## Kinetic analysis of the photo-Fenton/Fenton-like reaction by Ferrozine

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As well known, (Photo)-Fenton/Fenton-like reactions are the typical reactions in the atmosphere that can play a crucial role in the budget of the HxOy redox cycle  $(H_2O_2, HO, HO_2/O_2)^{-1}$ . Many studies have concluded that hydroxy radicals are the most efficient oxidant driving the daytime chemistry of the atmosphere. The iron reactivity through the (photo)-Fenton/Fenton-like processes appears to be significant to drive the HO production and budget, as shown in the following reactions (**Fig. 1**).

The previous studies illustrated that organic compounds such as carboxylate, amino carboxylate, and biological origin compounds like siderophore can complex free iron in the atmosphere <sup>2</sup>. Those organic iron complexes can generate HO<sup>-</sup> through the photo-Fenton and Fenton-like reaction at neutral pH. However, the HO<sup>-</sup> formation is mainly attributed to iron as free ions or aqua-complexes in the atmospheric chemical model leading to controversial evaluation of the contribution of such free radicals.

In our study, the Ferrozine reagent was chosen to measure the trend of the concentration of Fe<sup>II</sup> in (photo)-Fenton/Fenton-like reactions for the determination of the reaction constants. In **Fig. 2a and 2b**, the rate constants of Fenton and Fenton-like were determined to be 80.5  $M^{-1}$  s<sup>-1</sup> and 0.086  $M^{-1}$  s<sup>-1</sup>, which is consistent with the published data <sup>3, 4</sup>. In addition, the rate constants of Fe<sup>III</sup>-oxalate complex photolysis at different pH were presented in **Fig. 2c**.

In the future, the Ferrozine method will be used to obtain the rate constant of (photo) Fenton/Fenton-like reactions of different organic iron complexes. Moreover, the essential relationship between the Fenton/Fenton-like reaction efficiency or photolysis efficiency of those organic iron complexes and their complexation constants will be investigated.

## Reference

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$$\begin{aligned} \mathrm{F}\mathrm{e}^{\mathrm{II}} + \mathrm{H}_{2}\mathrm{O}_{2} + h\nu &\rightarrow \mathrm{F}\mathrm{e}^{\mathrm{II}} + \mathrm{H}^{+} + \mathrm{HO}^{\bullet} \mathrm{e}^{\mathrm{II}} \\ \mathrm{F}\mathrm{e}^{\mathrm{II}} + \mathrm{H}_{2}\mathrm{O}_{2} \rightarrow \mathrm{F}\mathrm{e}^{\mathrm{II}} + \mathrm{HO}^{-} + \mathrm{HO}^{\bullet} \mathrm{e}^{\mathrm{II}} \\ \mathrm{F}\mathrm{e}^{\mathrm{III}} + \mathrm{H}_{2}\mathrm{O}_{2} \rightarrow \mathrm{F}\mathrm{e}^{\mathrm{II}} + \mathrm{HO}_{2}^{\bullet} + \mathrm{H}^{+} \mathrm{e}^{\mathrm{II}} \end{aligned}$$

Fig. 1. The main reactions in the photolysis processes of  $Fe^{III}$ 



Fig. 2. The Fe<sup>II</sup> concentration as a function of time in Fenton (a) and Fenton-like reaction (b), the insert shows the spectra of  $Fe^{II}$ -Ferrozine complex at different reaction times; (c) the effect of pH on the rate constant of the photolysis of  $Fe^{II}$ -Oxlate complex at different pHs.