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Kinetics and Products of the Gas-Phase Reactions of Divinyl Sulfoxide with OH and NO_3 Radicals and O_3

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Using relative rate methods, rate constants for the gas-phase reactions of divinyl sulfoxide [$CH_2{=}CHS(O)CH{=}CH_2$; DVSO] with NO_3 radicals and O_3 have been measured at 296 ± 2 K, and rate constants for the reaction with OH radicals have been measured over the temperature range of 277−349 K. Rate constants obtained for the NO_3 radical and O_3 reactions at 296 ± 2 K were $(6.1 \pm 1.4) \times 10^{-16}$ and $(4.3 \pm 1.0) \times 10^{-19}$ cm^3 molecule^{-1} s^{-1}, respectively. For the OH radical reaction, the temperature-dependent rate expression obtained was $k = 4.17 \times 10^{-12} e^{(858 \pm 141)/T}$ cm^3 molecule^{-1} s^{-1} with a 298 K rate constant of $(7.43 \pm 0.71) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, where, in all cases, the errors are two standard deviations and do not include the uncertainties in the rate constants for the reference compounds. Divinyl sulfone was observed as a minor product of both the OH radical and NO_3 radical reactions at 296 ± 2 K. Using in situ Fourier transform infrared spectroscopy, CO, CO_2, SO_2, HCHO, and divinyl sulfone were observed as products of the OH radical reaction, with molar formation yields of 35 ± 11, 2.2 ± 0.8, 33 ± 4, 54 ± 6, and 5.4 ± 0.8%, respectively, in air. For the experimental conditions employed, aerosol formation from the OH radical-initiated reaction of DVSO in the presence of NO was minor, being ~1.5%. The data obtained here for DVSO are compared with literature data for the corresponding reactions of dimethyl sulfoxide.

Introduction

Volatile organic compounds (VOCs) emitted into the atmosphere are generally removed from the troposphere by one or more chemical processes, including photolysis at wavelengths ≥ 290 nm, reaction with OH radicals, reaction with NO_3 radicals, and reaction with O_3.[1] Organosulfur compounds are emitted into the atmosphere mainly from natural sources.[2,3] To date, most studies of the atmospheric reactions of this class of VOCs have been on methanethiol [CH_3SH],[4] dimethyl sulfide [CH_3SCH_3],[3,4] dimethyl disulfide [CH_3SSCH_3],[4] and dimethyl sulfoxide [$CH_3S(O)CH_3$],[3,5−13] the latter being a product of the OH radical-initiated reaction of dimethyl sulfide.[3,7,14−16] Reactions with OH and NO_3 radicals are important transformation processes for these organosulfur compounds in the troposphere,[3,17] and for simple organosulfur compounds such as CH_3SH, CH_3SCH_3, CH_3SSCH_3, and $CH_3S(O)CH_3$, these reactions can proceed by H-atom abstraction by OH radicals from C−H bonds and OH and NO_3 radical addition to the S atom.[3,4,13] While the kinetics of these reactions are reasonably well understood,[3,4] the reactions occurring after the initial step are much less well understood, especially for dimethyl sulfide and dimethyl sulfoxide.[3]

Divinyl sulfoxide, $CH_2{=}CHS(O)CH{=}CH_2$ (DVSO), is a volatile, commercially available sulfoxide which may have industrial uses in the formation of resins and polymers. DVSO is structurally related to dimethyl sulfoxide, with the methyl groups in dimethyl sulfoxide being replaced by vinyl groups in DVSO. The influence of the vinyl groups on the atmospheric reactivity of simple sulfoxides has not previously been investigated, and hence, in this work we have measured rate constants for the gas-phase reactions of DVSO with OH radicals over the temperature range of 277−349 K and with NO_3 radicals and O_3 at room temperature. In addition, we have used gas chromatography and in situ Fourier transform infrared spectroscopy (FT-IR) to investigate the products formed from the OH and NO_3 radical-initiated reactions of DVSO at room temperature. These kinetic and product data are compared with those for dimethyl sulfoxide.

Experimental Methods

Experiments were carried out in three different reaction chambers. A series of experiments to measure the OH and NO_3 radical and O_3 reaction rate constants and the products of the OH and NO_3 radical-initiated reactions were conducted at 296 ± 2 K and 735 Torr total pressure of dry purified air in a ~7000 L volume Teflon chamber,[18,19] equipped with two parallel banks of blacklamps for irradiation. Kinetics and products of the OH radical reaction were also carried out at 298 ± 1 K in a 5870 L Teflon-coated, evacuable chamber, with irradiation provided by a 24 kW xenon arc lamp filtered through a 6 mm thick Pyrex pane to remove wavelengths < 300 nm.[18−20] In this mode of operation, the chamber was equipped with a multiple reflection optical system interfaced to a Mattson Galaxy 5020 Fourier transform infrared (FT-IR) spectrometer.[18−20] Temperature-dependent experiments were carried out using a ~5000 L volume Teflon bag inserted inside of the 5870 L Teflon-coated chamber,[21] with irradiation again provided by the 24 kW xenon arc lamp filtered through a 6 mm thick Pyrex pane to remove wavelengths < 300 nm. The 5870 L volume Teflon-coated evacuable chamber is fitted with a heating/cooling system, allowing its temperature to be maintained to within ± 1 K over the range ~275−350 K.[21] All three chambers were provided with Teflon-coated fans to ensure rapid mixing of reactants during their introduction into the chamber. Temperatures of the

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gas mixtures inside of the chambers were measured by thermocouples, and in all experiments in all three chamber systems, the temperature rise during the irradiations was always ≤2 K.

Kinetic and Product Studies with Analysis by Gas Chromatography. Rate constants for the reactions of OH and NO_3 radicals and O_3 with DVSO were measured using relative rate techniques in which the concentrations of DVSO and a reference compound (whose OH radical, NO_3 radical, or O_3 reaction rate constant is reliably known) were measured in the presence of OH radicals, NO_3 radicals, or O_3.[18,22]

$$\left.\begin{matrix}\mathrm{OH}\\ \mathrm{NO_3}\\ \mathrm{O_3}\end{matrix}\right\} + \text{divinyl sulfoxide} \rightarrow \text{products} \qquad (1)$$

$$\left.\begin{matrix}\mathrm{OH}\\ \mathrm{NO_3}\\ \mathrm{O_3}\end{matrix}\right\} + \text{reference compound} \rightarrow \text{products} \qquad (2)$$

Provided that DVSO and the reference compound reacted only with OH radicals, NO_3 radicals, or O_3, then

$$\ln\left(\frac{[\text{divinyl sulfoxide}]_{t_o}}{[\text{divinyl sulfoxide}]_t}\right) - D_t = \frac{k_1}{k_2}\left[\ln\left(\frac{[\text{reference compound}]_{t_o}}{[\text{reference compound}]_t}\right) - D_t\right] \qquad (\mathrm{I})$$

where [divinyl sulfoxide]$_{t_o}$ and [reference compound]$_{t_o}$ are the concentrations of DVSO and the reference compound, respectively, at time t_o, [divinyl sulfoxide]$_t$ and [reference compound]$_t$ are the corresponding concentrations at time t, D_t is a factor to account for dilution caused by any additions to the chamber during the experiments ($D_t = 0$ for the OH radical reactions, $D_t = 0.0027$ per N_2O_5 addition to the chamber in the NO_3 radical reactions, and $D_t = 0.00135$ per O_3 addition to the chamber in the O_3 reactions), and k_1 and k_2 are the rate constants for reactions 1 and 2, respectively.

