Characterization by Theory of H-Transfers and Onium Reactions of $\text{CH}_3\text{CH}_2\text{CH}_2\text{N}^+\text{H}=\text{CH}_2$

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H-transfers by 4-, 5-, and 6-membered ring transition states to the π -bonded methylene of $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}^+=\text{CH}_2$ (**1**) are characterized by theory and compared with the corresponding transfers in cation radicals. Four-membered ring H-transfers converting **1** to $\text{CH}_3\text{CH}_2\text{CH}=\text{N}^+\text{HCH}_3$ (**2**) and $\text{CH}_3\text{N}^+\text{H}=\text{CH}_2$ to $\text{CH}_2=\text{NH}^+\text{CH}_3$ are high-energy processes involving rotation of the source and destination RHC= groups (R = H or C_2H_5) to near bisection by skeletal planes; migrating hydrogens move near these planes. The H-transfer **1** $\rightarrow$ $\text{CH}_3\text{C}^+\text{HCH}_2\text{NHCH}_3$ (**3**) has a higher energy transition-state than **1** $\rightarrow$ **2**, in marked contrast to the corresponding relative energies of 4- and 5-membered ring H-transfers in cation-radicals. Six-membered ring H-transfer-dissociation (**1** $\rightarrow$ $\text{CH}_2=\text{CH}_2$ + $\text{CH}_2=\text{N}^+\text{HCH}_3$) is a closed shell analog of the McLafferty rearrangement. It has a lower energy transition-state than either **1** $\rightarrow$ **2** or **1** $\rightarrow$ **3**, but is still a much higher energy process than 6-membered ring H-transfers in aliphatic cation radicals. In contrast to the stepwise McLafferty rearrangement in cation radicals, H-transfer and CC bond breaking are highly synchronous in **1** $\rightarrow$ $\text{CH}_3\text{N}^+\text{H}=\text{CH}_2$ + $\text{CH}_2=\text{CH}_2$. H-transfers in propene elimination from **1** are ion-neutral complex-mediated:

Intrinsic reaction coordinate tracing demonstrated that a slight preference for H-transfer from the methyl containing the carbon from which $\text{CH}_2=\text{NH}$ is cleaved is due to $\text{CH}_2=\text{NH}$ passing nearer this methyl than the other on its way to abstracting H, i.e., some memory of the initial orientation of the partners accompanies this reaction. (J Am Soc Mass Spectrom 2007, 18, 270–278) © 2007 American Society for Mass Spectrometry

Relative rates and transition-state energies for H-transfers by different ring sizes have long been of interest in gas-phase ion chemistry. The most prominent isomerization of aliphatic cation radicals with unsaturated functional groups is the 6-membered ring McLafferty rearrangement [1–3]. However, parallel 5- [4, 5] and 7-membered [6–8] ring H-transfers also occur, albeit at several times lower rates, and 4-membered ring H-transfers take place at high energies. Although closed shell aliphatic cations also undergo 4- and 6-membered ring H-transfers [9–13], their reactions are usually dominated by “onium” H-transfers (ion-neutral complex-mediated H-transfers in closed shell “onium” ions [14], an example being **1** $\rightarrow$ $\text{CH}_3\text{CH}=\text{CH}_2$ + $\text{CH}_2=\text{NH}_2^+$ (Scheme 1). To increase our understanding of H-transfers by 4-, 5-, and 6-membered rings and their competition with “onium” reactions, we used theory to characterize H-transfers by the immonium ion $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}^+=\text{CH}_2$ (**1**). Both the McLafferty rearrangement and onium ion reactions

have been studied experimentally in this system [9, 10], but its conventional 4- and 5-membered ring H-transfers are uncharacterized. We also explored why $\text{CH}_2=\text{NH}$ preferentially abstracts a hydrogen from the original α carbon of **1** following isomerization to a $[\text{i-C}_3\text{H}_7^+ \cdots \text{HN}=\text{CH}_2]$ complex [10].

Theory

All calculations were performed using the Gaussian 03 package of programs [15]. Geometries were obtained by B3LYP/6-31G*, B3LYP/6-311G** and QCISD/6-31G* theories. Energies were obtained at the same levels of theory and basis sets as the corresponding geometries, except QCISD(T)/6-311G** energies were obtained at QCISD/6-31G* geometries unless otherwise stated. Species were considered to be stable when they had only positive vibrational frequencies, and were considered to be transition states when they had one and only one imaginary vibrational frequency. Reaction pathways were traced by intrinsic reaction coordinate (IRC) methods [16, 17] utilizing B3LYP/6-31G* theory. Zero point energies were obtained by multiplying zero point energies derived from B3LYP/6-31G* frequencies by the scaling factor 0.9806 [18].

