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Kinetics for the Reactions of $H_3O^+(H_2O)_n$ with CH_3SOCH_3

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We have measured the rate constants and product branching fractions for the proton hydrate clusters $H_3O^+(H_2O)_n$ ($n = 0-4$), reacting with dimethyl sulfoxide. The reactions were studied over the temperature range 198−298 K. Larger clusters were only studied at low temperatures since they are unstable at higher temperatures. All reactions were fast, approaching the collisional limit. The small clusters are slightly slower than the collisional limit, especially at 298 K. The product distributions were measured only at 198 K. All reactions proceeded by formation of $H^+(CH_3SOCH_3)(H_2O)_n$. The major product was often the channel producing two neutral H_2O molecules. The product distributions for the larger clusters were probably effected by thermal decomposition as evidenced by production of endothermic products.

Introduction

Chemical ionization mass spectrometry (CIMS) is a powerful and sensitive tool for measuring trace gases in a variety of environments, including the atmosphere.[1] The technique relies on finding a suitable precursor ion that will react rapidly and selectively with the neutral to be detected. The product ion must be stable and nonreactive. Proton-transfer reactions often have these properties. In wet samples, such as the breath and the atmosphere, $H_3O^+(H_2O)_n$ ions are formed rapidly and are used often as chemical ionization agents.

To study the ion chemistry of CIMS precursor ions and their hydrated clusters, we have added a supersonic cluster ion source to our variable temperature selected ion flow tube (SIFT).[2] This source is ideally suited to study reactions of species such as $H_3O^+(H_2O)_n$. It allows us not only to measure quantitatively the rate constants involved but also to obtain detailed product distributions for many reactions. Particularly important is the ability to vary the temperature since many of the cluster ions are unstable at room temperature. We have used this system previously to look at CIMS schemes for detecting SO_2,[3] H_2SO_4,[4] and CH_3SCH_3.[5]

CH_3SOCH_3 is an important intermediate in the oxidation of CH_3SCH_3 to SO_2 and CH_3SO_3H.[6,7] Recently, CH_3SOCH_3 has been detected by CIMS using NH_4^+ as the precursor ion.[8] The goal of the present study is to look at the possibility of using proton hydrate ions, $H_3O^+(H_2O)_n$, as potential precursor ions for positive ion CIMS measurements of CH_3SOCH_3. To evaluate this, the rate constants for the reactions of $H_3O^+(H_2O)_n$ with CH_3SOCH_3 were measured as a function of temperature from 198 to 298 K, and product distributions were measured at 198 K.

Experimental Section

The measurements were made in a variable temperature SIFT equipped with a supersonic cluster ion source. This experimental setup has been described previously in detail.[9,2] The instrument is operated like any SIFT 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 (not used in the present experiments). To produce the $H_3O^+(H_2O)_n$ 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. 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 clusters $H_3O^+(H_2O)_n$ as well as Ar^+. The resulting distribution of ionic clusters was sampled with a blunt skimmer, passed into a quadrupole mass filter, and injected into the flow tube through 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. CH_3SOCH_3 was added 50 cm from the end of the flow tube.

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%.[10] The reaction time was obtained from previous measurements of the ion time-of-flight.

Kinetics were measured in several ways. Turning off the upstream quadrupole dc voltage allows all ions to pass and the rate constants for all thermally stable ions to be monitored simultaneously. This is possible since the ions are uncoupled in the absence of H_2O and there are no mass coincidences. Alternatively, kinetics and branching fractions were taken by injecting specific clusters. 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 selected intervals, we injected the cluster we were studying and then minimized breakup by lowering the injection energy until the point where further reduction resulted in loss of most of the signal. This works best for small values of *n*. Alternatively, we injected a cluster with one or more extra ligands and then set conditions so most of the selected cluster decomposed by a fixed number of ligands. Finally, we injected a broad distribution of clusters with masses greater than the cluster of interest by turning off the dc potential on the upstream quadrupole. The

