

Formation of the 3-Pentanone Ion from Ionized Propyl Propanoate Through Ion-Neutral Complexes

John C. Traeger

Chemistry Department, LaTrobe University, Bundoora, Victoria, Australia

Charles E. Hudson and David J. McAdoo

Marine Biomedical Institute, University of Texas Medical Branch, Galveston, Texas, USA

Formation of the 3-pentanone ion (**3**) from ionized propyl propanoate through the complex $[\text{C}_2\text{H}_5\text{CO}^+ \cdot \text{OC}_3\text{H}_7]$ is proposed based on data obtained by photoionization. The threshold and energy dependence for forming **3** relative to those for related processes support this proposal. The threshold for forming **3** coincides with that predicted for forming $[\text{CH}_3\text{CH}_2\text{CO}^+ \cdot \text{CH}_2\text{CH}_3]$, suggesting that that complex is also an intermediate in the pathway to **3**. 3-Pentanone ion formation is important much further above threshold than is alkane elimination through $[\text{RCO}^+ \cdot \text{R}]$ complexes. This adds to evidence that reactions between the partners in ion-dipole complexes take place over a wider energy range than do such reactions in complexes containing nonpolar neutral partners. (*J Am Soc Mass Spectrom* 1992, 3, 183-187)

Expulsion of an aldehyde from the alkoxy moiety of ionized esters to form ketone ions [1-3] is a very unusual mass spectral fragmentation. The aldehyde lost consists of the oxygen and the first carbon of the alcohol portion of the ester and species attached to that carbon [1, 2]. Deuteriums on this carbon do not exchange prior to aldehyde elimination [1]. The composition of the aldehyde eliminated and the direct formation of the ketone ion rather than an isomer thereof indicates that hydrogen transfer does not precede aldehyde expulsion [3]. This process is unique, in that other losses of interior portions of aliphatic ions take place by simple bond cleavages after rearrangements [4-7]. We have previously suggested that expulsion of the aldehyde and the associated C-C bond formation might either be concerted (**1a**) or involve ethyl migration to carbon followed by loss of the aldehyde (**1b**). However, pathway **1a** is dubious because concerted ejection of a fragment from the middle of an ion is unlikely [8]. A strike against both branches of Scheme I is that 4-membered ring processes are typically the least favorable rearrangements of ions [9]. In gas-phase ion chemistry, ion-neutral complexes are often intermediates when conventional mechanisms seem unlikely [10]. This

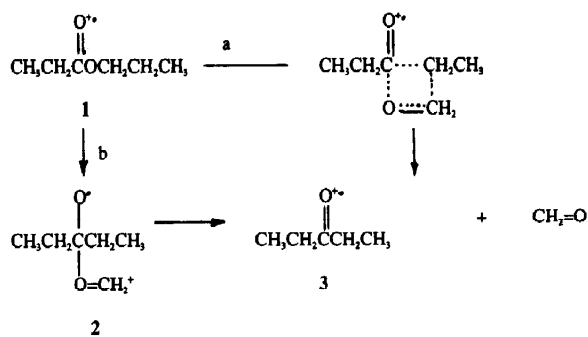
suggests that ketone ions may form from ionized esters through complexes, i.e., according to Scheme II or Scheme III.

The complex in Scheme II would be similar in origin to complexes proposed in alkane eliminations from ionized ketones [11-13]. However, in **4** the neutral partner is polar, whereas the alkyl radicals in the complexes that eliminate alkanes are nonpolar. The ion-dipole complex in Scheme II would be expected to be important over a wide energy range [14, 15], whereas the ion-induced dipole complex in Scheme III should be confined to a narrow energy range [11, 12, 16, 17]. Because of the novelty of the reaction, we examined formation of ionized 3-pentanone (**3**) from ionized propyl propanoate (**1**) by photoionization [18] to see if the energy dependence of the reaction supports or rules out Schemes II and III.

