

Relationship between effective temperature of thermalized ions and ion source temperature

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Abstract

The spontaneous dissociation of mixed proton bound dimers of nitrile bases has been studied using mass-analyzed ion kinetic energy spectra in a reverse geometry double focusing instrument coupled to a high pressure ion source. A linear correlation was found between the relative ion abundance ratios of the fragments and the ion source temperature. Proton exchange equilibria between the bases were studied using the time resolved capability of the high pressure mass spectrometry system, and relative ΔG° , ΔH° , and ΔS° values were extracted from the van't Hoff plots. The proton affinities (PA) of the nitriles studied were found to be $PA(\text{MeCN}) = 186.8$ kcal/mol, $PA(\text{EtCN}) = 189.9$ kcal/mol, $PA(\text{n-PrCN}) = 191.0$ kcal/mol, and $PA(\text{i-PrCN}) = 192.2$ kcal/mol. The effective temperatures of the metastable protonated nitrile dimers at different ion source temperatures were obtained from a plot of $\ln(I_{\text{RCN}}/I_{\text{ref}})$ versus ΔGB (relative gas phase basicity). From a plot of the effective temperature of the protonated metastable nitrile dimers reacting in the second field free region of the mass spectrometer versus the ion source temperature, it was found that the effective temperature decreases with increasing ion source temperature, which can be explained from qualitative considerations of the relevant thermal Boltzmann distributions. (Int J Mass Spectrom 176 (1998) 87–97) © 1998 Elsevier Science B.V.

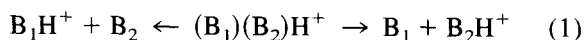
Keywords: Kinetic method; Effective temperature; Thermochemistry; Metastable ions; Nitriles

1. Introduction

1.1. Kinetic method

The kinetic method, originally introduced by Cooks et al. [1–3], has been used in a variety of novel ways. One of the most common applications has been the determination of relative gas phase proton affinities. When a proton bound dimer between two bases is formed and selectively isolated in the mass spectrometer, the collisionally activated or spontaneous disso-

ciation, Eq. (1), results in a distribution of both protonated monomers.



If it is assumed that no alternative reaction channel exists, then the unimolecular rate constant, k , for each reaction channel can be expressed [4] as

$$k = \frac{RT_{\text{eff}}Q^*}{hQ} e^{-\epsilon_d/RT_{\text{eff}}} \quad (2)$$

where R is the gas constant, h is Planck's constant, Q is the partition function for the ion, Q^* is the partition

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function for the activated complex, ϵ_o is the activation energy, and T_{eff} is the effective (nonequilibrium) temperature.

The probability of a reaction proceeding via a particular reaction channel depends on the rate of the reaction and thereby determines the relative abundance of the fragment ions [5]. Reaction rates depend on the internal energy content of the decomposing precursor ion [5], a quantity that is difficult to determine.

If the decomposing ion population is in thermal equilibrium with the environment (i.e. other ions, molecules, and the surroundings), the internal energy is defined by a temperature, which may define a mean value for the internal energy. Besides this, the temperature also describes the distribution of internal energies, the so-called Boltzmann distribution.

For a nonthermalized population of ions, the internal energy will be dependent on the ionization process and will typically not be in equilibrium with the environment. The internal energy is therefore not described by a real temperature, and the internal energy distribution cannot be described by a Boltzmann distribution. The mean value of the internal energy for a nonthermalized population of ions can be considered to be the effective internal energy. The effective internal energy is related to the effective temperature. Vékey [5] defines the effective temperature as a fictitious value that, when using equations developed for the case of thermal equilibrium, would describe the behaviour of ions with a nonthermal internal energy distribution and under nonequilibrium conditions. The effective temperature defines the effective rate constant, k_{eff} [5]:

$$k_{\text{eff}} = A e^{-\epsilon_o/kT_{\text{eff}}} \quad (3)$$

where A is a preexponential factor, ϵ_o , the activation energy, and T_{eff} , the effective temperature. This is a useful approximation.

