Regiospecificity for Water Elimination. A Mass Spectral Study of 1-Tetralol and 2-Tetralol

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In order to provide a comparison with the extensive research on the mechanism for elimination of water from various cyclohexanols, the mass spectra of 1-tetralol(1,2,3,4-tetrahydro-1-naphthalenol) and 2-tetralol(1,2,3,4-tetrahydro-2-naphthalenol) have been investigated. Deuterium labeling experiments show that the 1-tetralol molecular ion expels water by a highly specific 1,4 elimination, whereas 2-tetralol undergoes a 1,3 elimination. Both of these processes are competitive with cycloreversion reactions. The ionization potentials and appearance potentials for the major fragments $[M-H_2O]^{+\cdot}$ and the cycloreversion products have been measured using the Electron Distribution Difference method. In addition, the kinetic energy release in the metastable decompositions to lose water have been measured. It has been found that the 1,4 elimination for 1-tetralol releases over 50% of the available energy in the transition state, which is unexpected in view of the 6-membering ring transition state involved. This research also includes an investigation of the nature of the various $[C_{10}H_{10}]^{+\cdot}$ ions formed in the rearrangement reaction to lose water.

The specificity for elimination of water in mass spectral fragmentations is an intriguing question and consequently, this rearrangement has been the subject of many studies. The topic has been thoroughly discussed by Kingston, Hobrock, Bursey and Bursey in a recent review.[1] It is the primary purpose of this investigation to examine the regiospecificity for water expulsion in the mass spectra of 1-tetralol(1,2,3,4-tetrahydro-1-naphthalenol) and 2-tetralol(1,2,3,4-tetrahydro-2-naphthalenol). Other features of the electron impact induced decompositions of these molecules will be studied as a secondary objective.

Obviously the mechanism for water loss in cyclohexanol is of considerable relevance to this report. Deuterium labeling experiments demonstrate that the rearranging hydrogen comes almost equally from the 3 and 4 positions,[2] suggesting that the regiospecificity is not high. More recent studies show that the 1,4 elimination is highly stereospecific (a *cis* elimination), whereas the 1,3 elimination is preempted by ring opening and therefore is nonstereospecific.[3,4] An alternative theory states that the elimination is predominantly 1,4 with prior scrambling to explain the involvement of hydrogens in other positions.[5] The thorough work of Holmes *et al.*[4] shows that this is not the case.

More specificity is observed for the various substituted cyclohexanols. Both *trans*-4-*t*-butylcyclohexanol and *trans*-4-*iso*propylcyclohexanol lose water by *cis*-1,4 eliminations.[6,7] In the cases of methyl substitution,[8] 1,3 and 1,4 losses have been suggested, but the results are not conclusive. However, for isomeric podocarpinols, predominant, but not exclusive *cis*-1,3 and 1,4 dehydrations have been found.[9] Here, the itinerant hydrogens are tertiary and thus activated for transfer.

A logical extension of these researches is the investigation of the tetralols to test whether the fused benzene ring imparts a higher degree of regiospecificity than in the parent cyclohexanol. The results for substituted cyclohexanols would suggest that the benzylic hydrogens in the tetralols might be specifically activated for transfer. In addition, the charge localizing ability of the aromatic ring may minimize undesired hydrogen scrambling. Two reports of water loss in the tetralin system have appeared during the course of this investigation. Tetralin-1,2-diol undergoes two different 1,4 eliminations of water with the transferred hydrogen originating either from the oxygen group or from the 4 position.[10] The second study, primarily directed at the cycloreversion reaction in various 1-tetralols, has established that 4,4-dimethyl-1-tetralol shows a low abundance (<5% relative abundance) water loss by a predominant 1,3 process.[11] However, the mechanisms for water loss in the unsubstituted tetralols have not been established. Further interest in the tetralin system stems from our earlier studies of 1-phenyltetralin, a compound which loses C_6H_6 by a 1,4 elimination in the mass spectrometer.[12,13]

EXPERIMENTAL

Mass spectra were obtained with an Hitachi RMU-6D double focusing instrument with source and inlet temperatures at 100 °C or less. Higher temperatures caused dehydration of the tetralols, and the relative intensity of the $[M-H_2O]^{+\cdot}$ ion was observed to increase. Metastable ion studies were carried out using the defocusing techniques involving electric sector voltage scan and accelerating voltage scan. Isotopic compositions of the deuterium-labeled substances were obtained at sufficiently low ionizing energies such that $[M-1]^+$ and $[M-2]^{+\cdot}$ ions could not be observed for the unlabeled compounds.

1-Tetralol and 2-tetralol. These compounds were prepared by the lithium aluminum hydride reduction of the 1- and 2-tetralones, respectively, in diethylether solvent. Purification was by vacuum distillation and the purity was checked by infrared and mass spectrometry.

1-d_1-1-Tetralol. Lithium aluminum deuteride reduction of the 1-tetralone afforded this compound. Isotopic composition: 96% d_1, 4% d_0.

1-Tetralol-OD. This substance was prepared by lithium aluminum hydride reduction of 1-tetralone followed by hydrolysis with D_2O. Mass spectral studies of this compound were accomplished after two or three equilibrations of the source and inlet with D_2O. The best exchange in our hands gave 77.5% d_1 and 22.5% d_0.

