

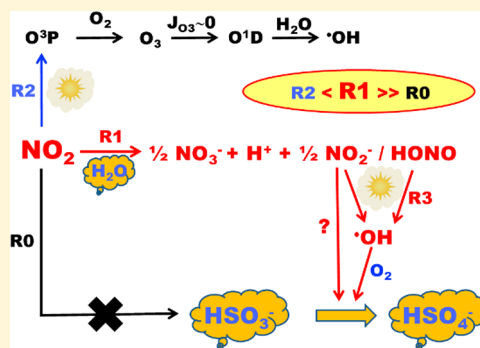
Role of Nitrogen Dioxide in the Production of Sulfate during Chinese Haze-Aerosol Episodes

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Supporting Information

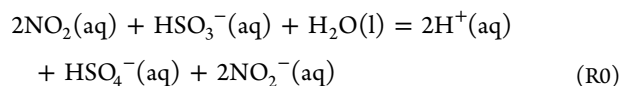
ABSTRACT: Haze events in China megacities involve the rapid oxidation of SO₂ to sulfate aerosol. Given the weak photochemistry that takes place in these optically thick hazes, it has been hypothesized that SO₂ is mostly oxidized by NO₂ emissions in the bulk of pH > 5.5 aerosols. Because NO₂(g) dissolution in water is very slow and aerosols are more acidic, we decided to test such a hypothesis. Herein, we report that > 95% of NO₂(g) disproportionates [2NO₂(g) + H₂O(l) = H⁺ + NO₃[−](aq) + HONO (R1)] upon hitting the surface of NaHSO₃ aqueous microjets for < 50 μs, thereby giving rise to strong NO₃[−] (*m/z* 62) signals detected by online electrospray mass spectrometry, rather than oxidizing HSO₃[−] (*m/z* 81) to HSO₄[−] (*m/z* 97) in the relevant pH 3–6 range. Because NO₂(g) will be consumed via R1 on the surface of typical aerosols, the oxidation of S(IV) may in fact be driven by the HONO/NO₂[−] generated therein. S(IV) heterogeneous oxidation rates are expected to primarily depend on the surface density and liquid water content of the aerosol, which are enhanced by fine aerosol and high humidity. Whether aerosol acidity affects the oxidation of S(IV) by HONO/NO₂[−] remains to be elucidated.



1. INTRODUCTION

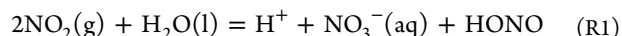
Chinese megacities often experience haze events (HEs)^{1–7} that severely impair visibility and induce acute health effects.^{5,6,8–11} Hazes mainly consist of sulfate aerosols produced in the atmospheric processing of SO₂ and NO₂ emissions under particularly adverse meteorological conditions.^{12–14} Current models of chemistry in HEs significantly underestimate sulfate formation, revealing that the mechanism of SO₂ oxidation is not well understood.^{15–17} The drastic attenuation of actinic radiation in hazes^{18–21} suggests that SO₂ is oxidized by NO₂(g) via heterogeneous processes on the aerosol itself, rather than by photogenerated oxidants in the gas-phase. The details of such a process are uncertain.

Known SO₂ atmospheric oxidation pathways include gas phase reactions with OH radicals and stabilized Criegee intermediates and aqueous phase reactions with O₃,²² H₂O₂, organic peroxides, and NO_x, as well as autooxidation catalyzed by transition metal ions. The low concentrations of photo-generated oxidants^{18,23–30} imply that the chemistries of SO₂ and NO₂ in HEs are intertwined. These observations have led to a hypothesis that HSO₃[−](aq) is rapidly oxidized by the NO₂(g) dissolved in aqueous aerosol phases assumed to be at pH > 5.5 (reaction R0):



on the basis of R0 rates measured in bulk water.^{31–33} Good agreement between field observations and model results on sulfate-aerosol formation in HEs could be obtained by

assuming that R0 proceeds on the surface pH > 5.5 aqueous aerosols at the rates previously reported at pH ~ 6 in bulk water.^{31–34} However, the assumptions that aerosols are at pH > 5.5 and NO₂(g) dissolves in large surface-to-volume aerosol droplets as NO₂(aq) as it does in bulk water may not apply.^{35–45} Most recent studies suggest that HE aerosols are in fact in the pH 3–5 range.^{46–52} Previous laboratory experiments have shown that collisions of NO₂(g) at parts per million level (i.e., in the absence of N₂O₄) with the surface of aqueous electrolyte solutions (but not on the surface of pure water) yield NO₃[−](aq) via a first-order in [NO₂] hydrolytic disproportionation catalyzed by anions (reaction R1).^{42,45}



