Carbocation-like Isomerisations at Radical Sites Precede Methyl Losses from Ionised Butanoic Acid

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The low-energy losses of methyl from ionised butanoic acid and isomeric ions have been further characterised utilising isotopic labelling, field ionisation kinetics, and translational energy releases. Long lived butanoic acid ions lose methyl groups containing C-2, C-3, and C-4. The loss of methyl containing C-2 follows migration of the protonated carboxy group to the radical site of $CH_3\dot{C}HCH_2$-$C(OH)_2^+$. Methyl containing C-3 is lost following a 1,2-shift of the terminal methyl from C-3 to C-2. 1,2- and 1,4-hydrogen shifts take place in all of the pathways to methyl loss. The 1,2-shifts of methyl and hydrogen may be permitted by a reduced electron density on the α carbon atoms of the intermediate ions $CH_3CH_2\dot{C}HC(OH)_2^+$ and $(CH_3)_2\dot{C}C(OH)_2^+$. The isomerisations of ionised butanoic acid can be rationalised as a mixture of free-radical-like and carbocation-like reactions.

Studies of ionised butanoic acid have contributed significantly to the understanding of reactions of radical cations in the gas phase. The ubiquitous McLafferty rearrangement[1] was first characterised in ^{13}C-labelled butanoic acid ions.[2] It was later concluded from exchange of the *O*-, β-, and γ-hydrogen atoms that the γ-hydrogen rearrangement and β-cleavage of the McLafferty rearrangement occur in separate steps.[3] Subsequent studies established that β-hydrogen rearrangement to the carbonyl oxygen followed by further isomerisation precedes loss of the terminal methyl.[4–6] The time course of hydrogen exchange prior to the loss of ethylene from ionised butanoic acid has been characterised,[7] butanoic acid has been studied by photoion–photoelectron coincidence methods,[8] and molecular orbital calculations of the energetic feasibility of several isomerisations of ionised butanoic acid have been carried out.[9] A preliminary study of the decompositions of ^{13}C-labelled butanoic acid ions as a function of ion lifetime demonstrated that some methyl groups lost at times exceeding $10^{-6.5}$ s contain C-2 or C-3.[10] We have now utilised additional isotopic labelling, translational energy release (T) determinations, and field ionisation kinetics (FIK) to establish detailed mechanisms for these processes.

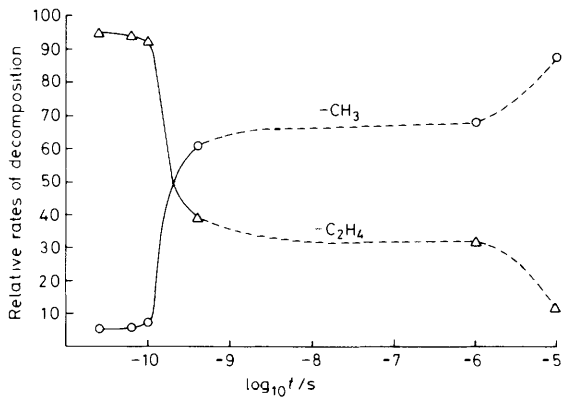


Figure. Time dependence of the losses of methyl and ethylene from ionised butanoic acid. Intensities at each time are expressed as percentages of their sum. Points at times shorter than 10^{-9} s were obtained by field ion kinetics experiments. Points at 10^{-6} s are from ref. 5, and the 10^{-5} s points are from the third field-free region of an MS 50 TA mass spectrometer

