lecular interaction between the carbonyl chromophore and the parent molecule. It is therefore more suitable to express that the origin of this rotational strength is the inherent ring chirality combined with the asymmetrically substituted methyl group.

The long-range zigzag path linked with the skeleton of the methyl substituent is identified to be a major path, making the locally symmetric carbonyl chromophore effectively couple with the dissymmetric environment, which is also consistent with the above-mentioned argument concerning the origin of this rotational strength.

Lastly, we are tempted to comment on the advantage of the present procedure and its possible extension. The expansion of CMO's in terms of LMO's makes it possible to evaluate quantitatively the degree of the localization and/or delocalization of CMO's concerned. The division of LMO's into the belonging fragment in this expansion enables one to make a discussion from the aspect of group MO's, which is useful for the characterizations of several kinds of substituents and chromophores. The electronic structural terminologies such as local and charge-transfer excitations derived from this procedure are helpful in understanding the intramolecular interactions. The approach using this procedure is promising for elucidating not only the essential feature of the coupling between the electronic and magnetic dipole transitions but also the origin and effective path generating the rotational strength, which neither the perturbation method nor the usual MO calculation can rationalize with sufficient accuracy. The application of the present procedure with some modifications to the induced CD, magnetic rotational strength, and other physical properties on the three or four interacting systems also will be available in the near future.

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Metastable Decompositions of $C_5H_{10}O^{+\cdot}$ Ions with the Oxygen on the Middle Carbon: A Test for Energy Randomization

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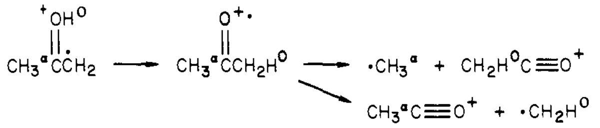
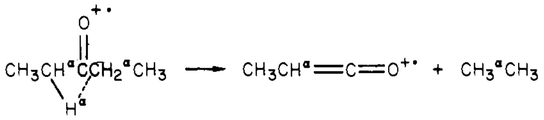
Abstract: This study was undertaken to define the mechanisms of metastable decomposition of $C_5H_{10}O^{+\cdot}$ ions with the oxygen on the middle carbon, and to test the assumption that internal energy becomes randomly distributed prior to the unimolecular decompositions of gaseous ions. $CH_3CH_2C({=}OH^+)CH_2CH_2\cdot$ (**2**), $CH_3CH_2C({=}OH^+)\cdot CHCH_3$ (**3**), and $CH_3CH_2C(OH^{+}\cdot)HCH{=}CH_2$ (**4**) all rearrange to $CH_3CH_2C({=}O^{+}\cdot)CH_2CH_3$ (**1**) prior to metastable decomposition. However, **2**–**4** lose ethyl 50–100 times as often as they lose ethane following rearrangement to **1**, while **1** formed by ionization of 3-pentanone loses exclusively ethane. These differences are attributed to excess energy in the isomerized ions. 3-Pentanone ions formed by isomerization of **2**–**4** lose ethyl and ethane from opposite sides at unequal rates, possibly owing to incomplete randomization of energy following isomerization.

Scheme I



$CH_3^{\alpha}C({=}OH^{+\,o})\dot{C}H_2 \rightarrow CH_3^{\alpha}C({=}O^{+\cdot})CH_2H^{o} \rightarrow \cdot CH_3^{\alpha} + CH_2H^{o}C{\equiv}O^{+}$; $CH_3^{\alpha}C{\equiv}O^{+} + \cdot CH_2H^{o}$

Scheme II



$CH_3CH^{\alpha}C({=}O^{+\cdot})CH_2^{\alpha}CH_3 \rightarrow CH_3CH^{\alpha}{=}C{=}O^{+\cdot} + CH_3^{\alpha}CH_3$

The quasi-equilibrium theory of mass spectrometry (QET) is based on the assumption that energy becomes randomly distributed among all internal degrees of freedom of a reactant ion more rapidly than reaction occurs.[1] If this assumption is valid, the decomposition pattern of an ion with a given internal energy will not depend on its mode of preparation.[2,3] Metastable decompositions are thought to be competitive processes, generally taking place over a narrow range of energies just above the threshold for decomposition. However, metastable decomposition patterns can vary with the energy content of the decomposing ion,[4] which in turn can be a function of the mode of preparation.[5,6] The energy randomization assumption of the QET can be tested by comparing the decompositions of metastable ions of the same structure prepared in different ways to see whether the patterns depend on the mode of ion preparation.[2,7] In support of the QET assumption, the decomposition patterns of many metastable ions with the same structure but different origins are very similar.[2,3] These tests are valuable, since they do not involve vibrational frequencies for ions and activated complexes, which are not available and must be estimated to carry out QET calculations. One such test is whether symmetric ions chemically activated by isomerization on one side lose symmetrically placed groups at equal rates.[8,9] The enolic isomer of the acetone ion apparently violates the energy randomization assumption of the QET upon metastable decomposition.[8] This rearranges to the symmetric acetone ion and then loses CH_2H^{o} about 1.3 times as often as it loses CH^{α}_3 (Scheme I). The inequality in the reaction rates was attributed to concentration of internal energy on the side of the ion on which rearrangement occurs, with decomposition taking place faster than