The O_3 reactions were carried out at 296 ± 2 K in the ~7000 L Teflon chamber. The initial concentrations of DVSO and *cis*-2-butene or propene (the reference compound) were ~2.4×10^{13} molecule cm^{-3} each, and 1.2×10^{16} molecule cm^{-3} of cyclohexane was also present to scavenge >97% of OH radicals formed in the O_3 reactions. Three to eight additions of 50 cm^3 aliquots of O_3 in O_2 (each addition corresponding to ~6×10^{12} molecule cm^{-3} of O_3 in the chamber) were made to the chamber during an experiment. The concentrations of DVSO and the reference compound were measured during the experiments by gas chromatography with flame ionization detection (GC-FID), as described below.

Nitrate radicals were produced from the thermal decomposition of N_2O_5,[18,19] and NO_2 was also included in the reactant mixtures. The initial reactant concentrations (molecule cm^{-3}) were DVSO and methacrolein or *trans*-2-butene (the reference compounds), ~2.4×10^{13} each, and NO_2, $(2.4-4.8) \times 10^{13}$ molecule cm^{-3}; and two to three additions of N_2O_5 (each addition corresponding to $(1.1-11.4) \times 10^{13}$ molecule cm^{-3} of N_2O_5 in the chamber) were made to the chamber during an experiment. The concentrations of DVSO and the reference compounds were measured during the experiments by GC-FID, as described below.

Apart from one experiment (see below), OH radicals were generated in the presence of NO by the photolysis of methyl nitrite in air at wavelengths > 300 nm.[18,19] The initial reactant concentrations (molecule cm^{-3}) employed for the OH radical reactions were CH_3ONO, ~2.4×10^{14}; NO, ~2.4×10^{14}; and DVSO and the reference compound, ~2.4×10^{13} molecule cm^{-3} each. In one experiment, the initial CH_3ONO and NO concentrations were a factor of 10 lower at ~2.4×10^{13} molecule cm^{-3} each. The reference compounds used were α-pinene and 1,2,4- and 1,3,5-trimethylbenzene, and irradiations were carried out at 20% of the maximum light intensity for up to 12 min in the ~7000 L Teflon chamber and for up to 22 min in the ~5000 L Teflon bag. While most experiments were carried out in air (21% O_2 content), experiments were also carried out with 1,3,5-trimethylbenzene as the reference compound at ~6 and ~78% O_2 content.

In additional experiments using 1,3,5-trimethylbenzene as the reference compound, two experiments were carried out with dimethyl sulfide present in the reactant mixtures at initial concentrations of 2.4×10^{13} and 2.4×10^{14} molecule cm^{-3}. A third experiment used the dark reaction of O_3 with 2-methyl-2-butene to generate OH radicals in the absence of NO_x,[23] with initial concentrations (molecule cm^{-3}) of DVSO, ~2.4×10^{13}; 1,3,5-trimethylbenzene, ~2.4×10^{13}; and 2-methyl-2-butene, 4.5×10^{13} molecule cm^{-3}; and with 6 additions of 50 cm^3 aliquots of O_3 in O_2 (each addition corresponding to ~6×10^{12} molecule cm^{-3} of O_3 in the chamber) being made to the chamber during the experiment.

An experiment was conducted to investigate the importance of dark decay and photolysis of ~2.4×10^{13} molecule cm^{-3} of DVSO in the chamber, with 2.4×10^{15} molecule cm^{-3} of cyclohexane being present to scavenge any OH radicals formed during the 60 min of photolysis. Two experiments were also carried out to measure the rate constant ratio k(OH + 1,3,5-trimethylbenzene)/k(OH + 1,2,4-trimethylbenzene) for comparison with previous data from this laboratory,[24] with initial reactant concentrations (molecule cm^{-3}) of CH_3ONO and NO, ~2.4×10^{14} each, and 1,2,4- and 1,3,5-trimethylbenzene, ~2.4×10^{13} molecule cm^{-3} each.

The concentrations of DVSO and the reference compounds were measured during the experiments by GC-FID. For the analyses of propene, *cis*-2-butene, and *trans*-2-butene, gas samples were collected from the chamber into 100 cm^3 volume all-glass gas-tight syringes and transferred via a 1 cm^3 gas sampling loop onto a 30 m DB-5 megabore column initially held at −25 °C and then temperature programmed to 200 °C at 8 °C min^{-1}. For the analyses of methacrolein, α-pinene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, DVSO and, in product studies (see below), divinyl sulfone, 100 cm^3 volume gas samples were collected from the chamber onto Tenax-TA solid adsorbent, with subsequent thermal desorption at ~205 °C onto a 30 m DB-1701 megabore column, initially held at −40 or 0 °C and then temperature programmed to 200 °C at 8 °C min^{-1}. For a number of the OH radical reactions, DVSO, α-pinene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene were analyzed using a 30 m DB-5MS megabore column, with the same temperature program as that for the DB-1701 column, and in some of these experiments, both columns were used for analyses (DVSO eluted before α-pinene, 1,2,4-trimethylbenzene, or 1,3,5-trimethylbenzene on the DB-5MS column but after them on the DB-1701 column). On the basis of replicate analyses in the chamber in the dark, the analytical uncertainties for DVSO and the reference compounds used were typically ≤3%.

A product of the reactions of OH and NO_3 radicals with DVSO was identified by combined gas chromatography−mass spectrometry (GC-MS) and was quantified by GC-FID using the DB-1701 column in selected (OH radical reaction) or all (NO_3 radical reactions) kinetic experiments. For the GC-MS analyses, samples were collected onto Tenax-TA solid adsorbent and thermally desorbed onto a 60 m DB-5MS column in a Hewlett−Packard (HP) 5890 Series II GC interfaced to a HP 5971B mass-selective detector operating in the scanning mode.

