Oxidation of atmospheric reduced sulphur compounds: perspective from laboratory studies

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SUMMARY

Results of laboratory experiments which address the course of the OH+DMS (dimethyl sulphide) reaction in the atmosphere are presented. It is shown that OH reacts via a complex sequence of reactions to produce CH₃S and other products, and argued that NO₃ is unlikely to be an important oxidizer of DMS in the marine boundary layer because it is very efficiently taken up by water droplets. A simplified mechanism for the oxidation of DMS in the troposphere is presented. This mechanism explains some of the field observations on the end products of DMS oxidation and their variations with temperature.

1. INTRODUCTION

Sulphur is a minor constituent of the Earth's atmosphere, yet it plays a significant role in various global scale phenomena, including the Earth's climate (Charlson *et al.* 1987; Restelli & Angeletti 1993) and the generation of acid precipitation. Many of the roles played by sulphur in the atmosphere have been discussed at this conference (see, for example, Dr Lovelock's article, this issue). The role of sulphur in providing a medium for heterogeneous reactions in the troposphere, and the consequent changes in the gas phase composition, have not been thoroughly examined and should be investigated. The majority of the sulphur for the stratospheric sulphuric acid aerosol is of volcanic origin. However, the contributions of OCS and even short-lived sulphur source gases to the stratospheric sulphur budget should not be neglected. Short-lived sulphur compounds such as dimethyl sulphide (DMS) can be transported from the marine boundary layer (MBL) and lower troposphere to the upper troposphere via convective activity, and then be transported to the stratosphere. This contribution is of particular importance during volcanically quiet periods. Even though the role of heterogeneous reactions for sulphuric acid droplets in the stratosphere has been well established, the role of such reactions in the troposphere has received little attention. The roles of anthropogenic sulphur dioxide in the formation of

aerosols and their contribution to the radiation budget have been discussed at this meeting. Naturally occurring sulphur compounds may also lead to aerosol formation. In addition to the direct climatic role via the interaction of the aerosol with radiation, heterogeneous reactions in the sulphur-containing media can alter the concentrations of greenhouse gases and, hence, the radiation field. The extent to which these phenomena are promoted by natural sulphur sources is not clear. However, understanding their role is necessary to gauge the magnitude of the anthropogenic contribution over natural levels. Also, such an assessment will depict the state of the atmosphere in the past, before the impact of human activities, and possibly in the future 'pollution'-free atmosphere.

The main atmospheric chemistry questions that need answering in order to assess the role of sulphur in the atmosphere are as follows. (1) In what form are sulphur compounds emitted into the atmosphere? (2) How much of these compounds are released into the atmosphere? (3) How rapidly are these compounds oxidized in the atmosphere and by what chemical agent? (4) What are the end products of this oxidation sequence, and what stable intermediates are produced in this process? (5) How does the presence of sulphur compounds and their chemical transformations affect the composition of the atmosphere? To answer these questions, a combination of field measurements, laboratory studies, and numerical modelling studies have been carried out. This paper focuses on the laboratory studies aimed at understanding the transformations of sulphur compounds in the atmosphere, in particular the lower troposphere.

The largest source of sulphur into the atmosphere is currently SO₂ from anthropogenic emissions (Houghton *et al.* 1995). The emissions of this compound into the Northern Hemisphere are much larger than they are into the Southern Hemisphere. The largest

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Figure 1. A skeletal representation of the atmospheric oxidation of H_2S based on available kinetics and products information and modifying the figure presented by Wang (1988).

natural contributor to sulphur in the troposphere appears to be CH_3SCH_3 (DMS) from oceanic emissions. Previously, terrestrial sulphur compounds, such as H_2S , received a lot of attention because of their possible contribution to acid precipitation (see, for example, Aneja & Cooper 1989). Some recent measurements have raised the possibility that H_2S may also be a significant oceanic source of sulphur (Saltzman & Cooper 1988). Therefore, attempts have been made to understand the atmospheric fluxes of all reduced sulphur compounds and the rates and products of their atmospheric oxidation reactions.

Ideally, the oxidation mechanism for a species entering the atmosphere should be completely delineated so that rates and products in the atmosphere can be calculated for any set of conditions. This is seldom the case for atmospheric species. In the case of sulphur compounds, the oxidation of H_2S comes closest to being understood. Figure 1 shows a skeletal view of H_2S oxidation. This oxidation mechanism is reasonably simple because the oxidation is initiated only by the OH radicals and the subsequent reactions involve O_2 , O_3 , and NO_2 . The rate coefficients and products for most of these reactions have been measured in the laboratory and, if one knows the atmospheric abundance of the oxidants, the overall rate and products of the oxidation can be calculated.

In contrast to the case of H_2S , the mechanism for the oxidation of DMS is very complex and still not well defined (Yin *et al.* 1990; Barone *et al.* 1995). A few of the end products from its atmospheric oxidation have been deduced from field observations, chamber studies,

and direct detection. The major product is believed to be SO_2 ; other important products are methane sulphonic acid (MSA), dimethyl sulphoxide (DMSO), and dimethyl sulphone (DMSO_2). However, the yields of these compounds are not well quantified. Therefore, laboratory, field and theoretical studies are needed. Part of this conference addresses these issues.

In this paper we focus mostly on the OH initiated oxidation of DMS in the MBL. We are focusing on DMS because it is the most important source of atmospheric natural sulphur. Whenever appropriate, reference is also made to other natural sulphur compounds and their oxidation. The reason for the focus on the MBL is that most of the DMS is present in this region and it is the place where measurements have been carried out.

