Isomerization and Decomposition Reactions of $C_4H_8O^{\cdot+}$ Ions[1-3]

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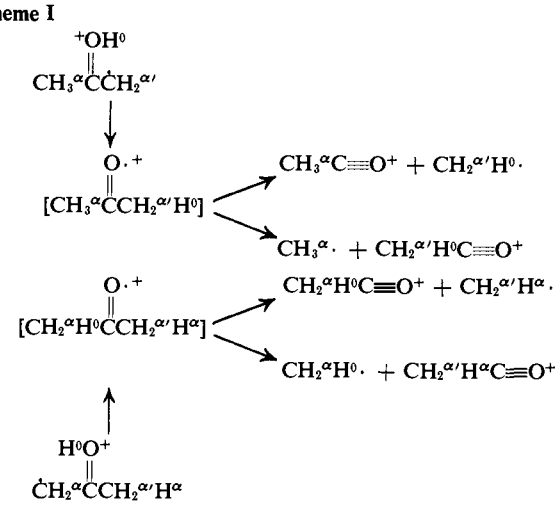
Abstract: The unimolecular reactions of the isomeric ions $C_2H_5C(OH)CH_2^{\cdot+}$ (**1**) and $CH_3CHC(OH)CH_3^{\cdot+}$ (**6**) are explicable in terms of stepwise rearrangement of individual hydrogen atoms leading to the ketonic ion $CH_3CH_2COCH_3^{\cdot+}$ (**5**); only **5**, not **1** or **6**, can undergo decomposition to give $C_2H_5CO^+$ and CH_3CO^+, which are the major final products observed from all three isomers. The results from this system appear to provide definitive evidence on the effect of the ring size of the rearrangement transition state on both the activation energy and the "looseness" of the activated complex of the reaction. For low-energy metastable decompositions the predominant pathway for isomerization of **1** → **5** involves two 1,4-hydrogen shift rearrangements, while that of **6** → **5** involves a 1,2-(favored over a 1,3-) followed by a 1,4-hydrogen shift. In the decomposition of higher internal energy ions, pathways involving 1,3-hydrogen rearrangements compete effectively with 1,4 rearrangements, indicating that the lower activation energy of the latter is offset by the looser activated complex of the 1,3-shift reaction. This also produces the unusual situation that hydrogen scrambling is *increased* in ions of higher internal energy. Isotope effects were found to be especially useful in elucidating these reaction mechanisms.

Aliphatic ketones have served as model compounds for the study of a variety of important fundamental aspects of mass spectral behavior.[4-7] Despite the impressively detailed knowledge that has been reported for these spectra, a recent study of the enolic form of the acetone ion, $CH_3C(OH)CH_2^{\cdot+}$, showed that several concepts required modification or deserved further attention.[3,8] The previously assumed decomposition through direct cleavage does not occur to an appreciable extent; ketonization apparently provides the main degradation pathway (Scheme I). In contrast to the well-known preference for 1,5-hydrogen transfers in mass spectra, in $CH_3C(OH)CH_2^{\cdot+}$ two 1,3-hydrogen shift reactions, ketonization and methyl-to-methylene transfer, occur competitively. The reactions of Scheme I exhibit primary and secondary isotope effects consistent with the proposed pathways, suggesting that isotope effect studies can provide valuable information on other mechanistic problems.

Scheme I



The present report[3] extends this investigation to the isomeric enolic ions $C_2H_5C(OH)CH_2^{\cdot+}$ (**1**) and $CH_3CHC(OH)CH_3^{\cdot+}$ (**6**); direct cleavage has been proposed as the degradation mechanism for the former,[5] in contrast to our findings for the $C_3H_6O^{\cdot+}$ case. For the **1** and **6** ions 1,2- and 1,4-, in addition to 1,3-, hydrogen shift reactions are possible. Little information on such competitive rearrangements has been reported, including the relationship of the transition-state geometry to the activation energy and the increase of rate constant with ion energy. Study of a system in which the 1,5 shift cannot occur is pertinent in view of the recent observation that 1,4- and 1,5-, but not 1,3-, hydrogen shifts occur in $CH_3CH_2CH_2COOH$.[9] It is of special interest to find evidence concerning the contrasting mechanisms for hydrogen scrambling in such ions; proposals include the concerted exchange of hydrogen atoms between two saturated carbon atoms,[7,10] and the stepwise rearrangement of H to a radical site.[8,9,11]

Results

Data for the metastable and collision-induced[12] decompositions of the $C_4H_8O^{\cdot+}$ ions from 2-butanone, 1-ethylcyclobutanol, and 3-methyl-2,4-pentanedione are given in Table I. These should represent the unimolecular decompositions of the lowest[7,11] and somewhat higher[12] energy ions, respectively; thus losses of a methyl or ethyl radical appear to be the principal degradation pathways of all of the $C_4H_8O^{\cdot+}$ ions studied.

(1) Metastable Ion Characteristics. XXI. Part XX: J. E. Coutant and F. W. McLafferty, *Int. J. Mass Spectrom. Ion Phys.*, submitted for publication.

(2) (a) Taken in part from the Ph.D. Thesis of D. J. M., Cornell University, 1971. (b) NIH Predoctoral Fellow, 1969–1970. (c) National Institutes of Health Postdoctoral Trainee, 1970–1971. (d) We are indebted to the Army Research Office, Durham, and to the National Institutes of Health for financial support.

(3) For a preliminary report of this work see D. J. McAdoo, F. W. McLafferty, and J. S. Smith, *J. Amer. Chem. Soc.*, **92**, 6343 (1970).

(4) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, Chapter 3.

(5) W. Carpenter, A. M. Duffield, and C. Djerassi, *J. Amer. Chem. Soc.*, **90**, 160 (1968).

(6) J. Diekman, J. K. MacLeod, C. Djerassi, and J. D. Baldeschwieler, *ibid.*, **91**, 2069 (1969).

(7) A. N. H. Yeo and D. H. Williams, *ibid.*, **91**, 3582 (1969).

(8) F. W. McLafferty, D. J. McAdoo, J. S. Smith, and R. A. Kornfeld, *ibid.*, **93**, 3720 (1971).

(9) J. S. Smith and F. W. McLafferty, *Org. Mass Spectrom.*, **5**, 483 (1971).

(10) A. N. H. Yeo, *Chem. Commun.*, 1154 (1970).

(11) F. W. McLafferty, *ibid.*, 78 (1966); F. W. McLafferty in "Topics in Organic Mass Spectrometry," A. L. Burlingame, Ed., Wiley-Interscience, New York, N. Y., 1970, p 223.

(12) F. W. McLafferty and H. D. R. Schuddemage, *J. Amer. Chem. Soc.*, **91**, 1866 (1969); F. W. McLafferty, I. Howe, R. Kornfeld, H. D. R. Schuddemage, and S.-C. Tsai, manuscript in preparation.

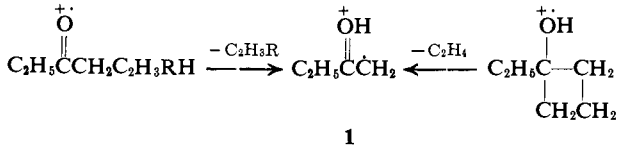
Table I. Unimolecular Metastable and Collision-Induced Dissociations of $C_4H_8O\cdot^+$ Ions[a]

Transition m/e 72 → m/e	$CH_3CH_2C(=\overset{+}{O}H)CH_3$ Unimol	Col ind	$CH_3CH_2C(=\overset{+}{O}H)CH_2$[b] Unimol	Col ind	$CH_3CHC(=\overset{+}{O}H)CH_3$[c] Unimol	Col ind
57	80	51	61	28	68	29
56	1.8	0.8	0.1	0.7	0.2	0.6
55	0.4	0.4	0.05	1.2	<0.04	.7
54	0.5	<0.2	0.3	0.7	0.3	0.6
44	0.4	0.3	0.9	4	0.4	2
43	100	100	100	100	100	100
42	0.3	4	0.3	2	0.3	2
30	<0.4	0.2	<0.05	0.3	<0.04	0.2
29	<0.4	3	0.05	6	<0.04	4
15	<0.4	<0.3	<0.05	0.3	<0.04	0.2

[a] These data were measured under somewhat different instrument conditions than the data of Table II. [b] Formed from 1-ethylcyclobutanol. [c] Formed from 3-methyl-2,4-pentanedione.

