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Why ketonization is favored over enolization in 5-membered ring H-transfers by $CH_3C(=OH^+)CH_2C^{\bullet}H_2$ and in 6-membered ring H-transfers by $CH_3(C=OH^+)CH_2CH_2C^{\bullet}H_2$

Charles E. Hudson [a], Lidenys Varela [a], Lawrence L. Griffin [b], David J. McAdoo [a,*]

[a] Department of Neurosciences and Cell Biology, The University of Texas Medical Branch, Galveston, TX 77555, USA
[b] Department of Marine Sciences, Texas A & M University at Galveston, Galveston, TX 77553, USA

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Abstract

The reactions leading to dissociation of the metastable enol isomers of 2-butanone have a puzzling feature: why does $CH_3C(=OH^+)CH_2C^{\bullet}H_2$ (**2**) isomerize to the less stable 2-butanone cation (**3**) and dissociate to the exclusion of conversion to $CH_2=C(OH^{+\bullet})CH_2CH_3$ (**1**) and $CH_3C(OH^{+\bullet})=CHCH_3$ (**4**)? To answer this, the stationary points on the pathways established previously are located using ab initio and hybrid density functional theory and their geometries and energies determined. Rate curves for some of the reactions are also obtained by RRKM theory. It is found that **2** isomerizes to **3** rather than to its more stable enol isomers **1** and **4** because ketonization has the lowest barrier, despite its giving the highest energy product. For **2** → **1**, this barrier arises from a strained, twisted transition state geometry being required in transfer of a hydrogen to the π-bonded methylene group in **1** whereas TS (**2** ⇌ **3**) is completely planar. The energy of the transition state for **4** ⇌ **2** is elevated by a different phenomenon, the need for an electron to go into an antibonding orbital in a 1,2-H-shift, raising its energy above that of TS (**2** ⇌ **3**). The critical energies for the 5-membered ring isomerizations of **1**–**2** and **2**–**3** are significantly higher than those of the 6-membered ring processes that ketonize and enolize $CH_3C(=OH^+)CH_2CH_2C^{\bullet}H_2$ (**6**). However, similarly to **2**, isomerization of **6** to $CH_3C(=O^{+\bullet})CH_2CH_2CH_3$ has a lower energy transition state and is preferred to isomerization to the more stable $CH_2=C(OH^{+\bullet})CH_2CH_2CH_3$. This is also attributable to twisting at the C1 methylene as hydrogen is transferred to and from it.

Keywords: Ab initio; $C_4H_8O^+$; $C_5H_{10}O^+$; 5-Membered rings; 6-Membered rings

1. Introduction

This work is dedicated to the memory of Chava Lifshitz, with deep regret at her passing and with gratitude for the many ways she influenced the work of the authors and gas phase ion chemistry. One of her interests was the chemistry of keto and enol ions [1–6]. Thus we present work in that area, including some reactions that she investigated [4,5], for this special issue in her honor.

In the early 1970s, McAdoo, McLafferty and coworkers [7,8] (MMP) reported that the metastable enol isomers $CH_2=C(OH^{+\bullet})CH_2CH_3$ (**1**) and $CH_3C(OH^{+\bullet})=CHCH_3$ (**4**) of the 2-butanone cation radical lose methyl and ethyl to similar degrees. They found the fragmentations of $CH_2=C(OH^{+\bullet})CH_2CD_3$ to be heavily dominated by losses of $C^{\bullet}H_2D$ and ${}^{\bullet}C_2H_3D_2$. This and similar results from other deuterium-labeled forms of **1** and **4** demonstrated that the third hydrogen forming the methyl group lost from **1** comes from C4 (In this work, carbons will be referred to by their IUC numbers.) and the fifth hydrogen in the ethyls lost from **1** and **4** comes from the oxygen, i.e., that **1** and **4** rearrange to $CH_3C(=OH^+)CH_2\ C^{\bullet}H_2$ (**2**) and then to the 2-butanone ion (**3**) before dissociating (Scheme 1). These reactions are prominent in the dissociation of most $C_4H_8O^{+\bullet}$ ions in the gas phase [9–11], although there are additional pathways to methyl loss from $C_4H_8O^{+\bullet}$ isomers with the oxygen on the first carbon [12].

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* Corresponding author at: Department of Neuroscience and Cell Biology, University of Texas Medical Branch, 301 University Boulevard, Galveston, TX 77555-1043, USA. Tel.: +1 409 772 2939; fax: +1 409 772 3222.

E-mail addresses: cehudson@utmb.edu (C.E. Hudson), lcvarela09@aol.com (L. Varela), griffinl@tamug.edu (L.L. Griffin), djmcadoo@utmb.edu (D.J. McAdoo).

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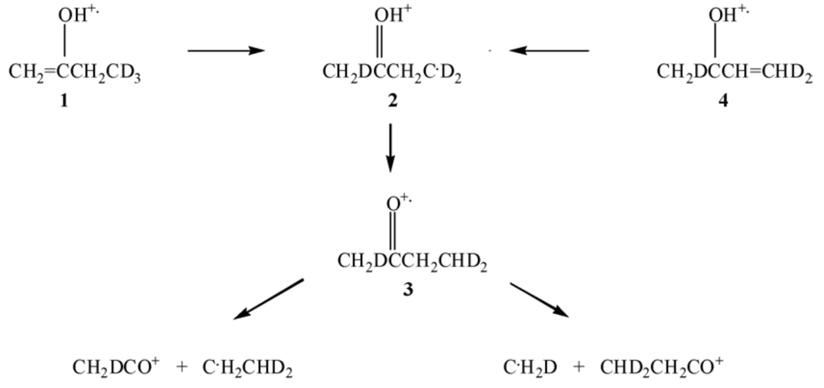


Scheme 1.

The absence of transfer of hydrogen from C1 to C4 in **2**, i.e., why **2** → **3** → products is at least 100 times faster than reversion of **2** to **1** when **1** is 49 kJ/mol more stable than **3** [13] has long been a puzzle. We address why **2** isomerizes preferentially to the less stable **3** than to the more stable **1**, even though both processes are 5-membered ring hydrogen rearrangements. We also explore why **4** → **2** is largely irreversible.

