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# Proton Affinities of Simple Amines; Entropies and Enthalpies of Activation and Their Effect on the Kinetic Method for Evaluating Proton Affinities

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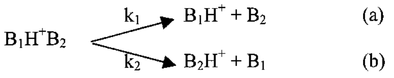
The competing unimolecular dissociations of a variety of proton-bound pairs of amino compounds of formula $R_1NH_2$, $R_1R_2NH$, where $R_1$ and $R_2$ are chiefly alkyl groups $C_1$ to $C_9$, have been investigated by tandem mass spectrometry. Metastable and collision-induced dissociations were studied. The relative product yields, $[B_1H^+]/[B_2H^+]$, from $B_1H^+B_2$ ions ($B_n$ = amine) have been related to the proton affinities (PA) of $B_1$ and $B_2$ by the kinetic method. In its simplest form, the method assumes no entropy effects and a zero reverse energy barrier for the competing dissociations. The general effects expected from nonzero entropies of activation are described in terms of how they influence log(rate constant) vs internal energy plots for such competing dissociations. For these homologous series such effects were observed to be minimal and the kinetic method well reproduces most of the reference PA values. In view of the very close agreement between many reference PA values obtained from equilibrium studies, it is possible that small reverse energy barriers (ca. 5 kJ $mol^{-1}$) may be identifiable by the kinetic method, in particular for $t$-$C_4H_9NH_2$, the homologous di-*n*-alkylamines, and possibly larger barriers for di-*sec*-alkylamines. The method is quite sensitive to small discrepancies in PA, and new values have been proposed for benzylamine, 924 ± 4 kJ $mol^{-1}$, $(CH_3)(n\text{-}C_4H_9)NH$, 951 ± 4 kJ $mol^{-1}$, and $(i\text{-}C_4H_9)_2NH$, 969 ± 4 kJ $mol^{-1}$. Results have also been obtained for some bidentate species, the 1,2-, 1,3-, and 1,4-diaminoethane, propane, and butane, respectively. Particular attention was given to the effects of activation entropies, $\Delta S^{\ddagger}$, and the possible presence of reverse energy barriers, $E_{rev}$, both of which are here a significant problem for the kinetic method. It was found that for 1,2-diaminoethane there was a $\Delta S^{\ddagger}$ effect, particularly for collisionally activated ions. The derived PA of 949 ± 4 kJ $mol^{-1}$ is quite close to the reference value for this compound, 952 ± 4 kJ $mol^{-1}$. It was concluded that for 1,3-diaminopropane (reference PA 987 ± 4 kJ $mol^{-1}$), the method failed due both to an activation entropy effect *and* the presence of a reverse energy barrier. The latter was estimated to be ca. 20 kJ $mol^{-1}$, making ca. 967 kJ $mol^{-1}$ the *apparent* PA resulting from the kinetic method. For 1,4-diaminobutane (reference PA = 1006 ± 4 kJ $mol^{-1}$), here too the kinetic method failed and similar difficulties arose with an estimated reverse energy barrier of ca. 32 kJ $mol^{-1}$. The overall results for these three compounds were compared with a recent report in this journal on low-energy collision-induced fragmentations. These results for species having a bidentate structure indicate that similar difficulties may apply to biomolecules and that PA values obtained by the kinetic method may be flawed.

## Introduction

The "kinetic method" has been used for the estimation of thermochemical data for some 22 years and has often been reviewed.[1] The experiments and their interpretation are deceptively simple but they have been steadily modified as results have accumulated which complicate the simplest approach. The best-known application of the method is for the determination of proton affinity (PA) values. For these to be evaluated, proton-bound dimers, $B_1H^+B_2$, are generated and isolated in a mass spectrometer and the competing reactions (a) and (b) yielding the individual protonated monomers are examined:



$$B_1H^+B_2 \xrightarrow{k_1} B_1H^+ + B_2 \quad \text{(a)}$$

$$B_1H^+B_2 \xrightarrow{k_2} B_2H^+ + B_1 \quad \text{(b)}$$

Upon fragmentation, the monomer having the greater proton affinity should preferentially carry the proton. The reactions are observed as metastable dissociations or induced by collisional excitation at low or high translational kinetic energies.

Canonical transition state theory (which is for species at an equilibrium thermodynamic temperature) has been applied to these systems. The rate constant, $k$, for a reaction is given by the statistical thermodynamics version of the Arrhenius equation:

$$\ln k = \ln Q^{\ddagger}/Q - E°/RT$$

where $Q$ and $Q^{\ddagger}$ are the partition functions for the reactant and the transition state, respectively, $E°$ is the activation energy, $R$ is the ideal gas constant, and $T$ is the temperature. When there are two competing dissociations, the ratio of their respective rate constants, $k_1$ and $k_2$ is given by

$$\ln k_1/k_2 = \ln \mathrm{Q}_1^{\ddagger}/\mathrm{Q}_2^{\ddagger} - (E_1° - E_2°)/RT \qquad (1)$$

In the kinetic method, $k_1$ and $k_2$ are replaced by the respective product ion intensities $[B_1H^+]$ and $[B_2H^+]$, and eq 1 is simplified to permit the evaluation of the difference in proton affinities, $E_2° - E_1° = \mathrm{PA}(B_1) - \mathrm{PA}(B_2)$:

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$$\ln[B_1H^+]/[B_2H^+] = \ln R = \{PA(B_1) - PA(B_2)\}/RT_{eff} \qquad (2)$$

>For eq 2 to apply, the most important assumption is that the proton-bound molecular pairs have internal energy distributions which can be described by an "effective temperature" term, $T_{eff}$. Note that, in general, a system of isolated ions generated or activated in a mass spectrometer cannot be assumed to have a Boltzmann distribution of internal energies, except where special efforts are made to generate thermal equilibria, such as in high-pressure mass spectrometry.

Also, to conform with reaction rate theory, the logarithm term should represent the ratio of the fractions of ions fragmenting that have internal energies from $E_1^\circ \rightarrow \infty$ and $E_2^\circ \rightarrow \infty$, respectively. This presents a problem when studying the dissociations of metastable ions in a sector mass spectrometer, reactions which take place in well-defined but narrow time frames. This has recently been discussed in a related publication.[2]

A third assumption is that neither dissociation involves a reverse energy barrier. This is a priori likely when only simple bond cleavages are involved. Finally, it is assumed that there are no net entropic effects, i.e., $Q_1^\ddagger = Q_2^\ddagger$.

To use eq 2 to obtain a new proton affinity value, reference bases of known PA are required.

For a series of molecules having a common functionality, it has generally been found that a plot of $\ln([B_1H^+]/[B_2H^+])$ vs PA yields a fairly straight line. Thus, from the slope of the plot, a temperature-like term, $T_{eff}$, has been obtained. It has been assumed that this parameter relates to the average internal energy of the ion population. If the ion population is not in thermal equilibrium with its surroundings, such as in an ion beam experiment, or in partial thermal equilibrium, as in the case of high-pressure experiments, the physical interpretation of the parameter obtained from the slope of the plot can be neither straightforward nor certain.