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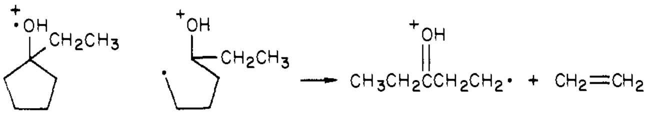
Table I. Metastable Decompositions of $C_5(H,D)_{10}O^{+}\cdot$ Ions

	species lost								
ion	C_2H_5	C_2H_4D	$C_2H_3D_2$	C_2H_2-D_3	C_2H_2-D_4	C_2D_5	C_2H_6	C_2H_5-D	$C_2H_4D_2$
$CH_3CH_2C(=O^{+}\cdot)CH_2CH_3$ [a] (**1**)	0.9						100		
$CH_3CH_2C(=OH^{+})CH_2CH_2\cdot$ [b] (**2**)	100						1.5		
$CH_3CH_2C(=OD^{+})CH_2CH_2\cdot$ [c] (**2**-*O*-d_1)	100	59						0.8	
$CH_2DCH_2C(=OH^{+})CH_2CH_2\cdot$ [d] (**2**-*1*-d_1)	91	100						1.5	
$CH_3CD_2C(=OH^{+})CH_2CH_2\cdot$ [e] (**2**-*2,2*-d_2)	100		92						
$CH_3CH_2C(=OH^{+})\dot{C}HCH_3$ [f] (**3**)	100						3		
$CH_3CH_2C(=OD^{+})\dot{C}HCH_3$ [g] (**3**-*O*-d_1)	100	80						1.0	
$CH_2DCH_2C(=OH)\dot{C}HCH_3$ [h] (**3**-*1*-d_1)	97	100						1.8	
$CH_3CD_2C(=OH^{+})\dot{C}HCH_3$ [i] (**3**-*2,2*-d_2)	100	7	85						
$CH_3CH_2C(=OH^{+})\dot{C}DCH_3$ [j] (**3**-*4*-d_1)	100	90							
$CH_3CD_2C(=OH^{+})\dot{C}DCH_3$ [k] (**3**-*2,2,4*-d_3)	3	83	100	3					
$CD_3CH_2C(=OH^{+})\dot{C}HCH_3$ [l] (**3**-*1,1,1*-d_3)	100	11	9	98					
$CD_3CD_2C(=OH^{+})\dot{C}DCH_3$ [m] (**3**-*1,1,1,2,2,4*-d_6)		80	1.5		2	100			
$CH_3CH_2C(OH^{+}\cdot)HCH=CH_2$ [n] (**4**)	100						2.2		
$CH_3CH_2C(OD^{+}\cdot)HCH=CH_2$ [o] (**4**-O-d_1)	100	80						1.3	
$CH_2DCH_2C(OH^{+}\cdot)HCH=CH_2$ [p] (**4**-*1*-d_1)	100	97						1.6	
$CH_3CH_2C(OH^{+}\cdot)DCH=CH_2$ [q] (**4**-*3*-d_1)	100	88							
$DCH_2CH_2C(OD^{+}\cdot)HCH=CH_2$ [r] (**4**-*O,1*-d_2)	30	100	27						0.17
$DCH_2CH_2C(OH^{+}\cdot)DCH=CH_2$ [s] (**4**-*1,3*-d_2)	11	100	2.8						0.15
$CD_3CH_2C(OH^{+}\cdot)HCH=CH_2$ [t] (**4**-*5,5,5*-d_3)	100	14	12	80					

