REARRANGEMENT REACTIONS FOLLOWING ELECTRON IMPACT ON ETHYL AND ISOPROPYL ESTERS

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ABSTRACT

The mass spectra of ethyl and isopropyl propionate and butyrate show rearrangement ions R_1COOH^+ and $R_1C(OH)_2^+$ formed by reactions [a] and [b]:

[a] $$R_1COOR_2^+ \rightarrow R_1COOH^+ + (R_2 - H),$$

[b] $$R_1COOR_2^+ \rightarrow R_1C(OH)_2^+ + (R_2 - 2H).$$

The mass spectra of ethyl-d_2 propionate and butyrate show that both [a] and [b] occur with essentially complete scrambling of the alkoxy hydrogens. For the isopropyl esters the mass spectra of the isopropyl-d_6 molecules show that reaction [a] occurs by transfer of one of the methyl hydrogens to the acid moiety while reaction [b] occurs predominately by transfer of two methyl hydrogens.

INTRODUCTION

The mass spectra of aliphatic esters of formula R_1COOR_2 show a number of characteristic rearrangement processes the general features of which have been elucidated (1, 2). When R_1 is three carbons or greater in length and contains hydrogen in the γ-position a rearrangement occurs to form the enol ion of the corresponding acetate (reaction [1]).

[1] $$RCH_2CH_2CH_2COOR_2^+ \rightarrow RCH{=}CH_2 + CH_2{=}C(OH)OR_2^+.$$

Deuterium labelling (3–6) has shown that reaction [1] involves a specific transfer of the γ-hydrogen to the oxygen, presumably through a cyclic intermediate (7).

When R_2 is ethyl or higher, further rearrangements may occur which lead not only to formation of the acid ion R_1COOH^+ (reaction [2]) but also to formation of the protonated acid ion $R_1C(OH)_2^+$ (reaction [3]). The formation of the latter ion has permitted estimation of the proton affinity of acids (8, 9). For the smaller R_1 groups reaction [2] occurs almost exclusively to give the charge on the $(R_2 - H)$ fragment.

[2] $$R_1COOR_2^+ \rightarrow R_1COOH^+ + (R_2 - H),$$

[3] $$R_1COOR_2^+ \rightarrow R_1C(OH)_2^+ + (R_2 - 2H).$$
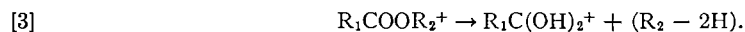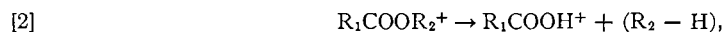
The evidence concerning the hydrogens transferred in reactions [2] and [3] is neither as extensive nor as conclusive as the evidence for reaction [1]. From the mass spectra of *sec*-butyl acetates mono-deuterated in the C_2 and C_3 positions, McLafferty and Hamming (10) concluded that the hydrogens of C_1, C_3, and C_4 of the butyl group were involved in reaction [3]. While the present work was in progress two papers (11, 12) have appeared concerning rearrangement reaction [3] in butyl and pentyl acetates. From the mass spectra of selectively deuterated *n*-butyl acetates it was suggested (11) that the rearrangement occurred by a selective transfer of one hydrogen from the C_3 position of the alcohol followed by a random selection of the second hydrogen. On the other hand, the results for the *n*-pentyl acetates indicated (12) that the first hydrogen was selected practically equally from the C_3 and C_4 positions, followed by random selection of the second from the remaining hydrogens. Godbole and Kebarle (8) concluded from the

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mass spectra of labelled ethyl acetates and formates that the hydrogen transfer reactions to the acid portion of the molecule involved essentially complete scrambling of the ethyl hydrogens. On the other hand, their results for isopropyl acetate show a pronounced preference for transfer of the hydrogens from the 1 and 3 positions of the propyl group.