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TABLE 1: Measured Rate Constants and Product Branching Fractions for the Reactions of $H_3O^+\cdot(H_2O)_n$ with CH_3SOCH_3 as a Function of Temperature; Reaction Efficiencies (in %) Are Shown in Parentheses

	rate constant (10^{-9} cm^3 s^{-1}) (efficiency) product branching fractions				
reaction ($\Delta H°$, kJ mol^{-1})	298 K	273 K	249 K	225 K	198 K
$H_3O^+ + CH_3SOCH_3 \rightarrow$ products	3.7 (70)	4.1 (75)	5.3 (92)	6.0 (100)	4.8 (75)
$\rightarrow H^+(CH_3SOCH_3) + H_2O$ (−193)					0.97
$\rightarrow H^+(CH_3SOCH_3)(H_2O)$ (?)					0.03
$H_3O^+\bullet(H_2O) + CH_3SOCH_3 \rightarrow$ Products	3.5 (84)	3.6 (83)	4.4 (97)	4.8 (102)	3.7 (75)
$\rightarrow H^+(CH_3SOCH_3) + 2H_2O$ (−55)					1.0
$H_3O^+\cdot(H_2O)_2 + CH_3SOCH_3 \rightarrow$ Products	3.16 (86)	3.1 (80)	3.9 (99)	4.2 (100)	3.4(76)
$\rightarrow H^+(CH_3SOCH_3) + 3H_2O$ (+33)					0.09
$\rightarrow H^+(CH_3SOCH_3)(H_2O) + 2H_2O$ (−30)					0.91
$H_3O^+\cdot(H_2O)_3 + CH_3SOCH_3 \rightarrow$ Products	3.1 (90)	2.9 (82)	3.8 (104)	4.1 (106)	3.3 (80)
$\rightarrow H^+(CH_3SOCH_3) + 4H_2O$ (+104)					0.12
$\rightarrow H^+(CH_3SOCH_3)(H_2O) + 3H_2O$ (+41)					0.10
$\rightarrow H^+(CH_3SOCH_3)(H_2O)_2 + 2H_2O$ (−13)					0.78
$H_3O^+\cdot(H_2O)_4 + CH_3SOCH_3 \rightarrow$ Products				4.0 (110)	3.5 (89)
$\rightarrow H^+(CH_3SOCH_3)(H_2O)_2 + 3H_2O$ (+50)					0.78
$\rightarrow H^+(CH_3SOCH_3)(H_2O)_3 + 2H_2O$ (+4)					0.22

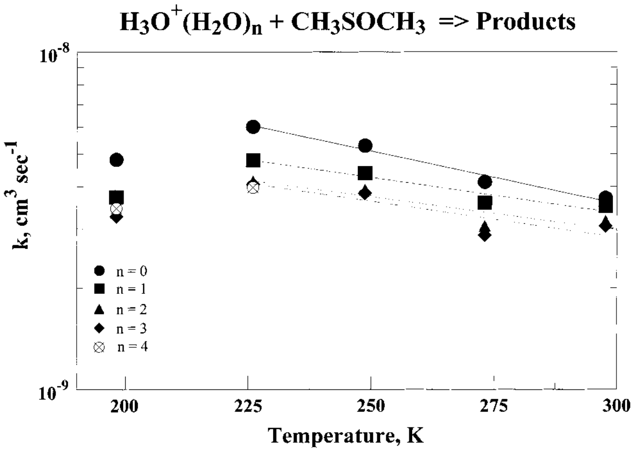

Figure 1. Rate constants for the reactions of $H_3O^+(H_2O)_4$ with CH_3SOCH_3 as a function of temperature.

ions decomposed (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.[2] Larger clusters can only be observed at low temperatures because of the lower bond strengths.[11] Rate constants were independent of the method within our 15% relative uncertainty. Branching fractions were measured only at 198 K.

The CH_3SOCH_3 reactant (99.9%) was obtained from Aldrich and was used without further purification except that several freeze/thaw cycles were performed to eliminate dissolved gases. Since CH_3SOCH_3 has a low vapor pressure, several modifications to our normal method of introducing gases were used. Helium flowed through a bubbler containing the CH_3SOCH_3. By assuming that the He/CH_3SOCH_3 mixture is saturated, the flow rate of CH_3SOCH_3 was calculated from the helium flow, the CH_3SOCH_3 vapor pressure, and the total pressure in the bubbler.