Results

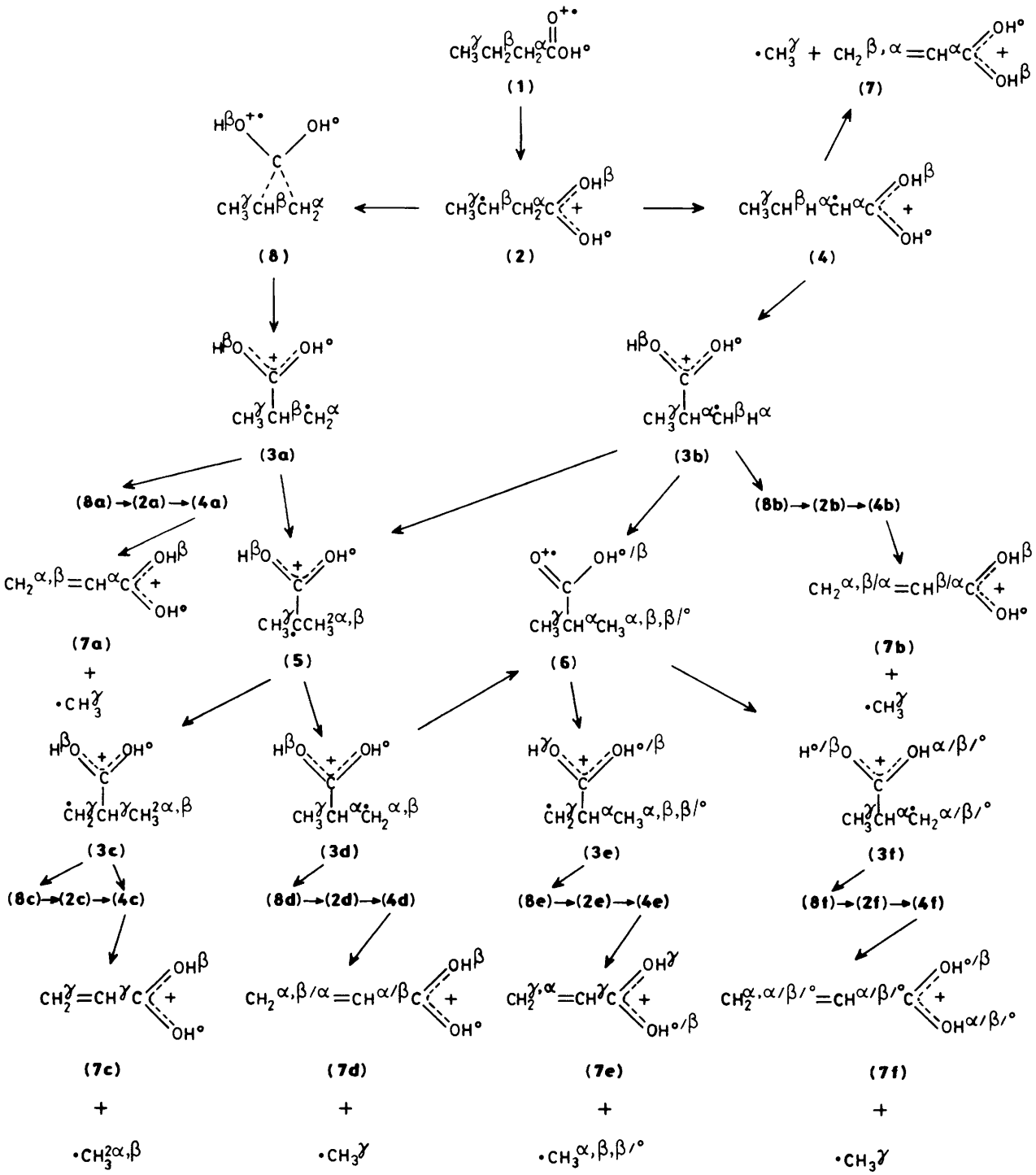
Methyl losses from a variety of ^{13}C- and D-labelled isomers of the butanoic acid have been characterised. Decomposition patterns of ^{13}C-labelled ions at three ion lifetimes are given in Table 1, and corresponding data for D-labelled ions are given in Table 2. The relative intensities of methyl and ethylene losses as a function of ion lifetime are given in the Figure. The field-free region spectra resemble those published previously.[5–7] Methyl groups lost at times shorter than 10^{-9} s contained only C-4. The fraction of methyl groups lost containing C-2 or C-3 increased with ion lifetime, until at 10^{-5} s only 50% of the methyl groups lost contained C-4. Hydrogen exchange became apparent at about 10^{-9} s and increased with increasing ion lifetime.

Collisionally activated decomposition (CAD) spectra[11] were determined for selected $C_3H_5O_2^+$ product ions (Table 3). A previously determined CAD spectrum of $C_3H_5O_2^+$ formed from n-butanoic acid matched that of protonated acrylic acid.[5] The CAD spectra of all $C_3H_5O_2^+$ ions produced by metastable decompositions agreed within experimental error, consistent with their being identical. (Some of the spectra were quite weak, since the products of metastable decompositions collided.)

Translational energies released were determined from peak widths at half height, $T_{\frac{1}{2}}$ (Tables 4 and 5). These sometimes varied more than two-fold for different methyl losses from the same initial ion. Parallel results were obtained when the peaks were measured at 20 and 80% of the maximum peak height.

