# Rate coefficients for the gas-phase reaction of OH radicals with dimethyl sulfide: temperature and O<sub>2</sub> partial pressure dependence

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Rate coefficients for the gas-phase reaction of hydroxyl (OH) radicals with dimethyl sulfide (CH<sub>3</sub>SCH<sub>3</sub>, DMS) have been determined using a relative rate technique. The experiments were performed under different conditions of temperature (250–299 K) and O<sub>2</sub> partial pressure (~0 Torr O<sub>2</sub>–380 Torr O<sub>2</sub>), at a total pressure of 760 Torr bath gas (N<sub>2</sub> + O<sub>2</sub>), in a 336 l reaction chamber, using long path *in situ* Fourier transform (FTIR) absorption spectroscopy to monitor the disappearance rates of DMS and the reference compounds (ethene, propene and 2-methylpropene). OH was produced by the photolysis of H<sub>2</sub>O<sub>2</sub>. The following Arrhenius expressions adequately describe the rate coefficients as a function of temperature (units are cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>):  $k = (1.56 \pm 0.20) \times 10^{-12} \exp[(369 \pm 27)/T]$ , for ~0 Torr O<sub>2</sub>; (1.31 ± 0.08) ×  $10^{-14} \exp[(1910 \pm 69)/T]$ , for 155 Torr O<sub>2</sub>; (5.18 ± 0.71) ×  $10^{-14} \exp[(1587 \pm 24)/T]$ , for 380 Torr O<sub>2</sub>. The results are compared with previous investigations.

## Introduction

Dimethyl sulfide (CH<sub>3</sub>SCH<sub>3</sub>, DMS) is the dominant natural sulfur compound emitted from the world's oceans,<sup>1,2</sup> accounting for about one quarter of global sulfur gas emissions. Oceanic DMS, through its oxidation products, is proposed to play an important role in climate regulation, especially in the remote marine atmosphere.<sup>3</sup>

At the low  $NO_x$  levels that characterizes the remote marine boundary layer, reaction with OH is the most important loss process for DMS:

$$OH + DMS \rightarrow products$$
 (1)

The kinetics of the reaction of OH radicals with DMS have been extensively studied by a variety of direct and competitive techniques. The early studies of the reaction<sup>4–18</sup> led to conflicting results both with regard to the magnitude of the rate coefficient and the activation energy where both positive and negative dependencies were reported. The situation with respect to the rate coefficient and activation energy for the reaction remained confused until it was demonstrated beyond doubt by several groups<sup>11,12,14</sup> that the rate coefficient was affected by the presence of O<sub>2</sub> in the reaction system and also that relative kinetic measurements performed in the presence of NO<sub>x</sub> resulted in erroneously high values for the rate coefficient.

In a comprehensive flash photolysis-resonance fluorescence (FP-RF) investigation Hynes *et al.*<sup>11</sup> found that the effective rate coefficient for OH + DMS and its deuterated analog (DMS- $d_6$ ) was dependent on the oxygen concentration, in-

creasing as the partial pressure of oxygen was increased. The "oxygen enhancement" was the same for both DMS and its deuterated analog, showing that there was no kinetic isotope effect and a significant negative temperature dependence was found.

The experimental kinetic observations of Hynes *et al.*<sup>11</sup> for the reaction of OH radicals with DMS and DMS-d<sub>6</sub> are consistent with a two-channel reaction mechanism involving both hydrogen abstraction (O<sub>2</sub>-independent channel) and reversible adduct formation in competition with adduct reaction with O<sub>2</sub> (O<sub>2</sub>-dependent channel):

$$OH + CH_3SCH_3 \rightarrow CH_3SCH_2 + H_2O$$
(1a)

$$\begin{array}{l} OH + CH_3SCH_3 \ (+M) \leftrightarrow \\ CH_3S(OH)CH_3 \ (+M) \end{array} (1b, 1-b) \end{array}$$

$$CH_3S(OH)CH_3 + O_2 \rightarrow products$$
 (1c)

$$OH + CD_3SCD_3 \rightarrow CD_3SCD_2 + HDO$$
 (2a)

$$\begin{array}{l} \mathsf{OH} \ + \ \mathsf{CD}_3\mathsf{SCD}_3\ (+\,\mathsf{M}) \leftrightarrow \\ \mathsf{CD}_3\mathsf{S}(\mathsf{OH})\mathsf{CD}_3\ (+\,\mathsf{M}) \end{array} \tag{2b, 2-b} \end{array}$$

$$CD_3S(OH)CD_3 + O_2 \rightarrow products$$
 (2c)

In the work of Hynes *et al.*<sup>11</sup> the temperature dependence of the rate coefficient for DMS + OH in 730  $\pm$  30 Torr air, together with temperature dependence of the branching ratio were determined. Using the data the authors derived the following expression for  $k_{obs}$  for one atmosphere of air:

$$k_{\rm obs} = \{T \exp(-234/T) + 8.46 \times 10^{-10} \exp(7230/T) + 2.68 \\ \times 10^{-10} \exp(7810/T)\} / \{1.04 \times 10^{11} T + 88.1 \exp(7460/T)\}$$

where  $k_{obs}$  is the total overall rate coefficient for the abstraction and addition reaction channels.

