ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Photochemistry and Photobiology A: Chemistry 157 (2003) 311–319

Journal of
Photochemistry
and
Photobiology
A:Chemistry

www.elsevier.com/locate/jphotochem

Temperature-dependent kinetics studies of aqueous phase reactions of SO_4^- radicals with dimethylsulfoxide, dimethylsulfone, and methanesulfonate

Lei Zhu [a], J.M. Nicovich [b], P.H. Wine [a,b,*]

[a] *School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332, USA*
[b] *School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332, USA*

Received 7 March 2002; received in revised form 9 June 2002; accepted 9 June 2002

Abstract

A laser flash photolysis-long path UV-Vis absorption technique has been employed to investigate the aqueous phase reactions between the SO_4^- radical and three organic sulfur species of atmospheric interest, dimethylsulfoxide (DMSO; $CH_3S(O)CH_3$), dimethylsulfone (DMSO2; $CH_3(O)S(O)CH_3$), and methanesulfonate (MS; $CH_3(O)S(O)O^-$). Rate coefficients at $T = 298$ K in units of $M^{-1}\,s^{-1}$ are found to be $(3.0 \pm 0.4) \times 10^9$ for DMSO, $<(3.9 \pm 0.5) \times 10^6$ for DMSO2, and $(1.1 \pm 0.3) \times 10^4$ for MS (zero ionic strength limit); reported uncertainties are estimates of accuracy at the 95% confidence level. Temperature-dependent studies have been carried out over the range 278–311 K; activation energies in units of $kJ\,mol^{-1}$ are found to be 12.0 ± 0.4 for DMSO, 11.3 ± 1.3 for DMSO2 and 20.7 ± 4.3 for MS (zero ionic strength limit), where uncertainties are 2σ and represent precision only. Accuracies of rate coefficients measured at the temperature extremes of our study are thought to be similar to those reported above for the 298 K rate coefficients. The implications of the kinetics results for understanding the atmospheric sulfur cycle are discussed.

Keywords: DMS; DMSO; DMSO2; MS; SO_4^-; Heterogeneous reactions; Aqueous phase; Laser flash photolysis; Reaction kinetics; Temperature dependence

1. Introduction

Dimethylsulfide (DMS, CH_3SCH_3) is the primary reduced sulfur compound emitted into the atmosphere. It is estimated that oceanic emissions of DMS account for about 15% of the atmospheric sulfur burden [1]. The free radical initiated oxidation of gas phase DMS can result in production of a number of relatively stable sulfur-containing products including dimethylsulfoxide (DMSO; $CH_3S(O)CH_3$), dimethylsulfone (DMSO2; $CH_3(O)S(O)CH_3$), methanesulfinic acid (MSIA; $CH_3S(O)OH$), methanesulfonic acid (MSA; $CH_3(O)S(O)OH$), SO_2 and sulfuric acid (H_2SO_4; $HO(O)S(O)OH$) [2]. If given time to equilibrate with the atmospheric condensed phase, all of the above DMS oxidation products are partitioned primarily (or almost exclusively in the cases of MSA and H_2SO_4) into the condensed phase [3–12]. As a result, condensed phase transformations are potentially important in the atmospheric sulfur cycle.

As first proposed by Charlson et al. [13], DMS oxidation may play an important role in modifying or regulating global climate. Currently, there is considerable interest in understanding the details of atmospheric sulfur oxidation in order to facilitate (1) our understanding of past climate as interpreted from ice core analyses; (2) the role sulfur compounds play in particle formation and growth in the atmosphere and its impact on current and future climate; and (3) the use of field observations of MS-to-NSS ratios (MS: methanesulfonate, $CH_3(O)S(O)O^-$; NSS: non-sea-salt sulfate) to infer the relative amounts of natural versus anthropogenic sulfur in atmospheric particulate matter.

As mentioned above, model studies and field observations have demonstrated that condensed phase processes play an important role in the atmospheric sulfur cycle [10–14]. Published studies of aqueous phase reactions of organic sulfur compounds with important atmospheric oxidants have been motivated by the interesting mechanistic behavior exhibited as well as by the desire to understand atmospheric chemical transformations. The available data base includes two studies that have demonstrated the atmospheric importance of the $O_3 + DMS$ reaction [15,16] as well as one study each of the reactions of DMS with OH [17], Cl_2^- [18], Br_2^- [18] and a series of hydroperoxides [19]. The DMSO data base includes two studies of the $O_3 + DMSO$ reaction (which show

---

[*] Corresponding author. Fax: +1-404-894-5638.
E-mail address: paul.wine@chemistry.gatech.edu (P.H. Wine).

1010-6030/03/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S1010-6030(03)00064-9

this reaction to be very slow) [15,20], one study of DMSO reactions with a series of hydroperoxides [19], two studies of the OH + DMSO reaction [21,22], and one study each of the reactions of DMSO with SO_4^- [23] and Cl_2^- [24]. One study of the OH + DMSO2 reaction is reported in the literature [22], as is one study of the reaction of methanesulfinate (MSI; $CH_3S(O)O^-$) with SO_4^- [25]. There have been two studies of the MSI + OH reaction [25,26] and three studies of the OH + MS reaction [22,27,28]; interestingly, the rate coefficients reported in the three studies of the potentially important (in atmospheric chemistry) OH + MS reaction are in very poor agreement with each other. In addition to the aqueous phase studies mentioned above, the NO_3 + DMS [29], NO_3 + DMSO [29], and Cl + DMS [30] reactions have been studied in non-aqueous solvents. All kinetic data reported to date have been obtained at room temperature.

As part of a research program aimed at developing a detailed understanding of DMS oxidation and its role in the global climate system, we are investigating the aqueous phase reactions between radicals commonly found in the atmospheric condensed phase (OH, SO_4^-, Cl_2^-, Br_2^-, and NO_3) and organic sulfur compounds of atmospheric interest. In this paper we report the results of a kinetics study of SO_4^- reactions with DMSO, DMSO2, and MS.

$$SO_4^- + CH_3S(O)CH_3 \rightarrow \text{products} \qquad (R1)$$

$$SO_4^- + CH_3(O)S(O)CH_3 \rightarrow \text{products} \qquad (R2)$$

$$SO_4^- + CH_3(O)S(O)O^- \rightarrow \text{products} \qquad (R3)$$

To our knowledge, this represents the first kinetics study of R2 and R3, and the first study of the temperature dependence of rate coefficients for any potentially important atmospheric reactions of free radicals with organic sulfur species. The implications of our results for understanding atmospheric sulfur chemistry are discussed.

