JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 105, NO. D11, PAGES 14,413–14,422, JUNE 16, 2000

Removal of SO_2 from the marine boundary layer over the Atlantic Ocean: A case study on the kinetics of the heterogeneous S(IV) oxidation on marine aerosols

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Abstract. Measurements of SO_2 and NSS-SO_4^{2-} were made over the Atlantic Ocean on board the RV Polarstern from October 9 to November 2, 1996, as part of the ALBATROSS campaign. The measurements were performed between 66.7°N and 37.8°S with a mean longitude of approximately 30°W. The most frequent background values for SO_2 were found to be 13 parts per trillion by volume (pptv) (0.54 nmol m^{-3} at standard ambient temperature and pressure (SATP)) in the Southern Hemisphere, and 15 pptv (0.62 nmol m^{-3} SATP) in the Northern Hemisphere. The mean values for total NSS-SO_4^{2-} in particles with a $d > 0.2$ μm were (5.99 ± 2.93) nmol m^{-3} (SATP) in the Southern Hemisphere, and (8.93 ± 5.29) nmol m^{-3} (SATP) in the Northern Hemisphere. An analysis of the size-fractionated aerosol samples ($d > 1$ μm and 0.2 μm $< d < 1$ μm) of NSS-SO_4^{2-} shows that (34 ± 13)% of the total NSS-SO_4^{2-} exists in coarse mode particles with $d > 1$ μm. The main fraction of this NSS-SO_4^{2-} is most likely produced by the oxidation of dissolved SO_2 via heterogeneous reactions occurring in the aqueous phase of coarse mode marine aerosols. A case study on the kinetics of this oxidation pathway was conducted during ALBATROSS. October 12, 1996, the ship sailed in the plume of a volcano on Iceland during its eruption from September 30 to October 13, 1996, as indicated by trajectory analysis and by the measurements of NSS-SO_4^{2-}, SO_2, CO, and Hg. An empirical physicochemical approach considering the atmosphere as a natural flow reactor is used for the presented case study. The determined pseudo-first-order reaction rate constant for the oxidation of SO_2 on marine aerosols is 3.31×10^{-4} s^{-1} at 25°C. Assuming that the occurrence of coarse mode marine aerosols is the rate-limiting variable of the reaction, the second-order reaction rate constant is found to be 1.32×10^{-6} cm^3 s^{-1} $particle^{-1}$ at 25°C. These values are in good agreement with results of previous field experiments as well as with the results of model studies.

1. Introduction

Large particles in the marine boundary layer (MBL) are usually produced due to the agitation of the sea surface by wind force. Small seawater droplets are brought into the MBL by the bursting of air bubbles when they reach the ocean surface [*Warneck,* 1988]. After evaporation of some of the original water content, the resulting aerosols still contain a certain amount of liquid water. This liquid water content (LWC) is in dependence on the relative humidity (RH) of the surrounding air. The aerosol water is able to dissolve gaseous compounds and therefore these aerosols act as potential sinks for water-soluble atmospheric trace gases like sulfur dioxide (SO_2), ammonia, or nitric acid. These gases undergo chemical conversion in the aerosol water. In particular, dissolved S(IV) species (SO_2aq, HSO_3^-, and SO_3^{2-}), are oxidized to S(VI) (SO_4^{2-}) by various pH-dependent reaction channels in the liquid phase [*Seinfeld and Pandis,* 1998]. This non-sea-salt SO_4^{2-} (NSS-SO_4^{2-}) production leads to an acidification of the aerosol water and an increase in the aerosol mass/volume. The removal of SO_2 from the MBL by sea-salt aerosols has been examined in a number of studies [*Clarke and Radojevic,* 1984; *Sievering et al.,* 1991; *Chameides and Stelson,* 1992; *Suhre et al.,* 1995; *Keene et al.,* 1998] over the last 2 decades. According to the recent model study of *Keene et al.* [1998] the acid-catalyzed reaction via hydrogen peroxide (H_2O_2) is the dominant sink for dissolved SO_2 at pH 3 of the aerosol water. The oxidation of S(IV) by dissolved ozone (O_3) is the most important pathway at pH 8 because of the enhanced solubility of SO_2 as well as its rapid reaction with O_3 in the higher pH regime. Furthermore, these authors postulate that the heterogeneous reactions of S(IV) with hypochlorous (HOCl) and/or hypobromous (HOBr) acid act as dominant sources of S(VI) in deliquescent sea-salt particles in the intermediate pH range. From our knowledge, however, there is no experimental proof so far about the occurrence of hypohalous acids and their reactions with S(IV) in sea-salt aerosols. Nevertheless, given the fact that the aqueous phase of coarse mode marine aerosols is believed to have a pH of 7-8.7, the later given reactions may be considered as potentially important sinks for SO_2 in the MBL [*Chameides and Stelson,* 1992; *Keene et al.,* 1998]. In contrast to these potential reactions, which are most likely to happen on freshly generated, coarse mode marine aerosols, the S(IV) + H_2O_2 reaction

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Paper number 1999JD900957.
0148-0227/00/1999JD900957$09.00

is mostly important for aged, acidified particles in the submicrometer range. The pH of these submicrometer aerosols is believed to be in the range of 1-3 [*Keene et al.*, 1998].

This is consistent with the studies of *Sievering et al.* [1992], who found that the S(IV) + O_3 reaction happens mostly in aerosols with a diameter of $d > 1$ μm due to the poor water content and low pH of smaller particles. These authors showed that marine aerosols with $d < 1.5$ μm have a water content of less than 0.1 μg m^{-3}, whereas particles with $d > 1.5$-15.5 μm contain a liquid water mass of 7.2 μg m^{-3} at 91% RH. Owing to their origin, these coarse mode aerosols contain a larger amount of liquid water with a higher pH than the smaller particles. These particles are usually produced by gas-to-particle conversion but also as a result of liquid water evaporation from the larger aerosols.

The kinetics of the S(IV) oxidation in deliquescent marine aerosols were investigated in a number of studies mostly by theoretical works [*Luria and Sievering*, 1991; *Chameides and Stelson*, 1992; *Suhre et al.*, 1995; *Keene et al.*, 1998], field experiments [*Sievering et al.*, 1991; 1995; *Leck and Persson*, 1996], and laboratory studies using a fog chamber/flow reactor [*Clarke and Radojevic*, 1984]. The drawback of the previous field studies and, of course, the model studies is that there have been no measurements of the direct removal of SO_2 from the MBL due to its oxidation in the LWC of marine aerosols. In these studies the SO_2 removal rate was usually determined indirectly by calculating the concentration of S(IV) and the corresponding oxidants in the aerosol water. With the calculated concentrations in the liquid phase the removal rate for SO_2 from the MBL can be estimated using the known rate constants for the reaction of S(IV) with its reaction partners taken from the literature, the amount and pH of the aerosol water, and the size distribution of marine aerosols. *Clarke and Radojevic* [1984] calculated the removal rate of SO_2 directly from its decrease in the gaseous phase, but their laboratory study focused on the chloride-catalyzed oxidation of dissolved SO_2. The observed loss in the S(IV) concentration, however, might be due to trace metal impurities in the alkali metal chloride reagents used by these authors. This metal-catalyzed (manganese(II), iron(III)) S(IV) oxidation by dissolved oxygen is less effective, especially if the poor solubility of the iron-hydroxo complexes at high pH and the poor occurrence of manganese in marine aerosols are considered. However, these reactions are negligible in the presence of strong oxidants like H_2O_2, HOCl, HOBr, or O_3 in the natural troposphere.

