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Review

Oxidation of organic substrates in aerated aqueous solutions by the Fenton reagent

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Abstract

There is only limited information about Fenton reactions involving organic substrates in oxygenated systems. In the presence of dioxygen, substrate radicals $^\bullet$R are generally converted rapidly into peroxyl radicals, $^\bullet$OOR, so that these radicals are the main reactive species in aerated aqueous systems under the majority of conditions. It is argued that the reactions of the peroxyl radicals with the transition metal complexes present in the solution are the key steps in determining the nature of the products and their yields.

Keywords: Fenton reactions; Organic substrates; Aerated solutions

1. Introduction

In 1894 Fenton reported that alcohols are oxidized in the presence of H_2O_2 and $Fe(H_2O)_6^{2+}$ [1]. ‘Fenton Reagents’ refer thus to a mixture of hydrogen peroxide and ferrous salts and ‘Fenton-like reactions’ are analogous reactions of peroxides with metal complexes, M^nL_m, in their low valent oxidation states (e.g. Fe(II), Cu(I), Ti(III), Cr(II), Co(II)). ‘Fenton-like’ reactions play an important role in a variety of catalytic and biological processes. In biology these reactions are believed to be the main source of reactive oxygen species (ROS) in the cell [2–6] causing a variety of diseases, e.g. cancer, arteriosclerosis, essential hypertension, Alzheimer’s disease, amyloidosis, osteoarthritis, etc. [7,8]. After more than 110 years of further research the active intermediate in, and detailed mechanism of, these kinds of reaction are still ambiguous and repeatedly discussed in many publications and

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reviews, e.g. [9–16]. In 1934 Haber and Weiss [17] suggested that the key step in this process is [14]:

$$H_2O_2 + Fe(H_2O)_6{}^{2+} \rightarrow {}^\bullet OH + OH^- + Fe(H_2O)_6{}^{3+}$$
$$k = 42\text{–}79\,M^{-1}\,s^{-1} \qquad (1)$$

The rates of Fenton-like reactions depend on the nature of M, L, ROOR′, and the medium. They might be orders of magnitude faster than reaction (1) e.g. for Fe^{2+} with suitable ligands:

$$ROOH + M^nL_m \rightarrow {}^\bullet OR + OH^- + M^{n+1}L_m \qquad (2)$$

Thus the $^\bullet OH/RO^\bullet$ radical is suggested to be formed as the active intermediate via an outer sphere mechanism and radical pathways are generally assumed throughout the remaining mechanism.

However, detailed kinetic studies and thermodynamic considerations indicate that hydroxyl radicals or $RO^\bullet$ radicals are not formed in all these reactions [10,11,13,18–24]. The detailed mechanism seems to involve the formation of a transient low-valent transition metal peroxide complex via an inner sphere mechanism [10,21]:

$$H_2O_2 + M^nL_m \rightleftarrows L_mM^{n\bullet}H_2O_2 \text{ or } L_{m-1}M^{n\bullet}H_2O_2 + L \qquad (3)$$

followed by one of the ensuing routes:

$$L_{m-1}M^{n\bullet}H_2O_2 \xrightarrow{+L} M^{n+1}L_m + {}^\bullet OH + OH^- \qquad (4a)$$

$$L_{m-1}M^{n\bullet}H_2O_2 \rightarrow L_{m-1}M^{n+2}{=}O + H_2O \qquad (4b)$$

$$L_{m-1}M^{n\bullet}H_2O_2 \xrightarrow{+RH} M^{n+1}L_m + R^\bullet + H_2O + OH^- \qquad (4c)$$

$${}^\bullet OH + RH \rightarrow R^\bullet + H_2O \qquad (5)$$

$$L_{m-1}M^{n+2}{=}O + RH \xrightarrow{+L} M^{n+1}L_m + R^\bullet + OH^- \qquad (6)$$

(H_2O_2 is used in these equations for simplicity purposes, but other peroxides might be involved).

Accordingly either the hydroxyl radical ($RO^\bullet$ radical) or a high valent transition metal species, e.g. a ferryl species, can be formed, or the organic substrate can be directly oxidized by the $L_{m-1}M^{n\bullet}H_2O_2$ transient. Obviously the rates of reaction of those species might well differ from those of the $^\bullet OH$ radicals with the substrate. In the presence of an organic substrate, RH, often the same radicals $R^\bullet$ are ultimately formed.

