Atmospheric Chemistry

International Edition: DOI: 10.1002/anie.201605266
German Edition: DOI: 10.1002/ange.201605266

Organosulfate Formation through the Heterogeneous Reaction of Sulfur Dioxide with Unsaturated Fatty Acids and Long-Chain Alkenes

*Monica Passananti, Lingdong Kong, Jing Shang, Yoan Dupart, Sébastien Perrier, Jianmin Chen, D. James Donaldson, and Christian George**

***Abstract:** The heterogeneous reaction between SO_2 and unsaturated compounds results in the efficient production of organosulfates for several fatty acids and long-chain alkenes. The presence of an acid group, the physical state of the reactants (solid or liquid), the nature of the double bond (cis, trans, terminal), and the use of light irradiation all have an impact on the reaction rate. The reaction was investigated using different set-ups (coated flow tube, aerosol flow tube, and diffuse reflectance infrared Fourier transform cell). The reaction products were identified by high-resolution mass spectrometry and the impact of this reaction on organosulfate formation in the atmosphere is discussed.*

Sulfur dioxide (SO_2) is an important atmospheric trace gas, which together with its oxidation products (e.g., sulfuric acid) can have profound effects on climate and atmospheric composition. Therefore, knowledge of the chemistry of SO_2 is essential for the understanding of some major atmospheric processes, such as particle formation.[1] Because SO_2 is a 1,3-dipolar molecule, it could also react with double bonds. Despite having similar electronic structures, SO_2 and O_3 react differently with alkenes. The well-known [3+2] cycloaddition of O_3 to alkenes is not favored for SO_2, while the [2+2] cycloaddition of SO_2 to the C=C bond is more favorable compared to the analogous reaction with O_3.[2]

The atmospheric formation of organosulfur derivatives through reaction with SO_2 is generally mediated by oxidants such as O_3 and $OH^{\bullet}$ radicals; recently we have proposed a direct reaction between SO_2 and unsaturated compounds as another possible pathway for organosulfate formation in the troposphere.[3] It was shown that a heterogeneous reaction between SO_2 and oleic acid (OA; an unsaturated fatty acid) takes place and leads efficiently to the formation of organosulfur products. Herein, we demonstrate that this reaction proceeds on various unsaturated compounds, and may therefore have a general environmental impact. We used different experimental strategies, namely, a coated flow tube (CFT), an aerosol flow tube (AFT), and a DRIFT (diffuse reflectance infrared Fourier transform) cell. The reaction products were analyzed by means of liquid chromatography coupled to a high-resolution mass spectrometer (LC-HR-MS).

In the CFT, the reaction between SO_2 and OA was investigated under different conditions, extending our previous work.[3] The uptake coefficients of SO_2 (γ_{SO_2}) on OA were measured for exposure of OA films to SO_2 in dry synthetic air, nitrogen, synthetic air with added O_3, synthetic air with 30 % relative humidity (RH), and in dry synthetic air under UV/Vis irradiation. There is no significant difference in the magnitude of γ_{SO_2} obtained under the different conditions. In the presence of O_3, both SO_2 uptake on OA and the formation of organosulfur products are observed.

Product analysis shows the presence of the same products as we have previously reported.[3] The ratios between the integrated peak area of products and OA obtained under different conditions are reported in Figure 1. When the reaction is carried out under N_2, all the oxygenated products are observed only in low amounts. Therefore the oxygen is directly involved in the product formation, but, as seen in Figure 1 a, it does not impact the uptake of SO_2 on OA. The amounts of the oxidation products are drastically increased with 30 % RH, possibly because of the interaction of water with reactive intermediates. Furthermore, under actinic irradiation (without O_3 formation or photolysis of the carboxylic function), the proportion of oxidation products increases compared to that obtained under dry conditions, or in the presence of O_3. Interestingly, the main organosulfur product $C_{18}H_{34}O_6S$ is more abundant under UV/Vis light, whereas the $C_9H_{18}O_6S$ is promoted under 30 % RH.

