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

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Registry No. **1**$^{•+}$, 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_3CHCH_2O, 75-56-9; CH_3OCHCH_2, 107-25-5; $CH_2OCH_2CH_2$, 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

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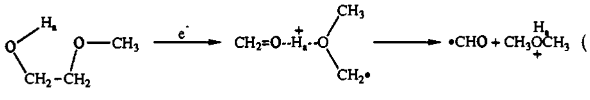
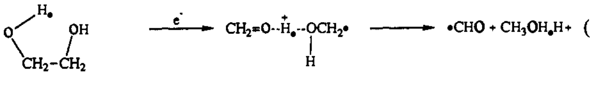
Abstract: The ions corresponding to metastable formyl loss from ionized ethylene glycol and 2-methoxyethanol are the conjugate acids of methanol and dimethyl ether, respectively. The structures of the fragments of deuterated analogues reveal that a hydroxylic hydrogen transfers to carbon to create the 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 [$Me_2O^{•+}$/formaldehyde] and [oxetane radical cation/water] complexes as the intermediates responsible for scrambling. The distonic ion $^•CH_2OCH_2CH_2OH_2^+$ is generated by unimolecular loss of CH_2O from $CH_3OCH_2OCH_2CH_2OH^{•+}$, 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]



1 **3** (1)



2 **4** (2)

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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Table I. Metastable Fragmentations (MIKES) of Deuterated 2-Methoxyethanol Molecular Ions and Distonic Isomers **6** Compared with Photoionization Results (PIMS[2]) and Statistical Predictions Based upon Complete Scrambling of the Six Hydrogens in the Hydroxyl and CH_3OCH_2 Portion of the Molecule

			[M − water]$^{\bullet+}$ proportions					
precursor structure	no.	[M − formyl]$^+$ obsd *m/z*	58	59	60	61	62	[M − water]$^{\bullet+}$: [M − formyl]$^+$
$HOCH_2CH_2OCH_3$	**1a**	47	1.0					0.37
PIMS			1.0					0.3
statistical			1					
$HOCHDCH_2OCH_3$	**1b**	47:48 = 1.65		>0.98				0.72
statistical				1				
$DOCH_2CH_2OCH_3$	**1c**	48	0.33	0.67				0.32
PIMS			0.4	0.6				0.34
statistical			1/3	2/3				
$HOCD_2CH_2OCH_3$	**1d**	48			>0.98			2.3
PIMS					>0.96			0.84
statistical					1			
$DOCD_2CH_2OCH_3$	**1e**	49			0.33	0.67		3.0
statistical					1/3	2/3		
$HOCH_2CH_2OCD_3$	**1f**	50		0.20	0.60	0.20		0.39
PIMS				0.23	0.57	0.20		0.31
statistical				1/5	3/5	1/5		
$DOCH_2CH_2OCD_3$	**1g**	51			0.42	0.52	0.06	0.37
PIMS					0.42	0.53	0.05	0.29
statistical					2/5	8/15	1/15	
$HOCH_2CD_2OCH_3$	**1h**	49	0.04	0.43	0.53			0.37
statistical			1/15	8/15	2/5			
$DOCH_2CD_2OCH_3$	**1i**	50		0.14	0.56	0.30		0.33
statistical				1/5	3/5	1/5		
$HOCH_2CD_2OCD_3$	**1j**	52				0.61	0.39	0.30
statistical						2/3	1/3	
$DOCH_2CD_2OCD_3$	**1k**	53					>0.98	0.30
statistical							1	
$^{\bullet}CH_2OCH_2CH_2OH_2^+$	**6a**	47	1.0					0.37
$^{\bullet}CH_2OCH_2CH_2OHD^+$	**6b**	48	0.34	0.66				0.39
$^{\bullet}CH_2OCH_2CD_2OH_2^+$	**6c**	48			>0.98			2.3
$^{\bullet}CH_2OCH_2CD_2OHD^+$	**6d**	49			0.34	0.66		1.5

wise specified, ICR experiments were performed by injecting reactant ions into a cell containing 5×10^{-8} Torr of neutral reactant from an external source followed by specific ejection of unwanted ions and then by a burst of argon from a pulsed valve to relax the ions prior to reaction.[5] Commercially available chemicals were used without further purification. Carbon-deuterated analogues of ethylene glycol and 2-methoxyethanol were purified by GLPC on a 3 m × $^1/_4$ in. Carbowax 20M column. Oxygen-deuterated molecules were formed in the source of the mass spectrometer by exchange with added D_2O. 2-(Methoxymethoxy)ethanol (**5a**) was prepared by $LiAlH_4$ reduction of methyl (methoxymethoxy)-acetate, which had been prepared from methyl glycolate and chloromethyl methyl ether. Deuterated analogue **5c** was prepared in the same fashion by reduction with $LiAlD_4$. The labeled 2-methoxyethanol **1b** was prepared by reduction of methoxyacetaldehyde with $NaBD_4$. Deuterated analogue **1f** was prepared by base-promoted O-methylation of methyl glycolate with CD_3I, followed by reduction with $LiAlH_4$. Analogues **1h** and **1k** were prepared by methylation of **5c** followed by acid-catalyzed removal of the methoxymethyl group. Compounds **1d** and **2c** were prepared as previously described.[2,6] Partially deuterated methanols were prepared by reduction of formic acid or gaseous formaldehyde with $LiAlD_4$ and purified by GLPC. Dimethyl ether-d_1 was prepared by reduction of bromomethyl methyl ether with $LiAlD_4$ and twice distilled before use. CD_3OCH_3 was prepared by reaction of CD_3OH with iodomethane in the presence of base.

Results

Metastable Ion Experiments. In order to approximate the low internal energies of the published 122-nm (Lyman α) photoionization mass spectra of 2-methoxyethanol,[2] metastable ion transitions of the molecular ions from 70-eV electron impact were examined using a mass spectrometer with reverse Nier-Johnson geometry. Two dominant processes, explusion of formyl radical (eq 1) and water loss, are seen in both the Lyman α and the metastable mass spectra. Unlabeled 2-methoxyethanol **1a** yields *m/z* 46 as the third most intense peak, $^1/_{200}$th the intensity of M − CHO (*m/z* 47). Under the more energetic conditions of collisionally activated decomposition (CAD), the elimination of CH_2OH is also observed (in both **1a** and **2a**).

Where possible, structures of the products of metastable ion transitions were determined by CAD of peaks that correspond to nonintegral masses in the first (magnetic) sector of the double-focusing instrument. The CAD of the M − H_2O ion from metastable **1a** shows the same pattern as does ionized oxetane. By comparison with the CAD spectra of authentic samples of oxetane and methyl vinyl ether (which are very different from one another[7]), we can rule out the formation of any ionized methyl vinyl ether in the *m/z* 76 → *m/z* 58 metastable transition. By the same method we confirm that formyl radical expulsion leads to protonated dimethyl ether for ion **1** and to protonated methanol for ion **2**.

