Ion Cyclotron Resonance Spectroscopy. Neighboring Group Effects in the Gas-Phase Ionization of β-Substituted Alcohols

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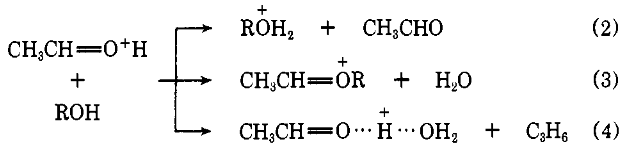
Abstract: The effects of structure and stereochemistry on the gas-phase ionization of β-substituted ethanols (XCH_2CH_2OH), propanols ($CH_3CH(OH)CH_2X$ and CH_3CHXCH_2OH), and cyclopentanols have been studied by ion cyclotron resonance techniques. Ionization to form $XC_2H_4^+$, $XC_3H_6^+$, or $XC_5H_8^+$, where X = F, Cl, Br, OR, SR, SH, and NH_2, occurs as the result of protonation of the alcohol and subsequent dissociation with H_2O as the leaving group. Only in the case of X = F and Cl was loss of HX competitive with loss of H_2O. The results are qualitative but indicate that product stability is a major factor determining the mode and importance of dissociation. Neighboring group effects, alkyl substitution, and configurational effects parallel those observed in solvolytic reactions of related compounds. An attempt has been made to assign structures to ions of composition $XC_2H_4^+$ derived from dissociation of the protonated β-substituted ethanols on the basis of the reactions of these ions with the parent alcohols compared to the related reactions of isomeric ions. The results are tentative but support cyclic sulfonium ion structures for X = SCH_3 and SH, and acyclic structures for X = OCH_3 and Br—that is, $CH_3CH{=}O^+CH_3$ and $CH_3CH{=}Br^+$.

Ion–molecule reactions in the gas phase can be conveniently studied using the techniques of ion cyclotron resonance[2a–d] (icr), chemical ionization, and high-pressure mass spectrometry.[2e,f] In this manner, the ion chemistry of simple alcohols has been investigated extensively[3–5] and the major reactions have been identified. In icr studies,[4] the major primary ions are α-cleavage products formed from the parent alcohols (ROH) on electron impact, as shown in eq 1 for the case of 2-propanol. These ions react with the parent alcohol to effect proton transfer (eq 2), condensation (eq 3), and dehydration (eq 4).

$$(CH_3)_2CHOH \xrightarrow{eV} CH_3CH{=}\overset{+}{O}H + CH_3\cdot + e \qquad (1)$$

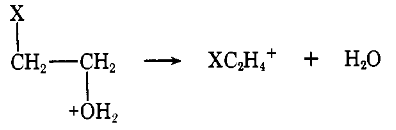


$$CH_3CH{=}O^+H + ROH \longrightarrow \begin{cases} \overset{+}{R}OH_2 + CH_3CHO & (2) \\ CH_3CH{=}\overset{+}{O}R + H_2O & (3) \\ CH_3CH{=}O\cdots\overset{+}{H}\cdots OH_2 + C_3H_6 & (4) \end{cases}$$

Of prime interest to the present work is the observation that, in certain instances, ROH_2^+ dissociates to R^+ and water (eq 5).[4,5] Since this is calculated to be an endothermic process (ΔH = 25 kcal/mol for 2-propanol[4a]), for it to occur, the reactant ions ROH_2^+ must possess excess internal energy greater than or equal to the endothermicity of dissociation. The needed energy is imparted to the neutral alcohol by the proton donor ($CH_3CH{=}O^+H$ in eq 2) and depends therefore on the internal energy of the proton donor and the relative proton affinities of the neutrals in eq 2. However, the question of how the dissociation of ROH_2^+ varies with the structure of the R group has not been extensively investigated, although its dependence on the structure and length of the alkyl chain has been noted.[5] We therefore initiated an icr study of the ion–molecule reactions of β-substituted ethanols XCH_2CH_2OH, where X = F, Cl, Br, OCH_3, OC_2H_5, SCH_3, SC_2H_5, SH, and NH_2, the intent being to see if the group X influences gas-phase dissociation of the protonated parent alcohol I in a manner comparable to that observed in related solution ionization reactions. We were particularly interested to see if neighboring group effects observed in solvolysis of derivatives of β-substituted alcohols II are also manifested in the related gas-phase ionization reactions of XCH_2CH_2OH, and whether or not the product ions of composition $XC_2H_4^+$ are the gas-phase counterparts of the bridged intermediates III which

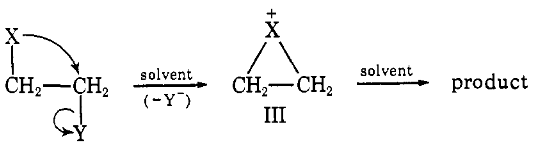
$$\overset{+}{R}OH_2 \longrightarrow R^+ + H_2O \qquad (5)$$

Gas-phase ionization



I

Solution-phase ionization



II III

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[1] This work was made possible through the financial support of the Petroleum Research Fund administered by the American Chemical Society (PRF No. 2357-AC 1, 4), and the NASA-Supported Facilities Fund of the Jet Propulsion Laboratories, Pasadena. The authors wish to gratefully acknowledge the support received.

[2] (a) For reviews, see (a) J. D. Baldeschwieler and S. S. Woodgate, *Accounts Chem. Res.*, **4**, 114 (1971); (b) G. C. Goode, R. M. O'Malley, A. J. Ferrer-Correia, and K. R. Jennings, *Nature* (*London*), **227**, 1093 (1970); (c) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971); (d) G. A. Gray, *Advan. Chem. Phys.*, **19**, 141 (1971); (e) for reviews, see F. H. Field, *Accounts Chem. Res.* **1**, 42 (1968); *Advan. Mass Spectrom.*, **4**, 645 (1968); (f) R. A. Durden, P. Kebarle, and A. Good, *J. Chem. Phys.*, **50**, 805 (1969); J. H. Futrell, T. O. Tiernan, F. P. Abramson, and C. D. Miller, *Rev. Sci. Instrum.*, **39**, 340 (1968).

[3] (a) L. W. Sieck, F. P. Abramson, and J. H. Futrell, *J. Chem. Phys.*, **45**, 2859 (1966); (b) J. M. S. Henis, *J. Amer. Chem. Soc.*, **90**, 844 (1968).

[4] (a) J. L. Beauchamp and R. C. Dunbar, *ibid.*, **92**, 1477 (1970); (b) J. L. Beauchamp, *ibid.*, **91**, 5925 (1969); (c) J. L. Beauchamp and M. C. Caserio, *ibid.*, **94**, 2638 (1972).

[5] F. H. Field, *ibid.*, **92**, 2672 (1970).

Table I. Icr Spectra of β-Substituted Ethanols (XCH_2CH_2OH) at 13 eV

		Product ions[b]						
X	Primary ions[a] m/e (RI)	MH^+ m/e (RI)	Precursor m/e	$MH^+ - H_2O$[c] m/e (RI)	M_2H^+ [d] m/e (RI)	Condensation reactions[e] Reactant (m/e) $\xrightarrow{M}$ product (m/e) (RI)	Other m/e (RI)	Precursor m/e
H	45 (45), 31 (29) 46 (26)	47 (86)	45, 31 46		93 (5)	MH^+ (47) → $M_2H^+ - H_2O$ (75) (9)		
CH_3	31 (35), 42 (30) 59 (18), 60 (17)	61 (37)	31, 42 59, 60 43	43 (12)	121 (18)	MH^+ (61) → $M_2H^+ - H_2O$ (103)(4)	73 (10)	60, 42
F	64 (50), 31 (50)	65 (56)	31	*f*	129 (12)	MH^+ (65) → $M_2H^+ - HF$ (109) (12)		
Cl	31 (73), 44 (25) 80, 82 (2)	81, 83 (55)	31	63, 65 (4)	161, 163, 165 (13)		45 (9)[g]	63, 65
Br	31 (14), 44 (39) 45 (36), 95, 97 (3) 124, 126 (4)	125, 127 (13)	45 44 31	107, 109 (23)	249, 251, 253 (4)	MH^+ (125, 127) → $M_2H^+ - H_2O$ (231, 233, 235) (9) $MH^+ - H_2O$ (107, 109) → $M_2{}^+H - H_2O - HBr$ (151, 153) (8)		
CH_3O	45 (55), 47 (24) 58 (12), 76 (11)	77 (24)	45 47	59 (5)	153 (7)	$CH_2{=}O^+CH_3$ (45) → $M + 45 - CH_3OH$ (89) (45) $MH^+ - H_2O$ (59) → $M_2H^+ - H_2O - CH_3OH$ (103) (4)		
C_2H_5O	59 (38), 43 (20) 72 (18), 31 (10) 41 (8), 45 (6)	91 (15)	31 45 43 41	73 (10)	181 (1)	$CH_3CH{=}O^+CH_3$ (59) → $M + 59 - CH_3OH$ (117) (18) $MH^+ - H_2O$ (73) → $M + 73 - C_2H_5OH$ $CH_2{=}O^+C_2H_5$ (59) → $M + 59 - C_2H_5OH$ (103) (19) $C_2H_3O^+$ (43) → $M + 43 - C_2H_5OH$ (87) (10)		
CH_3S	92 (67), 61 (33)	93 (17)	92	75 (9)	185 (2)	$CH_2{=}S^+CH_3$(61) → $M + 61 - CH_3SH$ (105) (12) $MH^+ - H_2O$ (75) → $M + 75$ (167) (2) $M^+ - H_2O$ (74) → $M + 74$ (166) (3)	74 (19)	92
C_2H_5S	75 (31), 106 (30) 63 (10), 47 (8) 62 (7), 60 (5)	107 (27)	63 47 41	89 (14)	213 (8)	$CH_2{=}S^+C_2H_5$ (75) → $M + 75 - C_2H_5SH$ (119) (16) $MH^+ - H_2O$ (89) → $M + 89$ (195) (9)	88 (18)	106
HS	60 (43), 78 (39), 48 (11), 44 (7)	79 (12)	44 48 60 78	61 (21)	157 (1)	$MH^+ - H_2O$ (61) → $M + 61 - H_2O$ (121) (5) $MH^+ - H_2O$ (61) → $M + 61 - H_2S$ (105) (12)		
H_2N	30 (71), 45 (20), 61 (9)	62 (75)	30 45	*h*	123 (10)			