2. METHODS

(a) Initiation of the atmospheric oxidation of reduced sulphur compounds

The first source of uncertainty in the oxidation of DMS is the reaction that initiates the oxidation. While the atmospheric oxidation of H_2S , CH_3SH , and CH_3SSCH_3 are all controlled by the OH radicals, DMS in the troposphere can be oxidized by either OH or NO_3 . The rate coefficient for the reaction of OH with DMS,

at 298 K is approximately $5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, while that for the NO_3 reaction,

is only four times slower (see, for example, Tyndall & Ravishankara 1991; DeMore *et al.* 1994). In contrast, the reactions of H_2S , CH_3SH , and CH_3SSCH_3 with NO_3 are, respectively, 6×10^3 , 40, and 5×10^3 times slower than their reactions with the OH radicals. Therefore, while NO_3 will not play a significant role in the oxidation of H_2S , CH_3SH , and CH_3SSCH_3 , it may play a large role in oxidizing DMS, depending on its atmospheric abundance. It appears that other atmospheric oxidants such as O_3 , NO_2 , and IO do not react with DMS fast enough to be important initiators (see Turnipseed & Ravishankara 1993). Recent work (Dunlea *et al.* 1997) in our laboratory has placed an upper limit of $< 3 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the rate constant for the $\text{IO} + \text{DMS}$ reaction; this limit is a factor of 2–5 lower than the previously reported values (Daykin & Wine 1990; Barnes *et al.* 1991; Maguin *et al.* 1991; DeMore *et al.* 1994). The role of halogen atoms in the oxidation of DMS, especially in the polar regions, is still uncertain and is worthy of investigation. Based on the current values for the rate coefficients for the initiation reactions, and the concentration of the oxidants in the atmosphere, the atmospheric lifetime of DMS is believed to be a few days, with the majority of the oxidation being initiated by OH in the warm sunny regions, and by NO_3 in the colder, darker regions. The atmospheric lifetime of DMS has been discussed elsewhere in this conference as well as in the literature

(Plane 1989; Yin *et al.* 1990; Tyndall & Ravishankara 1991; Turnipseed & Ravishankara 1993).

In addition to the rate coefficients for the initiation reactions, the products of the initiation steps are also known for H_2S , CH_3SH , and CH_3SSCH_3 . The reaction of OH, the only important initiator of oxidation, with H_2S and CH_3SH leads to $\text{HS} + \text{H}_2\text{O}$ and $\text{CH}_3\text{S} + \text{H}_2\text{O}$, respectively. The $\text{OH} + \text{CH}_3\text{SSCH}_3$ reaction leads to $\text{CH}_3\text{S} + \text{CH}_3\text{SOH}$ as well as a few other products (Domine & Ravishankara 1992). In contrast, the reaction of OH with DMS is quite complex and this complexity has to be understood to assess the role of DMS in the atmosphere and to interpret the field data on DMS and its oxidation end products. In the following section, we will show that the OH reaction with DMS involves the addition of OH to the sulphur as well as the abstraction of an H atom from the methyl group.

The identity and yields of the final oxidation products depend not only on the rates of the initiation reactions but also on the reactions of the intermediates. Such information has been derived from field and chamber studies, from which we know that DMS oxidation leads to the formation of SO_2 , MSA, DMSO, DMSO_2 , and, possibly, SO_3 ; a few other species have also been suggested. In the absence of detailed information, many approaches have been taken to construct a chemical mechanism that can predict the rates and yields of the end products in the oxidation of DMS. The most commonly used chemical mechanism is that developed by Yin *et al.* (1990) which is based mostly on measured yields of end products in chamber studies where the NO_x concentrations were quite large. The chamber studies, where reactive intermediates are not directly detected, can only assess the production of stable gas phase products. The generation of the end products may not be through a unique set of reactions, and, therefore, the reactions responsible for their production are not always clear. Yet, the mechanism of Yin *et al.* does provide for the formation of SO_2 , MSA, dimethyl sulphoxide (DMSO), and dimethyl sulphone (DMSO_2), which are known (or believed) to be formed in the atmosphere. Another approach has been to construct a mechanism to explain the field observations using known or speculated reactions (Bandy *et al.* 1992). We have opted to construct a mechanism based on individual elementary reactions studied in the laboratory, whenever possible, and rely on analogies to estimate the rate coefficients and products of unstudied reactions.

Field measurements of DMS and the oxidation products mentioned above have highlighted certain key aspects of the DMS oxidation mechanism. The ratio of MSA to non-sea salt sulphate (NSSS) in the remote MBL shows a dependence on latitude. This latitudinal dependence has been interpreted as the result of an increase in the extent of branching to MSA at lower temperatures (Hynes *et al.* 1986; Berresheim 1987; Hynes & Wine 1989). Support for this interpretation is also found in some ice core records of the $[\text{MSA}]/[\text{NSSS}]$ ratio, where there is a very strong correlation between the observed $[\text{MSA}]/[\text{NSSS}]$ ratio and temperature (Legrand *et al.* 1991). The increase in

MSA with DMS also shows that it is a product of DMS oxidation. If DMS oxidation is the main source of the MSA and NSSS measured in these studies, the oxidation mechanism must involve elementary steps which reflect this temperature sensitivity.

To connect DMS with the oxidation products observed in the atmosphere and chambers, and to elucidate the temperature dependence in the yields of the end products, we have investigated a large number of the elementary reactions. We have focused primarily on the reactions which initiate the oxidation and reactions of the CH_3S radical, a key intermediate in the atmospheric oxidation of DMS. We have paid particular attention to determining the dependencies of the yields on atmospheric composition and temperature.

In constructing our mechanism we have ignored some of the details, to simplify the mechanism, and have aimed at understanding certain features, such as the temperature dependence of the yields in the atmospheric oxidation of DMS. We have also incorporated our recent findings on the reactivity of the CH_3S radical towards O_3 , CH_3S addition to O_2 and the large temperature dependence of the bond scission reactions relative to atom transfer reactions (Barone *et al.* 1995). One of our main aims is to elucidate the pathways that produce MSA and SO_2 .

(b) *The intricacies of the OH + DMS reaction*

From previous work (Hynes *et al.* 1986; Wallington *et al.* 1986; Barnes *et al.* 1988; Hynes *et al.* 1989; Barnes 1993; Stickel *et al.* 1993; Wine 1994), it has become clear that the reaction of OH with DMS is complex, and proceeds via two pathways whose relative importance depends on atmospheric composition and temperature. In an attempt to characterize the details of the OH reaction with DMS, we have carried out a detailed study of this reaction, which is described elsewhere (Barone *et al.* 1996; Turnipseed *et al.* 1996).

