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Non-ergodic Behavior in Acetone–Enol Ion Dissociations

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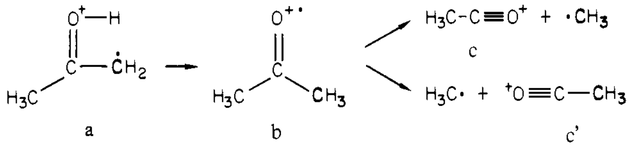
Abstract: A 1970 study[2] reported that enolic acetone cations ($C_3H_6O^{+\cdot}$) undergo threshold energy dissociation by isomerization to excited acetone ions which lose the newly formed CH_3 in preference (58:42) to the original methyl in forming $C_2H_3O^+$. The original postulate that this arises from non-randomization of vibrational energy has in recent years been challenged repeatedly. Questions concerning alternative dissociation pathways involving other $C_3H_6O^{+\cdot}$ or $C_2H_3O^+$ isomers are answered here. Mass spectra from collisionally activated dissociation show that only acetyl ions are formed at threshold energies by loss of either methyl. Dissociation of higher energy $CH_3C(OH)CH_2^{+\cdot}$ ions forms some $CH_2{=}C{=}O^+H$ ions by direct loss of the original methyl; corrected for this, the ^{13}C-labeling data of Heyer and Russell demonstrate that the proportion of non-ergodic dissociations increases with enol ion internal energy as expected. Thus there seems to be no reasonable alternative explanation for the characteristics of this ionic system, which are consistent[3] with thoroughly studied neutral systems shown to undergo non-ergodic behavior.[4]

Extensive studies of the kinetic behavior of neutral systems have led to well-established cases of vibrationally non-ergodic behavior, in which the rate of dissociation is fast relative to the rate of redistribution of energy among the vibrational degrees of freedom.[4] Most such cases involve high levels of excitation (40–100 kcal mol^{-1}) of the dissociating species. As has very recently been reviewed,[3] for unimolecular reactions of ions there has been a less successful search for such non-ergodic cases, for which the quasiequilibrium theory of mass spectra[5] would not be applicable. For example, laser multiphoton ionization of 3-phenyl-1-(*N*,*N*-dimethylamino)propane results in rapid intramolecular energy transfer out of each chromophore of the newly formed molecular ion before fragmentation.[6]

A 1970 study[2] used non-ergodic behavior to explain[7] the observation that acetone cations (b, eq 1) of high internal energy (≥49 kcal mol^{-1}), formed by isomerization of their enolic counterpart $CH_3CH(OH){=}CH_2^{+\cdot}$ (a), undergo dissociation in which the newly formed **CH_3** is lost more readily than the original CH_3. However, of a variety of recent further investigations of this system,[9–19] raise serious questions and offer explanations other than that of non-ergodic behavior. Resolving these questions is of particular importance because this ionic system is the largest, in terms of vibrational degrees of freedom, for which such non-ergodic behavior has been established experimentally. For larger systems this explanation has been offered in studies of the so-called "degrees of freedom" effect[8,20] for the apparent non-equilibrium partitioning of internal energy between the products formed in dissociations such as $CH_3CO(CH_2)_{29}H^{+\cdot} \rightarrow$ a + $C_{28}H_{56}$.[21]



ΔH_f: 158 221 172 191 kcal/mol[2,9–11]

(1)

Alternative mechanisms for such enol decompositions, such as concerted reactions[12] or a pair of 1,2- rearrangements,[13] have been suggested.[14] The intermediacy of the first excited electronic state of *b* (ΔH_f = 220 kcal mol^{-1}) and the isomeric propene oxide ion (ΔH_f = 214 kcal mol^{-1}) has been proposed.[16,22] The favored (58:42) loss of the newly formed CH_3 (eq 1) in metastable a decomposition was confirmed in independent studies[17,18] by using ^{13}C-labeled a. However, Heyer and Russell[17] reported that this loss did not increase with shorter ion lifetime or collisionally-activated dissociation (CAD) of a, the latter yielding a value of 56:44. Both conditions should increase the average internal energy of dissociating a and b ions, which for non-ergodic dissociation

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[2] McAdoo, D. J.; McLafferty, F. W.; Smith, J. S. *J. Am. Chem. Soc.* **1970**, *92*, 6343. McLafferty, F. W.; McAdoo, D. J.; Smith, J. S.; Kornfeld, R. *Ibid.* **1971**, *93*, 3720.

