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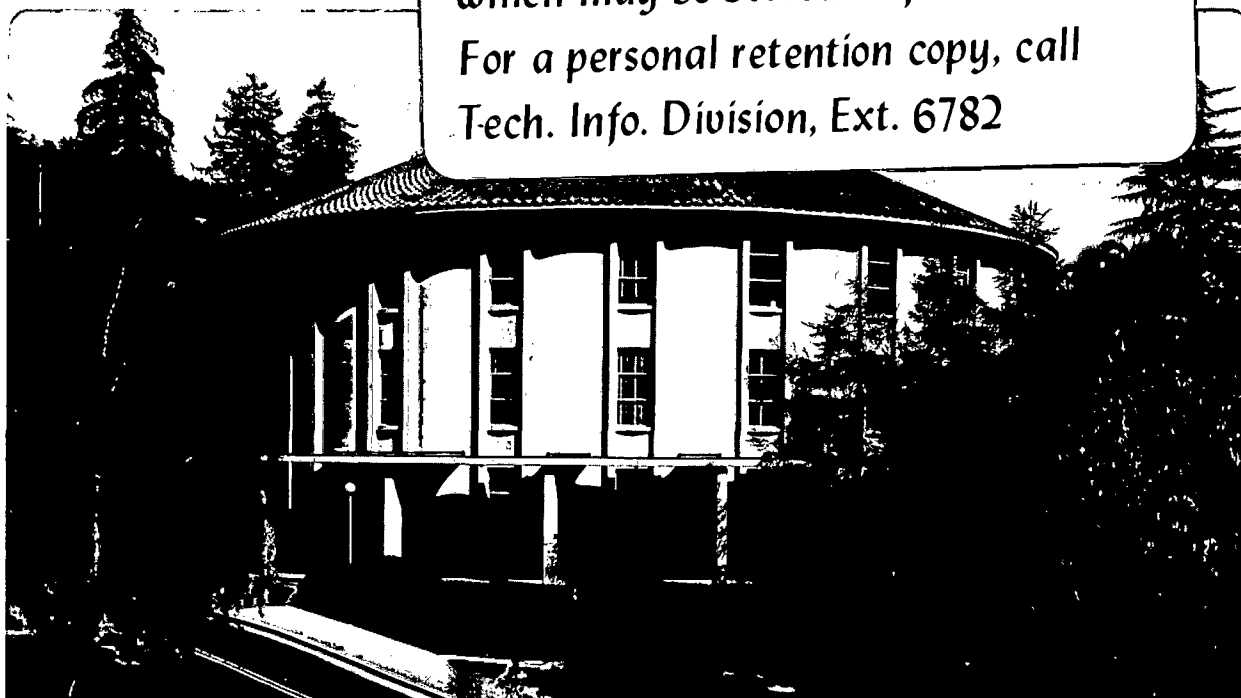
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June 1981

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CONFORMATIONAL DEPENDENCE IN THE MASS SPECTRUM
OF CYCLOHEXANECARBOXALDEHYDE. COMMENTS ON THE
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RADICAL CATIONS

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ABSTRACT: The mass spectrum of cyclohexanecarboxaldehyde (**1**) was shown to fit a composite of the mass spectra of the equatorial and axial conformers, utilizing experimental appearance energies and estimated energies of intermediate and product ions. Processes involving hydrogen abstraction by the oxygen atom as the initial step were attributed to the axial conformer because this step is favorable only in this conformer. Processes involving initial ring cleavage were attributed to the equatorial conformer. The lowest energy process was the formation of the M-H₂O ion from the axial conformer. In addition to the mechanisms of formation of the ions from **1**⁺, the mechanism of formation of the M-H₂O ion from hexanal⁺ and cyclohexanol⁺ was discussed.

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INTRODUCTION

The mass spectra of linear aliphatic aldehydes have been well investigated with major pathways being β -cleavage with hydrogen atom transfer (McLafferty rearrangement), β -cleavage with double hydrogen transfer, $M-CH_2=CH_2$ and $M-H_2O$.^{1,4} The initial step in these processes was considered to be hydrogen abstraction by the non-bonding electron on the carbonyl oxygen atom of the molecular ion. α -Cleavage was important only in the 2-substituted alkanals.²

The dependence of mass spectral fragmentation patterns on stereoisomerism was observed early in the study of organic mass spectrometry.⁵ To explain this dependence the removal of an electron to furnish the relaxed ionized state was assumed to have little effect on the overall arrangements of the atoms and that the fragmentations were controlled by both spatial relationships and energy considerations.⁵

Elie¹ has stated that the reactions of a mono-substituted cyclohexane should be considered as the discrete reaction of its equatorial and axial conformers.⁶ Thus the mass spectrum may be considered as a composite of the mass spectra of the equatorial and axial conformers.

Rej, Bacon and Eadon have studied the electron impact induced McLafferty rearrangement of a series of cyclohexylacetates and diethyl cyclohexylmalonates.⁷ From their results they proposed that γ -hydrogen abstraction was faster than chair \rightarrow chair interconversion.⁷ This proposal is in accord with the energetics of the McLafferty rearrangement in propyl-

acetates where the experimental and calculated appearance energy was equal to the ionization energy.⁸ There was no need for internal excitation of the molecular ion, in agreement with the extremely low relative abundance of the molecular ion.⁸ In contrast, an activation energy would be expected for the chair to chair interconversion in the molecular ions of the cyclohexylacetates.

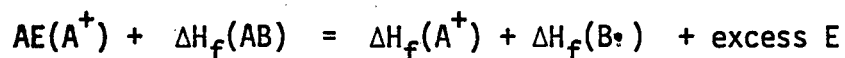
In this study, the fragmentation processes of cyclohexanecarboxaldehyde (1) were found to^{be} dependent on the initial stereochemistry of the aldehyde with only the axial conformer having the required geometry for hydrogen atom abstraction in a 6-membered transition state by the non-bonding electron on the carbonyl oxygen atom. Extensive use was made of gas phase basicity data⁹ together with experimental appearance energies in elucidating the most probable fragmentation pathways.

RESULTS

Appearance energies (AE) of the primary ions of I^+ were measured and are given in Table I. For comparison, product ion energy levels were calculated from the ΔH_f 's of the most likely structures of the product ions and the neutral fragments together with alternative structures and are given in the table. The empirical structures of the product ions were confirmed by high resolution data.

←————— Processes in which metastable ions were observed are given in the Experimental section.

For simple cleavage reactions, the calculated product ion energy levels should be similar to the experimental energy levels as calculated from the AE values. However, the calculated product ion energy levels are based on adiabatic ion energies whereas the appearance energies give vertical ion energies.¹⁰ Thus, the experimental energy levels may be slightly greater than the calculated energy levels. For rearrangement



reactions, the excess energy may be larger and the reaction may show an appreciable reverse activation energy.¹¹ The kinetic shift should be small for activation energies up to ~ 1 eV.¹²

In Scheme 1 is given the most probable structures for the intermediate and primary fragment ions, together with the ΔH_f 's (kcal/mol) of the intermediate ions and the calculated product ion energy levels. Those ΔH_f 's which involve an estimate are shown in parentheses. (See Appendix for method of estimation for the intermediate ions in this scheme as well as the intermediate and product ions in the other schemes.)

TABLE I. The Relative Abundances and the Calculated and Experimental Energy Levels of the Fragment Ions of 1⁺.

