Review of sulfur dioxide to sulfate aerosol chemistry at Kīlauea Volcano, Hawai‘i

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\section*{ABSTRACT}

Sulfur dioxide emissions from the Kīlauea Volcano on the island of Hawai‘i and the subsequent formation of sulfate aerosols have caused a public health hazard across the state of Hawai‘i since the volcano began erupting continuously in 1983. The University of Hawai‘i at Mānoa began to forecast the trajectory and dispersion of these emissions in 2010 to help mitigate the hazards to public health. In this paper a comprehensive review of potential conversion reactions is presented with the goal of more accurately representing the sulfate chemistry in the dispersion model.

Atmospheric sulfur dioxide chemistry and major processes responsible for sulfate formation are well documented in urban and industrial settings. The atmosphere in the vicinity of Kīlauea Volcano on the island of Hawai‘i differs from that in previous investigations by virtue of being far removed from both urban and industrial settings in a remote, tropical marine atmosphere. Additionally, the combination of the high rate of sulfur dioxide emissions and trace gases and metals from Kīlauea Volcano creates a unique circumstance that requires a new look at potential conversion pathways to determine the dominant reactions.

The theoretical analysis suggests that the dominant reaction in clear air will be between sulfur dioxide and hydroxyl radical (0.01–5% h\(^{-1}\)) and the dominant reaction in cloudy air involves hydrogen peroxide (0.01% s\(^{-1}\)). Moreover, given the high SO\(_2\) emissions from the Halema‘uma‘u Crater vent, the oxidation of sulfur dioxide by these reactants is limited by their rate of production.

\section{1. Introduction}

Since 1983, Kīlauea volcano has been continuously erupting from the Pu'u ‘Ō'ō vent, or East Rift vent, emitting large amounts of sulfur dioxide (SO\(_2\)). The rate of SO\(_2\) emissions has ranged from less than 50 tons per day (t d\(^{-1}\)) to more than 10,000 t d\(^{-1}\) (Elias and Sutton, 2007). In 2008, a second vent opened up in the Halema‘uma‘u Crater, or summit vent, with a typical emission rate of \(\sim 1000–3000\) t d\(^{-1}\) estimated from ground-based remote sensing observations (Elias and Sutton, 2012). This leads to annual SO\(_2\) emissions between 0.3 and 1.1 million tons. In comparison, the 50 dirtiest power plants in the United States emit between 0.04 and 0.2 millions tons of SO\(_2\) annually (Environmental Integrity Project, 2007).

Between 2007 and 2010, it is estimated that Kīlauea volcano was responsible for 6% of global sulfate load (Elias and Sutton, 2012). Due to their size, sulfate aerosols are considered a dominant component of particulate matter smaller than 2.5 micrometers (PM\(_{2.5}\)) and can impact human health and reduce visibility. Communities in close proximity to the volcano, such as the village of Volcano, are especially susceptible to episodes of poor air quality from SO\(_2\) pollution (Fig. 1), some of which have reached levels high enough that evacuations were ordered.

While the lifetime of sulfur dioxide in the atmosphere is generally found to be on the order of 1–3 days (Rotstyn and Lohmann, 2002), the lifetime of sulfates can be much longer. The lifetime of SO\(_4\)\(^{2-}\) is limited by ubiquitous photochemical sinks whereas the lifetime of sulfate is limited by a relatively slow rate of dry deposition and scavenging of soluble compounds by precipitation.
Given the persistent northeast trade winds in tropical North Pacific, emissions from Kilauea cause frequent episodes of poor air quality in the form of volcanic smog, or vog, over downwind and leeward communities on the island of Hawai‘i. Vog is composed of sulfur dioxide gas, the primary pollutant emitted by the volcano, and sulfate aerosols, a secondary pollutant that forms from the oxidation of sulfur dioxide.

The 2005 eruption of Kilauea was accompanied by widespread vog, which was observed by satellites (Pattantyus et al., 2015). The emissions from Kilauea are a significant source of sulfur aerosols in the troposphere, and the levels of sulfate aerosols can be measured at downwind sites. However, accurate measurements of these emissions are difficult due to the intermittent nature of the eruptions and the long residence time of the sulfate aerosols in the troposphere.

Fig. 1. Days per year when EPA 1-hr SO2 concentration exceeded the National Ambient Air Quality Standard of 75 ppb. HOVE stands for Hawaiian Ocean View Estates and HAVO OB stands for Hawaiian Volcanoes Observatory.

Many attempts have been made to measure sulfur dioxide loss rates from volcanic emissions, including some in the lower troposphere or planetary boundary layer (McGonigle et al., 2004; Rodríguez et al., 2005; Oppenheimer et al., 1998; Porter et al., 2002; Kroll et al., 2015). Generally, little care is taken during these experiments to attribute SO2 loss to a particular process because the goal is only to determine if SO2 flux measurements from correlation spectrometers are reliable proxies for source emissions of ash free tropospheric plumes (McGonigle et al., 2004). The loss rate of SO2 is important for evaluating the uncertainty of volcanic emissions. If a significant portion of SO2 is lost between emission and measurement then fluxes would not be representative of the real emission rate. Loss rates (s⁻¹), k, are calculated using an expression for the decay of SO2 in the atmosphere, considering various loss mechanisms such as deposition, wet and dry deposition, and chemical conversion.