[a] RI = relative intensities of primary fragments at 10^{-7} Torr. [b] RI = relative intensities (mass corrected) of product ions at 10^{-4} Torr. [c] Double resonance indicates precursor ion is MH^+ ($dk/dE_{ion} > 0$) and all ions leading to MH^+ ($dk/dE_{ion} < 0$). [d] Precursor ion is MH^+. [e] Product ions are identified here by their m/e values and composition; structure and mechanism are not implied. [f] $MH^+ - H_2O$ (m/e 47) and $MH^+ - HF$ (m/e 45) account for 15 and 7% of the total ionization at 10^{-5} Torr, 70 eV, respectively. [g] Represents ($MH^+ - HCl$). [h] $MH^+ - H_2O$ (m/e 44) accounts for 12% of the total ionization at 10^{-5} Torr, 70 eV.

are generally considered to be formed in anchimerically assisted solvolytic reactions.[6]

We have included in this study the ion–molecule chemistry of substituted propanols, $CH_3CH(X)CH_2OH$ and $CH_3CH(OH)CH_2X$, and cis and trans 2-substituted cyclopentanols. The overall objective was to see how the nature of the X substituent, the structure, and the stereochemistry of the carbon chain influence the ion–molecule chemistry of alcohols.

Results

To a large extent, the work reported here is a survey of the ion chemistry of a number of alcohols; hence it is impractical to discuss the chemistry of each compound in detail. The results are therefore summarized in tabular form to show the composition of the major primary fragment ions and the major secondary and tertiary product ions.[7] The data for the β-substituted ethanols are shown in Table I, those for the propanols in Table II, and those for the cyclopentanols in Table III. The relative ion intensities (RI) for the primary ions listed in these tables refer to a sample pressure of about 10^{-7} Torr which is sufficiently low that no significant ion–molecule reactions occur. The RI values for the product ions refer to a pressure near 5×10^{-4} Torr at which the secondary product ions account for most of the total ionization.

It is convenient to summarize the chemistry in the form of eq 6–10 using the notation M for the parent alcohol and RH^+ for a proton donor, which is usually a primary acidic fragment ion. Secondary product ions therefore include MH^+, ($MH^+ - H_2O$) and ($MH^+ - HX$) formed by reactions 6–8. Tertiary ions become dominant at pressures in excess of 10^{-4} Torr but are discernible at lower pressures and include protonated dimers (M_2H^+, eq 9) and condensation products (eq 10–12). In contrast to the behavior of 2-propanol[4a] and the butanols,[4bc] no dehydration reaction was observed (eq 4).

The precursors to each of the product ions listed in Tables I–III were identified by double resonance ex-

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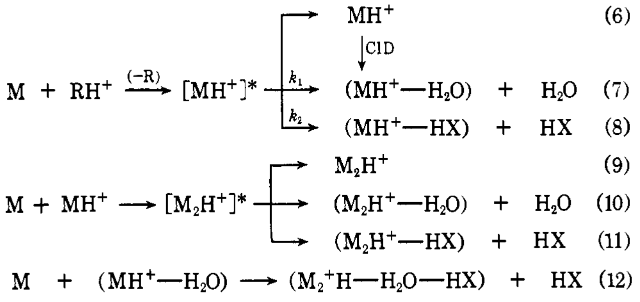
(6) For a review of neighboring group participation, see B. Capon, *Quart. Rev., Chem. Soc.*, 18, 45 (1964).

(7) Fragment ions produced by electron impact are usually referred to as *primary ions;* the first generation of product ions formed by reaction of the primary ions with the parent neutral are referred to as *secondary ions;* the second generation (or *tertiary ions*) are formed from the secondary ions and the parent neutral.

Table II. Icr Spectra of Substituted Propanols $CH_3C(OH)HCH_2X$ and $CH_3C(X)HCH_2OH$

		Product ions[b]						
X	Primary ions[a] m/e (RI)	MH^+ m/e (RI)	Precursor m/e	$MH^+ - H_2O$ m/e (RI)	M_2H^+ m/e (RI)	Condensation reactions Reactant (m/e) $\overset{M}{\rightarrow}$ product (m/e) (RI)	Other m/e (RI)	Precursor m/e
1-Cl	45 (90), 79, 81 (4)	95, 97 (60)	45	77, 79 (3)	189, 191, 193 (17)	$CH_3CH{=}O^+H \rightarrow M + 45 - H_2O$ (121, 123) (7) MH^+ (95, 97) $\rightarrow M_2H^+ - H_2O$ (171, 173, 175) MH^+ (95, 97) $\rightarrow M_2H^+ - HCl$ (153, 155) (2)	59 (5)[c]	45, 77, 79 95, 97
2-Cl	58 (62), 31 (37)	95, 97 (28)	31	77, 79 (8)	189, 191, 193 (12)	$C_3H_6O^+\cdot$(58) $\rightarrow M + 58$ (152, 154) (7) MH^+ (95, 97) $\rightarrow M_2H^+ - HCl$ (153, 155) (2)	59 (12)[c]	77, 79 95, 97 31
1-Br	45 (81), 44 (12) 123, 125 (2)	139, 141 (15)	45 44 123 125	121, 123 (11)	277, 279, 281 (4)	$CH_3CH{=}\overset{+}{O}H$ (45) $\rightarrow M + 45 - H_2O$ (165, 167) (30) MH^+ (139, 141) $\rightarrow (M_2H^+ - H_2O - HBr$ (179, 181) (4) MH^+ (139, 141) $\rightarrow (M_2H^+ - H_2O)$ (259, 261, (263) (10)		
2-Br	59 (80), 41 (10) 31 (7)	139, 141 (6)	59 31 41	121, 123 (20)	277, 279, 281 (1)	$C_3H_7\overset{+}{O}$ (59) $\rightarrow M + 59 - H_2O$ (179, 181) (25) MH^+ (139, 141) $\rightarrow M_2H^+ - H_2O)$ (259, 261, 263) (6)		
1-OCH_3	47 (73), 45 (25)	91 (44)	45, 47	73 (16)	181 (5)	$MH^+ - H_2O$ (73) $\rightarrow M + 73 - CH_3OH$ (131) 17)		
2-OCH_3	59 (93), 58 (6)	91 (5)	59	73 (5)	181 (1)	$CH_3CH{=}\overset{+}{O}CH_3$ (59) $\rightarrow M + 59 - CH_3OH$ (117) (47) $MH^+ - H_2O$ (73) $\rightarrow M + 73 - CH_3OH$ (131) (3)		
1-SCH_3	106 (45), 62 (41), 59 (4), 58 (3)	107 (11)	106	89 (12)	213 (2)	$MH^+ - H_2O$ (89) $\rightarrow M + 89$ (195) (2)	88 (29)[d] 212 (3)[d]	106 106
2-SCH_3	75 (7), 106 (32) 58 (6), 41 (4) 47 (4)	107 (15)	75 58	89 (19)	213 (1)	$MH^+ - H_2O$ (89) $\rightarrow M + 89$ (195 (1) $CH_3CH{=}SCH_3$ (75) $\rightarrow M + 75 - CH_3SH$ (133) (7)	88 (22)[d]	106
1-NH_2	30 (51), 31 (19) 32 (18), 60 (4)	76 (70)	30, 31 32	58 (0)[e]	151 (3)			

[a] RI is relative intensity of primary fragments at 10^{-6} Torr. [b] RI is relative intensity of product ions at 5×10^{-5} Torr; all intensities are mass corrected. [c] m/e 59 corresponds to $MH^+ - HCl$. [d] m/e 88 corresponds to $M\cdot^+ - H_2O$ and m/e 212 to $M_2\cdot^+$. [e] m/e 58 accounts for 8% of the total ionization at 10^{-5} Torr, 70 eV.