2,2,-d_2-1-Tetralol. 1-Tetralone (50 μl samples) was exchanged with D_2O using g.l.c. with a 10% FFAP on Chrom. W. ($\frac{1}{4}$ in ×5 ft) at 160–200 °C and a flow rate of 75–110 ml min^{-1} (helium). The column was conditioned with five 50 μl injections of D_2O prior to injection of the ketone. The process was repeated until mass spectrometric analysis indicated that suitable deuterium incorporation was achieved. Lithium aluminum hydride reduction gave the desired tetralol of isotopic composition 0.7% d_3, 91.4% d_2, 6.9% d_1 and 1.0% d_0.

4,4-d_2-1-Tetralol. 3-Benzoylpropionic acid (Aldrich) in glacial acetic acid-d_1 was converted into 4,4-d_2-4-phenylbutyric acid at three atmospheres of D_2 in a Parr hydrogenation apparatus using 10% Pd/C as catalyst for a period of 2 h. The procedure is that of Horning and Riesner.[14] The 4,4-d_2-phenylbutyric acid was cyclized to 4,4-d_2-1-tetralone by heating 0.5 g in 5 g of polyphosphoric acid at 100 °C for 1 h, followed by hydrolysis in ice-water and neutralization to pH=9. The product was extracted into ether, washed with sodium carbonate solution, dried and the ether removed. The crude ketone was purified by vacuum distillation. The 4,4-d_2-1-tetralol was obtained by lithium aluminum hydride reduction of the ketone to give an isotopic composition of 1.4% d_4, 10.1% d_3, 75.1% d_2, 11.2% d_1 and 2.2% d_0.

2-d_1-2-*Tetralol.* This substance was prepared by lithium aluminum deuteride reduction of 2-tetralone in ether to afford 97.5% d_1 and 2.5% d_0.

1,1,3,3-d_4-2-Tetralol. The 1 and 3 positions of 2-tetralone were exchanged with D_2O using the method discussed above. Lithium aluminum hydride reduction in ether afforded the final compound with an isotopic composition of 87.2% d_4, 7.6% d_3, 1.8% d_2, 1.8% d_1 and 1.6% d_0.

Ionization and appearance potentials were measured by a computerized 'Electron Distribution Difference' (EDD) technique using the Hitachi mass spectrometer as reported previously.[15] The electron energy scale was calibrated with benzene, furan and xenon as before.[15]

RESULTS AND DISCUSSION

Fragmentation pathways

The 70 eV spectra of 1- and 2-tetralol are given in Fig. 1 for comparison. The primary fragmentations of both compounds are the loss of water and the cycloreversion reactions. In addition, 1-tetralol shows an abundant cleavage of a hydrogen atom and less important losses of OH and C_3H_7, three processes which are of little importance for the 2-tetralol. It is noteworthy that all the primary fragmentations occur as metastables except for the cycloreversion reaction for 2-tetralol. These decompositions are shown in Eqns (1) and (2), and are confirmed to be dominant primary fragmentation by the mass spectra at low ionizing energy (Table 1).

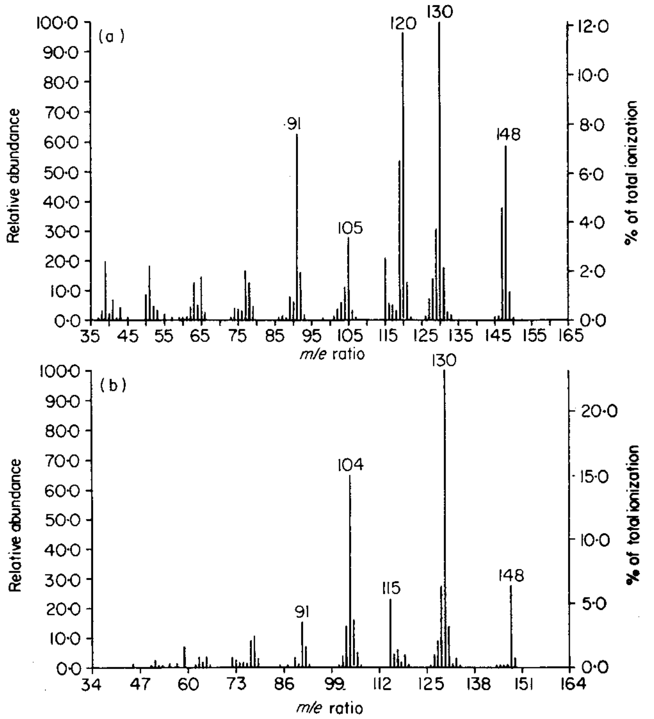
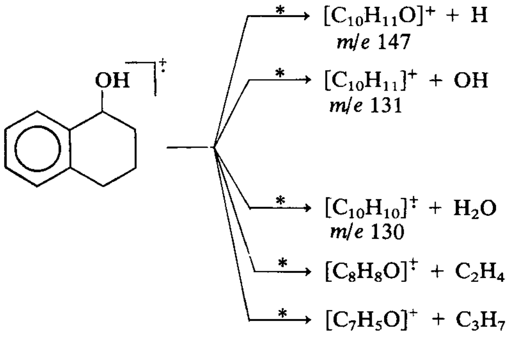
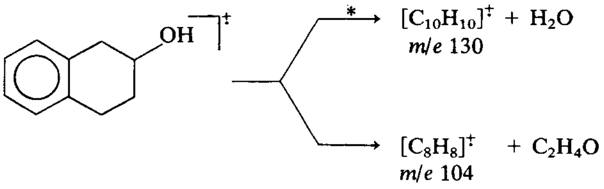


Figure 1. The 70 volt mass spectra of (a) 1-tetralol and (b) 2-tetralol.



