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Ion/molecule reaction kinetics using a modified Finnigan GCQ ion trap mass spectrometer: the energetics of the dehydration of proton-bound alcohol dimers

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Abstract

A Finnigan GCQ ion trap mass spectrometer has been modified for the measurement of ion/molecule reaction rate constants. The rate constants for the reactions between CH_3OH_2^+ and methanol, $\text{CH}_3\text{CH}_2\text{OH}_2^+$ with methanol and ethanol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}_2^+$ with methanol, ethanol, and *n*-propanol and protonated isopropanol with neutral isopropanol, all leading to products consisting of a protonated ether and neutral water, have been determined. All of the values, except that for the reaction involving isopropanol, are significantly lower than that predicted by the collision capture theory of Su and Chesnavich. Common to all the systems studied is an isomerization reaction that takes place in the proton-bound dimer that is initially formed in the reaction. This isomerization, which takes place via an internal $\text{S}_{\text{N}}2$ -type mechanism, leads to the formation of the protonated ether. The rate constants, in combination with Rice-Rampsberger-Kassel-Marcus modeling, allow the isomerization activation energies, E_{iso} , for the proton-bound dimers to be estimated. The E_{iso} values were found to decrease as the size of the alcohols increased, an observation consistent with the $\text{S}_{\text{N}}2$ -type rearrangement that has been predicted for these systems. (Int J Mass Spectrom 207 (2001) 183–193) © 2001 Elsevier Science B.V.

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

1. Introduction

Clusters of molecules are often viewed as an intermediate state of matter between the dilute gas phase and solution. Studying clusters allows the effects of solvation on the chemistry of gas-phase molecules and ions to be explored [1–5]. Ionic clusters (typically made up of a core ion surrounded by one or more solvating molecules) are known to be involved in the chemistry of the upper and mid

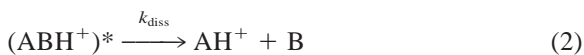
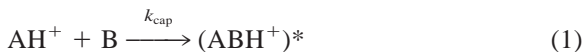
atmosphere [6]. A central issue, when studying the chemistry of all gaseous ions, is their propensity for rearrangement prior to reaction. Over the years, a variety of thermodynamically stable structures have been discovered and found to be involved in ion dissociation mechanisms, including distonic ions [7], ion–neutral complexes [8,9] and bridged ions [10]. The isomerization of organic ions is well known, and appears to be a common occurrence [11–15]. The isomerization of cluster ions, in addition to being a scientific curiosity, can also have an impact on the kinetics of the reactions between ions and molecules in the gas phase. Even though there may not be an

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activation barrier to an ion/molecule reaction, the presence of the isomerization on the reaction surface can make the reaction less efficient. Computational chemistry has made it possible to characterize isomerization pathways. However, as the ions under investigation get larger, it becomes increasingly more computationally intensive to reliably identify transition structures and intermediate equilibrium species on potential energy surfaces. Therefore, it is valuable to be able to experimentally estimate the net isomerization barrier height in a reaction, even though the exact mechanism for the process may not be known.

In the present study, we are interested in the formation of products due to the isomerization of proton-bound alcohol dimers. The family of proton-bound alcohol dimers has at least one common feature, they exhibit in their unimolecular chemistry the competition between simple bond dissociations and dehydration reactions. Calculations [16–18] and experiments [19–29] on the methanol dimer ion indicate that isomerization proceeds via an internal S_{N2} reaction. Essentially, the dehydration reactions consist of a back side nucleophilic attack of a neutral alcohol on the alkyl group of a protonated alcohol, forming in sequence, two stable intermediate complexes, $[\text{RO}(\text{H}) \cdots \text{R}'\text{-OH}_2]^+$ and $[\text{RO}(\text{H})\text{-R}' \cdots \text{OH}_2]^+$. The latter complex can then rearrange to the proton-bound dimer $(\text{RR}'\text{O})(\text{H}_2\text{O})\text{H}^+$ prior to H_2O loss [16–18].

These systems can also be approached from the point of view of an ion/molecule reaction. When an ion and molecule react in the gas-phase, there are several basic processes that can occur, as outlined in the following:



Initially, AH^+ and B must form an excited dimer ion, $(\text{ABH}^+)^*$. The rate constant for this process is de-

noted by k_{cap} . Once formed, $(\text{ABH}^+)^*$ can dissociate, k_{diss} , or be stabilized by collision with a third body, M, to form stable dimer ions, ABH^+ , ($k_s[\text{M}]$). The dimer can also react further to form products and the rate constant for this process is denoted above as k_p . Reactions (2) and (4) are both unimolecular processes whereas (3) is a bimolecular reaction. Radiative stabilization of the complex has been ignored here due to its long time scale.