For the competing reactions in Eq. (1), Eq. (4) can be written:

$$\ln\left(\frac{k_1}{k_2}\right) = \ln\left(\frac{Q_1^*Q_2}{Q_2^*Q_1}\right) + \frac{\Delta\epsilon_o}{RT_{\text{eff}}} \quad (4)$$

Because both product ions originate from the same reactant (the proton bound dimer), $Q_1 = Q_2$. The major difference in geometry between the activated complex $[B_1H^+ \cdots B_2]$ and $[B_1 \cdots B_2H^+]$ is in the hydrogen bond. Therefore, $Q_1^*/Q_2^* \approx \nu_1/\nu_2$, where ν_1 and ν_2 are the vibrational frequencies in the hydrogen bonds. If ν_1 and ν_2 are assumed to be equal, and if it is assumed that the frequency factors and the densities of rotational and vibrational states associated with either dissociation reaction do not differ significantly, it can be approximated that the difference in activation energy is equal to the difference in free energy. When Eq. (1) applies, the peak heights of B_1H^+ and B_2H^+ in the mass-analysed ion kinetic energy spectrum (MIKES) [6] of $(B_1)(B_2)H^+$ are determined by the rates of dissociation, k_1 and k_2 , and thus $k_1/k_2 = [B_1H^+]/[B_2H^+]$, provided the primary fragment ions do not dissociate further. Eq. (5) can now be written:

$$\ln\left(\frac{[B_1H^+]}{[B_2H^+]}\right) \approx \frac{-\Delta\Delta G^\circ}{RT_{\text{eff}}} \quad (5)$$

Because gas phase basicity (GB) $\equiv -\Delta G^\circ$ (for $B + H^+ \rightarrow BH^+$), Eq. (5) can be written as:

$$\ln\left(\frac{[B_1H^+]}{[B_2H^+]}\right) \approx \frac{\Delta GB}{RT_{\text{eff}}} \quad (6)$$

Assuming that $\Delta S \approx 0$ and because proton affinity (PA) $\equiv -\Delta H^\circ$ (for $B + H^+ \rightarrow BH^+$), Eq. (6) can be written as:

$$\ln\left(\frac{[B_1H^+]}{[B_2H^+]}\right) \approx \frac{\Delta PA}{RT_{\text{eff}}} \quad (7)$$

In summary, in the absence of entropy effects and assuming that the reverse activation energies are negligible, the relative abundances of the fragment ions, B_1H^+ and B_2H^+ , reflect the differences in proton affinities of B_1 and B_2 . To obtain the absolute proton affinity, a reference base with known proton affinity is needed.

Besides estimating proton affinities [1,2,7-13], the kinetic method has been used to estimate ionization energies of metal clusters [14], electron affinities [15], silver ion affinities [16], and metal and alkali metal

affinities [17–21]. Furthermore, the method has been used to examine the gas phase basicities or gas phase acidities of alcohols [22–24], alkylcarboxylic acids [2,22,25], nucleic acids [26], alkylamines [1,2,7], anilines [2], and pyridines [1,2,27].

Although many successful applications of the kinetic method have been reported that clearly illustrate the usefulness of the method, especially for compounds with low vapour pressure for which equilibrium measurements are difficult, it is nevertheless true that the applicability is restricted to special circumstances. The basis for and limitations of the kinetic method are still being elucidated because the method makes some rather demanding assumptions regarding several of the factors controlling the dissociation kinetics and, as a result, should ideally only be used in cases where alternatives do not exist [23].

The use of the kinetic method appears to be best justified when further fragmentation of the primary fragments from the dissociation of the protonated dimer is negligible, unless the further fragmentation is of the same proportion for both ions [2,28].

The frequency factors for dissociation of the two bases in the proton bound dimer should be very similar; that is, the dimer should consist of chemically similar species of the same functionality, and the hydrogen bond strengths should be similar and very weak compared with a covalent bond [2] (it should be emphasized that these are not absolute limitations). If this is so, we can expect the proton affinities of the two bases to be similar, which is important because bases with relatively large proton affinity differences cannot be compared accurately in a single experiment [2]. If ΔPA is too large, the spectra of such dimers either show only one peak, corresponding to the stronger base, or exhibit abundance ratios that are too large to be accurately determined.

The structure of the base should not change on protonation. If it does we can expect a barrier corresponding to the change of conformation, which would result in ΔPA (or ΔGB) $\neq -\Delta\epsilon_0$. If B_1H^+ and B_2H^+ have approximately the same structure, there should be no reverse activation energy and ΔPA (or ΔGB) $\approx -\Delta\epsilon_0$ [2].

With more than one functional group there is a

possibility of competitive protonation on different sites of the base and a possibility of intramolecular hydrogen bonding, which is known to increase proton affinities, decrease ΔS° , and thereby decrease the free energy change (ΔG°) [12,13]. It is thus appropriate to include the limitation that the base should only contain one functional group. In some special cases it has been possible to determine thermochemical properties for polyfunctional molecules such as amino acids [8,29,30], peptides [13,31–35], nucleosides, and nucleobases [26,36]. Furthermore, it has been shown by Hoke et al. [37] that “local” affinities, that is proton affinities for particular functional groups in complex polyfunctional molecules, can be measured.

