Rate Constants for the Reactions of $XO_3^-(H_2O)_n$ (X = C, HC, and N) and $NO_3^-(HNO_3)_n$ with H_2SO_4: Implications for Atmospheric Detection of H_2SO_4

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Relative rate constants for the reactions of $CO_3^-(H_2O)_n$, $HCO_3^-(H_2O)_n$, $NO_3^-(H_2O)_n$, and $NO_3^-(HNO_3)_n$ with H_2SO_4 have been measured for $n = 0-2$, $0-2$, $0-3$, and $0-3$, respectively. All rate constants have been found to occur in the ratio expected for the collisional values. This strongly indicates that the reactions proceed at the collision rate, and we assign absolute rate constants on the basis of this assumption. The present results show that all ions previously used for chemical ionization detection of H_2SO_4 concentrations in the atmosphere react rapidly, as has been previously assumed.

Introduction

Sulfuric acid is extremely important in the formation of atmospheric aerosols in several different environments.[1] Even when present in low concentrations, sulfuric acid condensation processes are often the dominant route to formation of new aerosols. Examples include the stratospheric aerosol layer[1] found at about 20 km and jet engine exhaust.[2,3] It is extremely difficult to detect H_2SO_4 in the low concentrations responsible for the aerosol formation. The only presently available technique to detect the gas-phase H_2SO_4 in the atmosphere is chemical ionization mass spectrometry (CIMS).[4−11] H_2SO_4 is detected by monitoring HSO_4^--containing product ions from the reactions of CO_3^- and NO_3^- core ions with H_2SO_4. Usually, the ions are solvated by HNO_3 or hydrated. For instance, in measuring jet exhaust emissions the following reactions have been used to derive H_2SO_4 concentrations,[10,12]

$$CO_3^-(H_2O)_n + H_2SO_4 \rightarrow HSO_4^-(H_2O)_m + HCO_3 + (n-m)H_2O \quad (1)$$

and

$$NO_3^-(H_2O)_n + H_2SO_4 \rightarrow HSO_4^-(H_2O)_m + HNO_3 + (n-m)H_2O \quad (2)$$

These reactions have been used although the rate constant for only reaction 2 with $n = 0$ had been previously measured,[13,14] and no calibration was used. Instead, the assumption that the reactions occurred at the collision rate independent of solvation was made. In the present study we have measured the rate constants for reaction 1, $n = 0-2$, and reaction 2, $n = 0-3$, relative to that for reaction 2, $n = 0$. In addition, we have measured

$$NO_3^-(HNO_3)_n + H_2SO_4 \rightarrow HSO_4^-(HNO_3)_n + HNO_3 \quad (3)$$

for $n = 1-3$,

$$HCO_3^-(H_2O)_n + H_2SO_4 \rightarrow HSO_4^-(H_2O)_m + H_2CO_3 + (n-m)H_2O \quad (4)$$

for $n = 0-2$, and

$$NO_3^-(HNO_2) + H_2SO_4 \rightarrow HSO_4^-(HNO_3) + HNO_2 \quad (5)$$

These include all the important primary ions used in CIMS detection of H_2SO_4.

Experimental Section

The experiments were performed in a variable temperature selected ion flow tube. The apparatus has been described in detail elsewhere,[15,16] and only details pertinent to the present experiments will be discussed. The ions were produced in a supersonic expansion ion source.[15] We could not make the $CO_3^-(H_2O)_n$ cluster directly. Instead, $O^-(H_2O)_n$ ions were made by expanding a mixture of N_2O, Ar, and H_2O, held at about 4 atm total pressure, through a 25 mm orifice and then ionizing the gas just downstream of the expansion with an electron filament (ThO_2/Ir) biased at about 50 V with respect to the expansion orifice. Other configurations were tried but with less success. Both $O^-(H_2O)_n$ and $OH^-(H_2O)_n$ ions were produced, at least in part, by reaction of hydrated electrons with N_2O.[17] The $O^-(H_2O)_n$ and $OH^-(H_2O)_n$ were sampled by a blunt skimmer and passed into a quadrupole mass filter. The quadrupole was operated in the "dc off" mode so that more than one ion species entered the flow tube, which made the determination of relative rates easier and more accurate. In the upstream inlet of the flow tube CO_2 was added in sufficient quantity to convert (completely) the $O^-(H_2O)_n$ ions into $CO_3^-(H_2O)_n$ and the $OH^-(H_2O)_n$ into $HCO_3^-(H_2O)_n$ upstream of the reactant inlet. The ions are as written and not CO_2 clustered to the original ions. The evidence for this comes from the fact that water ligands are displaced in this process and would not be if CO_2 simply clustered. The added CO_2 did not disrupt the kinetics measurements since all the ions were uncoupled from each other due to the lack of H_2O in the flow tube. We attempted to make the $CO_3^-(H_2O)_n$ ions in the source region with very limited success; addition of CO_2 and H_2O to the expansion mainly resulted in $HCO_3^-(H_2O)_n$ ions. For $CO_3^-(H_2O)_2$ and $HCO_3^-(H_2O)_2$, $C^{18}O_2$ was used to avoid mass coincidences with HSO_4^- and SO_4^-. The latter ion came from a small amount of SO_3 entering the flow tube from decomposition of H_2SO_4. We estimate that the [SO_3] was at most 10% of the [H_2SO_4] as evidenced by the relative intensities of the SO_4^- and HSO_4^- product signals. In most experiments [SO_3] was considerably less than 10% of the [H_2SO_4].

