J. Am. Chem. Soc. **1992,** *114,* 2017–2020

The Test of an Analogy: Are Intramolecular Hydrogen Bonds in β-Diols and β-Hydroxy Ethers Preserved in Their Molecular Ions?

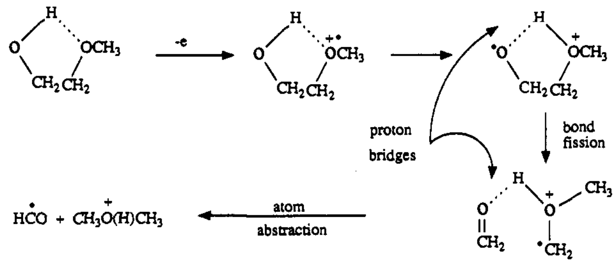
J. R. Cao,[†] M. George, J. L. Holmes,*[,†] M. Sirois,[†] J. K. Terlouw,[‡] and P. C. Burgers[§]

Contribution from the Chemistry Department, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5, Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1, and PFW (Nederland) B.V., Nijverheidsweg Zuid 7, 3812 EA, Amersfoort, The Netherlands. Received June 24, 1991

Abstract: An attractive proposal in gas-phase ion chemistry was that intramolecular hydrogen bonding in neutral molecules persisted in their molecular ions and directed their dissociation chemistry. The present mass spectrometric experiments demonstrate that this is not correct for ionized 1,2-ethanediol and 2-methoxyethanol, two species whose dissociation behavior was used initially to support the original hypothesis.

Introduction

In an important and influential review article in 1982, Morton[1] proposed that intramolecular hydrogen bonding in a neutral molecule can persist in the gas-phase molecular ion with a proton bridging the electronegative centers. This ionic species then becomes responsible for significant dissociation channels of the molecular ion. The archetype for such behavior was 2-methoxyethanol, **1**, and the mechanism shown below for the formation of the protonated dimethyl ether fragment ion is that proposed by Morton.[1]



We have used[2] this attractive and widely accepted proposal to rationalize one of the major dissociation reactions of ionized 1,2-ethanediol, **2**, viz., the formation of $CH_3OH_2^+$ ions and $HCO^{\bullet}$ radicals, by a mechanism similar to that shown above. Ab initio calculations[2] showed that the proposed hydrogen-bridged species $[CH_2O(H)\cdots H\cdots O{=}CH_2]^{\bullet+}$ was thermochemically more stable than $\mathbf{2}^{\bullet+}$, by 13 kcal mol^{-1}, providing an intermediate of sufficient stability to permit ionized **2** to be metastable. It should be emphasized that O···H···O hydrogen-bridged radical cations have been shown by calculation to have lower enthalpies of formation than their conventional molecular ion counterparts, and so they have been proposed to be key intermediates in a number of ionic dissociation mechanisms.[3]

In two other studies of ionized 2-methoxyethanol, the above mechanism was not specifically addressed. The first,[4] a photoionization study of normal mass spectra, focused attention on the possible intramolecular exchange of hydrogen between the CH_3 and OH groups, and the second[5] was concerned with the structure of the $C_2H_6O^{\bullet+}$ fragment ion. For 2-methoxyethanol, the Morton mechanism predicts that the hydroxyl hydrogen becomes the proton in the product ion and that the second methyl group contains a hydrogen atom from the 1-methylene group. Indeed, an indication that this mechanism may be incorrect was the report[5] that $CH_3O^+(D)CH_3$ was generated from $CH_3OCH_2CD_2OH$. Unfortunately this observation was not pursued further.

The present study describes experiments which have been performed on product ions generated by loss of $HCO^{\bullet}$ ($DCO^{\bullet}$) from deuterium-labeled 1,2-ethanediol and 2-methoxyethanol isotopomers. These experiments permit the unequivocal determination of label atom position in the product ions $CH_3O^+H_2$ and $CH_3O^+(H)CH_3$, respectively. The results described below constitute the evidence which necessitates a revision of the Morton mechanism. For 2-methoxyethanol the competing H_2O loss reaction was investigated insofar as that reaction relates to the $HC^{\bullet}O$ loss process.

