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Neutral and cationic heats of formation for ketene, methylketene, and dimethylketene

John C. Traeger

Department of Chemistry, La Trobe University, Bundoora, Victoria 3083, Australia

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Abstract

Threshold photoionization mass spectrometry has been used to measure appearance energies for the formation of $C_2H_2O^{+\cdot}$, $C_3H_4O^{+\cdot}$, and $C_4H_6O^{+\cdot}$ from several different precursors, leading to derived 298 K cationic heats of formation of 874.4 ± 1.0, 783.5 ± 0.3, and 719.3 ± 3.6 kJ mol^{-1}, respectively. Experimental appearance energies for the production of ionized phenol from phenyl acetate, phenyl propionate, and phenyl isobutyrate, and for ionized dimethylketene from tetramethyl-1,3-cyclobutanedienone, provide 298 K heats of formation for ketene (-53.6 ± 0.6 kJ mol^{-1}), methyl ketene (-66.9 ± 4.7 kJ mol^{-1}), and dimethyl ketene (≤ -86.4 kJ mol^{-1}). Apart from the value for the methylketene cation, these are all in excellent agreement with high level ab initio calculations. There is evidence to suggest that the experimental ionization energy for methyl ketene may be up to 0.15 eV too high. (Int J Mass Spectrom 194 (2000) 261–267) © 2000 Elsevier Science B.V.

Keywords: Ketene; Methylketene; Dimethylketene; Photoionization; Heat of formation

1. Introduction

Recent high level ab initio studies [1,2] of methyl ketene and dimethyl ketene have produced 298 K heats of formation for both the neutral and cationic species that are significantly (~40 kJ mol^{-1}) different from the evaluated gas-phase ion and neutral thermochemical (GIANT) values of Lias et al. [3]. However, the calculated ionization energies are in good agreement with experimental photoelectron spectroscopic measurements. In a recent examination of the effect of methyl substitution on the thermochemistry of ketene using energy-selected electron ionization (EI), Holmes and co-workers [4] obtained both neutral and ionic heats of formation, which were in essential agreement with the GIANT compilation. The aim of the present study is to use the technique of threshold photoionization mass spectrometry to try to resolve this large discrepancy between experiment and theory.

2. Experimental

The microcomputer-controlled photoionization mass spectrometer used in this study has been described in detail previously [5]. The hydrogen pseudocontinuum was used as the photon source with the band pass of the 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.

Dedicated to Jim Morrison who helped show me the value of a good appearance potential.

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All experiments were performed at 296 K, with sample pressures of 10^{-3} Pa in the ion-source region. Most compounds were obtained commercially and used without further purification. The phenyl esters were synthesized by standard procedures and base washed prior to use to remove interfering traces of phenol. GCMS analysis indicated purities were >99.5%.

3. Results and discussion

The experimental 298 K appearance energy (AE) based on a threshold linear extrapolation of the photoionization efficiency curve (PIE) for the process

$$AB + h\nu \rightarrow A^{+\cdot} + B + e^-$$

is related to the reaction thermochemistry by [6]

$$AE = \Delta H^\circ_{f,298}(A^{+\cdot}) + \Delta H^\circ_{f,298}(B) - \Delta H^\circ_{f,298}(AB) - \Delta H_{cor} \qquad (1)$$

where ΔH_{cor}, the thermal energy correction term, is given by

$$\{H^\circ_{298} - H^\circ_0\}(A^{+\cdot}) + \{H^\circ_{298} - H^\circ_0\}(B) - 5/2\ RT \qquad (2)$$

The various values for ΔH_{cor} can be obtained from standard statistical mechanical calculations [7] and the relevant data used in this work are given in Table 1. The stationary electron (ion) convention [6,8] has been used for all cationic heats of formation. For each appearance energy measured here, the extent of pre-threshold hot-band structure at photon energies below the linearly extrapolated AE was consistent with the thermal excitation observed for the corresponding molecular ion (typically ~0.1–0.2 eV).

