

CC1: 'Comment on acp-2021-58', Krzysztof Rudzinski, 09 Feb 2021

The authors thank Krzysztof Rudzinski for his active contribution in the review process and his comments which helped to improve the manuscript. In the following, we provide a response to your comment. Comments by the reviewer are given in black normal font, and our response to the comments is shown in blue. Newly added and modified text in the revised manuscript and supporting information (SI) is given in *italics*.

CC1-C1: This is a very interesting paper tackling an important aspect of atmospheric chemistry.

I would like to draw the authors' attention to our paper on isoprene oxidation coupled with manganese catalyzed autoxidation of sulfite (1), which is matching section 4.4. That paper shows the influence of acidity on the rate of autoxidation and on the rate of isoprene conversion based on experimental observation and detailed kinetic modelling. The kinetic model used includes autoxidation of Mn(II), autoxidation of S(IV) catalyzed by Mn and oxidation of isoprene. It explains the observed influence of pH on the reactions (with and without isoprene present) better than empirical rate equations shown in section 4.4.

Our another paper (2) describes the aqueous-phase transformation of isoprene in the presence of HONO. Also in this case the acidity of solutions had significant effect on the isoprene conversion demonstrated by experiments and explained by a model. However, in this case the role of acidity was simple - conversion of isoprene required undissociated HONO present.

The authors might consider using the quoted papers as a minor illustration to their valuable lecture. with best regards

Krzysztof J. Rudziński

(1) Rudziński KJ, Gmachowski L, Kuznietsova I (2009) Reactions of isoprene and sulphony radical-anions – a possible source of atmospheric organosulphites and organosulphates *Atmos Chem Phys* 9:2129-2140 doi:10.5194/acp-9-2129-2009

(2) Rudziński KJ, Szmigielski R, Kuznietsova I, Wach P, Staszek D (2016) Aqueous-phase story of isoprene – A mini-review and reaction with HONO *Atmos Environ* 130:163-171 doi:http://dx.doi.org/10.1016/j.atmosenv.2015.12.027

CC1-R1: According to the posted comment, we have cited the work of Dr. Rudziński on the S(IV) oxidation catalyzed by Mn(II) in section 4.4. The other mentioned publication (reference 2) has not been included as the indirect pH-dependency results just from the presence of HONO/NO₂⁻ under different acidity conditions.

"A detailed discussion of the mechanisms can be found in Brandt and van Eldik (1995) and Rudziński et al. (2009)".

References:

Brandt, C., and van Eldik, R.: Transition-Metal-Catalyzed Oxidation of Sulfur(IV) Oxides - Atmospheric-Relevant Processes and Mechanisms, *Chem. Rev.*, 95, 119-190, <https://doi.org/10.1021/cr00033a006>, 1995.

Rudziński, K. J., Gmachowski, L., and Kuznietsova, I.: Reactions of isoprene and sulphony radical-anions – a possible source of atmospheric organosulphites and organosulphates, *Atmos. Chem. Phys.*, 9, 2129-2140, <https://doi.org/10.5194/acp-9-2129-2009>, 2009.