Review article

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

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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 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 sulfur dioxide chemistry in the dispersion model.

Atmospheric sulfur dioxide chemistry and major process 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 the hydroxyl radical (0.01–5% h^{-1}) and the dominant reaction in cloudy air involves hydrogen peroxide (3–50% 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.

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 $\sim 1\,000$–$3\,000\ t\,d^{-1}$ 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).

Given the persistent northeast trade winds in tropical North Pacific, emissions from Kīlauea 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.

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 fine 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 (Rotstayn and Lohmann, 2002), the lifetime of sulfates can be much longer. The lifetime of SO_2 is limited by ubiquitous photochemical sinks whereas the lifetime of sulfate is limited by a relatively slow rate of dry deposition and the erratic nature of wet deposition. Due to longer residence times, sulfate impacts can become pervasive. Hand et al. (2012) showed that long range transport of sulfates from Asia impact air quality in the Pacific Northwest. It has also been demonstrated that Hawai'i is affected by Asian aerosols from March to May that includes measurable sulfate (Shaw, 1980; Perry et al., 1999; Holben et al., 2001).
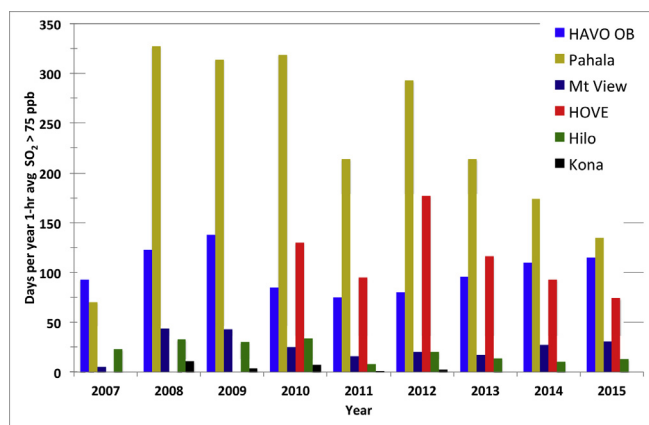
Fig. 1. Days per year when EPA 1-hr SO_2 concentration exceeded the National Ambient Air Quality Standard of 75 ppb. HOVE stands for Hawaiian Ocean View Estates and HAVO OB stands for Hawai'i Volcanoes Observatory.

Given the variety of negative impacts from sulfate aerosols (Businger et al., 2015), it is important to determine the rate of sulfate formation from sulfur dioxide emitted naturally and by industry. There are a number of active volcanoes worldwide that degas sulfur dioxide (http://so2.gsfc.nasa.gov/), leading to sulfates that regularly impact the air quality of a number of communities including those in Iceland, Nicaragua, Italy, and the Caribbean. Coal-burning power plants and industrial smelters also produce large amounts of sulfur dioxide and sulfates. The rapid expansion of coal power plants in China and India has led to hazardous air quality impacting local communities, neighboring countries, and locations far downwind (e.g., Hand et al., 2012).

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; Rodriquez 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 SO_2 loss to a particular process because the goal is only to determine if SO_2 flux measurements from correlation spectrometers are reliable proxies for source emissions of ash free tropospheric plumes (McGonigle et al., 2004). The loss rate of SO_2 is important for evaluating the uncertainty of volcanic emissions. If a significant portion of SO_2 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 exponential decay equation

$$\Phi = \Phi_0 e^{-kt} \tag{1}$$

where Φ and Φ_0 represent SO_2 fluxes estimated from transects with correlation spectrometers taken at various distances downwind separated by some time, t. An implicit assumption in equation (1) is that loss rates are a first order process with respect to SO_2 concentrations. A brief summary of previous SO_2 loss rate estimates at volcanoes found in the tropics are presented in Table 1. McGonigle et al. (2004) found

Table 1
Previously reported SO_2 loss rates reported from tropical volcanoes using correlation spectrometers.

Site	SO_2 loss rate, k (s^{-1})	SO_2 loss rate, % h^{-1}	Reference
Masaya, Nicaragua	1 ± 2e-5	0–10	McGonigle et al. (2004)
Soufrière Hills, Montserrat	1.5e-5 - 8.2e-4	5–95	Rodriquez et al. (2005)
Soufrière Hills, Montserrat	1.4e-3 - 5.4e-3	99.4 +	Oppenheimer et al. (1998)
Kīlauea, Hawai'i	1.9e-5 - 5.5e-5	7–18	Porter et al. (2002)
Kīlauea, Hawai'i	2.4e-6–5.3e-7	0.2–1.0	Kroll et al. (2015)

moderate loss rates at Mayasa volcano, Nicaragua. A majority of this loss rate was later attributed to plume dispersion caused by accelerated wind speeds between observation sites suggesting a very slow loss rate via gaseous conversion (Nadau, 2006). Comparatively, Rodriquez et al. (2005) estimated loss rates at Soufrière Hills volcano, Monserrat, British Virgin Islands that ranged from relatively slow conversion (5%) to nearly total depletion of SO_2 (95%) over the course of an hour. Oppenheimer et al. (1998) found rates an order of magnitude greater than Rodriquez et al. (2005) at Soufrière Hill, but noted that the plume was entrained into orographic clouds. There is a large difference in the conversion rates that can be explained by the various oxidation pathways responsible for the conversion. The implicit assumption is that most lost SO_2 is converted to sulfate aerosols. Oppenheimer et al. (1998) caution that their observations of the rapid loss of volcanic SO_2 in-cloud could lead to a global underestimation of volcanic SO_2 and subsequently underestimate tropospheric sulfate and its impacts on climate.

