What Are the Oxidizing Intermediates in the Fenton and Fenton-like Reactions? A Perspective †

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† This perspective is dedicated in honor of Professor Dov Lichtenberg on his 80th birthday.

Abstract: 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, there has been a debate whether the reaction of Fe II (H2O)6 2+ with H2O2 yields OH • radicals or Fe IV = Oaq. It is now known that this reaction proceeds via the formation of the intermediate complex (H2O)6Fe III (O2H) + / (H2O)6Fe III (O2H)2 + that decomposes to form either OH • radicals or Fe IV = Oaq, depending on the pH of the medium. The intermediate complex might also directly oxidize 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 (H2O)6 2+ + Fe III (OOH) aq → Fe IV = Oaq + Fe III aq. In the presence of ligands, the process often observed is Ln(H2O)5–nFe III (O2H) → Ln + + L + 1− + Fe III aq. Thus, in the presence of small concentrations of HCO3 − i.e., in biological systems and in advanced oxidation processes—the oxidizing radical formed is CO3 2−. It is evident that, in the presence of other transition metal complexes and/or other ligands, other radicals might be formed. In complexes of the type Ln(H2O)5–nM in–II (O2H + ), the peroxide might oxidize the ligand L without oxidizing the central cation M. OH • radicals are evidently not often formed in Fenton or Fenton-like reactions.

Keywords: OH •; Fe IV = Oaq; CO3 2−; pH effect; reactive oxidizing species

1. General Remarks

In 1894, Mr. Fenton reported that Fe II (H2O)6 2+ catalyzes the oxidation of tartaric acid by H2O2 [1]. No mechanism of this process was suggested by Mr. Fenton. Since then, the reaction Fe II (H2O)6 2+ + H2O2 has been called the Fenton reaction and the reactions M nL m + ROOR’—where M is either Fe or another low-valent transition metal, L is either H2O or another ligand, and R and R’ are either H or another substituent—are called Fenton-like reactions.

The Fenton and Fenton-like reactions are of major importance due to two reasons:
1. They are considered to be the major source of oxidative stress in all living systems.
2. They are used in the advanced oxidation technologies/processes that are of major importance in the environmental removal of pollutants.

Due to this prominence, a search in SciFinder for Fenton in 2021 results in 3286 references. The first mechanisms of the Fenton reaction were suggested in 1932 by two groups in parallel. Bray and Gorin [2] suggested that the mechanism is:

Fe II (H2O)6 2+ + H2O2 → Fe IV = O2+ aq

(1)

whereas Haber and Weiss [3,4] suggested that the mechanism of the Fenton reaction is:

Fe II (H2O)6 2+ + H2O2 → Fe III (H2O)6 3+ + OH • + OH −

(2)
The debate whether the oxidizing intermediate formed in the Fenton reaction is Fe$^{IV} = O^{2+}_{aq}$ or OH$^*$ has lasted for many decades. Thus, even as recently as this year, it has been suggested that reaction (1) is the correct mechanism, at least in neutral solutions [5], and that (2) is the only process even at pH 5 [6].

The difficulty in differentiating between the two mechanisms stems from the fact that both OH$^*$ radicals and Fe$^{IV} = O^{2+}_{aq}$ react with organic substrates, usually by abstracting a hydrogen atom, and often form the same, or similar, radicals. Using EPR to quantify the relative yields of the radicals formed in order to decide whether their sources are OH$^*$ radicals often fails due to their different lifetimes [7]. This difficulty was overcome by measuring the final products formed when a mixture of two alcohols is present. This technique requires that the low-valent metal cation initiating the Fenton-like reaction has a fast ligand exchange rate, i.e., it does not fit Fe$^{II} (H_2O)_6^{2+}$. Using this technique, it was shown that the reaction Cr$^{II} (H_2O)_6^{2+} + H_2O_2$ proceeds via a mechanism analogous to reaction (2), whereas the reaction Cu$^{I}_{aq}^+ + H_2O_2$ does not yield OH$^*$ radicals or Cu$^{III}_{aq}$ [8].

