ELSEVIER International Journal of Mass Spectrometry 210/211 (2001) 181–188 www.elsevier.com/locate/ijms

Heats of formation for the propen-1-ol and propen-2-ol cations by photoionization mass spectrometry

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Received 6 December 2000; accepted 2 February 2001

Abstract

Threshold photoionization mass spectrometry has been used to measure the appearance energies for $C_3H_6O^{+\cdot}$ formed via alkene elimination from several ionized aldehydes and methyl ketones. The derived 298 K heats of formation for the propen-1-ol and propen-2-ol cations are 681.1 ± 1.8 kJ mol^{-1} and 676.6 ± 0.7 kJ mol^{-1}, respectively. Although these values are ~16 kJ mol^{-1} higher than those derived from previous electron ionization data, they are both in excellent agreement with high level G2 ab initio calculations. (Int J Mass Spectrom 210/211 (2001) 181–188) © 2001 Elsevier Science B.V.

Keywords: Propen-1-ol cation; Propen-2-ol cation; Photoionization; Heat of formation; Appearance energy; McLafferty rearrangement

1. Introduction

The $C_3H_6O^{+\cdot}$ cation is often observed in the mass spectra of oxygen-containing organic molecules. Numerous structural isomers have been identified by theoretical calculations [1] with the propen-1-ol ($\mathbf{1}^{+\cdot}$) and propen-2-ol ($\mathbf{2}^{+\cdot}$) radical cations being the two most stable species. From a G2(MP2) ab initio study, Turecek and Cramer [2] calculated that the propen-2-ol cation ($\Delta H^\circ_{f,298} = 677$ kJ mol^{-1}) is 5 kJ mol^{-1} lower in energy than either the (E) or the (Z) forms of the propen-1-ol cation ($\Delta H^\circ_{f,298} = 682$ kJ mol^{-1}). By comparison, ionized acetone ($\mathbf{3}^{+\cdot}$) was calculated to be 40 kJ mol^{-1} higher in energy than $\mathbf{2}^{+\cdot}$, whereas ionized propionaldehyde ($\mathbf{4}^{+\cdot}$) was 93 kJ mol^{-1} less stable than $\mathbf{1}^{+\cdot}$. These correspond to 298 K cationic heats of formation of 717 kJ mol^{-1} and 775 kJ mol^{-1}, respectively, and agree to within 2 kJ mol^{-1} of the evaluated experimental data in the gas-phase ion and neutral thermochemical (GIANT) compendium of Lias et al. [3].

However, there is a significant discrepancy of 16 and 17 kJ mol^{-1} between the corresponding theoretical and experimental values for both $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$. Because of uncertainties in the neutral propenol heats of formation, the GIANT values were based on the electron ionization (EI) appearance energy (AE) measurements of Holmes and Lossing [4]. Although these were obtained using an electron monochromator, no allowance was made for the nonequilibrium thermal content of the fragmentation products, which could result in an underestimation of the cationic heat of formation by more than 20 kJ mol^{-1} [5]. Turecek and

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Dedicated to Professor Nico Nibbering in recognition of his many important contributions to mass spectrometry and gas-phase ion chemistry.

PII S1387-3806(01)00424-9

Cramer [2] recognized this in their comparison of theoretical and experimental values for $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$, and applied such a correction to the Holmes and Lossing measurement. The adjusted value of 684 kJ mol^{-1} for $\mathbf{2}^{+\cdot}$ was found to be in much better agreement with their corresponding G2 theoretical value of 677 kJ mol^{-1}.

The aim of the present study is to obtain accurate experimental heats of formation for these two important cations, extending our previous photoionization mass spectrometric investigation of the heat of formation for the related vinyl cation [6].

