Absolute Proton Affinity for Acetaldehyde

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Dissociative photoionization mass spectrometry has been used to measure appearance energies for the 1-hydroxyethyl cation ($CH_3CH{=}OH^+$) formed from ethanol and 2-propanol. Molecular orbital calculations for these two unimolecular fragmentation reactions suggest that only methyl loss from ionized 2-propanol does not involve excess energy at the threshold. The experimental appearance energy of 10.31 ± 0.01 eV for this latter process results in a 298 K heat of formation of 593.1 ± 1.2 kJ mol^{-1} for $CH_3CH{=}OH^+$ and a corresponding absolute proton affinity for acetaldehyde of 770.9 ± 1.3 kJ mol^{-1}. This value is supported by both high-level ab initio calculations and a proposed upward revision of the absolute isobutene proton affinity to 803.3 ± 0.9 kJ mol^{-1}. A 298 K heat of formation of 52.2 ± 1.9 kJ mol^{-1} is derived for the *tert*-butyl radical.

Introduction

The absolute proton affinity (PA) for acetaldehyde is one of a series of values used to anchor extensive compilations of interlocking PA ladders.[1−4] Like most of the reference values, it has been based on a photoionization (PI) appearance energy (AE) measurement substantiated by high-level ab initio calculations. In this case the threshold process used was H loss from ionized ethanol, from which Ruscic and Berkowitz had derived a 298 K heat of formation of ≤595.4 ± 0.4 kJ mol^{-1} for the $CH_3CH{=}OH^+$ cation.[5] On the assumption that there should be negligible excess energy associated with the AE, as a result of the fragmentation being the lowest-energy process and involving a simple bond cleavage, Hunter and Lias derived a 298 K PA for acetaldehyde of 768.5 ± 1.6 kJ mol^{-1}, which was then used as the selected reference value in their compilation.[1] This was supported by the corresponding PA of 770.2 kJ mol^{-1} calculated by Smith and Radom.[6]

Although it is likely that the above cationic heat of formation is close to the true thermochemical value, ab initio calculations suggest that there may be a small reverse activation energy involved in the loss of H from ionized ethanol, in which case any derived PA for acetaldehyde will be too low. The aim of the present study was to use dissociative photoionization mass spectrometry to investigate the thermochemistry associated with the formation of $CH_3CH{=}OH^+$ from several different alcohols, including ethanol, and to firmly establish the absolute proton affinity for acetaldehyde.

Experimental Section

The photoionization mass spectrometer (PIMS) used in this work has been described in detail previously.[7−9] Briefly, vacuum UV photons produced in a 1.5 kPa hydrogen gas discharge were energy-selected with a windowless 1 m Seya-Namioka monochromator. The resolution of the monochromator was fixed at 0.135 nm full width at half-maximum, and the photon energy scale was calibrated internally with known reference emission lines,[10] resulting in an absolute accuracy of better than 0.001 eV. All compounds were research grade commercial samples used without further purification. Experiments were conducted at ambient temperature (296 K), with typical sample pressures of 10^{-3} Pa in the ion-source region.

Apart from ethanol, analytical corrections were made to all *m/z* 45 threshold photoionization efficiency (PIE) curves to remove any ^{13}C contribution from a competing lower-energy *m/z* 44 fragmentation process. Linear extrapolations were used to obtain the 298 K AEs.[11] The prethreshold hot-band structure observed at energies below each assigned AE_{298} was consistent with that expected for thermal excitation of the neutral precursor. Standard deviations associated with the linear least-square fits used for the extrapolations and reproducibilities for repeat measurements were 0.005 eV or better. However, more conservative uncertainties have been assigned to each AE_{298} to compensate for errors in the absolute energy scale and any small variations introduced by the set of data points used for the actual fitting procedure.

All ab initio calculations were performed using the Gaussian 03 suite of programs[12] and carried out using either a dual 2.5 GHz PowerPC G5 Macintosh desktop computer or the Australian Partnership for Advanced Computing (APAC) supercomputer facility. Several different composite methods were used to calculate 0 K energies, including G2, G2(MP2), G3, G3 with B3LYP/6-31G* optimized geometries (G3B3), CBS-APNO, and W1U (Table S1). Unless specified otherwise, calculated thermochemical data, including $H°_{298} - H°_0$ values, were obtained from the G3 calculations. Transition states were characterized by a single imaginary vibrational frequency that corresponded to stretching of a C−X bond, the cleavage of which would result in the formation of the $CH_3CH{=}OH^+$ cation. RRKM rate constant calculations were carried out using a locally developed Macintosh program based on the Beyer−Swinehart algorithm.[13] Because the ion-source residence time for $CH_3CH{=}OH^+$ is in excess of several microseconds, there will be no kinetic shift associated with any unimolecular reaction that has a threshold rate constant $>10^6$ s^{-1}.[14]