To obtain further information on the hydrogens transferred in reactions [2] and [3] and to obtain information on the relative importance of reactions [1] and [2] we have prepared ethyl-1,1-d_2 propionate and butyrate and 2-propyl-1,1,1,3,3,3-d_6 propionate and butyrate and compared the spectra of the labelled and unlabelled molecules. The results obtained not only provide information on the rearrangement reactions discussed above but also provide information on a number of other fragmentation processes in these esters.

EXPERIMENTAL

Mass spectra were obtained with an A.E.I. MS-2 mass spectrometer at 50 V electron energy and 10 V cm^{-1} repeller field strength. Appearance potentials were determined in the usual manner (13) using xenon or krypton to calibrate the voltage scale.

The ethyl esters, both labelled and unlabelled, were prepared by the acid-catalyzed esterification of the free acid by the appropriate alcohol following the procedure given by Vogel (14). For the isopropyl esters this procedure gave poor yields. Much better yields were obtained by reaction of the appropriate acid anhydride with the labelled or unlabelled alcohol using zinc chloride catalyst (15). Final purification in all cases was by gas–liquid chromatography (g.l.c.) using a diisodecylphthalate column.

The ethyl-d_2 alcohol and isopropyl-d_6 alcohol were obtained from Merck, Sharp and Dohme, Montreal and were of better than 98% isotopic purity (16).

RESULTS AND DISCUSSION

Partial mass spectra of ethyl-1,1-d_2 propionate and 2-propyl-1,1,1,3,3,3-d_6 propionate are compared with the spectra of the unlabelled esters in Table I, while the spectra of the

TABLE I

Partial mass spectra of propionate esters

Mass	Ethyl propionate	Ethyl-d_2 propionate	Isopropyl propionate	Isopropyl-d_6 propionate
122				0.59
116			0.30	
104		6.61		3.88
102	7.26			
101			4.04	
77		0.17		8.72
76		1.92		1.14
75	4.08	5.06	10.73	2.34
74	3.93	2.14	1.81	0.42
73	2.83	0.65	0.36	
65				4.48
59			3.54	
57	31.53	29.84	31.83	32.30
49				23.67
48				2.76
47		2.08		1.43
46		0.71		3.78
45	3.86	0.90	1.25	3.26
44	0.14	0.68	0.17	0.41
43	1.83	0.29	19.67	1.78
33		1.05		0.50
32		0.49		0.10
31	0.91	14.47	0.51	0.39
30	0.40	3.02	0.10	0.57
29	27.12	14.69	9.45	11.01
28	4.22	5.35	1.44	1.38

corresponding labelled and unlabelled butyrates are compared in Table II. In all cases the spectra have been corrected for naturally occurring ^{13}C and the intensities are expressed as a percentage of the total ionization.

TABLE II

Partial mass spectra of butyrate esters

Mass	Ethyl butyrate	Ethyl-d_2 butyrate	Isopropyl butyrate	Isopropyl-d_6 butyrate
136				1.19
130			1.10	
118		1.85		2.39
116	2.03			
115			2.60	
108				1.79
103		1.77		
102			1.06	
101	1.75			
91		0.16		6.57
90		12.29		0.82
89	2.54	1.84	9.65	4.67
88	11.82	0.92	4.09	0.23
87	0.45	0.16	0.15	
75		0.49		
74		0.72		2.13
73	3.72	2.70	2.11	0.15
72		1.07		
71	18.52	19.15	22.04	19.91
70	2.20	0.56		
65				4.56
63		0.17		
62		1.15		0.41
61	1.56	1.41		4.46
60	3.86	3.73	4.41	
59			4.04	
49				18.92
47		1.37		1.25
46		0.63		2.51
45	3.39	1.11	1.05	2.20
44	0.77	0.53	0.25	0.40
43	15.48	14.49	28.10	10.58
31	0.89	9.77	0.41	0.18
30	0.22	1.13	0.85	1.32
29	10.68	2.06	1.06	1.66

Of particular interest in the present context are the rearrangement ions formed by reactions [2] and [3] which occur at masses[3] 74 and 75 for the unlabelled propionates and masses 88 and 89 for the butyrates, although, as will be shown below, a large fraction of the mass 88 ion current in the ethyl butyrate spectrum corresponds to the $CH_2=C(OH)OC_2H_5^+$ ion formed by reaction [1]. The ion current at mass 102 in the spectrum of isopropyl butyrate moves to mass 108 in the d_6 compound and obviously corresponds to the $CH_2=C(OH)OC_3H_7^+$ ion formed by reaction [1].

