CH₃CH₃⁺ Formation from Some C₃H₆O⁺ Isomers According to Theory

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Dissociations to alkane ions in gas phase ion chemistry are rare and poorly characterized. Therefore, the pathways to CH₃CH₃⁺ + CO from $\dot{\text{C}}\text{H}_2\text{CH}_2\text{O}^+=\text{CH}_2$ and some of its isomers are investigated by theory. The pathway found for this reaction is $\dot{\text{C}}\text{H}_2\text{CH}_2\text{O}^+=\text{CH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{O}^+=\text{CH} \rightarrow [\text{CH}_3\text{CH}_2-\text{H}-\text{CO}]^{++} \rightarrow \text{CH}_3\text{CH}_3^+ + \text{CO}$. The crucial intermediate in this pathway is the stable hydrogen-bonded ion-neutral complex $[\text{CH}_3\text{CH}_2-\text{H}-\text{CO}]^{++}$, a species held together by a strong hydrogen bond. CH₃CH₃⁺ + CO rather than CH₃CH₃ + CO⁺ is formed from $\dot{\text{C}}\text{H}_2\text{CH}_2\text{O}^+=\text{CH}_2$ and other C₃H₆O⁺ ions because the former pair is much more stable than the latter. The photoionization appearance energies of CH₃CH₃⁺ from CH₃CH₂CHO⁺ and from CH₃CH₂CO₂H⁺ demonstrate that the onsets of these reactions are at to just above their thermochemical thresholds, consistent with the intermediacy of ion-neutral complexes. We also found transition states for interconversion of CH₃CH₂CHO⁺ and CH₃CH₂O⁺=CH and transformation of CH₃CH₂ $\ddot{\text{C}}=\text{OH}^+$ to CH₃CH₂CHO⁺; the latter reaction occurs by a 1,2-H-shift from O to C. (J Am Soc Mass Spectrom 2002, 13, 1235–1241)
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The fragmentations of several C₃H₆O⁺ isomers to CH₃CH₃⁺ [1–7] constitute a majority of the dissociations known to produce alkane cations in gas phase ion chemistry, in contrast to the widespread occurrence of neutral alkane eliminations from radical cations [8, 9]. CH₃CH₃⁺ formation is observed in metastable decompositions of some ions with the CCCO or CCOC frame [e.g., in metastable dissociations -CO/-H = 0.04 [5]–0.07 [4] for $\dot{\text{C}}\text{H}_2\text{CH}_2\text{O}^+=\text{CH}_2$ (2), 0.01 for $\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}=\text{OH}^+$, CH₂=CHCH₂OH⁺ and $\dot{\text{C}}\text{H}_2\text{CH}_2\text{CHOH}^+$ [6], but missing for CH₃CH₂CHO⁺ [6]]. Corresponding ratios in the 70 eV mass spectra of CH₃CH₂CHO⁺ and CH₂=CHCH₂OH⁺ are 0.24 and 0.50 respectively [10]. Alkane eliminations usually take place by simple bond extension to an ion-induced dipole complex followed by an H-transfer between the partners in the complex to form the eliminated alkane [8, 9]. Dissociation of C₃H₆O⁺ isomers with the CCCO frame to CH₃CH₃⁺ + CO has also been suggested to involve H-transfer in intermediate ion-neutral complexes (Scheme 1) [6, 7, 9]. However, despite the potential surface for C₃H₆O⁺ ions with the CCCO and CCOC frames being a paradigm for elucidating radical cation chemistry in the gas phase [11–19], it is not clear how the transferred

Scheme 1

hydrogens, particularly the second one, get from the O=CH₂ methylene of $\dot{\text{C}}\text{H}_2\text{CH}_2\text{O}^+=\text{CH}_2$ (2) into CH₃CH₃⁺. A need to resolve this by theory has been recognized [6, 7]. Consequently, we here use theory to characterize reaction pathways from CH₃CH₂CHO⁺ (1), (2), and CH₃CH₂ $\ddot{\text{C}}\text{OH}^+$ (5) to CH₃CH₃⁺ + CO. Reactions investigated are summarized in Scheme 1. The reactions of some of these and other isomers with which they interconvert have been extensively characterized in previous studies [2, 5, 6, 7, 13, 17–19]. $\dot{\text{C}}\text{H}_2\text{CH}_2\text{O}^+=\text{CH}_2$ has been key to characterizing the properties of distonic ions [4, 5, 15, 16] and their bimolecular reactions [4, 20].