The branching ratio for the abstraction channel is given by:

$$k_{1a}/k_{obs} = 9.6 \times 10^{-12} \exp(-234/T) / k_{obs}$$

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For many years, the two-channel mechanism has been widely accepted as the operative mechanism for the OH-initiated oxidation of DMS, and expressions for the rate coefficient and inferred branching ratio recommended as the best currently available for mechanistic interpretation and atmospheric modeling purposes. The original expressions of Hynes *et al.* were also modified to take into account the  $O_2$  dependence of the reaction rate.<sup>19</sup>

A re-evaluation of the rate coefficient and the branching ratio has been made by Williams et al.<sup>20</sup> using the pulsed laser photolysis-pulsed laser induced fluorescence (PLP-PLIF) technique. The effective rate coefficient for the reaction of OH + DMS and OH + DMS- $d_6$  was determined as a function of  $O_2$ partial pressure at 600 Torr total pressure in  $N_2/O_2$  mixtures; measurements were made at 240 K for DMS and at 240, 261, and 298 K for DMS-d<sub>6</sub>. This new work showed that at low temperatures the recommended expression at that time<sup>11,19</sup> underestimated both the effective rate coefficient for the reaction and also the branching ratio between addition and abstraction. For example, at 261 K a branching ratio of 3.6 was obtained as opposed to the value of 2.8 obtained in the work of Hynes et al.<sup>11</sup> (the branching ratio is defined here as  $(k_{obs} - k_{1a})/k_{1a}$ ; at 240 K the discrepancy was found to increase between a measured value of 7.8 by Williams et al. and a value of 3.9 obtained from an extrapolation using the empirical expression of Hynes et al.<sup>11</sup> In addition, at 240 K the expression for  $k_{obs}$  in 760 Torr of air based on the work of Hynes et al.<sup>11</sup> predicts a value which is a factor of 2 lower then the measured value at 600 Torr of Williams et al.

The new work of Williams *et al.*<sup>20</sup> has been incorporated into the latest IUPAC Gas Kinetic Data Evaluation.<sup>21</sup> The preferred value for the rate coefficient of reaction (1a) from the review is now  $k_{1a} = 1.13 \times 10^{-11} \exp(-253/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 240–400 K ( $k_{1a} = 4.8 \times 10^{-12}$ cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K). This value is based on the studies on Wine *et al.*<sup>7</sup>, Hynes *et al.*,<sup>11</sup> Hsu *et al.*,<sup>13</sup> Abbatt *et al.*,<sup>16</sup> and Barone *et al.*<sup>18</sup> The preferred value for the rate coefficient of reaction (1b) from the review is now  $k_{1b} = 1.0 \times 10^{-39}$  [O<sub>2</sub>] exp(5820/T)/{1 + 5.0 \times 10^{-30} [O<sub>2</sub>] exp(6280/T)} cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the temperature range 240–360 K ( $k_{1b} = 1.7 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K, 760 Torr of air). This value is based on the studies of Hynes *et al.*<sup>11</sup> and Williams *et al.*<sup>20</sup>

The aim of the present study is to obtain an independent confirmation, using a relative kinetic technique, of the large increase in the rate coefficients for OH with DMS measured at low temperatures by Williams *et al.*<sup>20</sup> as opposed to the extrapolated values obtained with the empirical fit given by Hynes *et al.*<sup>11</sup>

## Experimental

The experiments were carried out in a 336 l glass reaction chamber equipped with a system for temperature regulation to within  $\pm 1$  K from 230 to 300 K and 2 types of lamps: 6 Philips TLA 40 W (300  $\leq \lambda \leq$  450 nm,  $\lambda_{max} =$  360 nm) and 6 Philips TUV 40 W ( $\lambda_{max} =$  254 nm). The reaction chamber is also equipped with an internally mounted multi-reflection White mirror system (47.7 m total optical path length) coupled to a FTIR spectrometer (Nicolet Magna 550, KBr beam splitter, MCT detector) for *in situ* detection of reactants and products. A detailed description of the experimental setup can be found elsewhere.<sup>22</sup>

The kinetic experiments to determine rate coefficients for the reaction of OH with DMS were performed at a total pressure of 760 Torr diluent gas (N<sub>2</sub>, synthetic air, or N<sub>2</sub>/O<sub>2</sub> mixture) at three different O<sub>2</sub> partial pressures (~0, 155 and 380 Torr) and six different temperatures (250, 260, 270, 280, 290 and 299 K). The photolysis of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was used as the OH radical source:

$$H_2O_2 + h\nu (\lambda < 370 \text{ nm}) \rightarrow 2OH$$

Ethene, propene and 2-methylpropene were used as the reference compounds in the investigations. The rate coefficients for the reactions of these compounds with OH are well established<sup>23</sup> and are listed in Table 1 as a function of temperature.

The starting concentrations (calculated at the working temperature) of DMS and of the reference organic compounds were typically in the range 1 to 3 ppm and that of  $H_2O_2$  was approximately 20 ppm. After introducing the reactants into the chamber, the reaction chamber was pressurized to 760 Torr with nitrogen, synthetic air, or nitrogen/oxygen depending on the desired partial pressure of  $O_2$ .

The concentration–time behavior of DMS and the reference organic compounds was followed over 40–50 min time periods by FTIR spectroscopy. Spectra were obtained by co-adding 64 scans which yielded a time resolution of 1 min.

Rate coefficients for the reactions of DMS with OH radicals were determined using a relative rate method in which the relative disappearance rates of DMS and a reference compound are monitored parallelly in the presence of OH radicals:

OH + DMS 
$$\rightarrow$$
 products  $k_{\text{DMS}}$   
OH + reference  $\rightarrow$  products  $k_{\text{ref}}$ 

Providing that DMS and the reference are removed solely by a reaction with the OH radicals, then

$$\ln\left\{\frac{[\mathrm{DMS}]_{t_0}}{[\mathrm{DMS}]_t}\right\} = \frac{k_{\mathrm{DMS}}}{k_{\mathrm{ref}}} \ln\left\{\frac{[\mathrm{ref}]_{t_0}}{[\mathrm{ref}]_t}\right\}$$
(I)

where  $[DMS]t_0$  and  $[ref]t_0$  are the concentrations of DMS and the reference compound, respectively, at time  $t_0$ ; [DMS]t and [ref]t are the corresponding concentrations at time t;  $k_{DMS}$  and  $k_{ref}$  are the rate coefficients for the reaction with OH radicals of DMS and the reference compound, respectively.

