Heat of Formation for the $CH_3CH{=}NH_2^+$ Cation by Photoionization Mass Spectrometry†

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The *m/z* 44 appearance energies for five primary amines have been measured by threshold photoionization mass spectrometry. Following an analysis of the thermochemistry associated with these unimolecular fragmentations, a value of 665.1 ± 1.4 kJ mol^{-1} is obtained for the 298 K heat of formation for the ethylidenimmonium cation ($CH_3CH{=}NH_2^+$). When combined with high-level ab initio calculations, this results in absolute proton affinities of 906.4 ± 2.7 and 909.2 ± 2.8 kJ mol^{-1} for the ethylidenimines *E*-$CH_3CH{=}NH$ and *Z*-$CH_3CH{=}NH$, respectively.

Introduction

In a previous study[1] the technique of threshold photoionization (PI) mass spectrometry was used to determine the heat of formation for the methylenimmonium cation ($CH_2{=}NH_2^+$). This resulted in a proton affinity (PA) for methylenimine ($CH_2{=}NH$) of 868.8 ± 2.5 kJ mol^{-1}, significantly increasing the range of experimental primary reference standards used as anchor points for relative PA measurements.[2,3] The present study aims to further extend this scale by measuring the heat of formation for the ethylidenimmonium cation ($CH_3CH{=}NH_2^+$) and thus derive an absolute PA for ethylidenimine ($CH_3CH{=}NH$).

The NIST recommended heat of formation for the ethylidenimmonium cation is 657 kJ mol^{-1},[3] which is based on a study of alkyl immonium cations by Lossing et al.[4] These workers used an electron monochromator to measure $CH_3CH{=}NH_2^+$ appearance energies (AEs) for four primary amines. Although their AE for H loss from ethylamine agreed well with an earlier quasi-monoenergetic electron ionization (EI) measurement,[5] there was a significant discrepancy associated with the corresponding AE for CH_3 loss from isopropylamine. No similar photoionization studies of the $CH_3CH{=}NH_2^+$ cation appear to have been made.[3]

There have been several experimental determinations of the PA for ethylidenimine. Ellenberger et al.[6] used ion cyclotron resonance (ICR) spectroscopy to study proton-transfer reactions between a range of bases and the $CH_3CH{=}NH_2^+$ ion, formed via methyl loss following EI of isopropylamine. From these bracketing experiments they were able to establish a PA of 892 ± 8 kJ mol^{-1} relative to ammonia, for which a PA of 851.9 kJ mol^{-1} was assumed.[7] The large error associated with their measurement was mainly due to the uncertainty surrounding the absolute PA for the ammonia reference that they used.

In a subsequent related ICR study, Peerboom et al.[8] obtained a value of 897 ± 5 kJ mol^{-1} for the ethylidenimine PA. This was also based on the PA of ammonia but instead used a critically assessed value of 853.5 kJ mol^{-1}.[9] Employing this reference, Peerboom et al. reevaluated the earlier Ellenberger et al. data to give a PA of 895 ± 8 kJ mol^{-1}, in excellent agreement with their own measurement.

Over the past decade there have been numerous adjustments made to the PAs of the various bases employed in both of these studies.[2,3] In some cases they have been quite substantial. If these latest values are applied to the bracketing measurements of Ellenberger et al.[6] and Peerboom et al.[8] the resultant PAs become 899 ± 3 kJ mol^{-1} and 897 ± 12 kJ mol^{-1}, respectively. In the first case the $CH_3CH{=}NH$ gas-phase basicity (GB) is found to lie between those of methylamine (GB = 864.5 kJ mol^{-1}) and 2-chloropyridine (GB = 869.0 kJ mol^{-1}). The larger uncertainty associated with the latter result is a consequence of using only two reference bases, hexane-2,5-dione (GB = 851.8 kJ mol^{-1}) and allylamine (GB = 875.5 kJ mol^{-1}), for the proton-transfer reactions. The Hunter and Lias[2] recommended PA for $CH_3CH{=}NH$ is 885.1 kJ mol^{-1} and uses a GB of 852.6 kJ mol^{-1} derived from the Ellenberger et al.[6] experiments. However, this significantly lower value is due to their use of a correspondingly low value for the GB of the reference base 3-aminotoluene (836 kJ mol^{-1}), the origin of which is unclear.

