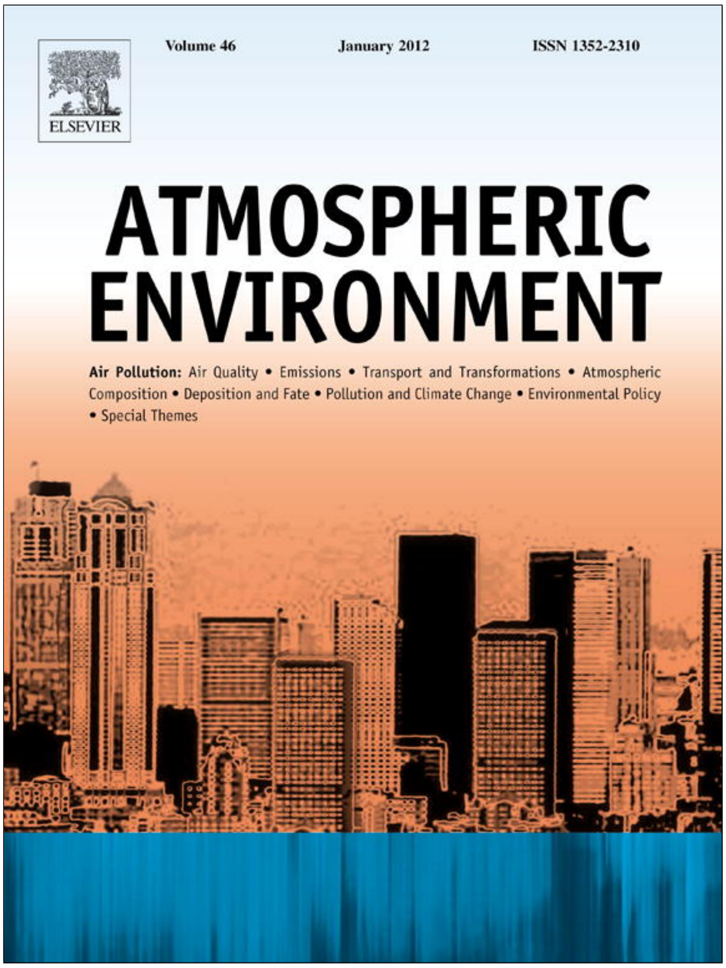

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Photodegradation of $(CH_3CH_2)_2S$ and $CH_3CH_2SCH_3$ initiated by OH radicals at atmospheric pressure. Product yields and mechanism in NOx free air

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ABSTRACT

The product distribution of the gas-phase reactions of OH radicals with diethyl sulfide $(CH_3CH_2)_2S$ and ethyl methyl sulfide, $CH_3CH_2SCH_3$, determined in the absence of NOx, is presented. The experiments were performed in a 1080 L quartz-glass photoreactor and a 405 L borosilicate glass photoreactor in synthetic air at (298 ± 2) K using long path "in situ" FTIR spectroscopy for the analysis of the reactants and products. SO_2 and CH_3CHO were identified as major primary products for both title reactions together with HCHO as a co-product in the photodegradation of $CH_3CH_2SCH_3$.

Formation of CO and HCOOH was observed, however, the concentration–time behavior of these products show that they are secondary in origin and are produced from the further oxidation of major primary products. Traces of OCS were observed; its concentration–time behavior suggests that it is a minor primary product. The yields of the products obtained for the reaction of OH radicals with $(CH_3CH_2)_2S$ were the following: $(50 \pm 3)\%$ and $(91 \pm 3)\%$ for SO_2 and CH_3CHO, respectively. While, for the reaction of OH radicals with $CH_3CH_2SCH_3$ yields of $(51 \pm 2)\%$, $(57 \pm 3)\%$ and $(46 \pm 4)\%$ were obtained for SO_2, CH_3CHO and HCHO, respectively.

The present results are compared with previous results for the well studied reaction of dimethyl sulfide, CH_3SCH_3, with OH radicals and simple atmospheric degradation mechanisms are postulated to explain the formation of the observed products.

1. Introduction

Sulfur is present in the Earth's crust at a mixing ratio of less than 500 parts per million by mass and in the Earth's atmosphere at a total volume mixing ratio of less than 1 ppm. Yet, sulfur-containing compounds exert a profound influence on the chemistry of the atmosphere and on climate (Seinfeld and Pandis, 2006). Natural emissions of sulfur compounds to the atmosphere occur from a variety of sources, including volcanic eruptions, sea spray, and a host of biogenic processes. It is well established that sulfur-containing organic compounds play an important role in atmospheric chemistry (Finlayson-Pitts and Pitts, 2000). By far, the largest natural source comes from the world's oceans in the form of dimethyl sulfide (CH_3SCH_3, DMS), which is generated by the biological activity of phytoplankton and volatilized to the atmosphere. The atmospheric fate of reduced sulfur compounds is determined mainly by chemical transformation, whereby reaction with OH radicals during the day, NO_3 radicals at night and Cl atoms and BrO radicals in the marine boundary layer (MBL) can play a role. Extensive work on the chemistry of DMS has shown that its main atmospheric loss pathway is OH radical initiated photooxidation, leading to the production of sulfur dioxide (SO_2) and minor amounts of methane sulfonic acid (CH_3SO_3H, MSA), dimethyl sulfoxide ($(CH_3)_2SO$, DMSO), and dimethyl sulfone ($(CH_3)_2SO_2$, $DMSO_2$) (Andreae and Crutzen, 1997). Sulfur dioxide reacts under tropospheric conditions with OH radicals and is converted rapidly to sulfuric acid. These processes lead to the formation of sulfur-containing species, which can promote the formation of aerosol, having a direct impact on the earth-atmospheric radiation budget by reflecting solar radiation. Additionally, atmospheric sulfate aerosols may participate in cloud condensation processes by serving as cloud condensation nuclei (CCN). Both aerosols and clouds formed from CCN can affect the heat balance of the atmosphere and possibly influence climate (Charlson et al., 1987).