**Table 1** Rate coefficients for reaction of the reference compounds with OH radicals ( $k = A e^{-E_a/RT}$ ,  $T \sim 250-425 \text{ K}$ )<sup>23</sup>

Reference compound	$10^{12} k (298 \text{ K})^a$	$10^{12} A^{a}$	$-E_{\rm a}/R$ (K)
Ethene	8.52	1.96	438
Propene	26.3	4.85	504
2-Methylpropene	51.4	9.47	504
$a \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$			

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Under the experimental conditions, DMS and the reference compounds may additionally undergo photodissociation and/ or be lost to the chamber surface.

The photostability of DMS and of each reference compound was established by irradiation of DMS–reference compound–diluent gas mixtures in the absence of OH radical precursors for a time period as long as that employed in the kinetic experiments, after switching on the lamps. The reference compounds employed were not photolysed and their wall losses were also very low, often below the detection limit. For DMS, wall losses accounted for approximately 5% of its measured decay at room temperature and increased gradually to around 30% at the lowest temperature employed in the experiments:

### DMS (+wall) $\rightarrow$ products $k_{\text{loss}}$

The wall loss of DMS was measured at the beginning of every experiment by recording 10–15 spectra prior to irradiation. To check that the wall loss of DMS was constant over the time period of the experiments the loss was measured on a regular basis after termination of the irradiation. No significant change in the DMS wall loss rate was ever observed between the pre- and post-irradiation periods. Incorporating the firstorder loss process of DMS into eqn (I) leads to eqn (II):

$$\ln\left\{\frac{\left[\mathbf{DMS}\right]_{t_0}}{\left[\mathbf{DMS}\right]_t}\right\} - k_{\text{loss}} \times t = k_{\text{DMS}} \left(\ln\left\{\frac{\left[\text{ref}\right]_{t_0}}{\left[\text{ref}\right]_t}\right\} / k_{\text{ref}}\right) \quad (\text{II})$$

where *t* is the reaction time and  $k_{\text{loss}}$  is the loss rate of DMS. According to eqn (II), a plot of  $\ln\{[\text{DMS}]t_0/[\text{DMS}]t\} - k_{\text{loss}} \times t$  against  $\ln\{[\text{ref}]t_0/[\text{ref}]t\}/k_{\text{ref}}$  gives straight lines directly yielding  $k_{\text{DMS}}$  as the slope. Eqn (II) allows the data for all reference hydrocarbons employed for a set of experimental conditions to be plotted and evaluated simultaneously and gives a direct visual view of the quality of the agreement of the experimental data obtained from the different reference compounds.

For each temperature and  $p_{O_2} = \sim 0$  Torr and  $p_{O_2} = 380$ Torr, one reference compound (ethene) was employed, and for each temperature and  $p_{O_2} = 155$  Torr, two or three different reference compounds (ethene, propene, 2-methylpropene) were employed. For each set of experimental conditions, at least three experimental runs were performed.

All the reactants were used without further purification. Dimethyl sulfide was supplied by Sigma Aldrich with a stated purity of 99%. H<sub>2</sub>O<sub>2</sub> (85% wt) was supplied by Peroxide Chemie GmbH. The reference hydrocarbons: ethene, propene, and 2-methylpropene, were supplied by Messer-Griesheim with stated purities of 99.95, 99.95, and  $\geq$  99%, respectively. The following gases were supplied by Messer-Griesheim: nitrogen (99.999%), oxygen (99.999%), and hydrocarbon free synthetic air (99.999%) with a N<sub>2</sub>:O<sub>2</sub> ratio of 20.5:79.5%.

## **Results and discussion**

The kinetic data obtained from the investigations on the reaction of OH with DMS at 6 temperatures for different partial pressures of  $O_2$  are shown plotted according to eqn (II) in Fig. 1. Reasonably linear plots were obtained in all cases. Significant scatter in the measurement points was only observed at the lowest temperature investigated, *i.e.* 250 K. Table

2 lists the reference compounds used for each set of experimental conditions, the measured rate coefficient ratios and the rate coefficients derived for the reaction of OH radicals with DMS. The errors given for the rate coefficient ratios in Table 2 are two least-squares standard deviations  $(\pm 2\sigma)$ ; the quoted errors for the rate coefficients in Table 2 are a combination of the  $2\sigma$  statistical errors from the linear regression analysis plus an additional 20% to cover uncertainties associated with the values of the reference rate coefficients. For every temperature and  $p_{O_2} = 155$  Torr, the rate coefficients were measured relative to two or three different references, thus, the final values given in Table 2 for these conditions of the rate coefficients (k<sub>DMS(average)</sub>) are averages of those determined using the two or three different reference compounds together with error limits which encompass the extremes of the individual determinations. Given in Table 2 is also the tropospheric lifetime of DMS at each temperature calculated using the annually averaged global tropospheric hydroxyl radical concentration of  $\sim 1 \times 10^6$  molecule cm<sup>-3</sup> (24 h average) (Prinn *et al.*<sup>24</sup>).

Several trends can be seen in the kinetic data listed in Table 2:

(i) at a fixed temperature the overall rate coefficient for DMS + OH increases with increasing partial pressure of oxygen;

(ii) at a constant O<sub>2</sub> partial pressure the rate coefficient is observed to increase quite appreciably with decreasing temperature, *i.e.* by factors of 3.6 and 3.0 for  $p_{O_2} = 155$  and 380 Torr between 299 and 250 K, respectively;

(iii) in N<sub>2</sub> with  $p_{O_2} = \sim 0$  Torr where the abstraction pathway for the reaction will dominate the rate coefficient for DMS + OH is observed to increase very slightly with decreasing temperature. However, the observed increase does not exceed the combined error limits of the measurements.

The data given in Table 2 are plotted in Arrhenius form in Fig. 2 for the three  $O_2$  partial pressures investigated. The solid lines are the least-squares fits to the data. The Arrhenius expressions derived from these fits are given in Table 3 for the individual  $O_2$  partial pressures.

