Four Isomers of [C₃H₈O]⁺ Distinguished by Collisional Activation

Frank W. Crow and Michael L. Gross†

Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588, USA

Maurice M. Bursey[†]

William Rand Kenan Jr Laboratories of Chemistry, The University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27514, USA

Collisional activation of the molecular ions of 1-propanol, 2-propanol and methyl ethyl ether, and of the m/z 60 ion from 1,2-dimethoxyethane provides evidence for four distinct forms of $[C_3H_8O]^+$. Collision induced decompositions may be explained either by simple cleavages, by cyclic processes involving adjacent substituents, or by bicyclic processes of adjacent substituents. Evidence for a form of $[C_3H_8O]^+$ in which charge and radical site are separate is assembled from the spectra.

The focus of this study is the nature of the C_3H_8O radical cation formed in the unimolecular decomposition of 1,2-dimethoxyethane¹ (Eqn (1)). The strategy is to investigate its collisionally induced decompositions (CID) and compare them with other $[C_3H_8O]^{+\cdot}$ ions. There are three stable C_3H_8O isomers that yield $[C_3H_8O]^{+\cdot}$: 1-propanol, 2-propanol and methyl ethyl ether.

$$[CH_3OCH_2CH_2OCH_3]^{+} \rightarrow [C_3H_8O]^{+} + CH_2O$$
(1)

It is known that the ion formed in Eqn (1) has the peculiar ability to transfer $[C_2H_4]^+$ to nitriles in low energy ion/molecule reactions observed using ion cyclotron resonance (ICR) spectrometry,² and so at least a fraction of these $[C_3H_8O]^+$ ions must possess a structure quite different than the other forms of $[C_3H_8O]^+$. This holds for times as long as the drift period in an ICR cell, i.e. about a millisecond.

1

The specific purpose of this work is to establish the actual structure of **1**. There is an additional need because so few studies of collisional activation of saturated odd electron ions exist. For example, only one investigation is listed in a recent compilation,³ and that is of the molecular ion of octane.⁴

EXPERIMENTAL

The 1-propanol, 2-propanol and 1,2-dimethoxyethane samples were commercial samples which had no impurities detectable by mass spectrometry. The methyl ethyl ether was prepared by a small-scale Williamson synthesis using methyl iodide and an ethanolic solution of sodium ethoxide at 37 °C; the reaction mixture was injected into the source after neutralization, and, since there were no impurities producing ions of the same mass as the desired product, only the molecular ion of the methyl ethyl ether was transmitted into the collision cell. A sample of 1,2-dimethoxyethane-1,1,2-2- d_4 was available from a previous study.⁴

CID spectra were obtained on a Kratos MS 50 triple analyzer mass spectrometer.⁵ The ions under study (here $[C_3H_8O]^+$) were selected at a mass resolution of 5000 using the first two sectors (EB). Collisional activation was accomplished in the third field free region, using helium as collision gas at a pressure sufficient to reduce the main beam by 20%, and the decomposition

Table 1. Collisional activation spectra of $[C_3H_8O]^+$ isomers (m/z 60)

