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Reactions of $H_3O^+(H_2O)_n$ and $H^+(H_2O)_n(CH_3COCH_3)_m$ with CH_3SCH_3

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Abstract

We have measured the rate constants and product branching fractions for the reactions of water clusters and mixed water/acetone clusters, $H_3O^+(H_2O)_n$ and $H^+(H_2O)_n(CH_3COCH_3)_m$, reacting with dimethylsulfide, CH_3SCH_3. The proton hydrates react rapidly. For $n = 0$–2, the reactions proceed at the collision rate within experimental error, while the reaction efficiency decreases slightly for $n = 3$ and further for $n = 4$ and $n = 5$. The product distributions for the higher clusters are mainly switching one H_2O for the CH_3SCH_3. The product distributions appear to be affected by thermal dissociation at higher temperatures. The reactions of $H^+(H_2O)_n(CH_3COCH_3)_m$ with CH_3SCH_3 are also rapid and proceed by switching both a CH_3COCH_3 and a H_2O out of the primary ion. The rate constant for $H^+(CH_3COCH_3)_2$ is very slow, although the addition of two H_2O ligands increases reaction by a factor of 13 and 21, respectively. The reactivity of $H^+(H_2O)(CH_3COCH_3)_3$ decreases to a value close to that of $H^+(CH_3COCH_3)_2$. These results indicate that $H_3O^+(H_2O)_n$ ions can be used as chemical ionization agents for CH_3SCH_3 detection in the atmosphere and that use of the mixed cluster ions, $H^+(H_2O)_n$ $(CH_3COCH_3)_m$, would be problematic. (Int J Mass Spectrom 179/180 (1998) 243–251) © 1998 Elsevier Science B.V.

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1. Introduction

Chemical ionization mass spectrometry (CIMS) has become a very important tool for measuring trace gas concentrations in the atmosphere [1]. The technique relies on finding a suitable precursor ion that will react rapidly and selectively with the neutral to be detected. Therefore, a prerequisite to any new CIMS method is a thorough understanding of the underlying ion chemistry. Since the atmosphere has a large concentration of water vapor, many of the precursor ions used in CIMS are hydrated [2]. In order to study the ion chemistry of likely CIMS precursor ions and their hydrated clusters, we have added a supersonic cluster ion source to our variable temperature selected ion flow tube (SIFT) [3]. This allows us not only to measure quantitatively the rate constants involved but also to obtain detailed product distributions for many reactions. Unlike flowing afterglow instruments, where reactants are coupled and erroneous rate constant measurements have resulted, making measurements in a SIFT guarantees that the reactants are not coupled and that the sensitivity to cluster size can be

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Dedicated to Professor Fulvio Cacace in recognition of his outstanding contributions for many decades to gas-phase ion chemistry and physics.

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measured. A key aspect of these measurements is the ability to vary the temperature since many of the species of interest are not stable at room temperature. Up to now, the modified SIFT apparatus has only been used to study systems involving negative cluster ions [3]. These studies have proven useful in understanding fundamental aspects of cluster ion stability and reactivity and in elucidating CIMS detection schemes for several neutral molecules including SO_2 [4] and H_2SO_4 [5]. In this article we report the first measurements taken with this apparatus involving positive cluster ions.

Our goal is to study potential CIMS schemes that could be used to determine atmospheric concentrations of dimethylsulfide, CH_3SCH_3. This molecule, which is produced from marine microorganisms and emitted from the oceans [6], is later oxidized to SO_2 and plays a role in aerosol sulfate formation in the remote marine regions. Kelly and Kenny [6] have previously shown that atmospheric pressure CIMS using a triple quadrupole detector can be both selective and sensitive for monitoring CH_3SCH_3. However, one potential application involves instrumenting a remotely piloted vehicle (RPV) to fly into the marine boundary layer to determine atmospheric CH_3SCH_3 concentrations. Because RPVs have extremely small payloads and power sources, it would be difficult to employ a triple quadrupole instrument for this purpose. Rather than relying on examination of daughter ion spectra from a triple quadrupole instrument for determination of CH_3SCH_3 concentrations, we hope to achieve the required sensitivity for CIMS through an appropriate choice of ion chemistry.

