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Energetics of the dehydration of nitrile-alcohol proton-bound dimers from ion/molecule reaction kinetics

Julie A.D. McCormack, Paul M. Mayer

Chemistry Department, University of Ottawa, OttawaK1N 6N5, Canada

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Abstract

An ion trap mass spectrometer has been used to measure the ion/molecule reaction rate constants for three reactions involving acetonitrile and primary alcohols. The values obtained for the reaction between CH_3CNH^+ and CH_3OH leading to the products $CH_3CNCH_3^+$ was $4.6 \pm 0.2 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. The reaction between CH_3CNH^+ and CH_3CH_2OH (to give $CH_3CNCH_2CH_3^+ + H_2O$) proceeds with a rate constant of $3.9 \pm 0.4 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, and that between $CH_3CH_2CH_2OH_2^+ + CH_3CN$ has a value of $2.1 \pm 0.4 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. These values for the rate constants have been used to extract the activation energy for isomerization of the initially formed proton-bound dimer in each case. (Int J Mass Spectrom 207 (2001) 195–203) © 2001 Elsevier Science B.V.

Keywords: Ion trap mass spectrometer; Ion/molecule kinetics; Cluster ions; Energetics

1. Introduction

The family of proton-bound mixed dimers consisting of nitriles and alcohols all have at least one common feature, they exhibit in their unimolecular chemistry the competition between simple-bond dissociations and dehydration reactions [1]. The dehydration of these simple clusters necessarily involves the isomerization of the proton-bound entity.

The isomerization of these clusters will also have an impact on the kinetics of the reactions between ions and molecules in the gas phase. Even though there is no activation barrier to an ion/molecule reaction, the presence of the isomerization barrier on the reaction surface can make the reaction less efficient. The cluster ion reaction can also be viewed from the point of view of an ion/molecule reaction

$$CH_3CNH^+ + CH_3OH \underset{k_{cap}}{\overset{k_{diss}}{\leftrightarrows}} (CH_3CN)(CH_3OH)H^+$$

$$(CH_3CN)(CH_3OH)H^+ \xrightarrow{k_{iso}} CH_3CNCH_3^+ + H_2O$$

The observed forward rate constant, k_{obs}, for the reactions studied (leading to the dehydration products) can be written as [2]

$$k_{obs} = \rho_{cap} k_{cap} \left(\frac{k_{iso}}{k_{iso} + k_{diss} + k_s[M]} \right) \quad (1)$$

where k_{iso} is the rate constant for the isomerization of the dimer ions (which eventually leads to the loss of water) and k_{diss} is the rate constant for the dissociation reaction of the dimer (both of which can be calculated

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* Corresponding author. E-mail: pmayer@science.uottawa.ca

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using Rice-Ramsperger-Kassel-Marcus (RRKM) theory [3]). The probability that a collision will lead to a long-lived excited intermediate complex is referred to as ρ_{cap} (the association reaction can normally be assumed to occur on every collision and ρ_{cap} is then assumed to be unity), and k_{cap} is the rate constant for capture collisions occurring between the reactant ion and neutral (calculated using the ion-dipole theory of Su and Chesnavich [4]) and $k_s[M]$ is the rate constant for collisional stabilization of the initially formed excited complex calculated employing the ion-induced dipole theory developed by Langevin [5]. The rate of stabilization of the initially formed excited cluster ion, $k_s[M]$ will depend on the pressure in the reaction chamber.

In the present study an ion trap mass spectrometer is used to measure the bimolecular rate constants for reactions between protonated acetonitrile and methanol and ethanol, and for the reaction between protonated *n*-propanol and acetonitrile. The goal is to compare the experimentally determined values with those obtained from theory, and to extract information about the cluster ion isomerization barrier.