We have also examined metastable and collisionally activated dissociations of proton-bound alkanol pairs,[2] the latter as a function of the target gas and its pressure. Plots of $\ln([R_1OH_2^+]/[R_2OH_2^+]$ vs PA were obtained to estimate new PA values and to investigate the significance of the "effective temperature" term. When the experiments were considered in detail, it was suggested that the kinetic method is essentially a semiempirical relationship, with $T_{eff}$ not relating to a true Boltzmann temperature.

A useful theoretical consideration of kinetic method plots in terms of the significance of their slopes (which relate to the internal energies or "effective temperature" of the fragmenting ions) has recently been made by Erwin.[3] His model is for metastable ions and uses ion source temperature as a parameter. In our earlier study on alkanols[2] we were not able to discern any ion source temperature effect on the behavior of metastable ions.

To date, with few exceptions, the kinetic method has been used to relate a known thermochemical datum (or data) with unknown values, most commonly for proton affinities (PA), where the need for PA values for biomolecules has provided a strong incentive. The lack of systematic studies to examine the kinetic method was well brought home by the three recent "commentary" articles in which the method was critically appraised but without any new data being presented.[1c−e]

We have recently briefly described the results of systematic kinetic method measurements on a series of simple amines[4] whose proton affinity values are established.[5] In this report these results are extended and examined further to include dialkylamines and α,ω-diaminoalkanes. Particular attention has been given to considering activation entropy effects and the problem of reverse activation energy barriers.

## Experimental Section

The proton-bound dimers were generated under chemical ionization conditions in the ion source of our modified triple sector (BEE) VG ZAB-2F mass spectrometer[2] by self-protonation. The metastable and collision-induced dissociations (MI and CID, respectively) of the mass-selected proton-bound dimers were studied in the second field-free region of the instrument. The ion acceleration energy was 8 kV.

The target gas was He (unless otherwise stated). The observed He pressure required to reduce the mass-selected ion flux by ca. 10% (i.e., single-collision conditions) was ca. $8 \times 10^{-8}$ mbar and was used in all these experiments. Note that the product ratios were insensitive to collision gas pressure from $2 \times 10^{-8}$ to $5 \times 10^{-7}$ mbar, showing that the small fraction of multiple collisions at the higher pressure did not effect the results.

Peak heights from the individual scans were used to measure the relative abundances of the fragment ions, the apparatus being set in low energy resolution mode. To separate the CID peaks from MI peaks, a potential of +500 V was applied to the collision cell, shifting the former to higher translational energies. Care was taken to ensure that neither the sign nor the magnitude of the voltage applied to the collision cell had any significant effect on the relative peak abundances. The CID peak heights were corrected for the small MI contribution.[2,6] Kinetic energy release values were measured by established methods.[7]

The ion source pressure was measured externally using an ion gauge. The ion source temperature was normally maintained at 423 ± 5 K and the inlet system was kept at a similar temperature. Compounds of research grade were purchased from Aldrich Chemical Co (Milwaukee, WI) and used without further purification.

Calculations of the log $k$ vs internal energy ($E$) curves were done using the standard RRKM expression, $k(E) = \sigma N^\ddagger/h\rho$ (no rotation effects considered), employing the sums and densities of states calculated via the direct count algorithm of Beyer and Swinehart.[8] The model compound used to generate the curves was the proton-bound methylamine−ethylamine dimer, and the vibrational frequencies were from ab initio calculations.[9] Transition-state frequencies were taken as the dimer frequencies, and the lowest five were scaled by a scaling factor to achieve a desired $\Delta S^\ddagger$. For $\Delta S^\ddagger < 0$, scale factors >1 were used; for $\Delta S^\ddagger > 0$, scale factors < 1 were used.

## Results and Discussion

Before discussing the present results, it is worthwhile to emphasize features of the experiments themselves and also some assumptions used in the first analyses of results.

For an homologous series of molecules, $B_n$, joined in pairs by a proton, it is reasonable to propose that the log $k$ vs $E$ curves for the species' dissociation into the two protonated monomers will be essentially parallel to each other, separated by the difference in their proton affinities. This applies when $\Delta(\Delta S^\ddagger) = 0$, a common assumption when homologous series are being investigated. For the kinetic method to be used to measure the proton affinity of an untested homologue, $B_1$, there are still some more assumptions which need to be considered:

1. That the internal energy distributions of $B_1H^+B_n$ ions dissociating as metastable ions are the same, irrespective of the species, $B_1$ and $B_n$. This appears to be a reasonable assumption

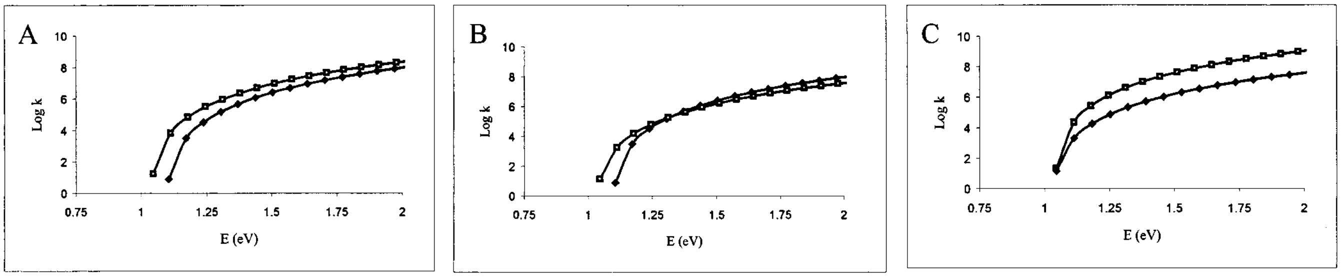

**Figure 1.** Log $k$ vs internal energy ($E$) curves for two competing dissociations. (a) Both dissociations have negligible activation entropies and $\Delta$PA is 7 kJ mol$^{-1}$, (b) $\Delta S^{\ddagger}$ for the dissociations of lower and higher energy are $-16$ and $\sim 0$ J mol$^{-1}$ K$^{-1}$, respectively; $\Delta$PA = 7 kJ mol$^{-1}$ (c) $\Delta S^{\ddagger}$ for dissociations of lower and higher energy are $+14$ and $-16$ J mol$^{-1}$ K$^{-1}$, respectively; $\Delta PA = 1$ kJ mol$^{-1}$.

provided that the distribution of the relevant internal energies is a simple exponential function.[2]

2. That the same criterion (but of course, a different internal energy distribution) applies to $B_1H^+B_n$ ions activated by high translational energy collisions. Note that the criterion of essentially parallel log $k$ vs $E$ curves does not rule out the possibility that the entropies of activation, $\Delta S^{\ddagger}$, are nonzero, but only requires that the entropies of activation for dissociating $B_1H^+B_n$ ions be *the same,* i.e., $\Delta(\Delta S^{\ddagger}) = 0$.