Estimates of sulfate production from Kīlauea calculated using ground-based remote sensing methods imply a rate between 7 and 18% an hour (Porter et al., 2002). This assumes no primary sulfate being emitted, which may be incorrect based on near-vent measurements by Mather et al. (2012) who found approximately 1% sulfate relative to SO_2 emissions during the early eruptive period of Halema'uma'u in 2008. This observation suggests a co-emitted catalyst (e.g., Fe^{2+}) may cause significant sulfate formation as SO_2 exits the vent, inflating conversion rates estimated further downwind. Such reactions have been implied previously (Eatough et al., 1984).

Kroll et al. (2015) measured ground-level sulfur dioxide and sulfate aerosols downwind of Kīlauea simultaneously. They found SO_2 oxidation by OH to be the likely conversion pathway but the conversion rate was much slower than previous estimates likely due to OH depletion from high SO_2 emissions.

Conversion rates and processes observed in other locales may not apply at Kīlauea given its unique features. Unlike many other volcanoes in the tropics that emit into the free troposphere, Kīlauea emits SO_2 into the marine boundary layer. The isolation of Kīlauea from major pollution sources within the tropical marine boundary layer results in a unique set of environmental conditions not previously documented. Ozone (O_3) and nitrogen oxides (NO_x) are found at much lower concentrations in the remote marine boundary layer than the oft-studied power plant plumes. The Hawai'i Department of Health (2013) estimated all anthropogenic sources of SO_2 on Hawai'i island amount to less than 0.5% of the annual SO_2 emissions from Kīlauea. The high SO_2 emission rate at Kīlauea is at least an order of magnitude greater than those observed at other volcanoes that SO_2 loss rates have been estimated (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., 2004) or 2014–2015 eruption of the Bárðarbunga volcanic system in Iceland (Gauthier et al., 2016). Sharma et al. (2004) estimated the total SO_2 load from Mauna Loa to be 1.0 ± 0.2 Mt in less than one month. Gauthier et al. (2016) estimated the SO_2 flux was 4–10 times the current flux at Kīlauea but lasted for less than a year. The persistent abundance of SO_2 at Kīlauea could deplete typical reactants rapidly, limiting conversion rates and increasing the likelihood that additional trace gases and/or metals either emitted or in the ambient environment could become important reactants themselves.

Chemical kinetic theory and observations have shown differences in the efficiency between cloud-free, gas phase oxidation of sulfur dioxide and aqueous, in-cloud oxidation. There are a number of variables that are thought to influence these processes. Among them are solar insolation, atmospheric mixing, temperature, relative humidity (RH), pH of cloud droplets, and species' concentrations (Eatough et al., 1994).

In this study, two dominant reaction pathways have been identified for the oxidation of sulfur dioxide in Hawai'i. The gas phase pathway is via reaction with the hydroxyl radical, OH. The aqueous phase pathway

is via reaction with hydrogen peroxide, H_2O_2. Given chemical kinetic theory, what range of conversion rates can one expect in the presence of SO_2 emissions from Kīlauea volcano? This will be addressed through a detailed examination of the reaction kinetics of SO_2 with the hydroxyl radical and hydrogen peroxide, including determinations of important variables that influence 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 Kīlauea volcano on the island of Hawaiʻi. 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 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.

Kīlauea 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 SO_2 and SO_4 by of 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 SO_2 to 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.

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 Kīlauea 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 (O_3) is considered the main precursor for OH formation while in the remote marine boundary layer OH is removed through reactions with carbon monoxide (CO) and methane (CH_4). At longer time scales, ozone concentrations follow an annual
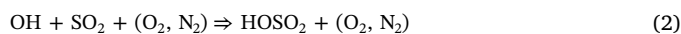
Table 2
Potential gas-phase SO_2 reactions. All values from Buckholder et al. (2015).

Reaction	k(298 K)
$OH + SO_2 -> HOSO_2$	1.6×10^{-12}
$O + SO_2 -> SO_3$	4.2×10^{-14}
$O_3 + SO_2 -> SO_3 + O_2$	$< 2.0 \times 10^{-22}$
$HO_2 + SO_2 ->$ products	$< 1.0 \times 10^{-18}$
$NO_2 + SO_2 ->$ products	$< 2.0 \times 10^{-26}$
$NO_3 + SO_2 ->$ products	$< 7.0 \times 10^{-21}$
$CH_3O2 + SO_2 ->$ products	$< 5.0 \times 10^{-17}$
$CH_2OO + SO_2 ->$ products	3.8×10^{-11}
anti-$CH_3CHOO + SO_2 ->$ products	2.2×10^{-10}
syn-$CH_3CHOO + SO_2 ->$ products	2.65×10^{-11}
$ClO + SO_2 -> Cl + SO_3$	$< 4.0 \times 10^{-18}$

cycle, with near surface concentrations nearly doubling from austral winter to summer in Fiji (Takashima and Shiotani, 2007). This implies an annual cycle in OH formation. Eatough et al. (1994) further suggest that OH formation is humidity dependent (via ozone), which will cause spatial and temporal variability on the scale of synoptic to mesoscale weather systems.