(1)



(2)

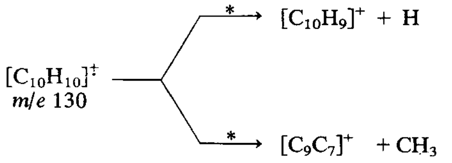
The elimination of water to form $[C_{10}H_{10}]^{+\cdot}$ is ideally suited for detailed study because of the strong propensity for this rearrangement. For both isomers $[C_{10}H_{10}]^{+\cdot}$ is the most abundant ion. The secondary fragmentations of the $[M-H_2O]^{+\cdot}$ ions are qualitatively the same for both tetralols; i.e. they continue to fragment by competitive losses of H and CH_3 as attested to by metastable ions [Eqn (3)].

The cycloreversion reactions of these isomers impart distinctive information which unambiguously allows identification of each. Loss of C_2H_4 from 1-tetralol produces the abundant $[C_8H_8O]^{+\cdot}$ (*m/e* 120) which yields secondary fragments at *m/e* 119, 105 and 92. Equation (4) illustrates these secondary decompositions as well as tertiary decompositions. 2-Tetralol expels C_2H_4O instead of C_2H_4 to give $[C_8H_8]^{+\cdot}$. No metastable can be found for this process which suggests either a high energy elimination, possibly occurring from an excited state of the molecular ion,[16a] or a stepwise process.[16b] The low voltage spectrum shows almost no $[C_8H_8]^{+\cdot}$, an observation which supports these ideas. The decomposing $[C_8H_8]^{+\cdot}$ ions give rise (m^*) to the signals at *m/e* 103 (loss of H) and *m/e* 78 (loss of C_2H_2).

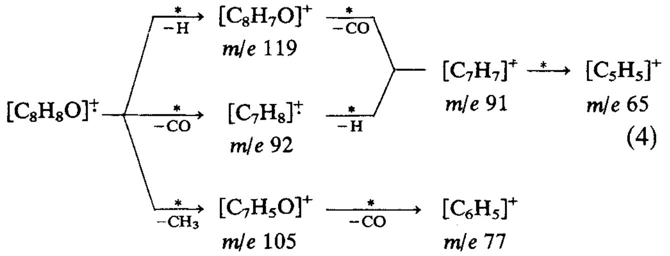
Table 1. Comparison of the low voltage (14 eV) spectra of 1- and 2-tetralol

m/e[a]	1-Tetralol	2-Tetralol
104	3.7	2.5
105	4.6	0.5
106	0.6	1.1
117	1.2	—
118	0.7	—
120	19.0	—
129	0.9	1.7
130	81.0	100.0
146	7.5	—
147	7.2	—
148	100.0	55.0

[a] Contributions from ^{13}C have been omitted.

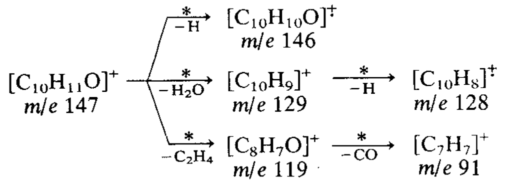


(3)



(4)

A second distinctive reaction, which is only important for 1-tetralol, is loss of a hydrogen atom. *A priori*, it would seem that the hydrogen in the 1 position is specially activated for cleavage by the adjacent aromatic ring and the hydroxyl group. Secondary reactions of the $[M-H]^+$ species include loss of H, H_2O and C_2H_4 (also observed for $[M]^{+\cdot}$). These decompositions explain in part the somewhat larger ion currents at *m/e* 146 and 129, for 1-tetralol *vis-à-vis* the 2 isomer [Eqn (5)]. A low abundance, direct cleavage of OH is also observed for only the 1-tetralol, presumably because of the benzylic location of this group.



(5)

Energetics

In order to obtain additional detail on the primary fragmentations, the ionization potentials of the isomeric tetralols and the appearance potentials for the major fragments were obtained using a computerized EDD technique.[15] The EDD procedure was chosen because it eliminates much of the ambiguity in assigning the thresholds for ionization or decompositions induced by electron impact. The results are presented in Table 2. Both compounds give nearly identical ionization potentials of approximately 8.7 eV, suggesting that the threshold electron is removed from the π-molecular orbitals of the aromatic ring. Energetically, the most facile decomposition of both isomers is the expulsion of water which requires 0.17 and 0.48 eV for 1- and 2-tetralol, respectively. This can be interpreted in terms of a concerted loss[17] of water from an intact ring. A stepwise mechanism would be of necessity, a high energy process with a barrier approximately as high as the appearance potentials for hydrogen and/or hydroxyl loss. Final verification requires a study of stereospecific deuterium labeled tetralols and this is in progress.

Table 2. Ionization and appearance potentials for 1- and 2-tetralols (in electron volts)[a]

Ion	1-Tetralol	2-Tetralol
148	8.70±0.01	8.67±0.02
147	9.67±0.11	11.6
130	8.87±0.07	9.15±0.02
120	10.42±0.03	—
104	—	11.68±0.04

[a] All measurements were averages of three determinations except A(147) for 2-tetralol.

