Communication

Triplet-Excited Dissolved Organic Matter Efficiently Promoted Atmospheric Sulfate Production: Kinetics and Mechanisms

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Abstract: Photochemical generation is an important pathway for atmospheric sulfate formation. However, the roles of atmospheric co-existing photosensitive dissolved organic matter (DOM) in sulfate formation are still unclear. The experimental results in this work provide evidence that atmospheric photosensitizers produce active intermediates to oxidize S(IV) into S(VI) under illumination. Quenching experiments of eight photosensitive model compounds (PS) demonstrate that their triplet-excited states \( (3\text{PS}^*) \) dominate sulfate formation for the photosensitizing pathway with a contribution of over 90%, and \( ^1\text{O}_2 \) plays an important role in sulfate formation. The results using humic acid (HA) and water-soluble organic carbon in vehicle exhaust particles (WSOC) as representatives of atmospheric photosensitizers further verify that triplet-excited DOM \( (3\text{DOM}^*) \) is the main reactive species for sulfate formation, which is consistent with the results of PS. Our findings provide new insights into the photochemical formation pathways of atmospheric sulfate.

Keywords: atmospheric oxidants; atmospheric sulfate; water-soluble organic carbon; aqueous-phase oxidation; triplet-excited states; photosensitization

1. Introduction

Globally, atmospheric aerosol nucleation contributes nearly half of all cloud condensation nuclei, thus having a significant impact on global climate change [1]. Under certain conditions, nucleated aerosol particles will grow into haze [2,3]. Sulfate is one of the main components in fine particulate aerosol samples during haze events. Oxidation of SO\(_2\) in the atmosphere produces sulfate aerosol particles, which can lead to air quality, climate, human and ecosystem health problems [4].

The formation of sulfate particles depends on several factors, including solar radiation, the background aerosol and volatile organic compound (VOC) concentrations, the availability of NH\(_3\), the temperature and the humidity [5]. As a precursor of sulfate, SO\(_2\) is extremely soluble in atmospheric water and forms SO\(_2\)-H\(_2\)O, HSO\(_3^–\) and SO\(_3^{2–}\), which increase the concentration of sulfate through the liquid phase oxidation pathway of SO\(_2\) in the atmosphere [6]. Some monitoring data have shown SO\(_3^{2–}\) concentrations in cloud droplets ranging from 17.3 to 211 \( \mu \text{M} \) [7], but some studies have also claimed that the average SO\(_4^{2–}\) concentrations in clouds, fog and rain observed in Southern California range from 9.4 to 475 mM [8]. The significant enhancement in sulfate concentrations observed in haze events since the 2013 Beijing haze incident has led to a growing interest and demand for studying sulfate formation mechanisms among scholars. Traditionally, sulfate formation mechanisms primarily include gas phase oxidation of SO\(_2\) by \( \cdot \text{OH} \) and the aqueous oxidation of S(IV) by H\(_2\)O\(_2\), O\(_3\), organic peroxides and O\(_2\) catalyzed by transition metal ions (TMs), such as Fe(III) and Mn(II), in cloud or fog water droplets [9]. However, the mechanisms behind sulfate formation remain poorly described, and its yield is also...
underestimated [10], indicating that many important pathways related to atmospheric sulfate formation have not been fully revealed.

