Low-energy, Low-temperature Mass Spectra. Part 7.[1] Terminal Alkenols

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The 12.1 eV, 75 °C, electron-impact mass spectra of four homologous alkenols $CH_2{=}CH[CH_2]_nOH$ (n = 1—4) are reported and discussed. For $n = 1$, simple cleavage of the molecular ion constitutes the major reaction; however, the importance of simple cleavages diminishes rapidly on ascending the homologous series. Rearrangement processes of three general kinds dominate the spectra of the higher homologues. Hydrogen transfer in $CH_2{=}CHCH_2CH_2OH^{+\cdot}$ leads to CH_2O expulsion; loss of H_2O gives rise to the base peak in the spectra of ionised pentenol and hexenol; and elimination of $CH_3^{\cdot}$ occurs to some extent from the molecular ion of butenol. Distonic ions are implicated as important intermediates in the reactions of these ionised alkenols.

Low-voltage, low-temperature electron-impact mass spectra offer features which are more attractive to analytical and mechanistic chemists than conventional 70 eV spectra.[2] The relatively low abundance of ions formed by secondary fragmentations of the primary daughter ions, coupled with the higher relative intensity of the molecular ion peak, leads to simpler spectra which are easier to interpret than their 70 eV counterparts. In addition, the importance of rearrangement processes, which often correspond to interesting chemical reactions, is enhanced in the low-energy spectra. In this paper, the 12.1 eV, 75 °C spectra of four homologous alkenols of general structure $CH_2{=}CH[CH_2]_nOH$ (n = 1—4) are reported.

Results and Discussion

The 12.1 eV, 75 °C, electron-impact mass spectra of the four terminal alkenols $CH_2{=}CH[CH_2]_nOH$ (n = 1—4) are reproduced in the Figure. Energy data relevant to the decomposition of ionised alkenols are given in the Table. Several interesting trends may be discerned in the spectra.

First, whereas allyl alcohol (**1**) shows an abundant molecular ion, the higher homologues (**2**)—(**4**) have spectra in which the $M^{+\cdot}$ peaks are smaller or absent. This behaviour can be interpreted in terms of the changes which occur in the relative energies of $M^{+\cdot}$ and plausible product combinations as the homologous series of ionised alkenols is ascended. Ionised allyl alcohol is thermodynamically more stable by some 60 kJ mol^{-1} than the energetically most favourable products accessible by simple bond cleavage ($CH_2{=}CHCH{=}OH^+ + H^{\cdot}$). Moreover, the products of water loss from $CH_2{=}CHCH_2OH^{+\cdot}$ also have a total enthalpy of formation substantially above (85 kJ mol^{-1}) the energy of the parent radical cation. Only one dissociation route, the mechanistically demanding process of production of $[CH_3CO]^+$ and $CH_3^{\cdot}$, leads to products of (marginally) lower energy than the molecular ion. In contrast, for n = 2, 3, or 4, $CH_2{=}CH[CH_2]_nOH^{+\cdot}$ is no longer thermodynamically stable with respect to $[C_mH_{2m-2}]^{+\cdot}$ and H_2O. It is probable that elimination of H_2O from the ionised alkenes involves a significant critical energy; nevertheless, it is clear that a fundamental change takes place in the energetics associated with decomposition of $CH_2{=}CH[CH_2]_nOH^{+\cdot}$ in progressing from $n = 1$ to $n \geqslant 2$. Other factors, including the possibility of the intervention of an optically excited state, may favour H_2O loss; this type of mechanism has been advanced to explain the ready appearance of $[M - H_2O]^{+\cdot}$ in the spectra of the analogous saturated alcohols, $CH_3[CH_2]_nOH$, for $n \geqslant 4$.[3]

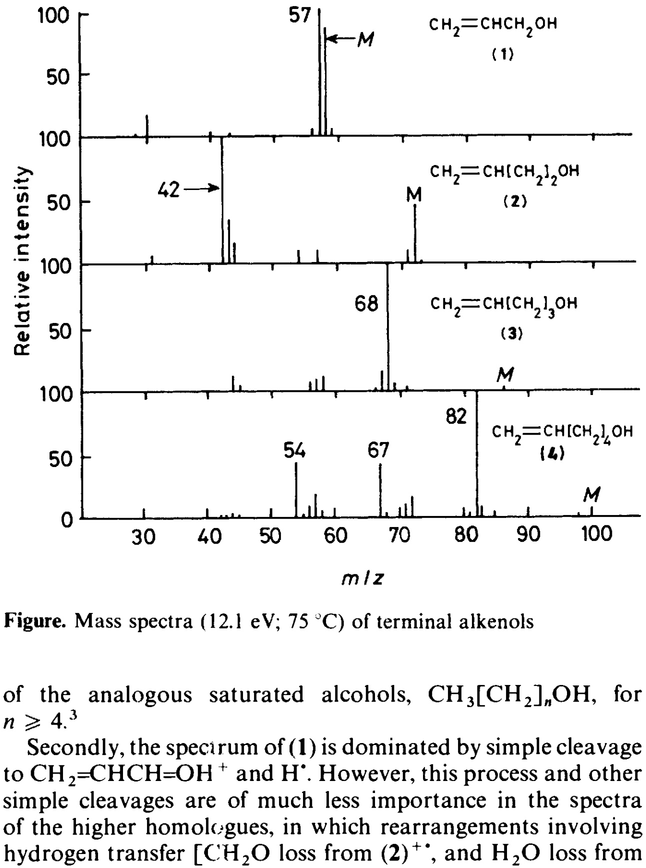


Figure. Mass spectra (12.1 eV; 75 °C) of terminal alkenols

Secondly, the spectrum of (**1**) is dominated by simple cleavage to $CH_2{=}CHCH{=}OH^+$ and $H^{\cdot}$. However, this process and other simple cleavages are of much less importance in the spectra of the higher homologues, in which rearrangements involving hydrogen transfer [CH_2O loss from (**2**)$^{+\cdot}$, and H_2O loss from (**3**)$^{+\cdot}$ and (**4**)$^{+\cdot}$] give rise to the base peak. This trend also has its origin in the energetics of the product combinations: only for (**1**)$^{+\cdot}$ is $H^{\cdot}$ loss (or any other simple cleavage) able to yield products that are thermodynamically preferable to those accessible by hydrogen-transfer reactions. Consequently, the abundance of $[M - H]^+$ declines sharply on ascending the homologous series.

