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Gas-Phase Heats of Formation for Alkylimmonium Cations by Photoionization Mass Spectrometry

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Photoionization mass spectrometry has been used to measure appearance energies for immonium cation formation from 25 alkyl amine precursors. A number of the unimolecular fragmentation processes are shown to involve excess energy at threshold so that, of the 11 different cations investigated, it is only possible to derive reliable 298 K heats of formation for $CH_2{=}NH_2^+$ (749.0 ± 0.9 kJ mol^{-1}), $CH_3CH{=}NH_2^+$ (666.1 ± 1.1 kJ mol^{-1}), $C_2H_5CH{=}NH_2^+$ (636.8 ± 2.5 kJ mol^{-1}), $CH_2{=}NH(CH_3)^+$ (706.1 ± 1.0 kJ mol^{-1}), $CH_2{=}NH(C_2H_5)^+$ (668.4 ± 1.3 kJ mol^{-1}), and $CH_2{=}N(CH_3)_2^+$ (668.0 ± 2.5 kJ mol^{-1}). When these are compared to those calculated by the G3, G3B3, G2, G2(MP2), CBS-APNO, and W1U composite ab initio methods, it is found that the smallest mean absolute deviation of 1.2 ± 0.8 kJ mol^{-1} is obtained from the G2 calculations.

Introduction

Some 25 years ago, Lossing and co-workers[1] carried out a comprehensive experimental study of the gas-phase heats of formation for C1−C3 alkyl immonium cations. Their results, obtained from monoenergetic electron ionization (EI) appearance energy (AE) measurements, represent the only systematic set of such data available and consequently have formed the basis of selected values found in several widely used thermochemical data compilations.[2,3]

Hammerum[4] has subsequently shown that these experimental heats of formation are uniformly lower than those obtained from a series of composite ab initio calculations and that much better agreement can be obtained if an allowance for a 298 K thermal enthalpy contribution is included with the AEs.[5] However, this correction was originally developed for photoionization (PI) AE measurements[6] and its use with EI data has been questioned by Holmes et al.[7]

One possible reason for the inconsistent agreement between the Lossing et al.[1] heats of formation and those calculated by Hammerum and Sølling[5] is that the experimental AEs were obtained from EI efficiency curves using a vanishing current technique. Such a method is highly dependent on instrumental sensitivity and the nature of the onset in the threshold region, which for many of the ions studied by Lossing et al. was found to be “unusually gradual”.[1]

Another source of variability in the derived experimental immonium cation heats of formation is the lack of consistent thermochemical data for both the precursor and the neutral fragment formed in the unimolecular dissociation process. Approximately 50% of the amine heats of formation used by Lossing et al.[1] were not available from experiment and were instead estimated using the group additivity scheme of Benson et al.[8] Furthermore, Baer and co-workers[9] have recently questioned some of these experimental data. They have proposed a set of revised values for several primary alkylamines and alkyl radicals as a result of their threshold photoelectron photoion coincidence (TPEPICO) study of the $CH_2{=}NH_2^+$ cation. However, despite a self-consistent set of data, it is not clear that their upward revisions of 1.7 and 1.3 kJ mol^{-1} to the NIST values[3] for the respective ethyl and *n*-propyl radical heats of formation are warranted, particularly given that such changes would need to be reconciled with the results of a large number of other independent experiments.

We have previously used PI mass spectrometry to obtain reliable values for the methylenimmonium ($CH_2{=}NH_2^+$) and ethylidenimmonium ($CH_3CH{=}NH_2^+$) cations.[10,11] The present study was undertaken to extend this work to a wider range of immonium cations, with the aim of producing a consistent set of experimental data that could be used to assess the reliability of some commonly used ab initio quantum chemical methods. For most of the AEs measured here, this represents the first time that they have been obtained using threshold dissociative PI or, in many cases by any technique, including EI.

Experimental Section

The La Trobe University photoionization mass spectrometer (PIMS) used in this work has been described in detail elsewhere.[12−14] Vacuum UV photons were generated in a 1.5 kPa hydrogen gas discharge and energy selected using a windowless 1 m Seya-Namioka monochromator equipped with a Jobin-Yvon holographically ruled 1200 grooves mm^{-1} diffraction grating. The resolution was fixed at 0.135 nm fwhm, with known reference emission lines[15] used to internally calibrate the absolute photon energy scale to better than 0.001 eV. The photon intensity was monitored with an EMI 9789B photomultiplier and sodium salicylate phosphor combination and a Philips Photonics X919BL channel electron multiplier used for photoion pulse counting. The data acquisition system was comprised of a 350 MHz Macintosh B&W G3 computer running LabVIEW 6.1 under OS 9.2.2 with a National Instruments PCI-6601 counter/timer used as the digital interface to the PIMS.

Photoionization efficiency (PIE) curves were obtained by dividing the photoion count rate by the photon count rate following a small correction for stray scattered background

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counts. Appearance energies were measured from linear extrapolations of the PIE curves in the threshold region.[6] Although standard deviations associated with the least-square fits to the data ranged between 0.003 and 0.007 eV, higher uncertainties have been assigned to the AEs to allow for any energy scale calibration errors and variations resulting from the selected set of data points used in the actual fitting process. The extent of prethreshold hot band structure associated with each linear extrapolation was consistent with the thermal excitation (typically ~0.1−0.2 eV) observed for the corresponding molecular ion PIE.

Experiments were conducted at room temperature (296 K), with sample pressures of 10^{-3} Pa in the ion-source region. All compounds were obtained commercially and of research grade purity. In each case, this was checked by gas chromatography−mass spectrometry (GC-MS) analysis. The dimethylamine and trimethylamine measurements were obtained using 40 and 30% aqueous solutions, respectively. PI mass spectra were recorded with the monochromator in a total reflection mode, that is, using all available light produced by the hydrogen pseudocontinuum (photons ~ 7.7−14.5 eV).

