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Key Points:

- Naphthalene-derived secondary organic aerosol (SOA) contains oxygenated aromatic compounds with photosensitizing properties
- Photosensitized oxidation of d-limonene and β-pinene by naphthalene-derived SOA results in particle growth
- Sulfate is formed through both dark and photosensitized chemical reactions between naphthalenederived SOA and SO₂

Supporting Information:

Supporting Information may be found in the online version of this article.

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Naphthalene-Derived Secondary Organic Aerosols Interfacial Photosensitizing Properties

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Abstract We investigated the photosensitizing properties of secondary organic aerosol (SOA) formed during the hydroxyl radical (OH) initiated oxidation of naphthalene. This SOA was injected into an aerosol flow tube and exposed to UV radiation and gaseous volatile organic compounds or sulfur dioxide (SO₂). The aerosol particles were observed to grow in size by photosensitized uptake of d-limonene and β -pinene. In the presence of SO₂, a photosensitized production (0.2–0.3 µg m⁻³ h⁻¹) of sulfate was observed at all relative humidity (RH) levels. Some sulfate also formed on particles in the dark, probably due to the presence of organic peroxides. The dark and photochemical pathways exhibited different trends with RH, unraveling different contributions from bulk and surface chemistry. As naphthalene and other polycyclic aromatics are important SOA precursors in the urban and suburban areas, these dark and photosensitized reactions are likely to play an important role in sulfate and SOA formation.

Plain Language Summary Organic compounds and sulfate anions are important components of atmospheric fine particles, which play an important role in air quality, visibility, climate, as well as human and ecosystem health. Photosensitized chemistry, which is driven by reactions of electronically excited organic molecules, is a proposed pathway for fine particle growth, producing highly oxygenated compounds and sulfate anions from gaseous volatile organics and sulfur dioxide, a key air pollutant. Aromatic hydrocarbons and their oxidation products are important components of fine particles in urban environments. This work shows that fine particles formed by oxidation of naphthalene, a common aromatic hydrocarbon, possess photosensitizing properties making them efficient catalysts for atmospheric oxidation of sulfur dioxide and volatile organics.

1. Introduction

Organic compounds and sulfate anions are ubiquitous in ambient aerosols, accounting for 20%–90% and 10%–60% of the fine particulate mass, respectively (Jimenez et al., 2009; Kanakidou et al., 2005). A large fraction of these organic compounds and sulfate are secondary in nature, that is, they are produced through atmospheric oxidation of volatile organic compounds (VOCs) (Hallquist et al., 2009) and sulfur dioxide (SO₂) (Eatough et al., 1994; Saxena & Seigneur, 1987). Both sulfate and secondary organic aerosol (SOA) significantly impact air quality, climate, as well as human and ecosystem health (Fuzzi et al., 2015; Nel, 2005). Despite extensive research spanning nearly a century, we still do not fully understand all possible pathways for their formation and transformation in the atmosphere (Wang et al., 2014; Zhang et al., 2007).

Many previous studies showed that photosensitized chemistry may be an important pathway for promoting the oxidation of VOCs (Kaur et al., 2019; Li et al., 2019a) in atmospheric particles, which can increase the mass of SOA. For example, irradiation of imidazole-2-carboxaldehyde (IC) and humic acid in the presence of various gaseous VOCs, such as d-limonene, has been shown to produce highly oxygenated compounds and thereby initiate aerosol growth by photosensitized mechanisms (Aregahegn et al., 2013; González Palacios et al., 2016; Monge et al., 2012; Rossignol et al., 2014; Tsui et al., 2017). Previous studies have suggested that the photosensitized chemistry of humic-like substances (HULIS) is not fast enough to compete with the conventional free-radical-driven growth under ambient concentrations of d-limonene (Fankhauser et al., 2020). However, while not being a major growth pathway of aerosols, photosensitized processes have the potential to change the particle phase oxidation capacity. For instance, significant amounts of

