

Viewpoint

Initial Steps in the Reaction of H₂O₂ with Fe²⁺ and Fe³⁺ Ions: Inconsistency in the Free Radical Theory

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Abstract: Consideration of the changes in free energy shows that the assumed initial steps in reactions of H₂O₂ with Fe²⁺ and Fe³⁺ in the free radical theory are not consistent. The free radical theory is unable to account for the Fe³⁺-initiated decomposition of H₂O₂ or for oxidations by it. In reactions with Fe²⁺ ions at high [H₂O₂], where O₂ evolution reaches a limit, such limit is not foreseen by the free radical model. At lower [H₂O₂], because of a disallowed substitution in the equation used, the interpretation is not valid. It appears, therefore, that free radicals derived from H₂O₂ do not provide a suitable basis for constructing models for these reactions. Non-radical models are more successful in interpreting experimental results.

Keywords: Fenton reaction; free radicals; free energy; Fe²⁺; Fe³⁺; H₂O₂; catalysis

1. Introduction

The search for the mechanism of the reaction of H₂O₂ with Fe²⁺ and Fe³⁺ ions has lasted for over a hundred years. The question has still not been settled satisfactorily, and many researchers are basing their interpretations of experimental results on the free radical theory that was introduced by Haber and Weiss [1]. The subject of the present discussion is to address some thermodynamic and kinetic aspects of O₂ evolution and oxidation in these systems. It is divided into two parts. In the first part, reactions involving Fe³⁺ and H₂O₂ are discussed. The corresponding reactions of Fe²⁺ are discussed in the second part.

2. Free Radical Model of the Fe³⁺ Ion-Catalyzed Decomposition of H₂O₂

In the free radical theory, free radicals originating from H₂O₂ are produced in the reaction between H₂O₂ and Fe²⁺ or Fe³⁺ ions. According to the version proposed by Barb et al., and shown in Appendix A, the initial steps of the respective reactions are [2,3]



H₂O₂ is presented in step 1 in its anionic form, Appendix A [4]. In these reactions, the molecule H₂O₂ is broken up in various ways to yield free radicals. In one way, the O–O bond is split by absorbing an electron and yielding the radical OH[•]



In another way, the radical HO₂[•] is formed by the ejection of an electron from the anion HO₂[−]



The donor and the acceptor of electrons in these processes is the oxidation–reduction pair Fe²⁺–Fe³⁺



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After coupling the appropriate processes, we obtain the following identities: (1) = (4) + (6) and (2) = (3) + (5). Denoting the total free energy changes accompanying various processes by F , we have $F_1 = F_4 + F_6$ and $F_2 = F_3 - F_6$ (note that $F_5 = -F_6$). Adding F_1 and F_2 we get $F_1 + F_2 = F_3 + F_4$. This sum is positive, because in reactions (3) and (4) free radicals are produced requiring the investment of free energy. On the other hand, the experiment shows that upon mixing Fe^{2+} and H_2O_2 react spontaneously and quantitatively. Therefore, F_2 must be negative (Appendix B). Consequently, F_1 must be positive. If F_1 is positive, then the initial and all the following steps of the Fe^{3+} ion-catalyzed decomposition of H_2O_2 cannot occur. In reality, the Fe^{3+} ion does catalyze the decomposition of H_2O_2 . Therefore, the conclusion must be drawn that, due to considerations of free energy, the model of Barb et al. failed to account for the occurrence of this reaction [3]. Modifications of Barb et al.'s scheme were suggested by including additional O_2 producing steps involving radical-radical reactions [5–7]. Since all these free radical models for the decomposition of H_2O_2 by Fe^{3+} start with step 1, the conclusion reached above applies to all of them. Mixtures of $\text{Fe}^{2+} + \text{H}_2\text{O}_2$ and of $\text{Fe}^{3+} + \text{H}_2\text{O}_2$ are able to oxidize a variety of organic compounds [8–10]. According to the free radical theory, the active intermediate involved in the oxidations is the OH^\bullet radical. In the case of Fe^{2+} , OH^\bullet is formed during step 2. In the case of Fe^{3+} , it is formed in a two-stage process: step 1 followed by step 2. Since a free energy barrier prevents step 1 from happening, the following step 2 cannot occur either. Under such circumstances, the oxidation of substrates by $\text{H}_2\text{O}_2 + \text{Fe}^{3+}$ becomes impossible. Summing up: *all free radical schemes beginning with reaction 1 are nonstarters* [3–10].

