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Ferryl for real. The Fenton reaction near neutral pH

Willem H. Koppenol †

According to the literature, the Fenton reaction yields HO^\bullet and proceeds with $53 \text{ M}^{-1} \text{ s}^{-1}$ at 25°C and low pH. Above pH 5, the reaction becomes first-order in HO^- , and oxygen atom transfer has been detected, which indicates formation of oxidoiron(2+), FeO^{2+} . These observations, and the assumption that the intermediate $[\text{FeOO}]^+$ decays approximately iso-energetically to FeO^{2+} , allow one to estimate an Gibbs energy of formation FeO^{2+} of $+15 \pm 10 \text{ kJ mol}^{-1}$, from which follows the one-electron $E^\circ(\text{FeO}^{2+}, \text{H}_2\text{O}/[\text{Fe}(\text{HO})_2]^+) = +2.5 \pm 0.1 \text{ V}$ and the two-electron $E^\circ(\text{FeO}^{2+}, 2\text{H}^+/\text{Fe}^{2+}, \text{H}_2\text{O}) = +1.36 \pm 0.05 \text{ V}$, both at pH 7. In the presence of HCO_3^- , formation of $\text{FeCO}_3(\text{aq})$ occurs which may facilitate formation of the $[\text{FeOO}]^+$ intermediate, and leads to $\text{CO}_3^{\bullet-}$. At pH 7, the product of the Fenton reaction is thus FeO^{2+} , or $\text{CO}_3^{\bullet-}$ if HCO_3^- is present.

Introduction

“Die Zahl der Untersuchungen, die sich mit dem Einfluß von Eisensalzen auf den Verlauf der durch Hydroperoxyd bewirkten Oxydationen befaßt, ist nicht gering. Trotzdem kann man mit Hilfe des vorliegenden Materials kein klares Bild von dem Gegenstand gewinnen, der unser Interesse im Rahmen des Oxydationsproblems in Anspruch nimmt.”

H. Wieland and W. Franke, *Justus Liebigs Ann. Chem.*, 1927, **457**, 1–70.

(The number of investigations into the effect of iron salts on the course of oxidations caused by hydrogen peroxide is not small. Nevertheless, with the present information, we cannot obtain a clear picture of the oxidation problem that occupies our interest.)

The oxidation of Fe^{2+} by H_2O_2 is named after H. J. H. Fenton (1854–1929). In 1876, he was inspired by a fellow student who had produced a violet colour by mixing reagents randomly. Fenton found that he could reproduce the colour by the addition of H_2O_2 or HOCl to a mixture of tartaric acid and FeSO_4 or FeCl_2 , followed rapidly by the addition of a base.¹ He showed that Fe^{2+} and H_2O_2 oxidized a number of organic compounds, and that Fe^{2+} was regenerated.² In 1893, he identified the product of the oxidation of tartaric acid as dihydroxymaleic acid.³ Fenton did not study the mechanisms of the oxidations he observed. Although Wieland and Franke praised Fenton's work in 1927,⁴ Haber and Weiss^{5,6} did not mention Fenton a few years later when they proposed that the one-electron reduction of H_2O_2 by Fe^{2+} yielded HO^\bullet . It took until 1946 for Fenton's paper to be cited. Baxendale and co-workers referred

to it in a publication on the initiation of a polymerization reaction by HO^\bullet generated from the reaction of H_2O_2 with Fe^{2+} .⁷

In 1927, Wieland and Franke wrote that the reaction of Fe^{2+} with H_2O_2 may yield a higher oxidation state of iron.⁴ In 1932, Bray and Gorin⁸ proposed that the disproportionation of Fe^{3+} would yield Fe^{2+} and FeO^{2+} – “a reversible and fairly rapid reaction” – which would limit $E^\circ(\text{FeO}^{2+}, 2\text{H}^+/\text{Fe}^{3+}, \text{H}_2\text{O})$ to about, or less than, $E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+})$, +0.77 V. Such a value is not compatible with the notion that FeO^{2+} is a strong oxidant. Bray and Gorin also proposed that FeO^{2+} would be produced by the reaction of H_2O_2 with Fe^{2+} .⁸ Numerous authors mentioned this proposal, which led to the ongoing dispute whether HO^\bullet or FeO^{2+} is the product of the Fenton reaction. As radical products are observed at low pH, it is generally accepted that under that condition HO^\bullet is formed. But not by all: Kremer, for instance, has claimed that FeO^{2+} is formed^{9,10} because simulations involving HO^\bullet under conditions of excess H_2O_2 over Fe^{2+} did not yield experimentally observed amounts of O_2 . However, this simulation has been questioned.¹¹ Thus, at low pH, there is no reason to invoke FeO^{2+} as a product of the Fenton reaction. FeO^{2+} is not an imaginary species: it is the product of the reaction of Fe^{2+} with O_3 .^{12,13} Although not stable, rate constants for several reactions have been determined.^{14,15} The archaic name for FeO^{2+} is ferryl,[‡] the systematic name is oxidoiron(2+).¹⁶

