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Reversible Tautomerization of Radical Cations. Photoionization of 2-Methoxyethanol and 3-Methoxy-1-propanol

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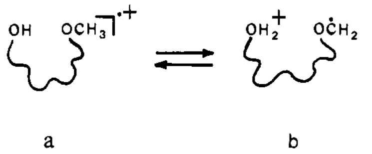
Abstract: Evidence for intramolecular hydrogen exchange between OH and OCH_3 groups is observed in PIMS studies of deuterated analogues of the title compounds. Isotopic labeling demonstrates the unimolecular tautomerization of the molecular ion **a**, $CH_3OCH_2(CH_2)_mCH_2OH^{+\cdot}$, to structure **b**, $\cdot CH_2OCH_2(CH_2)_mCH_2OH_2^+$. In the case $m = 0$, Lyman α photons (122 nm) from a hydrogen resonance lamp have an energy that corresponds to the first vertical IP. Irradiation of $DOCH_2CH_2OCH_3$ at this wavelength yields $CH_3OCH_2^+$ and $CH_2DOCH_2^+$ in a 2:1 ratio. Similarly, the d_3 analogue $HOCH_2CH_2OCD_3$ yields $CD_3OCH_2^+$ and $CD_2HOCH_2^+$ in a 2:1 ratio. Each of these compounds also yields both $[M - H_2O]^{+\cdot}$ and $[M - HOD]^{+\cdot}$. The d_3 analogue also yields $[M - D_2O]^{+\cdot}$, which must result from reversible $\mathbf{a} \rightleftarrows \mathbf{b}$ interconversion. The d_4 analogue $DOCH_2CH_2OCD_3$ yields $CD_3OCH_2^+$, $[M - HOD]^{+\cdot}$, and $[M - D_2O]^{+\cdot}$, but negligible quantities of $CD_2HOCH_2^+$ or $[M - H_2O]^{+\cdot}$. Isotopic scrambling must therefore be limited to the interchange of methoxy and hydroxy hydrogens. Examination of $HOCD_2CH_2OCH_3$ provides confirmation, since no scrambling is observed. The $\mathbf{a} \rightleftarrows \mathbf{b}$ interconversion is faster than bond cleavages, but the relative rate of cleavage increases with photon energy. Through-space interaction is discounted as a major effect on reactivity, because the tautomerization also occurs for $HOCH_2CH_2CH_2OCD_3$. A stepwise mechanism, $\mathbf{a} \rightleftarrows \cdot OCH_2(CH_2)_mCH_2O(CH_3)H^+ \rightleftarrows HOCH_2(CH_2)_mCH_2O(CH_2\cdot)H^+ \rightleftarrows \mathbf{b}$, is put forth to unify observed decomposition pathways.

The chemistry of radical cations has been a subject of much recent interest, with special attention paid to species derived from one-electron oxidation of saturated molecules containing two heteroatoms. Well-studied examples include the stable molecular ions from hydrazines[1] and bis(thioethers),[2] which have been prepared in condensed phases and examined spectroscopically. Symons and Wren[3] have lately reported ESR spectra from ionized bifunctional ethers that raise the possibility of through-space interaction between two oxygen atoms. In the gas phase, bifunctional radical cations exhibit a rich chemistry. Even at the lowest ionizing energies, molecular ions of many bifunctional ethers are unstable. Decomposition pathways frequently involve chemical reactions between remote functional groups.

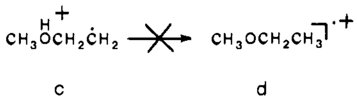
We report here the first examples of unimolecular hydrogen exchange between O-H and C-H bonds in molecular ions from saturated precursors. This reversible tautomerization, shown in reaction 1, competes with low-energy decomposition pathways that are well precedented in a variety of bifunctional ethers.[4,5] For instance, radical cations from dimethoxyalkanes $CH_3O(CH_2)_nOCH_3$ all expel a molecule of methanol. For $n = 3$, this is the sole reaction at the lowest ionizing energies. For the lower homologue $n = 2$, expulsion of a molecule of formaldehyde competes. For higher homologues, other reactions compete. Most of these involve regiospecific intramolecular hydrogen transfer (as revealed by deuterium labeling[5,6]), and variations with chain length can largely be explained in terms of preferences for six-member cyclic transition states.



(1)

Methoxy alcohols exhibit more complicated chemistry. Our attention has focused on reaction 1. Reaction 2 depicts a bimolecular analogue, which can be calculated to be exothermic by about 7 kcal/mol.[7] No better estimate for the thermodynamics of the $\mathbf{a} \rightarrow \mathbf{b}$ conversion is available. It is by no means obvious that it should be reversible, for other closely related reactions are not. As we first reported in 1975, ion **c** does not interconvert with the tautomeric molecular ion **d** on the millisecond time scale.[5] This result has been repeatedly confirmed by subsequent investigators,[8] and other noninterconverting tautomeric pairs have recently been described.[9]

$$[CH_3OCH_3]^{\cdot+} + CH_3OH \rightarrow CH_3O\dot{C}H_2 + CH_3OH_2^+ \quad (2)$$



$$CH_3\overset{\overset{+}{H}}{O}CH_2\dot{C}H_2 \not\longrightarrow [CH_3OCH_2CH_3]^{\cdot+} \quad (3)$$

c d

Background

Among our reasons for choosing to study ω-methoxyalkanols are the number of prior investigations of methyl cellosolve (2-methoxyethanol). As a commercial solvent, its UV photolysis[10] and anodic electrochemistry[11] have been published, in addition to several reports of its mass spectrometry and ion-molecule reactions.[5,6,12,13] Mass spectrometric data provide the background