The appearance potentials for the cycloreversion products (*m/e* 120 and *m/e* 104 for 1- and 2-tetralol respectively) seem surprisingly high for elimination of a neutral molecule, a process which at first thought would involve both bond making and bond breaking. As previously noted, the C_2H_4O loss in 2-tetralol does not occur on the metastable time scale and this process has an exceptionally high activation energy of *c.* 3 eV. 1-Tetralol does give a metastable for the cycloreversion reaction and the corresponding activation energy is somewhat less at 1.7 eV. The appearance potentials suggest these reactions are not as straightforward as simple considerations would indicate. The mechanism for the cycloreversion reaction in 1-tetralol is reported elsewhere.[18]

Water elimination—1-tetralol

Comparison of the mass spectra of the four deuterium labeled 1-tetralols in Fig. 2 with the unlabeled compound (Fig. 1) allows qualitative conclusions to be drawn about the elimination of water in this compound. Two of the isomers, 1-d_1- and 2,2-d_2-1-tetralol, predominantly expel H_2O, as evidenced by the shift of *m/e* 130 to *m/e* 131 and *m/e* 132, respectively. No extensive scrambling of the hydroxyl hydrogen is demonstrated by the spectrum of the OD compound; only loss of HOD is seen. The regiospecificity for water loss is finally revealed by the mass spectrum of the 4,4,-d_2-1-tetralol. Here *m/e* 130 is shifted to 131 for loss of HOD, indicating a 1,4 elimination of water. It is also interesting to note that the % of total ion current carried by *m/e* 131 is less than 7% compared with approximately 12% of the other 1-tetralols, which we take to be indicative of a small primary hydrogen isotope effect. The decrease in current at *m/e* 131 is compensated for by an increase at *m/e* 119 to 123, which means that the higher energy molecular ions show a greater propensity for ethene over water elimination in the 4,4-d_2 compound. The transition state for water loss must involve considerable C—H bond breaking (*vide infra*).

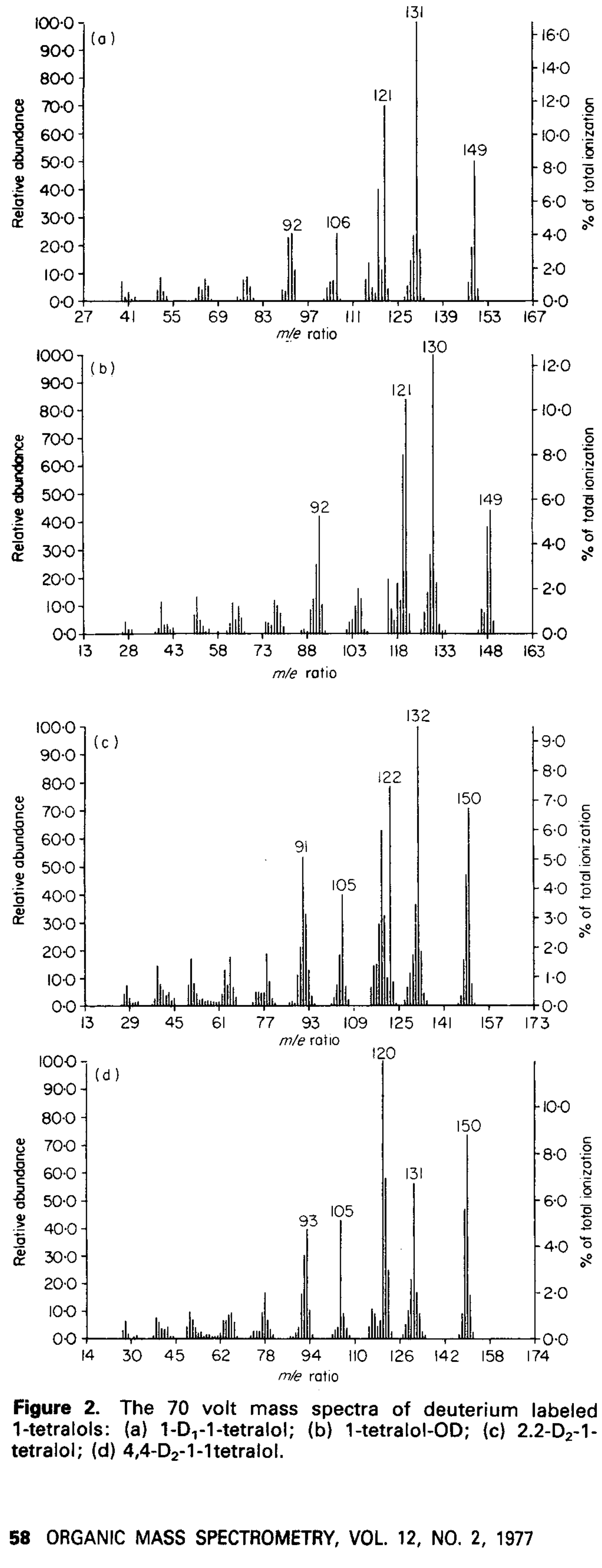


Figure 2. The 70 volt mass spectra of deuterium labeled 1-tetralols: (a) 1-D_1-1-tetralol; (b) 1-tetralol-OD; (c) 2.2-D_2-1-tetralol; (d) 4,4-D_2-1-1tetralol.