[3] Lifshitz, C. *J. Phys. Chem.* **1983**, *87*, 2304–2313.

[4] Oref, I.; Rabinovitch, B. S. *Acc. Chem. Res.* **1979**, *12*, 166. Forst, W. "Theory of Unimolecular Reactions"; Academic Press: New York, 1973. Baer, T. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 1, pp 153–196. Franklin, J. L. *Ibid.*, pp 273–303.

[5] Rosenstock, H. M.; Wallenstein, M. B.; Wahrhaftig, A. L.; Eyring, H. *Proc. Natl. Acad. Sci. U.S.A.* **1952**, *38*, 667.

[6] Lichtin, D. A.; Squire, D. W.; Winnik, M. A.; Bernstein, R. B. *J. Am. Chem. Soc.* **1983**, *105*, 2109–2117.

[7] The original papers should have acknowledged helpful discussions concerning non-ergotic behavior with B. S. Rabinovitch (see, for example, ref 8), J. C. Tou, and C. Lifshitz.[3]

[8] Lin, Y. N.; Rabinovitch, B. S. *J. Phys. Chem.* **1970**, *74*, 1769.

[9] Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1980**, *102*, 1591. Burgers, P. C.; Holmes, J. L. *Org. Mass Spectrom.* **1982**, *17*, 123.

[10] Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Am. Chem. Soc.* **1980**, *102*, 2246. Frenking, G.; Heinrich, N.; Schmidt, J.; Schwarz, H. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 1597.

[11] Lifshitz, C.; Tzidony, E. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *39*, 181. Lifshitz, C. *Ibid.* **1982**, *43*, 179. Lifshitz, C.; Berger, P.; Tzidony, E. *Chem. Phys. Lett.* **1983**, *95*, 109. Recent reports give evidence for the non-randomization of energy in the decomposition of metastable $C_2H_5C(OH)CH_2^{+\cdot}$ and $CH_3CHC(OH)CH_3^{+\cdot}$ (McAdoo, D. J.; Hudson, C. E. *J. Phys. Chem.* **1983**, *87*, 2451) and $CH_2C(OH)OD^{+\cdot}$ (McAdoo, D. J.; Hudson, C. E.; Griffin, L. L. *J. Phys. Chem.*, in press).

[12] Beynon, J. H.; Caprioli, R. M.; Cooks, R. G. *Org. Mass Spectrom.* **1974**, *9*, 1. Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1980**, *102*, 3732.

[13] Splitter, J. S.; Calvin, M. *J. Am. Chem. Soc.* **1979**, *101*, 7329.

[14] Experimental evidence (McAdoo, D. J.; Farr, W.; Hudson, C. E. *J. Am. Chem. Soc.* **1980**, *102*, 5156) for such non-ergodic behavior of a homologous system, the dissociation of excited 3-pentanone ions formed from the corresponding enolic ions, has been disputed convincingly with ^{13}C-labeling evidence.[15]

[15] Depke, G.; Schwarz, H. *Org. Mass Spectrom.* **1981**, *16*, 421.

[16] Bombach, R.; Stadelman, J.-P.; Vogt, J. *Chem. Phys.* **1982**, *72*, 259.

[17] Heyer, R. C.; Russell, M. E. *Org. Mass Spectrom.* **1981**, *16*, 236.

[18] Depke, G.; Lifshitz, C.; Schwarz, H.; Tzidony, E. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 792.

[19] Johnson, K.; Powis, I.; Danby, C. J. *Chem. Phys.* **1981**, *63*, 1. A persuasive argument against this interpretation has recently appeared: McAdoo, D. J. *Ibid.* **1980**, *80*, 203.

[20] McLafferty, F. W.; Pike, W. T. *J. Am. Chem. Soc.* **1967**, *89*, 5951. McAdoo, D. J.; Bente, P. F. III; Gross, M. L.; McLafferty, F. W. *Org. Mass Spectrom.* **1974**, *9*, 525. Bente, P. F., III; McLafferty, F. W.; McAdoo, D. J.; Lifshitz, C. *J. Phys. Chem.* **1975**, *79*, 713–721.

[21] Brand, Baer, and Klots (Brand, W. A.; Baer, T.; Klots, C. E. *Chem. Phys.* **1983**, *76*, 111) present kinetic energy release data in photoelectron–photoion coincidence experiments of 1- and 2-iodopropane cation dissociations suggesting that not all vibrational modes participate in the energy disposoal.

