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Short Communication

Concepts and errors in models for the mechanism of the Fenton reaction

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ABSTRACT

There is an inherent flaw in all free radical-based models for the Fenton reaction due to the demand of steady state kinetics, under all experimental conditions, for the evolution of O_2. Nonradical models do not have this drawback.

KEYWORDS: Fenton reaction, free radicals, catalysis, Fe^{2+}, H_2O_2.

Introduction

The mechanism of the Fenton reaction continues to intrigue researchers. It may be stated that the article of Haber and Weiss published in 1934 is still a source of inspiration for new investigations [1]. It is all the more remarkable since the theory of Haber and Weiss actually failed to account for the course of the Fenton reaction.

Discussion

The basic experimental fact to be explained in the reaction between Fe^{2+} and H_2O_2 is the evolution of O_2, obeying no rigid stoichiometric law, which accompanies the oxidation of Fe^{2+} at high $[H_2O_2]/[Fe^{2+}]$ and absence of any O_2 formation when $[H_2O_2]/[Fe^{2+}]$ is low. At the core of the theory of Haber and Weiss is the realization that the phenomenon must be due to a competition between a cyclic path for the evolution of O_2 and a unidirectional path for the oxidation of Fe^{2+} to Fe^{3+}. It was assumed that the cyclic path is a chain reaction carried by the free radicals $OH^{\cdot}$ and $HO_2^{\cdot}$ derived from H_2O_2. It was a mistake. Consider the individual steps of the model:

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

$$OH^{\cdot} + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \quad (2)$$

$$HO_2^{\cdot} + H_2O_2 \rightarrow OH^{\cdot} + O_2 + H_2O \quad (3)$$

$$OH^{\cdot} + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} \quad (4)$$

Step (1) initiates the reaction, steps (2) - (3) constitute the chain and step (4) terminates it. The chain, the site of O_2 production, is the cyclic (self-repeating) path. Steps (1) and (4) constitute the unidirectional path from Fe^{2+} to Fe^{3+}. Competition between the two pathways occurs in alternative reactions of $OH^{\cdot}$ with H_2O_2 or Fe^{2+} in steps (2) and (4), respectively. The balance between the two reactions depends on the ratio $[H_2O_2]/[[Fe^{2+}]$ and determines whether or not O_2 is evolved in the system. Up to this point, predictions of the model fit the results obtained experimentally. The radicals $OH^{\cdot}$ and $HO_2^{\cdot}$ are highly reactive species. They are present in very low concentrations in the reaction mixture. Their concentrations can be calculated by using the steady state approximation:

$$[OH^{\cdot}] = (k_1/k_4)\ [H_2O_2]$$

$$[HO_2^{\cdot}] = \{(k_1k_2)/(k_3k_4)\}\ [H_2O_2]$$

The rate of O_2 evolution becomes (ref 1, eq 6):

$$d[O_2]/dt = (k_1k_2/k_4)\ [H_2O_2]^2 \quad (5)$$

There is contradiction between this equation and results obtained in the experiments. According to

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the measurements, $d[O_2]/dt$ is a function of the ratio $[H_2O_2]/[Fe^{2+}]$, while according to eq (5) it depends solely on $[H_2O_2]$. The reason for the contradiction can clearly be found in the requirement of steady states for $[OH^{\cdot}]$ and $[HO_2^{\cdot}]$ during the reaction. But this condition exists necessarily for free radical intermediates, thus blocking agreement between theory and experiment. According to eq (5), the rate of O_2 evolution always increases with increasing $[H_2O_2]$. Experimentally, there exists an upper limit at high $[H_2O_2]$ to the amount of O_2 evolved in the reaction - in disagreement with eq (5). (It is to be noted that the existence of the limit was not yet known at the time Haber and Weiss investigated the reaction.)

Barb *et al*. proposed a different free radical model of the Fenton reaction [2]. They retained the basic ideas of Haber and Weiss, but to explain the existence of the upper limit which they discovered, they suggested to change the last step in the evolution of O_2 from a reaction between HO_2 and H_2O_2 (3) to a reaction between $HO_2^{\cdot}$ and Fe^{3+} (10). Their scheme consists of the following steps:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^{-} \quad (6)$$

$$OH^{\cdot} + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} \quad (7)$$

$$OH^{\cdot} + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \quad (8)$$

$$Fe^{2+} + HO_2^{\cdot} \rightarrow Fe^{3+} + HO_2^{-} \quad (9)$$

$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + O_2 + H^{+} \quad (10)$$

The revised model preserves the structure of the catalytic scheme: it consists of an O_2 producing cycle (6)-(8)-(10) and two pathways for oxidation of Fe^{2+} to Fe^{3+}: (6)-(7) and (6)-(8)-(9). The cycle is not a chain reaction, because the initiation step (6) is part of it (in a true chain reaction the initiation step cannot belong to the chain). On the basis of the revised model and assuming steady states, the concentrations of $OH^{\cdot}$ and $HO_2^{\cdot}$ are given by