3. That the competing dissociations have no reverse energy barrier. This is a reasonable assumption, especially when the dissociation can be viewed as a simple bond cleavage. If, however, the reverse reaction required a considerable geometry change in either reactant, this assumption may no longer apply. It has been customary to measure the kinetic energy releases associated with each reaction channel. Typically, for metastable $B_1H^+B_n$ ions the $T_{0.5}$ values have been 15−25 meV,[4,11] a range believed to be compatible with the cleavage of a simple covalent bond. Note, however, that this argument may be incorrect; if the bond is largely electrostatic in character and the transition state has no well-defined reaction coordinate (e.g., the $[CH_2\text{-}CH_2OH_2]^{+\bullet}$ ion dissociation by loss of $H_2O$[12]) then the kinetic energy release can be very small indeed, <1meV. If such a metastable ion had a large internal energy content, by for example being accessed via an energy barrier, a larger kinetic energy release would result.

In the ensuing discussion, assumptions 1−3 will initially be taken as correct, but will be modified as and when necessary.

Figure 1a,b illustrates, as an example, the effect of activation entropy on the curvature of calculated log $k$ vs $E$ curves (see Experimental Section) for two competing dissociations with an activation energy difference of 7 kJ mol$^{-1}$. If both dissociations have negligible entropies of activation (Figure 1a), their log $k$ vs $E$ curves are essentially parallel within the MI rate constant range which is from ca. $10^3$ to $10^6$ s$^{-1}$. Note, however, that they do tend slowly to converge at high internal energies. In Figure 1b, the greater curvature of the lower energy dissociation channel's plot arises from the transition state for this dissociation being *tighter* than that for the reaction of higher energy, (i.e., $\Delta\Delta S^{\ddagger}$, the activation entropy difference between the lower and higher energy channels, is negative. This convention is used throughout this work). The curves cross and this intersection in the example shown is at the upper end of the metastable ion time "window". Note that the smaller the activation energy difference between the two competing dissociations (in the present case the difference in PA), the more susceptible the system becomes to such entropic effects (i.e., the more likely the curves will cross). If, however, the transition state for the higher energy process is *looser* than that for the other dissociation channel (Figure 1c), then the curves will diverge. Experimentally, this should result in a CID ratio being greater than the MI ratio.

To illustrate and confirm the effect of very different log $k$ vs $E$ curves for competing reactions, a completely independent and well-studied system was selected. The ionized butylbenzene dissociations, reactions (c) and (d), were recorded in the MI and CID regimes:

$$C_6H_5C_4H_9^{+\bullet} \rightarrow C_7H_8^{+\bullet} + C_3H_6 \tag{c}$$

$$\rightarrow C_7H_7^{+} + C_3H_7^{\bullet} \tag{d}$$

From results of Baer et al.,[13] it is known that for this system the log $k$ vs $E$ curves for reactions (c) and (d) cross at $k \approx 10^{7.5}$ s$^{-1}$ with the activation energy difference $E_d - E_c \approx 60$ kJ mol$^{-1}$ and $\Delta S_d^{\ddagger} - \Delta S_c^{\ddagger} \approx 44$ J mol$^{-1}$ K$^{-1}$. The MI ratio ($k_c/k_d$) was 82 and this inverted, becoming 0.46, in the CID. The CID result was obtained using He, $O_2$, and Xe as target gases and the ratio was target gas independent, as has been found for all our recent kinetic method studies.[2,4,6] Target gas densities were the same for each gas and the pressures were well below single-collision conditions. Corrections for other collision-induced dissociations were minimal at such pressures.

Consider the absolute rate theory representation of the kinetic method, given by the equation

$$\ln k_1/k_n = \ln Q_1^{\ddagger}/Q_n^{\ddagger} + \mathrm{PA}(B_1)/RT_{\mathrm{eff}} - \mathrm{PA}(B_n)/RT_{\mathrm{eff}}$$

$$= \ln R = \ln Q_1^{\ddagger}/Q_n^{\ddagger} + \Delta\mathrm{PA}/RT_{\mathrm{eff}}$$

where $\Delta$PA is the difference between the proton affinity of the unknown, $B_1$, and the standards $B_n$. If there is no net entropy of activation, $Q_1^{\ddagger} = Q_n^{\ddagger}$, then

$$\ln R = \Delta\mathrm{PA}/RT_{\mathrm{eff}}$$

If for all MI dissociations the internal energies of the various fragmenting $B_1H^+B_n$ ions are the same, then a plot of ln $R$ vs PA($B_n$) will produce a straight line. With the same proviso for collision-induced dissociations a second straight line (of different slope) will be generated. These lines should intersect at ln $R$ = 0 and give PA($B_1$) at that point. If $\Delta\Delta S^{\ddagger}$ is not zero, then the intercept of each line on the ln $R$ = 0 axis occurs at an apparent gas-phase basicity value. These, in turn, are internal energy dependent (because a "$T\Delta S$" term is involved), and the intercept values will not therefore be identical for MI and CID plots. The lines will then cross above or below the ln $R$ = 0 axis—above if the $\Delta S^{\ddagger}$ for $B_1$ is greater than zero, and below if $\Delta S^{\ddagger}$ is less than zero, relative to any activation entropy for the standards, $B_n$.

It is important in tandem-sector mass spectrometer experiments that the residual pressure in field-free regions that contain collision cells is indeed so low that essentially only MI dissociations are observed. Two simple experimental tests

**TABLE 1: Proton Affinity Values from the NIST Data Base[5] or As Otherwise Indicated**

| compounds | PA (kJ/mol) NIST′98[a] | compounds | PA (kJ/mol) NIST′98[a] | compounds | PA (kJ/mol) NIST′98[a] |
|---|---|---|---|---|---|
| $CH_3NH_2$ | 899 ± 2 | $n$-$C_6H_{13}NH_2$ | 928 ± 2, 926 ± 4[b] | NH($s$-Pr)$_2$ | 972 ± 2 (968 ± 4[c]) |
| $C_2H_5NH_2$ | 912 ± 2 | $s$-$C_6H_{13}NH_2$ | 936 ± 4[b] | NH($n$-Bu)$_2$ | 968 ± 2 |
| $n$-$C_3H_7NH_2$ | 918 ± 2 | $n$-$C_7H_{15}NH_2$ | 923, 927 ± 4[b] | NH($i$-Bu)$_2$ | 958, 969 ± 4[b] |
| $s$-$C_3H_7NH_2$ | 924 ± 2 | $n$-$C_8H_{17}NH_2$ | 929 | NH($s$-Bu)$_2$ | 981, (976 ± 4[c]) |
| $n$-$C_4H_9NH_2$ | 922 ± 2 | $n$-$C_9H_{19}NH_2$ | 930 ± 4[b] | NH(Pe)$_2$ | 971 ± 4[b] |
| $i$-$C_4H_9NH_2$ | 925 ± 5 | NH(Me)$_2$ | 930 ± 2, 926 ± 4[c] | NH(Hex)$_2$ | 973 ± 4[b] |
| $s$-$C_4H_9NH_2$ | 930 ± 2 | NH(Me)(Et) | 942 ± 2 | $C_6H_5CH_2NH_2$ | 913, 923 ± 4[c] |
| $t$-$C_4H_9NH_2$ | 934 ± 3 (930 ± 4[c]) | NH(Me)($n$-Bu) | 952 ± 4[c] | $NH_2(CH_2)_2NH_2$ | 952 ± 2 (949 ± 4[c]) |
| $n$-$C_5H_{11}NH_2$ | 924 ± 2 | NH(Me)($n$-Pr) | 950 ± 4[c] | $NH_2(CH_2)_3NH_2$ | 987 ± 2 (971 ± 4[c]) |
| $neo$-$C_5H_{11}NH_2$ | 928 ± 2 | NH(Me)($n$-Hex) | 955 ± 4[b] | $NH_2(CH_2)_4NH_2$ | 1006 ± 2 (979 ± 4[c]) |
| $s$-$C_5H_{11}NH_2$ | 933 ± 4[c] | NH(Et)$_2$ | 952 ± 4 | | |
| $t$-$C_5H_{11}NH_2$ | 938 ± 4 | NH($n$-Pr)$_2$ | 962 ± 3 | | |