· · · · · · · · · · · · · · · · · · ·			
[CH ₃ CHOHCH ₃] ⁺	[CH ₃ CH ₂ CH ₂ OH] ⁺	[CH ₃ OC ₂ H ₅] ⁺⁻	1
			0.5
100.6ª	0.5 100.0ª		5.1
30.0ª	0.8 1.8		4.3
3.7ª	4.4	2.5	5.6
3.3	85.0ª	0.9	23.0ª
0.5	6.2	0.3	1.2
	1.1		
0.4	5.6		
0.1	1.9		
	1.3		
0.1	0.4	0.3	20
	1.1		3.3
4.6	100.0ª	4.2	100.0ª
0.6	4.7	1.6	5.4
3.1	21.0	12.0	20.0
0. 9	8.0	3.2	35 .0ª
2.4	19.0	5.4	29.0
1.5	9.5	3.2	19.0
0.3	1.9	0.6	2.9
0.1	0.4		0.7
0.1	0.3		0.2
	0.2		
0.2	0.2	0.3	1.0
3.0	2.4	4.7	10.0
1.2	1.9	1.6	5.4
0.3	0.9	0.6	1.8
0.1	0.4	0.2	0.5
	ICH ₃ CHOHCH ₃ J ⁺⁺ 100.6 ^a 30.0 ^a 3.7 ^a 3.3 0.5 0.4 0.1 0.1 4.6 0.6 3.1 0.9 2.4 1.5 0.3 0.1 0.1 0.2 3.0 1.2 0.3 0.1	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c c} \mbox{[CH}_3 \mbox{CHOHCH}_3]^{**} & \mbox{[CH}_3 \mbox{CH}_2 \mbox{CH}_2 \mbox{CH}_2 \mbox{OC}_2 \mbox{H}_6]^{**} \\ \hline 100.6^a & 0.5 & 100.0^a \\ 30.0^a & 0.8 & 1.8 \\ 3.7^a & 4.4 & 2.5 \\ 3.3 & 85.0^a & 0.9 \\ 0.5 & 6.2 & 0.3 \\ & 1.1 \\ 0.4 & 5.6 \\ 0.1 & 1.9 \\ & 1.3 \\ 0.1 & 0.4 & 0.3 \\ & 1.1 \\ 4.6 & 100.0^a & 4.2 \\ 0.6 & 4.7 & 1.6 \\ 3.1 & 21.0 & 12.0 \\ 0.9 & 8.0 & 3.2 \\ 2.4 & 19.0 & 5.4 \\ 1.5 & 9.5 & 3.2 \\ 0.3 & 1.9 & 0.6 \\ 0.1 & 0.4 \\ 0.1 & 0.3 \\ & 0.2 \\ 0.2 & 0.2 & 0.3 \\ 3.0 & 2.4 & 4.7 \\ 1.2 & 1.9 & 1.6 \\ 0.3 & 0.9 & 0.6 \\ 0.1 & 0.4 & 0.2 \\ \end{array}$

^a Peaks having unimolecular counterparts.

CCC-0030-493X/81/0016-0309\$01.50

[†] Authors to whom correspondence should be addressed.

Table 2. Collisional activation spectrum of $[C_3H_4D_4O]^+$ from CH₃OCD₂CD₂OCH₃

m/z	Rel. int.	m/z	Rel. int.	m/z	Rel. int.	m/z	Rel. int.	
50	0.7	42	0.3	30	44.1	18	2.1	
49	2.9	41	0.3	29	20.7	17	1.3	
48	1.6	40	0.3	28	21.9	16	3.4	
47	9.7	35	2.6	27	1.9	15	6.3	
46	14.3ª	34	21.4	26	1.9	14	2.4	
45	14.6ª	33	12.4	25	0.3	13	0.4	
44	4.2	32	95.3ª	24	0.3	12	0.3	
43	0.7	31	100.0 ^a	21	0.3			

^a Peaks having unimolecular counterparts.

products analyzed using the third sector (an ESA). Unimolecular metastable spectra were obtained in the absence of added collision gas; peaks occurring in the absence of collision gas are so noted in Tables 1 and 2. The CID spectra showed no significant change when the ionizing energy was reduced to 15 eV, nor when the beam was suppressed to 50% of its original value.

RESULTS AND DISCUSSION

The spectra of the molecular ions of the three stable neutral forms are clearly distinguished from each other (see Table 1) and the major fragments are for the most part easily related to the structure expected for the molecular ions. Thus, the spectrum of the molecular ion of 2-propanol is dominated by low energy processes; many other major ions are formed by simple high energy cleavages, though the ions of m/z 31, 29 and 27 are not. Even these can be accounted for by extrusion of adjacent portions of the molecule without the need for invoking an activated complex which is statistically unlikely. An acceptable complex, whose activation barrier is high but presumably accessible under CA conditions and whose geometry is not greatly distorted from the original structure-in general the energetics of the CA experiment imply the much greater importance of this latter restriction-is a, which could generate m/z 31 and 29.



The spectrum of the molecular ion of 1-propanol has no major ions easily derived by other than straightforward cleavages or 4-center rearrangements. The m/z 31 ion in the spectrum of the molecular ion of ethyl methyl ether offers the only challenge to the imagination in that spectrum. If it has the protonated formaldehyde structure, it may be accounted for by the activated complex b.



The spectrum of 1, the $[C_3H_8O]^+$ ion formed in the decomposition of the molecular ion of 1.2dimethoxyethane, is distinguished from the spectra of the other isomers by the abundance of at least four peaks: m/z 46, 33, 32 and 28. Although m/z 46 is a small peak, it corresponds to a loss of 14 mass units and implies the presence of a CH₂ group which can be easily cleaved from the ion. The decomposition requires a structural feature not present in the other isomers, two of which show substantial loss of terminal CH₃ according to simple rules of fragmentation and the other which shows a loss of CH₃ in about the same amount as this CH₂ loss. In that compound, 1propanol, loss of the terminal CH₃ would be expected to be a minor process.