We previously found that in enol-to-keto isomerizations of $CH_2{=}CHOH^{+\bullet}$, $CH_3C(OH^{+\bullet}){=}CH_2$ and $CH_2{=}C(OH)_2{}^{+\bullet}$ the methylenes destined to receive the itinerant hydrogens rotate to being perpendicular to the planes of the ions before there is much movement of the transferring H (H_t), i.e., the reactions are highly asynchronous [14,15]. From this we hypothesized that in **1** → **2** twisting of methylene to receive the itinerant hydrogen to its p-orbital might elevate the energy required to transfer H to that group. There is no comparable requirement for twisting that breaks off conjugation and creates non-planarity in TS (**2** ⇌ **3**). We performed density functional and ab initio calculations on the species in Scheme 1 to test our hypothesis that the energy required to twist CH_2 at TS (**2** ⇌ **1**) renders reaction through that transition state unable to compete with reaction through the lower energy, planar TS (**2** ⇌ **3**). Next we modeled the kinetics of **2** → **1** and **2** → **3** with RRKM calculations to establish further whether the former reaction is competitive with the latter. Then we used ab initio, density functional and RRKM theories to characterize the isomerizations of $CH_3C({=}OH^+)CH_2CH_2C^{\bullet}H_2$ (**6**) to $CH_3C({=}O^{+\bullet})CH_2CH_2CH_3$ (**7**) (the reverse of the first step of the McLafferty rearrangement [16–18]) and to $CH_2{=}C(OH^{+\bullet})CH_2CH_2CH_3$ (**5**) (the reverse of the second step of the double McLafferty rearrangement [16]). H-transfers through 6-membered ring transition states in these reactions also form higher energy keto ions in preference to lower energy enol ions [19].

Finally, we determined whether generating **1** by the McLafferty rearrangement rather than by fragmentation of the 1-ethylcyclobutanol ion, that is orienting the hydrogen on oxygen *cis* to the one carbon side of the molecule so that it is not positioned to participate in the rearrangement **2–3**, raises the energy required for that reaction. We found that *cis*/*trans* isomerization of the hydrogen on the oxygen of **1** is more facile than rearrangements **1–2** and **2–3**, rendering the fragmentation patterns of the *cis* and *trans* isomers of **1** indistinguishable.

2. Theory

The Gaussian 98 [20] and Gaussian 03 [21] suites of programs were employed to describe stationary points and the intrinsic reaction coordinate (IRC) for **1** ⇌ **2**. We found candidate transition states by first constraining the migrating hydrogen to be equidistant between the migration termini and optimizing all of the other parameters. The candidate structures were then fed into another run with the constraint to equal bond lengths removed and the route card specifying B3LYP/6-31G* opt = (*z*-matrix, ts, tight, calcall). The transition state geometry and force constants found at the B3LYP/6-31G* level were then used as starting points to locate the transition states at other levels of theory. This procedure did not work for finding TS (**6** ⇌ **7**) at the QCISD level. In that case, the distance from O to H_t was first constrained to 1.32 Å and the C–H_t distance to 1.28 Å. All other parameters were then optimized using QCISD theory. The resulting structure was fed into a transition state-finding routine with the constraints removed. Force constants calculated at the HF level were used. Zero-point energies were computed at the B3LYP/6-31G* level and scaled by 0.9806, as recommended by Radom for that level of theory [22]. Except for the QCISD(T) results, energies and geometries were obtained at the same levels of theory. Stationary points indicated in the tables as QCISD(T)/6-311G** are from QCISD(T)/6-311G**//QCISD/6-31G* theory. The structures in the figures were all optimized by QCISD/6-31G* theory. For RRKM calculations [23] the vibrational frequencies computed at the B3LYP/6-31G* level were scaled by Radom's factors of 1.0620 for frequencies below 600 cm^{-1} and by 0.9945 for frequencies above 600 cm^{-1} [22]. Reaction pathways were traced at the B3LYP/6-31G* level by IRC methods [24,25].

3. Results and discussion

3.1. $C_4H_8O^{+\bullet}$

3.1.1. $CH_2{=}C(OH^{+\bullet})CH_2CH_3$ (*1*) → $CH_3C({=}OH^+)CH_2C^{\bullet}H_2$ (*2*) → $CH_3C({=}O^{+\bullet})CH_2CH_3$ (*3*)

Figs. 1–3 depict the structures we obtained for the ground states of **1**, **2**, and **3** respectively. The skeleton and the H on O

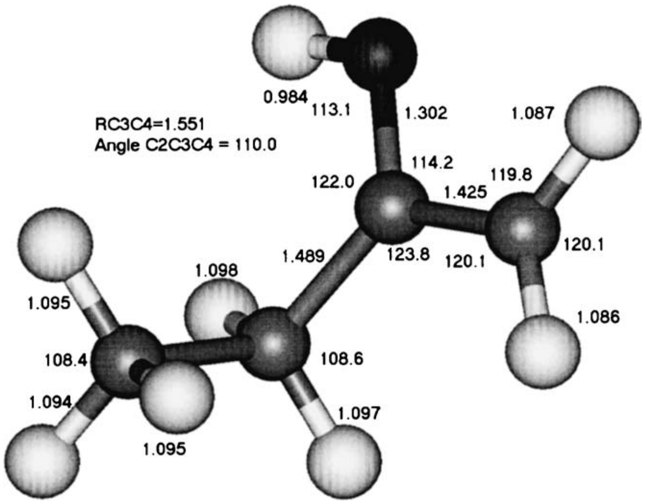


Fig. 1. Structure **1a**. In this structure, $C1H_2$, C1C2C3, O and the H on O are all within 3° of being in the same plane, and $C4H_3$ is bisected by that plane. However, the C4C3C2C1 dihedral angle is 80°, i.e., the C3C4 bond is almost perpendicular to the plane of the rest of the ion.

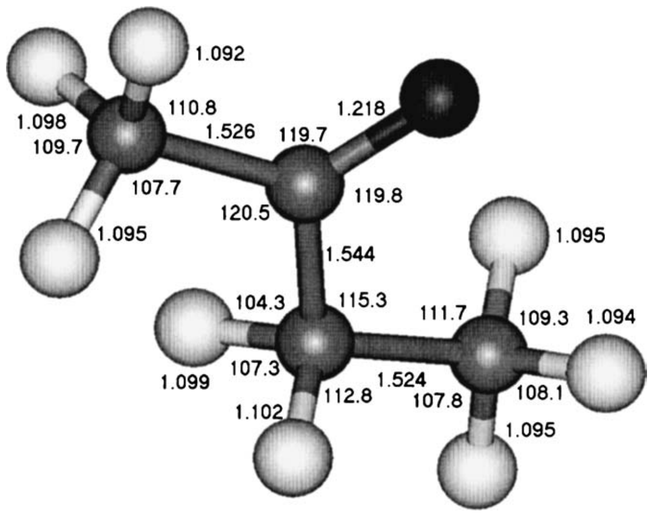


Fig. 3. The structure of **3**. C1C2C3O is planar in this structure with the C3C4 bond pointing slightly away from this plane (the dihedral angle C4C3C2C1 = −167°).

occupy a plane in **1**, except the C3–C4 bond is at an angle of 80° to that plane. The structures of the distonic ion **2** and the keto ion **3** are similar to that of **1**, except the hydrogens on their carbons are not symmetric to the skeletal plane and C4 is closer to the plane in **2** and **3** than in **1** (C4C3C2C1 dihedral angles of −172.6° and 167° versus 80°).

