# Characterization of Five $[C_4H_7O]^+$ Ion Structures. Fragmentation of the 2-Pentanone Molecular Ion

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The [C4H70]+ [CH<sub>2</sub>=CH-C(=OH)CH<sub>3</sub>]<sup>+</sup>  $[CH_3CH=CH-C(=OH)H]^+$ ions (1), (2),  $[CH_2 - C(CH_3)C(-OH)H]^+$  (3),  $[CH_3CH_2CH_2C=O]^+$  (4) and  $[(CH_3)_2CHC=O]^+$  (5) have been characterized by their collision-induced dissociation (CID) mass spectra and charge stripping mass spectra. The ions 1-3 were prepared by gas phase protonation of the relevant carbonyl compounds while 4 and 5 were prepared by dissociative electron impact ionization of the appropriate carbonyl compounds. Only 2 and 3 give similar spectra and are difficult to distinguish from each other; the remaining ions can be readily characterized by either their CID mass spectra or their charge stripping mass spectra. The 2-pentanone molecular ion fragments by loss of the C(1) methyl and the C(5) methyl in the ratio 60:40 for metastable ions; at higher internal energies loss of the C(1) methyl becomes more favoured. Metastable ion characteristics, CID mass spectra and charge stripping mass spectra all show that loss of the C(1) methyl leads to formation of the acyl ion 4, while loss of the C(5) methyl leads to formation of protonated vinyl methyl ketone (1). These results are in agreement with the previously proposed potential energy diagram for the [C<sub>5</sub>H<sub>10</sub>O]<sup>++</sup> system.

# INTRODUCTION

Although the chemistry of the  $[C_nH_{2n+1}O]^+$  ions, commonly observed as abundant fragment ions in the mass spectra of aliphatic alcohols and ethers, has been studied extensively,<sup>1-16</sup> the chemistry of their olefinic analogues, the  $[C_nH_{2n-1}O]^+$  ions, has received much less attention. A number of distinct stable  $[C_3H_5O]^+$  ion structures have been identified<sup>17</sup> from their collision-induced dissociation (CID) mass spectra. In addition, a number of more detailed studies<sup>18-21</sup> have shown that the  $[C_3H_5O]^+$  ion of nominal structure [CH2=CH-CH=OH]+ is distinct in its chemistry from the isomeric acylium ion  $[C_2H_5C\equiv O]^+$ . In recent work from this laboratory the thermochemistry<sup>22</sup> and unimolecular ion chemistry<sup>23</sup> of  $[C_4H_7O]^+$  ions of nominal structures 1-3 have been explored. These studies have shown that the three ions can be readily distinguished from the acylium ions 4 and 5 and that 1 can be readily distinguished from 2 and 3, but that 2 and 3 have similar thermochemistry and unimolecular fragmentation chemistry.

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In a related study<sup>24</sup> the unimolecular loss of CH<sub>3</sub> from the molecular ions of  $C_5H_{10}O$  olefinic alcohols has been investigated using isotopic labelling in conjunction with field ionization kinetics and metastable ion studies to elucidate the fragmentation reactions occurring and their lifetime/internal energy dependence. Of particular relevance to the present study is the observation<sup>24</sup> that the time-resolved fragmentation molecular ion of CH<sub>3</sub>-CH=CHof the CH(OH)CD<sub>3</sub> is extremely complex showing loss of both CD<sub>3</sub> (~60%) and CH<sub>3</sub>(~40%) at lifetimes of  $\sim 10^{-11}$  s, while at longer times  $(10^{-10} - 10^{-9} \text{ s})$  loss of  $CH_3$  predominates and at even longer lifetimes ( $10^{-6}$ - $10^{-5}$  s) loss of CD<sub>3</sub> increases in importance again. These results, supported by metastable ion studies of the fragmentation of electron impact (EI) produced ions, have been interpreted in terms of a complex fragmentation scheme, the essentials of which are summarized in the potential energy diagram of Fig. 1. Molecular ions  $(6-d_1)$  of short lifetimes (high internal energy) either undergo direct cleavage loss of CD<sub>3</sub> to form 2 or by two facile 1,2-H shifts rearrange to the enol of the 2-pentanone molecular ion  $(8-d_3)$  which fragments by loss of  $CH_3$  to form 1-d<sub>3</sub>. At lifetimes of  $\sim 10^{-9}$  s this latter reaction becomes the dominant fragmentation reaction. At longer lifetimes a 1,4-H migration in the intermediate  $7-d_3$  leads to the 2pentanone molecular ion  $(9-d_3)$  which fragments by

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Figure 1. Potential energy diagram for  $[C_5H_{10}O]^{+\cdot}$  system (vertical axis gives potential energy in kJ mol<sup>-1</sup>).

~100 °C

 $\alpha$ -cleavage to form the acyl ion 4. It is implicit from this scheme that the molecular ion of 2-pentanone (9) may fragment not only by  $\alpha$ -cleavage to form the acyl ion 4 but also by loss of the C(5) methyl group to form protonated vinyl methyl ketone (1); indeed, the overall scheme receives support from Krenmayr's observation<sup>25</sup> that the molecular ion of 2-pentanone-1,1,1,3,3-d<sub>5</sub> showed loss of both CH<sub>3</sub> and CD<sub>3</sub>. Krenmayr also showed that the two fragment ions thus formed had different metastable ion fragmentation reactions, although he postulated a cyclic structure for the ion resulting from CH<sub>3</sub> loss (which he assumed was the C(5) methyl).

