

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 the determination of a) the effective rate coefficients for the OH initiated oxidation of DMS under atmospheric conditions, b) 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: $(\text{CH}_3)_2\text{SO}$).

APPROACH

Our 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.

WORK COMPLETED

Our current proposal identified discrepancies in the experimental data base on DMS chemistry and led us to conclude that there was a significant possibility that the currently recommended rate coefficient for the reaction of OH with DMS under atmospheric conditions is 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

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14. ABSTRACT Dimethylsulfide (DMS, CH₃SCH₃) 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).					
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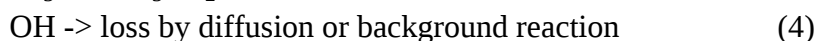
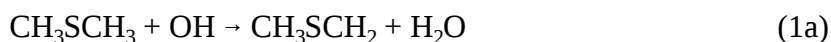
rate at which it is oxidized to products, some of which may act as condensation nuclei. We noted in our last report that we had completed a series of experiments measuring the effective rate coefficient for the reaction of OH with DMS and DMS-d₆ as a function of O₂ partial pressure, at 600 Torr total pressure (O₂ + N₂) at 296, 261 and 240 K. Currently recommended rates are based on an empirical fit to a two channel mechanism. This work shows 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. We completed additional measurements on the DMS reaction and this work has now been published in Chemical Physics Letters. A parameterization of the data has been proposed by the IUPAC data evaluation panel and will appear in their next evaluation. In addition we have measured additional equilibration rate coefficient for OH with both DMS and DMS-d₆ as a function of pressure in N₂. This together with recent chamber studies on the reaction continues to point to inconsistencies in the laboratory database. As a further check on our results in DMS we have performed a series of measurements on diethylsulfide (DES, (C₂H₅)₂S). These results confirm the very fast O₂ rate enhancement observed in the DMS reaction, and show an even larger enhancement under comparable conditions of pressure and temperature.

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.



The OH initiated oxidation of DMS proceeds via a complex mechanism which 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 O₂ at any total pressure.



Fig.1 shows the temperature dependence of the O₂ enhancement in the effective rate coefficient for reactions (1) and (2) obtained in 600 Torr of air at 298, 261 and 240 K in this work. For comparison the plot includes the data and 1986 expression from Hynes et al. for the enhancement which is the standard expression used in current models. The enhancements are calculated by subtracting the abstraction rate coefficient for DMS or DMS-d₆ from the observed rate coefficients. The abstraction rate coefficients are taken from the Arrhenius expressions reported by Hynes et al.[1]. As noted above, at 298 K we obtain good agreement with the 1986 data but at 261 K our measured enhancement in k_{obs} is approximately 30% larger than the values obtained with both DMS and DMS-d₆ in the 1986 work. At 240 K our results are a factor of 2 greater than the value calculated from the extrapolated 1986 expression. As we have noted above an expression based on this work will be included in the next IUPAC evaluation of rate coefficients for atmospheric chemistry, replacing the expression based on the 1986 work.