Discussion

Mechanisms of Methyl Loss.—Scheme 1 summarises the processes we propose to account for the time evolution of the decomposition patterns of the ions examined. The same numerical designations in Scheme 1 always represent the same ion structure, with a different letter suffix for each occurrence. In the superscripts, numbers indicate the numbers of hydrogen atoms from the initial position designated by the Greek letter, solidi (/) mean 'or' and commas represent 'and'; $CH_3^{\alpha,\beta,\beta/\alpha}$ depicts a methyl containing one α, one β, and one β or one



Scheme 1.

hydroxy hydrogen. This scheme is based on previous studies of the butanoic acid[4,8–10] ion and the following considerations. (1) Isomerisations are assumed to take place only by stepwise transfers to vacant sites, *i.e.* concerted interchange of atoms or groups does not occur.[12] (2) Analogous 1,2- and 1,4-shifts of hydrogen and 1,2-shifts of carbon with its substituents have been proposed for other carbonyl-containing ions.[13–17] MNDO Calculations[16] indicate that (**8**) is probably a transition state rather than an intermediate. (3) The 2-methylpropanoic acid ion and its enol isomer undergo the 1,4- and 1,2-hydrogen shifts proposed in Scheme 1, *i.e.* (**6**) ⟶ (**3**) and (**5**) ⟶ (**3**).* (4) Recent work by Schwarz and his co-workers[17] indicates that ionised methyl isobutyrate isomerises

* Directly generated (**5**)-3,3,3-$^2H_3$ and (**6**)-3,3,3-$^2H_3$ both lose CD_3 about twice as frequently as they lose CH_3 upon metastable decomposition (Table 2). This isotope effect demonstrates that the D transfers (**5**) ⟶ (**3**) and (**6**) ⟶ (**3**) precede the loss of CH_3 from both of these ions. Similar data have been utilised to demonstrate that hydrogen transfer precedes the loss of methyl from methyl 2-methylpropanoate ions.[13]

Table 1. Field ionisation and metastable spectra of ^{13}C-labelled butanoic acid ions

Ion	Designation	Species lost	$< 10^{-9}$ s	$10^{-6.5}$ s	10^{-5} s
$CH_3CH_2{}^{13}CH_2C\dot{O}_2\dot{H}$	[2-^{13}C]-(**1**)	CH_3	100	94	82
		$^{13}CH_3$		6	18
		C_2H_4	100	94	70
		$^{13}CCH_4$		6	30
$CH_3{}^{13}CH_2CH_2C\dot{O}_2\dot{H}$	[3-^{13}C]-(**1**)	CH_3	100	93	65
		$^{13}CH_3$		7	35
		C_2H_4		10	*a*
		$^{13}CCH_4$	100	90	*a*
$^{13}CH_3CH_2CH_2C\dot{O}_2\dot{H}$	[4-^{13}C]-(**1**)	CH_3		15	50
		$^{13}CH_3$	100	85	50
		C_2H_4		5	23
		$^{13}CCH_4$	100	95	77

[a] Accurate data not obtained.

Table 2. Field ionisation and metastable losses of methyl from $C_4(H,D)_8O_2^{+\cdot}$ ions

Ion	Designation	Species lost	$< 10^{-9}$ s	$10^{-6.5}$ s	10^{-5} s
$CH_3CH_2CH_2C\dot{O}_2\dot{D}$	[*O*-^{2}H$_1$]-(**1**)	CH_3	100	98	88
		CH_2D		2	12
$CH_3CH_2CD_2C\dot{O}_2\dot{H}$	[2,2-^{2}H$_2$]-(**1**)	CH_3	100	86	74
		CH_2D		2	5
		CHD_2		12	21
$CH_3CH_2CD_2C\dot{O}_2\dot{D}$	[*O*,2,2,2-^{2}H$_3$]-(**1**)	CH_3			65
		CH_2D			10
		CHD_2			24
		CD_3			1
$CH_3CH_2\dot{C}DC(OH)_2^+$	[2-^{2}H$_1$]-(**4**)	CH_3			94
		CH_2D			6
$CH_3CD_2CH_2C\dot{O}_2\dot{H}$	[3,3-^{2}H$_2$]-(**4**)	CH_3	100	88	77
		CH_2D		7	17
		CHD_2		5	6
$CD_3CH_2CH_2C\dot{O}_2\dot{H}$	[4,4,4-^{2}H$_3$]-(**1**)	CH_3		10	27
		CH_2D		1	8
		CHD_2		4	8
		CD_3	100	85	57
$CD_3CH_2CH_2C\dot{O}_2\dot{D}$	[*O*,4,4,4-^{2}H$_4$]-(**1**)	CH_3			20
		CH_2D			6
		CHD_2			4
		CD_3			70
$CD_3CH_2\dot{C}HC(OH)_2^+$	[4,4,4-^{2}H$_3$]-(**4**)	CH_3			5
		CD_3			95
$(CH_3)_2CHC\dot{O}_2\dot{D}$	[*O*-^{2}H$_1$]-(**6**)	CH_3		99	98.6
		CH_2D		1	1.4
$(CH_3)_2CDC\dot{O}_2\dot{H}$	[2-^{2}H$_1$]-(**6**)	CH_3	100	99	91.2
		CH_2D		1	7.8
$CD_3CH(CH_3)C\dot{O}_2\dot{H}$	[3,3,3-^{2}H$_3$]-(**6**)	CH_3	50	44	27
		CH_2D			0.3
		CHD_2		1	10
		CD_3	50	55	64
$CD_3\dot{C}(CH_3)C(OH)_2^+$	[3,3,3-^{2}H$_3$]-(**5**)	CH_3			31
		CH_2D			< 1
		CHD_2			≤ 1
		CD_3			67

