

New Product and Aerosol Studies On The Photooxidation Of Dimethylsulfide

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INTRODUCTION

Dimethylsulfide (DMS) is the major natural source of sulfur to the atmosphere with a source strength of between 12-54 Tg S yr⁻¹ (Andreae et al., 1994). The chemistry of DMS has been postulated to play a pivotal role in regulating the Earth's radiation budget. Although the atmospheric chemistry of DMS has been the subject of intense research an in-depth understanding of many facets of its chemistry still remain elusive.

Laboratory experiments show, that SO₂, HCHO, methanesulfonic acid (MSA: CH₃SO₃H), aerosols and recently also dimethylsulfoxide (DMSO: CH₃SOCH₃) and methane sulfinic acid (MSIA: CH₃S(O)OH), comprise the most important end products (Patroescu et al., 1999; Sørensen et al., 1994). Formation of carbonyl sulfide (OCS) has also been observed could make a significant contribution to the COS-budget (Barnes et al., 1996; Patroescu et al., 1999). The products of the OH-radical initiated oxidation of DMS have been investigated for the first time as a function of temperature and O₂ partial pressure.

EXPERIMENTAL

The experiments were performed in a temperature regulated 1080 litre volume quartz glass reactor. The 254 nm photolysis of H₂O₂ was used for the production of OH radicals. Mixtures of DMS/H₂O₂/(O₂ + N₂) were irradiated over a period of 20-30 min. All experiments were performed at 1000 mbar (O₂ + N₂) total pressure at O₂ partial pressures of 20, 200 and 500 mbar and temperatures of 284, 295 and 306 K.

Reactants and products were monitored using long path in situ FTIR spectroscopy. Methane sulfinic acid, methane sulfonic acid and sulphate were measured using ion chromatography. Samples of 10-40 l air were drawn through a U-tube immersed in an ethanol/liquid N₂ slush bath.

