SO$_2$ Uptake on Oleic Acid: A New Formation Pathway of Organosulfur Compounds in the Atmosphere

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S *Supporting Information*

ABSTRACT: Organosulfates are tracers for secondary organic aerosol (SOA) formation. We propose a new mechanism of organosulfur product formation in the atmosphere, in which sulfur dioxide (SO$_2$) reacts directly with alkenes. The experiments were conducted at the gas–liquid interface with a coated-wall flow tube reactor. It was shown, for the first time, that SO$_2$ reacts efficiently with the unsaturated bond in oleic acid under atmospheric conditions (without ozone), leading to the formation of C$_9$ and C$_{18}$ organosulfur products. The associated uptake coefficients were in excess of 10^{-6}, decreasing with initial SO$_2$ concentration and increasing with humidity. These results might explain a fraction of organosulfur products detected in atmospheric particles. This work tends to elucidate the role of organosulfates' interfacial chemistry as a potentially unrecognized pathway for their contribution to SOA formation; however, it remains to be determined how significant this pathway is to the overall organosulfate abundances measured in ambient aerosol.
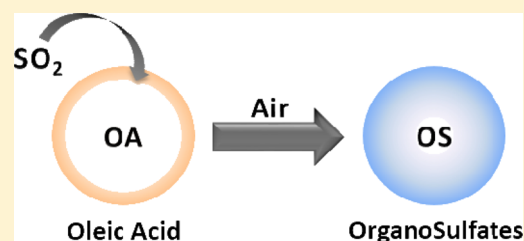
1. INTRODUCTION

Heterogeneous reactions have attracted much attention in recent years because of their potential importance in affecting the transformation of trace gas pollutants and properties of particles in the atmosphere.[1–4] Sulfur dioxide (SO$_2$) is an important trace gas, and its fate may have an impact on atmospheric chemistry; indeed, its oxidation by hydroxyl radical (OH$^•$) or in-cloud oxidation by various oxidants (including transition metals) and/or stabilized Criegee intermediates (sCIs) leads to sulfuric acid (H$_2$SO$_4$), which plays a key role in new particle formation.[5–8] SO$_2$ can also react at the surface of many aerosol particles such as mineral dust[9–12] and black carbon,[13–15] but there have been few studies about its reactions on organic surfaces and its contribution to organosulfate formation.

Organosulfates are ubiquitous in atmospheric aerosols and contribute up to 30% of the organic mass.[16,17] They are tracers for secondary organic aerosol (SOA) formation,[17–21] and they might influence the climate by light absorption and/or by affecting aerosol hygroscopicity.[22,23] Several organosulfate formation pathways have been suggested in the past few years,[24–26] and it is generally accepted that they are produced through heterogeneous and multiphase reactions of oxidized species (produced by ozone or OH$^•$) on sulfate-containing particles.[27–30] However, the knowledge of the spatial distribution of organosulfates, conditions of formation, and environmental impact is still limited.[21,31] We investigated the

possible direct chemical interactions of SO$_2$ with unsaturated compounds, i.e., oleic acid, as a source of organosulfates.

Oleic acid (OA), a monounsaturated long-chain fatty acid (pK_a = 9.85),[32] has been detected in urban, rural, and marine aerosols.[33–35] It is the most common fatty acid found in plant membranes and has been detected at concentrations of >25 ng m^{-3} in atmospheric aerosols.[34] Oleic acid is present in many cooking oils and for this reason is a marker for meat cooking aerosols.[15,36] The low vapor pressure of OA makes it suitable for studies of heterogeneous chemistry. Indeed, it has been chosen as an unsaturated model compound for atmospheric oxidation studies.[37–40]

The heterogeneous reaction of SO$_2$ with OA was investigated using a coated-wall flow tube reactor and was compared to the reactions of SO$_2$ with stearic acid and sodium oleate. We show for the first time that SO$_2$ reacts with OA without ozone or other reactive oxidants (e.g., OH$^•$), and we report the uptake kinetics and reaction products in the liquid and gas phases.

