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Review

Evidence for a New Oxidation Mechanism for Sulfur Dioxide from Laboratory Measurements

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Abstract

The oxidization of sulfur dioxide (SO_2) occurs in the gas and liquid-phase and this oxidation contributes to particulate matter and acid precipitation. The production of sulfate particles is significant because of their impacts on climate, precipitation acidification, and human health. In this paper the focus is on the oxidation of SO_2 and on the possibility of unknown heterogeneous reactions that may occur on sulfate aerosol surfaces. These results are based on aa reanalysis of a foundational set of SO_2 laboratory oxidation measurements. The experiments involved two sets of photochemical studies of nitrous acid (HONO), nitrogen oxides ($NO_x = NO + NO_2$), SO_2, carbon monoxide (CO) and water vapor (H_2O) mixtures made in molecular nitrogen (N_2) with trace of molecular oxygen or in synthetic air. The reanalysis strongly suggests that there are uncharacterized processes for the oxidation of SO_2 that are nearly three times faster than the known gas-phase reactions. The uncharacterized processes may involve sulfate aerosol surface reactions in the presence of nitrogen oxides. If these processes can be included in current atmospheric chemistry models, greater conversion rates of SO_2 to sulfate aerosol will be calculated and this may reduce modelling bias.

Keywords: particulate matter; sulfur dioxide; sulfate particles; aerosol; gas-oxidation; heterogeneous processes

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1. Introduction

The oxidation of sulfur dioxide (SO_2) produces products that are significant sources of atmospheric particulate matter and acid precipitation (acid rain) [1–4]. The products, small droplets of liquid sulfuric acid (H_2SO_4), bisulfate (HSO_4^-) and sulfate ($SO_4^=$) have consequences for health, agriculture, climate, etc. SO_2 is emitted from many natural and anthropogenic sources [4,5]. The greatest source of sulfur emissions into the atmosphere comes from biological processes in the Earth's oceans and this means that these sources are stronger in the southern hemisphere. Dimethyl sulfide (DMS, CH_3SCH_3) constitutes a significant fraction of the sulfurous emissions from the oceans [5–10]. Hydrogen sulfide (H_2S) is another biogenically emitted compound. H_2S and DMS are converted to SO_2 by a complicated chemical reaction mechanism [11].

Natural sources of SO_2 include volcanoes [5] and its photochemical production from biogenic emissions such as hydrogen sulfide (H_2S) and dimethyl sulfide (CH_3SCH_3) Biomass burning, i.e. wildfires, is an underappreciated source of sulfurous compound emissions [12]. The wildfire sources of sulfur compound emissions is increasing because of the increasing number and intensity of wildfires [13]. The major anthropogenic sources include the production of metals from sulfur containing ores (smelting) and the combustion of fossil fuels [14]. Coal is an example of a fossil fuel with sources that have large differences in sulfur content [15].

Sulfur dioxide is oxidized in the atmosphere to produce sulfate particles, i.e., H_2SO_4, HSO_4^- or sulfate $SO_4^=$, that are chemical components of particulate matter or aerosols [3]. This oxidation of sulfur dioxide to produce particulate matter is very important because of their effects on climate, precipitation patterns, amounts and acidification, and their health effects [4]. The chemistry may have possible applications to exoplanetary atmospheres too [16].

Sulfur containing particles have very significant effects on climate because they strongly scatter solar radiation which effects the Earth's radiation budget [4]. In fact, the emission of sulfate containing particles has been suggested as a method of cooling the Earth's atmosphere to counteract global warming [17].

Sulfate containing particles, along with other forms of particulate matter, contribute to the secondary aerosol effect [4]. Fine aerosol particles provide nucleation sites for the formation of cloud water droplets. If there is an increase in the concentration of fine aerosol particles, then there will be more, but smaller droplets formed for a given level of water vapor in the atmosphere. Depending upon conditions the secondary aerosol effect can affect the amount and geographical distribution of precipitation.

Sulfate compounds are acidic in liquid water, and they contribute strongly to the acidification of precipitation along with nitrates (NO_3^-) and organic acids such as formic (HCOOH) and acetic acid (CH_3COOH) [18]. For this reason and direct health effects, emissions of SO_2 have regulated in the United States by the Clean Air Act Amendments since 1970 [19]. Acid precipitation was recognized as a major problem in Europe, Canada and the United States [20,21] during the late 1970s and 1980s. One of the major driving political and scientific questions for public policy regarding acid precipitation was to determine if the production of sulfate was limited by the available sulfur dioxide (SO_2) or by the available oxidant; this uncertainty was known as the oxidant limitation question. This was a major issue of several international programs including the American National Acid Precipitation Program (NAPAP) and the U.S. Department of Energy's Processing of Emissions by Clouds Program (PRECP) [22–26].