[22] Tureček and McLafferty (Tureček, F.; McLafferty, F. W. *J. Am. Chem. Soc.*, following paper in this issue) demonstrate that the isomerization of propene oxide ions to b is not an important pathway at threshold energies.

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Table I. $C_2H_3O^+$ Isomers Predicted by Theory[23]

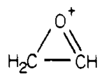
	$CH_3{-}C{\equiv}O^+$	$CH_2{=}C{=}O^+H$	$^+CH_2{-}CH{=}O$		$CH_3{-}O^+{=}C{:}$	$CH{\equiv}C{-}O^+H_2$
	c	d	e	f	g	h
ΔH_f, kcal/mol	157[26]	200	236	215	209	242
$\Delta H_f + \Delta H_f(CH_3)$	191	234	270	249	243	276

Table II. Spectra of $C_3(H,D)_6O^{+\cdot}$ Ions from Metastable and Collisionally Activated Dissociation[a]

		m/z					
precursor[b]	spectrum	41	42	43	44	45	46
$CD_3C(OH)CH_2^{+\cdot}$	MI		1	50	3	1	100
	CAD[c]	55	59	82	54	25	100
$CH_3C(OH)CD_2^{+\cdot}$	MI			100	3	93	
	CAD	31	18	100	47	89	
$CH_3C(OD)CD_2^{+\cdot}$	MI			95	37	45	100
	CAD	46	26	81	94	44	100

[a] Accuracy ±2. [b] Produced from the corresponding 1-methylcyclobutanols 1, 2, and 3, respectively. [c] *m/z* 47: 5.

should have instead *increased* the relative loss of the newly formed CH_3.[17]

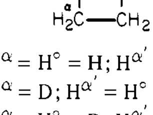
Recent elegant studies by Lifshitz[3,11] offer strong support for the non-ergodic hypothesis for threshold CH_3CO^+ formation from a (eq 1) and from its homologue $C_2H_5C(OH){=}CH_2^+$. For metastable a dissociations the kinetic energy release distributions for losses of the different methyls (eq 1) are bimodal, the higher energy component being of greater abundance for loss of the newly formed CH_3. Although a surprisal analysis[11] indicates non-randomization of internal energy before dissociation, a scaling law analysis[19] of the same data show these "to be consistent with the ergodic hypothesis".

Thus the only reasonable alternative to the non-ergodic hypothesis for explaining either the isotopic labeling[2,17,18] or kinetic energy release distributions[3,11] is that product $C_2H_3O^+$ ions are formed other than the $H_3C{-}CO^+$ and $^+OC{-}CH_3$ ions predicted by eq 1. A recent theoretical study[23] supported experimentally[24,25] indicates (Table I) the $C_2H_3O^+$ isomers c, d, and f to be stable (e isomerizes to c and f). Theory[23] also indicates g and h, not considered previously, to be stable. This product identification became particularly critical with the observation[24,25] that the $C_2H_3O^+$ ions formed by 70-eV electron ionization of acetone are themselves not pure c, containing ~5% of $CH_2{=}C{=}O^+H$ (d).

To answere these key remaining questions, this study utilizes CAD mass spectra to identify the possible $C_2H_3O^+$ isomeric products from dissociation of isotopically labeled a over a range of reaction energies, utilizing high resolution (~20 000) to ensure isobaric purity and low energy formation of $C_2H_3O^+$ to minimize precursor isomerization.[24,25]

Results and Discussion

Metastable ion (MI) and CAD spectra of $C_3(H,D)_6O^{+\cdot}$ ions prepared from the labeled 1-methylcyclobutanols **1**, **2**, and **3** by



1, $H^{\alpha} = H^{\circ} = H; H^{\alpha'} = D$
2, $H^{\alpha} = D; H^{\alpha'} = H^{\circ} = H$
3, $H^{\alpha} = H^{\circ} = D; H^{\alpha'} = H$

70-eV electron ionization are summarized in Table II. The MI spectra show only minor differences in comparison to the original data on which the non-ergodic hypothesis was based;[2] again, the loss of the newly formed methyl is favored by 58:42.[27] These data also confirm the absence of a primary isotope effect in the hydroxylic H migration; this reinforces the original argument[2] that loss of the newly formed methyl is not concerted, in contrast to more recent views.[12] The CAD data of Table II, which represent higher energy decompositions than the MI data,[28] are consistent with the ^{13}C-labeling results[17] but cannot be quantitated because of interference from $C(H,D)_4$ losses.