All our experiments utilized pulsed laser photolysis for generating OH and/or CH_3S and pulsed laser-induced fluorescence for detecting them. This apparatus, the experimental procedures and data analyses are described in detail elsewhere (Vaghjiani & Ravishankara 1989; Barone *et al.* 1994, 1996). The details of the findings are also described in two papers describing this work (Barone *et al.* 1996; Turnipseed *et al.* 1996). Therefore, here we will only briefly summarize the main points of our findings.

When OH is generated in the presence of DMS, its loss is governed by both its reversible addition to DMS and irreversible reaction with DMS. Separating the two reactions is critical for a successful characterization of their individual rate coefficients. The rate coefficient for the irreversible reaction of OH with DMS is approximately a factor of three faster than the reaction with the deuterated analogue of DMS, $\text{d}_6\text{-DMS}$ (Hynes *et al.* 1986). Hence, the use of $\text{d}_6\text{-DMS}$ decreased the rate of the irreversible reaction between OH and DMS and facilitated better separation of the two competing reactions. Use of $\text{d}_6\text{-DMS}$ had an added advantage in that it eliminated any possible secondary production of

OH radicals from reactions involving the methyl groups in DMS. Therefore, most of our experiments used d_6 -DMS, rather than DMS, as the reactant to study the OH initiation reactions:

(i) *Addition channel*

The OH + DMS reaction can proceed via several channels:

The symbol ' $\leftrightarrow$ ' refers to an equilibrium. Initially, we measured the overall rate coefficients for reactions 1 and 2 under pseudo first-order conditions ($[\text{DMS}]$ or $[d_6\text{-DMS}] \geq 100[\text{OH}]_0$) at 298 K in the absence of O_2 to be $k_1 = (4.95 \pm 0.35) \times 10^{-12}$ and $k_2 = (1.75 \pm 0.25) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. These values are in good agreement with other recent measurements (Hynes *et al.* 1986; DeMore *et al.* 1994; Turnipseed & Ravishankara 1993). (Note that reaction 2 has the same possible product channels as reaction 1.)

At $T \leq 240 \text{ K}$ the OH temporal profiles were not strictly single exponential in the presence of an excess d_6 -DMS (Barone *et al.* 1996). The [OH] temporal profiles were characterized by an initial rapid exponential decay followed by a slower exponential decay. Both the rate of the initial decay and the point of inflection varied with the concentration of d_6 -DMS. This behaviour is indicative of an equilibrium between OH and d_6 -DMS in combination with a slower first-order OH radical loss. Such temporal profiles were analysed using a nonlinear least squares fitting routine, FACSIMILE (Malleon *et al.* 1990), using the following mechanism:

Here, reaction 2bi represents the sum of reactions 2a, 2b and 2c (by analogy with reaction 1bi, which represents the sum of reactions 1a, 1b and 1c):

From these fits, the values of k_{2f} , k_{2r} , k_{2bi} and K_c ($= k_{2f}/k_{2r}$) the equilibrium constant, were calculated. The rate coefficient for the formation of the adduct is k_{2f} , and k_{2r} is the rate coefficient for the thermal decomposition of the adduct.

The equilibrium constant, K_c , was determined as a function of temperature and used to calculate ΔH_{2f}° ,

the enthalpy of reaction 2f, using the third law method. In this method, the entropy change for the equilibrium reaction, ΔS_{2f}° , was calculated from statistical mechanics. Measured equilibrium constants were converted into Gibbs free energy changes, ΔG_{2f}° , at each temperature. Using these values of ΔG_{2f}° and ΔS_{2f}° , the enthalpy of the reaction, ΔH_{2f}° , was calculated at each temperature. Using ΔS_{2f}° ($= -31.1 \text{ cal mol}^{-1} \text{ K}^{-1}$ at 229.5 K) and ΔC_p° calculated from statistical mechanics, the third law method yielded ΔH_{2f}° (298 K) =

$-10.7 \pm 2.5 \text{ kcal mol}^{-1}$. The error quoted is twice the standard deviation of the mean plus the estimated systematic uncertainty in the determination of $[d_6\text{-DMS}]$. Our analysis leads to a heat formation of $d_6\text{-DMS} \cdot \text{OH}$, ΔH° ($d_6\text{-DMS} \cdot \text{OH}$), of $-10.3 \pm 2.5 \text{ kcal mol}^{-1}$ at 298 K.

Knowledge of all the significant atmospheric loss processes of the OH·DMS adduct is needed to evaluate its atmospheric fate and, hence, the consequence of adduct formation to the branching to stable end products. Evidence from observation of OH temporal profiles in direct kinetics measurements, and of DMS loss in chamber studies, suggests that the OH·DMS adduct reacts with O_2 . Wallington *et al.* (1986) and Barnes *et al.* (1988) observed that the rate of reaction 1 increased systematically with increasing partial pressure of O_2 in their chambers. In addition, Hynes *et al.* (1986) found that the OH loss rate coefficient in the presence of an excess of DMS increased systematically upon the addition of atmospheric levels of O_2 .

Observation of the OH temporal profile in the presence of d_6 -DMS or DMS, O_2 , and a bath gas allowed us to determine the rate coefficients of reactions 5 and 6:

The details of these determinations are given elsewhere (Barone *et al.* 1996). Briefly, longtime ($t > 50 \mu\text{s}$) rate constant for the loss rate of OH, in the presence of an excess of d_6 -DMS or DMS, increased with the addition of O_2 . Numerical simulations of the observed enhancement in the loss rate of OH due to the presence of O_2 yielded the bimolecular rate coefficients for reactions 5 and 6 to be $k_5 = k_6 = (10.0 \pm 3.3) \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$. The error bars reflect 2σ of the standard deviation of the mean of many measurements and include estimated systematic uncertainties in the $[\text{O}_2]$ and $[d_6\text{-DMS}/\text{DMS}]$.