Intensities were determined for decompositions occurring between the ion source and the electric sector by adjusting the electric sector voltage. Values are corrected for ^{13}C contributions, but not for $C_2(H,D)_4$ and $C_2(H,D)_6$ losses. Ions were derived from the following compounds. [a] 3-Pentanone (determined on the MS-50). [b] 1-Ethylcyclopentanol. [c] 1-Ethylcyclopentanol-O-d_1. [d] 1-Ethyl-*2*-d_1-cyclopentanol. [e] 1-Ethyl-*1,1*-$d_2$cyclopentanol. [f] 4-Methyl-3-heptanone. [g] 4-Methyl-3-heptanone-*6,6*-d_2. [h] 4-Methyl-3-heptanone-*1*-d_1. [i] 4-Methyl-3-heptanone-*2,2*-d_2. [j] 4-Methyl-3-heptanone-*4*-d_1. [k] 4-Methyl-3-heptanone-*2,2*-d_3. [l] 4-Methyl-3-heptanone-*1,1,1*-d_3. [m] 4-Methyl-3-heptanone-*1,1,1,2,2,4*-d_6. [n] 1-Penten-3-ol. [o] 1-Penten-3-ol-d_1. [p] 1-Penten-3-ol-*1*-d_1. [q] 1-Penten-3-ol-*3*-d_1. [r] 1-Penten-3-ol-*O,1*-d_2. [s] 1-Penten-3-ol-*1,3*-d_2. [t] 1-Penten-3-ol-*5,5,5*-d_3.

Scheme III

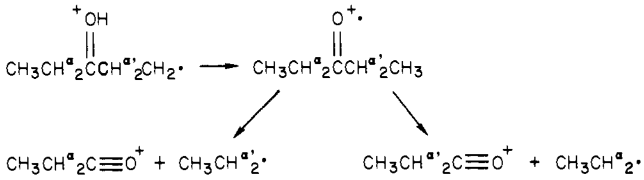


energy randomization following isomerization. Differing rates of reaction on opposite sides of symmetric neutral molecules have also been demonstrated for very fast reactions.[10,11] However, symmetric $[CH_2C(OH)_2]^{+}\cdot$ formed by McLafferty rearrangement[12] of ionized aliphatic acids undergoes complete energy randomization in the ca. 10^{-6} s that elapses prior to its metastable decompositions. Based on the behaviors of $C_3H_6O^{+}\cdot$[8] and $C_4H_8O^{+}\cdot$[13,14] ions, we expected $C_5H_{10}O^{+}\cdot$ ions with the oxygen on the middle carbon to isomerize to the 3-pentanone ion prior to decomposing, thereby providing symmetric, chemically activated ions to be examined for asymmetric decomposition. A study of the decompositions of $C_5H_{10}O^{+}\cdot$ ions with the oxygen on the middle carbon based on these expectations is presented here.

Results and Discussion

Mechanisms of Decomposition of $C_5H_{10}O^{+}\cdot$ Ions. The metastable spectra of $C_5H_{10}O^{+}\cdot$ ions and some deuterated analogues are given in Table I. Ionized 3-pentanone (**1**) underwent a strong loss of ethane and a weak loss of ethyl. Increasing the pressure in the region of decomposition drastically increased the relative intensity of the peak representing loss of ethyl, indicating that the peak largely resulted from collision-induced dissociation. Therefore metastable **1** loses ethane more than 100 times as often as it loses ethyl by unimolecular decomposition. Ionized 3-pentanone-*2,2,4,4*-d_4 loses $C_2H_3D_3$, demonstrating that **1** loses ethane according to Scheme II.[15]

Scheme IV



$CH_3CH_2C(=OH^{+})CH_2CH_2\cdot$ (**2**) was generated by loss of ethene from 1-ethylcyclopentanol (Scheme III). Such ethene losses seem to be a general mode of decomposition of cyclopentanols.[13] In contrast to **1**, metastable **2** loses ethyl about 70 times as often as it loses ethane. **2**-*O*-d_1 and **2**-*1*-d_1 both lost C_2H_4D and C_2H_5 to similar degrees (the inequality of the rates will be discussed below), and **2**-*2,2*-d_2 lost C_2H_5 and $C_2H_3D_2$ at similar rates. The only mechanism consistent with nearly equal losses of the original ethyl and ethyl containing all of the remaining hydrogens is rearrangement to **1** followed by loss of either ethyl (Scheme IV). $CH_3C(=OH^{+})CH_2CH_2\cdot$ generated from 1-methylcyclopentanol undergoes an analogous ketonization, followed by the loss of methyl or ethyl with a deuterium placed on the oxygen appearing exclusively in the ethyl.[13]