Furthermore, thermodynamic arguments [8] and kinetic arguments using the Marcus theory [9] indicate that the Fenton and Fenton-like reactions do not proceed via the outer sphere mechanism. Therefore, an inner sphere mechanism was proposed [8,9]:

$$ML_m^{n^+} + H_2O_2 \rightleftharpoons \{L_{m-1}M(H_2O_2)^{n^+} + L\}/\{L_{m-1}M(HO_2)^{(n-1)^+} + L + H^+\}$$

(3)

For simplicity, it will be assumed in that the complex formed is $L_{m-1}M(H_2O_2)^{n^+}$. Reaction (3) might be followed by a variety of routes, e.g., [8,9]:

$$\rightarrow ML_m^{(n+1)^+} + OH^* + OH^-$$

(4a)

$$L_mM(H_2O_2)^{n^+} \rightarrow ML_m^{(n+2)^+} + 2OH^-$$

(4b)

$$RH \rightarrow ML_m^{(n+1)^+} + R^* + OH^- + H_2O$$

(4c)

$$R=R \rightarrow ML_m^{(n+1)^+} + HOR-R^* + OH^-$$

(4d)

Naturally, $L_{m-1}M(H_2O_2)^{n^+}$ might also directly oxidize different substrates, e.g., inorganic reducing agents.

It was later discovered that when the central cation M has a too high redox potential, e.g., Co(II) [10], or cannot be oxidized, e.g.: Al$^{III}$, Ga$^{III}$, In$^{III}$, Sc$^{III}$, Y$^{III}$, La$^{III}$, Be$^{II}$, Zn$^{II}$, and Cd$^{II}$ [11–13], the binding of two or more peroxides to the central cation might lead to the formation of OH$^*$ radicals via disproportionation of the peroxides without involving oxidation of the central cation [10–13]:

$$M^{n_{aq}} + kH_2O_2 \rightleftharpoons M^{n}(HO_2^-)_{k-1}(H_2O_2)_{aq} + (k-1)H^+ \quad (k = 2 \text{ or } 3)$$

(5)

$$M^{n}(HO_2^-)_{k-1}(H_2O_2)_{aq} \rightarrow M^{n}(HO_2^*)(HO_2^-)_{k-2}(OH^-)_{aq} + OH^*$$

(6)

The observation that ligated H$_2$O$_2$ can oxidize a second ligated peroxide suggests that it might also oxidize other ligands. This was tested theoretically, by DFT [14], and experimentally for the oxidation of a carbonate ligated to Co$^{II}$ [15], thus proving this possibility.

2. The Fenton Reaction Is (Fe(H$_2$O)$_6^{2+} + H_2O_2$)

Efforts to determine whether the reaction Fe(H$_2$O)$_6^{2+} + H_2O_2$ forms OH$^*$ radicals via following the formation of the DMPO-OH$^*$ adduct by EPR failed, as it was shown that even mild oxidants, e.g., Fe$^{III}_{aq}$ oxidize DMPO via [16]:

$$DMPO + Ox \rightarrow DMPO^{**} + Red$$

(7)
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DMPO$^{•+}$ + H$_2$O $→$ DMPOH$^{•}$ + OH$^-$ (8)

The rate constant of the Fenton reaction in acidic media is $k(\text{Fe(H}_2\text{O}_2)_6^{2+} + \text{H}_2\text{O}_2) \sim 50$ M$^{-1}$s$^{-1}$. The measured rate constants depend on the pH and on the ratio [H$_2$O$_2$/[Fe(H$_2$O)$_6^{2+}$]; the latter dependencies mainly stem from the observation that in the presence of excess H$_2$O$_2$ reactions (9) [17] and (10) [17,18] contribute to the observed rate constants [17].

$$\text{Fe}^{III}_{\text{aq}} + \text{H}_2\text{O}_2 ⇌ \text{Fe}^{III}(\text{HO}_2) + \text{H}^+ \quad (k_0 = 69$ M$^{-1}$s$^{-1} \quad k_{-9} = 0.11$ s$^{-1}$ at pH 2.0) (9)$$

$$\text{Fe(H}_2\text{O}_6^{2+} + \text{Fe}^{III}(\text{HO}_2) → \text{Fe}^{III}_{\text{aq}} + [\text{Fe}^{III}_{\text{aq}} + \text{OH}^*]/[\text{Fe}^{IV} = \text{O}_{\text{aq}}] \quad (10)$$

$$K_{10} = 7.7 \cdot 10^5$ M$^{-1}$s$^{-1}$ at pH 1.0

The nature of the products of reaction (10) were later determined [19] to be $\text{Fe}^{III}_{\text{aq}} + \text{Fe}^{IV} = \text{O}_{\text{aq}}$; thus, clearly in acidic solutions when [H$_2$O$_2$/[Fe(H$_2$O)$_6^{2+}$] > 1, a mixture of OH$^*$ radicals and Fe$^{IV} = \text{O}_{\text{aq}}$ is formed.

