Ionic Cycloreversion Reactions in Tetralin Derivatives. Structure of C_8H_8O Ions from 1-Tetralol

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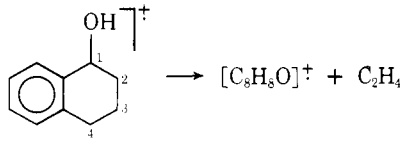
Abstract: By a combination of deuterium labeling and metastable ion measurements, it has been demonstrated that 1-tetralol ion (1,2,3,4-tetrahydro-1-naphthalenol) undergoes cycloreversion by two pathways to eliminate ethene bearing either carbons 2 and 3 or carbons 3 and 4. Although the two mechanisms are competitive for rapidly decomposing molecular ions, the elimination of ethene bearing carbons 3 and 4 is preponderant in the metastable time region. Each process produces a structurally distinct C_8H_8O radical cation and this is verified by isotopic labeling, comparisons of metastable ion intensities, and studies of kinetic energy release. The actual structure of $[C_8H_8O]\cdot^+$ produced by elimination of carbons 3 and 4 is the enol form of acetophenone, which undergoes methyl loss by abstraction of one of the randomized ring hydrogens. Expulsion of carbons 2 and 3 gives a structure similar to that produced by water loss from *o*-hydroxymethylbenzyl alcohol. These results sound a cautionary note for literal interpretations of metastable intensities and kinetic energy release data in ion structure determinations.

The extensive research in mass spectrometric decompositions using isotopic labeling experiments has produced numerous examples of competing mechanisms to produce a given daughter ion. The daughter may possess one or more structures depending on the mechanisms of formation. In the event of mixed structures, verification may be achieved by characterizing the subsequent decompositions using metastable techniques, provided each structure gives distinctive decompositions and no isomerization occurs prior to metastable decomposition. These are demanding constraints because there is considerable difficulty in sorting out decompositions from composite structures. As a result, new approaches for determining the structure of stable ions in the absence of solvent are undergoing development. Examples include low and high energy ion–molecule reactions. The former are conveniently studied by ion cyclotron resonance spectrometry[1] and the latter, which includes collisional activation, by metastable-ion methods.[2,3] Other recent developments include photodissociation[4,5] and the analysis of composite metastables, which yields information on parallel mechanisms to form a daughter ion.[2]

In this paper, we will report on a mass spectral fragmentation studied by a combination of deuterium labeling and unimolecular metastable methods, which is shown to occur by two mechanisms. The evidence clearly demonstrates tha two isomeric product structures are produced and preserved even in the subsequent decompositions of the daughter. The process of interest is the cycloreversion reaction in 1-tetralol (1,2,3,4-tetrahydro-1-naphthalenol). In a recent publication,[6] deuterium labeling studies were interpreted in terms of a single cycloreversion to eliminate ethene carbons 3 and 4 (eq 1).



$$\longrightarrow [C_8H_8O]^{\cdot+} + C_2H_4 \qquad (1)$$

During a study of the mechanism of water elimination in 1- and 2-tetralol,[7,8] certain inconsistencies in this interpretation were noticed and this prompted a more detailed investigation of the cycloreversion reaction in 1-tetralol and a reinterpretation of that reaction in tetralin itself.

Moreover, the product of the cycloreversion, $C_8H_8O\cdot^+$, has been the subject of other investigations which have been directed at the question of whether this ion, as the enol form of acetophenone, reketonizes prior to or concurrent with methyl loss.[9a-c] Our results are in agreement with the interpretation of Tomer and Djerassi[9a] and bring to light additional details on the question of keto–enol tautomerism for gas-phase ions.[9d]

Finally, this study demonstrates quite clearly a limitation of the techniques of competing metastable transitions and kinetic energy release as criteria for ion structure equivalence. These have been successfully applied and evaluated in many mass spectral investigations ever since the early work of McLafferty.[10] Hvistendahl and Williams[11] have recently pointed out one difficulty with comparing metastable abundance ratios. In a detailed investigation, they were able to show that one structural isomer of $C_3H_7O^+$, which was previously thought to be unique, underwent a rate determining isomerization prior to fragmenting. They concluded that metastable intensity ratios are not a reliable indicator of ion structure in this circumstance. An even less subtle failure of metastable techniques would occur if the ion under study possessed a mixture of structures whose composite metastable decompositions fortuitously coincided with yet another structure. The C_8H_8O ions produced in the cycloreversion reaction of 1-tetralol constitute such an example.