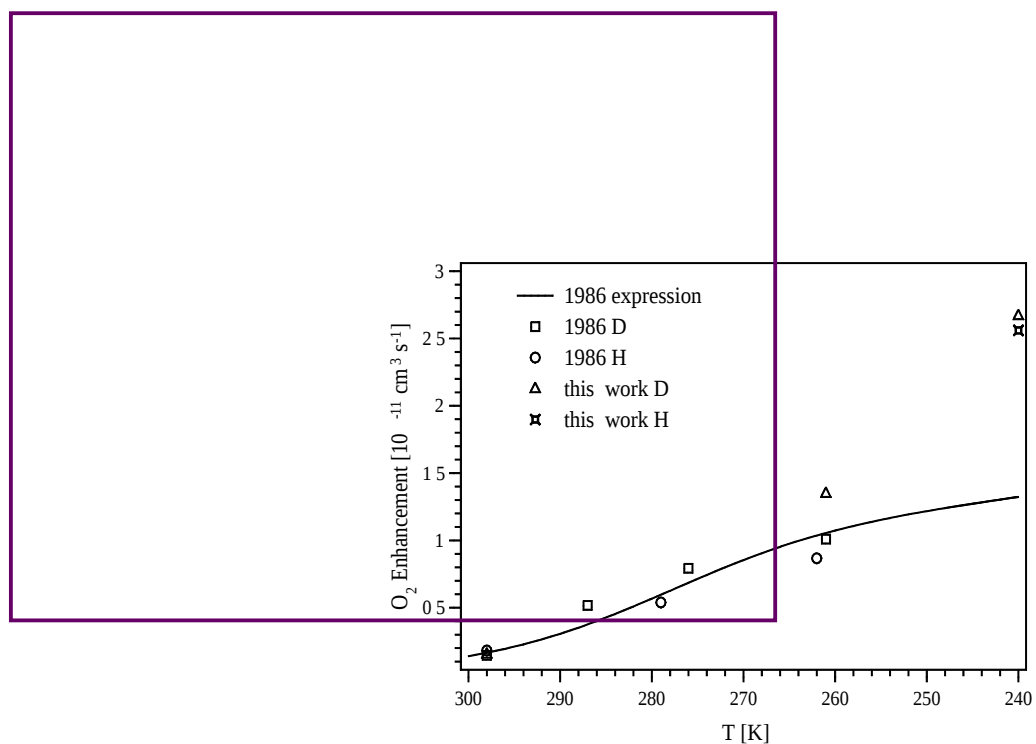


Figure1. Temperature dependence of the O_2 enhancement in the observed rate for reactions 1 and 2 in 600 Torr of air.

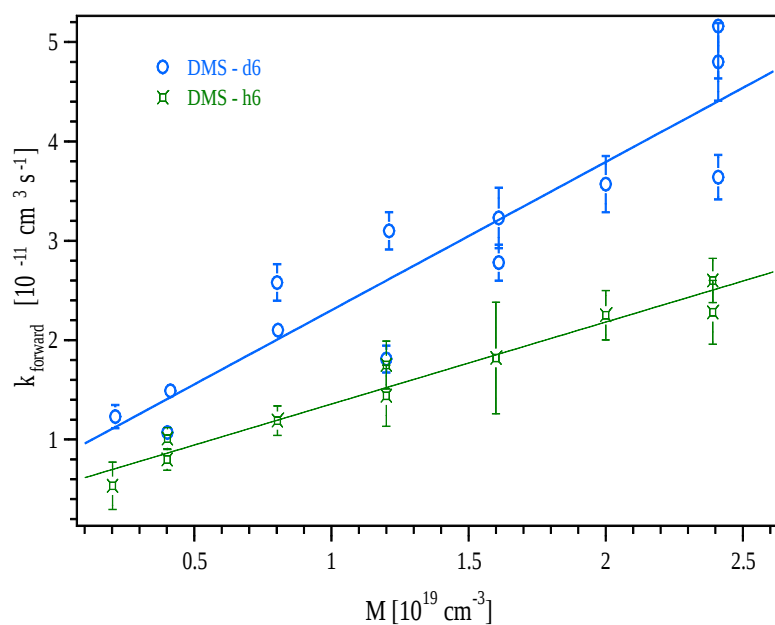


Figure 2. Pressure dependence of the adduct formation rates for the OHDMS and OHDMS-d6

Nevertheless some inconsistencies remain within our current results. The O₂ enhancement for reaction 1 and the DMS-d₆ analog, reaction 2 are consistent with a limiting enhancement of $\sim 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in the observed rate coefficient. This implies an adduct formation rate of $\sim 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for both adducts at 600 Torr and is consistent with a negligible kinetic isotope effect for an addition process. However, as shown in Fig. 2, we obtain significantly different pressure dependencies for the adduct formation rates for the DMS and DMS-d₆ isotopomers at 240 K.