It has been shown using alkoxides as the bases [24] that besides the fact that the two bases should have the same functionality, in the present example ROH they should not be different types of alkoxides (i.e. the proton bound dimer should consist of two primary alkoxides or two secondary alkoxides and so on). In the case in which the two bases are of the same functionality but differ in the type of base, the frequency factors will be different and not separable from the activation energy as required by the approximate Eqs. (4 to 7). This seems to be a very stringent condition that may, in fact, not be necessary.

The assumptions made for the kinetic method are not justified for very polar compounds [10]. It is usually assumed that $[\text{B}_1\text{H}^+ \cdots \text{B}_2]$ and $[\text{B}_1 \cdots {}^+\text{HB}_2]$ are separated by either no energy barrier or by only a small energy barrier without any effect on the rates of the dissociation, but if the proton bound dimer consists of a base with a very high dipole moment (like an amide) and a base with a considerably lower dipole moment, the ion–dipole interaction between the cation and the neutral highly polar base could become so large that even though the proton is attached to the less basic component, this may be energetically favoured, especially at low energy where the dissociation rates are slow and the dissociation is dominated by a reaction via the energetically most favoured reaction channel [10].

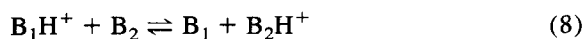
The kinetic method is not justified for systems that may produce covalently bound dimers that are isomeric with the electrostatically proton bound dimers

[38–42]. This is the case for the benzylacetate dimer, which has been shown to be covalently bound [41,43]. The appearance of alternate fragmentations is often an indication of a covalently bonded dimer structure.

If a sector instrument is used and the fragmentation is collision induced when using the kinetic method, it is desirable to use as low a collision energy as possible because of the mass discrimination in the collision cell. The extent of mass discrimination is determined by the instrument and the system studied. Another reason for using low internal energies, and hence low collision energies, is that this maximizes the ratio of the competing fragment ion abundances and makes the method more sensitive to small affinity differences. Therefore, when using the kinetic method, especially for proton affinity determinations, it is preferable to use a low collision energy or none at all (spontaneous dissociation). The fraction of each protonated base produced using collisional activation (CA) is dependent on the basicity of the bases, the collisional energy, and the target gas thickness [12,13,25,28].

1.2. Equilibrium method

One of the most common accurately quantitative methods to determine gas phase basicities and proton affinities is the equilibrium method [44] in which proton exchange occurs between two bases, Eq. (8), and the relative abundances of the protonated species are measured:



From the relative abundances of the two protonated bases at equilibrium and the partial pressure, P , for each of the two neutral bases, the equilibrium constant, K_{eq} , can be determined, Eq. (9):

$$K_{eq} = \frac{[B_2H^+]P_{B_1}}{[B_1H^+]P_{B_2}} \quad (9)$$

$$\Delta G^\circ = -RT \ln K_{eq} \quad (10)$$

$$\ln K_{eq} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

The free energy change, ΔG° , can now be derived from Eq. (10), and if the equilibrium constant is examined over a wide temperature range, both ΔH° and ΔS° may be derived from plotting $\ln K_{eq}$ versus $1/T$ (van't Hoff plot), Eq. (11). The reaction enthalpy for the equilibrium in Eq. (8) reflects the difference in proton affinity, ΔPA , and the free energy for the equilibrium reflects the difference in gas phase basicity, ΔGB , between the two neutral bases. To get the absolute proton affinity and the absolute gas phase basicity a reference base with known proton affinity or gas phase basicity is needed.

This method is restricted to volatile pure compounds of similar proton affinity, because bases with relatively large proton affinity differences cannot be compared accurately in a single experiment, as is also the case when using the kinetic method.

In the present work it has been our intention to investigate the equilibrium constant, K_{eq} , at various ion source temperatures for the proton exchange reactions between propionitrile and acetonitrile and isobutyronitrile and butyronitrile by using the equilibrium method to extract ΔG° (ΔGB), ΔH° (ΔPA), and ΔS° values from the van't Hoff plots. The spontaneous dissociation of the mixed metastable proton bound dimers can then be investigated using the kinetic method together with these accurate relative gas phase basicities, obtained from the equilibrium method, to measure the effective temperatures of the proton bound dimer reactions in the second field free region in the mass spectrometer (metastable ions). By varying the ion source temperature it is thereby possible to monitor the effect on the effective temperature of the dimers reacting in the second field free region. The results of this investigation are reported herein.