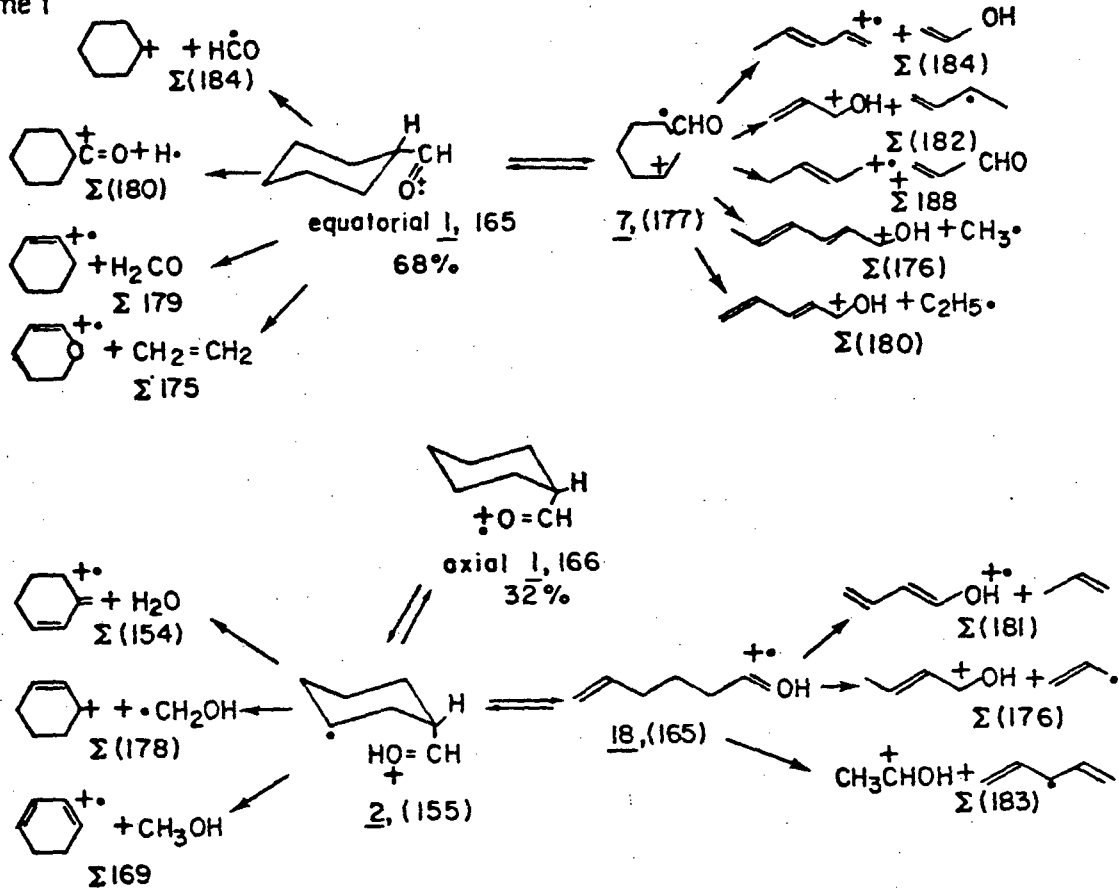
m/z	RA ^a (50eV)	Neutral fragment A	$\Delta H_f(298)$ A ^b kcal/mol	B ^c	$\Delta H_f(298)$ B ^{b,d} kcal/mol	IE B ^e eV	Calc.E ^f kcal/mol	Exp.E ^g kcal/mol	AE ^h eV
112	28	—	—	c-C ₆ H ₁₁ CHO	-56.2	9.6 ^h	—	165	9.6
94	31	H ₂ O	-57.8		19.0	8.4 ⁱ	154	158	9.7
		"	"	CH ₂ =CH(CH=CH) ₂ CH ₃	31.8	8.1 ^j	156		
80	2	CH ₃ OH	-48.0		25.9	8.3 ^{k,l}	169	—	(m)
		"	"	CH ₂ =CHCH=CHCH=CH ₂	39.6	8.3 ^j	182		
81	13	•CH ₂ OH	-6.1		30.0	6.7 ⁿ	178	189	10.6
		"	"	CH ₂ =CH•CH=CHCH ₃	40.4	6.7 ^p	188		
71	9	CH ₂ =CHCH ₂ •	39.1	CH ₃ CH=CH•CHOH	-8.4	6.3 ^q	176	181	10.3
		"	"	Δ •CHOH	9.4	6.4 ^r	196		
		"	"	CH ₃ CH ₂ •CHCHO	-11.4	7.5 ^s	200		
70	28	CH ₂ =CHCH ₃	4.9	CH ₂ =CHCH=CHOH	-17.7	8.4 ^u	181	184	10.4
		"	"	CH ₃ CH=CHCHO	-26.6	9.7	201		
45	3	CH ₂ =CH•CH=CH ₂	48.3	CH ₃ •CHOH	-16.6	6.6	183	184	10.4
68	41	CH ₂ =CHOH	-31.3	CH ₃ CH=CHCH=CH ₂	18.3	8.6 ⁱ	184	181	10.3
		CH ₃ CHO	-39.7	"	"	"	176		
84	6	CH ₂ =CH ₂	12.5		-29.9	8.35	175	—	(m)
		"	"	CH ₃ CH=CHCH ₂ CHO	-25.8	9.3 ^v	201		
56	10	CH ₂ =CHCHO	-18.8	CH ₃ CH=CHCH ₃	-2.7	9.1	188	188	10.6
97	5	CH ₃ •	34.9	CH ₃ (CH=CH) ₂ •CHOH	5.2	5.9 ^w	176	181	10.3
		"	"	CH ₃ CH=CH•(OH)CH=CH ₂	0.9	6.2 ^x	178		
		"	"		-12.3	6.0 ^y	161		
		"	"	CH ₂ =C(OH)C(CH ₃) ₂	-10.7	6.9 ^z	183		
57	14	CH ₂ =CH•CHCH ₃	30.3	CH ₂ =CH•CHOH	-0.6	6.6 ^{aa}	182	188	10.6
		"	"	CH ₃ •CHCHO	-6.4	7.6 ^t	199		
		CH ₂ =CHCH ₂ CH ₂ •	46.8	CH ₂ =CH•CHOH	-0.6	6.6 ^{aa}	198		
82	4	H ₂ CO	-26.0		-0.8	8.95 ⁱ	179	188	10.6
83	68	H•	9.0		13.9	7.0	184	188	10.6
	3	CH ₃ CH ₂ •	26.5	CH ₂ =CHCH=CH•CHOH	13.2	6.1 ^{bb}	180	—	—
111	1	H•	52.1		-22.1	6.5 ^{cc}	180	—	(m)
		"	"		-2.7	6.4 ^r	197		

FOOTNOTES TO TABLE I

- a Relative abundance (RA) at 50 eV corrected for isotope abundance.
See Experimental Section for the RA of other ions.
- b See Appendix for detail.
- c Fragment which carries the charge.
- d Not ionized.
- e Franklin, J. L.; Dillard, J. G.; Rosenstock, H. M.; Herron, J. T.;
Draxl K. Nat. Stand. Ref. Data Ser., Nat. Bur. Stand., NSRDS-
NBS 26, 1969 or see Appendix unless otherwise noted.
- f $\Delta H_f^{\circ}(g, 298)(A) + \Delta H_f^{\circ}(g, 298)(B) + IE(B)$.
- g AE (this work) + $\Delta H_f^{\circ}(g, 298)$ (precursor molecule). The ΔH_f° of
the axial form of 1 is -55.2 kcal/mol.¹³
- h ± 0.1 eV (this work).
- i Estimated to be 0.1 eV less than the IE of 2-methyl-1,3-
pentadiene.⁶⁷
- j Ref. 68.
- k Ref. 67.
- l Ref. 60 and Bischoff, P.; Heilbronner, E. Helv. Chim. Acta, 1970, 53, 1677.
- m RA too low.
- n Estimated to be 0.1 eV less than IE of 2-cyclopenten-1-yl.⁰ The
IE of cyclohexyl is 0.1 eV less than the IE of cyclopentyl.^{61,63}
- o See Appendix for estimation from the adjusted PA value of cyclo-
pentadiene.
- p Estimated to be 0.35 eV less than the IE for $CH_2=CH\dot{C}HCH=CH_2$
(see Appendix), the same amount that the IE of $CH_3\dot{C}HCH=CHCH_3$ ⁹ is
less than the IE of $CH_3\dot{C}HCH=CH_2$.⁹
- q See Appendix for estimation from the adjusted PA value of
2-butenal.

