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Interactive comment on "Aqueous phase oxidation of bisulfite influenced by nitrate photolysis" *by* Lu Chen et al.

Anonymous Referee #1

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Chen et al. investigated the formation of sulfate by nitrate photolysis in aqueous solutions. They also examined the effects of the presence of halides on sulfate formation. Nitrate photolysis has recently been proposed as one of the potential missing routes of sulfate formation (Gen et al., 2019ab). The major issue is the novelty of the work and it advances our understanding in light of the available literature. Gen et al. (2019ab) presented results of sulfate formation by nitrate photolysis in droplets upon uptakes of SO2, at 254 and 300 nm respectively. While the experimental approaches are slightly different, these papers essentially work on the same problem as the current ms. In addition, Zhang et al. (2020) also investigated the effect of halide ions on sulfate production rate during nitrate photolysis. They investigated the halide-induced enhancement of nitrate photolysis and potential halogen chemistry on sulfate formation, and

then concluded that halogen chemistry has little effect on sulfate formation compared to halide-induced enhancement of nitrate photolysis in particles. It is a natural expectation that the current ms needs to compare their results with the latest literature. As is the paper presents some interesting results but needs to improve on comparison with the literature results to identify substantiated scientific conclusions and key areas of discrepancies for future research. Furthermore, many discussions are somewhat qualitative, especially in the comparison of experiments done by themselves and others. More quantitative descriptions and comparison of the experimental conditions to go with the result discussions are needed. The interpretation of results without detailed examination of differences in experimental conditions could be erroneous.

1. Line 148: what are the light intensity and wavelength range of the Xe lamp? How is it compared to the 313-nm lamp? Discussions of experimental results should include the light source comparison.

2. Line 158 – 163: Again, please clarify the wavelength range of Xe lamp. ONOO- is one of the important photoproducts at wavelength below 290-nm. If wavelength range of Xe lamp falls in the longer wavelength, OH radical produced via HOONO decomposition may not be important. For example, Goldstein and Rabani observed no ONOO- formation during 300nm illumination (φ (ONOO-) < 0.2%) and Benedict et al. suggested that no ONOO- was observed at environmentally relevant wavelengths. In addition, it should be noted that ONOO- can undergo a rapid isomerization to nitrate at pH<6. As a result, ONOO- may not be an important product since pH is below 6 in the current study.

3. Line 177: Can the authors do more to identify which species is most important in the sulfate formation? I would suggest that they conduct a kinetic analysis to identify the contributions of different pathways to sulfate production.

4. Line 186: The authors concluded that nitrate itself can directly oxidize bisulfite by comparing S2 with S3. Kong et al. proposed that nitrate can oxidize sulfate on

hematite, but it does not mean that nitrate can do the same aqueous phase.

5. Line 195 – 198: Zheng et al. (2020) recently incorporated nitrate photolysis pathway into WRF-CMAQ, they found that nitrate photolysis pathway can explain about 15% (assuming an enhancement factor (EF) of 10) to 65% (assuming EF = 100) of the gaps between model estimations and observation in sulfate concentration during winter haze in Beijing. It is one of the very few papers which explicitly examines the role of nitrate photolysis in haze formation and should be cited. The authors in the current ms emphasize quite a bit that the results are consistent with others, including their own previous work, in a qualitative manner. With all these previous works including those already in the references of the current ms, this work needs to attempt to provide more quantitative analysis.

6. Line 200 - 211: Addition of (NH4)2SO4 or NH4HSO4 can adjust the pH but it can also affect other properties such as ionic strength. How would the authors confirm that other factors are not important? Gen et al. (2019) also investigated the effect of pH on SO2 uptake coefficient. They found that the SO2 uptake coefficient is not sensitive to initial pH and they attributed it to the similar stable final pH even with different initial pH values. Have the authors measured solution pH as the reaction took place? Variation of pH during the reaction may also affect sulfate production rate. Authors should also investigate a slightly higher pH too (e.g., 5 or 6). Such pH falls in the typical pH range during the haze events in China.