The mass spectra of the labelled and unlabelled propionates in the mass 70–80 region are compared in Table III and the ionic contributions for the various masses presented in detail. For the isopropyl esters little confusion can arise. The mass 75 of the unlabelled ester moves to mass 76 and 77 in the labelled ester corresponding to transfer of HD and 2D to the acid moiety, while the mass 74 moves to mass 75 corresponding to transfer of D in reaction [2]. The small mass 73 moves to mass 74 and therefore cannot be the

[3]*Since only singly charged ions will be discussed the m/e ratio will be referred to as the mass throughout.*

$C_2H_5COO^+$ ion formed by loss of the isopropyl group but is probably the $C_2H_4COOH^+$ ion formed by loss of H from $C_2H_5COOH^+$. Such a decomposition is known (17) to proceed with retention of the acid hydrogen.

TABLE III

Contributions to mass spectra of propionates in mass 73–77 region

Mass	Ethyl propionate		Ethyl-d_2 propionate	
	Intensity	Contribution	Intensity	Contribution
77			0.19	$C_2H_5C(OD)_2^+$
76			2.10	$C_2H_5C(OH)(OD)^+$
75	4.08	$C_2H_5C(OH)_2^+$	5.52	$2.12 = COOC_2D_2H_3^+$
				$1.59 = C_2H_5COOD^+$
				$1.81 = C_2H_5C(OH)_2^+$
74	3.93	$C_2H_5COOH^+$	2.34	$C_2H_5COOH^+$
73	2.83	$C_2H_5COO^+$, $COOC_2H_5^+$	0.71	$C_2H_5COO^+$

Mass	Isopropyl propionate		Isopropyl-d_6 propionate	
	Intensity	Contribution	Intensity	Contribution
77			8.72	$C_2H_5C(OD)_2^+$
76			1.14	$C_2H_5C(OH)(OD)^+$
75	10.73	$C_2H_5C(OH)_2^+$	2.34	$C_2H_5COOD^+$
74	1.81	$C_2H_5COOH^+$	0.42	$C_2H_4COOD^+$
73	0.36	$C_2H_4COOH^+$		

The calculations for the ethyl esters are more complex since the total intensities for the labelled and unlabelled spectra differ slightly and, in addition, a number of the masses in the deuterated spectrum may have more than one contributor. To make the calculations possible we have multiplied all intensities in the labelled spectrum by 1.10 to make total intensities equal and we have further assumed that the ion at mass 73 in the unlabelled ester is formed by loss of C_2H_5 and is therefore either the $COOC_2H_5^+$ or the $C_2H_5COO^+$ ion. Undoubtedly a small amount may arise by loss of H from $C_2H_5COOH^+$, however, comparison with the spectrum of the isopropyl ester suggests that this contribution will be small. With these assumptions the ionic contributions detailed in the final column are calculated for the ethyl-d_2 propionate spectrum.