Experiments with FT-IR Analyses. Irradiations of 2-propyl nitrite [$(CH_3)_2CHONO$)]−NO−DVSO−1,2,4-trimethylbenzene−air and 2-propyl nitrite−NO−DVSO−air mixtures were carried out in the 5870 L evacuable chamber. The photolysis of 2-propyl nitrite was used as the OH radical source to allow the formation of HCHO to be investigated.[18−20] Irradiations were carried out either continuously for 22 min, with FT-IR spectra being collected before the irradiation and every 1.5−3.5 min during the irradiation, or intermittently for up to a total irradiation time of 12 min and with FT-IR spectra being recorded before and after each 3 min irradiation period. The initial concentrations (molecule cm^{-3}) employed were 2-propyl nitrite, 1.97×10^{14}; NO, 2.46×10^{14}; DVSO, $(2.41-2.71) \times 10^{14}$; and 1,2,4-trimethylbenzene (when present), 2.88×10^{14} molecule cm^{-3}. The quantitative analysis of products and reactants by FT-IR spectroscopy was carried out by a subtractive procedure.[18−20] Components were successively subtracted from the spectrum of the mixture using calibrated spectra of the gaseous reactants and known products which have been recorded previously with the same instrument and identical spectral parameters.[18−20]

Aerosol Formation. CH_3ONO−NO−air irradiations of DVSO, DVSO + α-pinene, and α-pinene were carried out at 296 ± 2 K in the ~7000 L Teflon chamber, with the concentrations of DVSO and/or α-pinene being measured by GC-FID as described above and with the aerosol number density and size distribution being measured during the experiments using a TSI 3936L72 scanning mobility particle sizer (SMPS). The initial reactant concentrations were similar to those used for the OH radical kinetic experiments (see above).

Chemicals. The chemicals used (and their stated purities) were divinyl sulfone (97%), methacrolein (95%), α-pinene (99+%), 1,2,4-trimethylbenzene (98%), and 1,3,5-trimethylbenzene (98%), Aldrich Chemical Co.; divinyl sulfoxide (≥97%), Fluka; *cis*-2-butene (99%), Liquid Carbonic; and NO (≥99.0%), propene (≥99.0%), and *trans*-2-butene (>95%), Matheson Gas Products. Methyl nitrite, 2-propyl nitrite, and N_2O_5 were prepared and stored as described elsewhere,[18−20,25] and O_3 in O_2 diluent was generated using a Welsbach T-408 ozone generator. NO_2 was prepared as needed by reacting NO with an excess of O_2.

Results

Photolysis and Dark Decays. No decay (<5%) of DVSO was observed in the ~7000 L Teflon chamber over a period of 4.2 h with four 15 min periods of irradiation at the same light intensity and spectral distribution as that used in the OH radical rate constant determinations in the same chamber. These results show that dark losses and any photolysis of DVSO were negligible for the experimental conditions employed.

Rate Constant for Reaction with O_3. The rate constant for the reaction of O_3 with DVSO was measured at 296 ± 2 K in the ~7000 L Teflon chamber, using a relative rate method with sufficient cyclohexane being added to the reactant mixtures to scavenge >97% of the OH radicals produced from the reactions of O_3 with the reference compound and (possibly) DVSO. *cis*-2-Butene was used in an initial experiment as the reference compound, but while 70% of the *cis*-2-butene had reacted by the end of the experiment, only 1−2% of the DVSO had reacted, leading to the upper limit to the rate constant ratio k_1/k_2 given in Table 1. Subsequent experiments used propene as the reference compound, and the experimental data are plotted in accordance with eq I in Figure 1. Least-squares analysis of these data leads to the rate constant ratio k_1/k_2 given in Table 1. The intercept in Figure 1 is within three standard deviations of zero and within the analytical measurement uncertainties for DVSO of ≤3% (the intercept corresponds to 1.7% loss of DVSO); alternatively, this small intercept could be due to a small amount of a reactive impurity which coeluted with DVSO. Note that the maximum amount of DVSO reacted in these experiments was only 13%, while up to 92% of the propene was reacted away. The measured rate constant ratios k_1/k_2 are placed on an absolute basis using rate constants at 296 K of $k_2(O_3 + cis\text{-2-butene}) = 1.22 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} and $k_2(O_3 + \text{propene}) = 9.68 \times 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1},[1] and the resulting rate constants k_1 are given in Table 2. The upper limit to the rate constant obtained using *cis*-2-butene as the reference compound is consistent with that obtained using propene as the reference compound.

TABLE 1: Rate Constant Ratios k_1/k_2 and Rate Constants k_1 for the Reactions of Divinyl Sulfoxide with O_3 and with NO_3 Radicals at 296 ± 2 K

reaction with	reference compound	k_1/k_2[a]	k_1 (cm^3 $molecule^{-1}$ s^{-1})[b]
O_3	*cis*-2-butene	<0.021	$<2.6 \times 10^{-18}$
	propene	0.044 ± 0.010	$(4.3 \pm 1.0) \times 10^{-19}$
NO_3	*trans*-2-butene	<0.022	$<9 \times 10^{-15}$
	methacrolein	0.18 ± 0.04	$(6.1 \pm 1.4) \times 10^{-16}$

[a] Indicated errors are two least-squares standard deviations. [b] Placed on an absolute basis by use of rate constants (cm^3 $molecule^{-1}$ s^{-1}) at 296 K of $k_2(O_3 + cis\text{-2-butene}) = 1.22 \times 10^{-16}$, $k_2(O_3 + \text{propene}) = 9.68 \times 10^{-18}$, $k_2(NO_3 + trans\text{-2-butene}) = 3.89 \times 10^{-13}$, and $k_2(NO_3 + \text{methacrolein}) = 3.4 \times 10^{-15}$.[1,4] The indicated errors are two least-squares standard deviations and do not include the uncertainties in the rate constants k_2.

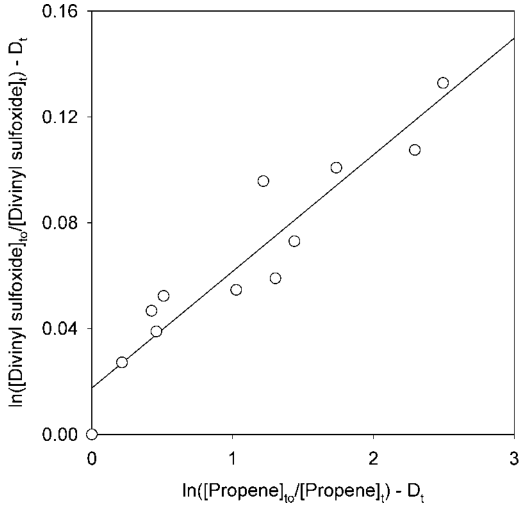

Figure 1. Plots of eq I for the reaction of O_3 with divinyl sulfoxide at 296 ± 2 K (~7000 L Teflon chamber), with propene as the reference compound. Analyses were by GC-FID.