2. Experimental

The measurements were made with a pulsed ionization, high pressure mass spectrometer constructed at the University of Waterloo, configured around a VG70-70 mass spectrometer whose configuration was changed from an E-B to a B-E instrument. The

apparatus and its capabilities have been described in detail previously [45].

2.1. MIKES measurements

Gas mixtures were prepared in a temperature controlled, 5-L stainless steel reservoir using methane as the high pressure bath gas and that served as the inert third body stabilization species to a pressure of 1200–1300 Torr. Other components of the mixture were present at pressures <4 Torr. The gas mixture was bled into the ion source through a heated stainless steel inlet line to a pressure of ~12 Torr. Ionization was accomplished by a beam of 2 keV electrons focused into the ion source through a 150- μm aperture. The ions diffuse out of the ion source through a 150- μm aperture into the source chamber where the pressure is 50 μTorr . The ions are then accelerated toward the first cone with a 50 V potential, where they enter the ion optics region and are accelerated up to 2.9 keV. Mass-selected ions were analysed with a 70-degree (20-cm) electrical sector, allowing the parent ions to pass at 232 V. The signal was monitored by a PC-based multichannel scaler signal acquisition system configured at a 3-ms dwell time per channel. A total of 1000 channels were acquired and 500 scans were accumulated. Representative data are shown in Fig. 1 for the spontaneous dissociation of the protonated metastable dimer between butyronitrile and propionitrile.

2.2. ΔG° , ΔH° , and ΔS° measurements

Gas mixtures were prepared in the same way using methane as the high pressure bath gas to a pressure of 900–1200 Torr. Other components of the mixture were present at pressures <1 Torr. The gas mixture was bled into the ion source to a pressure of 8 Torr. Ionization was accomplished by a 10- μs pulse of 2 keV electrons. Mass-selected ion temporal profiles were monitored by the same PC-based multichannel scaler signal acquisition system configured at a 50- μs dwell time per channel. A total of 250 channels were acquired by using a duty cycle of 10 ms greater than the most persistent ion, which prevents pulse-to-pulse

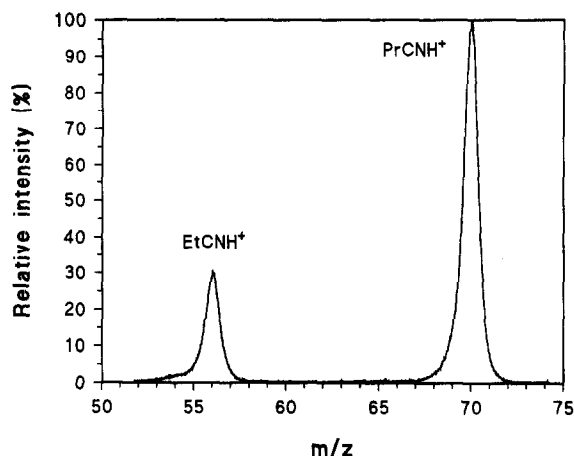


Fig. 1. MIKES of the protonated metastable dimer of propionitrile and butyronitrile after 500 scans have been accumulated at 305 K (32°C).

carry over in ion abundance. The results of 5000 electron gun pulses were accumulated. Representative data are shown in Fig. 2 for the proton exchange reaction between *iso*-butyronitrile and propionitrile.

All materials used were commercial products of the highest purity obtainable.

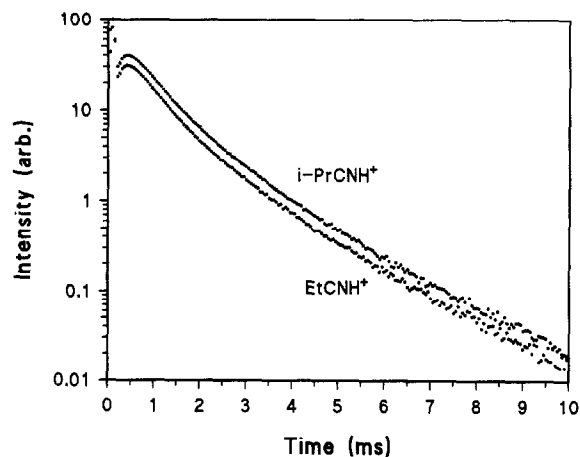


Fig. 2. Variation of absolute ionic abundances of protonated propionitrile and protonated isobutyronitrile as a function of time after a 10- μs electron beam pulse. A total of 5000 electron gun pulses were accumulated. Mixture composition: methane (968 Torr), propionitrile (590 mTorr), and isobutyronitrile (90 mTorr) at 569 K (296°C).