The proton hydrate ions, $H_3O^+(H_2O)_n$, are potential precursor ions for positive ion CIMS with atmospheric applications [2]. This is because of several reasons: these ions are rapidly formed upon ionizing air, partly because of the large water vapor concentration in the atmosphere, and these ions often react rapidly with molecules that have proton affinities greater than that of water [7], a class which includes many atmospheric species. For these reasons, we have examined the chemistry of $H_3O^+(H_2O)_n$ ions reacting with CH_3SCH_3 in order to evaluate the potential use of these ions in a CIMS detection scheme for dimethylsulfide. Both rate constants and products were measured as a function of temperature over the range 175–300 K.

While the reactions of $H_3O^+(H_2O)_n$ with CH_3SCH_3 may be fast enough for detection of CH_3SCH_3, they may or may not have sufficient selectivity to be useful for an atmospheric CIMS detection scheme. A simple way to make the chemistry more selective is to narrow the proton affinity difference between the core ion in the cluster series and the neutral to be detected. Since the proton affinity difference between H_2O and CH_3SCH_3 is 140 kJ mol^{-1} there are many molecules that fit this criterion [8]. For example, acetone (CH_3COCH_3) has a proton affinity only 19 kJ mol^{-1} less than that of CH_3SCH_3, making clusters of the type $H^+(H_2O)_n(CH_3COCH_3)_m$ potentially suitable precursor ions for CH_3SCH_3 detection. The second part of this study examined the reactivity of this mixed cluster system with CH_3SCH_3.

2. Experimental

The measurements were made in a variable temperature selected ion flow tube equipped with a supersonic cluster ion source. This experimental setup has been described previously in detail [3,9,10]. The instrument is operated like any selected ion flow tube except that the standard electron impact ion source is replaced by a supersonic expansion source consisting of a stagnation cell, an electron filament and an entrainment gas inlet. To produce pure water clusters, 1–2 atm of Ar and several milliliters of liquid H_2O were placed in the stagnation cell. The H_2O vapor concentration in the cell was controlled by resistively heating the stagnation cell which thereby determined the H_2O vapor pressure. The Ar/H_2O gas mixture was expanded from the stagnation cell through a 25 μm orifice into a vacuum chamber pumped by a 10 in. diffusion pump. The expanding gas was ionized with a negatively biased hot filament (ThO_2/Ir) to produce the primary clusters $H_3O^+(H_2O)_n$ as well as Ar^+. To produce ions containing CH_3COCH_3, one or both of the following were done. CH_3COCH_3 was added to the reservoir. This worked well for a short time before the CH_3COCH_3 completely evaporated from the reservoir due to its high vapor pressure. Alternatively, CH_3COCH_3 was added to an entrainment inlet just downstream of the expansion [3]. This provided longer term stability of the signal. However, with either method we found that both thoriated iridium and rhenium filaments had a short lifetime in the presence of CH_3COCH_3.

The resulting distribution of ionic clusters was sampled with a blunt skimmer and passed into a quadrupole mass filter. A single ionic cluster was mass selected and injected into the flow tube via a Venturi inlet. The ions were transported down the tube by a fast flow of He buffer gas maintained at a pressure on the order of 0.4 Torr. A portion of the clusters dissociated upon injection or by thermal decomposition in the flow tube. The extent of dissociation depended on the flow tube temperature, the size of the cluster, and the energy of injection. At times we injected the cluster we were interested in studying and then minimized breakup by lowering the injection energy until the point where further reduction resulted in loss of most of the signal. Alternatively, we injected a cluster with one extra ligand and then set conditions so most of the selected cluster decomposed by losing one ligand and not two. Finally, we injected a broad distribution of clusters with masses greater than the cluster of interest and let them decompose (mostly thermally) to the cluster to be studied. This final method can yield quite pure signals of a specific cluster but only over a narrow temperature range. This method also results in the largest signals since ions of many masses all decompose to the same ion. The maximum temperature at which a particular cluster could be observed is controlled by thermal decomposition in the flow tube [3]. Larger clusters that have weaker bond strengths [11] can only be seen at low temperatures.