MS^2 analyses were carried out on the main organosulfur products in order to determine their structures (see the Supporting Information). The absence of commercially available chemical standards means that it is difficult to characterize the structure unequivocally. The product detected at m/z 377.200 corresponding to $C_{18}H_{33}O_6S^-$ could be a cyclic organosulfate. The corresponding MS^2 spectrum (Figure S1) shows peaks at m/z 63.962, m/z 79.957 and m/z 96.960, corresponding to the loss of SO_2^-, SO_3^-, and HSO_4^- respectively. A similar fragmentation with the loss of SO_3^- (m/z 79.957) was also observed for dimethyl 2,3-*O*-

---

[*] Dr. M. Passananti, Dr. Y. Dupart, Dr. S. Perrier, Dr. C. George
IRCELYON, Institut de recherches sur la catalyse et l'environnement de Lyon, Université Lyon 1, CNRS, UMR 5256
2 avenue Albert Einstein, 69626 Villeurbanne (France)
E-mail: christian.george@ircelyon.univ-lyon1.fr

Dr. L. Kong, Prof. J. Chen
Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention, Department of Environmental Science and Engineering
Fudan University, Shanghai (China)

Dr. J. Shang
State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering
Peking University, Beijing, 100871 (P.R. China)

Prof. D. J. Donaldson
Department of Chemistry, University of Toronto
80 St. George St., Toronto, ON M5S 3H6 (Canada)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201605266.

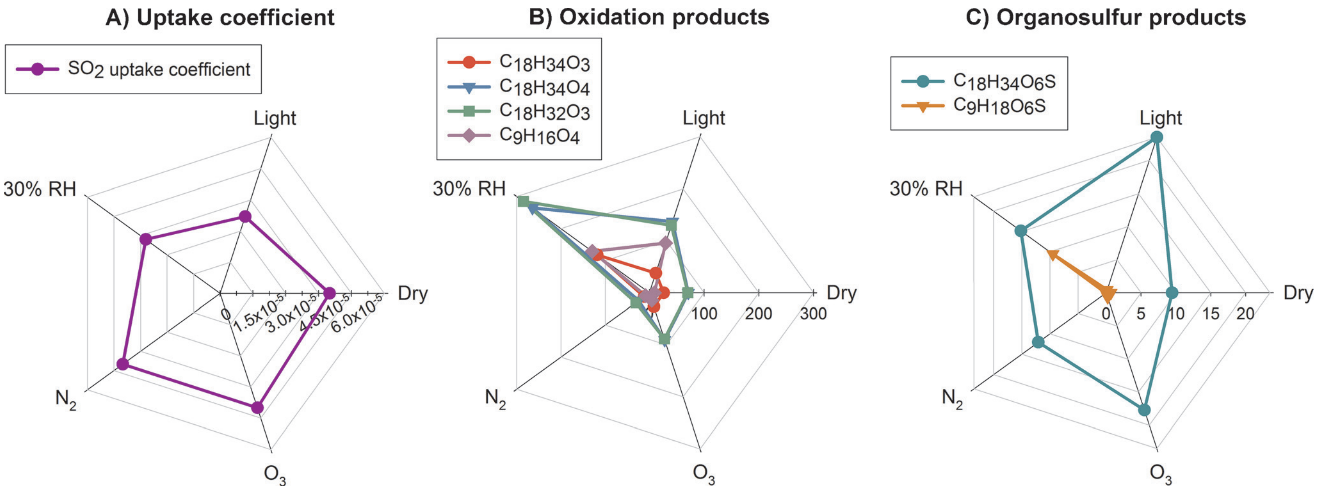
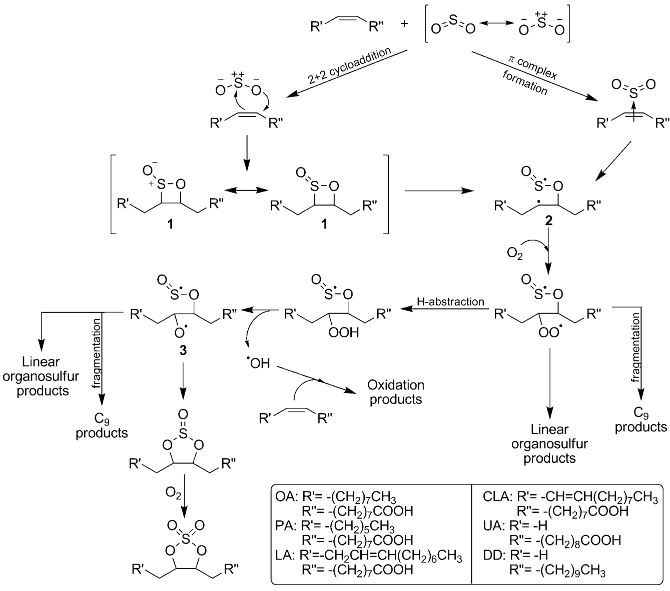