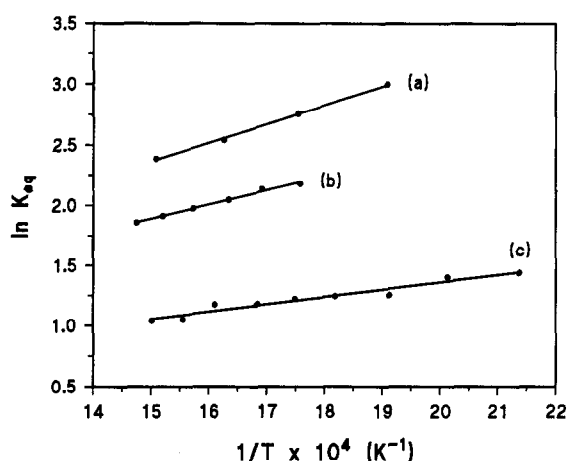


Fig. 3. Van't Hoff plots for the exchange reactions between propionitrile and acetonitrile (a), isobutyronitrile (b), and butyronitrile (c).

3. Results and discussion

Equilibrium measurements of the proton exchange reactions, Eq. (12) ($R = \text{Me}, n\text{-Pr}, i\text{-Pr}$), have been investigated and thermochemical data have been extracted from the van't Hoff plots (Fig. 3) and tabulated (Table 1).



As is evident from the van't Hoff plots (Fig. 3), the temperature dependence of the exchange reactions, Eq. (12), is, not surprisingly, very slight, which

indicates that ΔS° is small and therefore mainly accounted for by changes in symmetry numbers. This is verified by the experimentally determined ΔS° values in Table 1, which are all ~ 0 cal/mol \cdot K.

By using PA($i\text{-PrCN}$) from ref. [46] it has been possible to determine, besides relative proton affinities, the absolute proton affinities of the nitriles investigated (Table 1).

Staley et al. [47] have studied a series of nitriles using ion cyclotron resonance (ICR) techniques and found, among other things, the relative gas phase basicities, including the nitriles from the present work. It has become a well known fact that the temperature in the ICR cell is ~ 320 K (because of filament heating), rather than 298 K as assumed earlier. The ΔGB values from ref. [47] in Table 1 have, because of this, been corrected to 320 K and compared with the corresponding values from the present work at the same temperature. As is evident from Table 1 there is almost a perfect agreement between the values from the present work and the values from ref. [47].

We have studied the product ion ratios from spontaneous dissociation of metastable proton bound nitrile dimers using EtCN as reference base, Eq. (13) ($R = \text{Me}, n\text{-Pr}, i\text{-Pr}$):

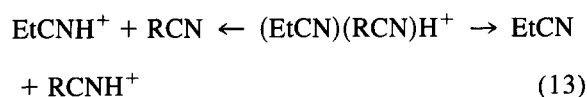


Table 1
Thermochemical data for the proton exchange reactions between RCN and EtCN

R ^a	ΔH^{ob} (kcal/mol)	ΔS^{oc} (cal/mol \cdot K)	PA(RCN) ^d (kcal/mol)	ΔGB^e (kcal/mol)	$\Delta\text{GB}(\text{literature})^f$ (kcal/mol)
Me	3.1	-0.1	186.8	-3.1	-3.1
Et	0.0	0.0	189.9	0.0	0.0
$n\text{-Pr}$	-1.2	0.3	191.0	1.3	1.3
$i\text{-Pr}$	-2.3	0.3	192.2	2.4	2.2

^aFrom Eq. (12).

^bEstimated experimental uncertainties are ± 0.2 kcal/mol.

^cEstimated experimental uncertainties are ± 0.4 cal/mol \cdot K.

^dThe PA($i\text{-PrCN}$) used here as a reference value has been reevaluated by J.E. Szulejko and T.B. McMahon on the basis of additional experiments, subsequent to the publication of [46].

^eAt 320 K.

^fFrom [47] at 320 K.

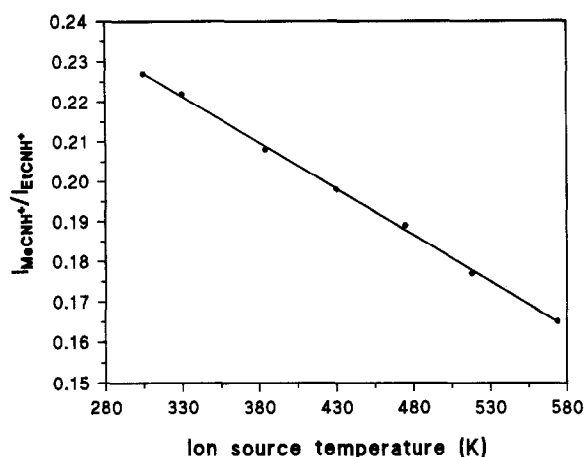


Fig. 4. Plot of the relative intensities between protonated acetonitrile and the protonated reference base propionitrile vs. the ion source temperature.