The CH_3SCH_3 reactant (99+%) was obtained from Aldrich and was used without further purification except that several freeze/thaw cycles were performed to eliminate dissolved gases. CH_3SCH_3 was used both neat and in He mixtures, the latter being necessary since the rates for many of the reactions were quite rapid. CH_3SCH_3 was introduced into the flow tube through a heated finger inlet [12]. Such an inlet was necessary because CH_3SCH_3 freezes in a standard inlet at temperatures where the larger cluster ions are stable. Even with the heated inlet, CH_3SCH_3 froze in the inlet line at temperatures much below 176 K, the lowest temperature used in this study. This temperature also determined the largest clusters that could be studied since clusters larger than those studied here were thermally unstable at temperatures of 176 K and above.

The reactant and product ions were sampled through a 0.2 mm orifice mounted on a blunt sampling cone and were mass analyzed in a second quadrupole mass spectrometer. To avoid excessive mass discrimination, the resolution of the downstream quadrupole was set as low as possible while still completely separating the reactant and product peaks. This has been shown previously to yield results accurate to approximately 10%. The reaction time was obtained from previous measurements of the ion time-of-flight.

Rate constants were determined by recording the semilogarithmic decrease in the reactant ion signal as a function of the CH_3SCH_3 flow rate. Product distributions were determined by monitoring the fractional product ion signal intensities as a function of CH_3SCH_3 flow rate. Extrapolation to zero flow yields the branching ratio for the primary reaction. At times several primary ions were present in the flow tube simultaneously, making corrections for the products of minor primary ions necessary. Typically the corrections are very small for ions with small numbers of ligands and increase with cluster size. We estimate that the reaction rate constants determined with this apparatus have an absolute uncertainty of ±25% and a relative error of ±15% [10].

3. Results and discussion

3.1. $H_3O^+(H_2O)_n$ clusters

Table 1 lists the rate constants, product branching fractions, and reaction efficiencies for the reactions of $H_3O^+(H_2O)_n$, $0 \leq n \leq 5$, with CH_3SCH_3. (Collisional rate constants were calculated using the param-

Table 1
Measured rate constants ($\times 10^{-9}$ cm^3 s^{-1}) and product branching fractions (shown in italics) for the reactions of $H_3O^+ \cdot (H_2O)_n$ with CH_3SCH_3 as a function of temperature; reaction efficiencies (in percent) are given in parentheses