In recent years, the triplet-excited state of dissolved organic matter (DOM*) in atmospheric liquid water (cloud droplets, mist droplets or aerosol water) has attracted a lot of attention as a special oxidant involved in liquid-phase photochemical reactions [11,12]. Xue et al. [13] and Wang et al. [14] suggested that atmospheric microaqueous reactions may contribute significantly to sulfate production. Photochemistry has been proposed as an important chemical trigger in tropospheric particles, and it has been emphasized that several photochemical mechanisms of sulfate production mainly occur in the liquid phase. Atmospheric brown carbon, mainly derived from forest fires, biomass burning and biorelease, was shown to act as a photosensitizer and produce a variety of reactive intermediates to modify the oxidation capacity and highlighted the positive dependence of sulfate production on relative humidity (RH) [15]. Wang et al. found that the triplet-excited state could induce the conversion of SO$_2$·H$_2$O and HSO$_3^-$ to sulfate through energy transfer, electron transfer or hydrogen atom extraction through liquid-phase reactions, suggesting that the photosensitization pathway may make a significant contribution to sulfate formation [16]. DOM* in natural water bodies promotes the photochemical oxidative degradation of pollutants in an aqueous environment [17,18]. Similarly, the atmospheric microaqueous phase can receive stronger sunlight, and the role played by atmospheric photosensitizers is gradually being emphasized. In fact, the discussion of the liquid-phase photosensitization pathway of sulfate in the atmosphere is still very limited. Although its important contribution has been recognized, the specific photosensitization mechanism is uncertain, and the atmospherically relevant affecting factors have not been investigated.

As the main driver of the sulfate photosensitization pathway, the types of photosensitizers in the atmosphere are closely related to local agricultural and industrial conditions. Many substances in the atmosphere can absorb light to produce DOM*, such as phenyl ketones [19], aromatic aldehydes [20] and benzoquinones [21]. These photosensitizers can produce certain photosensitizing effects in the atmosphere, which may impact sulfate formation. However, the effects of different photosensitizers on sulfate formation remained unclear.

This study examines the effects of photosensitizer model compounds (PS) and real environmental sample agents on sulfate formation under irradiated conditions. Active substance quenching experiments are carried out using eight types of PS, including phenyl ketones, benzaldehyde and benzoquinones, and the active intermediates in the reaction system were determined. The effect of atmospheric co-existing ions on the sulfate photosensitive formation pathway is studied by adding different concentrations of Cl$^-$ and NO$_3^-$ . In addition, the mechanism of photosensitized reactions of S(IV) with real environmental substances was explored based on the photochemical reactions of humic acid (HA) and water-soluble organic carbon in vehicle exhaust particles (WSOC) as agents of real environmental samples. This work reveals a potentially important force for atmospheric photosensitizers to drive haze events, particularly for regions with high vehicle exhaust emissions.

2. Materials and Methods

2.1. Chemicals

All chemicals were used as purchased: 4-benzoylbenzoic acid (CBBP, $C_{14}H_{10}O_3$, 99%), 3′-methoxyacetophenone (3-MAP, $C_9H_{10}O_2$, 99%), 4′-methoxyacetophenone (4-MAP, $C_9H_{10}O_2$, 98%), benzophenone (BP, $C_{13}H_{10}O$, 95%), xanthenone (Xan, $C_{13}H_{10}O_2$, 98.8%), 1,4-naphthoquinone (NP, $C_{10}H_8O_2$, 99%), p-benzoquinone (PBQ, $C_6H_4O_2$, 99%) and tetrahydroluran (THF, $C_4H_8O$, 99.5%) were purchased from Aladdin Inc. (Shanghai, China), 3,4-dimethoxybenzaldehyde (DMB, $C_9H_{10}O_3$, 98%) and sorbic acid (SA, $C_6H_8O_2$, 99%) were purchased from Rhawn (Shanghai, China), humic acid (HA, Cat no. 449752) was purchased from Sigma-Aldrich (Shanghai, China), tert-butanol (TB, $C_4H_{10}O$, 99.5%) was purchased from Macklin (Shanghai, China), and other reagents were purchased from Sinopharm
Chemical Reagent Co., Ltd. (Shanghai, China). In addition, all solutions were prepared using ultrapure water (18.2 MΩ·cm). We configured these hazardous chemical solutions in a fume hood and wore gas masks.