Figure 1. Radial plots that describe the results obtained for the exposure of the OA film to SO_2 in the CFT. The dark lines that cross the vertices of each pentagon represent the different experimental conditions, the distance of the points from the center of the pentagon represent the magnitude of the described quantity. OA films were exposed at 20 °C to 40 ppb of SO_2 under the following conditions: dry synthetic air (dry), nitrogen (N_2), dry synthetic air with 115 ppb of O_3 (O_3), synthetic air with 30% RH (30% RH) and synthetic air with 30% RH under UV/Vis irradiation (light). (A) shows the SO_2 uptake coefficients on OA. (B, C) show the data for the oxidation (B) and organosulfur (C) products formed upon exposure of the OA film to SO_2. The distance from the center of the pentagon represents the ratio (of the peak areas) between the product and OA.

sulfonyl-L-tartrate used as a standard cyclic organosulfate (Figure S2). By contrast, the linear organosulfate product detected at m/z 253.075 ($C_9H_{17}O_6S^-$) undergoes fragmentation with the loss of HSO_3^- (m/z 80.965; Figure S3).

We also carried out the reaction in a DRIFT cell in order to observe the double bond signal decay and product formation in situ during the reaction. The sensitivity of DRIFT is low compared to that of MS, therefore we had to increase the SO_2 concentration and the reaction time to 280 min. The infrared (IR) spectra indeed showed the decrease of the peak at 3007 cm^{-1} (corresponding to the C=C−H bond of OA) and an increase of features between 800 and 700 cm^{-1}, which could correspond to organosulfate and cyclic organosulfate functions (Figure S4). In order to investigate the SO_2 addition to the C=C bond under atmospheric conditions (in dispersed aerosols, as opposed to the macroscopic surfaces described above), we used an AFT to expose OA particles to SO_2, light, and SO_2 with light. The particles were then collected and analyzed by LC-HR-MS. During the reaction, the particle size distribution was observed to be constant. Some oxygenated products were observed under all the different conditions (Figure S5). Sulfur-product analysis shows the formation of the same organosulfur derivatives both in the presence and absence of light (Figure S6). In the presence of light the formation of organosulfur products increase and the major product detected is $C_{18}H_{34}O_6S$, as observed in the CFT. These results indicate that light can catalyze the addition of SO_2 to the double bond.

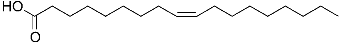
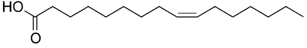
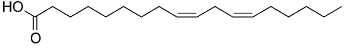
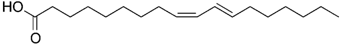
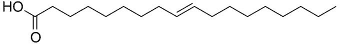
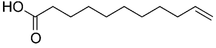
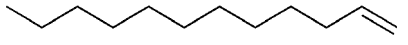
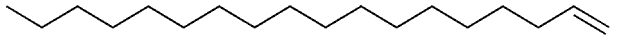
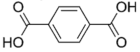
The reaction mechanism may involve the interaction of SO_2 with the double bond through a [2+2] cycloaddition, leading to a four-membered ring (**1**; Scheme 1). This species is high strained and could evolve into a diradical (**2**) by homolytic cleavage of S−C bond or through a π interaction between SO_2 and the C=C bond. SO_2 is known to form such π complexes with alkenes; these complexes can absorb UV/Vis light depending on the double bond substitutions, giving rise to the observed photoactivation.[4] Under irradiation, the SO_2 triplet state could be also involved, but is difficult to discern between the two pathways. The intermediates **1** and **2** have been previously proposed in the photosulfoxidation of alkenes and lead to formation of cyclic organosulfites.[5] The diradical **2** could also interact with oxygen to start a radical chain reaction. Radical-initiated H-abstraction, OH• production, and chain fragmentation could then lead to the oxygenated and C_9 products detected by LC-HR-MS. The intramolecular recombination of radicals in the intermediate **3** could form cyclic organosufites that could undergo oxidation to result in more stable cyclic organosulfates.