It is difficult to extract good quantitative data on the specificity for water loss from the 70 volt spectra, because of the lack of isotopic purity of the samples and the relatively abundant loss of H and H_2 from $[C_{10}H_{10}]^{+\cdot}$ (*m/e* 130). Two approaches were taken to surmount these problems.

At a sufficiently low voltage (14 eV) the *m/e* 130 region shows significant signals for only water loss and ^{13}C contributions for the unlabeled compound. Knowing the isotopic composition of the various labeled 1-tetralols enables us to calculate the % elimination of H_2O or HOD in each compound. The 1-d_1-1-tetralol undergoes greater than 98% loss of H_2O. The two d_2 compounds are compared in Table 3. The predicted set of relative intensities are calculated for two percentages of 1,4 elimination, to show the sensitivity of the data for small changes in mechanism. As can be seen, 99% of the molecular ions of 2,2-d_2-1-tetralol expel H_2O, whereas 95% lose HOD in the 4,4,-d_2-1-tetralol. The latter result points to a small contribution of 4–5% of 1,3 elimination or of isotopic scrambling. The 4,4-d_2 compound also shows some exchange of the deuteriums at position 4, possibly with the aromatic ring hydrogens prior to ethene elimination.[18] Therefore, we prefer the latter alternative to explain the H_2O loss in 4,4-d_2.

Table 3. Comparison of observed and calculated intensities in the *m/e* 130 region assuming various percentages of 1,4 elimination of H_2O in 1-tetralol

	2,2-d_2-			4,4-d_2-		
m/e	Obs.	Calc. (100%)[a]	Calc. (99%)[a]	Obs.	Calc. (100%)[b]	Calc. (95%)[b]
130	1.1	1.1	1.1	9.0	9.6	10.2
131	9.1	7.6	8.9	100.0	100.0	100.0
132	100.0	100.0	100.0	30.6	23.8	29.2
133	12.2	12.8	12.7	6.9	6.7	7.4
134	3.9	3.7	3.7	—	—	—

[a] Major % is 1,3 or 1,4 elimination; minor is 1,2.
[b] Major % is 1,4 elimination, minor is assumed to be 1,3.

The second approach is to compare relative intensities for loss of H_2O and HOD using defocused metastable studies (accelerating voltage scan method). It is expected that these data would be a more stringent test of mechanistic purity because metastable decomposing ions are more susceptible to scrambling reactions. Nevertheless, the metastable abundances confirm the results obtained by the low voltage measurements. The isotopic purity of the 1-d_1 and 2,2-d_2 compounds was sufficient in that no serious overlapping of metastable signals was found. The ratio for loss of H_2O to HOD for both these compounds was found to be 98:2. For 1-tetralol-OD the transition 149 → 131 was overlapped seriously with 150 → 131 (^{13}C of

149 → 130). Similarly in 4,4-d_2, the 150 → 132 metastable could not be resolved from 151 → 132. Both these problems occur because of the relatively large kinetic energy release in the loss of water fragmentation.

An attempt to obtain good metastable data was made using the mass analyzed ion kinetic energy (m.i.k.e.) technique. Unfortunately, the vapor pressure of 1-tetralol is too low for appropriate sample handling at an inlet temperature of 100 °C with the result that small signal-to-noise results were obtained. Nevertheless, a small signal corresponding to 150 → 132 could be observed along with the dominant 150 → 131 metastable. The high voltage scans also seemed to show some intensity for loss of H_2O from the 4,4-d_2 compound. We can only give an estimate that no more than 15% of the molecular ions decompose in the metastable time windows by loss of H_2O rather than HOD.

The interpretation shows quite clearly that 1-tetralol gives a highly regiospecific loss of water by a 1,4 elimination. Certainly no significant 1,1 or 1,2 elimination channels are important (<2%). However, a small amount (5%) of 1,3 elimination and/or isotopic scrambling do compete and assume greater importance at longer metastable times.

The low activation energy (≈0.2 eV) for water loss supports a concerted elimination reaction[17] as mentioned earlier. The transition state involves substantial carbon–hydrogen bond breaking for the transferred hydrogen. Evidence for this is found in the mass spectrum of the 4,4-d_2 compound (Fig. 2) in which the $[M-DOH]^{+\cdot}$ ion (*m/e* 131) carries less than 7% of the total ion current, compared with over 12% in the unlabeled 1-tetralol. A quantitative estimate of the isotopic effect (k_H/k_D) was made by obtaining the ratio of the metastable intensity for H_2O loss in the unlabeled compound normalized to all metastable fragmentations of the molecular ion (loss of H, H_2O, C_2H_4 and C_3H_7). This value (0.32) was compared with the relative metastable intensity for water loss in the 4,4-d_2-1-tetralol (0.16) to give a k_H/k_D estimate of 2.0. This value is approximately twice as large as found for acyclic alcohols. It has been argued that the small effects in the acyclics are a general indication of early transition states in mass spectral reactions.[19] However, for water loss in 1-tetralol, the transition state is somewhat more advanced.

