Enhancement of aqueous sulfate formation by the coexistence of NO2/NH3 under high ionic strengths in aerosol water

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Abstract

Current air quality models usually underestimate the concentration of ambient air sulfate, but the cause of this underestimation remains unclear. One reason for the underestimation is that the sulfate formation mechanism in the models is incomplete, and does not adequately consider the impact of the synergistic effects of high concentrations of multiple pollutants on sulfate formation. In this work, the roles of gaseous NO2, NH3 and solution ionic strength in the formation of sulfate in the aqueous phase were quantitatively investigated using a glass reactor and a 30 m3 smog chamber, separately. The results showed that sulfate formation was enhanced to different degrees in the presence of gas-phase NO2, NH3 and their coexistence as solutes in both liquid solution and aerosol water. NH3 enhances the aqueous oxidation of SO2 by NO2 mainly by accelerating the uptake of SO2 through increased solubility. More importantly, we found that high ionic strength in aerosol water could significantly accelerate the aqueous oxidation of SO2, resulting in unexpectedly high S(VI) formation rates. We estimate that under severe haze conditions, heterogeneous oxidation of SO2 by NO2 on aerosols may be much shorter than that through gas phase oxidation by OH, aided by high ionic strengths in aerosols. Considering the existence of complex air pollution conditions with high concentrations of NO2, NH3 and aerosol water, as expected in typical urban and suburban settings, the sulfate formation mechanisms revealed in the present work should be incorporated into air quality models to improve the prediction of sulfate concentrations.

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1. Introduction

In recent years, along with rapid social and economic development, many areas in China have suffered from frequent haze events (Li et al., 2017b; Shen et al., 2015; Sun et al., 2006; Tan et al., 2009). Similar air quality issues are also encountered in other rapidly growing countries (Fedorova et al., 2013; Pachauri et al., 2013). During such events, high concentrations (up to 100 ppb) of SO2, NOx and NH3 have been observed (Fu et al., 2015; Ianniello et al., 2010; Liu et al., 2013; Meng et al., 2011; Yang et al., 2009), and these gaseous precursors contributed to high concentrations of secondary species in PM2.5 (Yang et al., 2011; Ye et al., 2011; Zhang et al., 2015b; Zhao et al., 2013). Sulfate (SO42-) is a dominant component in PM2.5 during these haze events and plays a significant role in haze formation under high relative humidity (RH) conditions (Guo et al., 2014; He et al., 2001; Pathak et al., 2009; Wang et al., 2005; Zhang et al., 2011).

Sulfate is primarily generated from the homogeneous oxidation of SO2, mainly by OH radicals and Criegee intermediates (Mauldin III et al., 2012; Welz et al., 2012) in the gas phase, heterogeneous oxidation of SO2 on particle surfaces (He et al., 2014; Liu et al., 2012; Ma et al., 2008), and aqueous oxidation of dissolved S(IV) (the sum of SO2-, H2O2, HSO3-, and SO32-) by dissolved oxidants (e.g., H2O2, O3, NO2) and transition metals (e.g., Fe(III), Mn(II)) in cloud/fog droplets (Hung and Hoffmann, 2015; Li et al., 2017a; Quan et al., 2015; Seinfeld and Pandis, 2016; Xue et al., 2016). Both OH oxidation in
the gas phase and most aqueous oxidation reactions have been included in the Weather Research and Forecasting-Community Multiscale Air Quality (WRF-CMAQ) model system and most other air quality models, but simulation results have usually underestimated sulfate concentrations, especially under heavy haze pollution conditions (Cheng et al., 2016). Previous studies have demonstrated qualitative mechanisms for rapid sulfate growth under complex pollution conditions (Cheng et al., 2016; He et al., 2014; Li et al., 2018; Liu et al., 2012; Ma et al., 2008; Wang et al., 2016; Yang et al., 2016). For example, sulfate formation can be promoted by the coexistence of NOx on the surface of mineral dust particles; NH3 increases the surface alkalinity and leads to water film on the surface of mineral dust, which enhances SO2 adsorption on the surface and increases its oxidation to sulfate (Yang et al., 2016). However, the aqueous-phase oxidation of S(IV) by NO2 was ignored in the description of the mechanism because of the low solubility of NO2 under typical atmospheric conditions.

Due to the large discrepancies in the model-predicted pH of fine particles (Cheng et al., 2016; Guo et al., 2017; Liu et al., 2017; Wang et al., 2016), the mechanisms in model assumptions and inputs in those related studies (Song et al., 2018), the importance of the NO2 pathway for sulfate formation in the aqueous phase remains unresolved. The aqueous-phase oxidation pathway of S(IV) by NO2 has recently been shown to be a key mechanism in the formation of sulfate under fog/cloud conditions with high NO2 concentration levels (Cheng et al., 2016; Li et al., 2018; Wang et al., 2016). Wang et al. (2016) also indicated that the neutralization of NH3 could enhance sulfate formation from the reaction of S(IV) with NO2 under aerosol water or cloud conditions, implying that this reaction was greatly influenced by the pH values of the aqueous phase (Clifton et al., 1988; Huie, 1994; Nash, 1979; Spindler et al., 2003). Previous studies have shown that with increases in pH, the aqueous-phase equilibrium concentration of S(IV) increased, clearly caused by the increased solubility of SO2 (McVay and Ervens, 2017; Seinfeld and Pandis, 2016). Meanwhile, the reaction rate constant of S(IV) oxidation by dissolved NO2 also increased significantly (Littlejohn et al., 1993). Studies also found that the rate and efficiency of NO2 absorption could be enhanced during the process of simultaneous removal of SO2 and NO2 gases in alkaline solutions (Hu et al., 2010; Kameoka and Pigford, 1977; Takeuchi et al., 1977). The increased absorption of both SO2 and NO2 in alkaline solutions further enhanced the oxidation of sulfate (Shen and Rochelle, 1998). However, quantitative estimation of the increased absorption and oxidation rates in the presence of NO2 and NH3, for inclusion in a mechanism in air quality models to predict the sulfate concentration, is still lacking. This is one of the main subjects of this study.

