

Interactive
Comment

Interactive comment on “Evidence of the water-cage effect on the photolysis of NO_3^- and FeOH^{2+} , and its implications for the photochemistry at the air-water interface of atmospheric droplets” by P. Nissenon et al.

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We thank Dr. Olariu very much for his observations. The reviewer discusses two issues. The first issue concerns the initial formation rate of nitrite and acetone at high 2-propanol concentrations. The reviewer notes that at high [2-propanol], the initial formation rate of acetone (Racetone) appears constant while the initial formation rate of nitrite (Rnitrite) appears to decrease (Figure 2 of the manuscript). He suggests that there are additional reactions involving both products and/or some formation reactions are inhibited at high [2 propanol].

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It is possible that the observed behaviour of Rnitrite is due to the concentration dependence of the formation processes. However, the experimental data and the associated errors do not allow the authors to determine this. Warneck and Wurzinger (1988) showed that the kinetics of acetone formation can be accounted for better than the formation of nitrite by the known processes of nitrate photolysis. This is probably due to the presence of unaccounted, additional processes that yield nitrite (Mark et al., 1996). Therefore, the initial formation rate of acetone is a better measure of the quantum yield of OH photoproduction, $\Phi(\text{OH})$. The size of the error bars on Racetone at high [2-propanol] makes it difficult to determine the trend of Racetone in this region; Racetone may be decreasing in the same manner as nitrite, changing little, or increasing significantly. A more detailed discussion of the initial formation rate of nitrate and acetone at high [2-propanol] will be added to the manuscript.

The second issue raised by the reviewer concerns the relative concentrations of $\text{Fe}(\text{OH})_2^+$ and FeOH_2^+ at pH 2.5. At pH 2.5, the authors believe that the concentration of FeOH_2^+ is much greater than the concentration of $\text{Fe}(\text{OH})_2^+$ based on the following analysis:

The FeOH_2^+ and $\text{Fe}(\text{OH})_2^+$ equilibrium constants are,

$$K_1 = [(\text{FeOH})_2^+] [\text{OH}^-]^2, \quad (1)$$

$$K_2 = [(\text{Fe}(\text{OH})_2^+) [\text{OH}^-] \quad (2)$$

(Note: $[\text{Fe}(\text{OH})_3]$ is not considered in this analysis because it is a solid)

At pH 2, $[\text{OH}^-] = 10^{-12}$ M, and Equation (1) yields $[\text{FeOH}_2^+] = 2 \times 10^{-2}$ while Equation (2) yields $[\text{Fe}(\text{OH})_2^+] = 4 \times 10^{-5}$.

At pH 3, $[\text{OH}^-] = 10^{-11}$ M, and Equation (1) yields $[\text{FeOH}_2^+] [\text{OH}^-] = 2 \times 10^{-4}$ while Equation (2) yields $[\text{Fe}(\text{OH})_2^+] = 4 \times 10^{-6}$.

For both pH values, $[\text{FeOH}_2^+] \gg [\text{Fe}(\text{OH})_2^+]$. At intermediate pH values, such as pH 2.5, this relationship is true as well. The analysis above will be added to the manuscript.

References

Mark, G., Korth, H.-G., Schuchmann, H.-P., and von Sonntag, C., 1996. The photochemistry of aqueous nitrate ion revisited, *Journal of Photochemistry and Photobiology A: Chemistry*, 101, 89–103.

Warneck, P., and Wurzinger, C., 1988. Product quantum yields for the 305-nm photodecomposition of NO_3^- in aqueous solution, *Journal of Physical Chemistry*, 92, 6278–6283.

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