LBL-13303
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

CHEMICAL BIODYNAMICS DIVISION

OCT 9 1981

Submitted to the Journal of the American Chemical Society

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September 1981

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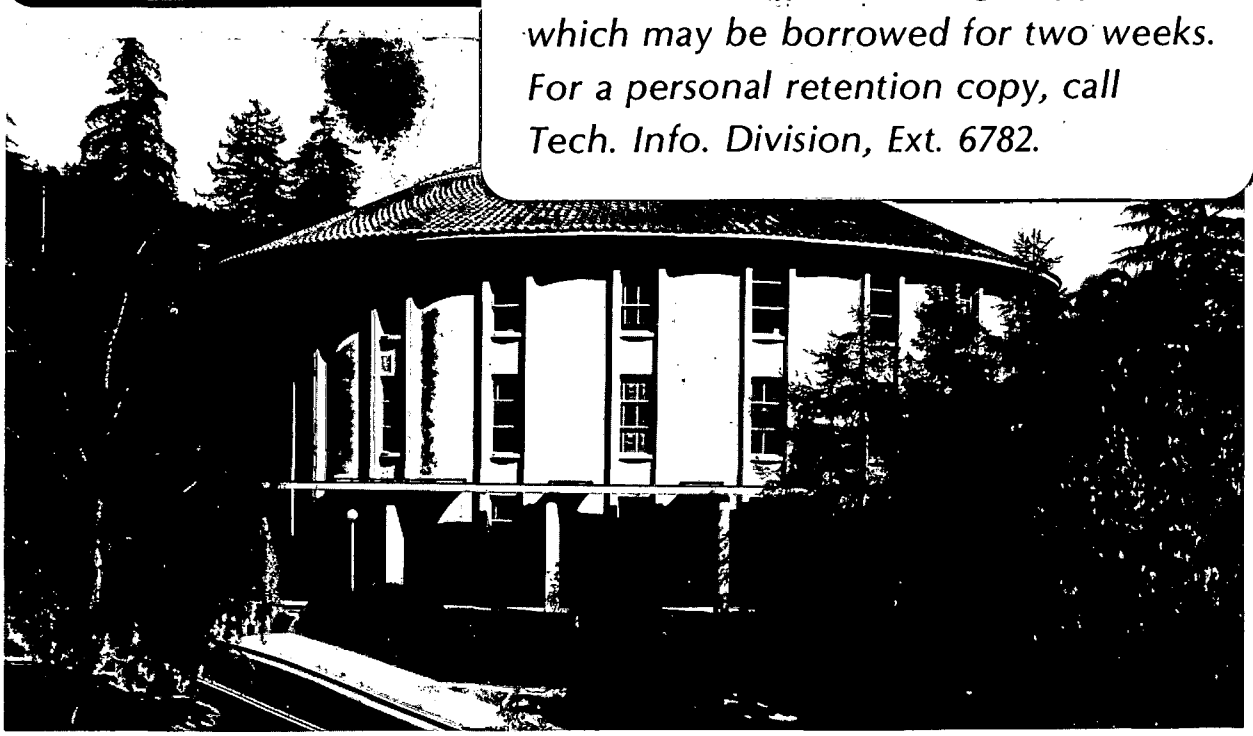

LBL-13303 c.2

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

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ON THE MECHANISM OF THE M-CH_3 PROCESS IN THE MASS SPECTRA OF CYCLOHEXENE AND 2-CYCLOHEXEN-1-OL

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Abstract

The M-CH_3 process in the mass spectra of cyclohexene (1) and 2-cyclohexen-1-ol (10) is proposed to occur via isomerization to the respective bicyclo[3.1.0]hexane (8) and 1-hydroxy-bicyclo[3.1.0]hexane (15) radical cations. The formation of intermediate ions 4 and 12 in this isomerization requires only one 1,2-H shift. H/D randomization before loss of $\cdot CH_3$ in labeled cyclohexene is then explained by a reversible isomerization of $1^{+\cdot}$ to $4^{+\cdot}$ instead of symmetry forbidden 1,3-allylic H shifts in $1^{+\cdot}$. Appearance energies indicated reverse activation energies for the M-CH_3 and M-H processes from $10^{+\cdot}$ which were attributed to an activation energy for the recombination of these radicals with the olefinic part of the product ion rather than with the cationic center. There was little evidence for the reversible isomerization of $10^{+\cdot}$ to 3-cyclohexen-1-ol$^{+\cdot}$ ($19^{+\cdot}$) consistent with ion 21, formed by a 1,2-H shift in $19^{+\cdot}$, having a higher energy than the ring-opened ion 20 and the M-H_2O process.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Chemical Sciences of the U.S. Department of Energy under Contract No. W-7405-ENG-48.

Recently, we commented on the possibility that the symmetry-forbidden sigmatropic 1,3-H shift in radical cations occurs via two successive 1,2-H shifts.[1] Examples of keto-enol tautomerism were discussed in which there were large barriers to the 1,3-H shift in the molecular ions. The estimated ΔH_f's of the intermediate radical cations formed by one 1,2-H shift were shown to be less than the energies of the transition states.