High-level ab initio calculations are now capable of providing accurate thermochemical information for gas-phase species. In many instances the theoretical measurements are considered to be more reliable than their experimental counterparts. For example, the Hunter and Lias[2] recommended PA for ammonia of 853.6 kJ mol^{-1} is largely based on an ab initio calculation by Smith and Radom.[10] Hammerum and Sølling[11] have carried out an extensive theoretical study of the proton affinities of imines and the corresponding imine and immonium cation heats of formation using a range of composite ab initio methods. Although there is no experimental imine thermochemical data available for comparison, several immonium cation heats of formation have been obtained from EI appearance energy measurements, primarily the experiments of Lossing et al.[4] Unfortunately the agreement between theory and experiment is mixed. Hammerum and Sølling recognized that part of the problem might have been due to the neglect of an internal thermal energy correction in converting the AEs to 298 K cationic heats of formation.[12] By taking this into account they were able to achieve an improved agreement for several ions. However, it is not clear that such an adjustment to EI data is warranted.[13]

Experimental Section

The photoionization mass spectrometer used in this work has been described in detail previously.[14−16] Briefly, the photon source used was the hydrogen pseudocontinuum, with known

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TABLE 1: Calculated[a] $H°_{298} - H°_0$ Values (kJ mol^{-1})

species	$H°_{298} - H°_0$
H	6.2[b]
CH_3	10.4[b]
C_2H_5	13.0
n-C_3H_7	15.6
i-C_3H_7	16.0
$CH_3CHNH_2^+$	13.5
$CH_3CH_2NH_2$	14.2
$CH_3CH(CH_3)NH_2$	17.4
$C_2H_5CH(CH_3)NH_2$	21.0
n-$C_3H_7CH(CH_3)NH_2$	24.6
i-$C_3H_7CH(CH_3)NH_2$	24.4

[a] From Gaussian HF/6-31G* calculations with vibrational frequencies scaled by 0.8929. [b] Reference 21.

reference emission lines[17] used to internally calibrate the absolute photon energy scale to better than 0.001 eV. Resolution of the Seya-Namioka monochromator remained fixed at 0.135 nm. The m/z 44 photoion count rates in the threshold region varied with each precursor compound, ranging from approximately 0.2 s^{-1} for ethylamine to 1.3 s^{-1} for isopropylamine. Background ion count rates were typically less than 0.01 s^{-1}.

Appearance energies were obtained from a linear extrapolation of each threshold photoionization efficiency (PIE) curve.[12] In each case the extent of hot band structure associated with the extrapolated AE was consistent with the thermal excitation observed for the corresponding molecular ion. The standard deviations associated with the various linear least-squares fits ranged between 0.003 and 0.005 eV. However, all AEs have been reported with a more conservative error to allow for both the above energy scale calibration errors and any small variations in the extrapolated AE as a result of the actual data points employed in the fitting procedure.

Experiments were conducted at room temperature (296 K) with pressures of 10^{-3} Pa in the ion source. PI mass spectra were recorded using the total light of all wavelengths produced by the hydrogen gas discharge lamp. All compounds were high purity commercial samples used without further purification. In each case sample purity was checked by GCMS analysis. The ethylamine and isopropylamine measurements were obtained using 70% aqueous solutions.

Potential energy surfaces for the various unimolecular reactions were explored using the Gaussian 03 suite of programs.[18] A more detailed discussion of this theoretical work is given elsewhere.[19] Ab initio calculations were performed with several composite methods, including G2, G2(MP2), G3, G3 using B3LYP/6-31G* optimized geometries (G3B3), CBS-APNO, and W1. The thermal energy corrections shown in Table 1 were calculated at the HF/6-31G* level of theory with vibrational frequencies scaled by 0.8929. Transition states were characterized by a single imaginary frequency and their connectivity to the reactants and products confirmed by intrinsic reaction coordinate calculations. RRKM rate constant calculations were carried out using a locally developed Macintosh program based on the Beyer−Swinehart algorithm.[20]

Results and Discussion

The conversion of a photoionization appearance energy to a 298 K reaction enthalpy has been discussed in detail elsewhere.[12] For the gas-phase reaction

$$CH_3CHRNH_2 + h\nu \rightarrow CH_3CHNH_2^+ + R^\bullet + e^- \qquad (1)$$

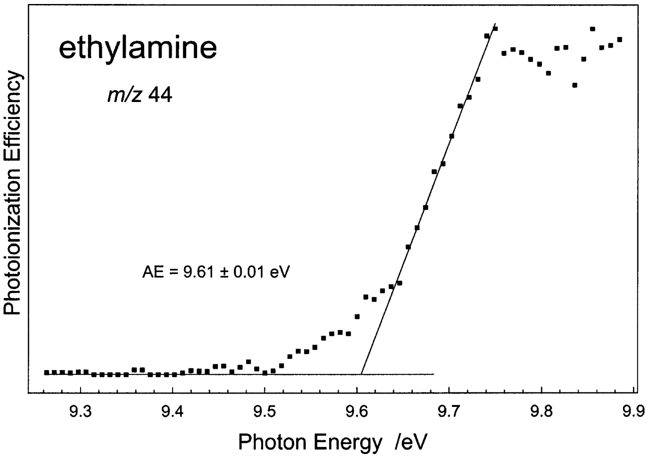

Figure 1. Threshold PIE curve for m/z 44 fragment ions produced from ethylamine.