Our experiment aims to directly measure the SO_2 loss rate in the MBL by the observation of the decrease in the SO_2 concentration during the Air Chemistry and Lidar Studies Above the Atlantic Ocean of Tropospheric and Stratospheric Species (ALBATROSS) experiment. The observed decrease represents the sum of all chemical and physical sinks for SO_2 in the MBL. These sinks are determined in this case study to calculate the reaction rate constants of the heterogeneous S(IV) oxidation in the LWC of coarse mode marine aerosols from direct field observations.

2. Experiment

The sampling systems for SO_2 and aerosols were both located on the compass deck of RV Polarstern, 25 m above sea level. The SO_2 inlet was installed on top of the differential optical absorption spectroscopy (DOAS) container and the aerosol filters on an outrigger, 3 m off the compass deck (bow direction). In order to prevent any contamination of the samples from emissions from the ship's exhaust, the sampling devices for SO_2 and aerosols were coupled with a wind direction cutoff system. Sampling was automatically interrupted if the relative wind direction was in a sector of ± 45° from the ship's exhaust with respect to the sampling location, and automatically reactivated after the wind direction was constantly 1 min out of the cutoff sector. Plastic funnels protected the inlets from seaspray and rainwater. Peroxy-radicals (RO_x·) were measured by means of a chemical amplifier technique [*Hastie et al.*, 1991] which was located in the crow's nest of RV Polarstern. A DOAS system was employed to measure hydroxy-radicals (HO·) by its UV absorption at 308 nm [*Hausmann et al.*, 1997]. Air sampling of O_3 and carbon monoxide (CO) was made on an outrigger, approximately 3 m off the compass deck (port side). O_3 was measured by UV absorption at 254 nm using a Dasibi (1003AH) instrument. The measurements of CO were performed by means of a gas chromatograph (GC) with a HgO-Detector (Wolters, RGA-3). Condensation nuclei (CN) were sampled on the top of the DOAS container on the starboard side of the ship approximately 1 m above and 5 m behind the SO_2 inlet by means of a Thermo Systems Inc. (TSI, 3010) counter. Its data were integrated at 60 s intervals. Measurements of gaseous elementary mercury (Hg) were performed in front of the DOAS container by means of a Tekran analyzer with a time resolution of 30 min [*Slemr et al.*, 1997]. Isentropic backward trajectories near the ocean surface were calculated by the German Weather Service in Offenbach/Germany. For further details about the ALBATROSS campaign and the instrumental setup aboard RV Polarstern see *Krischke* [1998].

2.1. SO_2

Atmospheric SO_2 was stripped from the gaseous phase by means of a filter technique, using an aqueous solution of tetrachloromercurate(II) as absorbents. Dissolved SO_2 forms a stable disulfitomercurate(II) complex in this absorbing solution. The samples were treated subsequently with an acidic cerium(IV) solution for analysis. The occurring chemiluminescence radiation was detected with a photomultiplier and integrated over 10 s by a photoncounter. The analysis of the SO_2 samples was performed every 2 or 3 days in the ship's laboratory. Calibration was performed in the liquid phase prior to each analytical series by means of eight sodium pyrosulfite standards. The concentration of the primary S(IV) standard was tested by iodometric titration. A detailed description of this technique is given by *Jaeschke et al.* [1997] and *Krischke* [1998]. The calculated (3σ) detection limit during ALBATROSS was 0.15 nmol m^{-3} (3.6 parts per trillion by volume (pptv)) at an average sampling volume of 420 L (SATP) which corresponds to 50 min sampling time. The average relative accuracy of the SO_2 measurements during ALBATROSS was ±9%.

2.2. NSS-SO_4^{2-}

A twin-filter device (Sartorius Teflon™-filter, cutoff: $d_{50\%}$ = 0.2 μm) was used for parallel sampling of bulk ($d > 0.2$ μm) and fine aerosols (0.2 μm < d < 1 μm). The separation of larger particles from the bulk aerosols was maintained by means of a preimpactor (cutoff: $d_{50\%} > 1$ μm) in front of the fine aerosol filter. The analysis of the filters was performed after the cruise at the Frankfurt laboratory. The filters were rinsed subsequently with 0.3 mL ethanol and 1 mL deionized water. Ion chromatography/conductivity detection (IC: Dionex DX-100, Column: Dionex CG12/CG12A for Na^+ and Dionex AG12A/AC12A for

SO_4^{2-}, Detector: Dionex CDM-2) was used for analysis. The NSS-SO_4^{2-} fraction of the total SO_4^{2-} amount collected on the filter was calculated according to the studies of *Keene et al.* [1986], assuming a constant $[SO_4^{2-}]$:$[Na^+]$ molar ratio of 0.0603. The (3σ) detection limit of the filter/IC technique for total SO_4^{2-} was 19.3 nmol m^{-3} for a 3600 L (SATP) (daytime) and 9.6 nmol m^{-3} for a 7200 L (SATP) (nighttime) sample, respectively. The time resolution was 6 hours during daytime and 12 hours during nighttime. The average relative accuracy of the SO_4^{2-} measurements during ALBATROSS was ±6%. For further details about this technique, see *Krischke* [1998].

3. Results

3.1. SO_2 and NSS-SO_4^{2-} Concentrations

Figure 1 shows the meridional variability of SO_2 and NSS-SO_4^{2-} in aerosols with $d > 1$ μm and 0.2 μm $< d <$ 1 μm in the MBL over the Atlantic during ALBATROSS. The measurements cover a latitudinal range from 66.7°N to 37.8°S with a mean longitude of 29.3°W ± 4.2°W.

The SO_2 concentrations cover several orders of magnitude with a maximum of 370.8 nmol m^{-3} (9.1 ppbv) at 16.3°N/29.3°W and a minimum of 0.15 nmol m^{-3} (3.6 pptv) at 51.4°N/33.2°W. The highest concentrations of SO_2 at 10°N-20°N are clearly due to anthropogenic emissions from the African shore and match the highest concentrations of NSS-SO_4^{2-}

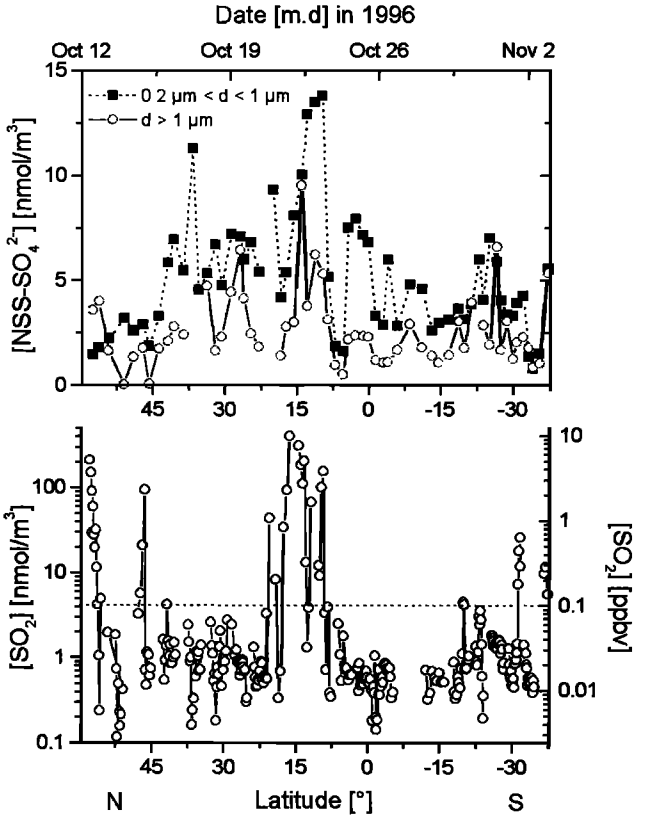

Figure 1. Meridional variability of NSS-SO_4^{2-} and SO_2 in the MBL over the Atlantic Ocean during ALBATROSS from October 9 to November 2, 1996. Horizontal dotted line denotes the upper SO_2 concentration limit for frequency analysis in Figure 2.

