

FENTON REACTION DRIVEN BY IRON LIGANDS

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ABSTRACT

One of the most important sources of reactive oxygen species (ROS) in biological systems is the Fenton reaction. In this, the Fe²⁺ or Fe³⁺ reacts with H₂O₂ to produce ROS as the hydroxyl radical (·OH), superoxide radical (O₂⁻) and singlet oxygen (¹O₂).

The main ROS, responsible for the high oxidizing power of the Fenton reaction, is not clear. Some authors claim that the principal reactive species is ·OH, while others propose a ferryl specie (Fe⁴⁺ or [FeO]²⁺)^(1,2). Recently, have been proposed that the kind of reaction species produced depends mainly of pH and the iron composition of the coordination sphere. This is highlighted for Fe³⁺, because in mono and (some) bis-complexes Fe³⁺ is reduced to Fe²⁺ and there are some positions occupied by water or hydroxide ligands, readily to be exchanged by H₂O₂. On the other hand, in tris-complexes there are not any positions occupied by water or hydroxide, avoiding the formation of peroxo-complexes, necessary for Fenton or Fenton like reaction.

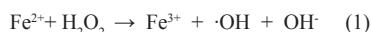
The 1,2-dihydroxybenzenes (DHBs) have been described as modulators of Fenton reaction. The DHBs driven Fenton reaction have been used for environmental applications as an advanced oxidation process. Furthermore, these systems participate in different biological process, as the wood biodegradation by fungi and oxidative stress in neurodegenerative diseases.

In this review, the effect of 1,2-dihydroxybenzenes on the activated species production by the Fenton and Fenton like reaction will be discussed and its participation in different systems.

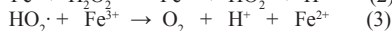
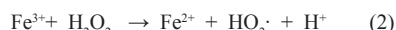
KEYWORDS Fenton reaction, iron ligands, ROS

1. ROS generated by Fenton reaction

The Fenton reaction was described by H.J.H. Fenton en 1894. Fenton was interested on the develop of a colored test for tartaric acid determination. For this, H₂O₂ was utilized catalyzed by FeSO₄ salt (Fenton's reagent)⁽³⁾. The mechanism of this reaction was proposed by Haber y Weiss at 1934⁽⁴⁾. This includes the hydroxyl radical (·OH) participation⁽¹⁾. This compound is the most reactive ROS (reactive oxygen specie) known⁽⁵⁾, have a standard redox potential of 2,8 V⁽²⁾ and consequently a low selectivity.



The Fe³⁺ reacts with H₂O₂ producing perhydroxyl radical (HO₂·). This reaction is named "Fenton like"⁽²⁾. The HO₂·, presents lower oxidant capacity than others ROS, but participate in the Fe³⁺ reduction to Fe²⁺ (3) to keep the ·OH production by (1).



Is highlighted that Fenton reaction (k=76 M⁻¹s⁻¹) (1) is four magnitude orders faster than Fenton like reaction (k= 0.01 M⁻¹s⁻¹) (2)⁽⁶⁾.

2. Iron speciation and Fenton reaction

The reactivity of Fenton reaction is pH dependent^(1,7). There are different approach to explain this effect^(1,2,7-9). Moffet and Zika⁽¹⁰⁾ determine different reaction rates for Fenton reaction from [Fe²⁺] and [Fe(OH)]⁺. Morgan and Lahav⁽¹¹⁾, determine that the constant rate for [Fe(OH)]⁺ is 9.2 x 10⁴ times higher than [Fe²⁺] rate constant. However, the concentration of [Fe(OH)]⁺ is 2.8 x 10⁶ times lower than [Fe²⁺] concentration at pH 3.0 and 2.8 x 10⁵ at pH 4.0 (figure 1-inset). This mean that [Fe(OH)]⁺ is the most reactive specie for Fenton reaction but its concentration is very lower to be main specie involves in Fenton reaction. Thus, both species are involved in Fenton reaction but [Fe²⁺] is the main one (specially at low pH). The [Fe(OH)]⁺ reach it maximum value at pH= 10 (Figure 1) and start to increase from pH= 4 (Figure 1-inset).