The results point out that the choice of the route to $R^\bullet$ depends on the nature of M, of L, of RH and its concentration, and on the medium, e.g. the pH [10,21,25,26].

Recent results demonstrate that for $M^nL_m = Fe(H_2O)_6{}^{2+}$ in strongly acidic solutions reaction (4b) is the dominant pathway [19,23]. For Fe(edta) the Fenton product was shown to be indistinguishable from the $^\bullet OH$ radical under the majority of conditions [25], whereas for Fe(nta) oxidations by ferryl species are more favored under most conditions [26]. Analogously it was shown that also in the aqueous Cu(I) and Cu(I)phen/H_2O_2 system the main product is not the hydroxyl radical [21,27,28].

An important source of H_2O_2 in biological and catalytic systems is dioxygen, which can react with low-valent transition metal complexes via the following sequence:

$$M^nL_m + O_2 \rightarrow M^{n+1}L_m + O_2{}^{\bullet-} \qquad (7)$$

$$2O_2{}^{\bullet-} + 2H^+ \rightarrow H_2O_2 + O_2 \qquad (8)$$

$$M^nL_m + O_2{}^{\bullet-} \xrightarrow{H^+} M^{n+1}L_m + H_2O_2 \qquad (9)$$

or analogous reactions.

Low-valent transition metal complexes can be formed in systems containing a reducing agent (e.g. ascorbate) and a higher valent transition metal complex. These kinds of systems are often referred to as Udenfriend reagents and serve as models for oxygenases [29,30]. Reactions (7)–(9) are also the main source of $O_2{}^{\bullet-}$ and H_2O_2 in biological systems and thus the source of biological deleterious processes.

2. Oxidation of organic substrates by Fenton reagents in aqueous solutions

The oxidation of organic substrates by Fenton reagents is reviewed in several recent publications [11–16]. Unfortunately there is only limited information about Fenton reactions in oxygenated systems.

In general the oxidation of organic substrates RH under anaerobic conditions is frequently described by Eqs. (10)–(12), following the production of the organic radicals $^\bullet R$ via one of the abovementioned routes:

General case:

$${}^\bullet R + M^{n+1}L_m \rightarrow M^nL_m + R^+ \xrightarrow[-H^+]{+H_2O} R\text{–}OH \qquad (10)$$

$${}^\bullet R + M^nL_m \rightarrow M^{n+1}L_m + R^- \xrightarrow[-OH]{+H_2O} R\text{–}H \qquad (11)$$

$${}^\bullet R + {}^\bullet R \rightarrow R\text{–}R \text{ or } R^+(ROH) + R^-(RH) \qquad (12)$$

Product distribution of R–OH, R–H, and R–R are obviously governed by the nature of the radical $^\bullet R$, the complex and the medium.

Organic substrates not containing activating substituents (e.g. alkanes) are usually studied mainly in organic solvents [31,32] and are not within the scope of this review.

2.1. *Reaction with alcohols*

The reaction of Fenton reagent's with alcohols (easily oxidizable substrates) under anaerobic conditions can be described according to Scheme 1 (example for 2-propanol [15,16], for simplicity the radical pathway based on $^\bullet OH$ radicals is shown, although in the following schemes the organic radicals ($R^\bullet$) can alternatively be produced via reactions (4b),

$$^{\cdot}OH + CH_3CH(OH)CH_3 \rightarrow H_2O + CH_3C^{\cdot}(OH)CH_3 \quad k_{\alpha} = 1.7\text{x}10^9\ M^{-1}s^{-1}[15, 16] \quad (13)$$

$$^{\cdot}OH + CH_3CH(OH)CH_3 \rightarrow H_2O + {}^{\cdot}CH_2CH(OH)CH_3 \quad k_{\beta} = 2.7\text{x}10^8\ M^{-1}s^{-1}\ [15, 16] \quad (14)$$

$$^{\cdot}OH + M^nL_m \rightarrow HO\text{-}M^{n+1}L_m\ (OH^- + M^{n+1}L_m) \quad k_{14(Fe_{aq}^{2+})} = 3.0\text{x}10^8\ M^{-1}s^{-1}\ [15, 16] \quad (15)$$

$$CH_3C^{\cdot}(OH)CH_3 + M^{n+1}L_m \rightarrow CH_3COCH_3 + H^+ + M^nL_m \quad (16)$$

$$2\,{}^{\cdot}CH_2CH(OH)CH_3 \rightarrow CH_3CH(OH)CH_2CH_2CH(OH)CH_3 \quad (17)$$

Scheme 1.