3.1. Ketene (1) and ketene radical cation ($\mathbf{1}^{+\cdot}$)

The AE for $\mathbf{1}^{+\cdot}$ from acetone was measured to be 10.38 ± 0.01 eV (Fig. 1), which corresponds to a 298 K heat of formation of 874.4 ± 1.0 kJ mol^{-1} (see Table 1 for supplementary thermochemical data). This is in good agreement with both the theoretical value of 875 kJ mol^{-1} [1,2] and the GIANT value of 879.6 kJ mol^{-1} [3]. Combination with the experimental adiabatic ionization energy (IE) of 9.6191 ± 0.0004 eV [9], which becomes 928.4 kJ mol^{-1} when converted to 298 K using data in Table 1, leads to a heat of formation for **1** of −54.0 ± 2.1 kJ mol^{-1}. Although this is lower than the experimental value of −47.5 ± 1.6 kJ mol^{-1} [10]; it is, however, in excellent agreement with theory (−52 kJ mol^{-1}) [1,2].

Table 1
Supplementary thermochemical data (1 eV = 96.4846 kJ mol^{-1})

Compound	$H^\circ_{298} - H^\circ_0$ (kJ mol^{-1})	Source
CH_2CO	11.7	[22]
$CH_2CO^{+\cdot}$	12.0	[22]
CH_3CHCO	14.9	[22]
$CH_3CHCO^{+\cdot}$	15.7	[22]
$(CH_3)_2CCO$	18.7	[22]
$(CH_3)_2CCO^{+\cdot}$	20.1	[22]
CH_4	10.0	[7]
CH_3OH	11.4	[23]
C_2H_4	10.5	[7]
C_2H_6	11.9	[24]
C_3H_8	14.7	[25]
C_6H_5OH	17.3	[26]
$C_6H_5OH^{+\cdot}$	18.1	[26]

Compound	$\Delta H^\circ_{f,298}$ (kJ mol^{-1})	Source
Methane	−74.4 ± 0.4	[10]
Methanol	−201.5 ± 0.3	[10]
Ethene	52.5 ± 0.4	[10]
Ethane	−83.8 ± 0.4	[10]
Propane	−104.7 ± 0.5	[10]
Acetone	−217.3 ± 0.7	[10]
Cyclopentanone	−192.1 ± 1.8	[10]
3-Pentanone	−257.9 ± 0.8	[10]
1-Hydroxy-2-butanone	−389 ± 2	[4]
2-Methyl-3-pentanone	−286.1 ± 1.0	[10]
2,4-Dimethyl-3-pentanone	−311.3 ± 1.2	[10]
Tetramethyl-1,3-cyclobutanedione	−307.6 ± 1.5	[10]
Phenol	−96.4 ± 0.9	[10]
Phenyl acetate	−279.7 ± 1.2	[10]
Phenyl propionate	−299.5 ± 1.8	Estimated [10]
Phenyl isobutyrate	−333.5 ± 2.0	Estimated [10]

The formation of ionized phenol and neutral ketene from phenyl acetate is the lowest energy photoionization process, with an AE of 9.62 ± 0.01 eV (Fig. 2). Furthermore, the small kinetic energy release of 7

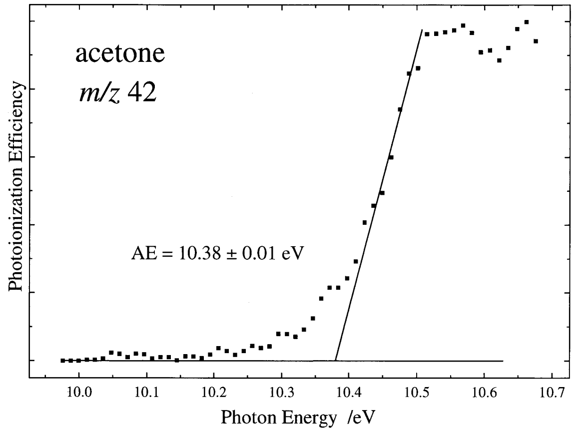

Fig. 1. Threshold PIE curve for *m/z* 42 fragment ions produced from acetone.