Similar calculations carried out for the mass 87–91 region of the labelled and unlabelled butyrates are presented in Table IV. Again the calculations for the isopropyl case are straightforward, however, the calculations for the ethyl esters are complex and it is not possible by equating intensities in the labelled and unlabelled spectra to solve directly for the ionic contributors at all masses. We have therefore made the logical assumption that the mass 88 intensity of the ethyl-d_2 spectrum corresponds entirely to $C_3H_7COOH^+$ formed by reaction [2] and that this reaction occurs by complete scrambling of the ethyl hydrogens as was found for the ethyl propionate. On this basis the contributions detailed in the last column of Table IV are obtained. The calculations show that approximately 92% of the mass 88 of the unlabelled ester has moved to mass 90 in the labelled spectrum and therefore must retain the two deuteriums. The major portion of the mass 88 therefore corresponds to the $CH_2=C(OH)OC_2H_5^+$ ion formed by reaction [1], while the remaining 8% corresponds to the $C_3H_7COOH^+$ ion formed by reaction [2]. This is in contrast to the results for isopropyl butyrate where reaction [1] produces an ion (mass 102) only 0.63 the intensity of the ion (mass 88) formed by reaction [2]. The presence of the isopropyl group appears to facilitate the rearrangement reaction [2].
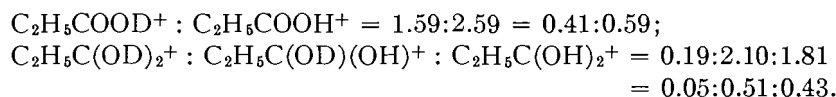
TABLE IV

Contributions to mass spectra of butyrates in mass 87–91 region

| | Ethyl butyrate | | Ethyl-d_2 butyrate | |
Mass	Intensity	Contribution	Intensity	Contribution
91			0.16	$C_3H_7C(OD)_2{}^+$
90			12.29	$1.44 = C_3H_7C(OD)(OH)^+$
				$10.85 = CH_2{=}C(OH)OCD_2CH_3{}^+$
89	2.54	$C_3H_7C(OH)_2{}^+$	1.84	$0.29 = CH_2COOCD_2CH_3{}^+$
				$0.61 = C_3H_7COOD^+$
				$0.94 = C_3H_7C(OH)_2{}^+$
88	11.82	$C_3H_7COOH^+$	0.92	$C_3H_7COOH^+$
		$CH_2{=}C(OH)OC_2H_5{}^+$		
87	0.45	$C_3H_7COO^+$	0.16	$C_3H_7COO^+$
		$CH_2COOC_2H_5{}^+$		

| | Isopropyl butyrate | | Isopropyl-d_6 butyrate | |
Mass	Intensity	Contribution	Intensity	Contribution
91			6.57	$C_3H_7C(OH)_2{}^+$
90			0.82	$C_3H_7C(OH)(OD)^+$
89	9.65	$C_3H_7C(OH)_2{}^+$	4.67	$C_3H_7COOD^+$
88	4.09	$C_3H_7COOH^+$	0.23	$C_3H_6COOD^+$
87	0.15	$C_3H_6COOH^+$		

From the calculations of Tables III and IV for the deuterated esters one obtains the following results for the transfer of H and D to form the R_1COOH^+ and $R_1C(OH)_2{}^+$ ions by reactions [2] and [3].

Ethyl-d_2 propionate:

$C_2H_5COOD^+ : C_2H_5COOH^+ = 1.59{:}2.59 = 0.41{:}0.59;$

$C_2H_5C(OD)_2{}^+ : C_2H_5C(OD)(OH)^+ : C_2H_5C(OH)_2{}^+ = 0.19{:}2.10{:}1.81$
$$= 0.05{:}0.51{:}0.43.$$

Ethyl-d_2 butyrate:

$C_3H_7COOD^+ : C_3H_7COOH^+ = 0.61{:}0.92 = 0.40{:}0.60 \text{ (assumed)};$

$C_3H_7C(OD)_2{}^+ : C_3H_7C(OD)(OH)^+ : C_3H_7C(OH)_2{}^+ = 0.16{:}1.44{:}0.94$
$$= 0.06{:}0.57{:}0.37.$$

Isopropyl-d_6 propionate:

$C_2H_5COOD^+ : C_2H_5COOH^+ = 2.34{:}0;$

$C_2H_5C(OD)_2{}^+ : C_2H_5C(OD)(OH)^+ = 8.72{:}1.14 = 0.88{:}0.12.$

Isopropyl-d_6 butyrate:

$C_3H_7COOD^+ : C_2H_5COOH^+ = 4.67{:}0;$

$C_3H_7C(OD)_2{}^+ : C_3H_7C(OD)(OH)^+ = 6.57{:}0.82 = 0.89{:}0.11.$
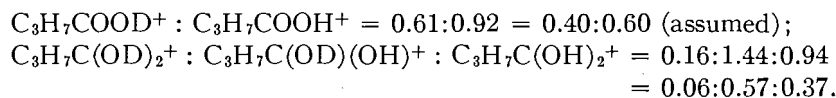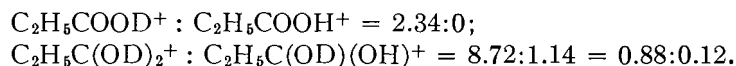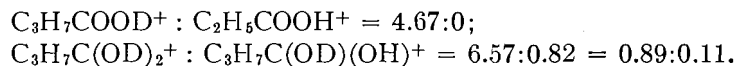
These results clearly show that the transfer of one H in reaction [2] involves complete scrambling of the ethyl hydrogens, while transfer of two hydrogens in reaction [3] for the ethyl esters proceeds with extensive scrambling of the the ethyl hydrogens, the experimentally observed ratio for transfer of $D_2{:}HD{:}H_2$ being close to the ratio 0.10:0.60:0.30 calculated for complete equivalence of the two D and three H. The results for the ethyl esters are in agreement with the results obtained by Godbole and Kebarle (8) for the

similar rearrangements in ethyl acetate. The results for the isopropyl esters, on the other hand, show that transfer of one hydrogen in reaction [2] proceeds, within experimental error, exclusively by transfer of the methyl hydrogen. Reaction [3] for the isopropyl esters occurs predominately by transfer of two of the methyl hydrogens as shown by the ratios for transfer of $D_2:DH = 0.88:0.12$. Complete scrambling of the isopropyl hydrogens would lead to $D_2:HD = 0.72:0.28$ while transfer of one of the methyl hydrogens followed by random selection of the second hydrogen would lead to the ratio $D_2:HD = 0.83:0.17$. The present results are in agreement with the results obtained for reaction [3] in $CD_3COOCD(CH_3)_2$ which showed transfer of H_2 : transfer of $HD = 0.88:0.12$ (8). It has been noted (12, 18) that rearrangement reaction [2] in the acetates leads almost exclusively to formation of the $(R_2 - H)^+$ ion rather than the R_1COOH^+ ion since the ionization potential of the olefin fragment is lower. For the esters studied in the present work the ionization potentials of the R_1COOH fragments are comparable to the ionization potentials of the olefin fragments with the result that appreciable intensities are noted corresponding to the acid ion.

It has been suggested (7, 18) that reaction [2] may occur through formation of a cyclic intermediate (I) involving transfer of the β-hydrogen of the alcohol moiety.
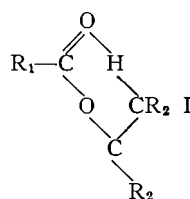
The results obtained in the present work for the isopropyl esters are clearly consistent with this interpretation since only the methyl (β) hydrogens are involved in reaction [2]. However, for the ethyl esters both the present results and previous work (8) show that the β-hydrogens are not transferred exclusively but that complete randomization of the ethyl hydrogens has occurred in the transfer process. This may be taken to indicate either that such a cyclic transition state is not applicable or that randomization of the ethyl hydrogens has occurred prior to formation of the intermediate. With regard to the latter possibility, it might be noted that for the ethyl esters a rather simple rearrangement of the parent ion (reaction [4]) could lead to essentially complete randomization of the hydrogens in reaction [2].