to $CH_3CH_2\dot{C}HC(\overset{+}{O}H)OCH_3$ prior to losing methyl. It is therefore assumed that methyl is lost from (**4**) but not (**3**). (5) At short times, 100% $CH_3{}^{\gamma}$ is lost, indicating that the earliest methyl losses take place by the process (**1**) ⟶ (**2**) ⟶ (**4**) ⟶ (**7**). (6) The equality at long times of the loss of $^{13}CH_3$ from [4-^{13}C]-(**1**) to the sum of $^{13}CH_3$ losses from [2-^{13}C]- and [3-^{13}C]-(**1**) suggests that by 10^{-5} s all the ^{13}C-labelled ions which lose methyl pass through structures [*i.e.* (**5**) and (**6**)] in which a methyl containing C-2 or C-3 is equivalent to the terminal methyl. However, in the D-labelled ions excessive loss of C-4 methyl occurs, presumably because the rates of formation of (**5**) and (**6**) and the subsequent losses of internal methyls are reduced by isotope effects. (7) Translational energies released in proposed pathways correlate with the translational energies released in decompositions of directly generated intermediates in those pathways (see later).

We estimated the relative contributions of the processes (**2**) ⟶ (**4**) ⟶ (**3b**) and (**2**) ⟶ (**8**) ⟶ (**3a**) to the decompositions in Scheme 1 from the ^{13}C distributions in the products formed after 10^{-5} s. The 2:1 ratio of the $^{13}CH_3$ loss from [3-^{13}C]-(**1**) to that from [2-^{13}C]-(**1**) demonstrates that the process (**2**) ⟶ (**4**) ⟶ (**3b**), which precedes the C-3 methyl

Table 3. Collisionally activated decomposition spectra of $C_3H_5O_2^{+\cdot}$ ions produced by decomposition of metastable $C_4(H,D)_8O_2^{+\cdot}$ ions

	Precursor ion				
m/z	$CH_3CH_2CD_2\dot{C}O_2^{+\cdot}H$ [2,2-$^2H_2$]-(1)	$CH_3CD_2CH_2\dot{C}O_2^{+\cdot}H$ [3,3-$^2H_2$]-(1)	$(CH_3)_2\dot{C}C(OH)_2^{+}$ [a] (5)	$(CH_3)_2CHCO_2^{+\cdot}H$ (6)	$(CH_3)_2CHCO_2^{+\cdot}H$ (10 eV) [b] (6)
26	25	35	28	25	21
27	55	48	46	56	48
29	16	22	14	18	16
45	54	54	55	58	51
46	21	*c*	20	21	18
53	20	26	18	21	22
55	100	100	100	100	100
71	12	9	14	13	11
72	84	74	62	82	65

[a] *m/z* 73 Formed by a first field-free metastable decomposition. [b] *m/z* Produced in the ion source. [c] Not measurable owing to overlap with *m/z* 45.

