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Reactions of $H_3O^+(H_2O)_n$ with Formaldehyde and Acetaldehyde

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Rate constants were measured as a function of temperature for the reactions of $H_3O^+(H_2O)_{0-4}$ with CH_3CHO and $H_3O^+(H_2O)_{0-5}$ with CH_2O. The CH_3CHO reactions all occur at the collision rate to within the experimental error. The $n = 0$ ion reacts via proton transfer, while the clusters react via ligand switching. In the CH_2O reactions, $n = 0$ reacts at 90% of the collision rate and proceeds by proton transfer. The $n = 1$ reaction is somewhat less efficient and proceeds by ligand exchange. The efficiencies for both reactions are independent of temperature. The $n = 2-5$ reactions are progressively slower, except for the point at the highest temperature at which a particular cluster has been studied for $n = 3-5$. Thermal dissociation is postulated to be the reason for the upturn at higher temperatures. Otherwise, the reactions involve mostly ligand exchange with some association occurring at low temperature. The use of these results in model calculations of particle formation in jet engine exhaust is discussed.

Introduction

Recently, Yu, Turco, and Kärcher[1] have speculated that charged particles in jet exhaust interact with volatile organic species that are also present in the exhaust stream, and together they may play a role in forming ultrafine aerosols. Their detailed model includes many charged particle reactions. In particular, the assumption is made that all aldehydes react rapidly with proton hydrates, $H_3O^+(H_2O)_n$, incorporating the aldehyde into the ion, where it remains. This reaction is illustrated in reaction 1 for formaldehyde. The positive ion clusters are then assumed to recombine with negative ion clusters, forming embryos for larger particles.

$$H_3O^+(H_2O)_n + CH_2O \rightarrow H^+(H_2O)_{n-1}(CH_2O) + H_2O \quad (1)$$

Previously, Fehsenfeld et al.[2] and Bohme et al.[3] studied the reactions of $H_3O^+(H_2O)_n$ with CH_2O. Both experiments found that the reaction with small clusters is fast, while larger clusters reached equilibrium with H_2O. Equilibrium measurements by Fehsenfeld et al.[2] demonstrated that reaction 1 is endothermic for $n \geq 2$. Rate constants for the reactions of $n \geq 2$ could not be measured in those two flowing afterglow experiments because both H_2O and CH_2O needed to be present in the flow tube simultaneously which resulted in back reactions also taking place; i.e., the system was in equilibrium.

Bohme et al.[3] also studied the reactions of $H_3O^+(H_2O)_n$ with acetaldehyde (CH_3CHO), an aldehyde whose proton affinity is greater than that of CH_2O.[4] The reactions of CH_3CHO with $H_3O^+(H_2O)_n$, $0 \leq n \leq 3$, were found to be fast at room temperature,

$$H_3O^+(H_2O)_n + CH_3CHO \rightarrow H^+(H_2O)_{n-1}(CH_3CHO) + H_2O \quad (2)$$

These experiments were also performed in a flowing afterglow instrument with both CH_3CHO and H_2O present in the flow tube simultaneously.

In examining similar cluster reactions, we have occasionally found rate constants measured in flowing afterglows to be in error because the reactant clusters are in equilibrium.[5] For example, if $H_3O^+(H_2O)_2$ reacts fast and $H_3O^+(H_2O)_2$ and $H_3O^+(H_2O)_3$ are in equilibrium, then the larger cluster appears to react rapidly regardless of the true rate constant. To circumvent these problems, we have added a supersonic expansion cluster ion source to a selected ion flow tube.[5,6] The source gas is excluded from the flow tube, and the reactant ions are therefore essentially uncoupled with the exception that larger clusters can thermally decompose in the flow tube into smaller-sized clusters. For small clusters, we are able to set conditions such that only one or two primary clusters are present in appreciable quantities. The apparatus is temperature controlled, allowing measurements of cluster reactions to be made at the temperatures of interest to aircraft cruise altitudes. The low-temperature capability also allows us to study larger clusters over a more extensive range of temperatures than has been possible in previous measurements, affording a better comparison of our data to many atmospheric kinetics models.

In this paper, we report measurements for the reaction of CH_2O with $H_3O^+(H_2O)_n$, $0 \leq n \leq 5$, at temperatures between 150 and 294 K and for the reaction of CH_3CHO with $H_3O^+(H_2O)_n$, $0 \leq n \leq 4$, at temperatures of 200 and 294 K. The larger clusters have been studied only at lower temperatures since they are thermally unstable in the flow tube at 294 K.