Table I compares the mass-analyzed ion kinetic energy spectra (MIKES) for isotopic analogues of **1**. A C–H of the CH_2OH group is specifically retained in the eliminated formyl radical both in **1** and in **2**, while an exchange among six hydrogen atoms precedes water elimination and, under CAD conditions, CH_2OH loss from **1**. The scrambling between the hydroxylic and methyl hydrogens has been proposed to take place via a distonic ion. Since expulsion of formaldehyde from methoxy compounds is a well-known way of producing distonic ions,[6] we have examined the ion resulting from expulsion of CH_2O from compound **5** and its deuterated analogues. The putative distonic ion, **6**, is drawn in eq 3 as a mixture of equilibrating tautomers. The MIKES of **6**, summarized in Table I, is nearly the same as that of methyl cellosolve: **6b–d** being very similar to **1c–e**, respectively.

The structures of the products of eqs 1 and 2 were investigated by CAD of fragment ions from metastable precursors. Ten deuterated analogues of methyl cellosolve were examined and the fragments corresponding to CHO loss compared with labeled protonated ethers. Authentic samples of these latter ions have

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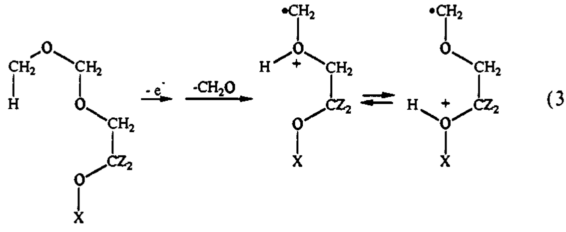
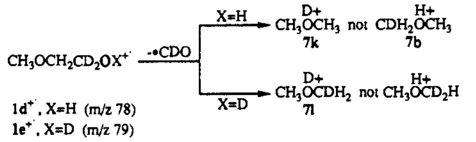


(3)

5a X=Z=H
5b X=D, Z=H
5c X=H, Z=D
5d X=Z=D

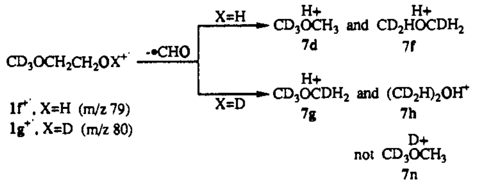
6a X=Z=H
6b X=D, Z=H
6c X=H, Z=D
6d X=Z=D

been generated either by chemical ionization of dimethyl ethers with water or from proton-bound dimers of labeled methanol (which can be produced in the source of the mass spectrometer). Expulsion of H_2O (or D_2O) from these proton-bound dimers leads, without scrambling, to the corresponding protonated dimethyl ethers. Pertinent features of the CAD spectra are listed in Table II, and the corresponding features of the CAD spectra of the fragment ions obtained from metastable ionized, labeled 2-methoxyethanols are summarized in Table III. The interpretation of the data is represented by eqs 4–6.



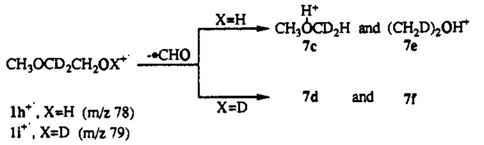
$$\mathrm{CH_3OCH_2CD_2OX^{+\cdot}} \xrightarrow{-\bullet\mathrm{CDO}} \begin{cases} \xrightarrow{X=H} \underset{\mathbf{7k}}{\mathrm{CH_3\overset{D+}{O}CH_3}} \text{ not } \underset{\mathbf{7b}}{\mathrm{CDH_2\overset{H+}{O}CH_3}} \\ \xrightarrow[X=D]{} \underset{\mathbf{7l}}{\mathrm{CH_3\overset{D+}{O}CDH_2}} \text{ not } \mathrm{CH_3\overset{H+}{O}CD_2H} \end{cases} \quad (4)$$

1d$^{+\cdot}$, X=H (m/z 78)
1e$^{+\cdot}$, X=D (m/z 79)



$$\mathrm{CD_3OCH_2CH_2OX^{+\cdot}} \xrightarrow{-\bullet\mathrm{CHO}} \begin{cases} \xrightarrow{X=H} \underset{\mathbf{7d}}{\mathrm{CD_3\overset{H+}{O}CH_3}} \text{ and } \underset{\mathbf{7f}}{\mathrm{CD_2H\overset{H+}{O}CDH_2}} \\ \xrightarrow[X=D]{} \underset{\mathbf{7g}}{\mathrm{CD_3\overset{H+}{O}CDH_2}} \text{ and } \underset{\mathbf{7h}}{\mathrm{(CD_2H)_2OH^+}} \\ \qquad \text{not } \underset{\mathbf{7n}}{\mathrm{CD_3\overset{D+}{O}CH_3}} \end{cases} \quad (5)$$

1f$^{+\cdot}$, X=H (m/z 79)
1g$^{+\cdot}$, X=D (m/z 80)



$$\mathrm{CH_3OCD_2CH_2OX^{+\cdot}} \xrightarrow{-\bullet\mathrm{CHO}} \begin{cases} \xrightarrow{X=H} \underset{\mathbf{7c}}{\mathrm{CH_3\overset{H^+}{O}CD_2H}} \text{ and } \underset{\mathbf{7e}}{\mathrm{(CH_2D)_2OH^+}} \\ \xrightarrow[X=D]{} \mathbf{7d} \text{ and } \mathbf{7f} \end{cases} \quad (6)$$

1h$^{+\cdot}$, X=H (m/z 78)
1i$^{+\cdot}$, X=D (m/z 79)

Because extensive exchange takes place between the hydroxylic and methyl hydrogens of the molecular ion of 2-methoxyethanol, the isotopic analogue **1d**, in which such exchange does not scramble in label, was chosen to determine the sites to which double hydrogen transfer occurs. The CAD of the M − CDO ion from metastable **1d**$^{\bullet+}$ was examined, and for purposes of comparison, the CADs of authentic samples of the dimethyl ether conjugate acids **7b** and **7k** were also recorded. The CAD of the fragment from the metastable precursor (m/z 78 → m/z 48) is nearly identical to the CAD of ion **7k**. Ion **7b** shows, among other features, equally intense peaks at m/z 15 and 16, while **7k** exhibits an m/z 15 that is 5 times more intense than m/z 16. In the same fashion the d_6-labeled 2-methoxyethanol **1k** produces $(CD_3)_2OH^+$ (**7j**) as the only detectable isomer from metastable formyl loss. A corresponding migration pattern is seen in the O-deuterated d_1 analogue **1c**. Here the deuterium is expected to scramble with other hydrogens, but the reaction produces **7b** regardless. The CAD spectrum of the M − CHO fragment from metastable **1c**$^{\bullet+}$ (m/z 77 → m/z 48) is the same as that of **7b** and contains no **7k** within our experimental limits of detection.