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For $NO_3^-(H_2O)$, two techniques were used. The first was simply to substitute NO_2 in the flow tube for CO_2. This allowed for rapid switching between CO_3^- and NO_3^- core ions. Alternatively, N_2O was left out of the expansion region and HNO_3 was added downstream of the expansion. At low flows of HNO_3 the resulting ions were mainly $NO_3^-(H_2O)_n$. At higher flows of HNO_3, the resulting ions were mainly $NO_3^-(HNO_3)_n$. A small amount of $NO_3^-(HNO_2)$ was made as well.

The cluster ions were unstable with respect to thermal decomposition at higher temperatures so that the larger the cluster, the colder the temperature at which the data were taken. In this manner small clusters were studied at or near room temperature, and larger ones could only be studied at temperatures of ~160 K.

The necessity of working at cold temperatures created problems in introducing H_2SO_4 into the gas phase. Previous experiments with H_2SO_4 had been made above room temperature by passing a dry gas over glass wool coated with H_2SO_4.[13,14,18] For the present experiments we settled on a modified version of a previous H_2SO_4 inlet design. A $^1/_4$ in. glass tube was blown so that a small bulbed section resided just inside the inlet flange of the flow tube. The bulb region was stuffed with glass wool. Approximately 1 mL of H_2SO_4 was added. The glass was wrapped with insulated nichrome wire in two zones: one around the bulb containing H_2SO_4 and one on the straight piece of glass tubing downstream from the bulb. An RTD monitored the temperature in each of the two zones. In order not to heat the buffer gas significantly, the inlet was wrapped with thermal insulation. The insulation was covered with stainless steel foil so that no electrically insulating surface was exposed to the ions. Insulating surfaces charge in the unipolar environment of a selected ion flow tube and cause disruption of the ion signal. Both zones of the inlet were typically run at ~373 K.

Decay curves were taken by varying the flow of helium over the hot H_2SO_4. The decays of two or more ions in the flow tube were monitored so that relative rates could be measured simultaneously. The relative rate constants were determined simply from the relative slopes in this case. When changing core ions, the NO_2 and CO_2 in the flow tube were switched rapidly, and decays were measured minutes apart. The gases were then switched back to check for any drift in the H_2SO_4 source.

No attempt was made to mass select the ions upstream since we were only attempting to measure relative rates. All product ions had HSO_4^- cores. No attempt was made to determine the distribution of ligands on the product ions. All data are the average of several runs, and the variation in the relative rates from run to run was within 10% and often only a few percent.

Results and Discussion

Figure 1 shows a typical decay plot for the reaction of $CO^{18}O_2^-(H_2O)_2$ with H_2SO_4 at 208 K. It shows the primary decay and four HSO_4^--containing products. Other primaries, namely $CO^{18}O_2^-(H_2O)$ and $HCO^{18}O_2^-(H_2O)_2$, were present in small quantities and are not included in the figure since our computer program can only monitor five masses at one time, and the decays were not recorded for this run. Other runs showed that all the primaries decayed at essentially the same rate. The decay of the primary is reasonably linear on this semilogarithmic plot. One concern in taking these data was that a considerable amount of the reaction was due to $(H_2SO_4)_n$ clusters. The data in Figure 1 address this issue. The data clearly show that the primary product ions are about 70% HSO_4^- and 30% $HSO_4^-(H_2O)$. The $HSO_4^-(H_2SO_4)$ and $HSO_4^-(H_2SO_4)_2$ are clearly secondary and tertiary products, respectively. No evidence was found for direct formation of any of these clusters. The possible conclusions are that (1) no neutral H_2SO_4 clusters are formed, (2) any H_2SO_4 clusters react just like unclustered H_2SO_4, or (3) any H_2SO_4 clusters are completely unreactive. We interpret our data to be due to either case 1 or case 3, since it seems likely that $(H_2SO_4)_n$ clusters would directly form some $HSO_4^-(H_2SO_4)_n$ ions. The total density of H_2SO_4 in the flow tube is between 10^{11} and 10^{12} cm^{-3}.