In addition, ionic species significantly affect the ionic strength of the reaction media and result in different reaction media for the aqueous oxidation of SO2 in bulk solutions (cloud droplets, fog) and aerosol water. Previous experimental studies have indicated that the ionic strength (I) of solutions could lead to changes in the rate constants (k) (Herrmann et al., 2015) for reactions leading to sulfate formation in the aqueous phase, such as the oxidation by H2O2, O3, and NO2. Studies have shown that an increase in solution ionic strength could increase the rate of oxidation of S(IV) by O3 (Maahs, 1983) and by H2O2 in aqueous solutions (Ali et al., 2014; Maal et al., 1990). However, with respect to the oxidation of S(IV) by NO2, there has been no report on the relationship of k and I, except for some plausible estimation (Cheng et al., 2016). The effects of ionic strength may be crucial for evaluating the importance of the aqueous-phase reactions, and need further investigation.

Hence, studying the synergistic effects among SO2, NOx and NH3 in sulfate formation is important to reveal the formation mechanisms of sulfate in aerosol water, especially during severe haze events with high levels of NOx and NH3. There is a need to evaluate the effects of the coexistence of NH3 and high ionic strength on the solubility and aqueous-phase oxidation of S(IV) by NO2 in different reaction environments. The present work was carried out to address this need and to determine the significance of these effects.

2. Experimental section

2.1. Simulation of aqueous-phase reaction in a glass reactor

Simulation of aqueous sulfate formation was carried out in a glass reactor as shown in Fig. S1 (Volume ~600 mL, see in Supporting Information SI). The specifications of the gases used are as follows: SO2 (100 ppm in N2, Beijing Huayuan), NO2 (100 ppm in N2, Beijing Huayuan), carrier gas N2 (99.999% purity, Beijing Huayuan). 6 mL ultrapure water (18.2 MΩ, Millipore Milli-Q) or 0.02 wt% NH3 solution (Sinopharm Chemical Reagent Co., Ltd, Guaranteed reagent) were firstly added at the bottom of the glass reactor. Then, steady concentrations of SO2 or/and NO2 carried by high purity N2 were introduced into the glass reactor at a flow rate of 2.0 L min\(^{-1}\) with Peclet number ~580, which indicated that the gas phase species were not transported to the interface of flow tube, so a mixing tube was used (see Fig. S1A, marked in red) to make sure the reaction gases were evenly mixed. As the reaction gases (SO2 or/and NO2) swept over the liquid surface, they would dissolve in the water, and aqueous-phase reaction would occur. After flowing the reaction gas for 10 min, the reaction cell was purged with 2.0 L min\(^{-1}\) of high purity N2 for 5 min. All the simulations were carried out under dark conditions and at constant temperature (~298 K). Four different reaction systems, namely SO2, SO2/NO2(aq), SO2/NO2 and SO2/NO2/NOx(aq) were designed, marked as GR-SO2, GR-SO2/NOx(aq), GR-SO2/NOx and GR-SO2/NOx/NOx(aq), respectively. The concentrations of SO2 or/and NO2 were controlled at about 300 ppb and 300 ppb, which were monitored with an interval of 1 min by a SO2 analyzer (Model 43i, Thermo Fisher Scientific, Inc. USA) and NOx analyzer (Model 42i-TL, Thermo Fisher Scientific, Inc. USA), respectively. The detailed conditions of the experiments are listed in Table 1. Additional parallel experiments in oxalic acid solution (Table S1) were also conducted. For each system, the simulation was repeated three times to understand the distribution due to experimental error, and the relative standard deviation (RSD) was also calculated to be less than 5%.

After reaction, the liquid samples were transferred to 5 mL vials (PolyVials™, Thermo Scientific, Inc. USA). 1 wt % formaldehyde (Sigma-Aldrich, ACS reagent, 37 wt % in H2O) was added in order to suppress sulfite oxidation and avoid overestimating sulfate (Kong et al., 2014). Then the samples were analyzed by ion chromatography (IC, Model DIONEX ICS-2100 and ICS-1100, Thermo Scientific, Inc. USA) to determine the concentrations of water-soluble ions (e.g., SO4\(^{2-}\), NO3, NH4\(^{+}\)) (SI, Section S1). Meanwhile, the pH of the solution at the end of the reaction was determined by a pH meter (FE28-Standard, Mettler-Toledo Instruments Co., Ltd).