Rate Constant for Reaction with NO_3 Radicals. Reactions of N_2O_5−NO_3−NO_2−DVSO−reference compound−air mixtures were carried out at 296 ± 2 K in the ~7000 L Teflon chamber, with GC-FID analyses of DVSO and the reference compound. *trans*-2-Butene was used as the reference compound in an initial experiment, and while at the end of the experiment 95% of the initial *trans*-2-butene had reacted, only 4% of the initial DVSO had reacted, leading to the upper-limit rate constant

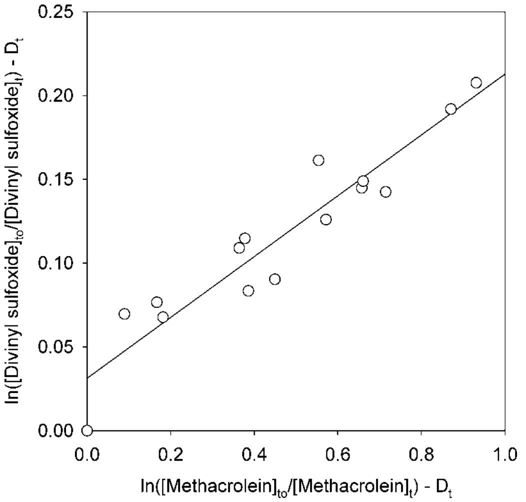

Figure 2. Plots of eq I for the reaction of NO_3 radicals with divinyl sulfoxide at 296 ± 2 K (~7000 L Teflon chamber), with methacrolein as the reference compound. Analyses were by GC-FID.

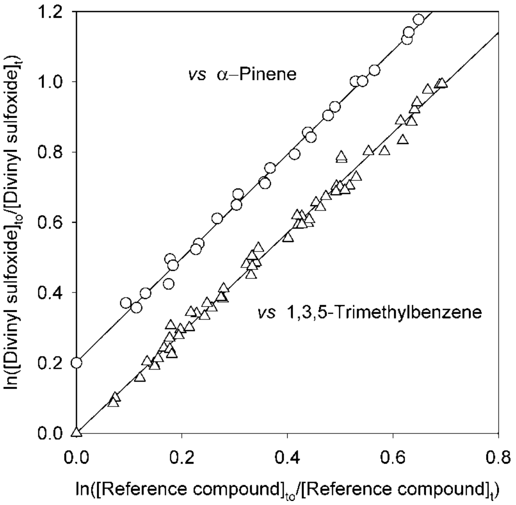

Figure 3. Plots of eq I for the reaction of OH radicals with divinyl sulfoxide at 296 ± 2 K (~7000 L Teflon chamber), with 1,3,5-trimethylbenzene and α-pinene as the reference compounds. Analyses were by GC-FID. The data with α-pinene as the reference compound have been displaced vertically by 0.2 units for clarity.

ratio listed in Table 1. Methacrolein was therefore used as the reference compound in subsequent experiments, and the data obtained are plotted in accordance with eq I in Figure 2. Least-squares analysis of these data leads to the rate constant ratio given in Table 1. The intercept in Figure 1 is just beyond three standard deviations of zero and almost within the analytical measurement uncertainties for DVSO of ≤3% (the intercept corresponds to 3.1% loss of DVSO). Alternatively, this intercept could be due to a small amount of a reactive impurity which coeluted with DVSO. This observation is similar to that for the O_3 reaction (see above).

The measured rate constant ratios k_1/k_2 are placed on an absolute basis using rate constants at 296 K of $k_2(NO_3 +$ *trans*-2-butene$) = 3.89 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} [1] and $k_2(NO_3 +$ methacrolein$) = 3.4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1},[1,4] and the resulting rate constants k_1 are given in Table 1. The upper limit to the rate constant obtained using *trans*-2-butene as the reference compound is consistent with that obtained using methacrolein as the reference compound.

Rate Constants for Reaction with OH Radicals. A series of CH_3ONO−NO−DVSO−reference compound−air irradiations were carried out in the three chambers, with α-pinene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene as the reference compounds. 1,2,4-Trimethylbenzene was used in the evacuable chamber experiment because of interferences in the IR spectrum from reaction products when 1,3,5-trimethylbenzene was used. Because the measured rate constant for the reaction of OH radicals with dimethyl sulfide shows a dependence on the O_2 concentration,[3,4] experiments were also carried out in $N_2 + O_2$ diluent with ~6 and ~78% O_2 content using 1,3,5-trimethylbenzene as the reference compound. The reaction of OH radicals with dimethyl sulfide has also been shown to be subject to secondary reactions when experiments are conducted in the presence of NO_x,[26−28] presumably due to CH_3SO_x (possibly CH_3SO_3) radicals formed from CH_3S radicals.[3] Hence, two experiments were carried out with added dimethyl sulfide (2.4×10^{13} and 2.4×10^{14} molecule cm^{-3}, the latter concentration corresponding to a similar OH radical reaction rate with dimethyl sulfide as that with DVSO) to determine if this had any effect on the rate constant for the reaction of OH radicals with DVSO. An additional experiment was carried out in the absence of NO_x, using the reaction of O_3 with 2-methyl-2-butene to generate OH radicals.[23]

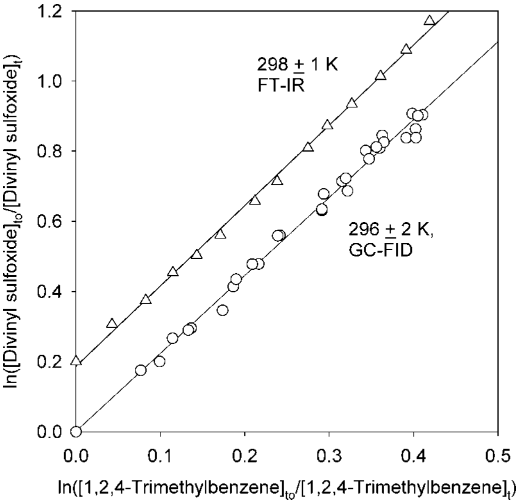

Figure 4. Plots of eq I for the reaction of OH radicals with divinyl sulfoxide at 296 ± 2 K (~7000 L Teflon chamber with analyses by GC-FID) and at 298 ± 1 K (5870 L Teflon-coated evacuable chamber with analyses by in situ FT-IR spectroscopy), both with 1,2,4-trimethylbenzene as the reference compound. The evacuable chamber data with FT-IR analyses have been displaced vertically by 0.2 units for clarity.