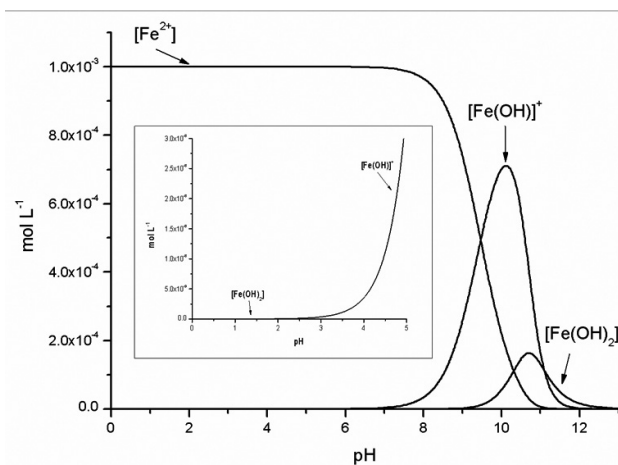


Figure 1. Speciation of a Fe(NO₃)₂ 1.00 x 10⁻³ mol L⁻¹ and H₂O₂ 1.00 mol L⁻¹ solution at different pH.

Nevertheless, at this pH value, all the Fe soluble species are unstable according to Pourbaix diagram (Figure 2). In consequence, a Fenton reaction is not possible at this conditions. The highest reactivity of [Fe(OH)]⁺ have been associated with its ligand lability to exchange H₂O by H₂O₂ to form a peroxo-complex [Fe(OOH)]⁽¹²⁾, postulated as an intermediary of the Fenton reaction⁽⁷⁾.

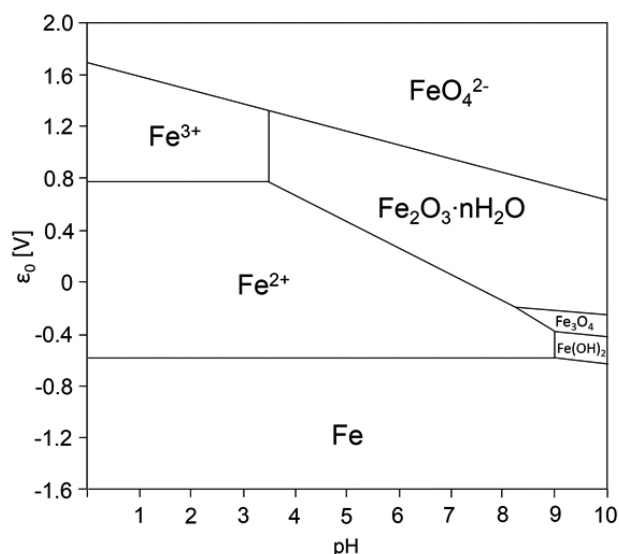


Figure 2. Iron Pourbaix diagram modified from Beverskoog et al 1996⁽¹³⁾

In this compound Fe^{2+} is oxidized through a inner sphere mechanisms (Figure 3). Keenan et al.⁽¹⁴⁾ propose a hydrogen peroxo-complex $[\text{Fe}(\text{H}_2\text{O}_2)]^{2+}$ as intermediary.

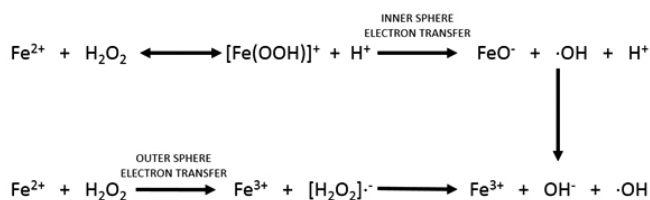


Figure 3. Inner sphere and outer sphere mechanism for Fenton reaction, modified from Mwebi et al 2005⁽¹⁵⁾.