Figure 1 shows the difference between a situation where the oxidation of SO_2 is limited by the available oxidant or not [27]. If there is a limited amount of oxidant relative to the amount of SO_2, left plot, then moderate reductions in SO_2 will not result in less sulfate produced; this condition was known as oxidant limited. The right panel shows that if there is more oxidant available then SO_2 then reductions in SO_2 will result in reductions in the amount of sulfate produced. Finding the chemical mechanisms for the oxidation of SO_2 is important for determining the emission reduction policies needed to reduce acid precipitation.

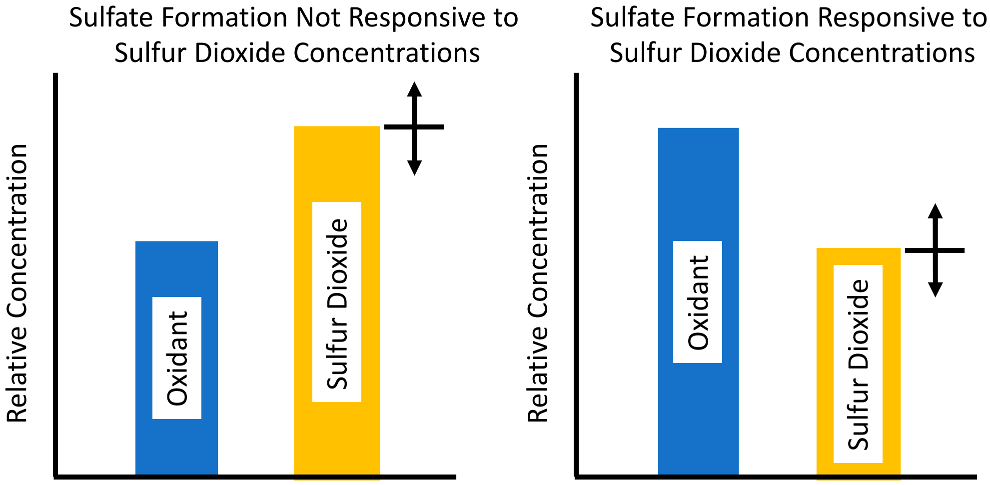

Figure 1. The plot to the right shows an oxidant limited condition. In that case reductions or increases in SO_2 concentrations do not affect the formation of sulfate. The plot to the right shows the case where there is sufficient oxidant to convert SO_2 to sulfate and decreases in SO_2 concentrations lead to decreases in sulfate production.

The oxidation of SO_2 may be important on local, urban scales as well as regional and global. In general, the particulate matter produced through atmospheric chemical reactions are fine particles with an aerodynamic dynamiter of 2.5 μm and these particles are known as $PM_{2.5}$. Larger particles with an aerodynamic dynamiter of 10 μm are known as PM_{10} [19]. As an example, the city of El Paso

Texas in the Paso Del Norte Border Region of the United States and Mexico has had problems with high concentrations of $PM_{2.5}$ and PM_{10} [28,29]. High emissions of SO_2, NO_x and volatile organic compounds and wind-swept mineral dust have occurred in El Paso which contributes to particulate pollution. Emissions of nitrogen oxides are significant because the region contains the American – Mexican border. Truck and auto traffic are queued near the border until they are cleared to pass the border into the United States.

1.1. SO_2 Oxidation Mechanisms

Many atmospheric chemical reactions produce products that condense to form particulate matter, $PM_{2.5}$ or PM_{10}. In general, SO_2 is oxidized in either gas or aqueous phases or it may be deposited directly to the ground. In this paper we present evidence that there many be chemical reactions that may involve nitrogen oxides and/or heterogeneous processed involving sulfate aerosols.