2. Experimental technique

The experimental approach involved coupling SO_4^- production by laser flash photolysis (LFP) of peroxydisulfate ($S_2O_8^{2-}$) with sensitive time-resolved detection of SO_4^- by multipass absorption spectroscopy at $\lambda \sim 445$ nm. A schematic diagram of the apparatus is shown in Fig. 1. It consists of an excimer laser photolysis light source, a xenon arc lamp probe light source, optics to direct the photolysis and probe beams including a set of White cell optics [31] for obtaining multiple passes of the probe beam through the photolyzed region of the sample, a Teflon reactor and liquid flow system, a monochromator to isolate the probe wavelength, an oscilloscope to record the temporal evolution of the transmitted probe radiation immediately before and after each laser flash, a photodiode to detect the laser flash and trigger the oscilloscope, a computer connected to the oscilloscope to store and average the waveforms from the oscilloscope, a thermostated bath to control the temperature of the liquid reservoir, and a Teflon-coated thermocouple to measure the temperature of the liquid in the reactor. Important features of the methodology include the following:

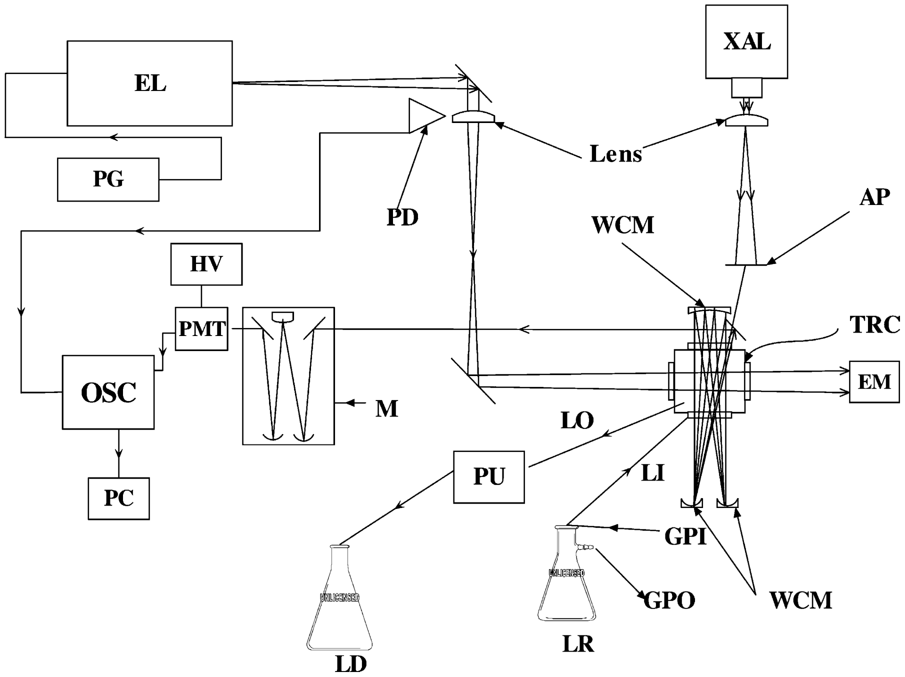

Fig. 1. Schematic diagram of the apparatus. AP, aperture; EL, excimer laser; EM, energy monitor; GPI, gas purge in; GPO, gas purge out; HV, high voltage; LD, liquid dump; LI, liquid input; LO, liquid output; LR, liquid reservoir; M, monochromator; OSC, oscilloscope; PC, personal computer; PD, photodiode; PG, pulse generator; PMT, photomultiplier; PU, pump; TRC, Teflon reaction cell; WCM, White cell mirror; XAL, xenon arc lamp.

(1) Reactive intermediates are probed in “real-time”, i.e. on time scales corresponding to their lifetimes under the experimental conditions employed (10^{-6} to 10^{-2} s); and (2) very low radical concentrations (5–100 nM) are employed. These two features eliminate many potential side reactions that could seriously complicate the interpretation of kinetic data. The experimental methodology was first developed in our laboratory in the late 1980s, and has been employed successfully in several previous studies of aqueous phase free radical kinetics [32–36].

The photolysis laser employed in this study was a Lambda Physik Compex 102 excimer laser operating with a KrF gas fill ($\lambda = 248$ nm, pulsewidth $= 2.5 \times 10^{-8}$ s). The laser fluence at the entrance to the reaction cell was typically 1.5×10^{16} photons cm^{-2} per pulse. In all experiments, the White cell was adjusted to give 46 passes of the probe radiation through the region of the reactor irradiated by the excimer laser, giving an absorption path length of ∼115 cm. With an electronic time constant of 1 μs, the detection limit is about 0.03% absorption (64 flashes averaged); assuming a peak (445 nm [33]) SO_4^- extinction coefficient of ∼1400 M^{-1} cm^{-1} [33], this gives a detection limit of $\sim 2 \times 10^{-9}$ M.

The stated minimum purities of the chemicals used in this study are as follows: sodium peroxydisulfate, 98%; sodium methane sulfonate, 98%; DMSO2, 98%; DMSO, 99.9%; all of these chemicals were used without further purification. The water used for preparing solutions was purified by a Millipore Milli-Q system equipped with filters to remove particles, ions and organics. All solutions were unbuffered with pH in the 5–6 range. Solutions were prepared in Pyrex volumetric flasks and were stored in 4 l Pyrex flasks. During experiments, the solutions were pumped through the reactor at a typical flow rate of 2.5 cm^3 s^{-1} without recycling. The laser repetition rate was 0.03 Hz and the reactor volume was ∼55 cm^3; hence no aliquot of solution was subjected to more than one laser flash. All reported kinetic data were obtained using air saturated solutions, as preliminary experiments showed that data obtained using N_2-saturated solutions gave identical results to data obtained using air saturated solutions. In most experiments, solutions were used immediately after preparation, although kinetics results for all three reactions were found to be unaffected by allowing the solution to sit for 1 h before being used in an experiment.

3. Results and discussion

The absorption spectrum of SO_4^- is well known [33,37–46]; it consists of a relatively strong band with peak absorbance around 445 nm and a weaker overlapping band with peak absorbance around 330 nm. As mentioned above, the extinction coefficient at the peak wavelength of the strong band is about 1400 M^{-1} cm^{-1} [33]. It is well-documented in the literature that UV photolysis of the peroxydisulfate anion results in production of sulfate radical with high yield:

$$S_2O_8^{2-} + h\nu(248\,\text{nm}) \rightarrow 2SO_4^- \tag{R4}$$

Under the experimental conditions employed, the rate of loss of SO_4^- by reaction with $S_2O_8^{2-}$ is negligibly slow compared to the rate of loss of SO_4^- by reaction with water [33,46]:

$$SO_4^- + H_2O \rightarrow HSO_4^- + OH \tag{R5}$$

At 298 K, $k_{R5} = 400 \pm 100\,\text{s}^{-1}$ [33,46], and, in agreement with two published studies [45,46], the results reported in this study suggest that k_{R5} increases a little as a function of temperature over the range 278–311 K (see Tables 1–3).