Reaction		298 K	225 K	203 K	178 K
$H_3O^+ + CH_3SCH_3$	$\rightarrow$ products	2.5 (96)	2.9 (104)	3.0 (103)	3.1 (103)
	$\rightarrow H^+ \cdot CH_3SCH_3 + H_2O$	*1.0*	*1.0*	*1.0*	*1.0*
$H_3O^+ \cdot (H_2O) + CH_3SCH_3$	$\rightarrow$ products	2.1 (103)	2.4 (109)	2.5 (108)	2.6 (108)
	$\rightarrow H^+ \cdot CH_3SCH_3 + 2H_2O$	*1.0*	*0.84*	*0.82*	*0.68*
	$\rightarrow H^+ \cdot H_2O \cdot CH_3SCH_3 + H_2O$		*0.16*	*0.18*	*0.32*
$H_3O^+ \cdot (H_2O)_2 + CH_3SCH_3$	$\rightarrow$ products	1.8 (100)	2.2 (110)	2.3 (110)	2.4 (111)
	$\rightarrow H^+ \cdot CH_3SCH_3 + 3H_2O$	*0.75*	*0.49*	*0.17*	0.04
	$\rightarrow H^+ \cdot H_2O \cdot CH_3SCH_3 + 2H_2O$	*0.25*	*0.18*	*0.34*	*0.16*
	$\rightarrow H^+ \cdot (H_2O)_2 \cdot CH_3SCH_3 + H_2O$		*0.33*	*0.49*	*0.80*
$H_3O^+ \cdot (H_2O)_3 + CH_3SCH_3$	$\rightarrow$ products	1.4 (82)	1.6 (89)	1.7 (89)	1.8 (90)
	$\rightarrow H^+ \cdot H_2O \cdot CH_3SCH_3 + 3H_2O$		*0.35*	*0.11*	
	$\rightarrow H^+ \cdot (H_2O)_2 \cdot CH_3SCH_3 + 2H_2O$		*0.06*	*0.09*	*0.25*
	$\rightarrow H^+ \cdot (H_2O)_3 \cdot CH_3SCH_3 + H_2O$		*0.59*	*0.80*	*0.75*
$H_3O^+ \cdot (H_2O)_4 + CH_3SCH_3$	$\rightarrow$ products		1.3 (74)	1.4 (78)	1.5 (79)
	$\rightarrow H^+ \cdot (H_2O)_3 \cdot CH_3SCH_3 + 2H_2O$			*0.47*	
	$\rightarrow H^+ \cdot (H_2O)_4 \cdot CH_3SCH_3 + H_2O$			*0.53*	*1.0*
$H_3O^+ \cdot (H_2O)_5 + CH_3SCH_3$	$\rightarrow$ products				1.4 (78)
	$\rightarrow H^+ \cdot (H_2O)_4 \cdot CH_3SCH_3 + 2H_2O$				*0.15*
	$\rightarrow H^+ \cdot (H_2O)_5 \cdot CH_3SCH_3 + H_2O$				*0.85*

etrized trajectory calculations of Su and Chesnavich [13,14].) For $n = 0$–3, the rate constants were measured from 178 to 298 K, although product branching fractions could only be determined at temperatures of $\leq$225 K for $n = 3$. For $n = 4$, rate constants were measured at temperatures of $\leq$225 K, whereas product branching fractions were determined at temperatures of $\leq$203 K. The reaction of $n = 5$ could be studied only at 178 K.

Fig. 1 shows the rate constants for all six reactions as a function of temperature. The rate constants decrease monotonically with increasing cluster size. Much of the decrease is explained by the decrease in the collisional rate constant with increasing molecular weight of the ion. For $n = 0$–2, the rate constants are collisional within experimental error. For $n = 3$, the rate constants appear to be approximately 90% of the collisional value. We believe this represents a real decrease in reaction efficiency since all rate constants were taken under the same conditions and were sometimes taken simultaneously for the different-sized clusters. This is reinforced by the fact that the decrease in efficiency for $n = 3$ is observed at four temperatures, eliminating random scatter for the decreased efficiency. Similarly, the reaction efficiencies for $n = 4$ and $n = 5$ reacting with CH_3SCH_3 decrease to approximately 78%.

The slight decrease in efficiency at $n = 3$ is probably related to the first solvation shell of $H_3O^+(H_2O)_n$ being filled. $H_3O^+(H_2O)_3$ has each of

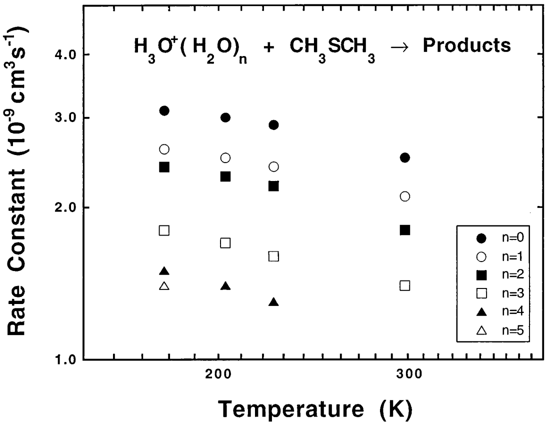

Fig. 1. Rate constants for the reactions of $H_3O^+(H_2O)_n$ with CH_3SCH_3 as a function of temperature.

the hydrogens of the H_3O^+ core ion bonded to a water molecule, and upon approaching the $H_3O^+(H_2O)_3$ cluster, a CH_3SCH_3 molecule cannot access the central core ion directly but instead interacts with a ligand initially. It appears this has a real, although small, effect on the reactivity. Similarly, ligands occupy the second solvation shell in the $n = 4$ and $n = 5$ clusters, further screening the ionic core, and the efficiency continues to decrease slightly. Evidence for such structural effects on reactivity have been observed previously [3].