oxygenated molecules with low-volatility have been observed during photosensitized oxidation of some VOCs (Rossignol et al., 2014; Smith et al., 2014; Yu et al., 2014). The importance of such processes is obviously linked to the concentration of triplet state in the condensed phase as underlined by Kaur et al. (2019), who pooled all active triplet state into a one single T* family. In other words, in contrast to well identified radicals (such as OH), the key feature of tropospheric photosensitization is related to numerous compounds with diverse sources. Understanding those is therefore key. To further illustrate this potential importance, it has been shown that photosensitized chemistry involving the humic fraction of aerosols during Chinese haze events can explain a significant fraction of the observed sulfate formation (Wang et al., 2020a). These authors highlighted the specific role played by biomass burning (for cooking and heating during the cold season) as the main source of the aerosol's photosensitizing properties.

Naphthalene, emitted primarily from fossil fuel combustion and biomass burning, represents the smallest, most volatile, and most abundant polycyclic aromatic hydrocarbon (PAH) in the atmosphere (Zhang et al., 2012). Naphthalene is ubiquitous in suburban and urban areas, with a median concentration of $0.94 \ \mu g \ m^{-3}$ in 11 U.S. cities (Sudakin et al., 2011). The OH-initiated oxidation of naphthalene produces a number of different oxygenated compounds with high molecular weight and low-volatility, which can partition into particles and contribute to SOA mass (Chan et al., 2009; Kautzman et al., 2010; Riva et al., 2015). Naphthoquinone, a naphthalene oxidation product (McWhinney et al., 2013), is commonly found in atmospheric aerosols (e.g., Shanghai, China [Wang et al., 2017]; Tempe, USA [Delhomme et al., 2008]; Kurashiki City, Japan [Oda et al., 2001]; Yangtze River channel [Wang et al., 2020b]), and is known to be an efficient photosensitizer, inducing redox chemistry or producing reactive oxygen species (De Lucas et al., 2014; Mc-Neill & Canonica, 2016). SOA derived from oxidation of naphthalene under high-NO_x conditions has been shown to be weakly fluorescent (Lee et al., 2014), resilient to photobleaching (Aiona et al., 2018), efficient in photosensitizing singlet oxygen in aqueous solutions (Manfrin et al., 2019), capable of photosensitized oxidation of halide ions (Gemayel et al., 2021), and moderately effective in photosensitized oxidation of d-limonene (Malecha & Nizkorodov, 2017). It is therefore likely that aerosol particles containing naphthalene oxidation products (as well as oxidation products of PAHs in general) contribute to photosensitized chemistry in the atmosphere.

In this study, we investigated the photosensitizing activity of naphthalene-derived SOA using both gaseous VOCs and SO₂ as reaction partners. The naphthalene-derived SOA was generated in a laminar-flow Gothenburg (Go:PAM) oxidation flow reactor, then its photosensitizing properties were investigated by explicitly measuring particle growth in aerosol flow tube (AFT) experiments, in which particles were exposed to near-UV radiation in presence of VOCs or SO₂. Our data suggests that these aerosols do indeed exhibit photosensitized chemistry, by converting SO₂ into sulfate and d-limonene and β -pinene into particle-phase organic products.

2. Materials and Method

As shown in Figure 1, the experimental setup mainly consisted of a Go:PAM oxidation flow reactor and an aerosol flow reactor.

