Accelerated Sulfur Oxidation by Ozone on Surfaces of Single Optically Trapped Aerosol Particles

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Abstract

The sulfur oxidation in mixed sodium thiosulfate/sucrose/aqueous micro-droplets by gaseous ozone is studied in this work via aerosol optical tweezers coupled with Raman spectroscopy, which can simultaneously determine various physicochemical properties and the heterogeneous reaction kinetics of single optically trapped micro-droplets, allowing for elucidating their complicate interplay. According to the kinetics measurement results at different relative humidities, ozone concentrations and stoichiometries of inorganic and organic solutes, this work finds that a high aerosol ionic strength can accelerate the ozone oxidation of thiosulfate at air-water interfaces, while a high aerosol viscosity prolongs the reaction timescales due to diffusion-limited kinetics. The kinetic multilayer model of aerosol surface and bulk chemistry (KM-SUB) is utilized to investigate the observed heterogeneous kinetics results and to retrieve the surface reaction rate coefficients. The KM-SUB simulations results indicate that the observed kinetics of sulfur oxidation in binary sodium thiosulfate aqueous micro-droplets with high ionic strengths is dominated by interfacial reactions, and the fitted surface reaction rate coefficients increase one order of magnitude when the droplet ionic strength increases around 40 M. Furthermore, this work demonstrated that including the effects of interfacial ion depletion in the kinetics simulations can lead to an excellent agreement with the experimental results, implying its potential role in the interfacial kinetics.

Introduction

The reactions in aerosol phase can play a key role in atmospheric chemistry. The oxidation of SO$_2$ in aqueous aerosol droplets is one of main sulfate sources in atmosphere, because of the fast kinetics of aqueous-phase sulfur oxidations. Large Criegee intermediates can survive at air-water interfaces, while water is also their major sink, allowing them to react with other species. The aqueous droplets can mediate the efficient production of atmospheric formic acid from gaseous formaldehyde. Furthermore, particle-phase oxidation reactions determine the formation, growth and aging of secondary organic aerosols. To better
quantify the effects of aerosols on environments, substantial progress has been made in recent years for better understanding these aerosol-phase reactions, including the complicate interplay between their reaction dynamics and physicochemical properties of aerosols.13,14

The chemical pathways of aerosols have a complicate interplay with the physicochemical properties of aerosols, which could be affected by the chemical composition of aerosols. Atmospheric aerosols usually contain both inorganic and organic species,15,16 which determine the ionic strength and viscosity of aerosols, respectively.17–20 These two physicochemical properties have been recognized to play key roles in the reaction kinetics of aerosols.3,19,20 A high ionic strength in aerosols can enhance the reactive uptakes of gaseous reactants, the reaction rate coefficients in aerosol bulks and the rates of aqueous photolysis.21–23 Several recent studies also found that high ionic strengths can enhance the reactive uptakes of SO2 by peroxides and the sulfate formations from the subsequent SO2 oxidation in deliquesced aerosol particles.24,25 Conversely, a high viscosity in organic aerosols can lead to slower diffusion times of molecular species and thus the longer time scales of dynamic processes in aerosols, while the relationship between viscosity and diffusivity could also highly depend on phase states of aerosols and molecular interactions.19,26–30

The roles of chemical composition in the heterogeneous reaction kinetics of aerosols are often rationalized in terms of the effects of ionic strength and diffusivity to the reactions in aerosol bulks. However, for the reactions at aerosol surfaces or interfaces, it still requires more advanced investigations to clarify the potential role of chemical composition. Such detailed understanding should promise to elucidate the mechanism of the accelerated droplet reactions found in recent studies.31–34 There have been extensive investigations which focused on the effects of ions to adsorption and gradients of concentration and pH at interfaces. The increasing number of ions in bulks can significantly modify the population of anions at interfaces.35–38 A very recent kinetics study of nitrite ozonolysis in aerosols investigated the significant dependence of interfacial nitrite concentrations on bulk nitrite concentrations and its potential role in the interfacial kinetics.39 The pH at surfaces of aerosols can also
be different from those in aerosol bulks,\textsuperscript{40} and a recent aerosol kinetics study observed the enhanced rates of catalyzed oxidations in aerosols and attributed this enhancement to the pH gradient at the air-water interfaces of aerosols.\textsuperscript{41}

