channel inside. The thermal elements are 4 cm × 4 cm × 4 mm with a honeycomb arrangement of 98 individual elements which decreases its effective cross-sectional area to 2 cm × 2 cm.

(31) This "stopped flow" experiment was designed to measure the heat effect, W_r, of a reaction under initial velocity conditions at zero flow rate. A very slowly reacting mixture of equal concentrations of KOH and EtAc was pumped through the calorimeter until steady state conditions were observed. At this point both pumps were turned off and the slowly decreasing signal was extrapolated back to zero time by correcting for the response time of the instrument. This correction is discussed in E. Calvet and H. Prat, "Recent Progress in Microcalorimetry", Macmillan, New York, N.Y., 1963, Chapter 4.

(32) J. M. Sturtevant and P. A. Lyons, *J. Chem. Thermodyn.*, **1**, 201 (1969); J. M. Sturtevant, *Fractions*, 1 (1969).

(33) P. Picker, C. Jolicoeur, and J. E. Desnoyers, *J. Chem. Thermodyn.*, **1**, 469 (1969); P. Picker, *Can. Res. Dev.*, **7**, 11 (1974).

Chain-Length Effects upon the Interaction of Remote Functional Groups. The Low Energy Electron Impact Mass Spectra of α,ω-Dialkoxyalkanes Examined by Ion Cyclotron Resonance Spectroscopy[1a]

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Abstract: The techniques of ion cyclotron resonance spectroscopy have been used to investigate the analogy between bimolecular ion-molecule reactions and intramolecular mass spectral rearrangements of a series of bifunctional ethers, $CH_3O(CH_2)_nOR$, $n = 1$-6 and R = H, CH_3, or C_2H_5. The first step in exploring this analogy has been the examination of the ion-molecule reactions of simple ethers. The second step has been the investigation of the rearrangement ions produced from bifunctional ethers by low energy electron impact. The third step has been a probe of selectivity using deuterium labels. It is found that intramolecular hydrogen transfer is highly regioselective, while the bimolecular analog is not. More pronounced deviations from the analogy arise with variation of the length of the methylene chain separating the functional groups. This indicates a selectivity in the rearrangement process which has no analog in ion-molecule reactions, and this chain-length selectivity has been probed by deuterium labeling and by examination of the ion-molecule reactions of the rearrangement ions. The term *vinculoselection* is proposed to designate a reaction of a polyfunctional molecule in which a specific chain length or spatial separation between functional groups is requisite for the reaction to occur. Thermodynamic and structural factors affecting vinculoselective reactions of cations from bifunctional ethers are discussed.

Interaction of functional groups within organic molecules is a well recognized aspect of chemical reactivity. Intramolecular reactions of bifunctional compounds are generally described by analogy to bimolecular reactions of the same functional groups, and this analogy is often useful in predicting the behavior of polyfunctional molecules. Such an approach has led, for example, to the development of stereoselective synthetic transformations in rigid cyclic systems,[3] the characterization of intramolecular strong hydrogen bonding in bifunctional molecules,[4] and the suggestion that mass spectral rearrangements in long chain bifunctional molecules resemble ion-molecule reactions,[5] as represented in reactions 1a and 1b.

$$RX^+ + RY \longrightarrow \text{ion-molecule reaction products} \qquad (1a)$$

$$\underbrace{X^+ \quad Y} \longrightarrow \text{mass spectral rearrangement ions} \qquad (1b)$$

The present study is an investigation of this analogy in the mass spectral rearrangements of bifunctional ethers of the general formula $CH_3O(CH_2)_nOR$, where R may be hydrogen, methyl, or ethyl, and n is varied from 1 to 6. Ethers have been chosen for examination because of the simplicity of their ion chemistry, their volatility, and the ease with which deuterium labels can be placed at specific positions within a molecule. The techniques of ion cyclotron resonance spectroscopy (ICR) have been used in this study for three reasons: (1) the relatively low spread in energy of the ionizing electron beam at energies near ionization thresholds;[6] (2) the ability to vary ion residence time from 10^{-3} to 1 sec and the pressure of neutrals from 10^{-7} to 10^{-3} Torr, which permits the observation of ion-molecule reactions; and (3) the capability of identifying reaction partners through ICR double resonance techniques.[7] As part of these studies, we have already described the examination of clustering reactions by ICR to detect intramolecular strong hydrogen bonding in bifunctional molecules.[4] More recent ICR studies have measured the strength of this form of interaction of remote functional groups.[8] In addition, ICR has been widely utilized for the identification of the structures of fragment ions arising from electron impact[7,9] and has revealed many details regarding the bimolecular reactions of organic ions with neutral molecules.[7,10]

The first step in exploring the analogy between reactions 1a and 1b has been the observation of the ion-molecule reactions of molecular ions from simple ethers. The second step has been the examination of the rearrangement ions produced from bifunctional ethers by low energy electron impact, with the result that the most prevalent rearrangement process corresponds to the intramolecular analog of a bimolecular ion-molecule reaction. The final step has been the realization that specific instances of major deviations from this analogy arise with variation of the methylene chain separating the functional groups. This indicates a selectivity not found in ion-molecule reactions, and this selectivity has been probed using deuterium labeling techniques and the examination of ion-molecule reactions of the rearrangement ions.

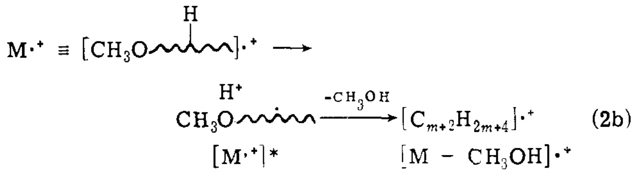
Selectivity is a prominent feature of many mass spectral rearrangements. The McLafferty rearrangement, which is regioselective by virtue of a six-member cyclic transition state, is the best known example.[11] A number of other hydrogen rearrangements have also been found to be regioselective;[12] in particular, five- and six-member cyclic transition states have been reported in the expulsion of water from the molecular ion of 1-hexanol[13] and in mass spectral hydrogen rearrangements of esters.[14] Stereoselectivity arising from the conformational requirements of a six-member cyclic transition state has been reported in the loss of water from the molecular ion of 2-hexanol.[15]

Previous studies of mass spectral rearrangements in polyfunctional ethers have shown that the introduction of additional functional groups promotes further selectivity. Stereochemical control has been reported in the mass spectral rearrangements of methyl ethers of diastereomeric cyclic polyalcohols,[16] and the 70 eV mass spectra of acyclic polyfunctional ethers show a variety of rearrangements which are regioselective.[17] The present investigation of the ion chemistry of ω-substituted 1-methoxyalkanes indicates that selectivity becomes pronounced at ionizing energies within a few eV of threshold. This selectivity falls into two general categories.

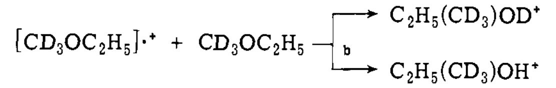
The first category is a regioselectivity in hydrogen rearrangements different from that usually inferred for monofunctional compounds. The source of itinerant hydrogen is determined not by the size of the cyclic transition state so much as by the positions of the functional groups. The second category is a form of chain-length control comparable to the stereochemical control found in the mass spectral rearrangements of cyclic polyfunctional compounds. Of the several pathways of rearrangement available to ω-substituted 1-methoxyalkanes, distinctive choices are made by certain molecules which differ from the rearrangements of longer and shorter chain-length homologues. Chain-length control has been reported in the mass spectral fragmentations of bifunctional carbonyl compounds,[18] but it is by no means general in the mass spectra of bifunctional molecules.[19] Nevertheless, this sort of selectivity appears throughout chemistry, and the term vinculoselection,[20] is proposed to designate a reaction of a polyfunctional molecule in which a specific chain length or spatial separation between functional groups is requisite for the reaction to occur.