The high regiospecificity for the elimination is undoubtedly due to two factors. First, the transferred hydrogen is activated because of its benzylic nature. Second, the cyclohexane moiety undergoes relatively facile conversion from a half-chair conformation[20] to the requisite boat form. A number of studies [21–23] estimate the energy cost of this conformational change to be between 5 and 7 kcal mol^{-1}. Moreover, i.r. studies show that the OH group in 1-tetralol prefers that quasi-axial conformation.[24,25]

Water elimination—2-tetralol

Inspection of the mass spectra of 2-d_1- and 1,1,3,3-d_4-2-tetralol (Fig. 3) and the unlabeled compound (Fig. 1) provides convincing evidence for a 1,3 elimination of water because these compounds show essentially no loss of HOD in their high voltage spectra. Quantitative comparisons, using both 70 eV and 14 eV spectra, show that more than 99% of the molecules lose H_2O in both cases. The relative abundances of metastable peaks confirm these results; i.e. loss of HOD in 2-d_1-2-tetralol is less than 0.5% and in the 1,1,3,3-d_4-2-tetralol an upper limit of 0.7% is established. Although these studies only directly rule out 1,1 and 1,2 eliminations, 1,3 loss is the only reasonable alternative. Unfortunately, we are unsure if scrambling of the benzylic hydrogens with the aromatic ring occurs prior to elimination. The high regiospecificity for water loss in 2-tetralol can be accounted for by the ease in establishing the 5-membered ring transition state (*a*) for transfer of an activated benzylic hydrogen. Prior ring opening seems less likely because of the low activation energy for water loss (≈0.5 eV, see Table 2). Green, Bafus and Franklin[26] have recently demonstrated that prior ring opening adds 0.6–0.8 eV to the energy requirement for water loss in cyclohexanol. It should be noted that examples of 1,3 eliminations of H_2O which proceed without ring-opening (stereospecific) have been reported.[8,9,41]

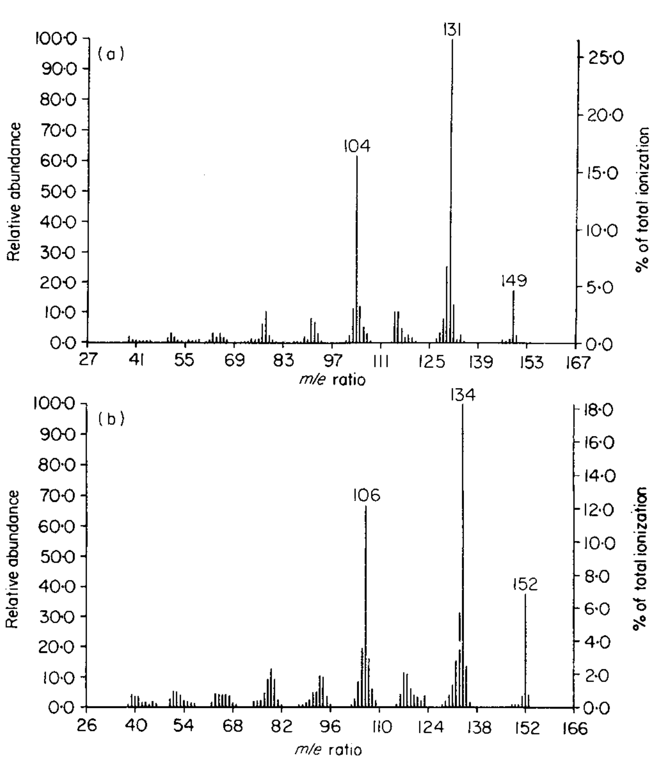
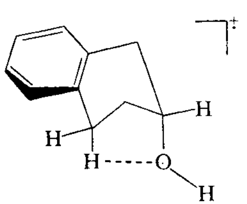


Figure 3. The 70 volt mass spectra of deuterium labeled 2-tetralols: (a) 2-D$_1$-2-tetralol; (b) 1,1,3,3-D$_4$-2-tetralol.



a

Kinetic energy release for water loss

A significant and surprising difference exists for the amount of translational energy released in the metastable losses of water from 1-and 2-tetralol as measured by the width of the metastables at half-height. For 1-tetralol a flat-top metastable is observed with release of 0.27 eV[†], whereas 2-tetralol gives a Gaussian peak with a release of 0.006 eV. The amount of energy released for 1-tetralol is independent of ion accelerating voltage over a range of 900–3600 volts, indicating that the energy release does not involve significant 'nonfixed' energy.[27]

Current views of energy release hold that flat-topped metastables arise in processes having appreciable reverse activation energy. More specifically, 'loose' transition states such as simple cleavages and 6-membered ring intermediates release only a small fraction of the reverse activation energy (typically less than 10%) whereas 'tight' transition states involving 3- and 4-membered ring intermediates release a significant fraction, *but usually not all*, of the available energy.[27–29] However, Holmes and Weese[30] have shown recently that H_2 loss from $[C_3H_7]^+$ occurs with release of virtually all of the reverse activation energy.