Experimental Section

Mass spectra were obtained with an Hitachi RMU-6D double focussing instrument with source and inlet temperatures at 100 °C or less for the various 1-tetralols. Studies of tetralin were obtained with source and inlet temperatures of 200 °C. Metastable ion studies were made using the defocussing techniques of ESA scan and accelerating voltage scan. Kinetic energy release was calculated from the peak width at half height. Appearance potentials were measured by a computerized EDD method as previously reported[12] and are discussed in more detail elsewhere.[8]

The various deuterium labeled compounds were prepared as outlined in the report of the mechanism for water loss in 1- and 2-tetralol.[8] *o*-Hydroxymethylbenzyl alcohol was prepared by a $LiAlH_4$ reduction of dimethyl phthalate. All other compounds are commercial samples and were found to be pure by mass spectrometry.

Results and Discussion

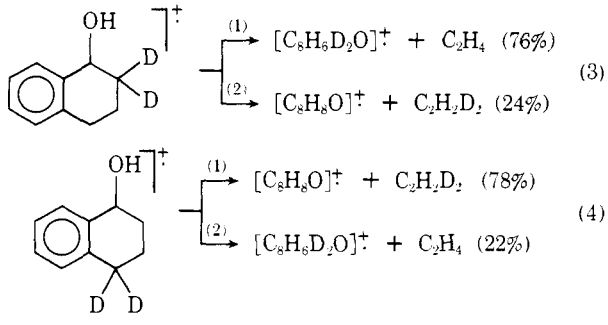
1-Tetralol. A facile cycloreversion reaction is observed in 1-tetralol at 70 V of ionizing energy to produce $C_8H_8O^+$ ion (*m/e* 120) with release of 14 meV of translation energy in the corresponding metastable transition (eq 1). To permit a closer examination of the cycloreversion reaction and the consecutive loss of a hydrogen atom in the various deuterium-labeled 1-tetralols, Table I has been compiled. The mass spectra of 1-

$$C_8H_8 \begin{cases} \longrightarrow C_8H_7O^+ + H \\ \longrightarrow C_7H_5O^+ + CH_3 \end{cases} \qquad (2)$$

tetralol-d_1 and -*2,2*-d_2 have been previously reported[6] and the present results are in good agreement with that study.

As was mentioned in the introduction, the earlier results were interpreted in terms of a single cycloreversion reaction. The existence of a second, parallel process becomes apparent upon close scrutiny of the *2,2*-d_2 and the *4,4*-d_2 compounds in Table I. In the former compound, the percent total ionization at *m/e* 122 is somewhat reduced compared to *m/e* 120 in the unlabeled compound. It would appear that *m/e* 119 is not shifted in this compound, leaving a significant *m/e* 120 peak to be accounted for. The situation is simply reversed in the 1-tetralol-*4,4*-d_2, which gives a significant *m/e* 122 peak which cannot be produced if the cycloreversion eliminates carbons 3 and 4 exclusively. Even more notable is the lack of an *m/e* 119 signal. If *m/e* 120 is the sole product of the cycloreversion, then loss of an hydrogen atom to give *m/e* 119 ranging between six and seven percent of the total ionization would be expected. Apparently, *m/e* 119 has shifted to *m/e* 121 and must originate by loss of H from *m/e* 122.