2.1. Go:PAM Description

The Go:PAM flow reactor (9.6 cm inner diameter, 100 cm length) is made of quartz glass and surrounded by two 30 W Philips ultraviolet lamps capable of producing 254 nm radiation (Watne et al., 2018). The gas flow injected into the Go:PAM chamber consisted of 250 mL min⁻¹ of pure air bubbled through hydrogen peroxide (H₂O₂, Sigma Aldrich, 26.4 wt. % in H₂O) solution, 20 mL min⁻¹ of pure air containing naphthalene (Sigma Aldrich, 99%) vapor, 1 L min⁻¹ of humidified air, and 2.78 L min⁻¹ of dry air, leading to a residence time of 1.8 min. The Go:PAM was operated at room temperature in the range of 297 ± 2 K, whilst a fan was used to homogenize and maintain the temperature. As calculated under the above conditions, the relative humidity (RH) and the concentrations of H₂O₂ and naphthalene in the Go:PAM reactor were around 29%, 5.2×10^3 ppb, and 5.5×10^2 ppb, respectively. The collection and analysis of naphthalene-derived SOA and its chemical characteristics are described in supporting information Texts S1–S2.





Figure 1. Schematic of the experimental setup with the Go:PAM flow and aerosol flow reactors.

2.2. Aerosol Flow Tube Experiment

The naphthalene-derived SOA air-flow was controlled by a needle valve and sent into a charcoal denuder $(100-160 \text{ mL min}^{-1})$ (Sigma Aldrich, Norit RBAA-3) to reduce concentrations of gaseous compounds and then into a differential mobility analyzer (DMA, TSI model 3081, impactor size 0.0508 cm) to produce monodispersed particles of desired size (mobility-equivalent diameter). The size selection by DMA further reduced the concentration of gaseous compounds in the flow. The size-selected SOA and VOC or SO₂ (Linde, France) were injected into a temperature-controlled horizontal jacketed aerosols flow tube (AFT) (6 cm internal diameter, 180 cm length) made of Pyrex (Wang et al., 2020a). In order to reduce the evaporative loss of the naphthalene-SOA particles that is known to happen after size selection (Li et al., 2019b; Yli-Juuti et al., 2017), the temperature and RH of the aerosol flow upon exiting the AFT. The AFT was surrounded by eight UV-lamps (Cleo, Philips, Netherlands) with a continuous emission spectrum over 300–420 nm and a total irradiance of 6×10^{15} photon cm⁻² s⁻¹ (Dupart et al., 2012).

As shown in Figure 1, the aerosol flow was diluted by a factor of ~2 with pure air before being sent to a scanning mobility particle sizer (SMPS, TSI 3936, impactor size 0.071 cm), an SO₂ analyzer (Thermo 43i) and an Aerodyne compact time-of-flight (cTOF) aerosol mass spectrometer (AMS), to characterize the particle size distributions in the range of 15–700 nm, gaseous SO₂ concentration, and particle-phase sulfate production, respectively. The diluted aerosol flow was further diluted with pure air before being analyzed by a stander SO₂ analyzer. More details about the SMPS and AMS measurements are provided in the supporting information section (Text S3). In some experiments, a selected VOC was continuously injected in the AFT together with the particles. For this purpose, a permeation tube placed in a temperature controlled oven (Dynacal, Valco Instruments Co. Inc., U.S., using VICI Metronics, U.S., Dynacalibrator, model 150) was used to generate a specific concentration of d-limonene or β -pinene (Rossignol et al., 2014). A high-resolution proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS 8000, Ionicon Analytik) was then used to measure their concentrations. The detailed setup and calibration of the PTR-MS were described in a previous study (Kalalian et al., 2020).

3. Results and Discussion

In previously published control experiments, only one VOC or SO_2 was injected into the AFT (without naphthalene-derived SOA) under similar conditions to other experiments (i.e., the same RH, UV exposure, temperature, and residence time). During these experiments, no loss of VOC or SO_2 and no particle





Figure 2. Median and mean diameter $(\pm 2\sigma)$ growths of naphthalene-derived secondary organic aerosol (SOA) exposed to UV light and SO₂ for 16 min in the aerosol flow tube (AFT) (a). The yellow region corresponds to the irradiation time. Sulfate production as measured by the cTOF-AMS of naphthalene-derived SOA exposed to SO₂ at different relative humidity (RH) (b), under different light intensities (c), and with different SO₂ concentrations (d). L4 means four lamps were turned on; and L8 means eight lamps were turned on.

formation were observed (Aregahegn et al., 2013), indicating that gas-phase oxidation of the VOC or SO_2 was not taking place in the AFT, due to an absence of gaseous oxidants.