Because of the paucity and uncertainty in thermochemical data, it is difficult to estimate what fraction of the reverse activation energy is released. Moreover, the structure of $[C_{10}H_{10}]^{+\cdot}$ is unknown. Nevertheless, an informative argument can be constructed based on a 1,2-dihydronaphthalene ion structure for the elimination product. Presumably, this should be the most stable isomeric $[C_{10}H_{10}]^{+\cdot}$ ion, but probably *not* the structure initially formed by water loss. Using an ionization potential of 8.0 eV[‡] for 1,2-dihydronaphthalene[33] and a ΔH_f of 30.3 kcal mol^{-1},[34] the $\Delta H_f[C_{10}H_{10}]^{+\cdot}$ is estimated to be 215 kcal mol^{-1}. The group additivity scheme[35] is used to estimate the ΔH_f of 1-tetralol as −35.5 kcal mol^{-1}, which now enables us to calculate the excess energy in the transition state [Eqn (6)] as 12 kcal mol^{-1}. The fraction released as kinetic energy is approximately 0.5 (6.4/12), a

$$A[C_{10}H_{10}]^{+} = \Delta H_f[C_{10}H_{10}]^{+\cdot} + \Delta H_f(H_2O) - \Delta H_f(\text{1-tetralol}) + E_{\text{exc}} \quad (6)$$

surprisingly large fraction considering that the transition state involves a 1,4 hydrogen shift *via* a 6-membered ring intermediate. This fraction is a *minimum* value because: (1) the 1,2-dihydronaphthalene ion structure for the $[C_{10}H_{10}]^{+\cdot}$ product is in all probability the most stable form of $[C_{10}H_{10}]^{+\cdot}$; (2) the ionization potential of 1,2-dihydronaphthalene is probably too small; and (3) the electron impact appearance potential of m/e 130 is undoubtedly an upper limit.

An estimate of the fraction of available energy released in the water elimination reaction of 2-tetralol can also be estimated using Eqn (6). The ΔH_f of 2-tetralol is calculated to be −37.4 kcal mol^{-1}[35] and $[C_{10}H_{10}]^{+\cdot}$ is again assumed to be the 1,2-dihydronaphthalene ion yielding an excess energy of 16 kcal mol^{-1} or less. The fraction released is 0.009 which, in contrast to water loss from 1-tetralol, is consistent with current views. A major mechanistic difference for water loss from these two compounds is that the 1-isomer must undergo a conformational change from the more stable half-chair to the boat, a change which costs approximately 7 kcal mol^{-1} for the neutral molecule.[21–23] It may be only fortuitous that nearly the same amount of energy is released in the metastable decomposition. More studies are in progress to understand this interesting difference.

Nature of $[C_{10}H_{10}]^{+\cdot}$

A comparison of the $[C_{10}H_{10}]^{+\cdot}$ ions can be developed by metastable abundance studies and kinetic energy release measurements. For both 1-and 2-tetralol, a significant fraction of the total ionization is carried by $[C_{10}H_{10}]^{+\cdot}$ which is formed in the water elimination reaction. Metastable ion studies demonstrate two competitive fragmentations of $[C_{10}H_{10}]^{+\cdot}$: loss of H and CH_3. The loss of methyl occurs from a structure which has undergone complete hydrogen scrambling, irrespective of which tetralol serves as origin (see Table 4). These data refer only to long-lived, metastable $[C_{10}H_{10}]^{+\cdot}$ ions, but inspection of the 115 a.m.u. region of the 70 eV spectra of the labeled compounds leads to a similar conclusion for the rapidly decomposing ions. Low activation energy hydrogen isomerizations are well-established phenomena in other congeneric hydrocarbon ions such as $[C_6H_6]^{+\cdot}$ from benzene[36] and 1,5-hexadiyne[37] and $[C_8H_8]^{+\cdot}$ from styrene.[38]

Table 4. Metastable ion intensities for methyl loss from various labeled $[C_{10}H_{10}]^{+\cdot}$ ions[a]

Ion	Source	$-CH_3$	$-CH_2D$	$-CHD_2$	$-CD_3$
$[C_{10}H_9D]^{+\cdot}$	1-*d*$_1$-1tetralol	69	31		
$[C_{10}H_9D]^{+\cdot}$	4,4-*d*$_2$-1-tetralol	73	27		
$[C_{10}H_9D]^{+\cdot}$	2-*d*$_1$-2-tetralol	74	26		
$[C_{10}H_9D]^{+\cdot}$	calc. for complete scrambling	70	30		
$[C_{10}H_8D_2]^{+\cdot}$	2,2-*d*$_2$-1-tetralol	54	40	6	
$[C_{10}H_8D_2]^{+\cdot}$	calc. for complete scrambling	47	47	6	
$[C_{10}H_6D_4]^{+\cdot}$	1,1,3,3-*d*$_4$-2-tetralol	19	48	28	5
$[C_{10}H_6D_4]^{+\cdot}$	calc. for complete scrambling	17	50	30	3

[a] From measurements of peak heights produced in high voltage scans.

It would seem reasonable that a common structure for $[C_{10}H_{10}]^{+\cdot}$ should be invoked to explain the hydrogen scrambling. Metastable abundances and energy release for various decomposing $[C_{10}H_{10}]^{+\cdot}$ ions attest to this hypothesis (see Table 5). We are uncertain as to

Table 5. Comparison of $[C_{10}H_{10}]^{+\cdot}$ metastable decompositions

Source	130→129	130→115
1,2-Dihydronaptha-lene	91[a] (48)[b]	9(24)
1-Tetralol	92[a] (48)[b]	8(32)
2-Tetralol	91[a] (63)[b]	9(30)

[a] Measured by high voltage scans.
[b] Kinetic energy release in meV.

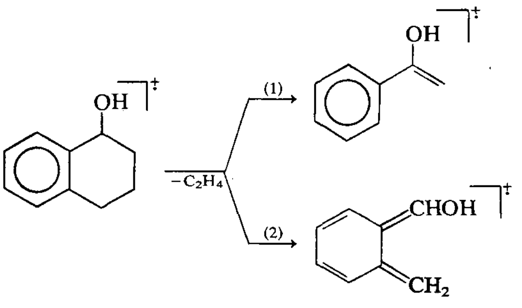
[†] A value of 0.30 eV was obtained using an A.E.I. MS-9 at Kansas State University. We thank Professor Michael Hoffman for this measurement.