2.2. Simulation of aqueous-phase reaction in the smog chamber

We also performed experiments by exposing oxalic acid seed aerosols to gaseous SO2, SO2/NOx, SO2/NO2/NOx(aq) respectively under dark and high relative humidity (RH = 98 ± 1.5 %) conditions in a 30 m\(^2\) smog chamber (SI, Section S2), these four experimental systems were marked as SC-SO2, SC-SO2/NOx, SC-SO2/NO2, and SC-SO2/NO2/NOx(aq), respectively. SO2 and NO2 were also monitored using a SO2 analyzer and a NOx analyzer mentioned...
above. For the concentration of NH₃, it was estimated according to the amount of NH₃ introduced and the volume of the chamber reactor. Aerosol particle size distributions and number concentrations were measured using a custom-built Scanning Mobility Particle Sizer (SMPS, TSI) with a 5-min cycle, which consists of a differential mobility analyzer (DMA, 3080 Classier, TSI, Inc., USA) coupled with a Condensation Particle Counter (CPC, 3776, TSI, Inc., USA). Also, the mass concentrations of sulfate, nitrate and ammonium were measured using a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research Inc. USA).

The wall loss of pollutants were measured in several specialized experiments at the beginning and the end of chamber experimental study. The deposition rate of the pollutants in these experiments turned out to be quite similar. The wall loss rates of gaseous SO₂ and NO₂ were (1.67 ± 0.25) × 10⁻⁴ and (3.32 ± 0.21) × 10⁻⁴, respectively. The wall loss rate (k_{dep}) of particles was in accordance with k_{dep} = 4.15 × 10⁻⁷ × D_{p}^{0.88} + 1.39 × D_{p}^{0.88} (D_p is the particle diameter (nm)), which is used to correct the wall loss of aerosol particles similarly as Takekawa et al. (2003). T and RH were monitored using a hydro-thermometer (Vaisala HMP110).

Prior to each experiment, the Teflon chamber was flushed with purified and dry zero air for about 24 h at a flow rate of 100 L min⁻¹ until there was almost no residual NO₂, SO₂, or NH₃, and the particle number concentration was <10 cm⁻³. Before the experiments, the Teflon chamber was humidified to the expected RH by passing purified air through ultra-pure water (18.2 MΩ, Millipore Milli-Q). Then the oxalic acid seed aerosols were injected into the Teflon chamber by atomizing 0.02 M oxalic acid solution and passed through a diffusion dryer before entering the chamber. These seeds would absorb water and even become deliquescent under high RH conditions (Peng et al., 2001), and formed a liquid reaction environment on their surface.

SO₂, NO₂, and NH₃ were then injected into the chamber in purified dry zero air. The concentrations of the gases were continuously monitored at a measurement point in the reactor. The initial concentration of gaseous NH₃ was approximately 300 ppb, as shown in Table 1, and the concentrations of SO₂ and NO₂ were similar to those in the simulation carried out in the glass reactor.

At the end of the experiments, filter samples were collected onto 47 mm pure quartz filters (0.3 μm pore size, Staplex Air Sampler Division, USA) by use of a vacuum pump with a flow rate of 10 L min⁻¹ during the first 6 h of the cleaning process. The sampling port for the filters was located in the middle of the east side, and the cleaning air inlet was located in the middle of the west side of the smog chamber. After that, the collected filter samples were extracted in 12 ml of ultra-pure water in an amber sample vial (Strg Vial Kit, Agilent Technologies, USA) by sonication (Ultrasonic Cleanser, KQ-300DE) for 30 min, and then samples were analyzed by the IC system as mentioned above for the concentration of water-soluble inorganic ions, including SO₄²⁻, NO₃⁻ and NH₄⁺. The trend of the SO₄²⁻ concentration of the filter samples determined by IC was consistent with the AMS results (Fig. S2).

### 2.3. Determination of reaction kinetics

In order to calculate the reaction kinetics of heterogeneous reactions, the mass transport in different media needs to be taken into account (Cheng et al., 2016). Considering the mass transport, a standard resistance model was adopted to describe the relationship between the aqueous-phase reaction rate and the overall reaction rate (Cheng et al., 2016; Seinfeld and Pandis, 2016):

\[
\frac{1}{R_{aq}} = \frac{1}{R_{at}} - \frac{1}{R_{aq,lim}}
\]

where \(R_{aq}\) is the aqueous-phase reaction rate, \(R_{at}\) is the overall reaction rate, and \(R_{aq,lim}\) is the limiting mass transfer rate. \(R_{at}\) could be derived by Eq. (2) using the experimental results:

\[
R_{at} = \frac{\Delta [SO_4^{2-}]}{dt}
\]

where \(\Delta [SO_4^{2-}]\) is the concentration of sulfate determined by IC or HR-ToF-AMS, and \(dt\) is the reaction time.

Correspondingly, the aqueous-phase reaction rate \(R_{aq}\) could be estimated by Eq. (3):

\[
R_{aq} = k(S/IV)|[NO_2]|
\]

where \(k\) is the reaction rate coefficient of the oxidation reaction, \([S/IV]\) and \([NO_2]\) are the concentrations of \(S/IV\) and \(NO_2\) in the aqueous phase, respectively, and \([NO_2]\) was determined by Henry's law:

\[
[NO_2] = p(NO_2) \cdot H^*(NO_2)
\]

where \(p(NO_2)\) and \(H^*(NO_2)\) are the partial pressure of \(NO_2\) in the gas phase and the effective Henry's constant with 1.00 × 10⁻² M atm⁻¹ at 298K, respectively.