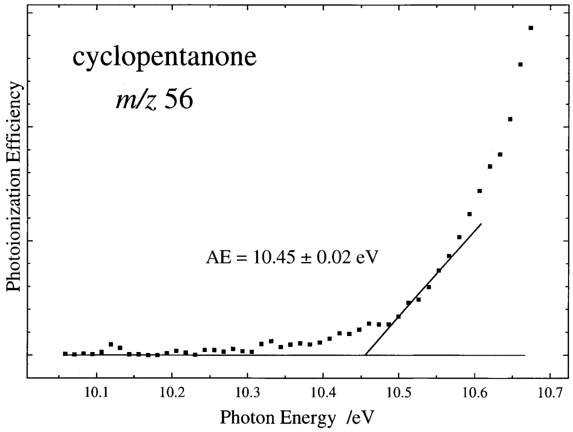

Fig. 3. Threshold PIE curve for *m/z* 56 fragment ions produced from cyclopentanone.

meV [4] indicates a negligible kinetic shift effect [11]. The adiabatic IE for phenol has been accurately measured to be 8.508 ± 0.001 eV [12–14]. This corresponds to a 298 K IE of 821.7 ± 0.1 kJ mol^{-1} and a cationic heat of formation of 725.3 ± 1.0 kJ mol^{-1}. Combination with the present AE leads to a 298 K heat of formation for **1** of −53.2 ± 3.2 kJ mol^{-1}, which supports both of the above values. It is also in good agreement with the recent value of −54 ± 5 kJ mol^{-1} obtained by Holmes and co-workers [4].

The average of the two present values for the ketene heat of formation (−53.6 ± 0.6 kJ mol^{-1}), together with $\Delta H_f(\mathrm{H}^+) = 1530.1$ kJ mol^{-1} [7] and $\Delta H_f(\mathrm{CH_3CO}^+) = 655.5 \pm 0.8$ kJ mol^{-1} [15], leads to a proton affinity (PA) for ketene of 821.0 ± 1.4 kJ mol^{-1}. This compares favorably with recent high-level theoretical values of 825.0 [16], 823.5 [17], and 820 kJ mol^{-1} [2], as well as a recent thermokinetic measurement of 817 ± 3 kJ mol^{-1} [18]. The Hunter and Lias evaluated PA for ketene is 825.3 kJ mol^{-1} [19].

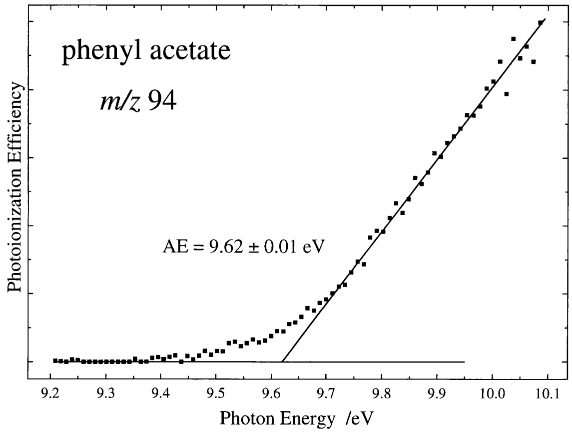

Fig. 2. Threshold PIE curve for *m/z* 94 fragment ions produced from phenyl acetate.

Apart from requiring a small adjustment to the experimentally determined value for **1**, experiment and theory are in accord for the heats of formation of both ketene and ionized ketene. The combined 298 K heats of formation for neutral and ionized ketene give a value of 821.2 ± 1.6 kJ mol^{-1}, compared to the GIANT value of 832 kJ mol^{-1} [3] and the theoretical value of 823 kJ mol^{-1} [1,2].