Experimental Section

All experiments were performed on the extended VG-ZAB 2F (geometry $B_1E_1B_2$) instrument at the University of Ottawa and on the VG-ZAB-R instrument (geometry $B_1E_1E_2$) at Hamilton. The label positions in the product ions from 1,2-ethanediol were determined by MS/MS/MS experiments. First the labeled molecular ion was selectively transmitted through B_1. The product ions from metastable molecular ions were then selectively transmitted through E_1 and were collisionally decomposed in the third field free region; its products are then selected by E_2 and detected. For details see ref 6. Collisional activation (CA) mass spectra of mass-selected ions were recorded using He as target gas, 90% transmission. Labeled compounds were synthesized by standard procedures. The OD labeled species were prepared in the inlet system and ion source of the mass spectrometer by exchange with excess D_2O.

Results and Discussion

1,2-Ethanediol. The molecular ion of this compound shows one intense peak in its metastable-ion (MI) mass spectrum corresponding to loss of $HC^{\bullet}O$ to generate $CH_3O^+H_2$. The latter ion has a structure-characteristic collisional activation (CA) mass spectrum. Upon collision, $CH_3O^+H_2$ dissociates to CH_3^+ (m/z 15) and $H_2O^{\bullet+}$ (m/z 18). According to the previously proposed mechanism,[2] the labeled molecular ion $DOCH_2CH_2OD^{\bullet+}$ should specifically eliminate $HC^{\bullet}O$ to generate $CH_3O^+D_2$ with both deuterium atoms being retained at oxygen. Figure 1 shows the CA mass spectrum of the $[H_3,D_2,C,O]^+$ ions generated by $HC^{\bullet}O$ loss from metastable $DOCH_2CH_2OD^{\bullet+}$ ions. It can be concluded immediately that the product ions are CH_2DOHD^+ and not $CH_3O^+D_2$. This conclusion is confirmed by a similar analysis of $HOCD_2CD_2OH^{\bullet+}$, where the $[H_2,D_3,C,O]^+$ product ion was found

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[†] University of Ottawa.
[‡] McMaster University.
[§] PFW (Nederland) B.V., Nijverheidsweg Zuid 7.

(1) Morton, T. H. *Tetrahedron* **1982**, *38*, 3195.

(2) Burgers, P. C.; Holmes, J. L.; Hop, C. E. C. A.; Postma, R.; Ruttink, P. J. A.; Terlouw, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 7315.

(3) For recent reviews, see: (a) Burgers, P. C.; Terlouw, J. K. In *Specialist Periodical Reports*: *Mass Spectrometry*; Rose, M. E., Ed.; Royal Society of Chemistry: London, 1989; Vol. 10, Chapter 2. (b) Heinrich, N.; Schwarz, H. In *Ion and Cluster Ion Spectroscopy and Structure*; Maier, J. P.; Ed.; Elsevier: Amsterdam, 1989; p 329. See also: (c) Schaftenaar, G.; Postma, R.; Ruttink, P. J. A.; Burgers, P. C.; McGibbon, G. A.; Terlouw, J. K. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 521.

(4) Biermann, H. W.; Morton, T. H. *J. Am. Chem. Soc.* **1983**, *105*, 5025.

(5) Burgers, P. C.; Holmes, J. L.; Terlouw, J. K.; van Baar, B. *Org. Mass Spectrom.* **1985**, *20*, 202.

(6) Kingsmill, C. D.; McGibbon, G. A.; Burgers, P. C.; Bateman, R. H.; Terlouw, J. K., manuscript in preparation.

