The Formation of $[CH_3CH_2C(=OH)CH_2]^+$ from 1-Hepten-3-ol

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The $[C_4H_8O]^+$ ion in the mass spectrum of 1-hepten-3-ol is shown to be $CH_3CH_2C(=OH)\dot{C}H_2$ by collisional activation spectra, appearance energies and comparison of the ratios of the intensities of metastable decompositions. $[C_4H_8O]^+$ appears to be formed by rearrangement of ionized 1-hepten-3-ol to $CH_3\dot{C}HC(=OH)CH_2CH_2CH_2CH_3$ followed by γ -hydrogen rearrangement- β -cleavage.

INTRODUCTION

A wide variety of metastable $[C_4H_8O]^{+\cdot}$ ions rearrange predominantly to the 2-butanone ion prior to decomposing,^{1,2} including $[C_4H_8O]^{+\cdot}$ in the mass spectrum of 1-hepten-3-ol.³ Grant and Djerassi³ proposed that $[C_4H_8O]^{+\cdot}$ ions arise from ionized 1-hepten-3-ol by one of the mechanisms of Scheme 1, but their data did



not indicate which. We have suggested² that c is the dominant product, and that it rearranges to the 2-⁺OH

butanone ion via CH₃CH₂CCH₂ d. [C₄H₇DO]⁺⁻ generated from 1-hepten-3-ol-O- d_1 specifically transfers D to neutral molecules in proton transfer reactions in an ion cyclotron resonance spectrometer.³ Therefore, ionized 1-hepten-3-ol does not isomerize to the 3heptanone ion and then form the $[C_4H_8O]^+$ ion by a McLafferty rearrangement. This contrasts with the demonstration by Willhalm and Thomas⁴ that ionized 3-penten-2-ol rearranges to the 2-pentanone ion and then forms $[C_3H_6O]^+$ by a McLafferty rearrangement. Metastable 3-buten-2-ol² and 1-penten-3-ol⁵ ions also rearrange to their keto isomers prior to decomposing. Ions b and c are probably much higher in energy than other $[C_4H_8O]^+$ ions, since neither the charge nor the radical sites are resonance stabilized. This suggested to us that $[C_4H_8O]^{+}$ formed from 1-hepten-3-ol might have a structure other than b or c, possibly $CH_3CH_2C(=OH)\dot{C}H_2^+$ (d). We demonstrate here

that *d* is formed from ionized 1-hepten-3-ol by examining dissociations induced by collision activation (CA), relative unimolecular metastable peak intensities, appearance energies and the decompositions of a possible intermediate in the formation of $[C_4H_8O]^+$ from ionized 1-hepten-3-ol.

RESULTS AND DISCUSSION

The CA spectra of $[C_4H_8O]^{+\cdot}$ obtained from 1hepten-3-ol and of *d* from 3-heptanone are given in Table 1. The spectra are essentially identical, and are distinctly different from those of 16 other $[C_4H_8O]^{+\cdot}$ ions.⁶ Therefore, both $[C_4H_8O]^{+\cdot}$ ions must have the same structure when they reach the collision chamber.⁷ The intensity ratio (-methyl/-ethyl) for the unimolecular metastable decompositions of $[C_4H_8O]^{+\cdot}$ from 1-hepten-3-ol was 1.57, which is within the range of the corresponding ratios for *d* obtained from 3-heptanone (1.51), 3-undecanone (1.64) and 1-ethylcyclobutanol (1.56). Identical unimolecular metastable peak intensity ratios demonstrate identity of ion structures.⁸ The (-CH₃/-C₂H₅) ratio for *d* is distinct from that of other $[C_4H_8O]^{+\cdot}$ ions, even, though all of those ions lose methyl and ethyl via the 2-butanone structure.² Therefore, the

Table 1. Collisional activation spectra of [C₄H₈O]⁺ ions^a

Precursor Product m/z	1-Hepten-3-ol 3-Heptanone Intensities		Precursor Product m/z	1-Hepten-3-ol 3-Heptanone Intensities	
12	0.2	0.1	38	2.0	1.7
13	0.5	0.4	39	4.4	3.7
14	1.7	1.5	41	3.9	3.5
15	2.2	2.1	42	8.5	8.0
25	1.0	1.0	43	24	24
26	3.7	3.3	53	3.9	3.7
27	7.8	7.0	54	1.1	0.9
28	2.1	1.7	55	1.8	1.8
29	6.1	5.5	56	0.5	0.5
31	2.1	1.7	57	17	17
37	1.3	1.3	71	9.6	9.4

 $^{\rm a}$ Spectra are corrected for unimolecular contributions at m/z 43 and 57, and are percentages of the sum of the total ion intensity.