3.2. Methylketene (2) and methylketene radical cation ($2^{+\cdot}$)

The $C_3H_4O^{+\cdot}$ appearance energies from cyclopentanone, 3-pentanone and 2-methyl-3-pentanone were determined here as 10.45 ± 0.02, 9.70 ± 0.02, and 9.75 ± 0.01 eV, respectively (Figs. 3–5). The corresponding 298 K heats of formation, obtained using Eq. (1) and data from Table 1, are 783.7 ± 4.1,

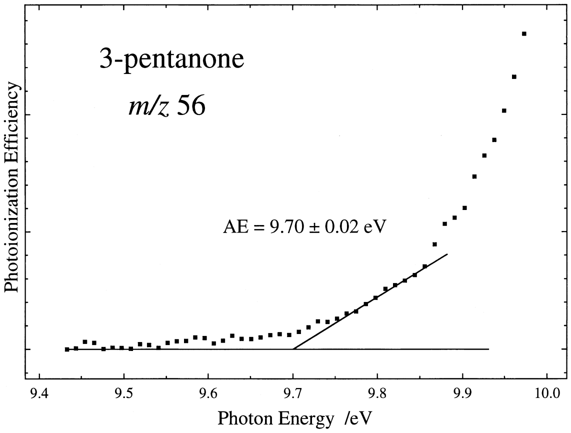

Fig. 4. Threshold PIE curve for *m/z* 56 fragment ions produced from 3-pentanone.

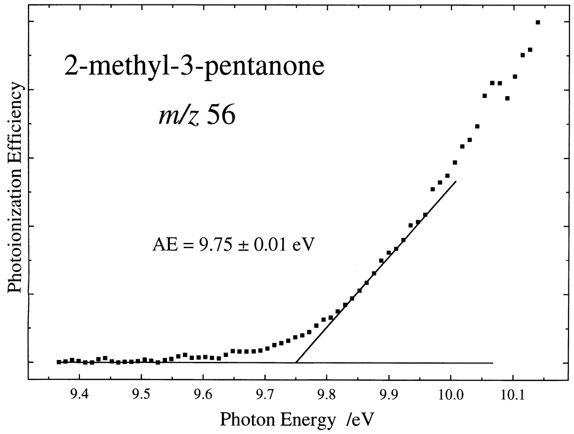

Fig. 5. Threshold PIE curve for *m/z* 56 fragment ions produced from 2-methyl-3-pentanone.

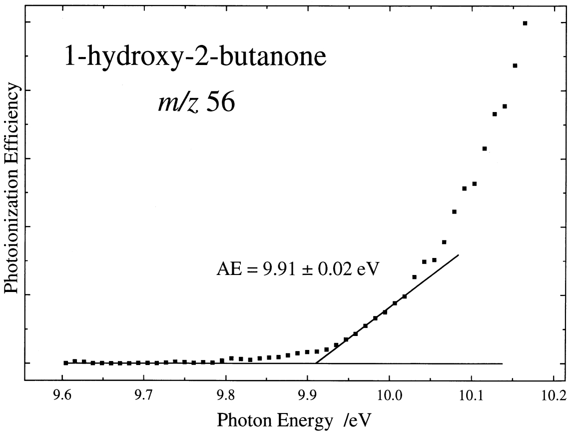

Fig. 6. Threshold PIE curve for *m/z* 56 fragment ions produced from 1-hydroxy-2-butanone.

783.2 ± 3.1, and 783.5 ± 2.5 kJ mol^{-1}, giving an average value of 783.5 ± 0.3 kJ mol^{-1} for $\Delta H_f(\mathbf{2}^{+\cdot})$. This is ~12 kJ mol^{-1} lower than the theoretical values of 795 [2] and 797 kJ mol^{-1} [1], but 24 kJ mol^{-1} higher than the GIANT value of 759 kJ mol^{-1} [3]. It is also significantly higher than the recent value of 765 ± 5 kJ mol^{-1} obtained by Holmes and co-workers [4]. However, their result was based on a single EI measurement of the *m/z* 56 AE for 1-hydroxy-2-butanone (9.88 ± 0.05 eV), where no experimental neutral heat of formation is available. The photoionization AE was measured here to be 9.91 ± 0.02 eV (Fig. 6) which, by using Eq. (1) and data from Table 1, results in $\Delta H_f(\mathbf{2}^{+\cdot}) = 789.6 \pm 4.2$ kJ mol^{-1}. This is slightly higher than the value derived from the other three ketone precursors, although it should be noted that the AE is identical to that for the *m/z* 57 ion and could therefore be subject to a competitive shift, i.e. the thermochemical AE could be lower.