Published online October 30, 2006

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Results

Reactants, transition states and reaction pathways of interest are characterized in the following sections. Energies of stationary points (ground and transition states) obtained at various levels of theory are given in Table 1 and Table 2. Carbons are numbered throughout this work as follows:

Four-membered ring H-transfers across double bonds, such as $CH_3CH_2CH_2N^+H=CH_2$ (**1**) $\rightarrow$ $CH_3CH_2CH=N^+HCH_3$ (**2**), are of interest because both open [20–22] and closed shell cations [11, 23] must either overcome orbital symmetry constraints or pass through highly strained antarafacial transition states [19]. Consequently, these reactions have high critical energies in both types of ions. The critical energy for **1** $\rightarrow$ **2** is 241 kJ mol^{−1} at probably our best level of theory (QCISD(T)/6-311G**). Figure 1a, b, and c give the structures of **1**, **2** and the transition-state for **1** $\rightarrow$ **2**, respectively. In **1**, C¹H₂, N⁺H⁺, and C² are all in the same plane, and the C⁴C³NC¹ dihedral angle is at 117.3° to this plane. In **2** with the methyl and ethyl trans to each other about the double-bond, all of the atoms attached to C¹ or N are very nearly in a plane (dihedral angles C³C²NC¹ = −179.48°, H^NNC²C³ = 0.76°). As expected, **2** is more stable than **1** at all levels of theory, e.g., 36.1 kJ mol^{−1} more so at QCISD(T)/6-311G**//QCISD/6-31G* theory. According to experimental data on deuterium exchange, **1** $\rightarrow$ **2** does not directly occur, at least not in metastable dissociations [9, 10]. However, analogous 4-membered ring H-transfers do occur [11, 23], as is described below for $CH_3N^+H=CH_2$.

Most 4-membered ring H-transfers across double bonds in both closed shell and radical cations circumvent orbital symmetry restrictions by transferring H in or near a plane containing the π -bonded atoms and the atoms attached to them after the destination CH₂ rotates to being bisected by a skeletal plane [11, 21, 22]. In such reactions, the transition-state is neither suprafacial nor antarafacial, but at the boundary between those two types of reactions, a point at which π -bonding does not exist. At the transition-state for **1** $\rightarrow$ **2**, the distances from the hydrogens on C¹ to H⁺ are 1.962 Å and 1.947 Å, so, similarly to other 4-membered ring transfers [11, 21,

Table 1. Ab initio energies (Hartrees) for potential energy minima and transition states on the C₄H₁₀N⁺ potential surface

	ZPE	B3LYP/6-31G*	B3LYP/6-311G**	QCISD/6-31G*	QCISD(T)/6-311G**
CH ₃ CH ₂ CH ₂ N ⁺ H=CH ₂ (1) ^a	361.7	−212.93718	−212.99640	−212.23539	−212.41211
CH ₃ CH ₂ CH ₂ N ⁺ H=CH ₂ (1) ^b	362.2	−212.93671	−212.99579	−212.23446	−212.41110
CH ₃ CH ₂ CH=N ⁺ HCH ₃ (2) (trans) ^c	360.8	−212.95538	−213.01388	−212.24973	−212.42533
CH ₃ C ⁺ HCH ₂ NHCH ₃ (3)	346.3	−212.86924	−212.92916	−212.15686	−212.33234
(CH ₃) ₂ CHN ⁺ H=CH ₂ (5)	360.7	−212.94156	−213.00052	−212.24035	−212.41702
CH ₃ CH=CH ₂ + CH ₂ =NH ₂ ⁺	346.4	−212.88166	−212.94905	−212.18037	−212.35880
CH ₂ =CH ₂ + CH ₂ =NH ⁺ CH ₃	345.9	−212.88797	−212.95284	−212.18511	−212.36197
1 $\rightarrow$ CH ₃ CH ₂ CH=N ⁺ HCH ₃ (2)	350.9	−212.83971	−212.90040	−212.13146	−212.31616
1 $\rightarrow$ CH ₃ C ⁺ HCH ₂ NHCH ₃ (3)	346.4	−212.84351	−212.90241	−212.12918	−212.30885
3 $\rightarrow$ CH ₃ CH ₂ CH=N ⁺ HCH ₃ (2)	345.9	−212.86736	−212.92797	−212.15444	−212.33268
1 $\rightarrow$ CH ₂ =CH ₂ + CH ₂ NHCH ₃	352.9	−212.87774	−212.93667	−212.16030	−212.34277
(1) $\rightarrow$ CH ₃ CH=CH ₂ + CH ₂ =NH ₂ ⁺ ^d	336.5	−212.84878	−212.91309	−212.14097	−212.32052
(5) $\rightarrow$ CH ₃ CH=CH ₂ + CH ₂ =NH ₂ ⁺ ^d	336.6	−212.86446	−212.92751	−212.15518	−212.33126
CH ₃ N ⁺ H=CH ₂ (6)	214.0	−134.30051	−134.33886	−133.87176	−133.97774
CH ₃ N ⁺ H=CH ₂ (6) $\rightarrow$ CH ₂ =N ⁺ HCH ₃ (6') ^e	203.2	−134.19291	−134.23359	−134.75939	−134.87365

^aA dihedral angle about the C²-N bond is 117.3° and a dihedral about the C²-C³ bond is −64.2°, making the configuration about the latter bond gauche.