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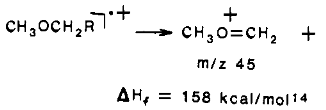
for our investigation. The bifunctional molecular ion exhibits two fragmentations characteristic of its monofunctional analogues, shown in reactions 4 and 5. Molecular ions of aliphatic ethers



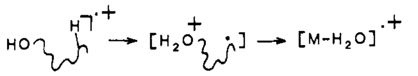
$$CH_3OCH_2R^{\cdot+} \longrightarrow CH_3\overset{+}{O}{=}CH_2 + R\cdot \quad (4)$$

m/z 45

ΔH_f = 158 kcal/mol[14]

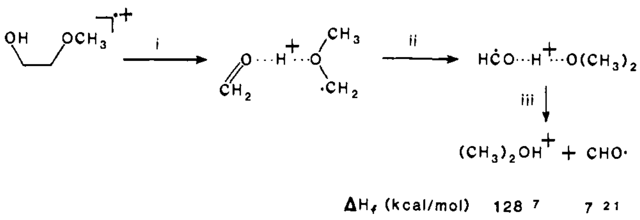
undergo simple cleavage. As depicted in reaction 4, methyl ethers of primary alcohols yield the methoxymethyl cation (m/z 45), and this is the base peak from 70-eV electron impact on 2-methoxyethanol.[6]

Molecular ions of aliphatic alcohols undergo hydrogen rearrangements, followed by expulsion of water.[15] This produces [M − 18] daughter ions, as represented in reaction 5. Van de Sande and McLafferty have shown, by use of collisional activation studies of 2-methoxyethanol, that the itinerant hydrogen can come from the methyl group or from the β-methylene.[13] When methyl hydrogen transfers, the daughter ion cannot be distinguished from the molecular ion of oxetane (whose heat of formation ΔH_f° = 202 kcal/mol[7]). Ab initio calculations suggest that this fragment may prefer a ring-opened structure, but its calculated energy is only 2.4 kcal/mol lower than that of the four-member ring.[17] When hydrogen transfers from the β-methylene, the daughter ion is the molecular ion of vinyl methyl ether. Thermodynamically, this is the most favored decomposition product.



(5)

At low ionizing energies, only one other fragment ion is seen, m/z 47.[6,7] An ion of the same exact mass (47.050) is observed from the isomeric compound, methylal (dimethoxymethane), and both correspond to the molecular formula $C_2H_7O^+$.[16] However, the ion from methylal vanishes as ionizing energy is lowered, while that from 2-methoxyethanol increases in intensity.[6] Ions at m/z 47 are unusual. A computer search shows that, of more than 12 000 C, H, O compounds in the EPA-NIH mass spectral data base,[18] only 80 exhibit m/z 47 peaks above 1% of the base peak intensity. Several (e.g., benzoic anhydride) surely produce the $CH_3O_2^+$ isobar, and about three-fifths of the rest are homologues of methylal. A collisionally induced decomposition study of the m/z 47 ion from 2-methoxyethanol shows that it is protonated dimethyl ether (Me_2OH^+), as distinct from protonated ethanol.[19] We have described a pathway for this fragmentation, which is summarized in reaction 6.[6] In this mechanism, the molecular ion decomposes to formaldehyde plus O-protonated methoxymethyl radical, step i. At low ionizing energies these remain bound by a strong hydrogen bond, whose strength is about 30 kcal/mol.[20] In this proton-bridged complex, the radical abstracts a hydrogen atom from the formaldehyde, as step ii shows. This complex then decomposes by expulsion of a formyl radical, shown by step iii.



(6)

Effects of hydrogen bonding can be inferred from photoelectron spectroscopy (PES). The He I PES of 2-methoxyethanol has been published,[22] and the spectrum of 3-methoxy-1-propanol is reproduced at the top of Figure 1. For purposes of comparison, the spectrum of 1,3-dimethoxypropane is displayed below it. We shall not discuss these spectra in detail, except to note that the two lowest bands in both spectra can be assigned to symmetric and antisymmetric combinations of oxygen lone pairs from the two functional groups.[23] In 1,3-dimethoxypropane, the splitting between the first two vertical IP's at 9.68 and 9.93 eV (which are more clearly separated in higher resolution spectra) is the same as in 1,2-dimethoxyethane. The separation between the first two bands is larger in methoxyalkanols, as would be expected, since the interacting lone pairs are on chemically nonequivalent oxygen atoms.