[a] The uncertainty given for the PA is the spread of the values given in the NIST tables unless otherwise indicated. Note that error limits are not provided therein and even their worst-case values are considered to be only ± 8 kJ mol$^{-1}$. Where no uncertainty is given, NIST quotes only one value. [b] Measured from their position on the ln $R$ vs PA lines in ref 4. Note that these values are all consistent with the PA vs ion size graphs (see text). [c] This work, from the crossover points (see text). Values in parentheses should not be quoted as new PA values because of the possible involvement of the reverse energy barrier, see text for discussion.

deserve emphasis in this part of the paper. The metastable acetyl ion, $[CH_3CO]^+$, loses CO to generate a very narrow Gaussian metastable peak, $T_{0.5} = 1.5$ meV.[14] The dissociation is, however, remarkably collision sensitive and a much broader peak ($T_{0.5} = \sim 20$ meV) is easily seen at very low but not negligible collision gas pressures (see Figure 1 in ref 14). An alternative and equally simple experiment is to observe the $m/z$ 41:$m/z$ 29 ratio for the dissociation of mass-selected $t$-$C_4H_9^+$ ions;[15] if this ratio is ca. 100:1, then it can be safely assumed that residual collision gas-induced dissociations can be neglected.

Although it has been common practice to take $T_{\mathrm{eff}}$ from the slopes of ln $R$ vs PA plots and use them to evaluate "entropies", there are serious problems with such an approach. The quantity $T_{\mathrm{eff}}$ does relate to the internal energy of the fragmenting ions but for metastable ions it is clearly not a temperature in the thermodynamic sense.[2] Note that where $T_{\mathrm{eff}}$ values have been used, the $\Delta(\Delta S^{\ddagger})$ results have been incorrectly ascribed to overall entropy effects,[11,16] i.e., entropies of protonation themselves. For CID ions a similar problem arises. The time frame of the CID observations is governed by the time the ions spend in the collision cell. In our apparatus this is ca. 0.2 μs and so all collisionally activated ions which fragment from time zero (the moment of collision) to 0.2 μs, are monitored. This encompasses a rate constant range upward from ca. $10^6$ s$^{-1}$. The mean rate constant for the ions' dissociation is unknown (other than that it lies in the range ca. $10^6$ to ca. $10^9$ s$^{-1}$, see Figure 1) and their internal energy distribution is also unknown. This precludes the application of absolute rate theory to evaluate $\Delta S^{\ddagger}$, which requires $\Delta H^{\ddagger}$, the enthalpy of activation, the temperature, $T$, and a known rate constant, $k$.

With regard to collisional activation itself, with the isolated CID observations (see Experimental Section) we again have been unable to see a center-of-mass energy effect on ln $R$ with different target gases, from He to Xe. Thus we believe that for ions of the size studied here, their post-collision internal energies are essentially collision gas independent.

**Alkylamines.** In Figure 2 the $\ln(B_1H^+/B_nH^+)$ values are plotted with $C_2H_5NH_2$ as the unknown using NIST[5] data and our earlier reported results[4] for PA values of the partner amines. Table 1 lists all the values relevant to this study. Note that the data in Table 1 are from the NIST database and are derived from equilibrium measurements, unless indicated otherwise. The uncertainty in the NIST values for all the amines used here as reference compounds is quite small and rarely exceeds ±3 kJ mol$^{-1}$. The inversion of the NIST values for $n$-$C_6H_{13}NH_2$ and $n$-$C_7H_{15}NH_2$ is certainly incorrect and in figures where these are required, our revised PA values[4] will be used.

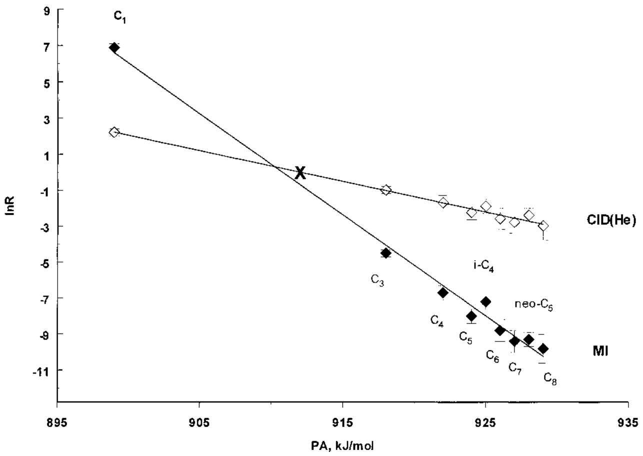

**Figure 2.** Plot of $\ln[C_2H_5NH_3^+/B_nH^+]$ as a function of PA values, where $B_n$ corresponds to a series of $n$-alkylamines. Point **X** is the NIST[5] value, 912 ± 2 kJ mol$^{-1}$ placed at ln $R = 0$. Error bars are those for the $R$ values.

In keeping with the requirement that ln $Q_1^{\ddagger}/Q_n^{\ddagger}$ is zero, the line for the metastable ion results crosses that for the CID observations very near $R = 0$, and gives a PA of 910 ± 4 kJ mol$^{-1}$, within experimental error the same as the reference value for $C_2H_5NH_2$, 912 ± 2 kJ mol$^{-1}$.[5]

Entropies of protonation[5] are closely similar for primary amines and so the above result is perhaps not unexpected, although it should strongly be emphasized that this being a kinetic method, *transition state* rather than product entropies must apply to the observations.

It was reported[4] that for *tert*-butylamine, there was an *inversion* of ln $R$ values for MI and CID observations when the PA of the reference $n$-alkylamine became close to but less than the PA of $t$-$C_4H_9NH_2$, 934 ± 3 kJ mol$^{-1}$ (derived from equilibrium studies[17]). This inversion was *not* reproducible and careful repeat experiments produced the results shown in Figure 3. The lines cross close to ln $R = 0$, eliminating the possibility of an entropy of activation; the derived PA value for *tert*-butylamine, 930 kJ mol$^{-1}$, is slightly but significantly lower than the reference value. Note that for a value of 934 kJ mol$^{-1}$ to be obtained in the present experiment, either all the reference PA values have to be too low by 4 kJ mol$^{-1}$ (e.g., moving the MI line bodily to the right) or some of the reference PA values have to be in error beyond the NIST quoted limits. This seems unlikely given the close fit of the data to a line.