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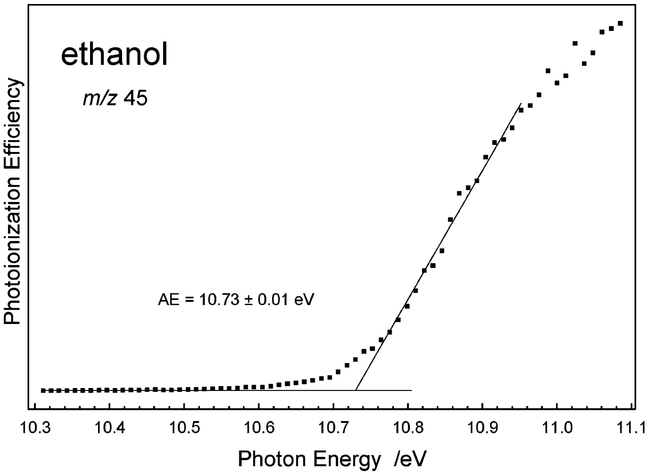

Figure 1. Threshold PIE curve for H loss from ethanol.

Results and Discussion

The derivation of absolute PAs from ionization threshold experiments involves the determination of heats of formation for protonated molecules.[1] There are several ways of obtaining reliable values for these from PIE curves, although they all require some allowance for hot-band structure as a consequence of the precursor thermal energy.[15] In addition, they also depend on the absence of any reverse activation energy associated with the fragmentation process.[14]

An early technique involved the measurement of PIE curves at several different temperatures followed by an extrapolation of the AEs to 0 K.[16,17] However, this has a limited application because of sample condensation at low temperatures and possible thermal decomposition and pyrolysis effects if high temperatures are used. Furthermore, extrapolations over large temperature ranges may lead to errors.[18] Alternatively, the effect of hot bands can be substantially reduced if a supersonic molecular beam is used for the sample introduction, resulting in effective temperatures of <50 K,[19] although it is not always possible to know the actual cooling achieved by the expansion process.[20]

The method used by Ruscic and Berkowitz[5] in their ethanol study is based on the generation of an arbitrary kernel function convoluted with a calculated thermal energy distribution to give a best fit to the experimental room-temperature PIE data.[21] This produces a 0 K AE, or enthalpy of reaction, from which it is possible to derive a 0 K cationic heat of formation that can then be modified to give a corresponding 298 K value.

An alternative approach[11] that we have used in previous PI experiments[22] is to obtain a 298 K AE from a linear threshold extrapolation. For the gas-phase reaction

$$\mathrm{CH_3CHROH} + h\nu \rightarrow \mathrm{CH_3CH{=}OH^+} + \mathrm{R^\bullet} + \mathrm{e^-} \quad (1)$$

AE_{298} is converted directly to a 298 K reaction enthalpy, and hence a 298 K cationic heat of formation, using the expression

$$\Delta H^\circ_{\mathrm{f},298}(\mathrm{CH_3CH{=}OH^+}) = \mathrm{AE}_{298} + \Delta H^\circ_{\mathrm{f},298}(\mathrm{CH_3CHROH}) - \Delta H^\circ_{\mathrm{f},298}(\mathrm{R^\bullet}) + \Delta H_{\mathrm{cor}} \quad (2)$$

where ΔH_{cor} is a thermal enthalpy correction, given by

$$\Delta H_{\mathrm{cor}} = \{H^\circ_{298} - H^\circ_0\}(\mathrm{CH_3CH{=}OH^+}) + \{H^\circ_{298} - H^\circ_0\}(\mathrm{R^\bullet}) - 6.2\ \mathrm{kJ\ mol^{-1}} \quad (3)$$