‡ Formulae, trivial names, and systematic (IUPAC)¹⁶ names: Fe^{2+} , *ferrous ion*, iron (2+); $[\text{FeH}_2\text{O}_2]^{2+}$, dioxidaneiron(2+); $[\text{FeHO}_2]^+$, dioxidanidoiron(+); Fe^{3+} , *ferric ion*, iron(3+); $[\text{FeHO}]^{2+}$, hydroxidoiron(2+); $[\text{Fe}(\text{HO})_2]^+$, dihydroxidoiron(+); $[\text{Fe}(\mu\text{-HO})_2\text{Fe}]^{4+}$, di- μ -hydroxido- κO -diiron(4+); FeO^{2+} , *ferryl*, oxidoiron(2+), CO_2 , carbon dioxide, or dioxidocarbon; HCO_3^- , *bicarbonate*, hydroxidodioxidocarbonate(1[−]); HO^\bullet , hydroxyl (allowed trivial name), hydridooxygen(°) or oxidanyl; HO_2^- , dioxidanide; H_2O_2 , hydrogen peroxide (allowed trivial name), dioxidane; HOCl , *hypochlorous acid*, hydroxidochlorine; $\text{CO}_3^{\bullet-}$, *carbonate radical*, trioxidocarbonate(1[−]); $(\text{CH}_3)_2\text{SO}$, dimethyl sulfoxide or methylsulfinylmethane; $(\text{CH}_3)_2\text{SO}_2$, dimethyl sulfone or methylsulfonylmethane.



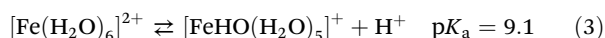
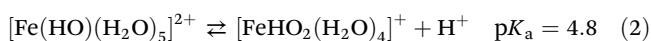
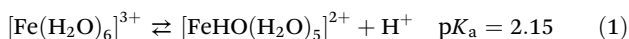
Given the importance of the Fenton reaction in physiology and for the remediation of soils, it is not surprising that, according to the Web of Science, there are close to 17 000 publications in which this reaction and its mechanism are discussed. Please note that none of the pre-1960 papers cited above can be found in this expertly curated database with the search term “Fenton reaction”. Thus, the true number is larger. The authors of these papers often use rate constants obtained at low pH to reaction schemes that pertain to neutral pH, and HO• is thought to be the reactive species responsible for physiological damage and destruction of organic compounds in soils. Furthermore, the simulations themselves are questionable.¹¹ Indeed, as stated by Wieland and Franke 95 years ago, more information has been collected, but it has not yet led to more insight. However, a better understanding of the Fenton reaction can be obtained by exploring its energetics and the increase of its rate constant with pH.

In this Review, I use the expression “Fenton reaction” for the reaction of H₂O₂ with Fe²⁺, but that does not necessarily imply that HO• is formed. I show here, based on thermodynamics and kinetics, that, near neutral pH, FeO²⁺ or CO₃^{•−} is the active agent. Reactions of multidentate Fe²⁺-complexes with H₂O₂ will not be discussed.

Thermodynamic data were obtained from literature compilations.^{17–19}

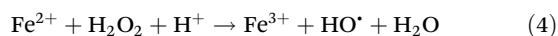
The Fenton reaction at low pH

For a discussion of the energetics of the Fenton reaction it is important to take into account the hydrolysis of Fe³⁺ and Fe²⁺. While the Fe³⁺-hexaquo complex loses two protons below pH 7, the Fe²⁺-complex does so at alkaline pH:

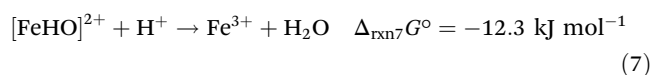
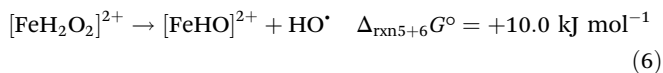
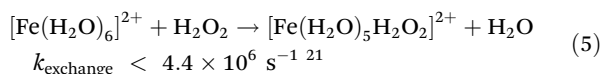


It must be emphasized that reactions (1) and (2) represent metastable equilibria, as both [Fe(HO)(H₂O)₅]²⁺ and [FeHO₂(H₂O)₄]⁺ will form haematite, Fe₂O₃.²⁰

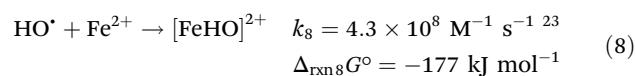
Generally, the Fenton reaction is written as in eqn (4).