$C_2H_3O^+$ from Threshold Dissociation of $CH_3C(OH)CH_2^{+\cdot}$. The CAD spectra of the $C_2(H,D)_3O^+$ ions (Table III) show unequivocally that only the acetyl isomer is formed by loss of either the original or the newly formed methyl (eq 1) in the threshold energy decomposition of a. Both the $C_2H_3O^+$ and $C_2D_3O^+$ ions formed by metastable decomposition from $CD_3C(OH)CH_2^{+\cdot}$, and $C_2H_3O^+$ from 2-hexanone, exhibit $[C(H,D)O^+]/[CO^+]$ ratios (0.56, 0.52, and 0.55, respectively) close to those for $C_2H_3O^+$ ions formed from CH_3CDO and CH_3COOCH_3 (0.48 and 0.50) under the same conditions[25] (allowing for isotope effects, the complete CAD spectra also show no differences outside experimental error). All other known $C_2H_3O^+$ isomers give much higher values;[24,25,29] $CH_2{=}C{=}O^+H$ (d), which would be formed by direct CD_3 loss (eq 2), and $\overline{CH_2CH{=}O}^+$ (f) give $[CHO^+]/[CO^+] = 4.3$ and 3.3, respectively.[25,29] Higher values (>0.9) were also obtained in attempts to prepare $^+CH_2CH{=}O$ (e), such as from $BrCH_2CHO$;[25] e presumably[23] isomerizes to c and f.

$$\underset{\text{a}}{H_3C{-}C({=}O^+H)CH_2\cdot} \rightarrow H_3C\cdot + \underset{\text{d}}{\mathbf{CH_2{=}C{=}O^+H}} \qquad (2)$$

Bombach, Stadelman, and Vogt[16] show that the heat of formation of the first excited electronic state (Ã) of acetone ions (b), 220 kcal mol^{-1}, corresponds closely to the threshold energy for eq 1; formation from a of b(Ã) could be more favorable than that of the ground state of b on the basis of orbital symmetry. Although they also give evidence that b(Ã) isomerizes to the unsymmetrical propene oxide ion,[22] this pathway could not account for the unsymmetrical loss of methyl; b(Ã) formed by eq 1 would be in its vibrational ground state with identical methyl groups. Thus the labeling[1,17,18] and kinetic energy release[3,11] data show that at least a substantial proportion of the acetone ions b from threshold isomerization of the enol ions a are not formed in the first electronically excited state b(Ã).

$C_2H_3O^+$ from Higher Energy Dissociation of $CH_3C(OH)CH_2^{+\cdot}$. The CAD spectra of CH_3CO^+ ions produced by 70-eV ionization of acetone (Table III) and other acetyl-containing molecules[25,29] show somewhat higher values (~0.68; 0.63 for CD_3CO^+) of $[C(H,D)O^+]/[CO^+]$, due to the presence of ~5% d in c presumably arising from partial isomerization of the molecular ion.[24,25] Despite this, the $C_2(H,D)O^+$ ions *retaining the original CH_3* produced by 70-eV ionization of **1** and **3** ($C_2D_3O^+$ from **1** and $C_2H_3O^+$ from **3**) show $[C(H,D)O^+]/[CO^+] = 0.62$, indicating that this process at higher energies produces almost exclusively (>95%) the CH_3CO^+ isomer. For $C_2D_3O^+$ from **1** this is confirmed by the CAD $[C_2D_2O^{2+}]/[C_2D_3O^{2+}]$ ratio of 7.2; the value

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(23) Nobes, R. H.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1983**, *105*, 309.

(24) Burgers, P. C.; Holmes, J. L.; Szulejko, J. E.; Mommers, A. A.; Terlouw, J. K. *Org. Mass Spectrom.* **1983**, *18*, 254.

(25) Tureček, F.; McLafferty, F. W. *Org. Mass Spectrom.* **1983**, *18*, 608–611.

(26) Traeger, J. C.; McLoughlin, R. G.; Nicholson, A. J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5318.

(27) Calculations as in ref 2, using $k_H/k_D = 1.125$.

(28) McLafferty, F. W.; Bente, P. F., III.; Kornfeld, R.; Tsai, S.-C.; Howe, I. *J. Am. Chem. Soc.* **1973**, *95*, 2120.