The optimal pH for Fenton reaction is close to 3.0^(1,2). The reason of this value can not be explained by $\text{Fe}(\text{II})$ speciation; because until pH close to 4, the main soluble specie is $[\text{Fe}^{2+}]$ and the rate of Fenton reaction increases with the pH⁽¹⁶⁾. After pH=4, almost all the Fe species are insoluble like Fe_2O_3 (Figure 2) or other colloidal hydroxide compounds. Thereby, the Fenton reaction (without Fe ligands), decrease its reactivity after pH=4. The reason for the optimal pH value for Fenton reaction can be explained by the $\text{Fe}(\text{III})$ speciation. The Fe^{3+} speciation is shown in Figure 4. The highest reactivity of Fenton reaction (at pH=3)⁽¹⁷⁾ is related to $[\text{Fe}(\text{OH})]^{2+}$ specie⁽¹⁸⁾. This specie could be related with the lability of water to be exchanged by H_2O_2 in a similar way than for Fe^{2+} species⁽⁴⁾. Pignatello et al⁽¹⁹⁾ and Ensing et al⁽²⁰⁾ propose the peroxo-complex ($[\text{Fe}(\text{OOH})]^{2+}$) participation in Fenton reaction (5). Gallard et al⁽²¹⁾, quantify this complex by a spectrophotometric method. From the equilibrium constants reported by Gallard et al⁽²¹⁾ and the NIST Database 46 Version 8, a $\text{Fe}(\text{III})$ speciation diagram was generated (Figure 4).

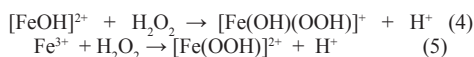


Figure 4 shows the speciation of soluble species of $\text{Fe}(\text{NO}_3)_3$ 1.00 x 10⁻³ mol L⁻¹ presence of H_2O_2 1.00 mol L⁻¹ from pH 0 to 5. In this plot is highlighted the maximum concentration of $[\text{Fe}(\text{OH})]^{2+}$ and $[\text{Fe}(\text{OOH})]^{2+}$ species at pH close to 3.0 (the optimum pH value for Fenton reaction). The rate-limiting step in Fenton reaction is the $[\text{Fe}(\text{OOH})]^{2+}$ or $[\text{Fe}(\text{OH})(\text{OOH})]^+$ decomposition (6, 7)⁽²¹⁾. The effective rate constant for both is 2.7x 10⁻³ s⁻¹. The individual rate constants are unknown⁽¹⁾.

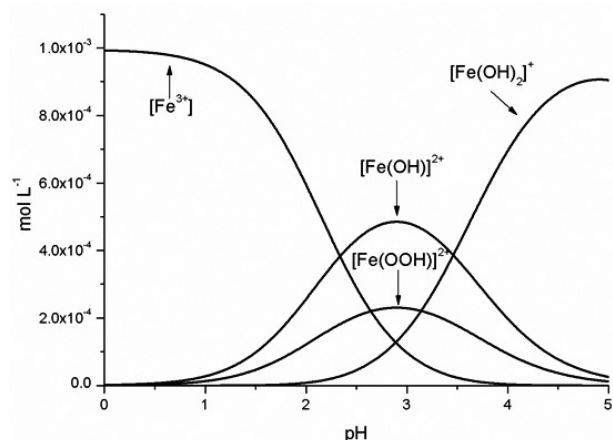
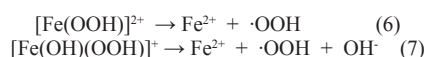


Figure 4. Speciation of a $\text{Fe}(\text{NO}_3)_3$ 1.00 x 10⁻³ mol L⁻¹ and H_2O_2 1.00 mol L⁻¹ solution at different pH.

The reaction 6 and 7 are sources of $\text{Fe}(\text{II})$ and HO_2^\cdot , which reduce $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$ ($k = 2 \times 10^3 \text{ s}^{-1}$). In this rate-limiting step, the $\text{Fe}(\text{II})$ is regenerated and the Fenton reaction can maintain the $\cdot\text{OH}$ by reaction (1).