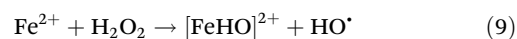
At pH 0, with $E^{\circ}(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.77$ V and $E^{\circ}(\text{H}_2\text{O}_2, \text{H}^+/\text{HO}^{\bullet}, \text{H}_2\text{O}) = +0.80$ V, $\Delta_{\text{rxn}4}G^{\circ} = -nF\Delta E^{\circ} = -F(+0.80 - 0.77)$ V = -2.3 kJ mol^{−1} with $n = 1$ electron and F the Faraday. Given that reaction (4) is an inner-sphere electron transfer, the first step is an exchange of a water molecule in the hydration sphere of Fe²⁺ for H₂O₂, which is probably slower than the H₂O exchange rate, followed by electron transfer:



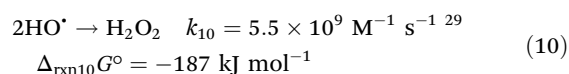
Equation 1 is the reverse of equation 7. It is noteworthy that the formation of HO•, reaction (6), is uphill. As $E^{\circ}(\text{H}_2\text{O}_2, \text{H}^+/\text{HO}^{\bullet}, \text{H}_2\text{O})$ decreases with 59 mV per pH, and $E^{\circ}(\text{Fe}^{3+}/\text{Fe}^{2+})$ is constant, $\Delta_{\text{rxn}4}G^{\circ}$ is 0 at pH 0.4, and at pH 1.0, the reaction is endergonic by +3.4 kJ mol^{−1}. Above pH 2.15, [FeHO]²⁺ will not become protonated, and thus the Fenton reaction remains unfavourable until pH 6.5 (Fig. 1). Nevertheless, the reaction proceeds because HO• is removed from equilibrium by hydrogen transfer from a second Fe(H₂O)₆²⁺,²² reaction (8):



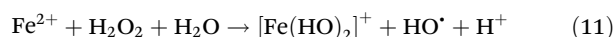
Although the energetics are pH-dependent, Hardwick found essentially the same rate constant at pH 0, 1.0, 1.9 and 2.8, at 20 °C.²⁴ The average is $43 \pm 2 \text{ M}^{-1} \text{ s}^{-1}$ which indicates that reaction (4) is better represented as reaction (9):



Depending on the pH, [FeHO]²⁺ may be stable, or proceed to Fe³⁺ or [Fe(HO)₂]⁺. The rate constant as a function of temperature is given by $k_4 = 4.5 \times 10^8 \text{ e}^{-39.5/RT} \text{ M}^{-1} \text{ s}^{-1}$ (modified from $k_4 = 5.4 \times 10^8 \text{ e}^{-39.5/RT} \text{ M}^{-1} \text{ s}^{-1}$ ²⁴), which yields $k_4 = 54 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C, and $12 \text{ M}^{-1} \text{ s}^{-1}$ at 0 °C, to be compared with experimental values of $53 \text{ M}^{-1} \text{ s}^{-1}$ and $12 \text{ M}^{-1} \text{ s}^{-1}$, respectively.^{25,26} At 37 °C, k_4 would be $99 \text{ M}^{-1} \text{ s}^{-1}$. Over the same range of temperature, but at 1 M ionic strength, Wells and Salam obtained $k_4 = 1.4 \times 10^7 \text{ e}^{-30.5/RT} \text{ M}^{-1} \text{ s}^{-1}$.²⁷ When one analyses $k_4 = 4.5 \times 10^8 \text{ e}^{-39.5/RT} \text{ M}^{-1} \text{ s}^{-1}$ by transition state theory (incorrect, but defensible), one finds $\Delta H^{\ddagger} = 35 \text{ kJ mol}^{-1}$ and $\Delta S^{\ddagger} = -96 \text{ J (K mol)}^{-1}$. While the activation enthalpy does not seem unusual, the negative entropy of activation could indicate that a specific orientation of Fe²⁺ to H₂O₂ is essential. This may reflect that a single electron transfer needs to be transferred from an iron 3d orbital into the empty σ* antibonding orbital of H₂O₂. Overlap between these two orbitals is sterically difficult.²⁸ As $\Delta_{\text{rxn}9}G^{\circ}$ also equals $-RT \ln k_9/k_{-9}$, and $k_9 = 53 \text{ M}^{-1} \text{ s}^{-1}$, it follows that $k_{-9} = 3.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C, in agreement with Stanbury.¹¹ It is difficult to experimentally verify k_{-9} , given its relatively low value and the fast reaction of HO• with itself, reaction (10).