Ion Chemistry of Monofunctional Ethers. The point of departure of the present investigation has been the comparison of the mass spectral rearrangements of monofunctional n-alkyl methyl ethers with the ion-molecule reactions of simple ethers. Although the base peak in the 70 eV mass spectra of n-alkyl methyl ethers (n-alkyl = butyl or longer) is the methoxymethyl cation (m/e 45), **1**, resulting from the simple cleavage shown in reaction 2a, the next most prominent ions result from hydrogen rearrangements.[21] In the present study, for example, methoxymethyl cation has been found to compose 27% of the total ionization (%Σ) from n-octyl methyl ether at 70 eV, while the $[\mathrm{M} - \mathrm{CH_3OH} - \mathrm{C_2H_4}]\cdot^+$ rearrangement ion (m/e 84, 7% Σ at 70 eV) is the next most prominent ion. At lower ionizing energies, the rearrangement ions become more prominent, and, at 12 eV, the methoxymethyl cation is not observed, while the $[\mathrm{M} - \mathrm{CH_3OH}]\cdot^+$ rearrangement ion (m/e 112, 27% Σ at 12 eV) is the base peak. The hydrogen rearrangement which produces this ion is represented schematically as a two-step process in reaction 2b.

$$\underset{\mathrm{M}\cdot^+}{[\mathrm{CH_3OCH_2}\text{—}(\mathrm{CH_2})_m\mathrm{CH_3}]\cdot^+} \longrightarrow \underset{\mathbf{1}}{\mathrm{CH_3OCH_2}^+} + \cdot\mathrm{CH_2(CH_2)_{\mathit{m}-1}CH_3} \quad (2a)$$


(2b)

A hydrogen transfer comparable to the first step of reaction 2b is observed in the ion-molecule reactions of simple ethers, which have been studied by high-pressure mass spectrometry,[22] ion trapping mass spectrometry,[23] and ICR.[9a] The characteristic reaction of an ether molecular ion with its parent neutral is shown in reaction 3. Reaction via path a and via path b occur to roughly equal extents,[9a,23] indicating no selectivity between methyl and ethyl as a proton source, even at 13 eV ionizing energy.[9a] These results have prompted the further study of ion-molecule reactions of simple ethers and the examination of the mass spectral rearrangements of bifunctional ethers at ionizing energies near threshold.



$$[\mathrm{CD_3OC_2H_5}]\cdot^+ + \mathrm{CD_3OC_2H_5} \begin{cases} \xrightarrow{a} \mathrm{C_2H_5(CD_3)OD^+} \\ \xrightarrow{b} \mathrm{C_2H_5(CD_3)OH^+} \end{cases} \quad (3)$$

Experimental Section

A standard Varian V-5900 series ion cyclotron resonance mass spectrometer equipped with a dual inlet system was utilized in the studies reported herein. The instrumentation and experimental techniques associated with ion cyclotron resonance spectrometry have been described in detail.[7] All ICR experiments were performed at ambient temperature. Mass spectral intensities and product distributions were determined from single resonance peak intensities and double resonance techniques using previously described methods of analysis. Pressures in the ICR cell greater that 10^{-5} Torr were measured using an MKS Baratron capacitance manometer. Reported lower pressures refer to calibrated ion gauge measurements.

Commercial dimethyl ether (Matheson), diethyl ether-d_{10} (98 atom % D, Merck Sharp and Dohme), 1,2-dimethoxyethane (MCB), and methyl cellosolve (Pierce Chemical Co.) were used without further purification. All other ethers were prepared from the corresponding alcohols by conventional Williamson ether synthesis.[17] The deuterium-labeled compounds utilized in the synthesis of the variously labeled bifunctional ethers included methyl-d_3 iodide (99 atom % D, Stohler Isotope Co.), lithium aluminum deuteride-d_4 (98 atom % D, Stohler Isotope Co.), methanol-d (99 atom % D, Stohler Isotope Co.), and deuterium oxide (99.7 atom % D, Columbia Organic Chemical Corp.).

Deuterium Substituted Compounds. The $\alpha,\alpha,\omega,\omega$-tetradeuterio-$\alpha,\omega$-alkanediols were prepared by reduction of the corresponding esters with lithium aluminum deuteride. Dimethyl ethers of these diols were prepared by Williamson ether synthesis.

1,1-Dideuterio-3-ethoxypropanol was prepared from the methyl ester of 3-ethoxypropanic acid. The ester was reduced with lithium aluminum deuteride and converted to the ether, **1,1-dideuterio-1-methoxy-3-ethoxypropane.** The ether was purified by preparative vpc on a 7 ft × 0.25 in. 8% FFAP (Carbowax 20 M-TPA), 60-80 mesh Chromosorb P column and characterized by nmr ($\mathrm{CCl_4}$): δ 1.14 (3 H, t, J = 7 Hz), 1.72 (2 H, broadened triplet, J = 6.5 Hz), 3.25 (3 H, s), 3.40 (2 H, t, J = 6.5 Hz), 3.41 (2 H, q, J = 7 Hz).

2,2-Dideuterio-1,3-dimethoxypropane. Diethyl 2,2-dideuteriomalonate was prepared from diethyl malonate by repetitive exchange with deuterium oxide in the presence of sodium acetate.[24] The ester was reduced with lithium aluminum hydride and converted to the dimethyl ether.

***gem*-Dideuterio-1-methoxy-4-ethoxybutanes** were prepared from 4-ethoxybutyric acid. The sodium salt of the acid was prepared from butyrolactone by the method of Fittig[25] and converted to the methyl ester. The 1,1-dideuterio compound was prepared by reduction of the ester with lithium aluminum deuteride and conversion of the resulting alcohol to the methyl ether, **1,1-dideuterio-1-me-**

thoxy-4-ethoxybutane. The 2,2-dideuterio compound was prepared by repetitive exchange of the ester in methanol-d_1 ca. 1 *M* in sodium methoxide; after two exchanges, the material remaining was reduced to the alcohol with lithium aluminum hydride and converted to the methyl ether, **2,2-dideuterio-1-methoxy-4-ethoxybutane,** 80 atom % D by ICR.

All synthesized compounds were purified by preparative VPC on a 10 ft × 0.25 in. 15% DEGS, 60-80 Chromosorb P column or on the FFAP column. The ICR mass spectra of deuterium labeled ethers prepared in the above manner showed isotopic purities to be greater than 98 atom % D, except where otherwise noted.

ICR mass spectra were recorded at 70, 30, 20, 16, 14, 13, 12, 11, and 10 eV ionizing energy. The important features of the variation of electron energy can be seen from the 70, 20, 16, and 12 eV spectra, and, except where otherwise noted, no appreciable change is seen when the ionizing energy is diminished below 12 eV. Observed ionization onsets of dimethyl and diethyl ether indicate that the nominal values of ionizing energy are in error by less than ±0.5 eV. Ion abundances are reported as % Σ, the ratio of normalized ion intensity, I_i/m_i, to total normalized intensity, $\Sigma I_i/m_i$, except where otherwise noted. Abundances are corrected for a natural abundance of 1.1% ^{13}C. Reported values have been rounded off to the nearest percent, and abundances less than 1% Σ are not reported.