^bDihedral angle about the C²-N bond (C¹NC²C³) is cis and the dihedral angle about the C²-C³ bond (NC¹C²C³) is trans.

^cMethyl and ethyl are trans about the double bond.

^dReactions occur through [C₃H₇⁺ NH=CH₂] complexes.

^eRelative to CH₃N⁺H=CH₂ = 0.

Table 2. Energies (kJ mol⁻¹) of stable species and transition states on the C₄H₁₀N⁺ potential energy surface

	B3LYP/6-31G*	B3LYP/6-311G**	QCISD/6-31G*	QCISD(T)/6-311G**
CH ₃ CH ₂ CH ₂ N ⁺ H=CH ₂ (1) ^a	0	0	0	0
CH ₃ CH ₂ CH ₂ N ⁺ H=CH ₂ (1) ^b	1.7	2.1	2.9	3.1
CH ₃ CH ₂ CH=N ⁺ HCH ₃ (2) ^c	-49.2	-47.3	-39.0	-36.1
CH ₃ C ⁺ HCH ₂ NHCH ₃ (3)	163.1	161.3	190.8	194.1
(CH ₃) ₂ CHN ⁺ H=CH ₂ (5)	-13.0	-12.3	-11.5	-14.4
CH ₃ CH=CH ₂ + CH ₂ =NH ₂ ⁺	130.5	109.0	129.1	124.6
CH ₂ =CH ₂ + CH ₂ =NH ⁺ CH ₃	113.4	98.6	116.2	115.8
CH ₃ CH ₂ CH ₂ N ⁺ H=CH ₂ (1) → CH ₃ CH ₂ CH=N ⁺ HCH ₃ (2)	245.1	241.2	262.1	241.1
CH ₃ CH ₂ CH ₂ N ⁺ H=CH ₂ (1) → CH ₃ C ⁺ HCH ₂ NHCH ₃ (3)	230.6	231.5	263.6	255.8
CH ₃ C ⁺ HCH ₂ NHCH ₃ (3) → CH ₃ CH ₂ CH=N ⁺ HCH ₃ (2)	167.5	163.9	196.7	192.7
CH ₃ CH ₂ CH ₂ N ⁺ H=CH ₂ (1) → CH ₂ =CH ₂ + CH ₃ N ⁺ H=CH ₂	147.3	148.0	188.4	173.2
CH ₃ CH ₂ CH ₂ N ⁺ H=CH ₂ (1) → CH ₃ CH=CH ₂ + CH ₂ =NH ₂ ⁺ ^d	206.9	193.5	222.7	215.3
(CH ₃) ₂ CHN ⁺ H=CH ₂ (5) → CH ₃ CH=CH ₂ + CH ₂ =NH ₂ ⁺ ^d	165.3	155.3	185.5	186.7
CH ₃ N ⁺ H=CH ₂ (6)	0	0	0	0
CH ₃ N ⁺ H=CH ₂ (6) → CH ₂ =N ⁺ HCH ₃ (6') ^e	271.7	265.6	284.2	262.5

^aA dihedral angle about the C²-N bond is 117.3° and a dihedral about the C²-C³ bond is -64.2°, making the configuration around the latter bond gauche.

^bDihedral angle about the C²-N bond (C¹NC²C³) is cis and the dihedral angle about the C²-C³ bond (NC¹C²C³) is trans.

^cMethyl and ethyl are trans about the double bond.

^dReactions occur through [C₃H₇⁺ NH=CH₂] complexes.

^eRelative to CH₃N⁺H=CH₂ = 0.

22], H^t attacks (or leaves) C¹ nearly in a plane that bisects the HC¹H angle. At the transition-state, the HC¹NC² dihedral angles were 96.0° and -103.9°, not quite symmetric to the C¹NC² plane. The HC¹NC² dihedral angles changed from 0.85° and -179.3° to 119.7° and -120.9° over the course of 1 → 2, and the HC²NC¹ dihedral angle changed from -115.0° to -0.2°. Thus C¹ and C² with their substituents rotate continuously throughout the course of the reaction as H is transferred from one carbon to the other. This contrasts with other systems studied [11, 21, 22] in which the methylenes and analogous groups rotate largely before and after rather than during H-transfer.

