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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Effects of NO_2 and C_3H_6 on the heterogeneous oxidation of SO_2 on TiO_2 in the presence or absence of UV irradiation" *by* Biwu Chu et al.

Anonymous Referee #1

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This manuscript describes a set of experiments looking at the effects of UV radiation, NO2, and C3H6 on heterogeneous SO2 oxidation. The authors demonstrate that on TiO2 aerosols the presence of NO2 alone or NO2 and C3H6 can suppress sulfate formation when in the presence of UV light. The authors also show that in dark conditions NO2 alone or NO2 and C3H6 can increase heterogeneous sulfate formation, but that the presence of C3H6 decreases heterogeneous sulfate formation compared to heterogeneous sulfate formation with NO2 only. That the presence of VOCs may suppress sulfate formation is an interesting and little focused on point. The authors need to add a bit more of a discussion of why they interpret their experiments as supporting their proposed mechanism. For example, the authors suggest that the presence of

C3H6 inhibited heterogeneous sulfate formation with NO2 by competing with SO2 for reactive oxygen species or active sites on the aerosol. It is not clear to readers how the authors reach this particular conclusion. The authors mention that the presence of NO2 induced the generation of reactive oxygen species, but the mechanism behind this is never satisfactorily explained. It is also unclear if the authors are saying that C3H6 competes with SO2 or with NO2 for active sites on the aerosol. A more detailed discussion of the mechanism behind the 'dark' oxidation of SO2 in the presence of NO2 and identifying the points in that mechanism in which C3H6 interferes could help clarify these issues. There are also some other outstanding issues listed below. Nevertheless, the key point that VOCs may suppress heterogeneous sulfate formation in dark conditions is a very important one. Altogether, the manuscript requires some important revisions before publication in ACP.

Other general comments:

1. The authors need to better explain why TiO2 is a good compound for approximating the heterogeneous oxidation of SO2 on mineral dust aerosols. The authors mention 4 studies using different types of mineral oxides (line 21 page 2). What were the differences between these studies attributable to the different mineral oxide used? Why did the authors in this study choose TiO2 instead of CaO, a-Fe2O3 or MgO, when calcium, magnesium, and iron are usually a much larger portions of mineral dust? What do the authors anticipate the effect of using different mineral oxides would be on their experiments?

2. Similar to the point in comment 1, the authors should elaborate further why propene was selected as a representative VOC. What evidence is there that propene is representative of different VOCs? How might the type of VOC used affect results?

3. As the authors are likely aware, it has also been proposed that a significant sulfate formation pathway for Chinese winter haze is heterogeneous oxidation of SO2 by NO2 (e.g. Wang et al., 2016; Cheng et al., 2016). The authors need to demonstrate that

this reaction is not significant in their experiments. This could be done by showing how NO_2 changes along with SO_2 in their experiments. In the proposed mechanism of the authors, NO_2 acts as a catalyst and therefore concentrations should not change. In the alternative mechanism NO_2 is the oxidizing agent and therefore should be depleted along with SO_2 as sulfate forms. If it turns out this other reaction is significant, this should be accounted for.

Wang, G., Zhang, R., Gomez, M. E., Yang, L., Zamora, M. L., Hu, M., et al. (2016). Persistent sulfate formation from London Fog to Chinese haze. Proceedings of the National Academy of Sciences, 113(48), 13630–13635. https://doi.org/10.1073/pnas.1616540113

Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., Wang, Z., et al. (2016). Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China. Science Advances, 2(12), e1601530. https://doi.org/10.1126/sciadv.1601530

4. The concluding paragraph of the introduction has multiple sentences that are oddly phrased.

5. In the IC section of the methods, what column type was used? Moch et al., 2018 found that certain IC column types could easily separate hydroxymethanesulfonate (HMS) and sulfate and others could not. Since the author's method involves adding a 1% formaldehyde solution to the samples, this would create HMS and possible an artifact in the IC measurements depending on the column type. Additionally, the authors mention that CH_2O was observed when the surface was exposed to NO_2 and C_3H_6, which might also indicate HMS formation

Moch, J. M., Dovrou, E., Mickley, L. J., Keutsch, F. N., Cheng, Y., Jacob, D. J., et al. (2018). Contribution of Hydroxymethane Sulfonate to Ambient Particulate Matter: A Potential Explanation for High Particulate Sulfur During Severe Winter Haze in Beijing. Geophysical Research Letters, 45(21), 11,969-11,979. https://doi.org/10.1029/2018GL079309

6. Many parts of the Results and Discussion section are better suited for placement in the methods section (e.g. the first and third sentence of section 3.1.1, large parts of the first paragraph of 3.3, etc.). The authors should consider moving sentences that describe how the experiments were conducted to the methods section and focus only on the results in the results section.

Other comments:

1. Line 12 on page 2 says that "SO_2 can be irreversibly converted into sulfite, bisulfite or sulfate." This is incorrect for sulfite and bisulfite. Even if the particular conditions of the particle mean that sulfite or bisulfite are stable, if conditions change the SO_2-HSO_3^-–SO_3^{2-} equilibrium can shift and the authors should therefore avoid the use of the word "irreversibly" as applied to HSO_3^- and SO_3^{2-} formation.

2. Line 14 on page 2 says the authors say "low concentrations (200 ppb)." Was this a typo and the authors meant to write ppt? If not and the authors may mean low for a laboratory setting, but this type of phrasing could be confusing to non-laboratory scientists who may be interested in the author's work since atmospheric propene concentrations are rarely more than a couple of ppb. Later the authors say they used pollutants are "close to ambient concentration" (line 28 page 8), but 200 ppb NO_2 and SO_2 is much higher than ambient concentrations of these pollutants even during the extremely severe winter haze in Beijing. The authors should either include reference values for the concentrations of these gases in the laboratory compared to the atmosphere, or drop the use of "low concentrations" or "ambient" all together.

3. Line 18 on page 2 regarding states "NO_2 was proposed to act as a catalyst to activate O_2 in the oxidation." This was a bit confusing, but I assume this means that the authors mean NO_2 catalyzed the oxidation of SO_2 by O_2. If that is correct the authors should change the sentence. Since there is also the heterogeneous oxidation of SO_2 by NO_2, the author be sure to clarify when the mechanisms involving NO_2 they are referring to have SO_2 oxidized by O_2 and catalyzed by NO_2 or have SO_2 oxidized

by NO_2. I believe in most instances the authors are referring to the former reaction (i.e. catalyzed by NO_2 and oxidized by O_2).

4. With regards to the formation of hydroxymethanesulfonate (line 26-27 page 2), it would be appropriate for authors to also cite Moch et al., 2018 (referenced above) which also proposed the reaction of CH_2O and sulfite/bisulfite in northern China winter haze.

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