. spectra are the means of at least two measurements. No dependence of the c.a. spectra on the electron energy was observed except for the processes of lowest activation energy (*m/e* 42 and 43). Appearance potentials were determined using the metastable ions and applying the semilog plot method. The unlabelled compounds were purchased from Fluka, butanoic [^{2}H]acid was prepared by exchange of butanoic acid with D_2O in the inlet system. [2,2-$^2H_2$]Butanoic acid was obtained by the Grignard reaction of [1,1-$^2H_2$]propyl bromide and magnesium (1 equiv.) in ether (10 ml) followed by treatment with dry-ice using standard procedures, yield 78%, isotopic purity 95%. From this compound [2,2-$^2H_2$]butanoic acid was prepared by exchange with D_2O in the inlet system of the mass spectrometer. Although the direct exchange in the inlet system led to a rather low degree of deuteriation (*ca.* 70%) isotopic impurities do not interfere with the measurements, as mass analysis precedes collisional activation.

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* $C_2H_4O_2^{+\cdot}$ Ions losing H_2O in the second field free region of the instrument have an internal energy of roughly 1.9 eV and a lifetime of 10^{-5} s. Thus if the potential barrier for isomerisation is $\leqslant$1.9 eV there should be some isomerisation prior to water loss, recognizable by a randomization of the hydrogen atoms.

[5] K. Levsen, *Tetrahedron*, 1975, **31**, 2431.