To obtain further information supporting the fragmentation scheme presented in Fig. 1 we have undertaken three interrelated studies. The first involved the characterization of the ionic structures 1-5 by CID and charge stripping mass spectra. The second involved a detailed study, using isotopic labelling, charge exchange mass spectrometry and collisional mass spectrometry of the fragmentation of the 2-pentanone molecular ion and the structures of the fragment ions therefrom. The third involved a detailed study, using charge exchange mass spectrometry and CID mass spectrometry, of the energy-resolved fragmentation of the 3-penten-2-ol molecular ion and the structures of the fragment ions formed as a function of the internal energy of the fragmenting molecular ions. The results of the first two studies are reported here; the results of the third study, which includes a detailed comparison of charge exchange mass spectrometry with field ionization kinetics and angle-resolved mass spectrometry will be presented elsewhere.<sup>26</sup>

## EXPERIMENTAL

Chemical ionization mass spectra were obtained using a DuPont 21-490 mass spectrometer equipped with a high-pressure chemical ionization source. Reagent gas pressures (H<sub>2</sub> or D<sub>2</sub>) were  $\sim 0.3$  Torr. Charge ex-

blved the stant electric sector voltage and constant magnetic field as described previously.<sup>30</sup> Kinetic energy release distributions (KERDs) were obtained from the metastable peak shapes, after correction for main beam width, by the method of Holmes and Osborne.<sup>31</sup> All metastable ion intensities (relative peak areas) and peak shapes were recorded at 7.5 kV accelerating voltage.

Unimolecular fragmentation reactions occurring in the second drift region (between magnetic sector and electric sector) of a ZAB-2F mass spectrometer (University of Ottawa) were recorded by mass-analysed ion kinetic energy spectral (MIKES) techniques. Similarly the CID mass spectra and charge stripping mass spectra were obtained by MIKES techniques with the ZAB-2F instrument using helium collision gas. Source temperatures for the ZAB experiments were ~150 °C and the ion accelerating potential was 8 keV.

change mass spectra were obtained using chemical

ionization techniques described previously27,28 using

the same instrument. The reactant ions (recombination

energies and reagent gas in brackets) were [COS]+

(11.2 eV, CO-10% COS) and Xe<sup>+-</sup> (12.5 eV, Xe). For

both the chemical ionization and charge exchange

experiments the source temperature was  $\sim 100$  °C and

samples were introduced from a heated inlet system at

The 70 eV mass spectra were obtained using an AEI

MS-902 mass spectrometer at a source temperature of  $\sim$ 150 °C. Fragmentation reactions (metastable ions)

occurring in the drift region between the ion source

and the electric sector of the MS-902 were examined

using the accelerating voltage scan technique<sup>29</sup> at con-

2-Pentanone-1,1,1- $d_3$  was prepared by the Grignard reaction of methyl- $d_3$ -magnesium iodide with butanal followed by oxidation of the resulting alcohol with CrO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> in acetone. 2-Pentanone-5,5,5- $d_3$  was prepared by the reaction of ethyl-2,2,2- $d_3$  bromide with ethyl acetoacetate in NaOEt/EtOH followed by hydrolysis and decarboxylation. 2-Pentanone-1,1,1,3,3- $d_5$  was prepared by base catalysed exchange of 2-pentanone with  $D_2O$ . 3-Ethyl-2-pentanone-1,1,1- $d_3$  was prepared by the Grignard reaction of methyl- $d_3$ -magnesium iodide with 2-ethylbutyraldehyde, with oxidation of the resulting alcohol with  $CrO_3/H_2SO_4$  in acetone. 3-(Ethyl-2,2,2- $d_3$ )-2-pentanone-5,5,5- $d_3$  was prepared by the reaction of two equivalents of ethyl-2,2,2- $d_3$  bromide with ethyl acetoacetate in NaOEt/EtOH followed by hydrolysis and decarboxylation. Final purification in all cases was by gas chromatography. The remaining samples used were commercial samples of high purity.

#### **RESULTS AND DISCUSSION**

# Characterization of [C<sub>4</sub>H<sub>7</sub>O]<sup>+</sup> ion structures

The isomeric  $[C_4H_7O]^+$  ions 1-3 were prepared by protonation of the corresponding carbonyl compounds, methyl vinyl ketone, crotonaldehyde and methacrolein; evidence favouring oxygen protonation rather than carbon protonation has been presented earlier.<sup>22</sup> Table 1 records the  $H_2$  and  $D_2$  CI mass spectra of these three carbonyl compounds while Table 2 records the metastable ion intensities observed (ZAB second drift region) for fragmentation of the protonated molecular ions and compares these intensities with those observed<sup>23</sup> for the same ions produced by electron impact methods. The three compounds are clearly distinguishable by their CI mass spectra particularly methyl vinyl ketone which is the only one to show a significant  $[C_3H_3O]^+$  (m/z 55) ion signal. The fragmentation reactions observed in the CI mass spectra are shown in Eqns (1)-(5). Reactions (1)and (2) may occur by direct hydride/methide ion abstraction rather than by protonation followed by decomposition. Of particular interest is the observation that, in the D<sub>2</sub> CI mass spectra, the m/z 43 observed for crotonaldehyde and methacrolein moves largely to m/z 44 indicating incorporation of the added proton in the fragment ion, while for methyl vinyl ketone the ion signal remains largely at m/z 43 indicating that the

#### Table 1. $H_2$ and $D_2$ CI mass spectra of $C_4H_6O$ isomers (intensities as a percentage of base peak)

	$\searrow$			0	//	
m/z	H₂ CI	D <sub>2</sub> Cl	H₂ CI	D <sub>2</sub> Cl	H₂ CI	D <sub>2</sub> Cl
72		31	_	45	_	25
71	47	15	58	19	63	16
70	4	3	7	7	8	5
69		_	15	13	19	9
55	20	14	1	0.5	1	0.5
54	_	1	_	13	—	2
53	5	10	52	60	7	11
44	_	26	_	100	—	100
43	100	100	100	4	100	30
42	1	19	2	64	3	47
41	14	4	72	22	72	25