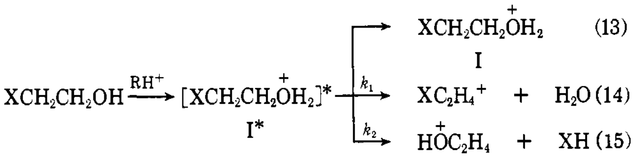
$$M + RH^+ \xrightarrow{(-R)} [MH^+]^* \begin{cases} \longrightarrow MH^+ \quad (6) \\ \quad\quad \downarrow \text{CID} \\ \xrightarrow{k_1} (MH^+{-}H_2O) + H_2O \quad (7) \\ \xrightarrow{k_2} (MH^+{-}HX) + HX \quad (8) \end{cases}$$

$$M + MH^+ \longrightarrow [M_2H^+]^* \begin{cases} \longrightarrow M_2H^+ \quad (9) \\ \longrightarrow (M_2H^+{-}H_2O) + H_2O \quad (10) \\ \longrightarrow (M_2H^+{-}HX) + HX \quad (11) \end{cases}$$

$$M + (MH^+{-}H_2O) \longrightarrow (M_2{}^+H{-}H_2O{-}HX) + HX \quad (12)$$

periments[8] and from the dependence of single resonance intensities on sample pressure. In most cases, the double resonance response corresponded to a decrease in product ion intensity with increasing reactant ion energy which is the usual response for an exothermic reaction (*i.e.*, $dk/dE_{ion} < 0$, where k is the rate constant for ion formation). An important exception was noted for the product ion ($MH^+ - H_2O$), the intensity of which *increased* on irradiation of MH^+ (*i.e.*, $dk/dE_{ion} > 0$). We conclude, therefore, that the initial proton transfer step involving RH^+ and M leads momentarily to ions $[MH^+]^*$ having a spectrum of internal energies such that some immediately dissociate (eq 7 and 8), and others with less energy become the observable product ions MH^+ of eq 6. Irradiation of MH^+ evidently increases the kinetic energy of the ion sufficiently to cause it to dissociate on collision with neutral molecules (*i.e.*, collision-induced decomposition (CID)[9]) and give the double resonance response $dk/dE_{ion} > 0$ on observing ($MH^+ - H_2O$).

The reactions of eq 6–8 are written out more explicitly for the β-substituted ethanols in eq 13–15. The



$$XCH_2CH_2OH \xrightarrow{RH^+} \underset{I^*}{[XCH_2CH_2\overset{+}{O}H_2]^*} \begin{cases} \longrightarrow \underset{I}{XCH_2CH_2\overset{+}{O}H_2} \quad (13) \\ \xrightarrow{k_1} XC_2H_4{}^+ + H_2O \quad (14) \\ \xrightarrow{k_2} H\overset{+}{O}C_2H_4 + XH \quad (15) \end{cases}$$

structure of the protonated alcohol I or I* is most simply written as $XCH_2CH_2OH_2{}^+$, but we wish to emphasize that the site of proton transfer is not known with certainty. Nevertheless, I* can dissociate in principle by loss of either HX or H_2O or both. However, *only loss of water* was observed for X = Br, OCH_3, OC_2H_5, SCH_3, SC_2H_5, SH, and NH_2 (eq 7 or 14). Also, the abundance of the product ion $XC_2H_4{}^+$ increased markedly with increasing abundance of acidic fragment

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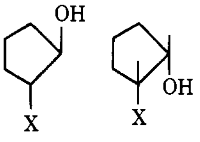
(8) L. R. Anders, J. L. Beauchamp, R. C. Dunbar, and J. D. Baldeschwieler, *J. Chem. Phys.*, 45, 1062 (1966).

(9) F. Kaplan, *J. Amer. Chem. Soc.*, 90, 4483 (1968).

Table III. Icr Spectra of 2-Substituted Cyclopentanols A and B at 13 eV



A B

		Product ions[b]					
						Other	
X	Primary ions[a] m/e (RI)	MH^+ m/e (RI)	Precursor m/e (RI)	$MH^+ - H_2O$ m/e (RI)	M_2H^+ m/e (RI)	(m/e) (composition) (RI)	m/e major precursor
Cl trans	57 (38) 102, 104 (24) 43 (3)	121, 123 (~1)		103, 105 (0)	241, 243, 245 (0)	(67) ($MH^+ - H_2O - HCl$) (30) 163, 165 159, 161 minor	57
cis	57 (32) 84 (18)	121, 123 (10)	57	103, 105 (0)	241, 243, 245 (4)	(85) ($MH^+ - HCl$) (19) 205, 207 (5) 169[c] (5)	121, 123, 57 85 85
OCH_3 trans	84 (45) 83 (14) 116 (5) 67 (4)	117 (6)	83, 84, 67	99 (12)	233 (2)	(98) ($M\cdot^+ - H_2O$) (11) $\left.\begin{matrix}169, 183\\199, 200\\215\end{matrix}\right\}$ minor	$M\cdot^+$ 116
cis	84 (50) 83 (15) 67 (6)	117 (34)	83, 84 67	99 (15)	233 (4)	98, 116, 155, 197 (minor)	
SCH_3 trans	132 (35) 84 (25) 56 (23) 83 (9), 67 (4)	133 (15)	83, 84 67	115 (31)	265 (0)	(114) ($M\cdot^+ - H_2O$) (34) (247) ($M_2H^+ - H_2O$) (1)	$M\cdot^+$ 132, 56 133
cis	132 (40) 56 (20), 84 (10) 83 (5), 67 (4)	133 (29)	83, 84 67	115 (10)	265 (0)	(114) ($M\cdot^+ - H_2O$) (29)	$M\cdot^+$ 132 56
SH trans	85 (8) 67 (13) 84 (8) 118 (9)	119 (0)		101 (30)	237 (0)	133, 167, 185, 201 (minor)	
cis	85 (8) 67 (15) 118 (25)	119 (12)	85, 67	101 (21)	237 (1)	(185) ($M_2H^+ - H_2O - H_2S$) (5)	119 (MH^+)

[a] Only primary reactive fragments are listed where RI is relative intensity at 10^{-6} Torr. [b] RI is relative intensity ot 10^{-4} Torr. [c] m/e 169 accounts for 47% of the total ionization at 10^{-8} Torr.

ions capable of exothermic proton transfer as determined by increasing the energy of the ionizing electron beam from 13 to 70 eV. However, loss of HX was not observed even at 70 eV. Aminoethanol (X = NH_2) ionized by loss of water at high electron energies only (70 eV), whereas fluoroethanol (X = F) and chloroethanol (X = Cl) ionized appreciably at 70 eV by loss of H_2O *and* HX. Ethanol itself protonates extensively, but reactions 14 and 15 were not observed although dissociation to form H_3O^+ and C_2H_4 at 50 eV has been reported.[3a]

Similar results were observed for the substituted propanols and cyclopentanols (Tables II and III). Dissociation of $[MH^+]^*$ by loss of water occurred exclusively for X = Br, OCH_3, SCH_3, and NH_2 and became increasingly important as the ionizing electron energy increased. The chloropropanols, however, lost both H_2O and HCl from $[MH^+]^*$. The chlorocyclopentanols were particularly interesting since their chemistry was dictated largely by the configuration of the starting alcohol. The cis isomer gave m/e 85 corresponding to ($MH^+ - HCl$), whereas the trans isomer gave m/e 67 corresponding to ($MH^+ - H_2O - HCl$). Neither isomer gave an ion of composition ($MH^+ - H_2O$).