1.1.1. The Gas-Phase Oxidation of Sulfur Dioxide

There are two gas-phase mechanisms known mechanisms for the gas-phase oxidation of sulfur dioxide. The hydroxyl radical (HO•) is the oxidant [30]. As shown by the reactions given below the HO• reacts with SO_2 to produce the adduct $HOSO_2$•, note that M is any molecule of air that stabilizes the formation of the adduct by absorbing excess collision energy.

$$HO\bullet + SO_2\ (+\ M) \rightarrow HOSO_2\bullet\ (+\ M) \tag{1}$$

$$HOSO_2\bullet + O_2 \rightarrow HO_2\bullet + SO_3 \tag{2}$$

$$SO_3 + H_2O \rightarrow H_2SO_4\ (+\ \text{liquid aerosol}) \tag{3}$$

The $HOSO_2$• adduct reacts with molecular oxygen to produce the hydroperoxyl radical (HO_2•) and sulfur trioxide (SO_3) [30]. SO_3 reacts with water vapor to produce sulfuric acid. In a nitrogen oxide polluted atmosphere, HO_2• reacts with NO to reproduce HO• as shown below.

$$HO_2\bullet + NO \rightarrow HO\bullet + NO_2 \tag{4}$$

The hydroxyl radical produced by Reaction 4 can react with SO_2 making this mechanism a chain mechanism. When the concentration of nitric oxide (NO) is low, HO_2• reacts with another HO_2• or with organic peroxy radicals to produce hydrogen peroxide (H_2O_2) or an organic peroxide.

Another gas-phase process for the oxidation of SO_2 reaction with Criegee intermediates [31,32]. Criegee intermediates are produced by reactions of ozone (O_3) with alkenes. An example of the mechanism for the production of Criegee intermediates from ethene (CH_2CH_2) and its oxidation of SO_2 is given below, Reactions 5–6.

$$O_3 + CH_2CH_2 \rightarrow CH_2OOOCH_2 \tag{5}$$

$$CH_2OOOCH_2 \rightarrow CH_2OO + CH_2O \tag{6}$$

$$CH_2OO + SO_2 \rightarrow SO_3 + CH_2O \tag{7}$$

The average total rates of the HO• radical and the Criegee intermediate mechanisms are a few percent per hour for a range of realistic conditions with a maximum rate of 6.13 % hr^{-1} [33].

In cloud water or water coated aerosols the H_2O_2 may react with SO_2 to produce sulfate [1,4,34] and in the gas-phase SO_2 does not affect the concentration of the HO•. Either way there is little or no oxidant limitation to sulfate production from SO_2 in the lower troposphere.

However, there is reason to suspect that could be additional oxidation processes. Relative to observations, air quality models underestimate sulfate production across the Eastern U.S and the models underestimate the effect of temperature on its production [35,36]. These newer modeling studies for United States, Alaska and Beijing, China indicate that estimates of particulate sulfur may

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be improved by the addition of additional heterogeneous chemical reactions [36]. In this paper we present an analysis of experimental data that suggests a process for the oxidation of SO_2 that is not included in models.

2. Materials and Methods

The experiments that are reanalyzed here were made with the objective to measure the rate coefficient of the HO• radical with SO_2 ($HO+SO_2$) reaction) relative to the rate coefficient of the HO• radical with carbon monoxide (HO+CO) reaction [30,37]. The reaction of HO• with SO_2 (Reaction 1) is given above and the reaction of with HO• with CO is given below.

$$HO\bullet + CO\ (+\ O_2) \rightarrow HO_2\bullet + CO_2 \tag{8}$$

The original analysis determined that HO• radical concentrations were not affected by SO_2 concentrations, and this observation led to the proposal of the mechanism given by Reactions 1 through 4 [30]. This study was cited as a landmark in sulfur oxide chemistry [38]. The proposed mechanism was verified by several independent studies [39,40].

Mixtures of SO_2, carbon monoxide (CO), nitrous acid (HONO), nitric oxide (NO) and nitrogen dioxide (NO_2) were photolyzed in molecular nitrogen (N_2) or synthetic air as a background gas, Table 1 [37]. The initial reactive nitrogen is the total molecular concentration of NO, NO_2 and HONO, Table 1 gives the initial conditions for the experiments made in N_2; note that there was a small trace of molecular (O_2) introduced during the filling of the chamber. Table 2 gives the initial conditions for the experiments made in synthetic air. Photolysis of nitrous acid produced HO• radicals.

$$HONO + h\nu \rightarrow HO\bullet + NO \tag{8}$$

The photolysis experiments were made using a long-path glass chamber that was 6m long and the concentration changes were measured with a Fourier Transform Spectrometer [30,37]. The concentrations of CO were sufficiently high so that they did not appreciably change during the experiments so the relative extent of the HO•+CO reaction was taken as the total CO_2 produced during each experiment. The rates of the HO•+SO_2 and HO•+CO reactions are given below where k_{SO2} and k_{CO} are rate coefficients for these reactions.