The fact that NO₂(g) is weakly soluble in pure water (Henry's law constant $H \sim 0.01 \text{ M atm}^{-1}$) and its uptake coefficient on pure water is very small ($\gamma \sim 1 \times 10^{-7}$)⁵³ the dissolution of NO₂(g) in pure water is unfavorable for both kinetic and thermodynamic reasons. The aqueous phase of most atmospheric aerosols, however, is not pure water. In 2009, we found that anions greatly enhance NO₂(g) uptake on water. The rate-determining step involves the capture of NO₂(g) by anions X[−] as X-NO₂[−] at air–aqueous interfaces,^{42,45} followed by the reaction of X-NO₂[−] with a second NO₂(g). This phenomenon accounts for the outstanding discrepancy (by a

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factor of $\sim 10^{3-4}$) between the $\text{NO}_2(\text{g})$ uptake coefficients measured in neat water^{41,53} and those determined on NaCl-seeded droplets in a cloud chamber.^{35,39,54} Because HE aerosols naturally contain organic and inorganic anions, the expectation was that the fate of $\text{NO}_2(\text{g})$ would be determined by reaction R1 at actual aerosol air–aqueous interfaces.

Given the societal and economic impact of HEs, we deemed it important to elucidate the actual role of $\text{NO}_2(\text{g})$ in the production of sulfate aerosol under relevant conditions. Herein, we describe experiments in which aqueous 1 mM NaHSO_3 microjets (containing 3 mM EDTA to inhibit the autoxidation of HSO_3^- catalyzed by pervasive transition metal ions) ejected from a stainless steel syringe are exposed to 5 ppm of $\text{NO}_2(\text{g})$ for $\leq 50 \mu\text{s}$ in 1 atm of $\text{N}_2(\text{g})$ at 298 K. Reactant and product ions formed on the outermost water layers of the liquid microjets are detected within 1 ms by online electrospray ionization mass spectrometry (o-ESI-MS). This technique has been used in our laboratory to investigate a suite of gas–liquid reactions at the air–water interface.^{55–61} The analysis of our experimental results focuses on the fate of $\text{NO}_2(\text{g})$, and the competition between reactions R0 and R1 during collisions of $\text{NO}_2(\text{g})$ with the surface of aqueous HSO_3^- solutions under conditions relevant to HEs. To the best of our knowledge, this is the first study to provide direct experimental evidence of the extent of S(IV) oxidation by $\text{NO}_2(\text{g})$ on the surface of aqueous electrolyte solutions over a wide pH range.

2. METHODS

Reactive interactions of $\text{NO}_2(\text{g})$ with $\text{HSO}_3^-(\text{aq})$ are investigated on the fresh surface of continuously flowing $\text{HSO}_3^-(\text{aq})$ microjets that are crossed by $\text{NO}_2(\text{g})/\text{N}_2(\text{g})$ beams in the spray chamber of an electrospray ionization (ESI) mass spectrometer maintained at 1 atm of $\text{N}_2(\text{g})$ and 298 K (Agilent 1100 Series G2445A Ion Trap LC-MS-MSD instrument) (Figure 1). This experimental setup has been described in more

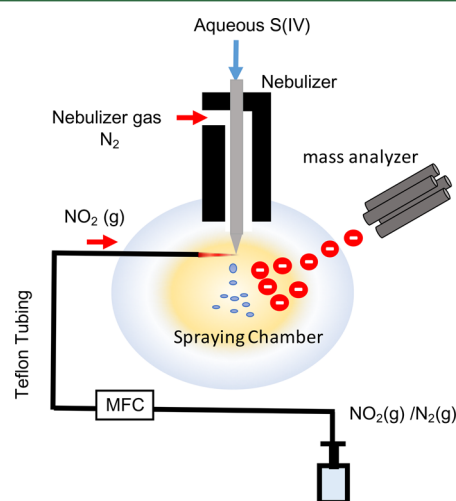


Figure 1. Schematic diagram of the experimental setup. MFC is the mass flow controller.

detail in previous reports from our laboratory.^{44,45,55,57,58,60–64} Aqueous 1 mM NaHSO_3 solutions (containing 3 mM EDTA to chelate pervasive traces of transition metal ions known to catalyze HSO_3^- autoxidation) are pumped at a rate of $50 \mu\text{L min}^{-1}$ through an electrically grounded stainless steel needle injector ($100 \mu\text{m}$ bore). These liquid microjets are intersected