2. Experimental

The La Trobe University photoionization mass spectrometer has been described in detail previously [7]. For this study the photon source was the many-lined hydrogen pseudocontinuum, with the resolution of the Seya–Namioka monochromator fixed at 0.135 nm. Atomic emission lines were used to calibrate the absolute energy scale to an accuracy of better than 0.003 eV. The experiments were performed at room temperature (296 K), with sample pressures of 10^{-3} Pa in the ion source. Photoionization mass spectra were obtained with the monochromator set in a nondispersive total reflection mode. This allowed photons produced by the discharge lamp with a range of wavelengths (~7.7–14.5 eV) to be available for ionization. All compounds were obtained commercially and used as supplied, with GCMS analyses used to confirm their high purity with respect to *m/z* 58 contamination.

3. Results and discussion

The heat of formation for a radical cation can usually be derived experimentally from the adiabatic ionization energy (IE) and heat of formation for the neutral precursor. Although several EI measurements have been made for the IE to form both $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$ [8–11], there is no direct experimental value available for the heat of formation of either **1** or **2**.

Appearance energies can often provide an alternative means of obtaining a reliable cationic heat of formation. It is, however, necessary that the fragmentation process does not involve a reverse activation energy and that any kinetic and/or competitive shift is negligible [5]. These errors may be minimized by the use of a range of precursor molecules, such as reported here, where these effects will usually be different. However, an AE can only ever produce an upper limit to the true thermodynamic value.

In the present study, several aldehydes and methyl ketones have been selected, as these are known to eliminate a neutral alkene and form the respective propen-1-ol and propen-2-ol cations via a six-centered intermediate following ionization [4]. This corresponds to the well known McLafferty rearrangement for either a methyl ketone or a 2-methyl substituted aldehyde.

The products of a unimolecular gas-phase fragmentation are not formed at any well-defined thermodynamic temperature. Thus, the experimental 298 K appearance energy for the process

$$C_3H_6OX + h\nu \rightarrow C_3H_6O^{+\cdot} + X + e^- \qquad (1)$$

does not directly represent ΔH^{o}_{298} for this reaction. It can be shown [12] that the cationic heat of formation, based on a stationary electron (ion) convention [12,13], is given by

$$\Delta H^{o}_{f,298}(C_3H_6O^{+\cdot}) = AE_{298} + \Delta H^{o}_{f,298}(C_3H_6OX) - \Delta H^{o}_{f,298}(X) + \Delta H_{cor} \qquad (2)$$

where AE_{298} is derived from a threshold linear extrapolation of the photoionization efficiency (PIE) curve and the thermal energy correction term is given by

$$\Delta H_{cor} = \{H^{o}_{298} - H^{o}_{0}\}(C_3H_6O^{+\cdot}) + \{H^{o}_{298} - H^{o}_{0}\}(X) - 6.2\ \text{kJ mol}^{-1} \qquad (3)$$

The enthalpy values used to derive ΔH_{cor} can be obtained from standard statistical mechanical calculations [14] and the relevant data used in this study are given in Table 1. Fig. 1 illustrates the overall thermochemical cycle involved.

The assignment of an appearance energy from a

Table 1
Supplementary thermochemical data

Compound	$H^\circ_{298} - H^\circ_0$ (kJ mol^{-1})	Reference
C_2H_4	10.5	[2]
C_3H_6	13.4	[2]
$i{-}C_4H_8$	16.8	[2]
$CH_3C(OH)CH_2^{+\cdot}$ ($\mathbf{2}^{+\cdot}$)	16.4	[2]
$CH_3CHCHOH^{+\cdot}$ ($\mathbf{1}^{+\cdot}$)	16.3	[2]

Compound	$\Delta H^\circ_{f,298}$ (kJ mol^{-1})	Reference
2-pentanone	-259.0 ± 1.0	[17]
2-hexanone	-279.8 ± 1.1	[17]
4-methyl-2-pentanone	-289.1	Estimated [18]
5-methyl-2-hexanone	-309.7	Estimated [18]
valeraldehyde	-228.5 ± 1.7	[17]
isovaleraldehyde	-236.8	Estimated [18]
2-methylvaleraldehyde	-255.5	Estimated [18]
3-methylvaleraldehyde	-257.4	Estimated [18]
hexanal	-248.1	Estimated [18]
ethene	52.5 ± 0.4	[17]
propene	20.0 ± 0.8	[17]
2-methylpropene	-16.9 ± 0.9	[17]

(1 eV = 96.4846 kJ mol^{-1})

threshold PIE curve is not always straightforward and may be influenced by a variety of factors. However, the common procedure adopted for each appearance energy assigned here is that the extent of prethreshold hot-band structure [5] apparent at photon energies less than the indicated linear extrapolation should be consistent with the thermal excitation observed for the corresponding molecular ion. This is typically ~0.1–0.2 eV.