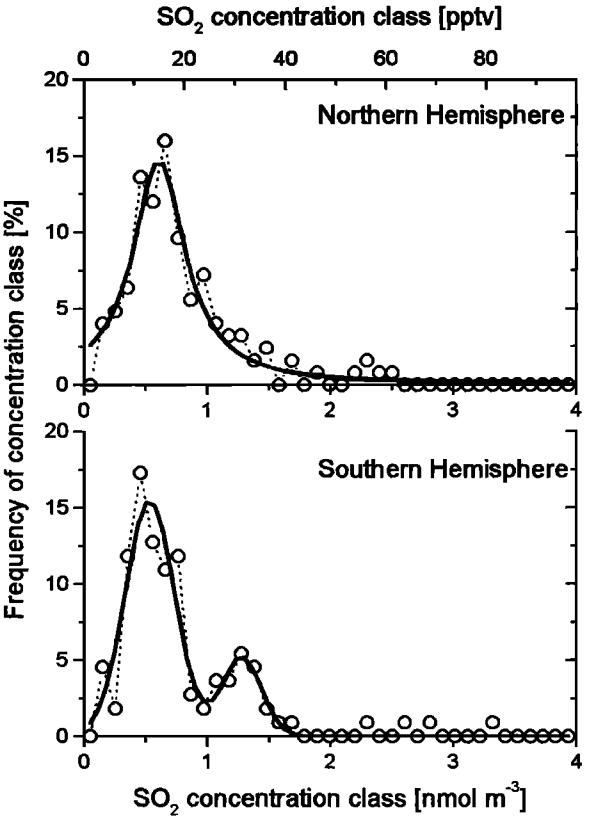

Figure 2. Estimation of the SO_2 background concentration in the range below 4 nmol m^{-3} over the Atlantic Ocean during ALBATROSS by means of a SO_2 concentration classes frequency analysis. The used step width is 0.1 nmol m^{-3} (2.5 pptv). Solid line is the Gauss fit of SO_2 concentration class frequency.

measured in this area. Considering all samples collected during the cruise, the mean concentration of SO_2 over the Atlantic during the cruise was (9.9 ± 40) nmol m^{-3} ((242 ± 978) pptv).

3.1.1. SO_2 background concentration. Trajectory analysis show that the measured SO_2 concentrations over 4 nmol m^{-3} are due to long-distance transport from strong, mainly anthropogenic, sources in coastal regions. For this reason, a frequency analysis was performed which included all samples with a concentration below 4 nmol m^{-3} (98 pptv) to calculate the natural SO_2 background concentration in the MBL over the Atlantic in the geographic Southern and Northern Hemisphere. This provides the statistical opportunity to exclude samples from the background value which are contaminated by emissions from anthropogenic sources. The chosen concentration range covers 73.5% of all measurements (125 of 170) on the Northern Hemisphere and 79.1% (110 of 139) of all measurements in the Southern Hemisphere.

Figure 2 shows slight differences between Northern and Southern Hemispheric SO_2 background concentrations. The highest frequency (14.5%) in the Northern Hemisphere was found at 0.62 nmol m^{-3} (15.2 pptv). The existence of two modes is conspicuous in the frequency analysis of the samples from the Southern Hemisphere. The frequency analysis shows one mode with 15.3% of all included samples at 0.54 nmol m^{-3} (13.2 pptv) and another mode with 5.2% at 1.28 nmol m^{-3} (31.3 pptv). All samples in the second mode belong to the same time interval (October 29, 1996) which corresponds to 22.5°S-28.4°S/(26.2 ±

0.4)°W. In this area, *Sciare et al.* [this issue] measured the highest dimethyl sulfide (DMS) concentrations in the Southern Hemisphere. The correlation of DMS and SO_2 is consistent with DMS being a precursor of SO_2. SO_2 is produced as a by-product of the DMS oxidation via HO- and NO_3-radicals. The corresponding arithmetic mean values for SO_2 in the concentration range < 4 nmol m^{-3} are (0.73 ± 0.51) nmol m^{-3} ((18 ± 12) pptv) for the Northern, and (0.78 ± 0.53) nmol m^{-3} ((19 ± 13) pptv) for the Southern Hemisphere. The observed SO_2 background concentrations are therefore slightly lower than the results of *Ockelmann* [1982], *Nguyen et al.* [1983], and *Herrmann and Jaeschke* [1984], but are in agreement with the results of the more recent studies of *Pszenny et al.* [1990] and *Leck and Persson* [1996]. These authors report a SO_2 concentration of (0.3-0.8) nmol m^{-3} in the Greenland Sea-Fram Strait area of the North Atlantic [*Leck and Persson,* 1996] and (< 0.6-2) nmol m^{-3} in the tropical region of the Atlantic Ocean [*Pszenny et al.,* 1990]. A possible explanation for the higher background concentrations found in the earlier studies may be the reduced sulfur emissions from the Northern industrial countries since the 1980s. Deviations in the DMS emissions as well as the different detection limits of the employed measurement techniques may also be considered as potential reasons for the deviating SO_2 concentrations measured during the different campaigns.