Next, Bakac et al. developed a new procedure to differentiate between OH$^*$ radicals and Fe$^{IV} = \text{O}_{\text{aq}}$ based on the different final products formed in the reactions of OH$^*$ radicals and Fe$^{IV} = \text{O}_{\text{aq}}$ with DMSO, (CH$_3$)$_2$SO [20]. This technique can only be used for iron. Using this technique, it was proved that, in acidic solutions, OH$^*$ radicals are formed by the Fenton reaction, whereas in neutral solutions, where pH > 6, the product is Fe$^{IV} = \text{O}_{\text{aq}}$ [20]. This proves that the Fenton reaction under physiological conditions does not form OH$^*$ radicals: However, this statement is not correct for the acidic organelles, e.g., lysosomes [21] and some peroxisomes [22]. This conclusion is correct for reactions of Fe(H$_2$O)$_6^{2+}$, but not for all Fenton-like reactions of Fe$^{II} \text{H}_2\text{O}_2$, as seen below.

Recently, it was shown that the Fenton reaction is dramatically accelerated in the presence of low concentrations of bicarbonate well below those present in living cells [19]. The oxidizing transient formed under these conditions is the carbonate anion radical, CO$_3^{•−}$ [19]. CO$_3^{•−}$ is a strong oxidizing agent, $E^0$(CO$_3^{•−}$/CO$_3^{2−}) = 1.57$ V vs. NHE [23] and is evidently somewhat stronger in neutral media. CO$_3^{•−}$ is still a considerably weaker oxidizing agent than OH$^*$ radicals and is, therefore, more selective as a ROS [24,25]. The reactions occurring were proposed to be [19]:

$$\text{Fe(H}_2\text{O}_6^{2+} + \text{H}_2\text{O}_2 ⇒ (H}_2\text{O}_3\text{Fe(O}_2\text{H})^+/(H}_2\text{O}_3\text{Fe(O}_2\text{H})^+ + \text{H}_3\text{O}^+) \quad (11)$$

$$\text{(H}_2\text{O}_3\text{Fe(O}_2\text{H})^+/(H}_2\text{O}_3\text{Fe(O}_2\text{H})^+ + \text{H}_2\text{O}_3^− → \text{Fe}^{III}_{\text{aq}} + \text{CO}_3^{•−}) \quad (12)$$

$$\text{Fe(H}_2\text{O}_6^{2+} + \text{H}_2\text{O}_3^− ⇒ (H}_2\text{O}_3\text{Fe(CO}_3)^+ + \text{H}_3\text{O}^+ + 2\text{H}_2\text{O} \quad (11a)$$

$$\text{(H}_2\text{O}_3\text{Fe(CO}_3)^+ + \text{H}_2\text{O}_2 → \text{Fe}^{III}_{\text{aq}} + \text{CO}_3^{•−}) \quad (12a)$$

Recent unpublished results [26] suggest that reaction (12) likely proceeds via:

$$\text{(H}_2\text{O}_3\text{Fe(O}_2\text{H})^+/(H}_2\text{O}_3\text{Fe(O}_2\text{H})^+ + \text{H}_2\text{O}_3^− → (CO}_3\text{Fe}^{IV}_{\text{aq}} \quad (13)$$

and reaction (12a) likely proceeds via:

$$\text{(H}_2\text{O}_3\text{Fe(CO}_3)^+ + \text{H}_2\text{O}_2 → (CO}_3\text{Fe}^{IV}_{\text{aq}} \quad (13a)$$

The (CO$_3$)Fe$^{IV}_{\text{aq}}$ thus formed might decompose via:

$$\text{(CO}_3\text{Fe}^{IV}_{\text{aq}} \quad (14)$$

$$\rightarrow \text{Fe}^{III}_{\text{aq}} + \text{CO}_3^{•−} \quad (14a)$$

$$\text{Substrate} \quad \rightarrow \text{Fe}^{III}_{\text{aq}} + \text{oxidized-substrate} + \text{H}_2\text{O}_3^− \quad (14b)$$
The competition between reactions (14a) and (14b) depends on the substrate. Thus, for DMSO $k_{14a} >> k_{14b}$, but for PMSO (phenyl-methyl-sulfoxide) $k_{14a}^{-1}k_{14b}$. 

3. Fenton-like Reactions Involving Fe$^{III}$L$_m$

Two types of Fenton-like reactions have to be considered.

