Ionic strength effect in Fenton reactions in the presence of sulfate

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Deliquescent aerosol particles are typically characterized by the presence of a high concentration of salts and organic compounds, resulting in non-ideal solutions with elevated ionic strength and low pH, typically varying from 0 to 3. These conditions alter the chemical equilibrium and kinetics of reactions that lead to the formation of OH radicals. One of the main sources of OH radicals in the aqueous particle phase is the decomposition of H_2O_2 by Fe^{2+}, called the Fenton reaction. Model predictions in non-ideal conditions considering Fe speciated as Fe^{2+} account for a decrease of 70 % in the Fenton rate constant. However, experiments conducted in the aqueous phase are often restricted to ideal solutions, and measured rate constants vary from 40 to 80 L mol^{-1} s^{-1}. In this work, the kinetics of Fenton reactions in acidic conditions and high concentrations of sulfate were investigated considering the prevalence of this ion in aerosols. For this, the Fe(II) conversion was monitored using the complexation with ortho-phenanthroline. Initially, the isolated effect of ionic strength was investigated with the addition of 3.6 mol L^{-1} of ClO_4^-, which does not alter the Fe^{2+} speciation in the investigated conditions. In this case, the rate constant decreased by 41 % if compared to the rate measured in diluted solutions (78.7 ± 4.3 L mol^{-1} s^{-1} at 298 K), considering values obtained from 278 to 318 K at pH 3. In another set of experiments, the effect of increased ionic strength was investigated in the presence of 1.2 mol L^{-1} of SO_4^{2-} (I = 2.7 mol L^{-1}), causing the Fe speciation to shift from Fe^{2+} to $FeSO_4$. In the presence of this complex, the rate constants increased by 85 %. After corrections considering the ionic strength and the Fe speciation, the value for the rate constant of the reaction between H_2O_2 and $FeSO_4$ at pH 3 was derived as 245 ± 7 L mol^{-1} s^{-1} at 298 K. Arrhenius expressions were derived for the Fenton reaction k(T) = (8.7 ± 0.8) × 10^7 × exp[(-4276 ± 520 K)/T] and the reaction in the presence of $FeSO_4$, k(T) = (7.5 ± 0.2) × 10^9 × exp[(-5153 ± 310 K)/T] in increased ionic strength conditions. This work provided means to characterize Fenton reactions in the presence of sulfate and high ionic strengths, showing that although ionic strength effects decrease the rate of the reaction, complexation with common inorganic ions surpasses this effect to yield faster rates, therefore increasing the importance of the Fenton chemistry in aerosol conditions.