The normal spectra of these compounds are also consistent with this. Data concerning the metastable and normal ion products of these decompositions from labeled and unlabeled 2-butanone, 1-ethylcyclobutanol, several 3-alkanones, 3-methyl-2,4-pentanedione, and 3-methyl-2-pentadecanone are given in Table II. Appearance potential data on these pathways are shown in Table III.

$C_2H_5C(OH)CH_2\cdot^+$ (**1**) was generated from both the



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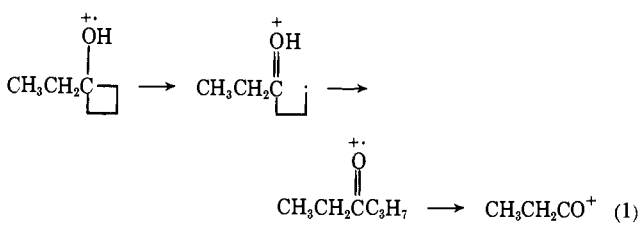
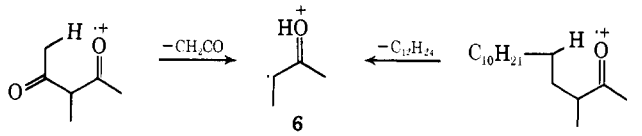
3-alkanones and 1-ethylcyclobutanol, following the methods used to form $CH_3C(OH)CH_2\cdot^+$.[3,4] Relative metastable ion abundances (Table II) for ions generated from these sources are similar; the variation of relative values observed for 3-hexanone probably reflects the variation of the $P(E)$ function (the distribution of the values of internal energy of the precursor ions) from the "degree-of-freedom" effect.[13] By analogy to the case of 1-methylcyclobutanol,[6,8] in the mass spectrum of 1-ethylcyclobutanol the $C_3H_5O^+$ and $C_2H_3O^+$ normal ions appear to be formed predominantly by decomposition of $C_4H_8O\cdot^+$; these three are the dominant product ions in this spectrum. A low energy tail on the appearance potential curve for $CH_3CH_2C{\equiv}O^+$ formed from 1-ethylcyclobutanol indicates that a small proportion of these ions are formed by a low-energy process. The most probable low-energy reaction, by analogy to a process established in the decomposition of 1-methylcyclobutanol,[8,14] is shown in eq 1.



$$CH_3CH_2CC_3H_7 \longrightarrow CH_3CH_2CO^+ \quad (1)$$

The isomeric enolic ion $CH_3CHC(OH)CH_3\cdot^+$ (**6**) was generated from 3-methyl-2,4-pentanedione and



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3-methyl-2-pentadecanone by γ-hydrogen rearrangement. The relative abundances of the metastable ions are surprisingly similar to those from the isomeric enolic ion **1** and from $C_2H_5COCH_3\cdot^+$ (**5**), which suggests that all of these ions isomerize to a common precursor before decomposition; this will be established in later discussion.

Significant isotopic scrambling during preparation and storage or in the molecular ion prior to its fragmentation was not apparent in the normal spectra of any of the compounds employed with the exception of the 3-methyl-2,4-pentanedione-*3-d*. This compound was found to contain ~18% of α′-methyl-*d* which gave rise to the abnormally high abundances of m*(**6d** → $C_2H_2DO^+$) and m*(**6d** → $C_3H_5O^+$). Ions formed from partially labeled molecular ions do not interfere in the metastable spectra obtained by the defocused mode,[8] except for ^{13}C contributions, for which appropriate corrections were made. The observation (Table II) of very abundant metastable ions corresponding to the formation of a single $C_3(H,D)_5O^+$ ion and a single $C_2(H,D)_3O^+$ ion in all cases (except **6d**) provides verification that isotopic scrambling prior to $C_4(H,D)_8O\cdot^+$ formation is small.

Appearance potential data of metastable and normal ions are given in Table III.

Discussion

The possible pathways for decomposition of the enolic ions **1** and **5** which will be considered here are shown in Scheme II. The predominant products of the metastable decomposition of **1** and **6**, as well as of the ketonic ion **5**, are $C_3H_5O^+$ and $C_2H_3O^+$. The figures on the arrows leading away from a particular precursor ion represent the approximate proportion of ions (as established in the following discussion) that decompose by each of those pathways for the metastable transitions, with the data from the higher energy normal ions in parentheses. The data have been corrected, where necessary, to represent the ion containing no deuterium assuming a primary isotope effect (k_H/k_D) of 2.2 and 1.4 for metastable[8] and normal ions,[15]

(13) F. W. McLafferty and W. T. Pike, *J. Amer. Chem. Soc.*, **89**, 5951 (1967); D. J. McAdoo, F. W. McLafferty, P. F. Bente III, M. L. Gross, and C. Lifshitz, manuscript in preparation.

(14) D. J. McAdoo, F. W. McLafferty, and T. E. Parks, manuscript in preparation.

(15) B. J.-S. Wang and E. R. Thornton, *J. Amer. Chem. Soc.*, **90**, 1216 (1968); I. Howe and F. W. McLafferty, *ibid.*, **93**, 99 (1971).

Table II. Metastable[a] (and Normal)[b] Ion Abundances Corresponding to the Decomposition of $C_4(H,D)_8O\cdot^+$ Ions