The measurements of the forward addition rate are extremely difficult to perform and the values of the rate coefficients are extracted from the analysis of biexponential decays. This is more difficult and requires much higher quality data than the measurement of pseudo-first order rates which are used to obtain the data in Fig. 2. Hence the extent to which these differences are artifacts of the experiments or the method of analysis is open to question. To shed additional light on these questions we have measured the rate coefficient for the reaction of OH with diethylsulfide.



We have measured the effective rate coefficients for reaction 5 as a function of O₂ concentration in O₂/N₂ mixtures at 200 and 600 Torr at 261 and 240 K. To a first approximation one might expect the rate in the absence of O₂ to be faster since the DES has four secondary H atoms which react with OH at

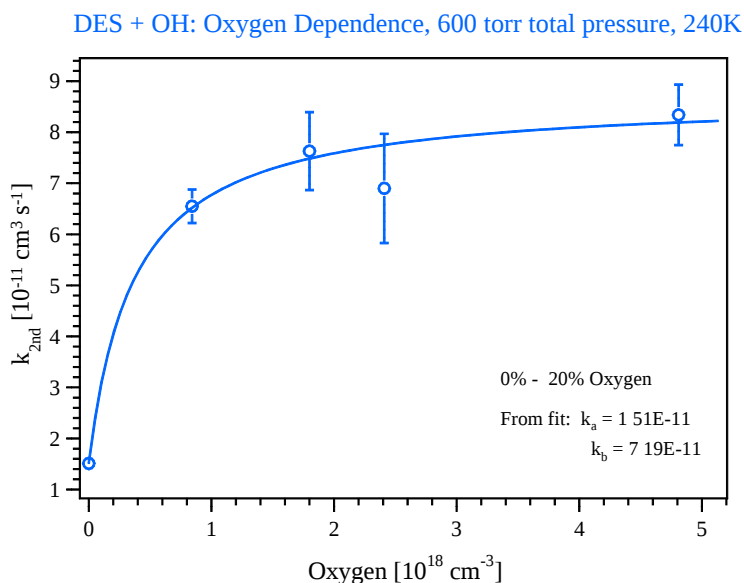


Figure 4. O₂ dependence of the observed rate coefficient for reaction 5 at 240 K and 600 Torr total pressure

a significantly faster rate than the primary H atoms on the methyl groups. One would expect addition to the sulfur group to be essentially independent of the alkyl substituents, hence the O₂ enhancements should be similar. In fact we see a large enhancement in the observed rate, the magnitude of which is even greater than that observed for reactions 1 and 2.

Figure 4 shows the variation in the effective rate as a function of [O₂] at 600 Torr and 240 K and should be compared with the results for reactions 1 and 2 shown in figure 2 for the same conditions. For reaction 5 we see a limiting rate enhancement of $\sim 7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, compared with a value of $\sim 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reactions 1 and 2. This is the first observation of an O₂ enhancement for a sulfide other than DMS and offers a further confirmation of the two channel mechanism. The magnitude of the enhancement again demonstrates that gaps remain in our understanding of the detailed mechanism and elementary rates.

IMPACT

These results show that 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.

TRANSITIONS

The data for OH + DMS has been adopted by the IUPAC kinetics data evaluation panel and will replace the current recommendation which is based on the 1986 data.

REFERENCES

1. Hynes, A.J., Wine, P.H. and Semmes, D.H., "Kinetics and Mechanism of OH Reactions With Organic Sulphides," *Journal of Physical Chemistry*, 90, 4148, 1986.

PUBLICATIONS

1. M. B. Williams, P. Campuzano-Jost, D. Bauer and A. J. Hynes, Kinetic and Mechanistic Studies of the OH-Initiated Oxidation of Dimethylsulfide at Low Temperature - A Reevaluation of the Rate Coefficient and Branching Ratio, *Chemical Physics Letters*, vol 344, pg61-67, 2001