Results

Selectivity in the bimolecular reactions of the molecular ions of simple ethers has been probed by low energy electron impact ionization of mixtures of ethers. At 3×10^{-5} Torr total pressure, bombardment of a mixture of dimethyl ether and diethyl ether-d_{10} produces only one primary ion, the molecular ion of diethyl ether-d_{10} (*m/e* 84), as the ionization potentials of dimethyl ether and diethyl ether are 10.0 and 9.5 eV, respectively.[26] Three ion-molecule reactions, 4a-c, may be envisaged to occur. Only the products of reactions 4a and 4b, *m/e* 85 and 86, are observed; no *m/e* 48 is detected. Double resonance confirms that *m/e* 84 is the only precursor to *m/e* 85 and 86.

$$\underset{m/e\ 84}{(C_2D_5)_2O\cdot^+} + (CH_3)_2O \longrightarrow \underset{m/e\ 85}{(C_2D_5)_2OH^+} + CH_3OCH_2\cdot \quad (4a)$$

$$\underset{m/e\ 84}{(C_2D_5)_2O\cdot^+} + (C_2D_5)_2O \longrightarrow \underset{m/e\ 86}{(C_2D_5)_2OD^+} + C_2D_5OC_2D_4\cdot \quad (4b)$$

$$\underset{m/e\ 84}{(C_2D_5)_2O\cdot^+} + (CH_3)_2O \longrightarrow \underset{m/e\ 48}{(CH_3)_2OD^+} + C_2D_5OC_2D_4\cdot \quad (4c)$$

Two causes may give rise to this selectivity. One possibility is that the bimolecular hydrogen transfer occurs only via atom abstraction, reaction 4a, and not via proton transfer, reaction 4c (reaction 4b may occur via either mechanism). Another possible cause is that the selectivity is based upon thermodynamic control of the reaction: ΔH for 4a is -50 ± 10 kJ/mol (-15 kcal/mol $\leq \Delta H \leq -10$ kcal/mol), the difference between the C-H bond dissociation energy of dimethyl ether[27] and the hydrogen atom affinity of the diethyl ether molecular ion,[7] and reaction 4b is expected to be somewhat more exothermic. Reaction 4c, however, is estimated to be thermoneutral, within experimental uncertainty.

The results of low energy electron bombardment of a mixture of ethyl methyl ether and diethyl ether-d_{10} show that atom abstraction is not the exclusive mechanism of bimolecular hydrogen transfer. The ionization potential of ethyl methyl ether is inferred to be lower than that of dimethyl ether, since no conditions were found to ionize diethyl ether without concomitant ionization of ethyl methyl ether. All possible ion-molecule reaction products from hydrogen transfer, the protonated and deuteronated parent ions of both ethers, are observed as secondary ions. ICR double resonance, however, indicates reaction 5, a proton transfer reaction, as a major source of the deuteromated parent of ethyl methyl ether, *m/e* 62.

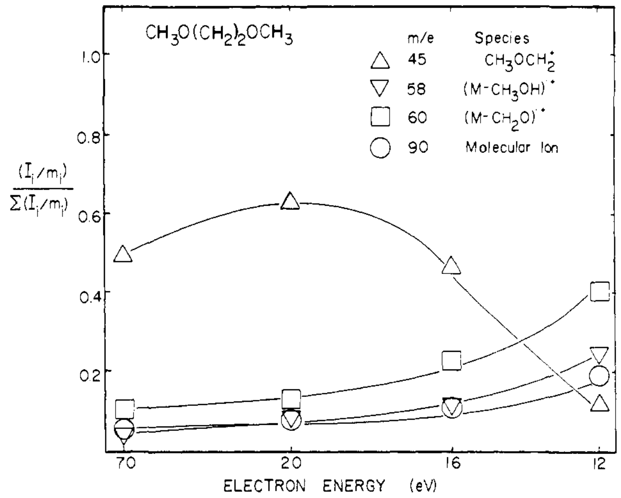


Figure 1. Mass spectral breakdown of 1,2-dimethoxyethane as a function of electron energy (only ions prominent at low ionizing energy are shown).

$$\underset{m/e\ 84}{(C_2D_5)_2O\cdot^+} + CH_3OCH_5 \longrightarrow \underset{m/e\ 62}{C_2H_5(CH_3)OD^+} + C_2D_5OC_2D_4\cdot \quad (5)$$

Mass Spectral Rearrangements of Bifunctional Ethers. Molecules which differ only in their chain lengths often fragment by expulsion of the same unit. In the mass spectra of a homologous series of compounds, members of the series may expel the same neutral species (e.g., methanol from the dimethoxyalkane molecular ions to produce $[M - CH_3OH]\cdot^+$ ions which are prominent in the low energy mass spectra) or the same ionic species (e.g., ion **1**, which gives the base peak for all the dimethoxyalkanes at 70 eV ionizing energy[17]). These homologous processes (production of homologous ions or expulsion of homologous neutrals) represent important trends in the mass spectra of dialkoxyalkanes, and deviations from the trends are suggestive of chain length selective processes. Significant trends are described in the following descriptions of the mass spectra.

Dimethoxymethane (Methylal). Two fragmentation processes, both simple bond cleavages, dominate the mass spectra of methylal at both high and low ionizing energies, viz., loss of a hydrogen atom and loss of a methoxy radical from the molecular ion. The resulting fragment ions, dimethoxymethyl cation (*m/e* 75)[17] and methoxymethyl cation (**1,** *m/e* 45), comprise 22% Σ and 42% Σ, respectively, at 70 eV and 77% Σ and 23% Σ, respectively, at 12 eV.

1,2-Dimethoxyethane (**Glyme**). The behavior of the ICR mass spectra of glyme as the energy of the ionizing electrons is decreased is shown in Figure 1. Methoxymethyl cation, **1,** is the base peak at 70 eV, but its abundance diminishes rapidly below 16 eV. Odd electron ions dominate the mass spectrum at low ionizing energies: molecular ion (*m/e* 90) and two ions which have rearranged to expel one of the methoxy functions, $[M - CH_2O]\cdot^+$ (*m/e* 60) and $[M - CH_3OH]\cdot^+$ (*m/e* 58). These two rearrangement ions show different reactions with the parent neutral: the latter reacts via hydride abstraction to produce the $[M - 1]^+$ ion of glyme, while the former reacts as a proton donor to form $[M + 1]^+$. The second-order rate constant for proton transfer from the $[M - CH_2O]\cdot^+$ ion to neutral glyme is computed to be $>1 \times 10^{-9}$ cm^3 molecule^{-1} sec^{-1} by the method of Marshall and Buttrill.[28]

1-Methoxy-2-ethoxyethane and 2-Methoxyethanol (Methyl Cellosolve). The low energy icr mass spectra of the

Table I. Low Ionizing Energy ICR Mass Spectra of ω-Ethoxy-1-methoxyalkanes

Compd	Electron energy, eV	Ions obsd *m/e* (% Σ)
(2) $CH_3OCH_2CH_2OC_2H_5$	12	60 (51), 72 (30), 59 (11), 104 (6), 86 (4)
(5a) $CH_3OCH_2CH_2CH_2OC_2H_5$	12	86 (47), 72 (43), 58 (6)
(8a) $CH_3OCH_2(CH_2)_2CH_2OC_2H_5$	12	103 (33), 71 (18), 58 (11), 59 (9), 72 (8), 88 (6), 56 (5), 87 (4), 117 (3)
(11) $CH_3OCH_2(CH_2)_3CH_2OC_2H_5$	11	117 (17), 114 (14), 85 (14), 100 (12), 99 (8), 72 (6), 102 (6), 68 (4), 75 (4), 73 (4), 71 (4), 70 (4)

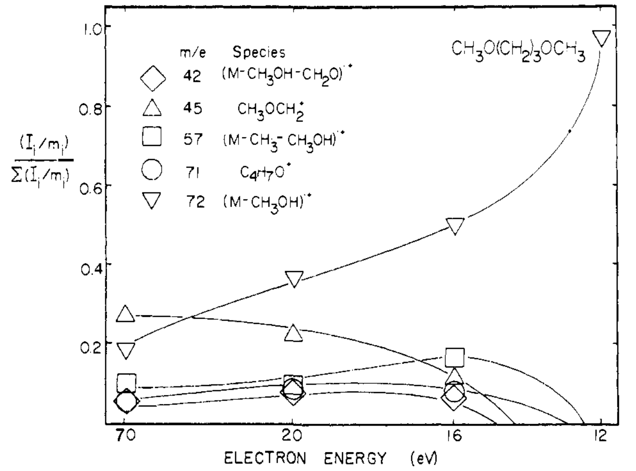


Figure 2. Mass spectral breakdown of 1,3-dimethoxypropane as a function of electron energy (only ions prominent at low ionizing energy are shown).