The results of the kinetic study on the $\text{OH} \cdot \text{DMS} + \text{O}_2$ reaction also provide insight into the mechanism of the OH + DMS reaction. Past studies of the mechanism of the OH + DMS reaction have assumed that the reaction proceeds by two separate reaction channels (addition and H atom abstraction).

Figure 2. The measured bimolecular rate constants for the loss of OH via reactions with DMS and d_6 -DMS as a function of concentration of O_2 in the reactor at 247 K. The error bars are the uncertainties in the individual rate constants that were measured. The lines are a fit of the data to the mechanism presented in the text. The difference between the asymptotes, A and B, is equal to the difference between the intercepts of the fits. This equality is argued to be due to the existence of two separate mechanisms for the reaction of OH with DMS.

This assumption excludes a possible mechanism consisting of an initial addition of OH to DMS followed by rearrangement to form the bimolecular products, $H_2O + CH_3SCH_2$:

Such a mechanism would imply that the two reactions cannot be treated separately in the atmosphere. We have measured the bimolecular rate constants for the loss of OH in the presence of high O_2 concentrations and DMS or d_6 -DMS. Figure 2 presents the results of the measurements at 247 K and provides the first qualitative evidence that two uncoupled reactive channels do indeed exist. The reaction of OH + DMS in the absence of O_2 exhibits a significant kinetic isotope effect (Hynes *et al.* 1986; Barone *et al.* 1996), indicating that direct H atom abstraction takes place at least part of the time. In a large concentration of O_2 , the OH· d_6 -DMS/OH·DMS adduct reacts exclusively with O_2 . Under these conditions, the presence of an isotope effect in the observed bimolecular rate constant, k_{obs} , which is a measure of OH loss rates, signifies a reaction mechanism composed of two separate reaction pathways. This behaviour arises because the adduct is scavenged by O_2 faster than it could decompose via the cleavage of C–H/C–D bonds. The above interpretation assumes that only the thermal decomposition and reaction with O_2 remove the adduct. Figure 2 clearly shows that as the O_2 concentration is raised, k_{obs} increases and levels off at two separate asymptotes for DMS and d_6 -DMS, respectively. The difference between asymptotes A and B is approximately

$3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, the same as the difference between k_1 and k_2 ($k_1 - k_2 = (3.2 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) at this temperature in the absence of O_2 . Experiments at 258 K also showed the same behaviour. Therefore, we conclude that the OH + DMS/ d_6 -DMS reaction proceeds through two independent reaction pathways, addition and H atom abstraction. This conclusion has an important consequence: the effective branching in OH initiated oxidation to form the adduct in air at any temperature (T) can be calculated simply by the expression,

$$\Phi_{\text{addition}}(T) = (k_{\text{obs}}(T) - k_{\text{abi}}(T))/k_{\text{obs}}(T).$$

The observed rate coefficient in an atmosphere of air has been measured as a function of temperature by Hynes *et al.* (1986); hence, branching ratios for abstraction and addition are easily calculated.

In addition to knowing the rate coefficient for the reaction of O_2 with the OH-DMS adduct, the products of this reaction need to be identified for atmospheric purposes. There are many thermodynamically feasible product channels for reaction 5:

The yield of HO_2 , channel 5a, in reaction 5 was measured by generating OH in a reaction mixture containing DMS, OH, O_2 and NO. The addition of NO converts HO_2 to OH via the reaction:

If HO_2 were produced in reaction 5, OH would be regenerated and change the temporal profile of OH. The changes in the OH temporal profiles upon addition of NO can be modelled to determine the branching ratio in reaction 5 that produces HO_2 . At 234 K the branching ratio for reaction 5a was determined to be $\Phi_{5a} = 0.50 \pm 0.15$, independent of the bath gas used, He or N_2 (100 Torr). The total rate coefficient for reaction 5 obtained by this analysis, (k_5) = $(1.1 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, is in excellent agreement with the value of k_5 mentioned earlier. Φ_{5a} and k_5 were also determined at 258 K to be $\Phi_{5a} = 0.49 \pm 0.12$ (in 200 Torr N_2) and $k_5 = (9.5 \pm 3.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. No variation in Φ_{5a} was observed when the reagent concentrations were varied. Such measurements were repeated at a few temperatures between 234 and 258 K and found to be the same. Hence, it appears that the branching ratio for channel 5a is $\Phi_{5a} = 0.50 \pm 0.16$, independent of temperature.

(ii) Abstraction channel

There is considerable evidence for the existence of an H atom abstraction channel in the OH + DMS reaction (reaction 1a). The kinetic isotope effect in the OH + DMS reaction rate coefficient at 298 K, i.e. k_1 versus

Figure 3. The temporal profiles of OH and CH₃S in the presence of DMS, O₂, and NO at 298 K, at which temperature the formation of the adduct is negligible and the OH reaction proceeds mainly via the abstraction of H atoms. The subsequent reactions lead to the formation of CH₃S according to the mechanism shown in the text. Analysis of the temporal profiles and signal levels lead to the yield of CH₃S in this system.

k_2 , strongly suggests that the H atom abstraction reactions have a significant activation energy and, hence, involve breaking the C–H bond. Stickel *et al.* (1993) directly measured the yield of HDO from the reaction of OD radicals with DMS to be $\Phi_{1a} = 0.84 \pm 0.15$. Also, end product studies have suggested that H atom abstraction is a major pathway for reaction 1 under atmospheric pressures and O₂ and NO concentrations.

In the present study, to determine the branching ratio for H atom abstraction in reaction 1 at 298 K, we used pulsed laser photolysis to produce OH and pulsed laser-induced fluorescence to detect OH and CH₃S. CH₃SCH₂ was not directly detected in this study. However, it can be converted to CH₃S, which was detected. The conversion of CH₃SCH₂ to CH₃S was accomplished by the addition of a high concentration of O₂ and sufficient NO via the sequence of reactions :

The yield that we measure is the amount of CH₃S formed from the sequence of reactions 1a, 9, 10 and 11, relative to the amount of OH lost.

