

# CH<sub>3</sub>CH<sub>2</sub>SCH<sub>3</sub> + OH radicals: temperature-dependent rate coefficient and product identification under atmospheric pressure of air<sup>†</sup>

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Relative rate coefficients have been determined for the gas-phase reaction of hydroxyl (OH) radicals with ethyl methyl sulfide (EMS) using isobutene as a reference compound. The experiments were performed in a 1080 L quartz glass photoreactor in the temperature range of 286–313 K at a total pressure of 760 ± 10 Torr synthetic air using *in situ* FTIR absorption spectroscopy to monitor the concentration-time behaviors of reactants and products. OH radicals were produced by the 254 nm photolysis of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>).

The kinetic data obtained were used to derive the following Arrhenius expression valid in the temperature range of 286–313 K (in units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>):  $k = (3.0 \pm 0.6) \times 10^{-15} \exp[(2457 \pm 65)/T]$

The rate coefficient displays a negative temperature dependence and low pre-exponential factor which supports the existence of an addition mechanism for the reaction involving reversible OH-adduct formation. The results are compared with previous data of other sulfides from the literature and are rationalized in terms of structure–reactivity relationships.

Additionally, product identification of the title reaction was performed for the first time by the FTIR technique under atmospheric conditions. Sulfur dioxide, formaldehyde, and formic acid were observed as degradation products in agreement with the two possible reaction channels (addition/abstraction). Copyright © 2010 John Wiley & Sons, Ltd.

**Keywords:** Arrhenius parameters, ethyl methyl sulfide, gas phase, hydroxyl radicals, tropospheric chemistry

## INTRODUCTION

It is well established that sulfur-containing organic compounds play an important role in atmospheric chemistry. Dimethyl sulfide (CH<sub>3</sub>SCH<sub>3</sub>: DMS), produced in the oceans by the biological activity of phytoplankton and volatilized to the atmosphere, is considered to be the dominant natural source of sulfur released to the atmosphere.<sup>[1]</sup> The main gas-phase degradation process of DMS in the troposphere is chemical oxidation initiated by OH radicals during the day and by NO<sub>3</sub> radicals at night. These processes lead to the formation of sulfur-containing species, such as sulfuric and methane sulfonic acids, which can significantly contribute to the acidity of the atmosphere.<sup>[2–5]</sup> It has been postulated that emissions of DMS from the oceans may have a significant influence on the Earth's radiation budget and possibly in climate regulation due to the formation of CCN (cloud condensation nuclei) from the oxidation of SO<sub>2</sub> formed in the photo-oxidation of DMS.<sup>[6–10]</sup> In this sense, it is necessary to determine rate coefficients for the reactions of organic sulfur compounds with tropospheric oxidants like OH and NO<sub>3</sub> radicals and Cl atoms, as well as the degradation pathways under atmospheric conditions. This information allows an assessment of the persistence, fate, and possible environmental effects of sulfides in the atmosphere.

While, there have been many studies of the photo-degradation reactions of DMS,<sup>[2,3,11–14]</sup> only limited information is available for other longer chain alkyl sulfides like ethyl methyl sulfide

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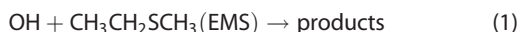
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(CH<sub>3</sub>CH<sub>2</sub>SCH<sub>3</sub>: EMS)<sup>[15–21]</sup> which have been observed in coastal areas.<sup>[22]</sup>

The OH-radical initiated oxidation mechanism of DMS includes reversible adduct CH<sub>3</sub>S(OH)CH<sub>3</sub> formation which gives rise to a negative temperature dependence for the rate coefficient. Since such behavior is expected for other longer chain sulfides, it is necessary to perform kinetic and product distribution studies of these compounds with typical oxidants under different conditions of temperature and pressure in order to understand the complexity of the reaction mechanisms.