A mass spectral study of labeled propene showed complete H/D randomization prior to loss of a hydrogen atom.[2] These observations were not consistent with 1,3-H shifts only but could be explained by a series of 1,2-H shifts. In addition, there was skeletal isomerization which could also lead to H/D randomization. The results were interpreted in terms of a reversible isomerization of propene$^{+\cdot}$ to cyclopropane$^{+\cdot}$ in competition with fragmentation.[2] In another study, a 1,2-H shift was postulated in 1,4-hexadiene$^{+\cdot}$ to explain the M-CH_3 ion formation.[3]

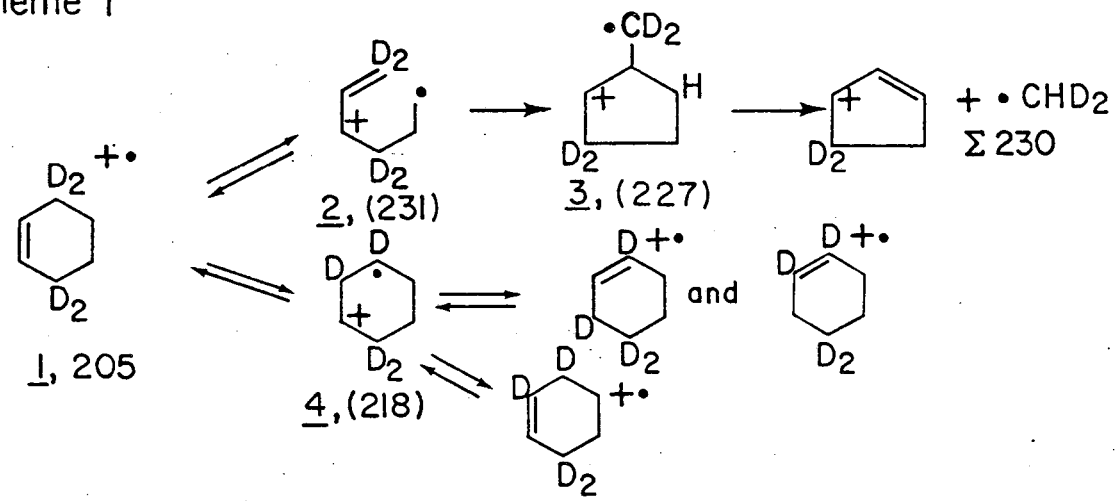
In this study, we have estimated the ΔH_f's of the intermediate ions formed by a 1,2-H shift in the molecular ions of cyclohexene (1) and 2-cyclohexen-1-ol (10) and show that these intermediate ions have lower energies than other possible first intermediate ions in the fragmentation processes. In order to explain the H/D mixing in labeled $1^{+\cdot}$,[4] we propose that this mixing can occur via the reversible process to the ion formed via one 1,2-H shift and that this ion is the intermediate ion in the reversible rearrangement of $1^{+\cdot}$ and bicyclo[3.1.0]hexane (8) radical cation.

Analysis of literature data on fragment ion appearance energies (AE) from $1^{+\cdot}$ and $8^{+\cdot}$,[5-7] kinetic energy releases (KER) for methyl loss in $1^{+\cdot}$ and $8^{+\cdot}$,[7] and deuterium labeling studies for $1^{+\cdot}$ [4] supports this mechanism. In addition to previous labeling studies on $10^{+\cdot}$,[8] we have determined AE's

for the major fragment ions which are consistent with a similar mechanism for $10^{+\cdot}$. Also discussed are the analogous thermal processes of 1[9] and 8.[10,11]

Cyclohexene (1). The molecular ion of cyclohexene-3,3,6,6-d_4 has been shown by FI to undergo 1,3-H shifts.[4] Only at the shortest times does the unrearranged ion fragment to the M-CH_2=CH_2 ion. Also at the shortest times, the M-CHD_2 ion is the most abundant ion whereas at longer times the M-CH_2D ion becomes more abundant. The mechanism proposed for the formation of the M-CHD_2 ion[4] is given in Scheme 1. Heats of formation (kcal/mol) are noted

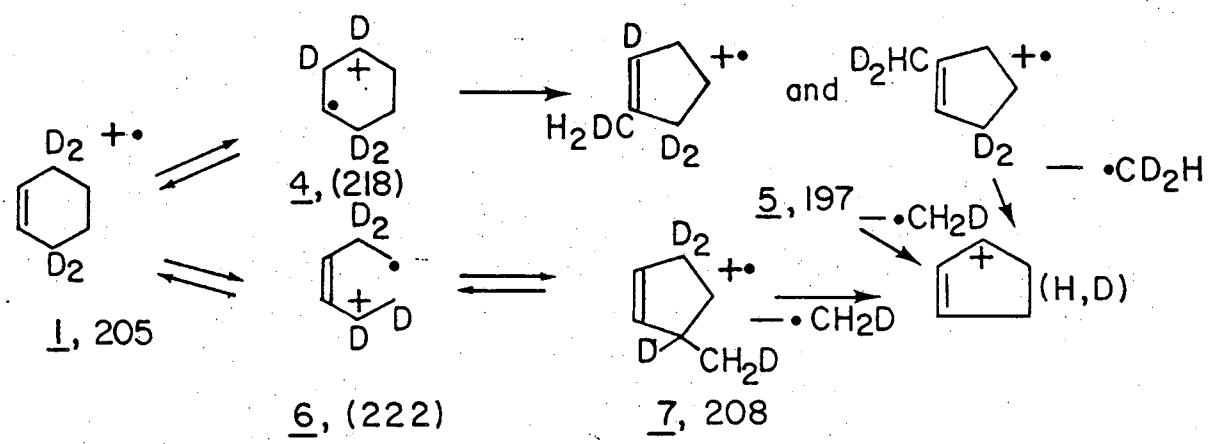
Scheme I



on the schemes with estimated values given in parenthesis (see Appendix for detail). With one 1,3-D shift which explains the increasing formation of M-$C_2H_2D_2$ as the M-CH_2=CH_2 ion formation decreases, the formation of M-CH_2D is not explained by this mechanism. Already at short times the abundance of the M-CH_2D ion is two-thirds the abundance of the M-CHD_2 ion and is more than