Thirdly, on progressing from $n = 1$ to $n = 4$, the relative abundance of ions formed from $CH_2{=}CH[CH_2]_nOH^{+\cdot}$ by dissociations involving hydrogen transfer increases dramatically. Thus, $[M - H_2O]^{+\cdot}$ is a minor peak in the spectra of (**1**) and (**2**), but it is the base peak in the spectra of (**3**) and (**4**). This reflects the growing stability of the $[C_mH_{2m-2}]^{+\cdot}$ daughter

Table. Energy data relevant to the decomposition of the ions $CH_2{=}CH[CH_2]_nOH^{+\bullet}$

Ion and ΔH_f†	Products and ΔH_f†	$\Sigma\Delta H_f$†
$CH_2{=}CHCH_2OH^{+\bullet}$ (800[8])	$CH_2{=}CH^+$ (1 110[a,b]) + $^{\bullet}CH_2OH$ (−25[c])	1 085
	$CH_2{=}CH^{\bullet}$ (250[b]) + $[CH_2OH]$† (705[d])	955
	$CH_2{=}CHCH_2^+$ (945[e]) + $^{\bullet}OH$ (40[f])	985
	$CH_2{=}C{=}CH_2^{+\bullet}$ (1 125[a]) + H_2O (−240[f])	885
	$CH_2{=}CHCH{=}OH^+$ (645‡,§,[g]) + $H^{\bullet}$ (215[f])	860
	CH_3CO^+ (650[h]) + $CH_3^{\bullet}$ (140[c])	790
$CH_2{=}CHCH_2CH_2OH^{+\bullet}$ (770¶)	$CH_2{=}CHCH_2^+$ (945[e]) + $^{\bullet}CH_2OH_2$ (−25[c])	920
	$CH_2{=}CHCH_2^{\bullet}$ (165[c]) + $[CH_2OH]^+$ (705[d])	870
	$CH_2{=}CHCH_2CH{=}OH^+$ (640‡,§) + $H^{\bullet}$ (215[f])	855
	$CH_2{=}CH\overset{+}{C}HCH_3$ (850[e]) + $^{\bullet}OH$ (40[f])	890
	$CH_2{=}CHCH{=}CH_2^{+\bullet}$ (985[f]) + H_2O (−240[f])	745
	$CH_3CH{=}CH_2^{+\bullet}$ (955[f]) + $CH_2{=}O$ (−115[f])	840
	$CH_3CH{=}CH_2$ (20[f]) + $CH_2{=}O^{+\bullet}$ (930[f])	950
	$CH_3\overset{+}{C}HCH_3$ (805[i]) + $H\dot{C}O$ (30[c])	835
	$CH_3\dot{C}HCH_3$ (80[j]) + HCO^+ (820[k])	900
	CH_3CO^+ (650[h]) + $CH_3CH_2^{\bullet}$ (115[j])	765
	$CH_3CH_2CH_3^{+\bullet}$ (965[f]) + CO (−110[f])	855
	$CH_3CH{=}O^{+\bullet}$ (830[f]) + $CH_2{=}CH_2$ (50[f])	880
	$CH_2{=}CHOH^{+\bullet}$ (770[l]) + $CH_2{=}CH_2$ (50[f])	820
$CH_2{=}CHCH_2CH_2CH_2OH^{+\bullet}$ (740¶)	$CH_2{=}CH\overset{+}{C}HCH_3$ (850[e]) + $^{\bullet}CH_2OH$ (−25[c])	825
	$CH_2{=}CH\dot{C}HCH_3$ (120[e]) + $[CH_2OH]^+$ (705[d])	825
	$CH_2CH_2CH_2CH_2CH^+$ (805[m]) + $^{\bullet}OH$ (40[f])	845
	$CH_3CH{=}CH\overset{+}{C}HCH_3$ (775[n]) + $^{\bullet}OH$ (40[f])	815
	$CH_2CH_2CH_2CH{=}CH^{+\bullet}$ (900[f]) + H_2O (−240[f])	660
	$CH_3CH{=}CHCH{=}CH_2^{+\bullet}$ (915[f]) + H_2O (−240[f])	675
	$CH_2{=}CHCH_2CH{=}CH_2^{+\bullet}$ (1 030[f]) + H_2O (−240[f])	790
	CH_3CO^+ (650[h]) + $CH_3CH_2CH_2^{\bullet}$ (75[k])	725
	$CH_2CH_2CH_2C{=}O^+$ (595**) + $CH_3^{\bullet}$ (140[c])	735
	$CH_2CH_2CH_2C{=}OH^+$ (610[o]) + $CH_3^{\bullet}$ (140[c])	750
	$CH_2{=}CHCH_2CH_2CH{=}OH^+$ (620‡,§) + $H^{\bullet}$ (215[f])	835
	$CH_2CH_2CH_2CH_2C{=}OH^+$ (495[o]) + $H^{\bullet}$ (215[f])	710
$CH_2{=}CHCH_2CH_2CH_2CH_2OH^{+\bullet}$ (715¶)	$CH_2CH_2CH_2CH_2CH{-}C{=}OH^+$ (445[o]) + $H^{\bullet}$ (215[f])	660
	$CH_2CH_2CH_2CH_2C^+CH_3$ (725‡,[p]) + $^{\bullet}OH$ (40[f])	765
	$CH_2CH_2CH_2CH_2CH{=}CH^+$ (830[f]) + H_2O (−240[f])	590
	$CH_2CH_2CH_2CH{=}C{-}CH_3^{+\bullet}$ (820††) + H_2O (−240[f])	580
	$CH_2{=}CHCH_2^{\bullet}$ (165[c]) + $CH_2CH_2CH_2OH^+$ (625‡)	790
	$CH_2{=}CHCH{=}CH_2^{+\bullet}$ (985[f]) + CH_3CH_2OH (−235[f])	750
	$CH_2CH_2CH_2CH{=}CH^{+\bullet}$ (900[f]) + CH_3OH (−200[f])	700
	$CH_2CH_2CH_2CH_2C{=}OH^+$ (495[o]) + $CH_3^{\bullet}$ (140[c])	635
	$CH_2CH_2CH_2CH_2CH{=}O^+$ (555**) + $CH_3^{\bullet}$ (140[c])	695