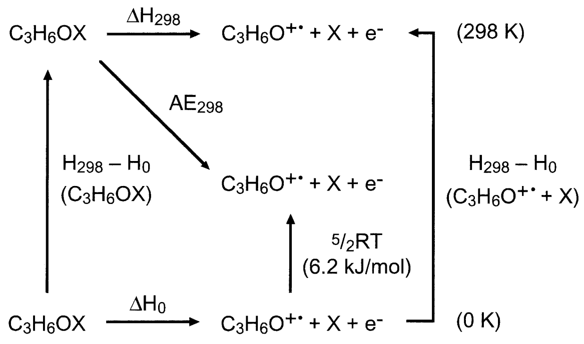


Fig. 1. Thermochemical cycle for the photoionization and unimolecular decomposition of C_3H_6OX.

3.1. Propen-2-ol radical cation ($2^{+\cdot}$)

The adiabatic ionization energies for the four methyl ketone precursors, listed in Table 2, are all in good agreement with previous photoionization measurements. Unfortunately, each of the PIE curves shown in Fig. 2, 3, 4, and 5 is affected by a low photoion count rate in the threshold region, with considerable curvature apparent. As a consequence, the selected 298 K appearance energies are somewhat less certain, due to the excellent reproducibility of the experimental data. Although other linear extrapolations could be made, those indicated on the Fig. have been selected on the basis of a plausible amount of hot-band structure, a criterion that alternative assignments do not satisfy. The AE errors indicated in Fig. 2, 3, 4, and 5 essentially reflect the confidence in assigning each particular extrapolation.

The significant threshold curvature is characteristic of the presence of either a kinetic or competitive shift. In their photoionization study, Murad and Inghram [15] commented on this behavior and the resulting uncertainty in the associated AEs. They estimated a kinetic shift of ~0.25 eV for the fragmentation process leading to $\mathbf{2}^{+\cdot}$, although Rice–Ramsperger–Kassel–Marcus calculations of the rates of the steps involved in the McLafferty rearrangement indicate that any kinetic shift should be negligible [16]. It is also possible that there is a competitive effect as the simple bond cleavage leading to loss of a methyl radical from ionized 2-pentanone, 2-hexanone and 4-methyl-2-pentanone occurs at a lower AE than the corresponding *m/z* 58 AE. Furthermore, there is a significant difference (≥0.5 eV) between all ionization and appearance energies listed in Table 2. The threshold formation of $\mathbf{2}^{+\cdot}$ occurs in a Franck–Condon gap [15], resulting in a low ionization cross section. This creates additional uncertainty with EI measurements because, due to a different threshold law, an electron ionization efficiency curve has a more poorly defined onset than a comparable PIE curve [5]. Because of these factors, the agreement with other experimental data shown in Table 2 is variable.

Despite the high purity of each methyl ketone (>99%), it was necessary to make a small analytical

Table 2
Thermochemistry for the gas-phase reaction at 298 K $CH_3COX + h\nu \rightarrow C_3H_6O^{+\cdot} + N + e^-$

Precursor	IE_{ad} eV	N	AE_{298} eV	ΔH_{cor} kJ mol^{-1}	$\Delta H^\circ_{f,298}(\mathbf{2}^{+\cdot})$ kJ mol^{-1}
2-pentanone	9.38[a]	C_2H_4	10.03[a]	20.7	676.9
	9.38[b]		10.07[c]		
	9.37[c]		10.08[d]		
2-hexanone	9.33[a]	C_3H_6	9.87[a]	23.7	676.2
	9.35[b]		10.00[c]		
	9.37[c]		10.04[d]		
4-methyl-2-pentanone	9.33[a]	C_3H_6	9.98[a]	23.7	677.5
	9.30[b]		10.1[c]		
	9.30[c]		9.98[d]		
5-methyl-2-hexanone	9.28[a]	$i-C_4H_8$	9.76[a]	27.0	675.9
	9.28[b]				