the 298 K cationic heat of formation, based on the stationary electron (ion) convention,[3,12] is given by

$$\Delta H°_{f,298}(CH_3CHNH_2^+) = AE_{298} + \Delta H°_{f,298}(CH_3CHRNH_2) - \Delta H°_{f,298}(R^\bullet) + \Delta H_{cor} \qquad (2)$$

where AE_{298} is derived from a linear threshold extrapolation of the PIE curve and

$$\Delta H_{cor} = \{H°_{298} - H°_0\}(CH_3CHNH_2^+) + \{H°_{298} - H°_0\}(R^\bullet) - 6.2\ \text{kJ mol}^{-1} \qquad (3)$$

The thermal enthalpy correction term, ΔH_{cor}, can be obtained from statistical mechanical calculations.[21] All data relevant to the present study are listed in Table 1. As discussed previously,[1] the 298 K AEs for eq 1 may be converted to the corresponding AE at 0 K using the expression

$$AE_0 = AE_{298} + \{H°_{298} - H°_0\}(CH_3CHRNH_2) - 6.2\ \text{kJ mol}^{-1} \qquad (4)$$

This facilitates comparison with the 0 K relative energies from ab initio calculations.

RRKM calculations showed formation of the $CH_3CH{=}NH_2^+$ cation from each of the ionized precursors studied here to be sufficiently fast on the mass spectrometer time scale that none of the m/z 44 AE measurements should be prone to a kinetic shift effect.[22] The absence of extended tailing in the threshold regions for all of the PIE curves is consistent with this.

Ethylamine. The threshold photoionization efficiency curve for H loss from ethylamine is shown in Figure 1. This is the lowest energy fragmentation process observed, having a 298 K AE of 9.61 ± 0.01 eV, in exact agreement with the EI value obtained by Solka and Russell.[5] It is however significantly higher than the monoenergtic EI measurement of Lossing et al.[4] that produced a value of 9.55 eV. Four different high-level ab initio calculations using composite methods (G2MP2, G2, G3 and G3B3) give the same 0 K energy difference of 9.62 eV between neutral ethylamine and ($CH_3CH{=}NH_2^+ + H^\bullet$). The present corresponding experimental AE is 0.07 eV higher (Table 2), which suggests the possibility of excess energy associated with this particular fragmentation process at threshold. The presence of a significant reverse activation energy barrier[23] is supported by G3 calculations that find a transition state located 18.0 kJ mol^{-1} higher in energy than the products, indicating

TABLE 2: Composite ab Initio[a] 0 K Appearance Energies (eV) for the Gas-Phase Reaction $CH_3CHRNH_2 + h\nu \rightarrow CH_3CHNH_2^+ + R^\bullet$

CH_3CHRNH_2	G2MP2	G2	G3	G3B3	average	experiment[b]
ethylamine	9.62	9.62	9.62	9.62	9.62	9.69
isopropylamine	9.24	9.23	9.19	9.20	9.22	9.22
2-butylamine	9.23	9.22	9.17	9.17	9.20	9.16
2-pentylamine	9.26	9.25	9.20	9.20	9.23	9.19
1,2-dimethylpropylamine	9.19	9.19	9.14	9.13	9.16	9.12

[a] Calculated using the Gaussian 03 suite of programs assuming no reverse activation energy. [b] Calculated using eq 4 and data from Tables 1 and 3.

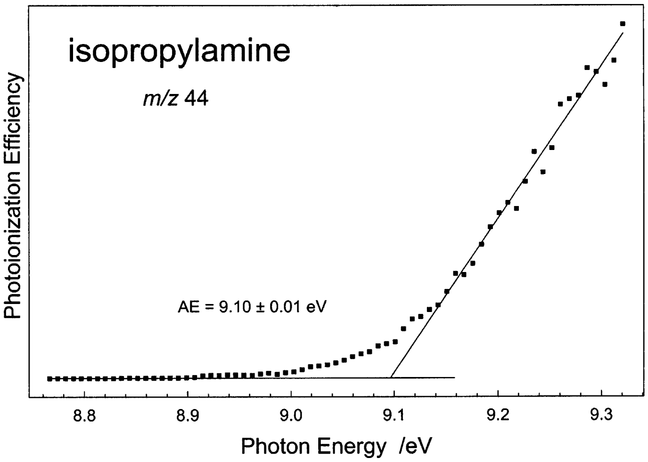

Figure 2. Threshold PIE curve for *m*/*z* 44 fragment ions produced from isopropylamine.