2.2. Environmental Sample Collection and Extraction

Particulate matter from vehicle exhaust was collected from the auto vent pipes of many vehicles traveling in Kunming, Yunnan Province. The collected particulate matter samples were placed in brown glass bottles, mixed well and stored away from light to dry. Then, 0.5 g of pellets were placed in a conical flask with 250 mL of ultrapure water and mixed by stirring and shaking in a constant-temperature shaking incubator at 25 °C for 24 h. The solid-liquid mixture was removed, and the suspension was filtered through a 0.45 µm polyethersulfone (PES) membrane before the filtrate (as WSOC stock solution) was collected and stored in a brown polyethylene bottle at 4 °C under refrigeration and protected from light. The dissolved organic carbon (DOC) concentrations of WSOC stock solution and HA (commercial chemical, in Section 2.3) were determined by TOC using a CD-800S total organic carbon analyzer from Hangzhou Qikun Technology Co. (Hangzhou, China).

2.3. Photochemical Experiments

An OCRS-PX32T merry-go-round photochemical reactor (Kaifeng Hongxing Technology Co., Ltd., of Henan province of China) was employed, with quartz tubes to contain the investigated solutions. A water-refrigerated, 500 W high-pressure mercury lamp surrounded by 290 nm cutoff filters was used as the light source. The irradiation spectral of the light source were reported in our previous study [22], and the main irradiation wavelengths consist of 297, 302, 313, 334, 365 and 366 nm. The average light intensity at the center of the solution was 0.23 mW/m² [22].

The initial concentration of NaHSO₃ in the photochemical experiment was 1 mM. CBBP, Xan, BP, 4-MAP, 3-MAP, DMB, NP and PBQ (80 µM) as PS were employed to investigate the reactivity between S(IV) and the model photosensitizers’ triplet-excited state (³PS*). HA and WSOC were used as DOM representatives, and the initial concentration of DOM was set at 10 mg C/L, falling within the typical range in the natural atmosphere [6]. H₂SO₄ and NaOH were used to keep the pH of the investigated solutions to a meteorological water value of six [7,23,24]. Pure water control experiments were performed under the same conditions to see if S(IV) underwent oxidation other than the photosensitive transformation. Aliquots were removed at the same selected intervals for further analysis. Each set of experiments was repeated three times.

To clarify the role of the reactive substances (RSs), quenching experiments were performed by adding 5 mM sorbic acid (SA) to quench the ³DOM* [25], 5 mM tert-butanol (TB) to quench the ·OH [26] or 5 mM tetrahydrofuran (THF) to quench the ¹O₂ [27]. Aliquots were removed at selected intervals for further analysis.

2.4. Analytic Methods

The SO₄²⁻ and SO₃²⁻ concentrations in quartz cuvettes in a photochemical reactor were analyzed using an ion chromatograph (Shunyu Hengping IC1800, Shanghai Shunyu Hengping Instrument Co., LTD., Shanghai, China). The system was equipped with an AS256 anion analysis column and an AES-100 anion suppressor. The reacted samples were sent to the ion chromatograph (IC) for SO₄²⁻ and SO₃²⁻ detection after the addition of 0.1% formaldehyde (HCHO) to protect the S(IV). The anions were determined at a flow rate of 1 mL/min using an eluent of 2.0 mM Na₂CO₃ and 8.0 mM NaHCO₃. In addition, both the Na₂CO₃ and NaHCO₃ used in the IC eluents have chromatographic-grade purity.
2.5. Kinetic Analysis

The observed transformation rate constants for the conversion of S(IV) could be expressed as in Equation (1):
\[
\ln \left( \frac{C_t}{C_0} \right) = -k_{obs}t,
\]
where \( k_{obs} \) (s\(^{-1}\)) is the pseudo-first-order rate constant of the S(IV), \( t \) (s) is the reaction time, \( C_t \) (M) is the concentration of S(IV) at \( t \) and \( C_0 \) (M) is the initial concentration of S(IV).