Table 2. Metastab ions	de f	ragmen	tation o	of [C₄]	<b>H</b> <sub>7</sub> O]⁺
		m*	*(CI)	m*	(EI) <sup>a</sup>
lon		~~ H <sub>2</sub> O	m/z 43	-H <sub>2</sub> O	m/z 43
<sup>+</sup> OH    CH₂—CHC—CH₃	(1)	16	84	15	85
⁺ОН    СН₃—СН—СН—СН	(2)	8	92	9	91
<sup>+</sup> OH    CH₂ <del></del> C(CH₃)CH	(3)	3	97	4	96
<sup>a</sup> Ref. 23.					

$$[C_4H_7O]^+ \xrightarrow{-H_2} [C_4H_5O]^+(m/z \ 69)$$
 (1)

CHC

$$\xrightarrow{-CH_4} [C_3H_3O]^+(m/z 55)$$
(2)

$$\xrightarrow{-\mathrm{H}_{2}\mathrm{O}} [\mathrm{C}_{4}\mathrm{H}_{5}]^{+}(m/z\ 53) \tag{3}$$

$$\xrightarrow{-\text{CO/C}_2\text{H}_4} [\text{C}_3\text{H}_7]^+ / [\text{C}_2\text{H}_3\text{O}]^+ (m/z \ 43) \quad (4)$$

$$\xrightarrow{\operatorname{CH}_2 O} [\operatorname{C}_3 \operatorname{H}_5]^+(m/z \ 41) \tag{5}$$

added proton is lost in the neutral fragment. This is in agreement with earlier conclusions<sup>23,24</sup> that ions 2 and 3 fragment largely by elimination of CO while 1 fragments largely by elimination of the vinyl group and the hydrogen bonded to oxygen. The formation of  $[C_3H_5]^+$  appears to occur with essentially complete hydrogen scrambling. In contrast to the higher energy fragmentation reactions observed in the CI mass spectra, metastable 1-3 ions were observed (Table 2) to fragment only by loss of H<sub>2</sub>O and CO/C<sub>2</sub>H<sub>4</sub>, again in agreement with earlier observations.<sup>23</sup> The acyl ions 4, prepared by dissociative electron impact ionization of methyl butyrate, 3-hexanone and butyryl chloride, and 5, prepared by dissociative electron impact ionization of 2,4-dimethyl-3-pentanone, 2-methyl-3pentanone, methyl isobutyrate and isobutyryl chloride, showed metastable peaks only for loss of 28 u (CO), in agreement with earlier studies.<sup>25,32</sup>

Table 3 records the CID mass spectra obtained for ions of nominal structures 1-3 prepared by proton transfer chemical ionization; in addition ion 1 was prepared by dissociative ionization of 2-methyl-3-buten-2-ol.<sup>24</sup> Table 4 records the CID mass spectra obtained for ions 4 and 5 prepared by dissociative ionization of the precursors indicated in the preceding paragraph. In all cases the CID spectra of the same nominal ion structure prepared from different sources are in excellent agreement. The CID spectra of the protonated carbonyl ions 1-3 are distinct from the spectra observed for the acyl ions 4 and 5 particularly in showing significant intensities at m/z 31, 40, 44 and 45 which are absent for the acyl ions; thus there is no significant interconversion of the protonated carbonyl and acyl structures. Within the protonated carbonyl series 1 gives a CID spectrum distinctly different from

Table 3. CID mass spectra of ions 1-3						
	~	⁺OH ↓↓	⁺OH	→OH		
m/z	CH₄ CI	Elª	CH₄CI	CH₄CI		
12	0.1	0.1	0.1	0.1		
13	0.3	0.3	0.2	0.1		
14	1.1	1.0	0.6	0.4		
15	4.2	4.0	1.7	1.7		
25	1.1	1.0	0.7	0.6		
26	5.6	5.3	3.4	2.8		
27	17.8	17.6	13.0	11.5		
28	1.4	1.4	1.3	1.3		
29	4.4	4.6	8.3	9.0		
30	0.2	0.3	0.8	0.9		
31	3.1	3.1	5.8	4.0		
37	1.8	1.9	2.8	3.2		
38	2.7	2.9	4.7	5.4		
39	8.4	8.7	19.7	20.5		
40	1.2	1.3	1.8	2.3		
41	6.7	8.3	15.0	13.7		
42	6.6	6. <del>9</del>	4.4	4.0		
43	<b>m</b> *	<b>m</b> *	m*	<b>m</b> *		
44	2.2	2.1	0.6	0. <del>9</del>		
45	1.3	1.2	0.2	1.2		
49	1.5	1.4	1.1	0.9		
50	5.4	5.1	3.6	3.1		
51	4.8	4.9	3.9	3.0		
52	1.5	1.4	0.8	0.8		
5 <b>3</b>	m*	m*	m*	m*		
54	1.1	1.0	0.5	0.6		
55	14.3	13.1	4.6	6.6		
56	1.3	1.0	0.5	1.0		
<sup>a</sup> Produced by dissociative ionization of $CH_2$ =CHC(OH)(CH <sub>3</sub> ) <sub>2</sub> .						

2 and 3, particularly in the intensities of the m/z 15, 29, 39, 41 and 55 ions. By contrast, 2 and 3 give very similar CID spectra and cannot be distinguished from each other on this basis. The two acyl ions 4 and 5 give similar CID mass spectra, but there are notable differences in the intensities of m/z 29, 42, 55 and 56; thus for 4 the  $[56]^+/[55]^+$  ratio is in the range 0.1–0.2 and the  $[56]^+/[28]^+$  ratio is in the range 0.3–0.4 while for 5 the same ratios are 3–4 and 3–5, respectively. These differences appear to be sufficient to distinguish between the two structures.