Meanwhile, \(J_{aq,lim}\) could be determined via Eq. (5) and Eq. (6) as follows:

\[
J_{aq,lim} = \min(J_{aq}(SO_2), J_{aq}(NO_2))
\]

\[
J_{aq}(X) = k_{MT}(X) \cdot p(X) \cdot H'(X)
\]

in which \(X\) refers to \(SO_2\) or \(NO_2\), and \(k_{MT}(X)\) is the mass transfer rate coefficient of species \(X\), which could be calculated by Eq. (7):

\[
k_{MT}(X) = \frac{R_p^2}{D_g} + \frac{4R_p}{3av}
\]

where \(R_p\) is the aerosol radius, \(D_g\) is the gas-phase molecular diffusion coefficient, \(a\) is the mass accommodation coefficient.
species X on the aqueous surface, with 0.11 (Seinfeld and Pandis, 2016) and 2.00 × 10⁻⁴ (Jacob, 2000) for SO₂ and NO₂, respectively. \( v \) is the mean molecular speed of species X.

3. Results and discussion

3.1. Description of the reaction process in different reaction systems

A simplified conceptual model of sulfate (S(VI) species will be mainly \( \text{SO}_4^{2-} \) under the pH conditions in GR reactions, while \( \text{SO}_4^{2-} \) and \( \text{HSO}_3^- \) may both exist under the pH conditions in SC reactions in this study) formation in the aqueous phase as investigated in this study is shown in Fig. 1, which includes the solubility of \( \text{SO}_2 \) and \( \text{NO}_2 \) (process I and II) and aqueous-phase oxidation (process III). \( \text{SO}_4^{2-} \) formation was determined in both a glass reactor with a water solution and in a smog chamber with aerosol water associated with oxalic acid seed aerosols. The experimental conditions for the reactions in the glass reactor (GR) and reactions in the smog chamber (SC) are summarized in Table 1. In the experiments GR-SO₂ and GR-SO₂/NO₂, dissolved \( \text{SO}_2 \) (mainly \( \text{HSO}_3^- \)) was oxidized by background oxidants in the water (e.g., dissolved oxygen), while in the experiments GR-SO₂/NO₂ and GR-SO₂(NO₂/\( \text{NH}_3(aq) \)), dissolved \( \text{NO}_2 \) (i.e., \( \text{NO}_2^- \)) also contributed to the oxidation of dissolved \( \text{SO}_2 \). Similar processes occurred in the aerosol water of the oxalic acid seed aerosols. The presence of \( \text{NH}_3 \) (in solution or in the gas phase) is expected to increase the alkalinity of the aqueous phase and influence both \( \text{SO}_2/\text{NO}_2 \) solubility and the oxidation rate of \( \text{HSO}_3^- \) by \( \text{NO}_2 \), which could be generated in the fast hydrolytic disproportionation of \( \text{NO}_2 \) (Li et al., 2018).

3.2. The role of \( \text{NO}_2 \) for \( \text{SO}_4^{2-} \) formation in the aqueous-phase oxidation

Fig. 2A summarizes the SO₄²⁻ concentrations resulting from reactions in the GR system. Ten minutes after the start of reaction in the experiment GR-SO₂, the concentration of \( \text{SO}_4^{2-} \), which came from the oxidation of dissolved \( \text{SO}_2 \) (mainly \( \text{HSO}_3^- \)) by background oxidants in the solution, was 0.005 ± 0.002 \( \mu \text{g mL}^{-1} \). In the experiment GR-SO₂/NO₂, the \( \text{SO}_4^{2-} \) generation was 0.041 ± 0.001 \( \mu \text{g mL}^{-1} \), which was increased by a factor of about 8 compared to GR-SO₂, suggesting a significant contribution of \( \text{NO}_2 \) to the oxidation of \( \text{SO}_2 \) in the water solution. The apparent reaction rate constant for the aqueous-phase oxidation of dissolved \( \text{S}^0 \) by \( \text{NO}_2(aq) \) was calculated to be 1.31 × 10⁻² to 2.68 × 10⁻¹ \( \text{M}^{-1} \text{s}^{-1} \) when \( \text{pH} < 5.0 \) and 2.00 × 10⁻¹ to 10⁻⁸ \( \text{M}^{-1} \text{s}^{-1} \) when \( \text{pH} > 5.8 \), while Clifton et al. (1988) calculated the rate constant to be 1.24 × 10⁻² \( \text{M}^{-1} \text{s}^{-1} \) and 1.67 × 10⁻¹ \( \text{M}^{-1} \text{s}^{-1} \) at \( \text{pH} \) of 5.3 and 8.7, respectively. In the present study, the \( \text{pH} \) of the solution was 4.1 at the end of the reaction. Considering the uncertainty in \( \text{pH} \), our experimental results for the reactions in water solution using the glass reactor are in the range of results from previous studies (Clifton et al., 1988; Huie and Neta, 1986; Lee and Schwartz, 1983).