Above pH 4.8, the Fenton reaction is given by reaction (11):



To be complete, in H₂SO₄, the rate constant of reaction (4) is slightly higher,²⁴ probably because a FeSO₄(aq) complex is formed,²⁷ $\log K = 2.4$.¹⁸



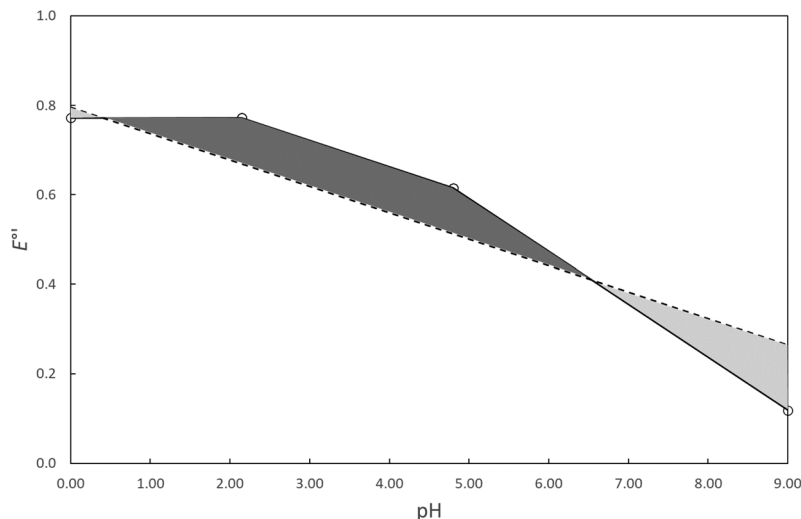


Fig. 1 Electrode potentials of three Fe(III)/Fe^{2+} couples (solid lines) and of the H_2O_2 , $\text{H}^+/\text{HO}^\cdot$, H_2O couple (dashed line) as a function of pH. The two pK_a values of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, 2.15 and 4.80, cause the breaks in the Fe(III)/Fe^{2+} potentials. Where $E^\circ(\text{H}_2\text{O}_2, \text{H}^+/\text{HO}^\cdot, \text{H}_2\text{O}) > E^\circ(\text{Fe(III)/Fe}^{2+})$, indicated by the light-gray shaded areas, the Fenton reaction is exergonic. The dark gray area shows where the Fenton reaction is endergonic. The species $\text{Fe}(\text{HO})^{2+}$ and $\text{Fe}(\text{HO})_2^{2+}$ are not stable with respect to haematite, Fe_2O_3 . The pK_a of $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ was thought to be 6.9,⁵⁰ but is 9.1.¹⁸

The catalytic function of iron in the disproportionation of excess H_2O_2 will not be discussed here. The mechanisms and rate constants involved have been reviewed by Stanbury.¹¹

The Fenton reaction near neutral pH

More than 30 years ago, it was published that the Fenton reaction is much faster in ocean water. Millero and Sotolongo,³⁰ in agreement with Moffett and Zika,³¹ reported that at pH 7 and 25 °C, the rate constant is $1.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, and at pH 8.0, $1.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, the present pH of ocean water. In that medium, one might expect $\text{Fe}^{2+}\text{-Cl}^-$ complexes to be formed. Although such complexes are weak,^{27,32} 85% of Fe^{2+} will be present as FeCl^+ , given that the concentration of Cl^- in ocean water is 0.55 M. For a physiological concentration of Cl^- of 0.10 M this number would be 50%. However, the rate constant of FeCl^+ is only slightly larger, $68 \text{ M}^{-1} \text{ s}^{-1}$, than that of $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ with H_2O_2 .²⁷ Thus, the presence of FeCl^+ does not explain the kinetics seen at higher pH. There, the Fenton reaction is first-order in $[\text{Fe}^{2+}]$, $[\text{H}_2\text{O}_2]$, and $[\text{HO}^\cdot]$.³⁰ When one extrapolates this dependence of the rate constant on pH, together with data from Bataneh *et al.*,³³ to lower pH values, the rate constant would intersect with the one at low pH, $53 \text{ M}^{-1} \text{ s}^{-1}$, at or close to pH 5.0, Fig. 2.

