

EGU2020-348

<https://doi.org/10.5194/egusphere-egu2020-348>

EGU General Assembly 2020

© Author(s) 2020. This work is distributed under the Creative Commons Attribution 4.0 License.



Photochemical production of sulfate from dissolved organic matter and atmospheric aqueous phases: Is there something in common?

Rachele Ossola¹, Baptiste Clerc¹, Julie Tolu^{1,2}, Lenny H. E. Winkel^{1,2}, and Kristopher McNeill¹

¹ETH, USYS, Zurich, Switzerland (rachele.ossola@usys.ethz.ch)

²EAWAG, Dübendorf, Switzerland

In a recent study, we showed that photodegradation of dissolved organic sulfur (DOS) from a wide range of natural terrestrial environments releases sulfate (SO_4^{2-}) and other small and highly oxidized S-containing compounds as degradation products, similar to what had already been reported for dissolved organic carbon, nitrogen and phosphorous. However, the underlying chemical mechanism of photoproduction of sulfate is still unknown.

To fill this knowledge gap, we selected cysteine as a DOS model compound and we investigated its photodegradation to sulfate using model sensitizers as the source of singlet oxygen ($^1\text{O}_2$) and triplet excited states ($^3\text{Sens}^*$), two photochemically produced reactive species ubiquitous in sunlit surface waters. Using a combination of steady-state photochemistry experiments, kinetic modeling and mechanistic knowledge from the biochemistry literature, we reconstructed the molecular events that likely lead to the release of sulfate. We found that the release of SO_2 via triplet-sensitized fragmentation of cysteine sulfinic acid, a $^1\text{O}_2$ degradation product of cysteine, is a key step in the reaction mechanism. In the presence of oxygen and a photosensitizer, SO_2 is then rapidly oxidized to SO_4^{2-} .

Interestingly, nowadays there is great interest in the atmospheric chemistry community on the same transformation (i.e., aqueous phase oxidation of SO_2 to SO_4^{2-}) in the context of extreme haze events. Triplet-induced SO_2 oxidation has already been proposed as a potential aqueous phase reaction that might explain the mismatch between measured and modelled sulfate concentrations, but the mechanism of this process is still not established. Our work provides an example of how mechanistic knowledge gained on the (photo)chemical behaviour of dissolved organic matter in aquatic systems can offer insights on processes occurring in atmospheric aqueous phases.

How to cite: Ossola, R., Clerc, B., Tolu, J., Winkel, L. H. E., and McNeill, K.: Photochemical production of sulfate from dissolved organic matter and atmospheric aqueous phases: Is there something in common?, EGU General Assembly 2020, Online, 4–8 May 2020, EGU2020-348, <https://doi.org/10.5194/egusphere-egu2020-348>, 2019