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The proton affinities of amin-alkanes. A test case for the kinetic method

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Abstract

Metastable ion and collision-induced dissociations of proton bound pairs of *n*-, sec-, and tert-alkyl amines have been studied by tandem mass spectrometry. The logarithms of the product ion ratios were found to be linear functions of the proton affinities (PA) of the amines as expected for the "kinetic method." However, the assumption that transition state entropies were closely similar for all pairs proved to be unjustified. Revised PA values for benzylamine and 2-phenylethylamine were proposed. (Int J Mass Spectrom 195/196 (2000) 525–532) © 2000 Elsevier Science B.V.

Keywords: Kinetic method; Proton affinity (PA); Amines

1. Introduction

The "kinetic method" has been used for the estimation of themochemical 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 over the years as recalcitrant results have accumulated that mar or 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, AH^+B, are generated and isolated in a mass spectrometer and the competing reactions (1) and (2) yielding the individual protonated monomers are investigated:

$$AH^+B \xrightarrow{k_1} AH^+ + B \qquad (1)$$

$$AH^+B \xrightarrow{k_2} BH^+ + A \qquad (2)$$

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.

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

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In appreciation of the scientific legacy of Bob Squires, a colleague who is greatly missed by the gas phase ion chemistry community.

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$$\ln k = \ln \frac{Q^*}{Q} - \frac{E^0}{RT}$$

where Q and Q^* are the partition functions for the reactant and the transition state, respectively, E^0 is the activation energy, R is the ideal gas constant, and T is the temperature. When there are two competing dissociations, their respective rate constants, k_1 and k_2, are given by:

$$\ln \frac{k_1}{k_2} = \ln \frac{Q_1^*}{Q_2^*} - \frac{E_1^0 - E_2^0}{RT} \quad (3)$$

In the kinetic method, k_1 and k_2 are replaced by the respective product ion intensities $[AH^+]$ and $[BH^+]$, and Eq. (3) is simplified to permit the evaluation of the difference in proton affinities, $E_2^0 - E_1^0 = PA_1 - PA_2$:

$$\ln \frac{[AH^+]}{[BH^+]} = \frac{PA_1 - PA_2}{RT_{\text{eff}}} \quad (4)$$

For Eq. (4) to apply, several assumptions are made. The most important is that the proton-bound molecular pairs have internal energy distributions that can be described by an "effective temperature" term, T_{eff}. Note that in general, a system of isolated ions generated 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 $E_1^0 \rightarrow \infty$ and from $E_2^0 \rightarrow \infty$, respectively. This presents a problem when studying the dissociation of metastable ions in a sector mass spectrometer, a point that has recently been addressed in a related publication [2].

The 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 entropic effects, i.e. $Q_1^* = Q_2^*$.

In order to use Eq. (4) to obtain a new proton affinity value, one or more reference bases of known PA is required.

For a series of molecules having a common functionality, it has generally been found that a plot of ln ($[AH^+]/[BH^+]$) versus PA yields a straight line. Thus, from the slope of the plot, a temperature-like term, T_{eff}, can be obtained. It is a common belief 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.

A recent report by McMahon et al. [3] describes a study of alkyl nitrile PA values by high pressure mass spectrometry (equilibrium measurements, ΔG values) and the above kinetic method (using metastable ion observations) in which inter alia the "effective temperature" question was directly addressed. It was concluded that in these experiments the ion source temperature may be related to the "effective temperature," but the inverse dependence observed could not be readily explained. In the interim, we have shown that the nitrile adduct ions in McMahon's work were not metastable but were dissociating as a result of collisional excitation [4].

We have also examined the application of the kinetic method to the proton affinities of the homologous primary alkanols, namely ethanol through *n*-octanol. Both metastable and collisionally activated dissociations of proton-bound alkanol pairs were studied, the latter as a function of the target gas and its pressure. Plots of ln ($[R_1OH_2^+]/[R_2OH_2^+]$) versus PA for both experiments were obtained to estimate new PA values and 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, T_{eff} not relating to a true Boltzmann temperature.

