

Atmos. Chem. Phys. Discuss., author comment AC1 https://doi.org/10.5194/acp-2022-13-AC1, 2022 © Author(s) 2022. This work is distributed under the Creative Commons Attribution 4.0 License.

## **Reply on RC1**

Haoyu Jiang et al.

Author comment on "Formation of organic sulfur compounds through SO<sub>2</sub>-initiated photochemistry of PAHs and dimethylsulfoxide at the air-water interface" by Haoyu Jiang et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-13-AC1, 2022

This is an interesting and new submission investigating the formation of organic sulfur compounds through the SO2 initiated (photo)chemistry of PAHs and DMSO at the airwater interface. A series of advanced analytical tools are employed to identify the products of these chemical interactions. This study is in line with previous investigations of the same group.

The fact that SO2 and/or PAHs could trigger photochemistry at the air/water interface is a topic that certainly falls with the scope of ACP, this is why I would certainly recommend the publication of this manuscript once the authors have dealt with the comments below.

## We would like to thank the reviewer for the constructing and encouraging comments.

While the title stresses the photochemical aspects of the chemistry presented, the actual text is a bit vague about the importance or not of the dark chemistry during the experiments (some figures in the SI points towards some active dark chemistry as well which is finally quite surprising for the poly-aromatic compounds). The same comment applies to the relative importance of the photochemistry of SO2 and PAHs. The text mentions that the SO2 dominates but pathway B stresses another possibility. It would be helpful if the authors could elaborate more on the relative importance of each pathway to avoid any confusion for the reader.

The reviewer is right that SO<sub>2</sub> reaction with PAHs/DMSO in absence of light can lead to the formation of product compounds. In dark, SO<sub>2</sub> can form  $\pi$  complexes with C=C bonds of PAHs upon ring opening which may undergo transformation to diradical organosulfur intermediates which in turn upon reaction with dissolved O<sub>2</sub> can lead to production of reactive oxygen species (ROS) such as OH radical. (Shang et al., 2016) These  $\pi$  complexes can absorb UV/Vis light depending on the double bond substitutions, leading to photoactivation and formation of product compounds (Passananti et al., 2016). The formation of diradical organosulfur intermediates and ROS have been suggested for reactions of SO<sub>2</sub> with alkenes and fatty acids (Shang et al., 2016, Pasananti et al., 2016), but here we suggest that the same mechanism may occur for the reaction of SO<sub>2</sub> with PAHs. While the SO<sub>2</sub> addition to the C=C bond would be responsible for the organic sulfur compounds, the CHO oxidation products could be explained by radical chain reactions triggered by ROS (Shang et al., 2016, Passananti et al., 2016) Additionally, the photosensitized degradation of DMSO initiated by excited triplets of PAHs can explain the formation of CHOS and CHO compounds. However, it is difficult to distinguish which mechanism is prevalent in the environment. Here, we suggest a mechanism that  $SO_2$  may indeed proceed on PAHs by  $SO_2$  addition on C=C bonds and it is supported by theoretical calculations of the reaction Gibbs energies, based on the information obtained from the detected tentative products. We show however, that under our experimental conditions,  ${}^3SO_2*$  oxidation of PAHs would prevail over PAH photodegradation and would lead to sulfur-containing PAHs. In this study highest number of observed CHOS compounds was observed upon reaction of  $SO_2$  with PAHs/DMSO highlighting the importance of the involved  $SO_2$ .

We added the following paragraph in the revised version of the manuscript including the cited papers:

"Alternatively, SO<sub>2</sub> can form  $\pi$  complexes with C=C bonds of PAHs upon ring opening, which may undergo transformation to diradical organosulfur intermediates which in turn can react with dissolved O<sub>2</sub> leading to production of reactive oxygen species (ROS) such as OH radical. (Shang et al., 2016) The formation of diradical organosulfur intermediates and ROS have been suggested for reactions of SO<sub>2</sub> with alkenes and fatty acids (Shang et al., 2016, Passananti et al., 2016), but here we suggest that the same pathway may occur for the reaction of SO<sub>2</sub> with PAHs. While the SO<sub>2</sub> addition to the C=C bond would be responsible for the OSs, the CHO oxidation products could be explained by radical chain reactions triggered by ROS (Shang et al., 2016, Passananti et al., 2016)"

If excited SO2 would create some OH radicals in the liquid phase it would certainly be scavenged by DMSO due to its very high concentration (it is used as cosolvent), with little interplay with the PAH photochemistry. In other, is there any synergy between PAH and SO2 or are the experiments looking at the PAH/DMSO and SO2/DMSO chemistry with finally no interaction.