[a] This work.
[b] Ref. [3].
[c] Ref. [15].
[d] Ref. [4].

correction to the 5-methyl-2-hexanone PIE curve (Fig. 5). Because this compound has a lower vapor pressure than the other ketones studied here, the interference from small traces of highly volatile acetone (IE = 9.71 eV [3]) was unduly magnified. This was apparent as superimposed fine structure in the threshold region of the uncorrected PIE.

The heats of formation for 2-pentanone and 2-hexanone are well established [17]. However, because no experimental data is available for either 4-methyl-2-pentanone or 5-methyl-2-hexanone, it is necessary to use a group equivalent estimation method for their heats of formation. For consistency, the Benson additivity scheme [18] has been used in the present work. Where possible, the corresponding Pedley et al. method [17] has been used for confirmation. Because these schemes produce good agreement with experiment for a range of ketones, it is expected that there will be little error associated with the estimated values listed in Table 2.

The mean of the cationic heats of formation for $\mathbf{2}^{+\cdot}$ given in Table 2 is 676.6 ± 0.7 kJ mol^{-1}, in excellent agreement with the theoretical value of 677 kJ mol^{-1} obtained by Turecek and Cramer [2]. It is, however, 16 kJ mol^{-1} higher than the Holmes and Lossing

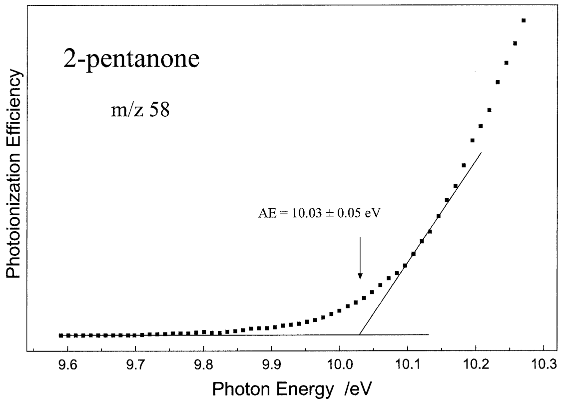


Fig. 2. Threshold PIE curve for *m/z* 58 fragment ions produced from 2-pentanone.

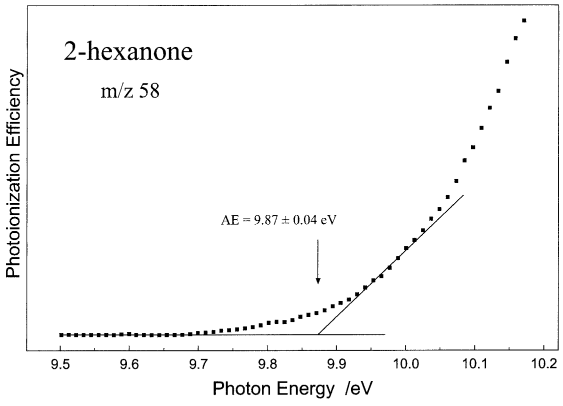


Fig. 3. Threshold PIE curve for *m/z* 58 fragment ions produced from 2-hexanone.