The structure for TS (**2** ⇌ **1**) is depicted in Fig. 4. Consistent with our hypothesis (see above), the methylene group containing C1 is twisted out of the C1C2C3 plane in TS (**1** ⇌ **2**). The $C1H_2$ methylene is coplanar with CCO in **1**, and therefore it might have to twist to achieve transfer of H_t to its face. The twisting amounts to 66.3° for the H on C1 *cis* to C3 (the H more nearly internal to the 5-membered ring), and 26.9° in the same sense for the remaining H on C1. The bond angles about C1 in this transition state (excluding the bond to H_t) total 347.2°, 12.8° less than required for a planar methylene group. The non-planarity of the transition state 5-membered ring is also evident in a bond angle sum about the ring of 530.9°, which is 9.1° less than the sum for

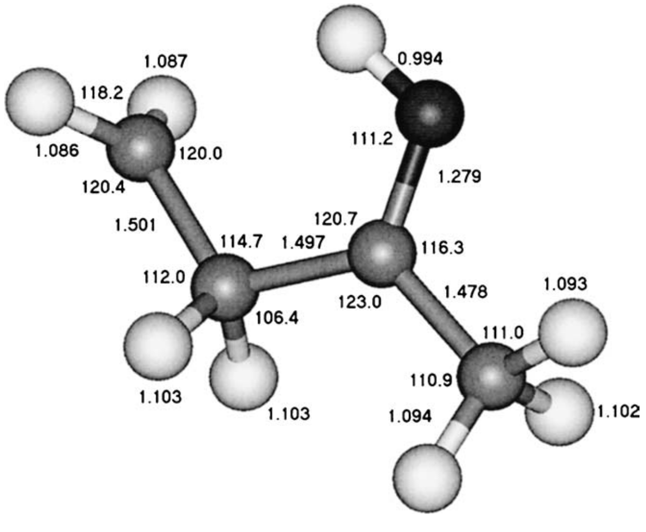


Fig. 2. The structure of **2a**. C1C2C3O and the H on oxygen are planar and the C3C4 bond is turned down away from the oxygen but still close to the plane of the rest of the skeleton (the C4C3C2C1 dihedral angle = −172.6°). None of $C1H_3$, $C3H_2$ and $C4H_2$ is symmetric to the skeletal plane.

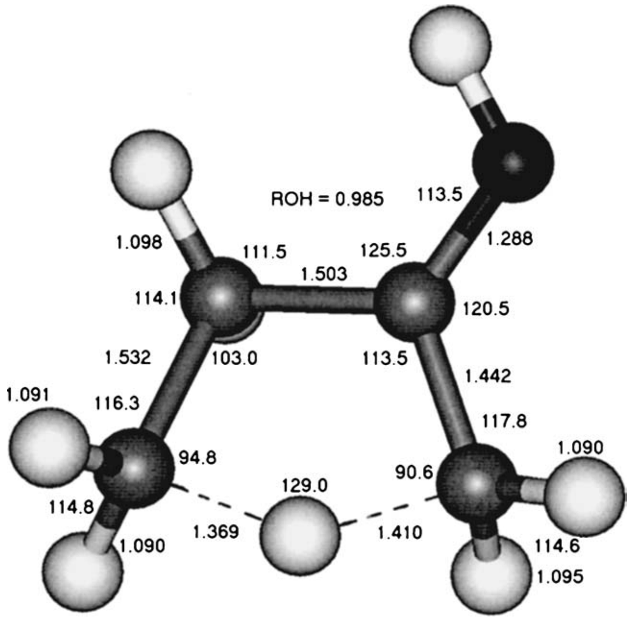


Fig. 4. TS (**2** → **1**) optimized at the QCISD/6-31G* level of theory. H_t is slightly closer to C1 than to C3 at this transition state. The dihedral angle OC2C3C4 = −146.4°, demonstrating that C4 is out of the skeletal plane. The dihedral angle $C3C2C1H_t$ is −28.7°, demonstrating that H_t is about the same degree outside and on the same side of the plane of the carbons as C4. The dihedral angles HC1C2C3 for the two hydrogens on C1 are 66.4° and −153.1° so these hydrogens are also substantially out of the C1C2C3 plane, allowing H_t to move to between the hydrogens on both the carbon it comes from and the one to which it goes. At the transition state, H_t is about equidistant from the two hydrogens on C4 (1.9665 and 2.0017 Å), but at differing distance from the hydrogens on C1 (1.8229 and 2.1328 Å). Thus the $C1H_2$ is twisted at the transition state relative to the $C1H_tC3$ plane, but $C4H_2$ is very nearly symmetric to that plane.

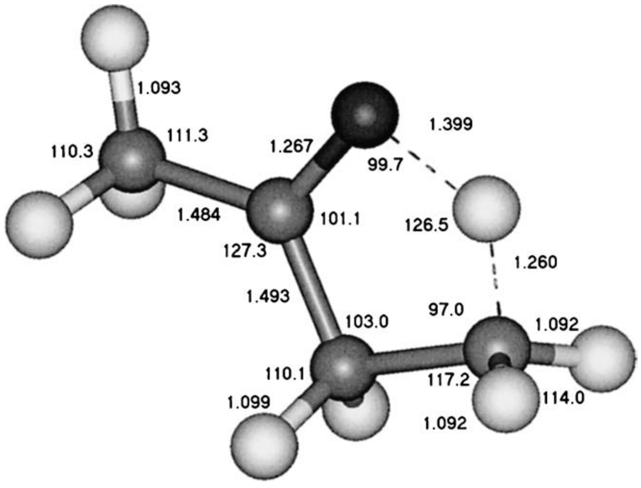


Fig. 5. TS (**2** → **3**). At this transition state, all of the heavy atoms, H_t and one hydrogen on C1 are in a plane and the remaining hydrogens are in CH_2 groups that are symmetric to that plane. Thus (**2** → **3**) is planar.