Once OH is formed the main reaction pathway with SO_2 is:

$$OH + SO_2 + (O_2, N_2) \Rightarrow HOSO_2 + (O_2, N_2) \qquad (2)$$

$$HOSO_2 + O_2 \Rightarrow SO_3 + HO_2 \qquad (3)$$

$$SO_3 + H_2O \Rightarrow H_2SO_4 \qquad (4)$$

A significant fraction of $HOSO_2$ eventually becomes H_2SO_4. Reaction 2, between OH with SO_2, is known to be the rate-limiting step in the oxidation of sulfur dioxide to sulfate aerosol. The formation rate of sulfate aerosol, S, can be solved via

$$S = k_c [SO_2][OH] \qquad (5)$$

where k_c is the conversion rate constant (cm^3 molecules^{-1} s^{-1}), and $[SO_2]$ and $[OH]$ are species concentrations (molecules cm^{-3}) (Raes et al., 1992; Simpson, 2010).

Many values have been obtained for k_c at different reference temperatures. The uncertainty of k_c, according to Atkinson et al. (1989), is of the order of a factor 2($\Delta \log(k) = \pm 0.3$). Based on this uncertainty, Raes et al. (1992) used a range of k_c values from 4.5×10^{-13} to 2.4×10^{-12} cm^3 molecules^{-1} s^{-1} to determine model sensitivity. They found that model results match smog chamber results for a range of values from 7.8×10^{-13} to 1.0×10^{-12} cm^3 molecules^{-1} s^{-1}. For comparison, the JPL recommended value for k = 1.6×10^{-12} cm^3 molecules^{-1} s^{-1} at a temperature of 300 K (Sander et al., 2011) falls within the range of estimates by Raes et al. (1992).

The reaction represented by equation (2) is thought to be a function of temperature and relative humidity (via OH production). Eatough et al. (1994) developed two equations to incorporate the moisture and temperature dependence into calculations for the first order rate coefficient, k_1. The moisture dependence is described by the dewpoint temperature (T_D) and reference values of k_1 and T_D at 25 °C (Eq. (6)). The temperature dependence was found through a linear regression fit of 109 k_1 values to 1/T (K) (Eq. (7)). This fit was performed by normalizing all values to 50% RH. The conversion rate at any temperature, T, calculated from equation (7) can be converted to any RH using equation (6) (Eatough et al., 1994). The resulting solution for k_1 is seen in equation (8).

$$\frac{\Delta \ln k_1}{\Delta T_D} = 0.0452°C^{-1} \qquad (6)$$

$$\ln k_1 = (24.91 \pm 0.41) - (8290 \pm 390)/T \qquad (7)$$

$$k_1 = e^{([(24.91 \pm 0.41) - (8290 \pm 390)/T] - \Delta T_D \times 0.0452°C^{-1})} \qquad (8)$$

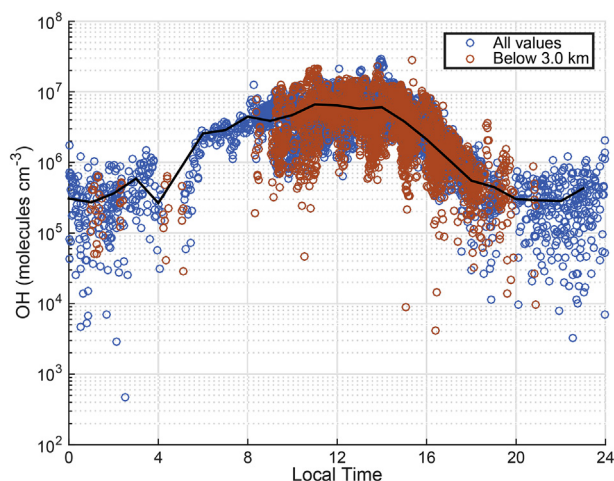The result of equation (8) is a unitless value. In order to use k_1 in

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.)

equation (5) we must put it in correct units and also scale it appropriately. Without scaling the value is simply a first order bulk conversion rate that does not take into account diurnal variations in OH. Based on reported values of k_c and values reported by Eatough et al. (1994), k_1 from equation (8) is scaled by 1.0×10^{-12} cm^3 molecules^{-1} s^{-1}.

In order to solve equation (5), OH concentrations have to either be measured or modeled with a photochemical model. Although OH is not routinely observed, past field campaigns have collected OH data. The most geographically specific data to Hawai'i is from INTEX-B (Singh et al., 2008), which was collected between 05 and 07 UTC 1 May 2006. Although this was an overnight flight, it provides a lower bound on the OH diurnal cycle. A mean OH concentration of approximately .01 ppt ($\sim 2.5 \times 10^5$ molecules cm^{-3}) is found.

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 $-180°$ W and $-140°$ W and 18°N and 40°N are displayed in Fig. 2. Several legs were flown near the surface during both day and night. Daytime concentrations peaked between 6×10^6 molecules cm^{-3} and 1×10^7 molecules cm^{-3} with nighttime concentrations approximately two orders of magnitude lower.

Further studies have found similar diurnal cycles of OH in the mid-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 4×10^6 molecules cm^{-3} during the day to a minimum that oscillated about $1–5 \times 10^5$ 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 $8–11 \times 10^6$ 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 Hawai'i 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 2.46×10^{11} molecules cm^{-3} (10 ppb). This value is used for both daytime and nighttime calculations. OH concentrations are obtained from INTEX-B flights presented in Fig. 2 to represent the diurnal range of concentrations with a daytime concentration of 1.0×10^7 molecules cm^{-3} and nocturnal concentration of 2×10^5 molecules cm^{-3}.

Table 3
Quantities used to calculate range of theoretical gaseous conversion rates.