The experimental adiabatic IE of 8.95 ± 0.01 eV [3] ($IE_{298} = 864.3 \pm 1.0$ kJ mol^{-1}), when combined with $\Delta H_f(\mathbf{2}^{+\cdot}) = 783.5 \pm 0.3$ kJ mol^{-1}, results in $\Delta H_f(\mathbf{2}) = -80.9 \pm 1.3$ kJ mol^{-1}, which is also between the theoretical values of −68 [1] and −69 kJ mol^{-1} [2], and both the GIANT value of −105 kJ mol^{-1} [3] and the Holmes and co-workers value of −95 ± 5 kJ mol^{-1} [4]. The ab initio calculations produced ionization energies ranging from 8.87 [2] to 8.93 eV [1] depending on the level of theory used.

The AE for production of ionized phenol and neutral methylketene from phenyl propionate was measured to be 9.65 ± 0.02 eV (Fig. 7), which corresponds to $\Delta H_f(\mathbf{2}) = -66.9 \pm 4.7$ kJ mol^{-1}, in excellent agreement with theory. Although an appearance energy can only represent a thermochemical upper limit, the small kinetic energy release of 9 meV [4] and the absence of any significant competing lower energy pathway suggests that there will be little, if any, excess energy involved in the threshold fragmentation process. This value, when combined

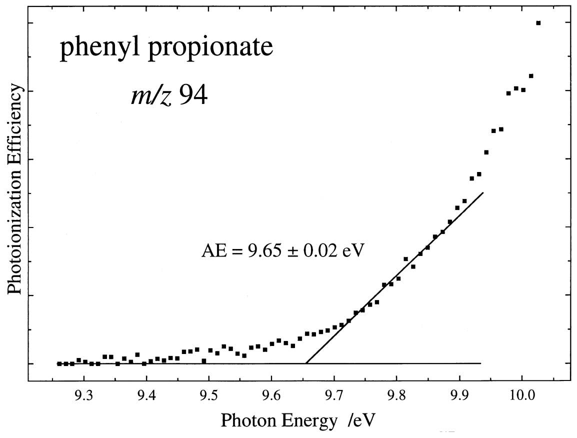

Fig. 7. Threshold PIE curve for *m/z* 94 fragment ions produced from phenyl propionate.

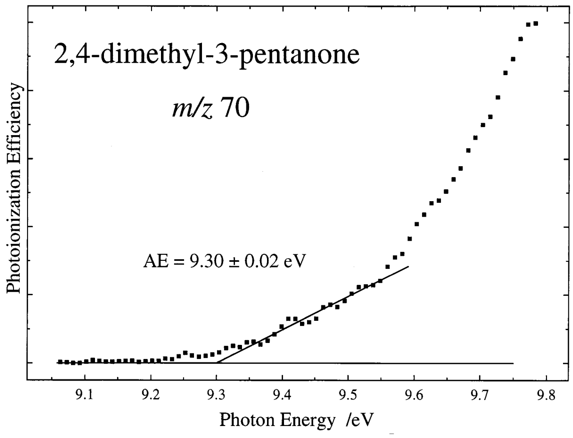

Fig. 8. Threshold PIE curve for *m/z* 70 fragment ions produced from 2,4-dimethyl-3-pentanone.

with $\Delta H_f(\mathbf{2}^{+\cdot}) = 783.5 \pm 0.3$ kJ mol^{-1}, results in $\mathrm{IE}_{298} = 850.3 \pm 5.0$ kJ mol^{-1}, which corresponds to an adiabatic value of 8.80 ± 0.05 eV, significantly lower than the experimental IE of 8.95 eV [3]. However, a close examination of the published photoelectron spectrum for methylketene [20] and the accompanying rare gas calibration peaks reveals that the energy assigned to the adiabatic transition may be too high by as much as 0.15 eV. Unfortunately this does not resolve the discrepancy with the theoretical calculations for $\Delta H_f(\mathbf{2}^{+\cdot})$.