The reactions involving protonated and neutral alcohols can be written as follows:



The rate constant, k_{obs} , for the formation of protonated ether and water can be written as [30]

$$k_{\text{obs}} = \rho_{\text{cap}} k_{\text{cap}} \left(\frac{k_p}{k_p + k_{\text{diss}} + k_s[\text{M}]} \right) \quad (6)$$

The probability that a collision will lead to a long-lived excited intermediate complex is denoted ρ_{cap} . The association reaction can normally be assumed to occur on every collision (i.e. $\rho_{\text{cap}} = 1$), though care must be taken when making this assumption [31]. The rate constant for capture collisions occurring between the reactant ion and neutral, k_{cap} , can be calculated using the ion-dipole theory of Su and Chesnavich [32], while $k_s[\text{M}]$ (the rate constant for collisional stabilization of the initially formed excited complex) is typically derived from the ion-induced dipole theory developed by Langevin [33]. In these systems, k_p most directly reflects the rate constant for the isomerization of the initially formed proton-bound dimer, k_{iso} , which ultimately leads to water loss. Since k_{iso} can be modeled using Rice-Ramsperger-Kassel-Marcus (RRKM) theory [34], information that can be obtained about it can yield the energetics of the isomerization of the dimer.

An ion trap mass spectrometer has been used to measure the bimolecular rate constants for ion/molecule reactions that take place between protonated and neutral alcohols. The goal is to measure the ion/molecule reaction rate constants and compare them to those obtained with theory, and to extract information about the cluster ion isomerization barrier.

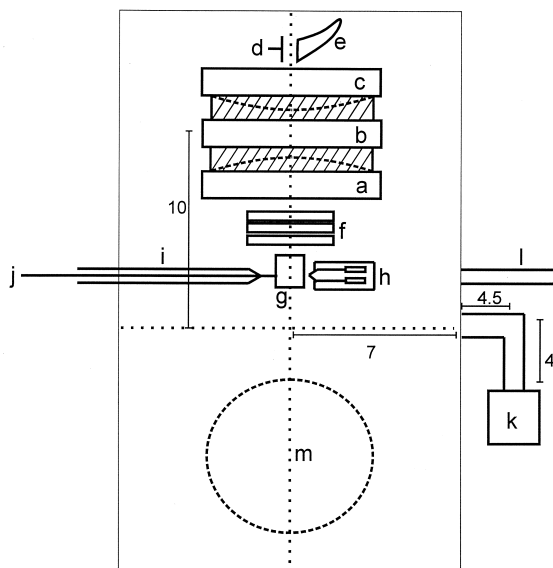


Fig. 1. Schematic of the Finnigan GCQ ion trap mass spectrometer: (a) entrance endcap electrode, (b) ring electrode, (c) exit endcap electrode, (d) conversion dynode, (e) electron multiplier, (f) ion injection/gate lens, (g) ion source volume, (h) filament, (i) heated capillary guide, (j) capillary from sample reservoir, (k) ionization gauge, (l) neutral reagent inlet, and (m) 100 L/s diffusion pump. Distances are shown in centimeters.

2. Experimental procedures

A modified Finnigan GCQ ion trap mass spectrometer, which incorporates an external ion source and running the XCALIBER software package, was employed for all experiments (Fig. 1). The gas chromatograph (GC) oven was 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 through 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

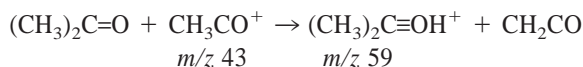
gas is introduced into the ion trap via a 0–10 psi pressure regulator and a capillary restrictor. It enters the trapping volume through a nipple on the entrance endcap electrode.

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 lens in the einzel lens assembly. Ion/molecule reactions were studied using the MS² 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} cm³ molecule⁻¹ s⁻¹.

2.1. Calibration reaction

When determining the absolute pressure of neutral reagent in the ion trap, two factors must be taken into consideration: the ionization gauge response to a particular compound 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:



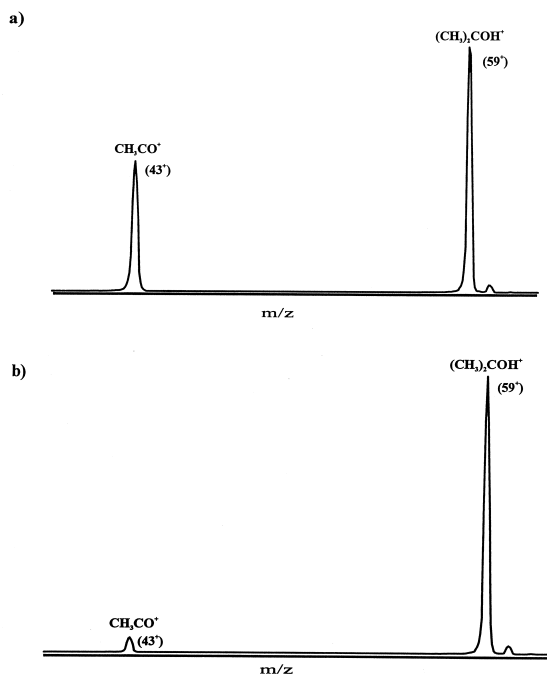


Fig. 2. Mass spectra corresponding to reaction times (a) 1 ms and (b) 30 ms for the ion/molecule reaction between CH_3CO^+ and acetone.

The resulting spectra contained only two peaks, m/z 43 and m/z 59. Experiments were performed at a series of different acetone pressures whereby the reaction times were varied from 1 to 30 ms (Fig. 2). The peak heights for the m/z 43 (H_{43}) and m/z 59 (H_{59}) ions were measured and a plot of $\ln[\text{H}_{43}/(\text{H}_{43} + \text{H}_{59})]$ versus reaction time was made for each pressure; the slope of each plot yielding a pseudo-first-order rate constant [Fig. 3(a)]. A plot of the pseudo-first-order rate constant as a function of acetone pressure yields the bimolecular rate constant for the reaction [Fig. 3(b)]. This experimentally derived value was then corrected to the literature value of $2.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [35,36] resulting in a correction factor for the neutral pressure in the ion trap volume. This calibration was performed numerous times over the course of the study, and the resulting correction factor (0.16) did not change significantly. When neutrals other than acetone were used, an additional correction was applied to account

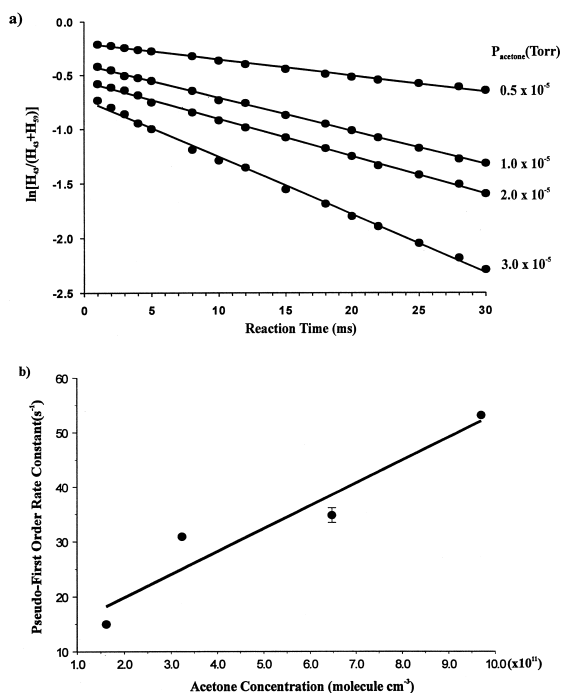


Fig. 3. (a) Pseudo-first-order plots for the reaction $(\text{CH}_3)_2\text{C}=\text{O} + \text{CH}_3\text{CO}^+ \rightarrow (\text{CH}_3)_2\text{COH}^+ + \text{CH}_2\text{CO}$ at four neutral acetone pressures (laboratory frame of reference). (b) Plot of the pseudo-first-order rate constant as a function of acetone pressure. Acetone pressures were corrected as outlined in the text to achieve a bimolecular rate constant of $2.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

for the different response of the ionization gauge between that neutral and acetone [37].

2.2. Temperature of the reaction

One question that arises is the temperature of the ions in the ion trap. The presence of helium buffer gas (~ 1 mTorr) should assist in the thermal equilibration of ions generated in the ion source of the instrument provided they are stored for sufficient time. There has been extensive previous work on estimating the temperature of ions in ion trap mass spectrometers [38–42]. McLuckey et al. [39] measured the rate constants for the desolvation reactions of protonated water and protonated methanol clusters under a variety of trapping conditions. Effective internal temperatures for the dissociating ions could be estimated using the known thermochemistry of the reactions. Under con-

Table 1

Comparison of the measured ion/molecule reaction rate constants, k_{obs} , with the collision-capture limit, k_{cap} , for the reactions leading to protonated ether and neutral water