It has been demonstrated in a variety of cases<sup>33-39</sup> that charge stripping mass spectra can be used to characterize the structures of gaseous ions even in those cases where CID spectra fail. Accordingly, we have determined the charge stripping mass spectra of the  $[C_4H_7O]^+$  ions of interest with the results shown in Table 5. Ions of nominal structures 1, 4 and 5 were prepared from several precursors and the results thus give an indication of the reproducibility of the measurements. As for the CID studies the charge stripping mass spectra clearly distinguish the acyl ions, 4 and 5, from the protonated carbonyl ions 1-3, in that only the latter form stable  $[C_4H_7O]^{2+}$  ions. The two acyl ions, 4 and 5, are clearly distinguished from each other by their charge stripping mass spectra, while 1 is clearly distinguished from 2 and 3. The distinction between 2 and 3 is more problematical, but given the reproducibility of the other measurements we are inclined to believe that the differences observed are significant and reflect differences in structure.

### Fragmentation of the 2-pentanone molecular ion

The 70 eV mass spectrum of 2-pentanone shows three major fragment ions, m/z 71 [M-CH<sub>3</sub>]<sup>+</sup>, m/z 58 [M-C<sub>2</sub>H<sub>4</sub>]<sup>+</sup> and m/z 43, which labelling studies in the present investigation show to be ~20% [C<sub>3</sub>H<sub>7</sub>]<sup>+</sup> and ~80% [C<sub>2</sub>H<sub>3</sub>O]<sup>+</sup>. Fragmentation of the molecular ion in the first drift region of the MS-902 formed only [M-CH<sub>3</sub>]<sup>+</sup> (63%) and [M-C<sub>2</sub>H<sub>4</sub>]<sup>+</sup> (37%). The present work concentrates on the mechanism of methyl loss and the structure(s) of the fragment ions so formed since this is the fragmentation reaction of relevance to the potential energy diagram of Fig. 1.

Table 6 records the relative intensities observed for  $C(H, D)_3$  loss from the molecular ions of 2-pentanone-1,1,1,3,3- $d_5$ , 2-pentanone-1,1,1- $d_3$  and 2-pentanone-5,5,5- $d_3$  for various internal energy windows listed in order of increasing mean internal energy of the fragmenting ions. Also included are the results obtained from the 70 eV mass spectra which sum over an unknown internal energy distribution. The observation windows were (i) metastable fragmentation reactions observed in the second field free region of the ZAB-2F mass spectrometer (m\*2FFR), (ii) metastable fragmentation reactions observed in the first field free region of the MS-902 (m\*1FFR), (iii) fragmentation reactions observed following charge exchange ionization with [COS]<sup>+</sup> (COS<sup>+</sup>CE) and (iv) fragmentation reactions observed following charge exchange ionization with  $Xe^{+}$ . Taking the ionization energy of 2-pentanone as  $9.4 eV^{40}$  the charge exchange experiments correspond to internal energies of the fragmenting ions of 1.8 and 3.1 eV, respectively. As indicated in Fig. 1 the critical energy for loss of CH<sub>3</sub> from ionized 2-pentanone is  $\sim 0.7 \text{ eV}$ ; the metastable fragmentation reactions correspond to internal energies slightly higher than this critical energy.

Clearly, under all conditions loss of the C(1) methyl and the C(5) methyl are the most important fragmentation processes occurring, although there is some loss of isotopically mixed methyls, the extent of isotopic mixing increasing with increasing lifetime (decreasing internal energy) of the fragmenting ions. The present results are in poor agreement with the earlier results of Beynon et al.41 who reported for the molecular of 2-pentanone-5,5,5- $d_3$  the loss ion ratio  $CD_3:CD_2H:CDH_2:CH_3 = 8:9:25:58$ ; in effect they observe much more isotopic scrambling, possibly because they examined ions of longer lifetimes. The good agreement of the results for 2-pentanone- $1,1,1,3,3-d_5$  and 2-pentanone- $1,1,1-d_3$  indicates that the C(3) hydrogens are not participating in the methyl loss process to a significant extent, and it is unlikely that the C(4) hydrogens are lost to any significant extent. The direct observation of the loss of the C(5)methyl provides confirmation of the assumption made by Krenmayr<sup>25</sup> that this methyl was lost in addition to C(1).

In the absence of isotope effects, and neglecting isotopic mixing processes, the fractional loss of  $CD_3$ 

			∕∕∕≡0⁺ (4	)		$\succ$	- <b>≡</b> O⁺ (5)	
m/z	Precursor			~, CI	$\succ \stackrel{\rm o}{\rightarrowtail} \prec$	≻ <sup>°</sup>	O ││ ──OMe	≻_cc
12		0.2	0.1	0.2	0.1	0.1	0.1	0.1
13		0.4	0.3	0.4	0.3	0.3	0.3	0.3
14		1.2	1.1	1.2	0.7	0.8	0.7	0.8
15		2.1	2.0	2.0	2.8	2.7	2.7	2.8
25		0.9	0.9	1.0	1.3	1.3	1.4	1.4
26		4.8	5.1	5.3	6.4	6.1	6.4	6.4
27		17.6	17.6	17.8	16.8	16.2	16.6	16.4
28		4.1	3.7	4.0	5.4	5.1	5.4	5.2
29		3.8	3.6	3.5	1.2	1.4	1.1	1.0
30		—				—		—
31		0.2	0.3	—	_	_	_	—
37		2.2	2.6	2.6	3.2	3.2	3.2	3.3
38		4.0	4.4	4.8	5.4	6.0	5.7	6.1
39		15.0	15.6	16.0	21.1	20.7	21.2	21.0
40				—	—	_	—	
41		14.0	14.8	13.6	13.8	13.7	13.1	12.6
42		18.8	16.5	17.4	11.1	11.0	11.6	11.5
43		<i>m</i> *	<i>m*</i>	m*	m*	m*	m*	m*
44			—	—		_	—	
45		—					_	_
49			0.3	0.2	0.3	0.3	0.1	0.2
50		0.7	0.8	0.7	0.7	0.8	0.7	0.7
51		0.5	0.6	0.5	0.5	0.6	0.5	0.5
52		0.3	0.2	0.2	0.3	0.4	0.3	0.3
53		0.9	2.3	0.9	1./	2.0	1.4	1.4
54		0.2	0.1	0.2	0.4	0.4	0.4	0.5
55 56		6.4 1.4	6.3 0.9	6.2 1.3	1.9 4.5	2.2 4.6	1.4 5.5	1.4 5.5