- r Estimated to be the same as the IE of $C_2H_5\dot{C}HOH$ ⁹ (see Appendix).
- s Estimated to be 0.1 eV less than the IE of $CH_3\dot{C}HCHO$.^t
- t Estimated to be higher than the IE of $CH_3\dot{C}HCH_3$ (see Appendix) by the amount (0.4 eV) that the IE of propenal is higher than the IE of propene.^e
- u Estimated to be 0.2 eV less than the IE of 1,3-pentadiene^j and 0.4 eV more than the IE of 1-methoxy-1,3-butadiene, 8.0 eV, (Sustmann, R.; Schubert, R. Tetrahedron Lett. 1972, 2739) similar to the IE of vinyl alcohol, 9.25 eV^{11b}, in relation to the IE of propene, 9.7 eV,^e and methylvinyl ether, 8.6 eV.¹⁵
- v Estimated to be intermediate between the IE of 2-pentene, 8.9 eV, (Lossing, F.P. Canad. J. Chem. 1972, 50, 3973) and pentanal, 9.7 eV.³⁴
- w Estimated to be 0.4 eV less than the IE of $CH_3CH=CH\dot{C}HOH$.⁹
- x Estimated to be 0.1 eV less than the IE of $CH_3CH=CH\dot{C}HOH$.⁹
- y Estimated to be the same as the IE of 1-hydroxycyclopentyl obtained from the adjusted PA of cyclopentanone.⁹ (see Appendix).
- z Estimated to be the same as the IE of $CH_2=CH\dot{C}(CH_3)_2$ (see Appendix).
- aa See Appendix for estimation from the adjusted PA value of propenal.
- bb Estimated to be 0.2 eV less than the IE of $CH_3CH=CH\dot{C}HOH$.⁹
- cc Estimated to be 0.1 eV less than the IE of $CH_3CH_2\dot{C}=O$.^e

Scheme 1



XBL 8011-2608A

It is possible that some fragment ions are formed by more than one mechanism and have different structures with different product ion energy levels. The AE values in these cases would be the AE value for the lowest activation energy (E_0) process. However, in order for there to be a significant contribution from a higher E_0 process to the abundance of an ion, the frequency factor for that process would have to be higher than for the lower E_0 process.¹¹

DISCUSSION

The equatorial conformation of $\underline{1}$ is more stable than the axial conformation; $-\Delta G_{298}^0 = 0.7$ kcal/mol for $\underline{1}$ in CD_2Cl_2 .¹³ At 150° , the ion source temperature, the equilibrium conformation of $\underline{1}$, was calculated to be 68% equatorial: 32% axial.¹³

For hydrogen abstraction to occur in linear aldehydes the allowable distance has been found to be 1.8 \AA or less between the hydrogen and the oxygen atoms.⁵ This distance is attainable in $\underline{1}$ in the axial conformer. The E_0 for the hydrogen abstraction in this conformer must be very low because the E_0 for the $M-H_2O$ process from $\underline{1}^+$ is only 0.1 eV (Table I). This E_0 is consistent with the low E_0 found for the hydrogen abstraction in the propylacetates.⁸ As shown in Scheme 1, the ΔH_f of the intermediate ion $\underline{2}$ formed by the initial hydrogen abstraction step is lower than the ΔH_f of the precursor molecular ion.

The molecular ion abundance due to the axial form would be expected to be low as is the molecular ion abundance in the acetates⁸ and the linear aldehydes.^{1,2} However, the molecular ion abundance is moderate in $\underline{1}^+$ (Table I) indicating the presence

of an isomer which is relatively stable to fragmentation. The equatorial conformer of $\underline{1}^+$ as shown in Scheme 1 fragments by higher energy processes than the axial conformer. Thus, the major part of the molecular ion abundance appears to consist of the equatorial conformer or isomeric ions derived from the equatorial conformer.

For an estimation of the percentage of the ion abundances due to the equatorial and axial isomers, those ions which are shown in Scheme 1 as derived from the equatorial conformer may also, in part, be derived from the axial isomer. The ion at 50 eV most likely to have a contribution from the unrearranged axial conformer is the abundant α -cleavage ion, M-HCO. We have assumed that the cyclohexyl cation is the initial structure of the M-HCO ion. However, there is evidence that this cation spontaneously rearranges to the 1-methylcyclopentyl cation.¹⁴ In competition with the M-HCO ion from the axial conformer are a number of lower energy pathways from the rearranged axial conformer so that the abundance of the M-HCO ion from axial $\underline{1}^+$ should be less than the abundance based on the percentage of the axial conformer in $\underline{1}^+$. If 10% of the M-HCO ion abundance is considered to be from the axial conformer, an estimation of the sum of the ion abundances above m/z 38, including secondary ions for the two conformers, gives a proportion of 67% equatorial:33% axial at 50 eV in agreement with the proportion of the conformers in $\underline{1}$ before ionization. Also, at low voltages as shown in Table II the sum of the ion abundances attributed to the equatorial isomer is ~60% of the total ion abundances with all of the molecular ion abundance considered to be in the equatorial conformation.

TABLE II. ABUNDANCES OF IONS
from 1 AT LOW VOLTAGES.

m/z	Abundances			
	9.5 eV ^a	10 eV ^a	10.5 eV ^a	11.0 eV ^a
112	10	60	238	595
94	6	41	185	475
68		6	39	170
70			9	44
71			9	34
83			5	34
97			5	18
82				2
45				5
81				6
56				4
57				6
% equatorial ^b	62	62	59	60

a Nominal voltage

b Sum of abundances of m/z 112, 68, 83, 97, 82, 56 and 57 as percent of abundances of all the ions listed.

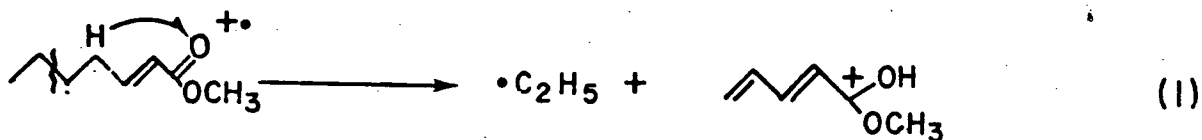
Primary Ions from Equatorial 1^{\ddagger}

The AE for the m/z 68 ion from 1^{\ddagger} indicates either or both M-CH₃CHO and M-CH₂=CHOH because there is only ~8 kcal/mol difference in the ΔH_f 's of the neutral compounds eliminated (Table I and Appendix). The ΔH_f of the 1,3-pentadiene radical cation is similar to the ΔH_f of the cyclopentene radical cation (Table I). There was little M-68 ion and this would be expected because the IE's of the neutral molecules, acetaldehyde, 10.2 eV and vinylalcohol, 9.25 eV (Appendix) are higher than the IE's of 1,3-pentadiene, 8.6 eV, and cyclopentene, 9.0 eV (Table I). The m/z 68 ion in the mass spectrum of cyclohexanecarboxylic acid^{3b} is of considerably greater abundance than the abundance of the M-68 ion whereas the opposite is true for the methyl ester of the acid.^{3b} This difference can be explained if the m/z 68 ion is the 1,3-pentadiene radical cation and the neutral molecule eliminated is CH₂=C(OH)₂ from the acid and CH₂=C(OH)(OCH₃) from the methyl ester. The IE of CH₂=C(OH)₂ is estimated to be 8.8 eV, higher than the IE of 1,3-pentadiene and the IE of CH₂=C(OH)(OCH₃) is estimated to be 8.4 eV, lower

than the IE of 1,3-pentadiene.¹⁵ Thus, the most probable structure for the m/z 68 ion from $\underline{1}^{\dagger}$ is the 1,3-pentadiene radical cation and the neutral molecule eliminated is vinylalcohol. However, the AE for the m/z 68 ion is clearly 0.1 - 0.2 eV lower than the AE of the m/z 70 ion, indicating the formation of acetaldehyde as the neutral molecule eliminated.

The m/z 68 ion should be a major ion from 5-heptenal because it is the base ion in the mass spectrum of 5-heptenoic acid¹⁹ and the comparable ion is the base ion in the mass spectrum of 5-hexenal.²⁰ If equatorial $\underline{1}^{\dagger}$ undergoes ring opening and isomerization to the 5-heptenal radical cation, ΔH_f 172 kcal/mol (Appendix), the m/z 68 ion should be the resultant product ion.