$CH_3CH_2C(=OH^{+})\cdot CHCH_3$ (**3**) was generated by the McLafferty rearrangement of 4-methyl-3-heptanone. The relative intensities of the peaks representing metastable losses of ethane and ethyl were similar to those of **2**. Both **3**-*O*-d_1 and **3**-*1*-d_1 lost C_2H_5 and C_2H_4D at similar rates, consistent with isomerization to **1** prior to metastable decomposition. Also consistent with ketonization, losses of C_2H_5 and of $C_2H_2D_3$ or $C_2H_3D_2$ dominated the metastable decompositions of **3**-*1,1,1*-d_3 and **3**-*2,2*-d_2. Ethyls exhibiting deuterium transfer from one side of the ion to the other were lost in about 8% of the decompositions of **3**-*1,1,1*-d_3 (allowing for the contributions of ethene and ethane to the data of Table I), and **3**-*2,2*-d_2 lost C_2H_4D in about 2% of its ethyl losses. Combining these results and ignoring isotope effects indicate that hydrogens are transferred across the oxygen-bearing carbon prior to about 10% of the metastable decompositions of **3**. Other

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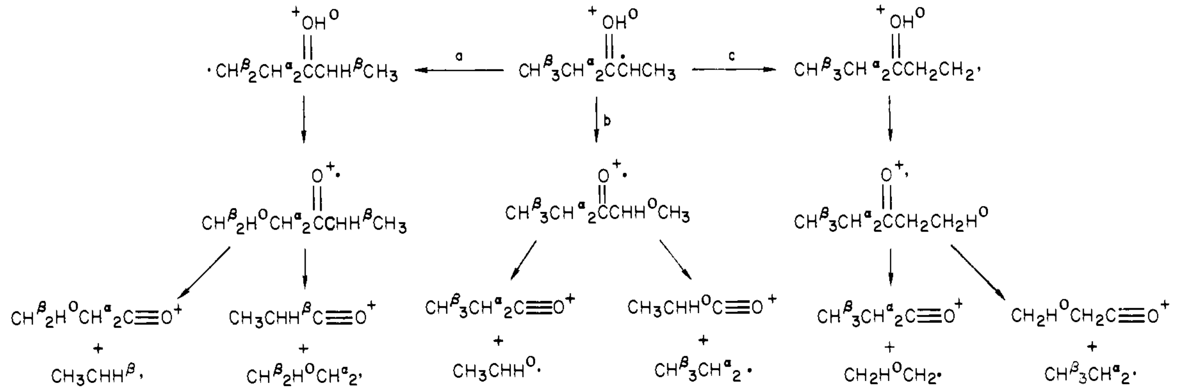
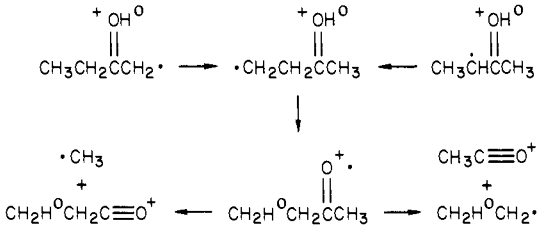
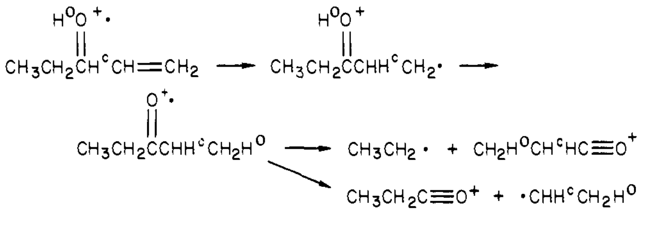
Scheme V



Scheme VI



Scheme VII



deuterated ions gave similar results. The decomposition patterns of the labeled ions rule out Va (Scheme V), but cannot be used to distinguish between pathways Vb and Vc. The losses of C_2H_4D and $C_2H_3D_2$ from 3-*1,1,1-d*$_3$ indicate that perhaps 8% of the losses of ethyl from 3 take place by Va. This contrasted with our expectations, as isomerization of $CH_3CH_2C(=OH^+)CH_2\cdot$ to the 2-butanone ion by the specific shift of a β hydrogen to the vacancy on the opposite α carbon has been reported to require less energy than the rearrangement of $CH_3CHC(=OH^+)CH_3$ to $\cdot CH_2CH_2C(=OH^+)CH_3$ (Scheme VI).[14] Vc is probably the major pathway, since three- and five-membered-ring hydrogen transfers are preferred to four-membered-ring rearrangements in the formation of carbonyl groups in other ions.[14,16] The strong similarity between the metastable decomposition patterns of 2–4 and the associated translational energy releases (Table III) may also indicate that all three ions rearrange to 1 by the same step, most likely 2 → 1. 2 and 3 may interconvert prior to decomposition, as this occurs in a related system.[16] In light of the differences between the decompositions of 1 and the other ions, differing rearrangements to 1 would probably result in substantially different decomposition patterns and energy releases.[5,6]