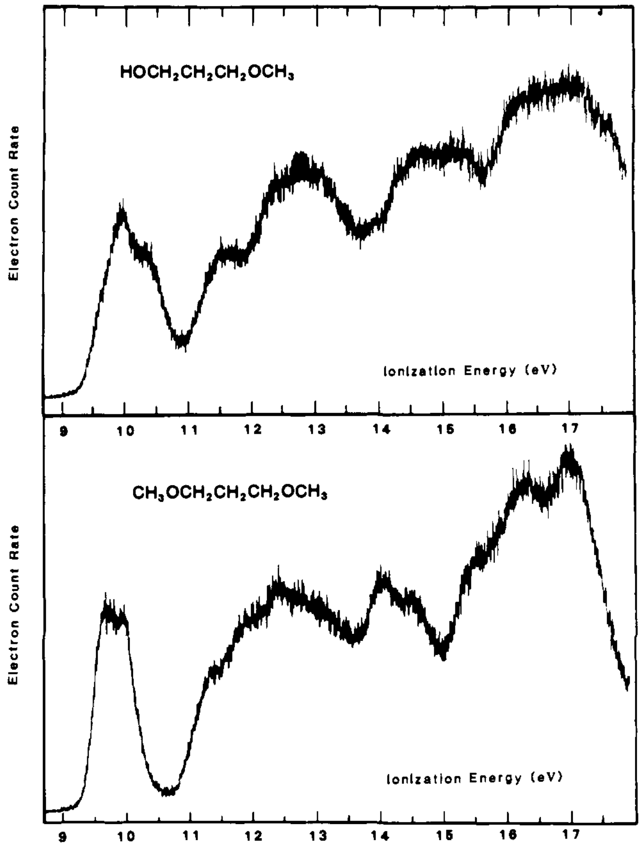


Figure 1. He I photoelectron spectra of 3-methoxy-1-propanol and 1,3-dimethoxypropane. Calibration with xenon internal standard not shown. Recorded by J. C. Schultz at the California Institute of Technology.

The first two bands of 3-methoxy-1-propanol are broad, more so even than the corresponding bands in 2-methoxyethanol (which are shown below in Figure 6). At 300 K, neutral 3-methoxy-1-propanol at equilibrium is approximately a 3:2 mixture of internally hydrogen-bonded and unbonded species.[24] We infer that the observed PES is a superposition of the spectra of these two forms. Neutral 2-methoxyethanol is virtually completely internally hydrogen bonded in the gas phase.[25] The effects of hydrogen

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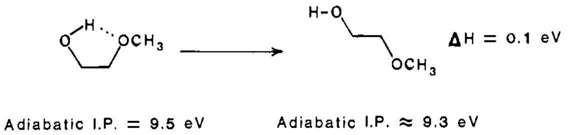
bonding on phtooelectron spectra have been well studied by Brown.[26] The splitting in 2-methoxyethanol, 0.45 ± 0.04 eV, is the same as reported for *cis*- and *trans*-2-methoxycyclohexanol and *cis*-2-methoxycyclopentanol, all of which exhibit internal hydrogen bonding, For *trans*-2-methoxycyclopentanol, which does not exhibit hydrogen bonding, the splitting is 0.4 eV greater than in the cis isomer. However, the mean ionization energy of the first two vertical IP's is the same for the cis and trans isomers. In other words, the effect of internal hydrogen bonding is to raise the first IP by 0.2 eV and lower the second IP by 0.2 eV.

In the absence of hydrogen bonding, the minimum energy conformation of 2-methoxyethanol ought to have the CH_3O group anti-periplanar to the HO group, instead of the gauche conformation that dominates the microwave spectra. The strength of the intramolecular hydrogen bond in the neutral molecule has been measured, and the value is $\Delta H = 2.2$ kcal/mol.[24] Breaking the hydrogen bond will therefore raise the heat of formation of the neutral molecule by 0.1 eV at the same time as it lowers the IP by 0.2 eV, as summarized in reaction 7. The heat of formation of the gauche molecular ion (which is the final state from vertical ionization) is thus at least 0.1 eV higher than that of a molecular ion in which the hydrogen bond geometry is disrupted. The ΔH for internal hydrogen bond formation does not vary greatly with chain length among the methoxyalkanols.[24] Therefore, the corresponding stable molecular ions should not maintain internal hydrogen bonds.



(7)

Experimental Section

The photoionization mass spectrometer has been previously described.[27] For 122- and 105–107-nm radiation, the photon source was a microwave discharge lamp with an LiF window, through which the appropriate gas mixture (1% hydrogen in helium, or pure argon) was allowed to flow.[28] For 130-nm radiation, a lamp with a CaF_2 window was used with a 1% oxygen in helium gas mixture. Attempts were made to use an oxygen discharge with LiF windows, but it was found that the presence of shorter wavelength emission required the use of the CaF_2 window (which cuts off just below 130 nm). For 3-methoxypropanol and for 130-nm PIMS, the ion extraction and focusing lens system of an Extranuclear Laboratories 020-2 ionizer control was inserted between the ionizing region and the entrance aperture to the Extranuclear Laboratories quadrupole mass filter.

Vapor from a cooled liquid sample was introduced directly into the ionizing region at a steady-state pressure on the order of 10^{-7} torr. Ion intensity was measured by integrating the ion counts over a 1-amu range, corresponding to 18 channels in the accumulated spectra stored in a Nuclear Data ND 100 multichannel analyzer. Ion intensities at 122 and 105–107 nm were normalized to constant photon flux by comparison with the *m/z* 78 intensity from a benzene internal standard, which was separately introduced into the ionizing region via a flow tube. Benzene absorption cross sections and ionizing efficiencies, as reported by Person,[29] were used for calibration.

2-Methoxyethanol (Aldrich Gold Label) was used without further purification. Other methoxyalkanols were prepared by Williamson ether synthesis, as exemplified by the procedure given below for $CD_3OCH_2CH_2CH_2OH$, except for $CH_3OCH_2CD_2OH$, which was prepared by reduction of methoxyacetic acid with $LiAlD_4$. The carbon-deuterated compounds were purified by preparative GLPC prior to PIMS. Oxygen deuterated analogues were prepared simply by dissolving the corresponding OH compound in excess D_2O. It was found that, because of internal hydrogen bonding, 2-methoxyethanol exchanges its hydroxylic hydrogen comparatively slowly. Therefore, it was not necessary to use a deuterated inlet to achieve O-deuteration to the extent of 88 ± 5%, which was observed for $DOCH_2CH_2OCH_3$ and $DOCH_2CH_2OCD_3$.