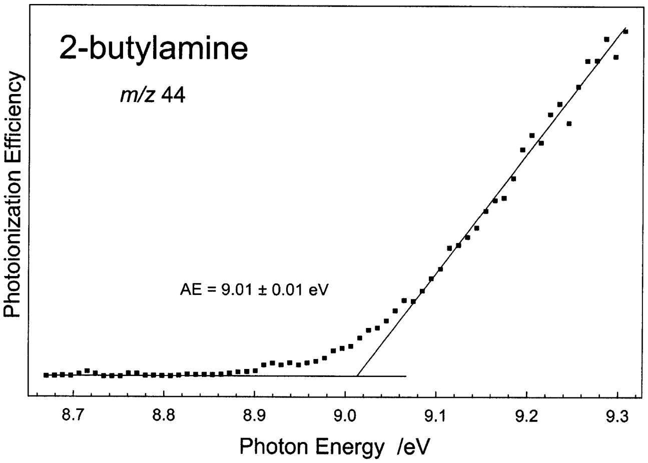

Figure 3. Threshold PIE curve for *m*/*z* 44 fragment ions produced from 2-butylamine.

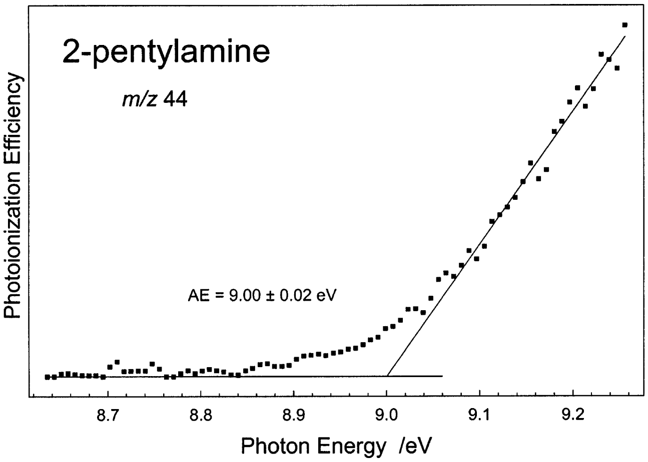

Figure 4. Threshold PIE curve for *m*/*z* 44 fragment ions produced from 2-pentylamine.

that this particular unimolecular reaction is unsuitable for deriving an accurate cationic heat of formation.

Isopropylamine. The loss of CH_3 from ionized isopropylamine is the major process observed in the isopropylamine PI mass spectrum. Although there are small peaks at *m*/*z* 58 and 30, these have much higher AEs, indicating that there is no competitive shift[23] associated with the PIE curve shown in Figure 2. The present AE of 9.10 ± 0.01 eV is close to the Lossing et al.[4] EI measurement of 9.12 eV but substantially higher than the corresponding Solka and Russell[5] value of 8.86 eV. However, there is excellent agreement with the calculated AEs shown in Table 2. The possibility of excess energy associated with the experimental AE cannot be discounted as G3 calculations find a transition state 5.1 kJ mol^{-1} higher in energy than the products ($CH_3CH{=}NH_2^+ + CH_3$). Given that a related study[1] showed no excess energy is involved in H loss from ionized methylamine, despite the calculation of a small reverse activation energy, it is quite likely that a similar situation also occurs here.

2-Butylamine. The *m*/*z* 44 peak dominates the PI mass spectrum for 2-butylamine. It has a 298 K AE of 9.01 ± 0.01 eV (Figure 3), which is slightly higher than the only other significant fragment ions at *m*/*z* 58 and 43, both having slightly lower AEs of 8.96 ± 0.02 and 8.91 ± 0.01 eV, respectively. By comparison, the corresponding monoenergetic EI AEs for loss of ethyl (*m*/*z* 44) and loss of methyl (*m*/*z* 58) from ionized 2-butylamine are 9.10 eV[24] and 9.03 eV,[4] respectively. Although there will be a small ^{13}C contribution to the *m*/*z* 44 PIE curve from the $C_2H_5N^+$ ion, in this case its relative abundance is too low (2.2% at 9.01 eV) to have any noticeable effect on the threshold data shown in Figure 3. The relatively sharp onset in the *m*/*z* 44 PIE curve indicates that the possibility of a competitive shift caused by the two lower energy processes is most unlikely. Furthermore, the absence of any excess energy at threshold is supported by the good agreement between the experimental and calculated 0 K AEs shown in Table 2, together with transition-state calculations that indicate no reverse activation energy.