Ab initio calculations for the various unimolecular reactions were performed using the Gaussian 03 suite of programs[16] and were carried out using either a dual 2.5 GHz PowerPC G5 Macintosh desktop computer or the Australian Partnership for Advanced Computing (APAC) supercomputer facility. A number of different composite methods were employed in this study, including G2, G2(MP2), G3, G3 with B3LYP/6-31G* optimized geometries (G3B3), CBS-APNO, and W1U. Unless specified otherwise, where no explicit reference is given in the text to the particular composite method employed, calculated AEs, reverse activation energies, and heats of formation were those obtained from G2 calculations. The transition state structures used to calculate reverse activation energies were characterized by a single imaginary frequency, and their connectivity to the reactants and products was confirmed by intrinsic reaction coordinate calculations.

Results and Discussion

We have shown[6] that, in the absence of any excess energy, the 298 K heat of formation for the cation formed in the gas-phase process

$$\mathrm{RX} + h\nu \rightarrow \mathrm{X}^+ + \mathrm{R}^\bullet + \mathrm{e}^- \tag{1}$$

is related to the 298 K PI AE by the expression

$$\Delta H_{\mathrm{f},298}°(\mathrm{X}^+) = \mathrm{AE}_{298} + \Delta H_{\mathrm{f},298}°(\mathrm{RX}) - \Delta H_{\mathrm{f},298}°(\mathrm{R}^\bullet) + \Delta H_{\mathrm{cor}} \tag{2}$$

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

$$\Delta H_{\mathrm{cor}} = \{H_{298}° - H_0°\}(\mathrm{X}^+) + \{H_{298}° - H_0°\}(\mathrm{R}^\bullet) - 6.2\ \mathrm{kJ\ mol^{-1}} \tag{3}$$

The individual $H_{298}° - H_0°$ values can be obtained from statistical mechanical calculations.[17] These involve vibrational frequencies that are generally unavailable from experiment so it is necessary to use theoretical data acquired from high-level molecular orbital calculations. All ΔH_{cor} values employed in this study have been obtained from G2 calculations using the harmonic oscillator approximation to internal motions. In using eq 2, it is assumed that the cationic heat of formation is based on the stationary electron (ion) convention[6,18] and that the AE_{298} can be derived from a linear threshold extrapolation of the relevant PIE curve.[6] Where appropriate, 0 K appearance energies for eq 1 have been converted to the equivalent 298 K AE using the expression

$$\mathrm{AE}_{298} = \mathrm{AE}_0 - \{H_{298}° - H_0°\}(\mathrm{RX}) + 6.2\ \mathrm{kJ\ mol^{-1}} \tag{4}$$

It should be recognized that an AE for eq 1 only ever provides an upper limit to the cationic heat of formation. However, in the absence of any excess energy at threshold due to factors such as a reverse activation energy and kinetic or competitive shifts,[19] a true thermochemical value should be possible provided that the auxiliary data used in eq 2 are reliable. Ab initio transition-state calculations can help to provide an insight into the possible presence of a reverse activation energy while a kinetic or competitive shift is generally characterized by a slowly rising onset of the PIE curve in the threshold region; both result in a higher than expected cationic heat of formation.

Ultimately, it is the quality of the neutral thermochemical data that plays a major role in being able to derive accurate cationic heats of formation from threshold PIE measurements. Because a large proportion of neutral precursor heats of formation required for this study are not available from experiment[3] and given the possibility of significant discrepancies with some of them,[9] it was proposed to use the Pedley group equivalence scheme[20] to obtain a self-consistent set of data. This method, which is based on atomic heats of formation and bond energies, has an advantage over the earlier Pedley et al. method[21] where several critical component enthalpies are not available. However, although the Pedley scheme has been shown to produce calculated heats of formation for a range of amines that are in good agreement with available experimental measurements,[20] it is not clear that this will necessarily apply across the wide range of amines studied here.

To assess the reliability of the Pedley scheme, all relevant amine heats of formation were calculated using the G3, G3B3, G2, and G2(MP2) composite methods. These involved 0 K energies, G2-calculated $H_{298}° - H_0°$ values, and the following experimental 0 K atomic gas-phase heats of formation: $H = 216.04 \pm 0.01$ kJ mol^{-1},[22] $C = 711.79 \pm 0.21$ kJ mol^{-1},[23] and $N = 470.57 \pm 0.05$ kJ mol^{-1}.[24] Because CBS-APNO and W1U calculations were not feasible for many of the larger amines, they have not been included in this part of the study.

The mean difference between the 26 Pedley estimated values and the corresponding average of the four composite ab initio methods was found to be -2.8 ± 2.6 kJ mol^{-1}, indicating a reasonable correlation between the two sets of data. However, excluding the three individual differences lying outside of the range −5.4 to −0.2 kJ mol^{-1} results in a slightly modified mean and a greatly reduced standard deviation of -2.3 ± 1.1 kJ mol^{-1}. It is clear from this that there are several anomalous results, but the question is which particular approach is likely to be in error? Because the ab initio calculations do not rely on data obtained from a range of different thermochemical experiments, they should be less likely to produce such irregular behavior. For this reason, all neutral amine heats of formation used in the present study (Table 1) were obtained from the average Gaussian calculated value, adjusted by −2.3 kJ mol^{-1}.