Figure 3 shows the temporal profiles of OH and CH₃S obtained in back-to-back experiments following the 248 nm photolysis of a mixture of DMS, H₂O₂, O₂ and NO. These temporal profiles can be described by the sequence of reactions shown in table 1. Measured temporal profiles were fitted to the mechanism using the nonlinear least squares fitting program mentioned earlier. An example of the calculated fits is also shown in figure 3 along with the experimental data. The

average value of Φ_{1a} obtained from the fits to the temporal profiles from 12 back-to-back runs was $\Phi_{1a} = 0.84 \pm 0.26$, in excellent agreement with the results of Stickel *et al.* (1993).

The temporal profiles of CH₃S obtained in the present study also yielded information on the rate coefficient for reaction 11. CH₃SCH₂O is thermally unstable at 298 K and dissociates to CH₂O and CH₃S (McKee 1993; Wine 1994). Wine (1994) has recently placed an upper limit of 30 μ s for the lifetime of CH₃SCH₂O at 261 K. The temporal profiles of CH₃S obtained in the present study constrain the lifetime of CH₃SCH₂O to be less than 10 μ s at 298 K, therefore corroborating the short lifetime of CH₃SCH₂O reported by Wine.

(iii) *Rate coefficient for the OH reaction with DMS in the atmosphere*

Rate coefficients for the loss of OH via reaction with DMS in an atmosphere of air have been measured by Hynes *et al.* (1986) as a function of temperature (figure 4). The values for the addition and abstraction pathways deduced by them are also shown in the figure. Our measured values for the abstraction pathway, also shown in the figure, are in excellent agreement with those of Hynes *et al.* In addition, the values of the overall rate constant calculated from the measured values of the rate coefficients for the forward and reverse reactions for the OH addition to DMS and the rate coefficient for the reaction of the OH·DMS adduct with O₂ are also shown. It is clear that the measured overall rate coefficients are in good agreement with those deduced from the individual elementary reactions. Note that because of the large error in calculating such a value, the uncertainty is quite large. Finally, based on the isotopic labeling studies described elsewhere (Turnipseed *et al.* 1996), we have concluded that the reaction of the OH·DMS adduct with O₂ cannot regenerate OH. Therefore, the rate coefficients measured by Hynes *et al.* in air are applicable to the atmosphere. This data set therefore provides the rate coefficients needed to calculate the atmospheric lifetime of DMS due to its reaction with OH.

(iv) *Summary of initiation reactions and their impact on the atmosphere*

Our work has quantified the kinetics and mechanisms of several elementary processes important in the atmospheric oxidation of DMS. We have shown that reaction 1 proceeds through a mechanism which involves two active channels: addition of OH to the sulphur atom and abstraction by OH of an H atom from the CH₃ group. Because the abstraction and addition channels are independent of each other, the respective rates and branching in the atmosphere can be accurately determined.

The rate coefficient for the loss of OH in air containing DMS measured by Hynes *et al.* agrees with that calculated from the individual reactions in the mechanism for the OH reaction with DMS. Therefore, the data of Hynes *et al.* can be used for calculating the lifetime of DMS in the atmosphere.

Table 1. Reactions used in the simulation of the temporal profiles of OH and CH₃S measured following OH production in the presence of DMS, O₂, and NO

reaction number	reaction	source of rate const
7	OH·DMS (+ M) → H ₂ O + CH ₃ SCH ₂	varied
9	CH ₃ SCH ₂ + O ₂ + M → CH ₃ SCH ₂ OO + M	varied
10	CH ₃ SCH ₂ OO + NO → CH ₃ SCH ₂ O + NO ₂	varied
11	CH ₃ SCH ₂ O + M → CH ₃ S + CH ₂ O + M	varied
12	CH ₃ + O ₂ + M → CH ₃ OO + M	DeMore <i>et al.</i> 1994
13	CH ₃ OO + NO → CH ₃ O + NO ₂	DeMore <i>et al.</i> 1994
14	CH ₃ O + O ₂ → HO ₂ + CH ₂ O	DeMore <i>et al.</i> 1994
15	HO ₂ + NO → OH + NO ₂	DeMore <i>et al.</i> 1994
16	NO + CH ₃ S → CH ₃ SNO	measured

Figure 4. A plot of the rate coefficient for the loss of OH in air at atmospheric pressure due to its reaction with DMS as a function of temperature. The upper curved line is the overall rate coefficient for OH loss rate coefficients measured by Hynes *et al.* 1986). The lowest straight line is the rate coefficient for the loss of OH due to the abstraction of an H atom from DMS, as measured by Hynes *et al.* The solid points are the abstraction rate constants measured in our laboratory. The lowest curved line is the calculated rate coefficient for the loss of OH via the addition channel. The dashed line is the rate coefficient for the loss of OH in air due to reaction with DMS calculated from the rate coefficients for the elementary reactions measured in our laboratory. The grey area is the approximate uncertainty in the calculated rate coefficient.

The abstraction channel predominately leads to CH₃S formation in the atmosphere. The value of $\Phi_{1a} = 0.84$ measured in the present study indicates that H atom abstraction is a major pathway in reaction 1. Our results also show that CH₃S will be an important intermediate in OH-initiated atmospheric oxidation of DMS as long as there is sufficient NO present to convert the CH₃SCH₂OO radical to CH₃SCH₂O. Recent work by Butkovskaya & LeBras (1994) has shown that the NO₃ + DMS reaction leads exclusively to CH₃SCH₂ and, hence, this reaction will also result in the production of CH₃S in the atmosphere. Therefore, the H atom abstraction by OH and the reaction of NO₃ both lead to the same set of products in the atmosphere.

Our study of the products of reaction 5 has shown that addition of OH to DMS followed by reaction with O₂ results in the formation of HO₂ a large fraction of the time. The co-product of HO₂ in this reaction must be DMSO. DMSO is likely to be rapidly scavenged by droplets in the marine troposphere and may comprise a significant sink of sulphur in the troposphere. Our measurements of the products of OH·DMS + O₂ suggest that there is a significant, as yet unidentified, active channel ($\Phi > 30\%$). This channel is likely to consist of one or more of the following reactions:

Further work is needed to quantify the remaining active channels of the OH·DMS + O₂ reaction and to directly ascertain the formation of DMSO.