$$[OH^{\cdot}] = (k_6/k_8)\,[Fe^{2+}]/\{1 + (k_7/k_8)\,([Fe^{2+}]/[H_2O_2])\} \quad (11)$$

$$[HO_2^{\cdot}] = k_6\,[Fe^{2+}]\,[H_2O_2]/\{(1 + (k_7/k_8)\,([Fe^{2+}]/[H_2O_2]))\,(k_9\,[Fe^{2+}] + k_{10}\,[Fe^{3+}])\} \quad (12)$$

The expression for the rate of O_2 evolution becomes

$$d[O_2]/dt = k_6\,[H_2O_2]\,F_1\,F_2 \quad (13)$$

where $F_1 = [Fe^{2+}]/\{1+ (k_7/k_8)\,([Fe^{2+}]/[H_2O_2])\}$ and $F_2 = (k_{10}/k_9)\,([Fe^{3+}]/[Fe^{2+}])/\{1 + (k_{10}/k_9)\,([Fe^{3+}]/[Fe^{2+}])\}$.

F_1 increases or decreases, by increasing or decreasing $[H_2O_2]$. Extreme forms of F_1 for high and low $[H_2O_2]$ are $[Fe^{2+}]$ and $(k_8/k_7)[H_2O_2]$, respectively. The value of F_2 depends on the ratio $[Fe^{3+}]/[Fe^{2+}]$. For high $[Fe^{3+}]/[Fe^{2+}]$, $F_2 = 1$, for low $[Fe^{3+}]/[Fe^{2+}]$, $F_2 = (k_{10}/k_9)([Fe^{3+}]/[Fe^{2+}])$.

Initially $[Fe^{3+}] = 0$, $F_2 = 0$ and $d[O_2]/dt = 0$. It is due to the fact that in step (10), unlike in the Haber Weiss model, Fe^{3+} ions are required to form O_2. Once the reaction has started, $[Fe^{3+}]$ and the ratio $[Fe^{3+}]/[Fe^{2+}]$ will increase, causing F_2 to increase. F_1 and $[H_2O_2]$ having positive values $d[O_2]/dt$ will be positive. It implies that according to the model of Barb *et al*., there will occur O_2 evolution under all circumstances, not only when the ratio $[H_2O_2]/[Fe^{2+}]$ is high, not in agreement with the observations. Of particular interest is the situation when $[H_2O_2]$ and $[Fe^{3+}]/[Fe^{2+}]$ are both high. In a large excess of H_2O_2, Fe^{2+} ions are rapidly oxidized to Fe^{3+} causing the ratio $[Fe^{3+}]/[Fe^{2+}]$ to reach very high values. According to the results listed above, it will exist: $F_1 = [Fe^{2+}]$ and $F_2 = 1$ The expression for the rate of O_2 evolution will become

$$d[O_2]/dt = k_6\,[Fe^{2+}]\,[H_2O_2] \quad (13a)$$

Obviously, such an equation cannot explain the existence of a limit to the evolution of O_2 at high $[H_2O_2]$, independent of $[H_2O_2]$. Thus, inserting Fe^{3+} instead of H_2O_2 in the O_2 production step did not solve the problem of the upper limit.

In free radical schemes of the Fenton reaction O_2 is formed from the precursor HO_2 in a one-equivalent oxidation step. The oxidizing species in the model of Haber and Weiss is H_2O_2, while in the model of Barb *et al.* it is Fe^{3+}. Both models failed to account for the experimental results at high as well as at low $[H_2O_2]$. It appears that the mandatory application of steady states for the free radical intermediates is at the root of blocking agreement with the experiment. Since beside

H_2O_2 and Fe^{3+} there are no other conceivable oxidizing agents in the reaction mixture, the conclusion can be generalized by stating that free radical models, with radicals derived from H_2O_2, are not able to account for the experimental results. O_2 formation *via* a radical-radical reaction

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow O_2 + H_2O_2 \qquad (14)$$

or

$$OH^{\cdot} + HO_2 \rightarrow O_2 + H_2O \qquad (15)$$

does not yield a new carrier of the cycle among the products: it does not fit in a cyclic process and therefore cannot be part of a model for the mechanism of the Fenton reaction [3].

In summary, examination of various free radical models indicates that a model for the mechanism of the Fenton reaction should rather be based on nonradical intermediates allowing more flexible kinetic forms [4].

CONFLICT OF INTEREST STATEMENT

There is no conflict of interest to declare.

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