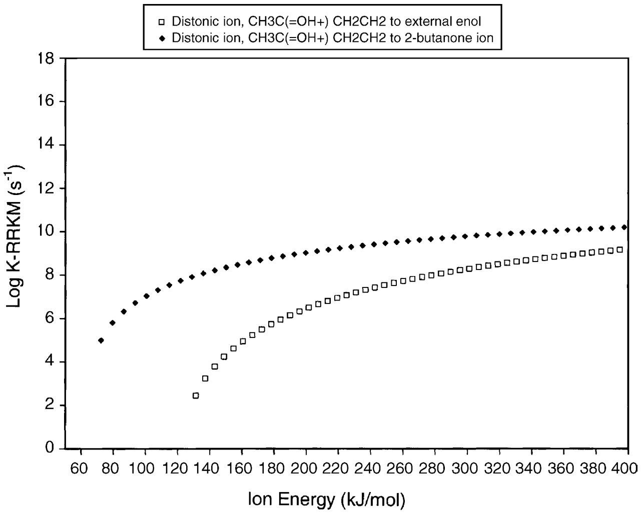


Fig. 6. Plot of the RRKM computed reaction rates of **2** → **3** (filled diamonds) and **2** → **1** (open squares) as a function of ion internal energy. Note that the reactions involving **1** are slower than those involving **2**.

a fully planar ring. In contrast, the ring in TS (**2** ⇌ **3**) (Fig. 5) is planar, creating a plane of symmetry for the whole transition state.

The energy of TS (**2** ⇌ **1**) exceeds that for TS (**2** ⇌ **3**) by 39–55 kJ/mol, depending on the computational method (Tables 1 and 2), with the lower number probably being our best result (QCISD(T)/6-311G**//QCISD/6-31G* results will be considered and referred to as our best results in all cases because that is the highest level of theory that we applied). In both B3LYP and QCISD calculations, larger (and therefore presumably better) basis sets gave smaller differences in the energies of the two transition states. The energy requirement of 130.5 kJ/mol that we obtained for **1** → **2**, which is also the energy requirement for the overall process **1** → **3**, is in good agreement with the difference of 125 ± 10 kJ/mol between the appearance energies of the products of metastable decomposition to $C_2H_3O^+$ and of **1** [8].

All but our lowest level calculations (B3LYP/6-31G*) predict that the energy required for **1** → **2** exceeds that of the fragmentation products of **3**, and our (QCISD(T)/6-311G**//QCISD/6-31G*) calculation predicted that the energy of TS (**1** ⇌ **2**) is 26 kJ/mol above that for $CH_3CO^+ + CH_3C^{\bullet}H_2$, the higher energy set of simple dissociation products of **3**. Fig. 6 gives the RRKM rate constants for **2** → **3** and **2** → **1** as a function of energy. When k for **1** → **2** equals $10^5\ s^{-1}$, i.e., in the region of metastable decompositions, *k* for **2** → **3** is $10^8\ s^{-1}$ and k for **2** → **1** is $1.6 \times 10^5\ s^{-1}$. Over the energy range considered, the rate for **2** → **3** is 10 to 6×10^5 times as fast as the rate of **2** → **1**, the greatest differences occurring near threshold. There is also an energy region below the theoretical threshold for **2** → **1** in which only **2** → **3** can occur. All of these results are fully consistent with the conclusions of MMP that **1** → **2** → **3** is essentially irreversible.

The QCISD(T) energy for TS (**2** ⇌ **3**) (91 kJ/mol) is about the same as those for the dissociations of **3** represented in Scheme 1 (103.7 and 88.2 kJ/mol). Thus significant **3** → **2** might be expected, although the lack of exchange in the dissociations of deuterated forms of **1** and **4** appears to indicate otherwise [8]. Possibly **3** → **2** occurs, but is not observable because reversion by **2** → **3** is faster than **2** → **1** and **2** → **4**. However, based on present results and previously calculated RRKM rate curves for the dissociations of **3** [26] near threshold, that ion should lose methyl about 100 times faster than it isomerizes to **2**, making dissociation much faster than isomerization, thereby suppressing **3** → **2**. This is also in keeping with the observations and conclusions of MMP.

To define better the factors that favor **2** → **3** over **2** → **1**, we traced the reaction coordinate of **1** → **2** by IRC calculations. Pertinent changes in angles and bond distances are plotted in Fig. 7. Twisting of the external methylene and rotation of the methyl so as to position the associated hydrogens to allow H_t-transfer occurs first and then H_t-transfer accompanied by little other

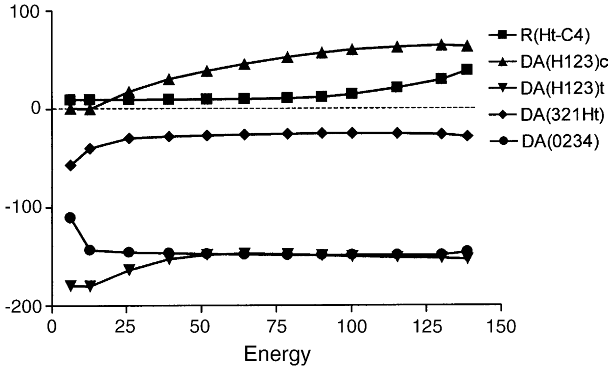
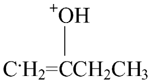
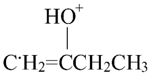
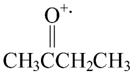
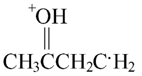
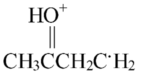
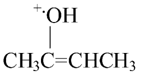
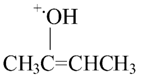
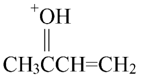


Fig. 7. Plots of parameters of the IRC of $CH_2{=}C(OH^{+\bullet})CH_2CH_3 \rightarrow CH_3C({=}OH^{+})CH_2C^{\bullet}H_2$ as a function of the energy of the reaction coordinate from the ground state of the first ion to the transition state for the rearrangement. The actual values of the angles are given, but the C1H distances were obtained by subtracting 1 Å from the actual values and then multiplying them by 20 to make the changes in the length of that bond apparent on the scale of the other traces in the plot. Note that the changes in bond angles largely precede the change in the C1H bond distances.

Table 1
Ab initio $C_4H_8O^+$ energies (hartrees)