The NIST database[3] has been used as the source of all radical heats of formation, with the exception of methyl and isopropyl. The methyl radical heat of formation was obtained from a critical evaluation by Ruscic et al.,[22] whereas the experimental measurement of Tschuikow-Roux and Chen[25] was used for the isopropyl radical. This latter value is supported by recent high-level ab

TABLE 1: Amine Thermochemical Data (kJ mol^{-1})

amine	$\Delta H_{f,298}°$[a]	$H_{298}° - H_0°$[b]
methylamine	−22.9	11.5
ethylamine	−50.1	14.2
n-propylamine	−69.5	17.7
n-butylamine	−89.3	21.2
isobutylamine	−97.4	21.0
isopropylamine	−85.0	17.4
2-butylamine	−102.9	21.0
2-pentylamine	−123.0	24.6
1,2-dimethylpropylamine	−128.2	24.4
dimethylamine	−18.2	14.3
N-methylethylamine	−45.9	17.6
N-methylpropylamine	−65.3	21.2
N-methylbutylamine	−85.5	24.5
N-methylisobutylamine	−93.6	24.6
3-pentylamine	−122.2	24.6
tert-butylamine	−121.2	20.7
tert-pentylamine	−138.1	24.3
N-methylisopropylamine	−77.6	21.0
diethylamine	−73.5	21.1
N-ethylpropylamine	−93.1	24.7
trimethylamine	−28.0	16.6
N,*N*-dimethylethylamine	−51.1	20.8
N,*N*-dimethylbutylamine	−90.7	28.1
N-methyl-tert-butylamine	−108.3	24.4
N-ethylisopropylamine	−105.4	24.6
N,*N*-dimethylisopropylamine	−75.2	24.1

[a] Average calculated values −2.3 ± 1.1 kJ mol^{-1} (see text). [b] G2 calculated values.

initio calculations[26] and is consistent with AE data for 1,2-dimethylpropylamine, as discussed in an earlier study of the $CH_3CH{=}NH_2^+$ heat of formation.[11]

$CH_2{=}NH_2^+$. The methylenimmonium cation heat of formation was determined previously to be 749.5 ± 1.3 kJ mol^{-1}.[10] In that study, experimental neutral precursor heats of formation[20] were used in the thermochemical calculations. However, the recent TPEPICO investigation by Baer and co-workers[9] has cast doubt on several of those values, as well as some of the radical heats of formation. Table 2 presents the previously published AE measurements[20] but instead uses neutral heats of formation from Table 1 to derive the corresponding value for $CH_2{=}NH_2^+$. The weighted average for all five precursors is 749.0 ± 0.9 kJ mol^{-1}.

This different result is largely a consequence of the 2.7 kJ mol^{-1} lower ethylamine heat of formation shown in Table 1. In their recent study of primary amines, Baer and co-workers[9] noted the anomalous experimental heat of formation for ethylamine and suggested a new value of −50.1 ± 1.5 kJ mol^{-1}, in excellent agreement with the present data. If the complete set of revised heats of formation and $H_{298}° - H_0°$ data proposed by Baer and co-workers[9] is used instead to derive the individual $\Delta H_{f,298}°(CH_2{=}NH_2^+)$ values in Table 2, a weighted average of 748.0 ± 0.9 kJ mol^{-1} is obtained. Although this is in agreement with the present PI result, it is 2.3 kJ mol^{-1} lower than the actual TPEPICO measurement of Baer and co-workers[9] and 2.4 kJ mol^{-1} lower than that obtained from an earlier related study of monomethylamine.[27] As noted previously by Baer and co-workers,[9] the source of such a discrepancy between similar threshold PI and TPEPICO derived results is not clear.

$CH_3CH{=}NH_2^+$. The heat of formation for the ethylidenimmonium cation has been obtained recently by dissociative PI in our laboratory.[11] A value of 665.1 ± 1.4 kJ mol^{-1} was derived based on AE measurements for three primary amine precursors; the value for H loss from ethylamine was excluded on the basis of a significant reverse activation energy, whereas uncertainty in the NIST heat of formation for the isopropyl radical precluded its use in the average.

If the previous experimental AE data are combined with the present estimated neutral amine heats of formation and the above preferred radical heats of formation, a weighted average of 666.1 ± 1.1 kJ mol^{-1} is obtained. Again, the higher value for ethylamine (Table 2) has been excluded on the basis of a calculated reverse activation energy of 22 kJ mol^{-1}. This increase of 1.0 kJ mol^{-1} in $\Delta H_{f,298}°(CH_3CH{=}NH_2^+)$, which is the result of using slightly different neutral thermochemical data, demonstrates the importance of such information for the determination of accurate cationic heats of formation from precise spectroscopic measurements.

$CH_2{=}NH(CH_3)^+$. The *m/z* 44 PIE curves for five different *N*-methylamino precursors each display a well-defined linear region extending over a range of at least 0.2 eV. There is no apparent indication of a kinetic or competitive shift with any of the processes, and all of the experimental AEs are supported by ab initio calculations.

The AE_{298} of 9.69 ± 0.01 eV for dimethylamine is in excellent agreement with a recent TPEPICO measurement by Bodi et al.;[27] their AE_0 of 9.768 ± 0.023 eV converts to a corresponding 298 K value of 9.685 ± 0.023 eV using eq 4. These are both close to the Lossing et al.[1] monoenergetic EI measurement of 9.65 eV but significantly higher than the 9.41 eV obtained by Solka and Russell[28] in their retarding potential difference EI study of dimethylamine. It is most likely that the AE involves a small amount of excess energy. The experimental breakdown results of Bodi et al.[27] were consistent with a 4 kJ mol^{-1} reverse activation energy, which is close to the G2 calculated value of 8 kJ mol^{-1}. Their data also indicated the presence of a small ~6 kJ mol^{-1} kinetic shift. Thus, any $CH_2{=}NH(CH_3)^+$ heat of formation derived from AE data for H loss from ionized dimethylamine is expected to be higher than the true thermochemical value.