2-Pentylamine. Figure 4 shows the threshold PIE curve for the loss of *n*-C_3H_7 from 2-pentylamine, with a 298 K AE of 9.00 ± 0.02 eV. The larger uncertainty associated with this particular measurement is due to the effect the slight threshold curvature has on making an accurate linear extrapolation. The present AE is substantially lower than the only other reported value of 10.43 ± 0.13 eV,[25] obtained by a nonmonoenergetic EI vanishing current measurement. As with 2-butylamine, two other fragmentation processes (loss of methyl and ethyl) are observed, both having lower energy onsets. Unfortunately the extended tailing in their PIE curves precludes any accurate AE assignment. However, the very low threshold ion count rates for both the *m*/*z* 72 and *m*/*z* 58 ions suggest that there should not be any significant competitive shift involved with the *m*/*z*

TABLE 3: Thermochemistry for the Gas-Phase Reaction $CH_3CHRNH_2 + h\nu \rightarrow CH_3CHNH_2^+ + R^\bullet$

			$\Delta H^\circ_{f,298}$ (kJ mol^{-1})		
R	AE_{298} (eV)	ΔH_{cor} [a] (kJ mol^{-1})	CH_3CHRNH_2[b]	R[c]	$CH_3CHNH_2^+$[d]
H	9.61 ± 0.01	13.5 ± 0.1	−47.4 ± 0.7	218.0 ± 0.0	675.3 ± 1.2
CH_3	9.10 ± 0.01	17.7 ± 0.1	−83.8 ± 0.6	147.0 ± 0.4[e]	664.9 ± 1.2
C_2H_5	9.01 ± 0.01	20.3 ± 0.1	−104.9 ± 1.0	119.0 ± 2.0	665.7 ± 2.5
n-C_3H_7	9.00 ± 0.02	22.9 ± 0.1	−125.6 ± 1.0[f]	100.0 ± 2.0	665.7 ± 3.0
i-C_3H_7	8.93 ± 0.01	23.3 ± 0.1	−132.0 ± 1.0[f]	90.0 ± 2.0	662.9 ± 2.5

[a] Calculated using eq 3 and $H^\circ_{298} - H^\circ_0$ values from Table 1. [b] Reference 26. [c] Reference 3. [d] Calculated using eq 2. [e] Reference 14. [f] Estimated from ref 26.

TABLE 4: Composite ab Initio[a] 298 K Heats of Formation (kJ mol^{-1})

	G2 (MP2)	G2	G3	G3B3	W1	CBS-APNO	average	experiment
$CH_2{=}NH$	86.9	86.7	89.9	88.4	86.7	90.1	88.1 ± 1.6	88.3 ± 2.1[b]
$CH_2{=}NH_2^+$	748.8	748.8	752.7	752.1	748.4	750.7	750.3 ± 1.9	749.5 ± 1.3[c]
E-$CH_3CH{=}NH$	43.1	41.5	43.9	42.6	37.4	40.5	41.5 ± 2.3	
Z-$CH_3CH{=}NH$	45.9	44.2	46.7	45.5	40.2	43.1	44.3 ± 2.4	
$CH_3CH{=}NH_2^+$	666.6	665.0	667.9	667.6	659.7	662.2	664.8 ± 3.3	665.1 ± 1.4[d]
n-$C_3H_7^\bullet$	110.5	106.4	100.7	101.3	94.9	94.9	101.5 ± 6.2	100.0 ± 2.0[e]
i-$C_3H_7^\bullet$	99.6	95.2	90.0	90.1	82.3	82.3	89.9 ± 6.9	90.0 ± 2.0[e]

[a] Calculated using the Gaussian 03 suite of programs. [b] W2 calculation.[28] [c] Reference 1. [d] This work. [e] Reference 3.