Method structure	B3LYP/6-31G*	ZPVE	B3LYP/6-311G**	QCISD/6-31G*	QCISD(T)/6-311G**
 $C^{\cdot}H_2{=}\overset{{}^{+}OH}{\overset{\vert}{C}}CH_2CH_3$ **(1a)**	−232.139855	291.7	−232.206692	−231.415448	−231.592732
 $C^{\cdot}H_2{=}\overset{HO^{+}}{\overset{\vert}{C}}CH_2CH_3$ **(1b)**	−232.137611	291.3	−232.204788	−231.413398	−231.590701
 $CH_3\overset{O^{+\cdot}}{\overset{\Vert}{C}}CH_2CH_3$ **(3)**	−232.132636	284.2	−232.195660	−231.407055	−231.590701
 $CH_3\overset{{}^{+}OH}{\overset{\Vert}{C}}CH_2C^{\cdot}H_2$ **(2a)**	−232.127341	285.0	−232.195045	−231.405599	−231.582554
 $CH_3\overset{HO^{+}}{\overset{\Vert}{C}}CH_2C^{\cdot}H_2$ **(2b)**	−232.127769	288.4	−232.195148	−231.403171	−231.581133
 $CH_3\overset{{}^{+\cdot}OH}{\overset{\vert}{C}}{=}CHCH_3$ **(4t)**	−232.155652	288.9	−232.222955	−231.427797	−231.604010
 $CH_3\overset{{}^{+\cdot}OH}{\overset{\vert}{C}}{=}CHCH_3$ **(4c)**	−232.155944	289.3	−232.223094	−231.428253	−231.604599
TS (**1a** → **2a**)	−232.085703	277.7	−232.154792	−231.352780	−231.537682
TS (**1b** → **2b**)	−232.086574	277.7	−232.155602	−231.353758	−231.538476
TS (**2a** → **3**)	−232.105207	274.7	−232.169769	−231.372522	−231.551535
TS (**2a** → **4t**)	−232.094994	279.0	−232.165096	−231.361172	−231.544072
TS (**2a** → **4c**)	−232.096340	279.3	−232.166224	−231.362479	−231.545423
TS (**1a** → **1b**)	−232.111415	284.6	−232.179292	−231.383825	−231.561000
TS (**2a** → **2b**)	−232.091920	274.3	−232.161568	−231.364246	−231.541196
CH_3CO^+	−152.923535	115.3	−152.968581	−152.495501	−152.597785
$C_2H_5^{\bullet}$	−79.157867	153.6	−79.183653	−78.869044	−78.946757
$C_2H_5CO^+$	−192.246649	190.5	−192.301551	−191.680455	−191.817561
$CH_3^{\bullet}$	−39.838292	76.8	−39.853758	−39.689122	−39.732301
 $CH_3\overset{{}^{+}OH}{\overset{\Vert}{C}}CH{=}CH_2$ **(8)**	−231.567786	264.5	−231.634585	−230.856087	−231.025905
$H^{\bullet}$	−0.498231	0.0	−0.499809	−0.498231	−0.499809

4t has C1C2C3C4 *trans* and OC2C3C4 *cis*; 4c has C1C2C3C4 *cis* and OC2C3C4 *trans*.

change in geometry follows. This sequence is similar to that of H-transfer in the ketonization reactions of $CH_2{=}CHOH^{+\bullet}$, $CH_2{=}C(OH)_2^{+\bullet}$ and $CH_3C(OH^{+\bullet}){=}CH_2$ [14,15]. The initial twisting takes about 2/3 of the energy required to reach TS (**1** ⇌ **2**). Thus twisting of $C1H_2$ as it is formed so H_t can depart the developing p orbital on this carbon contributes substantially to the higher energy requirement for **2** → **1** than for **2** → **3**. The remaining 1/3 of the critical energy is used during H-transfer, presumably to conduct that process.

Generation of **1** by a McLafferty rearrangement produces **1b** (**1** with the H on oxygen pointed toward the C1 end of **1**) rather than **1a** (**1** with the H on oxygen pointed toward the C4 end of **1**) required to form **3** from **2**. Maintenance of the HO orientation in **1b** would generate different reactivities for **1a** versus **1b**. Therefore, we determined whether **1a** and **1b** can interconvert at the energies required to form **3** from **1**. Fig. 8 represents the transition state for this isomerization. We obtained critical energies for **1a** → **1b** ranging from 65.5 to 76.2 kJ/mol. Since these are substantially less at all levels of theory than our computed critical energy of 120.8–150.5 kJ/mol for **1** → **2**, it is not surprising that it makes little difference in its reactions whether **1** is generated from 3-octanone (which should produce only **1b** initially) or from 1-ethylcyclobutanol (which should produce a mixture of **1a** and **1b**) [8]. The corresponding *cis*/*trans* isomerization of **2** requires more energy (117.9 kJ/mol relative to **1**) than does **1a** → **1b**, but its critical energy is nonetheless lower than that for **1** → **2**. Therefore reactivity would probably not be affected by *cis*/*trans* isomerization of **2**.

Table 2
$C_4H_8O^+$ relative energies

Method structure	B3LYP/6-31G*	B3LYP/6-311G**	QCISD/6-31G*	QCISD(T)/6-311G**
1a	0	0	0	0
1b	5.5	5.3	5.0	4.9
3	11.5	22.2	14.5	18.8
2a	26.2	23.9	19.2	20.0
2b	28.4	27.0	28.9	27.2
4t	−44.3	−44.8	−35.2	−33.5
4c	−44.6	−44.8	−36.0	−33.6
TS (**1a** → **2a**)	128.2	123.0	150.5	130.5
TS (**1b** → **2b**)	125.9	120.8	148.0	128.4
TS (**2a** → **3**)	74.0	80.6	95.7	91.2
TS (**2a** → **4t**)	105.1	97.2	129.8	115.1
TS (**2a** → **4c**)	101.8	94.6	126.7	111.8
TS (**1a** → **1b**)	67.6	65.5	75.9	76.2
TS (**2a** → **2b**)	108.5	101.1	117.0	117.9
$CH_3CO^+ + C_2H_5$	130.7	120.2	110.8	103.7
$C_2H_5CO^+ + CH_3$	119.8	110.5	96.0	88.2
8 + $H^\bullet$	166.7	162.6	133.3	148.8

4t has C1C2C3C4 *trans* and OC2C3C4 *cis*; 4c has C1C2C3C4 *cis* and OC2C3C4 *trans*.

MMP concluded from secondary isotope effects that $CH_3C(OH^{+\bullet})$=$CHCH_3$ (**4**) decomposes primarily by **4** → **2** → **3** → products (Scheme 1). Figs. 9 and 10 show the structures of **4a** (**4** with the H on oxygen pointed toward the C4 side of the ion) and TS (**2** ⇌ **4a**), respectively. According to our result, **4a** contains a plane of symmetry. Previously, only the C1 methyl in **4a** was found by MP2(FULL)/6-31+G(d,p) theory to be bisected by the plane containing the heavy atoms [27].

MMP obtained differences between the appearance energy of **4** and the peaks for metastable fragmentations of **4** to $C_3H_5O^+$ and $C_2H_3O^+$ of 164 and 193 kJ/mol^{-1}, respectively, both ±19 kJ/mol. Our computed threshold energy for these processes, the energy required to reach TS (**2** ⇌ **4**) from **4**, vary from 139.4 to 165.0 kJ/mol^{-1}, depending on computational method and the *cis/trans* isomer about the C2–C3 bond of **4** considered. Our best calculations gave values of 148.6 kJ/mol for the isomer with the carbon skeleton *trans* (**4t**) and 145.4 kJ/mol with the carbon skeleton *cis* (**4c**). Our computed values in the range of 162.7–165.0 kJ/mol may be somewhat too high, as those calculations did not incorporate polarization functions on hydrogen, which are important in computing the energies of [1,2]-H-shifts [28].