The AE for loss of methyl radical from ionized *N*-methylethylamine has also been measured by Solka and Russell (8.49 eV)[28] and Lossing et al. (9.15 eV).[1] Again, the present experimental measurement of 9.12 ± 0.01 eV is substantially higher than the former AE but in good agreement with the latter value. Calculations suggest that there should not be any reverse activation energy associated with this fragmentation process. This is also the case for the three other alkyl radical loss processes studied here that lead to formation of the $CH_2{=}NH(CH_3)^+$ cation (*N*-methylpropylamine, $AE_{298} = 9.03 \pm 0.01$ eV; *N*-methylbutylamine, $AE_{298} = 9.02 \pm 0.01$ eV; and *N*-methylisobutylamine, $AE_{298} = 8.97 \pm 0.01$ eV). No other AEs are available for comparison, with the exception of *N*-methylbutylamine; an EI value of 9.13 eV, obtained by Holmes et al.,[29] is significantly higher than the present measurement, reflecting the greater difficulty in obtaining reliable AEs from EI experiments.

Table 2 summarizes the thermochemistry for the five PI fragmentation processes producing $CH_2{=}NH(CH_3)^+$. It can be seen that the $\Delta H_{f,298}°[CH_2{=}NH(CH_3)^+]$ derived from dimethylamine is slightly higher than the other values, which is consistent with the presence of a small reverse activation energy. As there is not expected to be any excess energy associated with the other four processes, the weighted average of 706.1 ± 1.0 kJ mol^{-1} should represent the thermochemical value for the $CH_2{=}NH(CH_3)^+$ heat of formation. It is interesting to note that this is 11.6 kJ mol^{-1} higher than that obtained by Lossing et al.[1] but in exact agreement with the heat of formation

TABLE 2: Derived[a] 298 K Cationic Heats of Formation (kJ mol^{-1}) for the Gas-Phase Reactions RX + hν → X^+ + $R^\bullet$ + e^-

RX	X^+	$R^\bullet$	AE (eV)	$\Delta H_{f,298}°$ (X^+)
methylamine	$CH_2=NH_2^+$	H	10.16[b]	749.8 ± 1.5
ethylamine	$CH_2=NH_2^+$	CH_3	9.63[b]	747.0 ± 1.5
n-propylamine	$CH_2=NH_2^+$	C_2H_5	9.55[b]	750.1 ± 2.5
n-butylamine	$CH_2=NH_2^+$	*n*-C_3H_7	9.55[b]	751.9 ± 2.5
isobutylamine	$CH_2=NH_2^+$	*i*-C_3H_7	9.47[b]	748.6 ± 2.6
ethylamine	$CH_3CH=NH_2^+$	H	9.61[c]	672.6 ± 1.5
isopropylamine	$CH_3CH=NH_2^+$	CH_3	9.10[c]	664.0 ± 1.5
2-butylamine	$CH_3CH=NH_2^+$	C_2H_5	9.01[c]	667.7 ± 2.5
2-pentylamine	$CH_3CH=NH_2^+$	*n*-C_3H_7	9.00[c]	668.3 ± 3.0
1,2-dimethylpropylamine	$CH_3CH=NH_2^+$	*i*-C_3H_7	8.93[c]	668.8 ± 2.6
dimethylamine	$CH_2=NH(CH_3)^+$	H	9.69	712.1 ± 1.5
N-methylethylamine	$CH_2=NH(CH_3)^+$	CH_3	9.12	704.9 ± 1.5
N-methylpropylamine	$CH_2=NH(CH_3)^+$	C_2H_5	9.03	707.2 ± 2.5
N-methylbutylamine	$CH_2=NH(CH_3)^+$	*n*-C_3H_7	9.02	707.6 ± 2.5
N-methylisobutylamine	$CH_2=NH(CH_3)^+$	*i*-C_3H_7	8.97	707.2 ± 2.6
n-propylamine	$C_2H_5CH=NH_2^+$	H	<10.1	<703.4
2-butylamine	$C_2H_5CH=NH_2^+$	CH_3	9.10	649.0 ± 4.9
3-pentylamine	$C_2H_5CH=NH_2^+$	C_2H_5	8.86	636.8 ± 2.5
isopropylamine	$(CH_3)_2C=NH_2^+$	H	<9.6	<640.9
tert-butylamine	$(CH_3)_2C=NH_2^+$	CH_3	8.86	608.8 ± 1.5
tert-pentylamine	$(CH_3)_2C=NH_2^+$	C_2H_5	8.66	602.9 ± 3.0
N-methylethylamine	*E*-$CH_3CH=NH(CH_3)^+$	H	<9.9	<708.7
N-methylisopropylamine	*E*-$CH_3CH=NH(CH_3)^+$	CH_3	8.68	634.8 ± 1.5
N-methylethylamine	$CH_2=NH(C_2H_5)^+$	H	<9.9	<707.8
diethylamine	$CH_2=NH(C_2H_5)^+$	CH_3	8.99	667.9 ± 1.5
N-ethylpropylamine	$CH_2=NH(C_2H_5)^+$	C_2H_5	8.90	669.9 ± 2.5
trimethylamine	$CH_2=N(CH_3)_2^+$	H	9.61	697.8 ± 2.2
N,*N*-dimethylethylamine	$CH_2=N(CH_3)_2^+$	CH_3	8.80	672.1 ± 2.2
N,*N*-dimethylbutylamine	$CH_2=N(CH_3)_2^+$	*n*-C_3H_7	8.63	668.0 ± 2.5
N-methylisopropylamine	$(CH_3)_2C=NH(CH_3)^+$	H	<9.3	<621.0
N-methyl-*tert*-butylamine	$(CH_3)_2C=NH(CH_3)^+$	CH_3	8.46	584.8 ± 2.2
diethylamine	*E*-$CH_3CH=NH(C_2H_5)^+$	H	<9.2	<616.9
N-ethylisopropylamine	*E*-$CH_3CH=NH(C_2H_5)^+$	CH_3	8.61	603.5 ± 1.5
N,*N*-dimethylethylamine	$CH_3CH=N(CH_3)_2^+$	H	<9.8	<697.9
N,*N*-dimethylisopropylamine	$CH_3CH=N(CH_3)_2^+$	CH_3	8.43	617.0 ± 2.2

[a] Calculated using eq 2. [b] Ref 10. [c] Ref 11.

rederived by Hammerum and Sølling[5] to include an enthalpy correction given by eq 3.