All experiments were carried out under pseudo-first-order conditions with the stable reactant (DMSO, DMSO2, or MS) in large excess over SO_4^-. Concentrations of SO_4^- were kept small enough that the recombination reaction,

$$2SO_4^- \rightarrow S_2O_8^{2-} \tag{R6}$$

was an insignificant removal process even though this reaction proceeds at a near-diffusion-controlled rate [33,44–47]. Hence, observed absorption temporal profiles could be analyzed using simple first-order kinetics:

$$A = \log\left(\frac{I_0}{I}\right) = \varepsilon l[SO_4^-] \tag{1}$$

$$\ln\left(\frac{A_0}{A_t}\right) = \left\{k_{Ri}[Ri] + \sum_j (k_{M_j}[M_j]) + k_{bg}\right\} t \equiv k't \qquad (i = 1\text{–}3) \tag{2}$$

In Eq. (1), I_0 and I are the transmitted probe light intensities in the absence and presence of SO_4^-, A is the absorbance, ε the SO_4^- extinction coefficient at the probe wavelength, and l is the absorption path length. In Eq. (2), k_{bg} is the background first-order SO_4^- loss rate in the absence of added organic sulfur compound reactant Ri (dominated by R5 with a small contribution from reactions of SO_4^- with solvent impurities), k_{Ri} the bimolecular rate coefficient for Ri, k' the measured pseudo-first-order SO_4^- decay rate, M_j the jth impurity in the Ri sample, and k_{M_j} the rate coefficient for reaction of SO_4^- with M_j.

As predicted by Eq. (2), exponential SO_4^- decays were observed for all three reactions investigated, and linear dependencies of k' on reactant concentration were observed in the studies of R1 and R2. For all three reactions studied, observed SO_4^- decay rates were found to be invariant to changes in photolysis laser power and $S_2O_8^{2-}$ concentration. Typical kinetic data obtained in the study of R1 are shown in Figs. 2 and 3, and all kinetic data are summarized in Tables 1–3.

Since R3 involves two negatively charged reactants, k_{R3} is expected to increase with increasing solution ionic strength. Furthermore, since R3 is quite slow, the ionic strength of the solutions employed to study R3 increased with increasing

Table 1
Summary of kinetic data for the DMSO + SO_4^- reaction (R1)

T (K)	$[S_2O_8^{2-}]$ (10^{-4} M)	[DMSO] (10^{-6} M)	A_0[a]	k' (s^{-1})	$k_{R1} \pm 2\sigma$[b] ($10^9\ M^{-1}\ s^{-1}$)
278	0.988	0	0.024	311	2.10 ± 0.30
278	0.988	0.953	0.024	2040	
278	0.988	1.91	0.024	4320	
278	0.988	2.86	0.022	6660	
278	0.988	3.81	0.020	8840	
278	0.988	4.77	0.024	11000	
278	1.29	0	0.040	267	
278	1.29	1.46	0.040	3280	
278	1.29	3.64	0.029	8510	
278	1.29	7.29	0.030	14500	
278	1.29	8.75	0.030	19100	
287	0.988	0	0.023	358	2.52 ± 0.15
287	0.988	0.952	0.024	2390	
287	0.988	1.90	0.021	5200	
287	0.988	2.86	0.020	8010	
287	1.53	0	0.029	392	
287	1.53	0.728	0.027	2010	
287	1.53	1.46	0.023	4140	
287	1.53	2.19	0.026	5810	
287	1.53	2.91	0.025	7800	
287	1.53	3.64	0.025	9000	
294	1.60	0	0.042	378	2.78 ± 0.12
294	1.60	1.58	0.040	4770	
294	1.60	3.16	0.041	8880	
294	1.60	4.74	0.038	13800	
294	1.60	6.32	0.036	18300	
294	1.60	7.90	0.039	21600	
294	1.55	0	0.040	450	
294	1.55	2.40	0.041	5350	
294	1.55	4.80	0.038	12900	
294	1.55	7.20	0.039	20000	
294	1.55	9.60	0.035	27000	
298	1.29	0	0.036	400	3.00 ± 0.07
298	1.29	0.727	0.033	2260	
298	1.29	2.18	0.029	6630	
298	1.29	3.63	0.032	11200	
298	1.29	6.18	0.035	18300	
298	1.29	7.27	0.032	22100	
298	1.53	0	0.039	432	
298	1.53	0.950	0.034	2960	
298	1.53	1.90	0.032	5840	
298	1.53	2.85	0.030	8920	
298	1.53	3.80	0.034	11800	
298	1.53	5.09	0.030	16100	
308	1.29	0	0.052	498	3.47 ± 0.11
308	1.29	1.45	0.045	4640	
308	1.29	3.62	0.049	12300	
308	1.29	5.07	0.053	17700	
308	1.29	7.25	0.039	25600	
308	0.988	0	0.033	548	
308	0.988	0.947	0.034	3100	
308	0.988	1.90	0.032	6250	
308	0.988	2.84	0.026	10000	
308	0.988	3.79	0.028	12900	

[a] A_0: the SO_4^- absorbance immediately after the laser flash, i.e. when SO_4^- production is complete but no significant SO_4^- decay has occurred.

[b] Uncertainties represent precision only.

Table 2
Summary of kinetic data for the DMSO2 + SO_4^- reaction (R2)

T (K)	$[S_2O_8^{2-}]$ (10^{-4} M)	[DMSO2] (10^{-4} M)	A_0[a]	k' (s^{-1})	$k_{R2} \pm 2\sigma$[b] ($10^6\ M^{-1}\ s^{-1}$)
279	1.16	0	0.033	341	2.85 ± 0.33
279	1.16	2.46	0.032	980	
279	1.16	4.92	0.026	1910	
279	1.16	7.39	0.026	2520	
279	1.16	9.85	0.025	3180	
279	1.26	0	0.027	301	
279	1.26	3.15	0.056	1040	
279	1.26	6.31	0.032	2170	
279	1.26	9.46	0.024	3430	
279	1.26	12.6	0.03	3580	
286	1.26	0	0.029	353	3.29 ± 0.20
286	1.26	2.04	0.029	870	
286	1.26	4.08	0.028	1470	
286	1.26	6.13	0.024	2280	
286	1.26	8.17	0.027	2900	
286	1.26	10.1	0.026	3850	
289	1.26	0	0.033	308	3.43 ± 0.15
289	1.26	2.04	0.026	980	
289	1.26	4.08	0.026	1670	
289	1.26	6.12	0.026	2470	
289	1.26	8.16	0.025	3070	
294	1.58	0	0.028	387	3.73 ± 0.17
294	1.58	18.7	0.029	6130	
294	1.58	42.2	0.027	14900	
294	1.58	61.6	0.028	23300	
294	1.58	0	0.032	348	
294	1.58	10.3	0.031	4010	
294	1.58	25.7	0.029	10000	
294	1.58	35.9	0.029	14200	
294	1.57	0	0.035	364	
294	1.57	9.19	0.033	3790	
294	1.57	18.4	0.036	7250	
294	1.57	36.7	0.033	13200	
294	1.57	55.1	0.030	21700	
298	1.16	0	0.028	394	3.88 ± 0.17
298	1.16	2.46	0.027	1140	
298	1.16	4.91	0.026	2130	
298	1.16	7.37	0.026	3190	
298	1.16	9.82	0.023	4120	
298	1.16	12.3	0.024	5040	
298	1.53	0	0.042	443	
298	1.53	3.15	0.035	1350	
298	1.53	6.29	0.035	2430	
298	1.53	9.43	0.035	3780	
298	1.53	12.6	0.035	5120	
298	1.53	15.7	0.032	6500	

[a] A_0: the SO_4^- absorbance immediately after the laser flash, i.e. when SO_4^- production is complete but no significant SO_4^- decay has occurred.

