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Gas Phase Reaction of Sulfur Trioxide with Water Vapor

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Sulfur trioxide (SO_3) has long been known to react with water to produce sulfuric acid (H_2SO_4).[1] It has been commonly assumed that the gas phase reaction in the Earth's atmosphere between SO_3 and water vapor to produce sulfuric acid vapor is an important step in the production of sulfuric acid aerosol particles.[2,3] These aerosols are known to play an important role in stratospheric chemistry[4] and are also believed to have a significant effect on the climate, both through direct scattering of solar radiation and through the nucleation of cloud droplets which scatter both incident solar radiation and infrared radiation emitted from the Earth's surface.[5] It is generally accepted that atmospheric sulfur trioxide is formed in situ by the oxidation of sulfur dioxide.[2,3,6,7] There is also some evidence that gaseous SO_3 can be formed directly in the atmospheric oxidation of biogenically produced reduced sulfur compounds.[8,9] The degree to which atmospheric SO_3 reacts with water vapor, rather than condensed water in aerosols or cloud droplets, may be critical in determining the rates of new particle formation in the atmosphere.

The kinetics of the gas phase reaction of SO_3 with water vapor have previously been studied by Castleman and co-workers,[2] Wang et al.,[10] and Reiner and Arnold.[11] Each of these studies was carried out in a flow reactor, with the first two studies performed at low pressure (1–10 Torr) and the latter from ~30 to 260 Torr. Each of these studies measured SO_3 decays over a range of H_2O vapor levels, obtaining data consistent with interpreting the reaction of gaseous SO_3 and H_2O as a bimolecular process. Since the reaction is known to proceed rapidly on surfaces, the low apparent bimolecular rate constants measured by Wang et al.[10] and Reiner and Arnold[11] were reported as upper limits, because the contribution of wall loss to reactive uptake could not be independently determined. These studies suggest that the much higher apparent bimolecular rate constant measured by Castleman et al. was due to surface reactions. Hofmann-Sievert and Castleman also studied the gas phase reaction of SO_3 with small water clusters [$(H_2O)_n$, $n = 2–10$)], observing an apparently facile reaction to produce H_2SO_4 vapor.[12]

Castleman and co-workers[2,12,13] have interpreted the gas phase SO_3/H_2O reaction in terms of adduct formation followed by unimolecular rearrangement to H_2SO_4:

$$SO_3 + H_2O + (M) \rightarrow SO_3{\cdot}H_2O + (M) \qquad (1)$$

$$SO_3{\cdot}H_2O \rightarrow H_2SO_4 \qquad (2)$$

However, recent theoretical calculations by Popov et al.,[14] Hoffmann and Schleyer,[15] and Morokuma and Muguruma[16] have cast serious doubt on this interpretation. These studies find that the computed activation barrier for reaction 2 is significantly larger than the calculated binding energy for the $SO_3{\cdot}H_2O$ adduct, indicating that any adduct with sufficient internal energy to rearrange will more likely simply dissociate back to reactants.

Experimental kinetics results reported here also cast serious doubt on the mechanism represented by reactions 1 and 2. We have investigated the gas phase $SO_3 + H_2O$ reaction in an atmospheric pressure turbulent flow reactor designed to minimize the influence of wall reactions.[17] The reaction has been studied to date in a nitrogen carrier flow with added water vapor in the range of 5×10^{14} to 1×10^{16} molecules cm^{-3}. SO_3 is typically added at levels of $\sim 1 \times 10^{11}$ molecules cm^{-3} (although initial SO_3 levels up to three times lower or higher give the same results), and pseudo-first-order decays are observed using atmospheric pressure chemical ionization mass spectrometry initiated by either SF_6^- (from added discharged SF_6) or thermal electrons from an atmospheric pressure corona discharge. In the former case, $m/e = 99$, corresponding to SO_3F^-, is monitored, while in the latter case, $m/e = 80$, corresponding to SO_3^-, is detected. Both detection schemes yielded identical decay plots; note that both may also detect the $SO_3{\cdot}H_2O$ adduct at the same m/e as that at which unreacted SO_3 would appear (for example, electrons probably dissociatively attach to the adduct to produce SO_3^-). The H_2SO_4 product is also observed at $m/e = 97$ as HSO_4^- and at $m/e = 117$ as $(H_2SO_4{\cdot}F)^-$. An example of a set of decays observed for various water vapor concentrations at 22 °C is shown in Figure 1a. A small wall loss rate, k_w, is observed in the case where $[H_2O] = 0$. The pseudo-first-order rate constants derived from a least-squares fit of the decay data are plotted as a function of added water vapor in Figure 1b. If these decays are interpreted as representing a bimolecular rate constant for reaction 1, they yield values ranging from 9.2×10^{-16} to 7.3×10^{-15} cm^3 s^{-1} in general accord with the rate constant limits reported by Wang et al.[10] and Reiner and Arnold.[11] The curvature in Figure 1b clearly shows that the reaction is not first order in water vapor as suggested by reactions 1 and 2. Figure 1c presents a log/log plot of the same data shown in Figure 1b, with the k_w value subtracted out. The linear least-squares fit to this data (solid line) has a slope of 2.04, strongly supporting a reaction mechanism second order in water vapor.