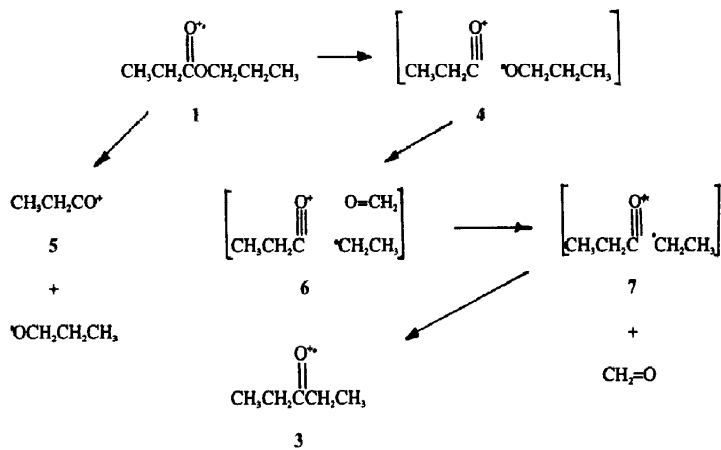
Experimental

Photoionization efficiency (PIE) curves were determined with a microprocessor-controlled photoionization mass spectrometer as described previously [18]. Appearance energy (AE) values were obtained by linear extrapolation of the initial rising portion of the curve to the abscissa. The AE measurements reported here are reproducible only to $\pm 3-5 \text{ kJ mol}^{-1}$ because of low count rates and tailing of curves near threshold. Metastable decompositions and collision-induced

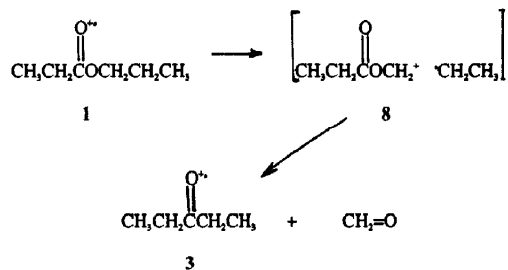
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Scheme I



Scheme II



Scheme III

dissociations were recorded on an electric sector-magnetic sector-electric sector mass spectrometer [19].

Results and Discussion

One characteristic of interest in complex-mediated dissociations is the degree of competition between the complex-mediated reaction and simple dissociation of the partners [11]. The direct cleavage 1 → 5 produces the base peak in the 70-eV mass spectrum of 1; 3 and CH₃CH₂CO₂CH₂⁺ are respectively 0.7% and 5% as abundant as the base peak. Thus, if 3 is formed through 4, that process competes weakly with the corresponding simple dissociation. The structure CH₃CH₂CO₂CH₂⁺ was assigned to C₄H₇O₂⁺ formed from 1 because this ion generates C₃H₅O⁺ in about 90% of its collision-induced dissociations. Loss of CH₂O would not dominate the decompositions of CH₃CH₂CH₂OCO⁺, the other reasonable product of ethyl loss from 1.

Photoionization AEs [18] for forming CH₃CH₂CO⁺CH₂CH₃ (3), CH₃CH₂CO⁺ (5) CH₃CH₂CO₂H₂⁺ and CH₃CH₂CO₂CH₂⁺ from 1 are given in Table 1. AE(3) is 49 kJ mol⁻¹ above AE(CH₃CH₂CO₂CH₂⁺) and 3 kJ mol⁻¹ below AE(5), the product of simple dissociation of complex 4. AE(3) being above AE(CH₃CH₂CO₂CH₂⁺) and below AE(5) suggests the intermediacy of 4 rather than of 8, because, without exception to date [12, 16, 17], products formed by reactions between partners in complexes containing alkyl radicals have thresholds 0–40 kJ mol⁻¹ below those for simple dissociation of the partners.