#### Possible source of errors in the system

Although we report here results from experiments performed in 760 Torr N<sub>2</sub> with  $p_{O_2} = 0$  Torr in reality the system will contain very small concentrations of O<sub>2</sub>. Apart from O<sub>2</sub> entering the system through leaks in the apparatus the use of hydrogen peroxide, as the OH radical source, can lead to production of O<sub>2</sub> via (i) heterogeneous decomposition on the reactor surface (possibly the largest source) and (ii) chemical reactions in the system. HO<sub>2</sub> radicals are produced in the reaction of OH with DMS and they are produced also by the reaction:

$$H_2O_2 + OH \rightarrow H_2O + HO_2 \tag{3}$$

The self-reaction of  $HO_2$  and reaction with OH result in the formation of  $O_2$ :

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{4}$$

$$HO_2 + OH \rightarrow H_2O + O_2 \tag{5}$$

The above reactions in combination with heterogeneous decay of  $H_2O_2$  will always provide small quantities of oxygen in the



**Fig. 1** Plot of the kinetic data according to eqn (II) for the reaction of DMS with OH radicals at different temperatures and oxygen partial pressures: (*a*) =  $\sim 0$  Torr O<sub>2</sub>, (*b*) = 155 Torr O<sub>2</sub>, (*c*) = 380 Torr O<sub>2</sub>; references:  $\bigcirc$ -ethene,  $\square$ -propene, and  $\triangle$ -2-methylpropene.

Temperature/K	O <sub>2</sub> partial pressure/Torr	Reference	$k_{\rm DMS}/k_{\rm ref}$	$k_{\rm DMS}  imes 10^{11a}$	$k_{\rm DMS\ (average)} \times 10^{11a}$	$ au_{\mathrm{DMS}} = 1/k_{\mathrm{DMS}}$ [OH] (h)
299	~0	Ethene	$0.59 \pm 0.01$	$0.50 \pm 0.10$		
	155	Ethene	$0.94\pm0.02$	$0.80\pm0.16$	$0.78\pm0.18$	35.6
		Propene	$0.28\pm0.01$	$0.75\pm0.15$		
	380	Ethene	$1.13\pm0.02$	$0.95\pm0.19$		
290	$\sim 0$	Ethene	$0.64\pm0.02$	$0.57\pm0.11$		
	155	Ethene	$1.13\pm0.02$	$1.00\pm0.20$	$0.98 \pm 0.23$	28.3
		Propene	$0.33\pm0.01$	$0.93\pm0.18$		
	380	Ethene	$1.51\pm0.04$	$1.34\pm0.27$		
280	$\sim 0$	Ethene	$0.67\pm0.02$	$0.62\pm0.13$		
	155	Ethene	$1.27\pm0.03$	$1.19\pm0.24$	$1.20 \pm 0.26$	23.1
		Propene	$0.42\pm0.01$	$1.22\pm0.24$		
	380	Ethene	$1.64\pm0.03$	$1.54\pm0.31$		
270 ~0	$\sim 0$	Ethene	$0.64\pm0.02$	$0.63 \pm 0.14$		
	155	Ethene	$1.53\pm0.06$	$1.52\pm0.31$	$1.51 \pm 0.34$	18.4
		Propene	$0.47 \pm 0.01$	$1.47\pm0.30$		
	380	Ethene	$1.87\pm0.05$	$1.85\pm0.37$		
260	$\sim 0$	Ethene	$0.60\pm0.03$	$0.64 \pm 0.13$		
	155	Ethene	$1.93\pm0.04$	$2.04\pm0.40$	$1.99 \pm 0.47$	13.9
		Propene	$0.58\pm0.01$	$1.97\pm0.39$		
		2-Methylpropene	$0.30\pm0.01$	$2.00\pm0.40$		
	380	Ethene	$2.25\pm0.12$	$2.38\pm0.47$		
250	$\sim 0$	Ethene	$0.58\pm0.05$	$0.66 \pm 0.14$		
	155	Ethene	$2.37\pm0.30$	$2.68\pm0.63$	$2.82\pm0.77$	9.85
		Propene	$0.77\pm0.04$	$2.80\pm0.57$		
		2-Methylpropene	$0.41\pm0.02$	$2.96\pm0.60$		
	380	Ethene	$2.51\pm0.23$	$2.83\pm0.62$		
<sup><i>a</i></sup> cm <sup>3</sup> molecule <sup>-1</sup>	$s^{-1}$					

**Table 2** Rate coefficient ratios  $k_{\text{DMS}}/k_{\text{ref}}$  and rate coefficients  $k_{\text{DMS}}$  for the gas phase reaction of OH radicals with DMS at different temperatures and O<sub>2</sub> partial pressures

system, leading to the formation of oxygenated compounds even when "nitrogen" is used as the bath gas. Using the known leak rate of the reactor under vacuum it is estimated that in the



Fig. 2 Arrhenius plots of the rate coefficients determined for DMS + OH in the temperature range 250 to 299 K for various  $O_2$  partial pressures.

"nitrogen" experiments  $p_{O_2}$  is probably less than 30 ppm. Based on the measured  $O_2$  enhancement on the rate coefficient for DMS + OH these low  $O_2$  concentrations in the  $N_2$ experiments will make a negligible contribution to the measured rate coefficient.

Another potential source of error is the reaction of  $HO_2$  radicals with DMS:

$$HO_2 + CH_3SCH_3 \rightarrow OH + CH_3S(O)CH_3$$
 (6)

An upper limit of the rate coefficient for reaction (6) of  $< 5 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K has been reported.<sup>21</sup> However, the good agreement between the rate coefficient for OH + DMS determined in N<sub>2</sub> at 299 K in this study with those obtained by other workers (as discussed later) leads to the conclusion that both reaction (6) and the low traces of O<sub>2</sub> have probably a negligible influence on the measurements.