2. Experimental procedures

The modified Finnigan GCQ ion trap mass spectrometer employed for this study has been described in a previous publication [6]. A gas chromatograph (GC) oven is used to house a heated inlet, consisting of the original GC injection septum attached to a stainless steel reservoir. Sample volatilized in the reservoir was introduced into the ion source of the GCQ by means of a fused-silica capillary of 0.25 mm i.d. The inlet temperature was held at 180 °C. Neutral reagent sample vapour was introduced into the vacuum chamber by way of a Granville-Phillips variable leak valve at ambient temperature. The neutral reagent used was the purest commercially available and was degassed by several freeze–pump–thaw cycles prior to use. Reagent gas pressure was monitored with a Bayert-Alpert type ionization gauge. The vacuum chamber is pumped by a 100 L/s oil diffusion pump backed by a rotary pump. Helium bath gas is introduced into the ion trap by means of 0–10 psi pressure regulator and a capillary restrictor. It enters the trapping volume through a nipple on the entrance end cap electrode.

Protonated molecules were generated in the chemical ionization ion source of the GCQ by self-protonation after ionization by 70 eV electrons. All ions thus generated were gated into the ion trap by applying a focusing potential to the central lense in the einzel lense assembly. Ion/molecule reactions were studied using the MS^2 mode of the GCQ. Ions with the *m/z* value of interest were isolated by applying a broadband rf field to the end cap electrodes (which resonantly excites all ions in the trap), out of which was notched frequencies corresponding to the ion *m/z* of interest. Isolation times were typically 2 ms, though longer times were tried and found to have no effect on the final rate constant.

Following isolation, the trapping mode was changed to store, for a variable length of time (between 1 and 30 ms), all product ions of the reaction between the isolated reactant ion and neutral reagent present in the trap. The mass spectrum for a given reaction time was acquired by sequentially scanning ions out of the trap where they were detected with a conversion dynode/electron multiplier assembly. The reaction time window and pressure regime that can be studied with the current instrument configuration limits observations to rate constants between 10^{-12} and 10^{-9} cm^3 $molecule^{-1}$ s^{-1}.

When determining the absolute pressure of neutral reagent in the ion trap, two factors must be taken into consideration: the ionization gauge response to that particular molecule and the relative pressures of the reagent in the vacuum chamber and inside the trapping volume. A correction for both these effects was obtained by measuring the rate constant for the well-studied reaction between acetone and the acetyl cation [7,8]:

$$(CH_3)_2C{=}O + \underset{m/z\ 43}{CH_3CO^+} \rightarrow \underset{m/z\ 59}{(CH_3)_2C{\equiv}OH^+} + CH_2CO$$

The procedure was outlined in detail in a previous publication [6]. In brief, the experiments were performed at a series of different acetone pressures whereby the reaction times were varied from 1 to 30 ms. The peak heights for the *m/z* 43 (H_{43}) and *m/z* 59 (H_{59}) ions were measured and a plot of $\ln [H_{43}/(H_{43}+H_{59})]$ versus time was made for each pressure to yield the pseudo-first-order rate constant for each experiment. These values were then plotted as a function of their respective pressures to yield the bimolecular rate constant for the reaction. The acetone pressures were adjusted to yield a rate constant of 2.1×10^{-10} cm^3 $molecule^{-1}$ s^{-1} [7,8]. When neutrals other than acetone were used, an additional correction was applied to account for the different response of the ionization gauge between that neutral and acetone [9].

There has been extensive previous work on estimating the temperature of ions in ion trap mass spectrometers. Estimates by McLuckey et al. [10] based on the measured rate constants for the desolvation reactions of protonated water and protonated methanol clusters give ion temperatures between 350 and 450 K under the present experimental conditions. Of course, this temperature applies only to the reacting ion in our experiments and not to the neutral reagent, which is expected to be near ambient. The ion/molecule reactions in this study do not exhibit large temperature dependence. If reactions showing greater temperature dependence were examined, a much better estimate of reactant ion internal temperatures would be required. Where the temperature plays a more important role in the current study is in the extraction of energy barrier values. The temperature dependence of the potential surface energetics will be discussed in the following.