In the present work, we choose the oxidation reaction of sodium thiosulfate (STS), Na$_2$S$_2$O$_3$, with O$_3$ as a model system of sulfur oxidation in aerosols, as such model reaction has been utilized in several studies associated with atmospheric aerosol chemistry.\textsuperscript{42–44} In particular, the present work exploited aerosol optical tweezers (AOT) combined with Raman spectroscopy to characterize the influences of chemical composition to the oxidation reaction kinetics of mixed STS/sucrose aqueous micro-droplets by gaseous O$_3$. The present work performed the kinetics measurements of the S$_2$O$_3^{2-} + O_3$ reaction in micro-droplets at different relative humidities (RHs), O$_3$ pressures and stoichiometries of STS and sucrose. The present work also performed the simulations of aerosol kinetics to retrieve the surface bimolecular reaction rate coefficients and the diffusivities of O$_3$ and S$_2$O$_3^{2-}$ at different solute strengths. Based on the data-model comparison, the potential role of surface ion depletions in the aerosol reaction kinetics will be addressed in this report.

**Experimental**

The aerosol optical tweezers apparatus utilized in our present work has been described elsewhere,\textsuperscript{23} and thus it is only briefly described here. A CW laser emitting at 532 nm was used as a trapping laser. After entering the microscope, the laser beam was focused by a high numerical aperture oil-immersion objective into an aerosol trapping chamber. When a single micro-droplet was trapped by this focused laser beam, the Raman scattering light emitted from it was collected by the same objective, imaged onto the entrance slit of a 0.5 m spectrograph, and dispersed by a 12001/mm grating. The dispersed Raman signals were detected by a TE-cooled spectroscopic CCD with 26 µm pixel size. The integrated time for acquiring time-resolved Raman spectra was 1.2 second. The spectral resolution employed in
the present work was about a couple of cm$^{-1}$, according to the FWHMs of observed whisper
gallery modes (WGMs) of optically trapped micro-droplets.

When the optical trapping experiments were performed, a dense flow of aqueous aerosols
(3 to 8 $\mu$m in diameter) containing binary aqueous STS or ternary aqueous STS/sucrose
mixtures was introduced into the trapping chamber for a few minutes, until the brightfield
imaging exhibited that a single micro-droplet was optically trapped. The RH in the trapping
chamber was maintained from 30% to over 80% via injecting a mixed flow of dry and
humidified nitrogen. The RH of the gas flow and the trapping chamber were monitored
by humidity sensors (Honeywell, HIH-4602-C, accuracy: 3.5%) which was calibrated by a
more accurate one (Rotronic, HC2A-S, accuracy: 0.5%). An ozone generator was utilized
to produce gaseous ozone from pure oxygen, and the generated O$_2$/O$_3$ gas mixture was fur-
ther diluted with dry nitrogen in the trapped chamber. When the measurements of aerosol
reaction kinetics were performed, the premixed O$_2$/O$_3$/N$_2$ gas flow was mixed with the RH
regulated nitrogen gas flow prior flowing into the trapping chamber. The concentration of
ozone in the mixed gaseous flow was on-line monitored via its UV absorption peak at 250 nm.

For the measurements of binary aqueous STS aerosols, the sample solutions for generating
aerosols contained 0.6 M or 0.9 M STS. For the measurements of ternary component aerosols
containing water, STS and sucrose, the sample solutions were prepared at several mass ratios,
for example, STS:sucrose:water = 2:4:15.

Results and discussion

Raman spectra of trapped droplets

The reaction schemes of the S$_2$O$_3^{2-}$ + O$_3$ reaction and the secondary chemistry in aqueous
phase are expected as following:

\begin{equation}
S_2O_3^{2-} + O_3 \rightarrow SO_4^{2-} + SO_2
\end{equation}
\[
S_2O_3^{2-} + O_3 \rightarrow S_2O_6^{2-}
\]  
(2)

\[
SO_2 + H_2O \rightleftharpoons SO_2 \cdot H_2O \rightarrow HSO_3^- + H^+
\]  
(3)

\[
HSO_3^- + O_3 \rightarrow HSO_4^- + O_2
\]  
(4)