From the results for *2,2*-d_2 and *4,4*-d_2, an accurate calculation of the percentage of each pathway in the 70-V spectra can be performed. Because the compounds are not isotopically pure (their compositions are reported in Table I), the following correction scheme was applied. The intensity at *m/e* 122 can only be due to fragmentation of the d_2 species and this intensity can be compared to the abundance of *m/e* 120 only after deducting the contributions from d_1 and d_0. This was done by multiplying the intensity at *m/e* 120 by the fraction of d_2 and d_3 in the isotopic mixture after both *m/e* 120 and 122 were corrected for ^{13}C from *m/e* 119 and 121, respectively. In this way, it can be established that 76% of the cycloreversion for *2,2*-d_2 eliminates carbons 3 and 4 and the corresponding percent for *4,4*-d_2 is 78%, demonstrating good consistency. Of course, the actual contribution of each reaction channel may be significantly different because each product ion undergoes subsequent fragmentation. The results are summarized in eq 3 and 4.



Low voltage spectra are in qualitative agreement with this analysis. At 14 V of ionizing energy, no significant *m/e* 119 can be detected in the unlabeled 1-tetralol. Correcting for ^{13}C in the 1-tetralol *2,2*-d_2, the ratio of *m/e* 122:121:120 is 88:0:12, demonstrating an enhanced preference for pathway 1. For *4,4*-d_2 the corresponding ratio is nearly reversed; i.e., 12:4:84. The small intensity at *m/e* 121 provides a clue that the hydrogen atoms at position 4 are susceptible to a small amount of scrambling probably with the aromatic ring hydrogens. This latter observation is substantiated by metastable ion studies, which will be discussed later. The greater preference for pathway 1 (see eq 3 and 4) at low ionizing energy suggests a lower activation energy for this cycloreversion channel.

The other two isotopically labeled 1-tetralols (-*1*-d_1 and -*O*-*d*) provide little new information on these competitive channels except to verify the interpretation presented above. In the *1*-d_1, *m/e* 120 cleanly shifts to *m/e* 121, as expected, and *m/e* 119 is unaffected. For the *O*-*d* compound again *m/e* 120 shifts to 121 and *m/e* 119 appears to be partitioned between *m/e* 120 and 119. No apparent hydrogen scrambling complicates the picture.

Table I. Comparison of the Ion Current as Percent of Total Ionization for the Cycloreversion Reaction in Various Deuterium Labeled 1-Tetralols

	m/e					
Compd[a]	123	122	121	120	119	Σ[b]
1-Tetralol		0.12	1.46	12.5	6.67	20.7
1-Tetralol-*1*-d_1		1.01	11.4	1.95	5.88	20.2
1-Tetralol-*O*-*d*		0.88	10.5	8.01[c]	1.49	20.9
1-Tetralol-*2,2*-d_2	0.89	8.08	1.05	3.35	6.47	19.8
1-Tetralol-*4,4*-d_2	0.40	3.30	7.81	10.9	0.82	23.2[d]

[a] Isotopic purity: *1*-d_1, 96% d_1, 4% d_0; *O*-*d*, 78% d_1, 22% d_0; *2,2*-d_2, 1% d_3, 91% d_2, 7% d_1, 1% d_0; *4,4*-d_2, 1% d_4, 10% d_3, 76% d_2, 11% d_1, 2% d_0. [b] Summation of percent of total ion current in the *m/e* 119–123 region. [c] Contamination with d_0, which enhances this percent. [d] A higher percentage is observed due to isotope effect, which discriminates against water loss.[8]

Defocussed metastable ion measurements (accelerating voltage scans) of the molecular ion fragmentations confirm the separate, yet parallel reaction channels. For 1-tetralol-*2,2*-d_2, an abundant metastable is observed for pathway 1 (i.e., 150 → 122) and 14 meV is released as translational energy. The metastable for pathway 2 (150 → 120) is only 0.7% of the 150 → 122 metastable ion. No detectable metastable is observed for 150 → 121, indicating no scrambling of the hydrogens at position 2. The extreme diminution of metastable abundance for pathway 2 indicates that the two reaction channels for cycloreversion are significantly less competitive in the 10^{-5} to 10^{-6} s time span than for times less than 10^{-6} s. This is in accord with the previous suggestion that pathway 2 has a higher activation energy. In addition, the rate constant for pathway 2 must exhibit a faster rise with internal excitation than for pathway 1.