The unimolecular dissociation of proton-bound dimers was studied with a modified triple sector VG ZAB-2HF mass spectrometer [11] incorporating a magnetic sector followed by two electrostatic sectors (BEE geometry). Protonated cluster ions were generated in the chemical ionization ion source of the instrument. The pressures in the ion source chamber, read with an ionization gauge located above the ion source diffusion pump, were typically between 10^{-5} and 10^{-4} Torr (the pressure in the ion source itself being approximately two orders of magnitude higher). Cluster ions were not observed when the pressure was below 10^{-5} Torr, and there was no evidence of higher order clusters at any of the pressures used in these experiments. Metastable ion (MI) mass spectra were recorded in the usual manner [12].

3. Computational methods

Ab initio calculations [13] were performed using the GAUSSIAN 98 suite of programs [14]. For the two reactions involving protonated acetonitrile, the corresponding dimer ions $(CH_3CN)(CH_3OH)H^+$ and $(CH_3CN)(CH_3CH_2OH)H^+$, have been modeled previously in our group at the MP2/6-31+G(*d*) level of theory [1,15]. Vibrational frequencies for these dimers were taken from those studies. The dimer $(CH_3CN)(CH_3CH_2CH_2OH)H^+$, was optimized in the present study at the HF/6-31G(d) level of theory. Relative energies in this system were determined at the MP2/6-31+G(d) level of theory employing scaled HF/6-31G(*d*) zero-point vibrational energies (scaled by 0.9135).

The dissociation and isomerization channels for each dimer ion were modeled with the standard RRKM expression:

$$k(E) = \frac{\sigma N^{\neq}(E - E_0)}{h\rho(E)} \tag{2}$$

where $N^*(E-E_0)$ and $\rho(E)$ are the sum and density of states of the transition state and reactant ion, respectively. They were calculated employing the direct-count algorithm developed by Beyer and Swinehart [3]. Transition state frequencies were taken to be the same as those of the reactant dimer ion, with one removed to represent the motion over the col. The lowest frequencies were then scaled to yield an entropy of activation, $\Delta S^\ddagger$ (600 K) of $+12$ $J\,K^{-1}\,mol^{-1}$ for a dissociation reaction and -12 $J\,K^{-1}\,mol^{-1}$ for an isomerization reaction. The vibrational frequencies are listed in Table 1. In the absence of ab initio calculated transition structures for the dissociation and isomerization processes in these cluster ions, the above RRKM treatment is strictly qualitative. The assignment of transition state fre-

Table 1.
Vibrational frequencies used in the RRKM modeling of the dissociation and isomerization reaction of the $(CH_3CN)(CH_3CH_2CH_2OH)H^+$ proton-bound dimer[a]

System	Harmonic vibrational frequencies (cm^{-1})
$(CH_3CN)(CH_3CH_2CH_2OH)H^+$	3, 34, 39, 87, 108, 122, 171, 227, 282, 404, 413, 460, 753, 807, 869, 878, 893, 940, 1008, 1067, 1071, 1072, 1159, 1214, 1283, 1321, 1355, 1423, 1427, 1438, 1462, 1462, 1494, 1500, 1507, 1512, 1716, 2401, 2791, 2936, 2942, 2960, 2986, 3006, 3020, 3024, 3044, 3044, 3093, 3650
TS (diss)	(−460),[b] 2, 21, 24, 54, 67, 122, 171, 227, 282, 404, 413, 432, 753, 807, 869, 878, 893, 940, 1008, 1067, 1071, 1072, 1159, 1214, 1283, 1321, 1355, 1423, 1427, 1438, 1462, 1462, 1494, 1500, 1507, 1512, 1716, 2401, 2791, 2936, 2942, 2960, 2986, 3006, 3020, 3024, 3044, 3044, 3093, 3650
TS (iso)	(−1008),[b] 4, 42, 48, 108, 135, 122, 171, 227, 282, 404, 413, 432, 460, 753, 807, 869, 878, 893, 940, 1067, 1071, 1072, 1159, 1214, 1283, 1321, 1355, 1423, 1427, 1438, 1462, 1462, 1494, 1500, 1507, 1512, 1716, 2401, 2791, 2936, 2942, 2960, 2986, 3006, 3020, 3024, 3044, 3044, 3093, 3650

[a] HF/6-31g(*d*) values scaled by 0.9135.
[b] Mode removed to represent the motion over the barrier.

quencies and the resulting values for $\Delta S^{\ddagger}$ (600 K) is one approach to deriving information from the ion/molecule reaction rate constant. This approach is particularly useful when reactions having similar characteristics are being compared, as is the case for the nitrile/alcohol pairs studied here. So, the relative values for the isomerization barrier may be expected to be reasonable. The impact on the final energy barrier values of different choices of $\Delta S^{\ddagger}$ (600 K) and different reactant ion temperatures was probed in our earlier publication [6].