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Table I. Collisional Activation Mass Spectra of $C_3H_6O^{\bullet+}$ Ions from $CH_3OCH_2CH_2OH$, Methyloxirane, Methyl Vinyl Ether, and Oxetane[a]

	m/z											
$C_3H_5O^{\bullet+}$ ions from	13	14	15	26	27	28	29	30	31	41	42	43
$CH_3OCH_2CH_2OH$; ion source	–	1	2	8	15	43	19	(39)	9	–	3	(9)
$CH_3OCH_2CH_2OH$; metastable	–	1	1	7	13	49	17	(37)	8	–	2	2
$CH_3\overline{CHCH_2O}$; ion source[b]	1	2	7	7	18	22	17	(14)	13	1	13	(59)
CH_3OCHCH_2; ion source	1	2	8	5	18	15	15	(4)	15	2	2	(29)
$\overline{CH_2OCH_2CH_2}$; ion source[b]	–	1	1	6	9	53	22	(31)	5	–	1	2

[a] Numbers in parentheses indicate peaks arising in part from metastable ions. [b] The relative cross sections for methyl oxirane and oxetane are 1:4.

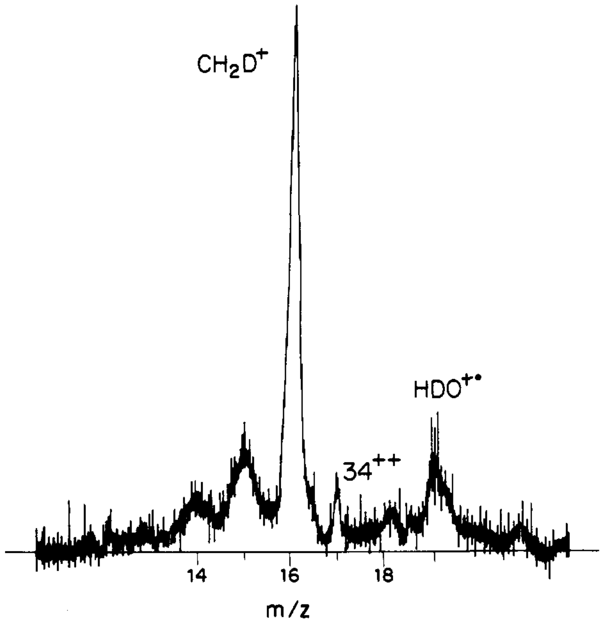
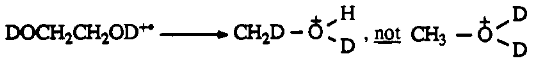


Figure 1. Partial collisional activation mass spectrum of the $[H_3,D_2,C,O]^+$ product ions generated from metastable $[DOCH_2CH_2OD]^{\bullet+}$.

to have the connectivity CHD_2OHD^+, again contrary to the original prediction that $CD_3O^+H_2$ would be generated.[2] Thus the following transformation is established:



$$DOCH_2CH_2OD^{+\bullet} \longrightarrow CH_2D-\overset{+}{O}\begin{smallmatrix}H\\D\end{smallmatrix},\ \underline{not}\ CH_3-\overset{+}{O}\begin{smallmatrix}D\\D\end{smallmatrix}$$

and so the earlier mechanism clearly must be revised.

When the molecular ion of $HOCH_2CH_2OH$ is activated by collision, another process comes into play, namely, loss of CH_2O leading to the ylidion $^{\bullet}CH_2O^+H_2$.[2] The labeled ion $DOCH_2CH_2OD^{\bullet+}$ specifically loses CH_2O, and the CA mass spectrum of the collisionally formed product ions (Figure 2) clearly shows that they are $^{\bullet}CH_2O^+D_2$. *Thus in the higher energy process, the (O)D migrates to oxygen, but in the lower energy process, it migrates to carbon.*

Ab initio calculations on the rearrangement/dissociation reactions of 1,2-ethanediol have confirmed[7] the earlier results of Radom et al.[8] that the syn-molecular ion can spontaneously rearrange to the distonic isomer $^{\bullet}OCH_2CH_2O^+H_2$, which can then lose CH_2O. However, the distonic ion cannot be the precursor for $HC^{\bullet}O$ loss (see above). The possibility that the anti conformer (which has a long C–C bond, 2.07 Å,[7] 2.05 Å[9]) leads to the $HC^{\bullet}O$ loss channel is also being explored.[7]

2-Methoxyethanol. The molecular ion of this compound shows two intense peaks in its MI mass spectrum, corresponding to losses of $HC^{\bullet}O$ and H_2O. It is necessary to describe the latter dissociation channel in some detail because it has a significant bearing on the discussion concerning the $HC^{\bullet}O$ loss which follows.