Like 2 and 3, metastable $CH_3CH_2C(OH^+)HCH{=}CH_2$ (4) undergoes a strong loss of ethyl and a weak loss of ethane. 4-*O-d*$_1$, 4-*1-d*$_1$, and 4-*3-d*$_1$ all lost C_2H_5 and C_2H_4D at similar rates, demonstrating that 4 also loses ethyl after isomerizing to the 3-pentanone ion. Ketonization of 4 probably occurs according to Scheme VII, since this would involve a common final step in the ketonization of 2–4. The alternate possibility, rearrangement of the hydroxyl hydrogen first, is unlikely, as there is no evidence for the formation of C–O-containing ions. Metastable $CH_3CH(OH^+)CH{=}CH_2$ rearranges to the 2-butanone ion prior to decomposing, probably by a pathway analogous to Scheme VII.[13]

Table II. Metastable Decompositions of $C_5H_{10}O^{+\cdot}$ Ions[a]

precursor molecule	species lost CH_3	H_2O	C_2H_4	C_2H_5	C_2H_6
$CH_3CH_2C(=O)CH_2CH_3$	0.3	<0.1	0.3	14[b]	100
$CH_2(CH_2)_3CH(OH)C_2H_5$	11	8	6	100	3
$C_2H_5C(=O)CH(CH_3)C_3H_7$	3.9	1.6	1.2	100	2.3
$CH_3CH_2C(OH)HCH{=}CH_2$	12.5	5	3.6	100	2.6
$CH_3C(=O)C_3H_7$	100	1.5	48	1.2	0.8
$CH_3CH{=}CHCH(OH)CH_3$	100	1	26	0.4	<0.6
$CH_3(CH_2)_3CHO$	33	16	100	14	1.3
$CH_2CH_2CH_2CH_2CHOH$	75	60	44	100	

[a] Results are from the first field-free region of a Du Pont 21-419B 21-419B mass spectrometer. [b] Almost totally collision induced.

Table III. Energies Released in Metastable $C_5H_{10}O^{+\cdot}$ Decompositions[a]

ion	$-C_2H_5$	$-C_2H_6$
$CH_3CH_2C(=O^{+}\cdot)CH_2CH_3$ (1)	2.8 ± 0.2	1.3 ± 0.1
$CH_3CH_2C(=OH^+)CH_2CH_2\cdot$ (2)	2.5 ± 0.1	3.8 ± 0.6[b]
$CH_3CH_2C(=OH^+)\dot{C}HCH_3$ (3)	2.3 ± 0.1	2.5 ± 0.2
$CH_3CH_2C(=OH^{+}\cdot)HCH{=}CH_2$ (4)	2.2 ± 0.15	3.2 ± 0.5

[a] Values are in kJ mol^{-1} and were determined from the peak widths at half height. Error limits are standard deviations of four or more determinations. [b] Peak shape visually corrected for contribution of an overlapping peak.

All of the *1-d*$_1$ and *O-d*$_1$ ions lost C_2H_5D, while their C_2H_6 losses were obscured by losses of C_2H_4D. This demonstrates that ethane losses also occur from both sides of 2–4, and therefore following rearrangement of those ions to 1.

It is surprising that 2 → 1 is preferred to 2 → 2′, a six-membered-ring isoenergetic rearrangement (note the low levels of exchange in *5,5,5-d*$_3$ ions). It is additionally curious that 2 → 1 is also preferred to 2 → 3, as 3 should be approximately 60 kJ mol^{-1} more stable than 1 (see below), and 2 → 1 and 2 → 3 are five-membered-ring rearrangements. A similar situation exists for $C_4H_8O^{+\cdot}$ ions.[14]

The metastable decomposition patterns of 1–4 are quite different from those of $C_5H_{10}O^{+\cdot}$ ions with the oxygen on the first or second carbons (Table II). $C_5H_{10}O^{+\cdot}$ ions with the oxygen on the second carbon ($CH_3CH_2CH_2C(=O^{+}\cdot)CH_3$, $CH_3CH_2CH_2C(=OH^+)CH_2\cdot$, $CH_3CH_2\dot{C}HC(=OH^+)CH_3$, $CH_3\dot{C}HCH_2C(=OH^+)CH_3$, and $CH_2CH_2CH_2CO^{+}\cdot HCH_3$) lose methyl and ethene, apparently by common pathways, since all of these ions have very similar metastable decomposition patterns.[17] $C_5H_{10}O^{+\cdot}$ ions with the oxygen on the first carbon lose methyl, ethyl, ethene, and water in a variety of patterns. Thus, $C_5H_{10}O^{+\cdot}$ ions with the oxygen on the middle carbon undergo at most minor isomerization to structures with the oxygen on the first or second carbon, and the

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Table IV. Appearance Energies for the Losses of C_2H_6 and C_2H_5[a]

ion	$-C_2H_5$	$-C_2H_6$
1		30
2	135 ± 20	
3	220 ± 20	200 ± 20

[a] Values are in kj mol^{-1} and are average results of two experiments several months apart; values were derived by 50-eV normalization.