Note that the kinetic data presented thus far give excellent straight lines. Figures 2 and 3 also show the effect of the

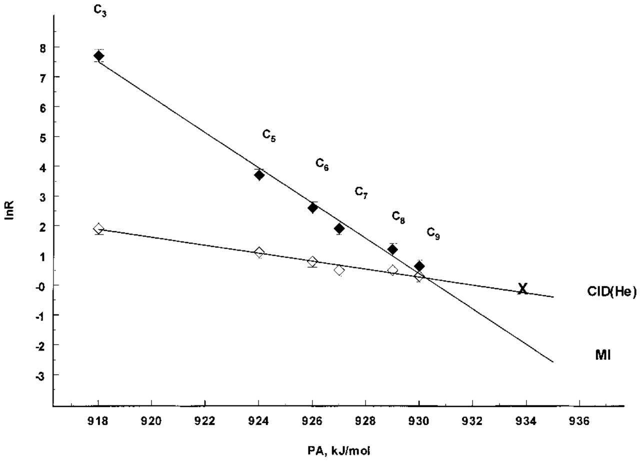

**Figure 3.** Plot of ln[$t$-$C_4H_9NH_3^+$/$B_nH^+$] as a function of PA values, where $B_n$ corresponds to a series of $n$-alkylamines. Point **X** is the NIST[5] value, 934 ± 3 kJ mol$^{-1}$ placed at ln $R = 0$. Error bars are those for the $R$ values.

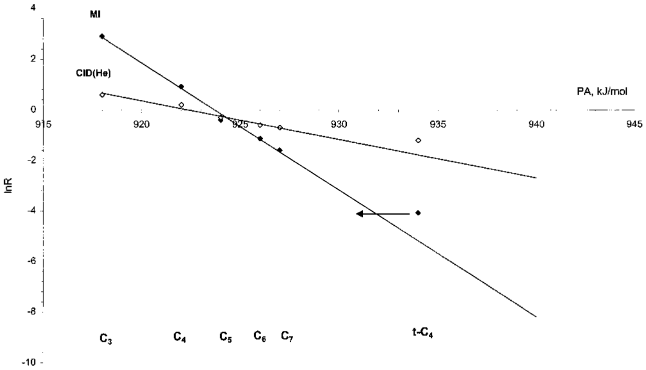

**Figure 4.** Plot of ln[$C_6H_5CH_2NH_3^+$/$B_nH^+$] as a function of PA values, where $B_n$ corresponds to a series of $n$-alkylamines. Arrow denotes new experimental value for $t$-$C_4H_9NH_2$; see text.

uncertainty in ln $R$. The $R$ values were reproducible to within 20% and so the ln $R$ uncertainty was only ≤ ±0.2. This is illustrated in Figure 3 where only direct ratios were involved; in contrast, Figure 2, where the range of $R$ values is huge, as many as four stepwise $R$ values were required giving rise to four times the above uncertainty. It is evident, however, from Figure 2 that this does not significantly affect the position of the crossover point and so the uncertainty in the final PA value (bearing in mind the consistency of the NIST values) is estimated to be no worse than ±4 kJ mol$^{-1}$.

Before leaving the $t$-$C_4H_9NH_2$ result, the effect of a reverse energy barrier in lowering the PA obtained by the kinetic method cannot be ignored. There are fifteen values quoted in ref 5 for this PA, all in close agreement. To force the result in Figure 3 to give a crossover at 934 kJ mol$^{-1}$, all the reference PA values for $C_5$−$C_9$ would have to be too low by up to 4 kJ mol$^{-1}$. We feel that this is unlikely and we propose that the above low value arises from a small reverse energy barrier ($E_{\rm rev}$). This problem will also arise later.

Note that the above graphical approach is not radically different from that adopted by Fenselau et al.,[16] who, however, evaluated a quasi temperature term ($T_{\rm eff}$) from the slopes of such plots. The absolute magnitude of the entropy of activation cannot be evaluated without a knowledge of the internal energies of the fragmenting ions. We have already indicated doubts as to the application of equilibrium thermodynamics to such systems, particularly with regard to metastable dissociations where $T_{\rm eff}$ was shown to not correspond to a thermodynamic temperature.[2]

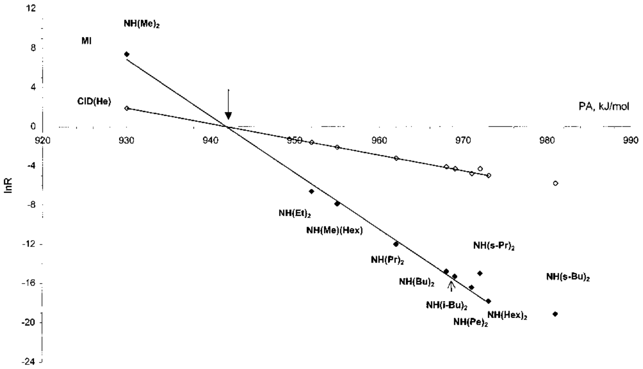

**Figure 5.** Plot of ln[$(CH_3)(CH_3CH_2)NH_2^+$/$B_nH^+$] as a function of PA values, where $B_n$ corresponds to a series of dialkylamines. The arrow shows the NIST[5] value for $(CH_3)(CH_3CH_2)NH$, 942 ± 2 kJ mol$^{-1}$.

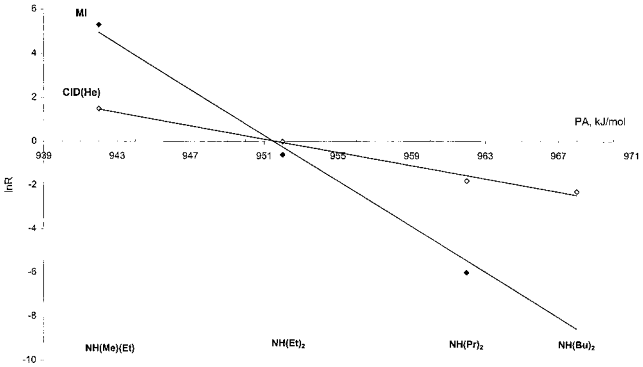

**Figure 6.** Plot of ln[$(CH_3)(C_4H_9)NH_2^+$/$B_nH^+$] as a function of PA values, where $B_n$ corresponds to a series of di-$n$-alkylamines. Note that $(CH_3)(C_3H_7)NH_2^+$ is not included, there being no NIST reference value.

A similar result was obtained for $sec$-propylamine as an unknown. The crossover point was at ln $R = 0$ and the PA thereat, 922 kJ mol$^{-1}$, is within experimental error the same as that given in the reference data (Table 1).