by beams of $\text{NO}_2(\text{g})$ diluted in $\text{N}_2(\text{g})$ at controlled flow rates (MKS). Gas–liquid encounters take place during $\tau \leq 50 \mu\text{s}$ contact times, which correspond to the estimated lifetimes of the intact microjets prior to their breakup by the nebulizing gas. The outermost layers of the liquid microjets issuing (at 11 cm s^{-1}) from the tip of the syringe are pneumatically stripped and nebulized into charged microdroplets by $\text{N}_2(\text{g})$ flowing at a rate of $>250 \text{ m s}^{-1}$ through a coaxial sheath. Anions contained in the charged microdroplets are detected by online ESI mass spectrometry in the m/z 50–100 range. Anion detection was optimized by setting the drying gas temperature to 325°C and the capillary voltage to 3250 V. Fresh solutions were prepared with Milli-Q water ($18.2 \text{ M}\Omega \text{ cm}$ at 25°C) that had been sparged with $\text{N}_2(\text{g})$ for 8 h to remove dissolved O_2 (except as indicated) within 5 min prior to injection, in a glovebox at $< 1 \text{ ppm O}_2(\text{g})$. The pH of solutions was adjusted by adding $\text{NaOH}(\text{aq})$ or $\text{HCl}(\text{aq})$ and measured with a calibrated pH-meter. Throughout, reported pH values correspond to those measured in the bulk of solutions. A sodium bisulfite solution [40% (w/w), Sigma-Aldrich], hydrochloric acid [$>30\%$ (w/w), Sigma-Aldrich], sodium hydroxide ($\geq 99.0\%$, Sigma-Aldrich), ethylenediaminetetraacetic acid (EDTA, $> 99.0\%$, Sigma-Aldrich), and $48.75 \pm 2 \text{ ppm}$ of $\text{NO}_2(\text{g})$ in $\text{N}_2(\text{g})$ (Airgas) were used as received. The actual $\text{NO}_2(\text{g})$ concentration at the surface of the aqueous microjets is 10 times lower (5 ppm) because of dilution by the nebulizer gas.

3. RESULTS

3.1. HSO_3^- Mass Spectral Intensities on Aqueous Surfaces. HSO_3^- m/z 81 mass spectral signal intensities (I_{81} values, normalized to their maximum value, $I_{81,\text{max}}$) measured by o-ESI-MS at the gas–aqueous interface of 1 mM NaHSO_3 aqueous microjets as a function of bulk pH are shown as blue data points in Figure 2. The red trace corresponds to $[\text{HSO}_3^-]/$

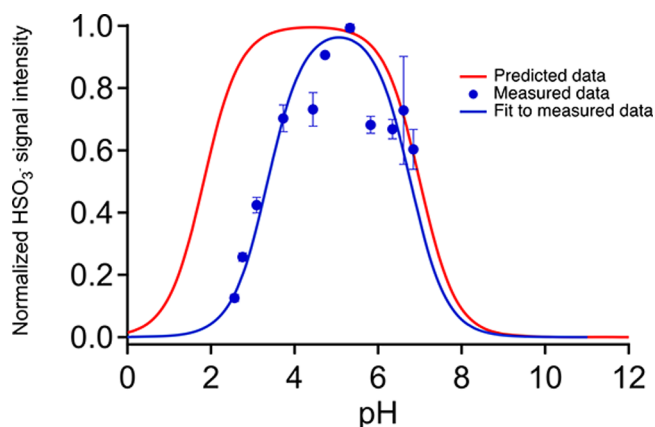


Figure 2. Normalized m/z 81 (HSO_3^-) signals measured by o-ESI-MS on the surface of 1 mM $\text{NaHSO}_3(\text{aq})$ microjets as a function of bulk pH (blue symbols and line). HSO_3^- mole fractions calculated from a $\text{p}K_{\text{a}1}$ ($\text{H}_2\text{O} \cdot \text{SO}_2 \rightleftharpoons \text{HSO}_3^- + \text{H}^+$) of 1.8 and a $\text{p}K_{\text{a}2}$ ($\text{HSO}_3^- \rightleftharpoons \text{SO}_3^{2-} + \text{H}^+$) of 7.2 in bulk water (red line).

$[\text{HSO}_3^-]_{\text{max}}$ values calculated from reported acidity constants in bulk water: $\text{p}K_{\text{a}1}$ ($\text{H}_2\text{O} \cdot \text{SO}_2 \rightleftharpoons \text{HSO}_3^- + \text{H}^+$) = 1.8, and $\text{p}K_{\text{a}2}$ ($\text{HSO}_3^- \rightleftharpoons \text{SO}_3^{2-} + \text{H}^+$) = 7.2. Experimental mass spectral data clearly display HSO_3^- deficits at $\text{pH} < 5$ relative to calculated values, which are due to losses of SO_2 to the gas phase. This is considered a feature particular to the $\text{HSO}_3^-/\text{SO}_2$ system because the titration curves of less volatile acids and bases

determined in this setup were in accordance with bulk pK_a values.^{58,65} The experimental HSO_3^- signal intensity versus pH data of Figure 2 provide the reference for analyzing the extent of S(IV) oxidation in the following sections.