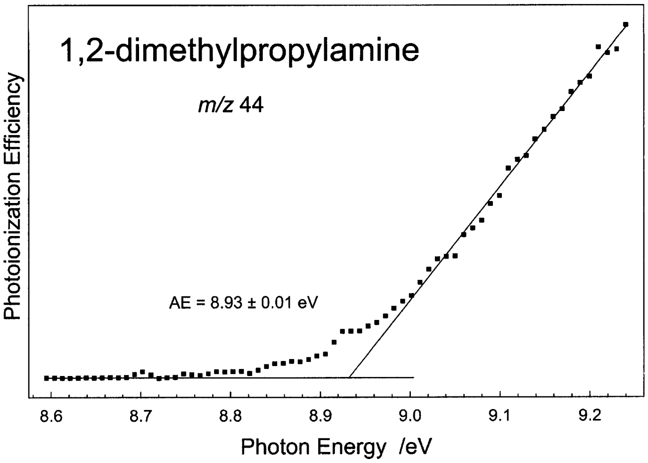

Figure 5. Threshold PIE curve for m/z 44 fragment ions produced from 1,2-dimethylpropylamine. The data have been corrected for the m/z 43 ^{13}C contribution.

44 onset. Ab initio transition state calculations indicate that there is no reverse activation energy associated with the loss of n-propyl radical from ionized 2-pentylamine. In addition, the good agreement between the calculated 0 K AEs and the corresponding experimental value shown in Table 2 provides evidence that there should not be any excess energy involved with this particular fragmentation process at its threshold.

1,2-Dimethylpropylamine. Like all other amines studied here, the m/z 44 ion forms the base peak in the PI mass spectrum for 1,2-dimethylpropylamine. The AE for this fragmentation process is found to be 8.93 ± 0.01 eV at 298 K (Figure 5), which is slightly higher than the corresponding AE for the m/z 43 ion (8.91 ± 0.01 eV), the only other significant fragment ion observed in the mass spectrum. No other experimental AE measurements appear to have been made.[3] The threshold ^{13}C isotope contamination from the m/z 43 peak (4.5% at 8.93 eV) was significantly greater than that observed for 2-butylamine, although still relatively small. To assess the effect of this on the AE, the m/z 44 PIE curve has had an appropriate analytical correction made to the experimental data. This is important if any possible underestimation of the AE is to be avoided.[14] However, both the isotopically corrected data, shown in Figure 5, and the uncorrected data produced identical AEs. Again the threshold PIE curve shape does not suggest the involvement of a competitive shift effect, despite the presence of a lower energy process. The theoretical 0 K AEs (Table 2) are in good agreement with the experimental 0 K value of 9.12 eV, which is to be expected given that the ab initio calculations show no reverse activation energy associated with the loss of isopropyl radical from ionized 1,2-dimethylpropylamine.

Thermochemistry. Table 3 summarizes the thermochemistry associated with the five ionization and fragmentation processes studied here. Because no experimental heats of formation for 2-pentylamine or 1,2-dimethylpropylamine are available these particular values have been calculated using the estimation procedure of Pedley et al.[26] The associated calculated error limits of ±1.0 kJ mol^{-1} are probably realistic. As expected, the derived $CH_3CH{=}NH_2^+$ heat of formation for ethylamine is noticeably higher than the other values shown in Table 3, reflecting the presence of excess energy in the form of a reverse activation energy. On the other hand the value for 1,2-dimethylpropylamine appears to be slightly lower than the others. A similar observation was made for the loss of isopropyl radical from ionized isobutylamine,[1] which suggests that there may be a problem with the radical heat of formation. It is interesting to note that the NIST value[3] of 90 ± 2 kJ mol^{-1} is that recommended by Tsang,[27] yet the "recommended value" listed in Tsang's table of data for the isopropyl radical is 88 ± 2 kJ mol^{-1}. The use of this lower radical heat of formation would increase the derived cationic heat of formation for 1,2-dimethylpropylamine by 2 kJ mol^{-1}, resulting in much better agreement with the other data.

The results of ab initio calculations shown in Table 4 also offer support for a lower isopropyl radical heat of formation. Although there are significant variations in the values obtained by the different composite methods, which is reflected by the rather large mean standard deviation of 6.9 kJ mol^{-1}, the average difference between the calculated n-propyl and isopropyl radical heats of formation is 11.5 ± 0.8 kJ mol^{-1}. Furthermore, both the W1 and CBS-APNO calculations, regarded as the most accurate of those used here, give identical heats of formation for both radicals with a difference of 12.6 kJ mol^{-1}. Assuming Tsang's value of 100 ± 2 kJ mol^{-1} for the n-propyl radical,[3,27] it would thus appear that the lower value of 88 ± 2 kJ mol^{-1} provides a more reasonable estimate. Further work needs to be done to resolve this particular issue.