Quantity	Daytime	Nighttime
Temperature (°C)	21.9	17.1
Relative humidity (%)	79	100
SO$_2$ (molecules cm^{-3})	2.46×10^{11}	2.46×10^{11}
k (molecules cm^{-3} s^{-1})	5.58×10^{-13}	4.04×10^{-13}
OH (molecules cm^{-3})	1×10^7	2×10^5
Conversion rate (% h^{-1})	2	0.03
Conversion rate range (k uncertainty) (% h^{-1})	0.8–5	0.01–0.07

Previous measurement campaigns have also found nocturnal OH concentrations in the range 2×10^5 to 10^6 molecules cm^{-3} (Brown and Stutz, 2012). Given that tradewinds are persistent near Halema'uma'u Crater, we assume that a persistent supply of OH is advected into the region of the plume for reaction with emitted SO$_2$. The subsequent k values calculated from equations (6) and (7) were 4.04×10^{-13} cm^3 molecules^{-1} s^{-1} and 5.58×10^{-13} cm^3 molecules^{-1} s^{-1} for night and day, respectively. The difference in k values is approximately 30%, given the relatively small ΔT (4.8 °C) and ΔRH (21%). If one assumes 100% conversion, this results in SO$_2$ to sulfate conversion rates of 1.98×10^4 cm^3 molecules^{-1} s^{-1} and 1.37×10^6 cm^3 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 SO$_2$ concentration for each time period that works out to a rate of 0.03% h^{-1} and 2% h^{-1} for nighttime and daytime.

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 are within the range of values for SO$_2$ loss found elsewhere (McGonigle et al., 2004; Rodriquez et al., 2005). The uncertainty in k, resulting from the temperature dependence represented in equation (7), results in a range from 2.29×10^{-13} to 1.42×10^{-12} molecules cm^{-3} s^{-1} during the day and 1.64×10^{-13} to 1.06×10^{-12} molecules cm^{-3} s^{-1} at night. The corresponding conversion rate range is 0.8–5% h^{-1} during the day and 0.01–0.07% h^{-1} at night. A more thorough treatment of the uncertainty in the conversion rate would take into account the variability in OH concentrations as well, however even when considering uncertainty in OH a majority of theoretical conversion rates will fall within the range of values found 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 1–100 ppt (2.46×10^7 molecules cm^{-3} to 2.46×10^9 molecules cm^{-3}), much lower than the concentration used above (10 ppb). SO$_2$ concentrations can easily exceed 100 ppm (2.46×10^{15} molecules cm^{-3}) above 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, the environmental formation rate can be approximated by the loss rate via 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 absence 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

$$\frac{d\text{OH}}{dt} = k_{CO}[\text{OH}][\text{CO}] + k_{CH4}[\text{OH}][\text{CH}_4] \tag{9}$$

where [CO] is the atmospheric concentration of carbon monoxide, [CH$_4$] is the concentration of methane, $k_{CO} = 3.45 \times 10^{-13}$ cm^3 molecules^{-1} s^{-1} (Baulch et al., 1980), and $k_{CH4} = 6.3 \times 10^{-15}$ cm^3
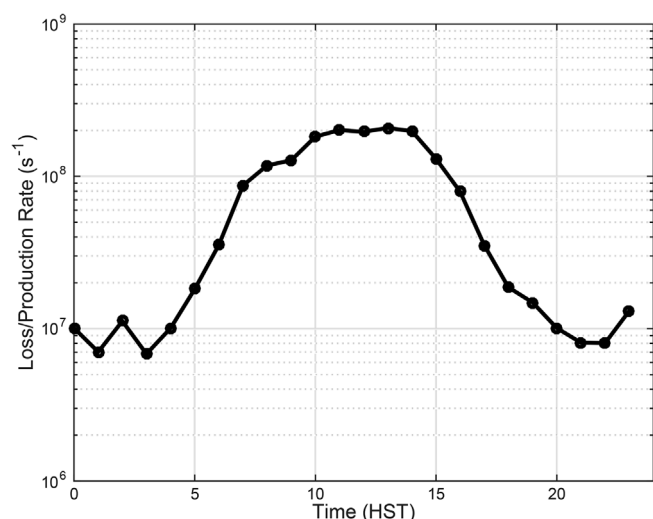
Fig. 3. Estimated loss/production rate (s^{-1}) of OH calculated from INTEX-B CO, CH4, and OH data.

molecules^{-1} s^{-1} (Sander et al., 2011). The loss/production rate of OH was approximately 2×10^{-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 1×10^{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 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 Kīlauea meaning actual HBr emission rates are two orders of magnitude lower at Kīlauea. Although some depletion may be occurring within the Kī-lauea 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., 2010; 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 values measured at Kīlauea. 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 temperatures (25–27 °C) - a temperature range typical of Hawai'i's climate. Additional uncertainty will arise from OH concentrations, including reduction of OH from in-plume halogen chemistry, and OH delivered to

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 in 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$_2$ mass transfer to coarse mode sea salt aerosols (SSA) in non-negligible. This 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 neutral 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 course SSA of 5–10% hr^{-1} at night and an average daytime loss of 5% hr^{-1}. Thus SSA uptake of SO$_2$ may be on the order 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 Kīlauea vents and prevailing wind patterns this pathway may be important during high wind events, when 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$_2$O·SO$_2$, SO$_3^{2-}$, the sum of which are known collectively as S$_{IV}$. The solubility of SO$_2$ is a function of temperature and pH of the solution. At pH 2–7, S$_{IV}$ is almost entirely in the form of the bisulfite ion (HSO$_3^-$) (Seinfeld and Pandis, 1998). At lower temperatures there will be higher solubility. The reaction rate will decrease with decreasing temperature, however, the increased reactant concentration will tend to counterbalance the decreased reaction rate HSO$_3^-$, H$_2$O·SO$_2$, SO$_3^{2-}$, (Eatough et al., 1994).