(6) or (4c) for those systems, where the Fenton reaction does not produce “free” $^{\bullet}OH$ radicals).

Hydrogen atoms are abstracted from alcohols (ROH) by $^{\bullet}OH$ preferably from the α-position (reaction (12)) and the distribution between α and β (and γ, etc.) abstraction products is specified by the relative rate constants [33]. The product of reaction (13) is oxidized fast by Fe(III) to yield the respective aldehyde or ketone (reaction (16), whereas that of reaction (14) accumulates to yield termination products; e.g. dimerization, reaction (17)).

However studies in the last 30 years [34] suggest that the reactions of the organic radicals with the transition metal complexes present in solution should be added to Scheme 1. Most of these reactions do not proceed via an outer sphere electron transfer mechanism but involve the formation of transient complexes with metal–carbon σ-bonds [11,34,35]. These transients decompose either via heterolysis, homolysis or β-elimination reactions in the presence of a suitable leaving group (reaction (18)) and the products of these reactions have to be considered [11,34,35]. In biological systems the decomposition of these transients, especially via β-elimination processes, cause irreversible structural modifications of the aliphatic residue, and are often deleterious.

$$\begin{aligned} &M^nL_m + {}^{\bullet}CH_2CH(OH)CH_3 \\ &\xrightarrow[-L]{} L_{m-1}M^{n+1}\text{–}CH_2CH(OH)CH_3 \\ &\rightarrow M^{n+1}L_m + CH_2{=}CHCH_3 + OH^- \qquad (18) \end{aligned}$$

Earlier reports, publishing mainly the relative reactivities of the intermediate of the original Fenton reaction toward various substrates and comparing them to those of hydroxyl radicals produced by radiation chemistry, established that the data are essentially in agreement with the $^{\bullet}OH$ radical being the active intermediate, unless ferryl species and $^{\bullet}OH$ radicals are kinetically equivalent [15]. But more recent findings demonstrate discrepancies in reactivity patterns on studying an extensive list of substrates and imply two active intermediates (presumably a ferryl species and an iron-peroxo complex) differing from the OH radical [24].

2.2. *Substrates in the presence of oxygen*

It should be mentioned, that according to Sawyer et al. [13], intermediates of the oxygenated Fenton chemistry (mainly in non-aqueous systems) are oxygen adducts derived from the products of reaction (3), $L_mM^{n\bullet}H_2O_2$ or $L_mM^n\text{–}^{-}OOH$. These intermediates supposedly react with the substrate to incorporate it (Scheme 2) and subsequently produce oxygenated products. Neither $^{\bullet}OH$ or carbon centered radicals are supposedly produced at any stage of the mechanism [13]. However, there is compelling evidence that, at least in aqueous solutions, radicals are major products of the reaction [11,16,36].

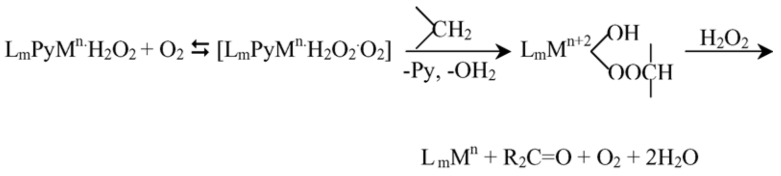
The possible follow-up reactions of the α-radicals formed in reaction (13) in oxygenated solutions are summed up in reactions (19)–(21) (incl. rate constants for RH = ethanol and $M^nL_m = Fe_{aq}^{2+}$) [37–39].

$$^{\bullet}R_{\alpha} + H_2O_2 \rightarrow ROH + {}^{\bullet}OH, \quad k_{17} = 1.6 \times 10^5\ M^{-1}\ s^{-1} \qquad (19)$$