twice the abundance of the M-CH_3 ion. If the 1,3-D shift occurs via two successive 1,2-D shifts[1] then with equal probability, if there is no isotope effect, the second shift could be a 1,2-H shift to give the other isomer. Considering, in addition, a reverse 1,2-H shift from ion 4, the abundance of the M-CH_2D ion would be expected to be no more than the abundance of the M-CH_3 ion. Thus, another mechanism for the formation of the M-CH_2D ion appears to be occurring. Two possible mechanisms are shown in Scheme 2.

Scheme 2



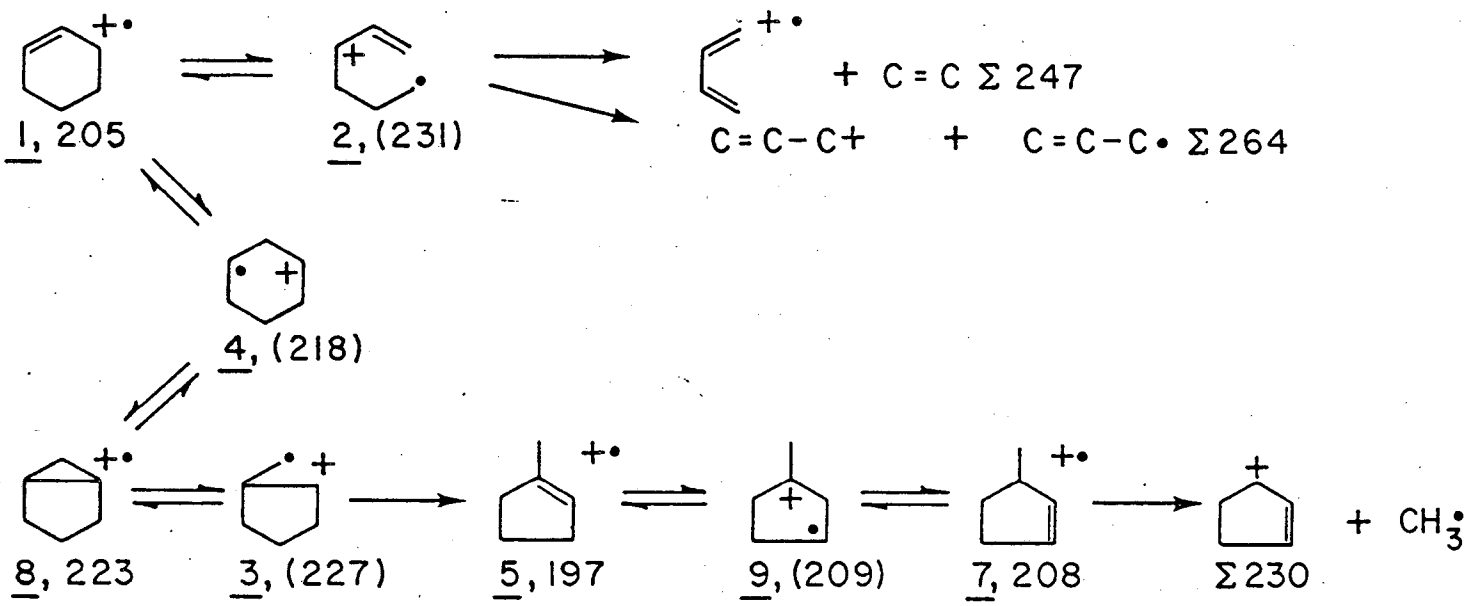
The mechanism via ion 4 would be preferred because of the lower energies of ion 4 and 1-methylcyclopentene radical cation ($5^{+\cdot}$) compared to ion 6 and 3-methylcyclopentene radical cation ($7^{+\cdot}$). In the following is a more detailed description of the mechanism via ion 4.

Recently, a study on AE's and metastable peak shapes of the methyl loss from ions 1, 5, 7 and 8 indicated that the fragmentation process had a common reaction pathway to give the cyclopentenium ion at threshold.[7] From labeling studies the authors proposed that both ions 1 and 8 irreversibly isomerized to ions 5 and/or 7 prior to fragmentation at or close to the thermochemical threshold for methyl loss. They assumed that the atom mixing

in labeled ion 1 prior to the loss of the methyl group took place via 1,3-allylic H atom shifts. The authors did not study labeled ion 8 and did not propose that ion 1 partially isomerized to ion 8.