Rate constants for the reactions of H_3O^+ and $H_3O^+(H_2O)$ with CH_3SCH_3 have been measured previously at 300 K. Passarella *et al.* [15] reported a rate constant of 2.1×10^{-9} cm^3 s^{-1} for the reaction of H_3O^+ with CH_3SCH_3, in good agreement with our value of 2.5×10^{-9} cm^3 s^{-1}. Williams *et al.* [16] reported a value of 1.7×10^{-9} cm^3 s^{-1} for both H_3O^+ and $H_3O^+(H_2O)$ reactions with CH_3SCH_3, over 30% less than the collision rate and the present measurements.

The temperature dependence of all the reactions is the same within experimental error and is equal to the dependence of the collisional rate constant on temperature. The values range from $T^{-0.4}$ to $T^{-0.6}$. No trend in the temperature dependences was observed even though the efficiencies for the larger clusters decrease slightly.

The reaction of H_3O^+ with CH_3SCH_3 proceeds exclusively by proton transfer:

$$H_3O^+ + CH_3SCH_3 \rightarrow H^+(CH_3SCH_3) + H_2O + 140 \text{ kJ mol}^{-1} \quad (1)$$

(The thermochemistry reported here is taken from the NIST Webbook [8] and from the compilation of Keesee and Castleman [11]. The thermochemistry of the mixed clusters is not known.) The reaction is a very exothermic proton transfer and proceeds rapidly as expected.

The first cluster ion, $H_3O^+(H_2O)$, produces primarily $H^+(CH_3SCH_3)$ and also some hydrated product ions:

$$\begin{aligned} H_3O^+(H_2O) + CH_3SCH_3 &\rightarrow H^+(CH_3SCH_3) + 2H_2O + 2 \text{ kJ mol}^{-1} \\ &\rightarrow H^+(CH_3SCH_3)(H_2O) + H_2O \end{aligned} \quad (2)$$

At 298 K the unhydrated product is formed exclusively, as also reported by Williams *et al.* [16]. However, as the temperature decreases, the hydrated product ion increases such that it accounts for a third of the reactivity at 178 K. Production of the bare ion, $H^+(CH_3SCH_3)$, is only 2 kJ mol^{-1} exothermic if one assumes two neutral water molecules, whereas formation of a water dimer increases the exothermicity by 23 kJ mol^{-1} [17]. The data for this reaction cannot distinguish if the measured product distribution is affected by thermal dissociation of $H^+(H_2O)(CH_3SCH_3)$ by collisions with the He buffer gas; however, data on the reaction of the next larger proton hydrate indicates that the product distribution must be affected by thermal dissociation.

For $H_3O^+(H_2O)_2$, the primary product ion at 298 K is also the unclustered $H^+(CH_3SCH_3)$. Because the channel that results in direct formation of this ion is significantly endothermic (~85 kJ mol^{-1}), the presence of $H^+(CH_3SCH_3)$ product ions indicates that thermal dissociation of the larger hydrated product ions must be occurring. Such thermal dissociation of cluster products has often been observed in previous experiments of this kind [3]. The temperature dependence of the branching fractions lends further support to this hypothesis. The data taken at low temperature (178 K), which should suffer little thermal dissociation, show that $H^+(H_2O)_2(CH_3SCH_3)$ accounts for 80% of the reactivity, while the $H^+(CH_3SCH_3)$ product accounts for only 4% of the reaction at 178 K. Although the 4% value at 178 K may result from fragmentation during sampling [18], this cannot account for the room temperature results since sampling fragmentation is at most on the order of several percent. The singly hydrated species accounts for less than one third of the total reactivity at all temperatures studied. This yields an odd product ion distribution at 225 K where the $H^+(CH_3SCH_3)$ and $H^+(H_2O)_2(CH_3SCH_3)$ products are more abundant than the $H^+(H_2O)(CH_3SCH_3)$ product.