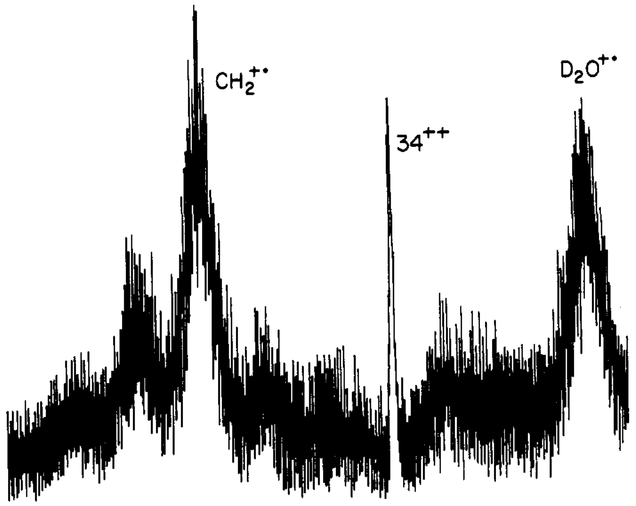


Figure 2. Partial collisional activation mass spectrum of the $[H_2,D_2,C,O]^+$ product ions generated from collisionally activated $[DOCH_2CH_2OD]^{\bullet+}$.

Loss of H_2O. The fragment ion *m/z* 58, $C_3H_6O^{\bullet+}$, produced by loss of H_2O, was shown to be a mixture of ionized oxetane (ΔH_f° = 204 kcal mol^{-1} [10]) and methyloxirane (ΔH_f° = 213 kcal mol^{-1} [10]), as described below.

The appearance energy (AE) values for the three dissociations of lowest energy requirement, *m/z* 58, $C_3H_6O^{\bullet+}$ (H_2O loss), *m/z* 47, $CH_3O^+(H)CH_3$ ($HC^{\bullet}O$ loss), and *m/z* 45, $CH_3OC^+H_2$ ($^{\bullet}CH_2OH$ loss), were measured using energy-selected electrons.[11] The AE values were 10.0, 9.96, and 10.42 eV, all ±0.05 eV, respectively. The respective threshold AE values calculated using established thermochemical data[12] were 10.10 eV (assuming ionized oxetane as the product ion), 9.90 eV, and 10.3 eV, all very close to the observed thresholds. Thus the three reactions take place close to their minimum required energies. The kinetic energy releases, $T_{0.5}$, for the first two (metastable) reactions, calculated from the half-height width of the Gaussian type metastable peaks, were 19 and 16 meV, respectively, in keeping with the reactions proceeding without a reverse energy barrier.

The *m/z* 58, $C_3H_6O^{\bullet+}$ ion displayed an MI mass spectrum with a broad, flat-topped peak at *m/z* 43 ($T_{0.5}$ = 710 meV) together with a very weak Gaussian type peak at *m/z* 30 and an intense $H^{\bullet}$ loss peak. The broad peak is only characteristic[14] of either ionized methyl vinyl ether (ΔH_f° = 182 kcal mol^{-1} [10]) or methyloxirane, $CH_3\overline{CHCH_2O}$.

The CA mass spectrum of the $C_3H_6O^{\bullet+}$ daughter ions generated from 2-methoxyethanol are given in Table I together with those of reference ions from appropriate compounds. The metastably

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(7) Ruttink, P. J. A.; Postma, R. Private communication.

(8) Yates, B. F.; Bouma, W. J.; McLeod, J. K.; Radom, L. *J. Chem. Soc., Chem. Commun.* **1987**, 204.

(9) Bellvile, D. J.; Pabon, R. A.; Bauld, N. L. *J. Am. Chem. Soc.* **1985**, *107*, 4978.

(10) Lias, S. G.; Bartmess, J. E.; Liebmann, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17* (Suppl. 1).

(11) Lossing, F. P.; Traeger, J. C. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *19*, 9.