[a] H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data Suppl. 1*, 1977, 6. [b] F. P. Lossing, *Can. J. Chem.*, 1971, **49**, 357. [c] Ref. 8. [d] F. P. Lossing, *J. Am. Chem. Soc.*, 1977, **99**, 7526. [e] F. P. Lossing, *Can. J. Chem.*, 1972, **50**, 3973. [f] Ref. 12. [g] Compare the quoted experimental value of 649 ± 13 kJ mol^{-1}, J. C. Traeger, *Org. Mass Spectrom.*, 1985, **20**, 223. [h] Mean of recent determinations: J. C. Traeger, R. G. McLoughlin, and A. J. C. Nicholson, *J. Am. Chem. Soc.*, 1982, **104**, 5318. [i] F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, 1970, **48**, 955. [j] Ref. 9. [k] P. M. Guyon, W. A. Chupka, and J. Berkowitz, *J. Chem. Phys.*, 1976, **64**, 1419. [l] Ref. 13. [m] J. J. Solomon and F. H. Field, *J. Am. Chem. Soc.*, 1976, **98**, 1567. [ΔH_f(t-$C_4H_9^+$) corrected to 695 kJ mol^{-1}, J. C. Traeger and R. G. McLoughlin, *ibid.*, 1981, **103**, 3647]. [n] Ref. 11. [o] G. Bouchoux and R. Houriet, *Tetrahedron Lett.*, 1984, **25**, 4755. [p] J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, 1977, **99**, 5417.

† All values in kJ mol^{-1} and rounded to the nearest 5 kJ mol^{-1}.

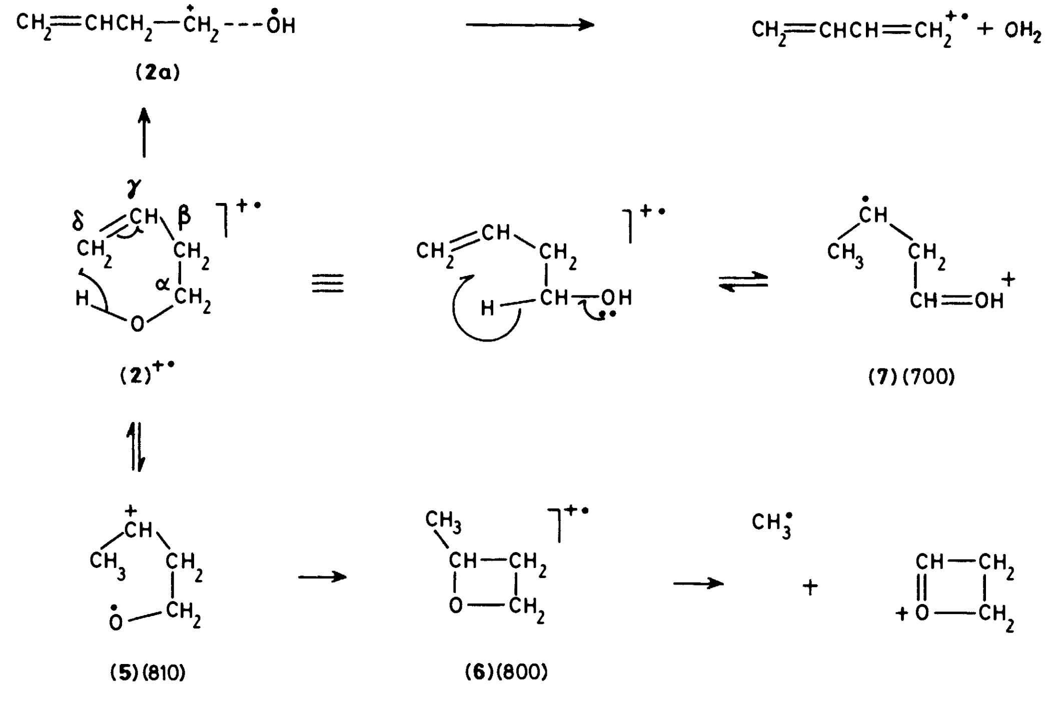
‡ Value obtained by estimating the proton affinity of the corresponding neutral species from those reported[p] for homologues and analogues.

§ Enthalpy of formation of corresponding neutral species obtained by use of group equivalent estimation procedures (ref. 12, appendix 2; see also J. L. Franklin, *Ind. Eng. Chem.*, 1949, **41**, 2029; *J. Chem. Phys.*, 1953, **21**, 2029).

¶ Value obtained from that of the corresponding ionised alkene[12] by use of an isodesmic substitution procedure.[7]

** Value estimated on the basis of a similar dissociation energy of RH to R^+ + H^- for cyclic ethers to that (960 kJ mol^{-1}) found[d] in acyclic ethers of comparable structure.

†† Value estimated on the basis that methylation of ionised cyclopentene confers the same stabilisation as that[12] (85 kJ mol^{-1}) produced by methylation of ionised *cis*-but-2-ene.