The larger $H_3O^+(H_2O)_n$ clusters are stable only at low temperatures. Therefore, the CH_3SOCH_3 vapor had to be introduced at temperatures where freezing would normally occur. We have often used a heated inlet in the past to extend the temperature range for which a particular neutral could be used.[2] Because CH_3SOCH_3 has such a low-vapor pressure, our normal heated inlet was not sufficient. We redesigned the heated inlet as follows. A 6 mm glass tube was wrapped with heating wire in two zones: 1) the tip (last cm) and (2) the rest of the tube. Resistance-temperature detectors monitored the temperature of each zone. A small layer of insulation was wrapped around the tube and heaters. Stainless steel foil was wrapped around the insulation so that no nonconductive surface was exposed to the unipolar ion stream. A similar inlet has been used to introduce H_2SO_4 into the system.[4] The two zones are needed only for the lowest temperatures and the temperature of the inlet was kept above room temperature; otherwise, it is not critical.

Rate constants were determined by recording the semilogarithmic decrease in the reactant ion signal as a function of the CH_3SOCH_3 flow rate. Product distributions were determined by monitoring the fractional product ion signal intensities as a function of CH_3SOCH_3 flow rate. Extrapolation to zero flow yields the branching ratio for the primary reaction. Frequently, several primary ions were present in the flow tube, making corrections for the products of the minor primary ions necessary. Typically, the corrections are small when *n* is small and increase with cluster size. Normally, we report uncertainties of ±25% and a relative error of ±15% in the measured values of the rate constants.[9] The double zoned heater is about 1.9 cm in diameter, causing a flow disturbance in the center of the flow tube where the ion concentrations are largest. This caused an error in the rate constant measurements. We calibrated this error by measuring a reaction for which the rate constant was known, namely, the Ar^+ reaction with CO_2. The calibration reaction indicated that the raw rate constants needed to be multiplied by a factor of 1.5. Taking this potential error into account, we reported rate constants to ±35%. A good test indicating that this gives us a conservative estimate is that the fastest reactions all are collisional. Relative rate constants between the various clusters at each temperature are still ±15%. Temperature dependencies also have a slightly larger error than normal. We estimated the rate constant variation with temperature to be accurate to ±25%.

Results and Discussion

The rate constants for the reactions of $H_3O^+(H_2O)_n$ with CH_3SOCH_3 are listed in Table 1 and shown in Figure 1. The rate constants are all large, reacting at or near the collision rate constant. The measured efficiency of reaction varies from 70% to just over 100%. The smallest efficiencies are found at room temperature and for the smaller clusters. The error in the relative rate constants between clusters indicates that the smallest clusters have an efficiency that is slightly less than the collisional rates.

The efficiency increases with decreasing temperature except at 198 K. The decrease in efficiency at 198 K is an experimental artifact due to CH_3SOCH_3 freezing in the inlet line or flow tube at that temperature. Similar behavior has been observed in our laboratory for other condensable liquids. At 198 K, the vapor pressure of CH_3SOCH_3 is only 3×10^{-5} Torr and yet a comparison to the collisional rate constant indicates that only about 20−25% of the CH_3SOCH_3 freezes. It is not possible to tell whether the CH_3SOCH_3 freezes in the inlet line or the flow tube. There does not appear to be a problem at 225 K since the rate constants are collisional at that temperature; the vapor pressure at 225 K is only 10^{-3} Torr.

The observed temperature dependence of the rate constants is due in part to the collision rate decreasing slightly with increasing temperature and in part to the efficiency decreasing with temperature. The collision rate decreasing with temperature is due to the ion−dipole interaction becoming less “locked” as the molecule rotates faster. The decrease in efficiency, which is just about at our error limits of detection, may be due in part to the inlet effect described in the Experimental Section. In any case, the rate constants are all fast.

The product distributions were only measured at the lowest temperature since past experiments of this type have shown that the products are disturbed by thermal dissociation, especially at higher temperatures.[2,5] The thermochemistry of the individual product channels listed in Table 1 is calculated from proton affinities in the NIST Webbook,[12] $H_3O^+(H_2O)_n$ cluster bond strengths from Keesee and Castleman,[11] and estimates of the $H^+(CH_3SOCH_3)(H_2O)_n$ bond strengths of 63, 54, 46, and 42 kJ mol^{-1}. The estimated bond strengths are based on values of several similar species. All neutral H_2O molecules are assumed to be monomers.