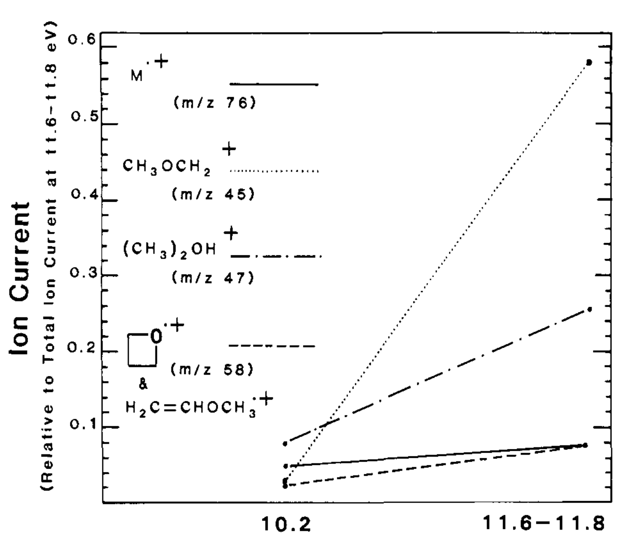


Figure 2. Ion yields (normalized to constant photon flux) from photoionization of 2-methoxyethanol using a hydrogen resonance lamp (Lyman α, 10.2 eV) and an argon resonance lamp (11.6–11.8 eV).

$CD_3OCH_2CH_2CH_2OH$. A 1.45-g portion of sodium hydride (6 mmol, freshly washed free of mineral oil) was dissolved in 31 g (0.4 mol) of 1,3-propanediol (Aldrich) with magnetic stirring. Then 7.5 g (50 mmol) of iodomethane-d_3 (Merck, >99 atom % D) was added and the reaction mixture allowed to reflux under mild heating. When refluxing ceased, the reaction mixture was allowed to cool, and the product was distilled under aspirator pressure to yield 2.95 g (32 mmol, 64% yield) of $CD_3OCH_2CH_2CH_2OH$, bp 62–67 °C (30 torr): NMR (90 MHz, CCl_4) δ 1.71 (quintet, $J = 6$ Hz, $CH_2CH_2CH_2$), 2.9 (broadened singlet, OH), 5.16 (triplet, $J = 6$ Hz, CH_2OCD_3), 5.30 (broadened triplet, $J = 6$ Hz, CH_2OH).

Results

The photoionization mass spectra of 2-methoxyethanol in two energy ranges studied are summarized in Figure 2. Ion abundances were normalized to a constant photon flux by means of the benzene internal standard. The total ion intensity from 2-methoxyethanol increases by a factor of 6.0 ± 0.5 when the wavelength is changed from 122 to 105–107 nm. The absolute yields of individual ions all increase with photon energy. Between 10.2 and 11.6–11.8 eV, the yield of the simple cleavage product jumps by a factor of 20, while molecular ion yield increases by a factor of only 1.8. The $[M - H_2O]^{+\cdot}$ and Me_2OH^+ fragment ion yields both increase by the same factors, 3.1 ± 0.2 and 3.4 ± 0.2, respectively. A 130-nm photoionization mass spectrum was measured, using an oxygen resonance lamp with a CaF_2 window. At this low ionizing energy (9.5 eV), molecular ion represented 95% of the total ionization, with Me_2OH^+ and $[M - H_2O]^{+\cdot}$ the predominant fragments, in an intensity ratio of 1.5. The ratio of Me_2OH^+ to the simple cleavage fragment was 7.3 at 9.5 eV, 2.4 at 10.2 eV, and 0.44 at 11.6–11.8 eV (standard deviations of these ratios is 2%).

$HOCD_2CH_2OCH_3$. Deuterium labeling confirms the structural assignments of the fragment ions. For $HOCD_2CH_2OCH_3$, the simple cleavage product ion remains at *m/z* 45, with *m/z* 46 <3% of its intensity (after correction for ^{13}C natural abundance). The molecular ion is almost completely dideuterated (98 atom % D). The Me_2OH^+ fragment is monodeuterated and appears at *m/z* 48, with *m/z* 47 and *m/z* 49 each ≤4% of its intensity (when corrected for incomplete deuteration of the parent and ^{13}C natural abundance). The $[M - H_2O]^{+\cdot}$ ion is dideuterated and appears at *m/z* 60, with d_1 and d_0 ions together comprising ≤4% of its intensity (after correction for incomplete deuteration of the parent). At 10.2 eV, the ratio of the fragment intensities is simple cleavage:Me_2OH^+:$[M - H_2O]^+$ = 0.72:1.15:0.97, and at 11.6–11.8 eV the ratio is 12:3.0:2.0 (all relative to molecular ion intensity = 1).