Hydrogen peroxide (H$_2$O$_2$) and ozone (O$_3$) are the most likely oxidants for SO$_2$ in the aqueous phase. However, ozone reactions are highly pH dependent and only become the leading oxidant at pH > 5.5 (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 Hawai'i yield an average pH = 4.5 (Miller and Yoshinaga, 1981) while Siegel et al. (1990) found 84% of rain samples downwind of Kīlauea had pH values less than 5.0. The large particle size of rain droplets relative to cloud droplets suggests that the pH of the smaller volume cloud droplets will likely be even lower and that the pH of rain droplets represents an upper limit. This suggests that hydrogen peroxide is the leading oxidant of sulfur dioxide in the aqueous phase in the vicinity of Kīlauea. 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 cloud water. Hydrogen peroxide is considered highly soluble and sulfur dioxide moderately soluble. Equilibrium between the gas and aqueous phase concentrations is reached on very short time scales relative to droplet lifetime so that equilibrium can be considered. This allows the use of Henry's Law constants to determine aqueous phase concentrations. Henry's Law has a strong dependence on temperature. This dependence has been found by Huang and Chen (2010) for hydrogen peroxide and can be expressed as

$$K_H[\text{H2O2}] = exp\left(\frac{a}{T} - b\right) \tag{10}$$

where a = 7 024 ± 138 and b = 11.97 ± 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 $K_H[\text{H}_2\text{O}_2] = 1.08 \times 10^5\,\text{M atm}^{-1}$ at 25 °C (Huang and Chen, 2010), where M, molarity, is the concentration of solute in solution expressed as $1\,\text{mol L}^{-1}$ or $1 \times 10^{-3}\,\text{mol cm}^{-3}$. The recommended value of $K_H[\text{H}_2\text{O}_2]$ by the JPL is $8.44 \times 10^4\,\text{M atm}^{-1}$ (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 $K_H[\text{SO}_2]$ from JPL is $1.36\,\text{M atm}^{-1}$ and the temperature dependence is given by

$$K_H[\text{SO2}] = exp\left(\frac{a}{T} - b + cT\right) \tag{11}$$

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

$$-\frac{d[\text{S}_{\text{IV}}]}{dt} = \frac{k\,[\text{H}^+][\text{H}_2\text{O}_2][\text{HSO}_3^-]}{1 + K\,[\text{H}^+]} \tag{12}$$

where the reaction constant, $k = 7.45 \times 10^7\,\text{M}^{-2}\,\text{s}^{-1}$, $K = 13\,\text{M}^{-1}$ at 298 K $[HSO_3^-] = [\text{SO}_2](\text{aq})K_s/\text{H}^+$ because it is assumed that most dissolved SO_2 is in the form of bisulfite, where K_s is the dissociation constant of $\text{SO}_2.\text{H}_2\text{O} = 1.3 \times 10^{-2}\,\text{M}$ and the concentration of the hydrogen ion, $[\text{H}^+]$, is the estimate of water droplet pH. Martin and Damschen (1981) provide another popular estimate of $k = 5.2 \times 10^6\,\text{M}^{-2}\,\text{s}^{-1}$. A pH of 4.5 is assumed here, which corresponds to an H^+ concentration of $3.16 \times 10^{-5}\,\text{M}$. Given this pH value and that the reaction is relatively independent of pH, the denominator is approximately 1, and equation (12) becomes

$$-\frac{d([\text{SO}_2](\text{aq}))}{dt} = k\,[\text{H}^+][\text{H}_2\text{O}_2][\text{SO}_2](\text{aq}) \tag{13}$$

where $k = 9.1\ (\pm\ 0.5)\ \text{x}\ 10^7\,\text{M}^{-2}\,\text{s}^{-1}$ 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

$$\frac{d([\text{SO}_4](\text{aq}))}{dt} = k\,[\text{H}^+][\text{H}_2\text{O}_2][\text{SO}_2](\text{aq}) \tag{14}$$