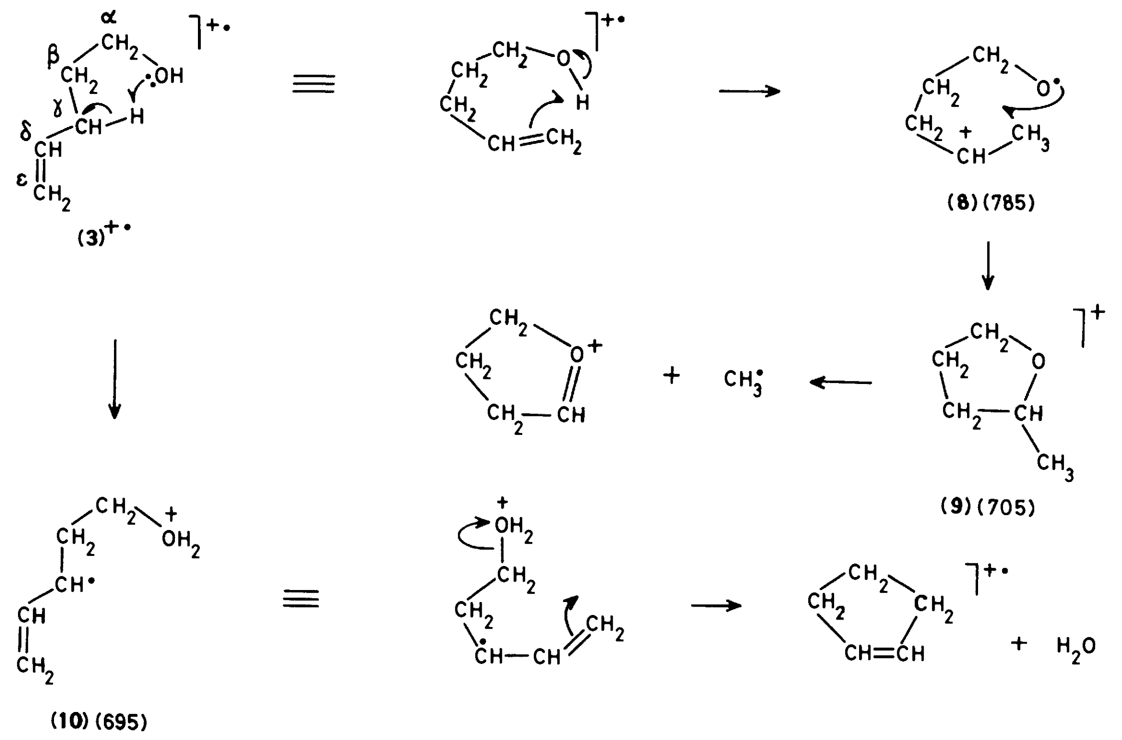
Scheme 1.

ions, especially when conjugated diene and relatively strain-free cycloalkene structures become possible for $m = 5$ and 6. However, another factor may operate in favour of H_2O elimination for $n = 3$ and 4; the greater conformational flexibility of ionised pentenol, as compared with ionised butenol, facilitates any rearrangement processes which are involved in loss of H_2O. The comparatively low abundance of $[M - H_2O]^{+\bullet}$ in the spectra of (**1**) and (**2**) cannot be attributed entirely to the relatively poor thermodynamic stability of the products because a metastable peak is present for H_2O loss from $(\mathbf{2})^{+\bullet}$. Moreover, the results of ^2H labelling on ionised butenol and pentenol in which the hydroxylic hydrogen is replaced by deuterium show a different specificity of hydrogen transfer in the selection of the atoms needed to make up the expelled water molecule. Thus, when D_2O is admitted into the source, the ratio of m/z 55 to 54 in a mixture of five parts $CH_2{=}CHCH_2CH_2OD$ and four parts $CH_2{=}CHCH_2CH_2OH$ is 1:1.8. The ratio calculated on the basis of complete retention of the hydroxylic hydrogen in the water molecule (model A) is 0:1. A similar calculation on the basis of statistical selection of the hydrogen and deuterium atoms (model B) gives a ratio of 1:1.4. An intermediate case, in which the hydroxylic hydrogen is reversibly exchanged with the hydrogens on the α- and δ-carbon atoms (model C), yields a ratio of 1:2.0. It is clear from these data that model A is not correct. A more sophisticated model (D) in which the hydroxylic hydrogen is reversibly exchanged with those of the δ-carbon, followed by a 1,2-elimination of water, gives a ratio of 1:1.7. The mass spectrum of $CH_2{=}CHCH_2CD_2OH$ contains peaks at m/z 56 (H_2O loss), 55 (HOD loss), and 54 (D_2O loss) in the ratios 6:1:0. The ratios calculated using models B, C, and D are 15:12:1, 3:6:1, and 1:0:0, respectively. Consequently, model D gives the best overall description of the behaviour of ionised ^2H-labelled butenols. Scheme 1 furnishes a mechanism for water loss which is consistent with these observations. Reversible exchange of the hydroxylic hydrogen, $(\mathbf{2})^{+\bullet} \rightleftharpoons (\mathbf{5})$, precedes 1,2-elimination of water. The final step probably proceeds with a very low degree of concert,[4] involving species such as (**2a**). Although interconversion of $(\mathbf{2})^{+\bullet}$ and (**7**) appears to be geometrically and energetically feasible, it is clear from the ^2H-labelling results that this process is slow in comparison with water loss.

In contrast, water loss from ionised pentenol involves a different specificity of hydrogen selection. Thus, when D_2O is allowed to exchange with the hydroxylic hydrogen of (**3**), the peaks at m/z 68 and 69 remain in similar relative intensity to the peaks in the spectrum of the undeuteriated compound. This suggests that the hydroxylic hydrogen is predominantly or exclusively retained in the expelled water molecule. Further insight is found in the mass spectra of $CH_2{=}CH_2CH_2CH_2$-CD_2OH and $CH_2{=}CHCH_2CD_2CH_2OH$; the base peaks in these spectra are at m/z 70 (H_2O loss) and 69 (HOD loss), respectively. These results are consistent with a 1,2-elimination of water from ionised pentenol.