[b] Uncertainties represent precision only.

[MS]. In relatively low ionic strength solutions such as those employed in this study, the following relationship is approximately obeyed if both reactants are singly charged [48]:

$$\log k = \log k^0 + \frac{2X\mu^{1/2}}{1+\mu^{1/2}} \tag{3}$$

Table 3
Summary of kinetic data for the MS + SO_4^- reaction (R3)

T (K)	$[S_2O_8^{2-}]$ (10^{-4} M)	[MS] (M)	A_0[a]	k' (s^{-1})	($k' - k_{bg}$) (s^{-1})	$(k' - k_{bg})_0$[b] (s^{-1})	$k^0_{R3} \pm 2\sigma$[c] ($10^3\ M^{-1}\ s^{-1}$)
293	1.58	0	0.050	343	0	0	9.59 ± 0.53
293	1.58	0.0105	0.047	458	115	92	
293	1.58	0.0149	0.046	516	173	134	
293	1.58	0.0275	0.050	704	361	259	
293	1.53	0	0.040	436	0	0	
293	1.53	0.0083	0.037	517	81	66	
293	1.53	0.0166	0.035	654	218	167	
293	1.53	0.0249	0.035	762	326	237	
298	1.26	0	0.028	419	0	0	10.9 ± 0.7
298	1.26	0.0115	0.027	592	173	137	
298	1.26	0.0209	0.028	743	324	240	
298	1.26	0.0317	0.029	913	494	346	
304	1.26	0	0.028	513	0	0	13.7 ± 0.9
304	1.26	0.0117	0.026	715	202	160	
304	1.26	0.0220	0.025	954	441	324	
304	1.26	0.0315	0.024	1150	637	446	
304	1.26	0.0409	0.025	1340	827	551	
311	1.16	0	0.022	469	0	0	15.4 ± 1.1
311	1.16	0.0122	0.022	750	281	221	
311	1.16	0.0335	0.023	1250	781	539	
311	1.16	0.0428	0.022	1470	1000	664	

[a] A_0: the SO_4^- absorbance immediately after the laser flash, i.e. when SO_4^- production is complete but no significant SO_4^- decay has occurred.
[b] $(k' - k_{bg})_0 \equiv (k' - k_{bg})$ in the zero ionic strength limit.
[c] Uncertainties represent precision only.

where k^0 is the rate coefficient in the limit of zero ionic strength, μ the ionic strength,

$$\mu = 0.5\sum_i (z_i^2[i]), \tag{4}$$

X is a collection of constants with values in water solvent that range from 0.492 at 278 K to 0.522 at 311 K [49], and z_i is the charge of species i. Analysis of our data for R3 employed Eq. (3) to convert each measured value of ($k' - k_{bg}$) to an appropriate value for the limit where $\mu \to 0$, thus allowing evaluation of the bimolecular rate coefficients $k^0_{R3}(T)$. Uncorrected and corrected values of ($k' - k_{bg}$) for data obtained at $T = 293$ K are plotted as a function of [MS] in Fig. 4.

Arrhenius plots for R1–R3 are shown in Fig. 5. Linear least-squares analyses of the $\ln k_{Ri}$ versus $1/T$ data give the following Arrhenius expressions (units are $M^{-1}\ s^{-1}$):

$$\ln k_{R1} = (26.643 \pm 0.161) - \frac{1440 \pm 100}{T} \qquad (A = 3.7 \times 10^{11})$$

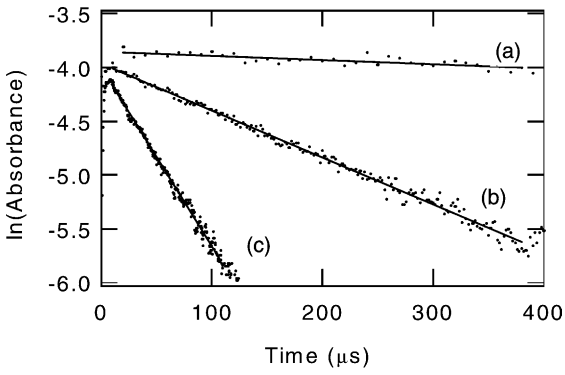

Fig. 2. Typical plots of ln(absorbance) vs. time. Reaction: $SO_4^- + DMSO$. Experimental conditions: $T = 294$ K; $[S_2O_8^{2-}] = 1.60 \times 10^{-4}$ M; [DMSO] = (a) 0, (b) 1.58×10^{-6} M, (c) 6.32×10^{-6} M; solid lines are obtained from least-square analyses which give the following pseudo-first-order decay rates (k'): (a) 378 s^{-1}, (b) 4770 s^{-1}, (c) 18,300 s^{-1}.

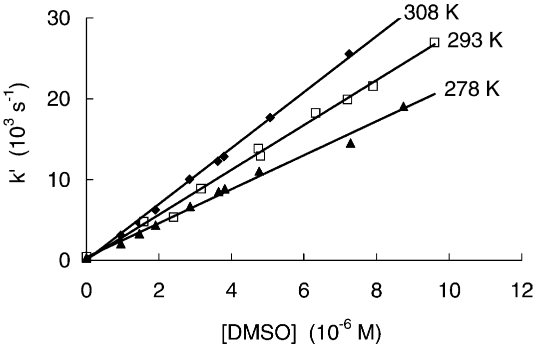

Fig. 3. Plots of k' vs. [DMSO] for data obtained at three different temperatures. Solid lines are obtained from linear least-square analyses. The following bimolecular rate coefficients are obtained from the slopes of the solid lines (units are $10^9\ M^{-1}\ s^{-1}$): 2.10±0.12 at 278 K; 2.77±0.12 at 294 K; 3.47±0.11 at 308 K. Uncertainties are 2σ and represent precision only.

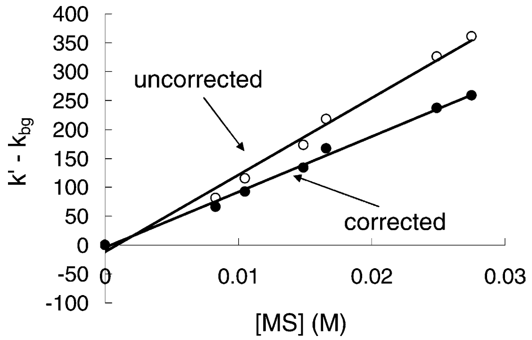

Fig. 4. Plots of uncorrected $(k'-k_{bg})$ and corrected $(k'-k_{bg})_0$ vs. [MS] for data obtained at 293 K. Solid lines are obtained from linear least-square analyses. From the slopes of the solid lines, the uncorrected data give $k_{R3} = (1.33 \pm 0.10) \times 10^4\,M^{-1}\,s^{-1}$ whereas the data corrected to zero ionic strength give $k^0_{R3} = (9.59 \pm 0.53) \times 10^3\,M^{-1}\,s^{-1}$. Uncertainties are 2σ and represent precision only.

$$\ln k_{R2} = (19.754 \pm 0.550) - \frac{1360 \pm 160}{T} \quad (A = 3.8 \times 10^8)$$

$$\ln k^0_{R3} = (17.684 \pm 1.711) - \frac{2490 \pm 520}{T} \quad (A = 4.8 \times 10^7)$$

Uncertainties in the above expressions are 2σ and refer to the precision of the Arrhenius parameters only. Potential effects of systematic errors on the measured rate coefficients are discussed below.