In the first series of experiments, naphthalene-derived SOA (\sim 5700 particles cm⁻³, median size \sim 46 nm) and SO₂ (1 ppm after dilution) were injected into the AFT with a residence time of 16 min at a high RH of 86%–90%. Figure 2a shows a typical profile for the evolution of the median and mean diameters of the particles at the outlet of the AFT. Notably, both the median and mean diameters of particles (before UV irradiation) were smaller than selected inlet sizes, indicating some particle evaporation in the first DMA and AFT. A small particle growth was observed once the UV lights were switched on, growing 2 nm in terms of median and mean diameters. In addition, the Diameter Growth Factor (DGF (%) = $((Dp - Dp_0)/(Dp - Dp_0))$ Dp) \times 100) was calculated for different experimental conditions (see Table 1). As RH decreases to 61%-65% and 40%-43%, the particle size measurements indicate particle shrinking instead of growth when naphthalene-derived SOAs were exposed to 1 ppm SO₂ and UV irradiation. This is likely due to the particle phase undergoing photodegradation when exposed to UV irradiation, resulting in smaller particle sizes. Indeed, it has been shown that the photodegradation of SOA particles could produce small oxygenated VOCs evaporating to the gas phase (Malecha & Nizkorodov, 2016, 2017; Wong et al., 2015). Notably, at RH 40%-49%, the DGF was even lower when SOA particles were exposed to SO₂ compared to control experiments, possibly due to the more acidic aerosol phase enhancing the evaporation of small organic acids from particles. Slade et al. (2017) suggested that degradation of SOA under viscous conditions (i.e., low RH), where diffusion into the bulk is prevented, tends to promote the production of multiple generations of oxidation of the same molecule, resulting in fragmentation and evaporation. Such processes could also be occurring in our experiments at low RH when SO₂ is present.

In the second series of experiments, 100 nm naphthalene-derived SOA particles, up to 6000 particles cm⁻³, were size-selected and exposed to 0.8 ppm SO₂ for sulfate production measurement experiments. The



Median Diameter Growth Factor (DGF, %) of Naphthalene-Derived SOA With Different Gaseous Compounds and RH						
Gaseous compounds	Concentration (ppm)	Residence time (min)	RH	$Dp_0(nm)$	Dp (nm)	DGF (%)
None	0	16	47%-49%	44.1±0.2	43.5±0.3	-1.4
	0	16	68%-71%	43.8±0.3	42.2±0.4	-3.8
	0	16	85%-89%	42.4±0.2	41.4±0.3	-2.4
SO ₂	1	16	40%-43%	44.8 ± 0.2	43.0±0.3	-4.2
	1	16	61%-65%	42.5±0.2	41.3±0.8	-2.9
	1	16	86%-90%	42.8 ± 0.4	44.7 ± 0.7	4.3
	0.7	16	86%-90%	42.9 ± 0.2	43.9±0.2	2.3
	0.4	16	86%-90%	42.9 ± 0.2	43.1±0.2	0.5
d-Limonene	0.1	25	39%-43%	36.4 ± 0.7	71.4±1.3	50.8
	0.1	25	84%-88%	34.0 ± 0.2	85.4±1.6	58.7
β-pinene	0.8	25	45%-47%	37.0 ± 0.4	40.6±0.3	8.9
	0.8	25	85%-89%	35.7±0.3	47.1±0.3	24.2

Table 1

Note. Dp₀, initial particle median diameter; Dp, particle median diameter after irradiation.