[‡] This value seems too low considering that the ionization potentials of tetralin and naphthalene are 8.44 eV,[32] and 8.12[31] respectively.

the actual structure of the $[C_{10}H_{10}]^{+\cdot}$ ion formed initially, but a reasonable possibility for the decomposing ions is the 1,2-dihydronaphthalene structure which scrambles by various hydrogen shifts.

Cycloreversion reaction mechanisms

As was discussed earlier, 1-tetralol undergoes a facile loss of C_2H_4 to produce $[C_8H_8O]^{+\cdot}$, whereas 2-tetralol eliminates C_2H_4O to give $[C_8H_8]^{+\cdot}$. Deuterium labeling and extensive metastable studies reveal that the cycloreversion in 1-tetralol occurs by two pathways to eliminate either carbons 2 and 3 or carbons 3 and 4. The actual structures for $[C_8H_8O]^{+\cdot}$ are shown in Eqn (7). The detailed evidence for these conclusions is discussed elsewhere.[18] It is noteworthy that whereas pathway (1) and (2) are competitive for rapidly decomposing molecular ions, pathway (1) dominates in the metastable time region. The metastable corresponding to pathway (2) is only barely detectable.



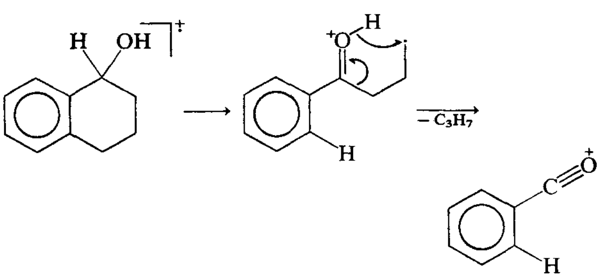
(7)

The deuterium labeling experiments presented here are not sufficiently extensive to pinpoint the mechanism for loss of C_2H_4O from 2-tetralol (i.e. either or both pathways that operate in 1-tetralol may be appropriate for the 2 isomer). However, if it is a general phenomenon that pathway (2) proceeds so rapidly as to preempt metastable decomposition in the tetralin series, then pathway (2) is the favored channel for 2-tetralol. As was mentioned earlier, no metastable is found for this process and the activation energy is relatively high (3 eV, see Table 2). Additional studies are in progress to answer this question.

Mechanism for formation of *m/e* 105 in 1-tetralol

As was mentioned previously, a major difference in the mass spectra of 1- and 2-tetralol is the abundant *m/e* 105 signal found in the 1-isomer. High resolution measurements show that the peak is predominantly $[C_7H_5O]^+$ (the ratio of $[C_7H_5O]^+$ to $[C_8H_9]^+$ is 9:1 after correcting the $[C_8H_9]^+$ contribution for ^{13}C from *m/e* 104). Defocused metastable studies show that *m/e* 105 originates from both the molecular ion (*m/e* 148) and from *m/e* 120, $[C_8H_8O]^{+\cdot}$, with the latter path accounting for *c.* 80% of the metastable pathways to *m/e* 105.

Metastable data for the various deuterated 1-tetralols allow us to speculate reasonably on a mechanism for the loss of 43 (C_3H_7) from the molecular ion. In both the 2,2-d_2 and the 4,4-d_2 compounds, loss of $C_3H_5D_2$ is found to be the major (>95%) route from the *m/e* 150 molecular ion. Whereas the 1-d_1 compound undergoes exclusive loss of C_3H_7, the 1-tetralol-OD loses predominantly C_3H_6D (<90%). A mechanism correlating these results [Eqn (8)] first includes ring opening, which may be accompanied by a 1,3 hydrogen shift or a series of 1,2 shifts, followed by transfer of the hydroxyl hydrogen to form the departing C_3H_7 group.



(8)

Of course, there is no evidence that the reaction occurs stepwise as shown. However, if it did, the ring opened intermediate is the structure formed in the first step of a two step mechanism for the McLafferty rearrangement. This system would then constitute additional experimental evidence for the existence of the intermediate, and support the argument drawn from theoretical studies[39] and isotopic labeling[40] that the McLafferty rearrangement does occur in two steps. Some corroboratory evidence is supplied by the fact that 4,4-d_2-1-tetralol eliminates ethene as $C_2H_2D_2$ (73%) and C_2H_3D (27) in the metastable cycloreversion.[18] We have postulated that the scrambling involves the aromatic hydrogens;[18] however, scrambling involving the hydroxyl hydrogen via the ring opened intermediate in Eqn (8) is equally plausible. Further studies are planned to test these ideas.

CONCLUSION

Unlike cyclohexanol, 1-tetralol and 2-tetralol undergo highly regiospecific 1,4 and 1,3 eliminations of water, respectively. Because both processes have low activation energies, we suggest that the rearrangements take place without prior ring opening. Moreover, the 1,4 elimination for 1-tetralol releases a significant fraction of the available energy in the transition state. This observation appears to contradict the current view that excess energy is preferentially partitioned among vibrational and rotational modes for 'loose' transition states.

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