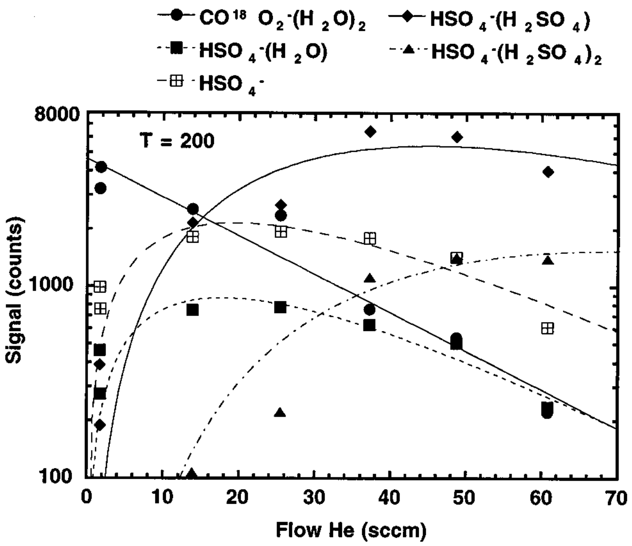

Figure 1. Ion signals as a function of He flow through the heated H_2SO_4 reservoir. The lines are crude fits to the data and are intended only as guides in viewing the data.

Table 1 lists the relative rate constants for the reactions studied here at five different temperatures. At 300 K, the only cluster ion that could be studied was $HCO_3^-(H_2O)$, and the rate constants are measured relative to that for bare CO_3^-. At 273 K, the rate constants are relative to that for NO_3^-, which in turn is assumed to be the same relative rate constant as found at 300 K. At 233 K the rate constants are relative to that of bare CO_3^-. The 200 K rate constants are relative to that of $NO_3^-(H_2O)$, which was assumed to be the same as found at higher temperatures. Finally, at 158 K the rate constants are relative to that of $NO_3^-(HNO_3)$, which is assumed to be the average of the relative rate constants found at higher temperatures. In all cases the relative rate constants are close to unity, ranging from 0.69 to 1.1 of that for CO_3^-.

For the most part the relative rate constants were found to be independent of temperature. However, for $NO_3^-(HNO_3)_2$ and $NO_3^-(HNO_3)_3$ the rate constants are larger at warmer temperatures. We believe this is due to the hot helium/H_2SO_4 mixture issuing from the H_2SO_4 bulb thermally decomposing some of these ions at the highest temperatures at which they were studied. The anomalous rate constants were measured at the highest temperature where the cluster of interest was thermally stable with respect to surviving the length of the flow tube. Thermal decomposition of a portion of the reactant ions down the length of the flow tube was certainly possible and indeed probable for the highest flow tube temperatures used. Therefore, a slight increase in buffer gas temperature (even locally) with increasing addition of the hot helium/H_2SO_4 mixture from the H_2SO_4 bulb could have had an appreciable effect on the ion signals and therefore the rate constants.

Table 1 contains a column where the relative rate constants for each temperature are combined to yield relative rate constants for each ion with respect to CO_3^-. For all reactions that did

TABLE 1: Relative Rate Constants of Chemical Ionization Primary Ions with H_2SO_4

	temperature (K)					relative			
ion	300	273	233	200	158	$\langle k\rangle^a$	$k_c{}^b$	$k/k_c{}^c$	$k_{300}{}^d$
CO_3^-	(1)[e]		(1)			(1)	(1)	(1)	(2.39)
$CO_3^-(H_2O)$			0.89	0.90		0.90	0.92	0.98	2.15
$CO_3^-(H_2O)_2$				1.0		1.0	0.87	1.15	2.39
HCO_3^-	1.1					1.1	0.99	1.11	2.63
$HCO_3^-(H_2O)$	0.83		0.82			0.83	0.92	0.9	1.98
$HCO_3^-(H_2O)_2$				0.99		0.99	0.86	1.15	2.37
NO_3^-	0.99	(0.99)	0.95			0.97	0.99	0.98	2.32
$NO_3^-(H_2O)$		0.86	0.85	(0.86)		0.86	0.92	0.94	2.06
$NO_3^-(H_2O)_2$				0.79		0.79	0.87	0.91	1.89
$NO_3^-(H_2O)_3$					0.79	0.79	0.82	0.96	1.89
$NO_3^-(HNO_3)$		0.75		0.80	(0.78)	0.78	0.76	1.03	1.86
$NO_3^-(HNO_3)_2$		{0.87}[f]		0.74	0.69	0.72	0.72	1.00	1.72
$NO_3^-(HNO_3)_3$				{1.1}	0.75	0.75	0.85	0.87	1.79
$NO_3^-(HNO_2)$				0.78		0.78	0.84	0.93	1.86