3.2. $\text{NO}_2(\text{g})$ Reactions on Aqueous Electrolyte Surfaces. Mass spectra acquired before and during exposure of pH ~ 5 (1 mM HSO_3^- and 3 mM EDTA) aqueous microjets to 5 ppm of $\text{NO}_2(\text{g})$ for $\leq 50 \mu\text{s}$ are shown in Figure 3. The main feature is the appearance of a strong NO_3^- m/z 62

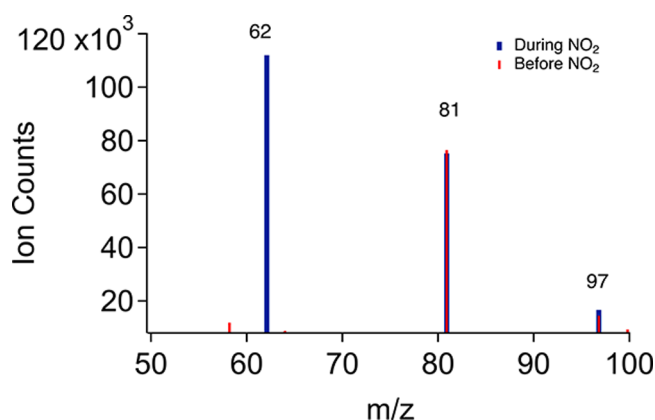


Figure 3. ESI mass spectra of the surface of aqueous 1 mM NaHSO_3 and 3 mM EDTA, pH ~ 5 microjets before and after exposure to 5 ppm of $\text{NO}_2(\text{g})$. Note the presence of minor HSO_4^- (m/z 97) impurities in the initial solutions.

signal, in contrast with the minimal variations displayed by both HSO_3^- m/z 81 and HSO_4^- m/z 97 signals upon exposure to $\text{NO}_2(\text{g})$. This outcome means that $\text{NO}_2(\text{g})$ molecules hitting the surface of pH ~ 5 HSO_3^- microjets mainly undergo fast (within $50 \mu\text{s}$) disproportionation, leaving barely any NO_2 for diffusing into the bulk liquid, and supposedly participate in reaction R0. The following section explores the effect of pH on the competition between reactions R0 and R1.

3.3. Oxidation of S(IV) on Aqueous Surfaces. The extent of $\text{HSO}_3^-(\text{aq})$ oxidation by $\text{NO}_2(\text{g})$, expressed by the ratio of $[\text{HSO}_3^-]/[\text{HSO}_4^-] \propto I_{81}/I_{97}$ signal intensities, as a function of pH is shown in Figure 4. I_{81} values correspond to measured I_{81} signals corrected for the depressing effect of the NO_3^- simultaneously produced via reaction R1 at the air–aqueous interface (see below).^{63,66} Figure 4 clearly shows that the extent of $\text{HSO}_3^-(\text{aq})$ oxidation via reaction R0 is minimal throughout, barely exceeding the experimental error in the pH 3–6 range that is relevant to HEs.

We quantified the fraction of $\text{NO}_2(\text{g})$ that oxidizes $\text{HSO}_3^-(\text{aq})$ at the air–aqueous interface as f_{R0} , defined by eq E1. In eq E1, Δ_{81}' is calculated from the decrease in the measured I_{81} signals, Δ_{81} , corrected for the NO_3^- depressing effect mentioned above, which is further multiplied by the ratio β (I_{62}/I_{82}) of the o-ESI mass spectra measured in 1 mM $\text{HSO}_3^-/1 \text{ mM } \text{NO}_3^-$ equimolar solutions at each pH to convert I_{81} decrements into equivalent $\Delta_{62} \text{ NO}_3^-$ changes.

$$f_{\text{R0}} = \frac{\Delta_{81}'}{\Delta_{81}' + \Delta_{62}} \quad (\text{E1})$$

We found that f_{R0} increases from $< 6\%$ within the pH range of 3.0–6.0 to 42% at pH 10.8. It also increases with acidity to 16% at pH 2.5 (Figure 5). This finding means that the anion-catalyzed hydrolytic disproportionation of $\text{NO}_2(\text{g})$ on aquated

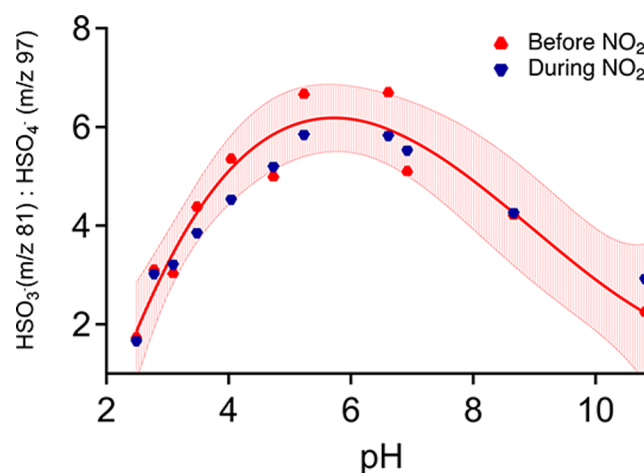


Figure 4. Red symbols, the red line, and the 95% confidence band correspond to the ratio of $\text{HSO}_3^-/\text{HSO}_4^-$ I_{81}/I_{97} signal intensities on the surface of 1 mM NaHSO_3 and 3 mM EDTA microjets in $\text{N}_2(\text{g})$ -sparged MQ water as a function of bulk pH. Blue symbols represent data after exposure to 5 ppm of $\text{NO}_2(\text{g})$ for $< 50 \mu\text{s}$.