[4]
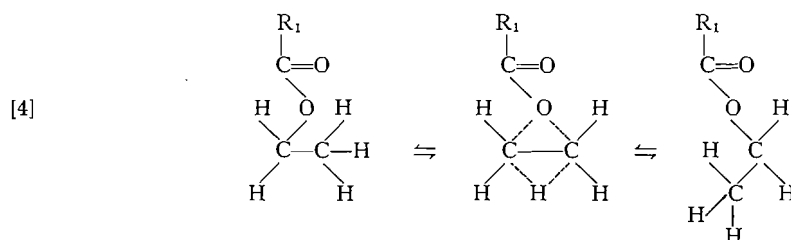
Such a rearrangement would be less likely for the isopropyl esters since it would involve shifting of the oxygen linkage from a secondary to a primary carbon rather than the symmetrical shift shown above. The above suggestion is clearly speculative since no other evidence can be found in the spectra of the ethyl esters to support such a rearrangement.

For reaction [3] it has been suggested (7) that the first hydrogen transfer also may occur by the cyclic intermediate I. It is not surprising therefore that the ethyl esters show extensive randomization of the ethyl hydrogens in reaction [3] as well as in reaction [2]. The results for the isopropyl esters are in accord with this suggestion while the results for the butyl (11) and pentyl (12) acetates suggest a selective transfer of the first hydrogen but through an intermediate of larger ring size. The major difference in the results for the isopropyl esters as compared to the butyl and pentyl esters is that transfer of the second hydrogen in the isopropyl esters appears to be specifically one of the terminal methyl hydrogens while for the other esters randomization of all the hydrogen has occurred.

A possible reason for this selectivity in the isopropyl case may be surmised from an examination of the energetics of formation of $R_1C(OH)_2^+$. The relevant data are summarized in Table V. The heats of formation of the neutral esters necessary for the thermochemical calculations were taken from Brion and Dunning (19) while the heats of formation of other neutral species were taken from the compilation of Bernecker and Long (20).

TABLE V

Energetics of formation of $R_1C(OH)_2^+$ from R_1COOR_2 (all data in eV)

R_1	$R_2 = C_2H_5$		$R_2 = CH(CH_3)_2$	
	$A(R_1C(OH)_2^+)$	$\Delta H_f(R_1C(OH)_2^+)$	$A(R_1C(OH)_2^+)$	$\Delta H_f(R_1C(OH)_2^+)$
CH_3	10.80±0.1*		10.42±0.1*	4.24
	10.75†	3.42	10.72±0.03‖	
	10.95‡			
	11.0±0.2§			
CH_3			10.48±0.07‖	4.28
			($R_2 = n$-propyl)	
C_2H_5	10.77‡	2.91	10.40±0.1*	3.74
	10.67±0.1*			

*This work.
†Reference 20.
‡Reference 8.
§Sharkey, Hickam, and Friedel, private communication to ref. 8.
‖Reference 19.

The average $A(CH_3C(OH)_2^+)$ from ethyl acetate leads to $\Delta H_f(CH_3C(OH)_2^+) = 3.42$ eV assuming C_2H_3 (vinyl) as the neutral fragment. On the other hand, $A(CH_3C(OH)_2^+)$ from isopropyl acetate leads to $\Delta H_f(CH_3C(OH)_2^+) = 4.24$ eV assuming C_3H_5 (allyl) as the neutral fragment. This higher heat of formation is also obtained from the appearance potential of $CH_3C(OH)_2^+$ in n-propyl acetate. This difference in the calculated heats of formation for $R_1C(OH)_2^+$ from the ethyl and isopropyl esters is also found in the propionates and it is clear that the neutral fragment (or fragments) for the isopropyl esters cannot be the allyl radical.

One may reverse the calculations and use $\Delta H_f(R_1C(OH)_2^+)$ derived from the ethyl esters in the thermochemical cycle for the isopropyl esters to calculate $\Delta H_f(C_3H_5) = 2.15 \pm 0.2$ eV. Although the heat of formation of the cyclopropyl radical is not known accurately it is probably about 2.4 eV and it is therefore possible that the C_3H_5 formed from the isopropyl esters in reaction [3] has the cyclopropyl structure. For the isopropyl esters transfer of one hydrogen from each methyl group in reaction [3] would permit the formation of the cyclopropyl radical without further hydrogen rearrangement and would also explain the selective transfer of the hydrogens in the rearrangement reaction.