The 70 and 12 eV mass spectra of both 1 and 8 are very similar[5,12] with the AE's of the m/z 67, 54 and 41 ions from both compounds giving the same ΔH_f for these ions.[5] The more abundant molecular ion of 1 would be expected from the lower ΔH_f of ion 1 compared to the ΔH_f of ion 8. With the exception of the fast formation of the M-CH_3 ion as shown in Scheme 1, we propose in Scheme 3 a mechanism which accounts for these data in which

Scheme 3



ions 1 and 8 reversibly isomerize before fragmentation to the cyclopentenium ion and the retro Diels-Alder (RDA) ion. The intermediate ion 4 in this isomerization is formed from ion 8 by simple bond cleavage and from ion 1 by a 1,2-H shift. H/D mixing in ion 1 prior to methyl loss then is accounted for by several successive 1,2-H shifts in the reversible step of ion 1 to ion 4 rather than by symmetry-forbidden 1,3-allylic H shifts in ion 1 prior to formation of ion 4. Ion 5 is shown as isomerizing to ion 7 because these

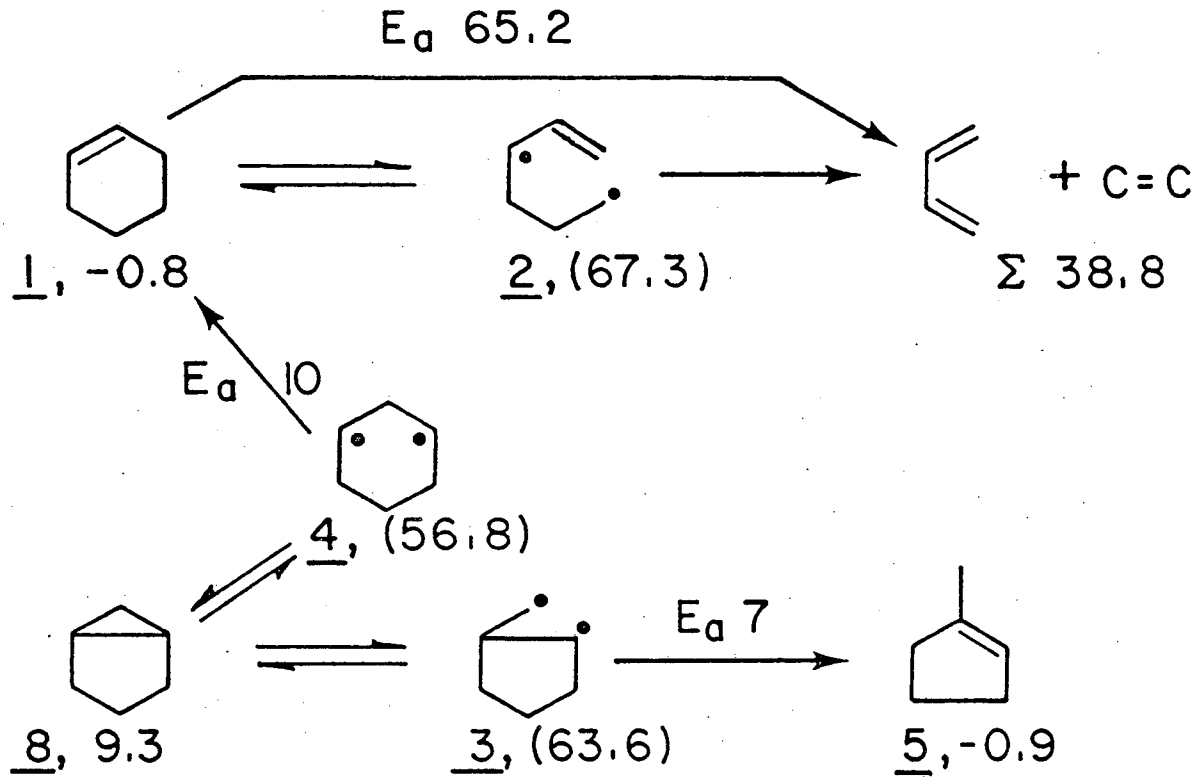
ions were shown to lose methyl by a common reaction pathway.[7] The loss of methyl via ions 3 and 7 is a lower energy process than the RDA process via ion 2 and also is a lower frequency factor process as shown by the FI studies.[4]

There is a possibility that ion 4 could isomerize directly to ion 9 because the cyclohexyl cation is known to isomerize to the 1-methylcyclopentyl cation under certain conditions.[13,14] Recently, however, the cyclohexyl cation was found to have a lifetime in excess of 10^{-7}s in the dilute gas state.[15] In a recent study of cyclohexanecarboxaldehyde$^{+\cdot}$,[16] the AE of the $C_6H_{11}^+$ ion indicated that the initially-formed ion was the cyclohexyl cation. Thus, ion 4 was considered not to isomerize directly to ion 9.

The m/z 41 ion has the highest energy level of the three fragmentation processes and has been shown from FI studies on cyclohexene-3,3,6,6-d_4 to be primarily from ion 2.[4] Formation of this ion from an intermediate 1,5-hexadiene radical cation [ΔH_f 234 kcal/mol[6]] appeared to be of minor importance from the small amount of H/D scrambling. The formation of this diene from ion 1 via ion 4 is a higher energy and lower frequency factor process than ring opening to give ion 2. Whereas ion 4 has lower energy pathways than the formation of this diene, ion 4 may be an intermediate ion in the formation of the cyclopentenium ion[3] and the m/z 54 ion from this diene. The abundances of the m/z 54 and 67 ions relative to the m/z 41 ion are much less in the mass spectrum of 1,5-hexadiene[17] than in the mass spectra of 1 and 8.