Oxidation of DMS is a complex process, however, it is now well established that the reaction of OH radicals with DMS proceeds through two channels: H-atom abstraction by OH from a methyl group and OH-radical addition to the S atom (Eqs. (1) and (2)). The

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relative importance of the addition *versus* abstraction channels is temperature dependent (Hynes et al., 1986). Attack of OH radicals at the CH_3 group produces water and the methylthiomethyl radical (CH_3SCH_2), while addition to the sulfur atom produces the dimethylhydroxysulphuranyl radical ($(CH_3)_2S{-}OH$), an adduct which can either dissociate back to reactants or react further to form products (Eqs. (-2) and (3)). Hence, the effective rate of the OH initiated oxidation and the branching ratio between the addition and abstraction channels depends on both temperature and the O_2 partial pressure.

The reactions involved are the following:

$$OH + CH_3SCH_3 \rightarrow CH_3SCH_2 + H_2O \text{ (abstraction pathway)} \tag{1}$$

$$OH + CH_3SCH_3 \rightarrow (CH_3)_2SOH \text{ (addition pathway)} \tag{2}$$

$$(CH_3)_2SOH \rightarrow OH + CH_3SCH_3 \tag{-2}$$

$$(CH_3)_2SOH + O_2 \rightarrow \text{products} \tag{3}$$

The further oxidation of the CH_3SCH_2 radical formed in the abstraction channel in the presence of NO_x produces the methylthyil radical (CH_3S) and formaldehyde (H_2CO) (Eqs. (4)–(6)) (Barnes et al., 2006).

$$CH_3SCH_2 + O_2 + M \rightarrow CH_3SCH_2OO + M \tag{4}$$

$$CH_3SCH_2OO + NO \rightarrow CH_3SCH_2O + NO_2 \tag{5}$$

$$CH_3SCH_2O \rightarrow CH_3S + CH_2O \tag{6}$$

In the marine boundary layer, where NO_x levels are relatively low, CH_3SCH_2OO radicals react with other peroxy radicals RO_2, where R is a H atom or organic entity, to form mainly CH_3SCH_2O radicals together with oxygen and RO radicals (Orlando et al., 2003). The main fate of the CH_3SCH_2O radical is decomposition to form CH_3S radicals and HCHO. Based on end product analyses in smog chambers, it has been postulated that the CH_3S radical is a key intermediate in the oxidation of reduced organic sulfur compounds in the atmosphere. The reactions of the CH_3 Sradical are important in the transformation of DMS to SO_2, MSA and H_2SO_4 (Yin et al., 1990a,b).

On the other hand, the $(CH_3)_2S{-}OH$ adduct produced in the addition channel, reacts with O_2 to form mainly other products. This reaction has been postulated to yield DMSO as the main product. The secondary products observed by further oxidation of DMSO include $DMSO_2$, SO_2, methanesulfinic acid (MSIA, $CH_3S(O)OH$) and MSA (Barnes et al., 1996; Sørensen et al., 1996; Arsene et al., 2001). The OH-addition pathway and the H-abstraction pathway leads partially to the same products, however, the H-abstraction channel is likely to be more efficient in producing new particles than the OH-addition pathway. This is due to the higher gas-phase H_2SO_4 production from the H-abstraction channel and the expected high losses (from heterogenic processes) of the products formed by the OH-addition pathway (DMSO, $DMSO_2$ and MSIA) before they can be oxidized further to SO_2 and then to H_2SO_4 (Sørensen et al., 1996).

One of the primary uncertainties in the oxidation of DMS is the yield of various final products under atmospheric conditions. The reaction of OH with DMS has been studied by Yin et al. (1990a) in the presence and absence of NO_x in air at 310 K. These authors found SO_2 yields ranging from 62 to 71% and yields of CH_3SO_3H and H_2SO_4 from 1 to 7% and 1 to 5%, respectively. Barnes et al. (1996) have measured the yield of the products from this reaction at 296 K in NOx-free air and found SO_2 and HCHO as major oxidation products with yields of $80 \pm 10\%$ and $90 \pm 6\%$, respectively. Additionally, they also observed formation of DMSO under the same conditions (Barnes et al., 1996). More recently, the products of the OH radical-initiated oxidation of DMS have been investigated as a function of temperature (284, 295, and 306 K) and different initial NOx concentrations (Arsene et al., 2001). Distinct trends in the yields of the various products have been observed as a function of temperature and initial NOx conditions. The major sulfur-containing products measured were SO_2 and DMSO whose yields were anti-correlated with temperature in line with current mechanistic understanding, *i.e.* the SO_2 yield decreased with decreasing temperature while that of DMSO increased due to the increasing importance of the addition pathway. Hence, the identity and yield of the final products in the reaction of OH with DMS depend on the oxidation steps of several intermediates for which a multitude of different possible reaction pathways exist and whose importance can vary with the prevailing atmospheric conditions (Arsene et al., 2001). This is also expected to be the case for other dialkyl sulfides.