Table	4.	CID	mass	spectra	of	4	and	5	prepared	from	various	precursors
Tanc	<b></b> .	<b>UID</b>	1110.00	specua	UL	-	anu	~	proparou	nom		procensors

from  $[CD_3COCH_2CH_2CH_3]^{+\cdot}$  should equal the fractional loss of the CH<sub>3</sub> from the complementarily labelled ion  $[CH_3COCH_2CH_2CD_3]^{+\cdot}$ . That they are not equal, at least for ions of low internal energy, must be attributable to the operation of significant secondary H/D isotope effects on the methyl loss process. Neglecting the minor isotopic mixing reactions, the relative losses of CH<sub>3</sub> and CD<sub>3</sub> from the molecular ions  $[CD_3COCH_2CH_2CH_3]^{+\cdot}$  and  $[CH_3COCH_2CH_2CD_3]^{+\cdot}$  can be expressed as follows:<sup>42</sup>

$[CD_3COCH_2CH_2CH_3]^+$	$\frac{-\mathrm{CH}_3}{-\mathrm{CD}_3} = \frac{(1-\alpha)i}{\alpha}$
[CH <sub>3</sub> COCH <sub>2</sub> CH <sub>2</sub> CD <sub>3</sub> ] <sup>+-</sup>	$\frac{-CH_3}{-CD_3} = \frac{\alpha i}{1-\alpha}$

Table 5. Charge stripping mass spectra of [C4	H <sub>7</sub> O] <sup>+</sup> ions
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			)H (1)	→OH (2)	<sup>+</sup> OH ↓↓ (3)		∕∕∍0⁺	(4)		)—=(	) <sup>+</sup> (5)	
lon	m/z	CI	Elª	СІ	СІ	Elp	El°	Ela	El®	Elf	El°	EI <sup>h</sup>
[C,HO] <sup>2+</sup>	32.5	_	_	_	_	_	_	_	1.9	1.4	1.3	1.4
[C.H.O]2+	33.0	_	_	0.4	0.9	6.2	6.8	5,8	20.7	18.5	20.8	20.3
IC.H.O12+	33.5	0.4		0.9	0.9	3.5	3.5	3.0	24.7	20.6	24.8	25.2
[C_H_O] <sup>2+</sup>	34.0	25.1	27.3	22.7	23.8	64.5	70.3	61.7	47.6	53.0	49.8	49.3
[C.H.O]2+	34.5	1.8	4.7	16.8	14.8	12.0	10.7	12.0	5.2	6.5	3.3	3.8
[C,H_O] <sup>2+</sup>	35.0	_	2.5	16.6	29.6	13.9	8.7	17.5			—	
[C_H_O] <sup>2+</sup>	35.5	72.7	65.5	42.5	30.0	_	—	—	_	—		

<sup>a</sup> From 2-methyl-3-buten-2-ol.

<sup>b</sup> From methylbutyrate.

° From 3-hexanone.

<sup>d</sup> From butyryl chloride.

\* From 2,4-dimethyl-3-pentanone.

<sup>f</sup> From 2-methyl-3-pentanone.

<sup>a</sup> From methyl isobutyrate.

<sup>h</sup> From isobutyryl chloride.

	-		-	-		-
Table	6.	Methyl	loss	from	labelled	2-pentanones

_		% of total met	thyl loss		
Observation mode	$CD_3$	CD₂H	CDH <sub>2</sub>	CH3	
$CD_3 - C (= 0) CD_2 CH_2 CH_3$					
m*(1FFR)	40.9	11.5	4.8	42.9	
[COS] <sup>+-</sup> CE	67.8	5.9	2.6	23.7	
Xe <sup>+.</sup> CE	69.2	3.1	2.3	25.4	
70 eV MS	61.4	3.4	1.8	33.4	
$CD_3C(=0)CH_2CH_2CH_3$					
m*(2FFR)	41.3	10.4	6.4	41.9	
m*(1FFR)	36.4	4.7	3.3	55.6	
[COS] <sup>+-</sup> CE	73.1	6.3	3.1	17.5	
Xe <sup>+•</sup> CE	67.3	1.0	1.9	29.8	
70 eV MS	62.3	1.2	4.0	32.4	
$CH_3C (= 0) CH_2 CH_2 CD_3$					
m*(2FFR)	18.4	7.5	21.4	52.6	
m*(1FFR)	28.2	2.6	6.1	63.0	
[COS] <sup>+-</sup> CE	11.4	8.4	11.4	68.7	
Xe <sup>+-</sup> CE	28.3	1.8	3.5	66.4	
70 eV MS	28.8	1.5	4.5	65.1	

where  $\alpha$  is the fractional loss of the C(1) methyl, 1- $\alpha$ is the fractional loss of the C(5) methyl and *i* is the apparent isotope effect  $k_{CH_3}/k_{CD_3}$ .<sup>43</sup> The results of the analysis made on this basis are presented in Table 7. Although the results show some scatter, metastable 2-pentanone molecular ions lose C(1) and C(5) in the approximate ratio 60:40 with an apparent isotope effect  $k_{CH_3}/k_{CD_3} \approx 1.8$ . With increasing internal energy of the fragmenting ions the isotope effect decreases significantly as expected.<sup>43</sup> In addition, in the higher energy charge exchange experiments loss of C(1) is increased in importance relative to the metastable ion fragmentation reactions. This also is expected since loss of C(1) is a direct cleavage reaction and should have a more favourable frequency factor than the rearrangement reaction leading to loss of C(5).