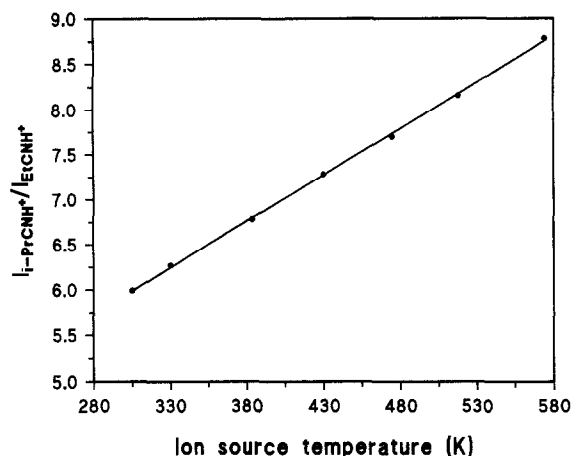


Fig. 6. Plot of the relative intensities between protonated isobutyronitrile and the protonated reference base propionitrile vs. the ion source temperature.

In Figs. 4–6 the product ion ratios are plotted against the ion source temperature. It is obvious that an apparent linear correlation is observed, which shows that when the ion source temperature increases the abundance of the protonated species with the higher basicity increases relative to that with the lower basicity.

From the equilibrium measurements we have the relative gas phase basicities between EtCN and RCN,

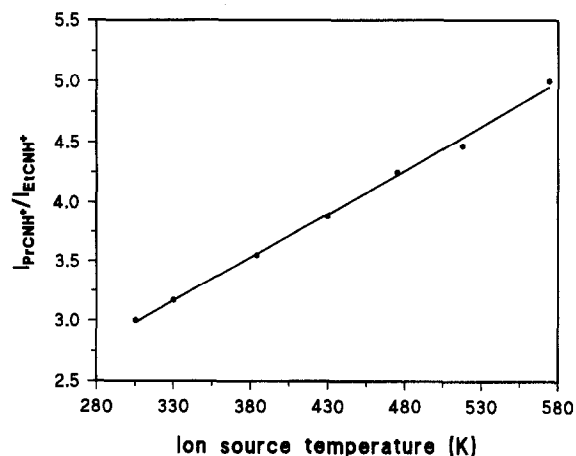
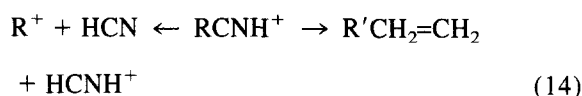


Fig. 5. Plot of the relative intensities between protonated butyronitrile and the protonated reference base propionitrile vs. the ion source temperature.

and from the MIKES measurements we have the product ion ratios from the spontaneous dissociation of the metastable proton bound nitrile dimers, $(EtCN)(RCN)H^+$. We now only have to ensure that the conditions for which the measurements have been performed justify the use of the kinetic method.

The only secondary daughter ions observed were ions corresponding to loss of HCN and alkene, Eq. (14). For all three systems investigated (at all temperatures) the amount of secondary ions observed were <3%, which can be considered to be negligible.



Formation of covalently bound dimers is not expected for aliphatic nitriles, which is supported by the observed absence of alternate fragmentation (other than loss of HCN and alkene).

The protonated dimers consist of chemically similar species of the same functionality (and only one functionality) with small proton affinity differences between the bases (Table 1), which ensure that the hydrogen bonds are similar and weak compared with a covalent bond. On the basis of this we can consider the frequency factors for dissociation of the two bases in the proton bound dimer to be similar.

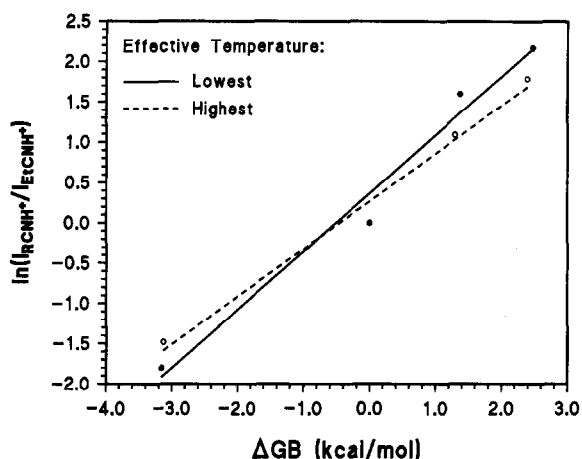


Fig. 7. Plot of the logarithm of the relative intensities between a protonated nitrile base and the protonated reference base propionitrile vs. the relative gas phase basicities of the nitriles investigated. The dashed line represents the highest measured effective temperature and the solid line the lowest.