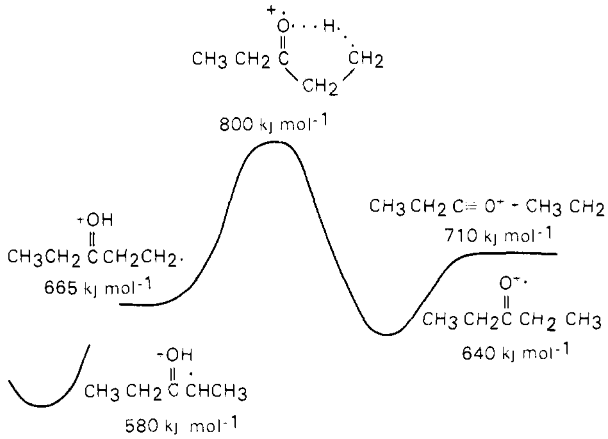

Figure 1. Potential surface for $C_5H_{10}O^{+}\cdot$ decompositions.

$C_5H_{10}O^{+}\cdot$ isomers decompose over a variety of different potential surfaces, in contrast to the $C_4H_8O^{+}\cdot$ ions, which decompose predominantly over the same potential surface.[13]

Cause of the Different Metastable Decomposition Patterns. The variation between the metastable decompositions of **1** and **2–4** is startling, since all of these ions must decompose from the 3-pentanone structure. Energy release (Table III) and appearance energy (Table IV) measurements were carried out to explore reasons for the difference. The energies released in the losses of ethyl from **2–4** were the same within experimental error (Table III). The peak representing the loss of ethyl appeared to be broader from **1** than from the other ions, consistent with the loss of ethyl from **1** being collision induced. About 1.7 kJ mol^{-1} more energy is released in the losses of ethane from **2–4** than from **1**.

The AE curves normalized to 50 eV[18] for precursor and products were parallel for **2** and **3**, while for **1** the curve for the metastable peak rose more slowly than the curve for the precursor. Figure 1 gives the potential surface for the decomposition of **3**. AE(**3**) − AE(**3** − ethyl) is about 220 kJ mol^{-1} (Table IV). About 70 kJ mol^{-1} is required to decompose the 3-pentanone ion to $CH_3CH_2C{\equiv}O^{+} + CH_3CH_2\cdot$,[19] and the relative heats of formation of the keto and enol forms of $C_3H_6O^{+}\cdot$ indicate that **3** should be approximately 60 kJ mol^{-1} more stable than **1**.[19] Therefore, $\Delta\Delta H_f$ between the products of the loss of ethyl from **3** and **3** should be about 130 kJ mol^{-1}, indicating that **1** formed by rearrangement of **3** contains about 90 kJ mol^{-1} more energy than it needs to lose ethyl.

The energy release and appearance energy measurements indicate that 3-pentanone ions formed by isomerization of **3** contain energy in excess of that needed for decomposition. This energy probably arises predominantly from reverse activation energies associated with the isomerizations, but could contain contributions from kinetic shifts. Since the peaks representing loss of ethane from **2** and **4** are also broadened, and the metastable decomposition patterns of those ions are very similar to those of **3**, all of the decomposing 3-pentanone ions formed by isomerization must contain substantially more energy than they need to decompose. Ion m/z 56 is 3.7% as intense as m/z 57 in the normal spectrum of 3-pentanone, so the metastable decomposition patterns of **2–4** approximate the fragmentation pattern of the high-energy 3-pentanone ion. Our results indicate that, as with systems recently studied by Williams and co-workers,[5,6] excess energy in the isomerized ions probably causes the difference between the metastable decomposition patterns of **1** and **2–4**. The loss of ethane must be the lowest energy decomposition of the 3-pentanone ion, and metastable ions formed by the direct ionization of 3-pentanone must contain only enough energy to lose ethane. At energies substantially above the threshold for the decomposition of the 3-pentanone ion, the simple cleavage loss of ethyl is faster than the elimination of ethane. If the peak reported in Table I for loss of ethyl from **1** arises mostly from a collision-induced process, the relative frequencies of the losses of ethane and ethyl change by more than four orders of magnitude with an increase of perhaps 90 kJ mol^{-1} in ion internal energy. Therefore loss of ethyl must occur very rapidly following ketonization, and isomerization, not fragmentation, must be the rate-determining step in the decompositions.