Large amounts of other volatile sulfur compounds are emitted into the atmosphere by natural and anthropogenic activities. Thioethers are widely used in various industries, for example, aryl, alkenyl and alkyl thioethers are important synthetic reagents and intermediates in organic synthesis. They have been employed in the synthesis of novel biologically active compounds (Robins and Wnuk, 1993), polymer materials (Masumura et al., 2001) and used as extracting reagents (Elmroth et al., 1992). Because of the frequent unpleasant smells associated with them, even at very low levels, thioethers are mixed into Liquefied Petroleum Gas and fuel cells as leakage sensor odorants (Imamura et al., 2005). Alkyl thioethers, which can be found in garlic, are synthesized and used as forage additives. These uses may result in their potential release into the atmosphere. Alkyl thiols, dialkyl sulfides and polysulfides are present in animals, animal manure, kerogens and are associated with sewage treatment plants and the wood-pulping industry (Visscher and Taylor, 1993). Consequently, it is therefore not unreasonable to expect that some of the more volatile alkyl sulfides will be released to the atmosphere. Alkyl sulfides like diethyl sulfide ($CH_3CH_2SCH_2CH_3$, DES) and ethyl methyl sulfide ($CH_3CH_2SCH_3$, EMS) have both natural and industrial sources and have been detected over seaweeds fields (Martin et al., 1985), and in soil atmospheres (Banwart and Bremner, 1974).

While there have been several kinetic studies of the reactions of OH radicals with DES and EMS (Martin et al., 1985; Nielsen et al., 1990; Kinnison et al., 1996; Williams et al., 2007; Oksdath-Mansilla et al., 2009, 2010), there is no product data available from which degradation mechanisms for these dialkyl sulfides can be elucidated. The pulsed laser photolysis – pulsed laser induced fluorescence study of Williams et al. (2007) has shown that the OH rate coefficients for both reactions show a O_2 partial pressure dependence. Their experimental observations are consistent with the OH initiated oxidation for both compounds proceeding via a two channel oxidation mechanism involving abstraction and addition pathways analogous to the mechanism outlined above for the OH initiated oxidation of DMS.

In this work we report the product distribution observed from the OH-radical initiated oxidation of two alkyl sulfides, DES and EMS, performed at room temperature and atmospheric pressure in NOx-free air:

$$OH + (CH_3CH_2)_2S \rightarrow \text{products} \tag{7}$$

$$OH + CH_3CH_2SCH_3 \rightarrow \text{products} \tag{8}$$

The aim of the work is the construction of atmospherically relevant chemical oxidation mechanisms, from the acquired product information, for the OH initiated photo-oxidation of the alkyl sulfides DES and EMS. To our knowledge no other product studies on the sulfides investigated in this work have been reported previously in the literature. Hence, this work is the first systematic product study of the title reactions.

2. Experimental

All the experiments were performed in a 1080 L quartz-glass chamber and a 405 L borosilicate glass chamber at (298 ± 2) K and a total pressure of 760 ± 10 Torr of synthetic air. A detailed description of the reactors can be found elsewhere (Barnes et al., 1994a; Bierbach, 1994), and only a brief description is given here. A pumping system consisting of a turbo-molecular pump backed by a double stage rotary fore pump was used to evacuate the reactors to 10^{-3} Torr. Three magnetically coupled Teflon mixing fans are mounted inside the chamber to ensure homogeneous mixing of the reactants. The photolysis system consists of 18 (405 L reactor) or 32 (1080 L reactor) superactinic fluorescent lamps (Philips TL05 40W: 320–480 nm, $\lambda_{max} = 360$ nm) and 3 or 32 low-pressure mercury vapour lamps (Philips TUV 40W; $\lambda_{max} = 254$ nm), which are spaced evenly around the reaction vessel. The lamps are wired in parallel and can be switched individually, which allows a variation of the light intensity, and thus also the photolysis frequency/radical production rate, within the chamber. Each chamber is equipped with a White type multiple-reflection mirror system for sensitive "in situ" long path absorption monitoring of reactants and products in the IR spectral range 4000–700 cm^{-1}. The White systems were operated at 32 and 82 traverses, giving a total optical path length of 50.4 m or 484.7 m in the 405 L and 1080 L environmental chambers, respectively. The IR spectra were recorded with a spectral resolution of 1 cm^{-1} using a Nicolet Nexus FT-IR spectrometer equipped with a liquid nitrogen cooled mercury-cadmium-telluride detector.

Hydroxyl radicals were generated by the photolysis of H_2O_2 with the mercury lamps:

$$H_2O_2 + h\nu \rightarrow 2OH \tag{9}$$

where possible, quantification of reactants and products was performed by comparison with calibrated reference spectra contained in the IR spectral database at the University of Wuppertal.

The initial concentrations used in the experiments for the alkyl sulfides in ppmV (1 ppmV $= 2.46 \times 10^{13}$ molecule cm^{-3} at 298 K and 760 Torr total pressure) were: 26.8 for diethyl sulfide and 45.9 for ethyl methyl sulfide. The concentration of hydrogen peroxide was typically around 11 ppmV.

The reactants and products were monitored at the following infrared absorption frequencies (in cm^{-1}): diethyl sulfide at 1260 and 1461; ethyl methyl sulfide at 1270 and 1446; hydrogen peroxide at 1266; carbon monoxide at 2169; carbonyl sulfide at 2054; sulfur dioxide at 1368; acetaldehyde at 1761; formic acid at 1776 and 1105; formaldehyde at 2766.

3. Materials

The chemicals used in the experiments had the following purities as given by the manufacturer and were used as supplied: synthetic air (Messer Griesheim, 99.995%) with a N_2:O_2 ratio of 20.5:79.5%, diethyl sulfide (Aldrich, 98.0%), ethyl methyl sulfide (Aldrich, 96%) and hydrogen peroxide (Peroxi Chemie 85.5%).

4. Results and discussion

To investigate the products of the OH-radical initiated oxidation of the alkyl sulfides, initial mixtures of H_2O_2/sulfide/air were irradiated for periods of 40–60 min for DES and 20–30 min for EMS, during the course of which infrared spectra were recorded with the FTIR spectrometer. Typically 64 interferograms were co-added per spectrum over a period of approximately 1 min and generally 15–20 such spectra were collected per experiment.