Bouchoux and Salpin [18] have experimentally measured the PA for methylketene using a thermokinetic technique. Their value of 842 ± 3 kJ mol^{-1} is significantly higher than the recent evaluated value of 834.1 kJ mol^{-1} [19]. It is however in close agreement with a high-level ab initio calculation of 843 kJ mol^{-1} [2]. In this theoretical study, Nguyen and Nguyen [2] proposed that the experimental heat of formation for the propanoyl cation of 591.2 ± 2.3 kJ mol^{-1} [21] was too low and, from their calculations, recommended a value of 618 kJ mol^{-1}. If the theoretical value is combined with the present heat of formation for methylketene, a PA of 845.2 ± 4.7 kJ mol^{-1} is derived, in good agreement with both of the above results. The apparent discrepancy of ~30 kJ mol^{-1} for $\Delta H_f(\mathrm{C_2H_5CO^+})$ is currently under investigation in our laboratory.

The combined 298 K heats of formation for neutral and ionized methylketene give a value of 716.5 ± 5.0 kJ mol^{-1}, in good agreement with the two theoretical values of 729 [1] and 726 kJ mol^{-1} [2] but significantly higher than either the GIANT value of 654 kJ mol^{-1} [3] or the Holmes and co-workers value of 670 ± 10 kJ mol^{-1} [4].

3.3. Dimethylketene (3) and dimethylketene radical cation ($\mathbf{3}^{+\cdot}$)

The AE for $\mathbf{3}^{+\cdot}$ from 2,4-dimethyl-3-pentanone was measured to be 9.30 ± 0.02 eV (Fig. 8), which gives a value of 719.3 ± 3.6 kJ mol^{-1} for $\Delta H_f(\mathbf{3}^{+\cdot})$. This is in good agreement with the theoretical results of 726 [1] and 723 kJ mol^{-1} [2] but is substantially higher than the GIANT value of 681 kJ mol^{-1} [3] and the Holmes and co-workers value of 683 ± 5 kJ mol^{-1} [4]. Combination of the present value with the experimental adiabatic IE of 8.45 ± 0.01 eV ($\mathrm{IE}_{298} = 816.7 \pm 1.0$ kJ mol^{-1}) for **3** [3] leads to $\Delta H_f(\mathbf{3}) = -97.4 \pm 4.6$ kJ mol^{-1}. As expected, this is close to the theoretical values of −92 kJ mol^{-1} [1] and from −89 to −86 kJ mol^{-1} [2] but considerably higher than either the GIANT value of −134 kJ mol^{-1} [3] or the Holmes and co-workers value of −137 ± 5 kJ mol^{-1} [4].

The formation of ionized phenol and neutral dim-

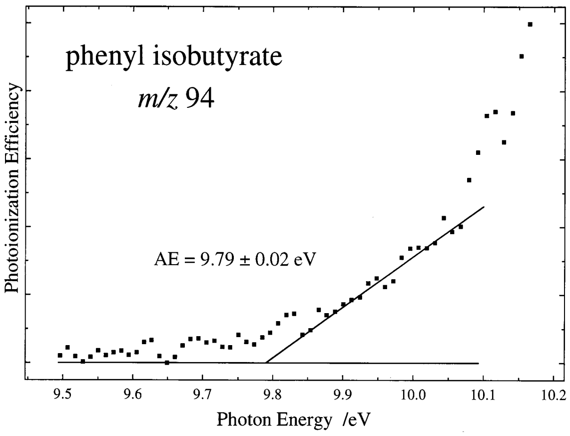

Fig. 9. Threshold PIE curve for *m/z* 94 fragment ions produced from phenyl isobutyrate.