particle size-selection was changed (from 46 to 100 nm) due to the low transmission efficiency of the cTOF-AMS for particles less than 60 nm. The total amount of all sulfates was then monitored (the cTOF instrument has limited capabilities to distinguish between the inorganic and organic sulfates). Figure 2b shows that at different RHs, particulate sulfate was produced from both dark and photosensitized chemistry. The dark production of particulate sulfate can be explained by a couple of factors. First, organic peroxides were found to account for $\sim 26.2\%$ of the total naphthalene-SOA mass (Kautzman et al., 2010), which are believed to oxidize SO₂ to sulfate and organosulfates (Wang et al., 2019; Yao et al., 2019; Ye et al., 2018a). In addition, dissolved S(IV) may react with aldehydes and quinones in naphthalene-derived SOA (Kautzman et al., 2010) to produce organosulfonates (LuValle, 1952; Olson & Hoffmann, 1989). All these pathways could contribute to the measured sulfates in the dark, which are in the range of $0.003-0.11 \ \mu g \ m^{-3}$. In addition, a previous study showed that the sulfate production from the reaction between SO₂ and α -pinene-derived SOA exhibits an exponential dependence on RH (Yao et al., 2019), which is similar to the result obtained in the present study (Figure 2b).

When the UV lights were switched on, 0.05–0.08 μ g m⁻³ of sulfate (i.e., 0.2–0.3 μ g m⁻³ h⁻¹) were produced at all RHs (Figure 2b). However, although the total sulfate production increases as the RH increases, the sulfate production attributable to the photosensitized oxidation at RH 81%-84% is the lowest. This indicates a more complex RH dependence on the photochemical mechanism. Saukko et al. (2012) have investigated the physical phase state (solid, semi-solid, or liquid) of SOA derived from various precursors by measuring their bounce behavior after inertial impaction on a solid substrate. The measured bounce fraction was evaluated as a function of RH and SOA oxidation level (O/C). In the case of naphthalene-derived SOA, the bounce factor was indicative of an amorphous solid or semi-solid state, up to RH close to 70%. At greater RH values, this factor decreased, indicating a phase change with particles having a less viscous, more "liquid-like" material. These trends are to be compared with the data shown in Figure 2b, where the dark chemistry was predominant only at high RH. Such chemistry could be driven, among other factors, by the peroxide, aldehyde, and quinone (i.e., naphthoquinone) compounds present in such particles (Kautzman et al., 2010) forming organosulfates, organosulfonates and sulfate (LuValle, 1952; Olson & Hoffmann, 1989; Wang et al., 2019; Yao et al., 2019; Ye et al., 2018a). But the fact that it occurs more efficiently at high RH (i.e., on more liquid particles), points toward a bulk process where the chemistry occurs after solubilization of the incoming SO₂ molecules. In addition, the sulfate formed from dark chemistry can also impact physical properties such as hygroscopicity, acidity, and phase state (Hodas et al., 2015; Saukko et al., 2012), which may further influence the solubility of S(IV) in the aerosol phase.

In contrast, the photochemical fraction of sulfate production is reduced at higher RHs but gains in importance at low RH, where potentially the surface, or a small shell close to the surface, is available for reaction.





Figure 3. Median diameter $(\pm 2\sigma)$ growths of Nap-derived secondary organic aerosol (SOA) exposed to UV-A light and 0.1 ppm d-limonene (A) and 0.8 ppm β -pinene for 30 min in the aerosol flow tube (AFT). The yellow region corresponds to the irradiation time.