When ligands, L, different from H$_2$O are ligated to The Fe$^{II}$ central cation, the effect of HCO$_3^-$ on the mechanism, discussed above, can be included herein. It should be noted that the technique to distinguish between OH$^\bullet$ radicals and Fe$^{IV}$=O$_{aq}$ developed by Bakac et al. [20], cannot always be applied here because the mechanism of the reaction LFe$^{IV}$=O with DMSO is not known. The mechanism of the reactions of Fe$^{III}$L$_m$ with H$_2$O$_2$ for the following ligands was studied.

- L = PO$_4^{3-}$ /HPO$_4^{2-}$ [20]. The results suggest that the Fenton reaction in the presence of phosphate in neutral solutions yields OH$^\bullet$ radicals and not (PO$_4^{3-}$)$_m$Fe$^{IV}$=O$_{aq}$ [20].
- L = edta [22]. The reaction Fe$^{II}$ (edta)$^{2-}$ + H$_2$O$_2$ was studied at pH > 5.5 using the technique developed by Masarwa et al. [8]. The results indicate that OH$^\bullet$ radicals are the product of this reaction [27].
- L = nta, nta = N(CH$_2$CO$_2^-$)$_2$ [28]. The reaction Fe$^{II}$ (nta)$^{2-}$ + H$_2$O$_2$ was studied. Surprisingly, though edta and nta are very similar ligands, the results differ considerably. The results suggest that the major product of the Fe$^{II}$ (nta)$^{2-}$ + H$_2$O$_2$ is a (nta)Fe$^{IV}$=O$_{aq}$ complex [28]. The yields of the final products are pH dependent [28].
- L = citrate [29]. The results of the reaction Fe$^{II}$ (citrate)$^{2-}$ with H$_2$O$_2$ was studied. This reaction is of importance because Fe$^{III}$ (citrate) is a major component of the non-transferrin iron mobile pool [30]. The results indicate that the reaction Fe$^{II}$ (citrate)$^{2-}$ + H$_2$O$_2$ in neutral solutions does not yield OH$^\bullet$ radicals. The results do not answer the question whether a Fe$^{IV}$ (citrate)$_{aq}$ species is a transient formed by this reaction. When low concentration of HCO$_3^-$ are added to this system, the kinetics and final products are changed dramatically, indicating that the CO$_3^{2-}$ radical anion is a major product of the reaction under these conditions [29].

The results presented in this section indicate that the mechanism of the Fenton-like reactions of Fe$^{III}$L$_m$ complex dramatically depend on the nature of the ligand. Therefore, one cannot assume that Fe$^{II}$ complexes with analogous ligands react via the same mechanism.

When different peroxides are used as oxidants in the Fenton-like reaction, such as in biological systems, the most important peroxides are the ROOH compounds, where R is an alkyl. The ROOH peroxides are formed in biological systems, mainly in lipids, via the chain reaction [30,31]:

$$\text{RH} + \text{Ox} \rightarrow R^\bullet + \text{Ox-H}/(\text{Ox}^- + \text{H}^+) \quad (\text{Ox} = \text{OH}^\bullet, R^\bullet, \text{Fe}^{IV}=\text{O}_{aq} \text{ etc.}) \quad (15)$$

$$R^\bullet + O_2^\bullet \rightarrow RO_2 \quad (16)$$

$$\text{RH} + RO_2^\bullet \rightarrow RO_2H + R^\bullet \quad (17)$$

Therefore, the mechanism of the reaction (CH$_3$)$_3$COOH + Fe(H$_2$O)$_6^{2+}$ was studied. The results indicate that in this system Fe$^{IV}$ = O$_{aq}$ is also formed in neutral solutions in the absence of bicarbonate. In the presence of low concentrations of bicarbonate, CO$_3^{2-}$ radical anions are the product of this Fenton-like reaction [32].

The S$_2$O$_8^{2-}$ and HSO$_3^-$ peroxides are of major importance in advanced oxidation technologies [33–36]. Therefore, the mechanisms of the reactions Fe(H$_2$O)$_6^{2+}$ + HSO$_3^-$ /S$_2$O$_8^{2-}$ were studied. The results indicate that in acidic media, SO$_4^{2-}$ radical anions are the active oxidizing species formed, in neutral solutions, Fe$^{IV}$=O$_{aq}$ is formed, and in the presence of low concentrations of bicarbonate, CO$_3^{2-}$ is the oxidizing intermediate formed [26].