3.1.2. NSS-SO_4^{2-} concentration. The mean values for total NSS-SO_4^{2-} in particles with a diameter larger than 0.2 μm were (5.99 ± 2.93) nmol m^{-3} in the Southern Hemisphere and (8.93 ± 5.29) nmol m^{-3} in the Northern Hemisphere. The NSS-SO_4^{2-} concentrations found during this cruise are slightly lower than the results of *Bürgermeister* [1991] on a similar cruise track who found (9.4-28.1) nmol m^{-3} between 35°N-5°N and (3.1-9.4) nmol m^{-3} between 0°S-10°S, respectively. The results of this study, however, are in good agreement with the measurements performed by *Sciare et al.* [this issue], who found a mean value of 7.8 nmol m^{-3} during the ALBATROSS campaign. An analysis of the size-fractionated aerosol samples (d > 1 μm and 0.2 μm < d < 1 μm) of NSS-SO_4^{2-} shows that (34 ± 13)% of the total NSS-SO_4^{2-} exists in coarse mode particles with d > 1 μm. This is consistent with the results of *Leck and Persson* [1996], who found that NSS-SO_4^{2-} is primarily associated with submicrometer particles. According to *Sievering et al.* [1991] the main fraction of the NSS-SO_4^{2-} in the coarse mode marine aerosols is produced by the oxidation of dissolved SO_2 via O_3 in a heterogeneous reaction occurring in the aqueous phase of these particles. Besides this oxidation pathway, the S(IV) + (HOCl, HOBr) reaction might also contribute to the NSS-SO_4^{2-} content in the larger particle fraction. Remarkably, the ratio of NSS-SO_4^{2-} in the coarse to fine mode aerosols reached 2.4:1 on October 12, 1996, at approximately 56°N, while the typical ratio during the entire cruise was 1:3. Two different possibilities have to be discussed to explain this phenomenon: Assuming that on October 12, 1996, the ship sailed in the plume of a volcano (for further explanation, see the following paragraph) NSS-SO_4^{2-} is enriched in coarse mode particles. This is either due to heterogeneous oxidation of atmospheric SO_2 on marine aerosols or the particles are directly emitted from the volcano. In the second case the SO_4^{2-} content of these volcanic particles is indistinguishable from the NSS-SO_4^{2-} content with the used [SO_4^{2-}]:[Na^+] correction of the samples. Though the occurrence of SO_4^{2-}-containing mineralic aerosols cannot be ruled out completely, the NSS-SO_4^{2-} production by heterogeneous S(IV) conversion seems to be more likely considering the fact that the erupted magma was basaltic andesite [*Gudmundsson et al.,* 1997] and that the large volcanic particles are supposed to suffer from rapid sedimentation.

3.2. SO_2 in Volcanic-Influenced Air Masses

On October 12, 1996 (54.6°N-59.7°N/30.9°W-32.4°W), the ship sailed in an air mass which was potentially influenced by a volcano on Iceland (64.31°N/17.22°W, Vatnajökull area) during its eruption from September 30, to October 13, 1996. Figure 3 shows the results of the SO_2 and CO measurements as well as the wind direction and the actinic flux on October 12, 1996.

3.2.1. Trace compounds. SO_2 and CO show a continuous decrease in concentration with increasing distance to the source until a change of the air mass at 1530 UTC. This is indicated by the vertical dotted line in Figure 3. Owing to the conservative chemical character of CO, its decrease in the remote marine troposphere may be attributed mainly to dry deposition and dilution by unpolluted air masses. Wet deposition of SO_2 and CO can be neglected due to the prevailing weather conditions on October 12, 1996 (see paragraph below). An additional CO production source, resulting from the oxidation of methane and volatile organic compounds by HO-radicals, is negligible due to the low concentrations of HO-radicals at high Northern latitudes during the measurement period. SO_2 shows a much stronger decrease in its concentration compared to CO. Additional sinks such as homogeneous and heterogeneous oxidation have to be considered due to the higher reactivity of SO_2. The results of additional gaseous Hg measurements [*Slemr et al.,* 1997] are not shown in Figure 3 due to the fact that there are no Hg data available during the strongest period of SO_2 decrease from 0830-1330 UTC on October 12, 1996. In the measurement period from 0110-0830 UTC on October 12, 1996, Hg shows a continuous, linear decrease in its concentration. A linear regression analysis of a $\ln([Hg]_t/[Hg]_0)$ versus time of transport plot (see Figure 5 for comparison) results in an overall Hg loss rate of 9.767×10^{-6} s^{-1} (regression analysis: $y = (-9.767\times10^{-6} \pm 3.939\times10^{-7})\,x$; R = 0.970). Because of the chemical inertia of elementary mercury in the troposphere, its decrease can be attributed mainly to dry deposition and dilution during the transport.

3.2.2. Meteorological observations. Figure 3 shows the wind direction and the actinic flux on October 12, 1996, in addition to the concentrations of SO_2 and CO. The wind direction was a stable (66.2 ± 7.5)° from the beginning of the SO_2 measurements until the change of the air mass at 1530 UTC. This indicates that the ship sailed in air masses of similar origin during the time of the stable wind directions. The course of the actinic flux as well as the observations of the ship's meteorologists indicate only short time periods with major cloud coverage during the SO_2 measurements. The only time period with an increased cloud coverage was between 1245-1415 UTC. This was at a time when the strongest decrease in the SO_2 concentration had already been observed. Table 1 provides an overview of the ship's meteorologists' observations during the SO_2 measurement period on October 12, 1996.

In order to determine the origin of the measured air masses an isentropic 60-hour back trajectory near the ocean surface was calculated by the German Weather Service. Figure 4 shows the ship's position and the 60-hour back trajectory on October 12, 1996.

The back trajectory shows that the track of the air masses is close to the eruption area of the volcano on Iceland. The results

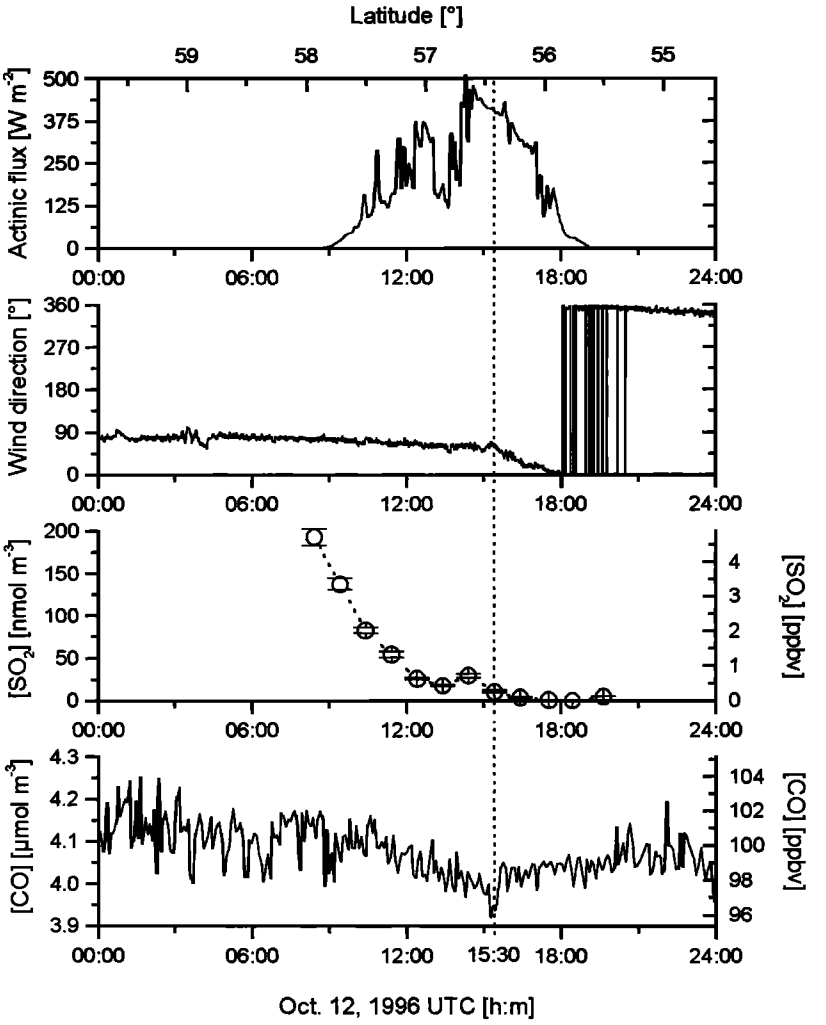

Figure 3. Measurements of volcanic influenced air masses on October 12, 1996. The vertical line indicates a change in the air masses which occurred at 1530 UTC. Error bars represent analytical errors (1σ) of the SO_2 measurements.

of the trajectory analysis as well as the results of the NSS-SO_4^{2-} (see Figure 1), Hg, and CO measurements indicate that the high concentrations of SO_2 measured at 55.5°N-57.9°N are due to this volcanic influence. This statement is even more valid because of the fact that the volcano was the only Hg, CO, and SO_2 source in this area with a sufficient source strength to explain the elevated concentrations measured for theses trace gases.