According to the IRC, the NC¹H^tC² dihedral angle starts at 0.56° in 1, increases to 9.34°, declines to 5.77° at TS(1 → 2) and diminishes to 0.27° at 2 without crossing the skeletal plane. This makes the reaction slightly suprafacial. H^t also stays on one side of the skeletal plane in CH₃N⁺H=CH₂ → CH₂=N⁺HCH₃ (see below), evidence that it is not only avoidance of the ethyl by H^t that pushes H^t out of the skeletal plane. While H^t stays near a plane containing N, C¹, and C², C¹H₂ goes from a tetrahedral configuration in the C¹ methyl to being in a plane that encompasses N, C¹, and C² in 2. The N-H^t distance is 2.153

Å in the transition-state, demonstrating that there is little bonding between those atoms in 1 → 2 at that point. The sum of the bond angles about N in the transition-state for 1 → 2 is 295.5°, compared with a sum of 360° that characterizes a planar structure. Thus the bonding to N in this transition-state is quite nonplanar.

CH₃C⁺HCH₂NHCH₃ (3) was located in a shallow potential minimum by B3LYP/6-31G*, B3LYP/6-311G**, QCISD/6-31G*, and QCISD/6-31G** but not QCISD(T)/6-311G** theories, so 3 may or may not be a stable species. The QCISD/6-31G* structure for 3 is given in Figure 1d, and the transition-state for the 5-membered ring H-transfer CH₃CH₂CH₂N⁺H=CH₂ (1) → CH₃C⁺HCH₂NHCH₃ (3) is depicted in Figure 1e. The critical energy for 1 → 3 is higher than that for the 4-membered ring 1 → 2 (Table 1), and even further above that of any other reaction characterized in this work. This contrasts with the situation in cation radicals, in which critical energies for 5-membered ring

Figure 1. (a) QCISD/6-31G* structure of the lower energy form of CH₃CH₂CH₂N⁺H=CH₂ (1). A dihedral angle about the C²-N bond is 117.3° and a dihedral about the C²-C³ bond is -64.2°, making the configuration about the latter bond gauche. (b) QCISD/6-31G* structure of CH₃CH₂CH=N⁺HCH₃ (2) with the methyl and ethyl attached to the double-bond trans to each other. (c) The QCISD/6-31G* transition-state for CH₃CH₂CH₂N⁺H=CH₂ (1) → CH₃CH₂CH=N⁺HCH₃ (2). (d) The QCISD/6-31G* structure for CH₃C⁺HCH₂NHCH₃ (3). Although this is a stable structure at this level of theory, it is not at QCISD/6-311G**/QCISD/6-31G* theory. (e) The QCISD/6-31G* structure for the transition-state for CH₃CH₂CH₂N⁺H=CH₂ (1) → CH₃C⁺HCH₂NHCH₃ (3). (f) The QCISD/6-31G* structure for the transition-state for the McLafferty-like rearrangement CH₃CH₂CH₂N⁺H=CH₂ (1) → CH₂=CH₂ + CH₂N⁺HCH₃. This structure is a transition-state rather than being at a stable energy minimum.

a

b

c

d

e

f

H-transfers are substantially lower than those for 4-membered ring H-transfers [5, 22]. Consistent with the high critical energy that we find for it, $1 \rightarrow 3$ is not observed experimentally, all fragmentation after H-transfer from C^2 and C^3 being accounted for by the onium reaction (see below). Nonetheless, theory does suggest that $1 \rightarrow 3$ would occur in the absence of competition from lower energy processes.

If **3** were formed, it would be followed by $3 \rightarrow 2$ (transition-state not shown), to which there is a slight to no barrier, generating a transition-state well below that for $3 \rightarrow 1$. As noted above, four levels of theory located a transition-state for $3 \rightarrow 2$ above the energy of **3** (2.6–5.9 kJ mol⁻¹, see Table 2), but the transition-state energy for $3 \rightarrow 2$ is 1.4 kJ mol⁻¹ below the energy of **3** at QCISD(T)/6-311G**//QCISD/6-31G* theory. Thus **3** may not be a stable species; if not, $1 \rightarrow 3 \rightarrow 2$ has two distinct stages. The H-transfer in the first stage, $1 \rightarrow 3$, would be largely complete (the $C^1H^{\dagger}$ distance = 1.096 Å, the $C^3H^{\dagger}$ distance = 3.054 Å, the $C^2H^{\dagger}$ distance = 1.116 Å; $H^{\dagger}$ is the H that shifts from C^2 to C^3) before H-transfer begins in the $3 \rightarrow 2$ stage.