Extension of the study of *n*-alkanols to isomeric species was not feasible because the simple dissociation of such proton bond dimers was often a minor process compared with other reactions, such as olefin elimination.

To date, no other single, thorough investigation of the limitations of the method has been undertaken with that intent alone. The kinetic method has been used almost exclusively to relate a known thermochemical datum (or data) with unknown values, most commonly for proton affinities where the need for PA values for biomolecules has provided a particular incentive. The lack of such studies was well documented in a recent trio of "commentary" articles in which the method was critically appraised but without any new data being presented [1c, d, e].

The present study investigates the dissociations of proton bound pairs of homologous and isomeric alkylamines, for which good reference PA data are available and for which the simple cleavage reaction is always dominant. The dissociation energy of proton bound amines pairs is ~100 kJ mol^{-1} [5]. The limitations of the method were examined with regard to the molecular structure surrounding a given functional group.

2. Experimental

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

The target gas was He (unless otherwise noted). The observed He pressure required to reduce the mass selected ion flux by ~10% (i.e. single collision conditions) was 6×10^{-8} mb.

Peak heights from individual scans were used to measure the relative abundances of the fragment ions. To separate the CID peaks from MI peaks, a potential of −500 V was applied to the collision cell, shifting the former to lower translational energies. The CID peak heights were corrected for the small MI contribution [2,4].

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.

3. Results and discussion

The results are given in Tables 1 and 2 and Fig. 1, where the ln(R) values are plotted against the PA values. The reproducibility of the observations was very good for both the MI and CID results where repeat measurements of AH^+/BH^+ ratios varied typically by less than 10%. For MI experiments, where the ratio was very large, care was taken to ensure that the residual pressure in the second field-free region was observed as $<1 \times 10^{-8}$ mb, thus making residual collision effects negligible. As was found for the aliphatic alcohols and nitriles, the MI ratio was independent of the degree of dissociation of the mass selected ion flux. This dissociation varied from ~2–20% depending on the ion source pressure.

The results will be discussed initially using the following assumptions, discarding or modifying them when necessary. (1) The rate ratio expressed as ln $[AH^+]/[BH^+]$ depends solely on the difference of the proton affinities of A and B, ΔPA. This requires that $\Delta\Delta S^\ddagger$ for the reactions (1) and (2) is zero. (2) Irrespective of the size and nature of the species A and B, the collisional activation by He of AH^+B at a constant target gas pressure, results in ion assemblages having essentially the same internal energy distribution. (3) The proton affinities of the simple amines described in this work are accurately represented by the values given in the NIST tables, to ±4 kJ mol^{-1} or better.

3.1. n-alkylamines

For metastable $[R_1NH_2H^+H_2NR_2]$ ions, where R_1 and R_2 are primary alkyl groups, the ln R plot versus PA values from the NIST database [6] is a satisfactory

Table 1
Product ion ratios for metastable (MI) and collision-induced dissociations (CID) of proton-bound *n*-alkyl amines

		C_1	C_2	n-C_3	n-C_5	n-C_7
R^a: MI	C_2	1000*[c]				
(CID)		(12)				
ln $R^{\#b}$: MI		6.9				
(CID)		(2.5)				
R: MI	n-C_3		91*			
(CID)			(3.6)			
ln $R^{\#}$: *MI*			4.5			
(CID)			(1.3)			
R: MI	n-C_4			9*		
(CID)				(2.7)		
ln $R^{\#}$: MI				6.7		
(CID)				(2.3)		
R: MI	i-C_4			14.7*		
(CID)				(3)		
ln $R^{\#}$: MI				(7.2)		
(CID)				(2.4)		
R: MI	n-C_5			33.5*		
(CID)				(4.8)		
ln $R^{\#}$: MI				8		
(CID)				(2.8)		
R: MI	neo-C_5			126*		
(CID)				(6.6)		
ln $R^{\#}$: MI				9.3		
(CID)				(3.2)		
R: MI	n-C_6			68*	2.2*	
(CID)				(7.1)	(1.6)	
ln $R^{\#}$: MI				8.7	8.8	
(CID)				(3.2)	(3.3)	
R: MI	n-C_7			115*	4*	
(CID)				(10)	(2.4)	
ln R$^{\#}$: MI				9.2	9.4	
(CID)				(3.6)	(3.7)	
R: MI	n-C_8					2*
(CID)						(1.9)
ln $R^{\#}$: MI						10
(CID)						(4.3)
R: MI	n-C_9					2.3*
(CID)						(2)
ln $R^{\#}$: MI						10.2
(CID)						(4.4)