These labelling experiments underline the profound change which takes place in the abundance of $[M - H_2O]^{+\bullet}$ on progressing from (**2**) to (**3**). Whereas the spectrum of (**2**) contains a substantial molecular ion and only a small peak for $[M - H_2O]^{+\bullet}$, the spectrum of (**3**) displays a negligible molecular ion and $[M - H_2O]^{+\bullet}$ becomes the base peak. One possible explanation involves invoking the increased conformational possibilities open to the longer alkyl chain in $(\mathbf{3})^{+\bullet}$ (Scheme 2). A hydrogen shift from the γ-carbon to oxygen leads to (**10**), which can eliminate water with π-participation to give ionised cyclopentene. However, such a mechanism, though energetically and geometrically plausible, cannot explain the spectrum of $CH_2{=}CHCH_2CD_2CH_2OH$, for which $[M - H_2O]^{+\bullet}$ would be expected as the base peak. A simple 1,2-elimination in $(\mathbf{3})^{+\bullet}$ yields only moderately favourable products ($CH_2{=}CHCH_2$-$CH{=}CH_2^{+\bullet}$ and H_2O). The possibility that $[M - H_2O]^{+\bullet}$ is formed *via* a mechanism involving an optically excited state, as has been suggested[3] for the saturated analogue, pentan-1-ol, is worthy of consideration. In any event, it is certain that if $[M - H_2O]^{+\bullet}$ does arise from $(\mathbf{3})^{+\bullet}$, then this water expulsion takes place exceptionally readily, occurring much more rapidly than hydrogen shifts to and from the oxygen atom.

On progressing to the next homologue $(\mathbf{4})^{+\bullet}$, there is indirect

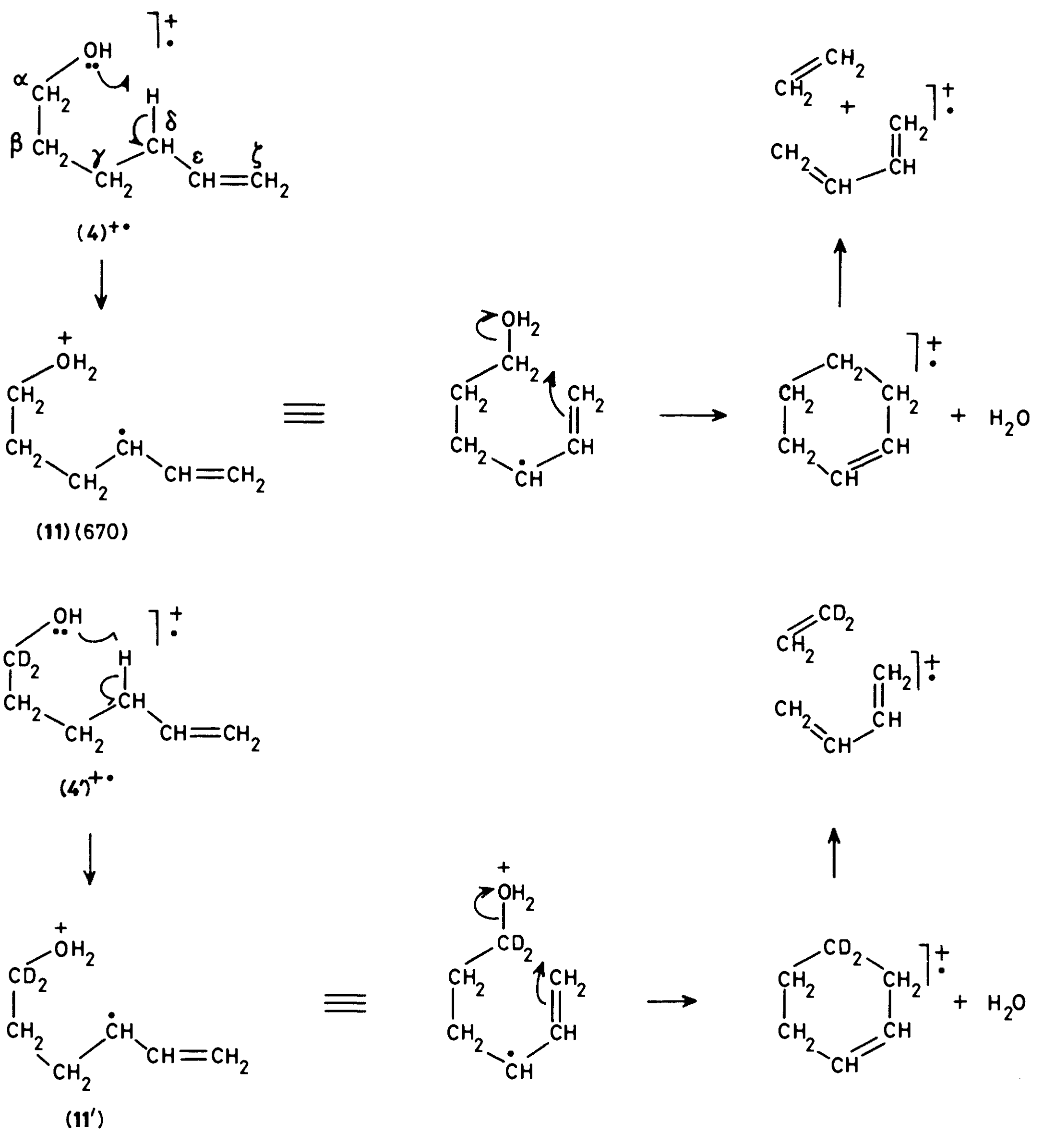


Scheme 2.

