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Journal

Angewandte Chemie International Edition, 64(49)

ISSN

1433-7851

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Publication Date

2025-12-01

DOI

10.1002/anie.202517261

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Iron (IV) Formation and the pH Dependent Kinetics of the Fenton Reaction

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Abstract

Despite its widespread importance for biological and environmental chemistry and decades of study, the mechanism underlying the Fenton reaction is still a matter of some controversy. To elucidate the pH dependence of this complex reaction, a new kinetic model is developed to explain the increase in rate and mechanistic shift that occurs from acidic to neutral conditions. This mechanism originated from a re-analysis of a previously proposed model, which neglected explicit iron speciation, leading to unrealistic rate constants. Accounting for speciation suggests a much faster formation rate of Fe(IV), which is estimated to be on the order of $10^6 \text{ M}^{-1}\text{s}^{-1}$. Expanding on prior kinetic studies that include speciation under acidic conditions, we propose a unified kinetic model that captures the pH-dependent rate acceleration in Fe(II) oxidation by H_2O_2 , which is a significant step toward resolving the long-standing mechanistic ambiguity of Fenton chemistry.

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Introduction

The Fenton reaction involves the oxidation of Fe^{2+} to Fe^{3+} by hydrogen peroxide, producing an intermediate with a stronger oxidizing ability. Since its discovery in 1894,¹ the Fenton reaction has been thoroughly examined in large part due to its central importance in biological,² environmental, and atmospheric³⁻⁶ chemistry as well as for its application in advanced oxidation processes for water remediation and wastewater treatment.⁷⁻⁹ Although the formation mechanism and identity of the strong oxidant produced by this reaction continues to be actively debated, there are two proposed mechanisms.^{10,11} The Haber-Weiss mechanism forms hydroxyl radicals:¹²



whereas the Bray and Gorin mechanism forms a highly reactive high-valent Fe(IV) intermediate:¹³

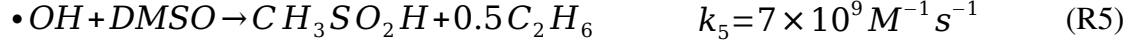


The formation of hydroxyl radicals in R1 is supported by many studies,¹⁴⁻¹⁶ and is broadly accepted. More recent investigations, however, report evidence that at certain reaction conditions, oxidation does not proceed solely or predominantly through the OH radical pathway.¹⁷⁻²⁰ Instead, it was hypothesized that at neutral and higher pH,²⁰⁻²⁴ Fe(IV) is formed.^{17,19,25-29}

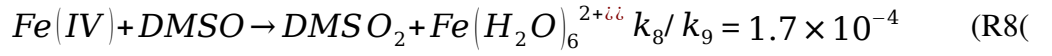
Important evidence for Fe(IV) formation was reported by Bataineh *et al.*,²² where the differences in the oxidation products of dimethyl sulfoxide (DMSO) were used to distinguish between the two reactive intermediates. DMSO oxidized by OH radicals produces methanesulfinic acid and ethane,^{30,31} whereas reaction with Fe(IV) produces dimethyl sulfone (DMSO₂).³² NMR measurements showed that the Fe(IV) pathway was undetectable in acidic conditions, but became substantial at pH = 6-7. This shift in product distributions with pH led Bataineh *et al.*²² to propose the following mechanism and rate coefficients:



Haber-Weiss Mechanism (OH Radical)



Bray-Gorin Mechanism (Fe(IV))



Fe(II) in R3 ultimately governs oxidant formation ($\bullet OH$ vs. Fe(IV)). $Fe(H_2O)_6^{2+}$ produces $\bullet OH$ radicals via the Haber Weiss mechanism, whereas $Fe(H_2O)_5OH^{+}$ forms Fe(IV) via the Bray-Gorin mechanism. Each oxidant can react with Fe(II) or with DMSO to yield the observed products.