Small aliphatic nitriles, like the ones investigated, are not suspected to change structures on protonation, so $\Delta GB \approx -\Delta \epsilon_o$ is justified.

All the measurements were performed without collision gas (spontaneous dissociation), so any contingencies of mass discrimination must be due to the ion optics, which is negligible.

In summary, all the conditions under which the measurements have been performed clearly justify the use of the kinetic method; that is, we can expect a linear correlation between the logarithm of the relative product ion abundances and the relative gas phase basicities, Eq. (6).

The logarithm of the product ion ratios from Figs. 4–6 have been plotted against the relative gas phase basicities (Fig. 7) (the highest and lowest temperatures measured are plotted), and the effective temperatures of the metastable ions reacting in the second field free region in the mass spectrometer have been calculated from the slopes.

In Fig. 8 the effective temperatures have been plotted against the ion source temperatures, which clearly shows that the effective temperature decreases with increasing ion source temperature.

The effective temperature is another way of describing the internal energy of the ions that dissociate.

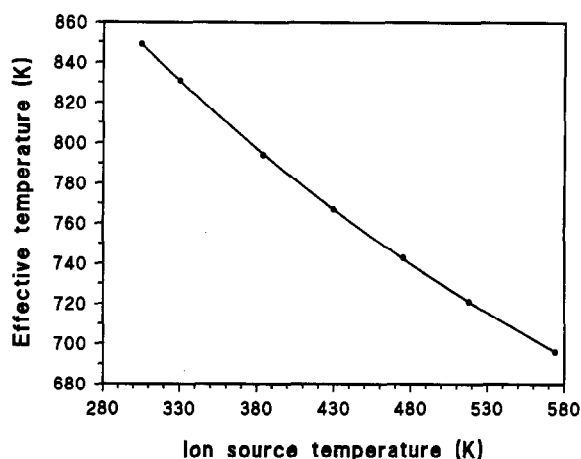


Fig. 8. Plot of the effective temperature of the protonated metastable nitrile dimers reacting in the second field free region of the mass spectrometer vs. the ion source temperature.

In Fig. 9 three situations are schematically illustrated with respect to the internal energies: E_1 , E_2 , and E_3 . As is evident from the figure, $PA(B_2) > PA(B_1)$. At internal energies, E_3 , intermediate between the two activation energies, only one protonated base will be formed, B_2H^+ , because this is the lowest energy decomposition route. At higher internal energies, E_2 , B_1H^+ will be formed and begin to compete with the other, more favourable, reaction channel. At even higher internal energies, E_1 , the population of B_1H^+ will have increased compared with the situation at E_2 .

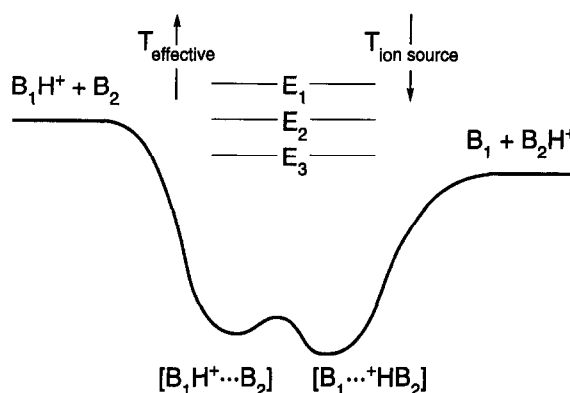


Fig. 9. Potential energy surface for the formation and dissociation of a proton bound dimer of two bases. E is the internal energy; E_1 , E_2 , and E_3 represents three situations.