In scheme 4 is given the thermal rearrangement processes of 1 and 8

Scheme 4



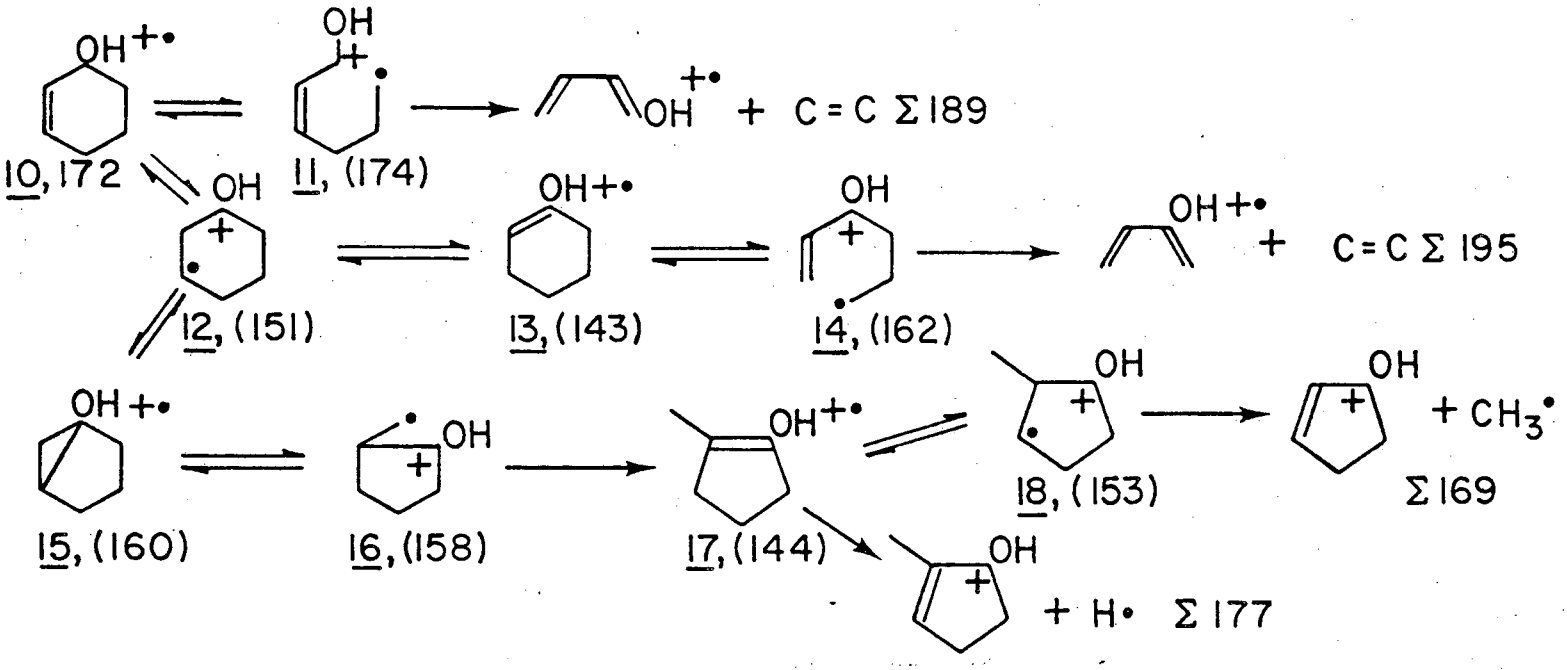
analogous to the rearrangement processes of ions 1 and 8 in Scheme 3. The major difference in the two schemes is the lack of rearrangement of 1 to 4 in Scheme 4 although the reverse rearrangement occurs. Cyclohexene is not known to form a methylcyclopentene via an uncatalyzed thermal process[9] whereas 8 forms both 1 and 5 in a ratio of 3:1.[10] A biradical mechanism was found to be consistent with the experimental results for the thermal rearrangement of 8.[11] There was no evidence of H/D mixing in labeled 1 before the RDA thermal reaction and the process was considered to be a symmetry-allowed concerted process.[9] The experimental activation energy (E_a) of 65.2 kcal/mol for this process was 3 kcal/mol less than the estimated E_a via 2.[9] Biradical 4 has an E_a of ∿10 kcal/mol for the 1,2-H shift to form 1[11] which is similar

to the E_a for the 1,2-H shift in the biradical from cyclopropane to form propene.[11] Thus, the E_a for the concerted RDA process in 1 is lower than the E_a to form biradical 4 and the rate of the RDA process is faster than rearrangement to biradical 4. In contrast, the 1,2-H shifts in radical cations have negligible barriers other than the differences in the enthalpies of the ions before and after the H shift[18] and the RDA process in ion 1 is considered to be a stepwise process via ion 2.[19] Thus, for ion 1 (Scheme 3) rearrangement to ion 8 via ion 4 is a lower energy process than ring cleavage to form ion 2.

2-Cyclohexen-1-ol (10). Recently, the loss of methyl from the molecular ion of 10 was shown to be predominantly from the C atom at the 2-position and the H atoms from the 1,2- and 3-positions[8] consistent with the mechanism via ion 4 rather than ion 6 for part of the M-CH_3 from $1^{+\cdot}$. Elimination of $\cdot CH_2OH$ corresponding to the fast elimination of methyl from the molecular ion of 1 was not found to occur in $10^{+\cdot}$ to any extent.[8] The M-CH_3 ion from the various methyl-substituted 2-cyclohexen-1-ols corresponded to the loss of the methyl substituent,[8] indicating that this process is a much faster process than the M-CH_3 ion derived from the ring contraction process.