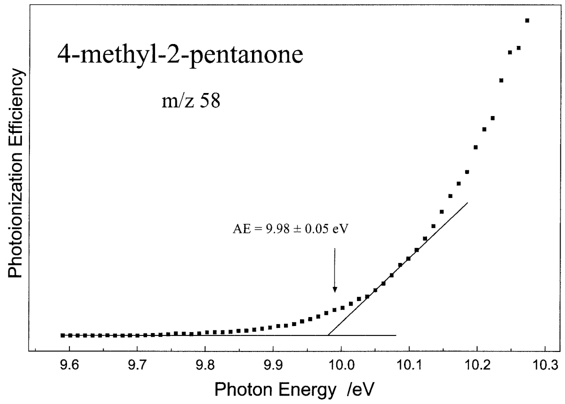
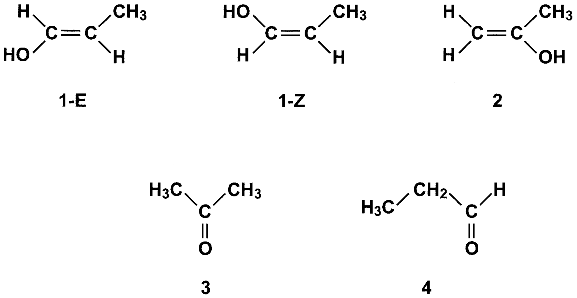


Fig. 4. Threshold PIE curve for *m/z* 58 fragment ions produced from 4-methyl-2-pentanone.

value [4], although this is to be expected since no enthalpy correction was employed in that study and ΔH_{cor} for their particular set of compounds varies between 20.6 and 23.7 kJ mol^{-1} (see Tables 2 and 3). Electron ionization AE values also tend to be higher than equivalent photoionization appearance energies because of the less distinct ionization efficiency threshold. The combined effect of these two factors would be to produce a heat of formation for $\mathbf{2}^{+\cdot}$ closer to the present value. Given the uncertainties with each of the appearance energies in Table 2, the small standard deviation of 0.7 kJ mol^{-1} is probably fortuitous. It is possible that there is some excess energy associated with the threshold products, but the close agreement of the present data, which involve a range of precursors and neutral fragments, suggests that this is unlikely.



Scheme 1

3.2. Propen-1-ol radical cation ($1^{+\cdot}$)

In contrast to the methyl ketones studied here, the five aldehydes each have very sharply defined appearance energies, with no evidence for any kinetic or competitive shift (Fig. 6, 7, 8, 9, and 10). Because they are all close to the corresponding IE, there is a good ionization cross section in the threshold region. Furthermore, apart from hexanal, the *m/z* 58 ion forms the base peak in each photoionization mass spectrum with no significant competition from other fragmentation pathways.

There is good agreement with IE measurements for valeraldehyde isovaleraldehyde and hexanal from

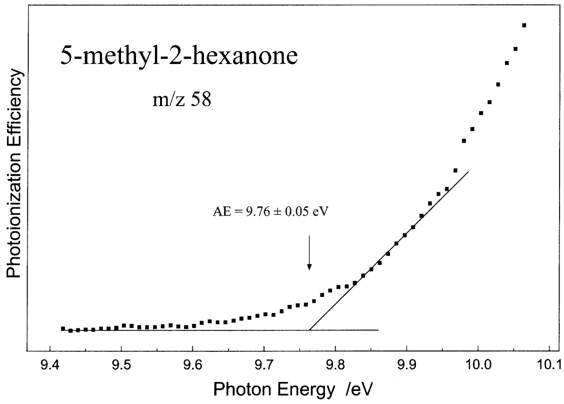


Fig. 5. Threshold PIE curve for *m/z* 58 fragment ions produced from 5-methyl-2-hexanone.

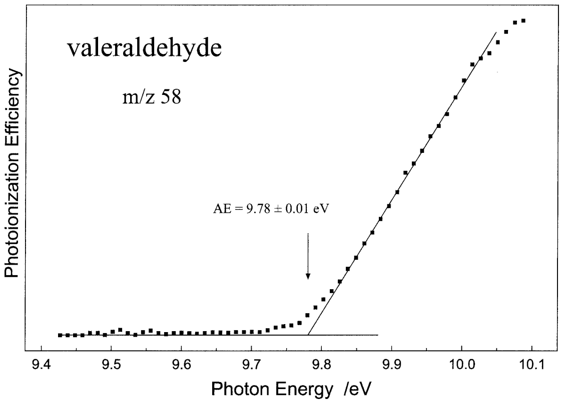


Fig. 6. Threshold PIE curve for *m/z* 58 fragment ions produced from valeraldehyde.