Experimental Section

The apparatus has been described previously in detail, and only a brief summary is given here.[5−7] A supersonic expansion of H_2O in Ar was ionized by electron impact. The ionized mixture was passed through a quadrupole mass spectrometer, which was operated in either a high-pass mode or a mass-selective mode. The cluster ions were injected into a helium buffer and carried along the length of a 1 m flow tube. The

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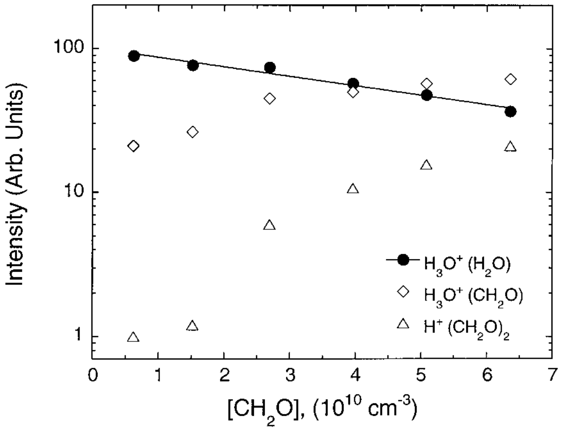

Figure 1. Kinetics plot for the reaction of $H_3O^+(H_2O)$ with CH_2O at 200 K.

aldehyde reactants were injected into the flow tube through a finger inlet located 50 cm from the sampling orifice. The reactant and product ions were sampled and detected by a second quadrupole mass spectrometer. The disappearance of the primary ions was monitored as a function of the reactant neutral flow rate. A typical example of the kinetics data is shown in Figure 1 for the reaction of $H_3O^+(H_2O)$ with CH_2O at 200 K. Both primary and secondary reaction products were observed. The slope of the logarithm of the decay rate along with the reaction time was used to derive rate constants. The accuracy of the measured overall rate constants is estimated to be ±25%, while the relative accuracy is estimated to be ±10%.

The CH_2O vapor was generated by heating paraformaldehyde to 70 °C. Both acetaldehyde and paraformaldehyde reactants were obtained commercially and were used without further purification except for pumping to remove trapped gases. To avoid freezing the aldehyde reactants within the instrument's inlet line, the CH_2O experiments could not be performed below 150 K and the CH_3CHO experiments could not be performed below 200 K.

For most of the present rate measurements, the upstream quadrupole was operated in the high-pass mode, where the dc component of the quadruple voltage was turned off, allowing a distribution of $H_3O^+(H_2O)_n$ clusters into the flow tube. Because H_2O was not present in the flow tube, the individual clusters remained essentially uncoupled from one another, with the exception that larger clusters in the distribution could decompose either upon injection into the flow tube or upon collisions with the helium buffer gas. Generally, these decomposition reactions are rapid and occur in the portion of the flow tube that is upstream of the neutral inlet. However, the largest cluster that remains thermally stable at a given flow tube temperature may partially decompose in the reaction region. This can be a source of added uncertainty and is discussed in more detail below. All product distribution measurements and additional rate measurements were made by operating the upstream quadrupole in the mass-selective mode. Generally, to study $H_3O^+(H_2O)_n$, we injected $H_3O^+(H_2O)_{m>n}$ at a relatively high energy that dissociated one or more of the solvent molecules. Product distributions are not reported in cases where we were unable to produce a relatively homogeneous signal of $H_3O^+(H_2O)_n$ using this method. It is important to note that, although product measurements were made at all temperatures, we have previously observed that product distributions of cluster reactions can be skewed by thermal dissociation of the product ions.[5] For a given cluster size, we observed no difference in the rate constants measured using either the high-pass mode or the mass-selective mode, indicating the clusters are not significantly affected by unimolecular dissociation and remain uncoupled from one another in the flow tube.

Results and Discussion

Acetaldehyde. Rate constants for the reactions of $H_3O^+(H_2O)_n$ with CH_3CHO are listed as a function of temperature in Table 1. Collisional rate constants were calculated using the parameterized trajectory method of Su and Chesnavich.[8,9] All the CH_3CHO rate constants are equal to the collision rate within the experimental error, indicating that both the cluster size dependence and the slight temperature dependence of the rate constants are due solely to the temperature dependence of the collision rate constant. The 294 K results presented here for $0 \le n \le 3$ are in good agreement with the previous study done by Bohme et al.[3] at 298 K, the present results being at most 20% higher.