(12) Using data from ref 10 and $\Delta H_f^{\circ}[CH_3OCH_2CH_2OH]$ = −87.4 kcal mol^{-1},[13] IE $[CH_3OCH_2CH_2OH]$ = 9.58 ± 0.05 eV, measured in this study.

(13) By group additivity. Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

(14) Lifshitz, C. *Org. Mass Spectrom.* **1988**, *23*, 303.

Table II. Low-Mass (*m/z* 14–18) Region of the Collisional Activation Mass Spectra of Isotopomeric $CH_3O^+(H)CH_3$ Ions[a]

ion	*m/z*				
	14	15	16	17	18
$CH_3O^+(H)CH_3$	8	90	2		
$CH_3O^+(D)CH_3$	7	91	2		
$CH_3OCH_2CD_2OH$	10	85	5		
$CH_3O^+(H)CD_3$	6	28	12	9	44
$CD_3OCH_2CH_2OH$	3	10	39	40	8.5
$CH_3OCD_2CD_2OD$	3	8	39	41	8.5
$CH_3O^+(H)CH_2D$	8	43	46	2.5	
$CH_3OCH_2CH_2OD$ (ion source)	8	43	47	3	
$CH_3OCD_2CD_2OH$	2.5	21	53	22	1

[a] Unless otherwise stated, product ions were generated from metastable molecular ions.

Table III. Metastable-Ion Mass Spectra of Protonated Dimethyl Ethers

ion	fragment-ion abundance at *m/z*			
	31	32	33	34
$CH_3O^+(H)CD_3$	1.0	–	1.4	–
m/z 50 from $CD_3OCH_2CH_2OH$	1.0	–	1.3	–
$CH_3O^+(D)CD_3$	–	1.0	–	1.4
m/z 51 from $CH_3OCD_2CD_2OD$	–	1.0	–	1.3
$CH_3O^+(H)CH_2D$	1.6	1.0		
m/z 48 from $CH_3OCH_2CH_2OD$[a]	~1.2	~1		
$CH_3O^+(H)CH_3$	1.0	–		
$CH_3O^+(D)CH_3$	–	1.0		
m/z 48 from $CH_3OCH_2CD_2OH$	–	1.0		

[a] Peak abundances uncertain due to artifact signals.

generated product ions from 2-methoxyethanol have a CA mass spectrum compatible with a mixture of ionized oxetane and methyloxirane, noting that oxetane is four times more collision sensitive than methyloxirane.

The proof that the second $C_3H_6O^{\bullet+}$ ion is methyloxirane comes from examination of deuterium-labeled methoxyethanols. First, ionized metastable $CH_3OCH_2CD_2OH$ loses only H_2O, showing that the 1-methylene hydrogens are not involved. Next, the losses of H_2O, HDO, and D_2O were examined for ionized metastable $CD_3OCH_2CH_2OH$, **1a**, $CH_3OCD_2CD_2OH$, **1b**, and $CH_3OCD_2CD_2OD$, **1c**. For the first isotopomer, the ratio 32:100:35 (for *m/z* 61, 60, and 59) is close to the ratio for randomization of the three D and three H atoms (33:100:33). However, complete atom scrambling is not taking place; the H_2O:HDO:D_2O losses for $CH_3OCD_2CD_2OH$ and $CH_3OCD_2CD_2OD$, 100:82:10 and 47:100:26, respectively, are significantly different from the appropriate random ratios (100:133:16 and 33:100:33, respectively).

For the $CD_3OCH_2CH_2OH$, **1a**, and $CH_3OCD_2CD_2OH$, **1b**, isotopomers, the MI and CA mass spectra of the three water-loss peaks were examined. For **1a**, the MI and CA mass spectra of the $[M - H_2O]^{\bullet+}$ ion (ion source or metastably generated) were identical with those reported for $CD_3\overline{CHCH_2O}$ by Turecek and McLafferty,[15] and the same result was obtained for the $[M - HDO]^{\bullet+}$ ion from **1b**, which was identical with $CH_3\overline{CDCD_2O}$. The HDO loss ion, *m/z* 60, from **1a** showed *no* broad peak in its MI mass spectrum, whereas its CA mass spectra for ion source or metastably generated ions displayed major peaks at *m/z* 30 and 32 which are compatible with ionized oxetane of the structure $\overline{CD_2CH_2CH_2O}$. (If the H_2O loss involved randomization of the six H atoms, the *m/z* 60 ions would have been a mixture of $\overline{CD_2CH_2CH_2O}$ and $\overline{CHDCH_2CHDO}$.) The D_2O loss peak, *m/z* 59, from **1a** could not be examined due to interference from artifact signals.