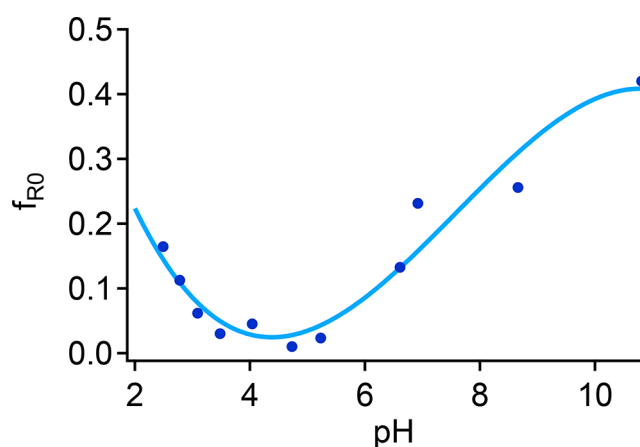


Figure 5. Fraction of $\text{NO}_2(\text{g})$ that contributes to S(IV) oxidation, f_{R0} (eq E1), as a function of pH.

aerosol surfaces (reaction R1) will outcompete reaction R0 throughout, particularly under atmospherically relevant acidic conditions.^{35,39,41,43,45,57} We have shown that most electrolytes increase the uptake coefficient of $\text{NO}_2(\text{g})$ from $\gamma < 1.0 \times 10^{-7}$ in pure water³⁷ to γ in the 10^{-3} – 10^{-4} range at air–aqueous electrolyte interfaces.^{35,39,41,45,57} The mechanism of enhancement involves trapping $\text{NO}_2(\text{g})$ by X^- as X-NO_2^- at the air–water interface, which can react further with $\text{NO}_2(\text{g})$.⁴⁵ This interfacial process is expected to dominate the fate of $\text{NO}_2(\text{g})$ during HEs due to the large surface-to-volume ratio of aerosol microdroplets. We have previously shown that the decay of $\text{NO}_2(\text{g})$ on aqueous aerosols via reaction R1 accounts for the similar $\sim 4 \text{ h}$ $\text{NO}_2(\text{g})$ decay half-lives measured by satellite sightings of urban plumes over world megacities ranging from Singapore to Moscow.⁴² We pointed out that if, as generally assumed, $\text{NO}_2(\text{g})$ were removed by gas phase OH radicals via the $\text{NO}_2(\text{g}) + \bullet\text{OH}(\text{g}) = \text{HNO}_3(\text{g})$ reaction, much longer decay half-lives would have been observed in winter and at high latitudes, given that “OH radicals follow the sun”.⁶⁷

Next, we performed experiments in which we analyzed, within 5 min via o-ESI-MS, freshly prepared HSO_3^- solutions in air-saturated water without added EDTA. We detected

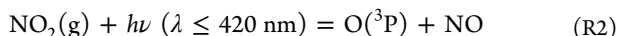
$\text{SO}_3^{\bullet-}$ m/z 80 signals whose intensities increase linearly with pH (Figure S3). The formation of $\text{SO}_3^{\bullet-}$ is ascribed to the autoxidation of HSO_3^- catalyzed by the omnipresent traces of transition metal ions in our solutions.⁶⁸ Whether this process makes a significant contribution to the oxidation of S(IV) under HE conditions is the subject of other studies.^{69,70} Additional experiments performed by exposing such HSO_3^- solutions (in air-saturated deionized water without added EDTA) to $\text{NO}_2(\text{g})$ (Figure S4) led to I_{81}/I_{97} ratios similar to those depicted in Figure 4 for $\text{NO}_2(\text{g})$, meaning that NO_2 makes negligible contributions to S(IV) autoxidation in our 50 μs time frames.

4. DISCUSSION

4.1. Indirect Role of $\text{NO}_2(\text{g})$ in the Oxidation of S(IV).

Our findings open up new perspectives on the mechanism of S(IV) oxidation by $\text{NO}_2(\text{g})$ during HEs. They underscore the fact that the stoichiometry of reaction R0 could not account for the formation of NO_3^- in HEs,^{32,33} because if $\text{NO}_2(\text{g})$ were the only available oxidant and were consumed in reaction R0, N(IV) O_2 could not be oxidized to N(V) O_3^- . Any valid mechanism should explain (1) how both S(IV) O_2 and N(IV) O_2 are oxidized to HS(VI) O_4^- and N(V) O_3^- and (2) how HONO is produced.