Compound	$C_4(H,D)_8O\cdot^+$	Ion no.	$\Sigma[m^*]^c / [C_4(H,D)_8O^+]$	Product ion abundance[d] $C_3H_5O^+$	$C_3H_4DO^+$	$C_3H_3D_2O^+$	$C_3H_2D_3O^+$	$C_3HD_4O^+$	$C_3D_5O^+$	$C_2H_3O^+$	$C_2H_2DO^+$	$C_2HD_2O^+$	$C_2D_3O^+$
$CH_3CH_2C(=O)CH_3$	$CH_3CH_2C(=O\cdot^+)CH_3$	**5**	0.00012	99 (36)						100 (440)			
$CH_3CD_2C(=O)CD_3$	$CH_3CD_2C(=O\cdot^+)CD_3$	**5a**				99	1.8					<2[e]	100
$CH_3CH_2C(=O)C_3H_7$	$CH_3CH_2\overset{+}{C}(=OH)\dot{C}H_2$	**1**	0.015	100 (240)						68 (545)			
$CH_3CH_2C(=O)C_4H_9$	$CH_3CH_2\overset{+}{C}(=OH)\dot{C}H_2$	**1**	0.010	77						100			
$CH_3CH_2C(=O)C_5H_{11}$	$CH_3CH_2\overset{+}{C}(=OH)\dot{C}H_2$	**1**	0.0088	73						100			
$CH_3CH_2C(=O)C_9H_{19}$	$CH_3CH_2\overset{+}{C}(=OH)\dot{C}H_2$	**1**	0.0048	74						100			
$C_2H_5C(OH)(CH_2)CH_2(CH_2)$	$CH_3CH_2\overset{+}{C}(=OH)\dot{C}H_2$	**1**	0.020	73 (66)						100 (85)			
$CD_3CH_2C(=O)C_5H_{11}$	$CD_3CH_2\overset{+}{C}(=OH)\dot{C}H_2$	**1a**	0.0098	0.4	1.0	70	1.0			1.2	100	0.6	
$CD_3CH_2C(OH)(CH_2)CH_2(CH_2)$	$CD_3CH_2\overset{+}{C}(=OH)\dot{C}H_2$	**1a**	0.013	0.4 (<2)	0.8 (<2)	70 (36)	0.6 (27)			1.1 (32)	100 (53)	0.8 (1)	
$CH_3CH_2C(OD)(CH_2)CH_2(CH_2)$	$CH_3CH_2\overset{+}{C}(=OD)\dot{C}H_2$[f]	**1b**	0.020	0.6 (9)	67 (62)					100 (64)	2 (16)		
$CD_3CH_2C(OD)(CH_2)CH_2(CH_2)$	$CD_3CH_2\overset{+}{C}(=OD)\dot{C}H_2$[f]	**1c**	0.014		0.2	3.2 (4)	73 (42)	1.1 (14)		1.0 (12)	100 (63)	5[g] (3)	0.1
$CH_3CD_2C(=O)CD_2C_2H_5$	$CH_3CD_2\overset{+}{C}(=OH)\dot{C}D_2$	**1d**				100						68	
$CH_3CD_2C(=O)CD_2C_4H_9$	$CH_3CD_2\overset{+}{C}(=OH)\dot{C}D_2$	**1d**			0.9	74	0.8			0.14	0.8	100	1.1
$CH_3C(=O)C(CH_3)HC(=O)CH_3$	$CH_3\dot{C}HC(=\overset{+}{O}H)CH_3$	**6**	0.011	70 (29)						100 (313)			
$CH_3C(=O)C(CD_3)HC(=O)CH_3$	$CD_3\dot{C}HC(=\overset{+}{O}H)CH_3$	**6a**	0.010		0.4 (8)	1.1 (8)	80 (46)			100 (380)	2.0 (34)	0.4 (15)	
$CH_3C(=O)C(CH_3)DC(=O)CH_3$[h]	$CH_3\dot{C}DC(=\overset{+}{O}H)CH_3$	**6b**	0.017	7.3	79					100	22		
$CD_3C(=O)C(CH_3)HC(=O)CD_3$	$CH_3\dot{C}HC(=\overset{+}{O}D)CD_3$	**6c**	0.0078	0.3	47	2.5					<0.03	2.4	100
$CD_3C(=O)C(CD_3)HC(=O)CD_3$	$CD_3\dot{C}HC(=\overset{+}{O}D)CD_3$	**6d**	0.010			<0.1	0.2	53	4.6		<0.1	6.0	100
$CD_3C(=O)C(CH_3)DC(=O)CD_3$	$CH_3\dot{C}DC(=\overset{+}{O}D)D_3$	**6e**	0.0095		0.2	54	1.9				0.4	3.1	100
$CD_3C(=O)C(CD_3)DC(=O)CD_3$	$CD_3\dot{C}DC(=\overset{+}{O}D)CD_3$	**6f**	0.0093						62				100
$C_{12}H_{25}C(CH_3)HC(=O)CH_3$	$CH_3\dot{C}HC(=\overset{+}{O}H)CH_3$	**6**	0.0023	100 (17)						92 (50)			
$C_{12}H_{25}C(CH_3)DC(=O)CD_3$	$CH_3\dot{C}DC(=\overset{+}{O}H)CD_3$	**6g**	0.0039	0.5 (17)	75 (6.3)	1.4 (0.8)	0.4 (1.0)			<0.04 (29)	0.2 (13)	0.8 (13)	100 (34)

[a] The intensity of the metastable ion on the basis that the intensity of the most abundant metastable ion arising from the $C_4(H,D)_8O\cdot^+$ ion equals 100. [b] The values in parentheses are the intensities of the $C_3(H,D)_5O^+$ and $C_2(H,D)_3O^+$ ions in the normal spectrum on the basis that the intensity of the corresponding $C_4(H,D)_8O\cdot^+$ ion equals 100. [c] The sum of the intensities of all of the metastables arising from the $C_4(H,D)_8O\cdot^+$ ions divided by the intensity of the corresponding $C_4(H,D)_8O\cdot^+$ ion. [d] Unless otherwise noted, standard deviations are generally better than ±5% of the value for values > 10, ±1.0% for 2–10, ±0.2 (absolute) for 0.4–2, and ±0.1 (absolute) for <0.4. The metastable abundances for the ions of structure **6** were obtained during the same day to minimize instrument variations between runs. [e] Uncertainty due to an instrumental problem. [f] The contributions of 1-ethylcyclobutanol-*O*-*d* species were subtracted from the spectra of these compounds. [g] This value was poorly reproduced for unknown reasons. [h] Contains *ca.* 18% α'-methyl-d_1.

Table III. Differences between the Appearance Potentials of the Precursor and Product Ions

Compound	Precursor ion	AP, eV	Ion measured	ΔAP eV[a]
$CH_3CH_2COCH_3$	**5**	9.6[b]	m*(**5** → $C_3H_5O^+$)	<0.4[c]
			m*(**5** → $C_2H_3O^+$)	0.7[c]
			$CH_3CH_2CO^+$	0.6[d]
			CH_3CO^+	1.5[e]
$CH_3CH_2COC_9H_{19}$	**1**		m*(**1** → $C_3H_5O^+$)	1.4
$CH_3CH_2C(OH)(CH_2)CH_2(CH_2)$	**1**	9.5	m*(**1** → $C_3H_5O^+$)	1.2
			m*($C_4H_8O^+$ → $C_2H_3O^+$)	1.3
			$CH_3CH_2CO^+$	1.5
			CH_3CO^+	1.7
$CH_3COCH(CH_3)COCH_3$	**6**	9.7	m*(**6** → $C_3H_5O^+$)	1.7
			m*(**6** → $C_2H_3O^+$)	2.0
			$CH_3CH_2CO^+$	2.2
			CH_3CO^+	2.3
$C_{12}H_{25}CH(CH_3)COCH_3$	**6**	10.2	m*(**6** → $C_3H_5O^+$)	1.8
			m*(**6** → $C_2H_3O^+$)	2.1
			$CH_3CH_2CO^+$	2.0
			CH_3CO^+	2.4
$CH_3C(OH)(CH_2)CH_2(CH_2)$	$CH_3C(OH)CH_2\cdot^+$	9.7	m*($C_3H_6O^+$ → $C_2H_3O^+$)	2.0

[a] Difference in the appearance potential of the ion and that of its precursor. Accuracy *ca.* ±0.2 eV. [b] Ionization potential. [c] Accuracy poorer because of low abundance. [d] Photoionization value, 0.69 eV (see text). [e] Photoionization value 0.74 eV.

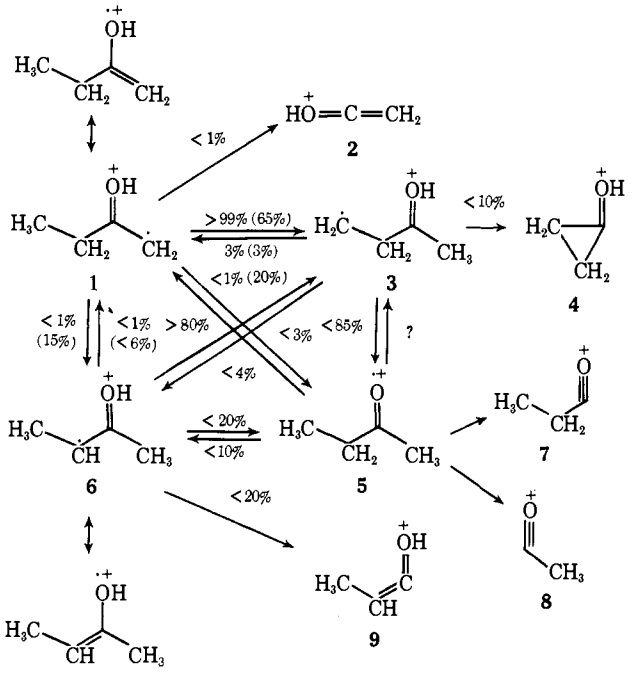
Table IV. Pathway Contributions Indicated in the Decomposition of Metastable (m*) and Normal (N) $C_4H_8O\cdot^+$ Ions from 1-Ethylcyclobutanol, Corrected for Primary Isotope Effects

	$C_3(H,D)_5O^+$ data			$C_2(H,D)_3O^+$ data			Composite value[a]	
Compd	Pathways	m*, %	N, %	Pathways	m*, %	N, %	m*, %	N, %
1a	**1** → **5**, **1** → **6**, eq 1	0.4	35	**1** → **2**, **1** → **5**, **1** → **6**	0.5	30	<1	35 ± 5
1b	**1** → **5**, eq 1	2	17	**1** → **2**, **1** → **5**	4	25	<4	20 ± 5
1c	**1** → **6**	0.7	19	**1** → **6**	0.5	12	<1	15 ± 4

[a] Assuming that pathways **1** → **2** and eq 1 are negligible.

respectively. Details of these data for 1-ethylcyclobutanols are shown in Table IV.