It was useful to extend and replot the data obtained earlier for benzylamine,[4] where the NIST value appeared to be too low by at least 10 kJ mol$^{-1}$. Figure 4 shows the analogous graph for benzylamine vs a series of $n$-alkylamines. The MI and CID lines cross close to ln $R = 0$, giving a PA value for benzylamine of 924 kJ mol$^{-1}$ and indicating, moreover, that there is apparently no significant *net* entropy of activation effect for this phenyl-substituted amine. It is noteworthy that the gas-phase basicity values given in the NIST tables are 879.3, 879.3, and 891.8 kJ mol$^{-1}$; the first two provide the listed PA value, 913 kJ mol$^{-1}$, whereas the latter gives a PA of 926 kJ mol$^{-1}$, in good agreement with the present result. Also shown in Figure 4 are the ln $R$ values when *tert*-butylamine was used as an additional standard. The data points are displaced from the $n$-alkylamine MI and CID lines by the difference between the reference and the new (crossover) PA values, providing support to the suggested $E_{\rm rev}$ for $t$-$C_4H_9NH_2$.

**Dialkylamines.** The kinetic method plots for dialkylamines having established PA values[5] are shown in Figure 5, the reference data are in Table 1, with new (estimated) values for di-$n$-pentylamine, di-$n$-hexylamine, and $(CH_3)(n$-$C_6H_{13})NH$ derived from ln $R$ results. Results for the previously unmeasured $N$-methyl, $n$-butylamine are shown in Figure 6. The MI and CID lines intersect at ln $R = 0$, giving a PA value of 951 ± 4 kJ mol$^{-1}$ for $(CH_3)(n$-$C_4H_9)NH$. Also shown in Figure 5 are the results for di-$sec$-propyl and di-$sec$-butylamines. The ln $R$ values for these di-$sec$-alkylamines, relative to other di-$n$-alkylamines, are not well compatible with their NIST PA values,

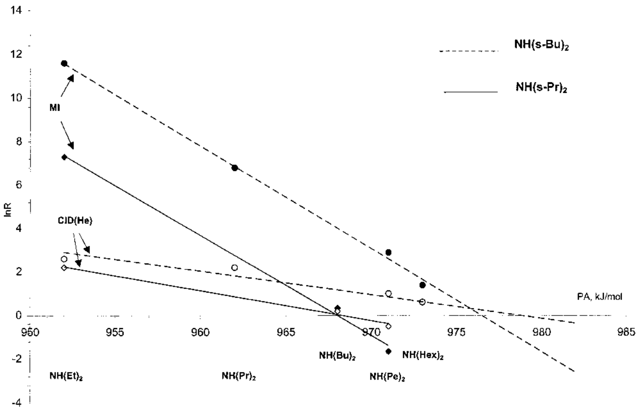

**Figure 7.** Plot of $\ln[(s\text{-}C_3H_7)_2NH_2^+/B_nH^+]$ and $\ln[(s\text{-}C_4H_9)_2NH_2^+/B_nH^+]$ as a function of PA values, where $B_n$ corresponds to a series of di-*n*-alkylamines.

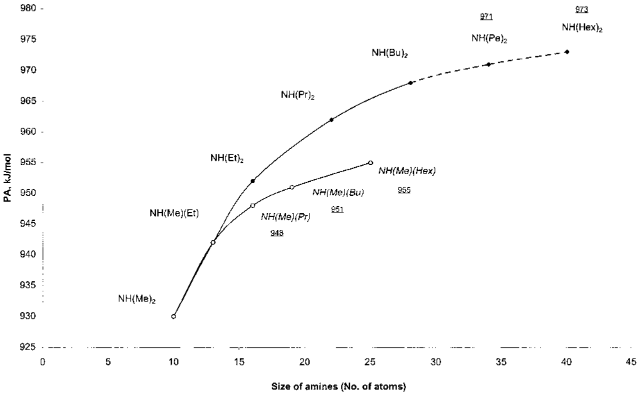

**Figure 8.** PA values of dialkylamines as a function of size; new PA values are shown on the graph.

972 ± 2 and 981 kJ mol$^{-1}$, respectively, which appear to be too high. These di-*sec*-alkylamines were measured as unknowns vs di-*n*-alkylamines and the results are shown in Figure 7. The crossover points are close to $\ln R = 0$ and are at 968 and 976 kJ mol$^{-1}$, respectively, both below the reference PA values. An entropy effect alone would have given a crossover point significantly below or above $\ln R = 0$ but at the reference PA value. These results mirror that for $t\text{-}C_4H_9NH_2$ and we again suggest that for these compounds, too, $E_{rev}$ is not zero but ca. 4−5 kJ mol$^{-1}$.

It is worth noting that the effect of ion size on the proton affinities of the di-*n*-alkylamines in which both substituents increase by a $CH_2$ group produce a smooth asymptotic curve, Figure 8. Also included in this Figure are $(C_5H_{11})_2NH$ and $(C_6H_{13})_2NH$, and these PA values are shown in Figure 5. That these values fall on the PA vs size curve indicates that they are certainly reasonable. Intermediate species with mixed alkyl groups have PA values which depend on the nature of the substituents rather than the size of the ion as a whole. This is also illustrated in Figure 8. Thus, for example, single substitution in $(CH_3)_2NH$ has very close to the same effect as alkyl group change in $CH_3NH_2$, but double substitution has less than twice the effect, e.g., (Table 1) $CH_3NH_2 \rightarrow C_2H_5NH_2$, $\Delta PA = 13$ kJ mol$^{-1}$; $(CH_3)_2NH \rightarrow (C_2H_5)_2NH$, $\Delta PA = 23$ kJ mol$^{-1}$. Now we must consider the $s\text{-}C_3H_7$ and $s\text{-}C_4H_9$ species. From the NIST data, $CH_3NH_2 \rightarrow s\text{-}C_3H_7NH_2$, $\Delta PA = 25$ kJ mol$^{-1}$; $CH_3NH_2 \rightarrow s\text{-}C_4H_9NH_2$, $\Delta PA = 31$ kJ mol$^{-1}$, and $(CH_3)_2NH \rightarrow (s\text{-}C_3H_7)_2NH$, $\Delta PA = 42$ kJ mol$^{-1}$; $(CH_3)_2NH \rightarrow (s\text{-}C_4H_9)_2NH$, $\Delta PA = 51$ kJ mol$^{-1}$, a remarkably consistent series of changes. This consistency is lost if the crossover values are used.

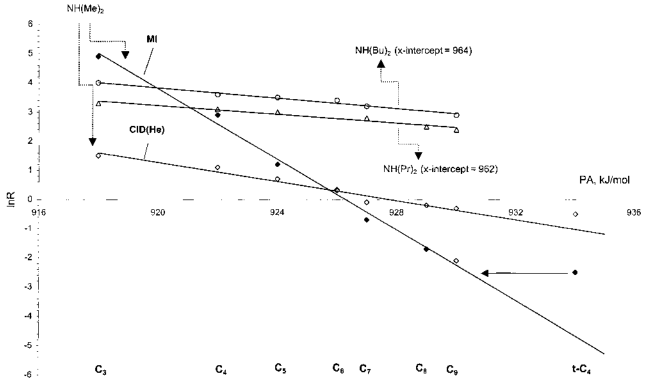

**Figure 9.** Plot of $\ln[(CH_3)_2NH_2^+/B_nH^+]$, $\ln[(n\text{-}Pr)_2NH_2^+/B_nH^+]$, and $\ln[(n\text{-}Bu)_2NH_2^+/B_nH^+]$ as a function of PA, where $B_n$ corresponds to a series of alkylamines. Note that only CID results are shown for (*n*-Pr)$_2$NH and (*n*-Bu)$_2$NH; see text for discussion. Solid arrow denotes new experimental value for $t\text{-}C_4H_9NH_2$; see text.