[a] R: relative product ion ratios of the selected proton bound pairs for MI and CID, R is always the ratio of compound in the column to that in the row.

[b] $R^{\#}$: ratios normalized to $[C_2H_5NH_3^+]$.

[c] R^*: ratios quoted for Fig. 1.

straight line (see Fig. 1). It could be argued that the line falls off slightly for the long chain amines, implying an earlier asymptote for the increase of the proton affinity with ion size, however, given the uncertainties in PA values this effect may not be significant. The CID experiments likewise produced a good line wholly compatible with the reference PA values. It would appear therefore that either experiment will produce good PA values for unmeasured primary alkylamines.

The kinetic energy release accompanying the metastable ion dissociation of the proton bound amines was typically ~15 meV, as obtained from the half height width of the energy resolved peak (see Sec. 2). For collisionally excited ions $T_{0.5}$ was ~30 meV, in keeping with these ions having a higher energy content.

As was observed for nitriles and alkanols, the product ion ratio was essentially independent of target gas, He, Ar, O_2, and Xe producing closely similar ratios with a reproducibility of ±10%. The ratios were also independent of target gas pressure at and below the 10% beam reduction levels.

3.2. Sec- and tert-alkylamines

As with ionization energies in analogous series, the PA values for these isomers are significantly larger than for the *n*-alkyl isomers, in keeping with greater charge delocalization resulting from the branched hydrocarbon chain.

The sec- and tert-amine plots were constructed as follows. As anchor points for sec-ions, sec-$C_3H_7NH_2$ was measured against n-$C_4H_9NH_2$ and the other sec-ions were measured relative to sec-$C_3H_7NH_2$. Similarly, t-$C_4H_9NH_2$ was measured relative to n-$C_3H_7NH_2$.

Note that beginning with sec-C_4, in general the ln R values for sec-sec proton bound pairs are larger than for the corresponding sec-n proton bound pairs, and tert-n pairs behave likewise. This may arise from a hidden activation entropy effect; see discussion below.

The MI results (see Tables 1 and 2 and Fig. 1) indicate that within experimental error, the isomeric

Table 2
Product ion ratios for metastable (MI) and collision-induced dissociations (CID) of proton-bound sec-, tert-alkylamines, and other selected amines