Reactants	k_{obs} ^{a,b}	k_{cap} ^a
$\text{CH}_3\text{OH}_2^+ + \text{CH}_3\text{OH}$	0.11 ± 0.01	2.3
$\text{CH}_3\text{CH}_2\text{OH}_2^+ + \text{CH}_3\text{OH}$	0.019 ± 0.005	2.1
$\text{CH}_3\text{CH}_2\text{OH}_2^+ + \text{CH}_3\text{CH}_2\text{OH}$	0.14 ± 0.03	2.1
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}_2^+ + \text{CH}_3\text{OH}$	0.061 ± 0.005	2
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}_2^+ + \text{CH}_3\text{CH}_2\text{OH}$	0.21 ± 0.05	2.3
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}_2^+ + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	0.63 ± 0.03	1.9
$(\text{CH}_3)_2\text{CHOH}_2^+ + (\text{CH}_3)_2\text{CHOH}$	1.1 ± 0.1	1.9

^aIn units of $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

^bUncertainties should be viewed as minimum values (see text).

ditions most similar to those in the present study (background pressure ~ 1 mTorr), their results gave ion temperatures between 350 and 450 K. 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. Few, if any, of the reactions we are exploring in this study are likely to have strong temperature dependencies, and so the results for the measured ion/molecule rate constants agree quite well with literature values reported at 300 K. If the ion/molecule reactions under study exhibited greater temperature dependencies, 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 below.

3. Results and discussion

The experimental results are summarized in Table 1.

3.1. Reactions not displaying a proton-bound dimer ion

The reaction between protonated and neutral methanol,

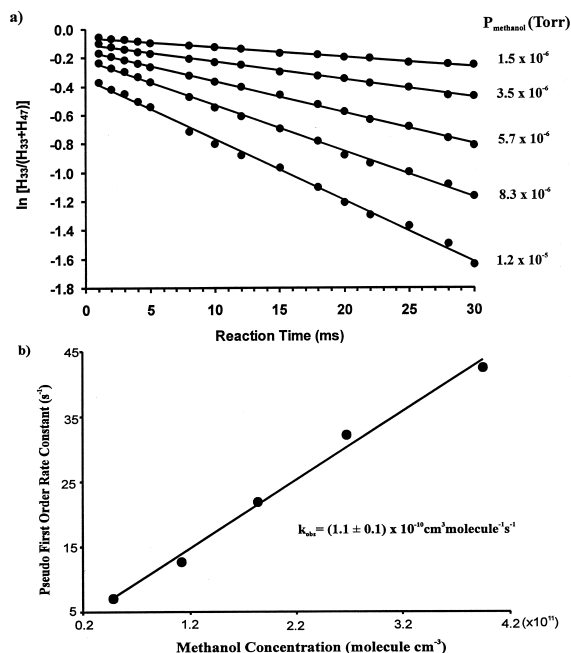
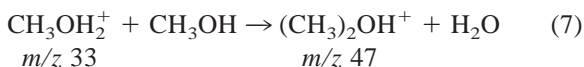


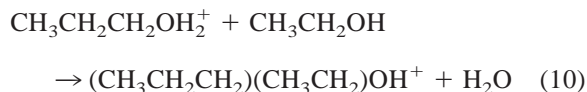
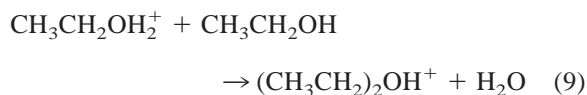
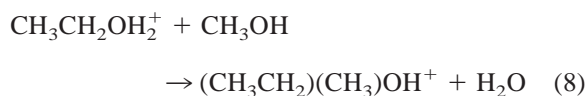
Fig. 4. (a) Pseudo-first-order plots for the reaction $\text{CH}_3\text{OH}_2^+ + \text{CH}_3\text{OH} \rightarrow (\text{CH}_3)_2\text{OH}^+ + \text{H}_2\text{O}$ at four neutral methanol pressures. (b) Plot of the pseudo-first-order rate constant as a function of methanol pressure. Methanol pressures were corrected as outlined in the text. No error bars were drawn as the experimental uncertainty in the data points was smaller than the points themselves.