The McLafferty-Like Rearrangement

The reaction $1 \rightarrow CH_2=CH_2 + CH_2=N^+HCH_3$ is of particular interest because it represents a McLafferty-like rearrangement by a closed shell cation, a type of process that has received some attention experimentally [9, 10, 12, 13], but little by theory. The transition-state for this reaction is given in Figure 1f. Its experimental observability is attributable to its critical energy (173 kJ mol⁻¹) being lower than those of $1 \rightarrow 2$, $1 \rightarrow 3$, and of ion-neutral complex-mediated $1 \rightarrow CH_3CH=CH_2 + CH_2=NH_2^+$ (respective critical energies are 241 kJ mol⁻¹, 256 kJ mol⁻¹ and 215 kJ mol⁻¹ according to QCISD(T)/6-311G** theory).

The critical energies predict a ring-size preference of $6 > 4 > 5$ for isomerizations of **1**, in contrast to the ring-size order for H-transfers in aliphatic radical cations, $6 > 5 \sim 7 > 4$ [6, 8, 24]. The critical energy of $1 \rightarrow CH_2=CH_2 + CH_2=N^+HCH_3$ is, however, much higher than those which typify McLafferty rearrangements in cation radicals [5, 25]. A transition-state (Figure 1f) but no energy minima were located on the reaction coordinate for $1 \rightarrow CH_2=CH_2 + CH_2=N^+HCH_3$. By the time the transition-state is reached, $H^{\dagger}$ is largely transferred from C^4 ($H^{\dagger}C^4$ distance = 1.955 Å) to C^1 ($H^{\dagger}C^1$ distance = 1.139 Å) in the IRC. Over the same time, the C^2-C^3 distance increases from 1.530 Å to 1.762 Å, so this reaction is both concerted and highly synchronous, in

contrast to the McLafferty rearrangement in cation radicals.

Based on the width at half height of the flat-topped peak produced by the metastable dissociation of **1** to $CH_2=CH_2 + CH_2=N^+HCH_3$, the translational energy released in that reaction is 65 kJ mol⁻¹ [9], an energy slightly exceeding the QCISD(T)/6-311G** difference between the energy of the transition-state and that of the products (57 kJ mol⁻¹). Therefore, essentially all of E_{rev} goes into the relative translational energy of the products. The release of translational energy in excess of the critical energy for the reverse reaction most likely reflects uncertainties in experiment and/or theory.

To get an idea as to why the energy release is so large with respect to the energy difference between the TS and the fragmentation products, we located the point on the IRC with the most rapid potential energy change. The net force on the atoms comprising the C_2H_4 portion, which is ejected is 0.018226 Hartree/Bohr, of which 99.5% or 0.018144 Hartree/Bohr was directed along a vector away from the center of mass. This corresponds to an acceleration of the C_2H_4 fragment of 3.2×10^{16} m/s², an acceleration that would be expected to produce a substantial energy release.

Propene elimination from **1** is an archetypal “onium” ion reaction in which a CN bond stretches to create an ion-neutral complex; *n*-propyl rearranges to *i*-propyl in the complex; a hydrogen transfers between the partners, and the complex then dissociates (Scheme 1). The transition-state energy for this reaction, 215 kJ mol⁻¹, is below those for $1 \rightarrow 2$ and $1 \rightarrow 3$, and above that for the 6-membered ring H-transfer $1 \rightarrow CH_2=CH_2 + CH_2=N^+HCH_3$ (QCISD(T)/6-311G** theory). C_3H_6 and C_2H_4 are lost to similar degrees in the metastable decompositions of **1** [9].

According to IRC B3LYP/6-31G* results, the onium reaction starts with extension of the NC^2 bond. We will first describe changes at an arbitrary point at which the C^2N bond has stretched from 1.521 Å to 1.954 Å. The increase in the C^2N distance continues beyond this point with little change in bond angles. The C^2N bond lengthens to 3.003 Å after the transition-state (Figure 2a) is passed in the direction of propene elimination, shortens slightly to 2.877 Å and then lengthens to 2.966 Å in a $[C_3H_6NH_2=CH_2^+]$ complex. $CH_2=NH$ stays nearer C^2 than C^4 over the course of this reaction. During the C^2N stretching up to the arbitrary point, the $C^3H^{\dagger}$ ($H^{\dagger}$ is the H shifting in C_3H_7) bond extends only from 1.098 Å to 1.112 Å and the $C^3C^2H^{\dagger}$ angle only changes from 101.2° to 95.2°, so the initial stages are quite asynchronous. At

Figure 2. (a) The QCISD/6-31G* transition-state for the ion-neutral complex-mediated elimination of propene from $\text{CH}_3\text{CH}_2\text{CH}_2\text{N}^+\text{H}=\text{CH}_2$ (**1**). This reaction begins with the stretching of the CN bond which is followed by the migration of an H from C3 to C2, and finally by the transfer of H from one of the methyls to N to eliminate propene. (b) QCISD/6-31G* structure for $(\text{CH}_3)_2\text{CHN}^+\text{H}=\text{CH}_2$ (**5**). (c) QCISD/6-31G* transition-state for the elimination of propene from **5** by way of an ion-neutral complex. (d) QCISD/6-31G* transition-state for the 1,3-H-shift in $\text{CH}_3\text{N}^+\text{H}=\text{CH}_2$. This structure has a plane of symmetry through N, H^{N} and H^{I} , but is not symmetric in relation to the skeletal plane because the N is fairly pyramidalized, and the methylenes are slightly rotated from being symmetrical to such a plane.