We analyzed the fate of $\text{NO}_2(\text{g})$ by considering its reactive uptake on the aerosol via reaction R1 and its photolysis by scattered solar radiation via reaction R2 under representative HE conditions.



Rate constants for the reactive uptake of $\text{NO}_2(\text{g})$, k_{R1} , were estimated with eq E2 from the kinetic theory of gases.

$$k_{\text{R1}} = \frac{1}{4} \gamma \nu_{\text{NO}_2} (S/V) \quad (\text{E2})$$

where ν_{NO_2} ($= 3.7 \times 10^2 \text{ m s}^{-1}$) is the mean thermal speed of $\text{NO}_2(\text{g})$ at 298 K, γ ($= 10^{-3}$ – 10^{-4}) is the estimated range of the reactive uptake coefficient of $\text{NO}_2(\text{g})$ on the surface of aqueous electrolyte solutions,⁴⁵ and S/V (in square micrometers per cubic meter) is the surface density of aerosols. Aerosols consist of submicrometer particles with S/V values of $\lesssim 2 \times 10^{-3} \text{ m}^{-1}$ during hazy days and values that are ~ 5 times smaller on clear days.³³ By assuming that $\gamma = 10^{-3}$ and $S/V = 2 \times 10^{-3}$ and $4 \times 10^{-4} \text{ m}^{-1}$, we estimate $k_{\text{R1}} \sim 2 \times 10^{-4} \text{ s}^{-1}$ and $k_{\text{R1}} \sim 4 \times 10^{-5} \text{ s}^{-1}$ on hazy and clear days, respectively.

The low $\text{O}_3(\text{g})$ concentrations measured during HEs indicate that the rate of photolysis of $\text{NO}_2(\text{g})$, which generates the $\text{O}(^3\text{P})$ atoms involved in $\text{O}_3(\text{g})$ formation [$\text{O}_2 + \text{O}(^3\text{P}) + \text{M} = \text{O}_3 + \text{M}$], is greatly reduced because of the severe attenuation of actinic sunlight during HEs. We estimated time- and space-averaged photolysis rate constants, k_{R2} , by using the National Center for Atmospheric Research Tropospheric Ultraviolet Visible (TUV) Radiation Model with environmental parameters within the ranges reported for aerosol optical properties and aerosol radiative forcing parameters (see Figure S3).^{24,25} Our estimates [$(k_{\text{R1}})_h/(k_{\text{R2}})_h \sim 0.5$ – 1.2 , and $(k_{\text{R1}})_c/(k_{\text{R2}})_c \sim 0.01$ – 0.1 (h, hazy; c, clear)] are semiquantitatively consistent with the premise outlined above and illustrate how the competition between reactions R1 and R2 shifts from hazy to clear days (see Figure S3). However, we suggest that TUV calculations on the competition between reactions R1 and R2 provide a lower bound to $(k_{\text{R1}})_h/(k_{\text{R2}})_h$ because $\text{NO}_2(\text{g})$ is not expected to be uniformly distributed but to accumulate in the

lower layers of dense hazes, where there is minimal actinic radiation and photochemical activity.

Together, our estimates and experimental results support the view that the leading pathway for $\text{NO}_2(\text{g})$ during HEs is its heterogeneous disproportionation into $\text{NO}_3^- + \text{HONO}/\text{NO}_2^- + \text{H}^+$ via reaction R1. Note that reaction R1 is autocatalytic because it ultimately contributes to the increases in the mass and S/V of the aerosols on which it takes place. The rapid development of HEs is in fact consistent with such an autocatalytic process. The fact that relative humidity increments are tracked by increased particle number concentrations and surface area density S/V (square micrometers per cubic meter) of $\text{PM}_{2.5}$, particularly in the accumulation mode, also supports the notion that the liquid particles present under such conditions grow from autocatalytic heterogeneous processes.⁷¹

Reaction R1 accounts for the direct formation of NO_3^- and HONO and would also account for the formation of HSO_4^- if the $\text{HONO}/\text{NO}_2^-$ produced in reaction R1 could ultimately oxidize S(IV) (see Figure 6).^{72–78} As a result, because $f_{\text{R0}} \leq 0.1$

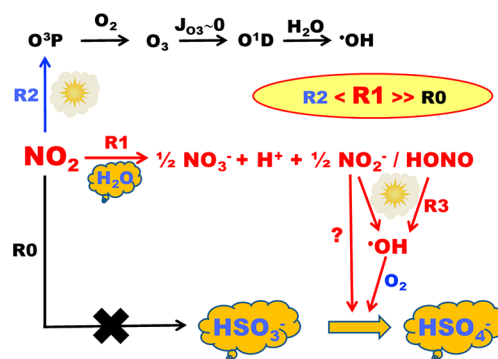


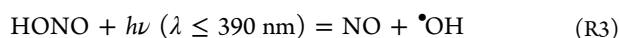
Figure 6. NO_2 reactions and their impact on S(IV) oxidation during haze-aerosol events.