The structures and ΔH_f's of the intermediate and product ions in the mass spectral fragmentation of 10 which are comparable to those shown for 1 are given in Scheme 5. The tert-H atom was shown to be the atom which shifts[20] and is consistent with the formation of ion 12 as the intermediate ion in the partial isomerization of $10^{+\cdot}$ to ions 13 and 15. Recently, 1,2-H shifts in linear alkenols similar to the 1,2-H shift in $10^{+\cdot}$ to form ion 12 were postulated to rationalize fragmentation results.[21]

Scheme 5



Because the M-CH_3 ion as shown in Scheme 5 could not be formed directly from the 5-methyl-1-cyclopenten-1-ol radical cation which is comparable to ion 7 in Scheme 3, ion 17 is shown as rearranging to ion 18. This ion can cleave to give the M-CH_3 ion without further rearrangement. However, the AE of 9.7 ± 0.1 eV for this ion (energy level 184 kcal/mol) indicates a reverse activation energy (E_0) of 15 kcal/mol. The alternative 2-cyclopenten-1-yl cation with the hydroxyl group in a position other than 1 has an energy level greater than the experimental energy level (Appendix). This reverse E_0 may be expected because the recombination of the radical and cation involves the addition of the methyl radical to the double bond rather than the cationic center. In addition, the M-H process which is important in the mass spectrum of 10 is shown as arising via ion 17. The AE of 9.9 ± 0.1 eV (energy level 188 kcal/mol) and the hydrogen atom eliminated[8] is consistent with this process. Other possible ions with the hydrogen atom eliminated corresponding to the

4-position in $\underline{10}^{+\cdot}$ except from ion 12 have energy levels greater than the experimental energy level. A reverse E_0 would be expected for the process shown in Scheme 5 and for the M-H ion from ion 12 for the same reason given for the M-CH_3 process. The reverse E_0 for the M-H ion from ion 17 is 11 kcal/mol whereas from ion 12 it is only 1 kcal/mol. Thus, the M-H ion is presumed to be from ion 17.

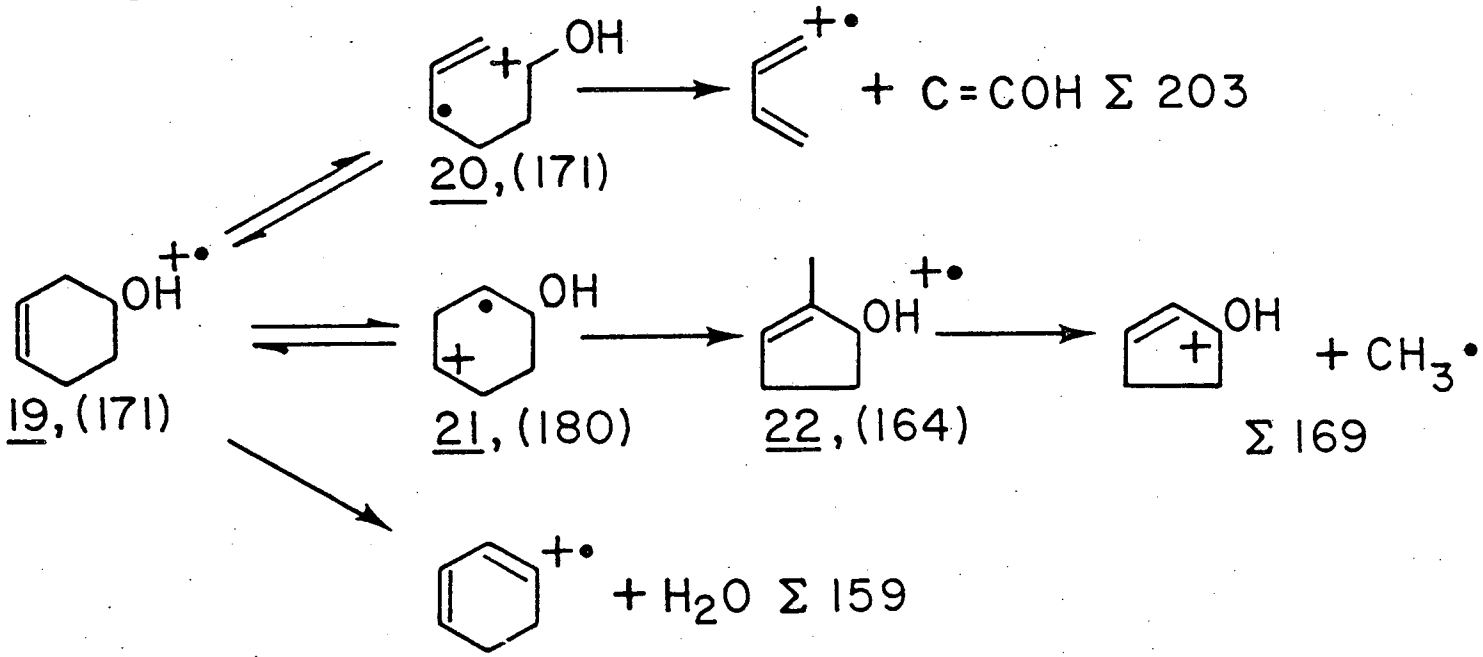
The major fragmentation path is the RDA reaction which is two-thirds from the isomeric ion 13.[8,20] This ion is of considerably lower energy than ion 10, with the intermediate ion 12 only 8 kcal/mol greater energy than ion 13. Thus, the intermediacy of ion 12 in the ring contraction process to give the M-CH_3 ion is consistent with the isomerization of ion 10 to ion 13 occurring via two successive 1,2-H shifts. The AE of 10.2 ± 0.1 eV for the RDA process (energy level 195 kcal/mol) indicates no reverse E_0 as would be expected for this process.[18] The mass spectrum of 13[17] is almost identical to the mass spectrum of 10[8] and this would be expected if the fragmentation processes occur as shown in Scheme 5.