2. MATERIALS AND METHODS

2.1. Heterogeneous Uptake of SO$_2$ on an Oleic Acid Film. The uptake experiments were conducted in a coated-wall flow tube (Figure S1) coupled to a SO$_2$ detector (Thermo

Scientific model 43i SO_2 analyzer) under atmospheric conditions (293 K, 1 atm). Oleic acid ($C_{18}H_{34}O_2$, Alfa Aesar, 99% purity) was used to coat the inner wall of a 20 cm long, 1.2 cm internal diameter (i.d.) Pyrex tube and then introduced into the flow tube. The deposited OA mass in Pyrex tubes ranged from 5.7 to 42.4 mg, corresponding to a calculated film thickness between 0.92 and 6.87 μm (see the Supporting Information). The SO_2 gas phase concentration ranged from 0.3 to 11.3 × 10^{12} molecules cm^{-3} (corresponding to 13−453 ppb), and the relative humidity (RH) was between 0.1 and 74%. The SO_2 flow in synthetic air was introduced into the flow tube through a horizontal movable injector at a flow rate of 150 or 300 mL min^{-1}. As seen for OA films, stearic acid (Alfa Aesar, 98% purity) and sodium oleate (Sigma-Aldrich, ≥99% purity) films were prepared. A detailed description of the experimental procedure is reported in the Supporting Information.

The uptake coefficient (γ) was determined by observing the loss of SO_2 as it was exposed to OA and was calculated from the measured first-order loss rate constant (see the Supporting Information).[41,42]

2.2. Characterization of Liquid Phase Products by Ultra-High-Performance Liquid Chromatography Coupled with High-Resolution Mass Spectrometry. The liquid phase was analyzed via ultra-high performance liquid chromatography coupled with high-resolution mass spectrometry (UHPLC−HRMS). Analyses were performed on a Dionex UltiMate 3000 UHPLC system with a C_{18} column coupled with a high-mass resolution Q-Exactive Hybrid Quadrupole-Orbitrap mass spectrometer (Thermo Scientific) equipped with a heated electrospray ionization source (H-ESI). Electrospray ionization was performed in negative mode. After the reaction of SO_2 with OA, the inner side of the flow tube was washed with a certain volume of methanol calculated according to the weight of the coated OA film to obtain a 20 mM OA solution. The solution was then diluted with acetonitrile and ultrapure water to obtain a 2 mM OA solution to be analyzed by UHPLC−HRMS. More details of UHPLC−HRMS analysis are reported in the Supporting Information.

2.3. Characterization of Gas Phase Products with a Switchable Reagent Ion Time-of-Flight Mass Spectrometer. A commercially available switchable reagent ion time-of-flight mass spectrometer (SRI-ToF-MS, Ionicon Analytik GmbH) using both H_3O^+ and NO^+ ionization modes was used to characterize gas phase products. The SRI-ToF-MS system was mounted at the exit of the flow reactor and sampled at a rate of 80 mL min^{-1} through 1.5 m of $^1/_4$ mm i.d. peek tubing heated at 60 °C. Measurements were performed at a drift voltage of 600 V, a drift temperature of 60 °C, and a drift pressure of 2.25 mbar, resulting in an E/N of approximately 130−135 Td (1 Td = 10^{-17} cm^2 V^{-1}), where E is the electric field strength and N the particle density number. The resolution of the spectra was approximately 4000 at m/z 100. A more detailed description of the instrument is given elsewhere[43] (see also the Supporting Information).