Figure S1 shows the representative Raman spectra of single aqueous STS droplets exposed to O₃ at two distinct RHs, and the observed molecular Raman bands can be assigned to the reactant \(S_2O_3^{2-}\) or products, such as \(SO_4^{2-}\) and \(HSO_4^-\),⁴⁵-⁴⁹ as depicted in Schemes 1 and 3-4. On the other hand, this work did not observe any distinguishable Raman feature of \(S_2O_6^{2-}\),⁵⁰ implying that any produced \(S_2O_6^{2-}\) may be subsequently oxidized to sulfates by O₃.⁵¹ Besides identifying molecular species in droplets, Raman spectroscopy of single aerosol particles can also be utilized to determine several physicochemical properties of each trapped droplet required for investigating the aerosol reaction kinetics, such as radius, concentrations of solutes and ionic strength.⁵²-⁵⁴ The present work utilized the measured Raman intensity ratios of solute and water to determine the absolute concentrations of STS, \(SO_4^{2-}\) and \(HSO_4^-\) inside each droplet, as well as aerosol ionic strength, and they are provided in Tables S1 and S4. The estimated droplet STS concentrations prior reaction, \([STS]_0\), agree with the predictions of E-AIM model,⁵⁵ as shown in Figure S6, justifying the methodology of concentration determination employed in this work.²³ In addition to spontaneous Raman scatterings, the optically trapped micro-droplets could also yield cavity-enhanced Raman scattering (CERS), which are WGMs amplified by stimulated Raman scattering, allow for determining aerosol radius and solute concentrations, as well as their time evolutions.¹,⁵⁴ For the case where no obvious CERS signals existed, we determined the droplet radius prior reaction via brightfield imaging.²³ The typical radius of droplets studied in this work is about 3 \(\mu m\).

Figure 1 shows the representative time evolutions of molecular Raman intensities and droplet radius from a binary aqueous STS droplet exposed to O₃. The rapid change of the droplet radius from 2750 nm to 2700 nm after 0 second is attributed to the sudden decrease of RH by \(\sim 3\%\), because of mixing the small premixed O₃ gas flow into the wet air flowing into
Figure 1: Representative time profiles of radius (squares) and integrated Raman intensities (lines) of $S_2O_3^{2-}$ (at 445 cm$^{-1}$ or 997 cm$^{-1}$, black), $SO_4^{2-}$ (at 980 cm$^{-1}$, red) and $HSO_4^{-}$ (1050 cm$^{-1}$, blue) from a trapped aqueous STS droplet exposed to O$_3$ ($\sim$14 ppm) after 0 second, as well as the representative error bars for droplet radius. See Table S1 (Expt.11) in ESI for details of the experimental conditions.

the trapping chamber. After O$_3$ flowed into the trapping chamber, the Raman intensities of $S_2O_3^{2-}$ and droplet radius decreased, and those of products $SO_4^{2-}$ and $HSO_4^{-}$ increased, until $S_2O_3^{2-}$ was completely used up. The existence of both $SO_4^{2-}$ and $HSO_4^{-}$ since the early reaction time scale indicates that the droplet pH is regulated in the range of 0.5 and $-0.5$ during the reaction progress.$^{48,49}$ Finally, according to Figure 1, the typical change of aerosol radius during the kinetic measurements of this work is about 200 nm, which is only about 7% of the typical droplet radius, and thus for simplifying the following data analysis the droplet radius is assumed constant.

**Kinetics measurements**

The present work carried out the kinetics measurements at different RHs, O$_3$ pressures and stoichiometries of STS and sucrose. Figure 2(a) shows the time evolutions of $S_2O_3^{2-}$ Raman intensities from single binary aqueous STS micro-droplets exposed to O$_3$ at two different RHs. It should note that the oxidation rate of $S_2O_3^{2-}$ at RH 32% is faster than those at
Figure 2: Typical kinetics measurement results (symbols) of micro-droplets containing (a) binary aqueous STS (Expt. 03 and 18 in Table S1 of ESI) and (b) ternary aqueous STS:sucrose mixtures at 2:4 mass ratio (Expt. 20–22 in Table S1 of ESI), exposed to ozone (∼12–15 ppm) at different RHs, as well as the simulations of KM-SUB (lines). The data shown here are the integrated Raman band intensities of $S_2O_3^{2−}$, and they are normalized to those prior reaction. Each data point represents the mean of 5 consecutive spectra, and for clarity, only the representative error bars are shown here.

RH 85%. As the measured droplet ionic strengths at RH 85% and RH 32% are 12 M and 60 M (see Table S1), respectively, the observed acceleration of the $S_2O_3^{2−} + O_3$ reaction in micro-droplets could be attributed to the enriched droplet ionic strength at lower RHs. For comparison, Figure 2(b) shows the representative kinetics measurements from ternary aqueous STS:sucrose micro-droplets at three distinct RHs. Unlike the case of binary STS, the decay rates of $S_2O_3^{2−}$ of ternary STS:sucrose mixtures become slower at lower RHs, agreeing with the observed trends of organic acid ozonolysis in aerosols. Such trend indicates that the observed reaction kinetics in aerosols containing organic species is limited by molecular diffusions when lowering RH and thus increasing the aerosol viscosities which are dominated by enriched organic species, such as sucrose.