TABLE 5: Composite ab Initio[a] 298 K Proton Affinities (kJ mol^{-1})

	G2 (MP2)	G2	G3	G3B3	W1	CBS-APNO	average	experiment
$CH_2{=}NH$	868.1	867.9	867.2	866.3	868.3	869.4	867.9 ± 1.1	868.8 ± 2.5[b]
E-$CH_3CH{=}NH$	906.5	906.5	906.0	905.0	907.7	908.3	906.7 ± 1.2	906.4 ± 2.7[c]
Z-$CH_3CH{=}NH$	909.3	909.2	908.8	907.9	910.5	910.9	909.4 ± 1.1	909.2 ± 2.8[c]

[a] Calculated using eq 6, with data from Table 4 and $\Delta H^\circ_{f,298}(H^+) = 1530.0$ kJ mol^{-1}.[2] [b] Reference 1. [c] This work.

If the results for ethylamine and 1,2-dimethylisopropylamine are excluded, for reasons discussed above, the average heat of formation for the $CH_3CH{=}NH_2^+$ cation is 665.1 ± 1.4 kJ mol^{-1}. This compares favorably with the mean value of 664.8 ± 3.3 kJ mol^{-1} obtained using six different high-level composite methods of calculation (Table 4). The best agreement is obtained with the G2 calculation, which also happens to be the case for the homologous $CH_2{=}NH_2^+$ cation shown in Table 4.

The proton affinity of a molecule is defined as the negative of the enthalpy change for a gas-phase protonation reaction.[2] For ethylidenimine, this corresponds to $-\Delta H$ for the reaction

$$CH_3CH{=}NH + H^+ \rightarrow CH_3CH{=}NH_2^+ \qquad (5)$$

which, at 298 K, is conveniently expressed as

$$PA(CH_3CH{=}NH) = \Delta H^\circ_{f,298}(CH_3CH{=}NH) + \Delta H^\circ_{f,298}(H^+) - \Delta H^\circ_{f,298}(CH_3CH{=}NH_2^+) \qquad (6)$$

Although the two cationic heats of formation in eq 6 are well-known it is not possible to derive an absolute proton affinity for $CH_3CH{=}NH$ because there is no experimental heat of formation available for this particular imine. This was also the situation for methylenimine in our previous related study.[1] However, there we were able to use the results of an accurate W2 calculation for the neutral imine heat of formation.[28]

In the absence of a W2 heat of formation for ethylidenimine we have carried out a series of high-level composite ab initio calculations for both the *E* and *Z* isomers. The results are shown in Table 4. If the related calculations for $CH_2{=}NH$ (Table 4) are compared to the W2 value of 88.3 kJ mol^{-1},[28] it can be seen that the density functional G3B3 calculation is in closest agreement. However, the average of the six different calculations is even closer. On this basis we have assumed that the average calculated value should also provide a reliable estimate for $\Delta H^\circ_{f,298}(CH_3CH{=}NH)$.

Taking a value of 41.5 ± 2.3 kJ mol^{-1} for the heat of formation for *E*-$CH_3CH{=}NH$, together with the well-known $\Delta H^\circ_{f,298}(H^+) = 1530.0$ kJ mol^{-1},[2] and $\Delta H^\circ_{f,298}(CH_3CH{=}NH_2^+) = 665.1 \pm 1.4$ kJ mol^{-1} from the present study, leads to a proton affinity of 906.4 ± 2.7 kJ mol^{-1}; the corresponding proton affinity for the *Z* isomer is 909.2 ± 2.8 kJ mol^{-1}. These two PAs are in excellent agreement with the average calculated values shown in Table 5. The similar agreement between the average calculated PA for $CH_2{=}NH$ and the experimental value[1] of 868.8 ± 2.5 kJ mol^{-1} demonstrates that these high-level ab initio methods are able to calculate accurate PAs, further supporting the present measurements.

The adjusted PA values of Ellenberger et al.[6] (899 ± 3 kJ mol^{-1}) and Peerboom et al.[8] (897 ± 12 kJ mol^{-1}) are slightly lower than the present result. Although this may reflect an overestimation of the *E*-$CH_3CH{=}NH$ heat of formation used here, it is more likely due to the uncertainties associated with the reference base GBs, particularly as they are ~50 kJ mol^{-1} higher than ammonia, the nearest absolute reference.[2] Obtaining a PA higher than the Hunter and Lias compilation[2] is consistent with our previous studies for molecules above ammonia on the PA ladder; the PA for methylketene was measured to be 11.3 kJ mol^{-1} higher[14] and the PA for methylenimine 15.8 kJ mol^{-1} higher.[1] This suggests that the upper end of the proton affinity scale may well contain significant errors that can only be resolved by additional absolute PA measurements.