The aim of this work was to investigate the kinetics of the reaction of OH radicals with EMS in the temperature range of 286–313 K:



The rate coefficient for the reaction of OH with EMS has been determined previously using the flash photolysis–resonance fluorescence (FP-RF) technique<sup>[15]</sup> at room temperature and 40 Torr total pressure of argon and by pulsed laser photolysis–pulsed laser induced fluorescence (PLP-PLIF) at 200 and 600 Torr in function of O<sub>2</sub> at three different temperatures.<sup>[20]</sup> More recently, the rate coefficient of reaction (1) has been determined in our laboratory in a large photoreactor in one atmosphere of air using a relative kinetic technique and FTIR to monitor the reactants.<sup>[21]</sup>

To the best of our knowledge, the present work is the first temperature-dependent study of the kinetics of the reaction of OH radicals with EMS at 760 Torr. The measured kinetic data are rationalized in terms of structure/reactivity relationships.

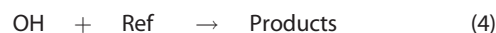
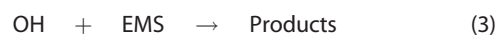
In addition, product identification using FTIR under atmospheric conditions was carried out for the first time for the title reaction and an atmospheric chemical mechanism is postulated.

## EXPERIMENTAL

All the experiments were performed in a 1080 L quartz-glass chamber in the temperature range of 286–313 K (±2 K) and at a total pressure of 760 ± 10 Torr of synthetic air. A detailed description of the reactor can be found elsewhere<sup>[23,24]</sup> and only a brief description is given here. Pumping systems consisting of a turbo-molecular pump backed by a double stage rotary fore pump enable the chamber to be evacuated to 10<sup>-3</sup> Torr. Magnetically coupled Teflon mixing fans are mounted inside the chamber to ensure homogeneous mixing of the reactants. The photolysis system consists of 32 low-pressure mercury vapor lamps (Philips TUV 40 W; λ<sub>max</sub> = 254 nm), which are spaced evenly around the chamber. The lamps are wired in parallel and can be switched individually, which allows a variation of the light intensity, and also of the photolysis frequency/radical production rate, within the chamber. The 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<sup>-1</sup>. The White mirror system was operated at a total optical path length of 484.7 m. IR spectra were recorded with a spectral resolution of 1 cm<sup>-1</sup> using a Nicolet Nexus FTIR spectrometer equipped with a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector. HO radicals were generated by the 254 nm photolysis of hydrogen peroxide:



In the presence of OH radicals, EMS and the reference compound (Ref) are consumed by the following reactions:



Provided that the reactant and the reference compound are lost only by reactions (3) and (4), respectively, it can be shown that:

$$\ln \left\{ \frac{[\text{EMS}]_0}{[\text{EMS}]_t} \right\} = \frac{k_{\text{EMS}}}{k_{\text{ref}}} \ln \left\{ \frac{[\text{Ref}]_0}{[\text{Ref}]_t} \right\} \quad (5)$$

where [EMS]<sub>0</sub>, [Ref]<sub>0</sub>, [EMS]<sub>t</sub>, and [Ref]<sub>t</sub> are the concentrations of the sulfide and reference compound at times *t* = 0 and *t*, respectively and *k*<sub>EMS</sub> and *k*<sub>ref</sub> are the rate coefficients of reactions (3) and (4), respectively.

Plots of ln([EMS]<sub>0</sub>/[EMS]<sub>t</sub>) vs. ln([Ref]<sub>0</sub>/[Ref]<sub>t</sub>) should yield straight lines with slope *k*<sub>EMS</sub>/*k*<sub>ref</sub> and zero intercept. The time decay of EMS was analyzed by obtaining the corresponding calibration factors, determined by subtraction with calibrated reference spectra at a single wavelength, that can replace the EMS and reference concentrations in Eqn (5) due to their proportional relationship.

The rate coefficients for the reaction of OH with EMS studied here were measured relative to the rate coefficient of OH with isobutene. Mixtures of the sulfide, reference compound, and H<sub>2</sub>O<sub>2</sub> were stable in the dark when left in the chamber for about 1 h. Moreover, in the absence of H<sub>2</sub>O<sub>2</sub>, no discernible decrease in the concentrations of the EMS and reference compound could be established upon irradiation of the mixture for more than 1 h.