The reaction with H_3O^+ was found to proceed mainly by proton transfer with a small amount of clustering. Above 198 K, no cluster product was observed. $H_3O^+(H_2O)$ exclusively formed $H^+(CH_3SOCH_3)$, a channel that is considerably exothermic. The absence of the $H^+(CH_3SOCH_3)(H_2O)$ cluster cannot be due to thermal dissociation since the higher clusters reveal at most partial dissociation of that ion. The reaction of $H_3O^+(H_2O)_2$ with CH_3SOCH_3 produced two channels. The bulk of the reaction forms an exothermic channel with one H_2O clustered to protonated CH_3SOCH_3, $H^+(CH_3SOCH_3)(H_2O)$. A minor endothermic channel forms bare $H^+(CH_3SOCH_3)$. The channel may be formed from decomposition of the H_2O cluster. However, there is enough uncertainty in the estimation of the thermochemistry to allow this to be a nascent product, especially if a neutral H_2O dimer is formed. Additionally, since four particles are formed, the reactions are more energetically allowed from the entropy term. We estimate this to be about 32−48 kJ mol^{-1} at 198 K.[11] If dissociation of clusters in the flow tube is the reason for the endothermic channel, it would be mainly from thermal dissociation. A small amount of dissociation also may occur in sampling by electric fields. A limit of no more than 10% dissociation due to electric fields has been observed for similar reactions in our laboratory.[10] For $n = 3$, three channels are formed, namely, $H^+(CH_3SOCH_3)(H_2O)_n$ with $n = 0-2$. The $n = 0$ and 1 channels are endothermic although the entropy term may make the $n = 1$ channel allowed. The $n = 0$ channel is sufficiently endothermic to rule out that effect. This may suggest that an electric field dissociation may be occurring to a small extent. The bulk of the product is the exothermic $n = 2$ channel. The largest cluster, $n = 4$, produces two products, $H^+(CH_3SOCH_3)(H_2O)_2$ and $H^+(CH_3SOCH_3)(H_2O)_3$. The $n = 3$ channel is estimated to be about thermoneutral and the $n = 2$ channel to be significantly endothermic although the entropy term may be enough to drive this channel. Alternatively, thermal dissociation may be effecting the product distribution. This is consistent with results for other systems.[2]

The product distributions indicate a propensity to form two neutral water molecules (or a water dimer). This is the main product channel when possible for every cluster studied except $H_3O^+(H_2O)_4$ where it is the second most abundant product channel. Whenever possible, we also observed the channel that forms three neutral water molecules.

The goal of the present study was to test whether proton hydrates may be useful chemical ionization agents for the detection of CH_3SOCH_3. The rate constants observed herein are fast and produce a unique series of ions that incorporates CH_3SOCH_3 in its entirety. These are important considerations in deriving chemical ionization schemes. Furthermore, the rate constants are not strongly dependent on cluster size, and variations in the cluster distribution will not have a major impact on the ability to derive neutral CH_3SOCH_3 concentrations accurately. Finally, the products are considerably less hydrated than the reactants, which decongests the spectra. If the chemical ionization chamber is heated, the hydration will be even less severe. Thus, the present study indicates that $H_3O^+(H_2O)_n$ ions are useful for the chemical ionization detection of CH_3SOCH_3. This is consistent with the previous use of NH_4^+ as a chemical ionization agent.[8,13] NH_3 has a much larger proton affinity than H_2O, and therefore, NH_4^+ should be as reactive or less reactive than the $H_3O^+(H_2O)_n$ series.

Both NH_4^+ and $H_3O^+(H_2O)_n$ should be useful source ions for CIMS detection of CH_3SOCH_3. The environment would determine which ion is best suited for CH_3SOCH_3 detection. NH_4^+ transfers protons to fewer species than $H_3O^+(H_2O)_n$ and, therefore, would be more selective in cases where many gases with high proton affinities are present. On the other hand, H_3O^+-$(H_2O)_n$ ions would detect more species, a useful attribute as long as there are no mass interferences.

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