Scheme 1. Proposed mechanisms for reactions between SO_2 and unsaturated compounds.

In order to generalize this reaction, we tested the reactivity of other unsaturated compounds with SO_2 in the CFT. The compounds used and the corresponding SO_2 uptake coefficient measured are reported in Table 1. As expected,[6] the aromatic ring in terephthalic acid is not reactive. A significant difference in reactivity is observed between unsaturated acids and alkenes (1-octadecene and 1-dodecene), thus suggesting that the acid function may catalyze the reaction, as proposed previously.[3]

Table 1: SO_2 uptake coefficient on studied molecules, their molecular structure, their melting points, and the nature the of double bond.

Compound	Double bond	Melting point [°C]	γ_{SO_2} [$\times 10^{-6}$][a]
Oleic acid (OA) 	*cis*	13–14	5.0 ± 0.5
Palmitoleic acid (PA) 	*cis*	0.5	1.4 ± 0.1
Linoleic acid (LA) 	*cis* and *cis*	-5	3.0 ± 0.3
Conjugated linoleic acid (CLA) 	conjugated *cis*–*trans*	-12	5.5 ± 0.5
Elaidic acid (EA) 	*trans*	42–44	0.10 ± 0.03[b]
10-Undecenoic acid (UA) 	terminal	23–25	0.85 ± 0.05 [c]
1-Dodecene (DD) 	terminal	-35	0.08 ± 0.01
1-Octadecene (OD) 	terminal	14–16	0.21 ± 0.01
Terephthalic acid (TA) 	aromatic	>300	not reactive

[a] Experimental conditions: 40 ppb of SO_2 in dry synthetic air, flow rate = 300 mL min^{-1}, $T = 293$ K. [b] This uptake was measured under 35 % of RH. [c] This uptake was measured at $T = 298$ K.

Terminal double bonds seem to be less reactive than internal bonds, but among the internal bonds the difference in reactivity between *cis* and *trans* is not so clear. Comparing the reactivity of linoleic acid (LA; two *cis* bonds) and conjugated linoleic acid (one *cis* and one *trans* bond), the reactivity of the latter is slightly higher. This difference may be explained by the possibility that SO_2 could react with conjugated double bonds through hetero-Diels–Alder and cheletropic additions.[7] The large difference between the measured SO_2 uptake on OA and eliadic acid (EA) is probably due to the different physical states of these compounds: OA is a liquid at room temperature and EA is a solid. The uptake coefficients of SO_2 on OA, LA, and 1-octadecene (OD) were measured in the temperature range between 5 and 25 °C (Figure 2). The SO_2 uptake drastically decreased when the compounds were in the solid phase. Therefore, viscosity could be also an important parameter; nevertheless there is no clear correlation between SO_2 uptake and the viscosity of the organic compound (Figure S7). The reactivity could depend on several factors: the nature of the double bond (*cis*, *trans*, etc.), the physical state (liquid, solid) and the viscosity of the reactants.

The fate of SO_2 in the atmosphere is generally modeled by considering only its multiphase oxidation that leads to the production of sulfuric acid, which contributes to particle formation and atmospheric acidity, and is efficiently taken up by various surfaces such as mineral dust or black carbon.[8] The reactive uptake of SO_2 by unsaturated organic compounds has not been taken into account to date. We have shown that SO_2 reacts with a variety of unsaturated compounds, and that even in the presence of ozone, SO_2 reacts with OA to form organosulfur products. A strong enhancement in product formation is observed under actinic illumination, and increases the atmospheric significance of this chemical pathway. This behavior is probably due to the chromophoric nature of the SO_2 adduct with $C{=}C$ bonds, and means that the contribution of this direct addition of SO_2 could even be more significant than the limit reported by Shang et al.,[3] of up to 3.3 %, which can now be interpreted as a lower limit. The detection in atmospheric aerosols of organosulfur compounds with the same chemical formulae as the products identified here (the list of these products is reported in the Supporting Information) seems to confirm the importance of this reaction in the atmosphere.[9]