Scheme II

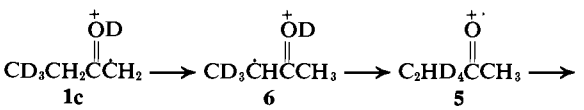


$CH_3CH_2C(OH)CH_2\cdot^+$ Reactions. The main decomposition products of the $CH_3CH_2C(OH)CH_2\cdot^+$ (**1**) enolic ion have been studied previously utilizing metastable ion decompositions of deuterium-labeled derivatives; these results were inconsistent with allylic cleavage, $CH_3CH_2C(OH)=CH_2\cdot^+ \rightarrow CH_3\cdot + CH_2C(OH)CH_2^+$, and were rationalized in terms of the formation of $CH_2=C=O^+H$ (**2**) and $CH_2CH_2C=O^+H$ (**4**) as shown in Scheme II.[5] However, the additional data of Table II rule out the production of $CH_2=C=OH^+$ through the direct cleavage **1** → **2**.[3] For example, $CD_3CH_2C(OH)CH_2\cdot^+$ (**1a**) yields mainly $C_2H_2DO^+$, not $C_2H_3O^+$, and $C_2H_5C(OD)CH_2\cdot^+$ (**1b**) yields $C_2H_3O^+$, not $C_2H_2DO^+$, as predicted by pathway **1** → **3** → **5** → **8**; correcting for the isotope effect on competing reaction **1** → **3**, the data (Table IV) for **1a** indicate that <1% of the $C_2H_3O^+$ ions can arise through the pathway **1** → **2**. This is consistent with our previous conclusion that the homologous $CH_3C(OH)CH_2\cdot^+$ ion does not decompose by direct cleavage.[8] By analogy to the mode of decomposition found for $CH_3C(OH)CH_2\cdot^+$ (Scheme I),[8] ketonization would provide a pathway for the formation of the stable acetyl ion, $CH_3C{\equiv}O^+$ (**8**); however, the same labeling data also show that <1% of the metastable decomposition of **1** occurs through the analogous direct ketonization **1** → **5** (or through **1** → **6**, to be discussed later). The alternative proposal **1** → **3** → **5** (Scheme II) involves two consecutive 1,4-hydrogen shifts (five-membered ring transition states). The formation of $C_2H_2DO^+$ from $CD_3CH_2C(OH)CH_2\cdot^+$ (**1a**) and $CD_3CH_2C(OD)CH_2\cdot^+$ (**1c**) supports the first hydrogen migration **1** → **3**, and the formation of $C_2H_3O^+$ from $C_2H_5C(OD)CH_2\cdot^+$ (**1b**) supports the migration **3** → **5**; the production of $C_2HD_2O^+$ from $CH_3CD_2C(OH)CD_2\cdot^+$ (**1d**) is also consistent with the overall process.

This establishment of the intermediacy of 2-butanone (**5**) in the decomposition of **1** demands that the formation of a substantial amount of $C_2H_5CO^+$ (**7**) accompany the formation of **8**, providing an additional or

even an alternative explanation for the formation of the $C_3H_5O^+$ ion. (The metastable ion abundances found for **5** ions formed from 2-butanone cannot be used for the quantitative prediction of this amount for reasons to be discussed later.) If the formation of **4** is competitive with the formation of **5** in the decomposition of **3**, there should be a significant primary isotope effect on their relative rate constants. When the hydroxylic H is replaced by D (**1** *vs.* **1b**, **1a** *vs.* **1c**), the rate of **3** → **5** should be reduced to approximately half,[8,15] enhancing the production of $C_3H_5O^+$ by **3** → **4**, and thus increasing $[m^*(C_4H_8O\cdot^+ \rightarrow C_3H_5O^+)]/[m^*(C_4H_8O\cdot^+ \rightarrow C_2H_3O^+)]$. If the proportion of **3** from **1** going to **4** were 10%, this ratio should thus increase from 0.73 in **1** to 0.80 in **1b**, so that the observed data show that <10% of the $C_3H_5O^+$ ions are formed by **1** → **3** → **4**.

The initial transfer of hydrogen to the α' carbon of **1** from the α position, **1** → **6**, might also be expected by analogy to the behavior of the enolic $C_3H_6O\cdot^+$ ion (Scheme I). This mechanism could account for the minor metastable decompositions of ion **1c**, eq 2. (The



1c **6** **5**

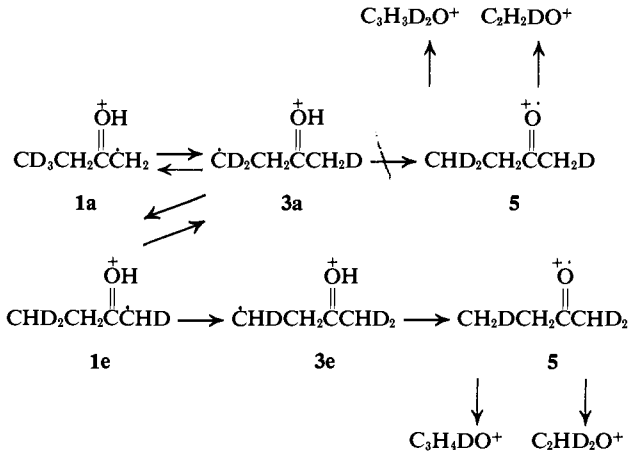
$$C_3HD_4O^+ + C_2H_3O^+ \quad (2)$$

details of pathway **6** → **5** will be discussed below.) Correcting for isotope effects, the data for **1c** indicate that <1% of the enol ions decompose through such a mechanism.

The normal (as distinguished from "metastable") $C_3H_5O^+$ and $C_2H_3O^+$ ions in the mass spectrum of 1-ethylcyclobutanol arise mainly by decomposition of $C_4H_8O\cdot^+$ (*vide supra*); the labeling results (Table IV) indicate that the competing pathways for **1** → **7** + **8** are of much more importance in the decomposition of these higher energy ions.[16] Within the limits of experimental accuracy, 20 and 15% of the normal $C_2H_5C(OH)CH_2\cdot^+$ ions decompose through direct initial isomerization to **5** and **6**, respectively.[17]

$CH_2CH_2C(OH)CH_3\cdot^+$ Reactions. Other reactions of the intermediate **3** should be considered in addition to the ketonization **3** → **5** established above. The data indicate that the reverse five-membered ring rearrangement **3** → **1** does not compete effectively with **3** → **5**. The alternative pathway of Scheme III accounts for approximately 3% of the decompositions of **3a**, after correction for isotope effects.[18] The higher energy normal ions show no appreciable increase in the products from this overall reaction (**1** → **3** → **1** → **3** → **5** → **7** + **8**), consistent with the expected tight transition states of the multiple rearrangements involved.[7,11,19,20]

Scheme III



Evidence will be given below that the path **3** → **6** accounts for <3% of the reactions of **3**. Thus the $\cdot CH_2CH_2C(OH)CH_3^+$ ion **3** appears to react principally by isomerization to the ketonic ion **5**.

$C_2H_5COCH_3\cdot^+$ Reactions. The main reactions of the ketonic ion **5** are the well-known decompositions to the acylium ions, **5** → **7** and **5** → **8**. The small $m^*(C_4H_3D_5O\cdot^+ \rightarrow C_3H_2D_3O^+)$ transition observed in 2-butanone-*1,1,1,3,3-d*$_5$ (**5a**) could be due to pathways **5** → **1** → **3** → **5** → **7** + **8** and/or **5** → **3** → **1** → **3** → **5** → **7** + **8**; a part of this peak is probably due to $m^*(C_4H_3D_5O\cdot^+ \rightarrow C_3D_4O^+)$. Because most of the **1** ions react by **1** → **3** → **5** → **7** + **8**, the data for **5a** show that <4% of the metastable reactions of the unlabeled **5** ions occur through the 1,3-hydrogen shift **5** → **1**. Collision-induced dissociation data indicate no relative increase in this pathway contribution, although $[C_3H_5O^+]/[C_2H_3O^+]$ is reduced to 0.69. The reversal **5** → **3** → **5** would not be apparent in the results for enolic ions as no interchange of labels would result from that process. A similar rearrangement of a β-hydrogen atom to a carbonyl group occurs to a substantial extent in the metastable decompositions of butyric acid,[9] but this may be more favorable as it involves migration of a secondary H in competition with the rearrangement elimination of C_2H_4.