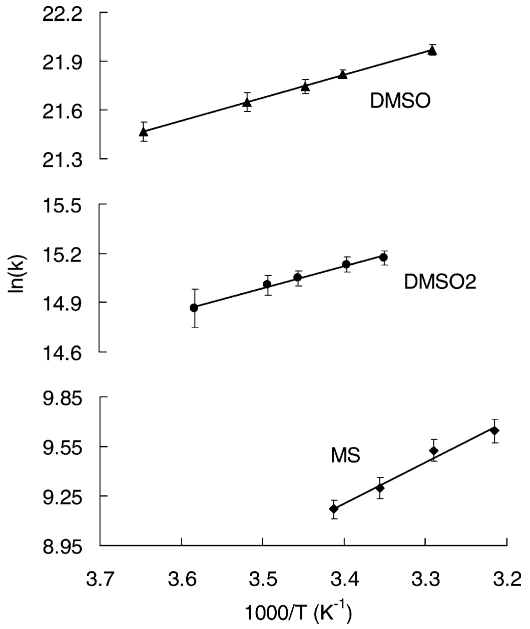

Fig. 5. Arrhenius plots for SO_4^- reactions with DMSO, DMSO2 and MS. Solid lines are obtained from least-square analyses which yield the Arrhenius expressions shown in the text.

The only kinetic study reported in the literature for R1–R3 is a room temperature measurement of k_{R1} by Kishore and Asmus [23] which was carried out using pulse radiolysis techniques; these authors report a rate coefficient of $(2.7 \pm 0.3) \times 10^9\,M^{-1}\,s^{-1}$, which is in excellent agreement with the result obtained in this study (see Table 1). The SO_4^- radical is a strong oxidant with a one-electron redox potential of about 2.5 V [50]. Kishore and Asmus [23] have demonstrated that R1 proceeds via an electron transfer mechanism:

$$CH_3S(O)CH_3 + SO_4^- \rightarrow CH_3S(O^+)CH_3 + SO_4^{2-}. \tag{R1a}$$

Kishore and Asmus [23] have also shown that the one-electron redox potential of DMSO is in the range 1.8–2.0 V. Both DMSO2 and MS are expected to have larger one-electron redox potentials than DMSO, and the much slower values for k_{R2} and k_{R3} (compared to k_{R1}) observed in this study suggest that R2 and R3 probably proceed via a H-abstraction mechanism rather than via an electron transfer mechanism. The similar activation energies obtained for R1 and R2 can be rationalized using the relationship [51]

$$k_{obs} = k_{diff}\left\{1 + \left(\frac{k_{diff}}{k_{react}}\right)\right\}^{-1} \tag{5}$$

where k_{obs} is the measured bimolecular rate coefficient, k_{diff} the encounter rate coefficient of the two reacting species, and k_{react} the rate coefficient that would be measured if diffusion was not rate-limiting. For the near-diffusion-controlled R1, the temperature dependence of k_{react} is presumably very small and the temperature dependence of k_{diff} exerts a strong influence on the observed activation energy. On the other hand, the observed temperature dependence of the much slower R2 should be due almost entirely to the temperature dependence of k_{react}. The value of k_{diff} for R1 can be estimated from the Smoluchowski equation [48],

$$k_{diff} = 4\pi(D_{SO_4^-} + D_{DMSO})(r_{SO_4^-} + r_{DMSO})N_A \tag{6}$$

where $D_{SO_4^-}$ and D_{DMSO} are the reactant aqueous phase diffusion coefficients, $r_{SO_4^-}$ and r_{DMSO} are the reactant radii, and N_A is Avogadro's number. Using the diffusion coefficients and molecular radii tabulated by Elliot et al. [51] as a guide, we estimate that $D_{SO_4^-} \sim D_{DMSO} \sim 1.05 \times 10^{-9}\,m^2\,s^{-1}$ and $r_{SO_4^-} \sim r_{DMSO} \sim 3.7 \times 10^{-10}$ m at $T = 298$ K. Substituting these parameters into Eq. (6) gives $k_{diff} \sim 1.2 \times 10^{10}\,M^{-1}\,s^{-1}$. Hence, it appears that for R1 at 298 K, $k_{obs} \sim 0.25\,k_{diff}$ and $k_{react} \sim 4 \times 10^9\,M^{-1}\,s^{-1}$.

The most likely source of systematic error in the rate coefficient determinations reported in this study is significant contribution to SO_4^- loss from reaction with background impurities in the DMSO, DMSO2, and/or MS samples. Because the DMSO sample purity is high and the observed rate coefficient is near the diffusion-controlled limit, impurity reactions can be ruled out as a source of error in the determination of k_{R1}. The MS sample used in the study of R3 had a stated minimum purity of 98%. However, according to the manufacturer, the major impurity in the MS sample was water. The large observed activation energy for R3 argues against fast reaction of SO_4^- with a minor impurity as the source of observed reactivity; however, some contribution from impurity reactions cannot be completely ruled out, so the error bars for measured values of k_{R3}^0 are adjusted upward to ∼30%. In the case of DMSO2, all observed reactivity could result from reaction of SO_4^- with a trace impurity (0.11 DMSO, for example); since this possibility cannot be ruled out, we consider the measured rate coefficients to represent upper limits to $k_{R2}(T)$.

4. Implications for atmospheric chemistry

The principal pathway for generating SO_4^- radicals in the atmospheric aqueous phase is thought to be via the OH-initiated oxidation of S(IV) [39,41,52–61]:

$$OH + HSO_3^- \rightarrow SO_3^- + H_2O \qquad (R7)$$

$$SO_3^- + O_2 \rightarrow SO_5^- \qquad (R8)$$

$$SO_5^- + HSO_3^- \rightarrow SO_4^- + SO_4^{2-} + H^+ \qquad (R9a)$$

$$SO_5^- + HSO_3^- \rightarrow SO_3^- + HSO_5^- \qquad (R9b)$$

$$SO_5^- + HSO_3^- \rightarrow 2SO_4^{2-} + H^+ \qquad (R9c)$$

The following reactions have also been suggested as sources of SO_4^- in cloud water [33,62]:

$$NO_3 + SO_4^{2-} \rightarrow SO_4^- + NO_3^- \qquad (R10)$$

$$OH + HSO_4^- \rightarrow SO_4^- + H_2O \qquad (R11)$$

although it has been suggested that the solubility of NO_3 in water might be too low for R10 to be important [63].