Table 4. Energies released ($T_{\frac{1}{2}}$)[a] in the losses of methyl from $C_4(H,D)_8O_2^{+\cdot}$ ions

Ion	$-CH_3$	$-CH_2D$	$-CHD_2$	$-CD_3$	$-C_2H_4$
$CH_3CH_2CH_2CO_2^{+\cdot}H$	15.9				3.7
$CH_3CH_2CH_2CO_2^{+\cdot}D$	19.8	10.6			
$CH_3CH_2CD_2CO_2^{+\cdot}H$	17.2	15.9	25.8		
$CH_3CH_2CD_2CO_2^{+\cdot}D$	20.2	13.0	28.3		
$CH_3CD_2CH_2CO_2^{+\cdot}H$	18.9	17.9	12.1		
$CD_3CH_2CH_2CO_2^{+\cdot}H$	26.3	10.3	12.9	23.8	
$CD_3CH_2CH_2CO_2^{+\cdot}D$	35.0	15.6	15.0	23.2	
$(CH_3)_2CHCO_2^{+\cdot}H$	19.5				10.3
$(CH_3)_2CDCO_2^{+\cdot}H$	18.0	29.7			
$CD_3CH(CH_3)CO_2^{+\cdot}H$	23.3		28.0	18.3	
$CH_3CH_2\dot{C}HC(OH)_2^{+}$	22.1				12.2
$(CH_3)_2\dot{C}C(OH)_2^{+}$	36.1				17.2
$CH_3C(CD_3)C(OH)_2^{+}$	39.6			36.4	

[a] Values are in meV and are averages of several signal-averaged determinations. Uncertainties are ± *ca.* 1.0 mV. Determined in the third field-free region of the MS 50 TA instrument.

Table 5. Energies released ($T_{\frac{1}{2}}$) in the losses of methyl from $^{13}CC_3H_8O_2^{+\cdot}$ ions

Ion	$-CH_3$	$-{}^{13}CH_3$
$CH_3CH_2{}^{13}CH_2CO_2^{+\cdot}H$	15.0	16.5
$^{13}CH_3CH_2CH_2CO_2^{+\cdot}H$ [a]	22.2	21.8

[a] Not corrected for main beam width.

loss, occurs twice as frequently as (2) ⟶ (8) ⟶ (3a), which leads to the C-2 methyl loss. This contrasts with $C_4H_8O^{+\cdot}$ and $C_5H_{10}O^{+\cdot}$ isomerisations in which pathways analogous to (2) ⟶ (8) are strongly preferred to those paralleling (4) ⟶ (3).[18] The differences could be due to a higher activation energy for (2) ⟶ (8) than for the corresponding $C_4H_8O^{+\cdot}$ and $C_5H_{10}O^{+\cdot}$ isomerisations.[16b]

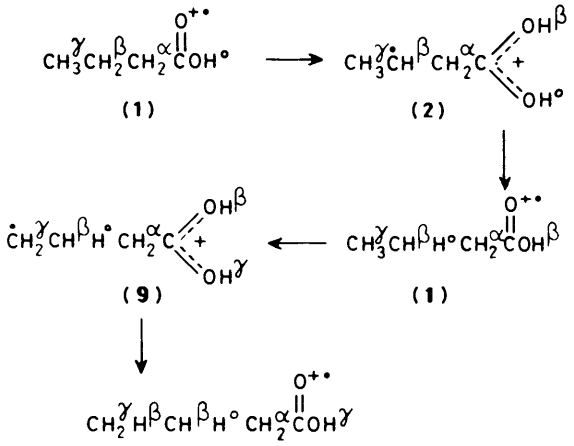
Following the initial formation of (3), the methyl groups containing hydrogen from C-2 and C-3 are assumed to be lost by the methyl shifts (3a)/(3b) ⟶ (5) ⟶ (3c) ⟶ (4c) ⟶ (7c) and (3) ⟶ (6) ⟶ (3e) ⟶ (4) ⟶ (7) [not shown in the Scheme, but (3c) ⟶ (4) is a methyl shift by a reaction identical with the reverse of (4) ⟶ (3b)] and the protonated carboxy shifts (3) ⟶ (5) ⟶ (3c) ⟶ (8c) ⟶ (2c) ⟶ (4c) ⟶ (7c) and (3b)/(3d) ⟶ (6) ⟶ (3e) ⟶ (8e) ⟶ (2e) ⟶ (4e) ⟶ (7e), the latter portions of these pathways being in part the reverse of pathways in the upper parts of Scheme 1. This is supported by kinetic energy release data to be discussed later.