RESULTS

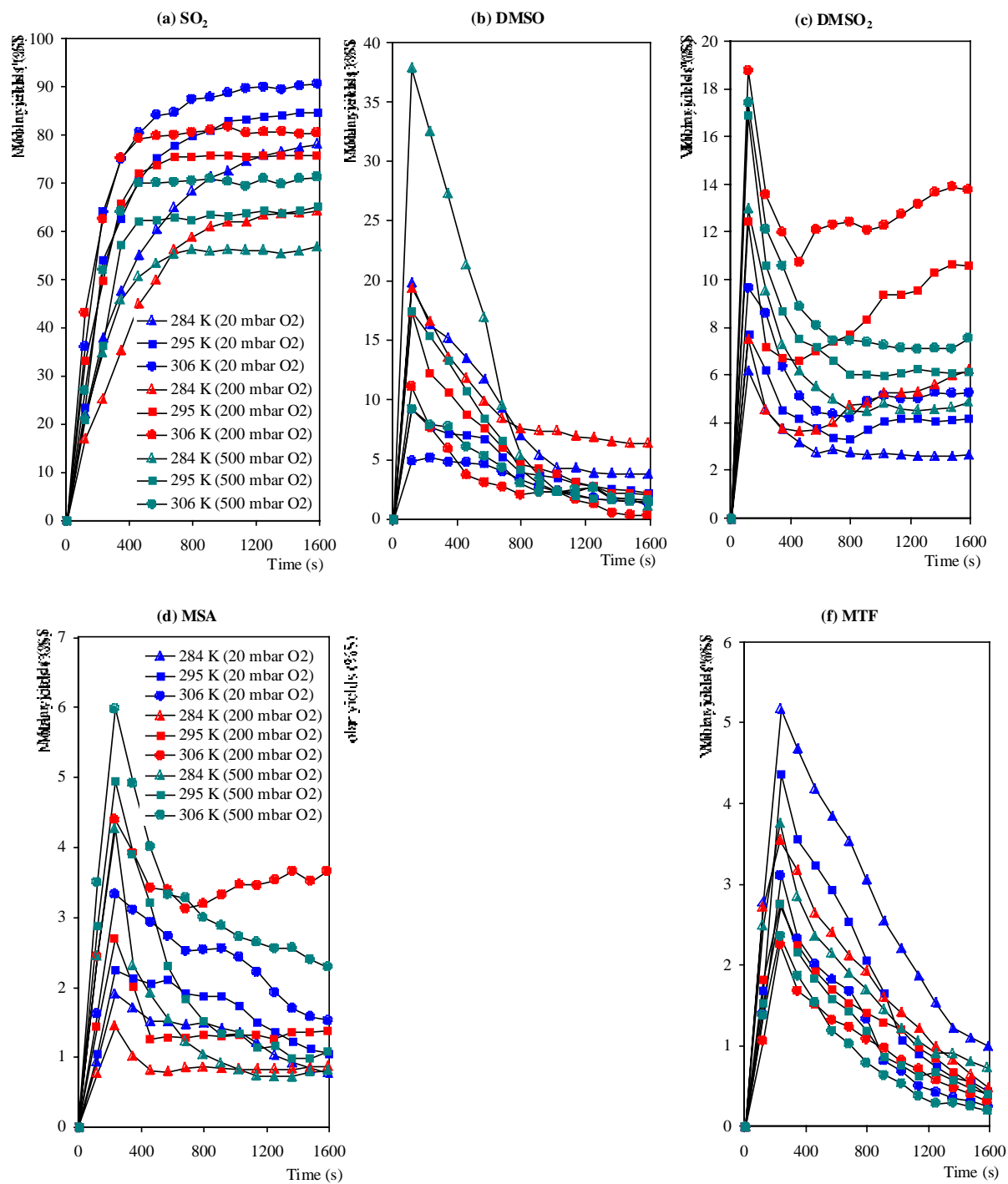
Yield/time profiles of the products formed in the OH + DMS reaction as a function of temperature and O₂ partial pressure are shown in Figure 2: a) SO₂, b) DMSO, c) DMSO₂, d) MSA, e) OCS, f) MTF. The yields have not been corrected for secondary loss processes: reactions with OH, photolysis and wall loss.

Table 1: Corrected yields for the formation of DMSO in the reaction of OH with DMS in 1000 mbar of synthetic air as a function of temperature. The yields are compared to the fractions of the reaction occurring via the addition pathway and abstraction pathways calculated using the results of Hynes et al. [1986] for the specific reaction conditions.

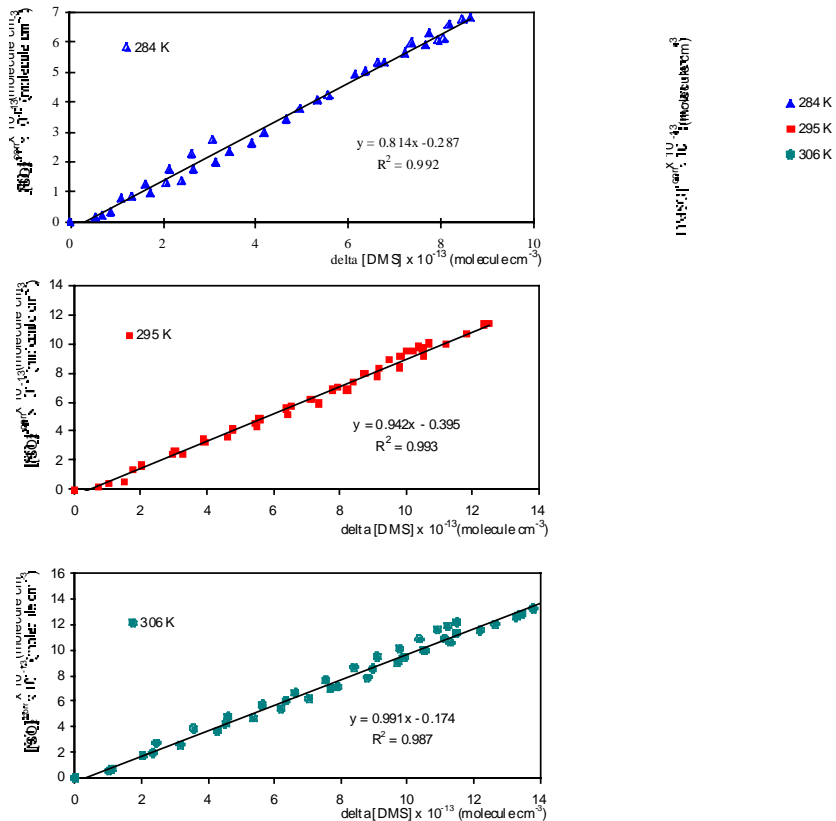
Temperature [K]	Corrected DMSO Yields [% molar yield, $\pm 2\sigma$]	Contribution of addition pathway [%]
284	46.3 ± 5.0	52
295	34.8 ± 7.6	33
306	24.4 ± 2.8	17