was studied and two peaks were observed in the mass spectrum: m/z 33 (CH_3OH_2^+) and m/z 47. The latter is known to be protonated dimethylether, $(\text{CH}_3)_2\text{OH}^+$, and is observed as a unimolecular dissociation product of proton-bound methanol dimer ions [16,19,20,22,25–27,43]. The peak heights of the m/z 33 (H_{33}) and m/z 47 (H_{47}) ions were measured and a first-order plot of ion intensity, $[\ln(\text{H}_{33}/(\text{H}_{33} + \text{H}_{47}))]$, versus reaction time yielded pseudo-first-order rate constants [Fig 4(a)]. These rate constants were then plotted against their respective methanol pressures to yield the bimolecular rate constant for the reaction. The correction factor obtained from the acetone calibration experiment was applied to the methanol pressures (plus a correction for the different ion gauge response between acetone and methanol [37]) to obtain the corrected experimental bimolecular rate constant of $(1.1 \pm 0.1) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [Fig.4(b)]. This value compares extremely well with those ob-

tained from ICR techniques. McMahon and Beauchamp [29] derived a value of $1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, whereas Karpas and Meot-Ner [19] obtained a value of $(1.08 \pm 0.22) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Bass et al. [24] derived a value of $(0.9 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, whereas Morris et al. [28] derived a value of $0.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The value derived with the ion trap lies within the experimental uncertainty of each group; all values lying an order of magnitude less than that obtained using the ion-dipole theory of Su and Chesnavich ($2.3 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) [32]. The polarizability and dipole moment of methanol were obtained from the literature [44,45]. The quoted uncertainty is based solely on the experimental data and does not take into account uncertainties in the calibration procedure. Therefore, all uncertainties quoted in this work for k_{obs} should be treated as minimum values.

3.2. Reactions displaying a proton-bound dimer ion

The three systems shown in the following contained only three ions in their mass spectra, the lowest energy protonated alcohol (A), the proton-bound dimer ion of the two reactants (B) and the protonated ether that is due to the dehydration of this proton-bound dimer ion (C):

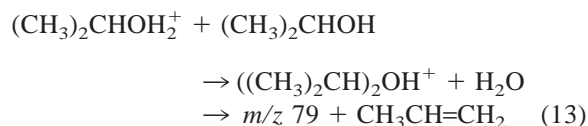
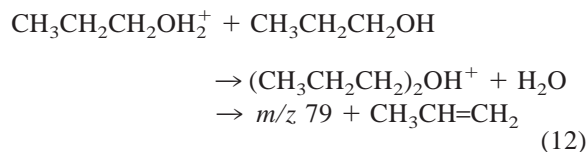
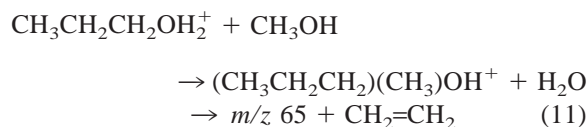


Since the proton-bound dimer is now present in the mass spectra, it must be taken into account when determining the rate constants. As such, plots of $\ln[\text{H}_A/(\text{H}_A + \text{H}_B + \text{H}_C)]$ were made to obtain the pseudo-first-order rate constants. The derived bimolecular rate constants for these three reactions increase in mag-

nitude from $(1.9 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reaction (8) to $(1.4 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reaction (9), and $(2.1 \pm 0.5) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reaction (10) (Table 1). McMahon and Beauchamp [29] derived a value of $2.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reaction (9), whereas Karpas and Meot-Ner [19] derived a value of $(0.68 \pm 0.11) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The present value lies in the middle of these two values. The temperature for these two literature values is quoted at $\sim 300 \text{ K}$. It might be expected that reactions displaying the proton-bound dimer exhibit a stronger temperature dependence than the $\text{CH}_3\text{OH}_2^+ + \text{CH}_3\text{OH}$ reaction. The fact that the observed rate constant for reaction (9) is similar to the two literature values suggests either that the effective ion temperatures are the same, or more likely, that the temperature dependence of reaction (9) is not very significant.

3.3. Reactions displaying a dimer ion and two product ions

The remaining systems exhibited two reaction products, the protonated ether resulting from dehydration of the dimer ion and a peak due to the loss of an alkene from the dimer ion



The appearance of the product ion due to alkene loss in the mass spectra of reactions (11) and (12) had no appreciable effect on the final bimolecular rate constant as it was a minor process in both cases (less than 3% of the total concentration). As such, its inclusion

was not necessary in the final kinetic treatment. It was, however, necessary to include this ion in the treatment of reaction (13) as it was a significant contribution to the reaction products. The rate constants varied in magnitude from $(6.1 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reaction (11) and $(6.3 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reaction (12) to $(1.1 \pm 0.1) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reaction (13), a value that is essentially the same as the collision-capture rate constant, k_{cap} ($1.9 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (Table 1). Karpas and Meot-Ner [19] obtained values of $(1.03 \pm 0.12) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reaction (12) and $(6.14 \pm 0.12) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reaction (13). These values are lower than those obtained with the ion trap. If the ions in the ion trap are at a temperature above ambient, the present results suggest that these two reactions may have significant temperature dependences. In the case of reaction (13), the present k_{obs} reflects the loss of both water and propene, and so will be larger than the rate constant for only water loss. However, the present value will permit the isomerization barrier to be derived as outlined in Sec. 3.4.