Conversion rates and processes observed in other locales may apply at Kilauea given its unique features. Unlike many other volcanoes in the tropics that emit into the free troposphere, Kilauea emits SO2 mainly into the marine boundary layer. The isolation of Kilauea from major pollution sources within the tropical marine boundary layer results in unique set of environmental conditions not previously documented. Ozone (O3) and nitrogen oxides (NOx) are found at much lower concentrations in the remote marine boundary layer than the off-shore power plant plumes. The Hawai‘i Department of Health (2013) estimated all anthropogenic sources of SO2 on Hawai‘i island amount to less than 0.5% of the total emissions.
is via reaction with hydrogen peroxide, $\text{H}_2\text{O}_2$. Given chemical kinetic theory, what range of conversion rates can one expect in the presence of $\text{SO}_2$ emissions from Kilauea volcano? This will be addressed through a detailed examination of the reaction kinetics of $\text{SO}_2$ with the hydroxyl radical and hydrogen peroxide, including determinations of important variables that influence $\text{SO}_2$ to sulfate conversion. Theoretical conversion rates are then estimated with locally observed quantities and compared with past research. Lastly, the uncertainty of theoretical conversion rates is discussed to highlight the difficulty in estimating the quantity and provides a baseline for conversion rate estimates from observations.

It is the goal of this research to quantify the conversion rate of sulfur dioxide to sulfate aerosol downwind of Kilauea volcano on the island of Hawai‘i. Several measurement campaigns found sulfur dioxide loss rates, but the distinction between the gas phase and aqueous phase conversion has not been made clear in many instances resulting in large uncertainty in loss rates. Observations during these campaigns suggest that sulfur dioxide emissions interacting with clouds or fog produce substantially more sulfate aerosols than through processes in clear air. It is the clear-air gas conversion that will impact ground-level concentrations of $\text{SO}_2$ and sulfate aerosols regularly and is of great interest here. Furthermore, only Porter et al. (2002) quantified sulfate production rates from volcanic emissions by measuring sulfur dioxide and aerosols simultaneously.

Kilauea is situated close (350 km) to large population centers (greater Honolulu ~population ~1 million) than most effusive volcanoes making the persistent eruptions an ongoing public health issue. The application of this work is to improve forecasts for ground level $\text{SO}_2$ and $\text{SO}_4$ by the University of Hawaii Vog Model (Businger et al., 2015). Preliminary model evaluation revealed poor forecast skill in both species at intermediate distances downwind. The goal is to improve forecast skill by replacing a constant $\text{SO}_2$ to $\text{SO}_4$ conversion rate, representative of bulk conversion at daily to monthly timescales, with first order conversion rates representative of gas and aqueous phase oxidation. A conversion scheme that follows the first-order conversion pathways is anticipated to improve forecast skill at timescales on the order of an hour and spatial scales on the order of kilometers while not resulting in a significant increase in computation time or resources that may delay forecast delivery to the public.

### Table 1

Previously reported $\text{SO}_2$ loss rates reported from tropical volcanoes using correlation spectrometers.

<table>
<thead>
<tr>
<th>Site</th>
<th>$\text{SO}_2$ loss rate, $k$ (s$^{-1}$)</th>
<th>$\text{SO}_2$ loss rate, % h$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Masaya, Nicaragua</td>
<td>1 ± 2e-5</td>
<td>0–10</td>
<td>McGonigle et al. (2004)</td>
</tr>
<tr>
<td>Soufrière Hills, Montserrat</td>
<td>1.5e-5 · 8.2e-4</td>
<td>5–95</td>
<td>Rodríguez et al. (2005)</td>
</tr>
<tr>
<td>Soufrière Hills</td>
<td>1.4e-3 · 5.4e-3</td>
<td>99.4 +</td>
<td>Oppenheimer et al.</td>
</tr>
</tbody>
</table>

### Table 2

Potential gas-phase $\text{SO}_2$ reactions. All values from Buckholder et al. (2000).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k$ (298 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{OH} + \text{SO}_2 \rightarrow \text{HOSO}_2$</td>
<td>$1.6 \times 10^{-12}$</td>
</tr>
<tr>
<td>$\text{O} + \text{SO}_2 \rightarrow \text{SO}_3$</td>
<td>$4.2 \times 10^{-12}$</td>
</tr>
<tr>
<td>$\text{O}_2 + \text{SO}_2 \rightarrow \text{SO}_3 + \text{O}_2$</td>
<td>$&lt; 2.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>$\text{HO}_2 + \text{SO}_2 \rightarrow \text{products}$</td>
<td>$&lt; 1.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>$\text{NO}_2 + \text{SO}_2 \rightarrow \text{products}$</td>
<td>$&lt; 2.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>$\text{NO}_3 + \text{SO}_2 \rightarrow \text{products}$</td>
<td>$&lt; 7.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>$\text{CH}_3\text{O}_2 + \text{SO}_2 \rightarrow \text{products}$</td>
<td>$&lt; 5.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OO} + \text{SO}_2 \rightarrow \text{products}$</td>
<td>$&lt; 2.2 \times 10^{-10}$</td>
</tr>
<tr>
<td>anti-$\text{CH}_3\text{CHO} + \text{SO}_2 \rightarrow \text{products}$</td>
<td>$&lt; 2.2 \times 10^{-10}$</td>
</tr>
<tr>
<td>syn-$\text{CH}_3\text{CHO} + \text{SO}_2 \rightarrow \text{products}$</td>
<td>$&lt; 2.6 \times 10^{-10}$</td>
</tr>
<tr>
<td>$\text{ClO} + \text{SO}_2 \rightarrow \text{Cl} + \text{SO}_3$</td>
<td>$&lt; 4.0 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