Table 3 Arrhenius expressions valid in the temperature range from 250 to 299 K  $\,$ 

O <sub>2</sub> partial presurre/Torr	$k_{\rm DMS}/{\rm cm}^3 {\rm \ molecule}^{-1} {\rm \ s}^{-1}$		
~0	$(1.56 \pm 0.20) \times 10^{-12} \exp[(369 \pm 27)/T]$		
155	$(1.31 \pm 0.08) \times 10^{-14} \exp[(1910 \pm 69)/T]$		
380	$(5.18 \pm 0.71) \times 10^{-14} \exp[(1587 \pm 24)/T]$		

Table 4 Room temperature rate coefficient for DMS + OH reaction in absence of  $O_2$ 

$k_{\text{DMS}} \times 10^{12}/\text{cm}^3$ molecule <sup>-1</sup> s <sup>-1</sup>	$T/\mathbf{K}$	Pressure (Torr)/bath gas	Technique	Ref.
$4.26 \pm 0.56$	298	50/Ar	FP-RF <sup>a</sup>	7
$3.22 \pm 1.16$	293	0.5/He	DF-EPR <sup>a</sup>	10
$4.09 \pm 1.16$	298	40/Ar	$FP-RF^{a}$	11
$4.44\pm0.23$	298	30/Ar	$FP-RF^{a}$	11
$4.75\pm0.15$	298	$500/SF_{6}$	PLP-PLIF <sup>a</sup>	11
$4.80 \pm 0.11$	298	$40/N_{2}$	PLP-PLIF <sup>a</sup>	11
$3.60\pm0.20$	297	50–400/Ar	$FP-RF^{a}$	12
$5.50 \pm 1.00$	298	0.8-3/He	$DF-RF^{a}$	13
$3.50\pm0.20$	295	760/År	PR-KS <sup>a</sup>	15
$4.98\pm0.46$	297	$10-100/N_2$	HPF-LIF <sup>a</sup>	16
$4.95\pm0.35$	298	$100/He/N_2/SF_6$	PLP-PLIF <sup>a</sup>	18
$5.30 \pm 0.50$	296	740/Ar	$DS-FTIR^{b}$	12
$4.40\pm0.40$	298	$760/N_{2}$	$CP-GC^b$	14
4.80	298		Review	21
$5.00\pm1.00$	299	$760/N_2$	$CP$ - $FTIR^{b}$	tw

<sup>*a*</sup> Absolute technique: FP = flash photolysis, RF = resonance fluorescence, DF = discharge flow, EPR = electron paramagnetic resonance, PLP = pulsed laser photolysis, PLIF = pulsed laser induced fluorescence, PR = pulse radiolysis, KS = kinetic spectroscopy, HPF = high pressure flow, LIF = laser induced fluorescence; <sup>*b*</sup> Relative technique: DS = dark source of OH (O<sub>3</sub> + N<sub>2</sub>H<sub>4</sub>), FTIR = Fourier transform infrared spectroscopy, CP = continuous photolysis, GC = gas chromatography; tw = this work.

## Comparison with previous work

For ease of comprehension, rate coefficients determined in the absence of  $O_2$  will first be discussed, followed by the determinations performed in the presence of  $O_2$ . Earlier determinations which are now thought to be flawed because of reactive impurities in the DMS samples<sup>4,5</sup> or heterogeneous effects<sup>8</sup> are not considered in the comparison. Also excluded from the comparison are relative studies where NO was present,<sup>6,9,12,15</sup> since the studies are believed to be in error due to secondary reactions in the systems. The exclusions, however, underline the variety of complications which can arise in studies of the kinetics of the DMS + OH reaction.

In Table 4 a comparison is made of the data obtained in this work at 299 K and 760 Torr N<sub>2</sub> ( $p_{O_2} = \sim 0$  Torr) with other room temperature values reported in the literature.

This comparison shows that the value obtained in this study  $(k_{\text{DMS}} = (5.00 \pm 1.00) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$  is in very good agreement with most of the other determinations obtained using absolute<sup>7,11,13,16,18</sup> and relative methods.<sup>12,14</sup> There are, however, three absolute studies<sup>10,12,15</sup> which re-

ported room temperature rate coefficient in the absence of  $O_2$ , which are substantially lower. Potential production of O impurities in the systems which can react with DMS to regenerate OH radicals on the time scale of the experiment and thus lead to a low effective rate constant has been postulated as an explanation for the low values. O atoms can be formed either in high concentrations from microwave discharges (which could affect flow tube experiments) or from high concentrations of OH, *via* the reaction OH + OH  $\rightarrow$  H<sub>2</sub>O + O. The experiments of Martin *et al.*<sup>10</sup> and Nielsen *et al.*,<sup>15</sup> for example, used extremely high OH radical concentrations.

The new recommended Arrhenius expression for reaction (1a) of  $k_{1a} = 1.13 \times 10^{-11} \exp(-253/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 240–400 K from the review of Atkinson *et al.*<sup>21</sup> gives  $k_{1a} = 4.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K. The value of  $(5.00 \pm 1.00) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  determined in this study at 299 K is in good agreement with the recommended value.

The Arrhenius expression derived in this work from the measurement in N<sub>2</sub> with  $p_{O_2} = \sim 0$  Torr for DMS + OH in the temperature range 250 to 299 K is compared with other determinations in the absence of O<sub>2</sub> and also with the most recent kinetic review given in Table 5.

The activation energy of reaction (1a) is still not well characterized. The studies of Wine et al.,<sup>7</sup> Hynes et al.,<sup>11</sup> Hsu et al.,13 Abbatt et al.16 report a positive Arrhenius activation energy, while Wallington et al.<sup>12</sup> report a negative Arrhenius activation energy. The latest IUPAC data evaluation recommends a *positive* Arrhenius activation energy. The observation of a *positive* activation energy has been taken as indicating the dominance of the hydrogen abstraction reaction (1a) in the systems used to study the reaction, while measurement of a negative Arrhenius activation energy has been taken as an indication that the association reaction (1b) is also probably contributing to the rate coefficient measurement under the conditions employed. In this work a negative Arrhenius activation energy has been obtained. Although we will always have very low concentrations of O<sub>2</sub> in our system even in 760 Torr N<sub>2</sub>, a reasonable agreement with other determinations of the rate coefficient would suggest that the  $O_2$  is not making a large contribution, at least at room temperature. However, with decrease in temperature, the formation of the (CH<sub>3</sub>)<sub>2</sub>S-OH adduct will become more important and it can not be excluded that the system may be more sensitive to the presence of small quantities of O<sub>2</sub> at