$$\frac{[SO_2]}{dt} = k_{HO+SO2}[HO *][SO_2] \tag{9}$$

$$\frac{[CO]}{dt} = k_{HO+CO}[HO *][CO] \tag{10}$$

Equations 9 and 10 may be rearranged to derive the ratio, k_{HO+SO2}/k_{HO+CO}. To derive Equation 11 for the experiments, note that the HO• concentrations cancel out, that the concentrations of SO_2 and CO may be averaged over the photolysis period ($[SO_2]_{AVG}$, $[CO]_{AVG}$) and that the change in CO is equal to the amount of CO_2 produced ($\Delta[CO_2]$. The change in the SO_2 concentration is given by $\Delta[SO_2]$.

$$\frac{k_{HO+SO2}}{k_{HO+CO}} = \frac{[CO]_{AVG}}{[SO_2]_{AVG}}\frac{\Delta[SO_2]}{\Delta[CO_2]} \tag{11}$$

The gas-phase rate coefficients for the Reactions 1 and 8 are well known now. These were used to calculate the literature k_{HO+SO2}/k_{HO+CO} ratio. The rate coefficients for the reaction of HO• with SO_2 is pressure and temperature dependent [41]. This reaction involves two small molecules forming a reactive intermediate that requires its collision energy to be dissipated through collisions with a third bodies. The rate coefficient n units of $cm^6 molecule^{-1} s^{-1}$ is calculated through the following equations.

$$k_0(T) = k_{0,298}\left(\frac{T}{298}\right)^{-n} \tag{12}$$

$$k_\infty(T) = k_{\infty,298}\left(\frac{T}{298}\right)^{-m} \tag{13}$$

$$k_{HO+SO2}(T,[M]) = \left\{\frac{k_{\infty}(T)k_0(T)[M]}{k_{\infty}(T)+k_0(T)[M]}\right\} 0.6^{\left\{1+\left[log_{10}\left(\frac{k_0(T)[M\}}{k_{\infty}(T)}\right)\right]^2\right\}^{-1}} \tag{14}$$

where: $k_{0,298}$ =2.90×10^{-31}, n = 4.1, $k_{\infty,298}$ =1.70×10^{-12} and m = -0.2; and [M] is the concentration of the total background gas in molecules cm^{-3} [41].

The rate coefficient for the reaction of HO• with CO in units of cm^{6}molecule^{-1}s^{-1} is given is given by equation 15 [42,43]:

$$k_{HO+CO} = 1.44 \times 10^{-13} \times \left(1.0 + \frac{0.8\times[N_2]}{4\times10^{+19}}\right) \tag{15}$$

These were used to calculate literature ratio of the coefficients given in the Results section of this work.

Table 1. Initial conditions for sulfur dioxide oxidation experiments that were made using molecular nitrogen as the background gas. All experiments contained a trace of molecular oxygen with a pressure assumed to be 4.64±0.06×10^{-5} atm [37]. The initial reactive nitrogen is the total initial sum of the HONO, NO and NO_2 concentrations.

Experiment Number	N_2 (atm)	Initial Reactive Nitrogen (Molec cm^{-3} ×10^{-15})	Initial CO (Molec cm^{-3} ×10^{-16})	Initial SO_2 (Molec cm^{-3} ×10^{-15})
1	0.921	0.817	2.31	2.96
2	0.954	0.882	3.43	3.88
3	0.925	0.917	2.31	2.23
4	0.924	1.09	1.60	2.07
5	0.922	1.23	1.62	1.69
6	0.925	2.17	1.10	1.70
7	0.933	2.38	1.03	1.28
8	0.921	1.91	1.07	2.01

Table 2. Initial conditions for sulfur dioxide oxidation experiments that were made using synthetic air as the background gas [37].

Experiment Number	N_2 (atm)	O_2 (atm)	Initial Reactive Nitrogen (Molec cm^{-3} ×10^{-15})	Initial CO (Molec cm^{-3} ×10^{-16})	Initial SO_2 (Molec cm^{-3} ×10^{-15})
O1	0.761	0.176	0.739	2.29	3.20
O2	0.748	0.171	1.43	2.32	2.26
O3	0.749	0.172	1.34	1.86	3.42
O4	0.746	0.175	0.828	1.83	2.31
O5	0.752	0.169	0.908	1.38	3.14
O6	0.742	0.176	1.02	1.39	2.36
O7	0.750	0.171	1.20	0.935	3.56

3. Results

Table 3 shows experimental results for the photolysis experiments.