The formation of the m/z 57 ion which occurs in low abundance in the mass spectra of 10 and 13 is analogous to the formation of the m/z 41 ion in the mass spectrum of 1. The M-H_2O ion which was shown to result from elimination of the hydroxyl group and a hydrogen atom from the adjacent methylene group occurs to a minor extent in the mass spectrum of 10.[8] Its energy level of 159 kcal/mol (Scheme 6) is consistent with the formation of the lower energy ion 12 being the faster process.

There is very little evidence of the molecular ion of 3-cyclohexen-1-ol (19) rearranging to the radical cation of 10.[22] The relative abundances of the M-CH_3, M-CH_2=CH_2 and the M-H ions are 8, 8 and 0%, respectively, from ion 19[22] compared to 35, 100 and 32%, respectively, for these ions from

ion 10.[8] The structures and ΔH_f's of the intermediate and product ions similar to those for $10^{+\cdot}$ are given in Scheme 6. In this scheme intermediate

Scheme 6



ion 21 in the rearrangement to the radical cation of 10 via two successive 1,2-H shifts is higher in energy than the cleavage in 20. Thus, the rearrangement reaction would not be favorable and is reflected in the low abundance of the M-CH_3 ion.

The molecular ion of 19 is barely visible, suggestive of a lower energy process than the M-CH_3 ion formation. The M-H_2O ion is a base ion with its energy level of 159 kcal/mol lower than the energy of intermediate ions 20 and 21. If this process occurs as a 1,2 elimination, a reverse E_0 would be expected, analogous to the reverse E_0 of 9 kcal/mol for the 1,2 elimination of H_2O from cyclohexanol.[23] However, a reverse E_0 of this magnitude for the M-H_2O ion from $19^{+\cdot}$ would not require an E_0 for the forward process.

The other major process is the RDA reaction via ion 20. Although the charge is shown on the butadiene fragment in Scheme 6, some of the charge is on the vinyl alcohol fragment.[22] Also not shown in Scheme 6 is the

RDA+1 ion, m/z 55, which may arise from an intermediate 4-hexenal radical cation formed from ion 20. It is noted that ion 20 is the intermediate ion in the McLafferty rearrangement of 5-hexenal.[24]

Conclusions

Evidence is presented which indicates that the M-CH_3 ion in $1^{+\cdot}$ and $10^{+\cdot}$ occurs via the reversible rearrangement of $1^{+\cdot}$ to $8^{+\cdot}$ and $10^{+\cdot}$ to $15^{+\cdot}$. This rearrangement involves a 1,2-H shift in $1^{+\cdot}$ and $10^{+\cdot}$ supporting the proposal that symmetry-forbidden 1,3-sigmatropic H shifts occur in $1^{+\cdot}$ and $10^{+\cdot}$ via two successive 1,2-H shifts.

Experimental

The ionization energy (IE) of 10 was determined by the semi-logarithmic method[25] from data obtained on an AEI MS-12 mass spectrometer at low repeller voltage, ion accelerating voltage 5 kV and ion source temperature 150°. Acetone was used as the internal standard: IE 9.7 eV; AE (m/z 43) 10.3 eV.[26] For the AE values of the fragment ions, m/z 97, 83 and 70, the semi-logarithmic curves were adjusted as described previously.[16] An example of the AE's from the unadjusted semi-logarithmic curves of $10^{+\cdot}$ with acetone at I/I_{50} = 0.001 is as follows: from acetone, m/z 43, 11.2 ± 0.1 eV; from $10^{+\cdot}$, m/z 97, 10.7 ± 0.1 eV; m/z 83, 10.4 ± 0.1 eV; m/z 70, 11.0 ± 0.1 eV. The intensity of the m/z 43 ion from acetone at 50 eV was corrected for the intensity of the m/z 43 ion from $10^{+\cdot}$ at 50 eV.

Acknowledgment. We thank Sherri Ogden for technical assistance in the mass spectral measurements. The work described in this paper was sponsored, in part, by the director, Office of Energy Research, Office of

Basic Energy Sciences, Division of Chemical Sciences, of the U.S. Department of Energy under Contract No. W-7405-ENG-48.

Appendix

The group additivity procedure[27] was used to calculate the ΔH_f's of the neutral molecules and radicals when no experimental values[28] were available. The ΔH_f's of 34.9 kcal/mol for ·CH3[29] and 39.1 kcal/mol for $CH_2{=}CHCH_2\cdot$[30] were recently determined. The group additivity value of 36.7 kcal/mol for $\cdot C\text{-}(C)(H)_2$ was derived from the ΔH_f of $\cdot C_2H_5$[27] and 41.0 kcal/mol for $\cdot C(C)_3$ was derived from the ΔH_f of $\cdot C\text{-}(CH_3)_3$.[31] The value of 31.4 kcal/mol for $\cdot C\text{-}(C)_2O$ was estimated to be the same as for $\cdot C\text{-}(C)(O)(H)$.[27] The value of 22.4 kcal/mol for $\cdot C\text{-}(C_d)(O)(H)$ was derived from an estimated bond dissociation energy of 81 kcal/mol for the α-CH bond in $CH_2{=}CHCH_2OH$. The value for $\cdot C\text{-}(C)(C_d)(O)$ was estimated to be ∿20.0 kcal/mol. The value of -46.2 kcal/mol for $O\text{-}(C_d)(H)$ was derived from the ΔH_f of -39.7 kcal/mol for the enol of acetone.[32] The value of -5.6 kcal/mol for $C\text{-}(C)(C_d)(O)(H)$ was estimated previously.[1] The ring correction for a radical which is part of a ring was assumed to be the average of the saturated and unsaturated ring correction values.[27]