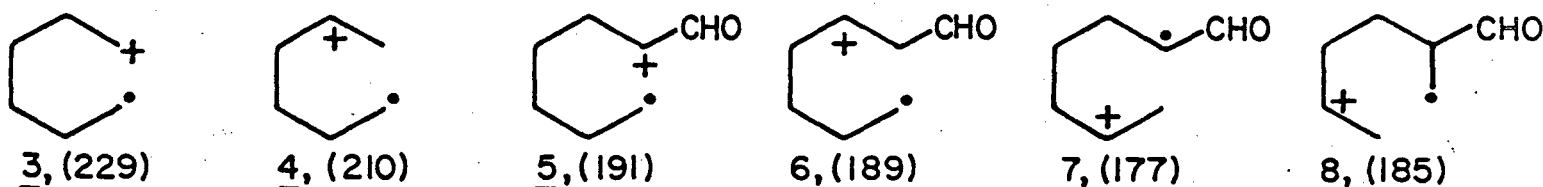
Recently, the molecular ion of cyclohexanecarboxylic acid methyl ester was shown to have a considerable barrier to ring opening to give either the α,β -unsaturated ester or the terminally unsaturated ester.²¹ However, the M-C₂H₅ ion from the cyclic ester could be derived from the α,β -unsaturated isomer (Eq.1).



Their data would allow for the possibility of the partial isomerization to this isomer. An alternative isomer, methyl 5-heptenoate which is known to give the m/z 68 and the M-68 ions,^{3b,c} was not investigated.

The $M-C_2H_5$ ion from $\underline{1}^{\ddagger}$ is of very low abundance by high resolution spectroscopy indicating little isomerization to the α,β -unsaturated isomer which has the $M-C_2H_5$ ion as a major ion.²²

The appearance energies for the fragment ions of cyclohexane have been measured²³ and indicate that the initial ring opening reaction of cyclohexane gives ion $\underline{4}$ ²⁴ rather than ion $\underline{3}$, involving a concerted 1,2-hydride shift during ring opening. The 1,2-hydride shift is considered to require little additional activation energy.²⁴ The AE for the base ion, m/z 56, gives a product ion energy level of 225 kcal/mol



which makes ion $\underline{3}$ unlikely as an intermediate ion. From its AE the m/z 56 ion has the 2-butene structure with a calculated product ion energy level of 219 kcal/mol. The $M-C_2H_5$ ion from cyclohexane presumably results from partial isomerization of the molecular ion of cyclohexane to the 2-hexene radical cation via ion $\underline{4}$.

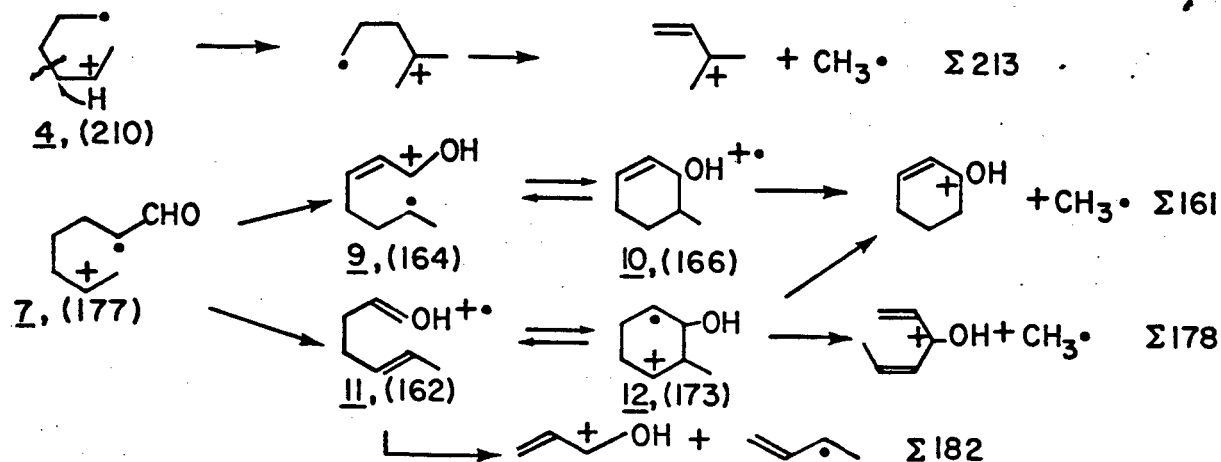
The ring opened structures from $\underline{1}^{\ddagger}$ analogous to ions $\underline{3}$ and $\underline{4}$ from cyclohexane are ions $\underline{5}$, $\underline{6}$, $\underline{7}$ and $\underline{8}$. Of these ions, ion $\underline{7}$ has the lowest energy and could partially isomerize to the 5-heptenal radical cation analogous to the partial isomerization of ion $\underline{4}$ to the 2-hexene radical cation. The McLafferty rearrangement would give the m/z 68 ion with vinylalcohol as the neutral molecule whereas a 1,3-allylic hydrogen shift with cleavage (see discussion below for the $M-H_2CO$ process) would give acetaldehyde as the neutral molecule.

Cleavage of ion 7 similar to the cleavage of ion 4 to give the m/z 56 ion occurs to a limited extent giving the m/z 56 ion. Cleavage of ion 6 analogous to the cleavage of ion 4 would give the m/z 84 ion. However, the product ion energy level for this reaction is 201 kcal/mol. A

faster reaction would be cleavage of ion 5 to give the 3,4-dihydropyran radical cation. The $M-CH_2=CH_2$ ion is of low abundance in the mass spectra of cyclohexanecarboxylic acid^{3b} and its methyl ester^{3b} although the m/z 56 ion is of moderate abundance in the mass spectrum of the acid.

The AE for the $M-CH_3$ ion from 1[†] indicates that this ion could arise from the intermediate isomer, 2-heptenal. However, the abundance of the $M-CH_3$ ion from cyclohexane and from the metastable and collision activation spectra of cyclohexanecarboxylic acid methyl ester²¹ indicates that this ion arises from another pathway in addition to being formed from the intermediate isomers, 2-hexene and methyl 2-heptenoate. The $M-CH_3$ ion from cyclohexane has been proposed to be $CH_2=CH\dot{C}(CH_3)_2$.^{24a} An analogous ion from 1[†] without hydrogen abstraction by the carbonyl group gives a product ion energy level greater than the experimental energy level (Table I). Thus hydrogen abstraction by the carbonyl group appears to be involved. A mechanism via ions 11 and 12 (Scheme 2) somewhat analogous to the mechanism for the $M-CH_3$ ion from cyclohexane gives an ion with a ΔH_f consistent with the AE for the process. Alternatively, the cyclic $M-CH_3$ ion may be formed, involving a 1,2-H shift in ion 12.

The cyclic ion may also be formed via ions 9 and 10. Formation of ion 9 from ion 7 involves a five membered transition state for the Scheme 2



hydrogen abstraction ^{process} /whereas the formation of ion 11 involves a seven membered transition state.²⁵ In both cases, the hydrogen atom abstracted is allylic. The 1,6-H abstraction process would be a faster process than the 1,4-H abstraction process which has a higher ^{energy} /and tighter transition state than the 1,6-H abstraction process (Scheme 2). The mass spectrum of ion 10 is known to give the M-CH₃ ion from loss of the substituent in 33% abundance with the base ion, m/z 70, from the retro Diels-Alder (RDA) reaction.²⁶ The abundance of the M-CH₃ ion from 11⁺ is low and if the process occurs via ions 9 and 10, the m/z 70 ion from 11⁺ may be expected to result in part from ion 9. However, a

faster process for the m/z 70 ion from axial 1^{\ddagger} is shown in Scheme 5 (see below).

Simple cleavage of ion 11 gives the M-55 ion. This process would be expected to have a much higher frequency factor than the M-CH₃ process and this is reflected in the abundances of the two ions. The M-55 ion is the base ion in the normal mass spectrum^{3b,c} and the collision activation spectrum²¹ of cyclohexanecarboxylic acid methyl ester whereas in the mass spectrum of 1, it is of much lower abundance.