		n-C_2	*n*-C_3	*n*-C_4	*n*-C_5	*n*-C_6	*n*-C_7	*n*-C_8	*n*-C_9	*s*-C_3	*s*-C_4	*s*-C_5	*s*-C_6	*t*-C_4	*t*-C_5	CH_2NH_2 
R^a: *MI*				**$1.2{*}^{c}$**	3.6^{-1}	8.1^{-1}	10^{-1}	19^{-1}	30^{-1}							
(CID)	*s*-C_3			**(1.2^{-1})**	(2.4^{-1})	(4.9^{-1})	(6.8^{-1})	(10.5^{-1})	(16.5^{-1})							
ln $R^{\#b}$: MI				**6.9**	6.7	6.7	7	7	6.8							
(CID)				**(2.1)**	(1.9)	(1.7)	(1.8)	(1.9)	(1.6)							
R: MI					5.8	2.4	**1.3**			32*						
(CID)	*s*-C_4				(1.5)	(1)	**(1.7^{-1})**			(3.4)						
ln $R^{\#}$: MI					9.8	9.7	**9.6**			10.4						
(CID)					(3.2)	(3.3)	**(3.2)**			(3.3)						
R: MI						8.8	4.2				5.6*					
(CID)	*s*-C_5					(2)	(1.3)				(2.3)					
ln $R^{\#}$: MI						11	10.7				12.1					
(CID)						(4)	(4)				(4.1)					
R: MI					50.5		14.4	9.2	4.9			3.2*				
(CID)	*s*-C_6				(4.8)		(2.4)	(2)	(1.3)			(1.8)				
ln $R^{\#}$: MI					11.9		12	12.2	11.8			13.3				
(CID)					(4.4)		(4.6)	(5)	(4.7)			(4.7)				
R: MI			2229*		36.6	13.7	**7**	**3.2**	**1.5**	199		1				
(CID)	*t*-C_4		(10.2)		(2)	(1.2)	**(1.2^{-1})**	**(1.9^{-1})**	**(2.1^{-1})**	(16.9)		**(1.4^{-1})**				
ln $R^{\#}$: MI			12.2		11.6	11.4	**11.2**	**11.2**	**10.6**	12.2		12.2				
(CID)			(3.6)		(3.5)	(3.5)	**(3.5)**	**(3.7)**	**(3.7)**	(4.9)		**(3.6)**				
R: MI								39*	23*					20.9*		
(CID)	*t*-C_5							(2)	(1.6)					(3.6)		
ln $R^{\#}$: MI								13.7	13.3					15.2		
(CID)								(5)	(4.9)					(4.9)		
R: MI	CH_2NH_2			2.5*	1.5^{-1}*					2.3*		43^{-1}*		59^{-1}*		
(CID)				(2.4)	(1.1^{-1})					(2.9)		(2.7^{-1})		(2.2^{-1})		
ln $R^{\#}$: MI				7.6	7.6					7.7		8.3		8.1		
(CID)				(3.1)	(2.8)					(3.2)		(3.1)		(2.8)		
R: MI	$CH_2CH_2NH_2$						7.5*		**$3{*}$**				1.6^{-1}*	4.3*		56*
(CID)							(1.6)		**(1.2^{-1})**				(1.7^{-1})	(4.4)		(3.1)
ln $R^{\#}$: MI							11.3		**11.3**				12.8	13.7		11.9
(CID)							(4.2)		**(4.2)**				(4.2)	(5.1)		(4.2)
R: MI		2.6^{-1}*		1285^{-1}*												
(CID)	$CH_2 = CHCH_2NH_2$	(1.6)		(24.5^{-1})												
ln $R^{\#}$: MI		−1		−0.5												
(CID)		(0.5)		(−0.9)												
R: MI					14.7*		**$2.1{*}$**									16.8*
(CID)					(2.2)		**(1.2^{-1})**									(1.6)
ln $R^{\#}$: MI					10.7		**10**									10.7
(CID)					(3.6)		**(3.5)**									(3.5)

[a] *R*: relative product ion ratios of the selected proton bound pairs for MI and CID; *R* is always the ratio of compound in the column to that in the row.

[b] $R^{\#}$: ratios normalized to $[C_2H_5NH_3^+]$; R^*: ratios quoted for Fig. 1.

[c] **R**: the inversion ratios (see text).