Here, we re-analyze both the experimental results and the kinetic model presented by Bataineh *et al.*²² Our analysis suggests that although the Bataineh *et al.*²² model qualitatively explains the branching between $\bullet OH$ and Fe(IV) via the acid-base equilibrium in R3, the rate constant for R7 appears to be derived from the total [Fe(II)] without explicitly accounting for its speciation. This oversight is particularly significant at pH 6-7 since $Fe(H_2O)_5OH^{+}$, the precursor for Fe(IV) in R7, is a small fraction (~0.1%) of the total Fe(II). As detailed below, our

reconstruction of the mechanism using the correct Fe(II) speciation, suggests that the rate coefficient for forming Fe(IV) in R7 is actually ~1500 times ($k_7 \sim 10^6 \text{ M}^{-1} \text{ s}^{-1}$) larger than originally reported by Bataineh *et al.*²² (*i.e.*, $k_7 = 592 \text{ M}^{-1} \text{ s}^{-1}$). Our reanalysis of Bataineh *et al.*²², together with recent work by Stanbury,³³ provides a foundation for constructing a new kinetic model. Stanbury's³³ analysis details how thermodynamic equilibria govern speciation, and thus, the Fenton mechanism at acidic pH. Incorporating Fe(IV) formation and expanding that analysis to higher pH, we develop a unified kinetic model that faithfully replicates the oxidation kinetics of Fe(II) by H₂O₂ from acidic to neutral pH conditions.

Results and Discussion

Kinetic simulations are performed in Kinetiscope,³⁴ a stochastic reaction-diffusion simulator that randomly selects outcomes from probability-weighted reaction steps. Like ordinary differential equation solvers, mechanisms are built up from elementary reaction steps and rate constants. The rate constants used by Bataineh *et al.*²² are obtained from prior literature for the Haber-Weiss mechanism (R4-R6)³⁰. The Bray-Gorin rate constants (R7-R9) were constrained by Bataineh *et al.*²² by fitting their experimental kinetics, which were obtained by monitoring Fe(III) formation through its absorbance at 270nm in a stopped flow apparatus. Although Bataineh *et al.*²² compare simulation results from Kinsim³⁵ with their observations (Fig. 3 in Ref ²²) there is insufficient information for us to replicate the mechanism (R3-R9). For example, there is no description of the forward and backward rate coefficients that comprise the iron acid-base equilibrium in R3, nor what values for the absolute rate constants were used for R8 and R9. Without these details, we reconstruct their mechanism using the following assumptions:

- 1) In R3, the backward rate coefficient for the acid-base equilibrium is diffusion-limited with a rate constant of $k_r=10^{10} M^{-1} s^{-1}$. The forward rate constant is set to a value that maintains the correct pKa, (*i.e.*, $k_f=k_r \times K_a=3.2 s^{-1}$).
- 2) R9 is set to be diffusion limited with a rate constant of $k_9=10^{10} M^{-1} s^{-1}$, with $k_8=1.7 \times 10^6 M^{-1} s^{-1}$ calculated to obtain the correct ratio of k_8/ k_9 reported by Bataineh *et al.*²².
- 3) The Fe(II) species produced in R8 and consumed in R9 is $Fe(H_2O)_6^{2+}$, which is appropriate, as this is the predominant Fe(II) species present at pH < 9.5.

Assumptions 1-3 preserve the rate constants that Bataineh *et al.*²² report as constrained by their experimental data and original model (*i.e.*, k_7 and k_8/ k_9). Assumptions 1 and 2 use rate coefficients at or near a kinetic upper limit to drive the overall reaction as fast as possible, since, as we will show below, the model proposed by Bataineh *et al.*²² substantially underpredicts the observed kinetics.

A comparison between reconstructed kinetic simulations and the experimental kinetics for Fe(III) formation recorded by Bataineh *et al.*²² is shown in Figure 1. The reconstructed kinetic model substantially underpredicts the rate of Fe(III) formation observed in the experiment. Complete conversion of the reagents should yield $[Fe(III)] = 2 \times 10^{-5} M$. However, we note that converting the raw absorbance provided by Bataineh *et al.*²² to concentration recovers a slightly smaller value (*i.e.*, $1.9 \times 10^{-5} M$). A comparison of the reconstructed model predictions as a function of [DMSO] is shown in the Supplementary Information (Figure S1), and similarly yields slower simulated kinetics than observed in the experiment.