$C_2H_5CH=NH_2^+$. The loss of H from ionized propylamine has a calculated reverse activation energy of 26 kJ mol^{-1}. In addition, there is competition with the lower energy ethyl loss process that occurs at 9.55 ± 0.01 eV.[10] This results in a PIE curve showing a long tail and a poorly defined onset with an AE < 10.1 eV. No other AE measurements are available.[3]

Like propylamine, the formation of $C_2H_5CH=NH_2^+$ from 2-butylamine showed a very low photoion count rate in the threshold region (~0.01 s^{-1}). Again, it was not possible to obtain a well-defined onset, although a tentative AE_{298} of 9.10 ± 0.05 eV has been assigned. This is 0.14 eV higher than the calculated AE_{298}, which is to be expected given that there is a calculated reverse activation energy of 12 kJ mol^{-1}. It is, however, 0.21 eV higher than the corresponding EI AE of Lossing et al.[1] Because there is significant competition from the *m*/*z* 43 and 44 fragment ions in the threshold region (AE_{298} = 8.91 ± 0.01 and 9.01 ± 0.01 eV, respectively)[11] with an expected resulting competitive shift, the source of the discrepancy is not clear. One possible reason is that the Lossing et al. measurement may have been compromised by a sample impurity. We previously obtained an AE_{298} of 8.96 ± 0.02 eV.[11] However, despite GC-MS analyses indicating no measurable *m*/*z* 58 impurity in the 2-butylamine sample, it was noticed that this AE shifted to higher energies following introduction into the PIMS for approximately 24 h. Such an effect is consistent with the removal of a more volatile isobaric impurity and once more demonstrates how sensitive threshold PI measurements can be to the presence of trace amounts of impurities.[12]

The loss of ethyl radical from ionized 3-pentylamine is not subject to any reverse activation energy or competitive shift. Consequently, the AE_{298} of 8.86 ± 0.01 eV should enable a reliable estimate to be made for $\Delta H_{f,298}°(C_2H_5CH=NH_2^+)$. No other AE measurements appear to have been made for 3-pentylamine.[3] In the absence of further data, the calculated cationic heat of formation shown in Table 2 (636.8 ± 2.5 kJ mol^{-1}) represents the best experimental estimate.

$(CH_3)_2C=NH_2^+$. Three amine precursors were available to provide an AE for $(CH_3)_2C=NH_2^+$. Like most H-loss processes in this study, the PIE curve for isopropylamine showed a long tail with a poorly defined threshold <9.6 eV. This is consistent with the presence of a competitive shift, caused by the more favorable lower energy methyl loss fragmentation (AE_{298} = 9.10 ± 0.01 eV)[11] and a calculated 35 kJ mol^{-1} reverse activation energy.

Although the AE_{298} for methyl loss from ionized *tert*-butylamine is not subject to any competitive shift, the well-defined onset of 8.86 ± 0.01 eV, which is in good agreement with that obtained by Lossing et al.,[1] almost certainly represents an upper limit because calculations show that there is a significant 23 kJ mol^{-1} reverse activation energy.

Despite the absence of any reverse activation energy or competitive shift associated with ethyl radical loss from ionized *tert*-pentylamine, the AE can also only represent an upper limit because there is no observed molecular ion in the PI mass spectrum, that is, the AE_{298} of 8.66 ± 0.02 eV represents a pseudo-IE. Thus, the derived cationic heat of formation of 602.9 ± 3.0 kJ mol^{-1} shown in Table 2 will probably be higher than the thermochemical value. No other amine precursors were available to verify this. However, a 0.04 eV lower calculated AE_{298} indicates that there is most likely some excess energy involved with the present experimental AE.

***E*-$CH_3CH{=}NH(CH_3)^+$.** H loss from ionized *N*-methylethylamine has a poorly defined onset ($<$9.9 eV) that is significantly higher than the G2 calculated AE_{298} of 9.12 eV. No other AE determinations appear to have been made.[3] The calculated reverse activation energy of 21 kJ mol^{-1}, together with a competitive shift due to the lower energy methyl loss process, ensures that the cationic heat of formation shown in Table 2 will be significantly higher than the true thermochemical value.

The AE_{298} of 8.68 ± 0.01 eV for methyl loss from ionized *N*-methylisopropylamine is 0.03 eV lower than that obtained by Lossing et al.[1] Although the onset is well-defined and no competitive shift is present, the derived cationic heat of formation of 634.8 ± 1.5 kJ mol^{-1} (Table 2) is most likely too high as a consequence of a reverse activation energy, calculated to be 8 kJ mol^{-1}. Ab initio calculations do indicate that the analogous fragmentation process of ethyl loss from *N*-methyl-2-butylamine should be free from any excess energy. However, to date, we have been unable to obtain a sample of the precursor to verify this.