To gauge the extent of isotopic exchange prior to formyl radical expulsion, the CAD spectra of metastably generated fragments from the two d_3 analogues were examined. The m/z 50 fragments from metastable **1f**$^{\bullet+}$ and **1i**$^{\bullet+}$ yield superimposable CAD spectra. If there were only the exchange between hydroxy and methyl hydrogens, both ions would yield products **7d** and **7f** in a statistical ratio of 1:3. If there were complete exchange between the hydroxy and all of the hydrogens in the CH_3OCH_2 portion of the molecule, then the two isomeric protonated dimethyl-d_3 ethers would be formed in a statistical ratio of 1:9. The experimental data are consistent with the latter ratio. Similar conclusions can be drawn from the CAD spectra of labeled fragment ions formed in the ion source.

Formyl loss has also been investigated in the deuterated ethylene glycols **2**. The resulting protonated methanols are observed as the only fragments in the MIKES. The structures of the ions from the isotopomers **2b** and **2c** were determined by comparing the CAD spectra of the fragment ions from metastable precursors ions with the CAD of authentic samples of the appropriate methanol conjugate acids. As eq 7 portrays, the pattern of double H transfer is the same as in 2-methoxyethanol.

$$\begin{aligned} &\underset{\mathbf{2b}}{\mathrm{DOCH_2CH_2OD^{+\cdot}}} \xrightarrow{-\bullet\mathrm{CHO}} \underset{m/z\ 35}{\mathrm{CH_2DOHD^+}} \text{ not } \mathrm{CH_3OD_2^+} \\ &\underset{\mathbf{2c}}{\mathrm{HOCD_2CD_2OH^{+\cdot}}} \xrightarrow{-\bullet\mathrm{CDO}} \underset{m/z\ 36}{\mathrm{CD_2HOHD^+}} \text{ not } \mathrm{CD_3OH_2^+} \end{aligned} \quad (7)$$

ICR Studies. We now ask if there is any ion–molecule reaction that yields the same products as the decomposition of **1**$^{\bullet+}$. If so, that result would give credence to the claim that ion–neutral complexes are intermediates in the unimolecular reaction.[8] Several ion–molecule reactions have been examined. Reactions of dimethyl ether and formaldehyde were investigated in the pressure range 10^{-8}–10^{-7} Torr. At low ionizing energies, the molecular ion of dimethyl ether reacts with its parent neutral exclusively to form protonated dimethyl ether.[6] Ionized dimethyl ether is the only ion initially formed by 10-eV electron impact on a mixture of dimethyl ether and formaldehyde, and subsequent ion–molecule reactions produce a mixture of methoxymethyl cation (m/z 45) and protonated dimethyl ether (m/z 47).

Because it is not possible to discern the origin of protonated dimethyl ether under those reaction conditions, another set of experiments was performed in which ionized dimethyl ether was injected from an external source into the ICR cell containing only formaldehyde. With a pressure of 5×10^{-8} Torr of formaldehyde in the cell, the reaction proceeds essentially to completion within a few seconds and yields m/z 45 and m/z 47 among the observed products in a ratio (extrapolated to zero time) of approximately 5:1. No m/z 58 ion is detected. With CD_2O as the target, no exchange to form $CH_3OCH_2D^{\bullet+}$ is observed, nor is there any $CH_3O(D)CH_2D^+$ (m/z 49) or CH_3OCHD^+ or $CH_2DOCH_2^+$ among the reaction products. The m/z 45 product still predominates, and the product corresponding to m/z 47 is now seen at m/z 48.

When ionized CD_3OCH_3 (m/z 49) is injected into formaldehyde, the parent ion disappears completely at long reaction times and is not replaced by any isobaric m/z 49 ion (except for the natural abundance ^{13}C satellite of $CD_3OCH_2^+$), showing that there is no exchange between the hydrogens of dimethyl ether radical cation and those of formaldehyde in the course of hydrogen atom abstraction. The product corresponding to m/z 45 is now observed as a pair of ions at m/z 47 and m/z 48 in the ratio 1:1.3. We assign the structures $CH_3OCD_2^+$ and $CD_3OCH_2^+$ to these products on the basis of high-resolution mass measurement. The protonated parent is also seen, which suggests that the intermediacy of ion–neutral complexes of the form [dimethyl ether radical cation/formaldehyde] must be considered.

An alternative hypothesis would involve the intervention of complexes between $^\bullet CH_2OH_2^+$ and oxirane. ICR studies exclude this option, since the only ion–molecule reaction detected (>98%) between these two partners is proton transfer from $^\bullet CH_2OH_2^+$ (generated from glycolic acid by loss of CO_2 from its molecular ion[9]) to oxirane.

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Table II. Proportions of Pertinent Fragment Ions in the Collisionally Activated Decomposition Mass Spectra of Deuterated Dimethyl Ether Conjugate Acid Ions from Various Precursors

			m/z					
precursor	no.	method	14	15	16	17	18	19
$CH_3OH^+CH_3$	**7a**	a	15	82	3			
		b	15	82	3			
$CH_3OH^+CDH_2$	**7b**	a	11	41	45	3		
		b	11	43	43	3		
$CH_3OH^+CD_2H$	**7c**	b	12	37	14	34	3	
$CH_3OH^+CD_3$	**7d**	a	7	27	13	7	45	1
		b	8	25	14	8	43	2
$CDH_2OH^+CDH_2$	**7e**	b	7	13	75	5		
$CDH_2OH^+CD_2H$	**7f**	b	6	11	39	40	4	
$CDH_2OH^+CD_3$	**7b**	b	5	7	37	9	37	5
$CD_2HOH^+CD_2H$	**7h**	b	6	8	21	61	4	
$CD_2HOH^+CD_3$	**7l**	b	4	4	14	38	39	1
$CD_3OH^+CD_3$	**7j**	b	4		14	1.5	80	0.5
$CH_3OD^+CH_3$	**7k**	a	16	78	6			
		b	15	79	6			
$CH_3OD^+CDH_2$	7l	a	12	38	40	5	5	
		b	12	38	40	5	5	
$CH_3OD^+CD_2H$	**7m**	b	12	36	14	35	3	
$CH_3OD^+CD_3$	7n	a	9	31	11	4	45	
		b	9	27	14	7	43	
$CDH_2OD^+CDH_2$	**7o**	b	9	17	64	7	3	
$CDH_2OD^+CD_2H$	**7p**	b	8	13	36	39	4	
$CDH_2OD^+CD_3$	**7q**	b	9	9	41	5	35	1
$CD_2HOD^+CD_2H$	**7r**	b	7	11	13	62	6	1
$CD_2HOD^+CD_3$	7s	b	8	6	15	31	39	1

[a] From chemical ionization of the corresponding dimethyl ether. [b] From the proton-bound dimer of the corresponding methanol.