3. RESULTS AND DISCUSSION

3.1. Uptake of SO_2 on Oleic Acid. While no significant loss of SO_2 was observed on the clean glass insert (Figure S2), a sharp and sustained decrease was observed upon its exposure to an OA film (Figure S3). The magnitude of the SO_2 signal clearly decreased with an increasingly exposed OA surface. After exposure, the injector was moved downstream and the SO_2 concentration returned to its original level, without any

indication of SO_2 desorption. This suggested an irreversible uptake of SO_2 on the OA surface under our experimental conditions. These experiments were conducted under clean carrier gas, in the absence of any additional gas phase oxidants (such as ozone), and are indicative of an efficient uptake of SO_2 onto these surfaces, which is reported here for the first time. Table S1 summarizes the uptake coefficients at different initial concentrations, humidities, and OA mass conditions.

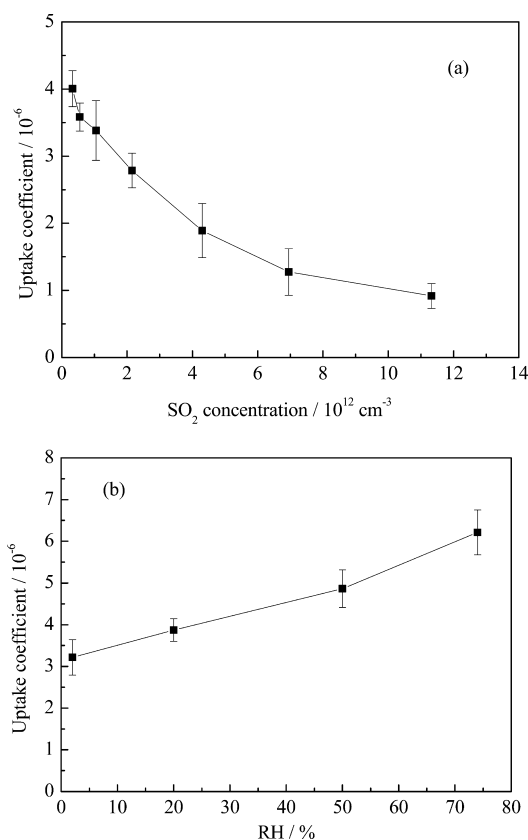While no dependence was observed as a function of the deposited OA mass (Figure S4), Figure 1a illustrates the

Figure 1. Dependence of the uptake coefficient on the initial SO_2 concentration (a) and relative humidity (RH) (b).

decrease in the uptake coefficient with an increasing initial SO_2 concentration, indicative of a Langmuir−Hinshelwood-type mechanism, characterized by the adsorption of SO_2 followed by a chemical reaction (on the surface or within the bulk). OA is a viscous liquid at room temperature (viscosity of 39.2 cSt at 20 °C);[44] thus, SO_2 still could diffuse into the bulk of the film. On the other hand, increasing humidity was seen to accelerate the uptake process (Figure 1b), either by promoting the adsorption of SO_2 or by increasing the water content of the film and therefore the SO_2 solubility, in both cases enhancing the rate of reaction of SO_2 with OA.

3.2. Comparison of the Reactivity of Stearic Acid, Sodium Oleate, and Oleic Acid Films. To improve our understanding of the reaction between SO_2 and OA, we measured the reactivity of stearic acid (a saturated C_{18} carboxylic acid) and sodium oleate (unsaturated C_{18} bearing a carboxylate function). For this purpose, stearic acid and sodium oleate were exposed to SO_2 as described above (Figure S5). While stearic acid did not show any reactivity, sodium oleate moderately reacted with SO_2 with a surface passivation

Table 1. Exact Masses, Detected by UHPLC−HRMS, of an Oleic Acid Film Exposed to Synthetic Air and to SO_2 (4.3 × 10^12 molecules cm^{-3})^a