(29) Terlouw, J. K.; Heerma, W.; Holmes, J. L. *Org. Mass Spectrom.* **1981**, *16*, 306.

Table III. CAD Spectra of $C_2(H,D)_3O^+$ Ions

precursor	product ion	ion formation	$[C(H,D)O^+]^a/[CO^+]$	$[C_2(H,D)_2O^{2+}]/[C_2(H,D)_3O^{2+}]$
CH_3COOCH_3	$C_2H_3O^+$	MI $45^+ \rightarrow 43^+$	0.50	
CH_3CDO	$C_2H_3O^+$	MI $45^+ \rightarrow 43^+$	0.48	
$CH_3COC_4H_9 \rightarrow CH_3C(OH)CH_2^{+\cdot}$	$C_2H_3O^+$	MI $58^+ \rightarrow 43^+$	0.55	
$CD_3C(OH)CH_2CH_2CH_2$ (I)	$C_2H_3O^{+b}$	70 eV	0.98	1.9
I $\rightarrow CD_3C(OH)CH_2^{+\cdot}$	$C_2H_3O^+$	MI $61^+ \rightarrow 43^+$	0.56	
1 $\rightarrow CD_3C(OH)CH_2^{+\cdot}$	$C_2H_3O^+$	CAD $61^+ \rightarrow 43^+$	0.85	
I	$C_2D_3O^+$	70 eV	0.62^c	7.2
I $\rightarrow CD_3C(OH)CH_2^{+\cdot}$	$C_2D_3O^+$	MI $61^+ \rightarrow 46^+$	0.52	
$CH_3C(OH)CD_2CH_2CD_2$ (2)	$C_2H_3O^+$	70 eV	0.75	4.3
$CH_3C(OD)CD_2CH_2CD_2$ (3)	$C_2H_3O^+$	70 eV	0.62	
$(CH_3)_2CHC(OH)CH_2CH_2CH_2$	$C_2H_3O^+$	70 eV	0.88	6.0
CH_3COCH_3	$C_2H_3O^{+b}$	70 eV	0.67	14
CD_3COCD_3	$C_2D_3O^+$	70 eV	0.63^c	7
$BrCH_2CHO$	$C_2H_3O^{+a}$	70 eV	0.91	5.4

[a] ±5%. [b] $([29^+ + 28^+])/[43^+] = 4.2 \pm 0.5 \times 10^{-3}$. [c] Corrected for $[C_2D_2^+]$ and $[C_2D_3^+]$.

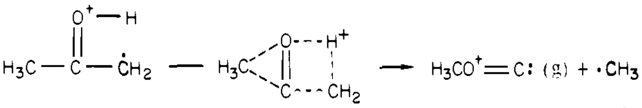
from reference CD_3CO^+ ions is 7.0 (CH_3CO^+ ions give a value of 14, consistent with an isotope effect on H/D loss).

However, the *loss of the original methyl* from higher energy a ions does form a $C_2H_3O^+$ isomer in addition to CH_3CO^+. $CD_3C(OH)CH_2^{+\cdot}$ ions formed from **1** by 70-eV ionization were dissociated by collisional activation to produce $C_2H_3O^+$ ions in the field-free region after the ion source; CAD of these gives $[CHO^+]/[CO^+] = 0.85$. Similarly, a value of 0.98 results from $C_2H_3O^+$ ions produced by 70-eV ionization of **1**, which also show $[C_2H_2O^{2+}]/[C_2H_3O^{2+}] = 1.9$. The latter value is consistent only with the formation of $CH_2{=}C{=}O^+H$ (d) (eq 2) in addition to CH_3CO^+ (c); a value of 0.04 is reported[24] for d, while the values for c, f, and the $C_2H_3O^+$ ion from $BrCH_2CHO$ (which could initially form e) are 14,[25] 25,[24] and 5.4,[25] respectively. This formation of 10–15%[30] $CH_2{=}C{=}O^+H$ by direct CD_3 loss from $CD_3C(OH)CH_2^{+\cdot}$ (eq 2) is consistent with the theoretical estimate[23] (Table I) of $\Delta H_f(CH_2{=}C{=}O^+H) = 200$ kcal mol^{-1}. Assuming a negligible reverse critical energy, this predicts (Table I) a threshold energy requirement of 234 kcal mol^{-1} for eq 2, well above that of 221 kcal mol^{-1} for eq 1.[9]