Summarized in Table 4 are estimated lifetimes of DMSO, DMSO2, and MS (or MSA) toward (a) gas phase destruction via reactions with OH, NO_3, and Cl, (b) loss from the gas phase by uptake into particles and/or aqueous droplets, and (c) aqueous phase destruction via reactions with OH and SO_4^- radicals. The diurnally averaged radical concentrations and rate coefficients that are needed for the lifetime estimates are obtained from this study and from a variety of other laboratory [21,22,64], field [10,65], and modeling [59,61,66] studies. It should be noted that the information used to evaluate the lifetimes of interest is representative of a wide-variety of conditions that could be encountered in the atmosphere and, therefore, the lifetimes in Table 4 should be considered rough estimates. The typical concentrations of OH(aq) and SO_4^-(aq) given in Table 4 are obtained from photochemical models. While there is good agreement between estimates of OH(aq) concentrations [61,66], estimated SO_4^- concentrations in cloud droplets range from 10^{-14} M [61] to 10^{-12} M [59]. We adopt the higher concentration for the purpose of making lifetime estimates in order to examine the *possibility* that reaction with SO_4^- is an important sink for organic sulfur species in the aqueous phase. Modeling studies suggest that diurnally averaged concentrations of Cl_2^- and Br_2^- radicals in the atmospheric aqueous phase may be as much as an order of magnitude larger than OH concentrations [61]. However, Cl_2^- and Br_2^- are considerably less reactive than OH and SO_4^- [67]. For the very reactive species DMS, the rate coefficients for reaction with OH (1.9×10^{10} M^{-1} s^{-1} [17]) is approximately a factor of 6 faster than the rate coefficients for reactions with Cl_2^- and Br_2^- (3.0×10^9 and 3.2×10^9 M^{-1} s^{-1}, respectively [18]). However, for the less reactive species DMSO, the Cl_2^- rate coefficient is only 1.2×10^7 M^{-1} s^{-1} [24], i.e. approximately a factor of 500 slower than the OH rate coefficient [21,22] (there are no data in the literature for the Br_2^- + DMSO reaction). It is typically the case for aqueous phase radical–molecule reactions that ratios of rate coefficients for reactions of a pair of radicals with the same molecular reactant increase in favor of the more reactive radical as the reactivity of the molecular reactant decreases [67]. Therefore, although kinetic data for the reactions of Cl_2^-

Table 4
Estimated lifetimes in hours of DMSO, DMSO2, and MSA/MS toward (a) gas phase destruction via reactions with OH, NO_3, and Cl, (b) uptake into aerosols under remote tropospheric conditions, and (c) aqueous phase destruction via reactions with OH and SO_4^- radicals

Process	Radical concentration	R = DMSO	R = DMSO2	R = MSA/MS
R(g) + OH(g)	1×10^6 cm^{-3}[a]	5[a]	>950[a]	
R(g) + NO_3(g)	7×10^6 cm^{-3}[a]	72[a]	>1.7×10^4[a]	
R(g) + Cl(g)	5×10^3 cm^{-3}[a]	1500[a]	2×10^6[a]	
R(g) → R(aq)		4[b]	4[b]	1–15[c]
R(aq) + OH(aq)	6×10^{-13} M[d]	0.1[e]	17[f]	10–40[f]
R(aq) + SO_4^-(aq)	1×10^{-12} M[g]	0.1[h]	>72[h]	2.5×10^4[h]

[a] [64].
[b] [10] (remote, cold conditions).
[c] [65] (remote, cold conditions).
[d] [61,66].
[e] Based on kinetic data from [21,22].
[f] Based on kinetic data from [22].
[g] [59].
[h] Based on kinetic data reported in this study.

and Br_2^- with DMSO2 and MS are certainly desirable, we consider it highly unlikely that these radicals will compete with OH and SO_4^- as a sink for the relatively unreactive species DMSO2 and MS under the conditions that exist in the atmospheric aqueous phase.

From the information in Table 4 it is clear that uptake into the condensed phase competes with gas phase oxidation for DMSO, and dominates gas phase oxidation for DMSO2 and MSA. In the aqueous phase, DMSO is oxidized very rapidly by both OH and SO_4^-. Since the DMSO oxidation product(s) are less volatile than DMSO itself (and, therefore, less likely to be re-introduced into the gas phase upon particle evaporation), aqueous phase oxidation of DMSO can contribute to particle growth via droplet formation/evaporation cycling. The lifetimes of DMSO2 and MS toward aqueous phase reactions are also short enough for aqueous phase oxidation to compete with droplet evaporation. While reactions with SO_4^-(aq) may be a significant sink for DMSO and DMSO2, it appears that MS oxidation is dominated by reaction with OH. In this regard, it is worth noting that we are in the process of carrying out temperature-dependent kinetics studies of OH reactions with organic sulfur compounds [68], and we find that the OH + MS reaction proceeds with a rate coefficient similar to the one reported by Olson and Fessenden [28], which is considerably slower than suggested by the results of two other published kinetics studies [22,27].

Acknowledgements

This research was supported by the National Science Foundation through Grant ATM-9910912.

References

[1] M. Pham, J.-F. Muller, G.P. Brasseur, G. Megie, A three-dimensional study of the tropospheric sulfur cycle, J. Geophys. Res.-Atmos. 100 (1995) 26061–26092.

[2] S.P. Urbanski, P.H. Wine, Chemistry of gas phase organic sulfur-centered radicals, in: Z.B. Alfassi (Ed.), S-Centered Radicals, Wiley, 1999, pp. 97–140.

[3] S.F. Watts, P. Brimblecombe, The Henry law constant of dimethylsulfoxide, Environ. Tech. Lett. 8 (1987) 483–486.

[4] A. Jefferson, F.L. Eisele, P.J. Ziemann, R.J. Weber, J.J. Marti, P.H. McMurry, Measurements of the H_2SO_4 mass accommodation coefficient onto polydisperse aerosol, J. Geophys. Res.-Atmos. 102 (1997) 19021–19028.

[5] W.J. De Bruyn, J.A. Shorter, P. Davidovits, D.R. Worsnop, M.S. Zahniser, C.E. Kolb, Uptake of gas-phase sulfur species methanesulfonic acid, dimethylsulfoxide, and dimethylsulfone by aqueous surfaces, J. Geophys. Res.-Atmos. 99 (1994) 16927–16932.

[6] P. Brimblecombe, S.L. Clegg, The solubility and behavior of acid gases in the marine aerosol, J. Atmos. Chem. 7 (1988) 1–18.

[7] G.R. Harvey, R.F. Lang, Dimethylsulfoxide and dimethylsulfone in the marine atmosphere, Geophys. Res. Lett. 13 (1986) 49–51.

[8] S.F. Watts, P. Brimblecombe, A.J. Watson, Methanesulfonic acid, dimethylsulfoxide and dimethylsulfone in aerosols, Atmos. Environ. 24 (1990) 353–359.

[9] F.L. Eisele, D.J. Tanner, Measurement of the gas phase concentration of H_2SO_4 and methanesulfonic acid and estimate of H_2SO_4 production and loss in the atmosphere, J. Geophys. Res.-Atmos. 98 (1993) 9001–9010.