Notably, the previous studies showed that in-particle diffusion is not rate-limiting to SO₂ uptake by α -pinene-derived SOA at low RH (<10%), whilst toluene-derived SOA starts to lose the resistance above 20% RH (Yao et al., 2019; Ye et al., 2016, Ye et al., 2018b). Therefore, a significant diffusion limitation is not expected in the present study. Besides, SO₂ could also be excited into the triplet state (i.e., SO₂) by direct absorption of light with wavelength from 240 to 330 nm, which could react with H₂O to produce sulfate (Kroll et al., 2018; Martins-Costa et al., 2018). However, this sulfate formation pathway was shown to be minor significant in our AFT system due to the weak overlap of SO₂ light absorption and spectral irradiance of our lamps (Wang et al., 2020a). Additionally, the bulk chemistry may also consume the existing photosensitizers and explain the reduced fraction of photochemically produced sulfate at high RHs. Thus, at higher RHs sulfate production is dominated by bulk phase solubilization and subsequent oxidation of SO₂, whereas photosensitized oxidation at the surface of the particles dominates at lower RHs.

It is notable that the mean particle size of SOA decreased from 93 to 85 nm as the RH increased from 37%– 39% to 81%–84% in the dark, possibly due to the moisture-induced changes in SOA morphology or phase and high evaporation of SOA at high RH (Li et al., 2019b; Wilson et al., 2015; Wong et al., 2015; Yli-Juuti et al., 2017), reducing the surface area and volume by ~16% and ~24%, respectively. Figures 2c and 2d show that sulfate production decreases as the light intensity and SO₂ concentration decrease.

Traditionally, SO₂ oxidation is known to be mainly driven by gas-phase reactions with OH radicals, ozone, H_2O_2 , nitrogen dioxide (NO₂), and transition-metal ions in the aqueous phase (Cheng et al., 2016), whilst interfacial SO₂ oxidation on acidic microdroplets (Hung & Hoffmann, 2015) and SO₂ triplet state chemistry (Kroll et al., 2018; Martins-Costa et al., 2018) were also suggested to play a role in the sulfate formation. However, the photosensitized oxidation of SO₂ has recently been discussed as an important contributor to sulfate formation on biomass burning type particles (Wang et al., 2020a). Our findings here now extend such observations also to more anthropogenic particles and are posing the question whether such photosensitized processes are widespread.

To test whether these particles exhibit photosensitized reactivity toward different partner molecules, we also exposed them to gaseous d-limonene or β -pinene. Control experiments using seed particles containing only ammonium sulfate or ammonium sulfate/succinic acid exposed to d-limonene and UV light did not lead to particle growth (Aregahegn et al., 2013; Monge et al., 2012). In contrast, as shown in Figure 3 and Table 1, the particle size of naphthalene-derived SOA particles (starting diameter of 37 nm) in the presence of 0.1 ppm limonene increased by 50.8% and 58.7% at RH 39%-43% and 84%-88%, respectively, corresponding to a residence time of 25 min. This is a remarkable amount of growth, implying that particle volume goes up by $(2.0-2.5)^3$ or by a factor of 8–16. In addition, the reaction with 0.8 ppm β -pinene at RH 45%–47% and 85%-89% resulted in similarly large DGFs of 8.9% and 24.2%. The RH dependence of particle growth is mainly driven by the enhanced solubility of naphthalene-derived SOA (Yao et al., 2019). Such experiments are meant to show that these particles are reactive toward unsaturated VOCs (Aregahegn et al., 2013; Monge et al., 2012), since d-limonene was found to be a more efficient SOA precursor compared to β -pinene, but are not meant to suggest a strong involvement in particle growth in the ambient atmosphere (due to the unrealistic experimental conditions). Similar to the study of Aregahegn et al. (2013), such growth is probably caused by the formation of highly oxygenated products through d-limonene or β -pinene reacting with the triplet state of the photosensitizers (Monge et al., 2012; Rossignol et al., 2014).