The large abundance of O₂ in the atmosphere ensures that, aside from unimolecular decomposition, reaction 6 will be the only fate of the OH·DMS adduct formed by the addition of OH to DMS. Therefore, the OH + DMS reaction constitutes the first possible fork in the oxidation mechanism which can lead to different products in the atmosphere. Based on the yields of HO₂ from the OH·d₆-DMS + O₂ reaction, it is very likely that DMSO will be a major product of the addition channel in the atmosphere. Direct observation of DMSO in the OH·DMS + O₂ reaction would strengthen this conclusion.

(c) NO₃ in the MBL: effect of heterogeneous uptake

To quantify the rate of DMS removal in the atmosphere requires not only the rate coefficients for the reaction of DMS with the initiating free radicals, but also their atmospheric concentrations in the regions where DMS is emitted. It appears that the measured atmospheric OH radical concentrations are not too far from those calculated (see Eisele & McMurry, this issue). We, however, should caution that there are no measurements of the OH radicals in the MBL into which most of DMS is emitted and where a large fraction of it is oxidized. However, based on our current understanding, it is very unlikely that the concentrations of OH in the MBL are too far from the values calculated using the measured abundances of

O₃ and water vapour. In contrast, our understanding of the concentrations of the NO₃ radical in the MBL is very uncertain. Even the levels of NO_x in this region of the atmosphere are not well measured. One of the processes that can greatly affect the NO₃ abundance in the MBL is its heterogeneous removal.

To characterize the heterogeneous night-time processing of NO₃ in the troposphere and its impact on cloud and MBL processes, we measured the uptake of NO₃ on pure water and on some solutions pertinent to the marine troposphere and to cloud droplets. These measurements were carried out using the wetted-wall flow tube technique developed in our laboratory and described elsewhere (Hanson *et al.* 1992; Utter *et al.* 1992; Rudich *et al.* 1996).

In these studies, Henry's law coefficient for NO₃ in aqueous solution was determined to be $H = 0.6 \pm 0.3 \text{ M atm}^{-1}$ at $273 \pm 1 \text{ K}$ (Rudich *et al.* 1996). In addition, we measured the rate coefficients for the reactions of NO₃ with various organic and inorganic ions (Rudich *et al.* 1996*a, b*; Imamura *et al.* 1997). One of the important implications of these studies is that NO₃ can be lost into water by reactive uptake, due to its liquid phase reaction with water:

The uptake of NO₃ by atmospheric hydrometeors differs from that of N₂O₅ because it forms reactive species in the liquid phase via the reaction of NO₃ with water and with other dissolved species. Therefore, NO₃ will be continuously removed from the atmosphere either via its reaction with liquid water or with dissolved species. Reactive uptake of NO₃ also produces reactive radicals such as Cl₂⁻, OH and SO₃⁻, which undergo further reactions in the liquid phase. Most importantly for the present discussions, the gas phase concentration of NO₃ in the atmosphere will be affected by the presence of water droplets and aerosols.

To assess the atmospheric implications of the laboratory findings we have constructed a zero dimensional (i.e. no transport) chemical kinetics model which focuses on the effect of NO₃ uptake on the lifetime of NO₃ in the presence of aerosols, and on the role of NO₃ uptake as a loss process for NO_x. The chemical kinetics model consisted of the pertinent gas phase and liquid phase reactions. It included mono-dispersed aerosols (10 μm radius, 100 particles cm⁻³, liquid water content, L, of $4.2 \times 10^{-7} \text{ cm}^3$ of liquid per cm³ of gas). Since NO₃ is an important oxidant only at night-time, the simulation modelled night-time processes. The gas phase part of the model was a simplified reaction scheme in which NO₃ was produced by the NO₂ + O₃ reaction. At the initiation of the calculations, NO₃ was assumed to be in thermal equilibrium with N₂O₅. Once the run was initiated, NO₃ abundance was explicitly calculated using all the gas phase and liquid phase reactions. The liquid phase reaction scheme of the model consisted of *ca.* 60 reactions. Reactions with dissolved organic compounds were not included in this study; the organics would decrease the NO₃ lifetime only slightly. All the simulations were carried out at 298 K. Gas-to-liquid mass transfers of NO₃, N₂O₅, SO₂, HO₂, and H₂O₂ were explicitly calculated using

Figure 5. Calculated NO₃ lifetime as function of salt concentration in the MBL in the presence of liquid particles specified in the text.

two coupled differential equations (Schwartz 1984, 1986; Hansen *et al.* 1994). The concentration gradient created due to the competition between diffusion and reaction in the liquid droplets was also taken into account (Schwartz 1986; Hanson *et al.* 1994). Such simulations were carried out at various concentrations of Cl⁻ in the droplets.

Due to the high concentration of Cl⁻ (0.1–1 M) in sea salt aerosols in the MBL, the uptake of NO₃ is very efficient. The lifetime of NO₃ in the presence of aerosols with different [Cl⁻] is shown in figure 5. The initial pH of the sea salt aerosols is 8, however, it rapidly decreases due to the very high NO₃ uptake which produces HNO₃. As seen in the figure, the lifetime of NO₃ in the presence of the condensed matter in the MBL will decrease very rapidly as the Cl⁻ concentration in the droplets increases.

Due to the efficient uptake by sea salt aerosol, the uptake of NO₃ can become the dominant loss of NO_x from the atmosphere in the MBL. In the MBL, H₂O₂ concentrations do not affect the NO₃ lifetime or gas phase concentration since the uptake of NO₃ is mainly due to its reaction with dissolved Cl⁻.