Relative rates of (3) ⟶ (6) and (3) ⟶ (5) can be derived from the decomposition patterns of [*O*-$^2H_1$]-(6) and [2-$^2H_1$]-(6), assuming that (6) ⟶ (3) precedes 100% of the metastable decompositions of (6). According to reactions given in Scheme 1, statistical effects reduce the loss of CH_2D from [*O*-$^2H_1$]-(6) twice as much as from [2-$^2H_1$]-(6) because one of two hydrogen atoms is transferred in (3) ⟶ (6), whereas there is only one possibility in (3) ⟶ (5). Results for the two ions would be affected similarly by isotope effects, assuming that the isotope effect on [*O*-$^2H_1$]-(3) ⟶ [3-$^2H_1$]-(6) is close to that on [2-$^2H_1$]-(3) ⟶ [3-$^2H_1$]-(5), which seems reasonable.*

Interchanges of the carboxy, γ-, and β-hydrogen atoms also appear to contribute to the patterns of deuteriated methyl losses. The increase in CD_3 loss from [4,4,4-$^2H_3$]-(1) (57%) to [*O*,4,4,4-$^2H_4$]-(1) (70%) and diminished associated CHD_2 expulsion (8% to 4%) indicates some exchange between the γ and carboxy hydrogens prior to C-4 methyl loss from these species in the third field-free region, in contrast to decompositions at shorter times.[7] The loss of CHD_2 from [*O*,4,4,4-$^2H_4$]-(1) cannot be accounted for by any pathway in the Scheme 1 or by interchange of the carboxy and γ-hydrogen atoms. Therefore we attribute this loss to transfer of a β-hydrogen to C-4 *via* an oxygen (Scheme 2). Such reactions appear to precede a large fraction of the ethylene eliminations from metastable butanoic acid ions.[3]

In summary, ionised n-butanoic acid isomerises to (4) by a variety of pathways and loses methyl. Decomposition of an ion to the same product by more than one pathway is not unprecedented; the loss of formaldehyde from the $(M - CH_3)^+$ ion in the mass spectrum of methoxymethyl isopropyl ether gives the same product ion *via* two different channels.[19]

Ion Lifetime Studies.—Available information[3,4-10] provides the following picture of the low-energy decompositions of butanoic acid ions. Initial hydrogen transfers (1) ⟶ (2) and (1) ⟶ $\dot{C}H_2CH_2CH_2C(OH)_2^{+}$ occur on average in about 6.5×10^{-11} s.[7] Since $\dot{C}H_2CH_2CH_2C(OH)_2^{+}$ decomposes directly, while (2) must undergo further isomerisation prior to decomposing, loss of ethylene appears sooner than the loss of methyl (Figure). Methyl loss becomes dominant at longer times owing to the more rapid disappearance of most ions which lose ethylene. The isomerisations which relocate the isotopes are relatively slow, taking nearly 10^{-6} s to manifest themselves in the methyl losses. In their FIK study of the ethylene losses from ionised butanoic acid, Weber and his co-workers[7] observed extensive interchange of γ and carboxy hydrogen atoms at times

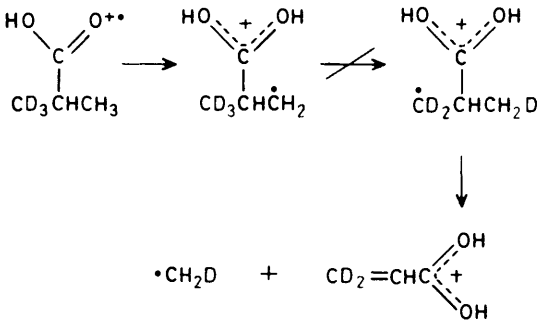


Scheme 2.

longer than 10^{-6} s, and considerable exchange of the β and carboxy hydrogen atoms starting at 10^{-7} s. The long period elapsing between the onset of the methyl and ethylene losses and the manifestation of exchange implies that the hydrogen transfers re-forming butanoic acid ions from (**2**) and (**9**) (see Scheme 2) are relatively slow processes. Ions undergoing (**2**) ⟶ (**8**) ⟶ (**3a**) and (**2**) ⟶ (**4**) at first lose only their terminal methyl groups (Scheme 1). A portion of (**4**) isomerises to (**3b**), and some (**3**) ions further isomerise to (**5**) and (**6**), permitting increasing loss of methyls containing the interior carbons after about 10^{-7} s. The long times elapsing between ionisation and the losses of methyl groups containing C-2 and C-3 indicate that the isomerisations preceding metastable losses of methyl from (**1**) do not precede ionisation, in contrast to a recent proposal that isomerisations of butanoic acid take place in super-excited neutral states prior to the more rapid losses of methyl from butanoic acid ions produced by photon impact.[8]