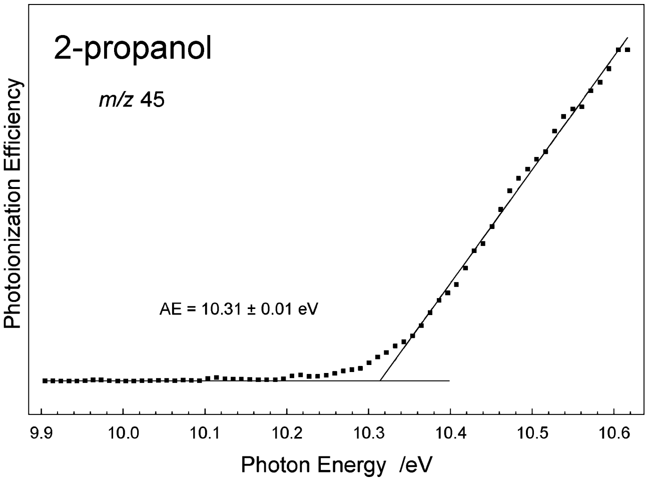

Figure 2. Threshold PIE curve for $\mathrm{CH_3}$ loss from 2-propanol. The data have been corrected for the ^{13}C contribution from the lower-energy $\mathrm{CH_4}$-loss fragmentation process.

It should be noted that the cationic heat of formation in eq 2 is based on the stationary electron (ion) convention.[11,23] For comparative purposes, a 298 K AE can be converted to the equivalent 0 K AE using the relationship

$$\mathrm{AE}_0 = \mathrm{AE}_{298} + \{H^\circ_{298} - H^\circ_0\}(\mathrm{CH_3CHROH}) - 6.2\ \mathrm{kJ\ mol^{-1}} \quad (4)$$

Ethanol. Figure 1 shows the *m*/*z* 45 threshold PIE curve for ethanol. The 298 K AE of 10.73 ± 0.01 eV converts to a 0 K value of 10.81 ± 0.01 eV using eq 4. This is slightly higher than the 10.78 ± 0.02 eV value obtained by Refaey and Chupka[24] and the 10.80 ± 0.05 eV measurement of Potapov and Sorokin,[25] cited in the NIST Chemistry WebBook,[2] but is in exact agreement with both the Ruscic and Berkowitz[5] analysis of photoelectron−photoion coincidence (PEPICO) data reported by Brehm et al.[26] and an unpublished PI measurement of Klemm and co-workers,[27] cited in the Hunter and Lias PA compendium.[1] It is also within experimental error of the Ruscic and Berkowitz value of 10.801 ± 0.005 eV.[5]

RRKM calculations show that H loss from ionized ethanol is a very fast process (Figure S5), so the AE will not be affected by any kinetic shift.[14] Furthermore, as it is the lowest-energy fragmentation process, there will also be no competitive effect on the PIE curve.[14] However, our ab initio calculations indicate that there is a small reverse activation energy barrier associated with this particular unimolecular decomposition. The G3, G2, and G3B3 0 K results of 13.1, 16.7, and 8.0 kJ mol^{-1}, respectively, imply that the above experimental AEs involve some excess energy, in which case any derived cationic heat of formation can only be an upper limit to the true thermochemical value, as correctly indicated by Ruscic and Berkowitz in their data analysis.[5]

2-Propanol. The threshold PIE curve for $\mathrm{CH_3CH{=}OH^+}$ formed from 2-propanol is shown in Figure 2. Unlike ethanol, this is not the lowest-energy process observed, with methane loss having a lower AE_{298} of 10.22 eV (Figure S1). H loss also occurs at lower energies but is only a very minor process.[28] The relative first differential PIE curves for these three fragmentation processes (Figure 2, ref 28) show that as soon as methyl loss becomes energetically feasible it very rapidly becomes the dominant process, indicating that there should be no competitive shift associated with the *m*/*z* 45 AE. In addition,

TABLE 1: Thermochemistry for the Gas-Phase Reaction $CH_3CHROH + h\nu \rightarrow CH_3CH{=}OH^+ + R^\bullet$

			$\Delta H°_{f,298}$ (kJ mol^{-1})		
R	AE_{298} (eV)	ΔH_{cor}[a] (kJ mol^{-1})	CH_3CHROH[b]	R[c]	$CH_3CH{=}OH^+$ [d]
H	10.73 ± 0.01	13.4 ± 0.1	−235.2 ± 0.3	218.0 ± 0.0	595.5 ± 1.1
CH_3	10.31 ± 0.01	17.6 ± 0.1	−272.6 ± 0.5	146.7 ± 0.3	593.1 ± 1.2

[a] Calculated using eq 3. The $H°_{298} - H°_0$ values used for H, CH_3, and $CH_3CH{=}OH^+$ were 6.2,[32] 10.4,[32] and 13.4 kJ mol^{-1}, respectively. [b] Reference 31. [c] Reference 38. [d] Calculated using eq 2.