Published online September 5, 2002

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Figure 1. QCISD/6-31G(d) geometry of $\text{CH}_3\text{CH}_2\text{CHO}^{\bullet+}$ (1). Distances are in angstroms and bond angles are in degrees in Figures 1–9.

Results and Discussion

Stationary Points

The species and reaction pathways of interest were characterized by ab initio and hybrid density functional theories with the Gaussian 98W package of programs [21]. The geometries obtained by QCISD/6-31G(d) theory for 1, 2, 3, 5, the stable $[\text{C}_2\text{H}_5-\text{H}-\text{CO}]^{\bullet+}$ complex (4) and several interconverting transition states are given in Figures 1–9. The structures of 1, 2, 3, 5 and $\text{TS}(2 \rightarrow 3)$ are quite conventional. The energies of the stationary points characterized are given at three levels of theory in Table 1, and a potential energy diagram based on that data from QCISD(T)/6-311G(d,p) + ZPVE [22] theory is given in Figure 10. Although 3 was characterized in a cis-configuration around the C2–O bond, the corresponding trans isomer was also found at essentially the same energy as the cis-configuration by B3LYP/6-31G(d) theory. The trans

Figure 3. QCISD/6-31G(d) geometry of $\text{CH}_3\text{CH}_2\text{O}^{\bullet+}-\text{CH}^{\bullet}$ (3).

configuration was not sought at other levels of theory. Where comparisons can be made, relative energies agree very well with ones obtained by Radom and coworkers in 1980 at lower levels of theory [16] (57 kJ mol^{-1} versus 55 kJ mol^{-1} for 2, 81 kJ mol^{-1} versus 81 kJ mol^{-1} for 3, and 25 kJ mol^{-1} versus 30 kJ mol^{-1} for 5; present results are the first in each pair). Too few corresponding experimental heats of formation are available to permit comparison of energies obtained by theory to experimental ones.

In the complex 4, O, C, H, and C are linearly arranged and the C–C bond of the ethyl in 4 makes an angle of 104.0° to the OCHC axis (Figure 5). The bridging H is 1.3099 Å from the CO carbon and 1.4959 Å from the methylene carbon of the ethyl in 4 according to QCISD/6-31G(d) theory, i.e., the H is shared almost midway between the carbons. In contrast in typical ion-alkyl radical complexes, the H to be transferred is much closer to the carbon in the ion than that in the radical. Thus the partners in 4 are not held in association simply by ion-dipole and ion-induced dipole forces, the dominant attractions in ion-alkyl radical

Figure 2. QCISD/6-31G(d) geometry of $^{\bullet}\text{CH}_2\text{CH}_2\text{O}-\text{CH}_2^+$ (2).

Figure 4. QCISD/6-31G(d) geometry of $\text{TS}(2 \rightarrow 3)$.

Figure 5. QCISD/6-31G(d) geometry of the proton bound ion-neutral complex [CH₃CH₂...H...CO]⁺ (4). Note that the hydrogen is well situated to be transferred to C₂H₅.

complexes [23–26]. The uniqueness of this H-bonded species is reinforced by 4 being 113 kJ mol^{−1} more stable than its dissociated partners, in the range of binding energies in H-bridged complexes [27–29]. This contrasts with typical binding energies of 10–20 kJ mol^{−1} between the partners in ion-alkyl radical complexes [23–26].

Mechanism of CH₃CH₃⁺ Formation

The central issue this work addresses is, “What are the pathways from 1, 2, and 5 to CH₃CH₃⁺?” Our location of TS(2 → 3) by theory demonstrates the feasibility of 2 → 3, a reaction that Wittneben and Grutzmacher proposed as the first step in the formation of CH₃CH₃⁺ + CO [4]. In TS(2 → 3) at QCISD/6-31G(d) theory, the distance from the migrating H to the CO carbon is 1.4239 Å and that to the ethyl carbon 1.3050 Å; these distances and the otherwise normal bond lengths in this transition state show that 2 → 3 involves a conventional H-transfer.

Another question is whether 3 → 1 is a step on the way from 2 to CH₃CH₃⁺. A transition state for 3 → 1

Figure 6. QCISD/6-31G(d) geometry for the transition state for the interconversion of 3 and 1. This assignment was made based on a combination of IRC tracing and ordinary optimizations.