In the SC experiments using oxalic acid seed aerosols, there was also similar enhancement of the \( \text{SO}_4^{2-} \) formation from the oxidation of \( \text{SO}_2 \) by \( \text{NO}_2 \) (Fig. 2B). The time series of \( \text{SO}_2, \text{NO}_2, \text{SO}_4^{2-} \) and \( \text{NO}_3^- \) during each SC experiment were shown in Fig. S3. Normalizing \( \text{SO}_4^{2-} \) formation with the initial \( \text{SO}_2 \) concentration, \( \text{SO}_4^{2-} \) formation increased by 15.2% in the presence of \( \text{NO}_2 \). As shown in Fig. 3, the consumption rate of gaseous \( \text{SO}_2 \) (after correction for wall loss) was 5.26 × 10⁻⁴ \( \text{min}^{-1} \) in the experiment SC-SO₂/NO₂, which is higher than in SC-SO₂ (4.33 × 10⁻⁴ \( \text{min}^{-1} \)). Meanwhile, the size distributions for different SC experiments were also given in Fig. S4. Compared with SC-SO₂, the slightly larger particle size were observed in the SC-SO₂/NO₂ (~250 nm, Figs. S4A and S4B). Meanwhile, the reaction rate constant was calculated to be 1.56 × 10⁻² to 4.67 × 10⁻⁸ \( \text{m}^{-3} \text{cm}^{-1} \text{s}^{-1} \) (Table 2), which is two orders of magnitude higher than that in the GR system. This was probably caused by the different reaction environments (e.g. the concentration of ionic species in the aqueous phase), and this influence will be discussed in detail later in this paper. Meanwhile, based on the concentrations of chemical species measured by HR-ToF-AMS, the molarity based pH (i.e., \( \text{pH}_k \)) of the aerosol water was estimated using the extended aerosol inorganic model (E-AIM, Model II) (Clegg et al., 1989; Wexler and Clegg, 2002; Jia et al., 2018). In the SC experiments, the gas-phase \( \text{NH}_3 \) concentration was estimated by considering the amount of \( \text{NH}_3 \) added and the volume of the smog chamber. Considering the uncertainty of the \( \text{NH}_3 \) concentration due to its strong stickiness with walls and other surfaces, and the presence of oxalic acid aerosols, which was not considered in the E-AIM model, the predicted \( \text{pH}_k \) of the aerosol by E-AIM model might have some uncertainty. In addition, recent studies have reported that organic compounds had an effect on \( \text{pH} \) (Guo et al., 2015; Jia et al., 2018; Pye et al., 2018). Therefore, the estimated \( \text{pH}_k \) was for reference only and was not used in the analysis of the results.

3.3. The role of \( \text{NH}_3 \) in \( \text{SO}_4^{2-} \) formation in the aqueous-phase reaction

Similarly, we studied the role of \( \text{NH}_3 \) in the aqueous-phase oxidation of \( \text{SO}_2 \). With the presence of \( \text{NH}_3 \) in the aqueous-phase reaction, the formation of \( \text{SO}_4^{2-} \) was enhanced to varying degrees (Fig. 2). In the GR system, 0.013 ± 0.006 \( \mu \text{g mL}^{-1} \) of \( \text{SO}_4^{2-} \) was formed in the experiment GR-SO₂/\( \text{NH}_3(aq) \), more than two times that in GR-SO₂. We attributed this increase in \( \text{SO}_4^{2-} \) formation to increased \( \text{SO}_2 \) dissolution due to the increase in the alkalinity of the reaction solution. In the experiment GR-SO₂/\( \text{NO}_2/\text{NH}_3(aq) \), \( \text{SO}_4^{2-} \) formation was further promoted by the presence of gaseous \( \text{NO}_2 \) and \( \text{NH}_3 \), and its concentration (0.22 ± 0.009 \( \mu \text{g mL}^{-1} \)) was about 44.0 times and 5.4 times that in the experiments GR-SO₂ and GR-SO₂/\( \text{NO}_2 \), respectively. These results are consistent with a previous study (Turisch et al., 2004) showing that the presence of \( \text{NH}_3 \) could promote \( \text{SO}_4^{2-} \) formation by a factor of 23 under aqueous droplet conditions. For the SC experiments, the presence of \( \text{NH}_3 \) in the experiment SC-SO₂/\( \text{NH}_3 \) enhanced the \( \text{SO}_4^{2-} \) formation by a factor of 4.4 compared to SC-SO₂ (1.19 \( \mu \text{g m}^{-3} \) vs 0.27 \( \mu \text{g m}^{-3} \), respectively). The promotion of \( \text{SO}_4^{2-} \) formation due to \( \text{NH}_3 \) is more significant in the SC experiments than that in the GR experiments. One possible reason is that the presence of \( \text{NH}_3 \) in the SC experiments also increased the volume of aerosol water, while this effect did not exist in the GR experiments. This could be supported by the size distribution observed in SC-SO₂/\( \text{NH}_3 \) and SC-SO₂, in which the former had the larger particle size (Figs. S4A and S4C). Meanwhile, in another separate SC experiment, \( \text{NH}_3 \) was injected into the chamber with similar RH and quantity of oxalic acid seed aerosol. The seed aerosol volume rose 23% after the injection of \( \text{NH}_3 \) into the chamber (24.0 \( \mu \text{m}^{3} \text{cm}^{-3} \) vs 29.6 \( \mu \text{m}^{3} \text{cm}^{-3} \).
respectively), indicating that the aerosol water was increased in the presence of NH3 (Chu et al., 2016). The reaction rate constants between NO2 and S(IV) in the experiments GR-SO2/NO2/NH3(aq) and SC-SO2/NO2/NH3 were calculated to be $1.63 \times 10^6 \pm 2.29 \times 10^5$ M⁻¹ s⁻¹ and $5.98 \times 10^8 \pm 5.44 \times 10^6$ M⁻¹ s⁻¹, respectively. These values are 1.2-fold and 3.8-fold those in the experiments GR-SO2/NO2 (1.31 $\times 10^6 \pm 2.86 \times 10^4$ M⁻¹ s⁻¹) and SC-SO2/NO2 (1.56 $\times 10^8 \pm 4.67 \times 10^6$ M⁻¹ s⁻¹), respectively, indicating an important role of NH3 in accelerating the aqueous-phase oxidation of SO2 by NO2.