For example, the excited photosensitizer can abstract a hydrogen from an organic molecule (i.e., d-limonene or β -pinene), through either a direct transfer or proceed via an electron transfer followed by a proton transfer (Rossignol et al., 2014). Since the initial step triggering the photosensitized uptake is a H-abstraction reaction (and not an addition to a double bond), VOCs having weak C-H bonds will react faster, which is observed here for d-limonene. The reduced photosensitizer radical can be oxidized to the original ground state in the presence of O₂, at the same time, producing superoxide radicals (HO₂^{-/}O₂⁻⁻) (Aregahegn et al., 2013). The photoproduct VOC and photosensitizer radicals can further react with other molecules or be oxidized

by HO_2 or O_2 , to produce new products. The study of Rossignol et al. (2014) found that highly oxygenated organic compounds including compounds retaining the same number of carbons as d-limonene were produced from the reaction of the IC triplet state and d-limonene in the aerosol phase through ring-opening and intramolecular isomerization during the d-limonene oxidation process.

Interestingly, both naphthalene-derived SOAs and seed particles containing photosensitizers grow efficiently even at low RH when exposed to d-limonene and β -pinene VOCs (Table 1) (Aregahegn et al., 2013; Monge et al., 2012). This indicates that the photosensitized process may occur at the surface and be sustained even on solid or semi-solid particles without passivation. This is in contrast to the expected behavior of a solid where it is expected that the high viscosities promote radical recombination and the surface is expected to be rapidly passivated. It is beyond the capabilities of these experiments to unravel the molecular reason for this observation, but one could speculate that the presence of a photochemically active surface may locally change the nature of the surface or induce chain reactions that may propagate some surface reactivity. Another possibility is the triplet states of these photoactive compounds convert molecular oxygen into reactive oxygen (e.g., O_2^- or 1O_2) sustaining surface reactivity, which would be in agreement with high 1O_2 yield from naphthalene-SOA in aqueous solutions (Manfrin et al., 2019). The produced oxygenated VOC may also form a new phase beneath the surface, thus keeping the surface open for more reactions. This type of liquid-liquid phase separation has been observed for various SOA types even under lower RH conditions observed here (Huang et al., 2021). Whatever the underlying reason, these observations tend to support that the surface of such solid or semi-solid particles will not passivate while being illuminated with actinic light.

Notably, the increased DGF under high RH conditions indicates that the underlying photochemical mechanisms are different for the VOCs and for SO₂. Wang et al. (2020a) suggested a direct reaction of SO₂ with the organic triplet states through different pathways, possibly influenced by pH. On the other hand, Rossignol et al. (2014) suggested that the underlying mechanism for the VOC uptake is H abstraction followed by the production of multiple generation products (by condensed phase autooxidation). As previously mentioned, at low RH, these first-generation products are concentrated at the surface (because they cannot diffuse to the bulk under highly viscous conditions) where they remain fully exposed to oxidants and undergo rapid further oxidation and fragmentation, yielding highly oxygenated products with lower molar mass. Those may therefore degas (or desorb) preferably at low RH compared to high RH where diffusion into the bulk is possible. Therefore, the different trends between the VOCs and SO₂ are possibly to a combination of mass transport limitations, and different chemistries being influenced by pH.

4. Conclusions

Naphthalene is ubiquitous in suburban and urban areas and its OH radical driven oxidation produces oxygenated aromatic compounds with low volatility forming secondary organic aerosols. Those particles are found to be reactive in the dark toward SO_2 where the reactions of dissolved S(IV) with naphthalene oxidation products such as quinones, aldehydes, and organic peroxides are expected to produce organosulfonates, organosulfates and sulfates. The dark production of sulfate was observed to increase at high humidity and hence on liquid like particles. In addition, these particles possess photosensitizing properties at all RHs, and can oxidize SO_2 even on solid or semi-solid particles. Moreover, the particle size of naphthalene-derived SOA grows efficiently under irradiation in the presence of VOCs, especially d-limonene. As the RH increases, the photosensitized particle growth becomes more efficient. These results indicate that the formation of sulfate and oxygenated organic compounds through naphthalene-derived SOA photoinduced reactions contributes to the sulfate concentration and size/mass of SOA particles.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

The data presented in this manuscript could be downloaded at https://osf.io/52ef9/.



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