3.3. Kinetic Studies

The following kinetic case study on the heterogeneous oxidation of S(IV) in the aerosol water of coarse mode marine aero-

Table 1. Overview of the Meteorological Observations on October 12, 1996, in the Period From 0830-1530 UTC

Parameter	Observation
Visibility	(10-20) km
Maximum cloud coverage	3/8-7/8
Precipitation	0 mm
Waves	(1-1.5) m

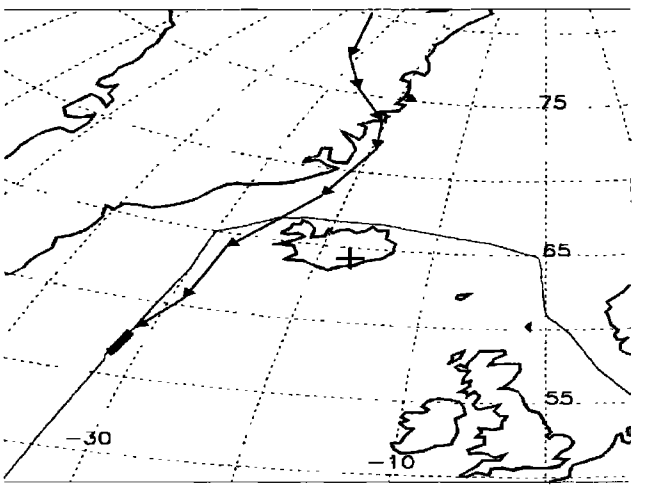

Figure 4. Ship's position at the start (0830 UTC) and at the end (1940 UTC) of the SO_2 measurements on October 12, 1996 (bold line). Sixty-hour back trajectory near the ocean surface starting at 0600 UTC on October 12, 1996 (triangles). Geographic position of the volcano on Iceland (64.31°N/17.22°W) (cross).

sols was performed by using the physicochemical approach to regard the atmosphere as a natural flow reactor. The case study was made by using only the samples collected on October 12, 1996, in the plume of the volcano. The study was based on the following assumptions:

1. Source strength and ratio for SO_2 and CO were approximately constant: Due to the fact that the time period of the measurements was at the end of the volcanic activity, which ended on October 13, 1996, the assumption of an almost constant source strength within the measurement period for SO_2 and CO is justified according to N. Oskarsson (personal communication, 1997). A detailed local and temporal description of the volcanic eruption is given by *Gudmundsson et al.* [1997] and *Lausch et al.* [1997].

2. Additional sources for SO_2 and CO along the path of transport were negligible: An additional SO_2 source due to DMS oxidation can be neglected due to the low concentrations of DMS [*Sciare et al.*, this issue] and the poor photochemical reaction conditions (see Figure 3) in the high Northern latitudes during the measurement period [*Collins et al.*, 1997]. For the same reason, the methane and volatile organic compound oxidation via HO-radicals, leading to CO, can be neglected.

3. The path of transport was approximately coaxial with the ship's heading: The trajectory analysis in Figure 4 shows that the path of transport was approximately coaxial with the heading of the ship on October 12, 1996.

4. Sinks for SO_2 and CO were dilution, dry deposition, and oxidation: Due to the prevailing meteorological conditions (see Table 1), no wet deposition has to be considered as an additional sink for CO or SO_2.

5. The dilution rates for SO_2 and CO were approximately identical: Identical dilution rates may be considered as valid for CO and SO_2.

3.3.1. Total removal rate. By making the above assumptions, a case study on the kinetics of the heterogeneous oxidation of SO_2 in the MBL was possible by considering the atmosphere as a natural flow reactor. The reaction rate constant for the total removal of SO_2 and CO from the MBL is given by the equation

$$k_{\Sigma}^{(1)'} = -\frac{1}{t}\ln\frac{[C]_t}{[C]_0} \quad (1)$$

with $k_{\Sigma}^{(1)'}$ being the pseudo-first-order total removal rate (s^{-1}), t being the time of transport (s), $[C]_t$ being the concentration at time t (mol m^{-3}), and $[C]_0$ being the concentration at time $t = 0$ (mol m^{-3}).

The time of transport is calculated from the distance between the SO_2 measuring sites and the average wind speed during the corresponding SO_2 sampling time. The wind speed data are taken from the ship's meteorological station and the distances $\overline{S_1S_{1+n}}$ (km) between the measurement sites 1 and 1+n are calculated by using the orthodromic equation

$$\overline{S_1S_{1+n}} = 111.2\times\cos^{-1}[\sin La_1\times\sin La_{1+n} + \cos La_1\times\cos La_{1+n} \times\cos(Lo_{1+n} - Lo_1)] \quad (2)$$

and the recorded ship's positions (La, latitude (°); Lo, longitude (°)). The maximum distance from site 1 (October 12, 1996, 0825 UTC, 57.9°N/31.4°W) to site 8 (October 12, 1996, 1530 UTC, 56.4°N/32.1°W) is 172 km. The measurement sites 1-8 cover all samples collected in the volcanic-influenced air mass until the change of air masses. The resulting maximum time of transport from measuring site 1 to 8 is 4 hours and 59 min.

The calculation of the total removal rate of SO_2 and CO is shown in Figure 5. The concentrations of CO are averaged over the SO_2 sampling periods assuming that the prevailing atmospheric conditions (especially dilution and potential contamination from foreign sources) have the same impact on the measurements of these two trace gases. CO as a tracer is used to calculate the contribution of dilution to the SO_2 decrease due to the fact that there are no Hg data available from 0825-1330 UTC on October 12, 1996.