3.4. Isomerization energy barrier

The rate constants determined above can be used to obtain information about the reaction surface. 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 for the dissociation is known, and appropriate vibrational frequencies are available for the two transition structures, the isomerization activation energy can be adjusted until Eq. (6) is satisfied.

Ab initio calculations [46] were performed using the GAUSSIAN 98 suite of programs [47]. For each reaction, the proton-bound dimer was optimized at the HF/6-31 G(d) level of theory and vibrational frequencies were calculated and scaled by 0.9135 [48]. The dissociation and isomerization channels were each modeled with the standard RRKM expression:

$$k(E) = \frac{\sigma N^\ddagger(E - E_0)}{h\rho(E)} \quad (14)$$

where $N^\ddagger(E - E_0)$ 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 [34]. 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, $\Delta S^\ddagger(600 \text{ K})$ of $+12 \text{ J K}^{-1} \text{ mol}^{-1}$ for a dissociation reaction and $-12 \text{ J K}^{-1} \text{ mol}^{-1}$ for an isomerization reaction (typical values for these processes). The vibrational frequencies are listed in Table 2.

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 frequencies and the resulting values for $\Delta S^\ddagger(600 \text{ K})$ 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 alcohol pair reactions 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 $\Delta S^\ddagger(600 \text{ K})$ and different assumed reactant ion temperatures will be probed in Sec 3.4.1.

3.4.1. $\text{CH}_3\text{OH} + \text{CH}_3\text{OH}_2^+$

Since the 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. (6):

$$\frac{k_{\text{iso}}}{k_{\text{iso}} + k_{\text{diss}}} = \frac{k_{\text{obs}}}{\rho_{\text{cap}} k_{\text{cap}}} \quad (15)$$

The activation energy for the dissociation reaction of $(\text{CH}_3\text{OH})_2\text{H}^+$ was taken from an equilibrium high-pressure mass spectrometry study conducted by Larson and McMahon, $131 \pm 8 \text{ kJ mol}^{-1}$ [49]. If

Table 2

Vibrational frequencies used in the RRKM modeling of the dissociation and isomerization reactions of the proton-bound dimer ions