Table 5 Arrhenius expressions for DMS + OH reaction in different ranges of temperature in the absence of  $O_2$ 

$k_{\text{DMS}}$ Arrhenius expression/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	T range/K	Pressure (Torr)/bath gas	Technique	Ref.
$(6.8 \pm 1.1) \times 10^{-12} \exp[(-138 \pm 46)/T]$	248-363	50–200/Ar	$FP-RF^{a}$	7
$(13.6 \pm 4.0) \times 10^{-12} \exp[(-332 \pm 96)/T]$	276-397	30–40/År	$\mathbf{FP}$ - $\mathbf{RF}^{a}$	11
$(2.5 \pm 0.9) \times 10^{-12} \exp[(130 \pm 102)/T]$	297-400	50/Ar	$\mathbf{FP}$ - $\mathbf{RF}^{a}$	12
$(11.8 \pm 2.2) \times 10^{-12} \exp[(-236 \pm 150)/T]$	260-393	0.8–3/He	$DF-RF^{a}$	13
$(13.5 \pm 6.2) \times 10^{-12} \exp[(-285 \pm 135)/T]$	297-368	$10 - 100/N_2$	$HPF-LIF^{a}$	16
$1.13 \times 10^{-11} \exp(-253/T)$	240-400		Review	21
$(1.56 \pm 0.20) \times 10^{-12} \exp[(369 \pm 27)/T]$	250-299	$760/N_2$	$CP$ - $FTIR^{b}$	tw

<sup>*a*</sup> Absolute technique: FP = flash photolysis, RF = resonance fluorescence, DF = discharge flow, HPF = high pressure flow, LIF = laser induced fluorescence. <sup>*b*</sup> Relative technique: CP = continuous photolysis, FTIR = Fourier transform infrared spectroscopy; tw = this work.

lower temperatures. As stated previously our observed increase in the DMS + OH rate coefficient in  $N_2$  with decreasing temperature does not exceed the combined error limits of the measurements at the temperature extremes. Similarly, for all of the other investigations the determined activation energy is associated with quite sizeable errors and the observed increase in the rate coefficient does not exceed the combined error limits of the measurements at the temperature extremes. Further measurements with higher precision are required to determine more accurately the Arrhenius parameters for the abstraction channel (1a) in DMS + OH.

The observed increase in the rate coefficient for the reaction of OH with DMS with increase in the partial pressure of O<sub>2</sub> for each temperature studied is in agreement with the observations from the studies at room temperature of Wallington et al.<sup>12</sup> and Barnes et al.,<sup>14</sup> and from the studies of Hynes et al.<sup>11</sup> and Williams et al.<sup>20</sup> made at different temperatures. In the work of Wallington et al.,<sup>12</sup> the experiments were carried out at 296 K and 740 Torr total pressure at different O<sub>2</sub> partial pressures between 0 and 740 Torr; the rate coefficient of  $5.3 \times 10^{-12} \text{ cm}^3$ molecule<sup>-1</sup> s<sup>-1</sup> measured with 0 Torr O<sub>2</sub> was found to increase by factors of 1.3, 1.6, and  $\sim 2.0$  in the presence of 50, 160, and 740 Torr O<sub>2</sub>, respectively. In the work of Barnes et al.<sup>14</sup> carried out at a total pressure of 760 Torr at 298 K, the rate coefficient was observed to increase from  $4.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in the absence of  $O_2$  by factors of 1.2, 1.5, 1.8, and 2.6 with 50, 100, 155 and 760 Torr partial pressures of O<sub>2</sub>. In this work at 299 K, the rate coefficient increases from 5.0  $\times$   $10^{-12}~{\rm cm}^3$ molecule<sup>-1</sup> s<sup>-1</sup> with ~0 Torr O<sub>2</sub> by factors of approximately 1.6 and 2.0 with 155 and 380 Torr of O<sub>2</sub>. In the work of Hynes et al.,11 at 298 K the measured rate coefficient was found to increase from  $4.8 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> in 40 Torr N<sub>2</sub> by a factor of 1.3 when using 750 Torr air, and at 261 K from  $4.29 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  in 700 Torr N<sub>2</sub> by a factor of approximately 3.0 when measured in 700 Torr air. In the work of Williams et al.<sup>20</sup> at a temperature of 240 K and a total pressure of 600 Torr, the rate coefficient was found to increase from  $5.4 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> with 5 Torr O<sub>2</sub> by factors of approximately 2.9, 3.9, and 5.2 when using 15, 30, and 120 Torr partial pressures of O<sub>2</sub>, respectively. In this work at 260 K, the rate coefficient increases from  $6.4 \times 10^{-12} \text{ cm}^3$ molecule<sup>-1</sup> s<sup>-1</sup> with ~0 Torr O<sub>2</sub> by factors of approximately 3.1 and 3.7 with 155 and 380 Torr of O<sub>2</sub>.

Table 6 shows a comparison between the overall rate coefficient obtained in this work for DMS + OH in 1 atm of synthetic air ( $p_{O_2} = 155$  Torr) at 299 K and those reported in other studies under similar conditions which are considered free of potential artifacts.