ω-ethoxy-1-methoxyalkanes are summarized in Table I. The 12 eV mass spectrum of 1-methoxy-2-ethoxyethane (**2**) reveals that the base peak (*m/e* 60) is the same as that of glyme at the same ionizing energy. This ion arises via the homologous process, elimination of the ethoxy function as acetaldehyde. It is interesting to note that this is the exclusive mode of expulsion of the ethoxy function at low energy, while elimination of methanol (to form *m/e* 72) is the sole mode of expulsion of the methoxy function. The remainder of the ions at 12 eV are comprised by molecular ion (*m/e* 104), $[M - H_2O]\cdot^+$ (*m/e* 86), and a cleavage fragment which is presumed to be ethoxymethyl cation, *m/e* 59.

Major ions in the 12 eV ICR mass spectra of ω-methoxyalkanols are summarized in Table II. The 13 eV ICR mass spectrum of 2-methoxyethanol (**3**) (Methyl Cellosolve) has been reported by Caserio and coworkers.[10c] The only odd electron ion observed, aside from the molecular ion (*m/e* 76), is the $[M - H_2O]\cdot^+$ rearrangement ion (*m/e* 58). The lack of $[M - CH_2O]\cdot^+$ ion (*m/e* 46) is perhaps attributable to intramolecular hydrogen bonding in the parent neutral.[29,30]

1,3-Dimethoxypropane. The breakdown of 1,3-dimethoxypropane (**4a**) as a function of ionizing energy is summarized in Figure 2. The most notable feature of the energy dependence of the mass spectra of **4a** is that only one ion, $[M - CH_3OH]\cdot^+$ (*m/e* 72), is observed at the lowest ionizing energies. This ion reacts with the parent neutral exclusively as a proton donor; the bimolecular rate constant from disappearance of $[M - CH_3OH]\cdot^+$ and appearance of $[M + 1]^+$ ions in the pressure range 10^{-6} to 10^{-4} Torr[28] is 3.5 ± 0.5 × 10^{-10} cm^3 molecule^{-1} sec^{-1}. This rate constant was also measured by trapped ion ICR methods in which the disappearance of reactant and the appearance of product are monitored at constant pressure as reaction time is increased.[10b] The bimolecular rate constant measured by this method at 4 × 10^{-6} Torr is 3.0 ± 0.5 × 10^{-10} cm^3 molecule^{-1} sec^{-1}.

Table II. ICR Mass Spectra (12 eV) of ω-Methoxyalkanols

Compd	Major ions obsd (>5% Σ) *m/e* (% Σ)
(3) $CH_3OCH_2CH_2OH$	45 (35), 47 (26), 76 (20), 58 (19)
(6) $CH_3OCH_2CH_2CH_2OH$	72 (74), 58 (14), 57 (9)
(9) $CH_3OCH_2CH_2CH_2CH_2OH$	58 (27), 45 (15), 76 (12), 47 (12), 89 (10), 86 (6)

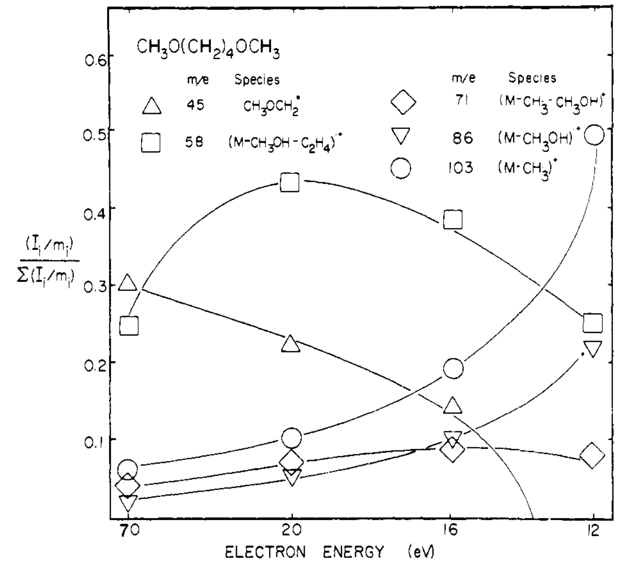


Figure 3. Mass spectral breakdown of 1,4-dimethoxybutane as a function of electron energy (only ions prominent at low ionizing energy are shown).

1-Methoxy-3-ethoxypropane and 3-Methoxy-1-propanol. The only ions observed in the 12 eV ICR mass spectrum of 1-methoxy-3-ethoxypropane (**5a**) are the $[M - CH_3OH]\cdot^+$ and $[M - C_2H_5OH]\cdot^+$ rearrangement ion (*m/e* 86 and 72, respectively). The ratio of these ions varies as a function of electron energy: *m/e* 72/*m/e* 86 = 1.5 at 70 eV, 1.2 at 16 eV, 0.9 at 12 eV, and 0.8 at 11 eV. To investigate this behavior further, the photoionization mass spectrum was examined.[31] The longest wavelength at which ionization can be observed is 1303 Å, corresponding to to 9.47 eV. No molecular ion is detected at onset; the two rearrangement ions are seen in the ratio 0.7 ± 0.2. Homologous rearrangement ions, $[M - H_2O]\cdot^+$ and $[M - CH_3OH]\cdot^+$ (*m/e* 72 and 58, respectively), are the major primary ions from 12 eV electron bombardment of 3-methoxy-1-propanol (**6**).

1,4-Dimethoxybutane, 1-Methoxy-4-ethoxybutane, and 4-Methoxybutanol. The breakdown of 1,4-dimethoxybutane (**7a**) as a function of ionizing energy is graphed in Figure 3. The base peak at the lowest ionizing energies (*m/e* 103) corresponds to the loss of a methyl radical from the molecular ion. The same ion constitutes the base peak from 1-methoxy-4-ethoxybutane (**8a**) and is inferred to result from loss of an ethyl radical. The ratio $[M - C_2H_5]^+/[M - CH_3]^+$ from **8a** equals 11 ± 2, independent of ionizing energy. The homologous process occurs to a far lesser extent in 4-methoxybutanol (**9**); at 12 eV $[M - CH_3]^+$ (*m/e* 89) composes only 10% Σ, and $[M - H]^+$ is not observed.

1,5-Dimethoxypentane. The breakdown of 1,5-dimethoxypentane (**10a**) is graphed as a function of electron energy in Figure 4. The base peak at low ionizing energy is the [M

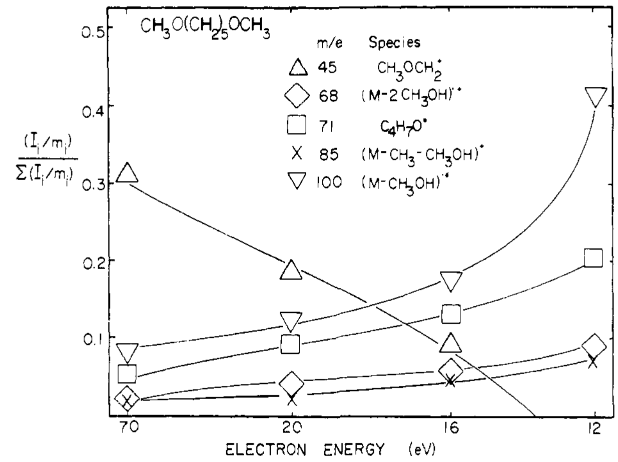


Figure 4. Mass spectral breakdown of 1,5-dimethoxypentane as a function of electron energy (only ions prominent at low ionizing energy are shown).