Table III. Collisionally Activated Decomposition (CAD) Spectra of [M − Formyl]$^+$ Ions from Metastable Decompositions of Labeled 2-Methoxyethanol Molecular Ions

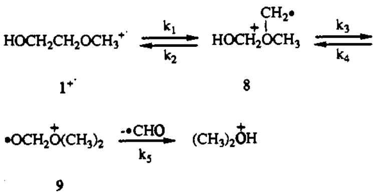
	m/z						
precursor	14	15	16	17	18	19	structure
1a		15	82	3			**7a**
1c		8	40	49	3		>0.95 **7b**
1d		16	77	7			>0.95 **7k**
1e		8	43	45	4		>0.95 7l
1f	4	12	34	41	9		0.9 **7f** + 0.1 **7d**
1g	5	6	27	38	22	2	0.6 **7h** + 0.4 **7g**
1h	8	23	46	21	2		0.6 **7e** + 0.4 **7c**
1i	3	10	34	42	9	2	0.9 **7f** + 0.1 **7d**
1j	2	3	10	43	42		>0.95 7l

Finally, we note that a third hypothesis, complexes of the form [oxetane radical cation/water], is ruled out by the fact that the molecular ion of oxetane does not react with water in the ICR to give the products observed from $1^{\bullet+}$. Oxetane radical cation (*m/z* 58) reacts with water to yield H_3O^+ (*m/z* 19), $C_3H_5O^+$ (*m/z* 57), and an isomeric *m/z* 58 ion that is much less reactive. With D_2O, we observe D_2OH^+ (which goes on to exchange with neutral D_2O to give D_3O^+). The product corresponding to *m/z* 57 in the H_2O experiment is a mixture of $C_3H_5O^+$ and $C_3H_4DO^+$ (*m/z* 58), and the isomerized starting material corresponds to a mixture of $C_3H_6O^{\bullet+}$ (*m/z* 58) and $C_3H_5DO^{\bullet+}$ (*m/z* 59). These ions are produced in an approximate ratio *m/z* 57:*m/z* 58:*m/z* 59 = 0.2:1:0.5 after 10-s reaction time with a D_2O pressure of 5×10^{-8} Torr. Use of a pulsed valve to relax the reactant ion permits the argon pressure to drop sufficiently during the reaction period that high resolution can be performed on the product ions, and the *m/z* 58 product contains 30–40% $C_3H_4DO^+$. The isomerized molecular ions do not react further with D_2O. Authentic samples of ionized propionaldehyde or methyl vinyl ether also do not react with D_2O under the reaction conditions, giving ≥1% $C_3H_5DO^{\bullet+}$ after a reaction time of 10 s.

Two $C_3H_5O^+$ isomers have low enough heats of formation to be formed by collision of oxetane radical cation with water: $CH_3CH_2C{\equiv}O^+$ or protonated acrolein (see Table IV in the Appendix). The latter would be expected to transfer a proton to diethyl ether, whose proton affinity is 26 kJ mol^{-1} greater than that of acrolein. When oxetane radical cation is injected into an ICR cell containing water vapor, allowed to react for 10 s, and then followed by a burst of ether from a pulsed valve (in lieu of a pulse of argon prior to the reaction with water), *m/z* 58 reacts completely (as would be expected, regardless of its structure) but unreacted *m/z* 57 ion remains. We conclude that *m/z* 57 has the more stable $CH_3CH_2C{\equiv}O^+$ structure and infer that oxetane radical cation isomerizes to propionaldehyde radical cation within [oxetane radical cation/water] complexes.

Discussion

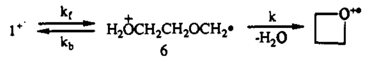
Expulsion of formyl radical from ionized ethylene glycol and its monomethyl ether, 2-methoxyethanol, involves the same net reaction. Double hydrogen transfer leads to migration of a hydroxylic hydrogen to carbon, while a hydrogen initially bound to carbon ends up attached to oxygen. This stands in contrast to previously proposed mechanisms[2,3] based upon proton-bridged complexes, which imply the transpositions of hydrogen from oxygen to oxygen and from carbon to carbon.



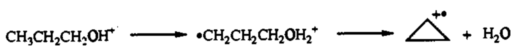
(8)

As will be discussed below, the heat-to-tail relationship indicated by the present results is consistent with the intermediacy of distonic ions **8** and **9** as eq 8 represents. This does not mean that proton-bridged complexes cannot be formed by unimolecular ion decompositions. Published calculations[3] and chemical intuition both suggest that they enjoy considerable stabilization. Our results, however, suggest that the reactive geometry is different. The low-energy products—the conjugate acid ions of methanol (from ethylene glycol) and of dimethyl ether (from methyl cellosolve)—are formed by a process that not only cleaves the central C–C bond but also requires the rotation of one fragment with respect to the other.

The First Hydrogen-Exchange Process. Expulsion of formyl is the only reaction observed in the metastable mass spectrum of ethylene glycol, while water loss is a competing process in its monomethyl ether. Because of the insight to be gained by studying this competition, we have focused on 2-methoxyethanol. The absence of water loss from ethylene glycol and the absence of methyl vinyl ether ions among the products of metastable water loss from methyl cellosolve lead us to infer that distonic ions are not formed at low internal energies by intramolecular hydrogen transfer via 4-membered cyclic transition states. The loss of water is presumed to result from the distonic ion **6**, as depicted in eq 9, whose intermediacy was proposed in the initial photoionization study.[2] Direct formation of several isotopomers of **6** are generated from **5a–d**, and these give the same MIKES as the corresponding isotopomers of $\mathbf{1}^{\bullet+}$. The tautomer of **6** drawn in eq 9 bears a resemblance to the distonic intermediate proposed for water loss observed in metastable 1-propanol ions[10] (eq 10). For the purposes of kinetic discussion, the net rate constant for water loss can be expressed as $k_6 = kk_f/(k_f + k_b)$.



(9)



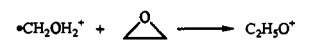
(10)

The metastable ion results agree qualitatively with the previously published photoionization results, which showed that the hydroxylic hydrogen equilibrates with the methoxy hydrogens (in other words, k_f and k_b are fast relative to the other rate constants). Unlike the distonic ion portrayed in eq 10, **6** forms reversibly from its precursor. It was reported that scrambling of the hydrogens on the methoxy-bearing methylene takes place more slowly than expulsion of water,[2] and we find here that is extensive but does not proceed to completion. No exchange of the hydrogens attached to the hydroxyl-bearing carbons is detected, neither in methyl cellosolve nor in ethylene glycol.

The Second Hydrogen-Exchange Process. The exchange among six hydrogens in the 2-methoxyethanol radical cation requires a second process in addition to the formation of **6**. As noted above, we consider the distonic intermediate $CH_3O\dot{C}HCH_2OH_2^+$ to be unlikely at low internal energies. In principle, scrambling could occur via any structure that renders two (and only two) carbons chemically equivalent. We can rule out the isomerization of 2-methoxyethanol ions to those of 1,3-propanediol or dimethoxymethane, since the mass spectra of these compounds differ from that of 2-methoxyethanol.