The initial concentrations used in the experiments for the organics in ppmV (1 ppmV = 2.46 × 10<sup>13</sup> molecule cm<sup>-3</sup> at 298 K and 760 Torr of total pressure) were: 9–57 for EMS and 3.5–12 for isobutene. The concentration of hydrogen peroxide was typically around 11 ppmV.

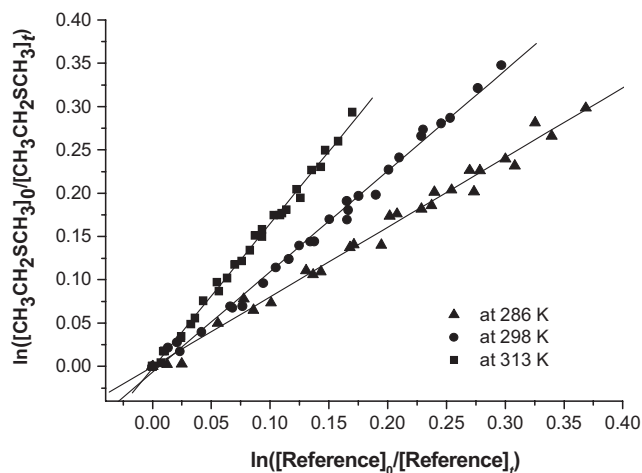
The reactants were monitored at the following infrared absorption frequencies (in cm<sup>-1</sup>): EMS at 1066 and 958 and isobutene at 890.

## 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<sub>2</sub>:O<sub>2</sub> ratio of 79.5:20.5%, nitrogen (Messer Griesheim, 99.999%), isobutene (Messer Griesheim, 99.995%), EMS (Aldrich, 96%), and hydrogen peroxide (Peroxide Chemie, 85.5%).

## RESULTS

Relative kinetic studies were performed at one atmosphere total pressure on the reaction of OH with EMS at temperatures of 286, 298, and 313 (±2 K). Figure 1 shows examples of the kinetic data obtained at the three temperatures plotted according to Eqn (5). Linear correlations with near zero intercepts were obtained for every temperature. Table 1 lists the experimental conditions, the rate coefficient ratios obtained from linear least-squares analyses of the data plotted according to Eqn (5), and the absolute rate coefficients obtained for OH with EMS derived from the rate ratios. To put the rate coefficients for the reaction of OH with EMS on an absolute basis, rate coefficients for the respective temperatures of the reference reaction OH + isobutene, derived



**Figure 1.** Relative kinetic plot of the data for the reaction OH + CH<sub>3</sub>CH<sub>2</sub>SCH<sub>3</sub> at 286, 298, and 313 K

from the following Arrhenius expression (in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> units), were used:<sup>[25]</sup>

$$k(\text{OH} + \text{isobutene}) = 9.51 \times 10^{-12} \exp\left[\frac{503}{T}\right]$$

The errors given for the rate coefficient ratios in Table 1 are the two least-squares standard deviations ( $\pm 2\sigma$ ). As can be seen in Table 1, the rate coefficients derived from the individual experiments at each temperature for the OH + EMS reaction are in excellent agreement. We therefore prefer to quote values for the reactions at the given temperature as an average of the individual values determined at that temperature. The final values of the rate coefficients at each temperature are listed as 'Average value' in Table 1.

For the reaction studied, the reaction rate coefficients were found to decrease slightly with increase in temperature in the range of 286–313 K. The average values of the rate coefficients