Product information was obtained for the $H_3O^+(H_2O)_{n=0-2}$ clusters at both 200 and 294 K. The bare ion reacts via proton transfer, while ligand switching is the only product ion of the $H_3O^+(H_2O)_{n=1,2}$ reactions. Qualitative data suggest ligand switching is also the predominant channel for the larger $H_3O^+(H_2O)_n$ reactions. However, a minor association channel could not be ruled out for these clusters. This uncertainty results from the fact that a small percentage of the larger $H_3O^+(H_2O)_{n+1}$ cluster was present in the flow tube (as described earlier, $H_3O^+(H_2O)_{m>n}$ clusters were injected such that $H_3O^+(H_2O)_n$ was the predominate species in the flow tube), and it is not possible to distinguish the association products resulting from reaction of $H_3O^+(H_2O)_n$ from the ligand switching products resulting from reaction of $H_3O^+(H_2O)_{n+1}$. The product ions of the CH_3CHO reactions were found to undergo fast secondary ligand switching reactions at 294 K to generate $H^+(CH_3CHO)_2$ ions. Higher order reactions yielding larger protonated acetaldehyde water clusters were also observed at 200 K.

Formaldehyde. Rate constants and product distributions for the reactions of $H_3O^+(H_2O)_n$ with CH_2O are listed as a function of temperature in Table 2. The rate constants and product distributions reported here for the reactions of CH_2O with $H_3O^+(H_2O)_n$ are more complicated than for the case of acetaldehyde.

The proton-transfer reaction of H_3O^+ with CH_2O is 5.2 kcal mol^{-1} exothermic.[2,3] As shown in a number of previous studies conducted at 298 K,[2,3,10,11] the reaction proceeds at approximately 90% of the collision rate.[8,9] We have demonstrated that this trend continues over the entire temperature range from 150 to 298 K, as shown graphically in Figure 2a where the reaction efficiencies are plotted as a function of temperature. Plotted this way, the temperature dependence of the collisional rate is factored out of the results.

The first hydrated cluster, $H_3O^+(H_2O)$, reacts with CH_2O exclusively via ligand switching from 150 to 294 K to form $H^+(CH_2O)(H_2O)$. This reaction is exothermic by only 0.51 kcal mol^{-1} [2] and proceeds at approximately 75% of the collision rate over the entire temperature range we have examined. The 294 K rate constant reported here is 25% lower than that reported by Bohme et al. at 298 K,[3] yet this is well within the combined error limits of the two experiments.

The addition of a second water solvent to the cluster makes the ligand switching reaction with CH_2O slightly endothermic, 0.58 kcal mol^{-1}.[2] In addition to the overall rate constant decreasing, the temperature dependence of the rate constant was found to decrease faster than does the collision rate, as shown in Figure 2a. At 150 K, the $H_3O^+(H_2O)_2$ cluster undergoes both ligand switching and association with CH_2O. We estimate that

TABLE 1: Temperature−Dependent Rate Constants and Collision Rate Constants for the Reactions of $H_3O^+(H_2O)_n$ with Acetaldehyde

reaction		rate const (10^{-9} cm^3 s^{-1}), [k_c]	
		200 K	294 K
$H_3O^+ + CH_3CHO \rightarrow$	$CH_2OH^+ + H_2O$	4.7 [4.7]	3.7 [3.9]
$H_3O^+(H_2O) + CH_3CHO \rightarrow$	$H_3O^+(CH_2O) + H_2O$	4.1 [3.8]	3.5 [3.2]
$H_3O^+(H_2O)_2 + CH_3CHO \rightarrow$	$H_3O^+(H_2O)(CH_3CHO) + H_2O$	3.7 [3.5]	3.1 [2.9]
$H_3O^+(H_2O)_3 + CH_3CHO \rightarrow$	products	3.4 [3.3]	2.9 [2.7]
$H_3O^+(H_2O)_4 + CH_3CHO \rightarrow$	products	3.5 [3.1]	

TABLE 2: Temperature Dependent Rate Constants, Collision Rate Constants, and Product Distributions for the Reactions of $H_3O^+(H_2O)_n$ with Formaldehyde