Finally, for the range of $O_3$ pressures used in this work, i.e., from 0.3 ppm to 15 ppm, the observed decay rates of $S_2O_3^{2−}$ is linearly proportional to $O_3$ pressures, as shown in Figure 3. The decay rate coefficient $k_1$ in this figure was obtained from phenomenologically fitting the data with the exponential decay form ($a \exp[−k_1 t]$). According to Langmuir-Hinshelwood mechanism, such linear relationship means that the surface coverage of $O_3$ does not saturate
Figure 3: Phenomenologically fitted decay rate coefficients $k_1$ with the exponential function form, $a \exp(-k_1 t)$, are plotted as a function of O$_3$ pressure, and the error bars shown here only represent fitting errors. See Table S1 (Expt. 1–10) in ESI for details of the experimental conditions.

the surface sites of aerosols yet.$^{57,58}$ If the O$_3$ pressure becomes larger than a threshold where the surface sites for O$_3$ are fully saturated, the value of $k_1$ reach a constant plateau and does not increase with O$_3$ pressures.$^{57}$

Model Simulations

In order to elucidate the observed ozone oxidation kinetics of S$_2$O$_3^{2−}$ in micro-droplets, such as the opposite trends of S$_2$O$_3^{2−}$ decay times with respect to RHs for binary STS and ternary STS:sucrose mixtures, this work utilized the kinetic multi-layer model of aerosol surface and bulk chemistry (KM-SUB)$^{59–61}$ to simulate the time evolutions of S$_2$O$_3^{2−}$ in aerosols. This kinetics model takes into account the following processes: gas-phase and bulk-phase diffusions, surface adsorption and desorption, surface-bulk exchange, and chemical reactions at the air-water interface and in the aerosol bulk. Table S2 summarizes the KM-SUB input parameters applied in the present work, which reflect the kinetics of above processes and physicochemical properties of reactants and each micro-droplet. The representative simu-
lation results for the kinetics measurements of both binary STS and ternary STS:sucrose mixtures are shown in Figure 2.

It should note that for the case of binary STS, the only free input parameter in the KM-SUB simulations for fitting the kinetics data is the second-order rate coefficient for the surface reaction of $S_2O_3^{2-}$ with $O_3$, i.e., $k_{SLR}$, and other input parameters are bound to values either provided by literature or determined from the present experiments. For example, the second-order rate coefficient for the bulk reaction of $S_2O_3^{2-}$ with $O_3$, i.e., $k_{BR}$, for each microdroplet is pinned down by the measured droplet ionic strength prior reaction, $I = 3[STS]_0$, and the empirical relationship of ionic-strength dependent $k_{BR}(I)$ from literature (see ESI for further details). The diffusion coefficients of $S_2O_3^{2-}$ and $O_3$ in binary STS droplets are fixed to those estimated from the Stokes-Einstein equation and parameterized viscosity of binary STS as a function of $[STS]_0$ (see ESI for further details). The viscosities of binary STS droplets at RHs from over 80% to 30% are estimated to be within the range of $\sim 10^{-3}$ Pas to $\sim 10^{-1}$ Pas. As a result, the surface reaction rate coefficient $k_{SLR}$ determined in this study can be decoupled from bulk reaction rate coefficient $k_{BR}$ and diffusion coefficients of reactants.