4.1. Diethyl sulfide oxidation (DES)

Fig. 1 shows typical product spectra recorded in the OH-radical initiated oxidation of DES. Trace (A) shows an IR spectrum of a mixture of DES and H_2O_2 in air acquired before irradiation and trace (B) shows a spectrum obtained after UV irradiation where residual absorptions due to DES and H_2O_2 have been subtracted. Traces (C) and (D) show reference spectra of SO_2 and acetaldehyde (CH_3CHO), respectively. It can be seen from a comparison of traces (C) and (D) with trace (B) that SO_2 and CH_3CHO are main products of the reaction of OH with DES. In the region 2000 to 2300 cm^{-1} absorptions unique to CO and carbonyl sulfide (OCS) were observed. As the reaction progressed formation of formaldehyde (HCHO) and formic acid (HCOOH) was also observed. The concentration–time behaviors of CO, OCS, HCHO and HCOOH show that they are being formed in secondary reactions.

After subtraction of the spectral features attributable to SO_2, CH_3CHO, HCHO and HCOOH from the spectrum in trace (B) the residual spectrum shown in Fig. 1, trace (E), was obtained in which weak broad absorptions centered at 1033, 1090, 1107, 1125, 1150, 1247, 1292, 1780, 2690, 2952, 2990, 3018 cm^{-1} are visible. It is difficult to attribute the absorptions in the spectrum to any of the other potential products which might be formed such as diethyl sulfoxide ($(CH_3CH_2)_2SO$, DESO), diethyl sulfone ($(C_2H_5)_2SO_2$, $DESO_2$), diethyl peroxide ($C_2H_5OOC_2H_5$, DEP), ethyl sulfinic acid ($C_2H_5S(O)OH$) and ethyl sulfonic acid ($C_2H_5SO_2OH$) since in addition to the bands being weak and diffuse gas phase IR spectra for these compounds are not available.

By analogy to the reaction of OH with DMS (Barnes et al., 1996) it is expected that, under the present experimental conditions, diethyl sulfoxide ($(CH_3CH_2)_2SO$, DESO) formed from reaction of an OH-DES adduct with O_2 will be an important product, and any of the weak absorptions in the vicinity of 1100 cm^{-1} could be due to

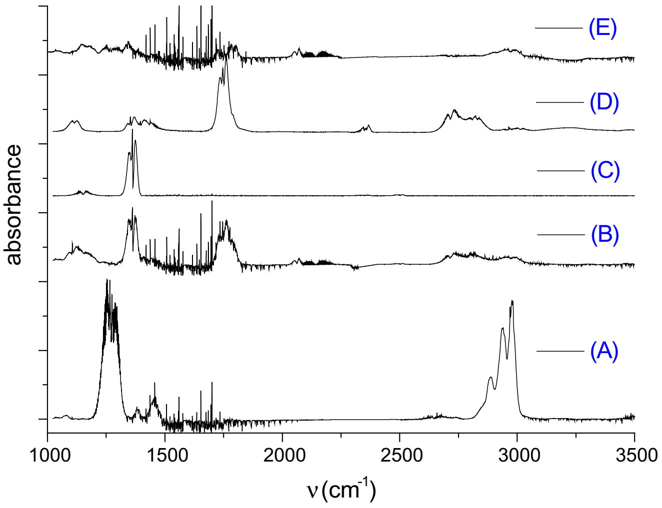

Fig. 1. Trace A shows the infrared spectrum of a $CH_3CH_2SCH_2CH_3$/H_2O_2/air reaction mixture before irradiation and B shows the IR spectrum after irradiation and subtraction of absorptions from residual $CH_3CH_2SCH_2CH_3$ and H_2O_2. Trace C shows a reference spectrum of SO_2, trace D a reference spectrum of CH_3CHO and E the residual product spectrum obtained after subtraction of features due to SO_2 and CH_3CHO from the spectrum in trace B.

DESO. However, the absence of any strong $S{=}O$ stretching absorption is consistent with fast removal of DESO by OH radicals as it was observed for the reaction of OH with DMSO ($k_{OH+DMS} \approx 1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (Barnes et al., 1989; Hynes et al., 1992; Urbanski et al., 1998).

Concentration–time profiles of DES and the identified products SO_2 and CH_3CHO are shown in Fig. 2. The concentration–time contours support the view that SO_2 and CH_3CHO are both primary products. Plots of the concentrations of sulfur dioxide and acetaldehyde as a function of the amount of diethyl sulfide consumed are linear as exemplified in Fig. 3. Both SO_2 and CH_3CHO, however, will be subject to oxidation by the OH radicals produced in the system and their concentrations need to be corrected for this loss. Using 298 K rate coefficients of $k(OH + SO_2) = 1.6 \times 10^{-12}$ (Sander et al., 2011) and $k(OH + CH_3CHO) = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006) the concentrations of SO_2 and CH_3CHO have been corrected for secondary consumption with OH radicals using the mathematical procedure described by Tuazón et al. (1986) and also by Arsene et al. (1999). Plots of the corrected SO_2 and CH_3CHO concentrations as a function of reacted DES, from a minimum of 3 experiments for this reaction, gave averaged molar formation yields of (50 ± 3)% and (91 ± 3)% for SO_2 and CH_3CHO, respectively (Table 1). The errors quoted are a combination of the 2σ statistical errors from the regression analysis together with the errors from the spectral subtraction procedure. The correction for secondary consumption of SO_2 with OH was negligible while for CH_3CHO the correction added ~5% to the yield. The oxidation of CH_3CHO is responsible for the formation of the HCHO which is observed in the system. The further oxidation of HCHO with OH will produce the levels of CO observed, however, as will be discussed in the section on the oxidation of EMS it is thought that the main loss process for HCHO is reaction with HO_2 and that this reaction is responsible for the formation of HCOOH which is observed.