$CH_2{=}NH(C_2H_5)^+$. As discussed above, H loss from ionized *N*-methylethylamine has an AE $<$ 9.9 eV that involves excess energy. Calculations show a reverse activation energy of 8 kJ mol^{-1} and a 298 K AE of 9.51 eV to form $CH_2{=}NH(C_2H_5)^+$. This calculated AE_{298} is 0.39 eV higher than the corresponding value for H loss from the methylene group leading to *E*-$CH_3CH{=}NH(CH_3)^+$ and 0.39 eV higher than the observed methyl-loss AE_{298} to form $CH_2{=}NH(CH_3)^+$. No other experimental AEs are available for comparison.[3]

The AE_{298} of 8.99 ± 0.01 eV for methyl loss from ionized diethylamine is 0.07 eV higher than the monoenergetic EI value obtained by Lossing et al.[1] but 0.56 eV higher than the nonmonoenergetic EI measurement of Collin and Franskin.[30] As there is no calculated reverse activation energy or competitive shift associated with this process, the derived cationic heat of formation given in Table 2 is expected to be close to the true thermodynamic value.

Like diethylamine, PI of *N*-ethylpropylamine to produce $CH_2{=}NH(C_2H_5)^+$ should not involve any excess energy at threshold. The well-defined AE_{298} of 8.90 ± 0.01 eV produces a derived cationic heat of formation in accord with that obtained from diethylamine and leads to a weighted average of 668.4 ± 1.3 kJ mol^{-1} for $\Delta H_{f,298}°(CH_2{=}NH(C_2H_5)^+)$.

$CH_2{=}N(CH_3)_2^+$. Three precursors were used to study the energetics of $CH_2{=}N(CH_3)_2^+$ formation. The loss of H from photoionized trimethylamine was also investigated by Bodi et al.[27] Despite this being the lowest energy process, and therefore not subject to any competitive shift, they found that there was a significant kinetic shift (∼0.20 eV) in addition to a reverse activation energy of 7 kJ mol^{-1}; the curvature in the threshold region of the PIE curve is consistent with such a kinetic shift effect. Bodi et al. were unable to derive a definitive AE from a detailed analysis of their TPEPICO data, although they did quote an AE_0 range of 9.414−9.458 eV (AE_{298} = 9.302−9.346 eV). This and the monoenergetic EI value of 9.38 eV obtained by Lossing et al.[1] are in essential agreement with one another; however, both are substantially lower than the present AE_{298} of 9.61 ± 0.02 eV. From an inspection of the threshold region, it is difficult to reconcile such a low AE, particularly given that the more favorable threshold law for PI usually results in a much greater threshold sensitivity than EI.[19] One possible explanation is that the use of the headspace from an aqueous solution of trimethylamine instead of a neat gas may have suppressed interference from any other *m*/*z* 58 ions of lower AE present in the sample. We have found that even very small traces of isobaric contaminants can have a significant effect on the threshold ion count rate and a corresponding appreciable downward shift in the observed AE.[12] Nevertheless, the presence of both a reverse activation energy and a kinetic shift eliminates trimethylamine as a suitable precursor for determining an accurate $CH_2{=}N(CH_3)_2^+$ heat of formation.

TABLE 3: Immonium Cation Heats of Formation (kJ mol^{-1}) Resulting from This Work

cation	$\Delta H_{f,298}°$
$CH_2{=}NH_2^+$	749.0 ± 0.9
$CH_3CH{=}NH_2^+$	666.1 ± 1.1
$CH_2{=}NH(CH_3)^+$	706.1 ± 1.0
$C_2H_5CH{=}NH_2^+$	636.8 ± 2.5
$(CH_3)_2C{=}NH_2^+$	$<$602.9 ± 3.0
E-$CH_3CH{=}NH(CH_3)^+$	$<$634.8 ± 1.5
$CH_2{=}NH(C_2H_5)^+$	668.4 ± 1.3
$CH_2{=}N(CH_3)_2^+$	668.0 ± 2.5
$(CH_3)_2C{=}NH(CH_3)^+$	$<$584.8 ± 2.2
E-$CH_3CH{=}NH(C_2H_5)^+$	$<$603.5 ± 1.5
$CH_3CH{=}N(CH_3)_2^+$	$<$617.0 ± 2.2

Methyl loss from ionized *N*,*N*-dimethylethylamine has an AE_{298} of 8.80 ± 0.01 eV with ab initio calculations finding no evidence for any reverse activation energy. This is in excellent agreement with both the Lossing et al.[1] EI value of 8.80 eV and the PI measurement of 8.81 ± 0.05 eV obtained by Loguinov et al.[31] However, it is 0.02 eV higher than that obtained from G2 calculations, which suggests the possible presence of excess energy despite the absence of any competitive shift.

The AE_{298} for loss of *n*-propyl radical from ionized *N*,*N*-dimethylbutylamine is found to be 8.63 ± 0.01 eV. In this case, no other experimental AE is available for comparison.[3] The absence of any calculated reverse activation energy or competitive shift indicates that this particular fragmentation process should be suitable for producing a reliable heat of formation for $CH_2{=}N(CH_3)_2^+$. From Table 2, it can be seen that the derived value is 4.1 kJ mol^{-1} lower than that for the corresponding methyl loss from *N*,*N*-dimethylethylamine, which is consistent with some excess energy being involved with the latter threshold process. For this reason, the preferred $\Delta H_{f,298}°(CH_2{=}N(CH_3)_2^+)$ from this study is 668.0 ± 2.5 kJ mol^{-1}.

$(CH_3)_2C{=}NH(CH_3)^+$. Two precursor amines were available to study the energetics of $(CH_3)_2C{=}NH(CH_3)^+$ formation. The PIE for H loss from ionized *N*-methylisopropylamine showed a long tail with a poorly defined threshold $<$9.3 eV. Given that there is a calculated reverse activation energy of 29 kJ mol^{-1} and that the major fragmentation process is methyl loss with a much lower AE, no meaningful cationic heat of formation can be derived from this AE.