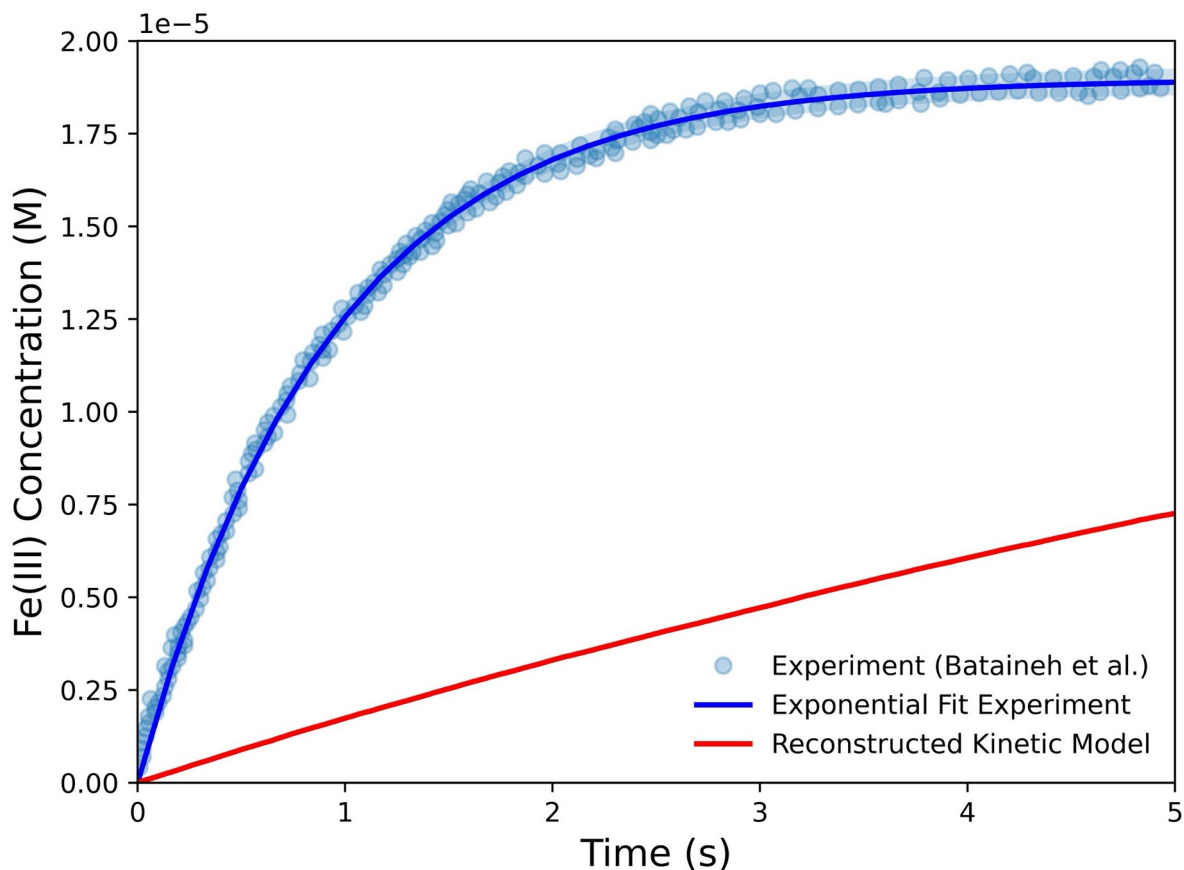


Figure 1 – Fe(III) concentration as a function of time for the reconstructed kinetic model (red) and experimental data (blue) reproduced from Fig. S6 in the Supplementary Information of Bataineh et al.²² and converted to concentration using their reported extinction coefficient. Experimental conditions: 0.02mM Fe(II), 0.78mM H_2O_2 , pH = 6.2 (buffered by 0.56mM MES (2-(N-morpholino)ethanesulfonic acid)).

When properly accounting for Fe(II) speciation in R3, the rate constant (k_7) for the formation of Fe(IV) as reported by Bataineh *et al.*²² is simply too small to replicate the experimental results (Figure 1). As a result, we are left to conclude that iron speciation was omitted from their kinetic simulations. To test this hypothesis, we replaced $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_5OH^{+}$ with a generic Fe(II) species, thereby effectively eliminating iron speciation from the reconstructed model. This species is used in R4 and R7 to form $OH\cdot$ and Fe(IV), respectively. As a result, the acid–base equilibrium no longer governs the reactivity of Fe(IV). A comparison of this non-

speciated version of the reconstructed model with the experimental results is shown in Figure 2. For this case, the simulations replicate the experiment.