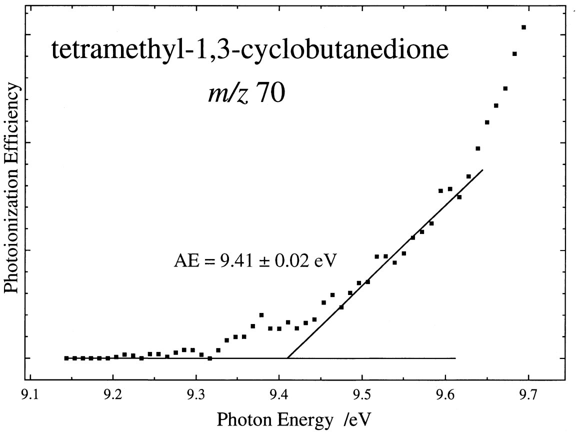

Fig. 10. Threshold PIE curve for *m/z* 70 fragment ions produced from tetramethyl-1,3-cyclobutanedione.

ethylketene is not the lowest energy fragmentation process observed in the photoionization mass spectrum of phenyl isobutyrate. Production of both *m/z* 70 and 71 was found to occur at energies approximately 0.2 eV lower. Thus, it is possible that the *m/z* 94 AE, measured here to be 9.79 ± 0.02 eV (Fig. 9), will be subject to some competitive shift, although the relatively small translational energy release of 18 meV [4] suggests that any kinetic shift will again be small. Despite the AE necessarily representing an upper limit, it is unlikely that the thermochemical value will be significantly lower. Using this AE, the calculated 298 K heat of formation for **3** is ≤ -83.6 kJ mol^{-1}, which is only 2–8 kJ mol^{-1} higher than that obtained by theoretical calculations [1,2]. In order to obtain agreement with the other available experimental data [3,4] the products would be required to have ~50 kJ mol^{-1} of excess energy.

Ionization of tetramethyl-1,3-cyclobutanedione produces the dimethylketene cation, together with neutral dimethylketene [4]. Although the AE for the *m/z* 84 fragment ion is 0.1 eV lower, this fragmentation process is rapidly replaced as the major fragmentation pathway at energies above the AE for $\mathbf{3}^{+\cdot}$. Using the $C_4H_6O^{+\cdot}$ appearance energy of 9.41 ± 0.02 eV measured here (Fig. 10), together with the above value of 719.3 ± 3.6 kJ mol^{-1} for $\Delta H_f(\mathbf{3}^{+\cdot})$, results in $\Delta H_f(\mathbf{3}) \leq -86.4$ kJ mol^{-1}, which again supports the ab initio calculations. In addition, the *m/z* 86 AE directly gives a combined 298 K heat of formation for neutral methylketene plus ionized methylketene of 632.9 ± 3.4 kJ mol^{-1}, in excellent agreement with the theoretical values of 634 kJ mol^{-1} [1] and 634–637 kJ mol^{-1} [2] but significantly higher than both the GIANT value of 547 kJ mol^{-1} [3] and the Holmes and co-workers value of 546 ± 10 kJ mol^{-1} [4].

4. Conclusion

From appearance energy measurements using threshold photoionization mass spectrometry, 298 K heats of formation have been obtained for ionized ketene (874.4 ± 1.0 kJ mol^{-1}), methylketene (783.5 ± 0.3 kJ mol^{-1}), and dimethylketene (719.3 ± 3.6 kJ mol^{-1}). Corresponding neutral heats of formation of -53.6 ± 0.6, -66.9 ± 4.7, and ≤ -86.4 kJ mol^{-1}, respectively, have also been determined. Apart from the value for the methylketene cation, these are all in excellent agreement with high level ab initio calculations. Evidence has been presented which suggests that the experimental adiabatic IE for methylketene could be up to 0.15 eV too high.

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