Mössbauer Evidence for an Fe(IV)=O Species in Acidic Aqueous Solution

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The Fenton reaction is used for the oxidation of aqueous Fe(II) ions with hydrogen peroxide in acidic aqueous solutions. It has been proposed that the reactive intermediate(s) involve hydroxyl radicals, Fe(IV)=O species or metal-coordinated peroxide. In some recent theoretical papers, Fe(IV)=O has been proposed as the most likely Fenton intermediate. The present work addresses the question whether an Fe(IV)=O species can be formed at pH 2.

Using stopped-flow we have mixed equimolar concentrations of $^{57}\mathrm{Fe(H_2O)_6}^{2+}$ and O_3 and trapped a reactive, short-lived intermediate, **Z**, by freeze-quenching on a 77 K brass surface. **Z** has quadrupole splitting $\Delta E_Q = -0.33$ mm/s and isomer shift $\delta = 0.38$ mm/s. Analysis of Mössbauer spectra recorded in applied fields up to 8 T proves that **Z** has *integer* electronic spin. An $S = 2$ spin Hamiltonian analysis reveals an axial species with zero-field splitting, $D = 9.7$ cm^{-1}, and magnetic hyperfine coupling tensor, $A_x = A_y = -27.8$ MHz; A_z is small. (A fit for $S = 1$ yields unreasonable A-values). These parameters are very similar to those of the $S = 2$ $\mathrm{Fe^{IV}{=}O}$ intermediate of *E. coli* taurine: α ketoglutarate dioxygenase; for the latter an Fe=O species has recently been established. We propose that **Z** is a high-spin $\mathrm{Fe^{IV}(O)(H_2O)_n}$ complex. Density functional theory calculations for an Fe(IV)=O species reproduce the hyperfine parameters quite well. Significantly, the reactivity pattern of the intermediate observed here is quite different from that observed in Fenton Chemistry.