The higher order reactant clusters, $H_3O^+(H_2O)_{3–5}$,

Table 2
Measured rate constants ($\times 10^{-9}$ cm^3 s^{-1}) and product branching fractions (shown in italics) for the reactions of $H^+ \cdot (H_2O)_n \cdot (C_3H_6O)_m$ with CH_3SCH_3 as a function of temperature; reaction efficiencies (in percent) are given in parentheses

Reaction	300 K	223 K	176 K
$CH_3CO^+ + CH_3SCH_3 \rightarrow$ products	1.5 (74)	1.7 (78)	2.1 (87)
$\rightarrow H^+CH_3SCH_3 + CH_2CO$	*0.95*	*0.93*	*0.86*
$\rightarrow CH_3CO^+ \cdot CH_3SCH_3$	*0.05*	*0.07*	*0.14*
$H^+ \cdot C_3H_6O + CH_3SCH_3 \rightarrow$ products	1.5 (80)	1.9 (93)	2.1 (95)
$\rightarrow H^+CH_3SCH_3 + C_3H_6O$	*1.00*	*1.00*	*0.95*
$\rightarrow H^+ \cdot C_3H_6O \cdot CH_3SCH_3$			*0.05*
$H^+ \cdot H_2O \cdot C_3H_6O + CH_3SCH_3 \rightarrow$ products	1.5 (87)	1.4 (73)	1.8 (89)
$\rightarrow H^+ \cdot C_3H_6O \cdot CH_3SCH_3 + H_2O$	*1.00*	*1.00*	*0.84*
$\rightarrow H^+ \cdot H_2O \cdot CH_3SCH_3 + C_3H_6O$			*0.16*
$H^+ \cdot (H_2O)_2 \cdot C_3H_6O + CH_3SCH_3 \rightarrow$ products		1.2 (69)	1.6 (80)
$\rightarrow H^+ \cdot H_2O \cdot C_3H_6O \cdot CH_3SCH_3 + H_2O$		*0.33*	*0.35*
$\rightarrow H^+ \cdot (H_2O)_2 \cdot CH_3SCH_3 + C_3H_6O$		*0.66*	*0.65*
$H^+ \cdot (H_2O)_3 \cdot C_3H_6O + CH_3SCH_3 \rightarrow$ products		1.2 (69)	1.3 (69)
$H^+ \cdot (C_3H_6O)_2 + CH_3SCH_3 \rightarrow$ products	0.0025 (0.2)	0.034 (2)	0.048 (3)
$H^+ \cdot H_2O \cdot (C_3H_6O)_2 + CH_3SCH_3 \rightarrow$ products		0.44 (26)	
$H^+ \cdot (H_2O)_2 \cdot (C_3H_6O)_2 + CH_3SCH_3 \rightarrow$ products		0.72 (43)	1.2 (66)
$H^+ \cdot H_2O \cdot (C_3H_6O)_3 + CH_3SCH_3 \rightarrow$ products		0.047 (3)	

show similar results. In the $H_3O^+(H_2O)_3$ reaction, thermal dissociation must also affect the rate constants since the direct $H^+(H_2O)(CH_3SCH_3)$ channel is endothermic, and this product ion disappears at lower temperatures where there is little thermal dissociation. The larger ions, $H_3O^+(H_2O)_4$ and $H_3O^+(H_2O)_5$, could only be studied at the two lowest temperatures, and thermal dissociation does not appear to be as important. Upon examining all the data taken at 178 K, where little disturbance of the product distribution by thermal dissociation should occur, one finds that a direct swap of one H_2O ligand for a CH_3SCH_3 molecule accounts for at least 75% of the reactivity for all species larger than $H_3O^+(H_2O)$.