4. Results and discussion

4.1. Determining k_{obs}

The procedure for determining the bimolecular rate constants, k_{obs}, for the three ion/molecule reactions discussed in this study is outlined below. The results are summarized in Table 2, which includes the theoretical collision capture rate constants, k_{cap}, for comparison.

4.1.1 $CH_3CNH^+ + CH_3OH$

The reaction between protonated acetonitrile and neutral methanol

$$\underset{m/z\ 42}{CH_3CNH^+} + CH_3OH \rightarrow \underset{m/z\ 56}{CH_3CNCH_3^+} + H_2O$$

occurs on the potential energy surface presented in [1]. The peak heights of the *m/z* 42 and *m/z* 56 ions (Fig. 1) were measured and a plot of $\ln[H_{42}/(H_{42}+H_{56})]$ versus reaction time was made for each different methanol pressure studied (1.4×10^{-6} Torr, 2.9×10^{-6} Torr, 4.9×10^{-6} Torr, 8.6×10^{-6} Torr, and

Table 2.
Comparison of the measured ion/molecule reaction rate constant, k_{obs}, with that predicted by collision theory, k_{cap}, for reactions leading to formation of neutral water[a]

Reaction	k_{obs}	k_{cap}[b]
$CH_3CNH^+ + CH_3OH$	0.046 ± 0.002	2.3
$CH_3CNH^+ + CH_3CH_2OH$	0.39 ± 0.04	2.2
$CH_3CH_2CH_2OH_2^+ + CH_3CN$	0.21 ± 0.04	3.7

[a] Rate constants are in units of 10^{-9} cm^3 $molecule^{-1}$ s^{-1}.
[b] Using the theory described by Su and Chesnavich [4].

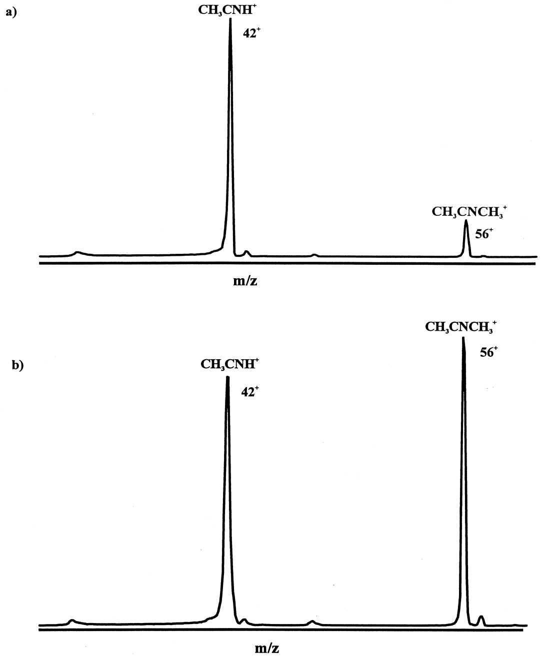

Fig. 1. Mass spectra corresponding to reaction times (a) 1 ms and (b) 30 ms for the ion/molecule reaction between CH_3CNH^+ and CH_3OH.