$DOCH_2CH_2OCH_3$. Deuterium labeling of the hydroxyl or the methyl group shows that these positions exchange hydrogen in the molecular ion prior to decomposition. Figure 3 reproduces

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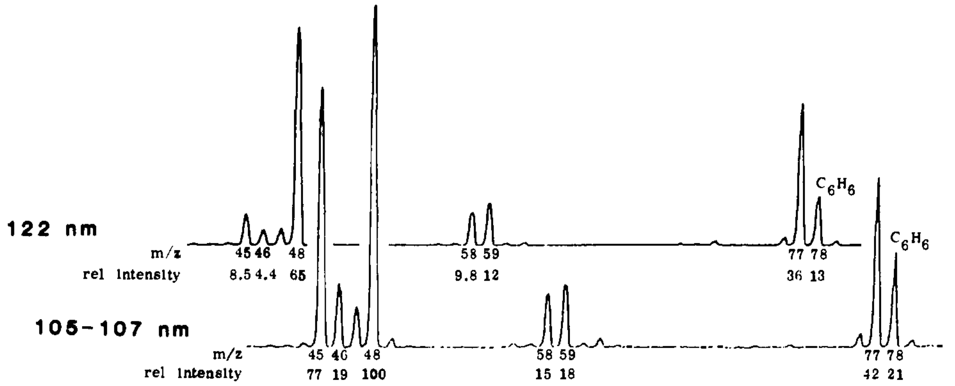


Figure 3. Photoionization mass spectra of $DOCH_2CH_2OCH_3$ containing benzene (*m/z* 78) as internal standard. Ion intensities are reported relative to the base peak at 105–107 nm. Intensities are not shown for peaks resulting from incomplete deuteration.

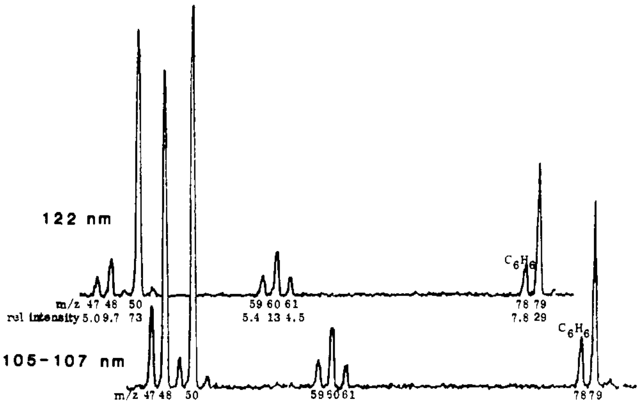


Figure 4. Photoionization mass spectra of $HOCH_2CH_2OCD_3$ containing benzene (*m/z* 78) internal standard. Ion intensities are reported relative to the base peak from the argon resonance lamp photoionization and are not corrected for ^{13}C natural abundance or incomplete deuteration.

the photoionization mass spectra of $DOCH_2CH_2OCH_3$, in two wavelength regions. Fragmentation via simple cleavage occurs to a smaller extent than in the undeuterated analogue. Moreover, this reaction produces both d_0 (*m/z* 45) and d_1 (*m/z* 46) ions in a ratio of 1.95 at 122 nm (this ratio is corrected for incomplete deuteration of the parent and has a standard deviation $\sigma = 0.15$). With the argon lamp, the ratio increases to *m/z* 45:*m/z* 46 = 4.

Intramolecular label scrambling also occurs prior to water loss: $[M - H_2O]^{+\cdot}$ (*m/z* 59) is more intense than $[M - HOD]^{+\cdot}$ (*m/z* 58). The ratio of these two ions is 1.5 (after correction for incomplete deuteration of the parent) and does not vary with ionizing wavelength within the experimental error ($\sigma = 0.1$). The protonated dimethyl ether fragment is monodeuterated, with undeuterated Me_2OH^+ representing <4% of its intensity (after correction for incompletel deuteration of the parent). This is consistent with the results for $HOCD_2CH_2OCH_3$, which show that the hydrogen in the expelled formyl radical comes from the methylene to which the hydroxyl is bound and that this methylene does not scramble with any of the other positions in the molecular ion prior to its decomposition.

$HOCH_2CH_2OCD_3$. Figure 4 reproduces the photoionization mass spectra of the deuteriomethyl analogue, normalized to constant photon flux using the *m/z* 78 intensity. The molecular ion is almost entirely d_3 (with only 2% of a d_2 impurity), and label scrambling is revealed by the masses of the fragments from reactions 4 and 5. The simple cleavage fragments appear at *m/z* 47 (d_2) and *m/z* 48 (d_3) in a ratio of 0.5 at 122 nm and 0.25 at 105–107 nm. The fragments from water expulsion appear at *m/z* 59 ($[M - D_2O]^{+\cdot}$), *m/z* 60 ($[M - HOD]^{+\cdot}$), and *m/z* 61 ($[M - H_2O]^{+\cdot}$).

$DOCH_2CH_2OCD_3$. The effect of deuterium-labeling of both the hydroxyl and the methyl groups is shown in Figure 5 and indicates that scrambling in the molecular ion occurs predominantly via hydrogen exchange between these two positions. Decomposition via simple cleavage produces only a d_3 fragment (*m/z* 48), and water elimination forms $[M - D_2O]^{+\cdot}$ (*m/z* 60) and $[M - HOD]^{+\cdot}$ (*m/z* 61) in a ratio of 0.8 (after correction for incomplete deuteration of the parent), with $[M - H_2O]^{+\cdot}$ (*m/z* 62) representing only a small fraction of the $[M - HOD]^{+\cdot}$ intensity.