the transition-state (B3LYP/6-31G* theory), the C^2N distance is 2.696 Å, and H^{I} is substantially transferred from C^3 (1.432 Å) to C^2 (1.242 Å), i.e., at the transition-state the *n*-propyl moiety is well on its way to becoming i-propyl. H transfer from C^3 to C^2 is nearly complete at the point of maximum C^2N extension. (At this point, the $\text{C}^2\text{H}^{\text{I}}$ distance is 1.100 Å and the $\text{C}^3\text{H}^{\text{I}}$ distance is 2.098 Å). H transfer from C^2 to N, i.e., between the partners, has barely begun (the C^2H distance = 1.163 Å versus 1.091 Å for an undisturbed H on the same carbon and the NH distance = 1.959 Å) at the point of maximum

C^2N extension. H-transfer is smoothly completed while the C^2N distance changes little. Thus, this reaction occurs in three stages while only passing one transition-state.

We also characterized the elimination of C_3H_6 from **5** (Figure 2b) by the pathway $\text{5} \rightarrow [(\text{CH}_3)_2\text{C}^+\text{H} \text{NH}=\text{CH}_2]$

$\rightarrow [\text{CH}_3\text{CH}=\text{CH}_2 \text{ H}_2\text{N}^+=\text{CH}_2] \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{CH}_2=\text{NH}_2^+$ to determine the effects of generating complexes of the same partners but starting with different orientations to each other. As in the dissociations of **1**, the IRC calculations demonstrate that in propene elimination from **5** the C²N bond stretches substantially (from 1.503 Å to 3.031 Å) before H is appreciably transferred between the partners. The CN bond is essentially fully broken at the transition-state (3.031 Å long), but the CH[†] bond is just beginning to stretch (1.144 Å). At the start of the reaction the *i*-propyl methyls are at similar distances from the nitrogen, the CN distances being 2.509 Å and 2.450 Å. This asymmetry increases over the course of the reaction [CN distances 3.587 Å and 3.190 Å at the transition-state (Figure 2c)], with C to NH transfer occurring from the nearer carbon. Therefore, in contrast to propene elimination from **1**, CH₂=NH stays between the methyls of (CH₃)₂CH⁺ over the course of bond breaking and H-transfer. Thus the IRC pathways of propene elimination from **1** and **5** are quite distinct, even though they involve complexes made up of the same partners.

The degenerate isomerization of **6** was characterized to determine whether the suprafacial trajectory of H[†] in **1** $\rightarrow$ **2** (see section on **1** $\rightarrow$ **2**) is due to effects of H[†] passing H versus ethyl. We found the transition-state (Figure 2d) for **6** $\rightarrow$ **6'** to have a plane of symmetry perpendicular to the skeletal plane and encompassing H[†], N, and the H^N. At the transition-state, the two methylene hydrogens on one side of the skeletal plane are 2.144 Å and the two on the other side are 2.182 Å from the N, so the skeletal plane does not precisely bisect the two HCH bond angles. H[†] is slightly closer to the two hydrogens (1.782 Å) on one side of the skeletal plane than to the two on the other side (1.836 Å). H^N was also closer to the same pair of hydrogens (2.327 Å from both hydrogens versus 2.945 Å from the other pair) at the transition state. The H[†]NH^N angle was 114.4° and in the plane of symmetry for the ion, demonstrating that at least one of those hydrogens was far from the C¹NC² plane.

Over the course of the IRC for the H-transfer **6** $\rightarrow$ **6'**, the NCH[†]C dihedral angle went from 3.1° to a maximum of 14.2° and then decreased to 4.3° at the transition-state. The trajectory for the second half of the reaction was similar, except inverted, with a maximum at 11.1°. This makes this reaction, like **1** $\rightarrow$ **2**, formally suprafacial. Although the IRC completed normally, it terminated at a NCH[†]C dihedral angle of 3.1° without going all the way to the energy minimum at **6**, at which the angle is close to 0°. Over the reaction coordinate, the H^NNCH[†] dihedral angle changed continuously. It started at 177.9°, declined to 100.7°, rose to 103.3° at the transition-state, declined again to 99.2° and ended at 179.8° in the newly formed methyl. As for **1** $\rightarrow$ **2**, this contrasts with 1,3-shifts in enol-keto isomerizations and in CH₃O⁺=CH₂ $\rightarrow$ CH₂=O⁺CH₃, in which H[†]s are in a

plane of symmetry at the transition-state and in which methylene twisting and H-transfer are largely separate stages [11, 21, 22]. One HNC bond angle goes from 117.8° to 121.0° to 111.5° at the transition-state, minimizes at 110.0° and becomes 115.6° at the product. Thus, this reaction passes very near a tetrahedral configuration (bond angles of which are 109.5°) in the vicinity of the transition-state. The bond angles about N in the transition-state for **6** $\rightarrow$ **6'** sum to 304.9°, further demonstrating significant pyramidalization about N.