1-Methylcyclobutanol may form $C_2H_3O^+$ ions by pathways other than that through a.[2,17] Loss of CD_3 from **1** molecular ions gives $C_4H_7O^+$ (5% of base peak) which could give $CH_2{=}C{=}O^+H$ by loss of C_2H_4. This does not appear to be an important pathway, as 1-isopropylcyclobutanol, for whose mass spectrum $C_4H_7O^+$ is the base peak,[32] yields $C_2H_3O^+$ ions containing a somewhat lower proportion of the $CH_2{=}C{=}O^+H$ isomer than the $C_2H_3O^+$ ions from **1** (Table III).

Increased Proportion of Non-ergodic Decompositions for $CH_3C(OH)CH_2^{+\cdot}$ Ions of Increased Energy. The above data show that a substantial fraction of the original methyl loss from a ions of higher internal energy does not involve b formation (eq 1). The ^{13}C data of Heyer and Russel[17] for CAD dissociation of a show that the high energy loss of newly formed methyl is favored by 56:44; correcting for 10% d formation[30] yields 56:(44 − 10), or 62:38, after a → b.[33] Such an increase vs. the lower energy value of 58:42[17] is expected if this excess loss is due to non-ergodic behavior.

Possible Formation of Other $C_2H_3O^+$ Isomers Such as $CH_3O^+{=}C$:. Even the very recent study of Holmes, Terlouw, and co-workers[24] concludes "We stress, however, that until all stable isomeric species (such as $CH{-}O^+{=}C$:) have been experimentally identified, the hypothesis of incompletely randomized energy should be used in reserve". With ergodic behavior for eq 1, the 58:42 ratio[2] favoring loss of the newly formed methyl would require that >16% of the $C_2H_3O^+$ ions be formed as a non-a isomer retaining the original methyl. This would require that the CAD spectrum of this new isomer be much more closely similar to that of a than are the CAD spectra of d–f (Tables III), which spectra eliminate these isomers as possible products of the threshold dissociation (eq 1). The theoretical predictions of $C_2H_3O^+$ isomers by Radom and co-workers[23] which for c–f are supported by these and other recent experiments,[24,25] indicate $CH_3O^+{=}C$: (g) and $CH{\equiv}CO^+H_2$ (h) to be stable also. Isomer h can be ruled out, as the H rearrangements required in its formation are inconsistent with the MI labeling data of Table II. For $CH_3O^+{=}C$: (g) the predicted heat of formation yields a minimum dissociation threshold (Table I) of 209 + 34 = 243 kcal mol^{-1}, higher by 22 kcal mol^{-1} than that observed for a dissociation.[9] Further, any reasonable mechanism for g formation, such as eq 3, would have



(3)

a tight activated complex and significant reverse activation energy; if the latter were 10 kcal mol^{-1}, the difference between the predicted[23] and actual heats of formation of g would have to be much greater than 32 kcal mol^{-1} if other than 16% of the $C_2H_3O^+$ product could be formed as g. Finally, these energetics require the formation with g of $\cdot CH_3$, not $:CH_2$ plus $\cdot H$. Although we concluded above that transfer of the hydroxylic H could not be involved in the rate-determining step, formation of the new methyl through a 1,3-H transfer (eq 3) would have to be concerted with the CH_3 transfer to oxygen. If the latter occurs first, H transfer would yield $CH_3O^+{=}CCH_3$, for which exothermic dissociation to $\cdot CH_3$ and c is predicted;[10a] initial 1,3-H transfer alone would yield the acetone ion of eq 1. The alternative initial 1,2-H transfer[13] yielding $CH_3{-}HC({-}O\cdot)CH_2^+$ appears no more attractive, as this intermediate would more likely rearrange to acetone[10a] or propene oxide[22] ions. We conclude that neither g nor any other rational $C_2H_3O^+$ isomer is a reasonable alternative either energetically or mechanistically.

Conclusion

The non-ergodic behavior proposed originally[2] still appears to be the only logical explanation for the favored loss of the new methyl from the newly formed acetone ion, as only acetyl ions are formed in threshold energy decompositions. At higher energies $CH_2{=}C{=}O^+H$ ions are also formed by direct CH_3 loss from the

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(30) The CAD $[CHO^+]/[CO^+]$ values of 0.85 and 0.98 correspond to ~10% and ~13%, respectively, d in c. Quantitation from the $[C_2H_2O^{2+}]/[C_2H_3O^{2+}]$ values is much more approximate,[24,25] indicating 25 ± 15%.