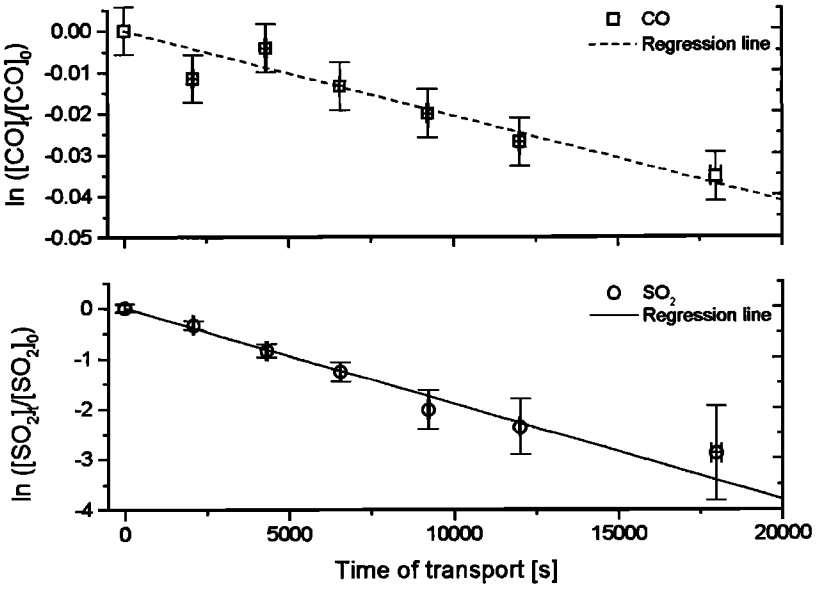

Figure 5. Estimation of the total removal rate of CO and SO_2 from the MBL on October 12, 1996, until the change of the air mass at 1530 UTC. Error bars: x = error (1σ) in the time of transport; y = analytical errors (1σ) of CO and SO_2 measurements, respectively. Regression analysis: CO, $y = (-2.075\times10^{-6} \pm 1.514\times10^{-7})\,x$, $R = 0.958$; SO_2, $y = (-1.906\times10^{-4} \pm 7.096\times10^{-6})\,x$, $R = 0.994$.

The total removal rates (s^{-1}) for SO_2 and CO are given by the slopes of the regression lines shown in Figure 5. Owing to random errors in the measurements and uncertainties in calculating the time of transport, the resulting total removal rates inhere errors themselves. The regression analyses are therefore weighted by the x and y error bars, and the lines are forced through the origin as suggested by the study of *Brauers and Finlayson-Pitts* [1997]. The resulting regression analyses indicate excellent linearities of the data points for both trace gases, considering the fact that the measurements were made in the field. The total removal rate of SO_2 is about 2 orders of magnitude larger than the removal rate of CO, as would be expected from the higher reactivity of SO_2 compared to CO. The removal rates of CO and Hg ($(2.075\times10^{-6} \pm 1.514\times10^{-7})$ s^{-1} and $(9.767\times10^{-6} \pm 3.939\times10^{-7})$ s^{-1}, respectively) are in good agreement considering the different reactivities, the deviating dry deposition velocities, and the different time periods in which the measurements of these two species were made. For this reason, it is possible to use CO as a tracer to calculate the contribution of the dilution to the SO_2 decrease during the measurement period.

In the next paragraph the reaction rate constant of the heterogeneous SO_2 oxidation in the water content of marine aerosols is calculated by subtracting all other chemical and physical sinks from its total removal rate. The reaction rate constant for the heterogeneous S(IV) oxidation on marine aerosols $k^{(1)'}_{\text{heteroOx},SO_2}$ (s^{-1}) may be calculated from the following equation:

$$k^{(1)'}_{\text{heteroOx},SO_2} = k^{(1)'}_{\Sigma,SO_2} - k^{(1)'}_{\text{homoOx},SO_2} - k_{\text{Depo},SO_2} - k_{\text{Dilution}} \quad (3)$$

with $k^{(1)'}_{\Sigma,SO_2}$ being the total removal rate for SO_2 (s^{-1}), $k^{(1)'}_{\text{homoOx},SO_2}$ being the reaction rate constant for the homogeneous oxidation of SO_2 (s^{-1}), k_{Depo,SO_2} being the dry deposition rate constant for SO_2 (s^{-1}), and k_{Dilution} being the dilution rate constant (s^{-1}). The contributions of the different sinks to the total removal rate of SO_2 from the MBL are quantified within the following paragraphs.

3.3.2. Contribution of homogeneous oxidation. SO_2 is homogeneously oxidized in the gaseous phase mainly by HO-, HO_2-, and CH_3O_2-radicals. The concentration of HO· at 30°W in October was calculated according to the study of *Collins et al.* [1997]. A comparison of the calculated HO· concentration with the results of the measurements performed by T. Brauers et al. (unpublished manuscript, 1999) on October 24 and 25, 1996, shows a good agreement for the diurnal variations. The resulting concentration of HO· for October at 55°N/30°W is given in Table 2. The concentrations of HO_2· and CH_3O_2· for October 12, 1996, were calculated from the results of the RO_x· measurements on October 13, 1996 (J. Burkert et al., unpublished manuscript, 1999). Assuming a constant $[HO_2\cdot]:[CH_3O_2\cdot]$ ratio of approximately 5:1 [*Lightfoot et al.*, 1992] and that the total sum of RO_x· consists only of HO_2· and CH_3O_2·, the resulting concentrations are given in Table 2. For further details about the calculated concentrations and diurnal variations of HO·, HO_2·, and CH_3O_2·, see *Krischke* [1998]. The reaction rate constants for the reaction of SO_2 with the radicals are shown together with the calculated mean concentrations of the radical species on October 12, 1996, from 0800-1550 UTC in Table 2.

According to the values given in Table 2, the reaction rate for the homogeneous oxidation of SO_2 is

$$\begin{aligned} k^{(1)'}_{\text{homoOx},SO_2} &= k^{(2)}_{HO\cdot} \times [HO\cdot] + k^{(2)}_{HO_2\cdot} \times [HO_2\cdot] + k^{(2)}_{CH_3O_2\cdot} \times [CH_3O_2\cdot] \\ &= 1.458\times10^{-6} + 7.835\times10^{-10} + 8.784\times10^{-8}\ (s^{-1}) \\ &= 1.547\times10^{-6}\ (s^{-1}) \end{aligned} \quad (4)$$

3.3.3. Contribution of deposition. Because of the prevailing meteorological conditions, a wet deposition along the path of transport between the measurement sites can be neglected. Assuming an altitude of 1500 m for the MBL and a deposition velocity of 4.5×10^{-3} m s^{-1} [*Warneck*, 1988], the rate constant for the dry deposition of SO_2 is $k_{\text{Depo},SO_2} = 3\times10^{-6}$ (s^{-1}).

3.3.4. Contribution of dilution. The value for the rate constant for dilution along the path of transport can be calculated from the total removal rate of CO as a tracer. This is possible due to the fact that homogeneous oxidation by HO-radicals in the gaseous phase acts as the only chemical sink for CO. A dry deposition velocity of $(0.8\text{-}5)\times10^{-4}$ m s^{-1} [*Conrad and Sailer*, 1985], a MBL mixing height of 1500 m, and a reaction rate constant for the reaction of CO with HO· of 1.68×10^{5} m^3 mol^{-1} s^{-1} (2.8×10^{-13} cm^3 $molecule^{-1}$ s^{-1}) [*Warneck*, 1988] are used together with the [HO·] from Table 2 to calculate the dilution rate constant according to the equation given below. It is assumed that the given deposition velocity (mean value equal to 2.9×10^{-4} m s^{-1}) of CO, determined for soils, is also applicable to water surfaces.

$$\begin{aligned} k_{\text{Dilution}} &= k^{(1)'}_{\Sigma,CO} - k^{(1)'}_{\text{homoOx},CO} - k_{\text{Depo},CO} \\ &= 2.075\times10^{-6} - 1.361\times10^{-7} - 1.933\times10^{-7}\ (s^{-1}) \\ &= 1.746\times10^{-6}\ (s^{-1}) \end{aligned} \quad (5)$$