Generation of $CH_3\overline{CHCH_2O}^{\bullet+}$ must take place via a specific loss of water involving the OH group and a 2-methylene hydrogen atom, but more significantly, the above results show that, for this reaction channel, the $[CH_3OCH_2CH_2OH]^{\bullet+}$ ions do not undergo any significant loss of positional identity of H atoms prior to that fragmentation. Rather, the *apparent* loss of positional identity of H atoms is due to two competing H_2O loss reactions of comparable importance.

Loss of HC•O. That the *m/z* 47 fragment ion from $[CH_3OCH_2CH_2OH]^{\bullet+}$ is protonated dimethyl ether is shown (a) by the AE of the ion and the small accompanying kinetic energy release (see above) and (b) by its dissociation characteristics, namely, the broad, flat-topped metastable peak at *m/z* 31 (CH_4 loss), $T_{0.5}$ = 830 meV (800 meV[16]), and the collisional activation mass spectrum (Table II).

Various metastable isotopomeric ions were studied, and they all show specific losses: $CD_3OCH_2CH_2OH^{\bullet+}$ and $CH_3OCH_2CH_2OD$ lose HC•O, whereas $CH_3OCD_2CD_2OH$, $CH_3OCD_2CD_2OD^{\bullet+}$, and $CH_3OCH_2CD_2OH^{\bullet+}$ eliminate DC•O. Thus for ions generated near threshold, complete mixing of *all* H and D atoms does not precede the molecular ions' fragmentation and one H (or D) from the 1-methylene carbon is always lost.

The MI mass spectra of the protonated dimethyl ethers produced from various labeled 2-methoxyethanols are shown in Table III, from which it can be readily seen that the hydroxyl hydrogen atom in **1** becomes a methyl hydrogen in the $CH_3O^+(H)CH_3$ while the 1-methylene hydrogen is attached to oxygen in the product. It should also be noted that there is *no* loss of positional identity of H atoms prior to the loss of the formyl radical; e.g., the $[M - HCO]^+$ ion from $CD_3OCH_2CH_2OH$ is exclusively $CD_3O^+(H)CH_3$ and not a mixture of $CD_2HO^+(H)CH_2D$ and $CD_3O^+(H)CH_3$.

The CA mass spectra of the metastably formed product ions from the above isotopomers are given in Table II. Only the *m/z* 14–18 regions are presented; the more intense peaks at *m/z* 28–34 contain overlapping contributions from adjacent masses and so are much less informative than the low-mass region, which in the unlabeled ion consists almost wholly of CH_3^+. It can immediately be inferred from the first entry in Table III that $CH_3OCH_2CD_2OH$ produces $CH_3O^+(D)CH_3$ and not $CH_3O^+(H)CH_2D$. This is opposite to the original prediction, but is in agreement with the earlier report[5] and also in keeping with results obtained for 1,2-ethanediol as described above.

Considering the results from the MI mass spectra of the *ion source* generated $[M - HCO]^+$ ions, one would expect the CA mass spectrum of the metastably generated $CD_3O^+(H)CH_3$ ion to be the same as that of the reference ion prepared by protonation of CD_3OCH_3, but instead it is a mixture of $CD_3O^+(H)CH_3$ and $CD_2HO^+(H)CH_2D$. This observation indicates that the CH_3 hydrogen, the 2-methylene hydrogens, and the OH hydrogen lose positional identity (in the metastable 2-methoxyethanol ions only) prior to fragmentation, ***unlike the H_2O loss channel.*** Hence the H_2O loss and HC•O loss processes do not involve a common intermediate, and any proposed mechanism for HC•O loss from *metastable* ionized 2-methoxyethanol must take into account the following: (1) the hydroxyl hydrogen atom becomes attached to the C-2 carbon atom; (2) one of the C-1 hydrogen atoms appears at the CH_3O oxygen atom; (3) the CH_3O, the 2-methylene, and the OH hydrogen atoms become virtually positionally indistinguishable, but the 1-methylene hydrogen atoms are not involved in the scrambling processes.