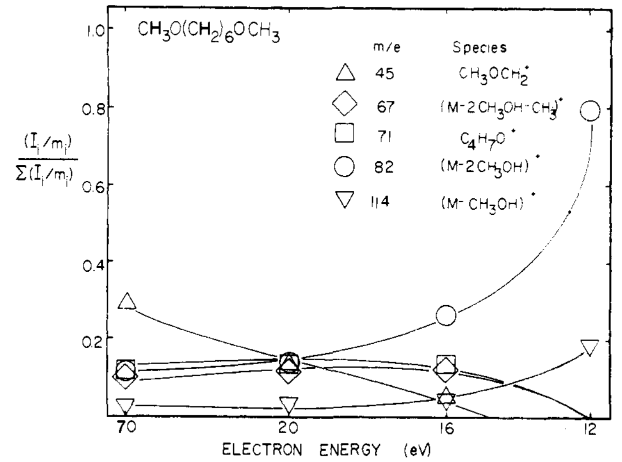


Figure 5. Mass spectral breakdown of 1,6-dimethoxyhexane as a function of electron energy (only ions prominent at low ionizing energy are shown).

$-$ $CH_3OH]^{\cdot+}$ rearrangement ion (*m/e* 100), and the other major peaks also result from rearrangements. The $[M - CH_3OH]^{\cdot+}$ and $[M - 2CH_3OH]^{\cdot+}$ (*m/e* 68) ions are observed by ICR double resonance to react as proton donors to the parent neutral, while the $C_4H_{10}O^+$ ion (*m/e* 71) reacts very slowly with the parent neutral, principally via aggregation at pressures above 10^{-4} Torr to form an $[M + 71]^+$ ion (*m/e* 203).

5-Ethoxy-1-methoxypentane and 1,6-Dimethoxyhexane . The major fragment ions seen in 5-ethoxy-1-methoxypentane (**11**) arise by rearrangements homologous to those of **10a** (Table I): $[M - CH_3OH]^{\cdot+}$ (*m/e* 114) and $[M - C_2H_5OH]^{\cdot+}$ (*m/e* 100) ions are seen in the ratio 1.1:1, and $C_4H_7O^+$ (*m/e* 71) and $[M - C_2H_5OH - CH_3OH]^{\cdot+}$ (*m/e* 68) ions are observed. In contrast to **11**, which yields a profusion of different ions at 11 eV, its isomer **12**, 1,6-dimethoxyhexane, exhibits a remarkably simple ICR mass spectrum at low ionizing energies, as shown in Figure 5. At 12 eV, only two ions are observed, $[M - CH_3OH]^{\cdot+}$ (*m/e* 114) and $[M - 2CH_3OH]^{\cdot+}$ (*m/e* 82).

Deuterium Labeling Studies. Isotopic labeling provides further information regarding the mechanisms of rearrangement in bifunctional ethers. The mass spectrum from 12 eV electron impact on the specifically labeled compound **5b** reveals that 90% of the total ionization results from loss

$CH_3OCD_2(CH_2)_{n-1}OC_2H_5$ $\quad$ $CH_3OCH_2CD_2CH_2CH_2OC_2H_5$

5b, $n = 3$ $\quad$ **8c**

8b, $n = 4$

of ethanol or methanol from the molecular ion. The ratio $[M - CH_3OH]^{\cdot+}:[M - C_2H_5OD]^{\cdot+}:[M - C_2H_5OH]^{\cdot+}$ is 7:5:1. The preference for loss of C_2H_5OD versus loss of C_2H_5OH indicates that the hydrogen rearrangement is regioselective, with the source of itinerant hydrogen being a methylene α to a methoxy function, as depicted in reaction 6.

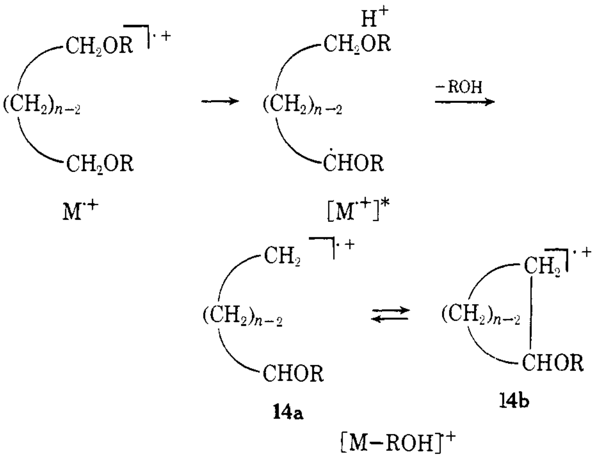
The mass spectra of various deuterium labeled α,ω-dimethoxyalkanes at 12 eV ionizing energy, summarized in Table III, indicate that a high degree of regioselectivity is manifested by the hydrogen rearrangements in all of these compounds, as well, in accordance with the mechanism shown in reaction 6.

Structure of Ions from which Loss of Alcohol has Occurred. Little is known about the structure of odd-electron ions. Structures **14a** and **14b**, shown in reaction 6, represent valence isomers possible for the $[M - ROH]^{\cdot+}$ ions from dialkoxyalkanes. The interconversion of **14a** and **14b** is of interest, for the bimolecular analog of the ring opening **14b** → **14a** is the expulsion of a radical fragment from a molecular ion, an endothermic process for which the enthalpy of activation, $\Delta H^{\ddagger}$, is presumed equal to the enthalpy of reaction.[26] If the analogy between bimolecular and intramolecular reactions is valid, the cyclization **14a** → **14b** is exothermic and should take place.

Table III. ICR Mass Spectra (12 eV) of Deuterium Labeled α,ω-Dimethoxyalkanes

Compd	$[M - ROD]^{\cdot+}/([M - ROH]^{\cdot+} + [M - ROD]^{\cdot+})^{a,b}$	Major ions obsd (>5% Σ)^b *m/e* (% Σ)
(13) $CH_3OCD_2CD_2OCH_3$	0.94	64 (47), 47 (23), 94 (20), 61 (7)
(4b) $CH_3OCD_2CH_2CD_2OCH_3$	0.96	75 (>95)
(4c) $CH_3OCH_2CD_2CH_2OCH_3$	0.05	74 (>95)
(4d) $CD_3OCH_2CH_2CH_2OCD_3$	⩽0.03	75 (>95)
(7b) $CD_3OCD_2(CH_2)_2CD_2OCH_3$	0.93	107 (26), 59 (24), 89 (20), 74 (8)
(10b) $CH_3OCD_2(CH_2)_3CD_2OCH_3$	0.87	103 (39), 72 (17), 73 (10), 71 (7,

^{a} ±0.02. ^{b} Corrected for ^{13}C natural abundance.



14a **14b** (6)

Cyclization of an ion may be probed in two ways. One method is examination of ions which are sufficiently energetic to undergo further fragmentation. For example, if the cyclization of the $[M - ROH]^{\cdot+}$ ion from **10a** ($n = 5$) occurs, then the ion **14b** ($n = 5$) resembles the molecular ion from cyclopentyl methyl ether, which is known to fragment at low ionizing energies via expulsion of a methyl radical to yield a $C_5H_9O^+$ (*m/e* 85) ion.[32] An ion of the same mass is produced by bombardment of **10a** by 12 eV electrons. Does this ion arise from loss of a methoxy methyl from the cy-

Table IV. Ratios of Deuteron to Proton Transfer from Hydrogen Rearrangement Ions of Labeled Dialkoxypropanes at 12 eV Ionizing Energy and 3 × 10^{-5} Torr

Parent neutral (M)	Acidic primary ion	[M + 2]/[M + 1]
4b	$[M - CH_3OD]^{\cdot +}$ (*m/e* 75)	0.61 ± 0.02
4c	$[M - CH_3OH]^{\cdot +}$ (*m/e* 74)	0.64 ± 0.02
4d	$[M - CD_3OH]^{\cdot +}$ (*m/e* 75)	0.06 ± 0.01
5b	$[M - C_2H_5OD]^{\cdot +}$ (*m/e* 73)	<0.15[a]

[a] The presence of $[M - CH_3OH]^{\cdot +}$ prevents further resolution of the contribution of this species to the $[M + 2]^+$ ion.

clized ion **14b?** If so, the corresponding ion from the tetradeuterio compound **10b** should be $C_5H_6D_3O^+$ (*m/e* 88). In fact, the analogous ions from **10b** appear at *m/e* 85, 86, 87, 88, and 89 in the ratio 1:4:4:6:3 (total of 7% Σ at 12 eV).