The structures of the fragment ions formed by loss of the C(2) and C(5) methyl groups from the 2pentanone molecular ions were investigated by unimolecular ion characteristics and collision-induced dissociation studies, including charge stripping mass spectra. The differing structures of the  $[C_4(H, D)_7O]^{\dagger}$ ions formed by loss of the C(1) methyl and the C(5)methyl were clearly demonstrated by the metastable ion abundances for fragmentation of the  $[M-CH_3]^+$ and  $[M-CD_3]^+$  ions observed in the mass spectrum of  $CD_3COCD_2CH_2CH_3$ . Thus, the  $[M-CH_3]^+$  fragment showed metastable peaks (MS-902 first drift region) for loss of  $C_2H_2D_2$ , CO and  $H_2O$  in the ratio 80:15:6, while the  $[M-CD_3]^+$  fragment ion showed metastable peaks for loss of 28 u and H<sub>2</sub>O in the ratio 98.5:1.5 (no metastable loss of  $C_2H_3D$  or  $C_2H_2D_2$ 

Table 7.	Fractional	losses	of	CH <sub>3</sub>	groups
	from 2-per	itanone			

	Loss of C <sub>1</sub>	Loss of C <sub>5</sub>	
Observation mode	α	1-α	$i = k_{CH_3}/k_{CD_3}$
m* (2FFR)	0.63	0.37	1.7
m* (1FFR)	0.55	0.45	1.9
[COS]+·CE	0.83	0.17	1.2
Xe⁺⁺CE	0.70	0.30	1.0 <sub>2</sub>
70 eV MS	0.68	0.32	1.0 <sub>8</sub>

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was observed). The first ratio is close to that observed<sup>23</sup> for metastable fragmentation of  $[CH_2=:CH-C(OD)CH_3]^+$  prepared by EI  $(C_2H_3D:CO:H_2O=72:14:13)$ , while the latter results are similar to the results observed<sup>23,25,32</sup> for fragmentation of  $[CH_3CH_2CH_2C=O]^+$  (CO = 100%).

The fragment ion structures are more clearly established from comparison with model compounds of the kinetic energy release distributions (KERDs) accompanying the metastable ion fragmentation reactions. Figure 2 shows the KERDs obtained for metastable loss of CO from the  $[M-CD_3]^+$  ion and metastable loss of  $C_2H_2D_2$  from the  $[M-CH_3]^+$ ion of CD<sub>3</sub>COCD<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>. The former metastable shows a KERD essentially identical to that observed (Fig. 3) for metastable fragmentation of the acyl ion 4 derived by dissociative ionization of ethyl butyrate. On the other hand metastable loss of C<sub>2</sub>H<sub>2</sub>D<sub>2</sub> from the [M- $CH_3$ <sup>+</sup> ion yields a flat-top metastable peak with a KERD essentially identical to that observed (Fig. 3) for metastable loss of  $C_2H_3D$  from 1-O-d prepared by dissociative ionization of  $CH_2 = CH - C(OD)(CH_3)_2$ . Similar results were obtained (Figs 4 and 5) for metastable fragmentation of the  $[M-CH_3]^+$  and  $[M-CH_3]^+$  $CD_3$ ]<sup>+</sup> ions derived from  $CD_3COCH_2CH_2CH_3$  and CH<sub>3</sub>COCH<sub>2</sub>CH<sub>2</sub>CD<sub>3</sub>. The ions derived by loss of the C(1) methyl show narrow Gaussian-type peaks for metastable loss of 28 u with KERDs essentially identical to that observed for metastable fragmentation of 4 (Fig. 3). On the other hand the ions derived by loss of the C(5) methyl group show flat-top metastables for loss of 28 u with KERDs essentially identical to that obtained for fragmentation of 1-O-d (Fig. 3). These results lead to the conclusion that loss of the C(1)methyl from the 2-pentanone molecular ion leads to the acyl ion 4 while loss of the C(5) methyl leads to



**Figure 2.** KERDs for fragmentation of  $[C_4H_5D_2O]^+$  and  $[C_4D_5H_2O]^+$  from 2-pentanone-1,1,1,3,3-d<sub>5</sub>.



Figure 3. KERDs for fragmentation of 1-O-d and 4, 1-O-d produced from  $CH_2$ =CHC(OD)(CH<sub>3</sub>)<sub>2</sub> and 4 produced from ethyl butyrate.

protonated vinyl methyl ketone, **1**. Further confirmation was obtained from CID mass spectra of the relevant fragment ions as well as from charge stripping mass spectra.

Table 8 compares the CID mass spectrum of the  $[C_4H_7O]^+$  ( $[M-C(5)]^+$ ) ion derived from 2-pentanone-5,5,5-d<sub>3</sub> with the CID mass spectrum of **1** as well as the CID spectrum of the  $[C_4H_7O]^+$  ([M-



Figure 5. KERDs for fragmentation of  $[C_4H_4D_3O]^+$  and  $[C_4H_7O]^+$  from 2-pentanone-5,5,5- $d_3$ .



**Figure 4.** KERDs for fragmentation of  $[C_4H_7O]^+$  and  $[C_4H_4D_3O]^+$  from 2-pentanone-1,1,1- $d_3$ .

C(1)<sup>+</sup>) ion derived from 2-pentanone-1,1,1- $d_3$  with the CID spectrum of 4. The spectra reported for 1 and 4 are the average of those reported in Tables 3 and 4.