A major difficulty in evaluating the importance of structure on the dissociation of $[MH^+]^*$ is the fact that the extent of dissociation is also dependent on the internal energy of $[MH^+]^*$ which is difficult to determine and varies from compound to compound. Thus, the exothermicity of proton transfer producing $[MH^+]^*$ is expected to vary with the nature of the proton donor and the parent alcohol with the result that the internal energies of $[MH^+]^*$ ions will vary likewise. A partial solution to this problem is to provide a common reference acid to form $[MH^+]^*$. Using mixtures of methane and the parent alcohol in mole ratios varying from 100:1 to 25:1 at 13 eV, the major proton donor is CH_5^+ (eq 16 and 17), and proton

$$CH_4 \xrightarrow{eV} CH_4\cdot^+ \xrightarrow{CH_4} CH_5^+ + CH_3\cdot \qquad (16)$$

$$CH_5^+ + M \longrightarrow MH^+ + CH_4 \qquad (17)$$

transfer to M is estimated to be exothermic by about 60 kcal/mol,[10] which is almost certainly sufficient energy to exceed the endothermicities of *both* reactions 7 and 8. The results are shown in Table IV which lists the major product ions observed for the various al-

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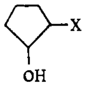
(10) This corresponds to the difference in proton affinities of methane (126 kcal/mol) and M (assumed to be close to that of ethanol, 186 kcal/mol).[2c] In the case of 2-aminoethanol, the exothermicity of proton transfer is likely to be as high as 90–100 kcal/mol with protonation occurring at nitrogen since there is approximately 30–40 kcal/mol difference in the proton affinities of structurally related alcohols and amines.

Table IV. Chemical Ionization Reactions of β-Substituted Alcohols with CH_5^+ [a]

	MH^+ [b] m/e (RI)	$MH^+ - H_2O$ m/e (RI)	$MH^+ - HX$ m/e (RI)	$MH^+ - H_2O - HX$ m/e (RI)
FCH_2CH_2OH	65 (25)	47 (37)	45 (38)	
F_2CHCH_2OH	83 (15)		63 (85)	
F_3CCH_2OH	101 (28)		81 (72)	
$ClCH_2CH_2OH$	81, 83 (18)	63, 65 (66)	45 (16)	
$HSCH_2CH_2OH$	79 (3)	61 (97)		
$CH_3CH(OH)CH_2Cl$	95, 97 (25)	77, 79 (42)	59 (25)	41 (8)
$CH_3CH(OH)CH_2Br$	139, 141 (4)	121, 123 (67)	59 (19)	41 (10)
$CH_3CH(Br)CH_2OH$		121, 123 (69)	59 (31)	
$CH_3CH(OH)CH_2OCH_3$	91, 92 (12)	73 (81)	59 (3)	41 (4)
$CH_3CH(OH)CH_2SCH_3$		89 (100)		
$CH_3CH(OH)CH_2NH_2$[c]	76 (32)	58 (68)		
				
X = Cl (cis)		103, 105 (7)	85 (5)	67 (88)
OCH_3 (trans)		99 (26.5)	85 (11.5)	67 (62)
OCH_3 (cis)		99 (49)	85 (11)	67 (40)
SCH_3 (trans)		115 (37)	85 (0)	67 (63)
SCH_3 (cis)		115 (36)	85 (0)	67 (64)
SH (trans)		101 (38.5)	85 (8.5)	67 (53)
SH (cis)		101 (42)	85 (7)	67 (51)

[a] Conditions correspond to 14.6 eV, total pressure near 10^{-4} Torr, and 100-fold excess of CH_4. [b] RI, relative intensities, are mass corrected and are normalized such that sum of product ions listed is 100. [c] The other major ion is m/e 60, the intensity of which varies widely with pressure; its origin is unclear.

cohols. Again the ($MH^+ - H_2O$) ions dominate the spectra except in the case of the fluoro and chloro alcohols. The intensity of MH^+ ions is relatively low or negligible confirming that extensive dissociation occurs when proton transfer is strongly exothermic. Ions of composition ($MH^+ - HX$) are important, as expected, for X = F and Cl, and appear as minor product ions for X = Br and OCH_3. Some dissociation to ions of composition ($MH^+ - H_2O - HX$) occurs, especially in the case of the cyclopentanols.

Table V. Thermodynamic Data for the Reaction
$HO^+C_2H_4(g) + HX(g) \longrightarrow X^+C_2H_4(g) + H_2O(g)$

X	ΔH_f (HX)[a]	ΔH_f ($X^+C_2H_4$)	$\Delta\Delta H$[b]
OH	−57.80	171[c]	0
F	−64.8	(164)[d]	0[i]
Cl	−22.06	(207)[d]	0[i]
Br	−8.7		
OCH_3	−48.1	169[e]	−12
SCH_3	−5.34	190[f]	−33
SH	−4.93	192[g]	−32
NH_2	−11.02	173[h]	−45[j]

[a] B. J. Zwolinski and R. C. Wilhoit, API Project No. 44, Thermodynamics Research Center, Texas A&M, 1968; all data in kcal/mol at 25°. [b] Calculated as $\Delta\Delta H = \Delta H_{f,H_2O} + \Delta H_{f,XC_2H_4^+} - \Delta H_{f,HX} - \Delta H_{f,HOC_2H_4^+}$. [c] Assumed to be protonated ethylene oxide (ref 4a). [d] Estimated assuming $\Delta\Delta H \sim 0$. [e] Estimated by assuming methylated ethylene oxide structure to be 28 kcal less stable than $CH_3CH{=}O^+CH_3$, $\Delta H_f = 141$ kcal/mol (ref 15) by analogy with protonated ethylene oxide being 28 kcal less stable than $CH_3CH{=}O^+H$ (ref 4a). [f] Estimated assuming difference in stability of ions $X^+C_2H_4$ where X = SH and SCH_3 equals difference where X = OH and OCH_3. [g] Calculated for ΔH_f (ethylene sulfide) = 19.93 kcal/mol [S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 69, 279 (1969)] and PA(ethylene sulfide) = 194 kcal/mol (estimated from PA data for related oxygen and sulfur compounds (see ref 2), and $\Delta H_f(H^+) = 366$ kcal/mol). [h] Estimated from ΔH_f(aziridine) = 27.7 kcal/mol (see reference in footnote *g*), PA(aziridine) = 221 kcal/mol (M. T. Bowers, private communication), and $\Delta H_f(H^+) = 366$ kcal/mol. [i] Assumed to be zero for the purpose of estimating a lower limit for $\Delta H_f(X^+C_2H_4)$. [j] This value is based on dissociation to neutral ammonia and protonated ethylene oxide. A more realistic figure is −22 kcal for dissociation to ethylene oxide and ammonium ion.

Discussion

While the internal energy of $[MH^+]^*$ clearly has an effect on the rates of dissociation and hence the abundance of product ions, the preferred mode of dissociation (H_2O *vs.* HX elimination) is unchanged with ion energy.[11] The preferred mode does in fact correspond to elimination of the most stable molecule of the pair, H_2O or HX, which is water in most cases and HF for the fluoro alcohols (see heats of formation of HX listed in Table V). This suggests that the relative importance of H_2O *vs.* HX elimination is determined by relative product stabilities. The structure and the stability the product ions $XC_2H_4^+$ and $HOC_2H_4^+$ must also be considered, but reliable data on the heats of formation of ($XC_2H_4^+$) are unavailable. However, estimates of ΔH_f values are listed in Table V and are based on the assumption (unjustifiable though it may be) that the ions have a cyclic structure III. The points to note from Table V are the following. (1) The calculated difference in endothermicity for reactions 14 and 15 appear in the $\Delta\Delta H$ column and clearly predict elimination of water to be energetically preferred for X = OCH_3, SCH_3, SH, and NH_2, as observed. (2) Since chloro- and fluoroethanol eliminate both HX and H_2O, the rates of the two dissociative pathways must be comparable. Further, if reaction rates and endothermicity correlate, then the difference in endothermicity $\Delta\Delta H$ must be small or zero. By this reasoning, estimates of ΔH_f for ions of composition $ClC_2H_4^+$ and $FC_2H_4^+$ are 207 and 164 kcal/mol, respectively. These estimates, which

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[11] A complete analysis of the product distribution by quasi-equilibrium theory is required in order to analyze the present data in more than a qualitative manner. However, the complexity of the system precludes this approach; see, for example, S. E. Buttrill, Jr., *J. Chem. Phys.*, 52, 6174 (1970).

are admittedly based on somewhat tenuous assumptions, are surprisingly close to independent estimates for CH_3CHCl^+ (ΔH_f = 195 ± 5 kcal/mol) and CH_3CHF^+ (ΔH_f = 165 ± 3 kcal/mol).[12] (3) The fact that chloroethanol loses HCl *competitively* with H_2O is as much due to the high energy of the chloronium ion relative to the oxonium ion as it is to the stability of water relative to HCl. (4) Table V shows that aminoethanol should lose water preferentially, which it does but only at 70 eV; this must be largely due to the high proton affinity of the amino group ($PA(CH_3NH_2)$ = 216 kcal/mol) which makes dissociation of MH^+ more strongly endothermic compared to the other alcohols with less basic substituents.