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The annual $\text{SO}_2$ emission rate at Kilauea is at least an order of magnitude greater than those observed at other volcanoes that $\text{SO}_2$ loss rates have been measured (McGonigle et al., 2004; Nadau, 2006; Oppenheimer et al., 1998). Large, periodic volcanic eruptions can be orders of magnitude larger, such as the 1984 eruption of Mauna Loa (Sharma et al., 2002, 2004; Oppenheimer et al., 2006) and the 2014–2015 eruption of the Barðarbunga volcanic system in Iceland (Gauthier et al., 2016). Sharma et al. (2004) estimated the total $\text{SO}_2$ flux was 4–10 times the ionic flux at Kilauea but lasted for less than a year. The presence of $\text{SO}_2$ emissions from Mauna Loa was 1.0 ± 0.2 Mt in less than one month. Gauthier et al. (2016) estimated the $\text{SO}_2$ flux was 4–10 times the ionic flux at Kilauea but lasted for less than a year. The presence of $\text{SO}_2$ emissions from Mauna Loa was 1.0 ± 0.2 Mt in less than one month. Gauthier et al. (2016) estimated the $\text{SO}_2$ flux was 4–10 times the ionic flux at Kilauea but lasted for less than a year. The presence of $\text{SO}_2$ emissions from Mauna Loa was 1.0 ± 0.2 Mt in less than one month. Gauthier et al. (2016) estimated the $\text{SO}_2$ flux was 4–10 times the ionic flux at Kilauea but lasted for less than a year. The presence of $\text{SO}_2$ emissions from Mauna Loa was 1.0 ± 0.2 Mt in less than one month. Gauthier et al. (2016) estimated the $\text{SO}_2$ flux was 4–10 times the ionic flux at Kilauea but lasted for less than a year. The presence of $\text{SO}_2$ emissions from Mauna Loa was 1.0 ± 0.2 Mt in less than one month. Gauthier et al. (2016) estimated the $\text{SO}_2$ flux was 4–10 times the ionic flux at Kilauea but lasted for less than a year. The presence of $\text{SO}_2$ emissions from Mauna Loa was 1.0 ± 0.2 Mt in less than one month. Gauthier et al. (2016) estimated the $\text{SO}_2$ flux was 4–10 times the ionic flux at Kilauea but lasted for less than a year. The presence of $\text{SO}_2$ emissions from Mauna Loa was 1.0 ± 0.2 Mt in less than one month.
This paper will be organized into three sections. Sulfur chemistry in the gas phase is presented in section two. Aqueous phase sulfur chemistry is discussed in section three. Section four provides a summary of the dominant sulfur dioxide reaction pathways around Kilauea Volcano.

2. Gas phase

Past research has determined that only the hydroxyl radical, OH, is important for the oxidation of sulfur dioxide to sulfate aerosol in the gas phase during daytime (Rattigan et al., 2000; Eatough et al., 1994 and references therein). The latest data from the Jet Propulsion Laboratory (JPL) shows that most reactions can be discounted based on their reaction rate constants (Table 2) (Buckholder et al., 2015). Oxidation via the Criegee intermediates can also be discounted because the requisite reactants to make Criegee radicals are absent.

The hydroxyl radical is formed through photolytic reactions and therefore has diurnal and seasonal cycles. OH is considered the most important oxidizing agent in the atmosphere because it is extremely reactive and able to oxidize most chemicals found in the atmosphere (ESPERE Climate Encyclopedia, 2006). Despite being highly reactive, OH concentrations remain relatively constant at timescales of days to weeks (1.0 part per trillion or ppt), meaning production and loss rates are in quasi-steady state. Ozone (O₃) is considered the main precursor.

\[
\Delta \ln k_1 = 0.0452 \frac{\Delta T}{T}
\]

\[
\ln k_1 = (24.91 \pm 0.41) - (8290 \pm 390)/T
\]

Fig. 2. Concentrations of OH measured during INTEX-B flights. Blue dots represent all 1-min averaged OH measurements and orange dots represent just those collected below 3.0 km AGL. The black line represents the hourly averaged OH values. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

\[\text{Table 3} \]

Quantities used to calculate range of theoretical gaseous conversion rates

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Daytime</th>
<th>Nighttime</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>21.9</td>
<td>17.1</td>
</tr>
<tr>
<td>Relative humidity (%)</td>
<td>79</td>
<td>100</td>
</tr>
<tr>
<td>SO₂ (molecules cm⁻³)</td>
<td>2.46 × 10¹⁰</td>
<td>2.46 × 10¹⁰</td>
</tr>
<tr>
<td>k (molecules cm⁻³ s⁻¹)</td>
<td>5.58 × 10⁻¹³</td>
<td>4.04 × 10⁻¹³</td>
</tr>
<tr>
<td>OH (molecules cm⁻³)</td>
<td>1 × 10⁷</td>
<td>2.2 × 10⁻¹³</td>
</tr>
<tr>
<td>Conversion rate (h⁻¹)</td>
<td>2</td>
<td>0.03</td>
</tr>
<tr>
<td>Conversion rate range (k uncertainty) (h⁻¹)</td>
<td>0.8-5</td>
<td>0.01-0.05</td>
</tr>
</tbody>
</table>