The efficient removal of NO₃ in the MBL results in a low abundance of NO₃. The steady-state concentration of NO₃ in the presence of sea salt aerosols will be determined by the rate of its removal by aqueous phase reactions. Figure 6 shows [NO₃] in the presence of sea salt aerosol ([Cl⁻] = 0.01 M) at three different scenarios: (1) No uptake of NO₃, (2) uptake only of N₂O₅, and (3) uptake of both N₂O₅ and NO₃. It can be seen that the concentration of NO₃ drops down to about one-fiftieth of the value calculated in the absence of the heterogeneous reactions. We calculated concentrations of < 0.01 pptv NO₃ for sea salt aerosol conditions with [Cl⁻] = 0.01 M, if the NO_x abundance is 10 pptv. Such low concentration in the MBL implies that NO₃ does not play an important role in the removal of various gas phase sulphur species pertinent to the MBL, most notably, DMS.

The above calculations show that in the presence of sea salt aerosol, which would be prevalent in the MBL,

Figure 6. The calculated gas phase concentration of NO_3 in the presence of liquid droplets in the MBL: (1) no heterogeneous losses take place (solid line); (2) only N_2O_5 uptake takes place (dashed line); (3) both NO_3 and N_2O_5 uptake occurs (dotted line). The parameters used for these simulations are: $[\text{Cl}^-] = 0.01 \text{ M}$, 100 pptv SO_2 , 100 pptv NO_x , 50 pptv H_2O_2 .

NO_3 will be very low. Therefore, as long as there are aerosol particles present, NO_3 is less likely to be a major oxidant for DMS in the MBL. If this conclusion is confirmed, OH will be the dominant oxidizer of DMS close to the regions where it is emitted.

The products of the OH reaction with DMS, which has an addition and an abstraction channel, can vary with temperature and, hence, can alter the yields of end

products in the atmosphere. This has been suggested in the past to be the source for the changes in the yield of $[\text{MSA}]/[\text{NSSS}]$ ratio with temperature (Berresheim 1987; Hynes & Wine 1989; Legrand *et al.* 1993). We have previously argued that the competition between addition and abstraction channels is an unlikely point for branching. The argument was partly based on the occurrence of the NO_3 reaction which diminishes the temperature dependence of the branching at the initiation. A lower NO_3 concentration leads to a larger role for OH in initiating DMS oxidation. Therefore, it also enhances the ability of the OH initiation step to alter products as a function of temperature. Yet, based on the modelling carried out earlier, we believe that the OH initiation reaction is not the place in the DMS oxidation mechanism which leads to the temperature dependence of the end products such as MSA and SO_2 , even in the absence of initiation by NO_3 (Barone *et al.* 1995).

(d) *The CH_3S radical intermediate and its subsequent oxidation: a mechanism for DMS oxidation*

Many chamber studies have shown that CH_3S is an important intermediate in the oxidation of reduced sulphur compounds such as DMS. Butkovskaya & LeBras (1994) have shown that the NO_3 -initiated oxidation of DMS leads to the production of CH_3S . We have shown that the abstraction path in the OH reaction with DMS leads to the production of CH_3S as

Figure 7. A simplified mechanism for the oxidation of DMS in the atmosphere. Various branching points in the mechanism are shown.

long as there is sufficient NO to react with the $\text{CH}_3\text{SCH}_2\text{O}_2$ radical. In the MBL, as long as there is *ca.* 10 pptv of NO_x , the $\text{CH}_3\text{SCH}_2\text{O}_2$ radical is likely to react with NO. However, the possibility that $\text{CH}_3\text{SCH}_2\text{O}_2$ (or any other subsequent peroxy radical) reacts with other peroxy radicals, in particular HO_2 , cannot be ignored (Berresheim 1995). It is possible that CH_3S will be generated even from the products of the peroxy radical reactions. Therefore, the oxidation of CH_3S in the atmosphere must hold an important key to the eventual formation of end products such as SO_2 and MSA.

Previous laboratory studies have shown that the CH_3S radical adds to O_2 to form a weakly bound adduct that can alter the course of CH_3S oxidation in the atmosphere (Turnipseed *et al.* 1992, 1993). Formation of weakly bound adducts appears to be quite prevalent in the case of sulphur-containing species. Such addition has been seen in the reaction of OH with CS_2 and DMS. Our previous work delineated the pathways by which the CH_3SO_2 radical, formed as an adduct in the $\text{CH}_3\text{S} + \text{O}_2$ reaction, can be converted to other species in the atmosphere. Based on the assumption that other sulphur-containing radicals also exhibit a propensity to form adducts, we have developed a mechanism for the oxidation of the CH_3S radical. A simple version of this mechanism is shown in figure 7. We have previously argued that this mechanism can account for the variation in the MSA to NSSS yield observed in the atmosphere, and this change is due to a competition between the unimolecular thermal decomposition of a CH_3SO_x radical to cleave the C–S bond and its reaction with a species such as HO_2 and CH_2O to yield MSA (Barone *et al.* 1995). In making that argument, we did not take into account the variation in the atmospheric concentration of species such as HO_2 with temperature. In this symposium, Ayers *et al.* (this issue) have argued that when allowance is made for the variation in the atmospheric concentration of HO_2 with temperature, one can better account for the observed ratio of MSA to NSSS. The main reason, as pointed by Ayers *et al.*, for such an accounting is that the concentration of the species from which an H atom can be abstracted also changes with temperature and, hence, alters the MSA to SO_2 ratio.

3. CONCLUSIONS

In this paper, we have described some of our laboratory measurements. We argue that OH is likely to be the dominant oxidizer for DMS in the MBL. One of the major uncertainties in this argument is the knowledge of the concentration of NO_x , and hence the NO_3 radical, in the MBL.

The rate coefficients for the reactions that initiate DMS oxidation are quite well known so that the atmospheric loss rates of DMS can be calculated if the free radical concentrations are known. The first step in the OH-initiated oxidation of DMS is reasonably well understood. This step involves a sequence of reactions consisting of addition of OH to DMS and the subsequent reaction of the adduct with O_2 to form,

50% of the time, HO_2 . The addition path is more prevalent at colder temperatures. Simultaneous with the addition reaction, OH also abstracts an H atom from DMS. This abstraction reaction is more important at warmer temperatures. The rate coefficients for the elementary reactions involved in the OH initiation reaction are known well enough to calculate the overall initiation rate and the branching between the abstraction and addition pathways.