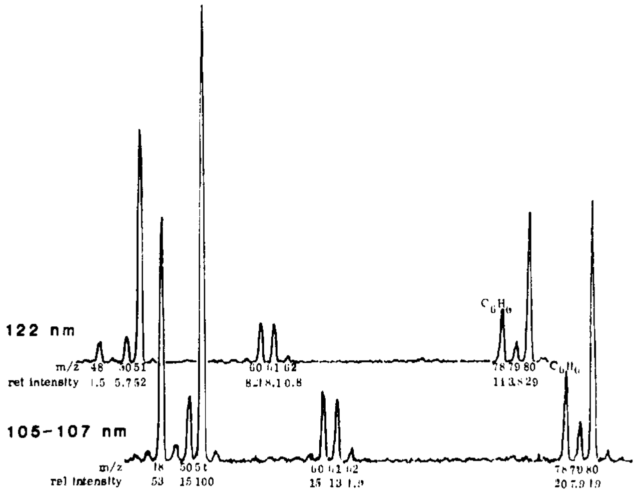


Figure 5. Photoionization mass spectra of $DOCH_2CH_2OCD_3$ containing benzene (*m/z* 78) internal standard. Ion intensities are reported relative to the base peak from the argon resonance lamp photoionization and are not corrected for ^{13}C natural abundance or incomplete deuteration.

There is no evidence for scrambling in the formation of *m/z* 51, which corresponds to protonated dimethyl ether, since the abundance of *m/z* 50 does not exceed the intensity expected on the basis of incomplete deuteration of the parent. All of the deuterated analogues show the same qualitative variation with wavelength as seen in the undeuterated 2-methoxyethanol.

$HOCH_2CH_2CH_2OCH_3$ and $HOCH_2CH_2CH_2OCD_3$. Molecular ion has not previously been reported in the mass spectra of 3-methoxypropanol.[5] At 122 nm, two fragments are observed, corresponding to $[M - H_2O]^{+\cdot}$ (*m/z* 72) and $[M - CH_3OH]^{+\cdot}$ (*m/z* 58) in a ratio of 6:1. Deuterium substitution shows that the itinerant hydrogen in the former ion can come from the methyl group as well as from the methylene chain. With a deuterated methyl group, the principal ions are $[M - H_2O]^{+\cdot}$ (*m/z* 75), $[M - HOD]^{+\cdot}$ (*m/z* 74), and $[M - CD_3OH]^{+\cdot}$ (*m/z* 58) in a ratio of 4:1:1, and the relative ion intensities are the same (within experimental uncertainty of ±10%) when the argon lamp is used. At 130 nm, a low intensity of molecular ion can be seen, and the peak intensity ratios are $M^{+\cdot}:[M - H_2O]^{+\cdot}:[M - HOD]^{+\cdot}:[M - CH_3OH]^{+\cdot} = 0.5:10:4:1$. At all three wavelengths $[M - CD_2HOH]^{+\cdot}$ (*m/z* 59) is observed at 0.05 the intensity of $[M - CD_3OH]^{+\cdot}$ (after correction for ^{13}C natural abundance). An ion at *m/z* 73 is also seen, approximately 0.05 the intensity of the *m/z* 74 ion. Though its intensity is greater than would be expected on the basis of incomplete deuteration of the starting material,

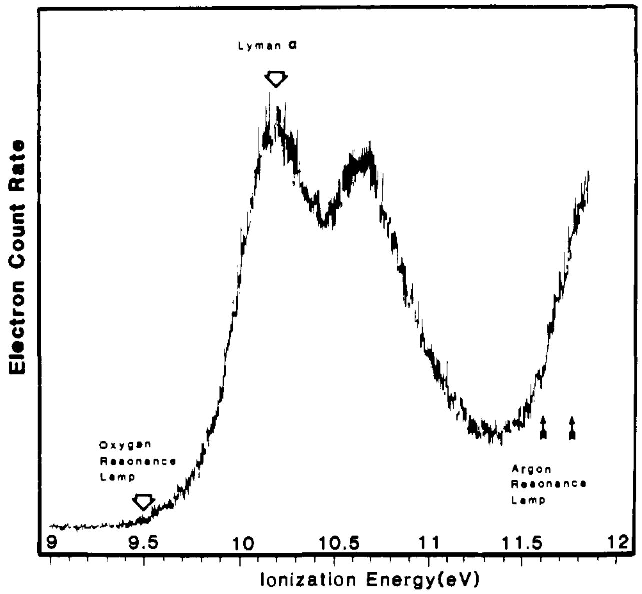


Figure 6. Detail of He I photoelectron spectrum of 2-methoxyethanol (recorded by J. C. Schultz at the California Institute of Technology). The resonance lines of the lamps used for the present studies are shown in relation to the ionization energies.

we cannot reliably estimate the fraction of this ion attributable to $[M - D_2O]^{+}\cdot$.