The value obtained in this work for atmospheric conditions is in reasonable agreement with the other values determined using relative kinetic techniques<sup>12,14</sup> but is approximately 20% higher than that determined using an absolute technique.<sup>11</sup>

Fig. 3 shows plots of the overall rate coefficients  $k_{\text{DMS}}$  (abstraction + addition channels) for DMS + OH as a function of temperature for:

(i) values calculated from the fit expression of Hynes *et al.*<sup>11</sup> for 760 Torr total pressure and  $p_{O_2} = 155$  Torr;

(ii) values measured in this work at 760 Torr and  $p_{O_2} = 155$  Torr;

 Table 6
 Rate coefficients for DMS + OH reaction at room temperature in air

$k_{\text{DMS}} \times 10^{12} / \text{cm}^3$ molecule <sup>-1</sup> s <sup>-1</sup>	$T/\mathrm{K}$	Pressure/Torr	Technique	Ref.
$\begin{array}{l} 6.28 \pm 0.10 \\ 8.50 \pm 0.20 \\ 8.00 \pm 0.50 \\ 7.80 \pm 1.80 \end{array}$	298 296 298 299	750 740 760 760	PLP-PLIF <sup>a</sup> DS-FTIR <sup>b</sup> CP-GC <sup>b</sup> CP-FTIR <sup>b</sup>	11 12 14 tw
<sup>a</sup> Absolute techniqu	ie: PLP =	= pulsed laser phot	tolysis, PLIF =	pulsed

laser induced fluorescence. <sup>b</sup> Relative technique: DS = dark source of OH (O<sub>3</sub> + N<sub>2</sub>H<sub>4</sub>), FTIR = Fourier transform infrared spectroscopy, CP = continuous photolysis, GC = gas chromatography; tw = this work.

(iii) values calculated from the new recommended fit expression of Atkinson *et al.*<sup>21</sup> for 760 Torr and  $p_{O_2} = 155$  Torr;

(iv) the values measured in this work at 760 Torr and  $p_{\rm O_2} = 380$  Torr; and

(v) values calculated from the new recommended fit expression of Atkinson *et al.*<sup>21</sup> for 760 Torr and  $p_{O_2} = 380$  Torr.

Unfortunately, the rate coefficient data in the paper of Williams *et al.*<sup>20</sup> was not given in a tabulated form and thus could not be plotted in Fig. 3. It is, however, incorporated into the fit expression given by Atkinson *et al.*<sup>21</sup> which is plotted in Fig. 3.

An inspection of Fig. 3 shows that for 760 Torr of air and in the temperature range 270 to 299 K, the values determined in this work are somewhat higher but are generally in fair agreement with those calculated from the old fit of Hynes *et al.*<sup>11</sup> and the new recommended fit given in Atkinson *et al.*<sup>21</sup> which incorporates the new Williams *et al.*<sup>20</sup> data. Also shown in Fig. 3, just for comparison purposes, is a plot of the rate coefficients measured in this study for  $p_{0_2} = 380$  Torr and the



**Fig. 3** Variation in the overall rate coefficient  $k_{\text{DMS}}$  for DMS + OH as a function of temperature as estimated or measured (see text for details).





Fig. 4 Temperature dependence of the branching ratio between the addition and abstraction channels for DMS + OH as estimated or measured (see text for details).

corresponding values calculated with the Atkinson *et al.* expression. The agreement here is also reasonably good.

At temperatures below 270 K our rate coefficient values show a strong increase compared to the values predicted by the empirical fit expression of Hynes *et al.*<sup>11</sup>. The values are, however, in good agreement with the new preferred values calculated from the recommended expression of Atkinson *et al.*<sup>21</sup> which took into account the data of Williams *et al.*<sup>20</sup> This work thus confirms the measurements reported by Williams *et al.*<sup>20</sup>

Fig. 4 compares the temperature dependence of the branching ratio between the addition and abstraction channel for DMS + OH obtained from:

(i) the empirical expression given in Hynes et al.;<sup>11</sup>

(ii) the values given in Williams et al.;<sup>20</sup>

(iii) the values measured in this study for the overall reaction at  $p_{O_2} = 155$  Torr and the value for the abstraction channel taken from Atkinson *et al.*<sup>21</sup>

The branching ratio is defined as  $(k_{obs} - k_{1a})/k_{1a}$ . As is to be expected from the kinetic data, above 270 K there is good agreement between the branching ratios calculated from the different data sets, while below 270 K there is a sharp increase in the branching ratio calculated using the data from this work which matches very well that obtained in the study of Williams *et al.*,<sup>20</sup> but deviates strongly from the values obtained from an extrapolation of the empirical expression of Hynes *et al.*<sup>11</sup>

#### Atmospheric implication

The results reported in this work have confirmed the sharp increase in the rate coefficient for OH with DMS at temperatures below 260 K observed by Williams *et al.*<sup>20</sup>

Although these results are of interest from a mechanistic viewpoint they will have no impact on DMS chemistry in the lower troposphere since at temperatures below  $\sim 273$  K emissions of DMS from the oceans will be extremely low. The

results will only be of atmospheric significance if DMS can reach the upper troposphere/lower stratosphere (UT/LS) where such low temperatures prevail. Updrafts in deep convective clouds can raise the boundary layer air into the upper troposphere within a matter of minutes. It has been suggested from observations of near-zero ozone concentrations over the convective Pacific that rapid convective transport of marine gaseous emissions such as DMS between the marine boundary layer and the uppermost troposphere could occur, which can lead to sulfate particle formation.<sup>25</sup>

The distribution of the products from the reaction of OH with DMS is dependent on the ratio of the two reaction channels, addition and subtraction, which is controlled by temperature and the oxygen partial pressure. The results of this study and that of Williams et al.<sup>20</sup> have shown that for 1 atm of air and at temperatures below  $\sim 260$  K the contribution of the addition pathway is considerably more than was predicted by extrapolation of the expression of Hynes *et al.*<sup>11</sup> Product studies on the OH initiated oxidation of DMS as a function of temperature and oxygen partial pressure<sup>26</sup> have shown that dimethyl sulfoxide (CH<sub>3</sub>SOCH<sub>3</sub>; DMSO) is the major product from the addition channel with molar yields of around 75% at 260 K in the presence of low levels of NO<sub>x</sub>. Only very low yields of SO<sub>2</sub> and DMSO<sub>2</sub> are observed. The products from the oxidation of DMSO at low temperature are not currently known. At room temperature it has been shown that the major product from the OH initiated oxidation of DMSO is methanesulfinic acid (MSIA; CH<sub>3</sub>S(O)OH).<sup>27-29</sup> The  $SO_2$  formed will be converted to  $H_2SO_4$  and eventually through gas-to-particle conversion to sulfate aerosol.