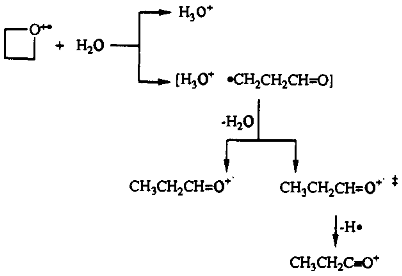
We now consider the alternative of ion–neutral complexes. A major supposition of a complex-mediated mechanism is that if one can create the same complex by another pathway, the same products ought to be observed.[8] One tempting option is to produce complexes involving the same partners by bimolecular, ion–molecule collisions. There are two conceivable drawbacks to this approach. First, the energy of an ion–molecule collision is often greater than the energy content of a complex formed by unimolecular dissociation. Second, the rotational angular momentum distribution differs considerably between the two regimes. It is not too drastic an approximation to say that the mean separation between two fragments increases with the overall total angular momentum (which is usually greater in the bimolecular than in the unimolecular case). Nevertheless, with these caveats in mind we can still inquire whether there are ion–molecule reactions that mimic the decomposition pathways of 2-methoxyethanol.

We consider three complexes whose intermediacy could account for the scrambling observed in deuterated 2-methoxyethanols. The first of these is the complex of oxirane with $^\bullet CH_2OH_2^+$. The energy of these separated species is more than 200 kJ mol^{-1} (>50 kcal mol^{-1}) higher than the heat of formation of $\mathbf{1}^{\bullet+}$. Moreover, the only reaction seen between these two fragments in the ICR is proton transfer, eq 11, to yield a product that is not observed in the metastable decomposition of $\mathbf{1}^{\bullet+}$.



(11)

The second possible complex contains two of the products of a major decomposition pathway: oxetane radical cation and water. However, the reaction of oxetane radical cation with water in the ICR does not yield the fragmentation products of 2-methoxyethanol radical cation. When these two reactants undergo ion–molecule collisions in the ICR, oxetane radical cation undergoes an exothermic rearrangement to an isomeric ion (eq 12) in competition with proton transfer and hydrogen loss. We interpret the experimental results in terms of an isomerization of oxetane radical cation to propionaldehyde radical cation induced by collision with water, for which eq 12 portrays a possible pathway. Reaction of oxetane radical cation with D_2O shows that isotopic exchange accompanies the isomerization (as expected on the basis of eq 12), and we observe $C_3H_6O^{\bullet+}$ and $C_3H_5DO^{\bullet+}$ in approximately equal proportions. Since $[M - H_2O]^+$ ion from metastable decomposition of $\mathbf{1}^{\bullet+}$ is oxetane radical cation, we conclude that the displacement in eq 9 leads to prompt expulsion of water and that the neutral does not linger to form a complex.



(12)

The last complex-mediated mechanism supposes that an ion–neutral complex of the form $[CH_3OCH_2^+/^\bullet CH_2OH]$, created by rupture of the C–C bond in $\mathbf{1}^{\bullet+}$, isomerizes to $[(CH_3)_2O^{\bullet+}/CH_2O]$. In this hypothesis the exchange prior to water loss requires that the first complex form reversibly from $\mathbf{1}^{\bullet+}$ and that the two complexes interconvert. Interconversion of two such complexes is not implausible (especially since the latter complex may occur as a transient en route to $CHO^\bullet$ loss), but the experimental evidence does not support the contention that the complex can revert to $\mathbf{1}^{\bullet+}$. Such a complex could account for the high yield of methoxymethyl cation in the photoionization of **1f**, in which isotopic label appears to have been scrambled, since ionized dimethyl ether reacts with formaldehyde to form methoxymethyl cation (and hydroxymethyl radical) as well as protonated dimethyl ether (and formyl radical). The former reaction is unusual, in that it represents the transfer of a hydrogen atom from a cation radical to a neutral molecule. However, no ion corresponding to oxetane radical cation is produced by the ion–molecule reaction, while such a product is produced by photoionization under similar energetic conditions.[11]

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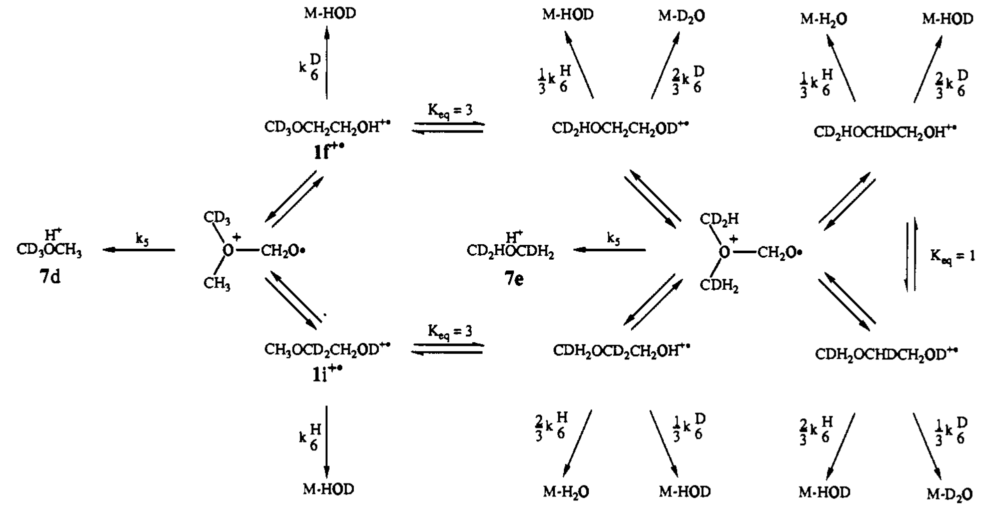
(10) Bowen, R. D.; Colburn, A. W.; Derrick, P. J. *J. Am. Chem. Soc.* **1991**, *113*, 1132–1137.

(11) Separated $Me_2O^{\bullet+}$ and CH_2O have an energy corresponding to $\mathbf{1}^{\bullet+}$ with an internal energy of about 1 eV. We have available the ion yields from $\mathbf{1}^{\bullet+}$ at two photon energies, 10.2 and 11.5–11.7 eV (ref 2, Figure 2). The photon energy of interest is between these two energies. We use the published slopes between the two photon energies to get a rough approximation of the ion yields from $\mathbf{1}^{\bullet+}$ when it has the same internal energy as the $[Me_2O^{\bullet+}\text{-}CH_2O]$ complex produced by the ion–molecule reaction in the ICR. From this calculation we should expect that m/z 58 ought to have composed more than 5% of the ion yield from $Me_2O^{\bullet+} + CH_2O$ in the ICR experiment if that reaction and $\mathbf{1}^{\bullet+}$ passed through a common intermediate. Experimentally, m/z 58 is not observed in the ICR experiment within our detection limits (1% of the most intense peak).

Scheme I



These results can be interpreted in either of two ways. It could be that the same type of ion–neutral complex is formed in both experiments, but the overall angular momentum of the complex formed in the ICR is large enough to prevent recombination leading to $1^{•+}$. Or else the unimolecular decompositions of $1^{•+}$ do not proceed via ion–neutral complexes but via distonic ions. Even though we cannot totally exclude the former interpretation, the latter seems more plausible for three reasons. It accounts for all of the experimental results. Moreover, heats of formation can be estimated for **8** and **9** (see Appendix), which place them within an accessible range. Finally, the interconversion **8** ⇄ **9** is a simple internal hydrogen transfer via a 5-membered cyclic transition state.