Published heats of formation of pertinent species are given in Table 2. The values in Table 2 give the following heats of formation for sets of products of interest:

$$\Delta H_f(\text{CH}_3\text{CH}_2\text{CO}^+) + \Delta H_f(\text{CH}_3\text{CH}_2\text{CH}_2\text{O}^\cdot)$$

$$= 550 \text{ kJ mol}^{-1}$$

$$\Delta H_f(\text{CH}_3\text{CH}_2\text{CO}^+) + \Delta H_f(\text{CH}_2 = \text{O})$$

$$+ \Delta H_f(\text{CH}_3\text{CH}_2^\cdot)$$

$$= 599 \text{ kJ mol}^{-1}$$

$$\Delta H_f(\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3^+) + \Delta H_f(\text{CH}_2 = \text{O})$$

$$= 531 \text{ kJ mol}^{-1}$$

Table 1. AEs^a for fragment ions from propyl propanoate

Ion	AE (kJ mol ⁻¹)
CH ₃ CH ₂ CO ⁺ CH ₂ CH ₃ (3)	1025
CH ₃ CH ₂ CO ⁺ (5)	1028
CH ₃ CH ₂ CO ₂ H ₂ ⁺	952 ^b
CH ₃ CH ₂ CO ₂ CH ₂ ⁺	976

^a Because of low threshold count rates and tailing of curves near threshold, these values are only reproducible to ± 3–5 kJ mol⁻¹.

^b Pseudo IE because the molecular ion is very weak, and because this is the lowest AE daughter ion.

AEs were predicted from the published heats of formation by means of the formula [18]

$$\text{AE}(A^+) = \Delta H_f(A^+) + \Delta H_f(B) - \Delta H_f(AB) - \Delta H_{\text{cor}}$$

where ΔH_{cor} is a statistical mechanical correction factor for the thermal energy content of the fragments. AE(3) predicted from published heats of formation [20, 21] and using $\Delta H_{\text{cor}} = 25.8 \text{ kJ mol}^{-1}$ [22]¹ was 990 kJ mol⁻¹, 35 kJ mol⁻¹ below the measured value. Ethane elimination from 3, a process thought to occur through [CH₃CH₂CO⁺CH₂CH₃] [12], has an onset 33 kJ mol⁻¹ above the ionization energy (IE) of 3 [21]. Therefore, formation of 3 by collapse of [CH₃CH₂CO⁺CH₂CH₃] would raise the threshold for formation of 3 by about 33 kJ mol⁻¹, in good agreement with the observed 35-kJ mol⁻¹ elevation. This coincidence is good evidence for formation of 3 by 6 → 7 → 3 rather than by one of the processes in Scheme I. AE(3) could also be raised above its thermochemical threshold by a reverse activation energy barrier to the elimination of formaldehyde. Such a barrier would be expected in the pathway depicted in Scheme II, because the products of formaldehyde elimination are 68 kJ mol⁻¹ more stable than the separated partners in 6.

The number of ions formed at a specific mass-to-charge ratio containing the energy on the abscissa minus the ionization energy of the parent molecule is proportional to the slope of the corresponding PIE curve of the ion at that point [23]. That is, at energies at which a curve is rising steeply, the corresponding

¹ This is based on vibrational frequencies given in JANAF thermochemical tables; see ref 22.

Table 2. Pertinent 298 K heats of formation (kJ mol⁻¹)

CH ₃ CH ₂ CO ₂ CH ₂ CH ₂ CH ₃	-484.2 ^a	CH ₃ CH ₂ CO ⁺ CH ₂ CH ₃	639.9 ^b
CH ₃ CH ₂ CO ⁺	591.2 ^c	CH ₃ CH ₂ CH ₂ O [·]	-41.4 ^d
CH ₃ CH ₂ ·	116.3 ^e	CH ₂ = O	-108.6 ^f
CH ₃ CH = C = O [·]	77.6 ^e	CH ₃ CH ₃	-83.8 ^f

^a From $\Delta H_f(\text{C}_2\text{H}_5\text{CO}_2\text{C}_2\text{H}_5) = -463.6 \text{ kJ mol}^{-1}$ [28] and addition of -20.6 kJ mol⁻¹ for the extra CH₂.

^b Ref 20.

^c Ref 21.

^d Ref 29.

