

Iron (III) carboxylate complex photolysis in aqueous particles and cloud droplets

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Absorption spectra and Fe^{2+} quantum yields of iron(III) coordination compounds with oxalate, malonate, succinate, glutarate, tartronate, tartrate, gluconate, glyoxalate and pyruvate were experimentally determined. Measured quantum yields of malonate, glutarate and gluconate complexes are in the range of $0.02 < \Phi < 0.05$, while succinate, tartrate, pyruvate, glyoxylate and tartronate complexes show values between $0.12 < \Phi < 1.21$. For some systems, the effect of dissolved oxygen on the quantum yields was considered. O_2 generally lowers the Fe^{2+} quantum yield for the complexes with tartronate, pyruvate, glyoxalate and gluconate. No oxygen effect was observed with tartrate and, surprisingly, in the case of succinate complexes a higher quantum yield under dissolved O_2 conditions at 351 nm was observed. In the case of oxalate, a dependence of the quantum yield on the initial concentration of iron(III) oxalato complexes was observed. A kinetic simulation of the reaction system after the photolysis was performed for oxalate, succinate, glyoxalate and tartrate complexes to characterize the influence of secondary thermal reactions on the quantum yield.

A tropospheric chemistry simulation with the multi-phase chemistry mechanism CAPRAM involving the photolysis of the studied complexes and subsequent reactions of the resulting fragments showed that the contribution of the iron complex photochemistry to the formation of oxidants such as $\text{O}_2^{\cdot-}/\text{HO}_2^{\cdot}$, $\cdot\text{OH}$ and H_2O_2 is low in comparison to other sources. It was shown that Fe(III) complex photolysis represents a major sink for some ligands in addition to the oxidation via free radicals.