The above discussion has been for conditions of 1 atm of air, however, in the UT/LS where temperatures between 210 and 260 K can prevail, the increase in the rate coefficient caused by the decrease in temperature will be compensated, at least in part, by the decrease in the O<sub>2</sub> partial pressure which will fall, for example, from approximately 110 Torr at 3 km altitude to approximately 40 Torr around 10 km. In regions of the troposphere with an  $O_2$  partial pressure of ~100 Torr where temperatures of approximately 250 K prevail, the present results show that the addition channel will account for  $\sim 70\%$  of the overall reaction of OH with DMS. Temperatures of 210 K prevail at 10 km altitude where the partial pressure of O<sub>2</sub> is approximately 40 Torr. We do not have kinetic data for these conditions but an extrapolation of the available data set suggests that under these conditions the addition channel could account for  $\sim 80\%$  of the overall reaction. Thus, it would appear that under the conditions prevailing in the UT/LS the contribution of the addition channel to the reaction of OH with DMS will vary within a relatively narrow range, i.e. approximately 70-80%, since the increase in rate with decrease in temperature is being more or less compensated by the decrease in the  $O_2$  partial pressure.

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## References

- H. Berresheim, P. H. Wine and D. D. Davis, in *Sulfur in the atmosphere, Composition, Chemistry, and Climate of the Atmosphere*, ed. H. B. Singh, Van Nostrand Reinhold, New York, 1995, pp. 251–307.
- 2 S. P. Urbanski and P. H. Wine, in *Chemistry of gas phase organic sulfur-centred radicals, S-Centred Radicals*, ed. Z. B. Alfassi, John Wiley and Sons, 1999, pp. 97–140.
- 3 R. J. Charlson, J. E. Lovelock, M. O. Andreae and S. G. Warren, *Nature*, 1987, **326**, 655.
- 4 R. Atkinson, R. A. Perry and J. N. Pitts Jr., Chem. Phys. Lett., 1978, 54, 14.
- 5 M. J. Kurylo, Chem. Phys. Lett., 1978, 58, 233.
- 6 R. A. Cox and D. Sheppard, *Nature*, 1980, **284**, 330.
- 7 P. H. Wine, N. M. Kreutter, C. A. Gump and A. R. Ravishankara, *J. Phys. Chem.*, 1981, **85**, 2660.
- 8 H. MacLeod, J. L. Jourdain, G. Poulet and G. Le Bras, *Atmos. Environ.*, 1984, **18**, 2621.
- 9 R. Atkinson, J. N. Pitts Jr. and S. M. Aschmann, J. Phys. Chem., 1984, 88, 1584.
- 10 D. Martin, J. L. Jourdain and G. LeBras, Int. J. Chem. Kinet., 1985, 17, 1247.
- 11 A. J. Hynes, P. H. Wine and D. H. Semmes, J. Phys. Chem., 1986, 90, 4148.
- 12 T. J. Wallington, R. Atkinson, E. C. Tuazon and S. M. Aschmann, Int. J. Chem. Kinet., 1986, 18, 837.
- 13 Y.-C. Hsu, D.-S. Chen and Y.-P. Lee, Int. J. Chem. Kinet., 1987, 19, 1073.
- 14 I. Barnes, V. Bastian and K. H. Becker, Int. J. Chem. Kinet., 1988, 20, 415.
- 15 O. J. Nielsen, H. W. Sidebottom, L. Nelson, J. J. Treacy and D. J. O'Farrell, Int. J. Chem. Kinet., 1989, 21, 1101.
- 16 J. P. D. Abbatt, F. F. Fenter and J. G. Anderson, J. Phys. Chem., 1992, 96, 1780.

- 17 A. J. Hynes, R. B. Stoker, A. J. Pounds, T. McKay, J. D. Bradshaw, J. M. Nicovich and P. H. Wine, *J. Phys. Chem.*, 1995, 99, 16967.
- 18 S. B. Barone, A. A. Turnipseed and A. R. Ravishankara, J. Phys. Chem., 1996, 100, 14694.
- 19 R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson Jr., J. A. Kerr, M. J. Rossi and J. Troe, *J. Phys. Chem. Ref. Data*, 1997, 26, 1329.
- 20 M. B. Williams, P. Campuzano-Jost, D. Bauer and A. J. Hynes, *Chem. Phys. Lett.*, 2001, 344, 61.
- 21 R. Atkinson, D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi and J. Troe, *Atmos. Chem. Phys.*, 2004, 4, 1461.
- 22 M. Albu, I. Barnes and R. Mocanu, in *Proceedings of the NATO ARW "Environmental Simulation Chambers-Application to Atmospheric Chemical Processes"*, ed. K. J. Rudzinski and I. Barnes, NATO Science Series, IV. Earth and Environmental Sciences, Kluwer Academic Publishers, Dordrecht, 2006, vol. 62, pp. 223–230.
- 23 R. Atkinson, J. Phys. Chem. Ref. Data, 1997, 26, 215.
- 24 R. G. Prinn, R. F. Weiss, B. R. Miller, J. Huang, F. N. Alyea, D. M. Cunnold, P. J. Fraser, D. E. Hartley and P. G. Simmonds, *Science*, 1995, **269**, 187.
- 25 D. Kley, P. J. Crutzen, H. G. J. Smit, H. Vömel, S. J. Oltmans, H. Grassl and V. Ramanathan, *Science*, 1996, 274, 230.
- 26 M. Albu, PhD thesis, Bergische University Wuppertal, Germany, 2005.
- 27 S. P. Urbanski, R. E. Stickel and P. H. Wine, J. Phys. Chem. A, 1998, 102, 10522.
- 28 C. Arsene, I. Barnes, K. H. Becker, W. F. Schneider, T. J. Wallington, N. Mihalopoulos and I. V. Patroescu-Klotz, *Environ. Sci. Technol.*, 2002, 36, 5155.
- 29 A. Kukui, D. Borissenko, G. Laverdet and G. Le Bras, J. Phys. Chem. A, 2003, 107, 5732.