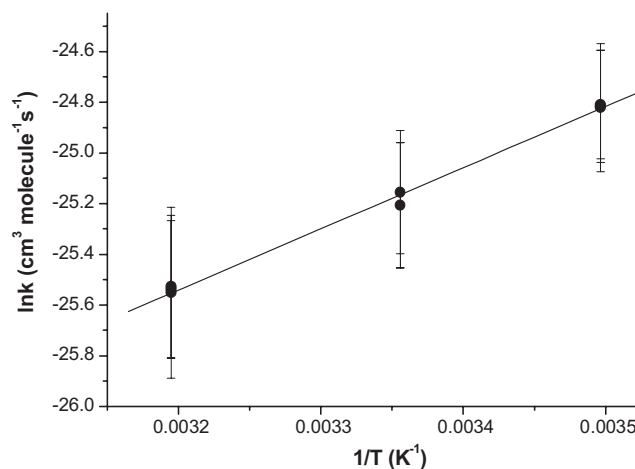
given in Table 1 are plotted in the Arrhenius form in Fig. 2. The following Arrhenius expression adequately describes the data in the temperature range of 286–313 K with  $k$  in units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>:

$$k(\text{OH} + \text{EMS}) = (3.0 \pm 0.6) \times 10^{-15} \exp\left[\frac{(2457 \pm 65)}{T}\right]$$

The errors in the activation term and the pre-exponential factor are the  $2\sigma$  random statistical errors from fits to the data presented in Table 1 and plotted in Figs. 1 and 2.

## DISCUSSION

To the best of our knowledge, there have not been previous studies of the temperature dependence of the overall rate coefficient of the reaction of OH radicals with EMS. In the present study, thus, the Arrhenius parameters (the activation energy and



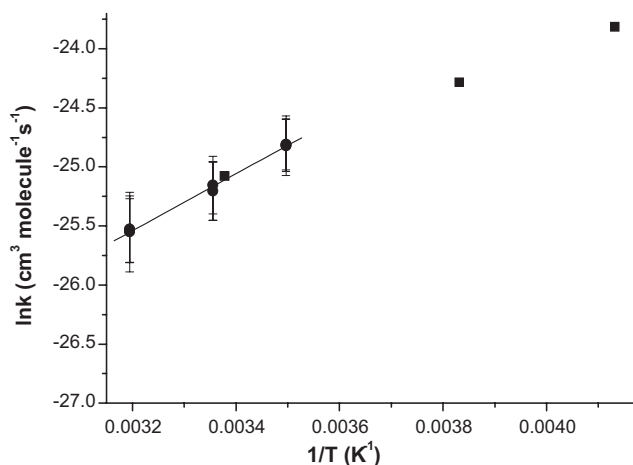
**Figure 2.** Arrhenius plot of the data for the reaction OH + CH<sub>3</sub>CH<sub>2</sub>SCH<sub>3</sub> between 286 and 313 K

**Table 1.** Rate coefficient ratios  $k_{\text{EMS}}/k_{\text{ref}}$  and rate coefficients obtained for the reaction of ethyl methyl sulfide with OH at different temperatures

Reaction <sup>a</sup>	Temperature/K	$k_{\text{EMS}}/k_{\text{ref}}$	$k_{\text{EMS}}$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )
CH <sub>3</sub> CH <sub>2</sub> SCH <sub>3</sub> + OH	286	0.30 ± 0.02	(1.66 ± 0.42) × 10 <sup>-11</sup>
	286	0.30 ± 0.01	(1.67 ± 0.37) × 10 <sup>-11</sup>
	286	0.30 ± 0.01	(1.68 ± 0.36) × 10 <sup>-11</sup>
	Average		<b>(1.67 ± 0.67) × 10<sup>-11</sup></b>
	298	0.23 ± 0.01	(1.19 ± 0.29) × 10 <sup>-11</sup>
	298	0.22 ± 0.01	(1.13 ± 0.28) × 10 <sup>-11</sup>
	298	0.22 ± 0.01	(1.13 ± 0.28) × 10 <sup>-11</sup>
	Average		<b>(1.16 ± 0.42) × 10<sup>-11</sup></b>
	313	0.17 ± 0.01	(0.81 ± 0.22) × 10 <sup>-11</sup>
	313	0.17 ± 0.02	(0.80 ± 0.27) × 10 <sup>-11</sup>
	313	0.17 ± 0.01	(0.82 ± 0.23) × 10 <sup>-11</sup>
	Average		<b>(0.80 ± 0.42) × 10<sup>-11</sup></b>

The error in the average rate coefficient is quoted as  $(\sum \sigma_i^2)^{1/2}$ .