evidence that $[M - H_2O]^{+\cdot}$ does arise by a mechanism involving hydrogen transfers and cyclisation to an ionised alkene (Scheme 3). Thus, when D_2O is allowed to exchange with the hydroxylic hydrogen of (**4**), the relative abundances of the peaks at *m/z* 82 and 83 in a mixture of five parts $C_6H_{11}OD$ and four parts $C_6H_{11}OH$ are consistent with reversible exchange of the hydroxylic hydrogen and any four of those bound to carbon. This formulation of the mechanism for formation of $[M - H_2O]^{+\cdot}$ is supported by the mass spectrum of $CH_2=CHCH_2CH_2CH_2CD_2OH$, which displays $[M - H_2O]^{+\cdot}$ as the base peak; $[M - HOD]^{+\cdot}$ is of negligible importance, and the hydrogen atoms on the α-carbon are not exchanged with the hydroxylic hydrogen before water is lost. The peak at *m/z* 54 ($C_4H_6^{+\cdot}$) in the spectrum of (**4**) is logically described as a secondary dissociation of ethylene expulsion from $[M - H_2O]^{+\cdot}$; when this reaction is investigated for $C_5H_9CD_2OH$, almost exclusive $C_2H_2D_2$ loss is observed. These results can be interpreted in terms of the mechanism of Scheme 3. After H_2O loss has taken place, the resultant ionised cyclohexene is set up to expel ethylene *via* a cycloreversion. Since the α-CH_2 of (**4**) becomes part of the ionised cyclohexene which is eliminated as ethylene in the secondary reaction, the consecutive loss of H_2O and $C_2H_2D_2$ from (**4′**)$^{+\cdot}$ is explained. On the other hand, if $[M - H_2O]^{+\cdot}$ arises from a 1,2-elimination, it is difficult to envisage a reason why the resultant $CH_2=CHCH_2CH_2CH=CD_2^{+\cdot}$ radical cation should eliminate predominantly $C_2H_2D_2$ in the secondary reaction. In order to accommodate the high relative abundance of the peak at *m/z* 54 ($C_4H_6^{+\cdot}$) in the spectrum of (**4′**), it would be necessary to postulate that this ion has its origin in a 1,2-elimination of ethanol from $M^{+\cdot}$. Such a possibility may seem unlikely, but it cannot be excluded on the basis of the present data. It is significant that some exchange of the carbon-bound hydrogens with the hydroxylic hydrogen does occur for (**4**)$^{+\cdot}$; this is in contrast with the situation which pertains for the lower homologue (**3**)$^{+\cdot}$. The allylic positions in (**4**)$^{+\cdot}$ (δ- and ζ-carbon atoms) are probably involved, but further labelling studies would be required to establish this possibility more firmly.

Ion radical species in which the notional charge and spin sites are separate are becoming known as 'distonic ions'.[5] These species are now known to be of great importance in the chemistry of isolated ions of diverse functionality. For instance, the important pseudo-α-cleavage process in the molecular ions of amines at low internal energies can be understood in terms of a mechanism involving hydrogen-transfer reactions and distonic ions.[6] Thus, the mechanisms given in Schemes 1—3 have an established precedent. Moreover, the enthalpies of formation of the distonic intermediates may be estimated using isodesmic substitution procedures[7] in conjunction with known values for hydrogen radical or hydride anion abstraction energies.[8,9] These estimated enthalpies of formation are given in parentheses in the Schemes, and it is clear that the intermediates should be accessible at energies below those needed to promote decomposition of (**2**)$^{+\cdot}$, (**3**)$^{+\cdot}$, and (**4**)$^{+\cdot}$.

Although water loss from ionised alkenols is the main reaction involving hydrogen transfer in the case of the higher homologues (**3**)$^{+\cdot}$ and (**4**)$^{+\cdot}$, elimination of a methyl radical is of some importance for ionised butenol. ^{2}H-Labelling experiments reveal that the hydrogen of the original hydroxy group undergoes extensive exchange with some or all of the carbon-bound hydrogens before methyl radical is lost. Thus, in a mixture of four parts $CH_2=CHCH_2CH_2OH^{+\cdot}$ and five parts $CH_2=CHCH_2CH_2OD^{+\cdot}$, the relative abundance of *m/z* 57 and 58 is 1.4:1. The ratio expected on the basis of irreversible hydrogen transfer [(**2**)$^{+\cdot}$ ⟶ (**5**) ⟶ (**6**) ⟶ products (model A)] would be 1.0:0. The ratios calculated on the basis of statistical selection of hydrogens (model B) and selection of any three of the five hydrogens bound to oxygen or the α- or δ-carbons (model C) are 1.5:1 and 2.6:1, respectively. Furthermore, the relative intensities of the peaks at *m/z* 59 ($CH_3^{\cdot}$ loss), 58 ($CH_2D^{\cdot}$ loss), and 57 ($CHD_2^{\cdot}$ loss) in the spectrum of $CH_2=CHCH_2CD_2OH$ are in the ratio 9:9:2. The

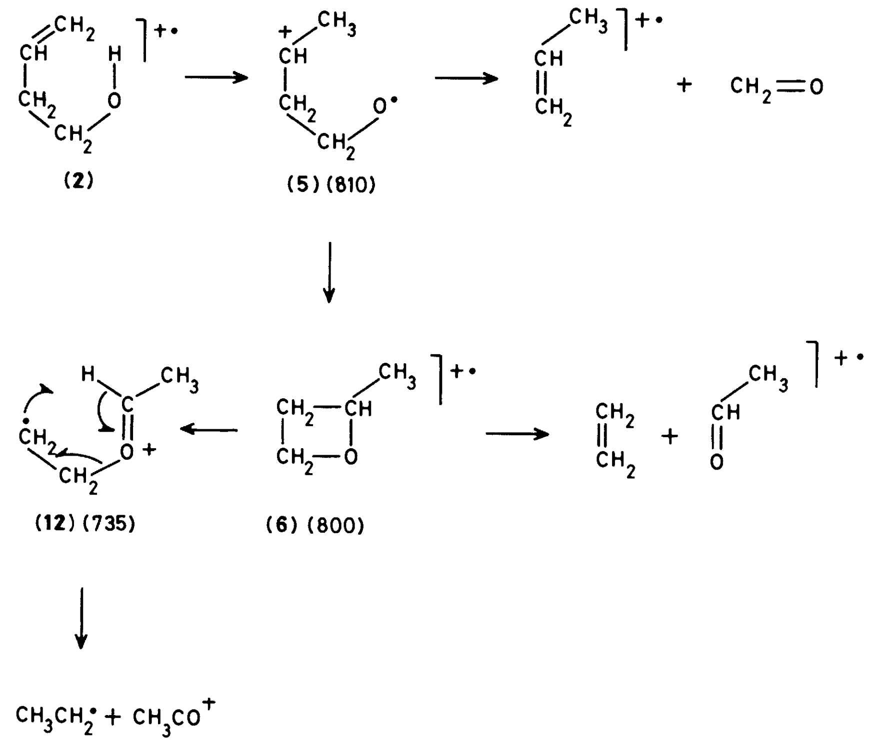


Scheme 3.