Discussion

H-Transfers

One goal of this work was to compare H-transfers through different ring sizes in closed shell carbocations to corresponding transfers in open shell cations. The ring-size preference order 6 > 4 > 5 for H-transfers predicted in **1** by the critical energies obtained here (173, 241, and 256 kJ mol⁻¹, respectively) differs from the order 6 > 5 > 4 generally obtained for radical cations [5, 8, 24]. Critical energies for carbonyl $\rightarrow$ enol or distonic C_nH_{2n}O⁺ ions in the order 6-, 5-, 4-membered rings are 15, 72, and 161 kJ mol⁻¹ (QCISD(T)/6-311G** theory) [5, 22], and for aliphatic amine $\rightarrow$ distonic ions, 18, 68, and 144 kJ mol⁻¹ (MP2/6-31G* theory) [24]. Thus, corresponding reactions differ substantially in their energy requirements and therefore in preference order between closed and open shell ions.

Four-membered ring isomerizations across π -bonds in open and closed shell systems encounter orbital symmetry restraints [11, 19–23]; avoidance of these by CH₂ twisting gives those reactions high critical energies in both open and closed shell ions, 196 [22], and 265 kJ mol⁻¹ (**6**). The four membered-ring H-transfers **1** $\rightarrow$ **2** and **6** $\rightarrow$ **6'** are similar to other 4-membered ring H-transfers across double bonds [11, 21–23] in that all of the departure and destination =CHRs (R = H or ethyl) for H_t rotate by about 90° and the H transfer occurs near a plane that bisects the destination CH₂. However, in **1** and **6** methylene twisting and H-transfer are somewhat synchronized rather than being strongly asynchronous, as in enol-keto interconversions. The transition-state has substantial pyramidalization about N; this, perhaps combined with repulsion of H^N by the lone pair being greater than repulsion by the bonding pairs [26], moves H^N out of the skeletal plane in **1** $\rightarrow$ **2** and **6** $\rightarrow$ **6'**. The substantial nonplanarity about N in present transition states and associated diminution in π -bonding allows 4-membered ring H-transfers to avoid Woodward-Hoffmann restrictions.

There are very large differences in critical energies for 5-membered ring H-transfers between open (72 [5] and 68 kJ mol⁻¹ [24]) and closed (256 kJ mol⁻¹) shell systems. The critical energy for the 5-membered ring H-transfer **1** $\rightarrow$ **3** is 184 kJ mol⁻¹ higher than that of 5-membered ring CH₃C(=O⁺)CH₂CH₃ $\rightarrow$ CH₃C(=OH⁺)CH₂CH₂. We attribute this primarily to the energy of **3** being elevated by

Scheme 2

its having one fewer bonds than **1** and the transition-state energy having to be at least as high as the energy of **3**. If **3** is a stable species, given that the transition-state for **1** → **3** is higher in energy than **3** → **2**, **3** formed by **1** → **3** would contain enough energy to continue on to **2**. The reaction **1** → **3** → **2** would be analogous to the sequence $\text{RCH}_2\text{CH}_2\text{C}(=\text{O}^+)\text{R} \rightarrow \text{RCHCH}_2\text{C}(\text{OH}^+)\text{R} \rightarrow \text{RCH}_2\text{CHC}(\text{OH}^+)\text{CH}_3$ [4–8] in cation radicals.

The critical energy for **1** → $\text{CH}_3\text{NH}^+=\text{CH}_2 + \text{C}_2\text{H}_4$ is 159 kJ mol^{-1} greater than that for $\text{CH}_3\text{C}(=\text{O}^+)\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{C}(=\text{OH}^+)\text{CH}_2\text{CH}_2\text{CH}_2$ [5], demonstrating that 6-membered ring H-transfers also require much more energy in closed shell than in open shell species.