Translational Energy Release.—There were marked differences (sometimes more than two-fold from the same initial ion) in the translational energy releases ($T_{\frac{1}{2}}$) associated with the losses of different methyl groups from ionised butanoic acid (Table 4). These large differences are somewhat surprising for decompositions to identical products starting from the same initial ion. The highest values are associated with fragmentations apparently reached by pathways through (**5**), *e.g.* loss of CHD_2 from [*O*,2,2-$^2H_3$]-(**1**) (28.3 meV), of CH_3 from [*O*,4,4,4-$^2H_4$]-(**1**) (35.0 meV), and of CH_2D from ionised 2-methyl[2-$^2H_1$]-propanoic acid (29.7 meV). The association of the largest $T_{\frac{1}{2}}$ values with passage through (**5**) is supported by the large value (36.1 meV) for methyl loss from (**5**). The elevated energy releases are attributed to passage of only higher energy ions over a barrier between (**3**) and (**5**), although the presence of such a barrier was not established by direct measurement. Isomerisation over a barrier is a common cause of increased translational energy releases.[20] There were only slight differences between the values for internal and terminal methyl losses from ^{13}C-labelled ions. Presumably this reflects both losses being preceded by similar proportions of the same isomerisations.

Directly generated (**4**) and (**6**) gave intermediate $T_{\frac{1}{2}}$ values (19—22 meV). Such values were generally observed when the terminal methyl was a large portion of the methyl lost starting from (**1**). Formation of (**7a**) and (**7b**) appears to contribute to terminal methyl loss, in addition to the pathways involving (**5**) and (**6**).



Scheme 3.

The two fragmentations which might be attributed totally to decompositions following formation of (**6**), loss of CH_2D from [2,2-$^2H_2$]-(**1**) and of CHD_2 from [3,3-$^2H_2$]-(**1**) have small $T_{\frac{1}{2}}$ values, 15.9 meV and 12.1 meV, respectively. The latter value is surprisingly low, as the lowest value obtained from any directly generated 2-methylpropanoic acid ion was 18.0 meV ($-CH_3$ from 2-methyl[2-$^2H_1$]propanoic acid). Very low values, 10.6, 10.3, and 12.9 meV, were also obtained for the losses of CH_2D from [*O*-$^2H_1$]-(**1**), and of CH_2D and CHD_2 from [4,4,4-$^2H_3$]-(**1**), respectively. The latter three processes are all preceded by hydrogen exchange between the carboxy group and C-4. A rationalisation as to how these energy releases can be substantially lower than those from directly generated intermediates in the proposed pathways involving (**3**) and (**4**) is needed. We hypothesise that most of the ions which reversibly transfer hydrogen between C-4 and oxygen, and perhaps C-3 and oxygen, contain less internal energy than the other metastable ions. This is supported by the small translational energy release associated with loss of ethylene from (**1**), which is preceded by considerable interchange of carboxy, β and γ hydrogen atoms.[3,5,6] Ions that exchange γ-hydrogen atoms may be restricted to very low energies by the rapid loss of ethylene from higher energy ions following γ-hydrogen transfer to oxygen. The present results indicate that different energy releases can accompany decompositions of the same initial ion to the same product from the same decomposing structure reached by differing pathways.

Transition State Preference in Hydrogen Transfers.—Ring-size preference for hydrogen transfers in ions in the gas phase has been of perennial interest.[4,21,22] In rationalising the decompositions of labelled butanoic acid ions, we have proposed 1,2-, 1,4-, and 1,5-, but not 1,3-hydrogen migrations. The absence of CH_2D loss from the 2-methyl[3,3,3-$^2H_3$]-propanoic acid ion rules out the process depicted in Scheme 3 and demonstrates that 1,3-hydrogen shifts involving saturated transition states are not competitive with reactions proposed in Schemes 1 and 2. Four-membered-ring transition states involving keto–enol tautomerism are also unfavourable, occurring only in the absence of competing processes.[23—27] The high activation energies of 1,3-hydrogen shifts interconverting keto and enol ions have been attributed to those processes being symmetry-forbidden.[25,26] However, the 1,3-hydrogen transfer depicted in Scheme 3 is not symmetry-forbidden, suggesting that strain in the transition state is also important in inhibiting four-membered-ring hydrogen transfers.