System	Unique modes	Common modes ^a
(CH ₃ OH) ₂ H ⁺	42, 71, 96, 113, 115	285, 358, 469, 879, 958, 988, 1044, 1160, 1172, 1199, 1305,
TS (diss)	(−311), ^b 26, 44, 60, 70, 94	1394, 1461, 1484, 1486, 1492, 1496, 1511, 1682, 2308, 2975,
TS (iso)	(−1044), ^b 53, 90, 121, 143, 191	3005, 3060, 3070, 3114, 3127, 3659, 3728
(CH ₃ CH ₂ OH) ₂ H ⁺	2, 44, 65, 83, 115	238, 260, 276, 361, 383, 407, 486, 762, 806, 808, 858, 952, 971,
TS (diss)	(−486, 15, 27, 41, 52, 72	1017, 1049, 1118, 1146, 1180, 1233, 1296, 1302, 1327, 1400,
TS (iso)	(−1017), ^b 30, 55, 82, 104, 144	1419, 1440, 1461, 1482, 1490, 1499, 1501, 1511, 1529, 1700,
		2506, 2933, 2953, 2979, 2988, 3017, 3019, 3026, 3033, 3094,
		3660, 3728
(CH ₃ OH)(CH ₃ CH ₂ OH)H ⁺	36, 65, 75, 90, 141	243, 279, 365, 383, 469, 757, 806, 945, 969, 996, 1037, 1144,
TS (diss)	(−469), ^b 22, 40, 46, 56, 87	1150, 1173, 1243, 1301, 1390, 1402, 1440, 1482, 1489, 1497,
TS (iso)	(−996), ^b 45, 81, 93, 113, 176	1499, 1510, 1512, 1698, 2573, 2953, 2972, 3019, 3025, 3033,
		3054, 3065, 3094, 3657, 3731
(CH ₃ OH)(CH ₃ CH ₂ CH ₂ OH)H ⁺	26, 35, 69, 79, 117	140, 202, 253, 325, 353, 448, 489, 728, 804, 855, 893, 960, 1000,
TS (diss)	(−489), ^b 16, 22, 43, 49, 73	1024, 1049, 1108, 1166, 1175, 1218, 1287, 1304, 1385, 1391,
TS (iso)	(−1000), ^b 32, 44, 86, 98, 146	1424, 1443, 1480, 1488, 1496, 1498, 1503, 1509, 1512, 1687,
		2574, 2934, 2942, 2972, 2972, 3004, 3020, 3020, 3054, 3064,
		3090, 3657, 3733
(CH ₃ CH ₂ OH)(CH ₃ CH ₂ CH ₂ OH)H ⁺	18, 36, 56, 92, 105	145, 208, 240, 277, 292, 329, 386, 454, 481, 755, 772, 806, 834,
TS (diss)	(−481), ^b 11, 22, 35, 57, 65	903, 930, 957, 975, 1044, 1073, 1118, 1146, 1164, 1231, 1274,
TS (iso)	(−1044), ^b 22, 45, 70, 116, 132	1288, 1306, 1350, 1389, 1402, 1437, 1439, 1456, 1482, 1488,
		1497, 1499, 1504, 1511, 1524, 1695, 2429, 2930, 2934, 2952,
		2967, 2977, 2992, 3009, 3018, 3022, 3026, 3033, 3091, 3657, 3738
(CH ₃ CH ₂ CH ₂ OH) ₂ H ⁺	17, 32, 34, 65, 78	124, 136, 187, 227, 227, 272, 289, 352, 425, 471, 481, 747, 752,
TS (diss)	(−480), ^b 11, 20, 21, 40, 49	820, 874, 881, 884, 895, 968, 989, 1011, 1024, 1068, 1125, 1145,
TS (iso)	(−989), ^b 22, 40, 43, 81, 98	1193, 1220, 1256, 1286, 1318, 1322, 1337, 1354, 1390, 1427,
		1436, 1438, 1446, 1493, 1494, 1500, 1501, 1507, 1509, 1512,
		1520, 1685, 2393, 2926, 2935, 2935, 2941, 2965, 2974, 2985,
		2993, 3005, 3013, 3017, 3023, 3027, 3089, 3662, 3723
((CH ₃) ₂ CHOH) ₂ H ⁺	12, 27, 37, 76, 97	209, 222, 229, 261, 271, 338, 350, 353, 382, 412, 449, 465, 500,
TS (diss)	(−500), ^b 8, 17, 23, 47, 60	690, 784, 859, 919, 934, 936, 943, 944, 963, 1056, 1113, 1128,
TS (iso)	(−963), ^b 16, 34, 46, 95, 122	1139, 1172, 1195, 1231, 1302, 1371, 1380, 1386, 1404, 1435,
		1441, 1445, 1447, 1478, 1485, 1485, 1492, 1495, 1499, 1503,
		1508, 1702, 2545, 2933, 2937, 2941, 2945, 2977, 2993, 3001,
		3008, 3009, 3011, 3019, 3021, 3032, 3058, 3658, 3730

^aCommon modes are used for the reactant ion and both transition states.^bCommon mode removed to represent the motion over the barrier.

CH₃OH and CH₃OH₂⁺ in the ion trap are initially 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 153 kJ mol^{−1} (131 kJ mol^{−1} plus the average thermal internal energy of the two reactants). Then by fixing ΔS^\ddagger (600 K) for the two unimolecular channels (−12 J K^{−1} mol^{−1} and + 12 J K^{−1} mol^{−1} for the isomerization and

dissociation processes, respectively), the only adjustable parameter becomes the activation energy for the isomerization channel. This value can be adjusted so that Eq. (15) is satisfied. With this procedure, the E_0 for the isomerization process was determined to be 132 ± 2 kJ mol^{−1} (Table 3). It should be noted that the quoted precision of this value was determined primarily by the precision in E_{diss} quoted by Larson

Table 3
Isomerization barriers extracted for the systems in this study

Proton-bound dimer	$E_{\text{diss}}^{\text{a,b}}$	$E_{\text{iso}}^{\text{a,c}}$
$(\text{CH}_3\text{OH})(\text{CH}_3\text{OH})\text{H}^+$	131	132 (125) ^d
$(\text{CH}_3\text{CH}_2\text{OH})(\text{CH}_3\text{OH})\text{H}^+$	122	128
$(\text{CH}_3\text{CH}_2\text{OH})(\text{CH}_3\text{CH}_2\text{OH})\text{H}^+$	131	126
$(\text{CH}_3\text{CH}_2\text{CH}_2\text{OH})(\text{CH}_3\text{OH})\text{H}^+$	123	123
$(\text{CH}_3\text{CH}_2\text{CH}_2\text{OH})(\text{CH}_3\text{CH}_2\text{OH})\text{H}^+$	126	118
$(\text{CH}_3\text{CH}_2\text{CH}_2\text{OH})(\text{CH}_3\text{CH}_2\text{CH}_2\text{OH})\text{H}^+$	131	109
$((\text{CH}_3)_2\text{CHOH})((\text{CH}_3)_2\text{CHOH})\text{H}^+$	131	107

^aValues in kJ mol^{-1} .