Formation of OCS has been observed in the photooxidation of DMS (Barnes et al., 1996, 1994b), DMDS (Barnes et al., 1994a) and methyl thioformate (CH_3SCHO, MTF) (Patroescu et al., 1996) in NOx-free air with molar yields a little under 1%. The source of the OCS is not entirely clear but is thought to possibly come from the further oxidation of methyl thioformaldehyde (H_2CS) which can be produced in the oxidation system via the reaction of O_2 with CH_3S radicals. In the present study formation of OCS is also observed from the OH + DES reaction, however, the yield calculated at the end of the experiments is only ~0.14%, *i.e.* nearly an order of magnitude lower than that observed in the DMS, DMDS and MTF oxidation systems. The potential source of OCS from the reaction of OH with DES could be production and further oxidation of ethanethial ($CH_3C(S)H$) formed in the reaction of O_2 with CH_3CH_2S radicals.

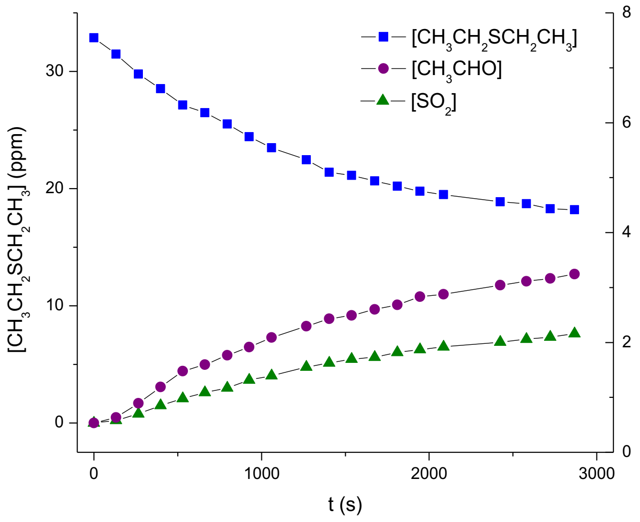

Fig. 2. Concentration–time profiles for reaction of OH radicals with DES and the formation of products acetaldehyde and SO_2.

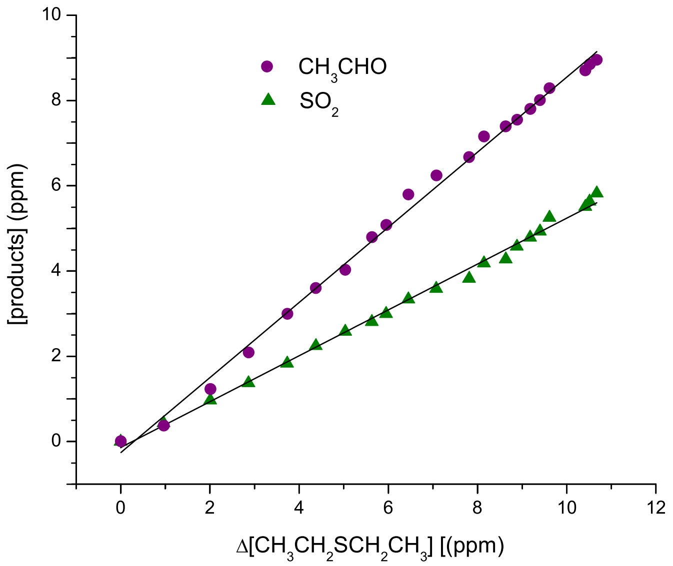

Fig. 3. Plot of the product concentrations of CH_3CHO and SO_2 as a function of reacted DES for the reaction of DES with OH radicals.

4.2. Ethyl methyl sulfide oxidation (EMS)

Fig. 4, trace A, shows an IR spectrum of a mixture of EMS and H_2O_2 in air acquired before irradiation and trace B shows a spectrum after irradiation and subtraction of residual absorptions due to EMS. Traces C, D, E and F in Fig. 4 show reference spectra of SO_2, CH_3CHO, HCHO, and HCOOH, respectively, which have all been positively identified as products in the photo-oxidation of EMS with OH radicals. Trace G in Fig. 4 shows the residual product spectrum obtained after subtraction of features attributable to SO_2, CH_3CHO, HCHO and HCOOH from trace B. In the residual spectrum weak unidentified bands centered at 789, 884, 1033, 1107, 1247,

Table 1
Oxidation products from the OH oxidation of DES, EMS and DMS (for comparative purposes) and their formation yields in one atmosphere of NOx-free air at room temperature.

Sulfide	Products	Yields (%)	Ref
$CH_3CH_2SCH_2CH_3$	SO_2	50 ± 3	This work
	CH_3CHO	91 ± 3	
	OCS[a]	~0.14	
$CH_3SCH_2CH_3$	SO_2	51 ± 2	This work
	HCHO	46 ± 4	
	CH_3CHO	57 ± 3	
	OCS[a]	~0.07	
CH_3SCH_3	SO_2	80 ± 10	Barnes et al., 1996
	HCHO	90 ± 6	
	OCS[a]	0.7 ± 0.2	
	SO_2	95 ± 4	Arsene et al., 1999

[a] The exact pathway for formation of OCS is not well established; the quoted yields are based on the consumption of the alkyl sulfide. The errors in the yields correspond to two standard deviations combined with estimated uncertainties in the spectral subtraction process.