$CH_3CHC(OH)CH_3\cdot^+$ Reactions. Direct decomposition of the isomeric enolic ion $CH_3CHC(OH)CH_3\cdot^+$ (**6**) through simple bond cleavage, **6** → **9**, should be no more facile than for **1** or **3**, and again the labeling data and metastable ion abundances are consistent with rearrangement to the ketonic ion **5** before decomposition; further evidence for this will be presented later. For metastable decompositions of the homologous $CH_3C(OH)CH_2\cdot^+$ ion (Scheme I), 1,3-hydrogen rearrangement from the α' to the α position occurred in 20% of the ions before ketonization; here for the $CH_3CHC(OH)CH_3\cdot^+$ (**6**) ion the analogous rearrangement **6** → **1** accounts for a much smaller proportion of the **7** and **8** final product ions. A value of <1% is indicated by the data for the ion $CD_3CHC(OH)CH_3\cdot^+$ (**6a**) which

(16) Forming the $C_3H_2D_3O^+$ and $C_2H_3O^+$ ions from **1a** by collision-induced dissociation increased their abundance to 3.4% relative to the total ions so produced; such dissociations provide unequivocal identification of the precursor ion, as do unimolecular metastables, but represent somewhat higher energy reactions.[12]

(17) The value for **5** would be reduced if both of the pathways **1** → **2** and eq 1 are important (the data are inconsistent with only one of these making an important contribution). However, eq 1 represents a low activation energy, tight complex reaction, so that its relative contribution should *decrease* with increasing energy.

(18) For ions originating from **1a** the rate of transfer of H (pathway **3a** → 1e) *vs.* D (**3a** → **1a**) would be 2:1 on a statistical basis; this value would be increased by the expected isotope effect.[8] Transfer of D from this product (1e → **3e**) would be favored over transfer of H (1e → **3a**) by a statistical factor of 2:1, except that the isotope effect would decrease this. Thus, the total contribution of **3** → **1** is approximately 2.4% of **3** → **5**. The value calculated from the **1c** data is somewhat larger; in this case the isotope effect (OD *vs.* OH) slows **3** → **5** so that the probability of the occurrence of **3** → **1** is increased.

(19) F. W. McLafferty, D. J. McAdoo, and J. S. Smith, *J. Amer. Chem. Soc.*, **91**, 5400 (1969).

(20) Reversible reactions similar to **1** → **3** → **1** could be invoked to explain the H–D scrambling reported recently in methyl acetate: $CH_3COOCD_3\cdot^+ \rightleftarrows CH_2DCOOCHD_2\cdot^+ \rightleftarrows CHD_2COOCH_2D\cdot^+ \rightleftarrows CD_3COOCH_3\cdot^+$: P. R. Briggs and T. W. Shannon, 18th Annual Conference on Mass Spectrometry, San Francisco, Calif., June 1970.

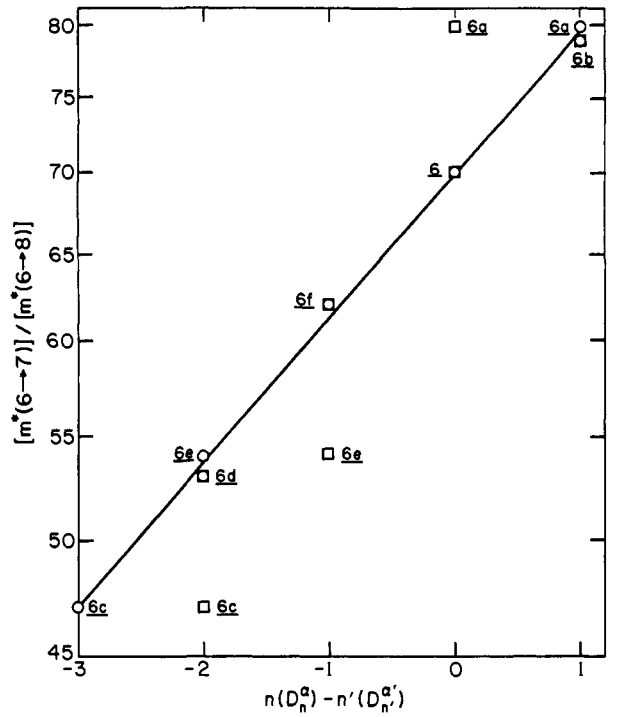


Figure 1. Semilog plot of $[m^*(C_4(H,D)_8O^{\cdot+} \rightarrow C_3(H,D)_5O^+)]/[m^*(C_4(H,D)_8O^{\cdot+} \rightarrow C_2H_3O^+)]$ arising from labeled 3-methyl-2,4-pentanediones *vs.* the difference in the number of deuterium atoms substituted at the α and α' positions in the postulated intermediate **5** of reactions 4 or 5: ○, data plotted assuming reaction 4 (**6** → **3** → **5**); □, data plotted assuming reaction 5 (**6** → **5**).

should yield $C_3H_3D_2O^+$ and $C_2H_2DO^+$ through this pathway (eq 3). Somewhat higher values result from

$$\underset{\textbf{6a}}{CD_3\dot{C}(\overset{+}{O}H)CCH_3} \longrightarrow \underset{\textbf{1}}{CD_3CH_2\dot{C}(\overset{+}{O}H)CH_2} \longrightarrow \underset{\textbf{3}}{\dot{C}D_2CH_2C(\overset{+}{O}H)CH_2D} \longrightarrow$$

$$\underset{\textbf{5}}{CHD_2CH_2\dot{C}(\overset{+\cdot}{O})CH_2D} \longrightarrow C_3H_3D_2O^+ + C_2H_2DO^+ \quad (3)$$

the data for **6c**, **6e**, and **6g** (Table IV). Data for **6a** indicate that the contribution of eq 3 in the reactions forming the higher energy normal ions is 6%, but the true value could be lower as there appears to be alternative pathways for the formation of $C_2(H,D)_3O^+$ and $C_3(H,D)_5O^+$ normal ions. Data from collision-induced decompositions of **6a** indicate that the importance of the pathway **6** → **1** is approximately doubled at these somewhat higher energies.

Two possible pathways for ketonization, **6** → **5** and **6** → **3** → **5**, remain; unfortunately the isotopic composition of the product ions ($C_3H^\alpha H_3^\beta H^0O^+$ and $C_2H_3^{\alpha'}O^+$) produced by pathway **6** → **3** → **5** (eq 4) should be identical with that produced by direct ketonization, eq 5.

The ratio of the abundances of the $C_3(H,D)_5O^+$ and $C_2(H,D)_3O^+$ products should show a secondary isotope effect[21] dependent on the identity (H or D) of the hydrogens on the carbon atoms of the bonds of **5** which are cleaved in forming these products. The intermediate ketonic ions **5** of eq 4 and 5 differ by the presence on the α carbon of hydrogens originating in the β or O positions; thus the labeled ions **6a**, **6c**, and **6e** should provide evidence for the relative importance of paths 4 and 5.

$$\underset{\textbf{6}}{CH_3^\beta\dot{C}H^\alpha C(\overset{+}{O}H^0)CH_3^{\alpha'}} \longrightarrow \underset{\textbf{3}}{\dot{C}H_2{}^\beta CH^\alpha H^\beta C(\overset{+}{O}H^0)CH_3^{\alpha'}} \longrightarrow$$

$$\underset{\textbf{5}}{CH_2{}^\beta H^0CH^\alpha H^\beta C(\overset{+\cdot}{O})CH_3^{\alpha'}} \longrightarrow$$

$$CH_2{}^\beta H^0CH^\alpha H^\beta C{\equiv}O^+ + CH_3^{\alpha'}C{\equiv}O^+ \quad (4)$$

$$\underset{\textbf{6}}{CH_3^\beta\dot{C}H^\alpha C(OH^0)CH_3^{\alpha'}} \longrightarrow \underset{\textbf{5}}{CH_3{}^\beta CH^\alpha H^0C(\overset{+\cdot}{O})CH_3^{\alpha'}} \longrightarrow$$

$$CH_3{}^\beta CH^\alpha H^0C{\equiv}O^+ + CH_3^{\alpha'}C{\equiv}O^+ \quad (5)$$