The rearrangement **2** → **4** is a [1,2]-H-shift in a cation radical, reactions to which there tend to be moderate barriers [28]. In simple radicals, such shifts are higher in energy than dissociation by loss of the hydrogen that migrates because the transition state is required to have an electron in an antibonding orbital [29]. However, when one of the reaction termini has a very strong electron withdrawing group attached to it, such as a protonated carbonyl group, the antibonding character of the HOMO is reduced, and rearrangement becomes the lower energy reaction [28]. Consistent with this, our calculations show this [1,2]-shift to be lower

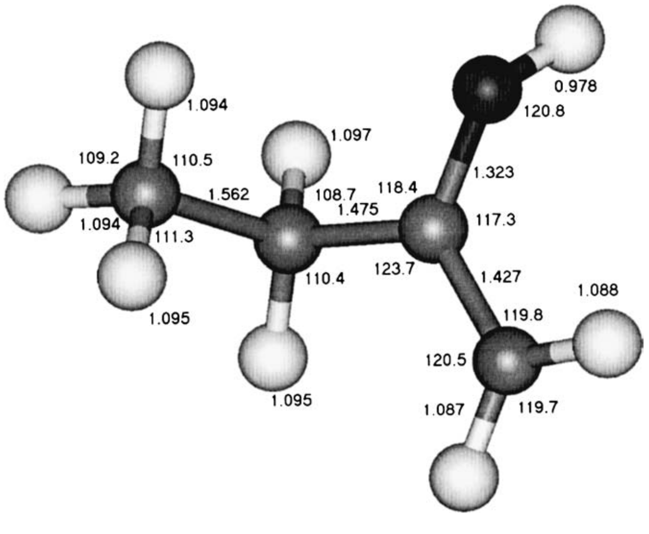


Fig. 8. TS for *cis*/*trans* isomerization of **1a** to **1b**. At the transition state, the HOC2C1 dihedral angle is 91.3°, as would be expected. The C4C3C2C1 dihedral angle is 96.9°, so the C3C4 bond is nearly perpendicular to the plane containing the heavy atoms other than C4.

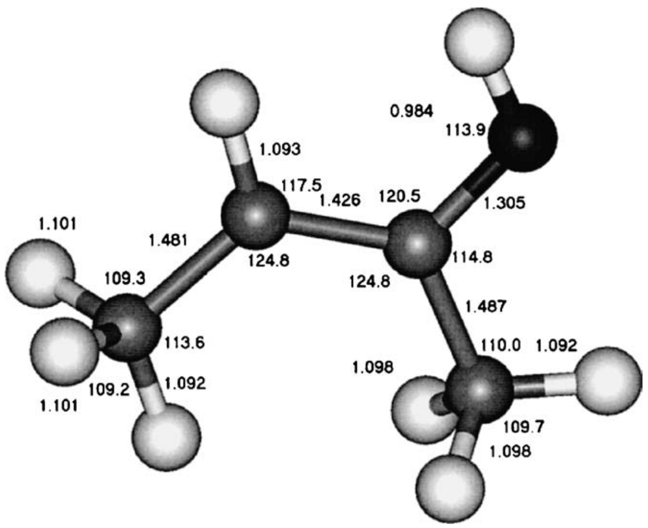


Fig. 9. The structure of **4c**. All of the heavy atoms, Ht and the H on C3 are in same plane.

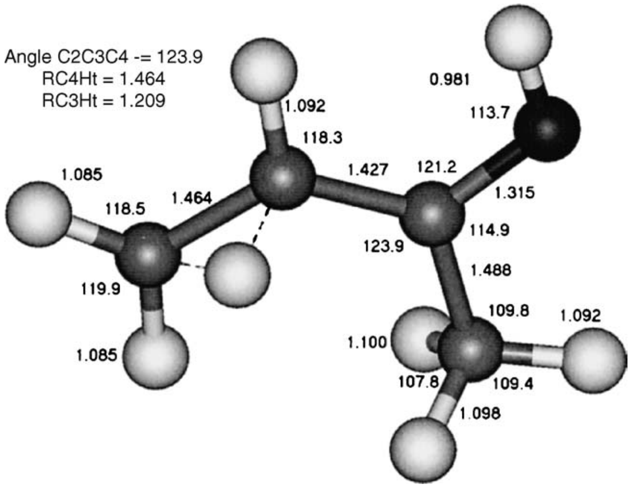


Fig. 10. TS (**2a** → 4**c**). The transferring H is closer to C3 (1.2094 Å) than to C4 (1.4620 Å) at this transition state, the C3C4 bond is rotated about 10° from the plane of C1C2C3O, and the methyl and $C4H_2$ are rotated out of the plane of the heavy atoms.

in energy at every level of theory than the products of H_t loss, with a best value for the difference of 37.0 kJ/mol.

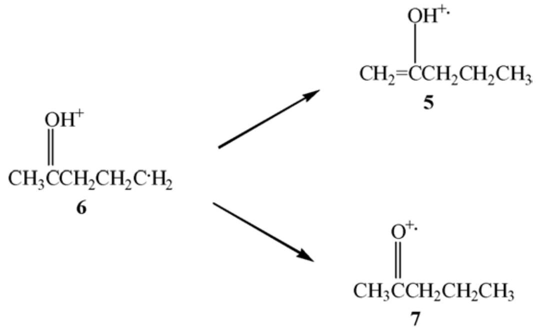
The results of B3LYP and QCI computations (Table 2) differ as to whether the fragmentation products of **3** are higher or lower in energy than TS (**4c** ⇌ **2**) and TS (**4t** ⇌ **2**). The hybrid density functional calculations place the fragmentation products higher, while the QCI calculations place them lower. This reflects that both higher transition state energies and lower fragment energies were obtained with QCI methods than with B3LYP methods. Ions **2** formed from **1** contain enough energy to rearrange to **4** because TS (**1** ⇌ **2**) is higher in energy than TS (**2** ⇌ **4**) at all levels of theory. However, the energy required for **2** → **4** is 20 kJ/mol greater than that needed for **2** → **3**, so the latter reaction should be substantially favored, as is observed [8]. Nonetheless, a few ions arriving at **2** from **1** might convert to **4** to form a reservoir of higher energy ions, because isomerization back to **2** would be very slow due to the deep well in which **4** resides.

3.2. $C_5H_{10}O^{+\bullet}$

We examined another enol ion → distonic ion → ketone ion sequence to extend our studies to 6-membered ring H-transfers because transfer of H from O to C5 of $CH_3C(=OH^+)CH_2CH_2C^\bullet H_2$ (**6**) occurs at least six times more frequently than does H-transfer from C1 to C5 [19]. The second step **7** → **6** is the reverse reaction of the McLafferty rearrangement [16–18], which has been characterized several times by theory [30–32]. The reactions we characterized are given in Scheme 2.