The M-H₂CO process from 1^{\ddagger} is presumably a 1,2 elimination from the intact ring and occurs with a reverse E_0 of ~ 5 kcal/mol when compared to the energy level for the M-HCO straight cleavage process which should not have a reverse E_0 . A 1,2-M-H₂O process from cyclohexanol⁺ occurs from the intact ring with an E_0 of ~ 7 and reverse E_0 of ~ 9 kcal/mol.²⁷ The moderately abundant M-C₂H₆ ion from ethylcyclohexane was shown by field ionization studies to be also from the intact ring.²⁸ Recently, the 1,2 elimination of methane from 2-methylpropane⁺ was shown to be a non-concerted elimination.^{29a} The evidence presented indicated that the hydrogen transfer to the carbon atom to be eliminated was already complete in the transition state. Thus, the 1,2 elimination can be considered to be a 1,3-H shift with cleavage. The reverse E_0 for this process was ~ 4 kcal/mol,^{29b} which may be expected from the distortion energy necessary for the process to occur.³⁰

The α -cleavage process leading to the M-HCO ion was briefly discussed above. The other α -cleavage process leading to the M-H ion is of very low abundance although the energy level appears to be lower than for the M-CHO process. This would indicate a much lower frequency factor for the M-H process. Discrimination against the M-H process has been noted by Bowen and Williams in other systems.²⁴

The acetaldehyde molecular ion also undergoes α -cleavage to give the M-CH₃ ion in greater abundance than the M-H ion at 70 eV although the AE for the M-H ion is 1.1 eV less than for the M-CH₃ ion.³¹

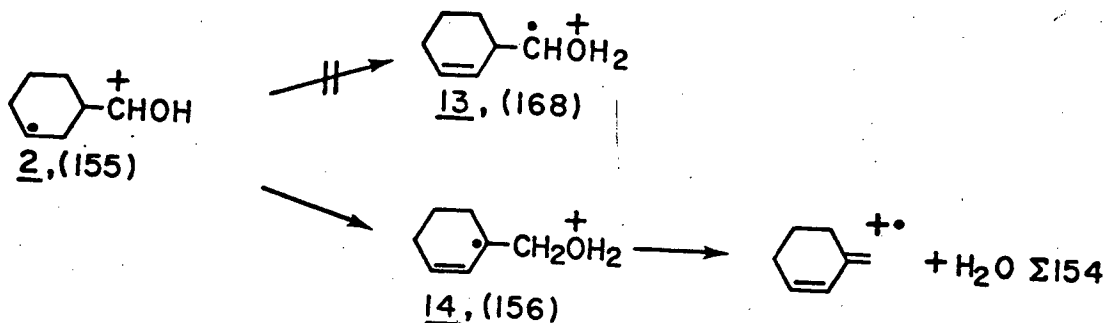
A molecular orbital study of the α -cleavage process from the acetaldehyde molecular ion showed that the α -cleavage process is the result of intramolecular energy transfer through intramolecular charge transfer from the initially formed radical cation where the electron removed is one of the lone pair electrons on the oxygen atom.³² The excess vibrational energy is transferred to the C-C stretching mode more effectively than to the C-H stretching mode, thus contributing to the discrimination against C-H bond cleavage.³²

As discussed above, the molecular ion of equatorial 1 appears to ring cleave in preference to interconversion to the axial form where the geometry is favorable for hydrogen abstraction. The barrier to the equatorial to axial conformation change in neutral cyclohexane is ~ 11 kcal/mol⁶ and thus the barrier to the interconversion in the molecular ion of 1 would be expected to be of similar magnitude if the IE of 1 does not change during the interconversion. The formation of ion 7 from equatorial 1⁺ would require an E₀ of 12 kcal/mol. The calculated ΔH_f of ion 7 may be high if the IE of the corresponding biradical is less than estimated. However, the frequency factor for ring cleavage would be expected to be greater than for the equatorial to axial interconversion of 1⁺, thus facilitating ring cleavage over ring interconversion.

Primary Ions from Axial 1⁺.

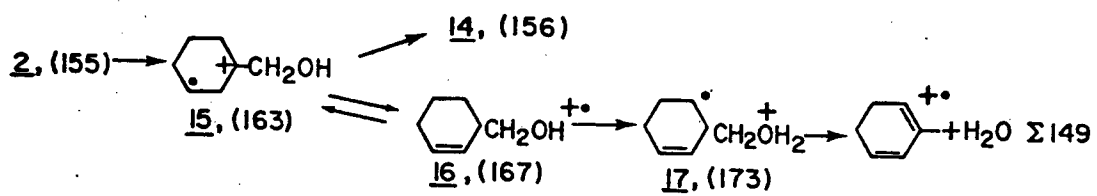
The AE for the M-H₂O ion indicates that the hydrogen abstraction process in axial 1⁺ to form ion 2 requires very little energy and also that the transition state energy for the M-H₂O process from ion 2 is of low energy. If the reaction were to proceed analogous to the mechanism proposed for the M-H₂O ion from n-hexanal molecular ion,¹ the intermediate ion 13 would be of similar energy to the experimental energy level. An alternative intermediate ion 14 which has 12 kcal/mol lower energy could be formed from ion 2 via two concerted hydrogen shifts, a 1,4-H shift to the oxygen atom and a 1,2-H shift of the tertiary hydrogen atom (Scheme 3). A simple cleavage then would give the M-H₂O ion.

Scheme 3



Stepwise formation of ion 14 from ion 2 would involve intermediate ion 15 which has a ΔH_f greater than the ΔH_f of ion 14 but less than the ΔH_f of ion 13 (Scheme 4). Instead of the 1,4-H shift to the

Scheme 4



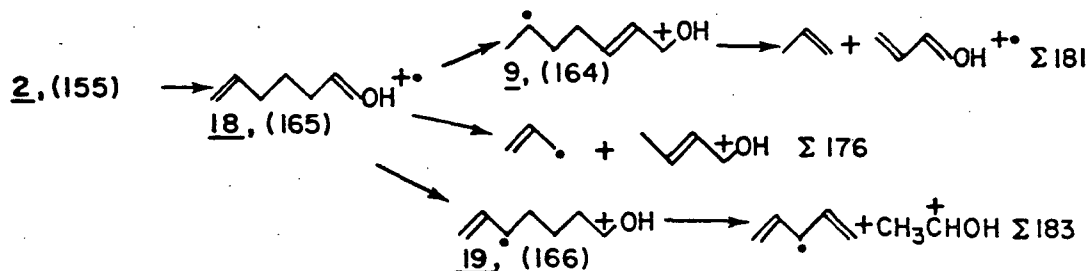
oxygen atom in ion 15 to form ion 14, a 1,2-H shift in the ring would give ion 16. However, this latter process is endothermic whereas the former process is exothermic and the M-H₂O process via ions 16 and 17 requires a transition state energy 5 kcal/mol greater than the experimental energy level.

Ion 16 would also be expected to undergo simple cleavage to give the M-CH₂OH ion. However, the M-CH₂OH ion occurs in 1⁺ with a reverse E₀ similar to that of the M-H₂CO ion, indicative of a 1,3-H shift with cleavage process. This process could occur directly from ion 2. A similar kind of 1,3-H shift with cleavage process has been proposed for the fast elimination of CH₃· from the intermediate ion in the field ionization mass spectrum of cyclohexene-3,3,6,6-d₄.³⁵

Whereas the M-H₂O and M-CH₂OH processes from 1⁺ can proceed via pathways other than via ion 16, the most probable process for the M-CH₃OH ion does involve ion 16. However, the M-CH₃OH ion is of very low abundance in 1⁺.