If eq 4 and 5 are the only paths producing $C_3H^\alpha H_3^\beta H^0O^+$ and $C_2H_3^{\alpha'}O^+$, the ions **6**, **6b**, **6d**, and **6f** formed from 3-methyl-2,4-pentanedione can serve to calibrate this secondary isotope effect, as the ions produced from these by either eq 4 or 5 should be identical. The further assumption[22] was made that replacing a hydrogen atom by a deuterium atom on the α-carbon atom would have the same relative effect on the rate of **6** → **7** as such a replacement on the α' carbon would have on the rate of **6** → **8**; if this is true there should be a linear relationship between the difference in the number of α-D and α'-D atoms and the logarithm of the metastable ion abundance ratio, $[m^*(\textbf{6} \rightarrow \textbf{7})]/[m^*(\textbf{6} \rightarrow \textbf{8})]$. Figure 1 shows that such a relationship holds within experimental error for these ions. The slope of this plot yields $k_H/k_D = 1.11$, consistent with the value of 1.10 found for the analogous reaction of $C_3H_6O^{\cdot+}$ (Scheme I),[8] and within the range of values expected for bond dissociation at an sp^3-hybridized carbon atom which proceeds through an sp^2-hybridized transition state.[23] The same value within experimental error is found from the data for ions **6** and **6g** formed from 3-methyl-2-pentadecanone.

Data for the labeled ions **6a**, **6c**, and **6e** are also shown in Figure 1, plotted according to the secondary isotope effect expected from the products of both eq 4 and eq 5. The former pathway, **6** → **3** → **5** → **7** + **8**, predicts the data within experimental error; thus <20% of the ketonic ions cleaved to form **7** and **8** appear to have been formed through the alternative pathway of direct ketonization, **6** → **5**.

The data of Figure 1 also provide evidence that the direct cleavage **6** → **9** is not important; exchange of H for D on the β-carbon atom should have no appreciable effect on the rate of this cleavage. In addition, the

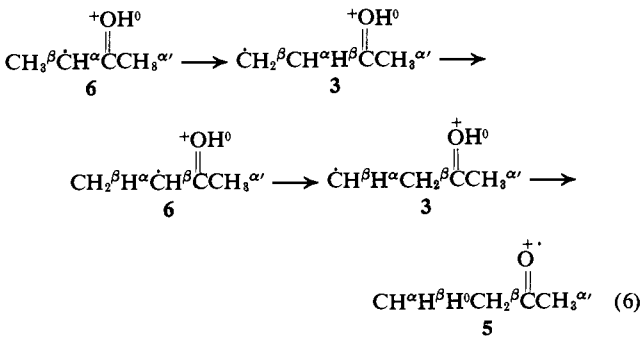
(21) Evidence from primary isotope effects on *total* metastable ion abundances was also considered for the elucidation of this pathway; such evidence was found to be indicative of reaction pathways of the $C_3H_8O^{\cdot+}$ ions,[8] although the experimental error was a substantial part of the differences observed. For the $C_4H_8O^{\cdot+}$ ions formed from the labeled 1-ethylcyclobutanols, the $\Sigma[m^*]/[C_4(H,D)_8O^{\cdot+}]$ values (Table II) appear to show differences outside experimental error consistent with reaction 1 → **3** as the rate-determining step in the proposed overall reaction 1 → **7** + **8**; however, most of the values for ions from 3-methyl-2,4-pentanedione do not exhibit differences that are significant in comparison to the experimental error.

(22) A similar assumption yielded consistent results in a previous study.[8]

(23) K. Humski, R. Malojcic, S. Borcic, and D. E. Sunko, *J. Amer. Chem. Soc.*, **92**, 6534 (1970), and references cited therein.

rate ratio $k(6 \rightarrow 9)/k(6 \rightarrow 3)$ should exhibit a primary isotope effect for the β-hydrogen atoms.

These data also show that another alternative pathway, hydrogen rearrangement from the α to the β carbon ($3 \rightarrow 6$), is of little relative importance. This would lead to H–D interchange through eq 6 for **6a**, **6b**,



6d, **6e**, and **6g**; the fact that the metastable ratios for these ions agree with those predicted within experimental error indicates that ions decomposing as shown by eq 6 represent <20% of the total. This value is probably <3%, based on evidence that the activation energy for $3 \rightarrow 6$ is greater than that for $3 \rightarrow 1$ (*vide infra*).

Relative Activation Energies of the Competing Reactions. Each of the possible decomposition reactions of a particular ion exhibit characteristic $k(E)$ functions which describe the rate constant for that reaction as a function of the ion internal energy.[11,24,25] For minimum energy reactions such as those in the metastable drift region, the relative rates of the competing decompositions depend mainly on the relative activation energies, as the kinetic shift values should be small and vary little between reactions. The 1,4-hydrogen shift rearrangements $1 \rightarrow 3$ and $3 \rightarrow 5$ are clearly favored over the competing 1,3-shift ($1 \rightarrow 5$ and $1 \rightarrow 6$) and 1,2-shift ($3 \rightarrow 6$) rearrangements. The substantially lower activation energy which this indicates is in keeping with the less-strained five-membered ring transition state of these reactions. This is also consistent with the clear preference for 1,4- and 1,5-hydrogen shifts in radical reactions;[27] rearrangements to carbon atoms exhibiting a high degree of carbonium ion character commonly involve three ring transition states.[28] This lower activation energy is confirmed by the differential appearance potentials (Table III); the values[29] of 2.0 and 2.2 eV found for the decomposition of $CH_3CHC(OH)CH_3 \cdot^+$ (**6**), which involves a 1,2-hydrogen shift, are significantly higher than those of 1.4 and 1.5 eV found for the decomposition of $CH_3CH_2C(OH)CH_2 \cdot^+$ (**1**), which involves only 1,4 shifts.

(24) M. L. Vestal in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Wiley-Interscience, New York, N. Y., 1968.

(25) It has now been quite well established that the Rice–Ramsperger–Kassel–Marcus theory adequately describes the $k(E)$ for unimolecular decompositions of smaller[24] and some larger[26] positive ions.

(26) F. W. McLafferty, T. Wachs, C. Lifshitz, G. Innorta, and P. Irving, *J. Amer. Chem. Soc.*, 92, 6867 (1970).

(27) E. A. Hardwidge, C. W. Larson, and B. S. Rabinovitch, *ibid.*, 92, 3278 (1970).

(28) W. Gerrard and H. R. Hudson, *Chem. Rev.*, 65, 697 (1965).

(29) The differential appearance potential values (ΔAP) for the metastable transitions are smaller than those of the corresponding normal products because they are affected by a smaller kinetic shift. The fact that this difference in the ΔAP values is relatively small indicates that the kinetic shift contributes little to the ΔAP values, and that the normal ion at threshold is formed by the same mechanism that is operative for the corresponding metastable.

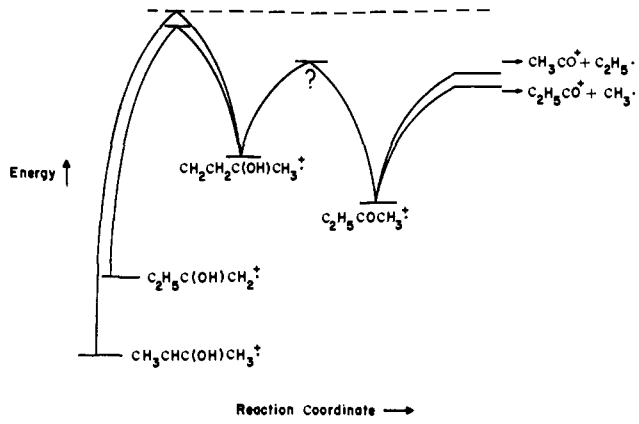


Figure 2. Schematic diagram of the approximate energy requirements for reactions occurring in conjunction with the metastable decompositions of particular $C_4H_8O \cdot^+$ isomers.