3. Results and Discussion

3.1. Transformation Kinetics of S(IV) with Triplet Photosensitizers

As shown in Figure 1, a significant increase in S(VI) was observed in the presence of photosensitive substances. The difference between the pure water and PS irradiated conditions suggests that the photosensitized substances promoted S(VI) production under illumination. The selected PS were triplet-excited precursors [19–21], which indicates that the increase in S(VI) could be attributed to the reactions between \(^3\)PS* and S(IV). It has been reported that \(^3\)PS* can also generate a variety of reactive oxidizing species (ROS) in the system through energy transfer or electron transfer, including \(^1\)O\(_2\), \( \cdot \)OH, \( \cdot \)HO\(_2\), \( \cdot \)O\(_2\)\(^-\) and H\(_2\)O\(_2\) [28,29], which may affect the transformation of S(IV). For this reason, the roles of \(^3\)PS* and ROS in the transformation of S(IV) to S(VI) need to be further explored.

![Figure 1](image-url). Comparison of observed sulfate concentration \((c(SO_4^{2-}))\) in different PS solutions \((PS = 80 \mu M, S(IV) = 1 mM and pH = 6)\).

3.2. Roles of Reactive Intermediates in Sulfate Production by Photosensitizers

Quenching experiments were conducted to study the photosensitive active intermediates among eight types of PS (Figure 2) and to explore the mechanism of the liquid-phase photosensitive pathway of S(IV).
Figure 2. Observed first-order photodegradation rate constants ($k_{\text{obs}}$) of S(IV) in different PS systems ($S(\text{IV}) = 1 \text{ mM}, PS = 80 \mu\text{M}, TB = 5 \text{ mM}, THF = 5 \text{ mM}, SA = 5 \text{ mM}, pH = 6, \text{ and radiation time} = 30 \text{ min}$). The error bars represent each sample’s standard deviation.

In the presence of CBBP, Xan, BP, 4-MAP, 3-MAP, DMB, PBQ or NP, the $k_{\text{obs}}$ values decreased by 15.5%, 20.6%, 6.5%, 9.1%, 1.96%, 19.6%, 5.9% or 7.7% with the addition of TB as a quencher of $^1\text{O}_2$. This observation indicates that PS can convert S(IV) through the photosensitized production of $^1\text{OH}$. Although $^1\text{OH}$ controls the natural atmospheric oxidation capacity under most atmospheric conditions [30,31], and the gas-phase pathway of sulfate aerosol production is mainly through the reaction of SO$_2$ with $^1\text{OH}$ [32], our work suggests that $^1\text{OH}$ plays a minor role in the indirect photochemical conversion of S(IV).

When THF was added as an $^1\text{O}_2$ quencher, the $k_{\text{obs}}$ value decreased by 20–60%. It was observed in PBQ that $^1\text{O}_2$ quenching resulted in a decrease of about 60% in $k_{\text{obs}}$, which was the largest decrease among the eight types of PS. The $k_{\text{obs}}$ of CBBP and 3-MAP decreased the least (about 20%), but overall, the effect of $^1\text{O}_2$ was significantly greater than the contribution of $^1\text{OH}$. This observation indicates that $^1\text{O}_2$ plays a nonnegligible role, and the contribution of several PS to $^1\text{O}_2$ is various, which is attributed to the difference in the energy transfer ability of $^3\text{PS}^*$ [33].

With the addition of SA as a $^3\text{PS}^*$ quencher, $k_{\text{obs}}$ decreased by more than 95% in all systems. As SA is a well-known triplet-excited state quencher, $^3\text{PS}^*$ is inferred to be predominant in inducing indirect photoconversion of S(IV). Wang et al. [16] also indicated that atmospheric $^3\text{DOM}^*$ played a main role in the photoconversion of S(IV). The addition of SA almost completely inhibits $k_{\text{obs}}$, and therefore we inferred that the $^1\text{OH}$ and $^1\text{O}_2$ in the system were derived from the electron transfer and energy transfer of $^3\text{PS}^*$, which confirms the role of $^3\text{PS}^*$.