<sup>a</sup>Experiments performed in 1080 L reactor in air. Isobutene as a reference compound. (Sulfide) = (9–57) ppmv. (Reference) = (3.5–12) ppmv.



**Figure 3.** Comparison of the temperature-dependent rate constants for the reaction  $\text{OH} + \text{CH}_3\text{CH}_2\text{SCH}_3$  between this work (filled circles with the Arrhenius fitting) and the previous absolute (PLP-PLIF) data from the sum  $k_{\text{obs}} = k_{\text{addition}} + k_{\text{abstraction}}$  obtained by Williams *et al.* (filled squares) at the  $\text{O}_2$  pressure regime

the pre-exponential factor) are presented for the first time and therefore no direct comparison with the literature can be made. However, we can compare our results with an absolute recent study of reaction (1) by Williams *et al.* performed at 600 Torr of  $\text{N}_2$  and  $\text{O}_2$  at three different temperatures (242, 261, and 296 K) in a PLP-PLIF system. The authors have studied the equilibration of the EMS-OH adduct in the absence of  $\text{O}_2$  and the dependence of the rate constant of reaction (1) with temperature and  $\text{O}_2$  partial pressure at high sulfide concentration.<sup>[20]</sup> The overall rate constants obtained by Williams *et al.* ( $k_{\text{obs}}$ ) from equilibration temporal profiles and their fittings of enhancement in the effective rate constants in the presence of oxygen are plotted in Fig. 3, as a sum of the addition and abstraction elementary processes ( $k_{\text{obs}} = k_{\text{abstraction}} + k_{\text{addition}}$ ) at the  $\text{O}_2$  pressure regime, from their experimental data at three different temperatures. Their results are compared in Fig. 3 with our temperature-dependent rate constants, where it is possible to observe a very good agreement between their absolute data and our 760 Torr relative data using an environmental chamber.

On the other hand, the Arrhenius parameters obtained for this reaction can be compared with the extensively studied reaction between OH radicals with DMS (Table 2). The pre-exponential factor A determined in this study for  $\text{OH} + \text{EMS}$  of  $(3.0 \pm 0.6) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and the value of  $E_a/R$  of  $2457 \pm 65 \text{ K}$  are not very dissimilar to the corresponding values for the reaction of OH with DMS in air of  $(1.31 \pm 0.08) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $1910 \pm 69 \text{ K}$ , respectively.<sup>[2,12]</sup>

Furthermore, the value of the rate coefficient determined at 298 K is in good agreement with that previously reported from this laboratory,  $(1.11 \pm 0.29) \times 10^{-11}$ ,<sup>[21]</sup> and is also in fair

agreement, within the experimental errors, with the value of  $(8.5 \pm 1.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  obtained by Hynes *et al.*<sup>[15]</sup> at 40 Torr total pressure in argon at 299 K using the FP-RF technique.

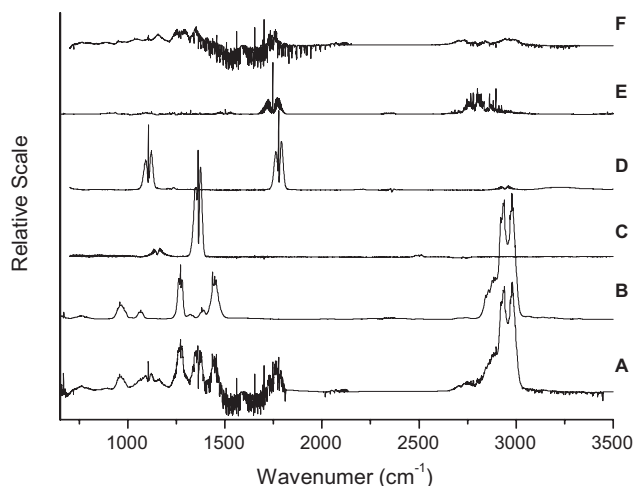
Regarding the reactivity trends for different organic sulfides towards OH radicals, it can be shown that the rate coefficients increase with the number of  $-\text{CH}_2-$  groups in the alkyl chain (in units  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K).<sup>[12,21]</sup>