To further assess the effect of X on the ionization of XCH_2CH_2OH, the intensities of the product ions $XC_2H_4^+$ (*i.e.*, $MH^+ - H_2O$) obtained at 13 eV relative to the total estimated abundance of $[MH^+]^*$ are plotted against sample pressure in Figure 1. Provided that ($MH^+ - H_2O$) ions are produced solely from $[MH^+]^*$, the quantity $I_{(MH^+ - H_2O)}/I_{[MH^+]^*}$ represents the fraction of ions formed by proton transfer that dissociate by loss of water and is therefore a relative measure of the rate of dissociation of $[MH^+]^*$. It should be independent of pressure if other reactions do not intervene significantly to deplete either MH^+ or ($MH^+ - H_2O$). This is approximately the case up to 10^{-5} Torr with the obvious exception of propanol (X = CH_3).[13] On comparing the data of Figure 1 for the several compounds, the extent of dissociation clearly decreases in the order X = Br > SH > SCH_3 > OCH_3 ≫ Cl, F.[14] The observed reactivity differences are undoubtedly due in part to differences in the internal energies of $[MH^+]^*$ derived from the various alcohols, and, in fact, the differences become significantly less as the internal ion energies are increased by raising the electron energy to 70 eV. However, the *order* of reactivity remains unchanged over the range 13–70 eV, and this order is strikingly similar to the effectiveness of X as a neighboring group in solvolytic reactions.[6] This suggests that the reactivity of $[MH^+]^*$ also reflects a structural dependence on X which is particularly prominent at low ion energies and which parallels the kinetic reactivities of analogous compounds on solvolysis; it lends support to the concept that solvolysis reactions involve two separate and independent processes: anchimeric assistance from a neighboring group and assistance from the solvent.[15] The present work substantiates that the former exists in the absence of the latter.

Neighboring group participation in solvolysis reactions is known to be enhanced by alkyl substitution at the carbon bearing the neighboring group, and the reasons for this have been the subject of much discussion.[16] The role of solvent is probably unimportant, however, as the alkyl effect is also evident in gas-phase ionization. This may be seen from Figure 2 showing the relative ion intensities $I_{(MH^+-H_2O)}/I_{[MH^+]}$ over the pressure range 10^{-6}–5×10^{-4} Torr for 1-bromo-2-propanol, 2-bromoethanol, and 2-bromopropanol. β-Methyl substitution clearly enhances the degree of dissociation of $[MH^+]^*$. Also, 80% of $[MH^+]^*$ dissociates for 2-bromopropanol as compared to 40% or less for 1-bromo-2-propanol. Since the products are presumably the same for both bromopropanols, the observed reactivity differences can be most simply explained as a preference for displacement of water by neighboring bromine from primary carbon over secondary carbon.

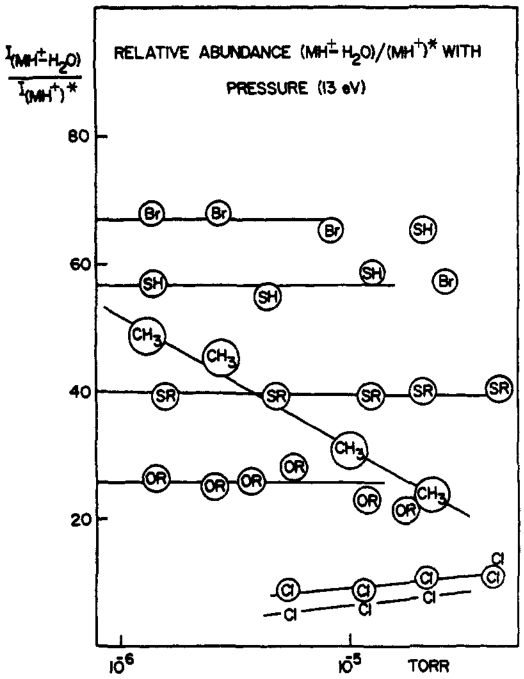
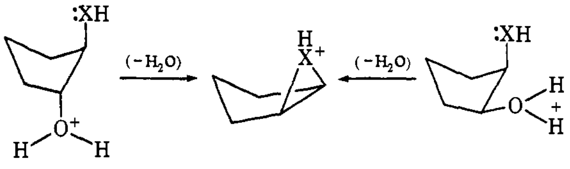


Figure 1. Relative ion abundance $I_{(MH^+-H_2O)}/I_{[MH]^*}$ is plotted against pressure where M refers to a series of β-substituted ethanols, XCH_2CH_2OH. The symbol inscribed in the data circles is the X group, R = CH_3. The intensities were measured for 13-eV electron energy. Values of $[MH^+]^*$ were taken as the summed intensities (mass corrected) of the observable MH^+, and those product ions obtained from the protonated parent (*i.e.*, $MH^+ - H_2O$, $MH^+ - HX$, M_2H^+). For X = F and NH_2, no dissociation of MH^+ was observed at 13 eV. Inscribed circles X = Cl refer to ($MH^+ - H_2O$) and plain X = Cl refers to ($MH^+ - HCl$).

The stereochemical dependence shown in the reactions of the cyclopentanols is also interesting (Table III). Dissociation of MH^+ is consistently more important for the trans isomers than for the cis isomers, as shown by the RI value for the ($MH^+ - H_2O$) ions in Table III. In conformity with evidence obtained from neighboring group effects in solvolysis reactions, the present results suggest that backside displacement of water by the group X is kinetically preferred (eq 18). Perhaps more surprising is the fact that the *cis*-MH^+ ions dis-



(18)

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(12) J. L. Beauchamp, private communication; R. M. O'Malley, K. R. Jennings, M. T. Bowers, and V. Anicich, *Int. J. Mass Spectrom. Ion Phys.*, 10, in press; see, however, J. M. Simmie and E. Tschuikow-Roux, *ibid.*, 7, 41 (1971).

(13) Double resonance data indicate that proton transfer from $C_3H_7^+$ to 1-propanol occurs; the intensity of $C_3H_7^+$ therefore falls off with increasing pressure of propanol. See also D. J. McAdoo, F. W. McLafferty, and P. F. Bente, III, *J. Amer. Chem. Soc.*, 94, 2027 (1972).

(14) The fraction of ($MH^+ - H_2O$) *m/e* 59 derived from $[MH^+]^*$ in the case of 2-methoxyethanol is overestimated in Figure 1 for the reason that the α-cleavage fragment $CH_3O^+{=}CH_2$ (*m/e* 45) is a specific ionic precursor to *m/e* 59 by a reaction that does not appear to involve proton transfer to the parent alcohol. The nature of this interesting reaction will be discussed elsewhere.

(15) For example, see P. v. R. Schleyer and C. J. Lancelot, *J. Amer. Chem. Soc.*, 91, 4297 (1969).

(16) See ref 6, pp 109–111.

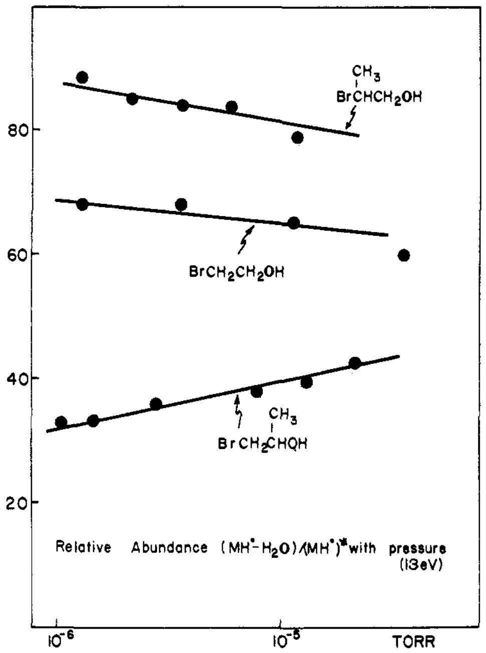


Figure 2. Relative ion abundance $I_{(MH^+-H_2O)}/I_{(MH)^*}$ is plotted against pressure where M refers to 2-bromoethanol, 2-bromopropanol, and 1-bromo-2-propanol. The intensities were measured for 13-eV electron energy. Values of $[MH^+]^*$ were taken as the summed intensities (mass corrected) of the observable MH^+ and those product ions obtained from the protonated parent.