Previous measurement campaigns have also found nocturnal OH concentrations in the range 2 × 10⁵ to 10⁹ molecules cm⁻³ (Brown et al., 2012). Given that tradewinds are persistent near Hālāmaʻumaʻu Crater, we assume that a persistent supply of OH is advected into the region of the plume for reaction with emitted SO₂. The subsequent values calculated from equations (6) and (7) were 4.04 × 10⁻¹³ molecules⁻¹ s⁻¹ and 5.58 × 10⁻¹³ molecules⁻¹ s⁻¹ for night and day, respectively. The difference in k values is approximately the same as the relatively small ΔT (4.8°C) and ΔRH (21%). If one assumes 100% conversion, this results in SO₂ to sulfate conversion rates of 1.98 × 10⁴⁹ molecules⁻¹ s⁻¹ and 1.37 × 10⁴⁹ molecules⁻¹ s⁻¹ for night and day, respectively. That works out to 7.13 × 10⁻⁷ molecules cm⁻³ h⁻¹ and 4.9 × 10⁻⁹ molecules cm⁻³ h⁻¹ for night and day, respectively. By percentage of SO₂ concentration for each time period, that works out to a rate of 0.03% h⁻¹ and 2% h⁻¹ for nighttime and daytime, respectively.

These rates of sulfate formation are similar to those of Kroll et al. (2015) and lower than those found by Porter et al. (2002) but within the range of values for SO₂ loss found elsewhere (McGee et al., 2004; Rodríguez et al., 2005). The uncertainty in k, resulting from the temperature dependence represented in equation (7), ranges in a range from 2.29 × 10⁻¹⁰ to 1.42 × 10⁻¹² molecules cm⁻³ for the day and 1.64 × 10⁻¹³ to 1.06 × 10⁻¹₂ molecules cm⁻³ for night. The corresponding conversion rate range is 0.8-5% h⁻¹ for the day and 0.01-0.07% h⁻¹ at night. A more thorough treatment is required.
The diurnal cycle of OH is best illustrated in Fig. 2 with data from the INTEX-B flights near Hawaii (region 4 in Singh et al., 2008). Flights were flown from April 17 to May 1 over the Pacific Ocean. Data collected between \(-180^\circ\) W and \(-140^\circ\) W and 18\(^\circ\)N and 40\(^\circ\)N are displayed in Fig. 2. Several legs were flown near the surface during both day and night. Daytime concentrations peaked between \(6 \times 10^6\) molecules cm\(^{-3}\) and \(1 \times 10^7\) molecules cm\(^{-3}\) with nighttime concentrations approximately two orders of magnitude lower.

Further studies have found similar diurnal cycles of OH in the middle latitudes during various seasons (Forberich et al., 1999; Hand et al., 1991). Hand et al. (1991) found a range of OH concentrations from a peak of \(4 \times 10^6\) molecules cm\(^{-3}\) during the day to a minimum that oscillated about \(1 \times 10^5\) molecules cm\(^{-3}\) overnight. Forberich et al. (1999) found a larger daytime range over several days from an early morning minimum on the order of \(10^5\) molecules cm\(^{-3}\) to a maximum of \(8 \times \sim 10^6\) molecules cm\(^{-3}\).

Hypothetical limits of sulfur dioxide oxidation by the hydroxyl radical can be calculated with the use of values from Fig. 2 and equation (5). For this calculation hourly average temperature and RH values from 20 July 2014 at Hawaii's Volcanoes National Park Observatory (HAVO-OB) were used to determine \(k\) (Table 3). This site is chosen for its proximity to the Halema'uma'u Crater vent. Over the period of measurement at HAVO-OB from initial deployment in 2011 to July 2014, the median SO\(_2\) concentration measured was approximately \(2.46 \times 10^{11}\) molecules cm\(^{-3}\) (10 ppb). This value is used for both daytime and nighttime calculations. OH concentrations are obtained from INTEX-B flight presented in Fig. 2 to represent the diurnal range of \(\sim 2 \times 10^8\) molecules cm\(^{-3}\) (Sander et al., 2011). The loss/production rate of OH was approximately \(2 \times 10^{-8}\) molecules cm\(^{-3}\) s\(^{-1}\) and was dominated by reactions with CO. This represents a cap on OH reactions with SO\(_2\), which would have been reached as SO\(_2\) concentrations approached \(1 \times 10^{14}\) (10 ppm) during maximum OH concentrations. This limit remained proportional to SO\(_2\) concentrations throughout the diurnal cycle (Fig. 3). For our purposes, we assume that mixing between the plume and the environment over periods of tens of minutes lead to near steady-state concentrations of OH even in the presence of SO\(_2\) plumes.

The model sensitivity study of Jourdain et al. (2016) found the depletion of O\(_3\) by halogen reactions led to decreases in OH, beyond the uncertainty in the conversion rate would take into account variability in OH concentrations as well, however even with this consideration in OH a majority of theoretical conversions will fall within the range of values above which were calculated with the extreme values of OH concentration measured during INTEX-B.