[a] Average relative rate constants. [b] Calculated collision rates ratioed to the calculated collision rate for CO_3^-. [c] Ratio of previous two columns. [d] Calculated rate constants at 300 K based on the relative rates and assumption that the CO_3^- rate is collisional. Units are $cm^3\ s^{-1} \times 10^{-9}$. [e] ( ) indicates the ion whose rate constant the other rate constants are relative to. [f] { } indicates the rate constant is not used in the average; see text for explanation.

not suffer from thermal decomposition, no temperature dependence was found, justifying taking relative rate constants at different temperatures and combining them. Averages were taken when an ion was studied at more than one temperature, with the anomalously high rate constants for $NO_3^-(HNO_3)_2$ and $NO_3^-(HNO_3)_3$ omitted from the averages for these ions. Also included is a column labeled k_c, for collision rate constants normalized to that for bare CO_3^-. Another column shows the ratio of the relative rate constants to the relative collisional rate constants. These numbers vary from 0.87 to 1.15. The two highest numbers are for the reactions of $CO_3^-(H_2O)_2$ and $HCO_3^-(H_2O)_2$ at the highest temperatures at which they were studied. This probably indicates that they also suffer from the thermal decomposition problem discussed above. This appears to affect the measured rate constant by 15%.

The fact that the relative rate constants are in the same ratio as that expected for the collision rates indicates that all the reactions occur at the collision rate within about 10%. With this in mind we set the rate constant for CO_3^- equal to its collisional value and scaled all values to this. Collision rate constants are calculated by the method of Su and Chesnavich,[19,20] and the molecular parameters are the same as those used by Viggano et al.[14] This is shown for 300 K in the last column of Table 1.

One should note, however, that the collisional value depends relatively strongly on temperature so that the appropriate rate constant for a stratospheric balloon mission is about 15% higher than the room-temperature value. The assumption that the reactions occur at the collisional value is supported by the work of Eisele and co-workers.[21,22] They titrate OH into H_2SO_4 and then use the reaction of $NO_3^-(HNO_3)$ with H_2SO_4 to detect the OH. Use of the collisional value for the H_2SO_4 reaction gives the same answer as a calibrated OH source within 10%.

It is difficult to put error limits on the data. Although the assumptions used to derive the rate constants warrant relatively large uncertainty, a number of factors indicate that the measurements are better than one might expect. Two indications that the relative rate constant measurements are probably precise to within 10−15% are the fact that there is such good reproducibility and the tight scatter about the ratio of rates to expected collisional values. The reactions where thermal dissociation may be occurring are obvious exceptions. The assumption that the rate constants are collisional is corroborated by the good agreement in the OH calibration mentioned in the previous paragraph.

The present findings of all negative ions reacting rapidly with H_2SO_4 are consistent with the previous findings of Viggiano et al.[13,14] that showed similar behavior for the reactions of H_2SO_4 with a number of negative ions. In that study it was found that the rate constant for $NO_3^-(HNO_3)_2$ was only 0.6 the collision rate. The present results show no such trend and indicate that $n = 3$ is also fast. The previous measurements were taken at 343 K, and the warmest temperature at which $NO_3^-(HNO_3)_2$ was reliably studied in the present set of experiments was 200 K. Normally, ion−molecule reactions become faster at lower temperatures so this may explain the discrepancy.[23] Alternatively, the previous data were taken in a flowing afterglow in which large amounts of HNO_3 were added. In similar comparisons of selected ion flow tube data to flowing afterglow data involving clusters, the flowing afterglow data were shown to be in error due to equilibrium processes occurring.[24,25] Tanner and Eisele[22] have concluded that the reactions of $NO_3^-(HNO_3)(H_2O)_n$ ions also did not depend on the level of hydration, consistent with the present results.

The present results show that all ions previously used for CIMS detection of H_2SO_4 concentrations in the atmosphere react rapidly with H_2SO_4, producing HSO_4^- core ions. Therefore, the assumption of calculating the collision rate constant for the ion of interest with H_2SO_4 has led to little error in previous measurements of H_2SO_4 concentrations. This is important since we have recently shown that for $CO_3^-(H_2O)_n$ reactions with SO_2 the rate constants do depend on the hydration number and that either in-flight calibration or a knowledge of the hydrate distribution is needed for the CIMS measurements of SO_2 with this series of core ions.[26]

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