Figure 7. QCISD/6-31G(d) geometry of the transition state for the interconversion of 1 or 3 and 4. Although its geometry is closer to that of 1, this transition might be accessed by either breaking of the C–C bond in 1 or the C–O bond in 3.

was located 145 kJ mol^{−1} above the energy of 1 (Figure 7). This transition state was demonstrated to be for 3 → 1 by a combination of intrinsic reaction coordinate (IRC) tracing [30, 31] and ordinary optimizations at the QCISD/6-31G(d) level of theory. Efforts to locate TS(3 → 1) by B3LYP/6-31G(d) theory failed; however, this transition state is probably real as QCISD theories are more reliable than B3LYP theory for describing bond extensions [32]. Location of a similar transition state by MP2 theory further supports its reality. Location of TS(3 → 1) demonstrates the feasibility of the conversion of 2 to 1 by 2 → 3 → 1 prior to dissociation to C₃H₅O⁺ + H[•]. CH₃CH₂CO⁺ is produced by H[•] loss from 2 [5], strongly supporting isomerization to 1 prior to loss of H[•] starting from 2. However, it is unlikely that reaction in the opposite direction — 1 → 3 — competes substantially with dissociation of 1, since the threshold for H[•] loss from 1, 74 kJ mol^{−1}, is 71 kJ mol^{−1} below TS(3 → 1).

Location of an appropriate transition state 43 kJ mol^{−1} above the energy of 4 and 97 kJ mol^{−1} above the energy of 1 (Table 1) establishes the feasibility of forming 4. This transition state is assigned to 1 ⇌ 4

Figure 8. QCISD/6-31G(d) geometry of the carbene ion CH₃CH₂COH⁺ (5).

Figure 9. QCISD/6-31G(d) geometry of the transition state for interconversion of $\text{CH}_3\text{CH}_2\text{CHO}^+$ and the carbene ion $\text{CH}_3\text{CH}_2\text{COH}^+$ (5) by a 1,2-H-shift between O and C1.

rather than to $3 \rightleftharpoons 4$ based on the ethyl CH_2 carbon being over the CH rather than over the CO of HCO (Figure 7). However, 4 should also form readily from 3 because 3 is 27 kJ mol^{-1} higher in energy than 4, even though a transition state for that reaction was not found. The transition state located is not for dissociation of 4 because it was not found on those reaction coordinates (see below) and because it is lower in energy than the pairs of dissociation products of 4 (24 kJ mol^{-1} below $\text{CH}_3\text{CH}_3^+ + \text{CO}$, further below other possible products). The finding of TS(3 $\rightarrow$ 1), TS(1 $\rightleftharpoons$ 4) and 4 by theory is good evidence that reactions between partners

Figure 10. Potential energy diagram for interconversions and dissociations of 1, 2, 3, and 4 based on QCISD(T)/6-311G(d,p) + ZPE energies in Table 1.

in complexes are important in the isomerizations and dissociations of 1, 2, and 3.

The H-bonded complex 4 is well situated to dissociate to $\text{CH}_3\text{CH}_3^+ + \text{CO}$. In search of the CH_3CH_3^+ -forming step, a minimum energy trajectory from 4 to $\text{CH}_3\text{CH}_3^+ + \text{CO}$ was sought with B3LYP/6-31G(d) theory by adjusting the C-H_i bond lengths away from the geometry of 4 in 0.1 Å steps and optimizing the rest of the structure at each step. A transition state was found at a C-C distance 5.457 Å and an energy of 143 kJ mol^{-1} . In the transition state, one CH bond in each

Table 1. Energies at points on the potential surface related to dissociation of $\text{C}_3\text{H}_6\text{O}^+$ isomers to CH_3CH_3^+