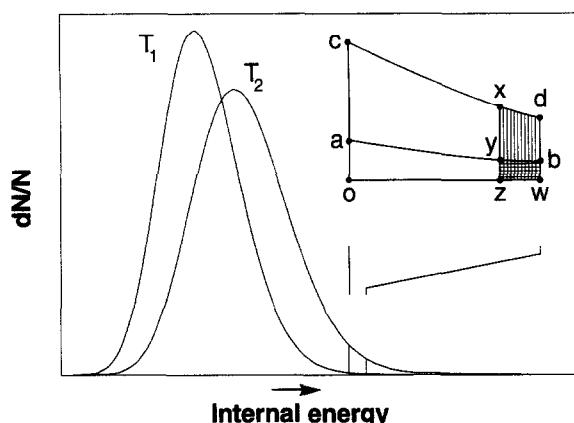


Fig. 10. Schematic representation of two Boltzmann distributions dN/N vs. internal energy of the dimer ions produced in a high pressure ion source where $T_1 < T_2$. Range between o and w indicates the energy range for the observation of metastable decomposition.

Thus, when the internal energy, and thereby the effective temperature, increases, the $[B_2H^+]/[B_1H^+]$ ratio approaches unity. Because the ion source temperature and the effective temperature apparently are inversely proportional for the systems investigated, the $[B_2H^+]/[B_1H^+]$ ratio approaches unity when the ion source temperature decreases.

From Fig. 10 we can qualitatively propose an explanation for the inverse proportionality between the effective temperature (the internal energy) and the ion source temperature. In Fig. 10, Boltzmann distributions for two arbitrary ion source temperatures, $T_2 > T_1$, are schematically presented with an arbitrary time window for the reactions of the metastable ions. Point a represents the population of metastable ions at T_1 with the smallest amount of internal energy, and Point b represents the population of metastable ions at T_1 with the largest amount of internal energy. Point c represents the population of metastable ions at T_2 with the smallest amount of internal energy, and Point d represents the population of metastable ions at T_2 with the largest amount of internal energy. It is obvious from Fig. 10 that the slope from c to d is steeper than slope from a to b . This means that the average internal energy of the population of decomposing ions is actually less for the higher ion source

temperature. This can also be understood from comparison of areas under the internal energy distribution. For example the high energy fraction of the decomposing population at the lower temperature, defined by area $zwyb$ compared with area $owab$, is greater than the high energy fraction for ions of the same lifetime range at higher temperature, defined by area $zwx d$ compared with area $owcd$. A similar conclusion might be arrived at by taking an "energy slice" in the internal energy distribution at an energy less than the maxima of the distributions. This situation seems improbable, in that we are observing a very small intensity of fragmenting ions compared with the intensity of the main beam of parent ions (1 part in 10^3-10^4). Based on this qualitative observation we can conclude that the actual time window for reactions of metastable ions must be located in the high energy tail of the Boltzmann distribution (on the right side of the maxima). If the interpretation for the temperature dependence is correct, the ratio between the sum of the product ions and the parent ions should increase with ion source temperature. A subtle increase has been observed that supports the contention that the fragmenting ions are in the high energy tail of the distribution.

The steepness of the slopes in Fig. 7 is dependent on the effective temperature (internal energy) of the ion undergoing dissociation. Less steep slopes are associated with higher effective temperatures (internal energies). The slope, that is the internal energy, is known to vary with experimental conditions [2,7,10,12,13,24,25,28] (i.e. collisional energy under CA conditions). The effective temperature (internal energy) has been observed typically to increase with collisional energy [10,13,25,28] under fixed target gas thickness conditions.

4. Conclusions

By applying the pulsed ionization high pressure mass spectrometry technique to an investigation of proton exchange reactions between propionitrile, acetonitrile, isobutyronitrile, and butyronitrile, using the equilibrium method, we have extracted ΔG° (ΔGB), ΔH° (ΔPA), and ΔS° values from the van't Hoff plots.

The relative gas phase basicities, ΔGB , were used together with an investigation of the spontaneous dissociation of the mixed metastable proton bound nitrile dimers, by applying the kinetic method, to measure the effective temperatures of the proton bound dimers reacting in the second field free region in the mass spectrometer. By varying the ion source temperature we have monitored its effect on the effective temperature (internal energy) of the dimers reacting in the second field free region and found an inverse relationship between the effective temperature (internal energy) and the ion source temperature. From a qualitative consideration of the Boltzmann distributions, the observed trend was explained and it was concluded that the actual time window for reactions of metastable ions must be located in the high energy tail of the Boltzmann distribution.

This investigation has clearly illustrated how useful the high pressure mass spectrometry technique is for the study of bimolecular reactions. The technique makes it possible to use thermalized ions when applying the kinetic method on protonated dimers and thereby makes it possible to get information about the relationship between the effective temperature and the ion source temperature. This is a new aspect not seen before in the otherwise broadly applied method.

Future work will involve a study of the effect of varying other experimental conditions pertinent to such measurements.

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