[10] H. Berresheim, J.W. Huey, R.P. Thorn, F.L. Eisele, D.J. Tanner, A. Jefferson, Measurements of dimethylsulfide, dimethylsulfoxide, dimethylsulfone, and aerosol ions at Palmer Station, Antarctica, J. Geophys. Res.-Atmos. 103 (1998) 1629–1637.

[11] D. Davis, G. Chen, P. Kasibhatla, A. Jefferson, D.J. Tanner, F.L. Eisele, B. Neff, H. Berresheim, DMS oxidation in the Antarctic marine boundary layer: comparison of model simulations with field observations for DMSO, DMSO2, H_2SO_4(g), and MSA, J. Geophys. Res.-Atmos. 103 (1998) 1657–1678.

[12] D. Davis, G. Chen, F.L. Eisele, B. Huebert, L. Mauldin, A. Bandy, D. Thornton, D. Lenschow, DMS oxidation in the equatorial pacific: comparison of model simulations with field observations for DMSO, SO_2, H_2SO_4(g), MSA(g), MS, and NSS, J. Geophys. Res.-Atmos. 104 (1999) 5765–5784.

[13] R.J. Charlson, J.E. Lovelock, M.O. Andreae, S.G. Warren, Oceanic phytoplankton, atmospheric sulfur, cloud albedo and climate, Nature 326 (1987) 655–661.

[14] G.P. Ayers, R.W. Gillett, DMS and its oxidation products in the remote marine atmosphere: implications for climate and atmospheric chemistry, J. Sea Res. 43 (2000) 275–286.

[15] Y.-N. Lee, X. Zhou, Aqueous reaction kinetics of ozone and dimethylsulfide and its atmospheric implications, J. Geophys. Res.-Atmos. 99 (1994) 3597–3605.

[16] M. Gershenzon, P. Davidovits, J.T. Jayne, C.E. Kolb, D.R. Worsnop, Simultaneous uptake of DMS and ozone on water, J. Phys. Chem. A 105 (2001) 7031–7036.

[17] M. Bonifacic, H. Moeckel, D. Bahneman, K.D. Asmus, Formation of positive ions and other primary species in the oxidation of sulphides by hydroxyl radicals, J. Chem. Soc., Perkin Trans. 2 (1975) 675–685.

[18] M. Bonifacic, K.D. Asmus, Stabilization of oxidized sulphur centres by halide ions. Formation and properties of $R_2S\,X$ radicals in aqueous solutions, J. Chem. Soc., Perkin Trans. 2 (1980) 758–762.

[19] P. Amels, H. Elias, K.J. Wannowius, Kinetics and mechanism of the oxidation of dimethylsulfide by hydroperoxides in aqueous medium—study on the potential contribution of liquid-phase oxidation of dimethylsulfide in the atmosphere, J. Chem. Soc., Faraday Trans. 93 (1997) 2537–2544.

[20] W.A. Pryor, D.H. Giamalva, D.F. Church, Kinetics of ozonation. Part 2. Amino acids and model compounds in water and comparisons to rates in nonpolar solvents, J. Am. Chem. Soc. 106 (1984) 7094–7100.

[21] A.P. Reuvers, C.L. Greenstock, J. Borsa, J.D. Chapman, Mechanism of chemical radioprotection by dimethylsulfoxide, Int. J. Radiat. Biol. 24 (1973) 533–536.

[22] P.L. Milne, R.G. Zika, E.S. Saltzmann, Rate of reaction of methanesulfonic acid, dimethyl sulfoxide, and dimethyl sulfone with hydroxyl radical in aqueous solution, in: E.S. Saltzman, W.J. Cooper (Eds.), Biogenic Sulfur in the Environment, ACS Symposium Series, vol. 393, 1989, pp. 518–528.

[23] K. Kishore, K.D. Asmus, Radical cations from one-electron oxidation of aliphatic sulfoxides in aqueous solution—a radiation chemical study, J. Chem. Soc., Perkin Trans. 2 (1989) 2079–2084.

[24] K. Kishore, K.D. Asmus, Nature of $2\sigma/1\sigma^*$ three-electron-bonded chlorine adducts to sulfoxides, J. Phys. Chem. 95 (1991) 7233–7239.

[25] R. Flyunt, O. Makogon, M.N. Schuchmann, K.D. Asmus, C. von Sonntag, OH-radical-induced oxidation of methanesulfinic acid. The reaction of methanesulfonyl radical in the absence and presence of dioxygen, J. Chem. Soc., Perkin Trans. 2 (2001) 787–792.

[26] K. Sehested, J. Holcman, A pulse radiolysis study of the OH radical induced autoxidation of methanesulfinic acid, Radiat. Phys. Chem. 47 (1996) 357–360.

[27] J. Lind, T.E. Eriksen, Pulse radiolysis of methanesulfonic acid, Radiochem. Radioanal. Lett. 21 (1975) 177–181.

[28] T.M. Olson, R.W. Fessenden, Pulse radiolysis study of the reaction of $OH^{\bullet}$ radicals with methanesulfonate and hydroxymethanesulfonate, J. Phys. Chem. 96 (1992) 3317–3320.

[29] S. Akiho, O. Ito, M. Iino, Flash photolysis study for reactions of $NO_3^{\bullet}$ with sulfur compounds in acetonitrile solution, Int. J. Chem. Kinet. 21 (1989) 667–676.

[30] T. Sumiyoshi, M. Katayama, Novel transient absorption of irradiated DMSO in carbon tetrachloride as studied by pulse radiolysis, Chem. Lett. (1987) 1125–1126.

[31] J.U. White, Long optical paths of large aperture, J. Opt. Soc. Am. 32 (1942) 285–288.

[32] P.H. Wine, R.L. Mauldin III, R.P. Thorn, Kinetics and spectroscopy of the NO_3 radical in aqueous ceric nitrate–nitric acid solutions, J. Phys. Chem. 92 (1988) 1156–1162.

[33] Y. Tang, R.P. Thorn, R.L. Mauldin III, P.H. Wine, Kinetics and spectroscopy of the SO_4^- radical in aqueous solution, J. Photochem. Photobiol. A: Chem. 44 (1988) 243–258.

[34] P.H. Wine, Y. Tang, R.P. Thorn, J.R. Wells, D.D. Davis, Kinetics of aqueous phase reactions of the SO_4^- radical with potential importance in cloud chemistry, J. Geophys. Res.-Atmos. 94 (1989) 1085–1094.

[35] M. Chin, P.H. Wine, A temperature-dependent kinetics study of the aqueous phase reactions $OH + SCN^- \rightarrow SCNOH^-$ and $SCN + SCN^- \leftrightarrow (SCN)_2^-$, J. Photochem. Photobiol. A: Chem. 69 (1992) 17–25.

[36] M. Chin, P.H. Wine, A temperature-dependent competitive kinetics study of the aqueous-phase reactions of OH radicals with formate, formic acid, acetate, acetic acid, and hydrated formaldehyde, in: G.R. Helz, R.G. Zepp, D.G. Crosby (Eds.), Aquatic and Surface Photochemistry, Lewis Publishers, Boca Raton, FL, USA, 1994, pp. 85–96.