The product distributions reported for the larger clusters may be due in part to collisions with the He buffer gas. The reactants first form a complex which then dissociates by losing a H_2O molecule. The remaining ion may still have enough energy to dissociate another H_2O molecule. However, if the lifetime of this species is long enough, a collision with He will occur before dissociation. The He collision can absorb enough energy to prevent the cluster from further dissociation. This would be more prevalent for larger clusters where the extra degrees of freedom will result in longer lifetimes. The lifetime, with respect to a He collision, in on the order of 10^{-7} s.

3.2. Mixed $H^+(H_2O)_n(CH_3COCH_3)_m$ clusters

Table 2 shows the rate constants, product branching fractions, and reaction efficiencies for the reactions of mixed water/acetone clusters, $H^+(H_2O)_n(CH_3COCH_3)_m$, with CH_3SCH_3 as a function of temperature. Also included in Table 2 is the reaction of CH_3CO^+ with CH_3SCH_3 because this ion is formed in small quantities upon injection of $H^+(CH_3COCH_3)$ and must be accounted for in determining branching fractions. The reaction of $H^+(CH_3COCH_3)$ occurs at 80%–95% of the collision rate; there is a slight increase in efficiency with decreasing temperature as is often observed for ion–molecule reactions [7]. Addition of a single H_2O ligand has little effect on the reactivity. Although $H^+(H_2O)_{2,3}(CH_3COCH_3)$ both react with slightly lower efficiencies, the reaction efficiency is never lower than 69% of the collisional value. Fig. 2 shows the efficiency as a function of the number of H_2O ligands at 176 K. The graph shows a monotonic decrease in efficiency with cluster size, with the

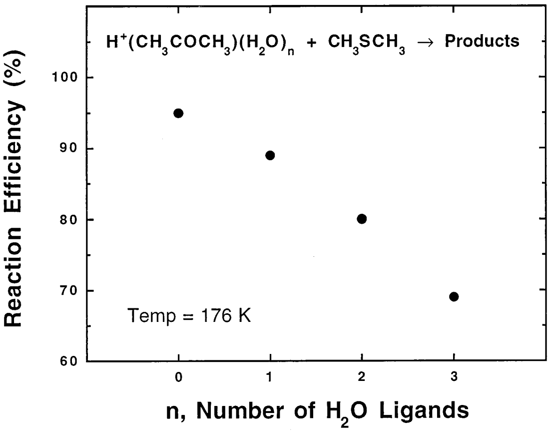

Fig. 2. Efficiencies for the reactions of $H^+(H_2O)_n(CH_3COCH_3)$ with CH_3SCH_3 as a function of n at 176 K.

efficiency decreasing by approximately 9% for each additional H_2O ligand. This trend is consistent with what is often found for cluster reactions. The trends at higher temperatures have more scatter.

In contrast to the minimal reactivity changes that occur upon increasing H_2O ligands in the mixed clusters, $H^+(H_2O)_n(CH_3COCH_3)$, the addition of more CH_3COCH_3 ligands has a dramatic impact on reactivity. For example, the addition of another CH_3COCH_3 ligand to the unhydrated species, $H^+(CH_3COCH_3)$, decreases the rate constant by a factor of 44–600, depending on temperature, with the lower number applying to higher temperatures. Similarly, the sequential addition of two more CH_3COCH_3 ligands to the singly hydrated mixed cluster, $H^+(H_2O)(CH_3COCH_3)$ decreases the rate constant at 223 K by factors of 3 and 30, respectively. Interestingly, it appears that increasing the level of hydration in mixed clusters that contain multiple CH_3COCH_3 ligands reverses this trend, as the rate constants increase. For example, sequentially adding two H_2O ligands to the $H^+(CH_3COCH_3)_2$ cluster increases the rate constant at 223 K by factors of 13 and 21, respectively.