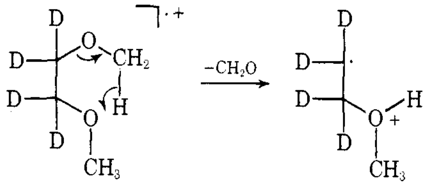
Subsequent fragmentations of the $[M - ROH]^{\cdot +}$ ions from dialkoxybutanes also show no evidence for cyclization of **14a** to **14b** ($n = 4$). If cyclization occurs in the $[M - CH_3OH]^{\cdot +}$ ion from **7a**, the ion formed will be identical to the molecular ion of cyclobutyl methyl ether, which is known to fragment via expulsion of ethylene.[33] The cyclization of the $[M - CH_3OD]^{\cdot +}$ ion (*m/e* 89) from **7b** will scramble a methylene with a methylene-d_2, and both *m/e* 61 and 59 daughter ions would be expected from further fragmentation. The observed ratio of *m/e* 59 to 61 from **7b** is >5 at 12 eV, indicating that cyclization, if it occurs, is much slower than subsequent fragmentation of the $[M - CH_3OD]^{\cdot +}$ ion.

Another probe for cyclization employs ion-molecule reactions to detect label scrambling in nonfragmenting ions.[9d] This method has been used to examine the dialkoxypropanes **4** and **5**, and there is evidence to suggest the cyclization of the $[M - ROH]^{\cdot +}$ ions to an alkoxycyclopropane molecular ion, **14b** ($n = 3$). The ratios of deuteron to proton transfer from the hydrogen rearrangement ions to the parent neutrals, summarized in Table IV, indicate that the acidic sites of the primary ions are the two methylene groups. The fact that the ions from **4b** and **4c** show the same ratios of deuteron to proton transfer, within experimental uncertainty, demonstrates that the two methylenes become completely scrambled on the time scale of the ion-molecule reaction ($k \approx 300\ sec^{-1}$ at 3 × 10^{-5} Torr).

The hydrogen rearrangements which give rise to the $[M - 2CH_3OH]^{\cdot +}$ ion (*m/e* 68) from **10a** differ from the rearrangement which leads to the $[M - CH_3OH]^{\cdot +}$ ion (*m/e* 100). Examination of the ion-molecule reactions of the mass spectral fragments of **10b** with the parent neutral using ICR double resonance[7] reveals that, of the three prominent ions *m/e* 71–73, only *m/e* 72 reacts rapidly as a proton donor. This implies that *m/e* 72 from **10b** is the analog of *m/e* 68 from **10a**, i.e., all four deuteria are retained in the rearrangement ion, and the sources of itinerant hydrogen are within the methylene chain in the β or γ positions, rather than the α positions, for loss of two molecules of methanol from the molecular ions of **10.**

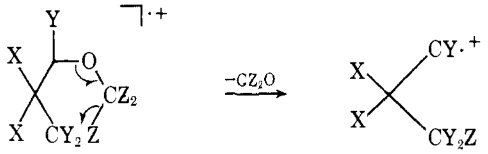
Vinculoselective Processes. The hydrogen rearrangement by which a molecule of alcohol is expelled from the molecular ion is prominent in the low energy mass spectra of all the bifunctional ethers studied save for methylal and 2-methoxyethanol (**3**). Other processes occur, though, which appear to be highly selective for certain chain lengths. The adjective *vinculoselective* is appended to these reactions.

One prominent vinculoselective reaction is the expulsion of an aldehyde molecule from the molecular ion, which gives rise to the base peaks from glyme and from 2-ethoxy-1-methoxyethane at low energy. This rearrangement does not figure so prominently in the mass spectra of any of the other dialkoxyalkanes studied, and a transition state for the expulsion of formaldehyde from the molecular ion of glyme-d_4, **13**, is depicted in reaction 7. The structure of ion **15** is confirmed by its ion-molecule reaction with parent neutral, for it reacts exclusively as a proton donor, demonstrating that the itinerant hydrogen has not become scrambled with any of the deuteria.



13 **15** (*m/e* 64) (7)

This rearrangement, which appears to require a six-member cyclic transition state in the α,ω-dimethoxyalkanes, is similar to the McLafferty rearrangement.[11] No analogous process is reported to be significant in the mass spectra of monofunctional acyclic ethers of the same chain length;[21,34] however, a comparable rearrangement is observed in the mass spectra of 1,3-dimethoxypropanes (**4**). A subsequent rearrangement of the ion **14** ($n = 3$) expels the second methoxy function as formaldehyde, reaction 8, to afford the ions **16.**



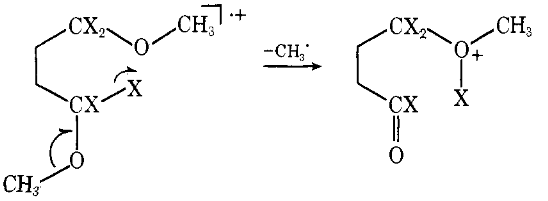
14 ($n = 3$) (8)

16a, X = Y = Z = H 7% Σ at 16 eV
b, X = Z = H; Y = D 6% Σ at 16 eV
c, X = D; Y = Z = H 9% Σ at 16 eV
d, X = Y = H; Z = D 3% Σ at 16 eV

There is no thermodynamic reason why expulsion of formaldehyde occurs in reactions 7 and 8, but in none of the homologous ions from α,ω-dimethoxyalkanes. The facts that $[M - CH_2O]^{\cdot +}$ is far more abundant in the mass spectra of *cis*-1,4-dimethoxycyclohexane than in the mass spectra of other dimethoxycyclopentanes, -hexanes, or -heptanes and that elimination of formaldehyde from dimethoxydecalins is dependent upon stereochemistry[16] confirm that this rearrangement is subject to stringent spatial and conformational constraints on the positions of the reactive center, the itinerant hydrogen, and the second functional center.

Another vinculoselective reaction is the expulsion of a methyl radical from the molecular ion of 1,4-dimethoxybutanes (**7**) which generates the base peak at the lowest ionizing energies, but is not seen in the homologous dimethoxyalkanes. Thermodynamic considerations suggest that this is not a simple cleavage. If the ionization potential of **7a** is assumed to be the same as that of its isomer **5a**, 9.5 eV, then the heat of formation of the molecular ion of **7a** is estimated to be 125 kcal/mol (520 kJ/mol).[35] Bond cleavages to expel radical fragments from molecular ions, such as reaction 2a, are usually endothermic, which necessitates that the ion be vibrationally activated before a simple bond cleavage will occur spontaneously. This explains why many even-electron species, such as methoxymethyl cation, **1**, which are prominent at 70 eV, are not observed at ionizing energies a few eV above threshold. The endothermicities of some cleavages may be estimated.

The cleavage to form methoxymethyl cation from the molecular ion of **7a**, based upon a heat of formation of **1** equal to 155 kcal/mol (650 ± 50 kJ/mol),[36] is estimated to be endothermic by 20 kcal/mol (85 ± 50 kJ/mol).[27] The cleavage of a methyl radical to leave an alkoxy cation is estimated to be 70 kcal/mol (300 ± 100 kJ-mol) endothermic, based upon reported ionization potentials of alkoxy radicals.[37] Nevertheless, $[M - CH_3]^+$ is the base peak from **7** at the lowest ionizing energies, where methoxymethyl cation is no longer observed. This anomaly may be resolved by the mechanism shown in reaction 9, which depicts an intramolecular hydrogen transfer concerted with cleavage of the alkyl radical. With the estimate that the proton affinity of 4-methoxybutanal is bracketed by that of dimethyl ether (186 kcal/mol[7]) and that of diethyl ether (199 kcal/mol[7]), reaction 9 is estimated to be thermoneutral within the limits of the uncertainty.