It has been reported that $^3\text{PS}^*$ has a strong oxidation potential (reduction potential of 1.4–1.9 eV [34]) and high energy (250 kJ/mol on average [35]), and thus it can directly degrade pollutants through oxidation or energy transfer. The difference of $k_{\text{obs}}$ corresponding to various PS is mainly attributed to different kinds of $^3\text{PS}^*$ redox potential [7,36–38] and the sensitivity of S(IV) to oxidants ($E_0 = −0.93 \text{ V}$), which may also be affected by the functional groups in PS.
3.3. Atmospheric Co-Existing Ions Influence Sulfate Photosensitization

The co-existing constituents (e.g., Cl\(^{-}\) and NO\(_3\)\(^{-}\)) in atmospheric waters may affect the transformation of S(IV) because of their importance in photochemical reactions [39–41]. Therefore, the effects of Cl\(^{-}\) and NO\(_3\)\(^{-}\) on S(IV) transformation were investigated (Figure 3).

As shown in Figure 3, the changes in \(k_{\text{obs}}\) for BP, DMB and NP were less than 6.8% when the concentration of Cl\(^{-}\) was less than 1 mM, indicating that the low concentration of Cl\(^{-}\) had little effect on S(VI) generation. In contrast, when the concentration of Cl\(^{-}\) was increased to 10 mM, the \(k_{\text{obs}}\) of BP, DMB and NP increased by 13.1%, rose by 30.8% and decreased by 2.6%, respectively, indicating that there were differences in the effects of high concentrations of Cl\(^{-}\) on the different types of PS. Parker and Mitch reported that \(^3\)DOM\(^*\) contributes to the formation of RHS, which in turn affects the oxidation of certain added organic compounds, and using a range of free radical quenchers, they found a strong linear relationship between \(^3\)DOM\(^*\) and RHS [26]. Therefore, we inferred that Cl\(^{-}\) may accelerate the oxidation of S(IV) by generating chlorine radicals.

Nitrate is a prevalent component of atmospheric aerosol particles [42]. Nitrate’s contribution was larger in a coarse fraction compared with PM\(_{2.5}\) instead of sulfate. Actually, there is a balance between nitrate and sulfate that depends on their concentrations of ammonium and on the meteorological conditions, as ammonium nitrate is relatively thermally unstable [43]. Multiphase photochemical oxidation of SO\(_2\) via photolysis of nitrate particles can make an important contribution to the formation of aerosol sulfate [44]. Therefore, it is of great importance to elaborate upon the effect of different concentrations of NO\(_3\)\(^{-}\) on sulfate in the presence of photosensitizers for us to investigate the specific mechanism. With the difference in \(k_{\text{obs}}\) between NO\(_3\)\(^{-}\) and Cl\(^{-}\) at the same ion concentration (Figure 3), we speculated that S(IV) oxidation was more affected by NO\(_3\)\(^{-}\) than Cl\(^{-}\). Compared with a <0.5 mM ion concentration, the same concentration of NO\(_3\)\(^{-}\) resulted in increases in \(k_{\text{obs}}\) all greater than 10%. Obviously, the addition of NO\(_3\)\(^{-}\) clearly had a stronger impact. In fact, there was an overall upward trend in \(k_{\text{obs}}\) after the addition of NO\(_3\)\(^{-}\). When 10 mM of NO\(_3\)\(^{-}\) was added, \(k_{\text{obs}}\) increased by 29.8%, 20.9% and 17.2% for BP, DMB and NP, re-
respectively. As a result, we suggest that the addition of $\text{NO}_3^-$ had a dramatic effect on $k_{\text{obs}}$. $\text{NO}_3^-$ is inherently photochemically active in the photochemical range (i.e., $\lambda > 290$ nm) and can photolyze to produce highly reactive substances such as $\text{NO}_2$, $\cdot\text{OH}$ and N(III) ($\text{NO}_2^-$ or HNO$_3$) [45], all of which have an oxidizing effect on S(IV). It can be inferred that in our work, it is the effect of the photolysis of $\text{NO}_3^-$ superimposed on the excited triplet state, rather than the conversion of other reactive substances caused by the excited triplet state as a precursor.