Figure 4: Bimolecular surface reaction rate coefficient $k_{SLR}$ (symbols) plotted as a function of droplet ionic strength prior reaction and the fit (lines) with eq 5. These values of $k_{SLR}$ were retrieved from fitting the kinetics data of binary STS with the KM-SUB model simulation results where the effects of interfacial ion depletions are (a) not included or (b) included, and the corresponding input parameters are provided in Tables S2 and S3, respectively.
Figure 4(a) plots the fitted $k_{\text{SLR}}$ from the data of binary STS at different droplet ionic strengths. As shown in Figure 4(a), the fitted $k_{\text{SLR}}$ exhibits a positive ionic-strength dependence, and its value increases about one order magnitude when the droplet ionic strength increases about 40 M. Indeed, the observed $S_2O_3^{2-}$ decay curve at RH 32% shown in Figure 2(a) exhibits the feature of an exponential decay, indicating the dominance of surface reactions at high ionic strengths. On the other hand, the time evolution of $S_2O_3^{2-}$ at RH 85% shown in Figure 2(a) exhibits a rather linear form, indicating that beside the surface kinetics, there is also a significant contribution of diffusion-limited kinetics in aerosol bulks at low ionic strengths. While the second-order rate coefficient for the bulk, $k_{\text{BR}}$, is expected to increase when increasing the droplet ionic strength, the values of this $k_{\text{BR}}$ for the most cases of binary STS measurements, which have the ionic strengths larger than 10 M, already reach the typical limit of diffusion-controlled reaction rates, $\sim 1.4 \times 10^{11} \text{M}^{-1} \text{s}^{-1}$, which is assumed as the upper limit of $k_{\text{BR}}$ in the simulations. As a result, the kinetics simulation ascribes the positive ionic-strength dependence of the $S_2O_3^{2-}$ decay rates observed in Figure 2(a) to the positive ionic-strength dependence of $k_{\text{SLR}}$. Figure 4(a) also shows a phenomenological fit applied to $k_{\text{SLR}}$, and this is based on the following equation from the Debye-McAulay approach for ion/neutral + neutral reactions:

$$\log k_{\text{SLR}}(I) = \log k_{\text{SLR},0} + bI$$  \hspace{1cm} (5)$$

where $b$ is an empirical constant, $I$ is droplet ionic strength prior reaction, and $k_{\text{SLR},0}$ is defined as the bimolecular surface rate coefficient corrected to zero ionic strength. The fitted values of $b$ and $k_{\text{SLR},0}$ are $(2.0 \pm 0.3) \times 10^{-2} \text{M}^{-1}$ and $(2.5 \pm 0.3) \times 10^{-14} \text{cm}^2 \text{s}^{-1}$, respectively.

For the case of STS:sucrose in 2:4 mass ratio, the empirically determined $k_{\text{SLR}}(I)$ (eq 5) was then employed in the corresponding KM-SUB simulations. Since both $k_{\text{SLR}}$ and $k_{\text{BR}}$ can be pinned down in the simulations via their empirical relationships and measured droplet ionic strengths, the aerosol viscosity becomes the only free KM-SUB input parameter.
instead, when assuming a valid Stokes-Einstein relationship. Table S2 summarizes the fitted diffusion coefficients of $S_2O_3^{2-}$ and $O_3$, which vary a few orders of magnitude at different RHs, and the corresponding fitted droplet viscosities at RH 89%, 49% and 37% are $7.9 \times 10^{-3}$ Pa s, $5.7 \times 10^{1}$ Pa s and $> 8.1 \times 10^{6}$ Pa s, respectively, as listed in Table S4. On the other hand, the increases of $k_{SLR}$ and $k_{BR}$ caused by lowering RH are relatively subtle and more or less within one order of magnitude, because of relatively low concentrations of STS in micro-droplets, as shown in Table S2. As a result, the reaction kinetics of aerosols is dominated by molecular diffusions in aerosol bulks, and the acceleration by means of enriching ionic strengths becomes negligible in such case. Finally, Table S4 shows that these fitted droplet viscosities are within the lower and upper limits defined by binary STS and sucrose at same RHs, $^{62,65,66}$ respectively, while they are closer to those of binary sucrose, justifying the methodology and the input KM-SUB parameters applied in the present work.

**Interfacial depletion of ions**

For the cases of binary STS at RH $>\sim 80\%$ and $<\sim 30\%$, the KM-SUB simulations with the input parameters listed in Table S2 can capture the entire reaction timescales of the kinetics data, as shown in Figures 5 and S2. However, for the kinetics data at RH between 60% and 80%, while the corresponding KM-SUB simulations with the same strategy can still perfectly capture more than the first half reaction timescales, the simulated time evolutions of $S_2O_3^{2-}$ exhibit more prolonged decays than the measured time decay traces at the later timescales, such as symbols (data) and blue lines (simulation) shown in Figures 6. The present work found that a phenomenological treatment of increasing the Henry’s law constants for $O_3$, $K_{sol,O3}$, by at least one or two orders of magnitude can yield a significantly better agreement between simulation and experimental results, particularly at the late time scales, such as red lines shown in Figures 6. Table S3 lists the corresponding values of $K_{sol,O3}$ applied in Figure 6.