Overnight observations at HAVO-OB on 20 July 2014 are used to estimate aqueous phase conversion rates because RH = 100% during this period. K_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 atm are $K_H[\text{H}_2\text{O}_2] = 1.78 \times 10^5\,\text{M atm}^{-1}$ and $K_H[\text{SO}_2] = 1.55\,\text{M atm}^{-1}$ for hydrogen peroxide and sulfur dioxide, respectively. When multiplied by the gas concentrations for H_2O_2 ($1 \times 10^{-9}\,\text{atm}^{-1}$) and 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 SO_2 gas ($[\text{SO}_2](\text{g})$) concentration is an order of magnitude greater than $[\text{H}_2\text{O}_2](\text{g})$, but the solubility of H_2O_2 results in dissolved concentrations of $[\text{H}_2\text{O}_2](\text{aq})$ four magnitudes greater than $[\text{SO}_2](\text{aq})$. Thus, $[\text{SO}_2](\text{aq})$ concentrations will be lower than $[\text{H}_2\text{O}_2]$ (aq) initially, however, higher $[\text{SO}_2](\text{g})$ concentrations will continue to dissolve and react with $[\text{H}_2\text{O}_2](\text{aq})$ and ultimately $[\text{H}_2\text{O}_2](\text{g})$ 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 $[\text{SO}_2](\text{aq})$ is $3.26 \times 10^{-6}\,\text{M s}^{-1}$, or roughly a 50% decrease in $[\text{SO}_2](\text{aq})$ per second. This rate is similar in magnitude to past theoretical conversion rates found by Seinfeld and Pandis (1998) (Fig. 4). Such rapid conversion
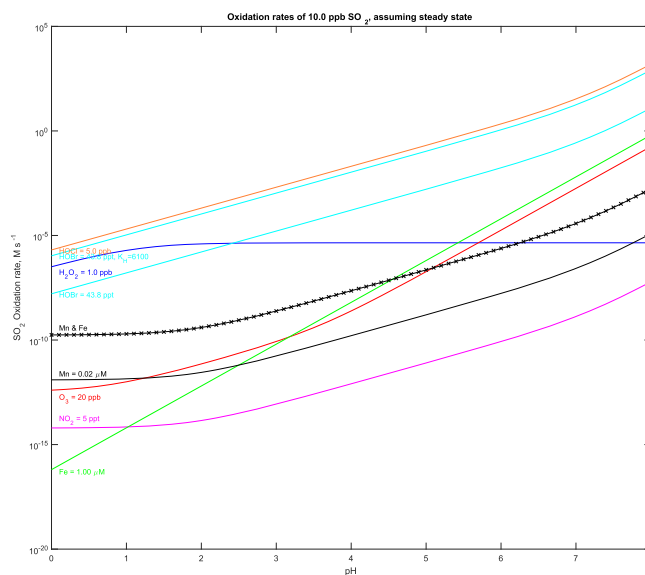

Fig. 4. Comparison of aqueous-phase oxidation paths near Kīlauea Volcano, Hawai'i. The rate of conversion of S(IV) to S(VI) as a function of pH. Condition assumed are: $[\text{SO}_2(\text{g})] = 10\,\text{ppb}$; $[\text{NO}_2(\text{g})] = 5\,\text{ppt}$; $[\text{H}_2\text{O}_2\ (\text{g})] = 1\,\text{ppb}$; $[\text{O}_3(\text{g})] = 20\,\text{ppb}$; $[\text{Fe(III)}] = 1.0\,\mu\text{M}$; $[\text{Mn(II)}] = 0.02\,\mu\text{M}$.

assumed a homogeneous H_2O_2 concentration within the cloud, however the reaction will likely be limited by mixing of the SO_2 plume into and within.

This reaction is known to be very fast and should deplete all H_2O_2 within a matter of minutes, which is the typical residence time of an air parcel in-cloud. Measurements by Daum et al. (1984) suggest that both reactants rarely coexist 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 removing hydrogen peroxide faster than it can be replaced.

Simpson (2010) took three approaches to estimate in-cloud oxidation of SO_2 to sulfate aerosols using project-averaged values from the Pacific Atmospheric Sulfur Experiment (PASE) conducted in 2007. Using chemical kinetic theory, the amount of SO_2 oxidized during a single cloud encounter lasting 7 min (based on updraft velocities below cloud and assuming a 500 m deep cloud) is 50 ± 30%. The ratio of dimethyl sulfide to SO_2 during individual cloud encounters is used to approximate the consumption of SO_2 using method two. Again the loss rate is found to be 50 ± 30%. The third approach estimates conversion with a sulfur flux budget. This method suggests 33–46% total SO_2 is consumed to produce 45–80% of the total sulfate. It is important to note that SO_2 concentrations during PASE are between 1 and 100 ppt, significantly lower than concentrations in the vicinity of Kīlauea.

In light of past observations and estimates of Simpson (2010) it is important to assess the uncertainty in the reaction rate calculated here because a significant depletion of H_2O_2 will make reactions between SO_2 and other reactants increasingly important.

Much of the uncertainty associated with the aqueous phase reaction of SO_2 with H_2O_2 stems from the uncertainty in the temperature dependence of the Henry's Law constants and the conversion rate coefficients. The uncertainty for $K_H[\text{SO}_2]$ is approximately 50% (Sander et al., 2011) while $K_H[\text{H}_2\text{O}_2]$ is less than 1% (1.76 (± 0.01) x $10^5\,\text{M atm}^{-1}$). Because the reaction is limited by H_2O_2 concentrations, any error resulting from uncertainty in SO_2 solubility is negligible. Estimates of k range from $5.2 \times 10^6\,\text{M}^{-2}\,\text{s}^{-1}$ to $9.6 \times 10^7\,\text{M}^{-2}\,\text{s}^{-1}$. By using the lower bound $[\text{SO}_2](\text{aq})$ loss will be 3% per second, or roughly a factor of 17.5 less than the upper bound estimate. While this lower conversion rate will deplete H_2O_2 more slower, estimates from Hua et al. (2008) suggest H_2O_2 production peaks at less than 1 ppb h^{-1},

meaning that over time (especially overnight) H_2O_2 may still be depleted. The lower bound estimates are closer to those of Simpson (2010) and differ in proportion to $[SO_2]$ used in the calculations.