^e Ref 18b.

^f Ref 28.

process is substantial, and at energies where the curve is horizontal, no ions containing the full energy $h\nu - IE$ are formed. In previous studies of alkane eliminations [12, 16, 24], PIE curves reached plateaus a few tenths of an electronvolt above the onset for simple loss of the alkyl radical, demonstrating that complex-mediated alkane eliminations are largely confined to a narrow energy range near threshold. However, small portions of alkane eliminations may occur up to very high energies [25]. If Scheme III were correct, the PIE curve for **3** should become horizontal within a few tenths of an electronvolt of threshold. The PIE curve for **3** rises rapidly from threshold (10.62 eV) to ~ 11.6 eV, and more slowly thereafter (Figure 1). The relatively wide energy range for forming **3** is additional evidence that **3** is formed according to Scheme II rather than Scheme III.

The 3-pentanone ion formed from **1** undergoes metastable loss of ethane [3], demonstrating that a portion of those 3-pentanone ions contained at least 54 kJ mol⁻¹ of internal energy. This confirms the conclusion from the AE curve that many of the 3-pentanone ions are formed at energies substantially above threshold. Formation of protonated ethanol from ion-

ized ethyl hexyl ether, clearly a complex-mediated process involving a polar neutral ethanol partner [14], also occurs up to well above the threshold for simple dissociation of the partners [14], as does complex-mediated formation of CH₃OH₂⁺ from ionized 2-methylpropanol, which involves a polar methanol partner [15]. Present observations add to evidence that the energy range over which complex-mediated fragmentations are important is considerably widened by the presence of a dipole moment in the neutral partner. When the partner in the complex is nonpolar, eliminations through that complex are generally the lowest threshold decompositions of the ion [10]. AE(CH₃CH₂CH₂CO₂H₂⁺) and AE(CH₃CH₂CO₂CH₂⁺) are substantially below AE(**3**), suggesting this restriction does not apply when the partner in the intermediate complex has a substantial dipole moment.

Alkoxy radicals readily dissociate to aldehydes plus alkyl radicals, so Scheme II is plausible. The simultaneous elimination of two benzene molecules from protonated oligophenylalkanes [26] is another possible three body complex-mediated reaction. Three partner complexes would be an interesting addition to the variety of known complex-mediated reactions [10, 27].

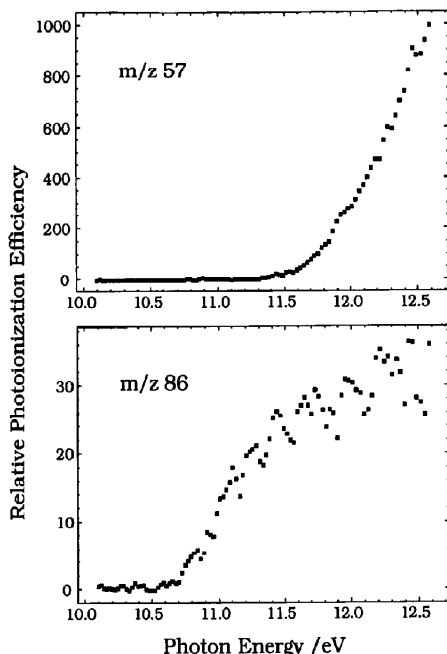


Figure 1. PIE curves for the formation of CH₃CH₂CO⁺CH₂CH₃ and CH₃CH₂CO⁺ from propyl propanoate. Note that the AE curve for C₅H₁₀O⁺ (m/z 86) rises steeply up to about 11.5 eV and then more gradually at higher energies. The curve for CH₃CH₂CO⁺, the product of simple dissociation, rises steeply through the energy range of the measurements.

Acknowledgments

We thank the Robert A. Welch Foundation (H-609), the Petroleum Research Fund, and the Australian Research Grants Scheme for financial support; Professor Michael Cross and the Midwest Center for Mass Spectrometry for use of their Kratos MS 50TA mass spectrometer; and Ms. Debbie Pavlu for typing.

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