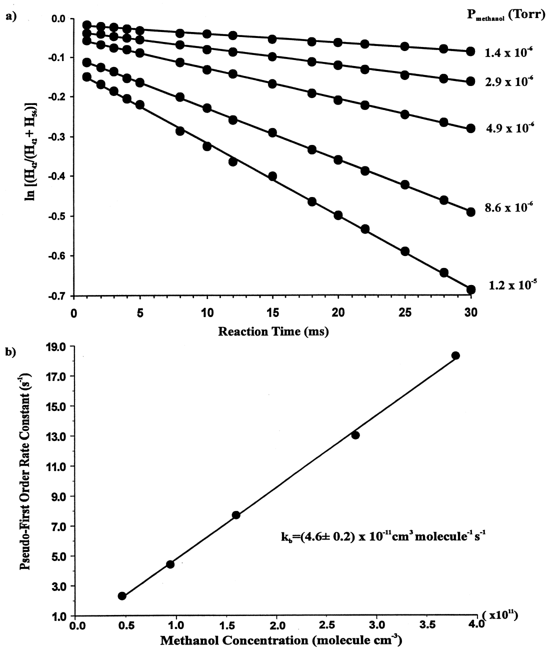

Fig. 2. (a) Pseudo-first-order plots for the reaction CH_3CNH^+ + $CH_3OH \rightarrow CH_3CNCH_3^+ + H_2O$ at five neutral methanol pressures and (b) plot of the pseudo-first-order rate constants as a function of methanol pressure. No error bars were presented as the experimental uncertainty of the data points was smaller than the points themselves.

1.2×10^{-5} Torr). The slope from each plot yielded pseudo-first-order rate constants [Fig. 2(a)]. These rate constants were then plotted against their respective methanol pressures to yield the bimolecular rate constant of $(4.6 \pm 0.2) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} [Fig. 2(b)]. The error is based upon five different experiments, but does not include errors due to assumptions made in the kinetic treatment such as a unity value for ρ_{cap}, and thus should be taken as a minimum error. This value is two orders of magnitude lower than k_{cap}, 2.3×10^{-9} cm^3 $molecule^{-1}$ s^{-1} (obtained using the ion–dipole theory of Su and Chesnavich [4]). The polarizability and the dipole moment of methanol were obtained from the literature [16,17]. This indicates that the presence of the isomerization barrier for the $(CH_3CN)(CH_3OH)H^+$ dimer ion hinders the ion/molecule reaction by creating a bottle neck in the overall availability of states for the reaction as it progresses from reactants to products.

4.1.2. CH_3CNH^+ + CH_3CH_2OH

The mass spectrum resulting from the ion/molecule reaction between CH_3CNH^+ and CH_3CH_2OH in the ion trap exhibits two peaks, *m/z* 42 (CH_3CNH^+) and *m/z* 70 ($CH_3CNCH_2CH_3^+$). A small peak at *m/z* 47 ($CH_3CH_2OH_2^+$) was minimized by increasing the pressure of CH_3CN. In the ensuing kinetic treatment, the original concentration of CH_3CNH^+ was approximated by the sum of the two peaks with *m/z* 42 and *m/z* 70 in the mass spectrum. The peak heights of *m/z* 42 and *m/z* 70 ions were measured and a plot of $\ln[H_{42}/(H_{42}+H_{70})]$ versus reaction time was made for each different ethanol pressure. A corrected experimental bimolecular rate constant value of $(3.9 \pm 0.4) \times 10^{-10}$ cm^3 $molecule^{-1}$ $^{-1}$ was obtained, which is an order of magnitude smaller than k_{cap} (2.2×10^{-9} cm^3 molecule $^{-1}$ s^{-1}) [4].

Table 3.
Comparison of the 0 K isomerization activation energy (E_{iso}) obtained from RRKM modeling of metastable ion (MI) mass spectra of proton-bound dimers with those obtained from the present study

		E_{iso} [a]	
Proton-bound dimer	E_{diss} [a,b]	MI[c]	Present work
$(CH_3CN)(CH_3OH)H^+$	112[d]	115 ± 10[d]	125 ± 10
$(CH_3CN)(CH_3CH_2OH)H^+$	152[e]	130 ± 10[e]	142 ± 10
$(CH_3CN)(CH_3CH_2CH_2OH)H^+$	131	114 ± 10	125 ± 10

[a] Values in kJ mol^{-1}

[b] See text.

[c] Estimated based upon relative peak heights in MI mass spectra of proton-bound dimers.

[d] See [1].

[e] See [14].

