

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

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## **LONG-TERM GOALS**

Dimethylsulfide (DMS,  $\text{CH}_3\text{SCH}_3$ ) produced by phytoplankton degradation 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 in evaluating the factors which control visibility in the marine boundary layer. The primary objective of this research effort is to determine the detailed mechanism of, and final product yields from, the OH initiated gas phase oxidation of DMS.

## **OBJECTIVES**

Our objectives include the determination of a) the effective rate coefficients for the OH initiated oxidation of DMS under atmospheric conditions, and b) the elementary rates for adduct formation and adduct reaction with  $\text{O}_2$ . By comparing these data sets we can evaluate the overall consistency of our proposed oxidation mechanism.

## **APPROACH**

Our studies utilize the Pulsed Laser Photolysis-Pulsed Laser Induced Fluorescence (PLP-PLIF) technique. Laser photolysis of a suitable precursor, either  $\text{H}_2\text{O}_2$  or  $\text{HNO}_3$ , is used to generate OH. The rate of loss of OH, and the appearance of potential products such as  $\text{SO}_2$ , SO and  $\text{CH}_3\text{S}$  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.

## **WORK COMPLETED**

There is considerable evidence that some of the impact of DMS oxidation on new particle formation and marine boundary layer (MBL) visibility occurs via oxidation in the upper troposphere. While DMS oxidation occurs rapidly in the MBL it has been suggested that the oxidation products will primarily condense on existing particles. This will, of course, modify the optical properties of those particles. DMS which is convectively pumped into the upper troposphere will undergo even more rapid

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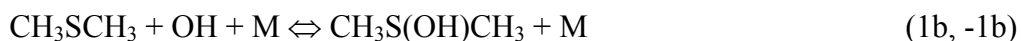
oxidation and the absence of preexisting particles enhances the probability of formation of condensation nuclei. These particles can then be entrained back into the MBL. Our current proposal identified discrepancies in the experimental database on DMS chemistry and led us to conclude that there was a significant possibility that the recommended rate coefficient for the reaction of OH with DMS under atmospheric conditions was too slow. An accurate value of this rate coefficient is critical in defining the lifetime of DMS in the marine boundary layer and hence the rate at which it is oxidized to products, some of which may act as condensation nuclei. We noted in our last report that we had completed a series of experiments measuring the effective rate coefficient for the reaction of OH with DMS and DMS-d6 as a function of O<sub>2</sub> partial pressure, at 600 Torr total pressure (O<sub>2</sub> + N<sub>2</sub>) at 296, 261 and 240 K. This work showed that at low temperatures the currently recommended expression underestimates both the effective rate coefficient for reaction together with the branching ratio between addition and abstraction. This work has now been published in Chemical Physics Letters and a parameterization of the data has been included in the latest IUPAC data evaluation. We also noted that our measured equilibration rate coefficient for OH with both DMS and DMS-d6 pointed to inconsistencies in the laboratory database. We have now completed a full suite of measurements of the O<sub>2</sub> dependence of effective rate coefficients of OH with DMS and DMS-d6, methylethyl sulfide (MES), diethylsulfide (DES), dipropylsulfide (DPS) and dibutylsulfide (DBS) at 600 and 200 Torr. In addition we have remeasured equilibration rates for OH with DMS, DMS-d6, and performed new equilibration measurements for MES and DES. These new measurements resolve the previous discrepancies in our results and present a completely consistent picture of the OH initiated oxidation of sulfides. This will allow us to provide a definitive expression for the OH initiated oxidation of DMS that will allow the calculation of accurate values for both the overall reaction rate coefficient and the branching ratio between addition and abstraction at any location in the troposphere.

## RESULTS

At the low NO<sub>x</sub> levels that are characteristic of the remote marine boundary layer, reaction with OH is the initial step in DMS oxidation.



The OH initiated oxidation of DMS proceeds via a complex, two channel, mechanism involving abstraction (1a) and reversible addition (1b, -1b). This can be described by the reaction sequence:



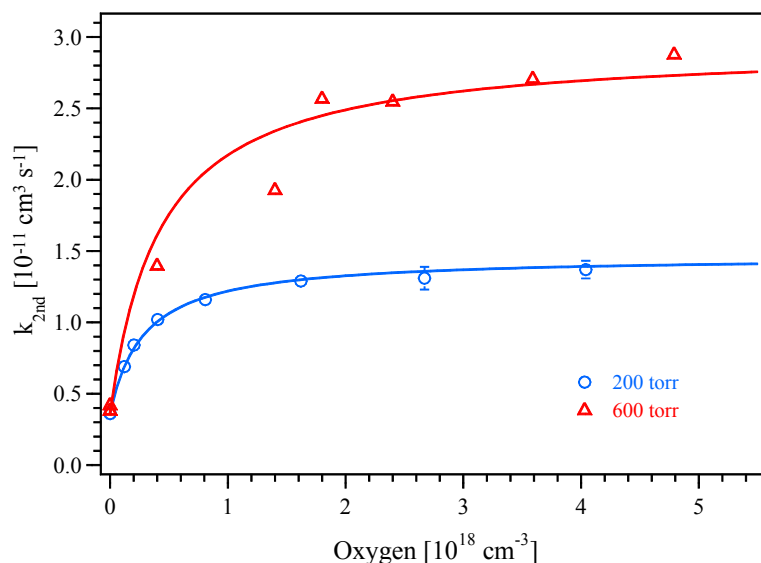
Because of this complex mechanism the effective rate coefficients for reaction (1) and its deuterated analog, reaction (2) depend on the partial pressure of O<sub>2</sub> at any total pressure.