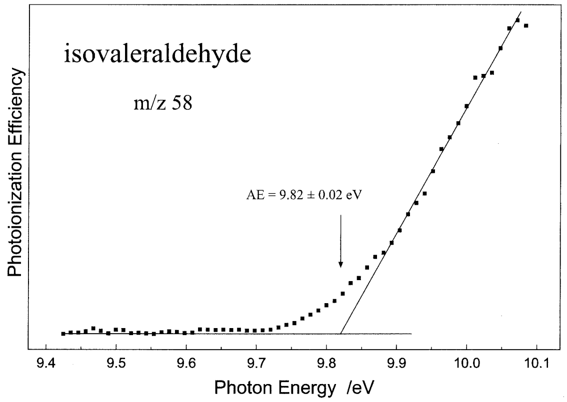


Fig. 7. Threshold PIE curve for *m/z* 58 fragment ions produced from isovaleraldehyde.

other photoionization experiments (Table 3). However, only EI data is available for either 2-methylvaleraldehyde or 3-methylvaleraldehyde and this is reflected by the wider discrepancy with these values.

No photoionization AE measurements are available for comparison. The literature values indicated in Table 3 were all obtained by electron ionization, involving either an electron monochromator [4] or a nonenergy resolved semilog analysis [19]. Although there is reasonable agreement with the former data, the unreliability of empirical techniques to obtain appearance energies is demonstrated by the poor agreement of the latter values, with a relative order in reverse to that found here.

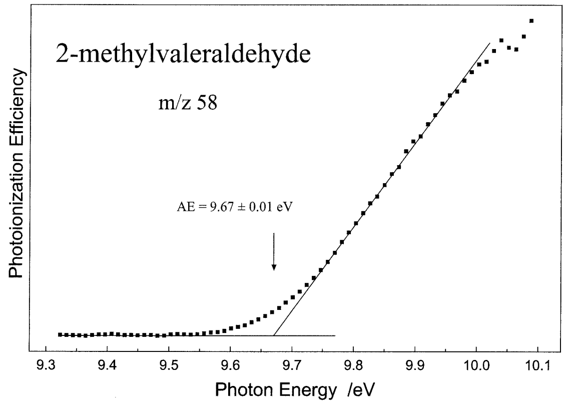


Fig. 8. Threshold PIE curve for *m/z* 58 fragment ions produced from 2-methylvaleraldehyde.

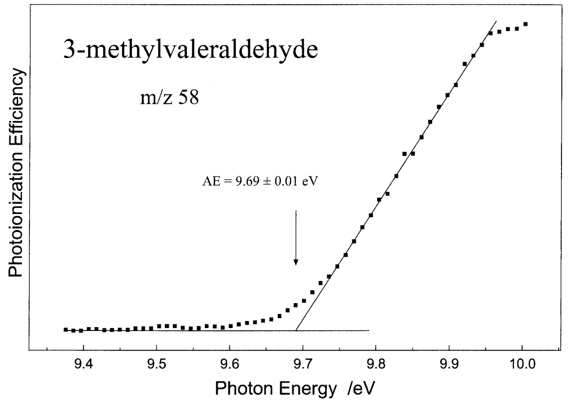


Fig. 9. Threshold PIE curve for *m/z* 58 fragment ions produced from 3-methylvaleraldehyde.

The *m/z* 58 AE for hexanal of 9.72 eV measured here is in exact agreement with the corresponding Holmes and Lossing measurement [4]. However, this does not represent a true thermochemical value as the IE of 9.72 eV dictates that *mz* 58 ions will not be formed below this particular energy. The somewhat higher calculated cationic heat of formation shown in Table 3 is a reflection of this restriction. Because a molecular ion is observed in the photoionization mass spectrum for hexanal, with a relative abundance ~50% of that for the *m/z* 58 fragment ion, the thermochemical AE is not expected to be substantially lower than the observed adiabatic IE of 9.72 eV.