Such increase of $K_{sol,O3}$ implies that the salt-out effect of STS at high ionic strengths...
Figure 5: KM-SUB simulations results including ($\theta_{ss} > 0$, red lines) and excluding ($\theta_{ss} = 0$, blue lines) the effects of STS surface depletions, comparing with the kinetics measurements (symbols) of (a) Expt. 16 (RH 33%), (b) Expt. 17 (RH 33%), (c) Expt. 18 (RH 32%) and (d) Expt. 19 (RH 29%). Dashed and dotted red lines in (c) correspond to $\theta_{ss} = 0.9$ and 0.99, respectively.

Figure 6: KM-SUB simulations results including ($\theta_{ss} > 0$, red lines) and without ($\theta_{ss} = 0$, blue lines) the effects of STS surface depletions, comparing with the kinetics measurements (symbols) of (a) Expt. 12 (RH 72%), (b) Expt. 13 (RH 71%), (c) Expt. 14 (RH 61%) and (d) Expt. 15 (RH 61%). Solid red lines correspond to $\theta_{ss} = (a) 0.67, (b) 0.55, (c) 0.8$ and (d) 0.8. Dashed and dotted red lines in (d) correspond to $\theta_{ss} = 0.75$ and 0.9, respectively. For clarity, only the representative error bars are shown here.
$(I > 10 \text{ M})$ is overestimated in the original strategy employed to the kinetics simulations. According to literature, the empirical relationship between $K_{\text{sol,O3}}$ in salt solutions and ionic strengths can be expressed as following:\textsuperscript{67}

$$\log\left(\frac{K_{\text{sol,O3,w}}}{K_{\text{sol,O3}}}\right) = \sum_i K_i [i]$$ \hspace{1cm} (6)

where $K_{\text{sol,O3,w}}$ is the Henry’s law coefficient of ozone in pure water, and $K_i$ and $[i]$ are the Sechenov constant and concentration of ion $i$, respectively.\textsuperscript{67} According to eq 6, if the underestimation of $K_{\text{sol,O3}}$ is mainly attributed to the overestimation of the values of $K_i$, the required values of $K_i$ has to be at least two to five times smaller than the literature values. However, these literature values of $K_i$ have only about 23\% percent error,\textsuperscript{67} and our previous work which also adopted this literature did not exhibit any evidence indicating that these values of $K_i$ are significantly overestimated.\textsuperscript{23} Thus, this potential overestimation of the salt-out effect would be instead attributed to the overestimation of $[\text{STS}]$ experienced by dissolving Oz. In particular, because of the fast kinetics of the $\text{S}_2\text{O}_3^{2-} + \text{O}_3$ reaction, the dissolved Oz from the air-water interface only diffuse through the surface layers beneath the interface during the most reaction timescale, until $\text{S}_2\text{O}_3^{2-}$ is completely used up. This means that at least $[\text{STS}]$ at the surface would be overestimated, and the present work proposes that the mechanism of overestimating the surface $[\text{STS}]$ could be associated to the depletion of interfacial ions. The similar argument can be applied to products $\text{SO}_4^{2-}$ and $\text{HSO}_4^-$, since they are supposed to maintain the ionic strengths and $K_{\text{sol,O3}}$ of droplets during the ozonolysis of $\text{S}_2\text{O}_3^{2-}$. See Table S4 for comparing the values of $K_{\text{sol,O3}}$ before and after reaction. Thus, not only STS, the required increase of $K_{\text{sol,O3}}$ also implies that the products $\text{SO}_4^{2-}$ and $\text{HSO}_4^-$ could be depleted at the air-water interfaces.