Asymmetric Decomposition of the Metastable $C_5H_{10}O^{+}\cdot$ Ions. The ratios of the peak intensities ($-C_2H_5$:$-C_2H_4D$) for the metastable decompositions of the *O*-d_1 ions are 1.2–1.8 times the corresponding ratios for the *1*-d_1 ions. Contributions from an unidentified process may have perturbed the ratio for **2**-*O*-d_1 or **2**-*1*-d_1 to give the value of 1.8. The differences in the ethyl losses from the complementarily labeled ions demonstrate that deuteration of the β carbon appreciably slows the rate of α-cleavage. Correction of the differences between each pair of labeled ions for secondary isotope effects (assuming that the effect of *1*-d_1 equals the effect for *O*-d_1) indicates that the ratios of the rates of loss of the ethyls from the opposite sides of the unlabeled ions vary from 1.10 to 1.36, and average 1.20, or 1.12 ignoring the value for **2**. The peaks for the losses of C_2H_5 in the second field-free region are about 5% wider than the peaks for the losses of C_2H_4D from both *1*-d_1 and *O*-d_1 ions, so correction of the intensity of the first field-free region peaks representing C_2H_5 loss for the differences in peak shape would slightly increase the $-C_2H_5/-C_2H_4D$ ratios. It is not simple to make such corrections to data obtained by lowering the electric sector voltage[20] (the method used here), but the preexisting ethyl must be lost slightly more than 10% more often than the ethyl formed by rearrangement in the metastable decompositions of **3** and **4**. Thus either the 3-pentanone ions formed by isomerization lose the original ethyl preferentially or an additional pathway for loss of the original ethyl exists.

Ethane containing the original ethyl of **2–4** also appears to be lost more rapidly than ethane from the other side of the ion. The peaks representing metastable losses of C_2H_5D from the *1*-d_1 ions were an average of 1.4 times as intense relative to the sum of the intensities of the peaks representing ethyl losses as were the peaks for C_2H_5D loss from the *O*-d_1 ions. Ethane losses appear to take place at least predominantly following rearrangement of **2–4** to **1** (see above). Loss of ethane containing the original ethyl and the hydrogen from the middle carbon would result in the loss of $C_2H_4D_2$ from **4**-*1,3*-d_2. However, the peak representing this process is less than 10% of the expected total intensity for ethane losses, and can be accounted for by intramolecular hydrogen transfers prior to the losses of ethyl and ethane. By similar logic, the weak loss of $C_2H_4D_2$ from **4**-*0,1*-d_2 appears to rule out appreciable loss of ethane containing the original ethyl and the hydroxyl hydrogen. Extra reactions would have to contribute about 20% of the ethane losses to make the loss of ethane containing the original ethyl 1.4 times the loss of the opposite ethyl.

Since we could not find evidence for significant elimination of ethane from 4 by another process, loss of ethane containing the original ethyl from 3-pentanone ions formed by isomerization appears to be favored over loss of ethane containing the opposite ethyl. If so, the favored losses of the original ethyls from isomerized **2–4** is probably also a property of the intermediate 3-pentanone ions. The preferred ethyl and ethane losses take place

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from the side opposite the one on which the rearrangements occur, in contrast to the acetone ion formed by isomerization from its enol isomer.[8] This is hard to explain, as a nonrandom distribution of energy presumably would stem from the isomerization step to **1**. Nonetheless, in light of the apparent asymmetry of their metastable decompositions, we conclude that the decomposing 3-pentanone ions generated by isomerizations probably contain a nonrandom distribution of internal energy. The above conclusion that loss of ethyl from these ions is orders of magnitude faster than the loss of ethane from **1** indicates that decomposition quickly follows slow isomerizations. Thus, the nonrandom distribution of energy would have to persist for at most 10^{-11}–10^{-10} s.

Experimental Section

Metastable peak intensities were recorded at 70 eV electron energy for decompositions occurring in the first field-free region of a Du Pont 21-491B or a Kratos-AEI MS 50 mass spectrometer by manually lowering the electric sector voltages. Energy releases were determined from uncorrected peak widths for decompositions taking place in the second field-free region of the MS 50. In this mode, metastable spectra were recorded free of normal spectra by deflecting the products of the metastable decompositions to a separate detector by means of a retarding potential. AE measurements were carried out on decompositions occurring in the first field-free region of the MS-50 by manually lowering the electron energy.