3.4. Sulfate Formation Promoted by DOM under Irradiation

Several pathways have been proposed to explain the sources of humic substances, including direct emissions from terrestrial or aquatic sources and biomass or fossil fuel combustion, as well as secondary production from the oxidative oligomerization of small organic molecules through atmospheric chemistry [46–48]. WSOC and HA were used as representatives of atmospheric DOM to explore the photosensitive conversion of S(IV).

In the pure water control, no significant S(VI) production was observed, while the $\ln(C_t/C_0)$ linear regression against time ($t$) indicated that photoconversion of S(IV) followed pseudo-first-order kinetics ($R^2 > 0.95$). The $k_{\text{obs}}$ values observed in pure water were $(0.11 \pm 0.08) \times 10^{-4}$ s$^{-1}$, and for HA and WSOC, the $k_{\text{obs}}$ values were $(1.05 \pm 0.09) \times 10^{-4}$ s$^{-1}$ and $(1.18 \pm 0.02) \times 10^{-4}$ s$^{-1}$, respectively, as shown in Figure 4. Thus, the photogeneration rate of S(VI) in solutions containing DOM was much higher than in pure water, indicating that DOM is an effective photosensitizer for the photoconversion of S(IV).

![Figure 4](image_url)

**Figure 4.** Comparison of observed first-order photoconversion rate constants ($k_{\text{obs}}$) of S(IV) in different DOM solutions (S(IV) = 1 mM, DOM = 10 mg C/L, TB = 5 mM, THF = 5 mM, SA = 5 mM and pH = 6). The error bars represent each sample’s standard deviation.

In the WSOC quenching experiments, the addition of TB, THF and SA resulted in a reduction in $k_{\text{obs}}$ of 15.5%, 50.3% and 92.1%, respectively. In the HA quenching experiments, the addition of THF and SA resulted in a $k_{\text{obs}}$ reduction of 39.1% and 92.1%, respectively. This achieved a high degree of agreement with the results of our quenching experiments for the photosensitizer model compounds. Significantly, in the quenching experiments of HA with $\cdot\text{OH}$, we found that the $k_{\text{obs}}$ was $(1.40 \pm 0.04) \times 10^{-4}$ s$^{-1}$ after the addition of TB, which was 33.7% expanded compared with the $k_{\text{obs}}$ without quenching, which
seems to be different from the results of our previous work. It has been suggested that alcohols as scavengers may have produced substances such as H$_2$O$_2$ during the scavenging process, leading to a wrong estimation of the ·OH concentration [49], which together with the complex composition of HA increased the possibility of H$_2$O$_2$ generation, resulting in higher $k_{\text{obs}}$ values after quenching than without the quencher instead.

### 4. Conclusions

In this work, we derived a rational pathway for the liquid-phase photosensitive oxidation of S(IV) and demonstrated that $^3$DOM$^*$ dominates the generation of S(VI). In this process, $^3$DOM$^*$ can directly convert S(IV) to S(VI), which is its main mechanism. Moreover, $^3$DOM$^*$ can also generate $^1$O$_2$ through energy transfer, which indirectly leads to S(IV) conversion, and this can even account for 50% of the conversion. Furthermore, $^3$DOM$^*$ is also capable of indirectly oxidizing S(IV) via electron transfer by generating very little ·OH. Previous studies [21] have documented that the concentration of triplets in typical fog water is much higher than the ·OH concentration, making the triplet state the main photooxidant.

To our knowledge, the liquid-phase photo-oxidation pathway for SO$_2$ has been explored to a very limited extent. In this work, we propose that an alternative pathway for sulfate aerosol generation is the photosensitive conversion of DOM in the atmospheric microaqueous phase, which as a new finding for rapid sulfate formation in the atmosphere can be considered an effective driver of haze events. More importantly, we demonstrate that the atmospheric DOM acts as a potential generator of ·OH, $^1$O$_2$ and $^3$DOM$^*$ in the troposphere under solar illumination. Therefore, more detailed studies are needed to understand the homogeneous and non-homogeneous photochemistry associated with atmospheric DOM.

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