What are the oxidizing intermediates in the Fenton and Fenton-like reactions?

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The Fenton and Fenton like reactions are of major importance due to their role as a source of oxidative stress in all living systems and due to their use in advanced oxidation technologies. For many years, probably till today, there was a debate whether the reaction of $Fe^{II}(H_2O)_6^{2+}$ with H_2O_2 yields OH· radicals or $Fe^{IV}{=}O_{aq}$. It is now known that this reaction proceeds via the formation of the intermediate complex $(H_2O)_5Fe^{II}(O_2H)^{+}/(H_2O)_5Fe^{II}(O_2H_2)^{2+}$ that decomposes to form OH· radicals or $Fe^{IV}{=}O_{aq}$ depending on the pH of the medium. The intermediate complex might also oxidize directly a substrate present in the medium. In the presence of Fe^{III}_{aq} the complex $Fe^{III}(OOH)_{aq}$ is formed. This complex reacts via $Fe^{II}(H_2O)_6^{2+} + Fe^{III}(OOH)_{aq} \rightarrow Fe^{IV}{=}O_{aq} + Fe^{III}_{aq.}$ In the presence of ligands often the process observed is $L_n(H_2O)_{5-n}Fe^{II}(O_2H) \rightarrow L^{\cdot+} + Fe^{III}_{aq}$. Thus, in the presence of small concentrations of HCO_3^-, *i.e.* in biological systems and in advanced oxidation processes, the oxidizing radical formed is $CO_3^{\cdot-}$. Also, the reactions of $Fe^{II}(H_2O)_6^{2+}$ with $HSO_5^-/S_2O_8^{2-}$ in neutral solutions form $Fe^{IV}{=}O_{aq}$ or $CO_3^{\cdot-}$. Clearly in the presence of other transition metal complexes and/or other ligands other radicals might be formed. OH· radicals are clearly often not formed in the Fenton or Fenton like reactions.

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