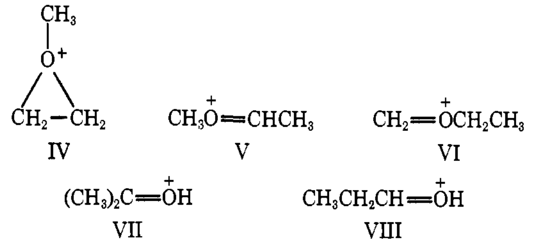
sociate as readily as they do, implying that front-side displacement may not be as unfavorable in the gas phase as it evidently seems to be in solution.

Also worth noting is the absence of any observable MH^+ ions in the spectrum of *trans*-2-mercaptocyclopentanol in spite of the fact that $(MH^+ - H_2O)$ is a major product ion. Evidently all of the MH^+ ions formed must dissociate to the product ions $(MH^+ - H_2O)$. This is unexpected in the sense that the favored site of proton transfer to *trans*-2-mercaptocyclopentanol is anticipated to be sulfur by analogy with the higher proton affinity of methanethiol (188 kcal) relative to methanol (180 kcal), and it is not easy to vizualize how a proton on sulfur gets transferred to a trans-disposed oxygen. Evidence that proton transfer to sulfur does indeed occur was obtained from the spectrum of a 1:100 mixture of *trans*-2-mercaptocyclopentanol and CD_4 at 15 eV. With CD_5^+ as the major proton donor (*cf.* eq 16 and 17), product ions *m/e* 101 and 102 corresponding to $(MD^+ - HDO)$ and $(MD^+ - H_2O)$ were observed in the ratio of 2.5:1. Retention of deuterium in the product ion $(MD^+ - H_2O)$ implies that deuteron transfer to sulfur to give MD^+ is followed by proton transfer from sulfur to oxygen and loss of H_2O. This process must occur more rapidly than MD^+ or MH^+ can be detected. Under comparable conditions, *cis*-2-mercaptocyclopentanol with CD_4 also gave *m/e* 101 and 102 in the ratio of 2.6:1, while 2-mercaptoethanol and CD_4 gave *m/e* 61 and 62 in the ratio of 2:1. We are reluctant to attach any significance to the magnitude of these ratios, but the retention of deuterium evidenced by $(MD^+ - H_2O)$ again implies deuterium transfer to sulfur and loss of H_2O.

Structure of Product Ions $(MH^+ - H_2O)$

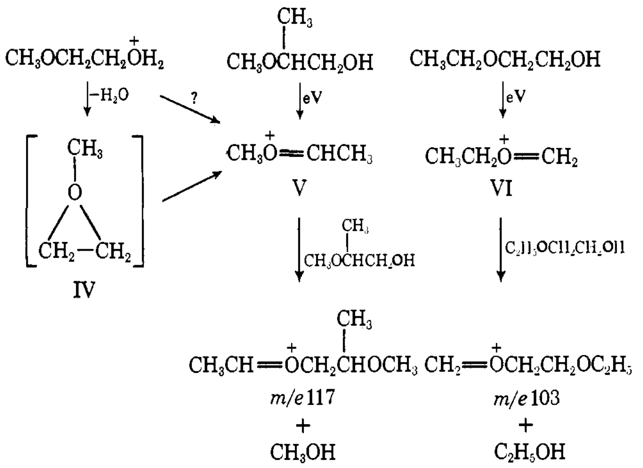
While the mode of dissociation of protonated alcohols suggests that the product ions $(MH^+ - H_2O)$ may have a bridged structure III, it is entirely possible that rearrangement to more stable structures may occur. Since mass spectral methods do not distinguish between isomeric ions, an indirect approach to structure determination is necessary. An approach often used in icr studies is to generate ions of the same elemental composition by different routes and to compare their behavior in chemical reactions. If the chemistry is indistinguishable, so are the ions. If, however, ions of comparable energies but produced from different sources react differently, a difference in structure is indicated.

Ions of Composition $C_3H_7O^+$, *m/e* 59. Plausible structures for the product ion $(MH^+ - H_2O)$ *m/e* 59 derived from the ionization of methoxyethanol are shown in IV–VIII. Structures VII and VIII can be



immediately excluded since $(MH^+ - H_2O)$ does not possess a labile proton and exhibits none of the reactions shown by VII and VIII.[4] Ions V and VI were generated respectively from 2-methoxypropanol and 2-ethoxyethanol. The icr spectra of these alcohols show *m/e* 59 as the major fragment ions on electron impact, and condensation reactions of these ions with the parent alcohols gave products by loss of methanol in the case of V, and ethanol in the case of VI (Scheme I). Some

Scheme I



rearrangement of VI to V evidently occurs since *m/e* 59 from 2-ethoxyethanol also condensed by loss of methanol. This rearrangement has been noted independently.[17] The key reaction, however, is that of $(MH^+ - H_2O)$ with methoxyethanol. Condensation occurs with loss of methanol (Table I, Scheme I) which means that *m/e* 59 generated from methoxyethanol is indistinguishable from V. While this result does not prove the two ions from different sources are identical, it lends credence to the possibility that they may be.

This situation resembles that found for protonated

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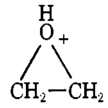
(17) C. W. Tsang and A. G. Harrison, *Org. Mass Spectrom.*, 3, 647 (1970).

ethylene oxide and acetaldehyde which could not be distinguished on the basis of ion–molecule reactions.[4a]



ΔH_f = 171 kcal/mol

$CH_3CH{=}\overset{+}{O}H$

ΔH_f = 143 kcal/mol

Since the heat of formation of $CH_3CH{=}OH^+$ is some 28 kcal less than that of protonated ethylene oxide, there is reason to expect that rearrangement of the cyclic ion to the acyclic form could ocur. By analogy, we suggest that if the cyclic oxonium ion IV is formed on dissociation of protonated methoxyethanol, it may also rearrange to the more stable acyclic form V; alternatively, V could be formed directly from MH^+ by loss of water accompanied by a hydride shift (Scheme I).

We also note that condensation reactions of ($MH^+ - H_2O$) *m/e* 73 derived from 2-ethoxyethanol and the methoxypropanols are entirely comparable to the condensation reaction of *m/e* 59 from methoxyethanol (Tables I and II). The probable structures of ($MH^+ - H_2O$) are IX from ethoxyethanol, and X or XI from the methoxypropanols. Condensation of IX with ROH results in loss of ethanol, whereas condensation of X or XI results in loss of methanol (eq 19–21) where ROH

$$\underset{\text{IX, } m/e\ 73}{CH_3CH{=}\overset{+}{O}CH_2CH_3} + ROH \longrightarrow \underset{m/e\ 117}{CH_3CH{=}\overset{+}{O}R} + CH_3CH_2OH \quad (19)$$

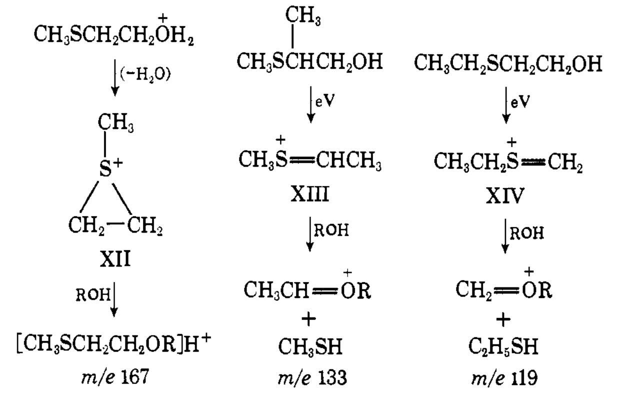
$$\underset{\text{X, } m/e\ 73}{(CH_3)_2C{=}\overset{+}{O}CH_3} + ROH \longrightarrow \underset{m/e\ 131}{(CH_3)_2C{=}\overset{+}{O}R} + CH_3OH \quad (20)$$

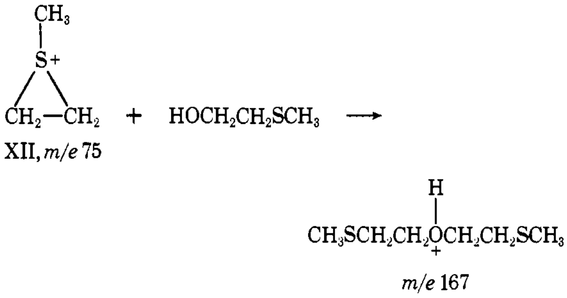
$$\underset{\text{XI, } m/e\ 73}{CH_3CH_2CH{=}\overset{+}{O}CH_3} + ROH \longrightarrow \underset{m/e\ 131}{CH_3CH_2CH{=}\overset{+}{O}R} + CH_3OH \quad (21)$$

is the parent alcohol from which the particular *m/e* 73 is derived.