Ring opening of ion 2 to give ion 18 (Scheme 5) is a process slightly greater in energy than the formation of ion 15 and less than the energy of

Scheme 5

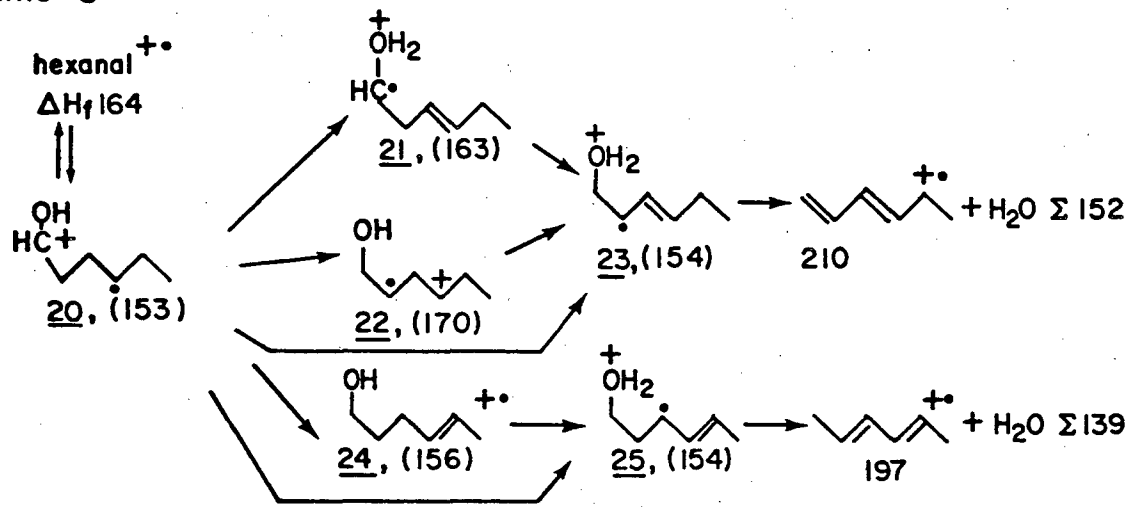


ion 16. A 1,5-H shift in ion 18 gives ion 9 which should cleave to give the $M-C_3H_6$ ion. Cleavage of ion 18, together with a 1,2-H shift, would give the $M-C_3H_5$ ion which occurs in low abundance. A 1,4-H shift in ion 18 would give ion 19 which should give the m/z 45 ion by a mechanism similar to the mechanism proposed for the m/z 45 ion from hexanal.¹ The m/z 45 ion is of low abundance, indicating a low frequency factor for this process. The AE for the formation of the m/z 45 ion indicates that ion 19 does not arise via ion 5.

The $M-H_2O$ Process from Hexanal[†]

Because the $M-H_2O$ ion is not characteristic of the mass spectrum of n-pentanal² the $M-H_2O$ ion in the mass spectrum of n-hexanal may be the 2,4-hexadiene radical cation instead of the 1,3-hexadiene radical cation formed via ion 21¹ (Scheme 6). The intermediate ion would be ion 25 instead of ion 23 formed by H-shifts from C-3 and C-4 to the oxygen atom and a H-shift from C-5 instead of C-2¹ to the C-1 atom (Scheme 6). The 1,2-shift of a secondary H atom would be less favorable than the 1,5-shift of a secondary H atom. In n-pentanal, this 1,5-shift would be of a primary H atom which would be less likely to shift. Stepwise formation of ion 25 instead of concerted formation would involve intermediate ion 24, the 4-hexen-1-ol radical cation, which is known to give the $M-H_2O$ ion in high yield.³⁶ Stepwise formation of ion 23 via ion 21 involves a higher energy intermediate ion than ion 24 and formation of ion 22 should not occur because the $M-H_2O$ ion occurs without an activation energy.^{1b} Formation of the 2,4-hexadiene radical cation from ion 25 would involve a 1,2-H shift with cleavage. A similar kind of cleavage has been postulated in various protonated alcohols.³⁷

Scheme 6



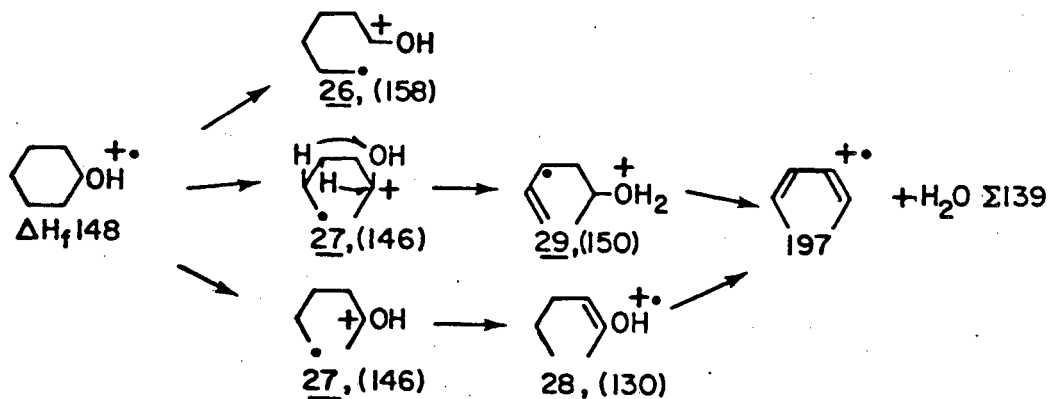
The 1,4-M-H₂O Process in Cyclohexanol[†]

One of the longstanding problems in mass spectrometry has been the M-H₂O process from cyclohexanol.³⁸ The transition state for the cis-1,4-elimination has been suggested to be the transition state to a boat form because this process shows stereospecificity in deuterated cyclohexanols and cis and trans 4-t-butyl cyclohexanol.^{38b, 38c} The IE of the cis-4-t-butyl cyclohexanol is less than 0.1 eV lower than the trans isomer.³⁹ Thus, the IE of the axial boat form of cyclohexanol would not be expected to be much less than the IE of the equatorial form. If the IE of the transition state is ~ 0.1 eV less, then the E₀ for the transition state from the equatorial form to the axial boat form may approximate the E_a of 11 kcal/mol for ring interconversion in cyclohexane⁶ less ~ 0.1 eV, giving an E₀ of $\sim 8-9$ kcal/mol. This is considerably higher than the measured E₀ of 0.2 eV for the 1,4 M-H₂O process.²⁷ The ΔH_f of the α -cleavage ion 25 (Scheme 7) indicates an E₀ of ~ 10 kcal/mol which is higher than the measured E₀ of 0.3 eV kcal/mol for the 1,2-elimination from the intact ring.²⁷

An alternative proposal for the stereospecific 1,4 M-H₂O process involves β -ring cleavage in which the ions with greater internal energy retain their stereospecificity. Metastable ions for this process have been shown to lose their stereospecificity and, therefore, must be of a low energy acyclic form.^{38b} Ion 27 is the result of β -cleavage with a 1,2-H shift and is of slightly lower energy than the molecular ion (Scheme 7). Ion 27 of low internal energy could give

ion 28 which would give nonstereospecific 1,4 elimination of H₂O. Ion 27 of higher internal energy could give ion 29 in which the hydrogen shifts

Scheme 7



are very rapid. The cis 4-H in equatorial cyclohexanol is closer to the oxygen atom than the trans 4-H so that in a fast 4-H shift to the oxygen atom, the cis 4-H shift could be preferred. Williams, *et al*⁴⁰ have shown that after extension of the bond to be broken in cations there can be incipient ion isomerization (e.g., 1,2-H shift) before final cleavage. A similar type of cleavage with isomerization has been shown to occur in molecular ions.^{24b,41} Thus, in the fast stereospecific 1,4 M-H₂O process, as the β-bond lengthens and the hydride ion shifts from the 1-position to the 2-position, the ring becomes more flexible in this region, allowing the OH group to rotate toward the cis 4-H atom. As the 1,5- H shift to the oxygen atom occurs above the ring, the 1,3-H shift to the carbon atom with the OH group occurs below the ring. Recently, a 1,3-hydride shift from a secondary carbon atom has been shown not to require an E₀ other than the difference in the enthalpy of the ions involved.^{37a,42} Field ionization studies of cis and trans 4-deuterocyclohexanol have shown that the cis-elimination is a faster process than the trans-elimination and the curves for the elimination are consistent with the formation of an intermediate ion.²⁷

Experimental

Secondary ions from $\underline{1}^+$ which are not given in Table I are: m/z (rel.int.); 79(24), 77(4), 69(9), 67(14), 66(7), 55(100), 53(8), 43(7), 41(42), 39(20). For the estimation of the percent of the ion abundances at 50 eV due to the equatorial conformer, the abundances of the following secondary ions were attributed to the equatorial conformer: m/z 67; 90% of m/z 55, 41, 39.