The dependence on $[\text{HO}^\cdot]$, indicates a change in mechanism. Moffett and Zika³¹ and Millero and Sotolongo³⁰ hypothesised that both Fe^{2+} and, to account for the dependence on HO^\cdot , FeHO^+ reduced H_2O_2 , and that the latter did so 5 orders of magnitude faster than Fe^{2+} . The rate constants $60 \text{ M}^{-1} \text{ s}^{-1}$ and $2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ allowed a reasonable fit to the experimentally rate data.^{30,31} These authors also assumed that both reactions yielded HO^\cdot . Bakac and co-workers³³ studied the ox-

idation of $(\text{CH}_3)_2\text{SO}$ by the Fenton reaction as a function of pH. At low pH, radical intermediates were formed as indicated by the products $\text{CH}_3\text{SO}_2\text{H}$ and C_2H_6 . However, near pH 6, the reaction was faster, and transfer of O, resulting in $(\text{CH}_3)_2\text{SO}_2$, was observed. Furthermore, Fe^{2+} was reformed. However, with phosphate present, radical products continued to be observed. Bakac and coworkers interpreted the O-transfer as evidence for FeO^{2+} , produced by the fast reaction of $[\text{FeHO}]^+$ with H_2O_2 .³³

FeO^{2+}

Below, in agreement with the conclusion of Bakac *et al.*,³³ thermodynamic arguments are made for FeO^{2+} as a product of the Fenton reaction near neutral pH. FeO^{2+} has the same charge as, but is larger than, Fe^{2+} , that does not hydrolyse until pH 9.1. Without experimental evidence to the contrary, no hydrolysis of FeO^{2+} is assumed to occur below pH 9.

Why $[\text{FeHO}]^+$ would generate FeO^{2+} rapidly and Fe^{2+} not at all, is puzzling. I propose a different hypothesis that is kinetically indistinguishable from the $[\text{FeHO}]^+$ pathway, namely that FeO^{2+} is formed from $[\text{FeHOO}]^+$: given that the pK_a of $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is 9.1,¹⁸ 6.6 units less than that of water, it is not unreasonable to assume that $[\text{Fe}(\text{H}_2\text{O}_2)(\text{H}_2\text{O})_5]^{2+}$ has a pK_a value that is 6.6 units less than that of H_2O_2 , or 5. If so, the kinetics would change above pH 5, which is experimentally observed as shown in Fig. 2. At this pH there is a change from a homolytic to a heterolytic mechanism.³⁴ The difference between the pK_a of H_2O_2 , 11.6, and that of $[\text{Fe}(\text{H}_2\text{O}_2)]^{2+}$, 5, results in $\Delta_{\text{rxn}12}G^\circ = -38 \text{ kJ mol}^{-1}$:



In cytochrome P-450, the intermediate $[\text{FeHOO}]^{2+}$ decays to FeO^{2+} and a porphyrin radical (compound I), in a reaction that



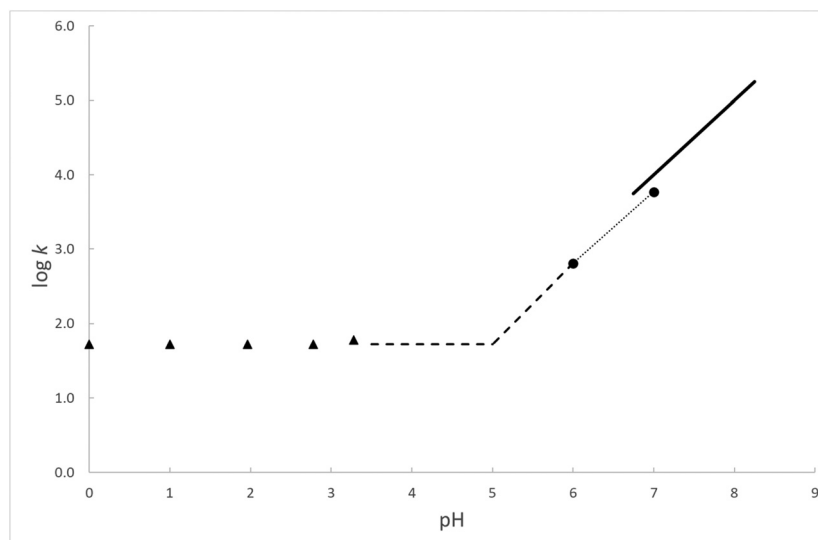
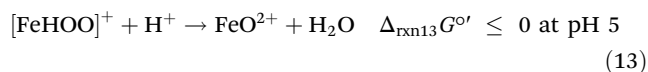


Fig. 2 Rate constants of the Fenton reaction as a function of pH. At low pH, data from Hardwick²⁴ adjusted to 25 °C was used (triangles). Data between pH 6.75 and 8.25 are from Moffett and Zika,³¹ and Millero and Sotolongo³⁰ (heavy bar) and were obtained in ocean water. The two points are from Bataineh *et al.*³³ (black circles) and lie below the bar because these rate constants were not influenced by HCO_3^- . The extrapolations (dashed lines) intersect at pH 5.0.