The excited triplet of  $SO_2({}^3SO_2*)$  can form OH radical as suggested by Martins-Costa et al., 2018 and Kroll et al., 2018

 ${}^{3}SO_{2}* + H_{2}O \square OH + HOSO$ 

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Alternatively, OH radicals can be also formed without assistance of light. Namely, SO<sub>2</sub> can form  $\pi$  complexes with C=C bonds of PAHs which may undergo transformation to diradical organosulfur intermediates which react with dissolved O<sub>2</sub> leading to formation of reactive oxygen species (ROS) such as OH radical. (Shang et al., 2016) While the SO<sub>2</sub> addition to the C=C bond would be responsible for the CHOS, the CHO oxidation products could be explained by radical chain reactions triggered by ROS (Shang et al., 2016, Passananti et al., 2016)

The reviewer is right that there is a high probability that OH is scavenged by DMSO due to its high concentration but the observed CHO compounds point out to the implication of ROS, thus OH radical in their formation through oxidation of PAHs.

We added the following paragraph to clarify this:

"Alternatively, SO<sub>2</sub> can form  $\pi$  complexes with C=C bonds of PAHs upon ring

opening, which may undergo transformation to diradical organosulfur intermediates which in turn can react with dissolved  $O_2$  leading to production of reactive oxygen species (ROS) such as OH radical. (Shang et al., 2016) The formation of diradical organosulfur intermediates and ROS have been suggested for reactions of SO<sub>2</sub> with alkenes and fatty acids (Shang et al., 2016, Passananti et al., 2016), but here we suggest that the same pathway may occur for the reaction of SO<sub>2</sub> with PAHs. While the SO<sub>2</sub> addition to the C=C bond would be responsible for the OSs, the CHO oxidation products could be explained by radical chain reactions triggered by ROS (Shang et al., 2016, Passananti et al., 2016)"

Finally, more experiments are need to clarify which mechanism would be prevalent in the real-life environment.

The chemical scheme involving PAH is not fully clear to the reviewer, as it seems that S(IV) is oxidized to S(VI) without any real explanation.

We supplemented the oxidation pathway in the Scheme 1 and added the following sentence to clarify this:

"The S(IV) in sulfite group of  $C_{10}H_6O_3S$  (10) would first undergo oxidation by the strong oxidizing agents in the system to result in more stable S(VI) in  $C_{10}H_8O_3S$  (12)."

Also, section 3.2 mixes some discussion on the actual results and the atmospheric context of the study. Some reediting here would certainly help the reader.

## We shifted one part (atmospheric context) of the discussion in section 3.2 to the section "Atmospheric Implications" (see revised version of the manuscript).

Finally, while this reviewer recognizes the need to perform such experiment at high concentrations. The observations made here cannot directly be used for realistic outdoors conditions. Therefore, some discussions on how to extrapolate these finding to authentic atmospheric conditions would beneficial for the manuscript.

## We are currently estimating the importance of the suggested chemistry here under environmentally relevant conditions. We added the following paragraph in the section "Atmospheric Implications":

"Based on the observed emission rates of OSs in this study, we estimate emission fluxes of MSA, and MSIA, among others, considering realistic environmental conditions, SO<sub>2</sub> mixing ratios ranging between 2 ppb and 50 ppb, surface UV-VIS irradiation, surface microlayer coverage with PAHs/DMSO, and surface wind speeds, (Brüggemann et al., 2018) to account the potential impact of the heterogeneous SO<sub>2</sub> (photo)chemistry with PAHs/DMSO, on the aerosol production in marine boundary layer, which results will be published elsewhere."