This circumstantial result lends some support to the proposed $E_{rev}$ effect.

Finally, to search for any activation entropy effects (or reverse energy barrier), selected di-*n*-alkylamines, as unknowns, were run with a series of *n*-alkylamines. The difference in PA values is not too great for $(CH_3)_2NH$, but for the higher homologues chosen, (*n*-Pr)$_2$NH and (*n*-Bu)$_2$NH, only CID observations could be made (MI ratios would exceed 10000 and so be subject to collisional activation by residual gas in the field-free region). The results are shown in Figure 9.

For $(CH_3)_2NH$, the crossover point is close to $\ln R = 0$ giving a PA $(CH_3)_2NH = 926$ kJ mol$^{-1}$. At the reference value for $(CH_3)_2NH$, 930 kJ mol$^{-1}$,[5] nonylamine and *tert*-butylamine are significantly favored as the proton carrier. Note that the above crossover PA value for *tert*-butylamine, 930 kJ mol$^{-1}$, is shown in Figure 9 and is very close to the line, consistent again with the above arguments.

Is the lower PA observed here for $(CH_3)_2NH$ due to an entropy of activation or a small reverse energy barrier for the dissociation in which the dialkylamine retains the proton? The former is unlikely; a $\Delta S^{\ddagger}$ acting against $(CH_3)_2NH$ would lead to a crossover point *below* the *x*-axis at PA = 930 kJ mol$^{-1}$. The wealth and narrow range of data[5] for the PA $(CH_3)_2NH$ again lead us to suggest that for this dialkylamine and its homologues a small $E_{rev}$ affects the kinetic method observations.

For (*n*-Pr)$_2$NH the *extrapolated* CID line intersects the PA axis at the reference value for this amine. The (*n*-Bu)$_2$NH line crosses the axis at 964 kJ mol$^{-1}$, reasonably close to the NIST value, 968 kJ mol$^{-1}$.[5] Considering the long extrapolation involved, a clear identification of an $E_{rev}$ for these species cannot be confirmed.

Thus for all the *n*-alkyl and di-*n*-alkylamines studied here, there are *no* clear effects in their "kinetic method" behavior which can be ascribed to activation entropies. There appears in some cases to be a small reverse energy barrier as considered above.

**Diaminoalkanes.** In a recent study by Siu et al.,[18] low translational energy collision-induced dissociations of $\alpha,\omega$-diaminoethane through pentane were described. In that work, three or four dialkylamines were used as standards. For the ln *R* vs PA(standard) plots, the slope was related to an apparent temperature. However, the "apparent PA" (where the ln *R* vs PA (reference molecule) line crossed the *x*-axis) was plotted against the translational energy of the ions, which typically was varied from ca. 0.6 to 2.5 eV. The intercept at 0 V was proposed to give the true PA value for the diaminoalkane. Calculations

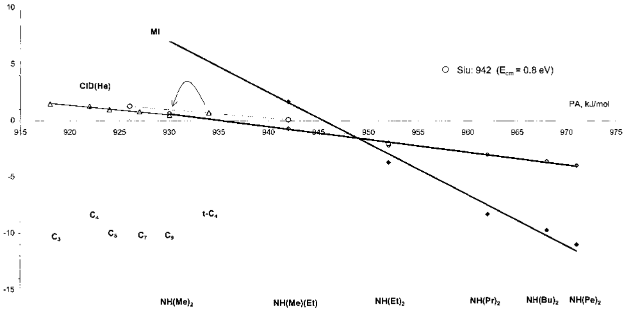

**Figure 10.** Plot of $\ln[H_2N(CH_2)_2NH_3^+/B_nH^+]$ as a function of PA values, where $B_n$ corresponds to series of alkylamines and dialkylamines. Arrow denotes new experimental value for $t$-$C_4H_9NH_2$; see text.

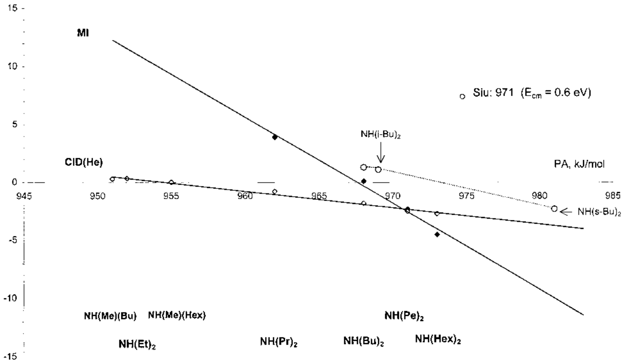

**Figure 11.** Plot of $\ln[H_2N(CH_2)_3NH_3^+/B_nH^+]$ as a function of PA values, where $B_n$ corresponds to a series of dialkylamines.

were also presented, using density functional theory, to describe the energies and equilibrium geometries of the protonated diamines and their adducts with some simple dialkylamines. The above approach sidestepped the problem of using the apparent temperature in the determination of the PA. They did, however, report that when an apparent temperature was extracted from the data and the method of Fenselau et al.[16] was applied, the resulting PA values were always higher than those derived from the apparent PA vs ion energy graphs.

**1,2-Diaminoethane.** The reference PA for this molecule, 952 ± 3 kJ mol$^{-1}$,[5] is sufficiently low that both $n$-alkyl and di-$n$-alkylamines can be used as standards. The results for MI and CID experiments are shown in Figure 10. The crossover point is not on the $x$-axis and the PA thereat, 949 kJ mol$^{-1}$, is close to the reference value. For collision-induced dissociations there appears to be a significant $\Delta S^{\ddagger}$ effect, acting against the diamino compound, giving an apparent $\Delta G^{\ddagger}$ of 935 kJ mol$^{-1}$.

Note too the inversion from positive to negative of ln $R$ for $(CH_3)(C_2H_5)NH$ and for $(C_2H_5)_2NH$, whose PA is the same as that of 1,2-diaminoethane, both ln $R$ values are negative. Note also that the *tert*-butylamine PA of 930 kJ mol$^{-1}$ appears again to be justifiable. If our $E_{\mathrm{rev}}$ argument for the di-$n$-alkylamines is also correct, then the heavy lines in Figure 10 should be moved 4 kJ mol$^{-1}$ to the left. The crossover point moves to 945 kJ mol$^{-1}$ and the intercepts to 941.5 and 931 kJ mol$^{-1}$ for MI and CID observations, respectively. The $\Delta S^{\ddagger}$ effect is unchanged but the crossover PA, 945 kJ mol$^{-1}$, is now 7 kJ mol$^{-1}$ below the NIST value.[5]

Also shown in Figure 10 are data from the work of Siu et al.[18] (open circles); these results were for the lowest translational energy for this diaminoalkane, 0.8 eV. As with their corresponding data at 1.5 and 2.0 eV translational energy, the three points are poorly collinear. The three intercepts for the three energies were 940, 940, and 938 kJ mol$^{-1}$, respectively. Their extrapolated PA value was 942 kJ mol$^{-1}$, and their calculated value was 959 kJ mol$^{-1}$. It is curious that their ln $R$ values are close to our results for high translational energy collisions, implying that the internal energies of the CID ions from the two experimental methods were similar. This however does not hold for the larger diaminoalkanes described below.