ratios expected on the basis of models A, B, and C are 1:0:0, 10:15:3, and 1:6:3, respectively. Model B gives the closest approximation to the observed ratios. However, in view of the uncertainty concerning the structure of the product ion (a cyclic oxonium ion is postulated in Scheme 1, though $CH_2=CHCH=OH^+$ would be a favourable alternative if further rearrangement occurred before methyl radical was lost), detailed discussion of the mechanism of this reaction is unwarranted. Notwithstanding this restriction, the statistical or near-statistical selection of hydrogen atoms in methyl loss from ionised ^2H-labelled butenols supports the proposal that distonic ions such as **(5)** and **(7)** are of importance in the chemistry of ionised alkenols.

The inability of methyl radical loss to compete effectively with water elimination from the molecular ions of pentenol and hexenol cannot be ascribed simply to the lack of stable product combinations. Production of cyclic oxonium ions and/or protonated cycloalkanones and methyl radical gives products of total energy similar to those formed by water loss (Table). Instead, the dominance of water elimination appears to reflect the ease of this process (see foregoing discussion), and perhaps the higher energy of the intermediates involved in methyl radical expulsion.

The fourth major trend in the spectra of the terminal alkenols concerns the abundance of ions produced by secondary decompositions of the primary ionic species. For n = 1—3, all such secondary ions are of negligible or only very minor importance. In contrast, for n = 4, significant peaks appear at m/z 54 and 67; these correspond to C_2H_4 and $CH_3^{\bullet}$ loss, respectively, from $[M - H_2O]^{+\bullet}$; these peaks also are present in the low-energy spectra of C_6H_{10} hydrocarbons such as cyclohexene.[10] Each of these reactions leads to products of low potential energy [$\Sigma\Delta H_f$ (cyclo-$C_5H_7^+$ + $CH_3^{\bullet}$) = 975 kJ mol^{-1} (refs. 8 and 11); $\Sigma\Delta H_f$ ($CH_2=CHCH=CH_2^{+\bullet}$ + C_2H_4) = 1 035 kJ mol^{-1} (ref. 12)]. Moreover, the presence at m/z 54.7 of a metastable peak corresponding to $CH_3^{\bullet}$ loss from $[M - H_2O]^{+\bullet}$ is consistent with the view that m/z 67 arises from m/z 82. It is interesting that the reaction of $[M - H_2O]^{+\bullet}$ which gives rise to a metastable peak is that ($CH_3^{\bullet}$ loss) which yields the products having the lower energy. The reaction leading to the higher-energy products (C_2H_4 loss) cannot compete effectively at energies appropriate to metastable transitions, though it does occur to a sizeable extent for $C_6H_{10}^{+\bullet}$ daughter ions of somewhat higher internal energies. As discussed previously, there is evidence that ethylene loss from $C_6H_{10}^{+\bullet}$



Scheme 4.

occurs *via* cycloreversion of ionised cyclohexene which is formed as the primary daughter ion by H_2O elimination from ionised hexenol (Scheme 3).

The presence of secondary ions corresponding to decomposition of $[M - H_2O]^{+\bullet}$ primary ions seems to be fairly general for low-energy spectra, particularly in compounds containing only one oxygen atom. This reflects the thermodynamic preference for eliminating an extremely stable neutral molecule [H_2O; $\Delta H_f = -240$ kJ mol^{-1} (ref. 12)] from $M^{+\bullet}$, and the relative ease of subsequent dissociation of the ionised unsaturated hydrocarbon which constitutes the primary daughter ion.

Finally, the peaks at *m/z* 42, 43, and 44 in the spectrum of $CH_2{=}CHCH_2CH_2OH$ are worthy of note. The first of these can be assigned to CH_2O loss from $M^{+\bullet}$ occurring *via* a pericyclic process (Scheme 4). Hydrogen transfer may well be a distinct step from dissociation to products. The distonic ion (**5**) is a plausible intermediate [ΔH_f(est.) = 810 kJ mol^{-1}] which is appreciably lower in energy than $C_3H_6^{+\bullet} + CH_2O$ [$\Sigma\Delta H_f$ = 840 kJ mol^{-1} (ref. 12)]. The peak at *m/z* 43 could be produced by either $^{\bullet}CHO$ loss or $C_2H_5^{\bullet}$ loss from $M^{+\bullet}$. High-resolution measurements show that *m/z* 43 is CH_3CO^+; therefore, $C_2H_5^{\bullet}$ is expelled. A reasonable mechanism for this unusual reaction is *via* ring closure of (**5**) to ionised 2-methyloxetane; ring opening to another type of distonic ion (**12**), followed by hydrogen transfer, then leads to CH_3CO^+ and $C_2H_5^{\bullet}$. Support for this proposal is found in the low-energy mass spectrum of 2-methyloxetane, in which a significant peak is present at *m/z* 43 (CH_3CO^+, by high-resolution measurements). A metastable peak for the transition $M^{+\bullet} \longrightarrow$ *m/z* 43 appears at *m/z* 25.7 in the spectra of but-3-enol and 2-methyloxetane. Therefore, it is evident that ethyl radical expulsion from these $C_4H_8O^{+\bullet}$ ions is an especially favourable process. In the spectrum of but-3-enol, the peak at *m/z* 44 is shown by high-resolution measurements to be $C_2H_4O^{+\bullet}$; a similar peak is present in the spectrum of 2-methyloxetane. A logical explanation of these observations is that *m/z* 44 in the spectra of both compounds is $CH_3CH{=}O^{+\bullet}$, produced by simple fission of (**6**). This ion could be formed either by simple cycloreversion of (**6**), or by a two-step mechanism involving the distonic ion (**12**). The latter explanation is perhaps the more likely, but the present data do not allow a definite decision to be made between the two alternatives. Formation of ionised vinyl alcohol, $CH_2{=}CHOH^{+\bullet}$, which is some 60[12,13] kJ mol^{-1} more stable than $CH_3CH{=}O^{+\bullet}$, is also to be considered. Whereas $CH_3CH{=}O^{+\bullet} + C_2H_4$ have a slightly higher enthalpy of formation than that of $C_3H_6^{+\bullet}$ + CH_2O, $CH_2{=}CHOH^{+\bullet} + C_2H_4$ lies lower in energy than the other two product combinations. Consequently, the production of $CH_2{=}CHOH^{+\bullet} + C_2H_4$ is thermodynamically preferable to CH_2O loss, and there would be a driving force favouring this process at low energies. This in turn would furnish an explanation for the appearance of a significant peak at *m/z* 44 in the spectrum of (**2**). In the absence of such a thermodynamic factor favouring C_2H_4 loss, it is difficult to see why the complex rearrangement required for formation of $C_2H_4O^{+\bullet}$ should compete with the mechanistically simpler process of CH_2O elimination.