	B3LYP/6-31G(d)// B3LYP/6-31G(d)	QCISD/6-31G(d)// QCISD/6-31G(d)	QCISD(T)/6-311G(d,p)// QCISD/6-31G(d)	ZPE ^a	E (kJ mol ⁻¹) ^b
$\text{CH}_3\text{CH}_2\text{CHO}^+$ (1)	-192.788003 ^c	-192.200867	-192.341978	209.5	0
$\text{CH}_2\text{CH}_2\text{O}^+=\text{CH}_2$ (2)	-192.768182	-192.184062	-192.321410	212.7	57
$\text{CH}_3\text{CH}_2\text{O}^+=\text{CH}^-$ (cis-3)	-192.756698	-192.173094	-192.312373	213.2	81
$\text{CH}_3\text{CH}_2\text{O}^+=\text{CH}^-$ (trans-3)	-192.756814			213.0	
$\text{CH}_3\text{CH}_2\text{COH}^+$ (5)	-192.776029	-192.190447	-192.334642	215.4	25
TS(2 $\rightarrow$ 3)	-192.726580	-192.134780	-192.280238	213.2	166
$[\text{CH}_3\text{CH}_2\text{OCH}]^+$ (TS(3 $\rightarrow$ 1))		-192.141478	-192.282591	198.2 ^d	145
$[\text{CH}_3\text{CH}_2\text{-H-CO}]^+$ (4)	-192.751597	-192.165020	-192.315377	193.2	54
$[\text{CH}_3\text{CH}_2\text{CHO}]^+$ (TS(1 $\rightarrow$ 4))	-192.741115	-192.153418	-192.300832	198.4	97
TS(5 $\rightarrow$ 1)	-192.712628	-192.123688	-192.272795	200.0	172
TS(4 $\rightarrow$ $\text{CH}_3\text{CH}_3^+ + \text{CO}$)	-192.724244			185.3	143
CO	-113.309454	-113.029616	-113.093770	13.0	
CH_3CH_3^+	-79.410498	-79.114215	-79.193846	175.1	
$\text{CH}_3\text{CH}_3^+ + \text{CO}$	-192.719952	-192.143831	-192.287616	188.1	121
HCO^+	-113.545291	-113.264071	-113.320724	42.6	
CH_3CH_2	-79.157867	-78.869044	-78.946757	153.6	
$\text{CH}_3\text{CH}_2 + \text{HCO}^+$	-192.703158	-192.133115	-192.267481	196.2	182
HCO^-	-113.850171	-113.545698	-113.616580	33.7	
C_2H_5^+	-78.860111	-78.582426	-78.654830	157.1	
$\text{C}_2\text{H}_5^+ + \text{HCO}^-$	-192.710282	-192.128124	-192.271410	190.8	167
T(1 $\rightarrow$ $\text{CH}_3\text{CH}_2\text{CO}^+ + \text{H}^-$)	-192.745239	-192.163829	-192.307253	194.2	76

^aValues given were obtained from those produced by B3LYP/6-31G(d) theory by multiplying by a scaling factor of 0.9806 as described in Reference [22].

^bQCISD(T)/6-311G(d,p) energies relative to 1 = 0.

^cNot comparable to other B3LYP values because a more stringent optimization criterion was applied; this was necessary to achieve optimization.

^dObtained at the MP2/6-61G(d) level of theory because this transition state could not be located by B3LYP/6-31G(d) theory.

Table 2. Threshold energies for CH₃CH₃⁺ production from propanal and propanoic acid

	IE	AE(CH ₃ CH ₃ ⁺) ^b	Predicted AE ^c
CH ₃ CH ₂ CHO ⁺	9.96 ^a	11.40 ± 0.05	11.29
CH ₃ CH ₂ CO ₂ H ⁺	10.51 ^b	11.45 ± 0.05	11.05

^aFrom Reference [30].^bObtained by photoionization AE measurements as described in Reference [39, 41].^cFrom Reference [34]. Values were adjusted for thermal energy content according to the expression (Reference [42]). AE(A⁺)₂₉₈ = ΔH_f^o(A⁺) + ΔH_f^o(B) – ΔH_f^o(AB) – ΔH_{corr}, where ΔH_{corr} = ΔH₂₉₈^o[A⁺] + ΔH₂₉₈^o[B] – 0.745 R, and ΔH₂₉₈^o represents H₂₉₈^o – H₀^o. ΔH₂₉₈^o(CH₃CH₃⁺) = 0.13 eV, ΔH₂₉₈^o(CO) = 0.09 eV and ΔH₂₉₈^o(CO₂) = 0.10 eV. ΔH₂₉₈^o values were obtained by B3LYP/6-31G(d) theory.

methyl is 1.151 Å long and the other two 1.090 Å long. Thus the ethane ion was essentially fully formed at this point. The energy of this transition state is 14 kJ mol^{–1} below the energy of the dissociated products in B3LYP/6-31G(d) theory, implying that **4** can dissociate to CH₃CH₃⁺ without a reverse barrier. However, this transition state could not be found by QCISD theory, raising doubts as to whether it really exists. Nonetheless, **4** should dissociate smoothly to CH₃CH₃⁺ + CO. In summary, the dissociation pathways are well described by the reactions postulated in Scheme 1.