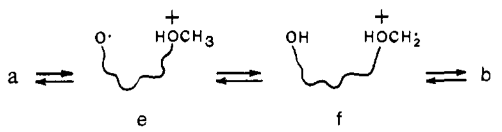
Discussion

The photon energies of the lamps used in these studies are shown in relation to the photoelectron spectrum in Figure 6. The 9.5-eV oxygen resonance line corresponds to the ionization onset, while the hydrogen resonance line corresponds to the first vertical IP. The two argon lines correspond to the onset of the third photoelectron band. The effect of changing lamps supports the interpretation that increasing the photon energy increases the average amount of internal energy available to the ground state of the molecular ion. Figure 2 shows this with straight lines drawn between ion abundances at two different angles. These straight lines are not meant to indicate the yields at intermediate energies, but are included to show that the slope between the two points correlates with the heat of formation of the corresponding products:[7] 154 kcal/mol for $CH_3OCH_2^+$ plus $HOCH_2\cdot$;[14] 135 kcal/mol for Me_2OH^+ plus $OCH\cdot$; and 123 kcal/mol for $H_2C{=}CHOCH_3^{+}\cdot$ plus water.[30,31] The relative ion abundances at 9.5 eV show that the trend continues as expected, with $CH_3OCH_2^+$ virtually vanishing and $[M - H_2O]^{+}\cdot$ increasing in intensity relative to $Me_2OH^{+}\cdot$. Thus, there is no evidence for the intervention of isolated states of the molecular ion. The greater the slope of a line in Figure 2, the greater the heat of formation of the fragmentation products. This is consistent with the theoretical interpretation of photoionization threshold behavior presented by Guyon and Berkowitz.[32] Also, as this theoretical treatment would predict, some of the fragmentation products (e.g., $CH_3OCH_2^+$ at 10.2 eV) are observed at photon energies below the expected appearance potential. This has been explained as a result of the thermal distribution of internal energies of the parent neutral molecules.

The most unusual result of this investigation is the observation of hydrogen exchange between hydroxy and methoxy groups. Competition between reaction 1 and fragmentation provides an economical explanation, which is supported by all of the deuterium-labeling data. In 2-methoxyethanol, extensive interconversion of tautomers **a** and **b** takes place prior to reactions 4 and 5, as revealed by the spectra in Figures 3 and 4. Scrambling, albeit to a lesser extent, is also detectable in the products from photoionization of deuterated 3-methoxy-1-propanol. Differences in reaction rates attributable to small energetic variations ($\approx$1 kcal/mol) in barrier heights can explain the different degrees of exchange in the homologous radical cations. Changes in decomposition patterns can be rationalized in thermochemical terms. For instance, reaction 6 does not occur for 3-methoxy-1-propanol because step i would be substantially more endothermic ($CH_3OCH_2\cdot$ is stabilized by 5–7 kcal/mol relative to propyl radical, whereas $CH_3OCH_2CH_2\cdot$ is not stabilized at all[7]).

A remarkable feature of reaction 1 is its apparent rapidity. In 2-methoxyethanol, scrambling competes effectively with simple cleavage, which is ordinarily among the fastest of molecular ion decompositions. The competition between hydrogen exchange and simple cleavage is energy dependent. At 122 nm, the photon energy is within 0.1 eV of the thermodynamic threshold for reaction 4. Exchange of isotopic label prior to expulsion of methoxymethyl cation is very extensive at this energy. At 105–107 nm, where the photon energy is roughly 35 kcal/mol higher, the abundance of unexchanged methoxymethyl cation is doubled with respect to the exchanged cation. This rules out the possibility that tautomer **b** somehow expels $C_2H_5O^+$ without reverting to **a**, for in that case the ratio should remain virtually unchanged. The energy dependence also argues against there being a separate pathway that leads to an exchanged isomer (e.g., protonated acetaldehyde, the one isomer that is more stable than methoxymethyl cation[14]). The abundance of the exchanged fragment increases dramatically with photon energy, by a factor of 3–4 with respect to every other ion except the unexchanged simple cleavage fragment. Such behavior is implausible for a decomposition that would required deep-seated rearrangement of the parent ion.

No evidence for reversible tautomerization has previously been reported for aliphatic alcohol radical ions.[15,33] Why, then, is reversible tautomerization so rapid for methoxy alcohols? We cite the substitution of oxygen for a methylene as the controlling factor. Reaction 8 presents an explanation for this in terms of two additional intermediates along the path from **a** to **b**. Tautomer **e**, the first intermediate, is the result of hydrogen transfer from the hydroxy to the methoxy oxygen. Reaction 4 is effectively prevented by this step, since only **a** can yield methoxymethyl cation via simple cleavage. This explains how isotopic scrambling can compete so well with simple cleavage in 2-methoxyethanol. Internal hydrogen atom abstraction by the oxy radical leads to tautomer **f**. The unpaired electron in **e** is localized, and its conversion to **f** should closely resemble intramolecular hydrogen transfer in neutral alkoxy radicals (the Barton reaction). The analogy between mass spectrometric hydrogen rearrangements and the Barton reaction has been extensively discussed by Green, who views alcohol molecular ions as O-protonated alkoxy radicals. In methoxy alcohols, transfer of the proton to the ether oxygen means that the charged center and the radical center are remote from one another. Therefore, the preferences of the Barton reaction should assert themselves more strongly in reaction 8 than they do in the rearrangements of simple aliphatic alcohol radical cations. Abstraction from δ carbon via a six-member cyclic transition state is even more highly preferred in neutral alkoxy radicals than in ions. Since the δ position of 3-methoxy-1-propanol is occupied by an oxygen, a six-member ring is not possible. Therefore tautomer **e** has a choice between five- and seven-member cyclic transition states, leading respectively to H_2O and HOD loss from $CD_3OCH_2CH_2CH_2OH$.