Table 3. Experimental Results for sulfur dioxide oxidation [37].

Experiment Number	Reaction Time (min)	Δ Reactive Nitrogen (Molec cm^{-3} ×10^{-14})	ΔCO_2 (Molec cm^{-3} ×10^{-14})	ΔSO_2 (Molec cm^{-3} ×10^{-14})	Experimental $\frac{k_{HO+SO2}}{k_{HO+CO}}$
1	29.12	0.088	1.60	2.53	12.9
2	25.37	0.52	1.01	1.03	9.1
3	16.98	0.060	1.58	1.38	9.4
4	25.57	-0.004	1.07	1.61	12.1
5	25.72	1.20	0.979	1.26	12.8
6	25.78	3.90	0.816	1.72	14.5
7	25.82	2.57	1.00	1.72	14.9
8	28.47	19.10	0.383	1.03	14.8
O1	28.20	0.100	1.50	2.34	11.6
O2	28.87	0.917	1.27	1.75	14.7
O3	28.37	-0.024	0.832	2.45	16.7
O4	28.62	-0.062	1.28	2.57	16.8
O5	28.87	-0.609	0.916	1.64	8.0
O6	28.32	0.382	0.962	2.45	15.9
O7	37.20	0.803	0.763	2.92	10.5

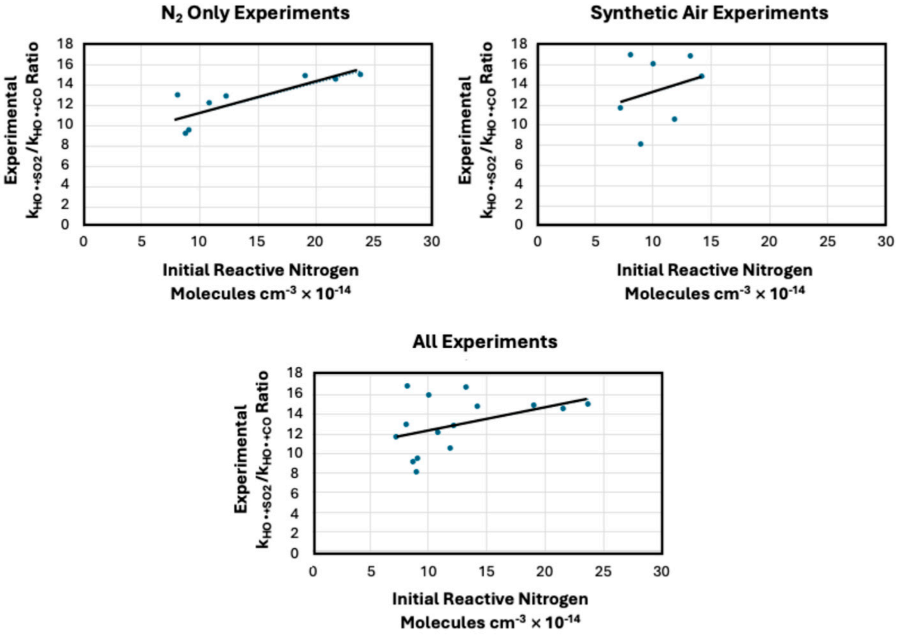
Table 3 shows the experimental k_{HO+SO2}/k_{HO+CO} ratios calculated using Equation 11 from the initial concentrations. The observed changes in SO_2 and CO_2 concentrations The ratios ranges from 9.1 to 14.9 for the experiments made with background N_2. The ratio ranges from 0.8 to 16.7 for the experiments made with background synthetic air.

Table 4 shows calculated k_{HO+SO2}/k_{HO+CO} ratios from the literature rate coefficients. The expected values of the ratios are between 4 and 4.5. The experimental values of the k_{HO+SO2}/k_{HO+CO} ratios are between 1.80 and 3.75 times greater than the literature calculated values.

Table 4. Comparison of experimental k_{HO+SO2}/k_{HO+CO} ratio with literature values. The values of k_{HO+SO2} and k_{HO+CO} were calculated for a temperature of 300K and the N_2 pressures given in Tables 1 and 2.