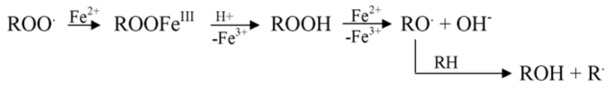
$$^{\bullet}R_{\alpha} + M^{n+1}L_m \rightarrow P + M^nL_m + H^+, \quad k_{18} = 3.8 \times 10^8\ M^{-1}\ s^{-1} \qquad (20)$$

$$^{\bullet}R_{\alpha} + O_2 \rightarrow RO_2{}^{\bullet}, \quad k_{19} = 4.6 \times 10^9\ M^{-1}\ s^{-1} \qquad (21)$$

The rates of reaction of most radicals with dioxygen are nearly diffusion controlled ($k > 10^9\ M^{-1}\ s^{-1}$). Thus, in the presence of dioxygen, alkyl radicals $^{\bullet}R$ are generally converted rapidly into peroxyl radicals, $^{\bullet}OOR$, so that these radicals are the main reactive species in aerated aqueous systems under the majority of conditions (excess substrate, etc.).



Scheme 2.



Scheme 3.

The possible follow-up reactions of the $ROO^{\bullet}$ radicals, formed in aerated solutions, are summarized very briefly by Gozzo [12] in Scheme 3. According to this scheme the peroxyl radicals are reduced by Fe^{2+} to form hydroperoxides. These hydroperoxides react in a Fenton-like reaction to form alkoxyl radicals, which abstract H from C–H bonds more selectively than $^{\bullet}OH$ radicals. If the $R^{\bullet}$ radical is a carbon centered radical of the type $^{\bullet}CR^1R^2OH$ then the final product is a ketone or an aldehyde (reaction (16)) [12].

The oxidation of ethanol in aerated aqueous solutions was described in more detail by Sychev [14] in Scheme 4. The mechanism includes the formation and ensuing potential reactions of the peroxyl radical derived from ethanol, entailing unimolecular elimination of $HO_2^{\bullet}$ to produce the aldehyde (reaction (22)), H-abstraction from the substrate ROH (reaction (23)), and reaction with iron(II) (reaction (24)). Possible metal-bound intermediates are not mentioned in this context. This scheme does not include the role of the $^{\bullet}R_{\beta}$ radicals. It should be noted that this scheme describes a chain process without a termination step.

Peroxyl radicals in general may undergo a number of unimolecular (e.g. $HO_2^{\bullet}$ and $O_2^{\bullet-}$ eliminations) and bimolecular processes (dimerization, reactions with organic solutes/substrates) as specified also in Scheme 4. However, the rates of the latter bimolecular processes are usually considerably slower than those of the reactions with M^nL_m [11,40]:

$$M^nL_m + RO_2^{\bullet} \leftrightarrows L_mM^{n+1}\text{–OOR} \tag{29}$$

These kinds of reaction are well documented in the literature for a number of transition metal complexes [35,41]. Moreover the reactions of $RO_2^{\bullet}$ (R: H, CH_3, CH_2COOH, CH_2CN, $CH_2C(CH_3)_2OH$, CH_2OH, $CHCl_2/CCl_3$) radicals with $Fe(H_2O)_6^{2+}$ were studied recently [40]. All these processes involve reaction (29) with an equilibrium constant of $K_{29} \sim 200\ M^{-1}$. (Surprisingly enough the K values are nearly independent of the redox potential of the radical and are considerably higher than calculated from the relevant redox potentials. These results indicate that the ROO^- ligands considerably stabilize the Fe(III) complex, this stabilization is smaller for radicals with electron withdrawing groups which raise the redox potential of the radical but decrease the basicity of the ROO^- ligands, two effects which seem to nearly cancel each other.) The values of k_{27} ($\sim 2.6 \times 10^6\ M^{-1}\ s^{-1}$) approach the ligand exchange rate of $Fe(H_2O)_6^{2+}$, implying that the rate determining step of these reactions is the ligand exchange step [42]. Thus these kinds of reaction are expected to compete efficiently with the abovementioned bimolecular processes of peroxyl radicals not involving metal complexes.