3. $\text{Fe}(\text{IV})$ and singlet Oxygen in Fenton reaction

There are experimental evidence for ferryl species formation ($[\text{FeO}]^{2+}$) in Fenton reaction. Some authors propose this compound as the oxidant in Fenton reaction more than $\cdot\text{OH}$ ^(22, 23). The main experimental evidence is based on the capacity of Fenton reaction to oxidate substrates in the presence of $\cdot\text{OH}$ quenchers⁽²⁴⁻²⁶⁾. Ferryl intermediary in Fenton reaction was proposed by Brainy Gorin⁽²⁷⁾, according to (8).



Some authors propose the coexistence of $\cdot\text{OH}$ and $[\text{FeO}]^{2+}$ on Fenton reaction. For this there are experimental evidence based on spin trapping⁽²⁸⁾, UV/Vis stopped-flow kinetic⁽²⁹⁾, pulse radiolysis on peroxo-complexes in aqueous solution⁽³⁰⁾ and chemiluminescence data^(31, 32).

Ferryl species have been detected in complexes that stabilize $\text{Fe}(\text{IV})$ ^(33, 34), in enzymatic reaction of peroxidases⁽³⁵⁾ and heterogeneous catalysis by zero valent iron^(36, 37). Some authors⁽³⁸⁻⁴¹⁾, have developed techniques to determine selectively the presence of $[\text{FeO}]^{2+}$ or $\cdot\text{OH}$ based on the reactivity again a substrate (Figure 5).

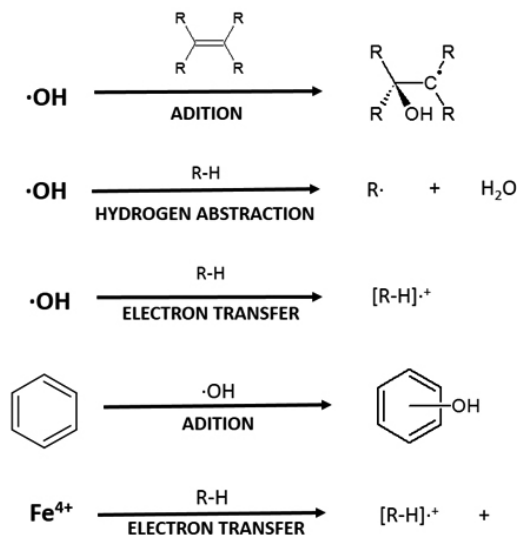
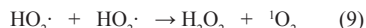


Figure 5. Hydroxyl radical and ferryl reactivity against organic substrates

There are several publications that probe the Haber-Weiss mechanisms of

Fenton reaction (mediated by $\cdot\text{OH}$ ^(28, 42) and others that probe the Bray-Gorin mechanism of Fenton reaction (mediated by $[\text{FeO}]^{2+}$)^(43, 44). However, in some of these publications have been proposed the formation of different oxidant species in dependence of reaction conditions (pH, reagents concentration, redox potential, etc.)⁽⁴⁵⁻⁴⁹⁾. Lee et al⁽⁴⁸⁾ and Bataineh et al⁽⁴⁹⁾ propose the pH as the main factor but these results are not concluding.

Recently, the singlet oxygen ($^1\text{O}_2$) have been postulated between the oxidant compounds generated by Fenton reaction^(50, 51) (9-11). This species is stronger oxidant than triplet oxygen^(52, 53).



The effect of pH in the iron species, the Fe(II) recycling mechanisms, limiting step and oxidant species generated are summarized in Figure 6.