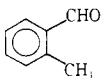
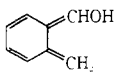
Final substantiation of these interpretations is obtained by a metastable ion study of the cycloreversion reaction in 1-tetralol-*4,4*-d_2. As expected, the metastable ion abundance for pathway 2 (now 150 → 122) is barely observable, such that a maximum intensity can be assigned of less than 4% of total metastable cycloreversions. The small extent of scrambling of hydrogens in position 4 detected in the low voltage spectra (vide supra) is substantiated by the observation of two metastable ions for pathway 1: 150 → 120 and 150 → 121 in the ratio 73:27. Because the 150 → 121 transition is *not* observed in the *2,2*-d_2 compound, it is postulated that *minor* equilibration of the hydrogens in position 4 and the aromatic ring hydrogens has occurred. Extensive scrambling, even with one aromatic ring hydrogen, would give preferential formation of *m/e* 121, and, therefore, is ruled out.

All of the above results clearly establish two parallel cycloreversion reactions to eliminate C_2H_4 in 1-tetralol. The favored channel involves expulsion of carbons 3 and 4 and is accompanied by an abundant metastable. A second, less facile channel involves elimination of carbons 2 and 3, and this path is only of consequence for short lived molecular ions. We will now turn our attention to the structures of the C_8H_8O ions produced by these parallel mechanisms.

Structure of $[C_8H_8O]^{+\cdot}$ Ions. Two reactions operating in parallel to produce the same mass daughter ion may lead to a common daughter structure formed concurrent with fragmentation or to two initially different structures, which then isomerize to a common structure or mixture of structures. A third possibility is formation of two different structures which do not interconvert or isomerize to a common species.

Our first approach to resolve these possibilities makes use of the established techniques of comparing metastable abundances and kinetic energy releases[2] for decomposition of var-

Table II. Comparison of Metastable Abundances and Kinetic Energy Releases for Decomposing C_8H_8O Ions (*m/e* 120)[a]

Source of C_8H_8O	*i* (120 → 119)	*i* (120 → 105)	Kinetic energy release (120 → 105)[b]
	90.9	9.1	50
	0.1	99.9	4[c]
 (from valerophenone)	1.0	99.0	42[d]
	97.2	2.8	42
	92.4	7.6	200
 (from *o*-hydroxymethylbenzyl alcohol)	99.6	0.4	[e]

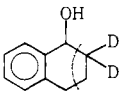
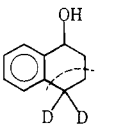
[a] Measured using accelerating voltage scans. [b] Millielectron volts. [c] Literature value ≃ 7 meV.[9b,13] [d] Literature value ≃ 52 meV.[9b,13] [e] Too weak to measure.

ious C_8H_8O ions. The results are tabulated in Table II. Two metastable transitions involving *m/e* 120 were found and they are loss of a hydrogen atom and loss of a methyl radical. A straightforward interpretation of both the kinetic energy release data and the metastable intensity ratios leads to the conclusion that the best representation of $[C_8H_8O]\cdot^+$ from 1-tetralol is the styrene oxide structure. However, the fact that two parallel mechanisms occur for the cycloreversion causes us to reject this conclusion and look more closely for a structural interpretation.

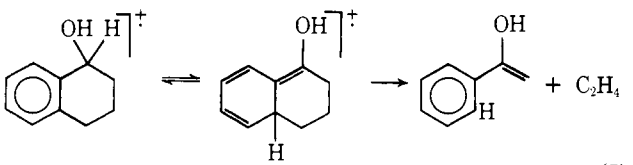
The separate C_8H_8O ions produced in the two mechanisms can be examined by a metastable study of *m/e* 120 from the *2,2-d*$_2$ and the *4,4-d*$_2$ compounds. For the former, *m/e* 120 is produced by pathway 1 and for the latter by pathway 2 (i.e., loss of carbons 2 and 3). The comparison is made in Table III. Now, an accurate picture emerges. Clearly, the two parallel processes produce two distinctive C_8H_8O ions. Elimination of carbons 2 and 3 gives rise to $[C_8H_8O]\cdot^+$, which fragments almost exclusively by loss of a hydrogen atom. The other cycloreversion product gives little hydrogen loss, but rather, dominant loss of methyl. There can be no doubt that the fragmenting metastable C_8H_8O ions have unique structures and their uniqueness must exist in the stable counterparts as well.