$$H_2O_2 + Fe(H_2O)_6^{2+} \rightarrow {}^{\cdot}OH + OH^- + Fe(H_2O)_6^{3+} \tag{1}$$

$${}^{\cdot}OH + C_2H_5OH \rightarrow {}^{\cdot}R_{\alpha} + H_2O \tag{5'}$$

$${}^{\cdot}R_{\alpha} + O_2 \rightarrow RO_2^{\cdot} \tag{21}$$

$$RO_2^{\cdot} \rightarrow CH_3CHO + HO_2^{\cdot} \tag{22}$$

$$RO_2^{\cdot} + ROH \rightarrow CH_3CH(OOH)OH + {}^{\cdot}R_{\alpha} \tag{23}$$

$$RO_2^{\cdot} + Fe^{2+} \xrightarrow{H+} Fe^{3+} + CH_3CH(OOH)OH \tag{24}$$

$$HO_2^{\cdot} + C_2H_5OH \rightarrow {}^{\cdot}R_{\alpha} + H_2O_2 \tag{25}$$

$$HO_2^{\cdot} + Fe^{2+} \xrightarrow{H+} Fe^{3+} + H_2O_2 \tag{26}$$

$$HO_2^{\cdot} + Fe^{3+} \longrightarrow Fe^{2+} + O_2 + H^+ \tag{27}$$

$$CH_3CH(OOH)OH \rightarrow CH_3CHO + H_2O_2 \tag{28}$$

Scheme 4.

The following reactions are subsequently involved in the decomposition of the peroxo iron complex [40]:

$$(H_2O)_5Fe^{III}\text{–}OOR^{2+} + H_3O^+/H_2O \rightarrow Fe(H_2O)_6^{3+} + ROOH + H_2O/OH^- \tag{30}$$

$$(H_2O)_5Fe^{III}\text{–}OOR^{2+} + 2Fe(H_2O)_6^{2+} \rightarrow 3Fe(H_2O)_6^{3+} + ROH \tag{31}$$

$$2RO_2^{\bullet} \rightarrow \text{products} \tag{32}$$

$$RO_2^{\bullet} + (H_2O)_5Fe^{III}\text{–}OOR^{2+} \rightarrow Fe(H_2O)_6^{2+} + \text{products} \tag{33}$$

The rate constant of reaction (31) (clearly not an elementary reaction), a Fenton-like reaction, was found also to approach the ligand exchange rate and thus is several orders of magnitude faster than the Fenton reaction. This result points out that the metal complex activates the peroxide towards the Fenton-like reaction [40].

The Fenton reaction is also used as an application for the determination of the concentrations of H_2O_2 and hydroperoxides in biological samples in the FOX assay [43]. In this assay the yield of Fe(III), produced in the Fenton reaction, is measured via the absorption of its complex with xylenol orange. The addition of alcohols to the aerated reaction mixture increases the Fe(III) yield. Thus for example in solutions containing 0.1 M sorbitol the yield is $[Fe(H_2O)_6^{3+}]/[H_2O_2] = 14$ [44]. This result clearly points out that the $Fe(H_2O)_6^{3+}$ is formed in a chain reaction. Two mechanisms were suggested in the literature for this process:

1. Wolff [43] suggested the following mechanism:

$$H_2O_2 + Fe(H_2O)_6^{2+} \rightarrow HO^{\bullet} + OH^- + Fe(H_2O)_6^{3+} \tag{1}$$

$$HO^{\bullet} + R_2CHOH \rightarrow H_2O + R_2C^{\bullet}OH \qquad (5')$$

$$R_2C^{\bullet}OH + O_2 \rightarrow R_2C(OO^{\bullet})OH \qquad (21')$$

$$R_2C(OO^{\bullet})OH \rightarrow R_2C{=}O + HO_2^{\bullet} \qquad (22')$$

$$HO_2^{\bullet} + Fe(H_2O)_6^{2+} \rightarrow H_2O_2 + Fe(H_2O)_6^{3+} \qquad (26)$$

However it is difficult to suggest which reaction terminates this chain process as the rates of reactions (5), (21) and (22) and (26) are known and are high. Thus second order reactions between the radicals are not expected to compete with these reactions.

2. Gebicki [45] proposed reaction (34) instead of (26) in the reaction mechanism (first four reactions analogous to Wolff):

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \qquad (34)$$

This mechanism is clearly wrong as it predicts a yield of $[Fe(H_2O)_6^{3+}]/[H_2O_2] = 2$.