It is important to note that theoretical conversion rate coefficients are meant to represent standard atmospheric conditions. A typical atmospheric concentration of SO\(_2\) is in the range of \(1-10\) ppb (\(2.46 \times 10^7\) molecules cm\(^{-3}\) to \(2.46 \times 10^9\) molecules cm\(^{-3}\)), lower than the concentration used above (10 ppb). SO\(_2\) concentrations can easily exceed 100 ppm (\(2.46 \times 10^{10}\) molecules cm\(^{-3}\)). Halema'uma'u Crater vent (Andrew Sutton, personal communication). Given such high concentrations of SO\(_2\), eight to nine orders of magnitude greater than OH, the reaction rate would be limited by OH concentrations and how rapidly OH can be produced.

Because the concentration of OH is considered steady state, environmental formation rate can be approximated by the loss rate. The loss rate for each gas is dominated by the carbon monoxide (CO) and methane (CH\(_4\)). CO and CH\(_4\) would be the leading reactants with OH in the marine boundary layer given the presence of volatile organic compound (VOC) sources upwind. Concentration data for these gases were available from the INTEX-B data set. The loss/production rate was estimated via

\[
\frac{d[OH]}{dt} = k_{CO} [OH][CO] + k_{CH_4}[OH][CH_4]
\]

the plume through mixing between the plume and environment.

### 3. Aqueous phase

If the SO\(_2\) plume encounters a cloud then SO\(_2\) can be taken up by cloud water and undergo oxidation via aqueous phase pathways. Though this discussion will be limited to in-cloud oxidation it is possible that some loss of gas-phase SO\(_2\) may occur due to mass transfer to aerosols.

Faloona et al. (2009) and Faloona (2009) have argued that SO\(_2\) transfer to coarse sea salt aerosols (SSA) in non-negligible process is highly dependent on aerosol pH with significant mass transfer occurring at higher pH values, but a review of past observations by Faloona (2009) suggests that supermicron, or coarse, SSA have near to slightly alkaline pH while submicron aerosols are very acidic. Observations from PASE allowed Faloona et al. (2009) to estimate aerosol mass transfer rates to coarse SSA of 5–10% hr\(^{-1}\) at a night time average daytime loss of 5% hr\(^{-1}\). Thus SSA uptake of SO\(_2\) may be of homogeneous reactions with OH, but remains dependent on aerosol pH such that rates vary from 0 to 10% based on atmospheric variability. Given the height of the Kilauea vents and prevailing patterns this pathway may be important during high wind events, when the coarse mode SSA are lofted high in the boundary layer, or when the plume descends down to sea level.

When SO\(_2\) dissolves in water it forms a weak acid that undergoes two dissociations to form a total of three species, HSO\(_3^\), H\(_2\)SO\(_3\), and SO\(_3^{2-}\), the sum of which are known collectively as H\(_2\)SO\(_3\). The solubility of SO\(_2\) is a function of temperature and pH of the solution. At pH 2–7, S\(_{HV}\) is almost entirely in the form of the bisulfate (H\(_2\)SO\(_3\)) (Seinfeld and Pandis, 1998). At lower temperatures there is a higher solubility. The reaction rate will decrease with decrease in temperature, however, the increased reactant concentration will tend to increase the reaction rate. Finally, the solubility of

\[
\text{H}_2\text{SO}_3 = \text{H}^+ + \text{SO}_3^{2-}
\]

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![Fig. 3. Estimated loss/production rate (s\(^{-1}\)) of OH calculated from INTEX-B CO, CH\(_4\), and OH data.](image-url)
those associated with reactions with SO$_2$ resulted in 30% longer SO$_2$ lifetimes. In their Ambrym simulations, halogen ratios such as HBr/SO$_2$ and HCl/SO$_2$, were estimated to be an order of magnitude more abundant than observations of halogens at Kilauea (Mather et al., 2012), while Ambrym SO$_2$ emissions were 4-6x as great as Kilauea meaning actual HBr emission rates are two orders of magnitude lower at Kilauea. Although some depletion may be occurring within the Kilauea plume due to halogen and SO$_2$ reactions, the magnitude is likely lower given the lower abundance of both SO$_2$ and halogens.

Other studies have found a reduction in O$_3$ in SO$_2$ plumes, which also limits the production of OH via halogen reactions (Vance et al., 2010; Oppenheimer et al., 1996; Schuman et al., 2011; Kelly et al., 2013; Surl et al., 2015). Surl et al. (2015) find the typical range of HBr/ SO$_2$ measured at various volcanoes to encompass the rates measured at Kilauea. These studies suggest the limit of OH production in SO$_2$ plumes is as much as 30% lower than the OH production rate calculation.

In summary, theoretical gas phase conversion rates estimated for conversion of SO$_2$ to sulfate aerosol display rates less than 10% h$^{-1}$. Daytime conversion rates are estimated to be 2.9 ± 2.1% h$^{-1}$, while nighttime conversion rates are estimated to be 0.04 ± 0.3% h$^{-1}$. Very high concentrations of SO$_2$ have been observed near the vents and could lead to this reaction being severely limited by availability of OH. Additionally, in-plume OH limiting reactions via HBr could further reduce SO$_2$ conversion rates by as much as 30%.