	chemical formula	detected mass (m/z)	Δppm	oleic acid film exposed to SO_2 in synthetic air		oleic acid film exposed to synthetic air	
				integrated peak area (×10^6 a.u.)	product/oleic acid ratio	integrated peak area (×10^6 a.u.)	product/oleic acid ratio
				Oxidation Products			
C_{18}	$C_{18}H_{33}O_2^-$	281.249	+0.4	1.71	1.00	1.25	1.00
	$C_{18}H_{33}O_3^-$	297.244	+0.8	49.34	28.91	0.72	0.57
	$C_{18}H_{33}O_4^-$	313.239	+0.8	29.83	17.48	2.90	2.32
	$C_{18}H_{35}O_4^-$	315.254	+0.7	3.97	2.33	1.81	1.45
	$C_{18}H_{31}O_4^-$	311.223	+0.9	1.84	1.08	0.03	0.03
	$C_{18}H_{31}O_3^-$	295.228	+0.6	15.40	9.02	−	−
C_9	$C_9H_{17}O_3^-$	173.118	+0.9	1.64	0.96	0.83	0.67
	$C_9H_{15}O_4^-$	187.098	+1.1	39.81	23.33	6.45	5.17
	$C_9H_{15}O_3^-$	171.103	+1.5	1.39	0.81	0.08	0.06
				Organosulfur Products			
C_{18}	$C_{18}H_{31}O_7S^-$	391.180	+1.4	1.00	0.59	−	−
	$C_{18}H_{33}O_6S^-$	377.201	+1.2	15.01	8.79	−	−
	$C_{18}H_{33}O_7S^-$	393.196	+1.3	5.26	3.08	−	−
	$C_{18}H_{35}O_7S^-$	395.211	+1.2	3.41	2.00	−	−
C_9	$C_9H_{17}O_5S^-$	237.080	+1.1	9.35	5.48	−	−

^{a}Experimental conditions: flow rate of 150 mL min^{-1} and relative humidity of 30%.

after 23 min. In comparison, the OA film sustained the reactivity for more than 3 h. This difference could be explained by the viscous nature of OA, while the oleate film was solid under these conditions. Thus, saturated compounds do not react, in contrast to the unsaturated oleic acid and sodium oleate. In addition, acidity could catalyze the uptake rate. These results highlight for the first time an efficient chemical reaction of SO_2 with double bonds.

3.3. Products, Mechanism, and Impact. Table 1 lists the main condensed phase products, when oleic acid is exposed to synthetic air or SO_2. Under air, UHPLC−HRMS analysis shows that OA is only slowly oxidized and that, as expected, no organosulfate products are formed. When OA is exposed to SO_2, in the absence of any other oxidant, the formation of sulfur-containing products is unambiguously observed as reported in Table 1. Moreover, compounds with the same formula (except $C_{18}H_{31}O_7S^-$) were also detected in atmospheric aerosols.[45,46] We have to underline the fact that in the absence of MS/MS analysis and chemical standards, these compounds could also correspond to isomeric compounds sharing the same formula, but arising from different sources. The most abundant products under laboratory conditions are detected at m/z 377.201 ($C_{18}H_{33}O_6S^-$) and m/z 237.080 ($C_9H_{17}O_5S^-$). The exposure of the film to SO_2 also increases the extent of formation of OA oxidation products. The product at m/z 377.201 is a C_{18} compound with the same degree of unsaturation as OA. It could therefore be a cyclic organosulfate, as previously observed in some photochemical reactions[47] and for addition of SO_2 to double bonds.[48]

Sulfur dioxide can react with alkenes via ene-reactions that generally lead to isomerization of the double bond and in some cases to sulfinic acids or polymeric products.[48−50] Sulfur dioxide can form π complexes with carbon−carbon double bonds;[51] in some cases (first step of the ene-reaction), the complex may undergo a transformation to the corresponding dipolar σ complex (with charge separation).[50] Under our conditions (nonpolar surface), radical, rather than ionic reactions might be promoted, leading to diradical intermediates (Figure 2). These kinds of intermediates have been proposed
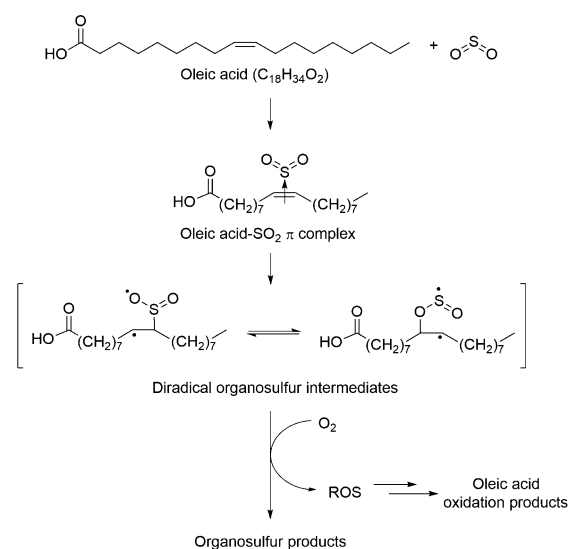