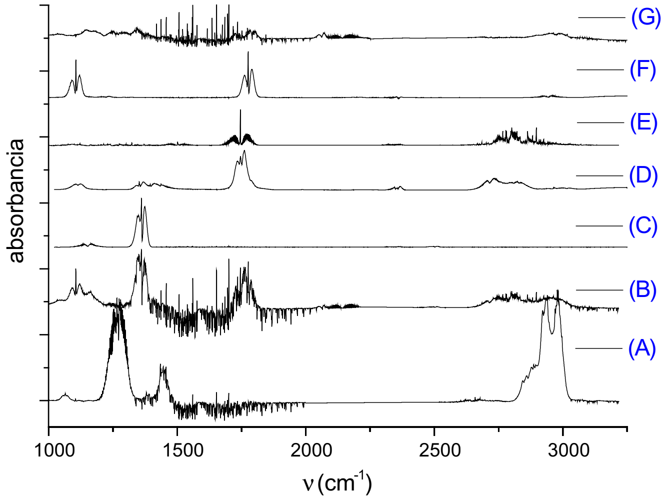

Fig. 4. Trace A shows the infrared spectrum of an $CH_3CH_2SCH_3/H_2O_2$/air reaction mixture before irradiation and B shows the IR spectrum after irradiation and subtraction of residual absorptions due to $CH_3CH_2SCH_3$ and H_2O_2. Trace C shows a reference spectrum of SO_2, trace D shows a reference spectrum of CH_3CHO, trace E shows a reference spectrum of HCHO, trace F shows a reference spectrum of HCOOH and G shows the residual product spectrum obtained after subtraction of features due to SO_2, CH_3CHO, HCHO and HCOOH from the spectrum in trace B.

1292, 2690, 2841, 2823, 2967, 2990, 3018 cm^{-1} are visible. CO and OCS could be also positively identified as reaction products by their weak absorption bands centered at 2169 $cm^{-1}$and at 2054 cm^{-1}, respectively. As in the OH initiated oxidation of DES, the lack of reference spectra render it very difficult to attribute the weak absorptions in the residual spectrum from the OH + EMS system to any of the other potential products. However, here again it is suspected that a major product will be ethyl methyl sulfoxide ($CH_3S(O)CH_2CH_3$, EMSO) formed from the reaction of a OH-EMS adduct with O_2. Also in this case a fast further reaction of EMSO with OH radicals is again consistent with the lack of a strong S=O stretching absorption in the vicinity of 1100 cm^{-1}.

The concentration–time profiles of EMS and the products show that both SO_2 and CH_3CHO are primary reaction products (see Fig. 5). Those for CO, and HCOOH show that they are secondary products. Only the profile for HCOOH is shown in Fig. 5. The concentration–time profile for HCHO shows that it is a primary product, however, the profile exhibits unusually strong curvature toward the end of the irradiation indicating a more pronounced secondary consumption compared to CH_3CHO. The reactions of OH with HCHO and CH_3CHO have recommended 298 K rate coefficients of 8.5×10^{-12} and 1.5×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, respectively (Sander et al., 2011; Atkinson et al., 2006). Hence, one would expect slightly more secondary consumption for CH_3CHO than for HCHO. In contrast to the OH + DES system considerable amounts of HCOOH are formed. As the reaction of OH with EMS progresses and the concentration of EMS is reduced to low levels, OH will react with the radical precursor H_2O_2 producing H_2O and HO_2 radicals. The reaction of HO_2 radicals with HCHO is relatively fast ($k = 7.9 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K) compared to its reactions with CH_3CHO and SO_2 which are much slower (Sander et al., 2011; Atkinson et al., 2006). The reaction of HO_2 with HCHO is known to produce HCOOH and the metastabile species $CH_2(OH)OOH$ (Su et al., 1979; Niki et al., 1980). We, therefore conclude that reaction of HO_2 with HCHO ismainly responsible for the formation of the HCOOH observed in both the reactions of OH with DES and EMS. The much higher amounts of HCOOH observed from the OH + EMS reaction compared to the OH + DES reaction is consistent with this hypothesis since HCHO is only a minor secondary product in the latter and a major primary product in the former systems. Also the amount of CO produced in the system is low which also supports that the main secondary loss of HCHO is not reaction with OH; a fact consolidated by the yield correction calculations mentioned below.

Plots of the concentrations of the primary products versus loss of EMS are linear (Fig. 6). Corrections to the yields for secondary consumption due to reaction with OH radicals were applied (Tuazón et al., 1986; Arsene et al., 1999). In the case of HCHO the analysis was made using only the initial 5 or 6 points to minimize the effect of the HO_2 reaction which is also occurring. The correction for SO_2 was negligible, for HCHO it was ~ 1% and for CH_3CHO ~3%. From least-squares analyses of the slopes of plots of the corrected product concentrations against reacted EMS yields of 51 ± 2%, 57 ± 3% and 46 ± 4% (Table 1) have been obtained for SO_2, CH_3CHO and HCHO, respectively, whereby the yield for HCHO is probably underestimated due to removal by HO_2 radicals.

The amount of OCS measured at the end of the OH + EMS experiments was even smaller than that observed in the OH + DES

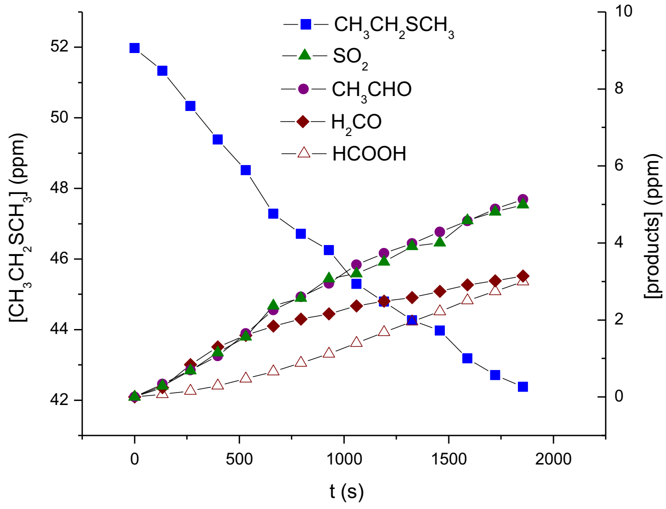

Fig. 5. Concentration–time profiles of EMS and products for the reaction of EMS with OH radicals.