There is some uncertainty in the OH conversion rate that stems from the temperature and moisture dependence of the reaction between OH and SO$_2$, which is represented in the conversion rate coefficient, k. Sander et al. (2011) suggest the uncertainty associated with the temperature dependence of the reaction is minimized near room temperature.

\[ K_{H}[H_2O_2] = \exp\left(\frac{a}{T} - b\right) \]

(10)

where \( a = 7024 \pm 138 \) and \( b = 11.97 \pm 0.48 \) and \( T \) (K) is the equilibrium temperature. Huang and Chen (2010) showed that this relation is relatively independent of solution pH in the range of 1–7. This relationship results in \( K_{H}[H_2O_2] = 1.08 \times 10^6 \text{M}^{-1} \text{atm}^{-1} \) at 25°C (Huang and Chen, 2010), where \( M \), molarity, is the concentration of solute in solution expressed as 1 mol L$^{-1}$ or 1 × 10$^{-3}$ mol cm$^{-3}$. The recommended value of \( K_{H}[H_2O_2] \) by the JPL is 8.44 × 10$^4$ M atm$^{-1}$ (for 278 K < \( T \) < 303 K) with temperature dependence values for \( a = 7,600 \) and \( b = 14.16 \) (Sander et al., 2011). The recommended value for \( K_{H}[SO_2] \) from JPL is 1.36 M atm$^{-1}$ and the temperature dependence is given by

\[ K_{H}[SO_2] = \exp\left(\frac{a}{T} - b + cT\right) \]

(11)

where \( a = 4250, b = 39.72 \), and \( c = 4.525 \) (Sander et al., 2011). The uncertainty in \( K_{H} \) is given as 10–50%.

The aqueous phase reaction of sulfur dioxide and hydrogen peroxide is expressed by Hoffman and Calvert (1985) as

\[ - \frac{d[SIV]}{dt} = \frac{k [H^+][H_2O_2][HSO_3^-]}{1 + K[H^+]} \]

(12)

where the reaction constant, \( k = 7.45 \times 10^7 \text{M}^{-2}\text{s}^{-1} \), \( K = 13 \text{M}^{-1} \) at 298 K [HSO$_3$] = [SO$_2$(aq)]K$_s$ because it is assumed that most dissolved SO$_2$ is in the form of bisulfite, where \( K_s \) is the dissociation constant of SO$_2$H$_2$O = 1.3 × 10$^{-2}$ M and the concentration of the hydrogen ion, [H$^+$], is the estimate of water droplet pH. Martin and Damschen (1981) provide another popular estimate of counterbalance the decreased reaction rate $SO_3^-$, H$_2$O$\cdot$SO$\cdot$H$_2$O$\cdot$SO$_3^-$ (Eatough et al., 1994).

Hydrogen peroxide (H$_2$O$_2$) and ozone (O$_3$) are the most limiting oxidants for SO$_2$ in the aqueous phase. However, ozone reactions are highly pH dependent and only become the leading oxidant at pH > 25 (Hegg, 1989; Seinfeld and Pandis, 1998). Hydrogen peroxide reactions are relatively independent of pH between pH 2–6. The pH of atmospheric water droplets reported is typically 3–6 (Eatough et al., 1994). Rainwater samples taken in Hawaii yield an average pH = 4.5 (Huang and Yoshinaga, 1981) while Siegel et al. (1999) found 84% of samples downwind of Kilauea had pH values less than 5.0. The particle size of rain droplets relative to cloud droplets suggests that the pH of the smaller volume cloud droplets will likely be even lower, thus the pH of rain droplets represents an upper limit. This suggests hydrogen peroxide is the leading oxidant of sulfur dioxide in the aqueous phase in the vicinity of Kilauea. Hydrogen peroxide, like the hydroxyl radical, is produced photochemically, both in the gas phase and aqueous phase (Warneck, 1999). The average concentration of hydrogen peroxide found during the Pacific Atmospheric Sulfur Experiment (PASE) was 1.0 ppb (Simpson, 2010). PASE was designed to study the chemistry in the trade wind regime that may influence cloud droplet chemistry and aerosol concentrations and composition (Bandy et al., 2011).

In order for the aqueous phase reaction to occur, both sulfur dioxide and hydrogen peroxide gases must be dissolved in water. Hydrogen peroxide is considered highly soluble and sulfur dioxide is moderately soluble. Equilibrium between the gas and aqueous phase concentration is reached on very short time scales relative to the droplet lifetime so that equilibrium can be considered. This allows the use of Henry's Law constants to determine aqueous phase concentrations.
\[ d([\text{SO}_2](aq)) \over dt = k [H^+][\text{H}_2\text{O}_2][\text{SO}_2](aq) \]

where \( k = 9.1 (\pm 0.5) \times 10^7 \text{M}^{-2}\text{s}^{-1} \) as proposed by Maass et al. (1999). Caffrey et al. (2001) found this kinetic relation to work best for their modeling of cloud particle growth. If we assume 100% conversion efficiency to sulfate aerosol, equation (13) can be treated as an aerosol production equation by changing the left hand term to

\[ d([\text{SO}_2](aq)) \over dt = k [H^+][\text{H}_2\text{O}_2][\text{SO}_2](aq) \]

Overnight observations at HAVO-OB on 20 July 2014 are used to estimate aqueous phase conversion rates because RH = 100% during this period. \( K_{\text{H}} \) values are corrected for pressure (altitude) using the 2014 annual mean station pressure from HAVO-OB. Values calculated from equations (10) and (11) at a temperature = 290.35 K and \( p = 0.867 \text{ atm} \) are \( K_{\text{H}}[\text{H}_2\text{O}_2] = 1.78 \times 10^8 \text{M}^{-1} \text{atm}^{-1} \) and \( K_{\text{H}}[\text{SO}_2] = 1.55 \text{ M atm}^{-1} \) for hydrogen peroxide and sulfurdioxide, respectively. When multiplied by the gas concentrations for \( H_2O_2 (1 \times 10^{-9} \text{ atm}^{-1}) \) and \( \text{SO}_2 (1 \times 10^{-8} \text{ atm}^{-1}) \) the aqueous phase concentrations are \( 1.78 \times 10^{-4} \text{M} \) and \( 6.37 \times 10^{-6} \text{M} \), respectively.