[37] E. Heckel, A. Henglein, G. Beck, Pulse radiolytic investigation of the radical anion SO_4^-, Ber. Bunsenges. Phys. Chem. 70 (1966) 149–154.

[38] E. Hayon, J.J. McGarvey, Flash photolysis in the vacuum ultraviolet region of SO_4^{2-}, CO_3^{2-}, and OH^- ions in aqueous solution, J. Phys. Chem. 70 (1967) 1472–1477.

[39] L. Dogliotti, E. Hayon, Flash photolysis of persulfate ion in aqueous solutions: study of the sulfate and ozonide radical anions, J. Phys. Chem. 71 (1967) 2511–2516.

[40] W. Robke, M. Renz, A. Henglein, Pulseradiolyse der anionen $S_2O_8^{2-}$ und HSO_5^- in wassriger losung, Int. J. Radiat. Phys. Chem. 1 (1969) 39–44.

[41] E. Hayon, A. Treinin, J. Wilf, Electronic spectra, photochemistry, and autoxidation mechanism of the sulfite–bisulfite, pyrosulfite systems: the SO_2^-, SO_3^-, SO_4^-, and SO_5^- radicals, J. Am. Chem. Soc. 94 (1972) 47–57.

[42] B. Lesigne, C. Ferradini, J. Pucheault, Pulse radiolysis study of the direct effect on sulfuric acid, J. Phys. Chem. 77 (1973) 2156–2158.

[43] K.J. Kim, W.H. Hamill, Direct and indirect effects in pulse irradiated concentrated aqueous solutions of chloride and sulfate ions, J. Phys. Chem. 80 (1976) 2320–2325.

[44] W.J. McElroy, S.J. Waygood, Kinetics of the reactions of the SO_4^- radical with SO_4^-, $S_2O_8^{2-}$, H_2O and Fe^{2+}, J. Chem. Soc., Faraday Trans. 86 (1990) 2557–2564.

[45] H. Herrmann, A. Reese, R. Zellner, Time-resolved UV-Vis diode-array absorption spectroscopy of SO_x ($x = 3, 4, 5$) radical anions in aqueous solution, J. Mol. Struct. 348 (1995) 183–186.

[46] Z.-C. Bao, J.R. Barker, Temperature and ionic strength effects in some reactions involving sulfate radical [SO_4^-(aq)], J. Phys. Chem. 100 (1996) 9780–9787.

[47] R.E. Huie, C.L. Clifton, N. Altstein, A pulse radiolysis and flash photolysis study of the radicals SO_2^-, SO_3^-, SO_4^-, and SO_5^-, Radiat. Phys. Chem. 33 (1989) 361–370.

[48] J.H. Espenson, Chemical Kinetics and Reaction Mechanisms, McGraw-Hill, New York, 1981, and references therein.

[49] G.G. Manov, R.G. Bates, W.J. Hamer, S.F. Acree, Values of the constants in the Debye-Hückel equation for activity coefficients, J. Am. Chem. Soc. 655 (1943) 1765–1767.

[50] L. Eberson, Electron-transfer reactions in organic chemistry, Adv. Phys. Org. Chem. 18 (1982) 79–185.

[51] A.J. Elliot, D.R. McCracken, G.V. Buxton, N.D. Wood, Estimation of rate constants for near-diffusion controlled reactions in water at high temperature, J. Chem. Soc., Faraday Trans. 86 (1990) 1539–1547, and references therein.

[52] L. Dogliotti, E. Hayon, Transient species produced in the photochemical decomposition of ceric salts in aqueous solution: reactivity of NO_3 and HSO_4 free radicals, J. Phys. Chem. 71 (1967) 3802–3808.

[53] L. Dogliotti, E. Hayon, Flash photolysis study of sulfite, J. Phys. Chem. 72 (1968) 1800–1807.

[54] R.E. Huie, P. Neta, Chemical behavior of SO_4^- and SO_5^- radicals in aqueous solutions, J. Phys. Chem. 88 (1984) 5665–5669.

[55] R.E. Huie, P. Neta, Rate constants for some oxidations of S(IV) by radicals in aqueous solutions, Atmos. Environ. 21 (1987) 1743–1747.

[56] W.L. Chameides, D.D. Davis, The free radical chemistry of cloud droplets and its impact upon the composition of rain, J. Geophys. Res. 87 (1982) 4863–4877.

[57] W.L. Chameides, The photochemistry of a remote stratiform cloud, J. Geophys. Res.-Atmos. 89 (1984) 4739–4755.

[58] D.J. Jacob, Chemistry of OH in remote clouds and its role in the production of formic acid and peroxymonosulfate, J. Geophys. Res.-Atmos. 91 (1986) 9807–9826.

[59] D.J. Jacob, E.W. Gottlieb, M.J. Prather, Chemistry of a polluted cloudy boundary layer, J. Geophys. Res.-Atmos. 94 (1989) 12975–13002.

[60] W.L. Chameides, A.W. Stelson, Aqueous-phase chemical processes in deliquescent sea-salt aerosols: a mechanism that couples the atmospheric cycles of S and sea salt, J. Geophys. Res.-Atmos. 97 (1992) 20565–20580.

[61] H. Hermann, B. Ervens, H.-W. Jacobi, R. Wolke, P. Nowacki, R. Zellner, CAPRAM2.3: a chemical aqueous phase mechanism for tropospheric chemistry, J. Atmos. Chem. 36 (2000) 231–284.

[62] W.L. Chameides, D.D. Davis, Possible role of NO_3 in the nighttime chemistry of a cloud, J. Geophys. Res.-Atmos. 91 (1986) 5331–5337.

[63] M. Mozurkewich, Comment on Ref. [55], J. Geophys. Res. 91 (1986) 14569–14570.

[64] H. Falbe-Hansen, S. Sorensen, N.R. Jensen, T. Pedersen, J. Hjorth, Atmospheric gas-phase reactions of dimethylsulfoxide and dimethylsulfone with OH and NO_3 radicals, Cl atoms and ozone, Atmos. Environ. 34 (2000) 1543–1551, and references therein.

[65] A. Jefferson, D.J. Tanner, F.L. Eisele, D.D. Davis, G. Chen, J. Crawford, J.W. Huey, A.L. Torres, H. Berresheim, OH photochemistry and methane sulfonic acid formation in the coastal Antarctic boundary layer, J. Geophys. Res.-Atmos. 103 (1998) 1647–1656.

[66] J. Lelieveld, P.J. Crutzen, The role of clouds in tropospheric photochemistry, J. Atmos. Chem. 12 (1991) 229–267.

[67] P. Neta, R.E. Huie, A.B. Ross, Rate constants for reactions of inorganic radicals in aqueous solution, J. Phys. Chem. Ref. Data 17 (1988) 1027–1284.

[68] L. Zhu, J.M. Nicovich, P.H. Wine, Temperature-dependent kinetics studies of aqueous phase reactions of hydroxyl and sulfate radicals with the important atmospheric sulfur species dimethylsulfoxide, dimethylsulfone, and methanesulfonate, 224th National ACS Meeting, Boston MA, August 2002, Paper PHYS 207.