(9)

7a, X = H
b, X = D

17a, X = H *m/e* 103
b, X = D *m/e* 107

Reaction 9 is inferred to be concerted, for, if it is stepwise, the first step is identical to the hydrogen transfer step of reaction 6, and there would be no rationale for the vinculoselectivity of the reaction. In the mechanism proposed, the vinculoselectivity results from the conformational and spatial restrictions of the six-member transition state which leads to ions **17.** Expulsion of methyl radical is not reported to occur to the same extent in any of the dimethyoxycycloalkanes that it does in **7.**[16]

The structure of ion **17** is confirmed by the ion-molecule reactions of deuterium substituted analog. Ion **17a** reacts as a proton donor to the parent neutral, while **17b** reacts exclusively as a deuteron donor. The analogous ions, $[M - C_2H_5]^+$ from **8b** and **8c,** react exclusively as proton donors.

Conclusion

Hydrogen transfer within the molecular ions of bifunctional ethers, reaction 6, is found to select between the methyl and methylene groups attached to oxygen, while the analogous ion-molecule reaction, reaction 3, does not. Bimolecular ion-molecule reactions are, however, found to select exothermic processes, e.g., reactions 4a-b, in preference to thermoneutral ones, e.g., reaction 4c. Generalization of these results suggests that endothermic rearrangements of vibrationally activated ions are more strongly affected by thermodynamic considerations than are exothermic bimolecular ion-molecule reactions.

The chain-length effects observed in the mass spectra of bifunctional ethers also represent a deviation from the analogy between bimolecular and intramolecular reactions. In solution phase studies, chain-length effects have been used to validate the analogy; for example, the length of a methylene chain between two electron acceptor moieties has been reported to affect the rate of intramolecular electron exchange in a manner analogous to the effect of concentration upon bimolecular exchange rates, and a quantitative relation has been suggested.[38] The chain-length selectivity observed in the mass spectral rearrangements of bifunctional ethers, however, has no analogy in the ion-molecule reactions examined.

The chain-length effects in the bifunctional molecules differ from the effects of chain length upon regioselective reactions, in which the selected region is determined on the basis of its position relative to an atom or functional group in the molecule.[39] Instead, vinculoselection is observed: reactions occur (e.g., the expulsion of an alkyl radical or an aldehyde molecule) which are specific for certain chain-length separations between functional groups. Vinculoselection, which denotes modes of reaction of polyfunctional molecules which are strongly dependent upon chain-length or spatial separation of the functional groups, is seen throughout the chemistry of polyfunctional compounds. Examples include the chemistry of selective ionophores,[40] synthetic organic cyclizations,[41] and structure-function relationships of drugs affecting cholinoreceptors.[42] Similar effects are also seen in intramolecular hydrogen bonding, both weak[43] and strong.[4,8] Additional examples and applications of vinculoselection are the subject of a continuing investigation.

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References and Notes

(1) (a) Taken in part from the Ph.D. dissertation of T.H.M., California Institute of Technology, 1973. Portions of this work have been presented before the Organic Section of the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 9–14, 1972; (b) Publication No. 4967.

(2) (a) Brown University; (b) California Institute of Technology, Dreyfus Teacher-Scholar.

(3) C. A. Stein and T. H. Morton, *Tetrahedron Lett.*, 4933 (1973).

(4) T. H. Morton and J. L. Beauchamp, *J. Am. Chem. Soc.*, **94,** 3671 (1972).

(5) E. White, V, S. Tsuboyama, and J. A. McCloskey, *J. Am. Chem. Soc.*, **93,** 6340 (1973), and references contained therein.

(6) D. P. Ridge and J. L. Beauchamp, *J. Chem. Phys.*, **51,** 470 (1969).

(7) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22,** 527 (1971).

(8) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **95,** 2699 (1973).

(9) (a) J. L. Beauchamp and R. C. Dunbar, *J. Am. Chem. Soc.*, **92,** 1477 (1970); (b) J. Diekman, J. K. MacLeod, C. Djerassi, and J. D. Baldeschwieler, *ibid.*, **91,** 2069 (1969); G. Eadon, J. Diekman, and C. Djerassi, *ibid.*, **92,** 6205 (1970); K. B. Tomer and C. Djerassi, *ibid.*, **95,** 5335 (1973); (c) M. L. Gross and F. W. McLafferty, *ibid.*, **93,** 1267 (1971); D. J. McAdoo, F. W. McLafferty, and P. F. Bente III, *ibid.*, **94,** 2026 (1972); (d) M. L. Gross, *ibid.*, **94,** 3744 (1972); (e) H. H. Jaffe and S. Billets, *ibid.*, **94,** 674 (1972); (f) J. R. Hass, M. M. Bursey, D. G. I. Kingston, and H. P. Tannenbaum, *ibid.*, **94,** 5095 (1972).

(10) (a) D. P. Ridge and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96,** 3595 (1974), and references contained therein; (b) R. J. Blint, T. B. McMahon, and J. L. Beauchamp, *ibid.*, **96,** 1269 (1974), and references contained therein; (c) J. K. Kim, M. C. Findlay, W. C. Henderson, and M. C. Caserio, *ibid.*, **95,** 2184 (1973), and references contained therein; (d) J. R. Eyler, P. Ausloos, and S. G. Lias, *ibid.*, **96,** 3673 (1974).

(11) D. G. I. Kingston, J. T. Bursey, and M. M. Bursey, *Chem. Rev.*, **74,** 215 (1974).

(12) J. T. Bursey, M. M. Bursey, and D. G. I. Kingston, *Chem. Rev.*, **73,** 191 (1973).

(13) P. J. Derrick, A. M. Falick, and A. L. Burlingame, *J. Am. Chem. Soc.*, **95,** 437 (1973).

(14) (a) J. H. Bowie, S.-Ö. Lawesson, G. Schroll, and D. H. Williams, *J. Am. Chem. Soc.*, **87,** 5742 (1965); (b) C. Djerassi and C. Fenselau, *ibid.*, **87,** 5756 (1965).

(15) M. M. Green, J. G. McGrew II, and J. M. Moldowan, *J. Am. Chem. Soc.*, **93,** 6700 (1971).

(16) J. Winkler and H.-F. Grützmacher, *Org. Mass Spectrom.*, **3,** 1117, 1139 (1970); H.-F. Grützmacher and K. H. Fechner, *ibid*, **9,** 152 (1974).

(17) H.-F. Grützmacher and J. Winkler, *Org. Mass Spectrom.*, **1,** 295 (1968).

(18) M. Sheehan, R. J. Spangler, M. Ikeda, and C. Djerassi, *J. Org. Chem.*, **36,** 1796 (1971).

(19) M. Sheehan, R. J. Spangler, and C. Djerassi, *J. Org. Chem.*, **36,** 3526 (1971).

(20) The prefix vinculo- is taken from the Latin word *vinculum*, meaning chain.

(21) F. W. McLafferty, *Anal. Chem.*, **29,** 1782 (1957).

(22) M. S. B. Munson, *J. Am. Chem. Soc.*, **87,** 5313 (1965).

(23) A. S. Blair and A. G. Harrison, *Can. J. Chem.*, **51,** 703 (1973).

(24) M. J. Caserio, W. H., Graham, and J. D. Roberts, *Tetrahedron*, **11,** 171 (1960).

(25) R. Fittig, *Justus Liebigs Ann. Chem.*, **267,** 186 (1891).

(26) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **No. 26** (1969).

(27) H. E. O'Neal and S. W. Benson, "Free Radicals", Vol. II, J. Kochi, Ed., Wiley, New York, N.Y., 1973, pp 275–359.