The new results here are in keeping with the calculations of Siu et al..[18] In protonated 1,2-diaminoethane, the ion is only weakly bidentate, with a long $-NH_3^+\cdots H_2N-$ bond, 1.87 Å (supplementary data, Siu et al.[18]). From the data presented for protonated 1,4-diaminobutane, coordination with an amino substrate lengthens the above bond from 1.54 to 1.76 Å, relaxing the bidentate structure. Considering the *reverse* reaction for the 1,2 compound, $R_2NH + H_3N^+CH_2CH_2NH_2$, a small activation energy may be required to allow the dialkylamine to achieve the optimum distance from the $-NH_3^+$ group. For the forward reaction, it is clear that the activation entropy for the looser transition state leading to $R_2NH_2^+ + H_2NCH_2CH_2NH_2$ will be greater than that for the proton remaining with the diamine.

**1,3-Diaminopropane.** In the same study, Siu and coworkers[18] reported a PA for this compound of 971 kJ mol$^{-1}$, the translational energy range used was 0.6– 2.0 eV. The NIST PA value for this molecule is 987 ± 2 kJ mol$^{-1}$.[5] Their calculated value was again high, 992 kJ mol$^{-1}$.

A problem which arises in the above study concerns the PA of diisobutylamine, whose PA should (by analogy with the monoamines) be greater than that of di-$n$-butylamine. The NIST values are 958 and 968 kJ mol$^{-1}$,[5] respectively. Accordingly we have measured the ln $R$ values for diisobutylamine against other dialkylamines and the derived PA, 969 ± 4 kJ mol$^{-1}$ shows that the NIST value is indeed too low by ca. 11 kJ mol$^{-1}$ (see also Figure 5 and Table 1). Moreover, this properly reflects the difference between the corresponding simple alkylamines. Replotting Siu's data using the revised PA value for diisobutylamine gives better lines and an extrapolated PA (by their method) of 975 kJ mol$^{-1}$.

Our results for 1,3-diaminopropane are shown in Figure 11. Only dialkylamines could be used as standards, and MI measurements were restricted to only four reference compounds. Note that all standard molecules having PA > 955 kJ mol$^{-1}$ preferentially retain the proton in CID experiments. The crossover point is at 971 kJ mol$^{-1}$, well below the reference value, and although their data do not fall close to our line (see Figure 11) this value is the same as that found by Siu et al.[18]

The new results differ from those for the diaminoethane in that there is a large $\Delta S^{\ddagger}$ effect, for CID ions amounting to a $\Delta G^{\ddagger}$ 31 kJ mol$^{-1}$ below the reference PA; the crossover point, 971 kJ mol$^{-1}$, is also low by 16 kJ mol$^{-1}$.

We propose that these results show the presence of both an activation entropy *and* a reverse activation energy barrier of about 20 kJ mol$^{-1}$, including the $E_{\mathrm{rev}}$ for dialkylamines. The above calculations of Siu et al. show an appreciably shorter $-NH_3^+\cdots NH_2-$ bond in the protonated 1,3 compound than in the 1,2 analogue; 1.65 vs 1.87 Å, respectively, but not as short as for the 1,4 diamine (1.54 Å). Therefore an energy barrier for the reverse reaction is indeed a reasonable proposal.

An additional experiment was performed to seek support for the suggestion that a reverse energy barrier was involved in the 1,3-diaminopropane fragmentations. The kinetic energy release values, $T_{0.5}$, for the Gaussian product ion peaks (from the MI and CID mass spectra) for the competing dissociations of $(C_2H_5)_2NH\cdots H^+\cdots(NH_2CH_2)_2$, ($m/z$ 134 → $m/z$ 61; $m/z$ 134 → $m/z$ 74) and the corresponding observations for $(C_4H_9)_2NH\cdots H^+\cdots H_2N(CH_2)_3NH_2$ ($m/z$ 214 → $m/z$ 75; $m/z$ 214 → $m/z$

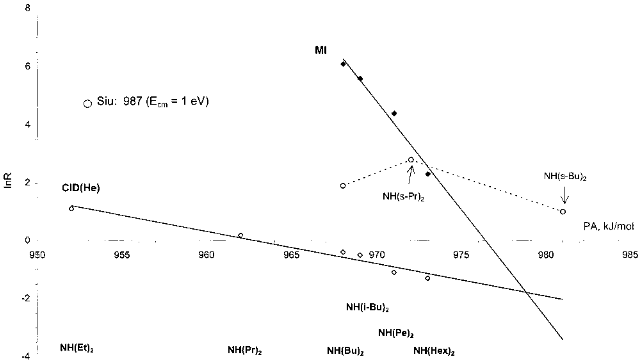

**Figure 12.** Plot of $\ln[H_2N(CH_2)_4NH_3^+/B_nH^+]$ as a function of PA values, where $B_n$ corresponds to a series of dialkylamines.

130) were measured. The MI fragmentations gave $T_{0.5}$ values of 14, 13, 18, and 14 meV and the corresponding CID $T_{0.5}$ results were 39, 30, 28, and 32 meV, respectively. The failure of this test does not, however, negate the proposal; the partitioning of a significant fraction of the (quite small) excess energy in the transition state into translational degrees of freedom of the products may not be occurring here.

**1,4-Diaminobutane.** The kinetic method graph for this compound with dialkylamines as the partner molecules is shown as Figure 12. The MI and CID lines cross below $\ln R = 0$ and the PA thereat, 978 kJ mol$^{-1}$, is far from the reference PA for this diamine, 1006 ± 1 kJ mol$^{-1}$. The lowest translational energy CID data of Siu et al.[18] are also shown; they are not collinear. We propose that much larger $\Delta S^{\ddagger}$ and $E_{\mathrm{rev}}$ effects are operative, the latter may be as great as 32 kJ mol$^{-1}$.

The results from these last three compounds illustrate the chief weaknesses of the kinetic method, which clearly does produce reliable results but *only* when entropies of activation and reverse energy barriers are negligible (as exemplified by the homologous compounds described here). Note that a crossover point at $\ln R = 0$ is *not* a guarantee that the PA thereat is correct. The effect of a reverse energy barrier, which in principle could give too high as well as too low an observed PA, cannot be discounted. That these difficulties arose for molecules having two proton binding groups in fairly close proximity gives cause for alarm as to how these problems will apply to simple biomolecules such as amino acids, where carbonyl and amino groups are both present. Work in this latter area will be presented in a future publication.

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**Supporting Information Available:** Tables for the product ion ratios for metastable and collision-induced dissociations of all the amines studied here are available free of charge via the Internet at http://pubs.acs.org.

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