The experimental data are plotted in accordance with eq I in Figures 3−5, and the rate constant ratios k_1/k_2 obtained from least-squares analyses of these data are given in Table 2. These rate constant ratios k_1/k_2 are placed on an absolute basis by use of rate constants k_2 of $k_2(OH +$ α-pinene$) = 1.21 \times 10^{-11} e^{436/T}$ cm^3 molecule^{-1} s^{-1}, $k_2(OH +$ 1,2,4-trimethylbenzene$) = 3.25 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 296−298 K, and $k_2(OH +$ 1,3,5-trimethylbenzene$) = 5.67 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 296 K.[1] The resulting rate constants k_1 are given in Table 2. The room temperature rate constants obtained in the three-chamber systems with α-pinene and 1,2,4- and 1,3,5-trimethylbenzene as the reference compounds are in generally good agreement. Although there are some differences which exceed the combined two standard deviation error limits (Table 2), these are within the combined estimated ±6% overall uncertainties in each rate constant ratio measurement when the small temperature differences are taken into account.

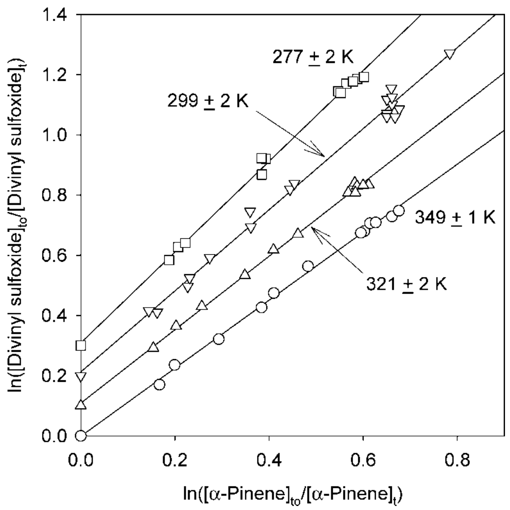

Figure 5. Plots of eq I for the reaction of OH radicals with divinyl sulfoxide at 277 ± 2, 299 ± 2, 321 ± 2, and 349 ± 1 K, with α-pinene as the reference compound. Experiments were carried out in a ~5000 L Teflon bag with analyses by GC-FID. The data at 321 ± 2, 299 ± 2, and 277 ± 2 K have been displaced vertically by 0.1, 0.2, and 0.3 units, respectively, for clarity.

As a check on the internal consistency of the rate constants used for the reference compounds, we measured the rate constant ratio *k*(OH + 1,3,5-trimethylbenzene)/*k*(OH + 1,2,4-trimethylbenzene) directly from $CH_3ONO-NO-$1,3,5-trimethylbenzene−1,2,4-trimethylbenzene−air irradiations in the ~7000 L Teflon chamber, with GC-FID analyses using both the DB-1701 and DB-5MS GC columns. The resulting data are plotted in accordance with eq I in Figure 6, together with previous data from Atkinson and Aschmann[24] (in that study, propene was used as the reference compound, and only one experiment had both 1,2,4- and 1,3,5-trimethylbenzene present in the reactant mixture). The agreement between the previous[24] and present data is excellent, with a rate constant ratio from the complete data set of *k*(OH + 1,3,5-trimethylbenzene)/*k*(OH + 1,2,4-trimethylbenzene) = 1.74 ± 0.02, where the indicated error is two least-squares standard deviations. This agrees with the rate constant ratio of 1.77 ± 0.10 derived from the rate constant ratios *k*(OH + 1,3,5-trimethylbenzene)/*k*(OH + propene) and *k*(OH + 1,2,4-trimethylbenzene)/*k*(OH + propene) determined by Atkinson and Aschmann[24] and is identical to the rate constant ratio derived from the recommended rate constants for 1,2,4- and 1,3,5-trimethylbenzene.[1] In addition, α-pinene and 1,3,5-trimethylbenzene were both present as reference compounds in a number of experiments carried out in the ~7000 L Teflon chamber at 296 ± 2 K, and the rate constant ratio *k*(OH + 1,3,5-trimethylbenzene)/*k*(OH + α-pinene) = 1.04 ± 0.04 at 296 ± 2 K (Figure 6) measured here is in good agreement with the ratio of 1.07 derived from the recommended rate constants[1] and with our previously measured values of 1.12 ± 0.02 at 296 ± 2 K[18] and 0.989 ± 0.021 at 298 ± 1 K.[21]

An Arrhenius plot of the rate constants k_1 for DVSO is shown in Figure 7. Using only the rate constants measured relative to those for α-pinene, then

$$k_1(\mathrm{OH}+\mathrm{DVSO}) =$$
$$4.06\times10^{-12}\mathrm{e}^{(858\pm141)/T}\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1} \qquad (277-349\ \mathrm{K})$$

where the indicated error is two least-squares standard deviations, and

$$k_1(\mathrm{OH}+\mathrm{DVSO}) =$$
$$7.23\times10^{-11}\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1} \qquad \text{at 298 K}$$

Using this temperature dependence to correct the rate constants measured at 296 and 299 K to 298 K, then the average 298 K rate constant obtained using all three reference compounds is

$$k_1(\mathrm{OH}+\mathrm{DVSO}) =$$
$$(7.43\pm0.71)\times10^{-11}\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1} \qquad \text{at 298 K}$$

where the error limit is two standard deviations. Combining this 298 K rate constant with the temperature dependence obtained relative to α-pinene leads to our recommended Arrhenius expression, shown as the solid line in Figure 7, of

$$k_1(\mathrm{OH}+\mathrm{DVSO}) =$$
$$4.17\times10^{-12}\mathrm{e}^{858/T}\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1} \qquad (277-349\ \mathrm{K})$$

Products of the Reaction with NO_3 Radicals. GC-MS analysis of a reacted $N_2O_5-NO_2-$DVSO−air mixture showed the presence of divinyl sulfone [$CH_2{=}CHS(O)_2CH{=}CH_2$], from matching the GC retention time and mass spectrum with those of an authentic standard. After calibration of DVSO and divinyl sulfone, analyses of the GC-FID data from the kinetic experiments provided the concentrations of divinyl sulfone formed and of DVSO reacted. Divinyl sulfone was present at concentrations of $(1.2-12)\times10^{10}$ molecule cm^{-3} in the initial prereaction analyses, compared to a maximum divinyl sulfone concentration in the postreaction analyses of 3.6×10^{11} molecule cm^{-3}. A plot of the amounts of divinyl sulfone formed against the amounts of DVSO reacted with the NO_3 radical was a good straight line, suggesting that divinyl sulfone is less reactive than DVSO toward the NO_3 radical (as is the case for dimethyl sulfone compared to dimethyl sulfoxide[9]) and that secondary reactions were relatively minor. A least-squares analysis of the data leads to a divinyl sulfone yield from the NO_3 radical reaction of 8.6 ± 2.3%, where the indicated error is two least-squares standard deviations combined with estimated overall uncertainties in the GC-FID response factors for DVSO and divinyl sulfone of ±5% each. Clearly, the reaction of NO_3 radicals with DVSO is slow, and the formation yield of divinyl sulfone from this reaction is low.