If the rate of H_2O_2 production cannot keep pace with removal through aqueous SO_2 reactions then secondary reaction pathways will become important. Although O_3 reactions are more dependent on solution pH, this pathway remains important at pH 3–6 should H_2O_2 be absent in significant concentrations (Eatough et al., 1994). Ozone concentrations in the marine boundary layer are higher than H_2O_2, with mean concentrations between 15 and 19 ppb, and it is moderately soluble with a Henry's Law coefficient of 1.3×10^{-2} M. The O_3 rate expression is given as

$$-\frac{d[S_{IV}]}{dt} = (k_0[SO_2 \cdot H_2O] + k_1[HSO_3^-] + k_2[SO_3^{2-}])[O_3(aq)] \tag{15}$$

where $k_0 = 2.4 \times 10^4\,M^{-1}\,s^{-1}$, $k_1 = 3.7 \times 10^5\,M^{-1}\,s^{-1}$, and $k_2 = 1.5 \times 10^9\,M^{-1}\,s^{-1}$ (Hoffman and Calvert, 1985), however, if all H_2O_2 is consumed in reactions with SO_2 then solution pH can easily drop below 3 making this reaction negligible. Additionally, the depletion of O_3 within volcanic plumes (Vance et al., 2010; Oppenheimer et al., 2010; Schuman et al., 2011; Kelly et al., 2013; Surl et al., 2015) will limit the impact of this pathway.

Emission estimates from Halemaʻumaʻu 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_2SO_4 so it is realistic to assume all Fe is dissolved in a cloud also impacted by the SO_2 laden volcanic. These reactants may be important conversion mechanisms near Halemaʻumaʻu Crater from pH 3.5 to 6 (c.f. figure 6.25 in Seinfeld and Pandis, 1998). The rate expressions are given as

$$-\frac{d[S_{IV}]}{dt} = k_{Fe}[Fe(III)][SO_3^{2-}] \tag{16}$$

$$-\frac{d[S_{IV}]}{dt} = k_{Mn}[Mn(II)][S_{IV}] \tag{17}$$

where $k_{Fe} = 1.2 \times 10^6\,M^{-1}\,s^{-1}$ for pH ≤ 5 (Hoffman and Calvert, 1985) and $k_{Mn} = 1\,000\,M^{-1}\,s^{-1}$ (Martin and Hill, 1987). Fe and Mn emissions are estimated by Mather et al. (2012) as Fe/$SO_2 = 7.7 \times 10^{-5}$ and Mn/$SO_2 = 1.4 \times 10^{-6}$. Given an SO_2 emission rate of $3\,000\,t\,d^{-1}$ this amounts to Fe emission of $0.231\,t\,d^{-1}$ and Mn emission of $4.2 \times 10^{-3}\,t\,d^{-1}$. Benitez-Nelson et al. (2003) measured Fe concentrations in cloud water near the volcano as 1×10^{-6} M and Sansone et al. (2002) estimated the Mn/Fe ratio near the volcano as 0.02. If all this Fe and Mn mass is dissolved in cloud water at a pH = 4.5, then the reaction rates for Fe(III) = $1.6 \times 10^{-8}\,M\,s^{-1}$ and Mn(II) = $1.2 \times 10^{-10}\,M\,s^{-1}$. The reaction with Mn can be neglected because of its magnitude but the reaction rate with Fe is secondary only to H_2O_2 at pH < 5.5. Fig. 4 shows the Fe reaction is highly dependent on solution pH suggesting such high conversion rates due to Fe may be unrealistic given the low pH of Hawaiian rainfall and implied lower pH of cloud water. However, given the relatively high emission rate of Fe, this reaction may be important near the vent when H_2O_2 could potentially be drawn down through SO_2 oxidation, especially in the presence of clouds or fog at the summit of Kīlauea. As the plume moves downwind and disperses, H_2O_2 removal through SO_2 oxidation will decrease meaning the likelihood that Fe reactions increasing in importance will remain low even though little to no Fe is being removed from the plume.

Seinfeld and Pandis (1998) mention a synergism between Fe and Mn that can increase reaction rates 3 to 10 times higher at low pH than would be predicted from the sum. The results of this calculation are uncertain however they are included in Fig. 4 for completeness. Also included in Fig. 4 is oxidation by NO_2. This pathway is pH dependent and due to low NO_2 concentrations around Hawaii (5 ppt) this reaction

would have a negligible impact on SO_2. For details of the NO_2 reaction see Seinfeld and Pandis (1998).

A further mechanism for SO_2 oxidation in solution with sea salt is proposed via halogen compounds HOCl and HOBr (Vogt et al., 1996). The reactions are described by Fogelman et al. (1989) and Troy and Margerum (1991) as follows

$$S_{(IV)} + HOCl \rightarrow S_{(VI)} + HCl \tag{18}$$

$$S_{(IV)} + HOBr \rightarrow S_{(VI)} + HBr \tag{19}$$

Simulations by Keene et al. (1998) found reactions with HOCl to be more rapid than H_2O_2 at pH 3–5.5 and HOBr more rapid than H_2O_2 at pH > 5.5. The HOCl estimate is highly uncertain since the rate constant is unknown but was assumed to be equal to that of SO_3^{2-} (Alexander et al., 2012).

Von Glasow et al. (2002) extended the work of Vogt et al. (1996) to account for SO_2 oxidation in aqueous solutions. They found that HOCl could be responsible for 5–10% of aqueous sulfate formation as a result of reactions with S(IV) and sea salt (high pH) in the remote marine boundary layer (MBL) while HOBr was responsible for 20–30% sulfate formation, with a majority forming in cloud water. It is important to note that estimates of Henry's Law constants for HOBr are a source of uncertainty, ranging from $93\,M\,atm^{-1}$ (Vogt et al., 1996) to $6\,100\,M\,atm^{-1}$ (Frenzel et al., 1998) and von Glasow et al. (2002) used the value of Vogt et al. (1996).