Note that the \( \text{SO}_2 \) gas \( ([\text{SO}_2](g)) \) concentration is an order of magnitude greater than \( [\text{H}_2\text{O}_2](g) \), but the solubility of \( \text{H}_2\text{O}_2 \) results in dissolved concentrations of \( [\text{H}_2\text{O}_2](aq) \) four magnitudes greater than \( [\text{SO}_2](aq) \). Thus, \( [\text{SO}_2](aq) \) concentrations will be lower than \( [\text{H}_2\text{O}_2](aq) \) initially, however, higher \( [\text{SO}_2](g) \) concentrations will continue to dissolve and react with \( [\text{H}_2\text{O}_2](aq) \) and ultimately \( [\text{H}_2\text{O}_2](g) \) will be the limiting reactant. Using the rate coefficient, \( k = 9.1 \times 10^7 \text{M}^{-2}\text{s}^{-1} \), provided by Maass et al. (1999) the loss rate of [SO\textsubscript{2}](aq) is meaning that over time (especially overnight) \( \text{H}_2\text{O}_2 \) may still be depleted. The lower bound estimates are closer to those of Simpson (2010) and differ in proportion to [SO\textsubscript{2}] used in the calculations.

If the rate of \( \text{H}_2\text{O}_2 \) production cannot keep pace with removal through aqueous \( \text{SO}_2 \) reactions then secondary reaction pathways will become important. Although \( \text{O}_3 \) reactions are more dependent on solution pH, this pathway remains important at pH 3–6 should \( \text{H}_2\text{O}_2 \) be absent in significant concentrations (Eaught et al., 1994). Ozone concentrations in the marine boundary layer are higher than \( \text{H}_2\text{O}_2 \), with mean concentrations between 15 and 19 ppb, and it is moderately soluble with a Henry's Law coefficient of 1.3 \( \times 10^{-2} \text{M} \). The \( \text{O}_3 \) rate expression is given as

\[ -d [\text{SO}_2] \over dt = k_0 [\text{SO}_2 \cdot \text{H}_2\text{O}] + k_1 [\text{HSO}_3^-] + k_2 [\text{SO}_2^-] [\text{O}_3(aq)] \]

where \( k_0 = 2.4 \times 10^4 \text{M}^{-1}\text{s}^{-1} \), \( k_1 = 3.7 \times 10^5 \text{M}^{-1}\text{s}^{-1} \), and \( k_2 = 1.5 \times 10^9 \text{M}^{-1}\text{s}^{-1} \) (Hoffman and Calvert, 1985), however, if all \( \text{H}_2\text{O}_2 \) is consumed in reactions with \( \text{SO}_2 \) then solution pH can easily drop below 3 making this reaction negligible. Additionally, the depletion of \( \text{O}_3 \) within volcanic plumes (Vance et al., 2010; Oppenheimer et al., 2010; Schumann et al., 2011; Kelly et al., 2013; Surl et al., 2015) will limit the impact of this pathway.

Emission estimates from Halema‘uma‘u Crater by Mather et al. (2012) show traces of Fe and Mn are being emitted, making conversion catalyzed via the Fe(III) and Mn(II) pathways possible. Mn is highly soluble and Fe is not water-soluble but would dissolve in an acidic solution such as H\textsubscript{2}SO\textsubscript{4} so it is realistic to assume all Fe is dissolved in a within a matter of minutes, which is the typical residence time of a parcel in-cloud. Measurements by Daum et al. (1984) suggest that these reactants rarely autoxidize in clouds or fog. Further evidence in measurements by Barth et al. (1989) reveal that aqueous concentrations of hydrogen peroxide are always below those expected in equilibrium from Henry's Law. This suggests that the sulfur dioxide sink is removed by hydrogen peroxide faster than it can be replaced.

Simpson (2010) took three approaches to estimate in-cloud oxidation of \( \text{SO}_2 \) to sulfate aerosols using project-averaged values from the Pacific Atmospheric Sulfur Experiment (PASE) conducted in 1985. Using chemical kinetic theory, the amount of \( \text{SO}_2 \) oxidized during single cloud encounter lasting 7 min (based on updraft velocities of 0.3 m/s) in cloud and assuming a 500 m deep cloud is 50 ± 30%. The rate of dimethyl sulhide to \( \text{SO}_2 \) during individual cloud encounters is used to approximate the consumption of \( \text{SO}_2 \) using method two. Again, the rate is found to be 50 ± 30%. The third approach estimates conversion with a sulfur flux budget. This method suggests 33-46% total \( \text{SO}_2 \) consumption to produce 45–80% of the total sulfate. It is important to note that \( \text{SO}_2 \) concentrations during PASE are between 1 and 100 ppb, significantly lower than concentrations in the vicinity of Kilauea.