We are now in a position to examine the actual structures of the C_8H_8O ions. Comparison of the metastable characteristics of the *m/e* 120 ions produced in pathway 1 (Table III) and by a McLafferty rearrangement in valerophenone (Table II) shows that these structures are identical and can be represented as the enol form of acetophenone. This structural isomer of $[C_8H_8O]\cdot^+$ cannot be formed by a straightforward elimination of C_2H_4; rather, a shift of the hydrogen at position 1 is required. An attractive and economical possibility is a 1,3-shift as shown in eq 5. A shift of this nature is forbidden by molecular orbital theory[14] and, therefore, would only occur with high activation energy. Because the heat of formation of

Table III. Comparison of Metastable Decomposition of *m/e* 120 Ions Produced by the Two Cycloreversion Reactions

Origin of *m/e* 120	*i* (120 → 119)	*i* (120 → 105)	Kinetic energy release (120 → 105)
	99.2	0.8	*a*
	8.1	91.9	50

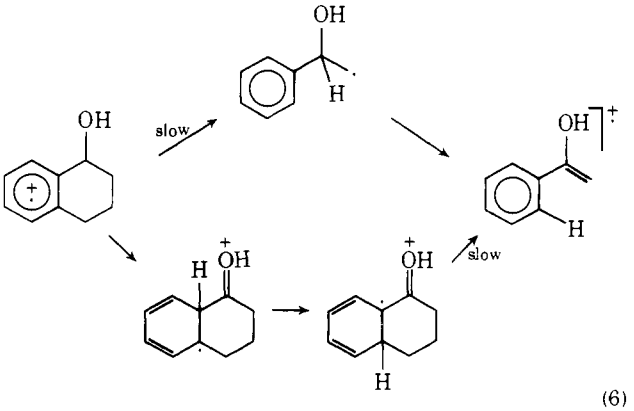
[a] Cannot be measured reliably because of overlap with the abundant 122 → 105 metastable signal.



(5)

the enol form of $[C_8H_8O]\cdot^+$ is not established, we cannot estimate whether the activation energy (1.72 eV), which is taken to be the difference of the appearance potential of *m/e* 120 and the ionization potential of 1-tetralol,[8] is excessive. If it were, a significant reverse activation energy would be expected and the metastable accompanying loss of C_2H_4 would show considerable kinetic energy release. Previous reports by Williams and Hvistendahl[15] show that release of large amounts of kinetic energy occurs for ionic decompositions proceeding through forbidden pathways. However, loss of C_2H_4 in 1-tetralol occurs with release of only 14 meV, which militates against a 1,3-shift. Moreover, there is no significant isotope effect for loss of C_2H_4 from 1-tetralol-*1*-*d*$_1$, a compound in which the itinerant hydrogen is replaced by deuterium. The evidence for this is contained in Table I. We note that the percent of total ionization carried by *m/e* 121 ($C_8H_7DO\cdot^+$) is not attenuated relative to the other tetralols. The existence of a 1,2-hydrogen shift has been diagnosed recently by observation of a kinetic isotope effect which operates against deuterium transfer.[16]

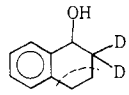
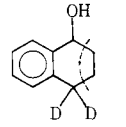
Therefore, we find no evidence for a 1,3-hydrogen shift, or indeed, for any shift of the hydrogen in position 1 in the transition state for expulsion of C_2H_4 via pathway 1. The two mechanisms given in eq 6 can explain the data. The molecular



(6)

ion can either undergo straightforward loss of C_2H_4 followed by consecutive 1,2-hydrogen shifts to ultimately give the enol form of $[C_8H_8O]\cdot^+$ or the hydrogen shifts can occur in fast steps prior to rate-determining expulsion of ethylene. Because these hydrogen shifts should be reversible, the proposed

Table IV. Comparison of Metastable Decompositions of *m/e* 122 Ions Produced by the Two Cycloreversion Reactions