Though initial calculations assumed these reactions were occurring the remote MBL subsequent research has revealed halogens in volcanic plumes at concentrations much higher than background levels. HOCl precursor OClO has been detected in volcanic plumes (Bobrowski et al., 2007), and ClO has been reported as well (Lee et al., 2005). Horrocks et al. (2003) and Aiuppa et al. (2007) found little evidence of HOCl SO_2 reactions in volcanic plumes due to limitations related to high acidity of cloud droplets and low background humidity.

HBr is a main volcanic emission compound and measurements of BrO in volcanic plumes (Bani et al., 2009; Bobrowski et al., 2003, 2015; Bobrowski and Platt, 2007; Boichu et al., 2011; Heue et al., 2011; Hörmann et al., 2012; Kelly et al., 2013; Kern et al., 2009; Lee et al., 2005; Oppenheimer et al., 2006; Theys et al., 2009) imply limits of HOBr concentrations in-plume. Concentrations of HOBr are also implied through observed O_3 depletion in volcanic plumes (Vance et al., 2010; Oppenheimer et al., 2010; Surl et al., 2015; Zerefos et al., 2006) since aqueous HOBr is a required reactant in the 'bromine explosion' reaction chain to form BrO as detailed in (Bobrowski et al., 2003).

The formation of sulfate via HOBr appears to be an important pathway, but may be limited due to the low pH (< 5) in Hawaiʻi (particularly in the volcanic plume itself). Results of Keene et al. (1998) and von Glasow et al. (2002) suggest the reaction is highly dependent on pH but even at pH = 4.5, it may account for ~25% sulfate formation. With the uncertainty around Henry's Law constant for HOBr, this reaction could be faster and even match that of H_2O_2. Von Glasow et al. (2002) also found little sulfate formation (< 10%) from HOCl under low pH values. Further research is needed to determine the magnitude of reactions in halogens and sulfur dioxide laden volcanic plumes.

4. Summary

Theoretical estimates of gas and aqueous phase oxidation of SO_2 at Kīlauea Volcano have been evaluated and the results suggest that hydroxyl radical and hydrogen peroxide are the dominant reaction pathways. For a frequently observed ground-level SO_2 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 the temperature and moisture dependence of the reactions. The estimated conversion rates represent results based on a single reactant concentration. Given that SO_2 is the limiting reactant (except near the

source area) the amount of sulfate aerosols formed via reactions can increase given higher SO_2 concentrations or decrease given lower SO_2 concentrations.

Oxidation of SO_2 in the gas phase is dominated by reactions with the hydroxyl radical, OH. Reaction rates are estimated for daytime and nighttime conditions observed at the Hawai'i Volcanoes Observatory. Daytime rates range from 0.8 to 5% h^{-1} and nighttime rates range from 0.01 to 0.07% h^{-1}. Because OH concentrations and production peak during the day and production ceases overnight, a diurnal signal is expected. Uncertainty in the conversion rate is addressed through the temperature and moisture dependence of the reaction is represented through a reaction coefficient, k. Additional uncertainty is the reaction rate results from concentrations of OH. Ozone depletion within volcanic plumes has been well documented (Jourdain et al., 2016 and references within), which reduces the formation of OH by as much as 30%. Under most circumstances the limiting agent will be SO_2, however, near Halema'uma'u Crater the SO_2 concentrations can exceed 100 ppm. Under such conditions OH would be completely depleted through reactions with SO_2 and will be the limiting agent. This reaction limit is reached with SO_2 concentrations as low as 10 ppm, however, concentrations of this magnitude are not common beyond a few kilometers downwind from the source.

The aqueous phase oxidation of SO_2 is dominated by reaction with hydrogen peroxide, H_2O_2. This is because of the independence of the 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_2 between 3 and 50% s^{-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 2010) and the observations of Daum et al. (1984) and Barth et al. (1989), the reaction estimate here is limited by the ambient H_2O_2 concentrations (1.0 ppb) and H_2O_2 production, which has been estimated by Martin et al. (1997) to be 0.85 ppb d^{-1}. Thus for an air parcel penetrating a cloud with 10 ppb SO_2 and 1 ppb H_2O_2, the maximum loss of SO_2 through conversion to SO_4 is 1 ppb or 10%.

Other aqueous phase reactions via O_3, Fe(III), and Mn(II), HOBr, and HOCl were considered to assess if the associated conversion rates are significant relative to H_2O_2. Ozone reactions are highly pH dependent and become important only in the event that H_2O_2 is drawn down first. A reduction in H_2O_2 via reaction with SO_2 will produce sulfuric acid, H_2SO_4, reducing solution pH limiting any contribution from O_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_2O_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 Kīlauea 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_2 from Kīlauea is dominated by the hydroxyl radical in the gas phase and hydrogen peroxide in the aqueous phase. Given high SO_2 emissions from the summit vent at Halema'uma'u Crater, the oxidation by these reactants may become limited by their modest ambient concentrations. Under such circumstances secondary reactions may become important, such as Fe(III) or HOBr for aqueous conversion. However these circumstances are limited to SO_2 concentrations ≥ 10 ppm and high

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 SO_2 and SO_4 is paramount to improving forecasts downwind of Kīlauea Volcano. For kilometers downwind the volcanic plume can often be observed traveling at or just above the ground under stable conditions. Ground level clouds are only occur near the summit of Kīlauea over of period of hours making the relative contribution 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 not as straight forward as gas-phase conversion. Oxidation via H_2O_2 is limited in-cloud by ambient concentrations but can reach 100% for SO_2 gas concentrations $< H_2O_2$ gas concentrations.

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