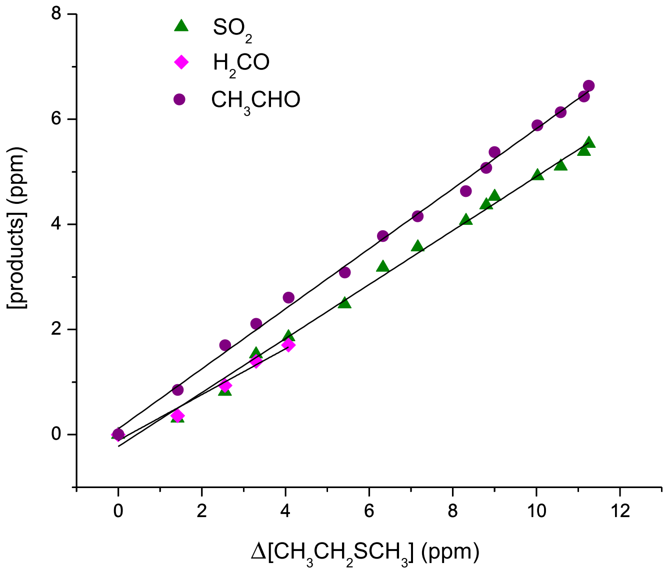

Fig. 6. Plots of product concentrations as a function of reacted EMS for the reaction of OH radicals with EMS.

systems with yields based on consumed EMS of typically around 0.07%. Pathways similar to those discussed for the reaction of OH with DES are thought responsible for the OCS formation.

4.3. Reaction mechanism and comparison of SO_2 and aldehyde yields

The product information from this work and previous kinetic studies (Hynes et al., 1986; Williams et al., 2007) supports a two-channel mechanism for the reactions of OH with the dialkyl sulfides, as previously proposed for the reaction of OH with DMS. The reactions involve a direct H-atom abstraction channel (O_2 independent) and a reversible OH addition channel forming an OH-SR_2 adduct which can react with molecular oxygen. The high yields of SO_2 observed in the reaction systems indicate that the H-atom abstraction channel is an important pathway for the reactions of OH radicals with both DES and EMS under the experimental conditions employed in this study (298 K, 760 Torr of NOx free air).

A tentative reaction mechanism describing the H-atom abstraction channel in the OH-radical initiated oxidation of the dialkyl sulfides DES and EMS is shown in Fig. 7. This mechanism only shows the pathways in the abstraction channel that lead to formation of SO_2 and the aldehydes; the possibility of other reaction pathways in the abstraction channel are discussed below together with the importance of the addition channel.

For both dialkyl sulfides abstraction of the secondary hydrogen atoms by OH is the dominant process (Hynes et al., 1986). In the case of EMS, Hynes et al. (1986) calculated that 26% of the H-abstraction reaction will occur from the CH_3S entity and only 2.2% from the CH_3 in the ethyl entity. The reactions of the radical intermediates $RSCHCH_3$ with molecular oxygen, result in the formation of alkylthio peroxy radicals ($CH_3CH(OO^{\bullet})SR$) which are converted to alkylthio alkoxy radicals ($CH_3CH(O^{\bullet})SR$) a major fate of which will be decomposition to give an aldehyde and an alkyl thiyl radical (RS) (Fig. 7, pathways a–d). However, as is discussed below other channels are probably also operative. The reactions of the alkyl thiyl radicals are important in the transformation of alkyl sulfides to SO_2. The reactions of methyl thiyl radicals (CH_3S) are known to be complex (Barnes et al., 1994a, 2006; Yin et al., 1990a,b; Turnipseed et al., 1992; Turnipseed and Ravisahankara, 1993), however, the present product investigations support the view (as argued below) that the main fate of the alkyl thiyl radicals formed in the OH initiated oxidation of DES and EMS is addition of O_2 to form a RSOO radicals, which mainly decompose to give SO_2 and alkyl radical (R) (Fig. 7, pathways e and f). The resulting alkyl radical (R) reacts rapidly, and exclusively, with O_2 under atmospheric conditions (Wallington et al., 1992) where the main resulting stable end product will be the corresponding aldehyde (Fig. 7).

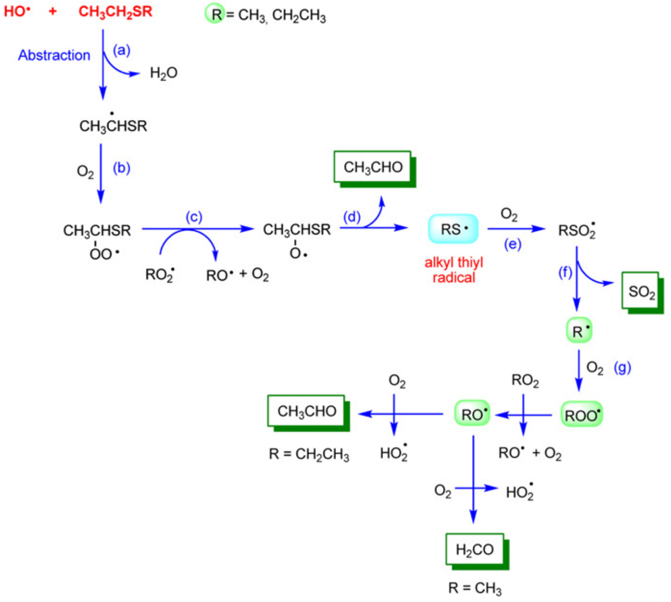

Fig. 7. Simplified mechanism for the OH-radical initiated oxidation of dialkyl sulfides in air showing only the more important possible H-atom abstraction pathways.