3.3.5. Heterogeneous S(IV) oxidation in cloud droplets. Another potential heterogeneous sink for dissolved SO_2 is its oxidation in cloud droplets. According to the studies of *Hegg and Hobbs* [1982], the pH of cloud droplets in the marine troposphere is > 5, and therefore the main oxidant for S(IV) is O_3. A recent study of *Keene et al.* [1998] also suggests that the S(IV) + (HOCl, HOBr) reaction might play an important role in this pH range. Nevertheless, the contribution of the in-cloud reaction pathway to the SO_2 decrease is considered to be of minor impor-

Table 2. Second-Order Reaction Rate Constants for the Radical + SO_2 Reaction and Calculated Concentrations of Radical Species on October 12, 1996, in the Period From 0800-1550 UTC

	HO·	HO_2·	CH_3O_2·
Concentration [pmol m^{-3}] ([molecule cm^{-3}])	0.81 ± 0.70 ($(4.88 \pm 4.21)\times10^{5}$)	65.29 ± 11.08 ($(3.93 \pm 0.67)\times10^{7}$)	14.64 ± 3.00 ($(8.81 \pm 1.81)\times10^{6}$)
$k^{(2)}_{\text{homoOx},SO2}$ [m^3 mol^{-1} s^{-1}] ([cm^3 $molecule^{-1}$ s^{-1}])	*Warneck* [1988] 1.8×10^{6} (3.0×10^{-12})	*Calvert* [1984] 1.2×10^{1} (2.0×10^{-17})	*Lightfoot et al.* [1992] 6.0×10^{3} (1.0×10^{-14})

tance in the presented case study due to the slight cloud coverage on October 12, 1996. However, a loss of SO_2 due to oxidation in cloud droplets would require a prior vertical SO_2 transport from the ocean surface to the clouds. This vertical transport can be considered as equal for CO and SO_2 and is therefore included in the $k_{Dilution}$ term (see paragraph above).

3.3.6. First-order reaction rate constant. Given the values of the reaction rate constants for dilution, dry deposition, and homogeneous oxidation, the resulting reaction rate constant for heterogeneous oxidation of S(IV) on marine aerosols is

$$k^{(1)'}_{heteroOx,\,SO_2} = 1.906\times10^{-4} - 1.547\times10^{-6} - 3\times10^{-6} - 1.746\times10^{-6}\ (s^{-1}) = 1.843\times10^{-4}\ (s^{-1}) \quad (6)$$

Corrected from the prevailing field temperature of (8.7 ± 0.9)°C to 25°C (using the Arrhenius equation, assuming that the oxidation of dissolved S(IV) via O_3 is the dominant reaction, and using an activation energy of 25.1 kJ mol^{-1} [*Martin*, 1984] for this reaction) the reaction rate constant found in this study is $k^{(1)'}_{heteroOx,\,SO_2} = 3.31\times10^{-4}$ s^{-1} for SATP. Reactions competitive with the S(IV) + O_3 oxidation channel cannot be ruled out completely, however, and therefore the given value represents the sum of all heterogeneous S(IV) reactions in the liquid phase of marine aerosols under the prevailing reaction conditions of the presented case study. At this point it is necessary to mention that the error in the SO_2 regression analysis (see Figure 5) is of the same order of magnitude as the sum of all other sinks (homogeneous oxidation, dilution, and dry deposition). A more detailed discussion of the errors is given in a later paragraph.

3.3.7. Second-order reaction rate constant. The reaction of S(IV) + O_3 in the liquid phase of marine aerosols is believed to be somewhat faster than in more dilute systems such as rain or cloud droplets because of the high ionic strength of aqueous marine aerosols. According to the studies of *Lagrange et al.* [1994], the reaction can be 2.6 times faster in a sea-salt particle with an ionic strength of 1 mol L^{-1} than in a solution with an ionic strength of zero. The actual LWC of the aerosols with $d <$ 1.5 μm in the case of October 12, 1996, is believed to be even smaller than the value reported by *Sievering et al.* [1992] (0.1 μg m^{-3} at 91% RH) due to the fact that the relative humidity was only (71.7 ± 2.8)% on that particular day. A lower LWC of the smaller particles causes an even faster S(VI) production by S(IV) oxidation via O_3 due to the higher ionic strength and pH of the aerosol water as well as the enhanced solubility of SO_2 at a higher pH. Subsequently, the reaction will lead to a rapid acidification of the smaller particles, followed by a shift of the predominant S(IV) + O_3 reaction regime at pH > 8, to the potential S(IV) + (HOCl, HOBr), and/or the S(IV) + H_2O_2 systems when the pH decreases successively to 5 and 3, respectively. Larger particles are freshly generated by braking waves and bubble burst at the water surface and should therefore meet the value of 7.2 μg m^{-3} given by *Sievering et al.* [1992]. Because of their origin, the pH of particles with $d >$ 1.5 μm is believed to be 7-8.7 [*Keene et al.*, 1998]. Owing to the fast reaction of O_3 and S(IV) in the liquid phase at pH > 6 and the surplus of O_3 in the gaseous phase (1.36 μmol m^{-3} (33.2 ppbv) in the case of October 12, 1996, from 0830-1530 UTC), the reaction rate constant is limited by the diffusion of gaseous SO_2 to the particle surface and its phase transition into the aerosol water. The maximum possible reaction rate constant depends therefore on the available surface of coarse mode marine aerosols. This surface is in dependence on the number distribution of particles with different diameters as well as on their shape (spherical, nonspherical). This information is not directly available from the measurements performed during ALBATROSS. Therefore the number density of particles with $d >$ 0.2 μm was used in this case study to estimate the second-order rate constant. Derived from the study of *Andreae et al.* [1995], the concentration of particles with $d >$ 0.2 μm $N_{d>0.2}$ (cm^{-3}) may be calculated from the number of CN (cm^{-3}) by the following equation:

$$N_{d>0.2} \approx 0.27 \times CN - 18.4 \quad (7)$$

With an average CN of approximately 1000 cm^{-3} on October 12, 1996, the resulting concentration of $N_{d>0.2}$ is about 250 cm^{-3}. The resulting second-order reaction rate constant for the heterogeneous oxidation of SO_2 in the aerosol water of marine aerosols with $d >$ 0.2 μm is found to be $k^{(2)}_{heteroOx,\,SO_2} \approx 1.32\times10^{-6}$ cm^3 s^{-1} $particle^{-1}$ at 25°C.

3.3.8. Error estimation. The results of the kinetic study presented in this work inhere some errors which are unavoidable due to the fact that the reaction rate constants are derived from field measurements. The largest error results from the assumptions which are necessary for the approach of considering the atmosphere as a natural flow reactor. These assumptions idealize the atmosphere in a way which may be considered as not totally valid under the prevailing field conditions. Unfortunately, the value of the deviations from the ideal conditions are hard to quantify from the performed measurements. For these reasons, the least error of the reaction rate constants was calculated from the analytical error of the performed measurements and the standard deviation of the performed regression analyses. Using the method of least squares for calculating the error of the reaction rate constant, the value for the second-order rate is found to be $(1.32 \pm 0.33)\times10^{-6}$ cm^3 s^{-1} $particle^{-1}$ at 25°C. Nevertheless, the absolute error of the reaction rate constant is believed to be larger than the given ±25%. Within the next paragraph the result of this case study is compared with the results of earlier field and model studies.