The formation of HO_2 suggests that its co-product is DMSO. If DMSO is rapidly removed from the atmosphere, without the formation of SO_2 , this step may explain the small yield of SO_2 from DMS oxidation under certain conditions. All the products of the reactions of O_2 with the OH·DMS adduct are not yet known.

It is clear that the oxidation of the CH_3S radical holds the key to identity and yields of the end products of DMS oxidation. A simplified reaction mechanism, which accounts for various observations, is presented in this paper. Many of the rate coefficients needed to place this mechanism on a quantitative footing are not available and will have to be estimated.

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Discussion

G. LE BRAS (*CNRS-LCSR, France*). Dr Ravishankara mentioned that the DMS oxidation (OH reaction (abstraction channel) and NO₃ reaction) produces the CH₃S intermediate through CH₃SCH₂O₂ and CH₃SCH₂O, which readily decomposes to CH₃S and CH₂O. Is there experimental evidence that the alternative pathway (CH₃SCH₂O + O₂) is negligible at the lowest temperature of the low troposphere? This pathway will produce CH₃SCHO.

A. R. RAVISHANKARA. The answer to this question is yes, there is evidence that CH₃SCH₂O falls apart to give CH₃S + CH₂O. The experimental evidence for this comes from the work of Wine *et al.* who have placed a lower limit of 30 μs for the thermal decomposition at 261 K. In our own work, we have been able to place a limit of 10 μs for the thermal decomposition at 298 K.

G. LE BRAS. To the answer of Dr Ravishankara, that this alternative channel will give the same products, I mention that CH₃SCHO has been suggested by Barnes *et al.* to produce small quantities of OCS. In such a case, the atmospheric impact of the two channels:

might be different, since OCS is a major source of stratospheric sulphur.

A. R. RAVISHANKARA. This comment addresses what can happen at lower temperatures and how the reaction of CH₃SCH₂O with O₂ can potentially change the oxidation mechanism. Dr Le Bras is absolutely correct that the mechanism can change. As the temperature goes down the thermal decomposition of CH₃SCH₂O will slow. The rate of the O₂ reaction is also likely to slow down. However, the O₂ reaction is unlikely to slow down more than the thermal decomposition, which has a much larger activation energy. Therefore, the reaction of CH₃SCH₂O with O₂ can be important at lower temperatures of the upper troposphere. It is also possible that such a reaction could yield OCS. However, it should be noted that as long as the CH₃S group is intact, it is likely to come back to the CH₃SO₃ radical. Dr Le Bras is also correct in noting that a switch in mechanism will impact on the atmosphere differently. I just want to point out that the mechanism I discussed focused on the MBL and in this region, the O₂ reaction with CH₃SCH₂O is unlikely to be important. Also, it should be remembered that there are other sources of OCS, such as CS₂. Yet, based on the points raised by Dr Le Bras, I agree that more work is needed to decipher the exact course of CH₃SCH₂O in the atmosphere, i.e. as a function of temperature.

D. J. FISH (*University of Reading, UK*). Have you considered the fate of MSA in the atmosphere? Is it possible that temperature-dependent loss processes for MSA could contribute to the temperature dependence of the ratio of MSA to non-sea salt sulphate?

A. R. RAVISHANKARA. No, we have not considered any chemical transformation of MSA in the atmosphere. The assumption is that it will condense out onto existing particles, as in the case of H₂SO₄. If the gas phase chemical transformation lifetime of MSA is shorter than its het-

erogeneous removal, the gas phase chemistry of MSA may change the MSA to NSSS ratio. I should add that MSA, until very recently, has been measured only in the condensed phase and the ratios of MSA to NSSS noted here are for such measurements. To be complete, let me note that we are assuming that MSA in the condensed phase is inert!

G. P. AYRES (*CSIRO, Australia*). What is the major difference between your DMS oxidation scheme and that of Yin *et al.*?

A. R. RAVISHANKARA. There are two major differences between the scheme of Yin *et al.* and ours. First, we have tried to simplify the oxidation scheme down to its bare bones, in order to understand the variations in the yields of MSA and NSSS. Second, we have incorporated the reactions of the CH_3SO_x radicals with O_2 to form weakly bound adducts. We have also included the reactions of some of these radicals with O_3 , NO , etc. We believe that the formation of the adducts plays a major role and the thermal decomposition of the adducts is an important step. Thus, some of the basic assumptions behind the two mechanisms are also different.

R. A. COX (*University of Cambridge, UK*). Could you explain in a little more detail the origin of the temperature dependence of the MSA yields in terms of the DMS oxidation mechanism, which has a number of 'branching points' where

competition between unimolecular (temperature dependent) and bimolecular (nearly temperature independent) is occurring?

A. R. RAVISHANKARA. First, to make MSA, the C–S bond has to be intact, i.e. the CH_3S group must stay together. Second, we are hypothesizing that the CH_3SO_3 radical can be produced via a sequence of O_2 addition steps and reactions with NO , etc. (Please see figure 10 in our paper.) Once the CH_3SO_3 group is produced, it can thermally decompose to give $\text{CH}_3 + \text{SO}_3$ or abstract an H atom from a molecule such as CH_2O or HO_2 . Note that the CH_3SO_3 cannot add any more O_2 to form adducts, i.e. it is at the end of the line for O_2 addition! It is the large temperature dependence of the thermal decomposition of CH_3SO_3 relative to its H abstraction reaction to make MSA that leads to the temperature dependence of the MSA to NSSS yield. We suggest that the main branching point is that between the thermal decomposition of CH_3SO_3 and the H atom abstraction. In this meeting, Greg Ayers pointed out a very important point: one needs to consider the temperature dependence of the concentration of species such as HO_2 and CH_2O from which the H atom can be abstracted by CH_3SO_3 . When this is taken into account, the yield of MSA may indeed decrease with temperature because the abstraction channel slows down. This is not because the rate coefficient is smaller, but because the reactant concentration is lower!