If hydrogen permutation in the low-energy decomposition of 2-methoxyethanol cannot be explained by reversible formation of ion–neutral complexes, we must interpret the isotopic scrambling results in terms of the distonic ions **6**, **8**, and **9**. Scheme I illustrates the implications of such a mechanism for several d_3 analogues. The distonic ions corresponding to **6** and **8** are not shown, to save space, and the rate constants k_1–k_5 are omitted. Experimentally we observe that **1f** and **1i** yield the same proportions of protonated CD_3OCH_3 and CD_2HOCDH_2, but different proportions of M − H_2O and M − D_2O. If the rate constants corresponding to k_4 in eq 8 are much larger that k_5, then we expect a **7e**:**7d** product ratio of 9:1, which is not significantly different from the experimental value. If k_5 were much larger than k_4, the two d_3 precursors would both give the protonated dimethyl-d_3 ether isomers in a ratio of 3:1.

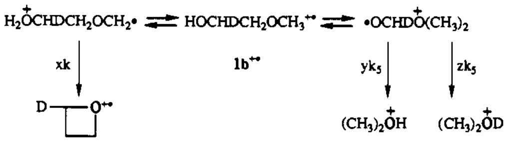
Isotope Effects. We discuss now isotope effects and relative timing of the steps in the decompositions of methyl cellosolve. Since deuteration of all of the six exchanging positions in **1k** does not greatly affect the [M − water]:[M − formyl] ratio, we conclude that $k^H{}_6/k^D{}_6$ cannot be very large. It seems less likely that there are large offsetting isotope effects that fortuitously cancel (for example, a primary isotope effect on k_3 that balances the effect of k_6), since there is not much variation of the product ratio in the deuteration series **1a**,**c**,**f**–**g**. The lack of a significant primary isotope effect for the H migration leading to H_2O loss is in agreement with the reversibility of the reaction **1** ⇄ **6** shown by hydrogen exchange. This strongly suggests that the ring closure with water expulsion is the final step in water loss.

In a similar fashion we conclude that the transfer of hydrogen from carbon to oxygen is the final step in formyl loss. The substantial isotope effect on the [M − water]:[M − formyl] ratio from **1d** and on the [M − CDO]:[M − CHO] ratio from **1b** implies that this hydrogen migration is considerably slower than the steps corresponding to k_3 and k_4.

In short, our arguments regarding the timing of steps are as follows. A hydroxylic and a methylene hydrogen migrate from the CH_2OH moiety to yield the M − formyl fragment ion. The hydroxylic hydrogen scrambles completely with all of the hydrogens of the CH_3OCH_2 moiety beforehand and is ultimately transferred to carbon. Therefore, this transfer step must be reversible. If we assume that the same process gives rise to the scrambling prior to both spontaneous fragmentations of $1^{•+}$ in the MIKES, it is difficult to conceive of a mechanism that does not convert the intermediates responsible for scrambling back to the molecular ion. On the other hand, this confirms that the migration from carbon to oxygen must be the second hydrogen-transfer step in formyl loss; otherwise, the isotope effect would have been washed out by interconversion with the molecular ion.

With regard to water loss, the scrambling of the hydroxyl with the methylene of the CH_2OCH_3 moiety is extensive but partial prior to water loss, while the scrambling with the methyl is complete. This means that the steps with rate constants k_f and k_b are very fast, and they shall be treated as a preequilibrium (for which we assume that the equilibrium constants $K_{eq} = k_f/k_b$ exhibit small isotope effects and have the values predicted by simple statistics). The interconversion steps corresponding to k_1 and k_2 are not that fast; otherwise, **1f** and **1i** would have given the same H_2O:HOD:D_2O ratios. Therefore, we infer that all of the steps are fast except those corresponding to k, k_1, k_2, and k_5. The departure of water corresponding to k is prompt, since we see none of the products expected from its subsequent reaction of oxetane radical cation with water. We believe, instead, that there must be at least three barriers of comparable height, as drawn schematically in Figure 1. While it would have been simpler to portray the mechanism in terms of a single rate-determining step corresponding to each product, the experimental data do not support such an interpretation.[12]

If we were to suppose product formation to be rate-limiting, some relative isotope effects could be extracted from the experimental data without recourse to a steady-state approximation. Substitution of the hydroxyl-bearing methylene would affect the final, irreversible steps for water loss (rate constant k) and formyl loss (rate constant k_5) much more than the preceding reversible steps. We could then consider only the secondary isotope effect on water expulsion ($k_H/k_D = 1/x$), the secondary isotope effect on hydrogen transfer ($k_H/k_D = 1/y$), and the primary isotope effect on hydrogen transfer ($k_H/k_D = 1/z$), as represented in eq 13.



(13)

We have two pertinent data available from the MIKES of **1b**$^{•+}$, the ratio [M − water]:[M − formyl] = 0.72, relative to the value of that ratio for **1a**$^{•+}$, for which we would write $2x/(y + z)$ = 0.72/0.30; and the ratio $(CH_3)_2OH^+$:$(CH_3)_2OD^+$ = y/z = 1.65.

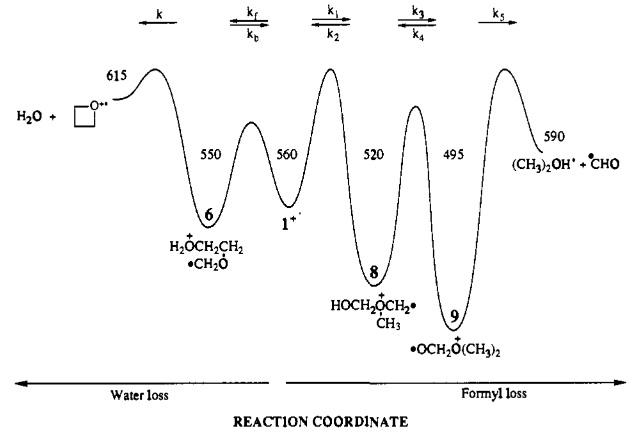


Figure 1. Estimated heats of formation for distonic intermediates (±20 kJ mol^{-1}) in the low-energy decompositions of 2-methoxyethanol molecular ion, $\mathbf{1}^{\bullet+}$, and literature values for $\Delta H_f°(g)$ of the final products (kJ mol^{-1}).

From these we solve to get $x/z = 3.20$ and $x/y = 1.92$ and check the accuracy of this calculation by using it to predict the fragment ion ratio for $\mathbf{1d}^{\bullet+}$. Here we would assume that the rate constant for the water expulsion step is x^2k and that the primary and secondary isotope effects for hydrogen transfer are multiplicative, so that the rate constant for the formyl expulsion step is $2yzk_5$. The predicted [M = water]:[M − formyl] ratio for $\mathbf{1d}^{\bullet+}$ relative to that for $\mathbf{1a}^{\bullet+}$ would be $x^2/yz = (3.20)(1.92) = 6.2$, while the experimental value is 8. The discrepancy between the calculated and experimental values conveys a sense of the influence of having at least one internal barrier comparable to the barriers for the final steps of product formation.