reaction		rate const (10^{-9} cm^3 s^{-1}), [k_c] (branching fraction)		
		150 K	200 K	294 K
$H_3O^+ + CH_2O \rightarrow$	products	4.4 [4.9]	3.8 [4.3]	3.3 [3.6]
	$CH_2OH^+ + H_2O$	(1.0)	(1.0)	(1.0)
$H_3O^+(H_2O) + CH_2O \rightarrow$	products	3.1 [4.1]	2.8 [3.6]	2.3 [3.0]
	$H_3O^+(CH_2O) + H_2O$	(1.0)	(1.0)	(1.0)
$H_3O^+(H_2O)_2 + CH_2O \rightarrow$	products	2.0 [3.8]	1.6 [3.3]	1.1 [2.8]
	$H_3O^+(H_2O)(CH_2O) + H_2O$	(∼0.5)	(1.0)	(1.0)
	$H_3O^+(H_2O)_2(CH_2O)$	(∼0.5)		
$H_3O^+(H_2O)_3 + CH_2O \rightarrow$	products	1.6 [3.6]	1.2 [3.2]	1.4 [2.7]
	$H_3O^+(H_2O)_2(CH_2O) + H_2O$	(∼0.5)	(1.0)	(1.0)
	$H_3O^+(H_2O)_3(CH_2O)$	(∼0.5)		
$H_3O^+(H_2O)_4 + CH_2O \rightarrow$	products	0.7 [3.5]	1.7 [3.1]	
$H_3O^+(H_2O)_5 + CH_2O \rightarrow$	products	1.1 [3.5]		

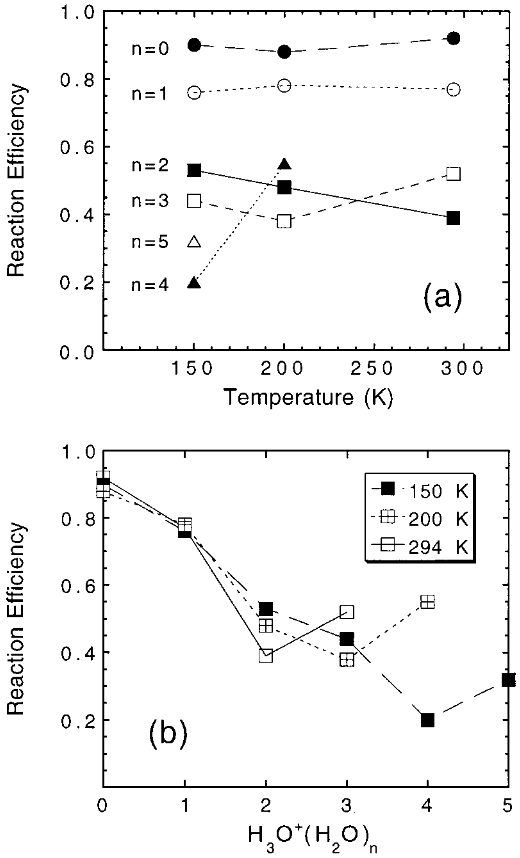

Figure 2. (a) Reaction efficiencies as a function of temperature for the reactions of $H_3O^+(H_2O)_n$ with CH_2O. (b) Reaction efficiencies as a function of cluster size at 150, 200, and 294 K.

the two channels are comparable at 150 K; the association product is not observed at the higher temperatures within our detection limit. The presence of the association channel probably explains why there is a small negative temperature dependence for this reaction despite the fact that the reaction is slightly endothermic.

The results for the reactions of $H_3O^+(H_2O)_{n\geq3}$ with CH_2O are significantly more complex. The ligand switching reaction of CH_2O with $H_3O^+(H_2O)_3$ is more endothermic, 1.1 kcal mol^{-1}, and the efficiency of this reaction decreases relative to that of the smaller clusters at 150 and 200 K. However, at 294 K the reaction efficiency for the $H_3O^+(H_2O)_3$ cluster increases unexpectedly to over 50% which is higher than that for the $H_3O^+(H_2O)_2$ reaction. Unusual behavior is also observed in the reactions with the larger proton hydrates. In the case of $H_3O^+(H_2O)_4$, we find the reaction efficiency is only 20% at 150 K, while it unexpectedly increases to over 50% at 200 K. Similarly, the reaction efficiency for $H_3O^+(H_2O)_5$ at 150 K appears higher than might be expected on the basis of the trends observed for the smaller clusters. Unfortunately, we were not able to explore this unusual behavior in the rate constants over a larger temperature range. This constraint results from the fact that large proton hydrate clusters are not stable at higher temperatures and that formaldehyde freezes in the inlet line at lower temperatures.