Metastable ions were observed for the following primary and secondary processes in $\underline{1}^+$: M-18, M-28, 94 \rightarrow 79, 83 \rightarrow 55, 82 \rightarrow 67, 81 \rightarrow 55.

High resolution measurements (CEC 21-110 mass spectrometer) on m/z 84, 83, 82, 81, 80, 79 (C_6H_7), 71, 70, 68, 57, 56 from $\underline{1}^+$ indicated the empirical structures given for the ions in Table I.

The ionization energy of $\underline{1}$ was determined by the semilogarithmic method⁴³ from data obtained on a duPont 21-491/492 double focussing mass spectrometer at low repeller voltage, ion accelerating voltage 2 kV, and ion source temperature 150⁰. Acetone was used as the internal standard; IE, 9.7 eV; AE (m/z 43) 10.3 eV.⁴⁴ For the AE values

of the fragment ions given in Table I, the semilogarithmic curves were adjusted in the following way. A curve (A) was drawn on the semilogarithmic plot exactly parallel to the curve of the molecular ion of the acetone internal standard from $\frac{I}{I_{50}} = 0.0002$ to 0.1 (I = intensity at low nominal voltage, I_{50} = intensity at 50 ev) with a voltage difference equal to the known value of the AE-IE of the m/z 43 ion of acetone. The experimental curve gave a greater AE-IE value. The vertical distances in arbitrary units (nonlogarithmic) from the experimental curve (E) of the m/z 43 ion of acetone to curve A were determined at intervals between $\frac{I}{I_{50}} = 0.0004$ on curve E to $\frac{I}{I_{50}} = 0.1$ on curve A. The experimental fragment ion curves EU of unknown AE were then made parallel (AU) to their molecular ion curve from $\frac{I}{I_{50}} = 0.0004$ to 0.1 such that the vertical distances from curve EU to curve AU at various $\frac{I}{I_{50}}$ values on curve EU were exactly proportional to the vertical distances from curve E to curve A at the same $\frac{I}{I_{50}}$ values on curve E of the acetone internal standard.

An example of the AE's from the unadjusted semilogarithmic curves of I^+ with acetone as internal standard at $\frac{I}{I_{50}} = 0.001$ is as follows: from acetone, m/z 43, 10.9 ev; from I^+ , m/z 94, 9.75 ev; m/z 68, 71, 97, 10.4 ev; m/z 45, 70, 10.6 ev; m/z 56, 57, 81, 82, 83, 11.0 ev. The accuracy of the determinations was estimated to be ± 0.1 ev. The adjusted and unadjusted values for m/z 56 and 57 in relation to the values for the other ions were considered to be more accurate from data taken without acetone as an internal standard.

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Appendix

The majority of the ΔH_f 's of the neutral molecules were from experimental values⁴⁵⁻⁴⁸ or estimated from the group additivity procedure.⁴⁶ The ΔH_f of $\cdot\text{CH}_3$ ⁴⁹ was a value recently determined. The value for $(\text{CH}_2=\text{CH})_2\dot{\text{C}}\text{H}$ was from a recent compilation.⁴⁵ The group additivity value of 36.7 kcal/mol for $\cdot\text{C}-(\text{C})(\text{H})_2$ was derived from the ΔH_f of $\cdot\text{C}_2\text{H}_5$.⁴⁶ The value of -3.1 kcal/mol for $\text{C}-(\text{H})(\text{C})_2(\text{CO})$ was derived from the ΔH_f of -52.1 kcal/mol for 2-methylpropanal.⁵⁰ The value of -46.2 kcal/mol for $\text{O}-(\text{H})(\text{C}_d)$ was derived from the ΔH_f of -39.7 kcal/mol for the enol of acetone.⁵¹ The ring correction for a radical which is part of a ring was taken to be the average of the saturated and unsaturated ring correction values.⁴⁶ The ring correction value of 1.6 kcal/mol for the exocyclic double bond was derived from the ΔH_f of methylenecyclohexane.⁵²

The ΔH_f of $\cdot\text{CH}_2\text{OH}$ was calculated from the bond dissociation energy (BDE) of 94 kcal/mol for $\text{H}-\text{CH}_2\text{OH}$;⁵³ $\text{CH}_3\dot{\text{C}}\text{HCHO}$ from the BDE of 91.2 kcal/mol for the α -CH bond of propanal;⁵⁴ $\text{CH}_2=\text{CH}\dot{\text{C}}\text{HOH}$ from an estimated BDE of 81 kcal/mol for the C-H bond in $\text{CH}_2=\text{CHCH}_2\text{OH}$, slightly less than the BDE of 82.5 kcal/mol for the C-H bond in $\text{CH}_2=\text{CHCH}_2\text{CH}_3$.⁴⁵ From these ΔH_f 's the following group additivity values (kcal/mol) were derived: $\cdot\text{C}-(\text{C})(\text{H})(\text{CO})$, 32.8; $\cdot\text{C}-(\text{C}_d)(\text{H})(\text{O})$, 22.4.

The value for $\cdot\text{C}-(\text{C})(\text{C}_d)(\text{O})$ was estimated to be ~ 20.0 kcal/mol.
 The value for $\cdot\text{C}-(\text{C}_d)_2(\text{O})$ was estimated to be 16.8 kcal/mol, lower than the value for $\cdot\text{C}-(\text{C}_d)(\text{H})(\text{O})$ (see above) by the same amount that the value of 18.6 kcal/mol for $\cdot\text{C}-(\text{C}_d)_2(\text{H})$ ⁴⁵ is lower than the value of 24.2 kcal/mol for $\cdot\text{C}-(\text{C}_d)(\text{H})_2$.⁵⁵

The IEs of the radicals in the tables and in the text were derived or extrapolated from experimental ΔH_f 's of cations which in most cases were determined from proton affinity values.⁹ A comprehensive PA scale⁹ was based on a ΔH_f of 166 kcal/mol for the t-butyl cation and ΔH_f of 367.2 kcal/mol for the H^+ ion. However, the ΔH_f of the t-butyl cation was recently determined to be 162.1 kcal/mol from the photoionization AE of the M-H ion from isobutane.⁵⁶ Thus, many of the ΔH_f values used in this study were based on the comprehensive PA scale⁹ adjusted to a ΔH_f of 162.1 kcal/mol for the t-butyl cation.⁵⁶

Vajda and Harrison⁵⁷ have measured the PA of propenal and 2-butenal relative to standards. After adjustment to the revised/PA scale of Aue and Bowers⁹ the PA of propenal was 197.3 kcal/mol and 2-butenal, 204.3 kcal/mol. To calculate the ΔH_f of the cations, accurate values for the ΔH_f of propenal and 2-butenal were needed. The ΔH_f (liquid) of 2-butenal, -34.45 kcal/mol,⁴⁷ and the ΔH_{vap} of butanal, 8.05 kcal/mol,^{47,48} were considered to be good values. The ΔH_{vap} of methyl and ethyl acrylates is 0.2 kcal/mol less than the ΔH_{vap} of the corresponding saturated compounds⁵⁸ and the ΔH_{vap} of propenal⁵⁸ is 0.2 kcal/mol less than the ΔH_{vap} of propanal.^{47,48} Thus, the ΔH_{vap} of 2-butenal was estimated to be 7.85 kcal/mol, 0.2 kcal/mol less than the ΔH_{vap} of butanal, giving a value for the ΔH_f (2-butenal) of -26.6 kcal/mol. There was no good value for the ΔH_f (liquid) of propenal.

However, by Benson's additivity method⁴⁶ the ΔH_f of propenal should be 7.8 kcal/mol greater than the ΔH_f of 2-butenal, giving a value of -18.8 kcal/mol for the ΔH_f of propenal. The additivity value for $C_d-(H)(CO)$ would be 4.0 kcal/mol instead of 5.0 kcal/mol.⁴⁶ The ΔH_f of $H_2C=CH-\overset{+}{C}HOH$ and $CH_3CH=CH-\overset{+}{C}HOH$ can now be calculated to be 151.1 and 136.3 kcal/mol, respectively.