Experiment Number	k_{HO+SO2} (cm^3 Molec^{-1} ×10^{13})	k_{HO+CO} (cm^3 Molec^{-1} ×10^{13})	Literature $\frac{k_{HO+SO2}}{k_{HO+CO}}$	Experimental/Literature $\frac{k_{HO+SO2}}{k_{HO+CO}}$
1	9.22	2.21	4.17	3.10
2	9.33	2.24	4.17	2.18
3	9.23	2.22	4.17	2.26
4	9.23	2.21	4.17	2.90
5	9.22	2.21	4.17	3.07
6	9.23	2.22	4.17	3.48
7	9.26	2.22	4.17	3.58
8	9.22	2.21	4.17	3.55
O1	9.27	2.08	4.46	2.60
O2	9.21	2.07	4.46	3.30
O3	9.22	2.07	4.46	3.75
O4	9.22	2.07	4.46	3.76
O5	9.22	2.07	4.45	1.80
O6	9.21	2.06	4.47	3.56
O7	9.22	2.07	4.46	2.36

Plots were made to examine the possibility that there was an effect of reactive nitrogen on the k_{HO+SO_2}/k_{HO+CO} ratios. Figure 2 shows plots of the experimental k_{HO+SO_2}/k_{HO+CO} ratios as functions of the initial reactive nitrogen oxides (HONO+NO+NO_2. Table 5 shows the average reactive nitrogen in the three sets of experiments, the average k_{HO+SO_2}/k_{HO+CO} ratio and the shared variance between them.


N₂ Only Experiments

Synthetic Air Experiments

All Experiments

Figure 2. Figure shows the relationship between the experimental k_{HO+SO_2}/k_{HO+CO} ratios and the initial reactive nitrogen used in the experiments. The initial reactive nitrogen is the total initial sum of the HONO, NO and NO_2 concentrations. The plot at the top left is for the experiments made with N_2 as the background gas. The plot at the top right is for the experiments made with synthetic air as the background gas. The plot at the lower center shows all experiments plotted together. The line in each plot is the regression line.

Table 5. Comparison of average experimental k_{HO+SO_2}/k_{HO+CO} ratio to the average reactive nitrogen concentrations and the shared variance between them as determined from the plotes shown in Figure 2.

Experimental Series	Average Reactive Nitrogen Conc. (Molec cm^{-3}×10^{-14})	Average k_{HO+SO_2}/k_{HO+CO} Ratio	Shared Variance (R^2)
N_2 Only	14.2	12.6	0.65
Synthetic Air	10.7	13.5	0.076
All	12.6	13.0	0.18

4. Discussion

This new analysis of photolysis experiments made with relatively high concentrations of HONO, NO, NO_2, SO_2 and CO showed that there may be an uncharacterized oxidation process for SO_2. The literature value of the k_{HO+SO_2}/k_{HO+CO} ratio for the experimental conditions is near 4 to 4.5 while the measured ratio is around three times greater for the N_2 only, synthetic air background gas experiments and both sets of experiments considered together.

The experimental ratio for the experiments with N_2 only as the background gas has a shard variance of 0.65 with the initial total reactive nitrogen concentration. However, the shard variance between the experimental ratio and the initial total reactive nitrogen concentration is much lower for the synthetic air case. Although there is much uncertainty, this could be due to an oxygen effect that is not taken into account in this analysis.

If there is a new oxidation process for SO_2 that is three times greater than the known hydroxyl radical reaction that occurs in NO_x polluted atmospheres then conversion rates in the range of 10 to

20% hr^{-1} may occur in urban regions such as El Paso, Texas with sources of SO_2 and NO_x (using reference 33 as the baseline).

Sulfuric acid has been produced on a commercial scale from the direct reaction of SO_2 and NO_x and H_2O. These were mixed at very high concentrations in large chambers, made from lead, where reactions produced H_2SO_4. [44] Based on our experiments we show that similar reactions may occur at lower concentrations. These reactions are probably heterogeneous and appear to be faster than the gas-phase reactions. The reactions may be important for converting SO_2 to sulfate on urban scales and therefore contribute to local $PM_{2.5}$ formation. Improved representation of these processes may improve the agreement between measurements and air quality modeling results [35,36] for the United States, China and elsewhere. New research involving laboratory studies and field measurements are needed to better characterize the oxidation of SO_2.because it is possible that heterogeneous reactions occurred on sulfate particles as soon as they were formed ans/or other reactive nitrogen catalyzed processes occure. Therefore, better measurements of formation and properties of the sulfate particles and their surface reactions are needed.

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Conflicts of Interest: The authors declare no conflicts of interest.

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