TABLE 2: Composite Ab Initio[a] 298 K Proton Affinities (kJ mol^{-1})

	G2 (MP2)	G2	G3	G3B3	CBS-APNO	W1U	average	experimental[b]
CH_3CHO	770.6	770.0	771.7	771.1	770.2	772.1	770.9 ± 0.8	770.9 ± 1.3
iso-C_4H_8	802.9	804.1	803.5	803.1	803.8	804.7	803.7 ± 0.7	803.3 ± 0.9

[a] Calculated using the Gaussian 03 suite of programs. [b] This work.

there should be no kinetic shift as RRKM calculations show that methyl loss from ionized 2-propanol is a fast process on the mass spectrometer time scale (Figure S6). Because of the lower-energy loss of methane, there will be a small ^{13}C contribution to the *m*/*z* 45 PIE curve that will have an affect on the observed AE. The PIE data in Figure 2 have been corrected for this interference. Transition-state calculations indicate the absence of any reverse activation energy associated with the formation of $CH_3CH{=}OH^+$ from 2-propanol.

The AE_{298} of 10.31 ± 0.01 eV, which becomes 10.41 ± 0.01 eV at 0 K, is slightly higher than both the Refaey and Chupka measurement of 10.40 eV[24] and the Potapov and Sorokin PI value of 10.40 ± 0.03 eV[25] but is significantly higher than that obtained by Wei et al.[29] in their recent PI study using synchrotron radiation (10.26 ± 0.02 eV). Although these latter workers used a molecular beam for their sample introduction, which should remove ∼80% of the internal energy for 2-propanol,[20] it is not clear how the actual AE was obtained as no experimental PIE curve is available. Wei et al. do mention however that their AEs were "determined by the onsets in each PIE curve". Given that, even with a molecular beam, there will still be some thermal energy associated with the 2-propanol molecules, the use of any vanishing current method with such threshold data must inevitably produce an AE lower than the true 0 K value. It is not unexpected that the present AE is higher than all previous PI experiments as none have reported making any ^{13}C correction to their PIE data. In support of the present result, the calculated AE_0 is just 0.02 eV higher at 10.43 eV.

2-Butanol, 2-Pentanol, and 3-Methyl-2-butanol. Although both ethanol and 2-propanol produce well-defined AEs for $CH_3CH{=}OH^+$ formation, this is not the case for the three larger alcohols studied here. All three PIE curves show no distinct linear region that could be used to provide a reliable AE_{298} (Figures S2−S4). For 2-butanol, RRKM calculations indicate that the dissociation process involving ethyl loss is sufficiently fast to have no kinetic shift effect (Figure S7). There is also no calculated reverse activation energy. However, in addition to competition from the associated *m*/*z* 44 alkane loss observed for 2-propanol, there are methyl and methane losses that also have lower AEs.[28] Unlike 2-propanol, there is a significant competitive effect from these latter two processes, resulting in a curved threshold region for the PIE curve. A similar effect is also observed for 2-pentanol and 3-methyl-2-butanol, with the former system having an additional competing lower-energy fragmentation corresponding to loss of H_2O.[30] There is no calculated reverse activation energy barrier for $CH_3CH{=}OH^+$ formation from these two precursors, but RRKM calculations do indicate that both PIE curves will almost certainly be subject to some kinetic shift effect as a result of the relatively slow unimolecular reactions (Figures S8 and S9).

Thermochemistry. The thermochemistry associated with the formation of $CH_3CH{=}OH^+$ from ethanol and 2-propanol is summarized in Table 1. As expected, the heat of formation for $CH_3CH{=}OH^+$ derived from the ethanol AE is slightly higher than the 2-propanol result, albeit within experimental error, reflecting the small reverse activation energy predicted by theory. Combining the lower cationic heat of formation of 593.1 ± 1.2 kJ mol^{-1} with $\Delta H_{f,298}(CH_3CHO) = -166.1 \pm 0.5$ kJ mol^{-1} [31] and $\Delta H_{f,298}(H^+) = 1530.05 \pm 0.04$ kJ mol^{-1} [32] results in an absolute PA for acetaldehyde of 770.9 ± 1.3 kJ mol^{-1}, which is in excellent agreement with the ab initio calculations given in Table 2.