(31) Proctor, C. J.; McLafferty, F. W. *Org. Mass Spectrom.* **1983**, *1*,, 193.

(32) This formation of $C_4H_7O^+$ has been shown to be accompanied by rearrangement: Stolze, R.; Budzikiewicz, H. *Tetrahedron* **1981**, *37*, 781.

(33) The ^{13}C-labeling value[17] of 58:42 for metastable dissociation also underestimates the favored loss of the newly formed methyl because prior hydrogen exchange between the CH_2 and CH_3 groups of a,[2] $CH_3C(OH)CH_2^{+\cdot} \rightleftarrows CH_2C(OH)CH_2H^+$, reverses the ^{13}C label. The H/D isotope effects on eq 1 and 3 lead to the marked differences in *m/z* 44 and 45 in the MI spectra (Table II) of **1** and **3**.[2]

enolic precursor; correcting for these shows that the proportion of non-ergodic dissociations increases with increasing precursor energy, as expected. Such behavior is also expected from the lifetime of $<10^{-12}$ s calculated[11] for the intermediate acetone ions b containing >49 kcal mol^{-1} excess internal energy, directly analogous to the behavior observed for non-ergodic neutral systems.[3,4]

Experimental Section

A tandem mass spectrometer[34] consisting of a Hitachi RMH-2 double-focusing mass spectrometer as MS-I, a molecular beam collision region, and an electrostatic analyzer as MS-II was used to obtain the CAD spectra. The temperatures of the all-glass sample inlet system and ion source were <130 °C. The collision gas pressure was adjusted to give 33% transmittance of the precursor ions. To measure the normal CAD spectra 7-keV ions were selected by the first MS at a resolution of ~ 20 000 to ensure the purity of the precursor ions. For example, precursor $C_2H_3O^+$ ions sampled at m/z 43.0175, 43.0184, and 43.0193 gave identical CAD spectra, demonstrating the exclusion of other precursors such as C_2HDO^+. In addition, precursor ions formed by metastable ion decompositions in the field-free region (FFR) before the electrostatic analyzer were selected by increasing the accelerating voltage from 7 to ~10 kV while maintaining the electrostatic and magnetic analyzers of MS-I at the same nominal values. For CAD formation of precursor ions the pressure in FFR was increased with helium to 2×10^{-5} torr (gauge), reducing precursor ion transmission in this region by 50%. Metastable ion spectra (Table II) correspond to ion decompositions within the collision chamber (pressure 4×10^{-7} torr) following MS-I, with ion lifetimes of ~22 μs for 7 keV ions, m/z 61. CAD spectra of doubly charged ions were measured separately with 9.9 keV ions at 33% transmittance of the precursor main beam.

$$\text{ions} \xrightarrow[\text{acceleration}]{10\text{ kV}} \text{FFR: MI or CAD} \xrightarrow{\text{ESA-I}} \xrightarrow{\text{magnet-I}} \text{collision chamber} \xrightarrow{\text{ESA-II}} \text{CAD spectrum}$$

1 was kindly supplied by Professor Chava Lifshitz. **2** was prepared from cyclobutanone-*2,2,4,4-d*$_4$[2] and methyl magnesium iodide, and **2** was converted to **3** with D_2O/CH_3OD, after conditioning the ion source and the inlet system with D_2O for 2 h before each measurement. Bromoacetaldehyde was prepared according to ref 35 and distilled immediately before use. 1-Isopropylcyclobutanol was prepared from cyclobutanone (Aldrich) and isopropyl magnesium bromide.

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Registry No. 1, 24300-66-1; **2**, 79523-37-8; **3**, 79523-38-9; CH_3COOCH_3, 79-20-9; $CH_3\underline{CDO}$, 4122-13-8; $CH_3COC_4H_9$, 591-78-6; $(CH_3)_2CH\underline{C(OH)CH_2CH_2CH_2}$, 78386-42-2; CH_3COCH_3, 67-64-1; CD_3COCD_3, 666-52-4; $BrCH_2CHO$, 17157-48-1; acetone enol radical cation, 34507-14-7.