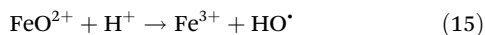
is thermoneutral or slightly exergonic.³⁵ I make the assumption that the energetics of reaction (13) are similar:



After addition of the ionisation of H_2O_2 , and reactions (12) and (13), one arrives at reaction (14):



From $\Delta_{\text{rxn14}} G^{\circ}$ follows $\Delta_f G^{\circ}(\text{FeO}^{2+}) \leq +16 \text{ kJ mol}^{-1}$. It is more likely that $\Delta_{\text{rxn13}} G^{\circ}$ is negative, which makes the value of $+16 \text{ kJ mol}^{-1}$ an upper limit. One can also make the assumption that, at pH 5, where the Fenton reaction produces equal amounts of HO^{\bullet} and FeO^{2+} , the Gibbs energies of these two reactions are similar, or close to $+8.5 \text{ kJ mol}^{-1}$ (Fig. 1) which would result in $\Delta_f G^{\circ}(\text{FeO}^{2+}) \approx +21 \text{ kJ mol}^{-1}$, somewhat above the upper limit. At low pH, FeO^{2+} decays slowly to HO^{\bullet} , reaction (15).¹²



Assuming that $\Delta_{\text{rxn15}} G^{\circ} \leq 0$, one arrives at $\Delta_f G^{\circ}(\text{FeO}^{2+}) \geq +10 \text{ kJ mol}^{-1}$. The lower limit of $+10 \text{ kJ mol}^{-1}$ eliminates from consideration *ab initio* results^{36,37} that imply much lower standard Gibbs energies of formation. A value of $\Delta_f G^{\circ}(\text{FeO}^{2+}) = +15 \pm 10 \text{ kJ mol}^{-1}$ seems reasonable and is adopted here. It must allow formation of FeO^{2+} from the reaction of Fe^{2+} with O_3 (see Introduction), and it does: $\Delta_{\text{rxn}} G^{\circ} = -52 \text{ kJ mol}^{-1}$. Electrode potentials based on $\Delta_f G^{\circ}(\text{FeO}^{2+}) = +15 \pm 10$ are listed in Table 1. They are in agreement with the estimate that $E^{\circ}(\text{FeO}^{2+}, \text{H}^+/\text{Fe}(\text{HO})_2^{2+}) > 1.95 \text{ V}$.³⁸ The value of $+2.5 \text{ V}$ for $E^{\circ}(\text{FeO}^{2+}, \text{H}_2\text{O}/\text{Fe}(\text{HO})_2^{2+})$ is valid at pH > 4.8 , which means that at pH 7 it is larger than $E^{\circ}(\text{HO}^{\bullet}, \text{H}^+/\text{H}_2\text{O}) = +2.31 \text{ V}$.³⁹ FeO^{2+}

Table 1 Electrode potentials involving FeO^{2+} , $\text{CO}_3^{\bullet-}$, and HO^{\bullet}

<i>n</i>	pH	Electrode potential	Volt
1	0	$E^{\circ}(\text{FeO}^{2+}, 2\text{H}^+, \text{Fe}^{3+}/\text{H}_2\text{O})$	+2.8
	0	$E^{\circ}(\text{HO}^{\bullet}, \text{H}^+/\text{H}_2\text{O})$	+2.73 ¹⁹
	>4.8	$E^{\circ}(\text{FeO}^{2+}, \text{H}_2\text{O}/\text{Fe}(\text{HO})_2^{2+})$	+2.5
	7	$E^{\circ}(\text{HO}^{\bullet}, \text{H}^+/\text{H}_2\text{O})$	+2.31 ⁴⁹
	7	$E^{\circ}(\text{CO}_3^{\bullet-}, \text{H}^+/\text{HCO}_3^-)$	+1.77
	>10.3	$E^{\circ}(\text{CO}_3^{\bullet-}/\text{CO}_3^{2-})$	+1.57 ¹⁹
2	0	$E^{\circ}(\text{FeO}^{2+}, 2\text{H}^+/\text{Fe}^{2+}, \text{H}_2\text{O})$	+1.78
	7	$E^{\circ}(\text{FeO}^{2+}, 2\text{H}^+/\text{Fe}^{2+}, \text{H}_2\text{O})$	+1.36