4. Other Fenton-like Reactions

Fenton-like reactions are reported for most low-valent transition metals and even for cations that are not involved in redox processes [11–13]. Herein, only Fenton-like reactions
involving Cu\textsuperscript{I} \cite{37} and Zn\textsuperscript{II} \cite{38–41} that are of biological importance and Co\textsuperscript{II}, due to its role in advanced oxidation technologies \cite{15}, are discussed.

The reaction of Cu\textsuperscript{I} with H\textsubscript{2}O\textsubscript{2} was long thought to yield OH\textsuperscript{*} radicals \cite{42}, but it was later shown that the active oxidizing agent is Cu\textsuperscript{I}(H\textsubscript{2}O\textsubscript{2}) \cite{8} or Cu\textsuperscript{II\textsubscript{aq}} \cite{43}. It was also proposed that the reaction of Cu\textsuperscript{I} with S\textsubscript{2}O\textsubscript{8}\textsuperscript{2–} yields Cu\textsuperscript{III\textsubscript{aq}} \cite{44}. Conversely, it was proposed that the reactions of Cu\textsuperscript{II} with HSO\textsubscript{5}– and S\textsubscript{2}O\textsubscript{8}\textsuperscript{2–} yield Cu\textsuperscript{III\textsubscript{aq}} and SO\textsubscript{4}\textsuperscript{2–} \cite{45}.

Surprisingly, Zn\textsuperscript{2+\textsubscript{aq}} and Zn\textsuperscript{II\textsubscript{aq}} complexes were shown to be involved in the formation of reactive oxygen species (see references \cite{38–41} for example.). However, no chemical mechanism initiating this process was forwarded. One possible mechanism is that suggested by Shul’pin et al. \cite{13}. According to this mechanism, the reactions involved are:

\begin{align*}
\text{Zn}^{2+\textsubscript{aq}} + \text{H}_2\text{O}_2 & \rightleftharpoons \text{Zn}^{II}(\text{O}_2\text{H}^-)\text{aq} + \text{H}^+ \quad (18) \\
\text{Zn}^{II}(\text{O}_2\text{H}^-)\text{aq} + \text{H}_2\text{O}_2 & \rightleftharpoons \text{Zn}^{II}(\text{O}_2\text{H}^-)(\text{H}_2\text{O}_2)\text{aq} \quad (19) \\
\text{Zn}^{II}(\text{O}_2\text{H}^-)(\text{H}_2\text{O}_2)\text{aq} & \rightarrow \text{Zn}^{2+\textsubscript{aq}} + \text{OH}^\cdot + \text{HO}_2^\cdot + \text{OH}^- \quad (20)
\end{align*}

As the steady state concentration of H\textsubscript{2}O\textsubscript{2} in biological media is very low, the probability that two H\textsubscript{2}O\textsubscript{2} will bind to the same Zn\textsuperscript{2+\textsubscript{aq}} is low. Therefore, it is tempting to propose that the process leading to the formation of reactive oxygen species catalyzed by Zn\textsuperscript{2+\textsubscript{aq}} is:

\begin{align*}
\text{Zn}^{2+\textsubscript{aq}} + \text{HCO}_3^- & \rightleftharpoons \text{Zn}^{II}(\text{HCO}_3^-)\text{aq} \quad (21) \\
\text{Zn}^{II}(\text{HCO}_3^-)\text{aq} + \text{H}_2\text{O}_2 & \rightleftharpoons \text{Zn}^{II}(\text{HCO}_3^-)(\text{H}_2\text{O}_2)\text{aq} \quad (22) \\
\text{Zn}^{II}(\text{HCO}_3^-)(\text{H}_2\text{O}_2)\text{aq} & \rightarrow \text{Zn}^{2+\textsubscript{aq}} + \text{OH}^\cdot + \text{CO}_3^\cdot - + \text{H}_2\text{O} \quad (23)
\end{align*}

These two plausible mechanisms must be studied experimentally to prove one or both of them.