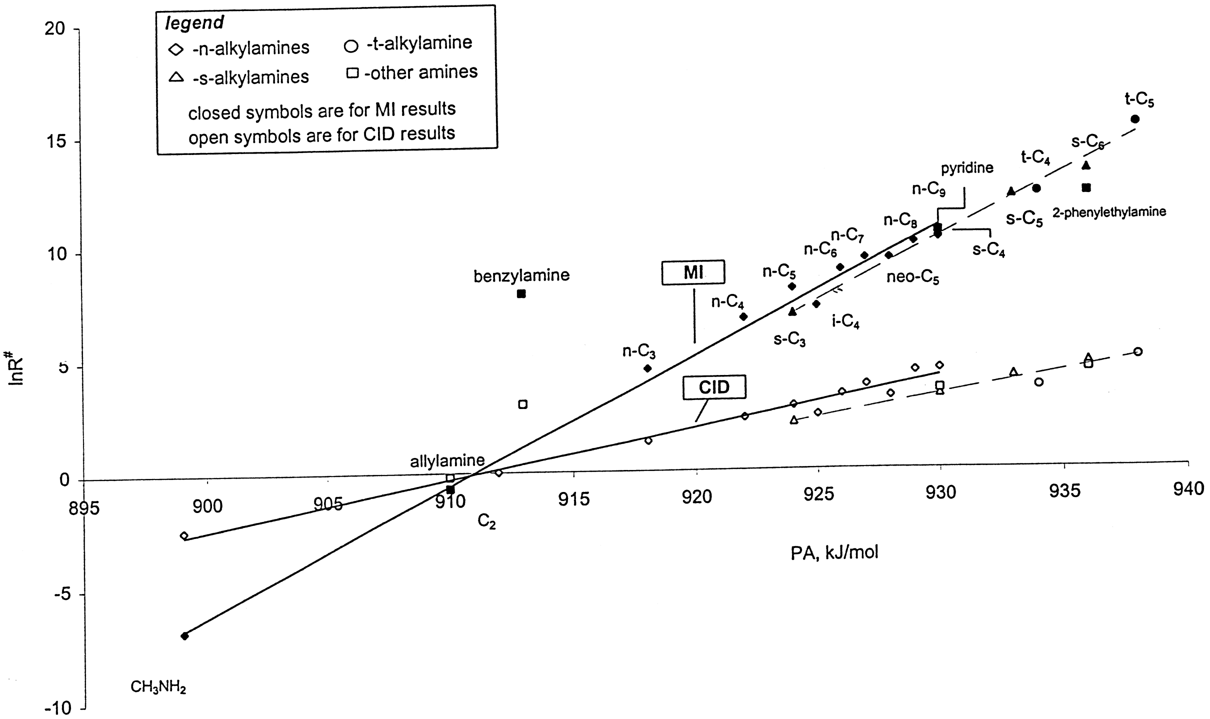

Fig. 1. Proton affinity measurement of amines by the kinetic method (MI: $T_{\text{eff}} = 212$ K; CID: $T_{\text{eff}} = 548$ K).

amines can be made to lie on a single line with a PA uncertainty of no more than ±2 kJ mol^{-1}.

In marked contrast, the CID plot, with its shallower slope, leads to a much greater uncertainty in PA values, about ±5 kJ mol^{-1}. However, this shortcoming of the graph and accompanying error estimate is outweighed by the R ratio inversions in going from MI to CID measurements; these are marked boldface in Table 2. The inversion of an R ratio implies an inversion of proton affinities and so is incompatible with the simple assumptions of the kinetic method.

Metastable ions dissociate in a limited timeframe, typically 2–20 μs and thus encompass first-order rate constants (k) of a limited range, ~10^3–10^6 s^{-1}. Their internal energy content above the dissociation limit, $E^{\neq}$, is generally low, on the order of 0.5 eV or less. Following collisional excitation however, the timescale for ion dissociation becomes 0 to ~20 μs and k values extend from ~10^3 to $>10^{13}$ s^{-1} and significantly higher internal energies are accessed. Clearly, in spite of uncertainties as to the magnitude of ion internal energies, the MI experiments must yield the more accurate results.

In terms of unimolecular reaction dynamics, rate–ratio inversions for MI and CID observations will arise if the ln k versus $E^{\neq}$ curves for reactions (1) and (2) are not parallel but cross each other such that the higher energy channel becomes favored at high internal energies.