In light of past observations and estimates of Simpson (2010) it is important to assess the uncertainty in the reaction rate calculated because a significant depletion of \( \text{H}_2\text{O}_2 \) will make reactions between \( \text{SO}_2 \) and other reactants increasingly important.

Much of the uncertainty associated with the aqueous phase reactions of \( \text{SO}_2 \) with \( \text{H}_2\text{O}_2 \) stems from the uncertainty in the temperature dependence of the Henry's Law constants and the conversion coefficients. The uncertainty in \( K_{\text{H}}[\text{SO}_2] \) is approximately 50% (Seinfeld et al., 2011) while \( K_{\text{H}}[\text{H}_2\text{O}_2] \) is less than 1% (1.76 (± 0.05) \( \times 10^8 \text{M atm}^{-1} \)). Because the reaction is limited by \( \text{H}_2\text{O}_2 \) consumption any error resulting from uncertainty in \( \text{SO}_2 \) solubility is negligible. Estimates of \( k \) range from \( 5.2 \times 10^4 \text{M}^{-2}\text{s}^{-1} \) to \( 9.6 \times 10^4 \text{M}^{-2}\text{s}^{-1} \), using the lower bound \( \text{SO}_2(aq) \) loss will be 3% per second, or roughly
hydroxyl radical and hydrogen peroxide are the dominant reaction pathways. For a frequently observed ground-level SO2 concentration (10 ppb) the range of conversion rates for the hydroxyl radical and hydrogen peroxide reaction pathways are estimated from kinetic theory, where the range is representative of the uncertainty associated with concentrations of Fe that are typically only found close to the emission source.

The importance of the gas-phase reaction to ground level concentrations of both SO2 and SO4 is paramount to improving forward modeling of plume downwind of Kilauea Volcano. For kilometers downwind the volcanic plume can often be observed traveling at or just above the ground due to stable conditions. Ground level clouds are only occur near the summit of Kilauea over of period of hours making the relative contributions of aqueous phase reactions to ground level concentrations minor over the course of the year. Gas phase oxidation via OH is expected in the range of 0.8–5% h−1. Theoretical estimates of in-cloud conversion are more straightforward as gas-phase conversion. Oxidation via H2O2 is limited in-cloud by ambient concentrations but can reach 100% for SO2 concentrations < H2O2 gas concentrations.

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reaction on solution pH and low ozone concentrations in the Central Pacific. Past observations of rainfall pH in Hawai‘i suggest a range of pH values between 3 and 5.5, which is likely an upper bound. Estimated reaction rates suggest a conversion rate of dissolved SO\textsubscript{2} between 3 and 50% s\textsuperscript{-1}. Such a rapid reaction coupled with a rapid diffusion process is unsustainable over long periods of time and will quickly lead to the depletion of the limiting reactant. Given that parcels of air spend no more than a few minutes in shallow marine cumulus clouds (Simpson et al. 2008) and the observations of Daum et al. (1984) and Barth et al. (1989), the reaction estimate here is limited by the ambient H\textsubscript{2}O concentrations (1.0 ppb) and H\textsubscript{2}O\textsubscript{2} production, which has been estimated by Martin et al. (1997) to be 0.85 ppb d\textsuperscript{-1}. Thus for an air parcel penetrating a cloud with 10 ppb SO\textsubscript{2} and 1 ppb H\textsubscript{2}O\textsubscript{2}, the maximum loss of SO\textsubscript{2} through conversion to SO\textsubscript{4}\textsuperscript{2-} is 1 ppb or 10%.

Other aqueous phase reactions via O\textsubscript{3}, Fe(III), and Mn(II) HOBr, and HOCI were considered to assess if the associated conversion rates are significant relative to H\textsubscript{2}O\textsubscript{2}. Ozone reactions are highly pH-dependent and become important only in the event that H\textsubscript{2}O\textsubscript{2} is drawn down first. A reduction in H\textsubscript{2}O\textsubscript{2} via reaction with SO\textsubscript{2} will produce sulfuric acid, H\textsubscript{2}SO\textsubscript{4}, reducing solution pH limiting any contribution from O\textsubscript{3}. Observed ozone depletion within volcanic plumes (Surl et al. 2015) further suggests this mechanism is negligible. Fe and Mn are emitted from HALEMA‘UMA‘U (Mather et al. 2012) and were measured by Sansone et al. (2002) and Benitez-Nelson et al. (2003). Measured concentrations and reaction kinetics for Fe(III) and Mn(II) suggest that catalyzed reactions with Mn(II) are negligible, whereas Fe(III) could be important should H\textsubscript{2}O\textsubscript{2} be depleted. The importance of this reaction is limited to the region around the vents because of low Fe emission rates, however periods of clouds near the summit of Kilauea can increase the significance of this rapid reaction rate. There is much uncertainty about the reaction rates of HOBr and HOCl but simulations suggest that HOBr may play as an important role as Fe(III) whereas HOCl is limited by pH.

Limits in both reaction rates theoretically exist based on environmental factors (i.e. temperature, relative humidity, solar insolation), emission rates, and ambient reactant concentrations. The oxidation of SO\textsubscript{2} from Kilauea is dominated by the hydroxyl radical in the gas phase and hydrogen peroxide in the aqueous phase. Given high SO\textsubscript{2} emissions from the summit vent at HALEMA‘UMA‘U Crater, the oxidation by these reactants may become limited by their modest ambient concentrations.

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