The measured yields of SO_2 and the aldehydes from the reactions of OH with DES and EMS obtained at atmospheric pressure at 298 K under NOx-free conditions are listed in Table 1 where they are compared with the corresponding yields for the reaction of OH with DMS obtained under similar conditions (Barnes et al., 1996; Arsene et al., 1999). The yields of SO_2 for the reaction of OH with DES and with EMS are both of the order of 50%. The yields of the aldehydes are approximately double that of SO_2. Assuming that there is no secondary production of SO_2 the results would suggest that approximately 50% of the reaction is proceeding by the abstraction pathway with the production of SO_2 and oxidation of both alkyl groups to the corresponding aldehyde as shown in the reaction mechanism in Fig. 7. This would also suggest that products from the OH addition pathway such as alkyl sulfoxides are not being further oxidized to SO_2 or aldehydes as has been observed in the oxidation of DMS under NOx-free conditions (Arsene et al., 1999).

In addition, the kinetic data reported by Williams et al. (2007) on the reactions of OH with DES amd EMS lead to the prediction that ~73% and ~76% of the reactions, respectively, will proceed via the abstraction channel for the following conditions: a total pressure ($N_2 + O_2$) of 600 Torr, an O_2 pressure of 150 Torr and 296 K. If these percentages are correct then approximately 20% of the $CH_2CH_2SCH(O^{\bullet})CH_3$ and $CH_2CH_2SCH_2(O^{\bullet})$ alkoxy radicals formed in the oxidation chain shown in Fig. 7 must, at least partly, react by other routes than decomposition. In the NOx-free studies on the reaction of OH with DMS formation of methyl thioformate (CH_3SCHO, MTF) was observed from the reaction of $CH_3SCH_2O^{\bullet}$ radicals with O_2 (Barnes et al., 1996; Arsene et al., 1999):

$$CH_3SCH_2O^{\bullet} + O_2 \rightarrow CH_3SCHO + HO_2 \qquad (10)$$

In the OH with DES and EMS reactions of the alkoxy radicals formed in the abstraction channel could lead to formation of *s*-ethyl thioacetate ($CH_3CH_2SC(O)CH_3$), *s*-methyl thioacetate ($CH_3SC(O)CH_3$) and *s*-ethyl thioformate (CH_3CH_2SCHO):

$$CH_3CH_2SCH(O^{\bullet})CH_3 + O_2 \rightarrow CH_3CH_2SC(O)CH_3 + HO_2 \qquad (11)$$

$$CH_3SCH(O^{\bullet})CH_3 + O_2 \rightarrow CH_3SC(O)CH_3 + HO_2 \qquad (12)$$

$$CH_3CH_2SCH_2(O^{\bullet}) + O_2 \rightarrow CH_3CH_2SCHO + HO_2 \qquad (13)$$

The gas phase IR spectrum of *s*-ethyl thioacetate exhibits a strong carbonyl stretching frequency at 1720 cm^{-1} (The Aldrich Library of FT-IR Spectra, 1989). In the residual product spectra for both the reactions of OH with DES and EMS there are absorptions in the region around 1720 cm^{-1} supporting that the reaction channels (10)–(13) are probably occurring to some extent. In contrast to DMS, the alkoxy radicals $CH_3CH_2SCH(O^{\bullet})CH_3$ and $CH_3CH_2SCH_2(O^{\bullet})$ formed from DES and EMS, respectively could isomerize by a 1,5-H shift through a six member transition state.

4.4. Atmospheric implications

As pointed out previously (Oksdath-Mansilla et al., 2009, 2010), the atmospheric lifetime of the alkyl sulfides studied here is determined primarily by reaction with OH radicals. The product studies reported here show that at 298 K under NO_x-free conditions the OH-radical initiated oxidation of the dialkyl sulfides DES and EMS will lead approximately 50% of the time to formation of sulfur dioxide and the corresponding carbonyl species as primary products via an H-atom abstraction mechanism. Approximately 50% of both the sulfur and carbon remain unaccounted for in the reaction system. Based on known DMS gas phase chemistry it is suspected that the addition reaction channel, estimated to account for approximately 25% of the overall reactions (Williams et al., 2007), will result in the formation of alkyl sulfoxides. These compounds will be rapidly further oxidized to products including SO_2 and alkyl sulfinic and sulfonic acids. There are also obviously other channels operative in the abstraction channel which could give products that will be further oxidized to SO_2 and sulfonic acids. Further studies utilizing methods capable of monitoring sulfoxides and sulfinic and sulfonic acids will be required to completely elucidate the mechanism for the OH radical initiated oxidation of dialkyl sulfides.

The fast reaction of the sulfides with OH means that they will be degraded near the emission sources producing SO_2, which will be further oxidized to H_2SO_4(g) and SO_4^{-2} (aq), and sulfinic and sulfonic acids. These compounds can be incorporated into particles to produce CCN thus affecting the Earth's radiation budget and climate regulation. They will also contribute to acid rain episodes.

The aldehydes that are formed play a central role in the chemistry of the troposphere since they are precursors of free radicals and peroxyacyl nitrates, which may lead to transport of NO_x to remote areas. The atmospheric degradation of aldehydes is controlled by photolysis and by reaction with OH radicals, for which the loss rates are of comparable magnitude (Mellouki et al., 2003). It is now known that they can also significantly contribute on secondary aerosol formation through heterogeneous reactions in the presence of an acid catalyst (Jang and Kamens, 2001).

To the best of our knowledge this is the first report of the product yields for the reaction of OH radicals with alkyl sulfides other than DMS. Such data will allow a more realistic representation of the tropospheric chemistry of other alkyl sulfides in the various types of CT-models which are used for designing environmental abatement strategies and making atmospheric policy decisions.

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