4.1.3. $CH_3CH_2CH_2OH_2^+ + CH_3CN$

The reaction,

$$\underset{m/z\ 61}{CH_3CH_2CH_2OH_2^+} + CH_3CN \rightarrow \underset{m/z\ 84}{CH_3CH_2CH_2CNCH_3^+} + H_2O$$

between protonated *n*-propanol and neutral acetonitrile results in three peaks in the mass spectrum, *m/z* 61 ($CH_3CH_2CH_2OH_2^+$), *m/z* 84 ($CH_3CH_2CH_2CNCH_3^+$) and the proton-bound dimer, *m/z* 102 $(CH_3CN)(CH_3CH_2CH_2OH_2^+)H^+$. The original concentration of $CH_3CH_2CH_2OH_2^+$ was approximated from the sum of all three peaks in the mass spectrum. The peak heights of *m/z* 61, *m/z* 84, and *m/z* 102 ions were measured and a plot of $\ln[(H_{61})/(H_{61} + H_{84} + H_{102})]$ versus reaction time was made for each acetonitrile pressure. A bimolecular rate constant of $(2.1 \pm 0.4) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} was obtained, which is also approximately an order of magnitude lower than k_{cap} (3.7×10^{-9} cm^3 $molecule^{-1}$ s^{-1}) [4]. Note the change in k_{cap} when acetonitrile is the neutral reagent (due to its greater dipole moment and polarizability).

4.2. Isomerization barrier energy

The rate constants derived previously can be used to extract information about the reaction surface. Referring to Eq. (1), the ratio of k_{obs} to k_{cap} can be used to obtain the ratio of the two competing unimolecular reactions of the proton-bound dimer, dissociation (k_{diss}) and isomerization (k_{iso}). If the activation energy of the dissociation is known, and appropriate vibrational frequencies are available for the two transition structures, the isomerization activation energy can be adjusted until Eq. 2 is satisfied. In previous work from this laboratory, the unimolecular reactions of the proton-bound dimers, $(CH_3CN)(CH_3OH)H^+$ and $(CH_3CN)(CH_3CH_2OH)H^+$, encountered in the present study were investigated [1,15]. High level ab initio calculations were used to model the unimolecular reaction surfaces and estimate their respective dissociation energies. Calculated vibrational frequencies were used to model the isomerization channel with RRKM theory [3], and extract isomerization barrier energies. To do this, the log *k(E)* versus *E* curves for dissociation and isomerization were adjusted to achieve an overlap that appeared reasonable based on the mass spectrum of metastable (low internal energy) dimer ions. The values that were obtained in this manner are summarized in Table 3. The vibrational frequencies quoted in those works [1,15] were used in the present study in the modelling of k_{obs} for these two dimer ions.

4.2.1. $CH_3CNH^+ + CH_3OH$

Since the intact proton-bound dimer ion was not observed in any of the mass spectra obtained for this reaction, we can use a simplified version of Eq. (1):

$$\frac{k_{iso}}{k_{iso} + k_{diss}} = \frac{k_{obs}}{\rho_{cap} k_{cap}} \tag{3}$$

where k_{iso} is the rate of isomerization from $(CH_3CN)(CH_3OH)H^+$ to $(CH_3CNCH_3)(H_2O)^+$ in Fig.1.

The 0 K binding energy of the $(CH_3CN)(CH_3OH)H^+$ complex was previously calculated to be 121 kJmol^{-1} [1] at the G2 [18] level of theory. If CH_3CNH^+ and CH_3OH are assumed to be at 298 K, then we need to extract from the RRKM modeling the k_{diss} and k_{iso} corresponding to an internal energy of the proton-bound dimer of 145 kJ mol^{-1} (121 kJmol^{-1} plus the average thermal internal energy of the two reactants). Then by fixing the $\Delta S^{\ddagger}$ for the two unimolecular channels [1], the only adjustable parameter becomes the activation energy for the isomerization channel. With this procedure, the E_0 value for the isomerization process was determined to be 125 ± 2 kJ mol^{-1}. This is slightly larger than the value of 115 ± 10 kJ mol^{-1} that was estimated from the mass spectrum of metastable proton-bound dimers [1]. The precision of the present value was difficult to determine because the RRKM analysis presented here is strictly qualitative. Based on our earlier work [6], an uncertainty of ±10 kJ mol^{-1} is not unreasonable.