A recent study [44] points out, that the length of the chain depends linearly on the number of CH_nOR ($n = 1$ or 2) groups in the alcohol. The reaction is accelerated by increasing $[Fe(H_2O)_6^{2+}]$ but this cation is also active in at least one of the termination steps of the chain reaction. Addition of ethanol to a solution containing sucrose shortens the chain lengths. Saturation with dioxygen, instead of air, increases the chain length. The increase in [alcohol] increases the chain length up to a limiting value [44].

An attempt to establish a complete, general scheme of all relevant reactions of the Fenton-like reactions with organic substrates in oxygenated aqueous solutions has to include the following reactions and considerations:

(1) choice of pathway and intermediate of the initial Fenton reaction, according to conditions, etc. (from reactions (3)–(6))

(2) reactions of the organic radicals derived from the organic substrates including its reaction with dioxygen, vide supra, and possible unique reactions (e.g. water-elimination reactions of α,β-diolic radicals (e.g. sugars) [46])

(3) reactions of the peroxyl radicals:
  - unimolecular reactions ($HO_2^{\bullet}$ elimination from hydroxyperoxyl radicals to yield the corresponding aldehyde or ketone) [46–48]
  - bimolecular reactions of the peroxyl radical
    (a) dimerization
    (b) hydrogen abstraction reactions, preferably from substrate
    (c) reaction with the metal complex to form a transient metal-bonded intermediate:

$$M^{n+} + ROO^{\bullet} \leftrightarrows (M^{n+1}{-}OOR)^{n+}$$

The rate of this reaction is usually controlled by the rate of ligand exchange, e.g. for Fe_{aq}^{2+} ca. $1 \times 10^6\ M^{-1}\ s^{-1}$. Thus this reaction is expected to compete efficiently with reactions (a) and (b).

(4) decomposition of the metalperoxo complex [11,40,41]:

these can generally decompose via a variety of possible reactions, but preferably decompose via heterolysis of the M–O bond to yield the hydroperoxide species, or via Fenton-like reactions [11,40]. In the case of Fenton systems, reactions (30), (31) and (33) have to be considered, vide supra [40]:

$$(M^{n+1}{-}OOR)^{n+} \leftrightarrows M^{n+1} + HOOR$$

(5) reactions of any other unstable species:

e.g. HOOR peroxides of the form HOOR′(OH) decompose further in the following possible reactions:

$$\begin{aligned} &HO_2CH(CHR'OH)OH \\ &\quad\rightarrow HC(O)(CHR'OH) \\ &\qquad + H_2O_2 \text{ or } C(O)(CHR'OH)OH + H_2O \qquad (35) \end{aligned}$$

The decomposition into the acid is acid catalyzed, whereas the aldehyde analogue preferably forms in more basic solutions and at higher temperatures [49].

Incorporating the experimental results and the above considerations a scheme describing Fenton reactions with alcoholic substrates in aqueous aerated solutions was derived [44,18,47,48,40,50]:

$$\begin{aligned} &Fe(H_2O)_6^{2+} + H_2O_2 \rightleftarrows [(H_2O)_5Fe^{II\bullet}H_2O_2] \\ &\quad\rightarrow (H_2O)_5Fe^{IV}{=}O^{2+} + H_2O, \quad 56\ M^{-1}\ s^{-1} \qquad (4b') \end{aligned}$$

$$\begin{aligned} &(H_2O)_5Fe^{IV}{=}O^{2+} + R^1R^2CHOH \\ &\rightarrow Fe(H_2O)_5(OH)^{2+} + R^1R^2C \cdot OH(\equiv R^{\bullet}) \qquad (6') \end{aligned}$$

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}, \quad k \geq 1 \times 10^9\ M^{-1}\ s^{-1} \qquad (21)$$

$$RO_2^{\bullet} \rightarrow R^1R^2C{=}O + HO_2^{\bullet}, \quad 400\ s^{-1} < k < 7000\ s^{-1} \qquad (22')$$

$$\begin{aligned} &RO_2^{\bullet}\backslash HO^{\bullet}_2 + Fe(H_2O)_6^{2+} \rightleftarrows (H_2O)_5Fe^{III}{-}OOR^{2+}, \\ &\quad k > 2 \times 10^6\ M^{-1}\ s^{-1},\ K \sim 200\ M^{-1} \qquad (29') \end{aligned}$$