Origin of *m/e* 122	*i* (122 → 121)	*i* (122 → 120)	*i* (122 → 107)	*i* (122 → 106)	*i* (122 → 105)
	9.1	*a*	*a*	*a*	90.9
	94.8	4.0	1.2	*a*	*a*

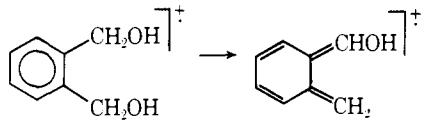
[a] Not detected.

mechanism would serve to scramble the hydrogen in position 1 and the four original aromatic hydrogens.

In fact, the specific hydrogen scrambling is verified by metastable studies for loss of methyl from $[C_8H_8O]\cdot^+$ and the various deuterated analogues of this ion. The 1-tetralol-*2,2-d*$_2$ gives $[C_8H_6D_2O]\cdot^+$ by pathway 1, which loses methyl exclusively as CD_2H, indicating *no* scrambling of the hydrogens at carbon 2 (see Table IV). However, 1-tetralol-*1-d*$_1$ loses CH_3 and CH_2D from *m/e* 121 in the ratio of 82:18 (Table V). A ratio of 80:20 would be expected for equilibration of four hydrogens and one deuterium prior to transfer to form the departing methyl. Loss of methyl then involves abstraction of one of the randomized hydrogens from the aromatic ring.

In a study of deuterated butyrophenones, Tomer and Djerassi have concluded that the hydroxyl hydrogen is *not* implicated in the methyl loss from $[C_8H_8O]\cdot^+$, formed as an enol ion in the McLafferty rearrangement. Thus, reketonization prior to methyl loss is ruled out. The evidence from the *O-d*$_1$ compound (Table V) clearly demonstrates that the hydroxyl hydrogen is also not involved in methyl loss. These combined results support our view that the structure of $[C_8H_8O]\cdot^+$ produced by elimination of ethene bearing carbons 3 and 4 is the enol form of the acetophenone radical cation. It is worthy of note that methyl loss from $C_8H_8O\cdot^+$ involves a rather elaborate mechanism of ring scrambling plus abstraction of an aromatic hydrogen instead of the simpler, but forbidden, 1,3-hydrogen shift to ketonize.

The second pathway followed in the cycloreversion reaction of 1-tetralol produces $[C_8H_8O]\cdot^+$, which gives metastable decompositions identical with the M − H_2O ion of *o*-hydroxymethylbenzyl alcohol (eq 7); see Tables II and III. Unfortu-

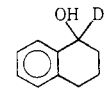
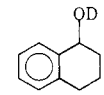


(7)

nately, the metastable ions for loss of CH_3 from *m/e* 120 are too weak to determine kinetic energy release, so this feature cannot be compared. Nevertheless, we conclude that the best representation for this C_8H_8O structure is that given in eq 6. Isomerization to the benzaldehyde ion followed by hydrogen loss seems to be excluded because there is a significant difference in the metastable abundance for methyl loss from benzaldehyde compared to $[C_8H_8O]\cdot^+$ from 1-tetralol and *o*-hydroxymethylbenzyl alcohol.

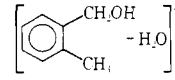
As noted previously, the second cycloreversion pathway has an activation energy higher than 1.7 eV and only a barely detectable metastable ion accompanying it. Although it cannot be firmly established whether the reaction shown by eq 8 is stepwise or concerted, a stepwise mechanism could explain the higher activation energy. The near absence of a metastable ion suggests that the fragmentation rate constant exhibits a

Table V. Comparison of Metastable Decompositions of *m/e* 121 Ions

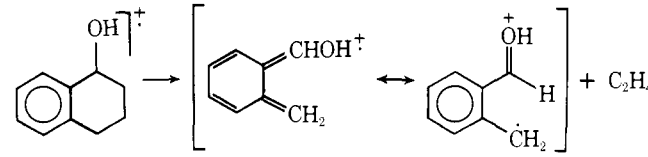
Origin of *m/e* 121	*i* (121 → 120)	*i* (121 → 119)	*i* (121 → 106)	*i* (121 → 105)
	36[a]	64	82[a]	18
	98	2	>99	<1

[a] Both loss of H(D) and loss of $CH_3(CH_2D)$ normalized to 100%.