Figs. 11–13 show the structures of **5**, **6**, and **7**, respectively. The ground state geometry of **5** has a plane of symmetry, and in **6** and **7** C1, C2, C3, O and the H on O in **6**, but not C4 and C5, are planar.

Table 3 gives the energies of the stationary points of pertinent $C_5H_{10}O^{+\bullet}$ isomers and connecting transition states. As inferred from experimental data for this reaction [19], and as in 5-membered ring H-transfers, 6-membered-ring transfer from **6** to give the higher energy keto isomer has a higher critical energy than isomerization to the lower energy enol isomer. Thus a higher critical energy for distonic → enol than for distonic → keto is again the reason for preferred rearrangement to the higher energy



Scheme 2.

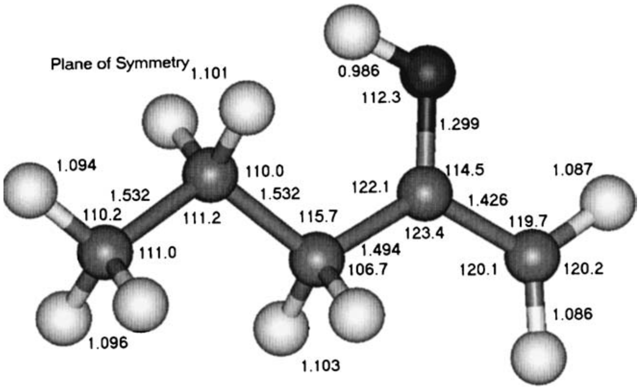


Fig. 11. The structure of **5**. The skeleton and hydrogens on C1, O and one H on C5 are in a plane and the other hydrogens are in or symmetrically placed in pairs relative to this plane.

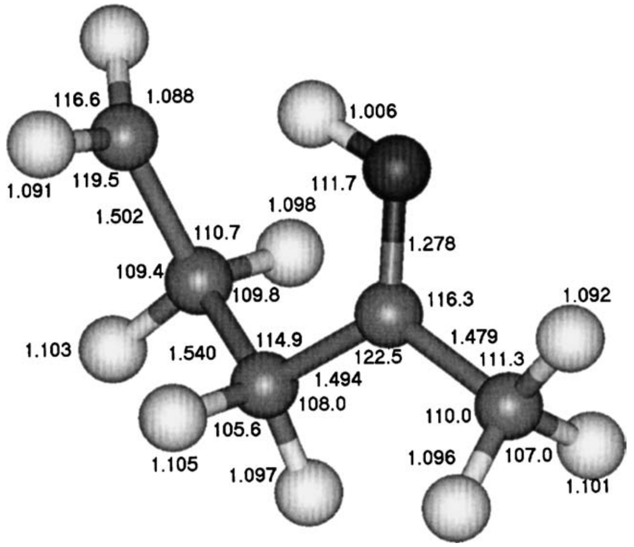


Fig. 12. The structure of **6**. This structure is without unusual features. C1, C2, C3, O and the H on the O are in the same plane, but the remainder of the ion is outside this plane. No CH_2 hydrogens are symmetric to this plane.

Table 3
$C_5H_{10}O^{+\bullet}$ energies

Method structure	B3LYP[a]	ZPVE	B3LYP[b]	QCISD[a]	QCISD(T)[c]
Enol$^{+\bullet}$ (**5**)	−271.457776 0	364.4	−271.535376 0	−270.596777 0	−270.809212 0
5a$^{+\bullet}$[d]	−271.456653 4.2	365.7	−271.534239 4.3	−270.595811 3.8	−270.808752 2.5
Distonic$^{+\bullet}$ (**6**)	−271.450636 13.6	359.3	−271.528207 13.7	−270.590525 11.3	−270.803642 9.5
Ketone$^{+\bullet}$ (**7**)	−271.454488 0.9	356.7	−271.527648 12.6	−270.587672 16.2	−270.799421 18.0
TS (**5** → **6**)	−271.426135 72.4	353.7	−271.504929 69.2	−270.555106 98.7	−270.775360 78.2
TS (**6** → **7**)	−271.446075 15.2	348.9	−271.521776 20.2	−270.575551 40.2	−270.790929 32.5

The values on the first line for each species are in Hartrees, and the values on the second line are in kJ/mol. All structures with a hydrogen atom on oxygen have it oriented toward the side of the longer chain.

[a] 6-31G*//6-31G*.

[b] 6-311G**//6-311G**.

[c] QCISD/6-311G(T)**//QCISD/6-31G*.

[d] **5a** is a conformational isomer of **5**.

isomer. Results of RRKM calculations (Fig. 14) gave rates of **6** → **7** six orders of magnitude faster than for **6** → **5** at the threshold for the latter, a much greater difference than indicated by experiments [19]. Additional isotope exchange reactions may have perturbed the latter results.

The differences between the critical energies for distonic ion → enol ion and distonic ion → ketone ion rearrangements are about the same whether the transition states contain 6-membered or 5-membered rings (45.7 versus 39.3 kJ/mol, respectively, by QCISD(T)/6-311G**//QCISD/6-31G* theory). The similar magnitudes of the differences suggest a common influence on H-transfers via 5- and 6-membered rings. Figs. 15 and 16 depict the transition states for **6** → **5** and **6** → **7**. HC1C2C3 dihedral angles of 168.5° and −51.6° for TS (**6** $\rightleftharpoons$ **5**) demonstrate that in this transition state the C1 methylene is twisted substantially out of the skeletal plane it occupies in **5**, as is H_t also. Thus, as in **2** → **1** and **2** → **3**, twisting of $C1H_2$ during transfer of H to and from it appears to be a substantial factor in the preference for **6** → **5** over **6** → **7**. Twisting of CH_2 seems to have comparable energy requirements in the 5- and 6- membered ring transition states studied. The energies required to twist CH_2 arise from disruption of the conjugation about C1C2O. H-transfer to C1 of both **1** and **5** have to disrupt this conjugation, the degree of which seems to depend little on ring size.