Conclusion

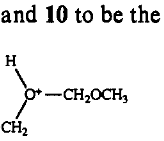
At low internal energies $\mathbf{1}^{\bullet+}$ has two major decomposition pathways and $\mathbf{2}^{\bullet+}$ has only one. The pathway that $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ share in common is formyl expulsion, which yields the conjugate acids of dimethyl ether and methanol, respectively. Examination of the distribution of deuterium in the ions from isotopically labeled precursors shows that CH_2OH methylenes undergo no hydrogen exchange but that every other type of hydrogen in $\mathbf{1}^{\bullet+}$ scrambles intramolecularly. The other major product from $\mathbf{1}^{\bullet+}$ is oxetane radical cation, and scrambling takes place prior to the water expulsion that forms it.

Three general sorts of stepwise mechanisms are considered in the decomposition of $\mathbf{1}^{\bullet+}$:those involving distonic ions (covalently bound), proton-bound complexes (hydrogen bonded), or ion–neutral complexes (electrostatically bound). Proton-bound complexes corresponding to stable structures might be formed; however, they are not intermediates in the isomerization/dissociation process. An ion–neutral complex of the form [$Me_2O^{\bullet+}$/formaldehyde] might occur en route to formyl loss, and therefore might be a transient intermediate, but there is no experimental evidence that such a complex interconverts with the molecular ion structure $\mathbf{1}^{\bullet+}$.

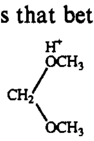
Distonic ion **6** made by a separate reaction gives the same chemistry as $\mathbf{1}^{\bullet+}$. This intermediate was proposed in the original photoionization study, and the present work affirms its equilibration with $\mathbf{1}^{\bullet+}$. Some of the isotopic scrambling cannot be explained by **6** and went unremarked in the photoionization study. Involvement of the methylene hydrogens of the CH_3OCH_2 in intramolecular isotopic exchange can be most easily explained by the intermediacy of distonic ions **8** and **9**. The interconversions $\mathbf{1}^{\bullet+} \rightleftarrows \mathbf{6}$ and $\mathbf{1}^{\bullet+} \rightleftarrows \mathbf{8} \rightleftarrows \mathbf{9}$ account for experimental results. Our conclusion that distonic intermediates offer the most parsimonious explanation leaves out, of course, mechanisms that are yet unimagined or which might have mistakenly been dismissed from consideration a priori. The present work shows that the most stable structures of an ion do not necessarily correspond to reactive intermediates in the decomposition pathway.

Appendix

Estimates of heats of formation of distonic intermediates are referenced to the distonic ion **10** (which does not intervene in the decomposition of 2-methoxyethanol radical cation, but whose $\Delta H°_f$ can be estimated as discussed below). We make three assumptions. First, we estimate the difference between the heats of formation of **8** and **10** to be the same as that between protonated methylal,



10



11

$(CH_3)_2\overset{+}{O}CH_2OH$

12

11, and its isomer **12**. This approximation assumes that the bond dissociation energy of a methyl C–H geminal to a positively charged, 3-coordinate oxygen is the same for both compounds.[14] Second, we suppose that the difference between the proton affinities of dimethyl ether[15] and methylal, PA(Me_2O) − PA($MeOCH_2OMe$), is the same as the difference between the methyl cation affinities of dimethyl ether[16] and methoxymethanol, MCA(Me_2O) − MCA($MeOCH_2OH$).

Third, we make use of the method of group equivalents, which states that the difference in heats of formation, ΔH_f($MeOCH_2OMe$) − ΔH_f(Me_2O), is equal to the difference ΔH_f($MeOCH_2OH$) − ΔH_f(MeOH). Given these three assumptions, we estimate the thermodynamic difference between **8** and **10** to be $\Delta H_f(\mathrm{MeOH}) + \Delta H_f(\mathrm{CH_3^+}) - \mathrm{MCA}(\mathrm{Me_2O}) - \Delta H_f(\mathrm{Me_2O}) - \Delta H_f(\mathrm{H^+}) + \mathrm{PA}(\mathrm{Me_2O}) = -202 + 1098 - 400 + 184 - 1530 + 804 = -45$ kJ mol^{-1}. In other words, **8** is estimated to be substantially more stable than **10**.

The heat of formation of **10** may be estimated as follows to be nearly equal to the heat of formation of ionized methylal, ΔH_f($MeOCH_2OMe^{\bullet+}$) = 568 kJ mol^{-1}. We assume that the hydrogen atom affinity of ionized methylal is the same as that of 1,3-dioxane, which can be calculated from its proton affinity and ionization potential to be 465 kJ mol^{-1}. The bond dissociation energy of a methyl C–H of protonated methylal is asssumed to be the same as that of protonated methanol, 465 ± 20 kJ mol^{-1}. If we give a hydrogen atom to an oxygen of methylal radical cation and then remove a methyl hydrogen from the resulting protonated methylal to form **10**, the net enthalpy change is close to zero (±20 kJ mol^{-1}). Since, as discussed above, the heat of formation of **8** is 45 kJ mol^{-1} lower than that of **10**, we estimate $\Delta H_f(\mathbf{8})$ = 520 kJ mol^{-1}. If we estimate the OH bond dissociation energy of **8** to be the same as that of simple, un-ionized alcohols (440 kJ mol^{-1}), isomerization of **8** to **9** should be exothermic by approximately −25 kJ mol^{-1} and we estimate $\Delta H_f(\mathbf{9})$ = 495 kJ mol^{-1}. Finally, we estimate the heat of formation of **6** by supposing that the proton affinity of the hydroxyl of non-hydrogen-bonded **1** is the same as that of ethanol and that the methyl C–H bond dissociation energy is the

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(12) In principle, we possess enough experimental data to perform a steady-state analysis of the kinetics to solve for the branching ratios and deuterium isotope effects. In practice, however, a steady-state analysis is not warranted. Previous analyses of MIKES using steady-state solutions of kinetic schemes have been justified by supposing that intermediates, once formed, do not return to the initial molecular ion structures but instead decompose completely to the observed fragment ions.[13] Under conditions where a reaction proceeds to completion, the steady-state approximation is equivalent to the exact solution of the first-order differential equations. In the present case, interconversions between the distonic ions and the original molecular ion are an essential feature of the mechanism, since this provides the means by which methylene hydrogens scramble with methyl hydrogens. Therefore, the reaction cannot be treated as though it has gone to completion.

(13) (a) Kondrat, R. W.; Morton, T. H. *J. Org. Chem.* **1991**, *56*, 952–957. (b) Kondrat, R. W.; Morton, T. H. *Org. Mass Spectrom.* **1991**, *26*, 410–415.

(14) Holmes, J. L.; Lossing, F. P. *Int. J. Mass Spec. Ion Proc.* **1989**, *92*, 111–122.

(15) Unless otherwise specified, thermodynamic values are taken from: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, supp. 1.