Table VI. Comparison of Metastable Decompositions of Various C_8H_8 Ions

Source	104 → 103	104 → 102	104 → 89	104 → 78
Tetralin	82.6	0.2	0.1	17.1 (155)[a]
Styrene	79.5	0.2	0.1	20.2 (130)[a]
	80.4	0.2	0.1	17.3 (160)[a]

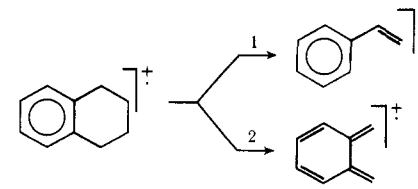
[a] Kinetic energy release in millielectron volts.



(8)

sharper increase with internal energy than does the rate constant for pathway 1. The nearly exclusive loss of a hydrogen atom from $[C_8H_8O]\cdot^+$ originates primarily from the 1-position of the starting tetralol and this is confirmed by both the 70-V spectra of 1-tetralol-*1-d*$_1$ (Table I) and the abundant 121 → 119 metastable for this compound (Table IV). The observed loss of H from *m/e* 121 in 1-tetralol-*1-d*$_1$ may be due to isotopic scrambling with the aromatic hydrogens or to an isotope effect which, by raising the activation energy for loss of D, allows other losses of H to become competitive.

Comparison with Tetralin. The most facile fragmentation in the 70-V spectrum of tetralin is the loss of ethene. This process has been recently studied by deuterium labeling and metastable ions[17] and by carbon-13 labeling.[18] The earlier results were interpreted in terms of an isomerization of the tetralin structure to a tetrahydroazulene ion prior to elimination of C_2H_4. The key piece of evidence supporting this hypothesis is the 1:2:1 loss of C_2H_4:$C_2H_2D_2$:C_2D_4 in tetralin-*1,1,2,2-d*$_4$. By analogy with 1-tetralol, we suggest as an alternative that tetralin undergoes two competitive cycloreversion reactions in the ratio of approximately 1:1 (eq 9). The



(9)

more recent ^{13}C-labeling results show that for tetralin labeled in the 1-position, expulsion of C_2H_4 occurs with 69% label retention, and the tetralin-*2*-^{13}C gives 34% label retention. A competitive cycloreversion mechanism can accommodate these data if the ratio of pathway 1 to pathway 2 is adjusted to 1.6:1.[19] It is more difficult to fit the results to a ring expansion

mechanism, which would give 75 and 25% label retention, respectively.

A more detailed study of metastable ion characteristics than employed in the original tetralin study[17] was made to determine if the two proposals can be distinguished (Table VI). As can be seen, no significant difference can be found in either the relative metastable abundances or the kinetic energy releases of the various C_8H_8 ions. Thus, no information can be extracted on the mode of formation of $[C_8H_8]^{\cdot+}$ in tetralin, as these data suggest isomerization of all C_8H_8 ions to a common structure prior to fragmentation. The behavior of various C_8H_8 ions should be compared with the C_8H_8O ion metastables presented in Table II. For this latter ion, distinctive metastable characteristics are found depending on the source of $[C_8H_8O]^{\cdot+}$ and the differences, with the aid of isotopic labeling, can be interpreted unambiguously in terms of structure. Unfortunately, this is not the case for the cycloreversion reaction in tetralin, and the overall mechanism for this process still requires further study.

Conclusion

It has been clearly established that 1-tetralol undergoes two cycloreversion reactions to eliminate ethene and thereby produces a mixture of structural forms for the $M - C_2H_4$ daughter. Although the two pathways are competitive to produce the normal mass spectrum, one process dominates the metastable decompositions. The daughter ions show extremely large differences in metastable abundances which are readily interpreted in terms of structure. Competitive cycloreversion reactions seem to be the case for tetralin as well, but further studies are needed to substantiate this.