Figure 2 depicts the approximate energy relationships for the ion decompositions occurring in the metastable drift region.

The enol $CH_3CHC(OH)CH_3 \cdot^+$ should be more stable than its isomer $C_2H_5C(OH)CH_2 \cdot^+$, as the partial radical character on the α carbon is stabilized by the adjacent methyl group. As a somewhat analogous case, the heat of formation of *trans*-2-butene is 0.56 eV less than that of 1-butene. $\Delta H_f(1) - \Delta H_f(6)$ should not be as great as 0.56 eV if the oxonium ion provides additional stabilization of the radical site of **1** and **6**; however, resonance stabilization of the neutral radical $CH_3COCH_2\cdot$ is negligible.[30] If **6** is 0.5 eV more stable than **1**, rearrangement of **6** will produce $C_2H_5COCH_3 \cdot^+$ ions of energies comparable to those from the rearrangement of **1** (Figure 2).

Although this conclusion is consistent in general with the relative metastable ion abundances, evidence of ion energies from the latter data must be used with caution. The rate ratio $k(C_2H_5COCH_3 \cdot^+ \rightarrow C_2H_5CO^+)/k(C_2H_5COCH_3 \cdot^+ \rightarrow CH_3CO^+)$ decreases with increasing ion internal energy, so that the metastable ratio $m^*(C_4H_8O \cdot^+ \rightarrow C_3H_5O^+)/m^*(C_4H_8O \cdot^+ \rightarrow C_2H_3O^+)$ should reflect the *average* internal energy of the $C_4H_8O \cdot^+$ ions which decompose in the metastable drift region.[11,31] This value is only an approximate indication of ion internal energy *at threshold;* however, note that the variation in this ratio with precursor molecules producing the same $C_4H_8O \cdot^+$ ion (**1** or **6**) is as great as the variation of the average ratios for **1** *vs.* **6**. This is probably due to the relatively wide range of internal energies of the **1** and **6** ions undergoing metastable decomposition, reflecting the slow change of rate constant with ion energy for such rearrangement reactions, which makes possible larger variation[32] in the relative metastable abundances with changes in the precursor $P(E)$. Note that the $C_2H_5COCH_3 \cdot^+$ ions undergoing metastable decomposition should exhibit a much narrower range of internal energies, as simple cleavages (loose activated complexes) are involved; the dra-

(30) K. D. King, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, 92, 5541 (1970).

(31) J. L. Occolowitz, *ibid.*, 91, 5202 (1969).

(32) It is also possible that this variation is due to nonrandomization of the excess energy in **5** formed by isomerization of **1** or **6** before decomposition to **7** and **8**; this explanation was postulated for the analogous decomposition of $CH_3COCH_3 \cdot^+$ formed by isomerization of $CH_3C(OH)CH_2 \cdot^+$.[8]

matically lower value for the total metastable abundance reflects this as well as a low probability in the metastable ion energy range of the $P(E)$ function.

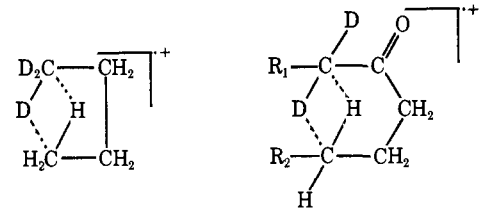
By analogy to the $C_3H_6O\cdot^+$ case,[8] the enol ion **1** should be somewhat (perhaps 0.4 eV) more stable than the keto form **5**.[33] The differential appearance potential value for **5** → **7**, Table III, indicates as expected that no appreciable excess ion energy is required for the decomposition of $C_2H_5COCH_3\cdot^+$.[38] However, for the formation of **7** from $C_2H_5C(OH)CH_2\cdot^+$ ion approximately 1 eV additional activation energy appears to be involved, only part of which should be due to the fact that the heat of formation of **1** is lower than that of **5** (Figure 2). Part appears to be due to the activation energy of the back reaction corresponding to **1** → **5**, so that **1** ions with sufficient internal energy to isomerize in the metastable drift region will usually form **5** ions with more than sufficient energy to decompose before leaving this region. Thus, these ions (and also those formed similarly from **6**) are probably of higher energies than the **5** ions formed by ionization of $C_2H_5COCH_3$ which decompose in the metastable drift region. It also follows that **5** ions formed from $C_2H_5COCH_3$ with sufficient energy to rearrange in the metastable region by **5** → **1** or **6** will exhibit much faster rate constants for **5** → **7** and **8**.

The heat of formation of $\cdot CH_2CH_2C(OH)CH_3^+$ (**3**) is probably higher than any of the isomeric **1**, **5**, and **6** ions. From the evidence above the lowest activation energy pathway is clearly **3** → **5**; the activation energy for the back reactions of either primary step **1** → **3** or **6** → **3** appears to be substantially higher, demonstrating that these primary steps are the rate-limiting reactions of the overall process. Note that the increased migratory aptitude of the hydroxyl hydrogen, **3** → **5**, in comparison to a methyl hydrogen atom, **3** → **1**, when both are undergoing a five-membered ring rearrangement is even more pronounced than the substantial factor (5:1) observed for the four-membered ring rearrangement in the $CH_3C(OH)CH_2\cdot^+$ ion.[8,20] As discussed above, reliable evidence could not be obtained for the activation energy of **5** → **3** relative to that of **5** → **7**.

Many more examples of 1,3-hydrogen shifts (four-membered ring transition states) have been postulated in mass spectral mechanisms than 1,2 shifts.[4,11] However, in this case, the 1,2-hydrogen shift **6** → **3** is clearly favored over the 1,3-hydrogen shifts **6** → **1** and **6** → **5**. (Note, however, that the ΔAP value, Table III, for **6** → **3** is comparable to that for the 1,3-hydrogen shift in $CH_3C(OH)CH_2\cdot^+$, Scheme I.) Assuming equilibrium bond angles and distances of the neutral species, the minimum distance from the α-carbon atom to the rearranging hydrogen atom in $CH_3CHC(OH)CH_3\cdot^+$ (**6**) is actually substantially shorter (*ca.* 0.5 Å) for **6** → **3** than for either **6** → **1** or **6** → **5** (note the unfavorable sp^2 bond angle at the carbonyl carbon for the transition state of the latter two reactions). Although these distances are comparable in a 1,2- and 1,4-hydrogen shift, the activation energy for the latter appears to be lower in the competitive decompositions of $\cdot CH_2CH_2C(OH)CH_3^+$ (**3** → **5** *vs.* **3** → **6** and **3** → **1**). It is also possible that the equilibrium ion geometries are quite different than those of their neutral counterparts; recent theoretical calculations indicate this for propyl ions.[40]

Activated Complex Configurations of the Competing Reactions. Reaction rate constants for ions with internal energies well above the minimum activation energy are also strongly influenced by the nature of the activated complex.[24-26] The rate constant of a loose complex reaction will rise more rapidly with increasing ion internal energy than that of a tight complex reaction, so that the former will be more competitive at higher internal energies. This offers an explanation for the substantial increase in importance of reactions pathways **1** → **5** and **1** → **6**, which increase from <1% of the metastable decompositions of $C_2H_5C(OH)CH_2\cdot^+$ to approximately 35% of the normal ion decompositions. It is concluded that the higher activation energy of the 1,3 shift relative to the 1,4 shift is offset by a looser activated complex for the former reaction, which makes the two reactions competitive at higher ion energies.

Alternative Mechanisms for Hydrogen Atom Scrambling. The mechanisms of Scheme II are consistent with those of many rearrangements which picture the stepwise transfer of a single hydrogen atom to a radical or carbonium ion center.[11] Another mechanism suggested to explain the migration of hydrogen atoms proposes the simultaneous exchange of two hydrogen atoms substituted on adjacent fully saturated positions.[7,10,41] It is difficult to rationalize the H–D exchange in *n*-butane observed by McFadden and Wahrhaftig[41] in terms of initial transfer of a single H to another carbon atom, although bonding similar to that in CH_5^+ might be operative. However, the hydrogen scrambling in alkane molecular ions is generally much smaller[42] than that in those with functional groups, such as alkanones, consistent with the involvement of the functional group in the scrambling process.