The adjusted PA of cyclopentadiene⁹ gives a ΔH_f for the 2-cyclopentenyl⁺ cation of 195.2 kcal/mol and an IE of 6.8 eV for the corresponding radical. The adjusted PA of 1,3-pentadiene⁹ gives an IE for $CH_3CH=CH\dot{C}HCH_3$ of 6.85 eV. These values are 0.2 eV lower than the IEs['] measured for these radicals.^{59,60} Thus, the IEs['] for $CH_2=CH\dot{C}(CH_3)_2$ and $CH_2=CH\dot{C}HCH=CH_2$ were estimated to be 6.9 and 7.05 eV, respectively, 0.2 eV less than the measured values.⁶⁰

The adiabatic IE of the cyclohexyl radical may be less than the reported IE^{59,61} by the amount that the IE of isopropyl, 7.2 eV, from the adjusted PA of propene⁹ is less than the reported IE.⁶² This correction would give a value of 7.0 eV for the adiabatic IE of the cyclohexyl radical. This value is similar to the value derived from recently determined PA of cyclohexene.⁶³ As noted in the text, the cyclohexyl cation rapidly rearranges to the 1-methylcyclopentyl cation.^{14,63}

A study of the destabilization effect of the hydroxyl substituent on alkyl cations showed that the effect on the IE of the corresponding radical was about the same as removing the substituent and the adjoining carbon atom when there were at least two carbon atoms between the substituent and the charged carbon atom.⁶⁴ The destabilization effect com-

pared to the unsubstituted cation was approximately 0.1 eV,⁶⁴ In this study, the destabilization effect of the carbonyl group in cations and ionized biradicals was estimated to be similar to the destabilization effect of the hydroxyl groups in cations.

In radical cations containing a double bond the destabilization effect relative to the unsubstituted radical cation was greater. For example, the IE of 4-t-butyl-2-cyclohexene-1-ol was 0.25 eV greater than the IE of 3-t-butylcyclohexene.³⁹ The destabilization effect in the radical cation was due to a stabilizing interaction with the double bond in the neutral molecule.³⁹

Estimated IE's of the neutral molecules, radicals and biradicals corresponding to the ions in the text are given as follows, with many of the reference IE's from the PA scale⁹ adjusted to the ΔH_f of 162.1 kcal/mol for the t-butyl cation:⁵⁶

- 2, 6.3 eV, same as the IE of $(\text{CH}_3)_2\text{CH}-\dot{\text{C}}\text{HOH}$;⁹
- 3, 7.6 eV, 0.4 eV greater⁶⁵ than the IE of the isopropyl radical;⁹
- 4, 7.0 eV, 0.2 eV less⁶⁵ than the IE of the isopropyl radical;⁹
- 5, 7.4 eV, 0.1 eV less than the IE for $\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HCHO}$ (Table I);
- 6, 7.1 eV, 0.1 eV greater than the IE of the biradical corresponding to ion 4 because of the destabilization effect of the CHO group on the cation (see above);
- 7, 8, 7.0 eV (see ion 4);
- 9, 6.3 eV, same as the IE of $\text{CH}_3\text{CH}=\text{CH}\dot{\text{C}}\text{HOH}$ (Table I);
- 10, 9.2 eV, 0.25 eV greater than the IE of cyclohexene⁶⁰ due to the destabilization effect of the hydroxyl group on the radical cation (see above);
- 11, 8.4 eV, same as the IE of 1-hydroxyl-1-butene;¹⁸

12, 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);

13, 14, the group additivity value of 134 kcal/mol for the OH_2^+ group when attached to a primary carbon atom was calculated from the ΔH_f^\ddagger of 110.8 kcal/mol for $\text{CH}_3(\text{CH}_2)_2\text{OH}_2^+$ derived from the PA of n-propanol⁹ adjusted to the ΔH_f^\ddagger of 162.1 kcal/mol for the t-butyl cation.⁵⁶ Orbital interaction between the radical and cation centers was assumed not to occur. The group additivity values for $\text{C}-(\text{H})_2(\text{O})(\text{C})^+$ and $\cdot\text{C}-(\text{H})(\text{O})(\text{C})^+$ were assumed to be the same as for $\text{C}-(\text{H})_2(\text{O})(\text{C})$ and $\cdot\text{C}-(\text{H})(\text{O})(\text{C})$;⁴⁶

15, 6.55 eV, 0.1 eV greater than the IE of 1-methylcyclohexyl radical due to the destabilization effect of the hydroxyl group on the cation (see above);

16, 9.15 eV, 0.2 eV greater than the IE of cyclohexene⁶⁰ due to the destabilization effect of the hydroxyl group on the radical cation (see above);⁶⁶

17, see ion 13;

18, 8.4 eV (see ion 11);

19, 20, 6.4 eV, same as the IE of $\text{CH}_3(\text{CH}_2)_3\dot{\text{C}}\text{HOH}$;⁹

21, see ion 13;

22, 7.0 eV (see ion 4);

23, see ion 13;

24, 8.9 eV, same as the IE of 2-hexene;⁶⁰

25, see ion 13;

26, 6.4 eV (see ion 19);

27, 6.1 eV, 0.05 eV less than the IE of $(\text{CH}_3)_2\dot{\text{C}}\text{HOH}$;⁹

28, 8.2 eV, same as the IE of 2-hydroxy-2-butene;¹⁸

29, the group additivity value of 132 kcal/mol for the OH_2^+ group when attached to a secondary carbon atom was estimated to be between the group additivity value of 134 kcal/mol for this group when attached to a primary carbon atom (see ion 13) and the value of 130 kcal/mol for this group when attached to a tertiary carbon atom. The latter value was calculated from the ΔH_f of 93.2 kcal/mol for $(\text{CH}_3)_3\text{COH}_2^+$ derived from the adjusted PA of $(\text{CH}_3)_3\text{COH}^+$.⁹ The group additivity value for $\text{C}-(\text{C})_3(\text{O})^+$ was assumed to be the same as for $\text{C}-(\text{C})_3(\text{O})$.⁴⁶

The IE of 5-heptenal was estimated to be 9.1 eV, 0.2 eV greater than the IE of 2-hexene⁶⁰ due to the destabilization effect of the CHO group on the radical cation (see above). The IE of 2-methyl-1,3-cyclohexadiene for the $\text{M}-\text{H}_2\text{O}$ ion from ion 17 was estimated to be 8.2 eV, 0.1 eV less than the IE of 1,3-cyclohexadiene⁶⁷ by the same amount that the IE of 2-methyl-1,3-butadiene is less than 1,3-butadiene.⁶⁸ The IE of hexanal is 9.7 eV;³⁴ 1,3-hexadiene, 8.54 eV;⁶⁰ 2,4-hexadiene, 8.1 eV.⁶⁸ The IE of cyclohexanol was estimated to be 9.5 eV, 0.1 eV less⁶⁹ than the IE of cyclopentanol which has been found to be 9.6 eV.⁷⁰

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- (15) See Ref. 11(b) and Appendix for IE of vinyl alcohol, 9.25 eV. The IE of $\text{CH}_2=\text{CHOCH}_3$ is estimated to be 8.6 eV, 0.1 eV higher than the IE of $\text{CH}_2=\text{CHOC}_2\text{H}_5$.^{16,17} An additional OH group would be expected to lower the IE so that a reasonable estimate for the IE of $\text{CH}_2=\text{C}(\text{OH})_2$ would be 8.8 eV and for $\text{CH}_2=\text{C}(\text{OH})(\text{OCH}_3)$, 8.4 eV. Also, see Ref. 18 for the ΔH_f of the radical cations of these compounds.
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Lack of H/D mixing in the metastable ions from the deuterated isomers^{24d} requires that the rearrangement of a to b be irreversible. However, if complex a and the product ion have the same energy level, product ion formation from b would be expected to have a much faster rate because the frequency factor for this process should be higher than reversion to a. (c) Steiner, B.; Giese, C. F.; Ingram, M. G. J. Chem. Phys. 1961, 34, 189. (d) Chupka, W. A.; Berkowitz, J. J. Chem. Phys. 1967, 47, 2921. (e) Wolkoff, P.; Holmes, J. L. J. Amer. Chem. Soc. 1978, 100, 7346.

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