Ions of Composition $C_3H_7S^+$, *m/e* 75. The sulfur analogs of the oxycations are structures XII, XIII, and XIV. Scheme II shows how each of these ions may be generated from the appropriately substituted alcohol and shows their respective condensation reactions with the parent alcohol (see also Tables I and II). The three ions react *differently* with their respective parent alcohols. Since XIII and XIV condense by loss of methanethiol and ethanethiol, respectively, they are assigned the acyclic structures shown. The ($MH^+ - H_2O$) ion does *not* condense with ROH but *associates* at 10^{-4} Torr and higher to give an ion of *m/e* 167. This behavior suggests that ($MH^+ - H_2O$) may have a cyclic sulfonium ion structure XII that reacts as an alkylating agent toward the nucleophilic alcohol ROH, possibly as depicted in eq 22.[18]

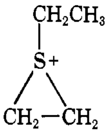
Scheme II



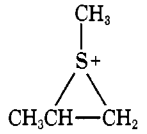


(22)

The ($MH^+ - H_2O$) ions from 2-ethylthioethanol, and the methylthiopropanols, similarly associate rather than condense with ROH (Tables I and II). Hence, they may be reasonably assigned cyclic structures XV add XVI.



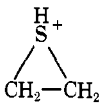
XV



XVI

The structural difference in the ($MH^+ - H_2O$) ions derived from β-methylthio alcohols compared to the β-methoxy alcohols is consistent with the greater stability of sulfonium ions relative to oxonium ions and the greater stabilization of carbon cations by oxygen relative to sulfur substituents.[19]

Unfortunately, we are unable to distinguish between open and cyclic structures for ($MH^+ - H_2O$) *m/e* 61 formed for 2-mercaptoethanol. Both structures XVII and XVIII possess a labile proton and would be expected to condense with ROH by loss of H_2O and H_2S, as is observed experimentally (Table I). However, we favor XVII by analogy with XII derived from 2-methylthioethanol.



XVII

$CH_3CH{=}\overset{+}{S}H$

XVIII

Ions of Composition $C_2H_4Br^+$, *m/e* 107, 109. The $C_2H_4Br^+$ ions from bromoethanol may have structures XIX or XX. The major reaction that $C_2H_4Br^+$ under-

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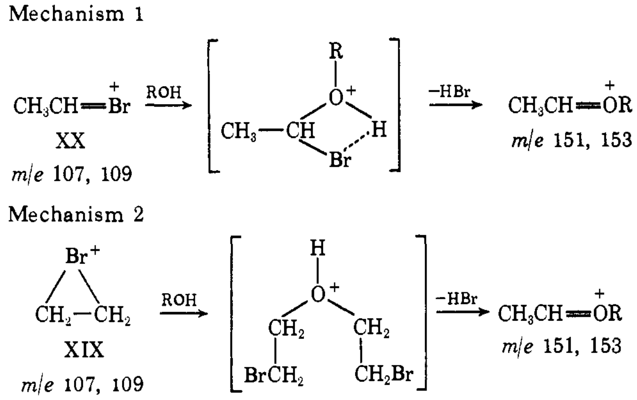
[18] The possibility exists that differences noted in the behavior of ions from different sources could be due to differences in states of excitation rather than differences in structure. The arguments pertaining to structure given in this paper are based on the assumption that this is not an important factor here.

[19] C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N. Y., 1962, Chapter 2; see also B. G. Keyes and A. G. Harrison, *J. Amer. Chem. Soc.*, 90, 5671 (1968); A. G. Harrison, C. D. Finney, and J. A. Sherk, *Org. Mass. Spectrom.*, 5, 1313 (1971).

goes corresponds to condensation with bromoethanol and loss of HBr. Two possible mechanisms for this reaction depending on ion structure are shown in Scheme III, where ROH is 2-bromoethanol.

Scheme III



They differ in one important respect: in mechanism 1, the bromine lost as HBr comes exclusively from the reactant ion; in mechanism 2, it comes equally from the reactant ion and the neutral since a symmetrical intermediate is involved. Experimentally, the two mechanisms can be distinguished by double resonance which unambiguously identify the precursor ions.[20] For example, all the possible combinations of reactant ions *m/e* 107, 109 with the neutral alcohol (mol wt 124, 126) having the natural abundance of ^{79}Br and ^{81}Br are shown in Table VI. The product ions *m/e* 151, 153 derived from these combinations for the two mechanisms are also listed. It can be seen that mechanism 1 predicts *m/e* 151 should arise equally from 107 and 109. In contrast, mechanism 2 predicts *m/e* 151 should come *unequally* from 107 and 109, actually in the ratio of 3:1. Similar arguments pertain to *m/e* 153. In actual fact, double resonance experiments produced an *equal* response on irradiating *m/e* 107 and 109 while observing either of the product ions *m/e* 151 or 153. This result is consistent with mechanism 1, and suggests that *m/e* 107, 109 has the acyclic structure $CH_3CH{=}Br^+$. Admittedly, there may be other mechanisms overlooked by us that could equally well accommodate the double resonance results but which do not demand an acyclic structure for the reactant ion. The only valid conclusion the results really allow is that the bromine lost as HBr comes exclusively from the reactant ion and any viable mechanism must be consistent with this. If mechanism 1 is indeed correct, then the cyclic bromonium ion XIX which may be formed in the dissociation of protonated bromoethanol must rearrange to the acyclic ion XX. This is surprising because the ethylenebromonium ion XIX can be formed from 1,2-dibromoethane in SbF_5–SO_2 solution at −60°[21] and evidently does not rearrange under these conditions. Alternatively, XX could be formed directly from MH^+, although the extensive dissociation of MH^+ in the case of bromoethanol (Figure 1) is more consistent with bromine participation to give XIX than with hydrogen participation to give XX.

Table VI. Isotopic Combinations in the Condensation $C_2H_4Br^+ + HOC_2H_4Br \longrightarrow BrC_4H_8O^+ + HBr$

Reactant ion *m/e*	Neutral *m*	Mechanism 1 Product ion *m/e*	Mechanism 2 Product ion *m/e*
107	124	151	151
107	126	153	1/2 (151 + 153)
109	124	151	1/2 (151 + 153)
109	126	153	153

Experimental Section

A standard Varian V-5900 series icr spectrometer equipped with dual inlet system and a standard drift cell was used in this study. A comparable instrument at the Jet Propulsion Laboratories, Pasadena, was also used for part of the work. Single resonance spectra were recorded by field, electron energy, or trapping plate modulation with comparable results. Standard double resonance methods were employed, the techniques of which are described elsewhere.[2] Ion abundance was taken as proportional to ion intensity divided by the mass of the ion.

The chemicals used in this work were obtained from commercial sources when possible and were purified by preparative glpc prior to use. Synthetic routes employed for the preparation of compounds which were not commercially available are summarized as follows: *trans*-2-chlorocyclopentanol was prepared according to a published procedure[22a] and had bp 80–82° (13 mm) [lit.[22a] 81–82° (15 mm)]; *cis*-2-chlorocyclopentanol was obtained from the reduction of 2-chlorocyclopentanone with lithium aluminum hydride by the method of Drefahl, *et al.*,[22b] bp 71° (16 mm) [lit.[18] bp 61–63° (15 mm)]; *trans*-2-methoxycyclopentanol was prepared from cyclopentene oxide and sodium methoxide in methanol according to the procedure of Bruice and Fife,[23] bp 88–90° (16 mm) [lit.[23] bp 96–97° (27 mm)]; *cis*-2-methoxycyclopentanol was prepared from the trans isomer according to the procedure of Buck, *et al.*,[24] bp 50–52° (20 mm) [lit.[24] bp 52° (20 mm)]; *trans*-2-mercaptocyclopentanol was prepared from cyclopentene oxide and sodium hydrosulfide in methanol according to the procedure by Goodman, *et al.*,[25a] bp 96–98° (15 mm) [lit.[25a] 97–98° (15 mm)]; *cis*-2-mercaptocyclopentanol was obtained by the addition of thioacetic acid to 1-cyclopentenyl acetate and the acid-catalyzed hydrolysis of the resulting *cis*-2-(thioacetyl)cyclopentyl acetate according to the procedure of Goodman, *et al.*,[25b] bp 80–80.5° (8 mm) [lit.[25b] 72.5° (7 mm)]; *trans*-2-methylthiocyclopentanol was prepared by the method of Goodman, *et al.*,[25b] bp 68° (1.5 mm) [lit.[25b] 68° (1.5 mm)].