Note that the entropies of protonation of primary amines [6] are all negative and closely similar in magnitude: -5 to -6 J mol^{-1} K^{-1}. Reactions (1) and (2) will thus involve little or no net entropy effect, i.e. $\Delta S_2 - \Delta S_1 \approx 0$. However, the kinetic method is not an equilibrium study and so only transition state entropies are relevant. For the ln k versus $E^{\neq}$ curves to cross, it is necessary that the "tightness" ($\Delta S^{\neq} < 0$) or "looseness" ($\Delta S^{\neq} > 0$) of the transition states be responsible for the curvatures in the ln k versus $E^{\neq}$ plots that lead to curve crossing (for example, the results of Baer et al. [7] on the bromobenzene ion dissociation, which nicely illustrates the effect on the

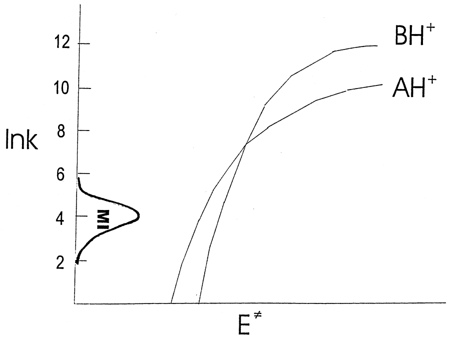

Fig. 2. Schematic of crossing ln k vs. $E^{\neq}$ curves for the Reaction $AH^+B \rightarrow AH^+ + B \rightarrow BH^+ + B$ where A has the higher PA. The area MI designates the metastable window.

ln k versus $E^{\neq}$ curves of varying $\Delta S^{\neq}$ from $+ve$ to 0 to $-ve$). For the proton bound amines reported here, the higher energy dissociation must be associated with $\Delta S^{\neq}$ values of larger magnitude, $\Delta S_2^{\neq} - \Delta S_1^{\neq} > 0$, i.e. it is entropically favored at high internal energies (Fig. 2). This seems to be the case in the present work, because CID results have not displayed any inverse effect, i.e. k_1/k_2 values larger than the MI ratios. It is disquieting, however, to realize that this entropic effect is only made evident by the inversion of k_1/k_2 values. This problem has similarly been addressed in the discussion of the kinetic method in a recent article by Armentrout [1c], in which earlier results of low energy collision-induced dissociations of alcohol pairs attached to Li^+ ions were described.

It is evident that transition state entropies cannot be neglected for even such simple systems as those studied here. There is a priori no reason to assume that the ln k versus $E^{\neq}$ curves for these and similar proton bound pairs are parallel, but without an experimental observation such as k_1/k_2 inversion, no firm conclusion can be drawn. Again, as in previous studies [2,4], different collision gases did not produce significantly different product ratios when the collision events were experimentally separated from MI dissociations and corrected for minor MI contributions. The results of Wesdemiotis et al. [8] on somewhat larger molecules show such an effect, but with data uncorrected for MI contributions. It is noteworthy that their results on entropy effects are reported as absolute entropies, even though the method can only lead to entropies of activation.

Further analysis of the present results will be described elsewhere.

3.3. Other selected amines

When averaged ln R values are used, allylamine and pyridine appear to fit the primary amines' line (Fig. 1) very well; the aromatic amines, benzylamine, and 2-phenylethylamine are less satisfactory. If these molecules are to fit the line for *n*-alkylamines, then the PA values for benzylamine need considerable revision upwards, from 913 kJ mol^{-1} to ~924 kJ mol^{-1}; 2-phenylethylamine may be too high, but only by ~5 kJ mol^{-1}.

In summary, the kinetic method has been successfully applied to simple proton bound amine pairs of formula $R_1NH_2H^+H_2NR_2$, insofar as the plots of ln AH^+/BH^+ versus PA were linear for both metastable ion and collision-induced dissociations. These monoamine results clustered around a single line, although it could be argued that sec- and tert-alkylamines produced a parallel, second line (see Fig. 1). In spite of the structural simplicity of the molecules involved in this study, it was apparent that transition state entropies could not be neglected; the ln k versus $E^{\neq}$ plots for some pairs must cross, making the higher energy dissociation favored at high internal energies.

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