(28) A. G. Marshall and S. E. Buttrill, Jr., *J. Chem. Phys.*, **52,** 2752 (1970);

computer program courtesy of S. L. Patt and T. B. McMahon.
(29) R. G. Azrak and E. B. Wilson, Jr., *J. Chem. Phys.*, **52**, 5299 (1970), report extensive intramolecular hydrogen bonding in the 2-haloethanols in the gas phase.
(30) L. P. Kuhn and R. A. Wires, *J. Am. Chem. Soc.*, **86**, 2161 (1964), report that, in carbon tetrachloride solution, about 90% of **3** exists in an intramolecularly hydrogen bound form at 300°K, while **6** and **9** show about 50 and 30% intramolecular hydrogen bonding, respectively.
(31) Spectra, courtesy of Dr. P. R. LeBreton, taken on joint Caltech-JPL photoionization mass spectrometer (J. M. Ajello, W. T. Huntress, A. L. Lane, P. R. LeBreton, and A. D. Williamson, *J. Chem. Phys.*, **60**, 1211 (1974).
(32) R. B. Jones, E. S. Waight, and J. E. Herz, *Org. Mass Spectrom.*, **7**, 781 (1973).
(33) W. G. Dauben, J. H. Smith, and J. Saltiel, *J. Org. Chem.*, **34**, 261 (1969)
(34) S. L. Bernasek and R. G. Cooks, *Org. Mass Spectrom.*, **3**, 127 (1970).
(35) H. K. Eigenmann, D. M. Golden, and S. W. Benson, *J. Phys. Chem.*, **77**, 1687 (1973).
(36) E. G. Jones, J. H. Beynon, and R. G. Cooks, *J. Chem. Phys.*, **57**, 2652 (1972).
(37) J. M. Williams and W. H. Hamill, *J. Chem. Phys.*, **49**, 4467 (1968).
(38) H. D. Connor, K. Shimada, and M. Szwarc, *Macromolecules*, **5**, 801 (1972). For a treatment of the chain-length dependence of the probability for ring closure of a polymer chain, see N. Goodman and H. Morawetz, *J. Polym. Sci. Part A-2*, **9**, 1657 (1971).
(39) M. A. Winnik, C. K. Lee, and P. T. Y. Kwong, *J. Am. Chem. Soc.*, **96**, 2901 (1974); M. A. Winnik, R. E. Trueman, G. Jackowski, D. S. Saunders, and S. E. Whittington, **98**, 4843 (1974), and references contained therein.
(40) W. Simon, *Helv. Chim. Acta*, **56**, 1780 (1973); J. Christiansen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 351 (1974).
(41) G. Stork, L. D. Cama, and D. R. Coulson, *J. Am. Chem. Soc.*, **96**, 5268 (1974); G. Stork and J. F. Cohen, *ibid.*, **96**, 5270 (1974).
(42) B. Belleau, H. Tani, and F. Lie, *J. Am. Chem., Soc.*, **87**, 2283 (1965); M. J. Michelson and E. V. Zeimal, "Acetylcholine", E. Lesser and M. Lesser, translators, Pergamon Press, Oxford, 1973; H. Wombacher and H. U. Wolf, *Mol. Pharmacol.*, **7**, 554 (1971).
(43) S. N. Vinogradov and R. H. Linnell, "Hydrogen Bonding", Van Nostrand, New York, N.Y., 1971, pp 134–138.

Studies in Chemical Ionization Mass Spectrometry. Secondary Alcohols with Isobutane

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Abstract: The major ions of the characteristic isobutane CI mass spectra of secondary alcohols can be accounted for in large part by the initial formation of a $(M + t\text{-}C_4H_9)^+$ association complex that is relatively long lived, but not always readily detectable. This complex may dehydrate to give $(M + 39)^+$, eliminate C_4H_8 to provide $(M + 1)^+$, eliminate C_4H_{10} to afford $(M - 1)^+$, or eliminate C_4H_9OH to give $(M - 17)^+$. Experiments with labeled secondary alcohols show that significant amounts of hydrogen atom scrambling occur in the $(M + 57)^+$ ions in these decompositions.

In an earlier report on the isobutane chemical ionization (CI) mass spectra of a number of saturated monohydroxylic alcohols, Field noted the presence of $(M + 57)^+$ and $(M + 39)^+$ ions, as well as very abundant alkyl ions, $(M - OH)^+$, and small amounts of $(M - 1)^+$ and $(M + 1)^+$ ions.[1] Separate mechanisms were suggested by Field to account for the formation of each of these ions.[1] We now wish to present evidence which suggests that in (at least) secondary alcohols these ions result in large part from the decomposition of a sometimes observable common intermediate $(M + t\text{-}C_4H_9)^+$ association complex.

Experimental Section

All chemical ionization spectra were obtained with a (Du Pont) CEC 21-110B mass spectrometer that had been modified for high-pressure operation.[2] Samples were introduced into the source region of the mass spectrometer by a direct insertion probe or through a variable leak from a heated glass oven.

The perdeuterated isobutane employed was obtained from Merck Sharp and Dohme of Canada. A high-pressure mass spectrum (P = 0.8 Torr) of this gas contained ions from m/e 29 to 140. The observed *tert*-butyl ions were $C_4H_9{}^+$ (6.1% of total ionization), $C_4H_8D^+$ (1.8%), $C_4H_7D_2{}^+$ (0.9%), $C_4H_6D_3{}^+$ (0.7%), $C_4H_5D_4{}^+$ (0.7%), $C_4H_3D_6{}^+$ (0.9%), $C_4H_2D_7{}^+$ (3.7%), $C_4HD_8{}^+$ (10.5%), and $C_4D_9{}^+$ (38.8%).

Cyclohexan-*1-d*-ol was prepared by lithium aluminum deuteride reduction of cyclohexanone employing an aqueous work-up procedure. Similarly, 2-adamantan-*2-d*-ol was prepared from adamantanone. Mass spectral analysis indicated that the cyclohexan-*1-d*-ol contained 86.3% d_1 and the 2-adamantan-*2-d*-ol, 96.3%. Cyclohexan-*2,2,6,6-d*$_4$-ol was obtained from the lithium aluminum hydride reduction of cyclohexan-*2,2,6,6-d*$_4$-one, which was prepared from cyclohexanone by repeated base-catalyzed equilibration with deuterium oxide. Mass spectral analysis showed that this labeled cyclohexanol contained 7.0% d_0, 2.1% d_1, 4.2% d_2, 11.9% d_3, 60.1% d_4, and 14.7% d_5. All samples were purified by glpc.

Results and Discussion

The isobutane CI data obtained in this study and those previously reported by Field[1] for a typical secondary alcohol, cyclohexanol, are compared in Table I. Although there are obvious differences in the relative abundances of the ions, the major ions observed are the same. Particularly striking are the $(M + 39)^+$ and the $(M + 57)^+$ ions. Field accounted for these ions by the formation of association complexes of the alcohol with the $C_3H_3{}^+$ and $t\text{-}C_4H_9{}^+$ ions of the isobutane plasma.[1] Alternatively, the $(M + 39)^+$ ion

Table I. Isobutane CI Spectra of Cyclohexanol

	% ionization ($100I_i/\sum_{\text{sample}} I_i$)		
Ion	70° [a]	110° [a]	180° [b]
M − 19	1.1	1.2	1.0
M − 17	22.8	39.9	65.8
M − 1	6.0	4.5	10.0
M + 1	9.2	7.0	7.2
M + 39	3.8	3.7	3.1
M + 57	23.6	13.7	2.3
2M + 1	6.3	3.4	

[a] The ion intensities reported are corrected for ^{13}C isotope. The reproducibility of the percent ionization is ±10% of the reported values. Pressure of isobutane is 0.6 Torr. [b] Reference 1; pressure of isobutane is 0.5 Torr.