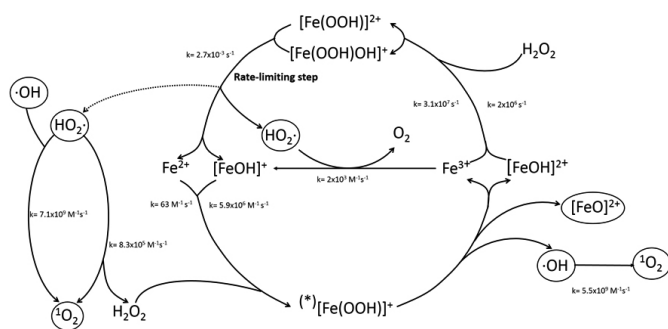


Figure 6. Redox cycle of Fenton reaction based in kinetic values from literature^(7, 54-56).

The Fenton reaction can be explained as a substrate oxidation by H_2O_2 catalyzed by Fe(II) establishing a redox cycle. Figure 6, shown how H_2O_2 (relative stable) is transform in very reactive species that reacts again substrates. Thus, soluble Fe(II) species bind H_2O_2 being obtained $[\text{Fe}(\text{OOH})]^{2+}$, this decomposes to $[\text{FeO}]^{2+}$ and $\cdot\text{OH}$. This last, can disproportionate to $^1\text{O}_2$. This is the main oxidant production stage in the Fenton reaction, after a Fe(II) recycling stage have to be established from Fe(III) soluble species. These species, are binding by H_2O_2 (reactive in excess) to peroxocomplexes in a fast step. Later, these complexes disproportionate to Fe(II) and $\text{HO}_2\cdot$ in the rate limiting step. From this step, Fe(II) is recuperated directly and $\text{HO}_2\cdot$ can reduce another Fe(III) to Fe(II). The $\text{HO}_2\cdot$ can reacts with $\cdot\text{OH}$ to $^1\text{O}_2$ in a secondary reaction, because both radicals are in low concentration.

4. Ligands effects on Fenton Reaction

The speciation of Fe^{2+} and Fe^{3+} hydroxide-complexes (pH dependent) are very important to define the reactivity of the Fenton and Fenton like systems. The importance of the iron coordination sphere constitution on Fenton reactivity can be applied for others iron ligands. In this way, some authors have been postulated that the coordination number of some organic ligands are mainly pH depending than concentration depending^(57, 58).

Sun and Pignatello⁽⁵⁹⁾ propose that ligands can modify the reactivity of Fenton's systems by three ways: (I) modification of redox properties of the metal, (II) create a labile coordination site that could be occupied by H_2O_2 , (III) competence with the substrate for the oxidant compounds.

According to way (I), organic ligands at higher pH values can chelate iron completely⁽⁶⁰⁻⁶²⁾, changing the redox potential of $\text{Fe}^{2+}/\text{Fe}^{3+}$ pair ($E^\circ = +0.771 \text{ V}$)⁽⁶³⁾. Considering the way (II) and highlighting that the first transition period are labile, following a dissociative mechanisms ($\text{S}_{\text{N}}1$)⁽⁶⁴⁾. The Fe^{3+} complexes can shows several labile positions to be substituted by H_2O_2 and, if the ligand is redox active, reduce Fe^{3+} ^(65, 66). Devanur et al.⁽⁶⁷⁾, synthesized a deferiprone bis-complex. This compound have two free coordination sites for water that can be replaced by H_2O_2 producing a peroxo-complex and releasing $\cdot\text{OH}$. This is not true for other ligands, Strlič y col.⁽⁶⁸⁾ determine that in 1,2-dihydroxybenzenes (DHB) bis-complexes of iron is not possible the H_2O_2 incorporation in the coordination sphere. In this way this ligand acts as an antioxidant. However, Kawabata et al.⁽⁶⁹⁾ determine the inclusion of H_2O_2 in the coordination sphere in DHB iron complexes and the production of oxidant species.

Tris-complexes show an antioxidant behavior, because the complete Fe^{3+} chelation. This avoids the access of H_2O_2 to the coordination sphere. Thus the Fenton reaction is inhibit⁽⁷⁰⁾. The complete Fe^{3+} chelation is improved at high pH values.