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Table 2. $\triangle AE$ values^a for the metastable decompositions of $[C_4H_8O]^+$

72→57	72→4 3	
1.1 eV	1.2 eV	
1.2 eV	1.3 eV	
	72→57 1.1 eV 1.2 eV	

* AE (m^*) – AE $([C_4H_8O]^{++})$.

match in these ratios confirms that $[C_4H_8O]^{+}$ ions generated from 1-hepten-3-ol have structure d.

Ionized 1-hepten-3-ol could either decompose directly to d, or the $[C_4H_8O]^+$ ion formed therefrom quickly rearrange to d. Differences between appearance energies (AE) for the metastable decompositions and those of the precursor $[C_4H_8O]^+$ ions were within experimental error for the $[C_4H_8O]^+$ ions from the two sources (Table 2). Ions b or c should be much less stable than d, and therefore should give a smaller difference formed, while ΔAE if initially $CH_3CHC = OH)CH_3$ gives a larger ΔAE difference.¹ Therefore, we conclude that the 1-hepten-3-ol molecular ion fragments directly to d.

Although we have proposed previously that both b and c can be formed,² the formation of b has since been ruled out,⁹ and present evidence indicates that c is not formed. Thus, there are no known examples of formation of $[C_4H_8O]^+$ isomers in which the charge cannot be resonance stabilized by the oxygen.

Grant and Djerassi³ demonstrated by deuterium labeling that a hydrogen from C-6 of ionized 1hepten-3-ol is transferred into the incipient $[C_4H_8O]^+$ ion, but not to the oxygen of that ion, ruling out the intermediacy of the 3-heptanone ion. Scheme 2 presents other possible pathways from ionized 1-hepten-3-ol to *d*. It is not possible to choose experimentally among these pathways, since each would place deuteriums from C-3 and C-6 in the ethyl of *d*, as was observed by Grant and Djerassi. $a \rightarrow g$ is improbable, since *g* is very similar in the placement of its charge and radical site to *b*, whose formation is ruled out in the present work.

There is no precedent for a specific, 7-membered ring hydrogen transfer when no special feature causes it to be preferred to a 6-membered ring hydrogen transfer, so the 7-membered ring hydrogen transfer $e \rightarrow h$ is unlikely, implying that $a \rightarrow e \rightarrow h$ does not occur. We generated $f-6, 6-d_2$ from 4-methyl-5nonanone-8,8- d_2 to verify that $f \rightarrow h \rightarrow d$ will occur. A strong $[C_4H_7DO]^+$ ion was observed in the normal spectrum of 4-methyl-5-nonanone- $8, 8-d_2$, and a metastable transition representing $f \rightarrow h \rightarrow d$ was observed. This [C₄H₇DO]⁺⁻ ion lost exclusively (>99% of methyl and ethyl) CH₃ and C₂H₄D, indicating that the deuterium was on the oxygen and/or the third carbon of that ion, as would be expected for the products of the double McLafferty rearrangements of the parent ion. Since $f \rightarrow h \rightarrow d$ will occur, those reactions are a highly probable part of the pathway between a and d. There remain two possible mechanisms for forming d, $a \rightarrow e \rightarrow f \rightarrow h \rightarrow d$ and $a \rightarrow f \rightarrow d$ $h \rightarrow d$. The loss of some CH₂D and C₂H₅ (15% of total methyl and ethyl losses) from $[C_4H_7DO]^+$ formed from 1-hepten-3-ol-3- d_1 may indicate that $a \rightarrow f$ occurs, since this would place the deuterium in a position to be partially transferred to the methyl lost in the decomposition of d.¹ However, this evidence is tenuous, because deuteriums placed initially in other positions in 1-hepten-3-ol are lost from d with comparable nonspecificity.³

EXPERIMENTAL

All results are for decompositions that occurred between the magnet and second electric sector of a Kratos MS 50 TA mass spectrometer. Peaks were recorded by scanning the electric sector voltage. The mass spectrometer was operated at an electron energy of 70 eV, 8000 V accelerating potential, a source temperature of 200 °C and a β -slit width of 0.050 in. CA spectra were determined by admitting helium to a collision chamber between the magnet (second sector)



and second electric sector of the mass spectrometer. Pressure readings at the vacuum wall outside the chamber were $1.0\pm0.1\times10^{-6}$ Torr during CA measurements. Appearance energies were determined from the semilog plots of intensities normalized to 50 eV.¹⁰

The 4-methyl-5-nonanone- $8, 8-d_2$ was prepared starting with butanol- $3, 3-d_2$ available from an earlier study.¹¹ The alcohol was converted to the bromide with HBr-H₂SO₄ and added to 2-methylpentanal via the Grignard reagent. The resulting 4-methyl-5-nonanol was oxidized to the ketone with H₂SO₄-

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CrO₃. It was found to be 97% d_2 and 3% d_1 by comparing the m/z 158 and 157 peak heights.

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