4.2. $CH_3CNH^+ + CH_3CH_2OH$

The unimolecular chemistry of the acetonitrile–ethanol proton-bound dimer has been studied in our laboratory [15] and found to be similar to that of $(CH_3CN)(CH_3OH)H^+$. The dimer exhibits three dissociation channels on the microsecond timescale, cleavage of the two hydrogen bonds to form CH_3CNH^+ and $CH_3CH_2OH_2^+$, and dehydration to form $CH_3CNCH_2CH_3^+$. The two simple dissociation reactions compete because the proton affinity (PA) values of acetonitrile and ethanol are similar (779.2 kJ mol^{-1} and 776.4 kJ mol^{-1}, respectively [19]). The formation of $CH_3CNCH_2CH_3^+$ involves the isomerization of the proton-bound dimer prior to water loss. From an analysis of the relative intensities of the peaks in the mass spectrum of metastable $(CH_3CN)(CH_3CH_2OH)H^+$ ions using RRKM theory, it was evident that the barrier to isomerization for this system was lower (relative to the products CH_3CNH^+ + CH_3CH_2OH) than was observed for the reaction involving methanol. An estimated value of E_{iso} of 130 ± 10 kJ mol^{-1} was obtained [15].

In the present study, a small peak is observed in the mass spectrum due to the proton-bound dimer, $(CH_3CN)(CH_3CH_2OH)H^+$, *m/z* 88. However, the bimolecular rate constant was found to be independent of its inclusion in the kinetic treatment, and so Eq. (3) was again used for determining the isomerization barrier energy.

The 0 K binding energy of the $(CH_3CN)(CH_3CH_2OH)H^+$ complex was previously calculated to be 152 kJ mol^{-1} [15] at the G2(MP2,SVP) level of theory. If CH_3CNH^+ and CH_3CH_2OH are assumed to be at 298 K, then we need to extract from the RRKM modeling the k_{diss} and k_{iso} corresponding to an internal energy of the proton-bound dimer of 182 kJ mol^{-1} (152 kJ mol^{-1} plus the average thermal internal energy of the two reactants). Employing the vibrational frequencies for the dissociation and isomerization states quoted in [15], the value of E_{iso} can be adjusted so that Eq. (3) is satisfied. The E_0 value for the isomerization process was determined to be 142 ± 10 kJ mol^{-1}. This is again slightly larger than the value of 130 ± 10 kJ mol^{-1} that was estimated from the mass spectrum of metastable proton-bound dimers [15].

4.3. $CH_3CH_2CH_2OH_2^+ + CH_3CN$

The mass spectra of the reaction between protonated *n*-propanol and neutral acetonitrile contained three peaks, *m/z* 61 ($CH_3CH_2CH_2OH_2^+$), *m/z* 84 (due to water loss from the proton-bound dimer) and a significant peak due to the intact proton-bound dimer $(CH_3CN)(CH_3CH_2CH_2OH)H^+$, *m/z* 102 and thus, Eq. (1) must be used. The stabilization rate constant, k_s [He], was calculated to be 1.75×10^4 cm^3 molecule^{-1} s^{-1}, based upon the polarizability of the helium atom (0.20×10^{-24} cm^3) [16] and a helium pressure of 1 mTorr.

The 0 K binding energy of the $(CH_3CN)(CH_3CH_2CH_2OH)H^+$ complex (relative to $CH_3CH_2CH_2OH_2^+$ + CH_3CN) was calculated in the present study to be 131 kJ mol^{-1} at the MP2/6-31+G(*d*) level of theory. If CH_3CN and

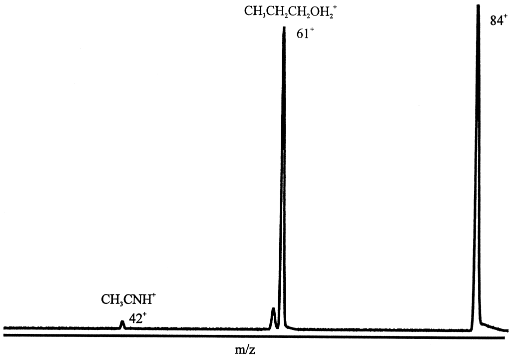

Fig. 3. MI mass spectrum of the $(CH_3CN)(CH_3CH_2CH_2OH)H^+$ cluster ion.