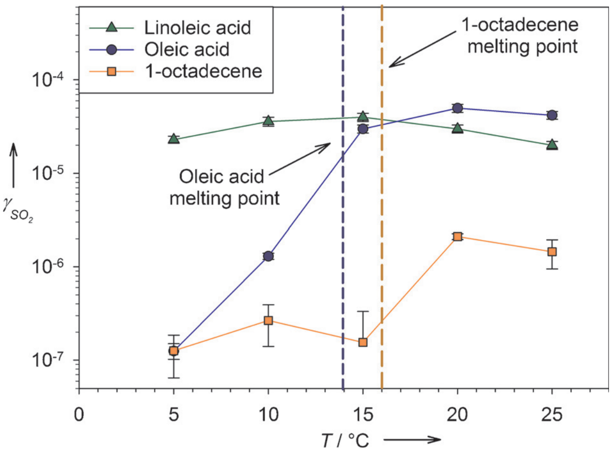


Figure 2. SO_2 uptake coefficient on LA, OA, and OD films measured at different temperatures. Experimental conditions: 40 ppb of SO_2 in dry synthetic air, flow rate = 300 mL min^{-1}.

Experimental Section

Detailed experimental procedures are provided elsewhere[3,10] and in the Supporting Information; the general conditions are summarized here. The experiments in the CFT were conducted using a glass tube coated on the inner wall with the pure organic product for analysis. The SO_2 flow was monitored at the outlet, allowing the determination of the γ_{SO_2}. The AFT experiments were carried out in a horizontal Pyrex double-wall aerosol flow tube. The OA particles were generated by atomizing an OA solution. The particles were collected on a filter at the flow tube outlet. The experiments in the DRIFT cell were carried out by flowing SO_2 in synthetic air through the sample. The samples were prepared by OA dispersion on glass beads.

Acknowledgements

This study was supported by the Agence Nationale de la Recherche through the COGNAC grant (ANR-13-BS06-0002-01), the Marie Curie International Research Staff Exchange project AMIS (Grant 295132), and the European Research Council under the European Union's Seventh Framework Programme (FP/2007–2013)/ERC Grant Agreement 290852-AIRSEA.

Keywords: aerosols · alkenes · atmospheric chemistry · organosulfates · sulfur dioxide

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 10336–10339
Angew. Chem. **2016**, *128*, 10492–10495

[1] M. Sipila, T. Berndt, T. Petaja, D. Brus, J. Vanhanen, F. Stratmann, J. Patokoski, R. L. Mauldin, A.-P. Hyvarinen, H. Lihavainen, M. Kulmala, *Science* **2010**, *327*, 1243.
[2] Y. Lan, S. E. Wheeler, K. N. Houk, *J. Chem. Theory Comput.* **2011**, *7*, 2104.
[3] J. Shang, M. Passananti, Y. Dupart, R. Ciuraru, L. Tinel, S. Rossignol, S. Perrier, T. Zhu, C. George, *Environ. Sci. Technol. Lett.* **2016**, *3*, 67.
[4] D. Booth, F. S. Dainton, K. J. Ivin, *Trans. Faraday Soc.* **1959**, *55*, 1293.
[5] P. W. Jones, A. H. Adelman, *Tetrahedron* **1974**, *30*, 2053.
[6] D. H. Stedman, H. Niki, *Environ. Lett.* **1973**, *4*, 303.
[7] D. Suarez, T. L. Sordo, J. A. Sordo, *J. Org. Chem.* **1995**, *60*, 2848.
[8] I. Faloona, *Atmos. Environ.* **2009**, *43*, 2841.
[9] a) B. Y. Kuang, P. Lin, M. Hu, J. Z. Yu, *Atmos. Environ.* **2016**, *130*, 23; b) X. K. Wang, S. Rossignol, Y. Ma, L. Yao, M. Y. Wang, J. M. Chen, C. George, L. Wang, *Atmos. Chem. Phys.* **2016**, *16*, 2285.
[10] Y. Dupart, S. M. King, B. Nekat, A. Nowak, A. Wiedensohler, H. Herrmann, G. David, B. Thomas, A. Miffre, P. Rairoux, B. D'Anna, C. George, *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 20842.

Received: May 30, 2016