The transition-state energy for 6-membered ring H-transfer **1** → $\text{CH}_2=\text{CH}_2 + \text{CH}_3\text{N}^+\text{H}=\text{CH}_2$ is 83 kJ mol^{-1} lower than that of 5-membered ring **1** → **3**. In $\text{C}_n\text{H}_{2n}\text{O}^+$ ions, the critical energy for $\text{CH}_3\text{C}(=\text{OH}^+)\text{CH}_2\text{CH}_2 \rightarrow \text{CH}_3\text{C}(=\text{O}^+)\text{CH}_2\text{CH}_3$ is 58 kJ mol^{-1} greater than the critical energy for $\text{CH}_3\text{C}(=\text{OH}^+)\text{CH}_2\text{CH}_2\text{CH}_2 \rightarrow \text{CH}_3\text{C}(=\text{O}^+)\text{CH}_2\text{CH}_2\text{CH}_3$. Thus, 6-membered ring H-transfers are similarly favored over 5-membered ring H-transfers in closed and open shell aliphatic cations.

In the McLafferty rearrangement in cation radicals, H-transfer to form an intermediate distonic ion is followed by cleavage of that intermediate [27] (Scheme 2). However, we could find no trace of a corresponding intermediate in the loss of ethene from **1**, revealing a fundamental difference between this closed shell McLafferty rearrangement and that in open shell species. H-transfer in **1** → $\text{CH}_2=\text{CH}_2 + \text{CH}_3\text{N}^+\text{H}=\text{CH}_2$ occurs simultaneously with bond cleavage in **1** → $\text{CH}_3\text{N}^+\text{H}=\text{CH}_2 + \text{C}_2\text{H}_4$, so this reaction is synchronous and without a stable intermediate, in contrast to the McLafferty rearrangement in cation radicals.

Dissociation of **1** through the $[\text{CH}_3\text{C}^+\text{HCH}_3 \text{ CH}_2=\text{NH}]$ Complex

In 1980, Bowen proposed that **1** dissociates by H-transfer between partners in the ion-neutral complex $[\text{CH}_3\text{C}^+\text{HCH}_3 \text{ CH}_2=\text{NH}]$ based on the relative degrees of H and D transfer from the carbons of **1** to $\text{CH}_2=\text{NH}$ [9], a seminal proposal that was later supported by a more detailed analysis of the dissociation of deuterium labeled forms of **1** by Veith and Gross [10]. We conclude that this reaction occurs in three temporally distinct stages, CN bond stretching to form an ion-neutral complex, isomerization from *n*- to *i*- C_3H_7^+ in an ion-neutral complex and H-transfer from *i*- C_3H_7^+ to

$\text{CH}_2=\text{NH}$ (see Results), refining the mechanism proposed previously [9, 10].

Veith and Gross found a small preference for H-transfer from C^1 of $\text{CH}_3\text{C}^+\text{HCH}_3$ relative to statistical predictions ($1:2:3 = 2.01:1.00:2.25$; predicted = $2:1:3$). They attributed this to preferential abstraction of H by $\text{CH}_2=\text{NH}$ from the C^2 end of $\text{CH}_3\text{C}^+\text{HCH}_3$ cleaved. Supporting this, in our IRC starting from **1**, $\text{CH}_2=\text{NH}$ abstracted H from C^2 . This supports the preferred H-transfer from C_2 being due to a minor fraction of the partners reacting with each other before all distinction between the two *i*-propyl methyls is lost. This could reflect some formation of a H-bonded $[\text{CH}_3\text{CHCH}_2-\text{H}^+-\text{NH}=\text{CH}_2]$ complex [28]; however, we could not locate such a species by minimum-seeking efforts. The approach of the H-transfer pattern of **1** to the statistically expected $2:1:3$ pattern [10] contrasts with the exclusive H abstraction from C^1 in the IRC results. Therefore, in actuality, the two partners in the complex formed from **1** must move around each other to such a degree that the memory of their original configuration is largely, but not completely, erased before H-transfer between the partners occurs.

Although preferential H abstraction from near the site of bond cleavage to form reacting partners in an ion-neutral complex has also been inferred for ethyl-substituted nonane ions [29], it is unusual behavior.

Summary

Present work compares H-transfers in open and closed shell aliphatic cations. H-transfers and bond breakings in radical cations occur in distinct steps while the rest of the ion maintains its connectivity. In closed shell cations, some consecutive H-transfers occur in separate, highly asynchronous stages with only one transition-state among them, but H-transfer and bond-breaking are synchronous in other closed shell systems. Avoidance of Woodward-Hoffmann restraints strongly influences the energies of 4-membered ring transition states in both open and closed shell systems. The 5-membered ring transition-state reaction for the closed shell system **1** → **3** is at high energies, while such transition states and their products are at low energies in open shell systems. In contrast to the low-energy, stepwise occurrence of the McLafferty rearrangement in radical cations, the McLafferty-like rearrangement **1** → $\text{CH}_3\text{NH}=\text{CH}_2^+ + \text{C}_2\text{H}_4$ is highly synchronous and concerted. H-transfer between the partners in the $[\text{CH}_3\text{C}^+\text{HCH}_3 \text{ HN}=\text{CH}_2]$ complex formed from **1** reflects some memory of the initial orientation of the partners relative to each other.

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