Table 3: Corrected yields for the formation of SO₂ in the reaction of OH with DMS in 1000 mbar of synthetic air as a function of temperature. The yields are compared to the fractions of the reaction occurring via the addition pathway and abstraction pathways calculated using the results of Hynes et al. [1986] for the specific reaction conditions.

Temperature [K]	Corrected SO₂ Yields [% molar yield, $\pm 2\sigma$]	Contribution of addition pathway [%]	Contribution of abstr. pathway [%]
284	84.3 ± 6.5	52	48
295	95.0 ± 3.8	33	67
306	99.0 ± 6.5	17	83

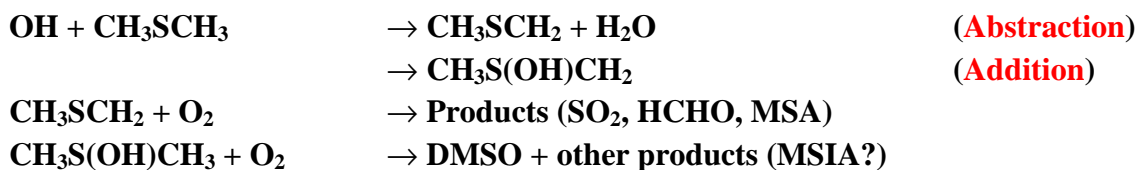


Figures 3 and 4 show plots of the corrected concentrations for SO₂ and DMSO against the amount of DMS consumed. The formation yields are tabulated in Tables 1 and 2 where they are compared against the contribution of the addition and abstraction channels.



DISCUSSION

The primary steps in the OH-radical initiated oxidation of DMS can be represented as follows:



- The observed variations in SO₂ and DMSO yields with experimental conditions are broadly in line with the above mechanism.
- The high yield of DMSO suggests that reaction of the OH.DMS adduct with O₂ results mainly in formation of DMSO.
- The DMSO yields are much higher than the 0.5 yield reported by Turnipseed *et al.* at low temperature and pressure.
- Earlier detection of OCS has been confirmed.
- Yields of gas phase MSA are low.
- High yields of methane sulfinic acid (MSIA) have been observed. Yields are lower limits because of the method of collection and oxidation of MSIA to MSA.
- A large fraction of DMSO is being oxidised to MSIA in line with a recent absolute measurement.

- The large overall formation yields of SO₂ support that SO₂ is formed in both the abstraction and addition channels.
- Further oxidation of MSIA must also result in formation of SO₂ under the present experimental conditions.

In the absence of heterogeneous processes, the gas phase oxidation of DMS in the atmosphere under conditions of low NO_x will result mainly in the production of SO₂.

The fate of DMSO and MSIA, other than gas phase oxidation, is likely to be a major factor in determining the efficiency of the conversion of DMS to SO₂.

LITERATURE

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Acknowledgement

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