The presence of m/z 32 suggests a structure from which CH₃OH is easily generated; it is three times as intense here as in the spectrum of 2-propanol.

The production of m/z 28 by a low energy process (it appears in the spectrum recorded without added collision gas and, therefore, is a true unimolecular product) is also more significant in the spectrum of **1** than in those of the other isomers.



These three pieces of information point to a structure for **1** which can lose CH_2 and CH_3OH and generate $[CH_2CH_2]^+$ easily. The formation of $[CH_3OH_2]^+$, m/z 33, is also accommodated by this form (Eqn (2)) within the restrictions of reactivity of adjacent substituents. The loss of water to give m/z 42 is a process visualized only on the level of processes for which activated complexes have been suggested

$$\begin{array}{ccc} H & H \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ &$$

previously in this paper. Thus, complexes c and d or their equivalents are required to rationalize a singlestep process in which water is lost. A multistep process in which the intermediate would be the molecular ion of 1-propanol or 2-propanol seems likely only to contribute a minor pathway, because the evidence is that these forms cannot account for a substantial fraction of the ions: the ions of masses between 37 and 40



which these forms produce are missing from the spectrum of 1, for example. Forms c and d require the same kinds of migrations as b.

In order to shed more light on these fragmentations, the decomposition of the m/z 64 ion from 1,2dimethoxyethane-1,1,2,2- d_4 upon collision was studied (see Table 2). The following points clarify the suppositions made above. First, the loss of water is primarily of HOH and HOD. That is, one of the hydrogens is defined as H, which we take to be the hydrogen bound to oxygen in **1**. The other may come either from the methyl group (via d) so that HOH is lost, or from the methylene groups (via c), so that HOD is lost. A further refinement of the analysis could come from the study of appropriate ions produced from the labeled compound $CD_3OCH_2CD_2$ -OCH₃, for example, but we have not prepared this model.

Likewise, the dominance of the reaction depicted as Eqn (2) in the formation of $[CH_3OH_2]^+$ is indicated by the shift of m/z 33 to 34 (CH_3OHD^+). Since m/z 32 may be either $[CH_3OH]^{++}$ or $[C_2D_4]^{++}$, it is of no value in confirming either process.

The two-carbon and one-carbon fragments show evidence of hydrogen scrambling. Based on a review of the highest mass ions in the spectrum of the labeled compound, we suggest a process by which this may occur. The m/z 46 peak in the spectrum of **1** appears to shift to m/z 50 in its labeled counterpart indicating a loss of CH₂. Further, the loss of CH₃ from **1** (to give m/z 45) appears to be divided between a loss of CH₃ (to give m/z 49) and at least CH₂D (to give m/z 48). The first observation suggests that there is an internal



- K. L. Busch, W. B. Nixon and M. M. Bursey, *J. Am. Chem. Soc.* 100, 1621 (1978).
- K. Levsen, Fundamental Aspects of Organic Mass Spectrometry, pp. 284–292. Verlag Chemie, Weinheim (1978).
- 4. K. Levsen, Org. Mass Spectrom. 10, 43 (1975).
- M. L. Gross, E. K. Chess, P. A. Lyon, F. W. Crow, S. Evans and H. Tudge, Anal. Chem. submitted for publication.



$$\begin{array}{c} H \\ \dot{O} - CD_2CD_2H \rightleftharpoons DH_2C \end{array} \xrightarrow{H} \overset{\dot{O}}{\longrightarrow} - CD_2\dot{C}DH \qquad (4)$$

hydrogen abstraction (Eqn (3)); the second, that it is reversible (Eqn (4)). Thus, the ion not only represents an example of structures differing from molecular ions in the clear separation of charged and radical sites,⁶⁻⁸ but it also provides another illustration of how the separation of these sites may provide a route for hydrogen scrambling.⁶

Acknowledgements

This research was supported by a grant to the Midwest Center for Mass Spectrometry, a National Science Foundation Regional Instrumentation Facility (Grant CHE 78-18572).

REFERENCES

- J. S. Smith and F. W. McLafferty, Org. Mass Spectrom. 5, 483 (1971).
- 7. H. H. Jaffé and S. Billets, J. Am. Chem. Soc. 92, 6965 (1970).
- B. C. Baumann, J. K. MacLeod and L. Radom, J. Am. Chem. Soc. 102, 7927 (1980).

Received 5 March 1981; accepted 21 April 1981

© Heyden & Son Ltd, 1981