Not only is the temperature dependence of the rate constants for $n \geq 3$ unusual but the cluster size dependence of the rate constants at a given temperature is atypical, as shown in Figure 2b. From previous cluster studies, the reaction rate constants are generally expected to either continually decrease with increasing cluster size or remain nearly equivalent until a solvation shell closing is reached and then decrease, sometimes relatively rapidly with increasing size.[5,12] In the present measurements, the reaction rate constant initially decreases as expected with increasing hydration and then increases unexpectedly for the largest cluster that could be studied at a given temperature. Stated another way, at each temperature the anomaly appears to occur at the cluster size where the reactant ion is only marginally stable in the flow tube with respect to thermal decomposition. Previous measurements[13,14] of the $H_3O^+(H_2O)_n$ thermal decomposition rate constants and ion lifetimes have indicated that $H_3O^+(H_2O)_3$ is partially decomposing in the flow tube at room temperature, while the $H_3O^+(H_2O)_4$ and $H_3O^+(H_2O)_5$ clusters are already partially decomposing at 200 and 150 K, respectively.

Erroneously high rate constants have been observed in previous cluster studies in which the reactant gas was introduced through a heated inlet line,[15] and this was attributed to increased thermal dissociation of the reactant ion by the small amount of extra heat added to the flow tube as the helium reactant carrier gas passed through the heated inlet. Although the reactant carrier gas/heated inlet system was not utilized in the present experiments, thermal dissociation of the reactant ions remains a possible explanation for the temperature-dependent rate constants that were measured for the larger cluster ions. This would suggest CH_2O is very efficient at causing thermal dissociation of the marginally stable species while helium is not. If this is the reason for the larger than expected rate constants, this could potentially cause an error in the rate constant measurement for the next smaller cluster. However, the fact that the rate measurements made using both high-pass and mass-selective modes were essentially identical indicates this was not a substantial problem.

An alternative explanation to the unexpected temperature dependence is that the presence of the association channel at low temperatures yields larger rate constants at low temperatures. For the reaction of $H_3O^+(H_2O)_3$, for example, the rate constants for the ligand switching channel alone yield a temperature dependence that is fairly typical for an endothermic reaction. However, this explanation does not account for the temperature dependence of $H_3O^+(H_2O)_2$, which is also an endothermic ligand switching reaction with an association channel observed at 150 K.

A number of product ions from the $H_3O^+(H_2O)_n$ reactions undergo secondary reactions with CH_2O. For example, $H^+(CH_2O)(H_2O)$ undergoes rapid ligand switching with CH_2O to form $H^+(CH_2O)_2$, in agreement with previous work.[2,3] The larger clusters also incorporate a second CH_2O solvent molecule. Although higher order CH_2O clusters have also been observed, mass coincidences prevent all of these clusters from being unambiguously identified. For example, $H^+(CH_2O)_3$ is nominally the same mass as $H_3O^+(H_2O)_4$.

Implications for Modeling of Particulates in Engine Exhaust. Models such as those used by Yu et al.[1] for examining the formation of particulates in engine exhaust contain many uncertainties in the various kinetics parameters. Despite questions that remain concerning the origin of the unusual temperature dependences measured for the reactions of formaldehyde with the larger proton hydrate clusters, the present results can be combined with the equilibrium measurements of Fehsenfeld et al.[2] to derive useful approximations of the rate constants for H_2O switching CH_2O out of the cluster product ion.

The primary $H_3O^+(H_2O)_n$ ions that are expected at airplane cruise altitudes are $n \geq 3$.[16] Because thermodynamic data exist only for $n \leq 3$, the most relevant overlap between the two data sets is for the $H_3O^+(H_2O)_3$ reaction. To combine the data, the total rate constant measurements need to be corrected for the fraction of the association channel observed at low temperature. We assume no association occurs at 200 and 294 K and therefore correct only the 150 K data. Using this assumption and the thermodynamic data of Fehsenfeld et al.,[2] we find the temperature-dependent rate of the back-reaction

$$H_3O^+(H_2O)_2(CH_2O) + H_2O \rightarrow H_3O^+(H_2O)_3 + CH_2O \quad (3)$$

to be $3.2 \times 10^{-10} e^{(387/T)}$ cm^3 s^{-1}. Thus, at 200 K, which is near the temperature of aircraft cruise heights, the rate constant for reaction 3 is 2.2×10^{-9} cm^3 s^{-1}, a value close to the collision rate. With the large abundance of water vapor that exists in jet engine exhaust, it seems very likely that CH_2O will come into equilibrium with $H_3O^+(H_2O)_3$.

Yu et al. adopted a value of 2.2×10^{-9} cm^3 s^{-1} for incorporation of CH_2O into the clusters. The combination of the present kinetics data and the equilibrium measurements indicates that this value may be much too large. The data for the other clusters are not terribly different, and the same conclusion should apply.

In contrast, the CH_3CHO reactions are rapid for all cluster sizes, and incorporation of CH_3CHO into the clusters should remain rapid, as assumed in the model of Yu et al.

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