$$k_{\text{CH}_3\text{SCH}_3} (0.78 \times 10^{-11}) < k_{\text{CH}_3\text{CH}_2\text{SCH}_3} (1.16 \times 10^{-11})^{\text{[this work]}} \\ < k_{(\text{CH}_3\text{CH}_2)_2\text{S}} (1.65 \times 10^{-11})$$

It is known that the presence of the  $-\text{O}-$  group in ethers leads to increased reactivity compared to the corresponding alkanes;<sup>[26]</sup> such an activating effect is also observed for the  $-\text{S}-$  moiety in sulfides.<sup>[25]</sup>

$$\frac{k_{\text{CH}_3\text{SCH}_3}}{k_{\text{C}_2\text{H}_6}} = 21; \frac{k_{\text{CH}_3\text{CH}_2\text{SCH}_3}}{k_{\text{C}_3\text{H}_8}} = 10 \text{ and } \frac{k_{(\text{CH}_3\text{CH}_2)_2\text{S}}}{k_{\text{C}_4\text{H}_{10}}} = 7$$

Experiments were also conducted to identify the products of the reaction of OH with EMS under similar conditions to the kinetic experiments. The main product was found to be sulfur dioxide ( $\text{SO}_2$ ), and traces of formaldehyde ( $\text{CH}_2\text{O}$ ) and formic acid ( $\text{HCOOH}$ ) were also detected. Figure 4 shows the product spectra recorded during the reaction of OH with EMS and the comparison with reference spectra of  $\text{SO}_2$ ,  $\text{CH}_2\text{O}$ , and  $\text{HCOOH}$ . Bands observed at 1362, 1746, and  $1105 \text{ cm}^{-1}$  correspond to the formation of  $\text{SO}_2$ ,  $\text{CH}_2\text{O}$ , and  $\text{HCOOH}$ , respectively.



**Figure 4.** Product spectra recorded during the reaction of OH radicals with  $\text{CH}_3\text{CH}_2\text{SCH}_3$ . (A) Product spectra after 10 min photolysis. (B) Reference spectra of  $\text{CH}_3\text{CH}_2\text{SCH}_3$ . (C) Reference spectra of  $\text{SO}_2$ . (D) Reference spectra of  $\text{HCOOH}$ . (E) Reference spectra of  $\text{CH}_2\text{O}$ . (F) Residual spectrum after subtractions of all the identified compounds

**Table 2.** Arrhenius parameters for the reactions  $\text{EMS} + \text{OH}$  <sup>[this work]</sup> and  $\text{DMS} + \text{OH}$  <sup>[12]</sup>

Reaction	$E_a/R$ (K)	A ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	$k_{(298 \text{ K})}$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	Reference
$\text{CH}_3\text{CH}_2\text{SCH}_3 + \text{OH}$	$(2457 \pm 65)$	$(3.0 \pm 0.6) \times 10^{-15}$	$(1.11 \pm 0.29) \times 10^{-11}$	This work
$\text{CH}_3\text{SCH}_3 + \text{OH}$	$(1910 \pm 69)$	$(1.31 \pm 0.08) \times 10^{-14}$	$(7.80 \pm 1.80) \times 10^{-12}$	[12]

The reaction products found, together with the observed reactivity trends, support that the reaction proceeds via two competitive reaction channels, abstraction and addition. A reaction mechanism for the reaction of OH with EMS detailing the possible reaction channels postulated is shown in Fig. 5. As in the H-abstraction reactions of alkanes by OH,<sup>[25]</sup> the two possible H-abstraction routes for OH with EMS produce CH<sub>3</sub>CH<sub>2</sub>SCH<sub>2</sub> and CH<sub>3</sub>CHSCH<sub>3</sub> radicals. The alkyl radicals thus generated react with O<sub>2</sub> to produce peroxy radicals, which by further peroxy–peroxy reactions mainly afford the corresponding alkoxy radicals.