Products of the Reaction with OH Radicals. GC-MS analysis of an irradiated $CH_3ONO-NO-$DVSO−air mixture also showed the presence of divinyl sulfone. Figure 8 shows plots of the amounts of divinyl sulfone formed against the amounts of DVSO reacted with the OH radical, as obtained from GC-FID analyses of data from a series of kinetic experiments. Divinyl sulfone was not present at detectable concentrations in the preirradiation analyses. While there is no information concerning the rate constant for reaction of divinyl sulfone with OH radicals, the reasonably good straight lines in Figure 8 suggest that divinyl sulfone is less reactive than DVSO toward OH radicals and that secondary reactions were relatively minor (this is analogous to the observation that dimethyl sulfone is much less reactive than dimethyl sulfoxide toward OH radicals[9]). The data in Figure 8 show that the divinyl sulfone yield depends on the O_2 concentration, being 4.4 ± 0.6% in air (21% O_2 content), 2.5 ± 0.3% at ~6% O_2 content, and 7.7 ± 1.2% at ~78% O_2 content, where the indicated errors are two least-squares standard deviations of the slopes of the plots in Figure 8 combined with estimated uncertainties in the GC-FID response factors for DVSO and divinyl sulfone of ±5% each (note that the yields at ~6 and ~78% O_2 content are from a single experiment each).

TABLE 2: Rate Constant Ratios k_1/k_2 and Rate Constants k_1 for the Reaction of OH Radicals with Divinyl Sulfoxide

temperature (K)	chamber[a]	reference compound	k_1/k_2[b]	$10^{11} \times k_1$[c] (cm^3 molecule^{-1} s^{-1})
277 ± 2	A	α-pinene	1.51 ± 0.06	8.82 ± 0.36
296 ± 2	B	α-pinene	1.48 ± 0.04	7.81 ± 0.22
296 ± 2	B	1,3,5-trimethylbenzene	1.42 ± 0.04[d]	8.05 ± 0.23[d]
296 ± 2	B	1,2,4-trimethylbenzene	2.22 ± 0.08	7.22 ± 0.26
298 ± 1	C	1,2,4-trimethylbenzene	2.29 ± 0.06[e]	7.44 ± 0.20[e]
299 ± 2	A	α-pinene	1.35 ± 0.06	7.02 ± 0.32
321 ± 2	A	α-pinene	1.22 ± 0.04	5.74 ± 0.19
349 ± 1	A	α-pinene	1.13 ± 0.04	4.77 ± 0.17

[a] A = ~5000 L Teflon bag inside of a 5870 L evacuable chamber; B = ~7000 L Teflon chamber; C = 5870 L evacuable, Teflon-coated chamber. [b] Indicated errors are two least-squares standard deviations. Estimated overall uncertainties in these rate constant ratios are ±6%. [c] Placed on an absolute basis by use of rate constants of k_2(α-pinene) = $1.21 \times 10^{-11}e^{436/T}$ cm^3 molecule^{-1} s^{-1}, k_2(1,2,4-trimethylbenzene) = 3.25×10^{-11} cm^3 molecule^{-1} s^{-1} at 296–298 K, and k_2(1,3,5-trimethylbenzene) = 5.67×10^{-11} cm^3 molecule^{-1} s^{-1} at 296 K.[1] The indicated errors are the two least-squares standard deviations and do not include the uncertainties in the rate constants k_2, which are likely to be ~±10%. [d] Includes experiments at ~6 and ~78% O_2 content, experiments with added dimethyl sulfide, and an experiment carried out in the absence of NO_x (see text). [e] From a single experiment.

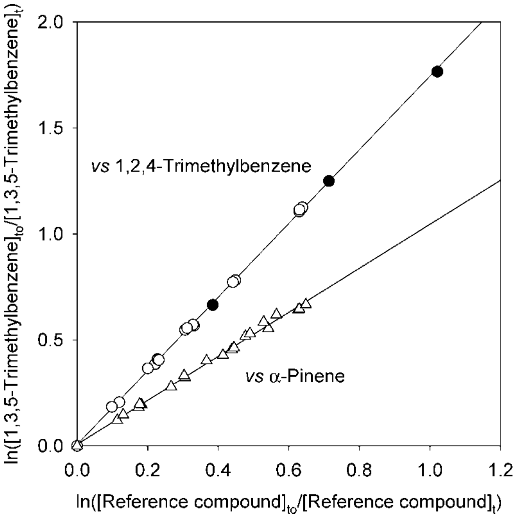

Figure 6. Plots of eq I for the reaction of OH radicals with 1,3,5-trimethylbenzene at 296 ± 2 K, with 1,2,4-trimethylbenzene and α-pinene as the reference compounds. Experiments were carried out in ~6400 or ~7000 L Teflon chambers with GC-FID analyses. ○, △: this work. ●: Atkinson and Aschmann.[24] The solid line for 1,2,4-trimethylbenzene as the reference compound is a least-squares fit to the complete data set.

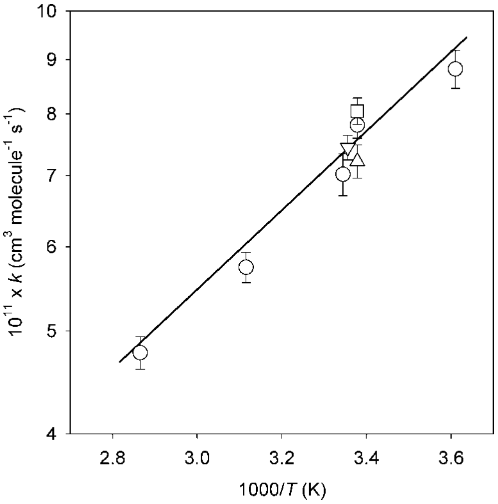

Figure 7. Arrhenius plot of rate constants for the reactions of OH radicals with divinyl sulfoxide. Rate constants are from ○ the ~5000 L Teflon bag inside of the evacuable chamber and the ~7000 L Teflon chamber, relative to α-pinene; □ the ~7000 L Teflon chamber, relative to 1,3,5-trimethylbenzene; △ the ~7000 L Teflon chamber, relative to 1,2,4-trimethylbenzene, ▽ the 5870 L evacuable chamber, relative to 1,2,4-trimethylbenzene. The solid line is our recommended Arrhenius fit (see text).