The PIE for loss of methyl radical from ionized *N*-methyl-*tert*-butylamine shows some curvature in the threshold region that increases the uncertainty associated with the observed AE_{298} = 8.46 ± 0.02 eV. In addition, there is a significant calculated reverse activation energy of 22 kJ mol^{-1}, which means that the derived $\Delta H_{f,298}°[(CH_3)_2C{=}NH(CH_3)^+]$ of 584.8 ± 2.2 kJ mol^{-1} shown in Table 2 can only be taken as an upper limit.

TABLE 4: Composite Ab Initio 298 K Cationic Heats of Formation (kJ mol^{-1})

cation	G3	G2	G2 (MP2)	G3B3	CBS-APNO	W1U	average	experiment
$CH_2{=}NH_2^+$	753.1	749.2	749.1	752.4	751.1	748.7	750.6	749.0
$CH_3CH{=}NH_2^+$	668.8	666.0	667.5	668.5	663.1	660.7	665.8	666.1
$CH_2{=}NH(CH_3)^+$	712.6	708.1	708.9	712.1	708.7	706.8	709.5	706.1
$C_2H_5CH{=}NH_2^+$	637.6	635.2	637.9	637.3	628.6	626.3	633.8	636.8
$(CH_3)_2C{=}NH_2^+$	594.1	591.4	594.3	594.4	584.7	583.0	590.3	<602.9
E-$CH_3CH{=}NH(CH_3)^+$	636.0	632.7	635.0	636.2	628.7	627.3	632.6	<634.8
$CH_2{=}NH(C_2H_5)^+$	674.0	670.3	672.1	673.9	667.3	665.8	670.6	668.4
$CH_2{=}N(CH_3)_2^+$	673.8	669.2	670.7	673.5	668.2	667.1	670.4	668.0
$(CH_3)_2C{=}NH(CH_3)^+$	571.0	568.0	571.6	572.0	560.4	560.1	567.2	<584.8
E-$CH_3CH{=}NH(C_2H_5)^+$	598.9	596.2	599.6	599.3	588.8	587.8	595.1	<603.5
$CH_3CH{=}N(CH_3)_2^+$	612.6	609.0	611.8	612.1	603.5	602.6	608.6	<617.0

TABLE 5: Difference between Composite Ab Initio and Experimental 298 K Cationic Heats of Formation (kJ mol^{-1})

cation	G3	G2	G2 (MP2)	G3B3	CBS-APNO	W1U	average
$CH_2{=}NH_2^+$	4.1	0.2	0.1	3.4	2.1	−0.3	1.6
$CH_3CH{=}NH_2^+$	2.7	−0.1	1.4	2.4	−3.0	−5.4	−0.3
$CH_2{=}NH(CH_3)^+$	6.5	2.0	2.8	6.0	2.6	0.7	3.4
$C_2H_5CH{=}NH_2^+$	0.8	−1.6	1.1	0.5	−8.2	−10.5	−3.0
$CH_2{=}NH(C_2H_5)^+$	5.6	1.9	3.7	5.5	−1.1	−2.6	2.2
$CH_2{=}N(CH_3)_2^+$	5.8	1.2	2.7	5.5	0.2	−0.9	2.4
mean absolute difference	4.3 ± 2.2	1.2 ± 0.8	2.0 ± 1.3	3.9 ± 2.2	2.9 ± 2.8	3.4 ± 4.0	2.2 ± 1.1

Unfortunately, no other suitable amine precursors were available to be investigated.

***E*-$CH_3CH{=}NH(C_2H_5)^+$.** Like most other H-loss processes studied here, the PIE for diethylamine has a long tail with a poorly defined threshold <9.2 eV. The calculated reverse activation energy of 21 kJ mol^{-1}, plus a competitive effect due to the lower energy methyl loss fragmentation process with $AE_{298} = 8.99 \pm 0.01$ eV, ensures that there will be excess energy at the threshold AE.

Although methyl loss from ionized *N*-ethylisopropylamine has a well-defined AE_{298} of 8.61 ± 0.01 eV with no competitive shift, there is a small calculated reverse activation energy of 9 kJ mol^{-1}, which implies that the derived $\Delta H_{f,298}°[E\text{-}CH_3CH{=}NH(C_2H_5)^+]$ of 603.5 ± 1.5 kJ mol^{-1} shown in Table 2 is almost certainly too high.

$CH_3CH{=}N(CH_3)_2^+$. The PIE for loss of H from ionized *N*,*N*-dimethylethylamine shows a long tail with a poorly defined AE < 9.8 eV. There is also a significant calculated reverse activation energy of 15 kJ mol^{-1}, together with competition from the methyl loss fragmentation process with the much lower AE_{298} of 8.80 ± 0.02 eV.

There is some curvature in the threshold region of the PIE curve for methyl loss from ionized *N*,*N*-dimethylisopropylamine, which increases the uncertainty associated with the AE_{298} of 8.43 ± 0.02 eV. Although there is no competitive shift present, there is a calculated reverse activation energy of 5 kJ mol^{-1}, which would suggest that the derived cationic heat of formation of 617.0 ± 2.2 kJ mol^{-1} given in Table 2 is probably higher than the true thermochemical value.

Calculated Cationic Heats of Formation. The use of ab initio calculations to evaluate gas-phase neutral and ion thermochemistry is now routine. For many small molecules and cations, the agreement between theory and experiment is often better than 1 kJ mol^{-1},[32] particularly when high-level methods are used.[33] However, computational requirements can very quickly become prohibitive for even relatively small species, necessitating the use of less demanding methods.

