



Photochemistry of iron(III)-carboxylato complexes in aqueous atmospheric particles

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Iron is always present in the atmosphere in concentrations from $\sim 10^{-9}$ M (clouds, rain) up to $\sim 10^{-3}$ M (fog, particles). Sources are mainly mineral dust emissions. Iron complexes are very good absorbers in the UV-VIS actinic region and therefore photo-chemically reactive. Iron complex photolysis leads to radical production and can initiate radical chain reactions, which is related to the oxidizing capacity of the atmosphere. These radical chain reactions are involved in the decomposition and transformation of a variety of chemical compounds in cloud droplets and deliquescent particles. Additionally, the photochemical reaction itself can be a degradation pathway for organic compounds with the ability to bind iron.

Iron-complexes of atmospherically relevant coordination compounds like oxalate, malonate, succinate, glutarate, tartronate, gluconate, pyruvate and glyoxalate have been investigated in laboratory experiments. Iron speciation depends on the iron-ligand ratio and the pH. The most suitable experimental conditions were calculated with a speciation program (Visual Minteq). The solutions were prepared accordingly and transferred to a 1 cm quartz cuvette and flash-photolyzed with an excimer laser at wavelengths 308 or 351 nm. Photochemically produced Fe^{2+} has been measured by spectrometry at 510 nm as $\text{Fe}(\text{phenantroline})_3^{2+}$. Fe^{2+} overall effective quantum yields have been calculated with the concentration of photochemically produced Fe^{2+} and the measured energy of the excimer laser pulse. The laser pulse energy was measured with a pyroelectric sensor.

For some iron-carboxylate systems the experimental parameters like the oxygen content of the solution, the initial iron concentration and the incident laser energy were systematically altered to observe an effect on the overall quantum yield. The dependence of some quantum yields on these parameters allows in some cases an interpretation of the underlying photochemical reaction mechanism. Quantum yields of malonate, glutarate and gluconate complexes lie in the range $0.02 < \Phi < 0.10$, whereas succinate, tartronate, pyruvate, glyoxalate and oxalate systems have values between $0.16 < \Phi < 1.26$. All quantum yields include contributions from secondary thermal reactions. Furthermore, an attempt was made to differentiate between contributions of individual iron-oxalato complexes to the overall measured quantum yield. The results will be discussed and compared with available literature.