On the basis of present and previous[4—6,14] observations, we conclude that ring-size preference in hydrogen transfers in cation radicals derived from carbonyl-containing ions is $6 > 5 \sim 3 > 4$ when the three-membered-ring hydrogen transfers are between positions α and β to carbonyl groups.

Hydrogen shifts directly from the β to the γ carbon [$\dot{C}H_2{}^{\gamma}CH_2{}^{\beta}CH_2{}^{\alpha}C(OH)_2{}^+ \longrightarrow CH_2{}^{\gamma}H{}^{\beta}\dot{C}H{}^{\beta}CH_2{}^{\alpha}C(OH)_2{}^+$] must be weak at most in the light of the slight loss (4%) of CHD_2 from [*O*,4,4,4-$^2H_4$]-(**1**), which can be accounted for by reactions depicted in Scheme 2. Thus, 1,2-hydrogen shifts between positions not adjacent to the functional group in $C_4H_8O_2{}^{+\bullet}$ ions appear insignificant. In simple terms the isomerisations of the ions studied here consist of five- and six-membered-ring hydrogen transfers and a variety of 1,2-shifts to and from C-2. Ions $C_5H_{10}O^{+\bullet}$ with the oxygen on the second carbon behave similarly.[15]

Free Radical, Carbocation, and $C_4H_8O_2{}^{+\bullet}$ *Isomerisations.*—Alkyl free radicals undergo major 1,5-, minor 1,4-, and negligible 1,2- and 1,3-hydrogen transfers.[28] Carbocations undergo ready 1,2-hydrogen transfers and skeletal isomerisations.[29,30] Thus the $C_4H_8O_2{}^{+\bullet}$ isomerisations parallel a combination of those of free radicals and carbocations.

We consider the 1,4- and 1,5-hydrogen transfers in $C_4H_8O_2{}^{+\bullet}$ ions to be free-radical-like (concepts developed by Green[31] and Schwarz[32]). Walling has rationalised the difference between the isomerisations of carbocations and free radicals by noting that 1,2-shifts in alkyl free radicals involve triangular transition states with one electron in a higher energy antibonding orbital, giving such reactions very high activation energies.[33] This electron is missing in carbocations and singlet carbenes, permitting ready 1,2-shifts. Such shifts dominate carbocation[29,30] and singlet carbene[34] isomerisations, but are absent in alkyl free radicals.[28] Free radicals undergo 1,2-shifts only when the odd electron can be substantially delocalised from the three-centre ring in the transition state.[34] Molecular orbital calculations indicate that there is considerable positive charge on the carbonyl and α-carbon atoms of enol ions,[35] which should permit 1,2-shifts to take place more readily than in free radicals. We suggest that the 1,2-hydrogen [(**2**) ⟶ (**4**) and (**3**) ⟶ (**5**)] and methyl [(**4**) ⟶ (**3**)] shifts are permitted by positive charge density on the α-carbon atoms in transition states for going to and from enol ions (**4**) and (**5**). The elevated translational energy release from (**5**) implies the the activation energy for (**5**) ⟶ (**3**) is above that for methyl loss from (**3**). Thus, the activation energies of 1,2-hydrogen shifts described here are appreciable, in contrast to the situation in carbocations.[36] Our interpretation of our observations supports the rationalisation of Walling of the differences between the reactivities of carbocations and free radicals.

Our proposal that $C_4H_8O_2{}^{+\bullet}$ ions undergo a combination of free-radical-like and carbocation-like reactions can also be applied to the previously studied reactions of $C_3H_6O^{+\bullet}$,[37] $C_3H_6O_2{}^{+\bullet}$,[38] $C_4H_8O^{+\bullet}$,[14a,23,39] and $C_5H_{10}O^{+\bullet}$[14b,15,40] ions in the mass spectrometer. Thus this proposal provides a unified view of the low-energy isomerisations of aliphatic radical cations in the mass spectrometer. It also improves our understanding of the role of the 'charge sites' and the 'radical sites' in mass spectral fragmentations.[41]

Experimental

Metastable ion spectra were recorded in the third field-free region of an MS 50TA mass spectrometer.[41] FIK Experiments were performed with a Varian MAT 711 mass spectrometer equipped with an EI/FI/FD source. Procedures for obtaining spectra have been previously described.[5,6,42,43] Corrections for main beam width[44] were made to obtain translational energy releases. CAD spectra were obtained at 20% beam reduction by admitting helium to a collision cell in the third field-free region of the MS 50TA instrument. The preparations of the labelled compounds are described elsewhere.[4,5,10,45]

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