The mass spectra obtained for the deuterium-labelled molecules provide information on some of the other fragmentation processes, particularly for the butyrate esters, and deserve some comment.

Formation of Mass 73 in Butyrate Esters

Both the ethyl and isopropyl butyrates show a significant ion current at mass 73. For the isopropyl ester a metastable at 60.6 indicates the decomposition

[5] $$C_3H_7COOH^+ \rightarrow CH_2CH_2COOH^+ + CH_3.$$
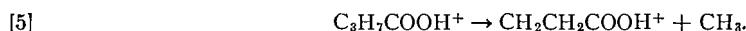
This is supported by the observation that the fragment ion moves to mass 74 and the metastable to 61.5 in the labelled ester since the precursor ion has become $C_3H_7COOD^+$. A similar fragmentation is observed in the spectrum of butyric acid.

For the ethyl-d_2 butyrate the major contribution remains at mass 73 with smaller contributions at masses 74 and 75. The contributions at 73 and 74 presumably arise by reaction [5] although no metastable was observed. That portion occurring at mass 75 must incorporate both deuteriums and probably originates by loss of methyl from the $CH_2=C(OH)OCD_2CH_3^+$ ion.

Formation of Mass 70 in Ethyl Butyrate

The ion current at mass 70 in ethyl butyrate has the empirical formula $C_4H_6O^+$ (2). In the d_2 compound approximately one-half of this intensity moves to mass 72 indicating retention of both deuteriums. The most probable reaction is the loss of H_2O from the mass 90 intermediate.

[6] $$CH_2=C(OH)OCD_2CH_3^+ \rightarrow CH\equiv COCD_2CH_3^+ + H_2O.$$
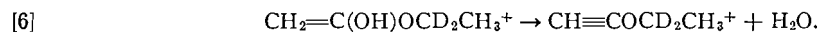
The remainder of the ion current is found at masses 70 and 71 and the mechanism of formation is not clear.

Formation of Masses 60 and 61 in Butyrate Esters

The mass spectrum of ethyl butyrate shows a mass 61 ion current which is considerably more intense than that observed for isopropyl butyrate. The precursor ion is undoubtedly the $CH_2=C(OH)OCH_2CH_3^+$ ion and the rearrangement is therefore similar to that occurring in the spectrum of ethyl acetate. The relative intensities at masses 63, 62, and 61 in the d_2 compound are in agreement with complete scrambling of the ethoxy hydrogens in the rearrangement process. A similar rearrangement might be expected from the enol form of the isopropyl acetate ion (mass 102), however, the intensity of the precursor ion is much lower.

Both the ethyl and isopropyl esters show large ion currents at mass 60. In the isopropyl-d_6 butyrate this peak moves to mass 61 indicating retention of one deuterium and suggesting reaction [7] similar to that observed in butyric acid, although one cannot eliminate a concerted mechanism proceeding from the parent ester ion.

[7] $$C_3H_7COOH^+ \rightarrow CH_2=C(OH)_2^+ + C_2H_4.$$
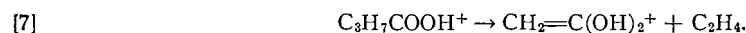
A similar reaction in ethyl butyrate will account for the observed results.

Formation of R_1^+ and R_2^+ from R_1COOR_2

For ethyl propionate and isopropyl butyrate R_1^+ and R_2^+ occur at the same mass for the unlabelled esters. The spectra of the labelled esters allows an estimate of the relative contributions. For ethyl-d_2 propionate approximately 50% of the mass 29 moves to mass 31 indicating that $C_2H_5^+$ is formed equally from both ends of the ester molecule. For the

isopropyl-d_6 butyrate approximately 66% of the mass 43 of the unlabelled ester is found at mass 49 in the labelled ester indicating the relative contributions $R_1^+:R_2^+ = 1:2$.

ACKNOWLEDGMENTS

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