The two channel reaction mechanism implies that in the absence of O<sub>2</sub> we measure k<sub>1a</sub>, the abstraction rate. As we add O<sub>2</sub> the effective rate increases until we measure a limiting rate (k<sub>1a</sub> + k<sub>1b</sub>). We can

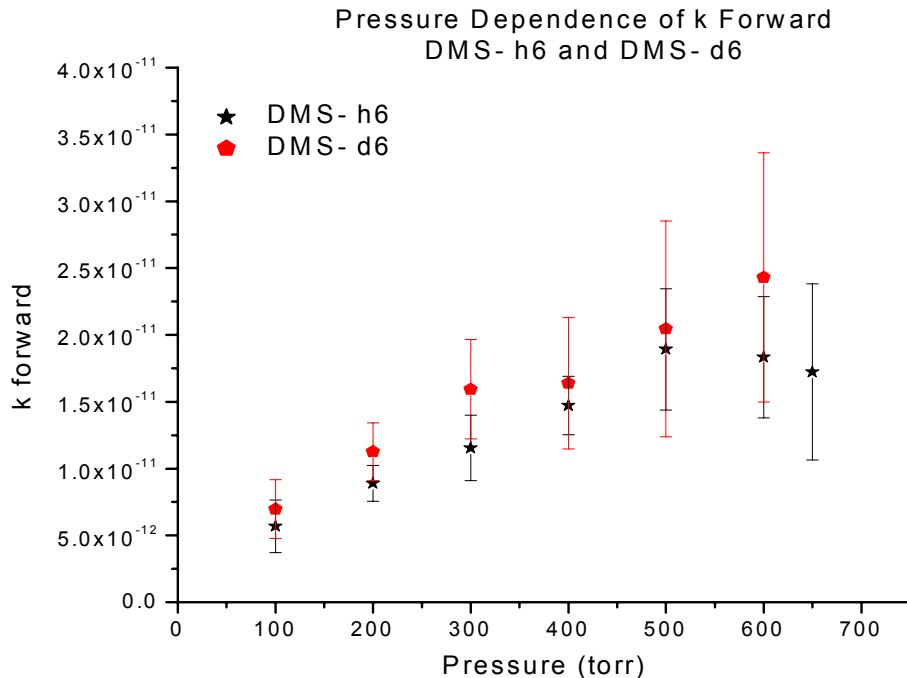
independently measure  $k_{1b}$  from equilibration measurements at high [DMS] in the absence of  $O_2$ . Clearly if our results are consistent we should obtain the same value of  $k_{1b}$  using both approaches. As

we noted in our last report, our previously measured rates for  $k_{1b}$  were different for DMS and DMS-d6 with the DMS-d6 values being considerably larger than the value obtained from  $O_2$  measurements. The equilibration measurements are particularly difficult to perform and require the extraction of elementary rates from a double exponential OH temporal profile. Fig. 1 shows the  $O_2$  enhancement in the effective rate coefficients for the reactions of OH with DMS at 240K and at total pressures of 200 and 600 Torr. The behavior is consistent with the two channel mechanism showing a characteristic “roll-off” at high  $O_2$ . The limiting value of the enhancement at 200 Torr is  $\sim 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and increases to  $\sim 2.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 600 Torr.



**Fig. 1** Variation of the effective rate coefficient for the reaction of OH with DMS as a function of  $O_2$  partial pressure at 600 and 200 Torr total pressure in  $N_2/O_2$  mixtures.

Fig. 2 shows values of  $k_{1b}$  measured directly from equilibration profiles. The equilibration profiles were performed at 247 K rather than at 240 K, the temperature of our previous measurements. Our signal-to-noise is much better at 247 K and we believe these measurements are more accurate than our previous data at 240 K, although scatter is still evident at high pressure. In our new data we find that, within the precision of the measurements, the forward addition rate is the same for both DMS and DMS-d6. The measurements are also consistent with the  $O_2$  enhancements shown in Fig. 1. At 200 Torr we measure a  $k_{1b}$  of  $\sim 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  in good agreement with the measured  $O_2$  enhancement from Fig. 1. We obtain reasonable agreement at 600 Torr, although, as noted above, the scatter in the data is rather higher at high pressure. The key point here is that we obtain elementary rates using very different approaches and we get consistent results. These observations also suggest that problems associated with OH regeneration from the reaction of OHDMS with  $O_2$  are not significant. Such a complication would result in our measured rates underestimating the true “effective rate” for atmospheric oxidation.