The critical energies for the 6-membered ring processes are 52 kJ/mol (distonic → keto)–59 kJ/mol (distonic → enol) lower in energy than the corresponding 5-membered ring processes in the $C_4H_8O^{+\bullet}$ ions. In intermolecular H-transfers, the preferred angle about H_t is nearly linear [33], so any small ring H-transfer will have a critical energy associated with it. The smaller the ring, the larger the critical energy is likely to be, with the exception of the 3-membered ring, whose energy is governed by other factors

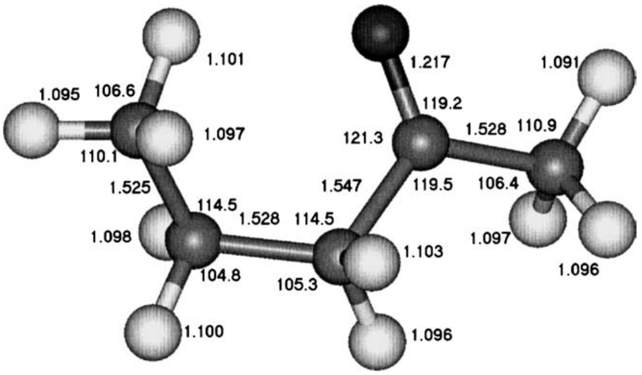


Fig. 13. The structure of **7**. C1, C2 C3 and O are planar with C4 and C5 out of the plane. There are no symmetries of hydrogens relative to the plane.

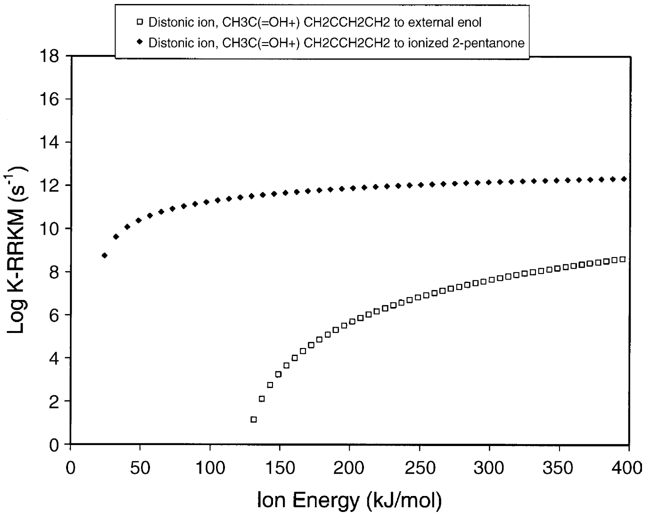


Fig. 14. RRKM computed reaction rates of **6** → **7** (upper curve) and **6** → **5** (lower curve) as a function of internal energy. Note that isomerization to the enol isomer **5** is much slower than to **7**.

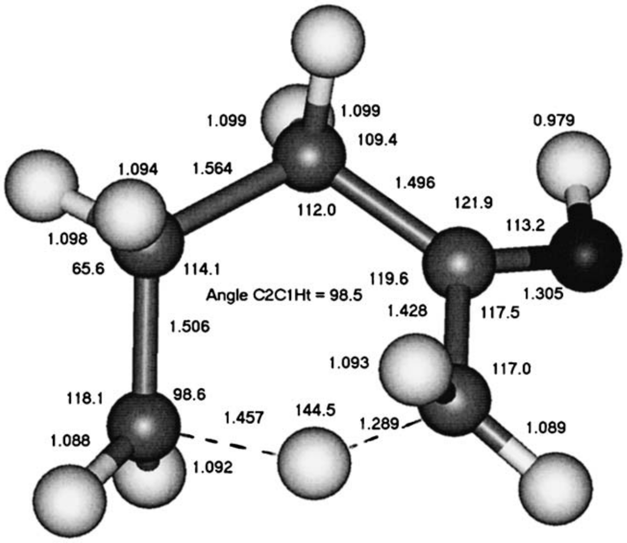


Fig. 15. TS (**6** → **5**). Note that the C1 methylene is substantially twisted out of the CCCO plane, as demonstrated by HC1C2C3 angles of 168.5° and −51.6°. The transferring H is also substantially out of the C1C2C3 plane, as the C3C2C1H_t dihedral angle is 49.0°. C5H_2 is also substantially rotated relative to the C3C4C5 plane, with HC5C4C3 dihedral angles of 152.9° and −60.7°. Thus this transition state is not planar.

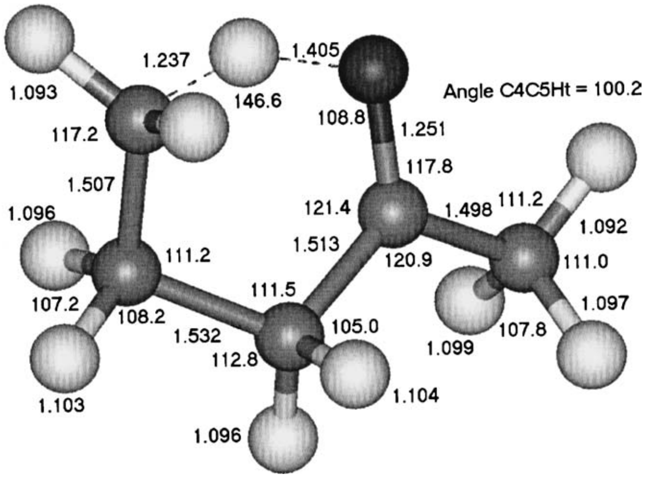


Fig. 16. TS (**6** → **7**). Dihedral angle C3C2OH_t = −1.6° and dihedral angle C2OH_tC5 = 1.99°. Dihedral angle C4C3C2O = 26.2°, so H_t and the skeletal atoms of this transition state excluding C4 are all essentially in the same plane.

[27,29]. The observed relationship between transition state ring size and transition state energy is in accord with the preceding predictions.

4. Summary

Why distonic $C_nH_{2n}O^{+\bullet}$ ions rearrange to their keto isomers rather than their more stable enol isomers is revealed for the first time. Using a combination of ab initio and RRKM theories, we established that twisting the hydrogens on C1 raises the energy for isomerization to enol structures, twisting that does not occur during isomerization to keto structures. This makes $CH_3C(=OH^+)(CH_2)_n^\bullet \rightarrow CH_3C(=O^{+\bullet})(CH_2)_{(n-1)}CH_3$ reactions much faster than $CH_3C(=OH^+)(CH_2)_n^\bullet \rightarrow CH_2{=}C(OH^{+\bullet})(CH_2)_{(n-1)}CH_3$ reactions. $RC(=OH^+)CH_2C^\bullet H_2 \rightarrow RC(=O^{+\bullet})CH_2CH_3$ reactions are faster than $RC(=OH^+)CH_2C^\bullet H_2 \rightarrow RC(OH^{+\bullet}){=}CHCH_3$ reactions for a different reason: 1,2-H-shifts in radicals and radical cations require the free electron to occupy a higher energy antibonding orbital in the transition state, thus raising the critical energy of that type of reaction above that for ketonization. Finally, as concluded in the original work [8], barriers to **1** → **2** → **3** and **4** → **2** → **3** produce energized **2** that dissociates by simple cleavage reactions faster than it can undergo the reverse reaction **3** → **2**.

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