^bSee [49], quoted uncertainty $\pm 8 \text{ kJ mol}^{-1}$.

^cMinimum uncertainty 2 kJ mol^{-1} (see text).

^dSee [16].

and McMahon [49], and as such, should be considered a minimum value for the uncertainty.

In the previous calculations, two somewhat arbitrary parameters are used, $\Delta S^\ddagger (600 \text{ K}) = \pm 12 \text{ J K}^{-1} \text{ mol}^{-1}$, and a reactant temperature of 298 K. When the average thermal energy for the reactants is determined at 400 K, the fit to Eq. (15) also yields an E_{iso} of 132 kJ mol^{-1} . In other words, at a $\Delta S^\ddagger (600 \text{ K}) = \pm 12 \text{ J K}^{-1} \text{ mol}^{-1}$, the ratio of k_{iso} to k_{diss} is not strongly temperature dependent. Increasing the difference in ΔS^\ddagger between the two channels to $\pm 20 \text{ J K}^{-1} \text{ mol}^{-1}$ does significantly alter the value for E_{iso} , 125 kJ mol^{-1} . The present result compares well with the theoretical value of 125 kJ mol^{-1} calculated by Bouchoux and Choret [16] using the MP2/6-31G* level of theory (taking into account at least a $\pm 10 \text{ kJ mol}^{-1}$ uncertainty in the calculated value at this level of theory).

3.4.2. Other systems

The mass spectra of all the other reaction systems studied contained the intact proton-bound dimer and so Eq. (6) must be used. The rate constant for collisional stabilization of the initially formed excited complex, $k_s[\text{M}]$, was calculated to be $1.75 \times 10^4 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ based upon the polarizability of the helium atom ($0.20 \times 10^{-24} \text{ cm}^3$) [44] and a helium pressure of 1 mTorr. The extraction of E_{iso} for the initially formed proton-bound dimer was done in a manner similar to that described above for the $\text{CH}_3\text{OH}_2^+ + \text{CH}_3\text{OH}$ reaction. The vibrational frequen-

cies employed in the RRKM analysis are listed in Table 2. The values for E_{diss} were all either experimentally measured by Larson and McMahon [49], or derived using the empirical formula developed by them for asymmetric proton-bound dimers. All values can be found in Table 3.

An $\text{S}_{\text{N}}2$ -type mechanism has been established for the dehydration of these proton-bound alcohol dimers. It has been confirmed for the methanol dimer by experiments [28] and theory [16–18] and experiments also suggest this type of mechanism for the propanol dimers [23]. The present results are consistent with this general mechanism. The value of E_{iso} decreases as the size of the alkyl groups in the reacting system increase. This is most evident in the series of reactions involving protonated *n*-propanol and the homologous series of alcohols: methanol, ethanol, and *n*-propanol. The value of E_{iso} drops by 14 kJ mol^{-1} across the series, which is consistent with greater charge stabilization in the intermediate $[\text{RO}(\text{H}) \cdots \text{R}'\text{OH}_2]^+$ and $[\text{RO}(\text{H})\text{--R}' \cdots \text{OH}_2]^+$ complexes. The trend is also consistent with a weaker $\text{R}'\text{--OH}_2^+$ bond strength which is expected if the water loss occurs from the methanol, ethanol and *n*-propanol moieties. This would need to be confirmed with isotopic labeling experiments.

4. Conclusions

A Finnigan GCQ ion trap mass spectrometer was used to measure the rate constants for the ion/molecule reactions involving protonated and neutral alcohols. RRKM modeling of the unimolecular reactions of the initially formed excited proton-bound dimer allowed the activation energy for the isomerization of the proton-bound dimers to be estimated. These values decrease with increasing size of the dimer, which is consistent with the previously proposed $\text{S}_{\text{N}}2$ -type mechanism for the reaction, which ultimately leads to the loss of a molecule of water.

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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 reaction between CH_3OH_2^+ and CH_3OH with FT-ICR mass spectrometry and obtained a value at 293 K of $0.111 \pm 0.001 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, in excellent agreement with the present result. Their experiments show that the rate constant decreases to $0.060 \pm 0.003 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 338 K. Modeling of their results indicated that this ion/molecule reaction does not initially proceed via the proton-bound dimer.

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