The fate of the alkoxy radicals includes decomposition by C—C scission to produce aldehydes (CH<sub>2</sub>O and CH<sub>3</sub>CHO) and RS radicals (CH<sub>3</sub>S and CH<sub>3</sub>CH<sub>2</sub>S). These thiyl radicals can react with O<sub>2</sub> to produce SO<sub>2</sub> and alkyl radicals that in the presence of O<sub>2</sub> will finally form CH<sub>2</sub>O.

On the other hand, the existence of an OH-radical addition mechanism which leads to the formation of an intermediate CH<sub>3</sub>CH<sub>2</sub>S(OH)CH<sub>3</sub> adduct (labeled addition in Fig. 5) can also take place. The fate of this hydroxysulfide radical includes: (1) reaction with O<sub>2</sub> to produce subsequently sulfoxides, sulfones, and ethanesulfonic acid and (2) decomposition to CH<sub>3</sub> radical (to form CH<sub>2</sub>O) and ethane sulfenic acid (CH<sub>3</sub>CH<sub>2</sub>SOH), which by a subsequent reaction with OH is converted into CH<sub>3</sub>CH<sub>2</sub>SO radicals. Different reaction channels are possible for these last radicals: (2a) reaction with O<sub>2</sub> to produce CH<sub>3</sub>CH<sub>2</sub>S(O)OO radicals which afford CH<sub>3</sub>CH<sub>2</sub>S(O)O radicals by reaction with other peroxy radicals; (2b) reaction with HO<sub>2</sub> to give CH<sub>3</sub>CH<sub>2</sub>S(O)O radicals, and

(2c) decomposition in CH<sub>3</sub>CH<sub>2</sub> and SO fragments to finally produce SO<sub>2</sub> and CH<sub>2</sub>O.

The fate of CH<sub>3</sub>CH<sub>2</sub>S(O)O radicals generated in channels (2a) and (2b) will be mainly production of SO<sub>2</sub>.

According to the observed products, it is not possible to discriminate the main route of the OH-initiated degradation of EMS (abstraction or addition) since similar reaction products are expected from both reaction pathways. Further experiments need to be conducted in the presence and absence of NO<sub>x</sub>, different O<sub>2</sub> partial pressures, and at different temperatures to elucidate this complex reaction mechanism.

Regarding the formation of sulfoxides, sulfones, and sulfonic acid in the reaction of OH with EMS, no evidence could be found in the infrared spectrum for the formation of these sulfur-containing compounds in the gas-phase indicating that either the formation of these compounds is fairly negligible or they are quickly removed from the gas-phase through particle formation. The sulfoxide if formed will have a very low vapor pressure and could be quickly removed by heterogeneous reactions, however, the results from the kinetic experiments<sup>[15]</sup> indicate that H-atom abstraction from the secondary hydrogen atoms will dominate the reaction mechanism.

According to the atmospheric lifetime of EMS calculated in a recent study, the main homogenous sink of EMS in the atmosphere is its OH-initiated oxidation during day which results in a lifetime of about 8 h.<sup>[21]</sup> The sulfide will thus be degraded near the emission sources producing SO<sub>2</sub> which will be further

