Kinetics, Mechanism and Product Yields in the Atmospheric Oxidation of Dimethylsulfide

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LONG-TERM GOALS

Dimethylsulfide (DMS, CH_3SCH_3) produced by phytoplankton emission is thought to be the major source of the sulfate and methanesulfonate aerosol found in the marine boundary layer. An understanding of the mechanism of formation of these aerosols is critical to understanding the factors which control visibility in the marine boundary layer. The primary objective of this research effort is the determination of the detailed mechanism of, and final products yields from, the OH initiated gas phase oxidation of dimethylsulfide (DMS).

OBJECTIVES

Our objectives include a) the determination of the elementary rates for adduct formation, decomposition and reaction, b) direct confirmation of production, and quantitative product yields of potential reaction products and intermediates such sulfur dioxide (SO_2) and dimethyl sulfoxide (DMSO: $(CH_3)_2SO$), c) determination of the homogeneous and heterogeneous removal rates of the stable primary products of DMS oxidation.

APPROACH

Our gas phase studies utilize the Pulsed Laser Photolysis-Pulsed Laser Induced Fluorescence (PLP-PLIF) technique. Laser photolysis of a suitable precursor, either H_2O_2 or HNO_3, is used to generate OH. The rate of loss of OH, and the appearance of potential products such as SO_2 , SO and CH_3S are monitored by a second "probe" laser using laser induced fluorescence. Kinetic information is obtained by varying the delay between the photolysis and probe lasers, mapping out a temporal profile of the species of interest. Heterogeneous studies utilize an aerosol flow tube. We measure the rate of loss of SO_2 as a function of time and as a function of aerosol surface area. We use the TSI aerodynamic particle and scanning mobility particle sizers for aerosol measurements and laser induced fluorescence to monitor SO_2 .

WORK COMPLETED

We have observed a large enhancement in the observed rate coefficient for the reaction of OH with both DMS and DMS-d_6 in the presence of nitric acid.

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$$OH + CH_3SCH_3 \rightarrow products \quad (1)$$
$$OH + CD_3SCD_3 \rightarrow products \quad (2)$$

As we noted in our last annual report [1], these results cast some doubt on the currently accepted mechanism of the OH initiated oxidation of DMS . Because of the implications of these results we have gone to great lengths to avoid the possibility of systematic errors. We reconfigured our experimental configuration to allow us to independently monitor the concentrations of DMS and nitric acid entering our reaction vessel using photometry with Cd and Zn lamps in separate absorption cells. The concentrations are then obtained from the known flows and concentrations in each cell. The gas flows are mixed after the absorption cells, flow through the reactor for kinetic experiments and then exit downstream through a third absorption cell in which the combined absorption of the HNO_3 / DMS mixture is measured using an optical multichannel analyzer (OMA) and deuterium lamp. Knowing the absorption spectrum of each component and the initial concentrations, we can calculate a final absorption spectrum for the mixture. We obtain excellent agreement between our initial concentrations and the spectrum of the mixture indicating that DMS is not lost via dark reaction with HNO_3.

One possible artifact that could explain a rate enhancement and which we had not considered is that HNO_3 is subject to an autocatalytic decomposition to NO_2 in the presence of DMS. To exclude this we have reconfigured the OMA to attempt to simultaneously monitor DMS, HNO_3 and any NO_2 which might be formed. This is somewhat tricky because of the differences in absorption cross sections and the wavelengths of absorption bands. We can find no evidence for production of NO_2 at concentration levels which could explain the observed enhancements. However at the highest nitric acid concentrations we have used we see see some evidence for an autocatalytic decomposition to NO_2. Clearly this can complicate our interpretation of the enhancement in these cases.

Based on the large enhancement in nitric acid, we identified an examination of any water vapor effect on OH-DMS as a priority in the proposal for this contract period. We have examined the water vapor dependence of reaction 1 at 300K and 283K in the presence of up to 6 Torr of water vapor in 500 Torr total pressure of N_2. Concentrations of DMS and H_2O were determined independently using absorption of the Cd 228 nm line for DMS and the Hg 184.9 line for H_2O.

We have found that an artifact is possible in measurements of OH with sulfur containing species. If the metastable electronically excited state of diatomic sulfur, $S_2(a^1\Delta)$ is formed with vibrational excitation i.e. in the v=2 level, an accidental spectroscopic overlap produces an interference signal. We have found that this artifact is present in the photolysis of gas mixtures of several sulfur containing molecules. We have completed a detailed characterization of the spectroscopy of $S_2(a^1\Delta)$ in the OH overlap region and examined potential routes to its formation. This work has been written up and published [2,3].