Perhaps this odd pattern of reactivity reflects the difficulty of transferring the proton: In the protonated acetone dimer, the proton is presumably hydrogen bonded to both oxygen atoms, making it relatively inaccessible; whereas, the addition of a single H_2O molecule to the cluster will probably yield a cluster with a H_3O^+ core [19,20], leaving the proton more accessible. Addition of a second H_2O could add more sites for reaction.

Product information for the reactions of CH_3SCH_3 with the mixed clusters was possible only for the reactions of $H^+(H_2O)_{0-3}(CH_3COCH_3)$. Clusters containing more than one CH_3COCH_3 ligand could not be injected so that one ion dominated the spectra in the absence of the neutral reactant. Therefore, the corrections necessary to derive the branching fractions were larger than the branching fractions. The unhydrated ion reaction proceeds primarily by proton transfer with some clustering also occurring:

$$\begin{aligned} H^+(CH_3COCH_3) + CH_3SCH_3 &\rightarrow H^+(CH_3SCH_3) + CH_3COCH_3 + 19\ \text{kJ mol}^{-1} \\ &\rightarrow H^+(CH_3COCH_3)(CH_3SCH_3) \end{aligned} \tag{3}$$

The clustering channel is negligible except at 176 K where it accounts for 5% of the total reactivity. The reaction of CH_3SCH_3 with $H^+(H_2O)(CH_3COCH_3)$ also produces two product ions:

$$\begin{aligned} H^+(H_2O)(CH_3COCH_3) + CH_3SCH_3 &\rightarrow H^+(CH_3SCH_3)(CH_3COCH_3) + H_2O \\ &\rightarrow H^+(H_2O)(CH_3SCH_3) + CH_3COCH_3 \end{aligned} \tag{4}$$

Switching H_2O out of the cluster ion accounts for most of the reactivity; however, at 176 K 16% of the product ions result from the channel that switches out CH_3COCH_3. The addition of a second H_2O molecule produces more equal amounts of the two channels:

$$H^+(H_2O)_2(CH_3COCH_3) + CH_3SCH_3 \rightarrow H^+(H_2O)(CH_3SCH_3)(CH_3COCH_3) + H_2O \rightarrow H^+(H_2O)_2(CH_3SCH_3) + CH_3COCH_3. \quad (5)$$

For this reaction, approximately 2/3 of the product ions correspond to switching out a H_2O for CH_3SCH_3 and 1/3 correspond to switching out the CH_3COCH_3. This indicates that the energetics for the two channels are probably comparable.

Unfortunately, we could not obtain product information for the reactions in which the primary had two or more CH_3COCH_3 molecules. This would have helped shed some light as to why the large reactivity changes are found as more CH_3COCH_3 and H_2O ligands are added to clusters that have incorporated more than one CH_3COCH_3.

4. Conclusions

The goal of this study was to find a chemical ionization scheme for detecting CH_3SCH_3 in the atmosphere, and the results presented here demonstrate that the reactions of $H_3O^+(H_2O)_n$ with CH_3SCH_3 should work well for this purpose. The reactions are all fast, and they all produce $H^+(H_2O)_n(CH_3SCH_3)$ as the exclusive ion product series. The rate constants do decrease slightly with cluster size indicating the need for care in making the concentration derivations since the average reaction rate will vary slightly with H_2O content of the atmosphere (by changing the cluster distribution). However, the average cluster size should change by only one or two units over wide ranges of the water content. Therefore, the error caused by this problem should be on the order of 20% or less. For more accurate measurements, one should either calibrate or know the cluster size distribution accurately.

In contrast, the mixed water/acetone clusters, $H^+(H_2O)_n(CH_3COCH_3)_m$, do not seem to be ideal for making CIMS measurements of CH_3SCH_3. The rate constants depend strongly on the CH_3COCH_3 content of the clusters, and in practice, it would be difficult to restrict the primary ions to $m = 1$ in a field experiment. Even for $m = 1$, where the rate constants are fast and roughly independent of water content, two product series are formed, complicating the ion spectra.

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