Barriers indicated experimentally for CH₃CH₃⁺ formation from **1** are at most low, as the photoionization appearance energy of C₂H₆⁺ is only 0.11 ± 0.05 eV (11 ± 5 kJ mol^{–1}) above the thermochemical threshold for that dissociation of **1** (Table 2). The approach of the photoionization efficiency (PIE) curve for this process to the abscissa is shallow (Figure 11), consistent with an influence of a competitive shift induced by the lower energy H loss on this reaction. The possible presence of a competitive shift makes the measured appearance energy an upper limit for the onset of the reaction.

Ethyl formate [33] and propanoic acid ions also decompose to CH₃CH₃⁺ (Scheme 2), so the neutral

Figure 11. Photoionization efficiency curve for the formation of C₂H₆⁺ from the propanal ion (**1**). This curve was obtained on a photoionization mass spectrometer [39, 41]. Note the shallow approach of the curve to its onset. **Scheme 2**

fragment is CO or CO₂ in all dissociations to alkane ions of which we know. This charge allocation is attributable to the relatively high ionization energies of CO and CO₂ [34] causing preferential association of the charge with CH₃CH₃ rather than with CO or CO₂ [35–38], as the former location gives much more stable products (Table 2). Formation of CH₃CH₃⁺ from propanoic acid radical cations 39 kJ mol^{–1} above the thermochemical threshold for that reaction (Table 3) demonstrates that any barriers in that pathway are not very far above the energies of the products. This is also an upper limit, as the shallow approach of the PIE curve to threshold (Figure 12) is consistent with an effect of a competitive shift on this reaction.

The carbene ion CH₃CH₂ĊOH⁺ (**5**) also dissociates to CH₃CH₃⁺ + CO, at least upon collision [3]. A transition state for **5** → **1** by shift of H from O to C was found at 172 kJ mol^{–1}. The identities of the species connected through this transition state were verified by tracing the reaction coordinate by IRC calculations. According to theory, the analogous interconversion of CH₃ĊOH⁺ and CH₃CHO⁺ requires a similar amount of energy, 171 kJ mol^{–1} [42, 43]. However, the transition state for that interconversion is higher in energy than those for the abundant H-losses from both species it connects, so the interconversion of CH₃ĊOH⁺ and CH₃CHO⁺ does not compete significantly with dissociation. TS (**5** → **1**) is 98 kJ mol^{–1} above TS(**1** → CH₃CH₂CO⁺ + H), so, as with the C₂H₄O⁺ reactions, **1** → **5** is probably not competitive with simple dissociation of **1**. To test if **5** can dissociate directly to CH₃CH₃⁺, the C–CO bond in **5** was extended to 3.6 Å, a point 273 kJ mol^{–1} above the ground state of **1** and with the H still fully on the oxygen. This pathway might serve to produce CH₃CH₃⁺ + CO in the collision-induced dissociation of **5** [3], but it is too high in energy to be significant in the dissociations of C₃H₆O⁺ species other than **5**.

According to photoelectron-photoion coincidence studies, CH₃CH₃⁺ is formed from **1** over a relatively

Table 3. Energies^a for products from C₃H₆O⁺ and C₃H₆O₂⁺ with an oppositely located charge

CH ₃ CH ₃ ⁺	1028	CH ₃ CH ₃	–84
CO	–111	CO ⁺	1241
CO ₂	–394	CO ₂ ⁺	935
ΣΔ _f H (Products)	917	634	1157 851

^aValues from Reference [34].

Figure 12. Photoionization efficiency curve for the formation of $C_2H_6^+$ from the propanoic acid ion.

narrow energy range above its onset [6], also a characteristic of many alkane eliminations from radical cations [9, 23, 44, 45]. This and present plus previous work on alkane eliminations [23–26] together demonstrate that alkane eliminations and formations of charged alkanes are closely related reactions, differentiated by the charge location giving the most stable products and by formation through an H-bonded rather than an ion-induced dipole intermediate complex. This study adds to the significance of the $C_3H_6O^+$ system as a model for understanding the chemistry of radical cations in the gas phase.

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