RESULTS

At the low NO_x levels that are characteristic of the remote marine boundary layer, reaction with OH is the initial step in DMS oxidation. Hynes et al. [4] found that the effective rate of reaction 1 and its deuterated analogue, reaction 2, is dependent on oxygen partial pressure and proposed that the reaction proceeds by a two channel mechanism, involving either hydrogen abstraction or OH addition to form a weakly bound adduct . In earlier ONR supported work we reported the first direct observation of equilibration between OH and DMS-d_6 and obtained values for the adduct binding energy and the rate coefficient for its reaction with O_2 [5]. Our initial observations on the rate enhancement of reactions 1 and 2 in nitric acid and the implications of this for the atmospheric oxidation mechanism of DMS have been discussed previously [1].

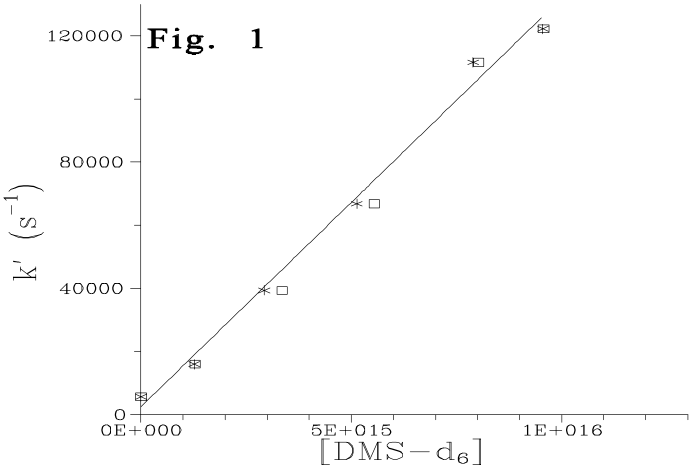

Fig. 1

Figure 1 shows data obtained with our new experimental configuration. It shows a typical plot of the pseudo-first order decay rate vs DMS-d_6 in a mixture containing slightly less than 1 Torr of nitric acid at a total pressure of 700 Torr of N_2 at 282 K. The observed rate coefficient, $(1.29\pm0.11)10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} is given by the best fit to DMS-d_6 concentrations measured before the reaction cell and noted by ✳. Concentrations obtained from OMA measurements, noted by □, are in excellent agreement. Under these conditions NO_2 formation is negligible indicating that nitric acid is responsible for the observed enhancement.

We have measured the rate coefficient for reaction 1 in a gas mixture containing 6 Torr of water vapor at a total pressure of 500 Torr at 298 K. The observed rate coefficient $(4.92\pm0.16)x10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} is indistinguishable, within the combined error bars, to the value we obtain in pure N_2. We find no difference in the measured rates in the presence and absence of H_2O at 300 K and 282 K, indicating that there is no significant enhancement in the observed rate at these temperatures. There have been no prior studies of this effect because of the difficulty of using laser induced fluorescence (lif) to monitor OH in the presence of high concentrations of water vapor, a very efficient quencher of OH lif. These results cannot exclude an effect at lower temperatures but this would require any H_2O-OHDMS interaction to be strongly temperature dependent. Experiments at much lower temperatures at significant H_2O concentrations are difficult in this system because of the low vapor pressure of water/ice and condensation problems within the reaction vessel.

IMPACT

There have been no direct determinations of the rate coefficients for the elementary processes in DMS oxidation under conditions which are representative of the marine boundary layer. Such rates are required for a detailed model of the atmospheric oxidation mechanism. An accurate model of the oxidation process is critical in predicting new particle formation rates in areas in which DMS is the major precursor of condensation nuclei. Our results indicate inconsistencies in the interpretation of laboratory results on the DMS oxidation process which imply that the simple two channel mechanism requires some modification. Direct measurements of the OHDMS adduct formation rate as a function of pressure up to at least one atmosphere and preferably up to the high pressure limit would do much to clarify this issue. We find that water vapor has no effect on the observed rate coefficient for reaction 1 at temperatures between 300 K and 278 K. Our work on $S_2(^1\Delta)$ production indicates that this has not been a problem in our studies of the reaction of OH with DMS. It may be a problem in other studies which use lif to monitor OH in the presence of other sulfur species, particularly CS_2, H_2S and COS.

TRANSITIONS

The potential implications of this work for particle formation in the marine boundary layer will require a completion of the laboratory work and modeling studies.

RELATED PROJECTS

In our NSF sponsored work on HO_x cycling we have shown that the quantum yield for O^1D formation from ozone photolysis has a significant long wavelength component, part of which is spin forbidden. This implies that current models underestimate OH concentrations, particularly at low temperatures and high zenith angles. Since OH is a primary oxidant for both DMS and SO_2 these results will feedback into models of marine boundary layer chemistry and imply higher oxidation rates of both DMS and SO_2. In related ONR sponsored work we are attempting to develop novel laser based instrumentation to allow near real-time sodium measurements on individual, size-segregated marine aerosols. The development and deployment of such an instrument would improve our understanding of the size distribution of seasalt aerosols in marine air and provide data for relating the abundance of these aerosols to remotely observable parameters related to the physical state of the atmosphere and surface ocean. It would allow us to calculate the influence of sea salt-derived particles on the optical properties of the marine aerosol and characterize and predict the variability of this signal.

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