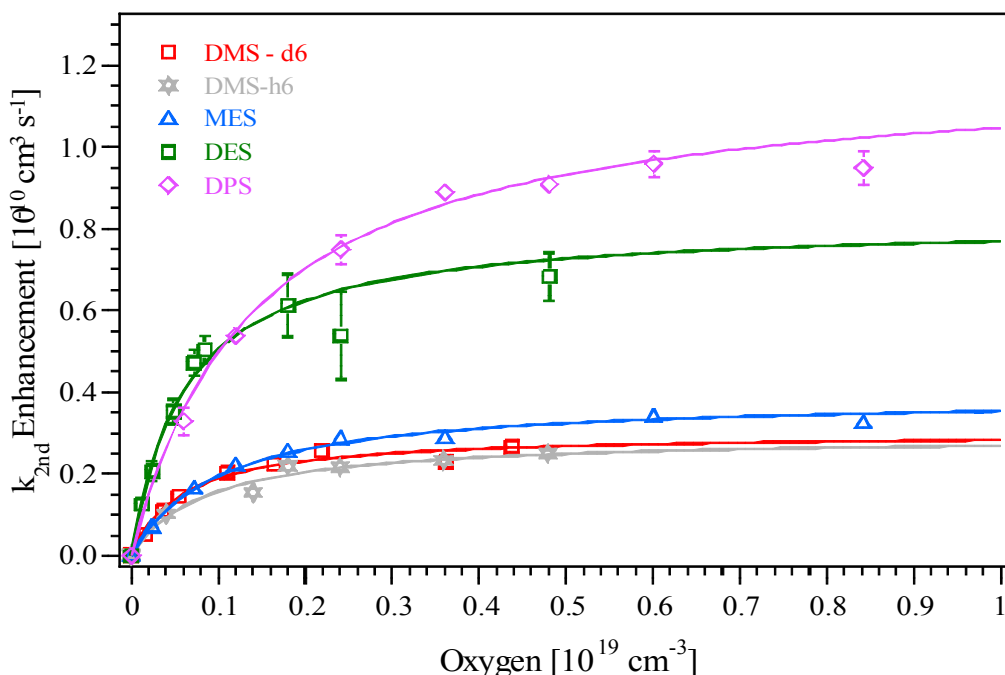
**Fig. 2** Pressure dependence of the forward addition rate for the reaction of OH with DMS and DMS-d6 at 247 K.

Fig 3 shows the O<sub>2</sub> dependence of the effective rate coefficient for reactions of OH with a series of sulfides at 600 Torr total pressure and 240 K. These results show that all the measured sulfide rate coefficients show an O<sub>2</sub> rate enhancement which is consistent with the basic two channel mechanism first proposed by Hynes et al. in 1986. The solid lines show fits to the data using our equilibration measurements for DMS and a value for the adduct scavenging rate (ie OHsulfide + O<sub>2</sub>) of  $\sim 1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . We also have equilibration data for MES and DES that give values for the forward equilibration rates which are consistent with the O<sub>2</sub> enhancements. We now believe we have a consistent picture of the OH initiated oxidation of the sulfides. We are completing our data analysis and this should allow us to propose a new expression for the effective rate of DMS oxidation based on actual elementary rates. This will allow oxidation rates to be calculated at all temperatures and pressures in air, rather than the current parameterization, which is only appropriate at 600 Torr. This work will form the basis for the Ph. D. thesis of Margaret Williams. We expect to produce three manuscripts describing this work.

## IMPACT

These results show that the 1986 expression of Hynes et al. for the effective rate of the OH initiated oxidation of DMS significantly underestimates both the effective rate and branching ratio between abstraction and addition at low temperatures. Current models of the high latitude oxidation of DMS should be significantly impacted by these results. This work was selected for oral presentation at three recent international conferences, most recently the International Conference on Gas Kinetics in Essen

Germany (August 2002). Margaret Williams presented the paper and was the only graduate student and one of the two female scientists who gave oral presentations.



**Fig. 3**  $O_2$  enhancement in the observed rate coefficient for reaction of OH with a series of sulfides. Measurements were made at 240 K and 600 Torr total pressure.

## TRANSITIONS

Our published data for OH + DMS has now been adopted by the IUPAC kinetics data evaluation panel and replaces the recommendation which is based on the 1986 data. It should be widely used for modeling DMS oxidation.

## REFERENCES

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