This study is a classic example of the dangers inherent in a literal interpretation of measurements of metastable abundances and kinetic energy release. In the unlabeled 1-tetralol, the metastable characteristics of $[C_8H_8O]^{\cdot+}$ are a composite of two isomeric structures undergoing decomposition, and these characteristics are fortuitously matched by a third structure from styrene oxide, which is not involved. The combination of deuterium labeling and metastable measurements allows the correct conclusions to be drawn.

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References and Notes

(1) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).
(2) R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, "Metastable Ions", Elsevier, Amsterdam, 1973.
(3) J. Winkler and F. W. McLafferty, *J. Am. Chem. Soc.*, **95**, 7533 (1973), and references cited therein.
(4) R. C. Dunbar, *J. Am. Chem. Soc.*, **97**, 1382 (1975).
(5) See, for example, P. K. Pearson, H. F. Schaefer III, J. H. Richardson, L. M. Stephenson, and J. I. Brauman, *J. Am. Chem. Soc.*, **96**, 6778 (1974).
(6) H. Heimgartner, P. A. Weibel, and M. Hesse, *Helv. Chim. Acta*, **57**, 1510 (1974).
(7) M. L. Gross and E. Chiu, American Society for Mass Spectrometry, 22nd Annual Conference on Mass Spectrometry and Allied Topics, Philadelphia, Pennsylvania, 1974.
(8) M. L. Gross, E. Chiu, D. Pokorny, and F. L. DeRoos, *Org. Mass Spectrom.*, in press.
(9) (a) K. B. Tomer and C. Djerassi, *Org. Mass Spectrom.*, **6**, 1285 (1972); (b) J. H. Beynon, R. M. Caprioli, and T. W. Shannon, *ibid.*, **5**, 967 (1971); (c) ref. 1, p 119. (d) For a recent review of this matter, see M. A. Winnik, *Org. Mass Spectrom.*, **9**, 920 (1974).
(10) T. W. Shannon and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 5021 (1966).
(11) G. Hvistendahl and D. H. Williams, *J. Am. Chem. Soc.*, **97**, 3097 (1975).
(12) M. L. Gross, C. L. Wilkins, R. C. Williams, and G. Leung, *Org. Mass Spectrom.*, **9**, 1217 (1974).
(13) Reference 2, p 119.
(14) R. B. Woodward and R. Hoffmann, *Angew. Chem. Int. Ed. Engl.*, **8**, 781 (1969).
(15) D. H. Williams and G. Hvistendahl, *J. Am. Chem. Soc.*, **96**, 6753 (1974); D. H. Williams and G. Hvistendahl, *ibid.*, **96**, 6755 (1974).
(16) I. Howe, *Org. Mass Spectrom.*, **10**, 767 (1975).
(17) H.-F. Grützmacher and M. Puschmann, *Chem. Ber.*, **104**, 2079 (1971).
(18) M. I. Gorfinkel, N. S. Bugreeva, and I. S. Isaev, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 88 (1974).
(19) Gorfinkel et al.[18] also point out the possibility of a mixed cycloreversion mechanism.

Application of the Principle of Least Motion to Organic Reactions. 4.[1a] More Complex Molecular Rearrangements

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Abstract: The principle of least motion technique has been applied to a wide variety of unimolecular rearrangements involving large and relatively complex systems lacking symmetry. Results, with two exceptions, are in excellent agreement with the qualitative overlap considerations of the Woodward-Hoffmann approach where applicable and experimental observations when available.

The first application of the principle of least motion (PLM) technique to molecular rearrangements was reported[2a] a few years ago. It was recognized at that time that, despite the classical nature of the approach, the stereochemical predictions arising from the results parallel those based on the conservation of orbital symmetry (COS) method when applicable. Although this initial study utilized relatively few and rather simple model systems, it provided valuable information with regard to the wide scope of potential applicability of the PLM technique. For example, it was suggested that systems that lack suitable elements of symmetry, and thus cannot be rigorously treated by the COS approach, should be amenable to investigation by the present method, since the latter does not require the presence of any particular symmetry. Also, in those cases where