The new observations cannot be used to define a unique mechanism to describe the loss of HC•O from the diol and its methyl ether. Several plausible mechanisms can be formulated a priori, including C-1–C-2 bond elongation leading to transformations involving ion/radical, ion/molecule, or CHO-bridged, odd electron ion intermediates. Unfortunately there is no current experimental technique which unequivocally can identify such complex ions or even distinguish between them. A solution to this intriguing mechanistic problem should come from an extensive ab initio computational study of the system.

Nevertheless, the present work rules out the attractive Morton mechanism, in which preservation of the intramolecular H-bond

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(15) Turecek, F.; McLafferty, F. W. *J. Am. Chem. Soc.* **1984**, *106*, 2528.
(16) Jarrold, M. F.; Kirchner, N. J.; Liu, S.; Bowers, M. T. *J. Phys. Chem.* **1986**, *90*, 78.

in the neutral molecule directed the dissociation chemistry of the molecular ion.

Acknowledgment. J.L.H. and J.K.T. acknowledge continuing financial support from the Natural Sciences and Engineering Research Council of Canada. M.S. acknowledges the FCAR Studentship provided by the Quebec Provincial Government. We thank Dr. F. P. Lossing for appearance energy measurements and many stimulating discussions, and we also thank Dr. P. J. A. Ruttink, Dr. R. Postma, and H. van Garderen for communicating results of their calculations.

Registry No. **1**$^{\bullet+}$, 86012-96-6; **1a**, 97840-77-2; **1b**, 138667-25-1; **1c**, 138667-26-2; **2**, 83957-60-2; $DOCH_2CH_2OD$, 2219-52-5; $CH_3\overline{CHCH_2O}$, 75-56-9; CH_3OCHCH_2, 107-25-5; $\overline{CH_2OCH_2C}H_2$, 503-30-0; $CH_3OCH_2CD_2OH$, 51255-53-9; $CH_3OCH_2CH_2OD$, 86012-98-8; $CH_3O^+(H)CH_3$, 17009-82-4; $CH_3O^+(D)CH_3$, 131295-07-3; $CH_3O^+(H)CD_3$, 138408-93-2; $CH_3O^+(H)CH_2D$, 138408-91-0.

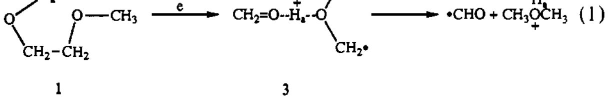
Unimolecular Decompositions of the Radical Cations of Ethylene Glycol and Its Monomethyl Ether in the Gas Phase. Distonic Ions versus Ion–Neutral Complexes

Henri Edouard Audier,* Arielle Milliet, Danielle Leblanc, and Thomas Hellman Morton*,†

Contribution from the Laboratoire des Mécanismes Réactionnels—Département de Chimie, Ecole Polytechnique, 91128 Palaiseau Cedex, France. *Received July 17, 1991*