in the realistic pH range of 3–6, i.e., nearly independent of pH (Figure 5), the acidity/basicity of HE aerosols could be a parameter relevant to S(IV) oxidation rates if subsequent processes were to depend on aerosol pH.^{79,80} Therefore, our conclusion that the main pathway for $\text{NO}_2(\text{g})$ in HEs is reaction R1 will stand regardless of future assessments of aerosol pH. The parameters that may affect a heterogeneous process such as reaction R1 could be a combination of aerosol S/V and aerosol liquid water content, both of which depend on relative humidity.^{79,80} We suggest that the apparent dependence of sulfate formation rates on ammonia neutralization of aerosol particles may be the result of cross-correlations between aerosol acidity and the actual causal parameters. In this connection, we point out that the enhancing “ammonium” effect on the rates of oxidation of $\text{SO}_2(\text{g})$ by $\text{NO}_2(\text{g})$ on aqueous solutions might be due to the presence of HSO_4^- anions that capture $\text{NO}_2(\text{g})$ at the aerial interface, as explained above.³³ It is also important to realize that the results of Clifton et al.,⁵⁴ on the homogeneous reaction rates of $\text{HSO}_3^-(\text{aq})$ with the $\text{NO}_2(\text{aq})$ produced in situ within the bulk solution via $\text{NO}_2^-(\text{aq})$ radiolysis, cannot be applied to the heterogeneous processes being considered here, which involve $\text{NO}_2(\text{g})$ as a reactant.

4.2. HONO and NO_2^- as S(IV) Oxidizers. Aqueous HONO and NO_2^- can oxidize HSO_3^- to HSO_4^- in the pH range of 3–5 of HE aerosols. Reductions of HONO and NO_2^- to NO [$E^\circ(\text{HONO} + \text{H}^+ + \text{e} = \text{NO} + \text{H}_2\text{O}) = 0.75 \text{ V}$, and

$E^\circ(\text{NO}_2^- + 2\text{H}^+ + \text{e} = \text{NO} + \text{H}_2\text{O}) = 1.08\text{ V}$] or to N_2O [$E^\circ(2\text{HONO} + 4\text{H}^+ + 4\text{e} = \text{N}_2\text{O} + 3\text{H}_2\text{O}) = 1.06\text{ V}$, and $E^\circ(2\text{NO}_2^- + 6\text{H}^+ + 4\text{e} = \text{N}_2\text{O} + 3\text{H}_2\text{O}) = 1.04\text{ V}$] could also drive the thermal (dark) oxidation of HSO_3^- to HSO_4^- [$E^\circ(\text{HSO}_3^- + \text{H}_2\text{O} = \text{HSO}_4^- + 2\text{H}^+ + 2\text{e}) = 0.15\text{ V}$] at pH 4, depending on the concentrations of the reactants and products. The oxidation of HSO_3^- by HONO and NO_2^- , however, is complex and proceeds slowly via a free radical mechanism through S- and N-containing intermediates.^{81–83} In the presence of air, O_2 could participate in this process (see below).⁸⁴

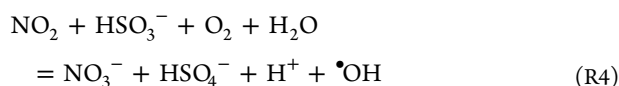
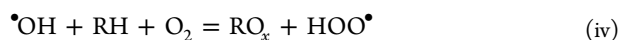
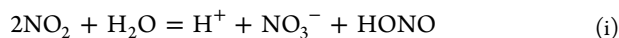
HONO and NO_2^- , however, could also produce $\bullet\text{OH}$ radicals at significant rates via photolysis, even in optically thick hazes. Estimates made by using the TUV radiation model show that the photolysis of HONO (from reaction R1) (reaction R3)



is a stronger and more direct source of OH radicals than the photolysis of $\text{O}_3(\text{g})$ even at the $[\text{HONO}] = 0.01[\text{O}_3]$ relative abundances measured during HEs.²⁸ This is due to the much larger solar irradiance in the $\lambda \leq 390\text{ nm}$ actinic range compared with that in the $\lambda \leq 310\text{ nm}$ range where $\text{O}_3(\text{g})$ dissociates into $\text{O}(^1\text{D})$: $\text{O}_3 + h\nu = \text{O}_2 + \text{O}(^1\text{D})$. Our estimates furthermore suggest that rates of production of OH radicals from HONO during hazy and clear days could be comparable, because faster production and slower HONO photolysis under hazy conditions are offset by slower production and faster HONO photolysis during clear days (Table S1 and Figure S3). We therefore suggest that the production of $\bullet\text{OH}$ via HONO photolysis during HEs could play a significant role in sulfate formation.⁸⁵