The reaction Co(H\textsubscript{2}O\textsubscript{6})\textsuperscript{2+\textsubscript{aq}} + H\textsubscript{2}O\textsubscript{2} to yield OH\textsuperscript{*} radicals is endothermic due to the high redox potential of the Co\textsuperscript{III/II} couple \cite{10}. However, it was shown that the following reactions replace the simple Fenton-like reaction \cite{14}:

\begin{align*}
\text{Co}(\text{H}_2\text{O})\textsuperscript{6+\textsubscript{aq}} + 3\text{H}_2\text{O}_2 & \rightleftharpoons (\text{H}_2\text{O})\text{Co}^{II}(\text{H}_2\text{O}_2^-)\text{aq}\textsubscript{2}(\text{H}_2\text{O}_2) \quad (24) \\
(\text{H}_2\text{O})\text{Co}^{II}(\text{H}_2\text{O}_2^-)\text{aq}\textsubscript{2}(\text{H}_2\text{O}_2) & \rightarrow (\text{H}_2\text{O})\text{Co}^{II}(\text{H}_2\text{O}_2^-)(\text{H}_2\text{O}_2^+)(\text{OH}^-) + \text{OH}^\cdot \quad (25)
\end{align*}

In the presence of bicarbonate, the complex cyclic-(CO\textsubscript{4})Co\textsuperscript{II}(H\textsubscript{2}O\textsubscript{2})\textsubscript{2}(H\textsubscript{2}O) is formed. This complex decomposes via \cite{15}:

\begin{equation}
\text{cyclic-(CO}_4\text{Co}^{II}(\text{H}_2\text{O}_2^-)\text{aq}\textsubscript{2}(\text{H}_2\text{O}) \rightarrow (\text{H}_2\text{O})\text{Co}^{II}(\text{H}_2\text{O}_2^+)(\text{OH}^-)_2 + \text{CO}_3^\cdot - \quad (26)
\end{equation}

The reaction of HSO\textsubscript{5}– with Co(H\textsubscript{2}O\textsubscript{6})\textsuperscript{2+\textsubscript{aq}} and with Co\textsuperscript{II}(P\textsubscript{2}O\textsubscript{7})(H\textsubscript{2}O\textsubscript{2})\textsuperscript{2–} require more than one peroxymonosulfate to form radicals \cite{46}.

Finally, it should be pointed out that it is likely that ligands other than carbonate, with the proper redox potential, might also be oxidized directly by peroxides \cite{14}.

5. Heterogeneous Fenton-like Processes

A variety of heterogeneous catalysts react with H\textsubscript{2}O\textsubscript{2} in Fenton-like processes. Thus, ZnO-nanoparticles induce the formation of reactive oxygen species in biological systems. However, this is attributed to the dissolved Zn\textsuperscript{2+\textsubscript{aq}} ions \cite{39} and is, therefore, not truly heterogeneous.

The most important heterogeneous catalysts of Fenton-like processes have iron atoms/cations as the active participants, e.g., zero-valent iron \cite{47}, MgFe\textsubscript{2}O\textsubscript{4} (e.g., Fe\textsubscript{3}O\textsubscript{4} \cite{48} and MgFe\textsubscript{2}O\textsubscript{4} \cite{49}), and LaFeO\textsubscript{3} \cite{50}. These systems are used in advanced oxidation processes and not in biological ones. Therefore, their mechanisms are not discussed herein.
6. Concluding Remarks

The major conclusions of this perspective are:

I. The reaction Fe\(^{II}\)(H\(_2\)O\(_6\))\(^{2+}\) + H\(_2\)O\(_2\) yields OH\(^*\) radicals as the active oxidizing agent in acidic solutions when [Fe\(^{II}\)(H\(_2\)O\(_6\))\(^{2+}\)] > [H\(_2\)O\(_2\)], a mixture of OH\(^*\) radicals and Fe\(^{IV}\)=O\(_{aq}\) in acidic solutions when [Fe\(^{II}\)(H\(_2\)O\(_6\))\(^{2+}\)] < [H\(_2\)O\(_2\)], Fe\(^{IV}\)=O\(_{aq}\) in neutral solutions, and CO\(_3\)^{−} in solutions containing even low concentration of HCO\(_3\)^{−}, i.e., under physiological conditions.

II. It is important to note that mechanisms of the reactions H\(_2\)O\(_2\) + Fe\(^{II}\)L\(_m\)(H\(_2\)O\(_n\))\(_k\), where L are ligands different than water, depend dramatically on the properties of L. Thus, one must study the mechanism for each ligand separately.

III. The study of the mechanisms of Fenton-like reactions with other peroxides requires separate studies.

IV. The mechanisms of Fenton-like reactions of other low-valent metal cations differ from each other and thus require separate studies.

Therefore, it must be concluded that the mechanism of each Fenton-like reaction should be studied before concluding which oxidizing transient is formed in that reaction.

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