Abstract: The ions corresponding to metastable formyl loss from ionized ethylene glycol and 2-methoxyethanol are the conjugate acids of methanol and dimethyl ether, respectively. The structures of the fragments of deuterated analogues reveal that a hydroxylic hydrogen transfers to carbon to create the new methyl group, while a hydrogen originally attached to carbon migrates to oxygen in the course of this double hydrogen transfer. This is the only metastable decomposition of ethylene glycol radical cation, while 2-methoxyethanol radical cation also loses water to form oxetane radical cation. Hydrogen scrambling prior to the fragmentations of 2-methoxyethanol radical cation takes place via the interconversion of three distonic ions with the parent structure. Comparison between unimolecular and bimolecular reactions is used as a criterion to test for ion–neutral complexes, and they are ruled out on the basis of reactions observed in the ICR. Ionized dimethyl ether reacts primarily with neutral formaldehyde by donating a hydrogen atom from the cation to the neutral and less frequently by abstracting a hydrogen atom from the neutral, but no product corresponding to oxetane radical cation is detected. Ionized oxetane reacts with neutral water via proton transfer to yield at least three products, including an isomer of oxetane radical cation, but none of these products are observed among the fragments of 2-methoxyethanol. These results are taken as excluding [$Me_2O^{\bullet+}$/formaldehyde] and [oxetane radical cation/water] complexes as the intermediates responsible for scrambling. The distonic ion $^{\bullet}CH_2OCH_2CH_2OH_2^+$ is generated by unimolecular loss of CH_2O from $CH_3OCH_2OCH_2CH_2OH^{\bullet+}$, and its isotopic analogues give the same results as for the corresponding 2-methoxyethanols. Two other distonic ions are inferred to form in kinetically significant steps from the molecular ion.

In the gas phase, cleavage of covalent bonds in acyclic ions does not always lead to prompt separation of the molecular fragments. Often the charged and neutral cleavage products remain held together for a sufficiently long time for them to undergo subsequent ion–molecule reactions. Transient species of this nature have been described as falling into two categories: (i) those held together by proton bridges (strong hydrogen bonds) and (ii) ion–neutral complexes, which are held together by ion–dipole and ion-induced dipole attraction.[1] Some of the earliest evidence for proton-bridged intermediates comes from a photoionization mass spectrometric (PIMS) study of 2-methoxyethanol (methyl cellosolve).[1,2] The molecular ion of this compound, **1**, expels formyl radical to yield protonated methyl ether, and the mechanism that was proposed is drawn in eq 1. More recently, Burgers, Holmes, Terlouw, and their co-workers have reported the unimolecular decomposition of ethylene glycol molecular ion (**2**) and infer the same kind of pathway, as depicted in eq 2, for expulsion of formyl radical to produce protonated methanol.[3]



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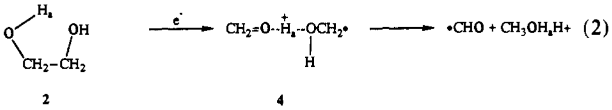

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In both cases the starting neutral alcohols enjoy extensive intramolecular hydrogen bonding. The distinctive reactions that follow removal of an electron have been attributed to cleavage of the carbon–carbon bond and conversion of the internal hydrogen bond into a proton bridge. The proton-bridged species **3** and **4** contain formaldehyde and an oxygenated methyl radical, which are presumed to be held together by the strong hydrogen bond. Naive application of this model suggests that the bridging hydrogen (labeled H_a in eqs 1 and 2) should become directly bound to oxygen in the product. However Burgers et al. report that $CH_3OCH_2CD_2OH$ appears to yield $(CH_3)_2OD^+$, an apparent contradiction.[4] Here, we present the results of a series of experiments that show that H_a is indeed transferred to carbon rather than to oxygen. Moreover, we find that the hydroxylic hydrogen of 2-methoxyethanol undergoes exchange with all five hydrogens of the CH_2OCH_3 portion of the molecule prior to decomposition. The results call into question the necessity for inferring a proton-bridged intermediate.

Experimental Section

Metastable ion mass spectra were recorded on a VG ZAB 2F double-focusing mass spectrometer. Ion cyclotron resonance (ICR) experiments were performed on a Bruker CMS 47X FT-ICR. Unless other-

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† Present address: Department of Chemistry, University of California, Riverside, CA 92521-0403.

(1) Morton, T. H. *Tetrahedron* **1982**, *38*, 3195–3243.

(2) Biermann, H. W.; Morton, T. H. *J. Am. Chem. Soc.* **1983**, *105*, 5025–5030.

(3) Burgers, P. C.; Holmes, J. L.; Hop, C. E. C. A.; Postma, R.; Ruttink, P. J. A.; Terlouw, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 7315–7321.

(4) Burgers, P. C.; Holmes, J. L.; Terlouw, J. K.; Van Baar, B. *Org. Mass Spectrom.* **1985**, *20*, 202–206.

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