Validation of different theoretical predictions with experimental measurements requires that such data are available.[32] Unfortunately, this is not always the case.[5] The group of immonium cation heats of formation determined in the present study (Table 3) provides for the first time a set of reliable experimental data for benchmarking a number of commonly used composite ab initio methods available with the Gaussian 03 suite of programs.[16]

Six different methods have been used to determine 298 K cationic heats of formation via the atomization method described by Radom and co-workers.[34] The results for all 11 cations studied here are given in Table 4, from which it can be seen there is general good agreement between theory and experiment. A comparison of the relative accuracy of each method, based on the set of six cations for which thermochemical values were able to be obtained, is given in Table 5. Overall, the best performance is obtained from the G2 method, which produces a mean absolute deviation from experiment of just 1.2 ± 0.8 kJ mol^{-1} and a maximum deviation of 2.0 kJ mol^{-1}. Surprisingly, the nonempirical W1U method, which requires the greatest computing power [e.g., a W1U calculation for the $(CH_3)_2C{=}NH(CH_3)^+$ cation used 232 GB of mass storage and over 234 h of CPU time at the APAC supercomputer facility, as compared to 12 GB of mass storage and just 81 min of computing time for a similar G2 calculation], gives a noticeably poorer agreement. Some of the divergence may be a consequence of limitations in the auxiliary thermochemical data used to derive the experimental cationic heats of formation. Nevertheless, the present results demonstrate that G2 calculations are able to provide reliable results for a range of immonium cations with relatively modest computational demands.

Conclusions

Threshold dissociative PI mass spectrometry has been used to measure the appearance energies for immonium cation formation from 25 alkyl amine precursors. These were combined with a set of neutral amine heats of formation calculated by G3, G3B3, G2, and G2(MP2) composite ab intio methods to derive 298 K cationic heats of formation for 11 different cations. Because of excess energy at threshold for many of the unimolecular fragmentation processes, it is only possible to obtain reliable values for $CH_2{=}NH_2^+$ (749.0 ± 0.9 kJ mol^{-1}), $CH_3CH{=}NH_2^+$ (666.1 ± 1.1 kJ mol^{-1}), $C_2H_5CH{=}NH_2^+$ (636.8 ± 2.5 kJ mol^{-1}), $CH_2{=}NH(CH_3)^+$ (706.1 ± 1.0 kJ mol^{-1}), $CH_2{=}NH(C_2H_5)^+$ (668.4 ± 1.3 kJ mol^{-1}), and $CH_2{=}N(CH_3)_2^+$ (668.0 ± 2.5 kJ mol^{-1}). When these are compared to those calculated by each of the G3, G3B3, G2, G2(MP2), CBS-APNO, and W1U composite ab initio methods, it is found that the smallest mean absolute deviation of 1.2 ± 0.8 kJ mol^{-1} is obtained from the G2 calculations.

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Supporting Information Available: Twenty-four PIE curves (Figures S1−S24) with G2-calculated $H_{298}° - H_0°$ values (Table S1) and calculated 298 K heats of formation (Table S2) and 0 K energies (Table S3) obtained with the 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.

References and Notes

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

(2) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

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

(4) Hammerum, S. *Int. J. Mass Spectrom. Ion Processes* **1998**, *165/166*, 63−69.

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

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

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

(8) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O' Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279−324.

(9) Bodi, A.; Kercher, J. P.; Bond, C.; Meteesatien, P.; Sztáray, B.; Baer, T. *J. Phys. Chem. A* **2006**, *110*, 13425−13433.

(10) Harvey, Z. A.; Traeger, J. C. *Eur. J. Mass Spectrom.* **2004**, *10*, 759−765.

(11) Traeger, J. C.; Harvey, Z. A. *J. Phys. Chem. A* **2006**, *110*, 8542−8547.

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

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

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

(15) 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.

(16) 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 03*, revision D.01; Gaussian, Inc.: Wallingford, CT, 2004.

(17) 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.

(18) Bartmess, J. E. *J. Phys. Chem.* **1994**, *98*, 6420−6424.

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

(20) Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; Thermodynamics Research Center: College Station, TX, 1994.

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

(22) Ruscic, B.; Boggs, J. E.; Burcat, A.; Császár, A. G.; Demaison, J.; Janoschek, R.; Martin, J. M. L.; Morton, M. L.; Rossi, M. J.; Stanton, J. F.; Szalay, P. G.; Westmoreland, P. R.; Zabel, F.; Bérces, T. *J. Phys. Chem. Ref. Data* **2005**, *34*, 573−656.

(23) Tasi, G.; Izsák, R.; Matisz, G.; Császár, A. G.; Kállay, M.; Ruscic, B.; Stanton, J. F. *ChemPhysChem* **2006**, *7*, 1664−1667.

(24) Tang, X.; Hou, Y.; Ng, C. Y. *J. Chem. Phys.* **2005**, *123*, 074330/1−7.

(25) Tschuikow-Roux, E.; Chen, Y. *J. Am. Chem. Soc.* **1989**, *111*, 9030−9031.

(26) Lau, K.-C.; Ng, C. Y. *J. Chem. Phys.* **2006**, *124*, 044323/1−9.

(27) Bodi, A.; Sztáray, B.; Baer, T. *Phys. Chem. Chem. Phys.* **2006**, *8*, 613−623.

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

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

(30) Collin, J. E.; Franskin, M. J. *Bull. Soc. Roy. Sci. Liege* **1966**, *35*, 285−306.

(31) Loguinov, Y.; Takhistov, V. V.; Vatlina, L. P. *Org. Mass Spectrom.* **1981**, *16*, 239−241.

(32) Lau, K.-C.; Ng, C.-Y. *Acc. Chem. Res.* **2006**, *39*, 823−829.

(33) Karton, A.; Rabinovich, E.; Martin, J. M. L.; Ruscic, B. *J. Chem. Phys.* **2006**, *125*, 144108/1−17.

(34) Nicolaides, A.; Rauk, A.; Glukhovstev, M. N.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 17460−17464.