***cis*-2-Methylthiocyclopentanol.** A mixture of 1-cyclopentenyl acetate (25 g, 0.2 mol), 50 ml of methanethiol, and catalytic amount of benzoyl peroxide was placed in a pressure-bottle and was illuminated with a Hanovia uv lamp (140 W) for 3 hr with occasional shaking. After the evaporation of methanethiol, the liquid residue was distilled at reduced pressure. There was obtained 26.6 g (76%) of *cis*-2-methylthiocyclopentyl acetate; bp 55–57° (0.2 mm); nmr δ 5.25 (m, 1, $CHOOCCH_3$), 3.03 (m, 1, $CHSCH_3$), 2.00 (s, 3, $OOCCH_3$), 2.07 (s, 3, SCH_3), and 1.80 (m, 6, $(CH_2)_3$). The hydrolysis of *cis*-2-methylthiocyclopentyl acetate (17.3 g, 0.1 mol) with the aid of *p*-toluenesulfonic acid (8 g) in methanol (130 ml)

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[20] See J. L. Beauchamp, L. R. Anders, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **89**, 4569 (1967), for related double resonance experiments in the icr spectrum of chloroethylene. See also G. A. Gray, *ibid.*, **90**, 2177 (1968), for double resonance using ^{15}N-labeled acetonitrile. Using ^{18}O-labeled *tert*-butyl alcohol, double resonance icr experiments have established that this alcohol condenses with its α-cleavage ion $(CH_3)_2C{=}O^+H$ to lose water, the oxygen of which comes exclusively from the neutral alcohol: J. L. Beauchamp and M. C. Caserio, unpublished results.

[21] G. A. Olah, J. M. Bollinger, and J. Brinich, *J. Amer. Chem. Soc.*, **90**, 2587 (1968); G. A. Olah, J. M. Bollinger, Y. K. Mo, and J. M. Brinich, *ibid.*, **94**, 1164 (1972); J. W. Larsen and A. V. Metzner, *ibid.*, **94**, 1614 (1972).

[22] (a) H. B. Donahoe and C. A. Vanderwerf, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 157. (b) G. Drefahl, G. Heublein, and B. Noll, *J. Prakt. Chem.*, **293**, 208 (1963).

[23] T. C. Bruice and T. H. Fife, *J. Amer. Chem. Soc.*, **84**, 1973 (1962).

[24] K. W. Buck, A. B. Foster, A. Labib, and J. M. Webber, *J. Chem. Soc.*, 2846 (1964).

[25] (a) L. Goodman, A. Benitez, and B. R. Baker, *J. Amer. Chem. Soc.*, 80, 1680 (1958); (b) L. Goodman, A. Benitez, C. D. Anderson, and B. R. Baker, *ibid.*, 80, 6582 (1958).

produced *cis*-2-methylthiocyclopentanol (9.8 g, 74%), bp 52–54° (0.3 mm); nmr δ 4.05 (m, 1 C*H*OH), 3.03 (d, 1, J = 2.5 Hz, OH), 2.95 (m, 1, C*H*SCH$_3$), 2.08 (s, 3, SCH$_3$), and 1.74 (m, 6, (CH$_2$)$_3$).

2-Methoxy-1-propanol and 1-methoxy-2-propanol were prepared by the acid-catalyzed ring opening of propylene oxide in methanol according to a known procedure,[26] and the isomers were separated by preparative glpc.

1-Methylthio-2-propanol was prepared by the procedure of Bordwell and Andersen:[27] bp 67–69° (20 mm) [lit.[27] bp 55–58° (10 mm)].

2-Methylthio-1-propanol was prepared as follows: a mixture of 1-propenyl acetate (10 g, 0.1 mol), methanethiol (60 g), and benzoyl peroxide (0.5 g) was illuminated with a uv lamp as described earlier for *cis*-2-methylthiocyclopentanol. The 2-methylthiopropyl acetate obtained (4.8 g, 34%, bp 128°) was hydrolyzed with 10% KOH solution (60 ml) at room temperature. The mixture was extracted with ether several times, and the combined extracts were washed with water saturated with sodium chloride, dried (MgSO$_4$), and concentrated. The product was separated and purified by preparative glpc; overall yield 18%; bp 65–71° (12 mm); nmr (CDCl$_3$) δ 3.55 (d, 2, J = 6.0 Hz, C*H*$_2$OH), 2.85 (s, 1, OH), 2.79 (m, 1, C*H*SCH$_3$), 2.05 (s, 3, SCH$_3$), and 1.27 (d, 3, J = 6.0 Hz, CHC*H*$_3$).

Acknowledgment. We are indebted to Dr. Wesley Huntress of the Jet Propulsion Laboratories, Pasadena, for his help with regard to both the instrumental and conceptual aspects of this work.

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[26] S. Winstein and L. L. Ingraham, *J. Amer. Chem. Soc.*, **74**, 1160 (1952).

[27] F. G. Bordwell and H. M. Andersen, *ibid.*, **75**, 4959 (1953).

Anodic Oxidations. IX. Anodic Oxidation of 2-Methoxyethanol

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Abstract: The anodic oxidation of 2-methoxyethanol in the presence of tetraethylammonium fluoroborate as supporting electrolyte results in the formation of formaldehyde, bis(2-methoxyethyl)formal (I), 2-hydroxyethyl-2′-methoxyethylformal (II), and 2,4,6,9-tetraoxadecane (III), with the major oxidation products resulting from attack on the ether rather than the alcohol function of 2-methoxyethanol. With tetraethylammonium nitrate as supporting electrolyte, an additional product, 3-hydroxymethyl-2,4,7-trioxaoctane (IV), is obtained. The mechanisms of these oxidations have been discussed.

The saturated aliphatic alcohols and ethers have ionization potentials exceeding 9 eV.[1,2] Since there is a parallelism between anodic oxidation potentials and gas-phase ionization potentials,[3] it is not surprising that the anodic oxidation of aliphatic alcohols and ethers requires extreme positive potentials.[4] By using fluoroborates as the supporting electrolyte, it is possible to extend the potential range to beyond 3.0 V *vs.* Ag|Ag$^+$ (10^{-2} M),[5] and to determine the half-wave potentials for oxidation of aliphatic alcohols by cyclic voltammetry.[6]

Sundholm[7] has shown that methanol and ethanol can be electrooxidized to give, in good yield, aldehydes with sodium alkoxides as the supporting electrolytes and acetals with perchlorates or fluoroborates as the supporting electrolytes. The proposed mechanism involves reaction I as the primary process, with subsequent chemical steps leading to products. Shono and Matsumura[8] have anodically methoxylated saturated ethers in methanol containing a methoxide, a nitrate, or a p-toluenesulfonate as the supporting electrolyte. This reaction introduces methoxy groups in the α position of the ether and fails when no α hydrogens are available. The authors, therefore, favored a mechanism in which an anodically generated radical abstracts hydrogen from the α position of the ether.

$$RCH_2OH \longrightarrow R\overset{+}{C}HOH + 2e + H^+ \qquad (I)$$

A mechanism involving direct electron transfer from an ether to form a cationic species should be possible, since such a mechanism has been observed for the alcohols.[6,7] To explore this possibility, the anodic oxidation of 2-methoxyethanol, which contains both the alcohol and the ether function, has been investigated. The products formed indicate the locus of attack, and the extent of attack at the two available sites affords some indication of the relative ease of anodic oxidation of the two functions.

Results

Cyclic voltammograms of a solution of 0.1 M tetraethylammonium fluoroborate in acetonitrile over the potential range -1.20 to $+2.1$ V *vs.* E (Ag|Ag$^+$ (0.1 N)) at scan rates of 100 and 200 mV sec^{-1} are comparable to those previously reported[9] for a more concentrated solution of this salt and show an increase in current at $E > 1.8$ V. The addition of 0.47 M 2-methoxy-

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[1] A. Streitwieser, Jr., *Progr. Phys. Org. Chem.*, **1**, 1 (1963).

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

[3] L. L. Miller, G. D. Nordblom, and E. A. Mayeda, *J. Org. Chem.*, **37**, 916 (1972), and references cited therein.

[4] C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York, N. Y., 1970, Chapter 8.

[5] M. Fleischmann and D. Pletcher, *Tetrahedron Lett.*, 6255 (1968).

[6] G. Sundholm, *Acta Chem. Scand.*, **25**, 3188 (1971).

[7] G. Sundholm, *J. Electroanal. Chem. Interfacial Electrochem.*, **31**, 275 (1971).

[8] T. Shono and Y. Matsumura, *J. Amer. Chem. Soc.*, **91**, 2803 (1969).

[9] E. J. Rudd, M. Finkelstein, and S. D. Ross, *J. Org. Chem.*, **37**, 1763 (1972).