Unlike the methyl ketones, the errors associated

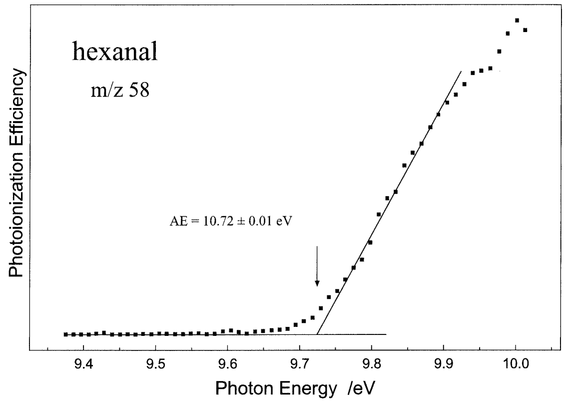


Fig. 10. Threshold PIE curve for *m/z* 58 fragment ions produced from hexanal.

Table 3
Thermochemistry for the gas-phase reaction at 298 K XCHO + $h\nu \rightarrow C_3H_6O^{+\cdot} + N + e^-$

Precursor	IE_{ad} eV	N	AE_{298} eV	ΔH_{cor} kJ mol^{-1}	$\Delta H^{\circ}_{f,298}(\mathbf{1}^{+\cdot})$ kJ mol^{-1}
valeraldehyde	9.74[a] 9.74[b]	C_2H_4	9.78[a] 10.00[c] 9.82[d]	20.6	683.2
isovaleraldehyde	9.73[a] 9.70[b]	C_2H_4	9.82[a]	20.6	678.8
2-methylvaleraldehyde	9.53[a] 9.70[b]	C_3H_6	9.67[a] 10.30[c] 9.80[d]	23.6	681.1
3-methylvaleraldehyde	9.64[a] 9.68[b]	C_3H_6	9.69[a] 10.10[c]	23.6	681.1
hexanal	9.72[a] 9.67[b] 9.72[d]	C_3H_6	9.72[a] 10.20[c] 9.72[d]	23.6	693.3

[a] This work.
[b] Ref. [3].
[c] Ref. [19].
[d] Ref. [4].

with the $C_3H_6O^{+\cdot}$ appearance energies for each aldehyde measured here are small. However, the accuracy of a derived cationic heat of formation also depends on reliable auxiliary thermochemical data, and only valeraldehyde has a neutral heat of formation determined by experiment. In addition, by comparison with ketones, the success of group equivalent methods applied to aldehydes is less reliable [17]. If hexanal is excluded from the average, the mean cationic heat of formation for $\mathbf{1}^{+\cdot}$ given in Table 3 is 681.1 ± 1.8 kJ mol^{-1}, which is 4.5 kJ mol^{-1} higher in energy than $\mathbf{2}^{+\cdot}$. This is in excellent agreement with both the theoretical value of 682 kJ mol^{-1} and the 5 kJ mol^{-1} energy difference calculated by Turecek and Cramer [2]. The slightly larger standard deviation of 1.8 kJ mol^{-1} is probably due to the less certain precursor heats of formation used in Table 3.

4. Conclusion

Dissociative photoionization mass spectrometry has been used to measure appearance energies for $C_3H_6O^{+\cdot}$ cations formed via neutral alkene elimination from a range of ionized methyl ketones and aldehydes. The 298 K cationic heats of formation derived for ionized propen-1-ol ($\mathbf{1}^{+\cdot}$) and propen-2-ol ($\mathbf{2}^{+\cdot}$) are 681.1 ± 1.8 kJ mol^{-1} and 676.6 ± 0.7 kJ mol^{-1}, respectively. Both values are supported by recent high-level ab initio calculations, indicating that the previous experimental heats of formation obtained from electron ionization measurements are too high by ~16 kJ mol^{-1}. It is suggested that this discrepancy is largely due to the exclusion of an appropriate thermal enthalpy correction factor when deriving the cationic heat of formation.

Acknowledgement

This work was financially supported by the Australian Research Council.

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