

Formation of Ketone Ions Upon the Loss of CH₂O from Ionized Esters

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Unimolecular and collision-induced decompositions of the products of CH₂O loss from propyl propanoate and butyl butanoate demonstrate that the respective products are the 3-pentanone and 4-heptanone ions.

INTRODUCTION

Fragmentations involving losses of interior portions of ionized esters take place,^{1,2} but are not well understood. One of these reactions is the very weak loss (0.5–1% of base peak intensity) of C_nH_{2n}O neutrals containing the oxygen plus the first carbon and its substituents from the alcohol moiety.¹ McFadden and coworkers¹ speculated that the retained alkyl portion of the alcohol migrates to the oxygen, while Budzikiewicz *et al.*³ suggested that ketone ions are formed. Because of the novelty of the reaction, we sought to determine the structures of the ionic products. We concluded that loss of CH₂O from ionized aliphatic esters produces ketone ions.

RESULTS AND DISCUSSION

[C₅H₁₀O]⁺ ions from propyl propanoate (**1**) and ionized 3-pentanone (**2**) have matching collision-induced (Table 1) and metastable (Table 2) spectra indicating that the two ions are the same. Ions from propyl propanoate with a deuterium in one methyl

Table 1. Collision-induced mass spectra of [C₅H₁₀O]⁺ ions from propyl propanoate (**1**) and 3-pentanone (**2**)

m/z	Intensities	
	1	2
26	1	2
27	5	5
28	3	2
29	11	12
39	1	1
41	1	1
42	1	1
43	1	1
53	1	1
55	1	1
56	32	29
57	100	100

Table 2. Third field free region metastable fragmentations of [C₅(H,D)₁₀O]⁺ ions

Precursor compound	Product m/z		
	56	57	58
Propyl propanoate (1)	100	34	
3-Pentanone (2)	100	30	
4-Ethyl-3-heptanone	6	100	
Propyl propanoate-3-d ₁ (1a)	83	100	5
Propyl-3-d ₁ propanoate (1b)	81	100	7

group or the other formed m/z 56 products 81–83% as often as m/z 57 products. Correcting the m/z 57 intensities for C₂H₄D contributions, by assuming that the C₂H₄D loss was 92% of the C₂H₅ loss due to an isotope effect based on a secondary isotope effect on the loss of ethyl from 3-pentanone ions observed elsewhere,⁴ gives a –C₂H₆/–C₂H₅D ratio of 1.14 for **1a** and 1.16 for **1b**. We conclude from the identity of these ratios that the imbalance in [C₃H₄O]⁺ and [C₃H₃DO]⁺ intensities is entirely due to an isotope effect, and that the ethanes lost from the intermediate [C₅H₁₀O]⁺ ions have equal probabilities of containing the stationary and migrating ethyls. Therefore, the two ethyls are equivalent, further indicating that the intermediate [C₅H₉DO]⁺ ions are 3-pentanone ions. CH₃CH₂C(=OH)CHCH₃, CH₃CH₂CHÖHCH=CH₂, CH₃CH₂C(=OH)CH₂CH₂, CH₃CH₂CH₂CHC(=OH)-H, CH₃CH₂CH₂CH₂CHÖ and CH₃CH₂CH₂CH₂CHÖH all isomerize to 3-pentanone ions to some degree in their metastable decompositions and, as illustrated in Table 2 for CH₃CH₂C(=OH)CHCH₃, all of these isomerizations are followed by much more intense losses of ethyl than of ethane.^{4–6} Formation of predominantly one of these [C₅H₁₀O]⁺ isomers by CH₂O loss from ionized propyl propanoate is, therefore, ruled out, so we conclude that the 3-pentanone ion is the direct product of the loss of CH₂O from ionized propyl propanoate. The metastable propyl propanoate ion loses H and C₃H₅, but not CH₂O.

Third field free region unimolecular dissociations of 4-heptanone (**4**) ions and of m/z 114 generated from ionized butyl butanoate (**3**) (Table 3) were identical, both undergoing losses of CH₃, C₂H₄, C₃H₇ and C₃H₈. Thus loss of CH₂O from ionized butyl butanoate probably forms the 4-heptanone ion.