4. Discussion

In order to calculate the maximum possible second-order reaction rate constant k_{Diff} (cm^3 s^{-1} $particle^{-1}$) for the removal of SO_2 from the MBL by the oxidation on marine aerosols, *Luria and Sievering* [1991] performed a model study based on diffusion theory. In this study these authors calculated k_{Diff} for three different particle diameters and the correlating number distribution of marine aerosols. Table 3 shows the results of this model study.

Table 3 shows that the second-order rate constant of 1.32×10^{-6} cm^3 s^{-1} $particle^{-1}$ found in the presented study is below

Table 3. Second-Order Reaction Rate Constants for the Diffusion-Controlled SO_2 Removal by Marine Aerosols in Dependence of the Aerosol Diameter

Particle Diameter, μm	Particle Concentration, cm^{-3}	k_{Diff}(25°C), cm^3 s^{-1} $particle^{-1}$
0.23	229	7.0×10^{-6}
1.5	2.3	4.7×10^{-5}
5.9	0.5	1.8×10^{-4}

From *Luria and Sievering* [1991].

the maximum possible rate constant as predicted by diffusion theory. The resulting first-order reaction rate constants for diffusion are in the range $(9.0\times10^{-5}\text{-}1.6\times10^{-3})$ s^{-1} which agrees with the first order constants presented in this study. The largest value is found for particles with a chosen diameter of 0.23 μm, even if the corresponding second-order rate is the smallest given in Table 3. This is due to their high concentration in the MBL compared to the occurrence of larger particles. Therefore the removal of SO_2 seems to be determined by the abundance of marine aerosols with a diameter of about 0.2 μm.

A semiempirical study on the SO_2 removal from the MBL was performed by *Sievering et al.* [1995] during the Atlantic Stratocumulus Transition Experiment/Marine Aerosol and Gas Exchange (ASTEX/MAGE) experiment in the Azores region of the North Atlantic. From their measurements these authors derived an average first-order rate constant of 1.1×10^{-4} s^{-1} at 20°C. Another empirical study on SO_2 degradation was performed by *Jaeschke et al.* [1982] in the plume of the volcano Mount Etna/Italy. These air masses contained marine aerosols as well as particles of volcanic origin because of the location of Mount Etna on the Sicily island in the Mediterranean Sea. Therefore the reaction conditions of this study may be considered as quite similar to the conditions found during ALBATROSS on October 12, 1996. *Jaeschke et al.* [1982] found a first-order reaction rate constant of $(1.7\times10^{-4}\text{-}5.0\times10^{-4})$ s^{-1} (22°C-23°C) for the total chemical sink (heterogeneous and homogeneous oxidation) in the MBL. As can be seen from the presented study, the major part of this value may be attributed to the heterogeneous oxidation on marine aerosols. The calculated first-order rate constant of 3.31×10^{-4} s^{-1} (SATP) presented in this study is in excellent agreement within the spread of the prediction, considering the fact that the measured rate constant covers an integral of all particle diameters and the sum of all heterogeneous oxidation channels, as well as with the empirical results of other authors.

The fact that the strong decrease in the SO_2 concentration on October 12, 1996, is recovered only in a slight increase in the NSS-SO_4^{2-} concentration of the aerosols might be attributed partially to the comparatively long aerosol sampling interval. The two aerosol samples on October 12, 1996, were made between 0800-1400 UTC and 1400-2000 UTC. Whereas the first sample was made in the same air mass as the SO_2 measurements, the second sample represents an integral over two different air masses, as indicated by the change of the air mass at 1530 UTC on October 12, 1996, with a longer time period in the second air mass. Therefore the temporal changes in the NSS-SO_4^{2-} and SO_2 concentrations are not directly comparable. Another important fact that has to be considered is the chemical composition of the volcanic aerosol. According to *Gudmundsson et al.* [1997] the erupted magma was basaltic andesite which consists to approximately 75% of feldspaths. In the case of andesite the most abundant of these minerals is albite ($Na[AlSi_3O_8]$). Also, the occurrence of SO_4^{2-}-containing minerals in the volcanic aerosol cannot be ruled out completely. $[SO_4^{2-}]$:$[Na^+]$ was supposedly different on October 12, 1996, from the molar ratio given by *Keene et al.* [1986] for seawater because of the complex chemical composition of volcanic aerosols. Therefore the used $[SO_4^{2-}]$:$[Na^+]$ correction might be inappropriate, as well as SS-SO_4^{2-} corrections using other ions than Na^+ and SO_4^{2-}, to calculate the NSS-SO_4^{2-} concentration in the plume of a volcano. Moreover, the actual ratio changed with time on October 12, 1996, due to a change of the air mass as well as due to sedimentation of coarse volcanic particles and the continuous introduction of freshly generated sea-salt aerosols into the MBL. Regarding these facts, the given concentrations of NSS-SO_4^{2-} on October 12, 1996, have to be treated cautiously. Considering the impact of different air masses and the uncertainties of the aerosol composition on the result of the NSS-SO_4^{2-} measurements on October 12, 1996, it is rather unlikely that the observed SO_2 loss can be reflected completely in an increase of the NSS-SO_4^{2-} concentration.

5. Conclusions

Measurements of SO_2 and NSS-SO_4^{2-} were performed over the Atlantic Ocean during the ALBATROSS experiment from October 09 to November 02, 1996, between 66.7°N and 37.8°S with a mean longitude of 29.3°W ± 4.2°W. An analysis of the size-fractionated aerosol samples shows that (34 ± 13)% of the total NSS-SO_4^{2-} was found to exist in aerosols with $d > 1$ μm. Whereas earlier studies [*Chameides and Stelson,* 1992; *Sievering et al.,* 1992] suggest that the major part of this fraction is produced by a heterogeneous oxidation of dissolved SO_2 by O_3, the reaction of S(IV) with HOCl and HOBr in the liquid water of coarse mode marine aerosols might also contribute to the NSS-SO_4^{2-} concentration [*Keene et al.,* 1998]. A kinetic study on the heterogeneous pathway of removing atmospheric SO_2 from the MBL was performed by using a physicochemical approach by considering the atmosphere as a natural flow reactor. The pseudo first- and second-order reaction rate constants were found to be 3.31×10^{-4} s^{-1} and 1.32×10^{-6} cm^3 s^{-1} $particle^{-1}$ at 25°C, respectively. The reaction rate constant for the heterogeneous oxidation of S(IV) on marine aerosols presented in this work is in good agreement with the theoretical prediction [*Luria and Sievering,* 1991] as well as the results of earlier empirical studies on the kinetics of the SO_2 removal from the MBL [*Jaeschke et al.,* 1982; *Sievering et al.,* 1995]. The value of the reaction rate constant found in this study indicates that the heterogeneous oxidation of dissolved SO_2 in the liquid phase of coarse mode marine aerosols plays an important role in the removal of gaseous SO_2 from the MBL.

Acknowledgments. The authors would like to express their gratitude to all ALBATROSS participants and the crew of the RV Polarstern for their help and cooperation. This work was funded by the Sonderforschungsbereich 233 of the Deutsche Forschungsgemeinschaft and the Alfred-Wegener-Institut. The authors also would like to thank the referees for their comments which helped to improve the original manuscript.

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(Received April 12, 1999; revised September 8, 1999;
accepted September 12, 1999.)