Extrapolation of these yields to the high-O_2 limit from a plot of 1/yield against 1/[O_2] suggests that there is a minor reaction pathway, accounting for ~8% of the overall reaction (i.e., α ~ 0.08), which leads to an intermediate, presumably the adduct $CH_2{=}CHS(O)(OH)CH{=}CH_2$, which then reacts with O_2 to form divinyl sulfone in competition with another process

$$\mathrm{OH} + \mathrm{DVSO} \rightarrow \alpha\ \text{adduct} \qquad (1a)$$

$$\text{adduct} + \mathrm{O_2} \rightarrow \text{divinyl sulfone} \qquad (3)$$

$$\text{adduct} \rightarrow \text{other products} \qquad (4)$$

Two irradiations of 2-propyl nitrite–NO–DVSO–air mixtures were also carried out in the evacuable chamber with in situ FT-IR analyses, showing formation of CO, CO_2, SO_2, HCHO, and divinyl sulfone. As noted above, the quantitative analysis of products and reactants by FT-IR spectroscopy was carried out by a subtractive procedure in which components were successively subtracted from the spectrum of the mixture using calibrated spectra of the gaseous reactants and known products recorded previously with the same instrument and identical spectral parameters. Minor corrections to the measured concentrations of HCHO and CO_2 were made to account for formation from the photolysis of 2-propyl nitrite,[18−20] and the HCHO concentrations were also corrected for secondary reaction with OH radicals, using a rate constant of 8.5×10^{12} cm^3 molecule^{-1} s^{-1} for HCHO[4] and the value measured here for DVSO. Any corrections for secondary reactions for CO, CO_2, or SO_2 were negligible, and the maximum correction to the measured HCHO concentration was 4.6%. Least-squares analyses of the data resulted in formation yields of 35 ± 11% for CO, 2.2 ± 0.8% for CO_2, 33 ± 4% for SO_2, 54 ± 6% for HCHO, and 5.4 ± 0.8% for divinyl sulfone, where the errors are two least-squares standard deviations combined with estimated overall uncertainties in the IR calibrations of ±5% for DVSO, ±5% for divinyl sulfone, ±5% for SO_2,[20] ±5% for HCHO,[18] ±7% for CO,[18] and ±7% for CO_2.[18] The formation yield of divinyl sulfone obtained from the experiments with in situ FT-IR analyses (5.4 ± 0.8%) agrees within the experimental uncertainties with that of 4.4 ± 0.6% in air determined from independent experiments with GC-FID analyses. This agreement suggests that artifactual formation of divinyl sulfone during the GC-FID sampling and analysis procedures was not significant.

Figure 9 illustrates spectra recorded from one of the irradiations. Trace A is the spectrum of the initial DVSO, and trace B

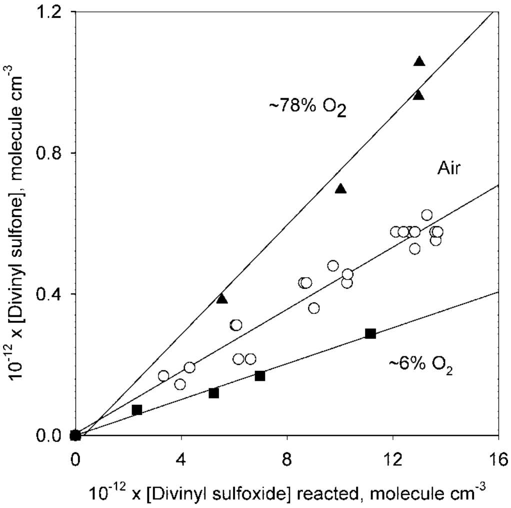

Figure 8. Plots of the amounts of divinyl sulfone formed from the reactions of OH radicals with divinyl sulfoxide in air (21% O_2 content) and in N_2-O_2 mixtures with ~6 and ~78% O_2.

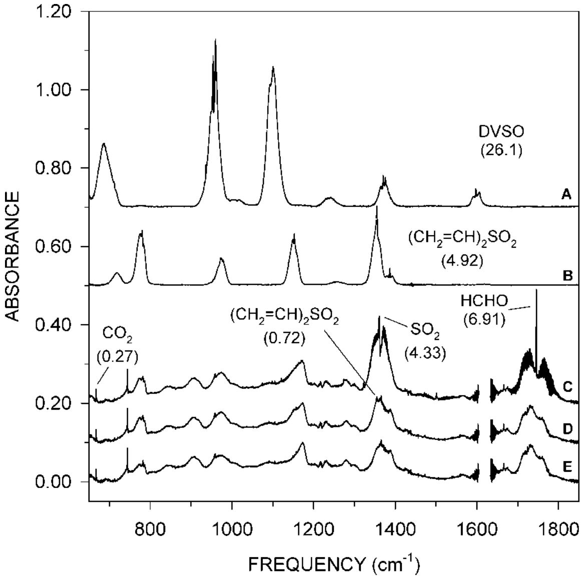

Figure 9. FT-IR spectra recorded from an irradiation of a 2-propyl nitrite−NO−divinyl sulfoxide (DVSO)−air mixture (numbers in parentheses are the concentrations in units of 10^{13} molecule cm^{-3}). Trace (A) is the spectrum of the initial DVSO; (B) is a reference spectrum of divinyl sulfone; (C) is the spectrum of products formed from DVSO after ~51% reaction, after subtraction of absorptions due to DVSO and products formed from 2-propyl nitrite and NO_x; (D) is after subtraction of the absorptions of HCHO and SO_2 from (C); and (E) is after subtraction of absorptions of divinyl sulfone from (D).

is a reference spectrum of divinyl sulfone, where the numbers in parentheses are the concentrations in units of 10^{13} molecule cm^{-3}. Trace C is the spectrum of products attributed to arise from DVSO after ~51% reaction of the initial DVSO (i.e., absorptions of the parent compound and of products formed from 2-propyl nitrite and NO_x have been subtracted). Trace D is obtained after subtraction of the absorptions of HCHO and SO_2 from C, revealing the presence of a detectable amount of divinyl sulfone. Subtraction of absorptions due to divinyl sulfone from D leaves a significant set of absorptions by unidentified products in trace E. By comparison of residual spectra such as E at different times of the reaction, it was possible to derive two qualitative sets of absorptions. One of these is composed of three distinct absorption bands at 1740, 1365, and 1217 cm^{-1}, which are most likely from a single product which increased in concentration at longer irradiation times (i.e., with the extent of reaction). The presence of these frequencies at 1740 (C=O bond stretch), 1365 (region of $=CH_2$ "scissor" motion), and 1217 cm^{-1} (consistent with an "influenced" S=O bond stretch) makes possible a tentative assignment to $CH_2{=}CHS(O)CHO$, a product which is predicted on the basis of plausible reaction mechanisms (see below). The shift in the vapor-phase S=O stretch frequency to a higher position relative to those in DVSO (~1100 cm^{-1})[29] and dimethyl sulfoxide (1101 cm^{-1})[30] is consistent with the presence of an electron-withdrawing aldehyde group in $CH_2{=}CHS(O)CHO$. The other set of absorptions indicates other unidentified carbonyl-containing products from DVSO.