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Intramolecular hydrogen transfer is not the only pathway available for tautomer **e**. Cleavage of its carbon–carbon bond is equivalent to step i of reaction 6. Reaction 8 thus links two of the photoionization reactions of 2-methoxyethanol. Hydrogen transfer via a four-member ring represents an alternative pathway for molecular ion **a** and ultimately leads to loss of water to give the molecular ion of vinyl methyl ether. This step is irreversible (and is not depicted). The overall water elimination is exothermic, since the *calculated* appearance potential is below 9 eV, far lower than the ionization potential of 2-methoxyethanol. Every other decomposition observed for the molecular ion is endothermic. The kinetic preference for a six-member cyclic transition state allows reaction 8 to compete, in spite of the large thermodynamic preference for vicinal elimination.

With PIMS[34] we can examine gaseous radical ions with near-thermal energy distributions. Detailed kinetic schemes for tautomerization and decomposition of the molecular ion of 2-methoxyethanol can be drawn, and there are, in principle, enough data to solve for relative rate constants and primary isotope effects. In practice, though, the uncertainties in our experimental measurements translate into huge fluctuations in the derived values, making it currently impossible to extract meaningful quantitative conclusions. With further refinement of PIMS techniques, it will in the future become possible to obtain relative rates for decompositions and isomerizations of gaseous cations that are as reliable as the data for neutral species.

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Registry No. $CH_3OCH_2CH_2OH^{+\cdot}$, 86012-96-6; $CH_3OCH_2CH_2CH_2OH^{+\cdot}$, 86012-97-7; $\cdot CH_2OCH_2CH_2OH_2^+$, 86023-99-6; $\cdot CH_2OCH_2CH_2CH_2OH_2^+$, 86024-00-2; $DOCH_2CH_2OCH_3$, 86012-98-8; $DOCH_2CH_2OCD_3$, 86012-99-9; $HOCD_2CH_2OCH_3$, 51255-53-9; $HOCH_2CH_2CH_2OCD_3$, 86013-00-5; 2-methoxyethanol, 109-86-4; 3-methoxy-1-propanol, 1320-67-8; 1,3-propanediol, 504-63-2; iodomethane-d_3, 865-50-9.

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[34] This acronym has two meanings: Photoionization Mass Spectrometry or Primary Ion Mass Spectrometry (see Maccoll, A. *Org. Mass Spectrom.* **1982**, *17*, 1–9). In the present context, both are meant.

A Product Study of 1-Adamantyl and 1-Bicyclo[2.2.2]octyl Radicals in Hydrocarbon Solvents. An Unusually Large Hydrogen Isotope Effect

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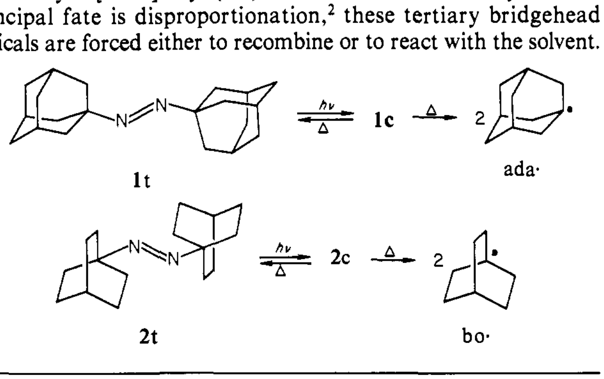
Abstract: 1-Adamantyl (ada·) and 1-bicyclo[2.2.2]octyl (bo·) radicals have been generated by photolysis of the corresponding azoalkanes in various hydrocarbon solvents. Both radicals abstract hydrogen readily from saturated hydrocarbons and they add to aromatic rings much faster than *tert*-butyl· does. Despite its reactivity, ada· is remarkably selective in hydrogen atom abstraction, preferring a benzylic hydrogen 25:1 over a cyclohexane hydrogen. The effect of solvent viscosity indicates that formation of the radical dimers biada and bibo occurs in the solvent cage. The most striking result of this work is a deuterium isotope effect of 25 for hydrogen transfer from cyclohexane to ada· at 65 °C. Steric compression in the transition state is postulated to cause an unusually large tunnel correction and hence a large k_H/k_D.

We have recently shown that irradiation of *trans*-azo-1-adamantane (**1t**) and *trans*-azo-1-bicyclo[2.2.2]octane (**2t**) produces the cis isomers (**1c** and **2c**) which undergo competing loss of nitrogen and reversion to trans.[1] Since thermolysis of these cis isomers occurs at relatively low temperatures and produces only nitrogen as a byproduct, irradiation of **1t** and **2t** at 65 °C is a particularly clean method for generating 1-adamantyl (ada·) and 1-bicyclo[2.2.2]octyl (bo·) radicals. Unlike *tert*-butyl·, whose principal fate is disproportionation,[2] these tertiary bridgehead radicals are forced either to recombine or to react with the solvent. Most previous product studies[3-6] of bridgehead radicals were qualitative only and were confined to a limited number of solvents. These earlier studies employed peresters to generate the desired radicals, leading to additional *tert*-butoxy-containing products. Presently, we show that unlike peresters, **1t** and **2t** give the symmetrical recombination products 1,1′-biadamantyl (biada) and 1,1′-bis(bicyclo[2.2.2]octyl) (bibo) in up to 50% yield. The free ada· and bo· add more readily to the ring of benzene and toluene than does *tert*-butyl; however, the two radicals seem to exhibit comparable reactivity toward side-chain hydrogen abstraction from toluene. Finally, extremely large isotope effects are demonstrated for hydrogen abstraction by bridgehead radicals.



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