3. Free Radical Model of the Fenton Reaction

A new direction in the search for the mechanism of the reaction of Fe^{2+} and H_2O_2 started when Haber and Weiss introduced their model in 1934 (Appendix A) [1]. It was a chain reaction based on the participation of OH^\bullet and HO_2^\bullet radicals. This mechanism was criticized later as it could not account for the existence of a limit in the evolution of O_2 when $[\text{H}_2\text{O}_2]$ was increased at a constant $[\text{Fe}^{2+}]$. The discoverers of this limit, Barb et al., modified the scheme of Haber and Weiss, by substituting Fe^{3+} for H_2O_2 in the O_2 evolution step (Appendix A) [2]. *With the change, the chain reaction has been turned into a catalytic reaction.* Namely, as the result of this substitution, (1) the cycle of the two chain-carrying radicals has been eliminated and (2), in the O_2 -producing step, Fe^{2+} has been regenerated. Fe^{2+} became thus a catalyst, as it was both a reactant in the initial step and was regenerated in the product-forming step [11]. This fact is generally overlooked, although it is significant for understanding the free radical model (it is to be noted, that there is no regeneration of Fe^{2+} in the Haber–Weiss scheme). The modified scheme of Barb et al. is shown in Appendix A. It is a combined model for both the Fenton reaction and the Fe^{3+} ion catalyzed decomposition of H_2O_2 . The set of reactions A2 to A6 present the Fenton part. Concerning the limit to the evolution of O_2 , it is observed in a large excess of $[\text{H}_2\text{O}_2]$ over $[\text{Fe}^{2+}]$. In the model, it causes step A3 to become insignificant beside A4. The same excess will cause a rapid oxidation of Fe^{2+} to Fe^{3+} and will cause A5 to become insignificant beside A6. The model will then be reduced to steps A2–A4–A6. *This combination is a catalytic cycle for the conversion of H_2O_2 to O_2 , carried by the free radicals OH^\bullet and HO_2^\bullet .* Due to their high reactivity, (a) their concentrations are in steady states and (b) the rates of all reactions in the cycle are equal: $v_2 = v_4 = v_6$ (v denoting rate). By inserting $v_6 = d[\text{O}_2]/dt$ and $v_2 = k_2 [\text{Fe}^{2+}] [\text{H}_2\text{O}_2]$, we obtain

$$d[\text{O}_2]/dt = k_2 [\text{Fe}^{2+}] [\text{H}_2\text{O}_2] \quad (7)$$

(Indexing of rate constants follows the numbering of the corresponding Equation in the Appendix A with the omission of the prefix A.)

Clearly, an equation of this form cannot explain the phenomenon of an upper limit to O_2 . Barb et al. also performed O_2 evolution experiments at lower $[\text{H}_2\text{O}_2]$, but still in excess

over $[\text{Fe}^{2+}]$. In this range, the following relation exists between the amount of O_2 evolved (per 1 dm^3 of the reaction mixture) and $[\text{Fe}^{2+}]$ at various times [2,11,12]

$$\Delta\text{O}_2 = (k_6/k_5) ([\text{Fe}^{2+}]_0/2) \{ \ln([\text{Fe}^{2+}]_0/[\text{Fe}^{2+}]) + ([\text{Fe}^{2+}]/[\text{Fe}^{2+}]_0) - 1 \} \quad (8)$$