Mautner[4] has shown that the relative PA measurements of Sieck[3] from pulsed high-pressure mass spectrometry experiments are in good accord with the evaluated data of the Hunter and Lias compilation.[1] Because the PA for isobutene was used as an anchor point in Mautner's analysis of the Sieck data, it is possible that this important reference value may also require a small upward revision. The Hunter and Lias recommended value of 802.1 ± 1.4 kJ mol^{-1} was based on a 298 K heat of formation for the *tert*-butyl cation obtained from a PEPICO measurement for *tert*-butyl iodide[33] and a threshold PIE for isobutene.[34] A subsequent evaluation,[14] which also considered the *tert*-$C_4H_9^+$ AE from neopentane, produced a slightly higher value of 711.5 ± 0.2 kJ mol^{-1} for the cationic heat of formation and a correspondingly lower PA for isobutene of 801.7 ± 0.9 kJ mol^{-1}. However, all of these determinations used a value of 19.5 kJ mol^{-1} for $(H°_{298} - H°_0)$ *tert*-$C_4H_9^+$ that was obtained from HF/6-31G* calculations in which the harmonic oscillator approximation was used.[6] Radom and co-workers[35] subsequently showed that a free rotor model should instead be used for *tert*-$C_4H_9^+$, which reduces its calculated $H°_{298} - H°_0$ value to 17.9 kJ mol^{-1}. Use of this thermal correction would result in a decreased value of 709.9 ± 0.2 kJ mol^{-1} for $\Delta H_{f,298}$(*tert*-$C_4H_9^+$) and a corresponding increased PA for isobutene of 803.3 ± 0.9 kJ mol^{-1}, in accord with the proposed small upward revision to the acetaldehyde PA. Again, this experimental PA is supported by a range of high-level composite ab initio calculations (Table 2).[36]

The revised heat of formation for the *tert*-butyl cation also may be used to provide an estimate of the *tert*-butyl radical heat of formation. This does however require the use of a reliable adiabatic ionization energy for the radical. Although several photoelectron spectroscopic determinations of this quantity have been made,[2] there is good evidence that they are too low,[14,36] presumably as a result of hot-band complications associated with the thermally generated radicals. An unpublished PI measurement of 6.82 ± 0.02 eV was obtained recently by Klemm et al.[37] This value, which corresponded to the first clearly defined peak in the first differential PIE curve, involved the production of *tert*-butyl radicals in a flow tube via a reaction of F atoms with either isobutene or *tert*-butyl iodide rather than via a pyrolytic decomposition process. It is in excellent agreement with that obtained from corresponding ab initio calculations (6.81 ± 0.06 eV).[36] The Klemm et al. experimental adiabatic ionization energy becomes 657.7 ± 1.9 kJ mol^{-1} at 298 K, using $H°_{298} - H°_0$ values of 17.9 and 17.6 kJ mol^{-1} for the radical and cation, respectively.[36] This, when combined with the above revised cationic heat of formation, results in a 298 K heat of formation for the *tert*-butyl radical of 52.2 ± 1.9 kJ mol^{-1}. A recent International Union of Pure and Applied Chemistry critical evaluation of thermochemical properties of selected radicals[38] lists a number of measurements, ranging from 36.4 ± 4.2 to 51.8 ± 1.3 kJ mol^{-1}. The highest value, which is based on a kinetic study by Seetula and Slagle,[39] although slightly lower than that calculated using a variety of high-level theoretical procedures (57 ± 7 kJ mol^{-1}),[36] provides good support for the presently derived value.

Conclusions

Threshold PIE curves have been measured for $CH_3CH{=}OH^+$ formed from five alcohols. Because of competitive and kinetic effects, it only has been possible to obtain reliable AEs for ethanol and 2-propanol. Molecular orbital calculations for the unimolecular reactions associated with these two precursors suggest that only methyl loss from ionized 2-propanol does not involve excess energy at threshold. A 298 K heat of formation for $CH_3CH{=}OH^+$ of 593.1 ± 1.2 kJ mol^{-1} has been derived from the AE_{298} (10.31 ± 0.01 eV) for this latter process, leading to an absolute proton affinity for acetaldehyde of 770.9 ± 1.3 kJ mol^{-1}. This value is supported by both high-level ab initio calculations and a proposed upward revision of the absolute isobutene proton affinity to 803.3 ± 0.9 kJ mol^{-1}. The corresponding *tert*-butyl cation heat of formation (709.9 ± 0.2 kJ mol^{-1}), when combined with an experimental adiabatic ionization energy obtained by PIMS (6.82 ± 0.02 eV),[37] results in a 298 K heat of formation of 52.2 ± 1.9 kJ mol^{-1} for the *tert*-butyl radical.

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Supporting Information Available: Threshold PIE curves for *m*/*z* 44 cations formed from 2-propanol and *m*/*z* 45 cations formed from 2-butanol, 2-pentanol, and 3-methyl-2-butanol (Figures S1−S4), RRKM curves (Figures S5−S9), and 0 K energies (Table S1) obtained with G3, G2, G2(MP2), G3B3, CBS-APNO, and W1U methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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