(16) (a) Sharma, D. K. S.; Kebarle, P. *J. Am. Chem. Soc.* **1982**, *104*, 19–24. (b) Szulejko, J. E.; Fisher, J. J.; McMahon, T. B.; Wronka, J. *Int. J. Mass Spectrom. Ion Proc.* **1988**, *83*, 147–161. (c) Wang, D.; Squires, R. R.; Farcasiu, D. *Int. J. Mass Spectrom. Ion Proc.* **1991**, *107*, R7-R8.

Table IV. Gas-Phase Heats of Formation (kJ mol^{-1}; Rounded Off to the Nearest 5 kJ mol^{-1}) of Reactants, Intermediates, and Products Discussed in the Text (Except As Discussed in the Appendix, Values Are Taken from Reference 13)

$CH_3OCH_2CH_2OH^{\bullet+}$ ($\mathbf{1}^{\bullet+}$)	560
$^{\bullet}CH_2OCH_2CH_2OH_2^+$ (**6**)	550
$^{\bullet}CH_2O^+(CH_3)CH_2OH$ (**8**)	520
$(CH_3)_2O^+CH_2O^{\bullet}$ (**9**)	495
oxetane radical cation + H_2O	615
$CH_3OCH_3^{\bullet+} + CH_2{=}O$	675
oxirane + $^{\bullet}CH_2OH_2^+$	775
$(CH_3)_2OH^+ + {}^{\bullet}CH{=}O$	590
$CH_3OCH_2^+ + {}^{\bullet}CH_2OH$	620
propionaldehyde$^{\bullet+}$ + H_2O	530
methyl vinyl ether radical cation + H_2O	520
$CH_3CH_2CO^+ + H^{\bullet} + H_2O$	570
protonated acrolein + $H^{\bullet} + H_2O$	620
protonated oxirane + $^{\bullet}CH_2OH$	660

same as that of dimethyl ether. This gives a value slightly lower than that of $\mathbf{1}^{\bullet+}$, $\Delta H_f(\mathbf{6}) = 550$ kJ mol^{-1}. Heats of formation of relevant reactants, products, and intermediates are summarized in Table IV.

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Registry No. **1a**, 109-86-4; **1b**, 138408-76-1; **1c**, 86012-98-8; **1d**, 51255-53-9; **1e**, 138408-77-2; **1f**, 97840-77-2; **1g**, 86012-99-9; **1h**, 51255-54-0; **1i**, 138408-78-3; **1j**, 138408-79-4; **1k**, 138408-80-7; **2b**, 138408-89-6; **2c**, 138408-90-9; **5a**, 4484-61-1; **5b**, 138408-84-1; **5c**, 138408-85-2; **5d**, 138408-86-3; **6a**, 86023-99-6; **6b**, 138408-81-8; **6c**, 138408-82-9; **6d**, 138408-83-0; **7a**, 17009-82-4; **7b**, 138408-91-0; **7c**, 138408-92-1; **7d**, 138408-93-2; **7e**, 138408-94-3; **7f**, 138408-95-4; **7g**, 138408-96-5; **7h**, 138408-97-6; **7i**, 138408-98-7; **7j**, 138408-99-8; **7k**, 131295-07-3; **7l**, 138409-00-4; **7m**, 138409-01-5; **7n**, 138409-02-6; **7o**, 138409-03-7; **7p**, 138409-04-8; **7q**, 138409-05-9; **7r**, 138409-06-0; **7s**, 138409-07-1; **8**, 138408-87-4; **10**, 138408-88-5; methyl (methoxymethoxy)acetate, 50918-08-6; methoxyacetaldehyde, 10312-83-1; methyl glycolate, 96-35-5; oxetane radical cation, 74181-62-7; ethylene glycol, 107-21-1.

Supplementary Material Available: Tabulated CAD spectral data for $C_3H_6O^{\bullet+}$ isomers, isotopic analogues of methanol conjugate acids, and M − formyl ions from **2a–c** (1 page). Ordering information is given on any current masthead page.

A Remarkably Stable Organic Radical Cation: The Distonic Isomer of the Unstable Radical Cation of Dimethyl Propyl Phosphate

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Abstract: A new isomer of the radical cation of dimethyl propyl phosphate has been synthesized in the gas phase by transferring ionized ethylene to trimethyl phosphate. Examination of the dissociation reactions of this ion suggests that it is covalently bound, and has spatially separated radical and charge sites (a distonic ion). In contrast to most known radical cations with a formally localized charge (when using classical valence electron description), this ion is remarkably unreactive toward strong bases, nucleophiles, and reductants. A slow transfer of ionized ethylene is observed for phosphorus nucleophiles only. This reaction is proposed to take place by a radical-type mechanism. These findings contrast sharply with the recent suggestion that distonic ions are expected to be highly reactive toward neutral molecules in the gas phase.

Introduction

Gaseous radical cations with spatially separated radical and charge sites, the so-called distonic ions, have attracted considerable interest during the last nine years.[1] Many distonic ions are thermodynamically as well as kinetically more stable than their conventional counterparts, molecular ions generated by removal of an electron from a stable neutral molecule.[1] However, the current knowledge on the properties of gaseous distonic ions with the charge and radical sites separated by at least one heavy atom is almost exclusively limited to unimolecular reactions. Thus far, bimolecular reactions of four β-distonic ions and one γ-distonic ion (two heavy atoms between the charge and the radical site, when written using the valence electron formalism) have been investigated.[1-5] These ions include two protonated radicals ($^{\bullet}CH_2CH_2NH_3^+$ and $^{\bullet}CH_2CH_2O^+(H)CH_3$),[1,2] and the ring-opened forms of ionized cyclopropane[3] ($^{\bullet}CH_2CH_2CH_2^+$), ionized trimethylene oxide[4] ($^{\bullet}CH_2CH_2O^+{=}CH_2$), and ionized cyclobutanone ($^{\bullet}CH_2CH_2CH_2C{\equiv}O^+$).[5] The results obtained[1-5] suggest that bimolecular reactions predominantly involve the charge site of these ions. Deprotonation dominates the chemistry of the acidic ions (protonated radicals).[1-4] For the ion $^{\bullet}CH_2CH_2O{=}CH_2^+$, addition of the attacking nucleophile to the unsaturated charged center has been proposed to be the initial step in the reactions with acetonitrile and pyridine.[4b]

This study focuses on the synthesis and properties of a novel gaseous distonic ion that does not have acidic functional groups or unsaturation near the charge site. This ion was found to be nearly unreactive toward strong bases, nucleophiles, and reductants, in sharp contrast with the recent suggestion[4b] that distonic ions may be highly reactive in ionic as well as in radical reactions.

Experimental Section

The prototype Extrel FTMS 2001 mass spectrometer used in this study has a differentially pumped 2-in. dual cell aligned collinearly with a magnetic field produced by a 2.8-T superconducting magnet. The dual cell is pumped with two turbomolecular pumps (Balzars TPU 330). The base pressure in both sides of the cell is less than 1×10^{-9} Torr, as measured by an ionization gauge on each side. The trapping plates parallel to the magnetic field were kept at +2 V, including the conductance limit plate separating the two cells. The conductance limit plate was grounded for 100–200 μs when ions were transferred from one side of the dual cell into the other side. Reagents were added to the system

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