

Interactive comment on “Effects of NO₂ and C₃H₆ on the heterogeneous oxidation of SO₂ on TiO₂ 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

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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, α-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

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this reaction is not significant in their experiments. This could be done by showing how NO₂ changes along with SO₂ in their experiments. In the proposed mechanism of the authors, NO₂ acts as a catalyst and therefore concentrations should not change. In the alternative mechanism NO₂ is the oxidizing agent and therefore should be depleted along with SO₂ 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 CH₂O was observed when the surface was exposed to NO₂ and C₃H₆, 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>

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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 “SO₂ 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 SO₂-HSO₃⁻-SO₃²⁻ equilibrium can shift and the authors should therefore avoid the use of the word “irreversibly” as applied to HSO₃⁻ and SO₃²⁻ 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 NO₂ and SO₂ 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 “NO₂ was proposed to act as a catalyst to activate O₂ in the oxidation.” This was a bit confusing, but I assume this means that the authors mean NO₂ catalyzed the oxidation of SO₂ by O₂. If that is correct the authors should change the sentence. Since there is also the heterogeneous oxidation of SO₂ by NO₂, the author be sure to clarify when the mechanisms involving NO₂ they are referring to have SO₂ oxidized by O₂ and catalyzed by NO₂ or have SO₂ oxidized

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by NO₂. I believe in most instances the authors are referring to the former reaction (i.e. catalyzed by NO₂ and oxidized by O₂).

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 CH₂O and sulfite/bisulfite in northern China winter haze.

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