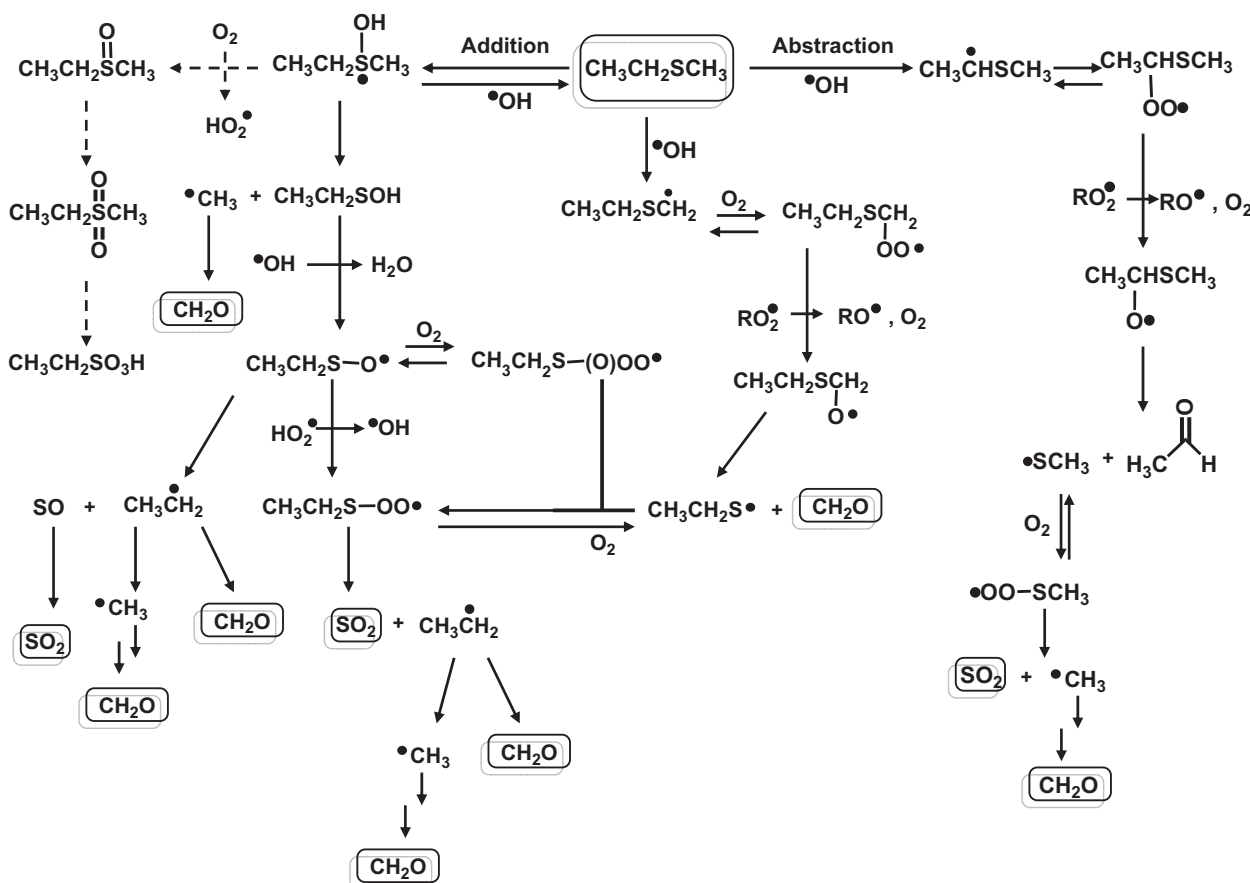


Figure 5. Postulated mechanism for the OH-initiated degradation of CH<sub>3</sub>CH<sub>2</sub>SCH<sub>3</sub>

oxidized to  $\text{H}_2\text{SO}_4(\text{g})$  and  $\text{SO}_4^{2-}(\text{aq})$ . These anions can be incorporated into particles to produce CCN affecting the Earth's radiation budget and climate regulation as well as to participate in acid rain episodes.

## SUMMARY AND CONCLUSIONS

The temperature-dependent rate coefficient of the reaction  $\text{OH} + \text{CH}_3\text{CH}_2\text{SCH}_3$  was determined by the relative method in an environmental chamber with FTIR detection of reactants at 760 Torr of air. Although the Arrhenius parameters are reported for the first time for this reaction, they are consistent with the previously reported rate constants by PLP-PLIF results at 600 Torr and the parameters for the reaction of OH with DMS. Previous data from reactivity trends were analyzed in terms of the structure of the sulfide.  $\text{SO}_2$ ,  $\text{CH}_2\text{O}$ , and  $\text{HCOOH}$  are found as the reaction products and a degradation mechanism leading to the products is postulated.

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