

Small Particles, Big Impact: Exploring How Iron Chemistry Transforms Our Atmosphere

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Reactions between Fe(II) and peroxides, known as Fenton reactions, take place in deliquescent aerosols particles, being regarded as major sources of oxidants in the atmosphere. Hydroxyl radicals (HO \cdot) are the most important oxidizers formed in this environment [1]. Modeling studies have demonstrated that the high concentration of salts and dissolved organic compounds present in aerosols affect the rate constants and oxidant yields coming from these reactions [2]. This work aims to experimentally describe how the Fenton chemistry is affected by salt concentrations and inorganic ligands typically found in aerosols. For this, Fenton reactions were investigated in the presence of two major aerosol components, sulfate and oxalate. The isolated effect of ionic strength (I_c) was initially investigated in the presence of an inert anion, perchlorate. At $I_c = 4\text{M}$, the rate constant of the Fenton reaction decreased when compared to the measured rate constant in diluted solutions (24 ± 1 vs. $44 \pm 1 \text{ M}^{-1} \text{ s}^{-1}$ at pH 3 and 293 K). In the presence of sulfate (SO_4^{2-} , $I_c = 2.7 \text{ M}$), the Fe(II) speciation was shifted to FeSO_4 , and the rate constants increased to $245 \pm 10 \text{ M}^{-1} \text{ s}^{-1}$. When oxalate was added to the system, different oxalate complexes were formed, and the rate constant significantly increased, reaching $(3.5 \pm 0.3) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$. The HO \cdot production remained unchanged in the presence of FeSO_4 and H_2O_2 , but was notably reduced when perchlorate and oxalate were present. This study reveals how the Fenton chemistry is modified in aerosol conditions, showing that interactions between iron and anions can counterbalance the ionic strength effect, and enhance the role of Fenton chemistry in aerosol particles. This study provides valuable insights for improving the accuracy of atmospheric models, such as those developed using the Chemical Aqueous Phase Radical Mechanism (CAPRAM) [3].

REFERENCES

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