Table 8. CID spectra of [C <sub>4</sub> H <sub>7</sub> O] <sup>+</sup> ions							
Ĵ_/	CD₃	+OH	$\sim$	0 <sup>+</sup> 0 D <sub>3</sub> C			
m/z	m/z 71	1	4	m/z 71			
12	0.1	0.1	0.2	0.1			
13	0.3	0.3	0.4	0.3			
14	1.0	1.0	1.2	1.1			
15	4.0	4.1	2.0	1.9			
25	1.9	1.0	0.9	0.9			
26	5.2	5.5	5.1	4.8			
27	16.8	17.7	17.6	17.0			
28	1.6	1.4	3.9	3.5			
29	4.4	4.5	3.6	3.8			
30	0.3	0.2		0.1			
31	3.0	3.1	0.2	0.6			
37	1.9	1.9	2.5	2.5			
38	2.8	2.8	4.4	4.4			
39	8.5	8.6	15.5	15.6			
40	1.5	1.3					
41	7.6	7.5	14.1	14.8			
42	6.7	6.8	17.6	15.2			
43	m*	<i>m</i> *	<b>m</b> *	<b>m</b> *			
44	2.2	2.2	—	—			
45	1.2	1.3					
49	1.6	1.5	0.2	0.3			
50	5.1	5.3	0.7	1.0			
51	4.7	4.9	0.5	0.8			
52	1.5	1.5	0.2	0.3			
53	<b>m</b> *	<i>m</i> *	1.4	2.5			
54	0.9	1.1	0.2	0.2			
55	12.8	13.7	6.3	6.1			
56	1.5	1.1	1.2	0.8			

Table 9	). Charge [C <sub>4</sub> H <sub>7</sub> O]	stripping ] <sup>+</sup> ions	mass	spectra of
Å	D <sub>3</sub>	⁺он Щ	∕∕=0	+ 0 D <sub>3</sub> C
m/z	m/z 71	1	4	m/z 71
32.5				_
33.0	<del></del>		6.3	6.7
33.5	1.6	0.2	3.3	3.9
34.0	40.1	26.2	65.5	69.7
34.5	4.4	3.3	11.6	11.2
35.0		1.3	13.4	8.5
35.5	53.9	69.1		

The agreement of the spectrum of the  $[C_4H_7O]^+$  ion derived by loss of C(5) with that of 1 and the agreement of the spectrum of the  $[C_4H_7O]^+$  ion derived by loss of C(1) with that of 4 leaves little doubt as to the structures of the fragment ions. Further confirmation comes from the charge stripping mass spectra reported in Table 9. Here the spectra reported for 1 and 4 are the averages of the spectra reported in Table 5. The charge stripping spectrum of the  $[C_4H_7O]^+$  ion derived from  $CD_3COCH_2CH_2CH_3$  (loss of C(1)) is in excellent agreement with that obtained for the acyl ion 4. The spectrum observed for the  $[C_4H_7O]^+$  ion derived from  $CH_3COCH_2CH_2CD_3$  (loss of C(5)) is in reasonable agreement with that obtained for 1 although the m/z 35.5 intensity is decreased and the m/z 34.0 intensity is increased for the ion derived from 2pentanone relative to the reference ion 1. This may indicate that fragmentation of the 2-pentanone molecular ion by loss of the C(5) methyl involves to a minor extent formation of the acyl ion 4 through the sequence of Scheme 1. Some support that this may happen on the  $[C_5H_{10}]^+$  potential energy surface comes from the observation<sup>26</sup> that the molecular ion of 3-penten-2-ol-1-<sup>13</sup>C (**6**-<sup>13</sup>C) shows metastable loss of <sup>13</sup>CCH<sub>4</sub> as well as C<sub>2</sub>H<sub>4</sub> (~7% loss of <sup>13</sup>CCH<sub>4</sub>), indicative of a 1,3-hydroxyl shift prior to fragmentation. Hoppilliard and Bouchoux<sup>44</sup> have concluded from MINDO/3 studies that such an hydroxyl migra-



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tion in the 3-penten-2-ol molecular ion is a relatively facile process. Thus it is possible that in the rearranged 2-pentanone molecular ion such a migration may occur to a minor extent leading to minor formation of **4** by loss of C(5) and to minor formation of **1** by loss of C(1). The effect that this will have on the charge stripping mass spectra will depend in part on the relative cross-sections for charge stripping of the two isomeric ions. In any event the mass of data supports the conclusion that loss of C(1) forms primarily the acyl ion **4** while loss of C(5) proceeds by formation of protonated vinyl methyl ketone 1 in agreement with the reaction scheme outlined in Fig. 1.

## Fragmentation of the enol ion of 2-pentanone

The potential energy diagram of Fig. 1 implies that the enol ion 8 should fragment by loss of both the C(1)and C(5) methyl groups. A limited study of the fragmentation of the labelled enol ions [CD3- $C(OH)H=CHCH_2CH_3]^{+-}$  (derived from  $CD_3COCH-(CH_2CH_3)_2$ ) and  $[CH_3-C(OD)=CHCH_2CD_3]^{+-}$  (derived from CH<sub>3</sub>COCH(CH<sub>2</sub>CD<sub>3</sub>)<sub>2</sub> was carried out. Because of overlap of the  $[C_4(H, D)_7O]^+$  ions with C<sub>5</sub> hydrocarbon ions only metastable fragmentation of the enol ions was examined. The results obtained are summarized in Table 10. Clearly, loss of both C(1) and C(5) is occurring in the metastable time-frame. Analysis of the results in the same manner as the 2-pentanone data leads to  $k_{CH_3}/k_{CD_3} = 1.2$  and to 31% loss of C(1) and 69% loss of C(5). Compared to the 2-pentanone molecular ion loss of C(5) is favoured. This is not surprising since for the enol loss of C(5) is a simple bond cleavage while loss of C(1) involves a rearrangement. For the 2-pentanone molecular ion the reverse is true.