We have also studied the reaction of SO_3 and H_2O vapor as a function of temperature over the range of −30 to +60 °C, observing a significant (>10×) increase in reaction rate as the temperature is lowered over this range. This observation,

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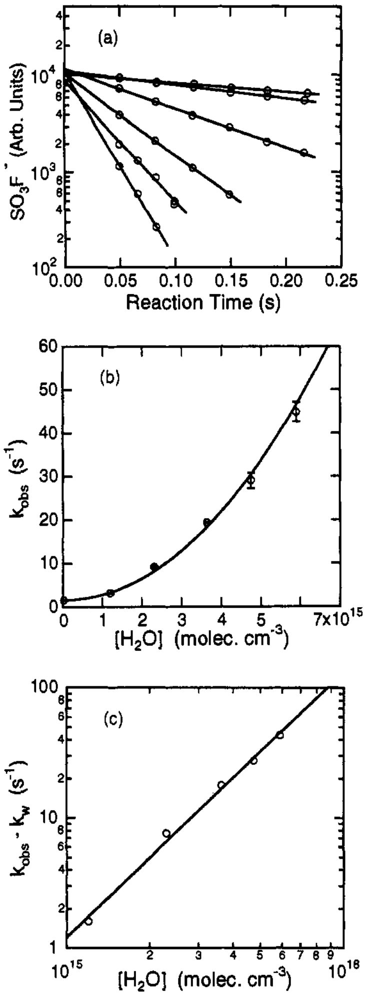

Figure 1. (a) Decay of SO_3 (monitored as SO_3F^-) as a function of reaction time at 22 °C. Top curve, no added H_2O vapor; second curve, $[H_2O] = 1.2 \times 10^{15}$; third curve, $[H_2O] = 2.3 \times 10^{15}$; fourth curve, $[H_2O] = 3.6 \times 10^{15}$; fifth curve, $[H_2O] = 4.8 \times 10^{15}$; and steepest curve, $[H_2O] = 5.9 \times 10^{15}$ molecules cm^{-3}. (b) Pseudo-first-order rate constants derived from the data in part a plotted as a function of $[H_2O]$. Curvature shows that reaction is not first order in $[H_2O]$. Solid line is a plot of the least-squares line generated from part c, with the value of k_w added. (c) Data from part b (minus the k_w value) replotted on log/log scale. Slope of 2.04 indicates that reaction of SO_3 with H_2O vapor is second order in $[H_2O]$.