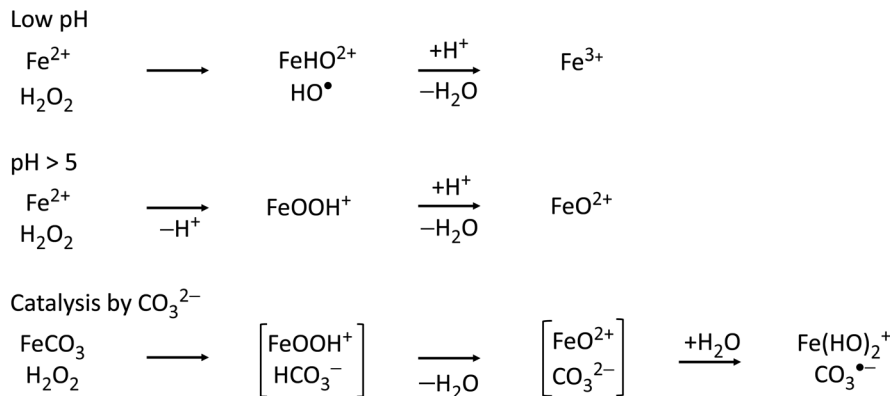
The Fe-potentials are based on $\Delta_f G^{\circ}(\text{FeO}^{2+}) = +15 \pm 10 \text{ kJ mol}^{-1}$. *n* is the number of electrons. The error in the $1e^-$ potentials is therefore 0.10 V, and 0.05 V in the $2e^-$ potentials.

can also transfer its oxygen, and thus the two-electron potentials $E^{\circ}(\text{FeO}^{2+}, 2\text{H}^+/\text{Fe}^{2+}, \text{H}_2\text{O})$, $+1.78 \text{ V}$ at pH 0, and $+1.36 \text{ V}$ at pH 7, are relevant. FeO^{2+} has been partially characterised.^{12,40}

CO₂

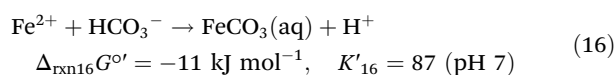
There are conditions where the $p\text{CO}_2$ can be appreciable: in physiology, $p\text{CO}_2 \approx 0.05 \text{ atm}$,⁴¹ and 0.1 atm is possible in water-logged soils.⁴² HCO_3^- accelerates the Fenton reaction. Present day sea water contains 2 mM HCO_3^- , and when Millero and Sotolongo³⁰ increased that concentration, the Fenton reaction became faster. More recently, Meyerstein and coworkers confirmed that HCO_3^- accelerates the Fenton reaction.⁴³ They proposed that, instead of HO^{\bullet} , trioxidocarbonate ($\cdot\text{O}_3^-$), $\text{CO}_3^{\bullet-}$, is formed. This proposal is not based on a direct observation of this radical, but on the absence of oxidation products – from either $1e^-$ or $2e^-$ oxidation – of dimethylsulfoxide when HCO_3^- was present.⁴³ How could HCO_3^- catalyse the Fenton reaction? The formation of FeO^{2+} , reaction



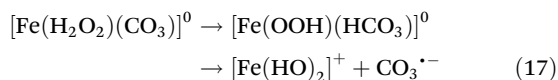


Scheme 1

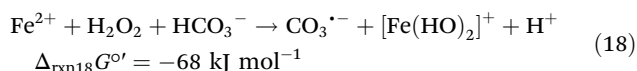
(14), is, overall, pH-independent but it involves a deprotonation and a protonation. A compound that can take up a proton and then give it back at little or no cost would catalyse the Fenton reaction. HCO_3^- fulfills that role, as with Fe^{2+} it forms $\text{FeCO}_3(\text{aq})$:¹⁸



As the physiological concentration of HCO_3^- is $\approx 25 \text{ mM}$, nearly 2/3 of any uncomplexed Fe^{2+} would be present as $\text{FeCO}_3(\text{aq})$. CO_3^{2-} , being a bidentate ligand, would leave 4 H_2O molecules in the inner solvation sphere of Fe^{2+} , of which 1 or 2 could be replaced by one H_2O_2 . One can then imagine the following inner-sphere reaction sequence:



$\text{CO}_3^{\bullet-}$ is a strong oxidant, $E^{\circ}(\text{CO}_3^{\bullet-}/\text{CO}_3^{2-}) = +1.57 \text{ V}$,¹⁹ but less so than HO^{\bullet} or FeO^{2+} (Table 1). The energetics of the overall reaction at pH 7 can be calculated:

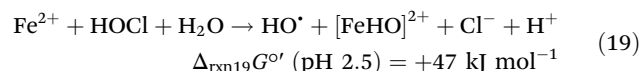


As the conditions in soil are not very different, it is reasonable to assume that soil remediation involves the same reactions.