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(34) McLafferty, F. W.; Todd, P. J.; McGilvery, D. C.; Baldwin, M. A. *J. Am. Chem. Soc.* **1980**, *102*, 3360. Todd, P. J.; McGilvery, D. C.; Baldwin, M. A.; McLafferty, F. W. In "Tandem Mass Spectrometry"; McLafferty, F. W., Ed.; John Wiley: New York, 1983; Chapter 13.

(35) Yanovskaya, L. A.; Terentyev, A. P. *Zh. Obsh. Khim.* **1952**, *22*, 1598.

Rearrangement and Methyl Loss from Ionized Propene Oxide and Methyl Vinyl Ether

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Abstract: Molecular cations of propene oxide (a) and methyl vinyl ether (b), despite a large difference (35 kcal mol^{-1}) in their heats of formation, undergo two very similar metastable methyl loss dissociations; for both of these dissociations a and b exhibit the same kinetic energy release values and produce acetyl ions. Deuterium labeling shows that a ions undergo little direct methyl loss, but instead isomerize by ring opening and 1,4-H transfer to b. The latter reversible reaction causes hydrogen exchange in metastable b ions prior to methyl loss by b → $CH_3C{=}OCH_3^{+\cdot}$ → CH_3CO^+. For long-lived a ions of energies below the decomposition threshold, nearly complete hydrogen exchange occurs between the methyl and methylene groups. Low-energy a ions also lose a methyl incorporating the ring methylene group and the methine hydrogen, consistent with the symmetry-allowed rearrangement to acetone ions in their first electronically excited state postulated recently by Bombach, Stadelmann, and Vogt. High-energy a ions also lose the methylene plus methine H, possibly through a non-ergodic process.

The gaseous $C_3H_6O^{+\cdot}$ isomers have been the subject of a variety of investigations,[1-13] including a recent comprehensive ab initio molecular orbital study.[8] Ionized propene oxide $CH_3\overline{CHCH_2O}^{+\cdot}$ (a) appears to be unique among these isomers in several aspects. It is stable,[6,8,10] in contrast to ionized ethene oxide, which spontaneously ring opens.[14] Its heat of formation, 214 kcal mol^{-1},

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(1) Diekman, J.; MacLeod, J. K.; Djerassi, C.; Baldeschwieler, J. D. *J. Am. Chem. Soc.* **1969**, *91*, 2069.

(2) Eadon, G.; Diekman, J.; Djerassi, C. *J. Am. Chem. Soc.* **1969**, *91*, 3986; **1970**, *92*, 6205.

(3) McLafferty, F. W.; McAdoo, D. J.; Smith, J. S.; Kornfeld, R. *J. Am. Chem. Soc.* **1971**, *93*, 3720.

(4) McLafferty, F. W.; Kornfeld, R.; Haddon, W. F.; Levsen, K.; Sakai, I.; Bente, P. F., III; Tsai, S.-C.; Schuddemage, H. D. R. *J. Am. Chem. Soc.* **1973**, *95*, 3886.

(5) Pritchard, J. G. *Org. Mass Spectrom.* **1974**, *8*, 103.

(6) Van de Sande, C. C.; McLafferty, F. W. *J. Am. Chem. Soc.* **1975**, *97*, 4617.

(7) (a) Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1980**, *102*, 1591. (b) *Ibid.* **1980**, *102*, 3732.

(8) Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Am. Chem. Soc.* **1980**, *102*, 2246, 7928.

(9) Terlouw, J. K.; Heerma, W.; Holmes, J. L. *Org. Mass Spectrom.* **1981**, *16*, 306. Burgers, P. C.; Holmes, J. L.; Szulejko, J. E.; Mommers, A. A.; Terlouw, J. K. *Ibid.* **1983**, *18*, 254.

(10) Bombach, R.; Stadelmann, J. P. Vogt, J. *Chem. Phys.* **1982**, *72*, 259.

(11) Turecek, F.; McLafferty, F. W. *J. Am. Chem. Soc.*, preceding paper in this issue.

(12) Turecek, F.; McLafferty, F. W. *Org. Mass Spectrom.* **1983**, *18*, 608-611.

(13) Lifshitz, C. *J. Phys. Chem.* **1983**, *87*, 2304-2313.

(14) Corderman, R. R.; Le Breton, P. R.; Buttrill, S. E.; Williamson, A. D.; Beauchamp, J. L. *J. Chem. Phys.* **1976**, *65*, 4929. Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Chem. Soc., Chem. Commun.* **1978**, 724.

0002-7863/84/1506-2528$01.50/0