However, because $\text{pK}_a(\text{HONO}) \sim 3$,⁸⁶ some $\text{N}(\text{III})$ will be also present as $\text{NO}_2^-(\text{aq})$ in the pH range of 3–5. The photolysis of $\text{NO}_2^-(\text{aq})$ also produces $\bullet\text{OH}$, but at rates much lower than that of $\text{HONO}(\text{g})$, both because of the integrated molar absorptivity of $\text{NO}_2^- \sim 15$ times smaller than that of HONO and because the quantum yield of $\bullet\text{OH}$ production [$\phi(\text{NO}_2^-(\text{aq}) \rightarrow \bullet\text{OH}) \sim 0.04$] is 25 times smaller than [$\phi(\text{HONO}(\text{g}) \rightarrow \bullet\text{OH}) = 1.0$],⁸⁷ due to solvent cage effects. Because the reaction of HSO_3^- with $\bullet\text{OH}$ from the photolysis of HONO and NO_2^- and, presumably, also the thermal (dark) reaction between NO_2^- and HSO_3^- both proceed via free radicals, O_2 is expected to participate in these processes and lead to chain oxidation mechanisms.

The preceding considerations lead us to suggest that $\text{NO}_2(\text{g})$ oxidizes $\text{S}(\text{IV})$ indirectly via the free radical mechanism shown below, rather than directly via reaction R0.



Steps iii and iv as written are not elementary reactions but may proceed via $\text{R-OO}\bullet$ and $\text{H-OO}\bullet$ intermediates. The overall stoichiometry of reaction R4 indicates that NO_2 and HSO_3^-

produce equimolar amounts of NO_3^- and HSO_4^- , plus an $\bullet\text{OH}$ radical that can oxidize HSO_3^- as well as other species, RH. If $\bullet\text{OH}$ reacts with organics RH instead of HSO_3^- , the $\text{HOO}\bullet$ produced in reaction iv will regenerate $\bullet\text{OH}$ via reaction v as long as there is sufficient NO remaining. Therefore, although NO_2 may not be the direct oxidizer of SO_2 during HEs, the oxidative capacity of the atmosphere will still be determined by the initial NO_2 concentrations. As noted above, a related thermal chain oxidation mechanism may be initiated by $\text{NO}_2^- + \text{HSO}_3^-$.

4.3. Atmospheric Implications. This work focused on the particular heterogeneous chemistry that takes place during the severe wintertime HEs observed in major Chinese cities. We show that the rapid formation of sulfate aerosols during HEs cannot be due to the direct reaction of HSO_3^- with NO_2 . Instead, $\text{S}(\text{IV})$ could be oxidized indirectly by NO_2 via the HONO and NO_2^- produced in its fast hydrolytic disproportionation [$2\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) = \text{H}^+ + \text{NO}_3^-(\text{aq}) + \text{HONO}$ (reaction R1)], a process that is catalyzed by anions at air–aqueous aerosol interfaces. The proposed mechanism naturally accounts for the formation of NO_3^- in the aerosol phase and the significant concentrations of HONO in the gas phase reported by all field studies. It is expected to be favored at the high relative humidity and high S/V aerosol densities that are prevalent during HEs. We show that the photolysis of HONO and NO_2^- can be a significant source of OH radicals even under hazy conditions and point out that the thermal reaction between NO_2^- and HSO_3^- also proceeds via free radicals,⁸² both of which can initiate oxidative chains in the presence of O_2 . These findings suggest that future field campaigns should focus on OH radical measurements during winter HEs, an issue that has not been properly addressed in the literature. The main insight is that the relevant parameter for a heterogeneous process such as reaction R1 is the surface density S/V of aerosol hazes, which is related to the particle size distribution, and the fluidity of the interfacial layers, rather than to the acidity of aerosol particles. The apparent dependence of sulfate formation rates on ammonia neutralization of aerosol particles may be the result of cross correlations between aerosol acidity and the actual causal parameters. Whereas it remains true that the oxidation of SO_2 during HEs is driven by primary NO_2 emissions, our work, by clarifying the actual mechanism by which this process is initiated, could guide future research efforts and help optimize future air pollution control strategies.

In summary, the direct reaction of $\text{NO}_2(\text{g})$ with HSO_3^- on the surface of aqueous aerosols is insignificant in the pH range of 3–6. On the surface of aqueous electrolyte solutions, such as those of HE aerosols, $\text{NO}_2(\text{g})$ is mainly converted to NO_3^- and $\text{HONO}/\text{NO}_2^-$ via hydrolytic disproportionation. The implication is that the oxidation of HSO_3^- during HEs could be mostly due to thermal (dark)⁸⁸ and/or photochemical reactions initiated by $\text{HONO}/\text{NO}_2^-$. The acidity/basicity of HE aerosols could be a parameter relevant to $\text{S}(\text{IV})$ oxidation rates only if such processes were to depend on aerosol pH.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b05222.

Figures S1–S4, explanatory note (section S0), TUV calculations (section S1), estimated rates of HONO and OH production (section S2), and Table S1 (PDF)

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