Conclusions

Threshold photoionization mass spectrometry has been used to measure the $CH_3CH{=}NH_2^+$ appearance energies for five primary amines. From an analysis of these data a 298 K heat of formation of 665.1 ± 1.4 kJ mol^{-1} is obtained for the ethylidenimmonium cation. When this is combined with theoretically calculated heats of formation for the ethylidenimines *E*-$CH_3CH{=}NH$ and *Z*-$CH_3CH{=}NH$, absolute proton affinities of 906.4 ± 2.7 and 909.2 ± 2.8 kJ mol^{-1}, respectively, are derived. These results, which are in excellent agreement with high-level ab initio calculations, further extend the absolute proton affinity scale.

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References and Notes

(1) Harvey, Z. A.; Traeger, J. C. *Eur. J. Mass Spectrom.* **2004**, *10*, 599−766.

(2) Hunter, E. P. L.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413−656.

(3) Linstrom, P. J.; Mallard, W. G. Eds.; *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, June 2005, National Institute of Standards and Technology, Gaithersburg MD, 20899 (http://webbook.nist.gov).

(4) Lossing, F. P.; Lam, Y.-T.; Maccoll, A. *Can. J. Chem.* **1981**, *59*, 2228−2231.

(5) Solka, B. H.; Russell, M. E. *J. Phys. Chem.* **1974**, *78*, 1268−1273.

(6) Ellenberger, M. R.; Eades, R. A.; Thomsen, M. W.; Farneth, W. E.; Dixon, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 7151−7154.

(7) Ceyer, S. T.; Tiedemann, P. W.; Mahan, B. H.; Lee, Y. T. *J. Chem. Phys.* **1979**, *70*, 14−17.

(8) Peerboom, R. A. L.; Ingemann, S.; Nibbering, N. M. M.; Liebman, J. F. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1825−1828.

(9) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695−808.

(10) Smith, B. J.; Radom, L. *J. Am. Chem. Soc.* **1993**, *115*, 4885−4888.

(11) Hammerum, S.; Sølling, T. I. *J. Am. Chem. Soc.* **1999**, *121*, 6002−6009.

(12) Traeger, J. C.; McLoughlin, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3647−3652.

(13) Holmes, J. L.; Lossing, F. P.; Mayer, P. M. *J. Am. Chem. Soc.* **1991**, *113*, 9723−9728.

(14) Harvey, Z. A.; Traeger, J. C. *J. Mass Spectrom.* **2004**, *39*, 802−807.

(15) Traeger, J. C. *Int. J. Mass Spectrom. Ion Processes* **1984**, *58*, 259−271.

(16) Traeger, J. C.; McLoughlin, R. G. *J. Mass Spectrom. Ion Phys.* **1978**, *27*, 319−333.

(17) Junkes, J.; Salpeter, E. W.; Milazzo, G. *Atomic Spectra in the Vacuum Ultraviolet from 2250 to 1100 Å, Part One − Al, C, Cu, Fe, Ge, Hg, Si, and H_2*; Specola Vaticano: Vatican City, 1965.

(18) Gaussian 03M, Revision B.04, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

(19) Harvey, Z. A.; Wilson, D. J. D. To be published.

(20) Baer, T.; Mayer, P. M. *J. Am. Soc. Mass Spectrom.* **1997**, *8*, 103−115.

(21) Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1.

(22) Lifshitz, C. *Mass Spectrom. Rev.* **1982**, *1*, 309−348.

(23) Traeger, J. C.; Kompé, B. M. in *Energetics of Organic Free Radicals*; Simões, J. A. M., Greenburg, A., Liebman, J. F., Ed.; Blackie Academic & Professional: Glasgow, Scotland, 1996; pp 59−109.

(24) Holmes, J. L.; Lossing, F. P.; Maccoll, A. *J. Am. Chem. Soc.* **1988**, *110*, 7339−7342.

(25) Svec, H. J.; Junk, G. A. *J. Am. Chem. Soc.* **1967**, *89*, 790−796.

(26) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London 1986.

(27) Tsang, W. In *Energetics of Organic Free Radicals*; Simões, J. A. M., Greenburg, A., Liebman, J. F., Eds.; Blackie Academic & Professional: Glasgow, Scotland, 1996; pp 22−58.

(28) De Oliveira, G.; Martin, J. M. L.; Silwal, I. K. C.; Liebman, J. F. *J. Comput. Chem.* **2001**, *22*, 1297−1305.