combined with the data shown in Figure 1a–c and the calculations of Morokuma and Muguruma,[16] leads us to propose that a significant portion of the observed SO_3 consumption likely involves reaction with the water dimer:

$$SO_3 + (H_2O)_2 \rightarrow H_2SO_4 + H_2O \qquad (3)$$

which Morokuma and Muguruma calculate proceeds through a six center transition state with a very small activation energy.[16] The observed negative temperature dependence is presumably due to the higher abundance of water dimer at lower temperatures as well as a more favorable competition between reaction 3 and the alternative path to form an $SO_3{\cdot}H_2O$ adduct:

$$SO_3 + (H_2O)_2 \rightarrow SO_3{\cdot}H_2O + H_2O \qquad (4)$$

Reaction 4 is calculated to be approximately 3.5 kcal/mol exothermic.[16] It is reasonable to assume that the fraction of reaction between SO_3 and $(H_2O)_2$ proceeding through the six-center transition state[16] computed for reaction 3 will also increase with decreasing temperature. At this time it is unclear whether H_2SO_4 is also formed directly through the reaction of the $SO_3{\cdot}H_2O$ adduct with water vapor:

$$SO_3{\cdot}H_2O + H_2O \rightarrow H_2SO_4 + H_2O \qquad (5)$$

Calculations indicate that this reaction has an activation barrier of approximately 5.3 kcal/mol.[16] The $SO_3{\cdot}H_2O$ adduct reactant for this process can be formed in either reaction 1 or 4.

It is safe to assume that, under the atmospheric pressure reaction conditions used in our work, the concentrations of the $SO_3{\cdot}H_2O$ adduct and $(H_2O)_2$ are in equilibrium with the SO_3 and H_2O vapor concentrations. Although there is considerable uncertainty in calculating equilibrium water dimer concentrations for either laboratory or atmospheric conditions,[18–21] we have chosen one of the equilibrium constant analyses recommended by Slanina (based on the calculated intermolecular potential he designates BJH/G).[20,21] This analysis predicts equilibrium concentrations of $(H_2O)_2$ ranging from 8×10^9 to 2×10^{11} for the water vapor concentrations represented in Figure 1a–c, suggesting a second-order rate constant of $\sim 2 \times 10^{-10}$ cm^3 s^{-1} at 22 °C if reaction 3 alone is responsible for the irreversible consumption of SO_3. Alternatively, using thermochemical parameters for the $SO_3{\cdot}H_2O$ adduct provided by Morokuma and Muguruma, we can estimate initial equilibrium concentrations of the adduct to range from 2×10^8 to 1×10^9 cm^{-3}, suggesting that reaction 5 must have a room temperature rate constant of $\sim 1.4 \times 10^{-12}$ cm^3 s^{-1} if it dominates irreversible loss of SO_3. We are currently fitting the kinetic data which we have measured over a wide range of water vapor concentrations and temperatures to a model invoking reactions 1–5, with the goal of deriving rate constants and/or equilibrium constants for each fundamental process discussed above. The rate parameters derived from this model along with experimental details will be published in a subsequent report.[22]

It is not clear why previous experimental studies of this system[2,10,11] failed to observe a nonlinear dependence of SO_3 consumption on water vapor concentration. The earliest study[2] was performed over a limited range of water vapor concentrations (about a factor of 3), and both of the first two studies[2,10] were performed at low pressure, making first-order wall reactions more likely. Futhermore, we have observed that kinetic runs utilizing high initial SO_3 concentrations ($>5 \times 10^{11}$ cm^{-3}) and high water vapor lead to the formation of both hydrated sulfuric acid vapor species and, in some cases, sulfuric acid/water vapor condensation aerosols from binary homogeneous nucleation. The latter are signaled by a precipitate drop in product ions associated with sulfuric acid vapor and, in the worst cases, significant scattering of light from a HeNe laser beam. SO_3 can be expected to react with both acid hydrates and acid/water condensation nuclei, and we see an increase in the apparent reaction rate and loss of second-order dependence on water vapor under conditions where significant levels of these species are present. Since both of the initial experimental studies apparently used high levels of SO_3 relative to our work, their results may have been influenced by SO_3 loss on acid hydrates and/or acid/water condensation nuclei. The most recent study[11] uses a discharge flow reaction source of SO_3 and operates in a flow regime with substantial axial and radial reactant gradients, requiring significant data corrections.

As a final observation, it is probable that sufficient water dimer exists in much of the Earth's atmosphere to allow reaction 3 to participate in sulfuric acid vapor formation (equilibrium concentrations vary from as much as $\sim 10^{14}$ cm^{-3} at ground level to $\sim 10^4$ cm^{-3} at 40 km[19–21]).

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