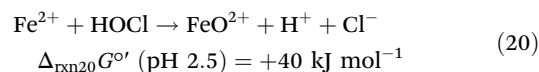
HOCl

As mentioned in the Introduction, Fenton noted that HOCl can substitute for H_2O_2 to obtain the purple colour.¹ However, HOCl is a poor one-electron oxidant, $E^{\circ}(\text{HOCl}/\text{HO}^{\bullet}, \text{Cl}^-) = +0.26 \text{ V}$,⁴⁴ a value that is not pH dependent. It would be identical to the pH-dependent $E^{\circ}(\text{H}_2\text{O}_2, \text{H}^+/\text{HO}^{\bullet}, \text{H}_2\text{O})$ at pH 9 (Fig. 1). Instead, it is a powerful two-electron oxidant, $E^{\circ}(\text{HOCl}, \text{H}^+/\text{Cl}^-, \text{H}_2\text{O}) = +1.50 \text{ V}$, and $+1.28 \text{ V}$ at pH 7⁴⁵ (the value of $+1.08 \text{ V}$ published in 1994⁴⁴ was based on an incorrect pH dependence). Given the pK_a values of tartaric acid of 2.9 and 4.4, and concentrations between 10 and 100 mM, the

pH during Fenton's experiment is estimated at between 2 and 3. There the energetics to generate HO^{\bullet} are not favourable:



But could FeO^{2+} be formed? Conocchioli *et al.*⁴⁶ oxidised Fe^{2+} with H_2O_2 , Cl_2 , HOCl, and O_3 , with Fe^{2+} present in large excess. Only the latter two oxidants generated $[\text{Fe}(\mu\text{-HO})_2\text{Fe}]^{4+}$, the transient product of Fe^{2+} and FeO^{2+} . As the authors⁴⁶ wrote: "... it suggests that iron(IV) is an intermediate in these reactions." It is therefore likely that the reaction of Fe^{2+} with HOCl yields FeO^{2+} ;



Although the $\Delta_{\text{rxn}} G^{\circ'}$ values of reactions (19) and (20) are positive, formation of FeO^{2+} is energetically less costly than formation of HO^{\bullet} . Both oxidants would seem oxidising enough⁴⁷ to abstract the C-2 hydrogen from tartaric acid and to form the transient deep purple colour, presumably from the charge-transfer complex of the tartaric acid radical with Fe^{3+} . Thus, Fenton may have produced both HO^{\bullet} and FeO^{2+} in 1876. Indeed, that these species mimick each other led to the nearly 90 years old question as to what the product of the Fenton reaction is.

Conclusions

Up to about pH 5, the Fenton reaction produces HO^{\bullet} . Above that pH, it is FeO^{2+} (except in the presence of phosphate). The mechanisms of the reaction of Fe^{2+} with H_2O_2 are summarised in Scheme 1. The proposal for formation of FeO^{2+} from Fe^{2+} and H_2O_2 near neutral pH is based on two observations and one assumption. The observations are that, above pH 5, the rate of the reaction is first-order in HO^- and that non-radical products are formed. From the first observation followed a pK_a of 5 of the Fe^{2+} - H_2O_2 complex. The assumption is that that complex decays to FeO^{2+} thermoneutrally or with a slightly



negative Gibbs energy change. Interestingly, Fenton may have produced HO[•] with H₂O₂, and FeO²⁺ with HOCl.

In many Fenton studies, or simulations thereof, carried out at or near neutral pH, the reactive product is thought to be HO[•]. Instead, it is likely to be FeO²⁺, or, in the presence of HCO₃⁻, CO₃^{•-}. Most certainly, one should not use $k_4 = 53 \text{ M}^{-1} \text{ s}^{-1}$, but a value closer to $1.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ (Fig. 2). Additionally, the simulations should not violate the principle of detailed balancing.¹¹ The role of phosphate in redirecting the product of the Fenton reaction to HO[•] needs to be experimentally investigated.^{33,48}

Conflicts of interest

There is no conflict of interest.

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