$CH_3CH_2CH_2OH_2^+$ are assumed to be at 298 K, then to satisfy Eq. (1), we need to extract from the RRKM modeling the k_{diss} and k_{iso} corresponding to an internal energy of the proton-bound dimer of 162 kJ mol^{-1} (131 kJ mol^{-1} plus the average thermal internal energy of the two reactants). The E_0 value for the isomerization process that ultimately satisfies Eq. (1) was found to be 125 ± 10 kJ mol^{-1}. This value can be compared with an estimate based on the MI mass spectrum of metastable $(CH_3CN)(CH_3CH_2CH_2OH)H^+$ ions (Fig.3). The MI mass spectrum exhibits two major peaks, *m/z* 61 and *m/z* 84 in nearly a 1:1 ratio. Two minor peaks are present at *m/z* 42 (CH_3CNH^+) and *m/z* 60 (propene loss). The log $k(E)$ versus E curves for the dissociation and isomerization reactions of the proton-bound dimer can be adjusted so that they overlap in the internal energy range of the dimer appropriate for observations in the second field-free region of the ZAB mass spectrometer. The estimated value of E_{iso} that results is 114 ± 10 kJ mol^{-1}, which is 11 kJ mol^{-1} lower than that predicted from the ion/molecule reaction modeling.

The isomerization of nitrile/alcohol proton-bound dimers is believed to take place by a mechanism similar to that predicted for the proton-bound alcohol dimers, namely an S_N2-type attack by CH_3CN on the alcohol carbon adjacent to the OH_2 moiety, e.g. $[CH_3CN \cdots CH_3OH_2]^+$ [15]. The values for E_{iso} obtained in this study, when viewed relative to the activation energy for the simple dissociation, E_{diss}, are consistent with this type of mechanism. The cluster $(CH_3CN)(CH_3CH_2OH)H^+$ has the strongest hydrogen bonds due to the similarity in the PA values for acetonitrile and ethanol. Although the larger alkyl group should stabilize an intermediate $[CH_3CN \cdots CH_2(CH_3)OH_2]^+$ complex, and the $CH_3CH_2-OH_2^+$ bond is weaker than the CH_3-OH_2^+ bond, the E_{iso} for the isomerization is larger for this cluster than for that involving methanol. If the S_N2 mechanism is valid, the strength of the H bonding in the proton-bound dimer must result in a higher energy initial rearrangement to form $[CH_3CN \cdots CH_2(CH_3)OH_2]^+$. The value for k_{obs} is affected most by the relative values of E_{diss} and E_{iso}, and so is still larger than that measured for the reaction involving methanol.

4. Conclusions

A Finnigan GCQ ion trap mass spectrometer was used to measure the rate constants for three reactions between acetonitrile and alcohols, methanol, ethanol and *n*-propanol. The values were all significantly lower than those predicted from collision theory due to the presence of an isomerization reaction of the initially formed excited proton-bound dimer. The relative magnitudes of the isomerization barrier extracted from the kinetic data are consistent with an S_N2-type rearrangement of the dimer, which involves backside attack of the nitrile on a protonated alcohol.

Acknowledgements

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Note Added in Proof: Upon completion of this manuscript, Fridgen et al. [50] measured the rate constant for the ion/molecule between CH_3CNH^+ and CH_3OH with FT-ICR mass spectrometry and obtained a value at 293 K of 0.0349 ± 0.0008 × 10^{-9} cm^3 molecule^{-1} s^{-1}, in good agreement with the present result. Their experiments show that the rate constant decreases to $0.0189 \pm 0.007 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} at 335 K.

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