As shown in Fig. 1, SO4²⁻ formation in the aqueous phase is dependent on solubility of SO2 and NO2 (process I and II) and aqueous-phase oxidation (process III). Therefore, the increased ratio of SO4²⁻ concentration ($R[SO_4^{2-}]$) should be equal to the increase ratio of SO2 dissolution ($R[SO_2]$) multiplied by the increase ratio of NO2 dissolution ($R[NO_2(aq)]$), then multiplied by the increase ratio of the reaction rate constant ($R_k$), i.e., $R[SO_4^{2-}] = R[S(IV)] \times R[NO_2(aq)] \times R_k$. Gas-phase NH3 increases all these processes mentioned in Fig. 1, leading to increased SO4²⁻ formation. The effects of NH3 on the three processes were evaluated separately in this study. First, the influence of NH3 on the dissolution of SO2 was studied in the experiments GR-SO2/H2O2(aq) and GR-SO2/NH3/H2O2(aq) (SI, Table S1). Considering that the reaction rate constant between SO2 and H2O2 ($k = 7.45 \times 10^7$ M⁻¹ s⁻¹) is constant when the solution pH is > 2.5 (Seinfeld and Pandis, 2016), the increased SO4²⁻ formation in the experiment GR-SO2/NH3/H2O2(aq) compared with that in GR-SO2/H2O2(aq) can be attributed to the increased solubility of SO2 by NO2.

As shown in Fig. 2, the generated concentration of SO4²⁻ (A) in GR under different experimental conditions, i.e., 300 ppb SO2, 310 ppb SO2/312 ppb NO2, 302 ppb SO2/NH3(aq), and 300 ppb SO2/310 ppb NO2/NH3(aq), and (B) in SC under analogous experimental conditions, i.e., 298 ppb SO2, 288 ppb SO2/307 ppb NO2, 288 ppb SO2/NH3 (~300 ppb), and 284 ppb SO2/317 ppb NO2/NH3 (~300 ppb). The error bars represent the standard deviations.

**Fig. 3.** (A) Time-resolved concentration and (B) consumption rate constant of SO2 in the SC experiments under different conditions.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Reaction rate constant (M⁻¹ s⁻¹)</th>
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<tr>
<td>This study</td>
<td>GR-SO2/NO2</td>
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<tr>
<td>GR-SO2/NO2</td>
<td>$1.31 \times 10^6 \pm 2.86 \times 10^4$ (pH &gt; 4.1)</td>
</tr>
<tr>
<td>Lee and Schwartz, 1983</td>
<td>$1.40 \times 10^5$ (pH &lt; 5.0)</td>
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<tr>
<td>Clifton et al., 1988</td>
<td>$1.24 \times 10^7$ (pH &gt; 5.3)</td>
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of NH₃. These two ratios in processes I and II could not fully explain the 5.3-fold higher SO₄²⁻ formation in the experiment GR-SO₂/NO₂/NH₃(aq) compared to GR-SO₂/NO₂. The remaining increase was attributed to the promotion of the oxidation rate constant, namely process III in Fig. 1. An increase of 12% in the oxidation rate constant with the coexistence of NH₃ was needed to match the total increase of SO₄²⁻ formation. This slight increase in the oxidation rate constant might be attributed to the change in the pH of the aqueous solution. In summary, our estimation showed that the enhancement effects of NH₃ on the solubility of SO₂ and NO₂ were the main factors in promoting SO₄²⁻ formation in the aqueous-phase reaction.

3.4. Influence of ionic strength on aqueous-phase reactions

The electrolyte (i.e., hygroscopic oxalic acid) concentrations were higher in the aerosols in the SC experiments than those in the solution in the GR experiments. Previous studies have shown that electrolyte concentrations can alter the rate constant for a reaction involving a neutral species (e.g., the reactions of nitrogen trioxide (NO₃)) by about one order of magnitude (Herrmann and Zellner, 1998). For the H-abstraction reactions of chlorine radical anion (Cl₂) with formaldehyde and formic acid, higher rate constants were observed with increasing ionic strength (Jacobi et al., 1999). Therefore, it is reasonable to attribute the higher reaction rate constant derived from the SC experiments compared to that from the GR experiments to the higher ionic strength (Herrmann et al., 2015) in the aerosol water, where the products and pre-existing electrolyte were highly concentrated.