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#### REFERENCES

- 1. D. Van Raalte and A. G. Harrison, Can. J. Chem. 41, 3118 (1963).
- 2. A. G. Harrison, A. Ivko and D. Van Raalte, Can. J. Chem. 44, 1625 (1966).
- 3. T. W. Shannon and F. W. McLafferty, J. Am. Chem. Soc. 88, 5021 (1966). K. M. A. Refaey and W. A. Chupka, J. Chem. Phys. 48, 5205
- (1968). 5. M. A. Haney and J. L. Franklin, Trans. Faraday Soc. 65,
- 1794 (1969). 6. C. W. Tsang and A. G. Harrison, Org. Mass Spectrom. 3,
- 647 (1970). 7. J. L. Beauchamp and R. C. Dunbar, J. Am. Chem. Soc. 92, 1477 (1970).
- 8. F. W. McLafferty and I. Sakai, Org. Mass Spectrom. 7, 971 (1973).
- 9. C. W. Tsang and A. G. Harrison, Org. Mass Spectrom. 7, 1377 (1973).
- 10. F. W. McLafferty, R. Kornfeld, W. F. Haddon, K. Levsen, I. Sakai, P. F. Bente, S.-C. Tsai and H. D. R. Shuddemage, J. Am. Chem. Soc. 95, 3886 (1973).
- 11. B. G. Keyes and A. G. Harrison, Org. Mass Spectrom. 9, 221 (1974).
- 12. G. Hvistendahl and D. H. Williams, J. Am. Chem. Soc. 97, 3097 (1975).
- 13. R. D. Bowen, J. R. Kalman and D. H. Williams, J. Am. Chem. Soc. 99, 5481 (1977).
- 14. R. Botter, J. Pechine and H. M. Rosenstock, Int. J. Mass Spectrom. Ion Phys. 25, 7 (1977).
- 15. F. P. Lossing, J. Am. Chem. Soc. 99, 7526 (1977).
- 16. R. D. Bowen, D. H. Williams, G. Hvistendahl and J. R. Kalman, Org. Mass Spectrom. 13, 721 (1978).
- 17. F. W. McLafferty, T. Wachs, C. Koppel, P. Dymerski and F. M. Bockhoff, Adv. Mass Spectrom. 7, 1231 (1978). 18. J. Mead and D. H. Williams, J. Chem. Soc. (B) 1654 (1971).
- 19. C. E. Hudson and D. J. McAdoo, Org. Mass Spectrom. 17, 366 (1982).
- 20. G. Bouchoux, Y. Hoppilliard, R. Flamang, A. Maquestiau and P. Meyrant, Org. Mass Spectrom. 18, 340 (1983).
- 21. J. J. Zwinselman and A. G. Harrison, Org. Mass Spectrom. 19, 573 (1984).
- 22. J. Hegedus Vajda and A. G. Harrison, Int. J. Mass Spectrom. Ion Phys. 30, 293 (1979).
- 23. A. G. Harrison, N. E. Middlemiss and J. Hegedus Vajda, Adv. Mass Spectrom. 8, 853 (1980).

- 24. J. J. Zwinselman, N. M. M. Nibbering, N. E. Middlemiss, J. Hegedus Vajda and A. G. Harrison, Int. J. Mass Spectrom. Ion Phys. 38, 163 (1981).
- 25. P. Krenmayr, Monatsh. Chem. 106, 925 (1975).
- 26. J. J. Zwinselman and A. G. Harrison, Int. J. Mass Spectrom. Ion Phys. in press.
- Y.-H. Li, J. A. Herman and A. G. Harrison, Can. J. Chem. 59, 1753 (1981).
- J. A. Herman, Y. H. Li and A. G. Harrison, Org. Mass 28. Spectrom. 17, 143 (1982).
- 29. M. Barber and R. M. Elliott, paper presented at the 12th Annual Conference on Mass Spectrometry and Allied Topics, Montreal, Canada (1964).
- 30. N. E. Middlemiss and A. G. Harrison, Can. J. Chem. 57, 2827 (1979).
- 31. J. L. Holmes and A. D. Osborne, Int. J. Mass Spectrom. Ion Phys. 28, 189 (1977).
- 32. D. H. Williams, Philos. Trans. Roy. Soc. London (A) 293, 117 (1979).
- 33. R. G. Cooks, J. H. Beynon and J. F. Litton, Org. Mass Spectrom. 10, 503 (1975).
- 34. A. Maguestiau, Y. V. Haverbeke, R. Flammang, C. D. Meyer and A. Mino, Org. Mass Spectrom. 12, 706 (1977)
- 35. G. L. Glish and R. G. Cooks, J. Am. Chem. Soc. 100, 6720 (1978).
- 36. R. D. Bowen, M. P. Barbalas, F. P. Pagano, P. J. Todd and F. W. McLafferty, Org. Mass Spectrom. 15, 51 (1980).
- 37. J. L. Holmes, J. K. Terlouw, P. C. Burgers and R. T. B. Rye, Org. Mass Spectrom. 15, 149 (1980).
- W. Wagner, K. Levsen and C. Lifschitz, Org. Mass Spec-38. trom. 15, 271 (1980).
- 39. W. Wagner-Redeker, K. Levsen, H. Schwarz and W. Zummack, Org. Mass Spectrom. 16, 361 (1981).
- 40. H. M. Rosenstock, K. Draxl, B. W. Steiner and J. T. Herron, J. Phys. Chem. Ref. Data 6, Suppl. 1 (1977).
- 41. J. H. Beynon, R. M. Caprioli and R. G. Cooks, Org. Mass Spectrom. 9, 1 (1974).
- 42. F. Meyer and A. G. Harrison, J. Am. Chem. Soc. 86, 4757 (1964).
- 43. P. J. Derrick, Mass Spectrom. Rev. 2, 285 (1983).
- 44. Y. Hoppilliard and G. Bouchoux, Org. Mass Spectrom. 17, 534 (1982).

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