The prooxidant ability of ligands through a Fenton reaction, have been observed in several compounds. Between these are highlighted 2,4-dimethylaniline⁽⁴⁶⁾, EDTA, DTPA and desferal⁽⁷¹⁾, humic acids⁽⁷²⁾, oleuropein⁽⁷³⁾, malonic acid, oxalic acid⁽⁷⁴⁾, ascorbic acid⁽⁷⁵⁾ and DHBs⁽⁷⁶⁾. The prooxidant ability has been associated to the Fe^{3+} reduction to Fe^{2+} and the establish of a redox cycle⁽⁷⁷⁾. A similar effect have been describe for Cu(I) Fenton reaction⁽⁷⁸⁾.

The antioxidant ability of iron ligands has been associated to radical scavenger, radical deactivation and inhibition of the initiation reaction by metal chelation. Between these are highlighted ferulic acid⁽⁷⁹⁾, carotenoids⁽⁸⁰⁾, tannic acid⁽⁸¹⁾, DHB⁽⁸²⁾, flavonoids⁽⁸³⁾.

Several ligands, known for their antioxidant properties, have shown pro-oxidant activity, and vice versa⁽⁶⁸⁾. This dual behavior have been attributed to reaction variables like reagents concentration and pH^(84, 85). Between these are highlighted flavonoids⁽⁸⁶⁾, carotenoids, ascorbic acid, tocopherols⁽⁸⁷⁾ and DHB⁽⁸⁸⁻⁹¹⁾.

The DHB have special interest because its participation in several biological systems like metabolic pathways in mammals, fungal mechanisms for wood biodegradation, etc.^(1, 92-94).

5. DHB driven Fenton reaction

The Fenton reaction driven by DHB has been studied in different systems like metabolic pathways in biological systems⁽⁹⁵⁻⁹⁷⁾ and advanced oxidation process (AOPs) to water or wastewater treatment^(76, 89, 98, 99). This phenomenon has been explained by several authors through distinct reaction pathways: (I) DHBs can form complexes with Fe^{3+} and then reduce it to Fe^{2+} ⁽¹⁰⁰⁾. In this process the DHB is oxidized to the corresponding semiquinone^(77, 101), whereby the pKa of the hydroxyl groups has high importance because the ligand is the deprotonated DHB⁽¹⁰²⁾. The semiquinone can reduce another Fe^{3+} to Fe^{2+} forming the corresponding quinone (Figure 7)⁽¹⁰²⁾. Evidence of the formation of semiquinone- Fe^{2+} complex, has been found through Mössbauer spectroscopy⁽⁶⁶⁾ and by magnetic moment measure⁽¹⁰³⁾. (II) Semiquinone is also an oxidant specie, therefore in addition to oxidize substrates may also react with H_2O_2 ^(104, 105)(12). (III) Peroxo-complex intermediaries stabilization^(25, 106). (IV) "Redox cycle" (quinone-hydroquinone). This amplifies the reduction of Fe^{3+} to Fe^{2+} through hydroxy hexadienyl products formed in the oxidation of 1,2-DHB by $\cdot\text{OH}$ radicals which also possess reductive capacity. It is also known that while quinones are reduced may cause oxidation of other molecules involved in the redox cycle like other 1,2-DHB^(107, 108). The quinones can also be oxidized to CO_2 while reducing Fe^{3+} ⁽¹⁰⁹⁾. (V) O_2 a $\text{O}_2\cdot^-$ reduction by semiquinone. $\text{O}_2\cdot^-$ can also react with H_2O_2 to give $\cdot\text{OH}$ radicals, O_2 y OH^- ^(110, 111).

In the DHBs ligands are biological catecholamines (dopamine, epinephrine and norepinephrine). These compounds are high importance in the human physiology and pathophysiology. Thus, these compounds have been related with the etiology and development of Parkinson's disease⁽¹¹²⁻¹¹⁴⁾, stress-induced arrhythmias, cardiopathies⁽¹¹⁵⁾ and inflammatory damage caused by chronic stress⁽¹¹⁶⁾.