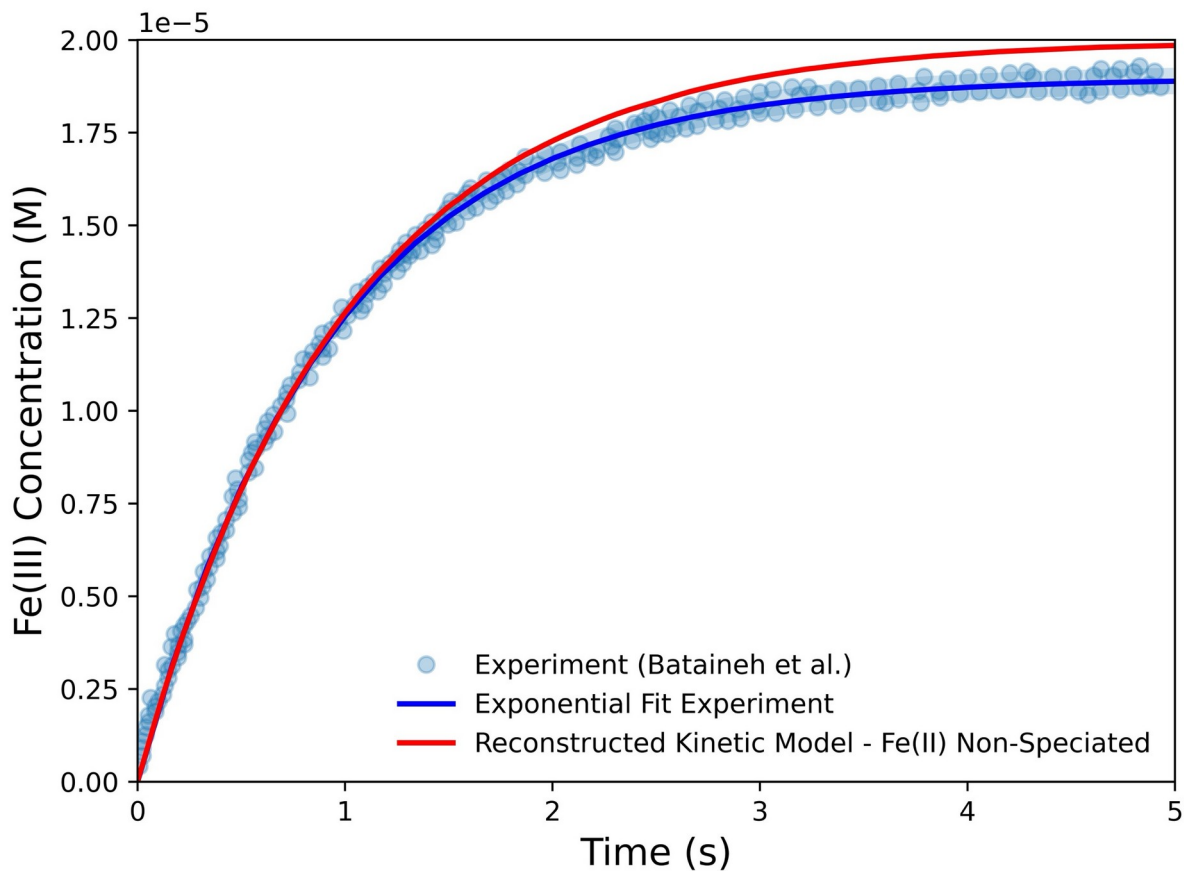


Figure 2 – Fe(III) concentration as a function of time for the reconstructed kinetic model with no Fe(II) speciation (red) and experimental data (blue) reproduced from Fig. S6 in supplementary information of Bataineh *et al.*²². Experimental conditions: 0.02mM Fe(II), 0.78mM H_2O_2 , pH 6.2 (buffered by 0.56mM MES).

The rate constant (k_{Fe}) for the Fenton reaction when one of the reagents is in excess is defined as $\frac{-d[H_2O_2]}{dt} = \frac{-1}{2} \frac{d[Fe(II)]}{dt} = k_{Fe}[Fe(II)][H_2O_2]$. Consequently, k_{obs} in Bataineh *et al.*²² is the observed rate, not corrected for stoichiometry, measured by the Fe(III) formation rate when H_2O_2 is in excess, *i.e.* $k_{obs} = 2k_{Fe}$ in units of $M^{-1}s^{-1}$. Shown in Figure 3 is the observed rate of Fe(III) formation (k_{obs}) as a function of [DMSO] reported in Bataineh *et al.*²² compared with