The loss of CH₂O from ionized esters can be represented as occurring by concerted ejection of CH₂O

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Table 3. Third field free region metastable fragmentations of $[C_7H_{14}O]^{+}$ ions from butyl butanoate (3) and 4-heptanone (4)

Product m/z	Intensities	
	3	4
70	4	4
71	6	7
86	100	100
99	4	5

or as transfer of the alkyl group from the alcohol to the carbonyl carbon to form an intermediate which then loses CH_2O (Scheme 1). Our data do not permit choosing between these possibilities.

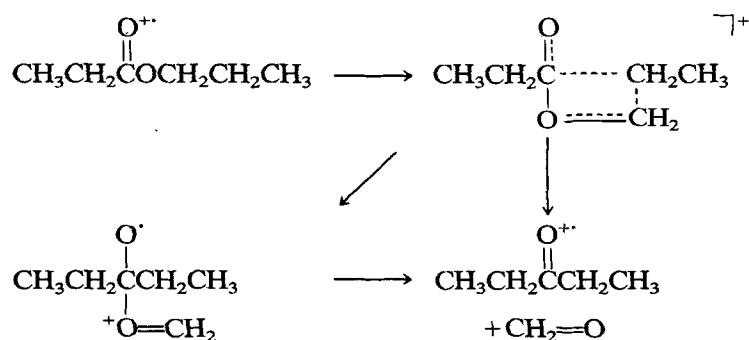
EXPERIMENTAL

Unimolecular and collision-induced decomposition spectra^{7,8} were determined in the third field free region of an MS 50 TA mass spectrometer.⁹ Helium was used as a collision gas at a pressure which gave a 40%

reduction in beam intensity. Propyl propanoate was prepared by adding a slight excess of propionic anhydride and a trace of sulfuric acid to 1-propanol, washing the product with a sodium bicarbonate solution and distilling out the ester. Butyl butanoate was prepared by adding a slight excess of butanoic acid and a trace of sulfuric acid to *n*-butanol at reflux temperatures. Benzene was added and the water distilled out as an azeotrope. Propyl propanoate-3- d_1 was prepared by reduction of ethylene oxide with $LiAlD_4$, conversion of the alcohol to the bromide with HBr/H_2SO_4 , carboxylation of the Grignard to form propanoic acid-3- d_1 , conversion to the acid chloride with $SOCl_2$, and formation of the ester by reaction with propanol. Propyl-3- d_1 propanoate was prepared by reducing propanoic acid-3- d_1 (see above) with $LiAlH_4$ and esterification of the resulting alcohol with propionic anhydride.

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Scheme 1

REFERENCES

- D. R. Black, W. H. McFadden and J. W. Corse, *J. Phys. Chem.* **68**, 1237 (1964).
- R. Ryhage and E. Stenhagen, in *Mass Spectrometry of Organic Ions*, ed. by F. W. McLafferty, p. 399, Academic Press, New York (1963).
- H. Budzikiewicz, C. Djerassi and D. H. Williams, in *Mass Spectrometry of Organic Compounds*, p. 187, Holden-Day, San Francisco (1967).
- D. J. McAdoo and C. E. Hudson, *Org. Mass Spectrom.* **18**, 159 (1983).
- D. J. McAdoo, W. Farr and C. E. Hudson, *J. Am. Chem. Soc.* **102**, 5165 (1980).
- C. E. Hudson and D. J. McAdoo, *Org. Mass Spectrom.* **19**, 1 (1984).
- F. W. McLafferty, P. F. Bente, R. Kornfeld, S. C. Tsai and I. Howe, *J. Am. Chem. Soc.* **95**, 2120 (1973).
- F. W. McLafferty, R. Kornfeld, W. F. Haddon, K. Levsen, I. Sakai, P. F. Bente, S. C. Tsai and H. D. R. Schuddemage, *J. Am. Chem. Soc.* **95**, 3886 (1973).
- M. L. Gross, E. K. Chess, P. A. Lyon and F. W. Crow, *Int. J. Mass Spectrom. Ion Phys.* **42**, 243 (1982).

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