The ionic strength (I) of a solution is defined as:

\[ I = \frac{1}{2} \sum_{i=1}^{n} c_i z_i^2 \]  

where \( c_i \) is the concentration of species \( i \) and \( z_i \) is the ionic charge of species \( i \) in aqueous solution.

For a reaction \( A \rightarrow \text{products} \), where reactants A and B form an intermediate product \( \text{[A-B]} \), which then quickly converts into the final product P, the relationship between the reaction rate constant \( k \) and the ion strength \( I \) can be described by the following equation (Herrmann, 2003):

\[ \log \frac{k}{k(I = 0)} = \log \gamma_A + \log \gamma_B - \log \gamma_A \times B \]  

where \( \gamma_i \) is the activity coefficient of species \( i \), and \( k(I = 0) \) is the kinetic rate constant at the infinite dilution condition, namely \( I = 0 \) M.

According to the previous reported mechanisms for the reaction of NO₂ with S(IV) (Clifton et al., 1988; Huie, 1994; Nash, 1979; Spindler et al., 2003), the rate-controlling step of this oxidation process involves an ion (i.e., HSO₃⁻, SO₃²⁻) reacting with a neutral molecule (i.e., NO₂). For the neutral species, the expression for the activity coefficient \( \gamma_i \) can be described by equation (10), which indicates that \( \gamma_i \) of the neutral species could be positively influenced by I via the ion-pair interaction (Herrmann, 2003).

\[ \log \gamma_i = bI \]  

where \( b \) is the kinetic salting coefficient.

As a result, the relationship between \( k \) and \( I \) for the reaction of NO₂ with S(IV) should be expressed as:

\[ \log \frac{k}{k(I = 0)} = bI \]  

In the light of previous studies (Kameoka and Pigford, 1977), B should be a positive value. Therefore, the reaction rate constant \( k \) increases with increases in the ionic strength \( I \) of the solution.

Based on the concentrations of water-soluble ions (mainly SO₄²⁻, NO₃, NH₄) (SI, Table S2), the ionic strength of the reaction systems was low \( I = 2.40 \times 10^{-6} \) M and \( 7.20 \times 10^{-6} \) M for GR-SO₂/NO₂ and GR-SO₂/NO₂/NH₃(aq), respectively) in the GR experiments. In a previous study conducted by Lee et al. (Lee and Schwartz, 1983), the initial reaction solution concentration \( ([\text{HSO}_3^-]_0 = 1.3 \times 10^{-6} \) M\) was also low. Hence, it is reasonable that the reaction rate constants derived from the GR experiments in our study are comparable to the results by Lee et al. (Lee and Schwartz, 1983). On the other hand, under a higher S(IV) concentration \( ([\text{S(IV)}] = 5 \times 10^{-4} - 2 \times 10^{-3} \) M\) condition, Clifton et al. (1988) derived higher reaction rate constants compared to Lee et al. (Lee and Schwartz, 1983) and this study (Table 2). The comparison suggests that higher concentrations of solutes, namely higher ionic strengths in the solution can result in higher rate constants. To test this hypothesis, we performed experiments on the oxidation of SO₂ by NO₂ in solutions with different concentrations of oxalic acid (Table S1). Higher SO₄²⁻ concentrations (Table S2), resulting from higher formation rate constants, were indeed observed for higher concentrations of oxalic acid in solution. A linear relationship between \( \log k \) and \( I \) (\( R^2 = 0.95 \), blue solid line, Fig. 4) was obtained, which is consistent with equation (11) and thus confirms the hypothesis.

Meanwhile, for the SC experiments SC-SO₂/NO₂ and SC-SO₂/ NO₂/NH₃, the oxalic acid seeds were deliquescent under the experimental conditions of RH = \( 98 \pm 1.5 \% \) (Peng et al., 2001), providing an aerosol water reaction medium in which the reactions occurred. Using similar methods as in Guo et al. (2015) (SI, Section S3), the volume of aerosol water was estimated, allowing the concentrations of water-soluble ions (mainly HC₂O₄⁻, SO₄²⁻, NO₃, and NH₄) in this aerosol water (SI, Table S3) and the ionic strength of the solution to be calculated. The ionic strength was much higher \( I = 3.29 \times 10^{-1} \) M and \( 1.14 \) M for the experiments SC-SO₂/NO₂ and SC-SO₂/NO₂/NH₃, respectively) in the SC experiments than that in the GR experiments. The higher higher strengths can explain the high reaction rate constants for SO₄²⁻ formation in the aerosol water. Together with the GR experiments with further reduced ionic strength (i.e., in total 5 experimental data points), an empirical relationship between reaction rate constants for SO₄²⁻ formation in the aerosol water.

![Fig. 4. Relationship between reaction rate constant (k) and ionic strength (I). Each data point refers to an experiment listed in Table 1 and Table S1, and the log(k)-I data corresponding to the all points are given in Table S4. An linear relationship \( \log k = 3.1 \times I + 6.1, R^2 = 0.98 \) was obtained when combining GR and SC experiments.](image-url)
relationship between log k and I could also be obtained ($R^2 = 0.98$, black dashed line, Fig. 4). According to this empirical relationship, the reaction rate constant may increase linearly with the increase of ionic strength in aerosol water, but the increase progressively diminish. Although there is no scientific explanation for this phenomenon yet, it is supported by previous studies investigating the salt effect in reactions between ions and dipolar molecules (Amis and Jaffe, 1942; Castanedaagullo et al., 1961). These empirical relationships in Fig. 4 might provide a parameterized solution to the air quality models for simulation of SO4$^{2-}$ formation in cloud/fog droplets and aerosol water.