Many of the IE's of the radicals in the schemes were derived or extrapolated from experimental ΔH_f's of cations determined from proton affinity (PA) values. These ΔH_f's were based on a comprehensive PA scale[33] adjusted to a ΔH_f of 162.1 kcal/mol for the t-butyl cation.[34] The PA's of propenal and 2-butenal[35] when adjusted as above gave ΔH_f's of 151.1 kcal/mol for $H_2C{=}CHC^+HOH$ and 136.3 kcal/mol for $CH_3CH{=}CHC^+HOH$.[16]

The adjusted PA's of cyclopentadiene and 1,3-pentadiene[33] gave IE's of 6.8 and 6.85 eV, respectively, for the corresponding radicals.

These values are 0.2 eV lower than the measured IE's for these radicals.[36,6] Thus, the IE for $CH_2{=}CH\dot{C}HC_2H_5$ was estimated to be 7.1 eV, 0.2 eV less than the measured value.[6] The adiabatic IE's of the cyclohexyl and cyclopentyl radicals may be less than the reported IE's[36,37] by the amount that the IE of isopropyl from the adjusted PA of propene[33] is less than the reported IE.[38] This correction would give values of 7.0 and 7.1 eV, respectively, for the IE's of cyclohexyl and cyclopentyl radicals. These values are similar to the values derived from the recently determined PA's of cyclohexene and cyclopentene.[14]

The destabilizing effect of a hydroxyl group on an alkyl cation when not on the carbon atom holding the charge has been found to be ~0.1 eV.[39] Thus, the IE of 2-cyclopenten-1-yl when substituted by a hydroxyl group other than in the 1-position was estimated to be 6.9 eV. With the hydroxyl group in the 2- or 3- position, the ΔH_f of the cation was estimated to be 153 kcal/mol and in the 4- or 5- position, 158-9 kcal/mol.

The IE's of 1-hydroxy-2-cyclopenten-1-yl, 1-hydroxy-2-methyl-2-cyclopenten-1-yl and 1-hydroxy-3-cyclohexen-1-yl were estimated to be 6.0 eV, similar to the IE of 1-hydroxycyclopentyl obtained from the adjusted PA of cyclopentanone.[33]

The IE's of allyl, butadiene and 1,3-cyclohexadiene have been found to be 8.1,[40] 9.05 [41,42] and 8.3 eV,[41,42] respectively. The ΔH_f of 2-hydroxybutadiene$^{+\cdot}$ has been determined to be 182 kcal/mol and the ΔH_f of 1-hydroxybutadiene$^{+\cdot}$ estimated to be 176 kcal/mol.[20]

The ΔH_f's of ions 1, 5, 7 and 8 have been reported.[7] The IE of 9.2 eV for 2-cyclohexen-1-ol (10) was determined (Experimental). Estimated IE's of the neutral molecules and biradicals corresponding to the other

ions in the schemes are given as follows:

2, 7.1 eV, same as the IE of $CH_2{=}CH\dot{C}HC_2H_5$ (see above);

3, 7.1 eV, same as the IE of cyclopentyl (see above);

4, 7.0 eV, same as the IE of cyclohexyl (see above);

6, 6.85 eV, same as the IE of $CH_3CH{=}CH\dot{C}HCH_3$;[33]

9, 6.5 eV, same as the IE of 1-methylcyclopentyl;[33]

11, 6.3 eV, same as the IE of $CH_3CH{=}CH\dot{C}HOH$ (see above);

12, 6.0 eV, same as the IE of 1-hydroxycyclopentyl;[33]

13, 8.2 eV, same as the IE of 2-hydroxy-2-butene;[43]

14, 6.0 eV, 0.15 eV less than the IE of $(CH_3)_2\dot{C}HOH$;[33]

15, 8.4 eV, 0.9 eV less than the IE of 8 by the same amount that the IE (9.6 eV) of cyclopentanol[44] is less than the IE (10.5 eV) of cyclopentane;[45]

16, 6.0 eV (see ion 12);

17, 8.2 eV, 0.1 eV less than the IE of 2,3-dimethyl-2-butene;[46]

18, 6.0 eV (see ion 12);

19, 9.2 eV, same as the IE of 10;

20, 6.4 eV, same as the IE of $CH_3(CH_2)_3\dot{C}HOH$;[33]

21, 7.1 eV, 0.1 eV greater than the IE of the cyclohexyl radical due to the destabilization effect of the hydroxyl group on the cation (see above);

22, 8.8 eV, 0.2 eV greater than the IE of 1-methylcyclopentene[6] similar to the difference in IE's of 1 and 10.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Chemical Sciences of the U.S. Department of Energy under Contract No. W-7405-ENG-48.

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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