The interfacial partitioning of ions has been extensively investigated and recognized, but it is not trivial yet to clarify its role in the aerosol reaction kinetics yet. For the case of sulfate salts, such as $\text{Na}_2\text{SO}_4$ and $(\text{NH}_4)_2\text{SO}_4$, both cations and anions were found to be significantly depleted from the air-water interface, and the interface depth of such depletion
could be in an order of sub nm. The present work assumes that not only \( \text{SO}_4^{2-} \) and \( \text{HSO}_4^- \), but also STS may exhibit the similar effect at the air-water interface. From the viewpoint of the heterogeneous kinetics, the smaller solute strength inside the interfacial depletion depth can lead to the larger Henry’s law constant and diffusion coefficient for \( \text{O}_3 \), leading to a more efficient penetration of \( \text{O}_3 \) from gas phase into this ion-depleted layer. On the other hand, since the aqueous phase \( \text{S}_2\text{O}_3^{2-} + \text{O}_3 \) reaction will occur at the boundary between the STS-depleted layer and the STS-rich core, the ionic strength affecting their reactions and the viscosity experienced by diffusing \( \text{S}_2\text{O}_3^{2-} \) should remain more or less the same as those of aerosol bulks. To implement such scenario into the KM-SUB simulation, the present work assumed that the interfacial concentration, \([\text{STS}]_{ss}\), is equal to the product of the bulk concentration, \([\text{STS}]_b\), and \((1 - \theta_{ss})\), where \( \theta_{ss} \) is defined as the partial coverage of surface sites. This assumption was realized in KM-SUB by relating the rate constants for surface-to-bulk transport, \( k_{ssb} \), and vice versa, \( k_{bss} \), as following: \( k_{bss} = k_{ssb}(1 - \theta_{ss})K_{bs} \), where \( K_{bs} \) is surface equilibrium constant, which remains as a constant in the simulations. As a result, \( \theta_{ss} \) becomes an additional input parameter for simulating the observed kinetics. For simplifying the simulations, the present work assumes that \( \theta_{ss} \) does not depend on the reaction time, and the influences of STS to KM-SUB input parameters are used to present those from all ions in droplets, i.e., \( \text{Na}^+, \text{S}_2\text{O}_3^{2-}, \text{SO}_4^{2-} \) and \( \text{HSO}_4^- \), during the entire reaction progress. Thus, the Henry’s law constant and the diffusion coefficient for \( \text{O}_3 \) were estimated from \([\text{STS}]_{ss} \) prior reaction, and the diffusion coefficient for \( \text{S}_2\text{O}_3^{2-} \) and the ionic strength used to determine \( k_{\text{BR}} \) were estimated from \([\text{STS}]_b \) prior reaction.

The simulated time evolutions of \( \text{S}_2\text{O}_3^{2-} \) which include the depletion effects for the kinetics measurements of binary STS (red lines, \( \theta_{ss} > 0 \)) are shown in Figures 5, 6 and S2, as well as those without the surface depletion (blue lines, \( \theta_{ss} = 0 \)) and the corresponding experimental results (symbols) for comparison. It should note that in these simulations, only \( k_{\text{SLR}} \) and \( \theta_{ss} \) are the only free input parameters for capturing the time scales of the observed kinetics. For the data in Figure 6, where the ionic strength is between \( \sim 15 \text{ M} \) and \( \sim 30 \text{ M} \), including
the effects due to surface STS depletion and assuming \( \theta_{ss} = 0.5 \) to 0.8 (50\% to 80\% of STS on the surface is depleted) can lead to a significantly better agreement between simulation and experimental results than assuming no depletion (\( \theta_{ss} = 0 \)). Particularly, the comparison between the simulations of \( \theta_{ss} > 0 \) and \( \theta_{ss} = 0 \) in Figure 6 exhibits that \( k_{SLR} \) and \( \theta_{ss} \) only affect the kinetics at early and late reaction timescales, respectively, and thus they can be decoupled and retrieved independently from the model-data comparison. For example, while the simulation results of both \( \theta_{ss} = 0.8 \) and \( \theta_{ss} = 0 \) shown in in Figure 6(d) can capture the early time scale of the observed kinetics, which is dominated by surface reactions, that of \( \theta_{ss} = 0 \) exhibits a slower diffusion-limit kinetics in bulk layers at the later time scale than the observed kinetics. On the other hand, for \( \theta_{ss} = 0.8 \), the significant ion depletion at the surface promotes the dissolution of gaseous O\(_3\) and the diffusivity of O\(_3\) by factors of \( \sim 420 \) and \( \sim 14 \), respectively, lowering the resistance attributed by the diffusion-limited kinetics. Actually, the effect of \( \theta_{ss} > 0 \) to the aerosol kinetics shown in Figure 6 is to enhance the decay rate due to bulk kinetics, while it should note that the surface depletion of STS can suppress the decay rate due to surface kinetics. As a result, for the data in Figure 6, the fitted value of \( k_{SLR} \) for \( \theta_{ss} > 0 \) has to be larger than that for \( \theta_{ss} = 0 \) by a factor of \( 1/(1 - \theta_{ss}) \) (see Tables S2 and S3 for comparison).