1-Ethylcyclopentanol was prepared by the addition of the ethyl Grignard to cyclopentanone. Ethanol-*1,1*-d_2 was prepared by reduction of acetic anhydride with $LiAlD_4$,[21] and converted to 1-bromoethane-*1,1*-d_2 with HBr/concentrated H_2SO_4. 1-Bromoethane-*2,2,2*-d_3 was similarly prepared starting with reduction of acetic-d_6 anhydride with $LiAlH_4$, and 1-bromoethane-*2*-d_1 was obtained starting with reduction of ethylene oxide with $LiAlD_4$. **1-Ethyl-*2*-d_1-cyclopentanol** and **1-ethyl-*1,1*-d_2-cyclopentanol** were prepared by addition of the corresponding ethyl Grignard reagents to cyclopentanone.

4-Methyl-3-heptanone was obtained from Pfaltz and Bauer, Flushing, N.Y. **4-Methyl-3-heptanone-*6,6*-d_2** (98% d_2, 2% d_1) was prepared by the $CuBr(CH_3)_2S$-catalyzed addition of CH_3CD_2MgBr to 2-methyl-1-penten-3-one.[22] **4-Methyl-3-heptanone-*4*-d_1** (93% d_1, 5% d_0) was prepared by the addition of C_2H_5MgBr to the same enone followed by workup with D_2O/DCl. **4-Methyl-3-heptanone-*1*-d_1** (99% d_1, 1% d_0) was prepared by addition of DCH_2CH_2MgBr to 2-methylpentanal followed by Jones oxidation. **4-Methyl-3-heptanone-*1,1,1*-d_3** (94% d_3, 6% d_2) and **4-methyl-3-heptanone-*2,2*-d_2** (96% d_2, 4% d_1) were prepared from the appropriate ethyl bromides and 2-methylpentanoyl chloride via the cadmium reagents.[23] **4-Methyl-3-heptanone-*2,2,4*-d_3** (86% d_3, 14% d_2) was prepared by refluxing 4-methyl-3-heptanone in $DCl/D_3PO_4/D_2O$. **4-Methyl-3-heptanone-*1,1,1,2,2,4*-d_6** (77% d_6, 20% d_5, 3% d_4) was similarly prepared from 4-methyl-3-heptanone-*1,1,1*-d_3.

1-Penten-3-ol, **1-penten-3-ol-*1*-d_1** (91% d_1, 9% d_0), and **1-penten-3-ol-*5,5,5*-d_3** (>54% d_3) were prepared by adding ethyl Grignard reagents to acrolein. **1-Penten-3-ol-*3*-d_1** (>88% d_1) and **1-penten-3-ol-*1,3*-d_2** (>53% d_2) were prepared by oxidation of 1-penten-3-ol and 1-penten-3-ol-*1*-d_1 to the corresponding 1-penten-3-ones in ether with chromic acid[24] followed by reduction with $LiAlD_4$.

1-Ethylcyclopentanol-*O*-d_1 (90% d_1, 10% d_0) and **1-penten-3-ol-*O*-d_1** (93% d_1, 7% d_0) were prepared by mixing the unlabeled compounds with D_2O followed by introduction with D_2O into the batch inlet of the mass spectrometer.

All synthesized compounds were either shown to be pure or were purified by gas chromatography.

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The Quinones of Azulene. A Theoretical Prognosis

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Abstract: Azuloquinones are unknown species of great interest because they are both quinones, which have important redox chemistry and appear in a variety of biologically important molecules, and derivatives of a nonalternant hydrocarbon. MINDO/3, Hückel, PPP, and ab initio SCF calculations with the STO-3G basis set have been used to predict the structures, stabilities, spectral properties, and reactivities of all members of this class of molecules.

Introduction

Quinones constitute one of the oldest known and most interesting classes of compounds in all of chemistry.[2] Naturally occurring quinones were exploited by the Chinese for medicinal purposes as early as 2700 B.C.,[3] and many more recently have been found to exhibit significant antifungal, antibiotic, antimalarial, or antitumor activity.[2,3] The birth of our organic chemical manufacturing industry in the middle 1800s was built around quinone pigments, some of which had been used for the dyeing of cotton since the days of ancient Egypt.[4] Still other quinones are known to play vital roles in photosynthesis[5] and in the respiratory electron transport chain,[6] in the biosynthesis of tetra-

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