7. Line 246 – 249: Please refer to Figure 4a and 4b in Gen et al. (2019), their results also suggested that sulfate formation rate during NH4NO3 photolysis is slightly higher than that during NaNO3 photolysis. The type of cation has little influence on the quantum yield of nitrate photolysis, but it does not necessarily mean that the sulfate yield is comparable regardless of type of cations. As authors suggested in the main text, NH4+ may play a role in the sulfate formation.

8. Line 263 – 265: Low pH is favorable to the formation of HONO, but the presence

of NH3 will increase pH. Any suggestion why the presence of NH3 can promote the hydrolysis of NO2 and induce the explosive growth of HONO?

9. Line 287 – 289: Have the authors conducted experiments in the absence of NH4NO3, i.e., compared Dark+O2 with 2-propanol+ Dark+O2, which is a direct way to investigate the role of O2 in sulfate formation.

10. Line 291 – 293: It is not clear what the authors would like to prove. The role of O2 in the direct oxidation of HSO3- by nitrate? Or just want to show the direct oxidation of HSO3- by O2? Please clarify the role of O2 in the presence and absence of irradiation.

11. Line 297 - 303: How is O2 related to the OH formation from nitrate photolysis? Gen et al. (2019) did not present that OH generation from nitrate photolysis requires O2. The statement presented in Gen et al. is that oxidation of dissolved SO2 by OH radicals requires O2. Again, it would be useful to compare the contribution of NO2 pathway, NO2- pathway and OH pathway to sulfate formation? Gen et al. (2019) found that direct oxidation of dissolved SO2 by NO2- is an efficient pathway for sulfate formation.

12. Line 309 – 314: In the presence of O2, O(3P) will react with O2 to produce O3. As displayed in the Figure 1a, a larger difference between S1 (NH4NO3+Light+Air) and S4 (NH4NO3+Light+N2) may be also attributed to the O3 pathway.

13. Line 329: Figure S2 is the “First-order photodegradation of 2NB under 313 nm UV irradiation”. The trend of H2O2 concentration should be in Figure 6. Please revise.

14. Line 331 – 334: It should be noted that reaction of O3 with OH can produce HO2. Hence, there is no strong evidence to conclude that H2O2 is owing to the recombination of OH.

15. Line 352 – 353: Figure S5 shows that the sulfate production rate under 100 mW/cm2 is comparable to that in 50 mW/cm2. Any suggestions?

16. Line 355: Zhang et al. (2020) found that sulfate production rate will be enhanced

during nitrate photolysis in the presence of halide ions. And they suggested that presence of halide ions can enhance nitrate photolysis, as a result, more oxidants will be produced from nitrate photolysis, which will promote sulfate formation further. While the halide related reactions are possibilities, have the authors conducted any simulation to investigate if enhanced sulfate production is attributed to the enhanced nitrate photolysis? In Zhang et al. (2020) halogen chemistry was included in their box modeling and was not found to play an important role in the enhanced sulfate production.

Reference: Gen, Masao, et al. "Heterogeneous SO2 oxidation in sulfate formation by photolysis of particulate nitrate." Environmental science & technology letters 6.2 (2019a): 86-91.

Gen, Masao, et al. "Heterogeneous Oxidation of SO2 in Sulfate Production during Nitrate Photolysis at 300 nm: Effect of pH, Relative Humidity, Irradiation Intensity, and the Presence of Organic Compounds." Environmental science & technology 53.15 (2019b): 8757-8766.

Goldstein, S.; Rabani, J. Mechanism of Nitrite Formation by Nitrate Photolysis in Aqueous Solutions: The Role of Peroxynitrite, Nitrogen Dioxide, and Hydroxyl Radical. J. Am. Chem. Soc. 2007, 129 (34), 10597−10601.

Benedict, Katherine B., Alexander S. McFall, and Cort Anastasio. "Quantum yield of nitrite from the photolysis of aqueous nitrate above 300 nm." Environmental Science & Technology 51.8 (2017): 4387-4395.

Zheng, Haotian, et al. "Contribution of Particulate Nitrate Photolysis to Heterogeneous Sulfate Formation for Winter Haze in China." Environmental Science & Technology Letters (2020).

Zhang, Ruifeng, et al. "Enhanced Sulfate Production by Nitrate Photolysis in the Presence of Halide Ions in Atmospheric Particles." Environmental Science & Technology 54.7 (2020): 3831-3839.

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