For the cases with ionic strengths larger than \( \sim 35 \) M (see Figure 5), where all the measured kinetics exhibit the exponential decay form, Figure 5(c) shows that the simulation result with \( \theta_{ss} \) up to \( \sim 0.9 \) still maintains the feature of the exponential decay, indicating the dominance of surface reactions even under such surface-STS-depleted condition. However, when \( \theta_{ss} \) increases to 0.99, the simulated results exhibit a rather linear decay form, which indicates the significant contribution of bulk kinetics, contradicting with the observed kinetics. Thus, \( \theta_{ss} = \sim 0.9 \) could be regarded as an upper limit of the surface STS depletion. Finally, for the cases of ionic strengths smaller than \( \sim 15 \) M (see Figure S2), including the depletion effects does not bring any significantly better agreement between the simulation and experimental results than the case without surface depletion, when taking the experimental
errors into account. It should also note that for each data in Figure S2, the corresponding surface and bulk kinetics have the similar reaction timescales, leading to an ambiguity of determining $\theta_{ss}$ and $k_{SLR}$. As a result, the present work assumes that $\theta_{ss}$ for these data of low ionic strengths is negligible.

Figure 7: $[\text{STS}]_{ss,0}$ (symbols) in Table S3 (Expt. 01–04 and 10–15) are plotted as a function of $[\text{STS}]_{b,0}$. Dashed line: $[\text{STS}]_{ss,0} = [\text{STS}]_{b,0}$.

Briefly speaking, including the effects due to depletion of surface ions in the simulations can lead to a better agreement to the experiment results with high droplet ionic strengths, while such treatment does not yield any contradictory simulation result for the kinetics measurements with low droplet ionic strengths. Figure 4(b) summarizes the fitted $k_{SLR}$ when taking the STS surface depletion into account, and the corresponding value of $b$ in eq 5 is equal to $(4.8 \pm 1.1) \times 10^{-2} \text{M}^{-1}$. Comparing with the value of $b$ determined from the bulk measurements (see ESI), $0.27 \text{M}^{-1}$, the value determined in the present work is significantly smaller, and such difference may also imply that the effective ionic strength at the interface layers where the surface reactions occurs is smaller than that in the aerosol bulks. Indeed, the fitted values of partial coverage $\theta_{ss}$ suggest that the surface STS concentration remains around $1.3 \times 10^{14} \text{ cm}^{-2}$ (or around $2.5 \text{ M}$), such as $[\text{STS}]_{ss,0}$ plotted in Figure 7, when the bulk STS concentration is larger than $\sim 4 \text{ M}$. Such kind of dependence has also been found
in the cases of nitrites and nitrates, and it was rationalized in terms of Langmuir adsorption model,\textsuperscript{39} where the surface sites for these ions are also limited, leading to a constant plateau of surface concentrations at higher bulk concentrations. However, it should note that $\theta_{ss}$ employed in the present work is assumed to be independent of time, and thus in principle it takes into account the surface depletions of all ions ($\text{Na}^+$, $\text{S}_2\text{O}_3^{2-}$, $\text{SO}_4^{2-}$ and $\text{HSO}_4^-$) appeared at different reaction time scales. Thus, the trend reported in Figure 7 could also be regarded as the averaged surface concentrations for these ions as a function of droplet ionic strength.

**Conclusion**

The kinetic measurements of single optically trapped micro-droplets performed in the present work demonstrate that the chemical pathways in aerosols can be significantly affected by chemical composition. The organic species in aerosols usually can increase the aerosol viscosity and thus decrease the molecular diffusivity in aerosols, further limiting the reaction kinetics of aerosols at low RHs, as demonstrated by numerous studies\textsuperscript{29,56,59} and also the present work, which utilized the ternary system of aqueous STS and sucrose mixtures. On the other hand, the inorganic salts in aerosols can cause high aerosol ionic strengths, which can enhance not only the bulk-phase but also the surface reaction rate coefficients. The present work demonstrates that such effect of ionic strength leads to the acceleration of the sulfur oxidation reactions on the surfaces of binary aqueous STS micro-droplets, as a proxy of inorganic aerosol, at low RHs. However, for inorganic aerosols, the depletion of interfacial ions at high ionic strengths may also affect the aerosol kinetics. The model-observation comparison performed in the present work implies the existence of interfacial ion depletions which reduces the salt-out effect in first surface layers and thus increases the solubility of $\text{O}_3$, actually leading to an acceleration of the bulk kinetics dominated at the later reaction timescales of the aerosol reaction kinetics associated with high ionic strengths.
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Supporting Information Available

The following files are available free of charge.

- STS-AOT-ESI.pdf: experimental conditions, input parameters of kinetic simulations, calculations of input parameters, error analysis, supplementary figures and tables.

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