$$\begin{aligned} &(H_2O)_5Fe^{III}{-}OOR^{2+} \xrightarrow{H^+} Fe(H_2O)_6^{3+} + HOOR, \\ &k \sim 1500\ M^{-1}\ s^{-1} \qquad (30) \end{aligned}$$

$$\begin{aligned} &(H_2O)_5Fe^{III}{-}OOR^{2+} + Fe(H_2O)_6^{2+} \\ &\quad \xrightarrow{H^+} (H_2O)_5Fe^{IV}{=}O^{2+} + Fe(H_2O)_6^{3+} + ROH, \\ &k \sim 5 \times 10^5\ M^{-1}\ s^{-1} \qquad (31a) \end{aligned}$$

$$(H_2O)_5Fe^{IV}{=}O^{2+} + Fe(H_2O)_6^{2+} \xrightarrow{2H^+} 2Fe(H_2O)_6^{3+},$$

$$k < 3 \times 10^{6}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1} \tag{36}$$

Moreover in principle two types of radicals $R^{\bullet}$ are formed, depending on the substrate:

a. A terminal, α, ω, radical $^{\bullet}CH(CHR'OH)OH \equiv {}^{\bullet}R^{1}$,
b. A β radical $^{\bullet}C(CHR'OH)(CHR''OH)\ OH \equiv {}^{\bullet}R^{2}$.

Both these radicals react with dioxygen to yield the $R^{i}O_2{}^{\bullet}$ radicals. However the latter eliminate $HO_2{}^{\bullet}$ at considerably different rates [47,48]:

$$^{\bullet}O_2CH(CHR'OH)OH \rightarrow HO_2{}^{\bullet} + CH(O)(CHR'OH),$$
$$k = 400\,\mathrm{s}^{-1} \tag{22a'}$$

$$^{\bullet}O_2C(CHR'OH)(CHR''OH)OH$$
$$\rightarrow HO_2{}^{\bullet} + C(O)(CHR'OH)(CHR''OH), \quad k = 2600\,\mathrm{s}^{-1} \tag{22b'}$$

For sugars there is an additional faster elimination step for the group next to the ether linkage ($k > 7000\,\mathrm{s}^{-1}$) [47,48]. For substrates other than alcohols reactions analogous to reaction (22) are expected to be considerably slower if they occur at all.

In order to explain the effect of $[O_2]$ on the yield of $Fe(H_2O)_6{}^{3+}$ in aerated solutions, it was concluded that the dioxygen effect, at least in the ethanol system, is due to the reaction of dioxygen with one of the reactive intermediates [44]. No such reaction is known and a plausible one is [44]:

$$(H_2O)_5Fe^{III}\text{–}OOR^{2+} + O_2$$
$$\xrightarrow[H^{+}]{} (H_2O)_5Fe^{IV}\text{–}OOR^{3+} + HO_2{}^{\bullet} \tag{37}$$

followed by

$$(H_2O)_5Fe^{IV}\text{–}OOR^{3+} \xrightarrow{H_2O} Fe(H_2O)_6{}^{3+} + RO_2{}^{\bullet} \tag{38}$$

or by

$$(H_2O)_5Fe^{IV}\text{–}OOR^{3+} \xrightarrow{H^{+}} (H_2O)_5Fe^{VI}{=}O^{4+} + ROH \tag{39}$$

The larger dioxygen effect for systems with adjacent CH_nOR groups is attributed to the competition between reactions (9) and (26) (β-elimination of water from 1,2-diol type radicals) [46]:

$$^{\bullet}CH(CHR'OH)OH \rightarrow O{=}CH(C^{\bullet}HR') + H_2O \tag{40a}$$

$$^{\bullet}C(CHR'OH)(CHR''OH)OH$$
$$\rightarrow O{=}C(C^{\bullet}HR')(CHR''OH) + H_2O \tag{40b}$$

It should be noted that if $RO^{\bullet}$ radicals are formed in the process they are considerably less reactive than the $^{\bullet}OH$ radicals. If the $RO^{\bullet}$ radical is of the type $CHR^1R^2O^{\bullet}$ it usually isomerizes into $^{\bullet}CR^1R^2OH$ [51].

3. Concluding remarks

This review clearly demonstrates that the mechanism of the Fenton reaction and Fenton-like reactions, in aerated aqueous solutions containing organic substrates is considerably more complex than usually assumed.

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