The symbol $[]_0$ denotes initial concentration. Since the measurement of pairs of simultaneous values of ΔO_2 and $[\text{Fe}^{2+}]$ at different times was not feasible due to the speed of the reaction, Equation (8) was applied to the “total amount of O_2 ” evolved in the Fenton reaction (ΔO_2^T). If $\Delta\text{O}_2 = \Delta\text{O}_2^T$ then $[\text{Fe}^{2+}]$ is the concentration of Fe^{2+} at the end of the reaction ($[\text{Fe}^{2+}]_{\text{end}}$). $[\text{Fe}^{2+}]_{\text{end}}$ can be calculated by solving the rate equation for $d[\text{Fe}^{2+}]/dt = 0$. It was found to be zero [11,12]. This implies that the logarithmic term and the entire r.h.s. of Equation (8) became infinite. As a consequence, at this point Equation (8) has lost its physical meaning. In an attempt to treat the problem, Barb et al. added A1 to the set of reactions from A2 to A6. Consider then all reactions occurring in the system when Fe^{2+} and H_2O_2 are mixed with no Fe^{3+} being present initially. Reaction A1 can be neglected in the initial phase (phase A, Fenton reaction). As the reaction progresses, $[\text{Fe}^{2+}]$ will decrease with simultaneous increase of $[\text{Fe}^{3+}]$. The reaction will reach a stage at which initiation will occur via both steps A1 and A2 (phase AB). With further decrease of the ratio $[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$, step 1 will become the only starting point of the reaction (phase B, Fe^{3+} catalysis). During phase B, $[\text{Fe}^{2+}]$ will reach a steady state denoted as $[\text{Fe}^{2+}]_{\text{s.s}}$ [3]. There is no identity between the steady state during phase B and the endpoint of phase A. In the calculations, Barb et al. have inserted a quantity defined in phase B ($[\text{Fe}^{2+}]_{\text{s.s}}$) in an equation the validity of which is restricted to phase A. This substitution is not permissible. There is also problem with the determination of ΔO_2^T : in the transition phase, O_2 evolved in the Fenton reaction path and in Fe^{3+} catalysis are inseparable [12]. Finally, there is a very short proof of inadequacy of the free radical model. A rate equation should be able to describe the course of the reaction from the beginning to the end. If it leads to an infinity catastrophe at the end, it is sign that the model is wrong.

4. Conclusions

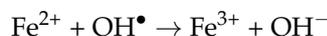
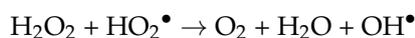
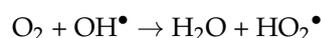
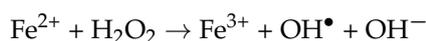
Consideration of kinetics and of free energy changes in reactions of Fe^{2+} and of Fe^{3+} with H_2O_2 shows that there are deficiencies in proofs for free radical models of these reactions. Thus, the concept of Haber and Weiss, according to which *interatomic bonds in H_2O_2 can be broken to form free radicals in thermal reactions with ions of iron in an aqueous media is not well supported by experimental evidence*. The reactions can proceed through non-radical intermediates of the type FeO^{2+} and FeO^{3+} [11–14]. A non-radical model on this basis was able to offer an explanation for the existence of an upper limit to O_2 evolution—70 years after it has been found experimentally [2,13].

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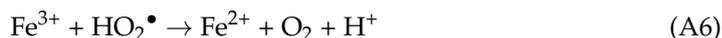
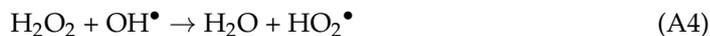
Appendix A

The free radical model of Haber and Weiss consists of the following reactions [1]

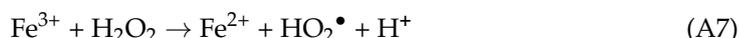


The free radical model of Barb et al. is a unified model of the reactions of H_2O_2 with Fe^{2+} and Fe^{3+} ions. Both ions play a part in both reactions.

The unified model consists of the following steps:



The complete model represents the free radical mechanism of the catalytic decomposition of H_2O_2 by Fe^{3+} ions. Reactions in the range A2 to A6 comprise the mechanism of the Fenton reaction. Barb et al. wrote step A1 differently



It does not affect the change of the free energy in step A1. Namely, by taking the difference of the free energy (F) changes in steps (A7) and (A1), we obtain the following:

$$F_{\text{A7}} - F_{\text{A1}} = F_{\text{H}_2\text{O}_2} - F_{\text{H}^+} - F_{\text{HO}_2^-}$$

Because of the equilibrium between H_2O_2 and its dissociation products, the r.h.s. of this equation must be zero. Thus, $F_{\text{A7}} = F_{\text{A1}}$.

Appendix B

This statement requires qualification. It is not valid for chain reactions. Once a chain reaction has started, the chain carriers will continue it even if initiation has stopped.

It is valid, however, for catalytic reactions. A catalytic reaction stops when the initial step has stopped. The free radical model of the Fenton reaction is a catalytic reaction. It consists of a catalytic kernel A2-A4-A6 and two reactions that inhibit the reaction: A1 and A3. They remove carriers of the catalytic cycle: Fe^{2+} , OH^\bullet , and HO_2^\bullet .

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