different versions of the reconstructed kinetic model. There is general agreement between the experimental results and the *non-speciated* reconstructed kinetic model across varying DMSO concentrations. In contrast, when including Fe(II) speciation in R3, k_{obs} predicted by the reconstructed model is an order of magnitude smaller and somewhat invariant to [DMSO]. Although the *non-speciated* reconstructed model agrees with the experimental results, it does so by assuming Fe(II) speciation that is unphysical. At pH=6, the experimental conditions are more than three pH units away from the pKa of Fe(II). This means that the concentration of $Fe(H_2O)_5OH^{+i.i}$, the species required for Fe(IV) formation, is less than 0.1% of the total Fe(II) in solution. As a result, the model's agreement arises from an unrealistic assumption rather than an accurate mechanistic representation. Moreover, the original premise of the Bataineh *et al.*²² model was to link Fe(IV) formation to the iron acid-base equilibrium (R3) in order to construct a predictive kinetic model across varying pH conditions. Yet, without including explicit Fe(II) speciation, the model is fundamentally unable to capture pH dependence. In addition to explicit kinetic simulations, Bataineh *et al.*²² provided a closed-form approximation to predict how k_{obs} varies with [DMSO] (See Eq. 10 in Ref. ²²). Our re-derivation of that equation (see SI Section S2) points to the same conclusion; that the derivation of this equation neglects Fe(II) speciation.

Thus, we conclude that the rate constant suggested by Bataineh *et al.*²² for the formation of Fe(IV) in R7 must be substantially underestimated since it is derived without considering the actual concentration of $Fe(H_2O)_5OH^{+i.i}$ at pH = 6. As a result, reproducing the experimental results requires increasing the Fe(IV) formation rate constant k_7 from $592 M^{-1} s^{-1}$ to $1.4 \times 10^6 M^{-1} s^{-1}$ (Figure 3 - red line and Fig. S4).