Aerosol formation was measured during $CH_3ONO-NO-$air irradiations of DVSO, DVSO + α-pinene, and α-pinene carried out in the ~7000 L Teflon chamber at 296 ± 2 K. The initial reactant concentrations and experimental procedures were as those in the kinetic experiments, with three irradiation periods and GC-FID analyses of DVSO and/or α-pinene before and after each irradiation period. The fraction of the initially present DVSO and/or α-pinene reacted by the end of the experiments was DVSO alone, 46−50%; DVSO + α-pinene, 50−64 and 38−53%, respectively; and α-pinene alone, 31%. Aerosol number and size distribution were measured during the experiments using a TSI 393672L scanning mobility particle sizer (SMPS). The aerosol loadings prior to beginning the irradiations and with all of the reactants present in the chamber were in the range of 4−38 μg m^{-3} (4 μg m^{-3} for both DVSO experiments and one of the two DVSO + α-pinene experiments). The SMPS data showed that new particle formation occurred during the first irradiation period in one of the two DVSO alone experiments and in the DVSO + α-pinene experiment with the lowest initial aerosol loading, with the increase in aerosol mass during the second and third irradiation periods being due to the growth of existing particles. In the other experiments (one DVSO alone, the α-pinene alone, and the DVSO + α-pinene experiment with the highest initial aerosol loading), the increase in aerosol mass during all three irradiation periods was due to the growth of existing particles. Assuming that the aerosol had the same density as the reactants, the aerosol yield at the end of the reaction was 1.5% for the DVSO alone experiments, and within the measurement uncertainties, the aerosol yield was constant throughout each experiment. Clearly, aerosol formation in the OH radical-initiated reaction of DVSO was minor. The aerosol yield at the end of the α-pinene alone experiment was 8−9%. However, factors of ~3−6 higher amounts of aerosol were formed in the DVSO + α-pinene experiments if the aerosol yields from DVSO alone and α-pinene alone were additive.

Discussion

While DVSO reacts slowly with O_3 with a rate constant at 296 ± 2 K of 4.3 × 10^{-19} cm^3 $molecule^{-1}$ s^{-1} (Table 1), only an upper limit to the rate constant of <1 × 10^{-19} cm^3 $molecule^{-1}$ s^{-1} at 295 ± 2 K has been reported for the reaction of dimethyl sulfoxide with O_3.[9] Our observation of a reaction of DVSO with O_3, with a rate constant a factor of ~3−4 lower than that for ethene,[1] suggests that the reaction of O_3 with DVSO occurs at the C=C bonds and that the C=C bonds in DVSO are of roughly similar reactivity as those in ethene. In contrast to the O_3 reaction, DVSO is markedly less reactive than dimethyl sulfoxide toward NO_3 radicals, with room-temperature rate constants of 6.1 × 10^{-16} (Table 1) and ~2 × 10^{-13} cm^3 $molecule^{-1}$ s^{-1},[5,9] respectively. Again, the rate constant for the reaction of DVSO with NO_3 radicals is of similar magnitude to that for ethene,[1] possibly suggesting that the NO_3 radical reaction with DVSO proceeds mainly by addition to the C═C bonds. This would be in contrast to the NO_3 radical reaction with dimethyl sulfoxide, which is believed to react mainly by addition to the S atom and form dimethyl sulfone as the only observed product, in 10−94% yield.[9]

The measured rate constant for the reaction of OH radicals with DVSO, of 7.43×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298 K, is invariant of O_2 content (∼6−78%), the presence of dimethyl sulfide, and the presence or absence of NO_x. The magnitude of this rate constant, together with the negative temperature dependence, indicates that the reaction proceeds by initial OH radical addition. The rate constants for the reactions of OH radicals with DVSO and dimethyl sulfoxide both have similar room temperature rate constants (7.4×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for DVSO and $\sim 8 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} for dimethyl sulfoxide[5,6,8,9,12]) and negative temperature dependencies ($E/R = -858 \pm 141$ K for DVSO and -800 ± 540 K for dimethyl sulfoxide[6]). Experimental[8,10,12] and theoretical[11,13] studies of the reaction of OH radicals with dimethyl sulfoxide indicate that the reaction proceeds by initial OH radical addition to the S atom to form an adduct, which then decomposes to $CH_3S(O)OH$ (methanesulfinic acid) plus CH_3

$$OH + CH_3S(O)CH_3 \leftrightarrow [CH_3S(O)(OH)CH_3] \rightarrow CH_3S(O)OH + CH_3 \quad (5)$$

In the case of DVSO, the OH radical reaction could proceed by initial addition to the S atom to form the adduct $CH_2{=}CHS(O)(OH)CH{=}CH_2$ and/or by addition to the carbons of the C═C bonds to form the radicals $CH_2{=}CHS(O)C^{\bullet}HCH_2OH$ and $CH_2{=}CHS(O)CH(OH)C^{\bullet}H_2$. Presumably, reaction of the $CH_2{=}CHS(O)(OH)CH{=}CH_2$ adduct with O_2 leads in part to formation of divinyl sulfone, and extrapolation of our GC-FID data to limiting high O_2 concentration suggests that this accounts for ∼8% of the overall OH radical reaction. The carbon-centered radicals formed after OH radical addition to the C═C bonds are anticipated to form, after addition of O_2 and reaction with NO, the $CH_2{=}CHS(O)CH(O^{\bullet})CH_2OH$ and $CH_2{=}CHS(O)CH(OH)CH_2O^{\bullet}$ alkoxy radicals. By analogy with simple alkoxy radicals formed from alkanes, these may be expected to react by

$$CH_2{=}CHS(O)CH(O^{\bullet})CH_2OH \rightarrow CH_2{=}CHSO + HOCH_2CHO \quad (6a)$$

$$CH_2{=}CHS(O)CH(O^{\bullet})CH_2OH \rightarrow CH_2{=}CHS(O)CHO + {}^{\bullet}CH_2OH \quad (6b)$$

$${}^{\bullet}CH_2OH + O_2 \rightarrow HCHO + HO_2 \quad (7)$$

and

$$CH_2{=}CHS(O)CH(OH)CH_2O^{\bullet} \rightarrow CH_2{=}CHS(O)C^{\bullet}HOH + HCHO \quad (8)$$

$$CH_2{=}CHS(O)C^{\bullet}HOH + O_2 \rightarrow CH_2{=}CHS(O)CHO + HO_2 \quad (9)$$

If the $CH_2{=}CHSO$ radical is formed, it may ultimately lead to $CH_2{=}C^{\bullet}H + SO_2$, with the vinyl radical reacting with O_2 to form HCHO + CO. However, since $HOCH_2CHO$ was not observed in the FT-IR analyses, reaction 6a cannot occur to any significant extent. The products observed and quantified in air account for 38 ± 5% of the sulfur and 28 ± 4% of the carbon reacted, and aerosol formation (1.5%) increases these numbers only very slightly. Obviously, a large fraction of the reaction products is presently not accounted for.

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