Figure 2. Suggested reaction mechanism of addition of SO_2 to oleic acid.

for photoreactions of SO_2 with alkenes, and their interaction with oxygen can lead to formation of reactive oxygen species (ROS).[47,52] Organosulfur products could be generated via addition of SO_2 to the double bond,[47,53] whereas the OA oxidation products could be explained by radical chain reactions triggered by ROS. Indeed, the observed products at m/z 297.244 ($C_{18}H_{33}O_3^-$) and m/z 187.098 ($C_9H_{15}O_4^-$) are common lipid oxidation products.[54] Gas phase products were analyzed by connecting an SRI-ToF-MS to the exit of the flow tube reactor. Both H_3O^+ and NO^+ ionization modes were used to analyze the gas phase. Gaseous sulfur-containing products were not observed, probably because of their low volatility. However, the formation of gaseous oxygenated compounds was observed. In the H_3O^+ ionization mode, the main product signals detected were at m/z 143.134 [$(C_9H_{18}O)H^+$], m/z 145.122 [$(C_8H_{16}O_2)H^+$], m/z 131.143 [$(C_8H_{18}O)H^+$, octanol], and m/z 117.127 [$(C_7H_{16}O)H^+$, heptanol]. In NO^+ ionization

mode, an increase in the level of typical fragments of nonanoic acid and aldehydes[55,56] was observed when the film was exposed to SO_2.

To the best of our knowledge, this is the first time that a direct heterogeneous reaction between SO_2 and OA has been reported (i.e., without any further oxidant being required). This reaction leads to the formation of organosulfur compounds in addition to other possible major pathways, including the acid-catalyzed chemistry of epoxides, such as the isomeric isoprene epoxydiols (IEPOX).[57,58] The direct SO_2 addition could be relevant in highly polluted regions such as in some urban areas of China, where average concentrations of SO_2 and ozone of 15 and 65 ppbv, respectively, were reported for 2014, with peak concentrations of SO_2 of >34 ppbv.[59] Under such pollution levels and by taking into consideration the reported uptake coefficient of ozone on oleic acid at long reaction times,[39] and the data presented here, we were able to estimate that approximately 1.6−3.3% of the double bonds will still react directly with the addition of SO_2 in regions with high sulfur loadings.[60] This simple calculation, based on the reported relative uptake rates, also tends to support the fact that SO_2 addition, while being a minor pathway as compared to ozone addition, will still exist in the presence of other oxidants. As such heterogeneous SO_2 addition could be generalized to other alkenes, we suggest that it could be one of several pathways of organosulfur compound formation in the atmosphere. Moreover, this reaction triggers oxidation reactions that might change the hygroscopicity of particles. Determining the exact structure of the sulfur-containing product by this addition and their existence in ambient air remains a challenge because of the lack of standards. Nevertheless, these preliminary results are a starting point for investigating in more detail the addition of SO_2 to alkenes under environmental conditions using, for instance, atmospheric simulation chambers or aerosol flow tubes to assess its real significance for ambient atmospheric aerosols.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.6b00006.

Additional information regarding the flow tube experiments and product analysis (PDF)

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Author Contributions

J.S. and M.P. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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