(33) Calculations[34] based on photoionization data[35] indicate that $\Delta H_f(CH_3COCH_3\cdot^+) - \Delta H_f(CH_3C(OH)CH_2\cdot^+) = 0.5$ eV. Alternatively, the ionization potential of $CH_3C(OH)CH_2$ has been estimated to be 0.4–0.8 eV[36] below that of CH_3COCH_3; assuming that the heat of enolization of acetone is 0.5 eV,[37] $\Delta H_f(CH_3COCH_3\cdot^+) - \Delta H_f(CH_3C(OH)CH_2\cdot^+) = -0.1$ to +0.3 eV.

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(38) Heats of formation, ΔH_f, for **5**, **7**, **8**, $CH_3\cdot$, and $C_2H_5\cdot$ are 161, 143, 152, 33, and 25 kcal/mol,[34] respectively, so that ΔH(**5** → **7**) = 0.69 eV and ΔH (**5** → **8**) = 0.74 eV.[39]

(39) The large ΔAP value for **5** → **8** is due to the competition of the lower energy reaction **5** → **7**, and to the very low abundance of $C_2H_5COCH_3\cdot^+$ ions formed with internal energies corresponding to the threshold energy for this reaction.[35]

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The simultaneous exchange pictured for the ketone[7] postulates no role for the carbonyl function, although hydrogen rearrangement to this group has been established in a variety of mass spectral reactions, including many of low activation energies.[3-9] Qualitatively, such a concerted exchange reaction should have an even tighter activated complex than the stepwise H rearrangements, suggesting that the latter might be more applicable to cases such as the ketone scrambling as well as the $C_4H_8O\cdot^+$ reactions cited here. For example, the interesting labeling results found for the $(M - H_2O)\cdot^+$ ion in ethyl acetate[10] could alternatively be explained on the basis of stepwise hydrogen rearrangements involving the carbonyl oxygen as well as the alkyl moieties.

Effect of Ion Internal Energy on the Extent of Isotopic Scrambling. Several studies of the mass spectra of deuterium-labeled alkanones have noted that fragment ions show evidence of positional scrambling of H and D atoms, and that the extent of this scrambling is increased by decreasing the internal energy of the reacting ions, such as by lowering the ionizing electron energy or by utilizing metastable ion transitions.[4,5,7-11,19] In contrast, we find that scrambling of H and D positions in the ions **7** and **8** produced from $CH_3CH_2C(OH)CH_2\cdot^+$ (**1**) is *reduced* sharply by lowering the internal energy from that required to produce normal ions to that producing metastable decompositions. The mechanistic pathways of Scheme II provide a logical explanation for this, and represent an alternative general way in which the abundance of isomeric product ions can be increased in a mass spectrum.[43] In this case, higher ion internal energies make the alternative degradation paths **1** → **5** → **7** + **8** and **1** → **6** → **3** → **5** → **7** + **8** competitive with the lowest energy path **1** → **3** → **5** → **7** + **8**, producing isomeric (scrambled) **7** and **8** product ions. In the low-energy case scrambling arises through isomerization (isotopic or structural) which can take place only at the low ion internal energies where such rearrangement reactions can compete with the degradation pathways.

Reactions of Larger Ions. The 1,2-, 1,3-, and 1,4-hydrogen shift reactions in this $C_4H_8O\cdot^+$ system appear to be explicable in terms of a stepwise radical site mechanism in which the activation energy is lowered but the activated complex geometry is tightened by increased ring size in the transition state. The analogous $C_5H_{10}O\cdot^+$ system is currently under investigation, as it presents additional reaction possibilities such as the ubiquitous 1,5-hydrogen shift[45] and the newly postulated cyclobutanol formation.[46]

(43) Another case which could be considered as an example of this is the formation of $C_3H_7^+$ in the mass spectrum of C_3H_8. The activation energy for the loss of the secondary hydrogen atom from $C_3H_8\cdot^+$ is lower than that for loss of the primary hydrogen; the latter reaction has a looser activated complex, and so will compete at higher ion internal energies to form n-$C_3H_7^+$ in addition to s-$C_3H_7^+$.[44]

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Experimental Section

All data were obtained on an Hitachi RMU-7 double focusing mass spectrometer using 70-eV electron energy, 3.6-kV accelerating voltage, and a 10-V repeller potential as described previously.[8] In measurements of normal ion intensities sufficient resolving power was used to distinguish between isobaric species. Metastable ion intensities were recorded by the Major modification of the Barber–Elliott defocusing technique.[47] Collision-induced decomposition measurements were made with a drift region pressure of 3×10^{-5} Torr. Appearance potentials of metastable and normal ions were obtained by the 50-eV normalization–semilog plot method of Lossing and coworkers.[48]

3-Octanone-*1,1,1-d*$_3$. Ethanol-*1,1,1-d*$_3$ was prepared by reduction of 10 g of acetic anhydride-d_6 with $LiAlH_4$ in 200 ml of dry diglyme[49] at 70° for 2 hr. The mixture was cooled, 350 g of diethylene glycol monobutyl ether was added, and ethanol-*1,1,1-d*$_3$ was recovered by distillation. This was converted to 1-bromoethane-*1,1,1-d*$_3$ by means of 12 ml of 48% aqueous HBr mixed with 6 ml of concentrated H_2SO_4. The organocadmium reagent of the distilled bromide and hexanoyl chloride were used to prepare 3-octanone-*1,1,1-d*$_3$ (>98% d_3).

1-Ethylcyclobutanol was prepared from the Grignard reagent of 1-bromoethane prepared under nitrogen in ether by the dropwise addition of cyclobutanone followed by the addition of sufficient 10% H_2SO_4 to clarify the solution. The 1-ethylcyclobutanol was extracted with diethyl ether, dried over $MgSO_4$, and distilled.

1-Ethyl-*1,1,1-d*$_3$-cyclobutanol was prepared from the 1-bromoethane-*1,1,1-d*$_3$ described above and cyclobutanone by the method used to prepare 1-ethylcyclobutanol (92% d_3, 8% d_2).

3-Methyl-*d*$_3$-2,4-pentanedione was prepared from the potassium salt of 2,4-pentanedione and methyl-d_3 iodide by a procedure analogous of that of Sprague, Beckham and Adkins[50] (<1% d_1, 2% d_2, 97% d_3).

3-Methyl-2,4-pentanedione-3-*d* was prepared by stirring 0.30 g of the commercially available 3-methyl-2,4-pentanedione with 1.0 g of D_2O in 1 ml of dioxane for 48 hr at ambient temperature.

The following compounds were prepared by passage of unlabeled compounds through a 10% Carbowax 20M–10% KOD gas chromatography column:[51] **2-butanone-*1,1,1,3,3-d*$_5$** (70% d_5, 25% d_4, 5% d_3); **3-hexanone-*2,2,4,4-d*$_4$** (60% d_4, 34% d_3, 6% d_2); **3-octanone-*2,2,4,4-d*$_4$** (89% d_4, 10% d_3, 1% d_2); **3-methyl-2-pentadecanone-*1,1,1,3-d*$_4$** (71% d_4, 25% d_3, 5% d_2); **3-methyl-2,4-pentanedione-*1,1,1,3,5,5,5-d*$_7$** (1% d_4, 15% d_5, 69% d_6, 15% d_7).

3-Methyl-2,4-pentanedione-d_{10} was prepared from 3-methyl-d_3-2,4-pentanedione (1% d_6, 2% d_7, 11% d_8, 62% d_9, 24% d_{10}).

The following compounds were prepared by exchange with D_2O in the mass spectrometer inlet: **1-ethylcyclobutanol-*O-d*** (78% d_1, 22% d_0); **1-ethyl-*2,2,2-d*$_3$-cyclobutanol-*O-d*** (69% d_4, 24% d_3, 7% d_2). All compounds were purified by gas chromatography.

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