The ratios of the intensities of the peaks at *m/z* 45, 44, 43, and 42 in the spectrum of a mixture of four parts C_4H_7OH and five parts $C_4H_7OD^{+\bullet}$ are 12:29:100:56. On the basis of the mechanisms given in Scheme 4, and the assumption that hydrogen transfer from oxygen to carbon is irreversible (model A) the calculated ratios for these peaks are 11:35:92:60. When calculations are made on the assumption of random distribution of the hydroxylic hydrogen before decomposition (model B) or equilibration of the hydroxylic hydrogen with those on the α- and δ-carbon atoms (model C), the expected ratios are 5:26:88:78 and 7:23:80:85, respectively.

Reversible exchange of hydrogen between oxygen and the δ-carbon atom (model D) gives the same values as model A. Thus, models A and D give the nearest fit to the observed intensities. However, none of the models makes any allowance for isotope effects, and the results are somewhat difficult to interpret on account of the similar intensities of the group of peaks between *m/z* 42 and 45. Nevertheless, the formulation of loss of formaldehyde as a reaction involving expulsion of the α-CH_2 group is supported by the presence of an intense peak (100% relative intensity) at *m/z* 42 (CD_2O expulsion) in the spectrum of $CH_2{=}CHCHCD_2OH$. The peaks at higher mass (*m/z* 43, 44, 45, and 46, relative intensities, 9, 24, 7, and 8%, respectively) are of comparatively minor importance. Extensive hydrogen transfers to and from the α-carbon atom prior to formaldehyde loss can certainly be excluded by these observations. This is in stark contrast to the behaviour found for methyl radical loss, in which essentially random selection of the hydrogen atoms takes place.

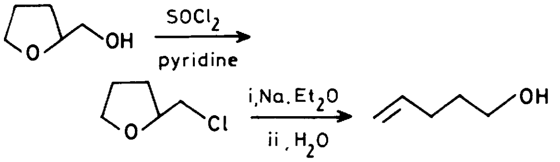
Conclusions

The reactions of ionised alkenols of structure $CH_2{=}CH[CH_2]^n OH$ can be understood in terms of the energetics of the product combinations. Several interesting rearrangement reactions, some of which involve reversible hydrogen transfers, are observed, including loss of $CH_3^{\cdot}$, $C_2H_5^{\cdot}$, and C_2H_4. Distonic ions are of central importance in the chemistry of these ionised enols.

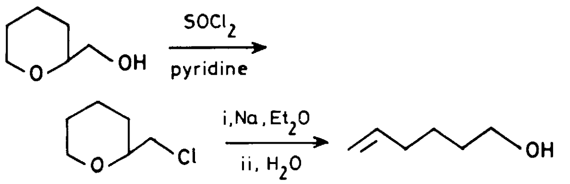
Experimental

The mass spectra were obtained using a modified A.E.I MS9 double-focusing mass spectrometer equipped with a water-cooled source maintained at *ca.* 350 K. Ionisation was effected by bombardment of the vaporised sample at a source pressure of *ca.* 2×10^{-6} Torr using an electron energy of 12.1 eV. Details of the experimental procedure, including the method for accurately calibrating the electron energy, have been published elsewhere.[2]

Allyl alcohol and but-3-enol were commercial samples of high purity and showed no significant impurities. Pent-4-enol and hex-5-enol were synthesised by treatment of tetrahydrofurfuryl chloride and tetrahydropyranylmethyl chloride, respectively, with sodium metal suspension in dry diethyl ether [reactions (1) and (2)].[14] A minor amount of starting material remained in these samples even after fractional distillation; consequently, preparative h.p.l.c. was performed prior to the measurement of the mass spectra of these compounds.



(1)



(2)

^2H-Labelled alkenols were prepared by the routes shown [reactions (3)—(6)]. The purity of these alkenols was checked by 400 MHz n.m.r. (^1H and/or ^2H); with the exception of $CH_2{=}CHCH_2CD_2CH_2OH$, which showed a minor amount of deuterium incorporation other than at the β-position, the labelled alkenols showed no significant impurities.

$$CH_2{=}CHCH_2COCl \xrightarrow[Et_2O]{LiAlD_4} CH_2{=}CHCH_2CD_2OH \qquad (3)$$

$$CH_2{=}CHCH_2CH_2CO_2Me \xrightarrow[\text{ii, repeat}]{\text{i, MeOD-MeONa}} CH_2{=}CHCH_2CD_2CO_2Me \xrightarrow[Et_2O]{LiAlH_4} CH_2{=}CHCH_2CD_2CH_2OH \qquad (4)$$

$$CH_2{=}CHCH_2CH_2CO_2Me \xrightarrow[Et_2O]{LiAlD_4} CH_2{=}CHCH_2CH_2CD_2OH \qquad (5)$$

$$CH_2{=}CHCH_2CH_2CH_2CO_2H \xrightarrow[Et_2O]{LiAlD_4} CH_2{=}CHCH_2CH_2CH_2CD_2OH \qquad (6)$$

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