4. Conclusions and atmospheric implications

As the major inorganic constituent of atmospheric particle matter (PM), SO4$^{2-}$ plays an important role in haze pollution not only over North China (Guo et al., 2014; Sun et al., 2016), but also other rapidly developing countries (Gordon, 2003). Based on the present understanding of SO4$^{2-}$ formation mechanisms, the observed SO4$^{2-}$ levels cannot be accurately simulated in air quality models, which indicates the presence of reactions and factors in addition to the current formation mechanisms (Gao et al., 2016a; Zheng et al., 2015a). In the present study, model reaction kinetics of aqueous oxidation of SO2 by NO2 under different atmospheric conditions were quantitatively evaluated. The GR experimental results, in which we found that SO2 oxidation by NO2 contributed significantly to SO4$^{2-}$ formation, may be applicable to SO4$^{2-}$ formation in fog and clouds. Meanwhile, the coexistence of NH3 would mainly enhance the dissolution of SO2 and NO2 and subsequently promote SO4$^{2-}$ formation. The SC experimental results may be applied to SO4$^{2-}$ formation in aerosol water. Unexpectedly high reaction rate constants for the oxidation of S(IV) by NO2 were observed in aerosol water, which was attributed to the high ionic strength in the aerosol water.

In severe haze episodes (Gao et al., 2016b), ground-level photochemical reactivity can be weak due to radiative attenuation and the ozone concentration can be low (Zheng et al., 2015b). Gas-phase oxidation of SO2 by OH and aqueous-phase oxidation of dissolved SO2 by O3 and H2O2 can be suppressed to a great extent because of the low oxidant levels. Under these situations, the oxidation of S(IV) by NO2 in the liquid phase may become an essential pathway of SO4$^{2-}$ formation when RH, NO2 and NH3 levels are all high. Such conditions exist in the winter season in cities such as Beijing (Zhang et al., 2015a) and Shanghai (Ye et al., 2011), China, where haze episodes were frequently observed but oxidant levels represented by O3 were low, yet SO4$^{2-}$ was high (He et al., 2014; Wang et al., 2016). Using observed NO2, NH3 and PM concentrations in such haze episodes (Cheng et al., 2016), the atmospheric lifetime of SO2 due to oxidation by NO2 in aerosol water is estimated to be approximately 24 h based on the present laboratory study results (SI, Section S4), which is shorter by an average factor of about 2 than the atmospheric lifetime of SO2 due to OH oxidation by assuming an daytime average OH concentration of 5.2 × 105 molecules cm$^{-3}$ (Lu et al., 2013). Atmospheric OH concentrations varied a lot ($<1 \times 10^5$–$1.7 \times 10^6$ molecules cm$^{-3}$) in different seasons and at different latitudes and altitudes (Lu et al., 2013; Seinfeld and Pandis, 2016; Wang et al., 2016; Yang et al., 2017), while ranged from 2.4 × 105 molecules cm$^{-3}$ to 3.6 × 106 molecules cm$^{-3}$ in Beijing winter (Tan et al., 2018). The atmospheric lifetime of SO2 due to OH oxidation will increase with decreasing OH concentration in winter time during haze episodes. These SO2 lifetime analyses suggest that heterogeneous oxidation of SO2 by NO2 in aerosol water, especially with the coexistence of NH3, high concentrations of PM and high RH, is a major pathway for SO4$^{2-}$ formation in the atmosphere in severe haze episodes. Such a high oxidation rate was clearly promoted by high ionic strengths in aerosol water. High aerosol ionic strengths have been observed in typical haze events in Beijing (Guo et al., 2017), at 12 times higher than that under our experimental conditions. Given the finding of the already large impact under the ionic strength conditions of our laboratory study, the impact of I under real-world haze conditions should be even stronger, and hence should be considered in air quality models to improve simulations of haze formation process.

There have been questions about the importance of the oxidation of SO2 to SO4$^{2-}$ by NO2 based on low pH value predictions for aerosols (Cheng et al., 2016; Guo et al., 2017; Liu et al., 2017; Song et al., 2018; Wang et al., 2018). Our results indicated that SO4$^{2-}$ formation by NO2 oxidation can still be significant in acidic aerosol water under high ionic strength conditions (Table 2). Expanding and continuing the present work to include more atmospherically relevant conditions may provide more accurate kinetic parameters for simulation of SO4$^{2-}$ formation in air quality models.

Competing financial interests

The authors declare no competing financial interest.

Acknowledgments

This work was supported by the National Key R&D Program of China (2016YFC0202700), National research program for key issues in air pollution control (DQCG0103), the National Natural Science Foundation of China (41877304), the Young Talent Project of the Center for Excellence in Regional Atmospheric Environment, CAS (CERAE201801), Strategic Priority Research Program of the Chinese Academy of Sciences (XDB05010300), the Youth Innovation Promotion Association, CAS (20180606), and Key Research Program of Frontier Sciences, CAS (QYZDB-SSW-DQC018).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2019.05.119.

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https://doi.org/10.1016/j.envpol.2019.05.119.


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