Catecholamines form complexes with Fe^{3+} by the catecholate group. The coordination number is pH dependent⁽¹¹⁷⁾. At acidic pH mainly mono-complex are formed this are very unstable since quickly reduce Fe^{3+} to Fe^{2+} by inner-sphere mechanism. At neutral pH bis-complexes are formed, this are more stable than mono-complex. At basic pH the stable tris-complexes are formed⁽¹¹⁸⁾.

Recent results (unpublished) are showed that catecholamines are able to drive a Fenton reaction in a similar way than other DHB^(18, 70). These systems are able to degrade recalcitrant compounds. However, the degradation is closely pH related and only is performed by the mono-complexes.

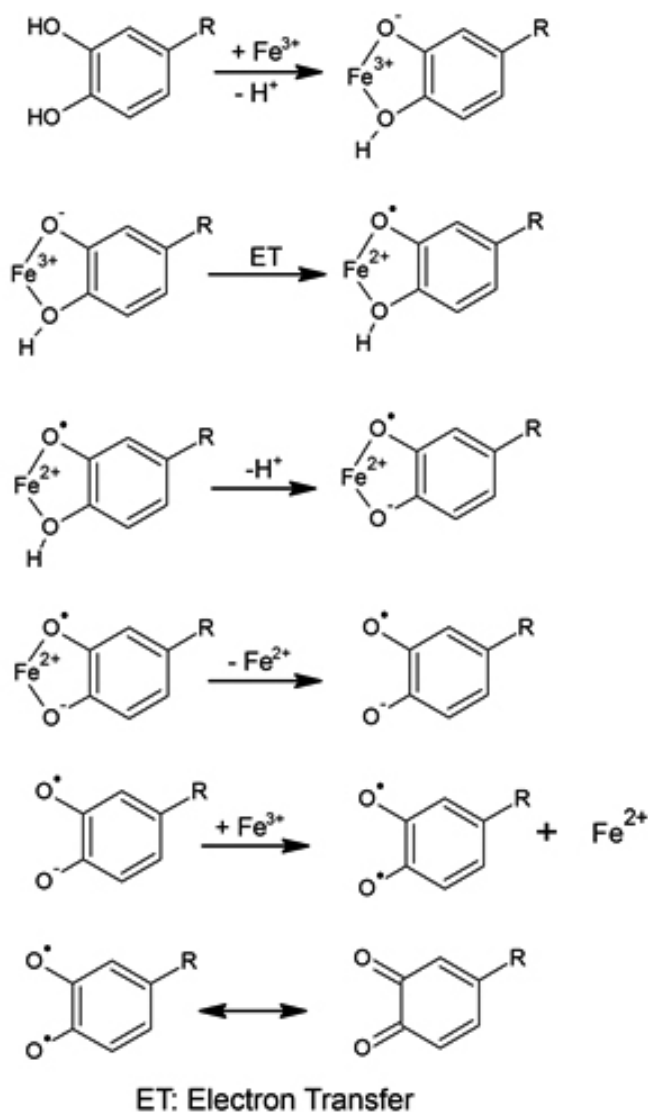


Figure 7: Fe^{3+} reduction mechanisms by DHBs.



CONCLUSION

There are several controversial reports about the kind and amount of oxidant species generated by a Fenton reaction. Some authors relate this variability with the reaction conditions. Notwithstanding these differences, there are accordance about the importance of the ligands in the coordination sphere of Fe^{2+} (or Fe^{3+} in Fenton-Like) for the reactivity of a Fenton system. The prooxidant and antioxidant effect of the ligands depends of the nature and coordination number. These factors in turn depend on the reaction conditions (pH, reagents concentration, etc.). The DHBs have special importance because are involve in several biological systems and AOPs, also this compound can increase, induce or inhibit a Fenton reaction by several pathways depending of the reaction conditions. The understanding of these systems can be very important to modify biological process (fungal wood biodegradation, neurological diseases, etc.) and develop AOP technologies.

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