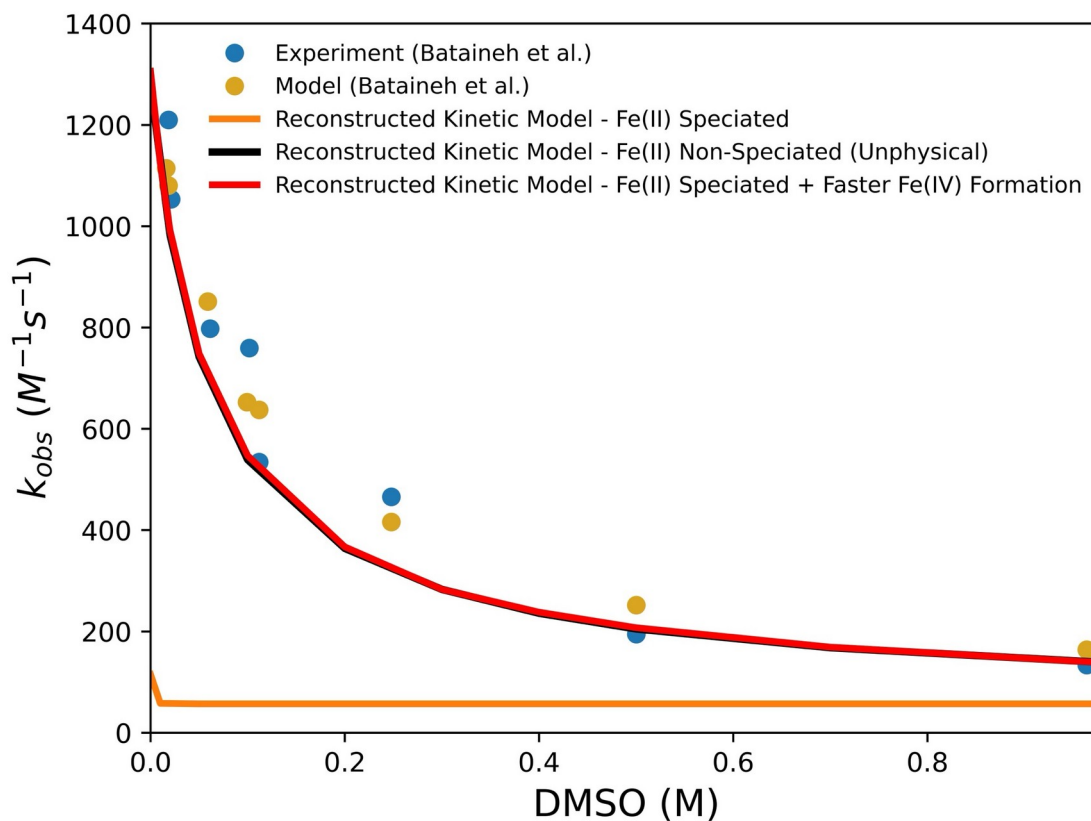


Figure 3 – k_{obs} is plotted as a function of DMSO concentration showing Bataineh et al.²² experimental results at pH=6 (blue circles) and model simulation (gold circles) reproduced from their Fig. 3. The reconstructed kinetic model with three variations is shown with lines connecting each model prediction to guide the eye. Assuming correct Fe(II) speciation (orange line) does not match experimental results, while assuming no speciation (black line) closely matches the experimental data, but this agreement is unphysical because it neglects the known speciation behavior of Fe(II). Reconstructed kinetic model that includes both Fe(II) speciation and a faster formation rate of Fe(IV) $k_7 = 1.4 \times 10^6 M^{-1} s^{-1}$ is shown with a red line. This version of the model matches the experimental trend and maintains consistency with realistic Fe(II) speciation.

The reconstructed model incorporating faster Fe(IV) formation and explicit Fe(II) speciation gets closer to a realistic representation of the Fenton reaction (Figure 3 – red line) but remains unsatisfactory, since it omits Fe(III) speciation, which is known to vary substantially with pH (see Sanz et al.³⁶ Fig. 2 or Remucal and Sedlak²¹ Fig. 3). Furthermore, because the Fe(IV) formation rate was adjusted to fit the experimental data at pH=6, the model performs well under

these conditions. However, when extended to pH=7, it underpredicts the observed reaction rate (Figure S4), suggesting that in its current form, it does not fully capture the pH dependent increase in Fe(II) oxidation.

Recently, Stanbury³³ conducted an exhaustive survey of Fenton reaction kinetics, identifying more than 200 published kinetic models that violate the principle of detailed balancing, *i.e.* that the ratio of forward and reverse rate constants for each elementary step must equal the corresponding equilibrium constant. In addition to this critical analysis, Stanbury³³ presented a validated radical mechanism for the Fenton reaction under acidic conditions. Expanding on this work, we develop a unified reaction mechanism spanning acidic to neutral conditions that incorporates both Fe(IV) formation and the correct thermodynamic speciation of iron and radical species (*i.e.*, $\cdot OH$, $HO_2\cdot$, $\wedge O_2^{\cdot-}$). The full reaction mechanism, including literature references for reaction steps and rate constants, is shown in Table 1.

Table 1: Fenton Chemistry Kinetic Model From Acidic to Neutral pH.^a

Reaction	Equilibrium/Rate Constants	Ref.	#
$H O_2 \cdot \rightleftharpoons H^{+} + O_2^{\cdot -}$	$K=1.3 \times 10^{-5} M$ $k_f=1.3 \times 10^5 s^{-1}$ $k_r=10^{10} M^{-1} s^{-1}$	33,37	M1
$F e^{3+} + H_2 O \rightleftharpoons F e(OH)^{2+} + H^{+}$	$K=4 \times 10^{-3} M$ $k_f=4 \times 10^7 s^{-1}$ $k_r=10^{10} M^{-1} s^{-1}$	33,38*	M2
$F e^{3+} + H_2 O_2 \rightleftharpoons F e(OH O_2)^{2+} + H^{+}$	$K=2 \times 10^{-3}$ $k_f=27 M^{-1} s^{-1}$ $k_r=1.35 \times 10^4 M^{-1} s^{-1}$	33,38,39†	M3
$F e(OH O_2)^{2+} \rightleftharpoons F e^{2+} + H O_2 \cdot$	$k_f=1.6 \times 10^{-3} s^{-1}$ $k_r=2.1 \times 10^6 M^{-1} s^{-1}$	33	M4
$F e(OH O_2)^{2+} + F e(OH)^{2+} \rightleftharpoons 2 F e^{2+} + H_2 O_2$	$k=5.0 M^{-1} s^{-1}$	33	M5
$F e^{2+} + H_2 O_2 \rightarrow F e(OH)^{2+} + \cdot OH$	$k=68 M^{-1} s^{-1}$	33	M6
$\cdot OH + H_2 O_2 \rightarrow H O_2 \cdot + H_2 O$	$k=1.7 \times 10^7 M^{-1} s^{-1}$	33	M7
$F e^{3+} + O_2^{\cdot -} \rightarrow F e^{2+} + O_2$	$k=4 \times 10^8 M^{-1} s^{-1}$	33	M8
$F e^{2+} + \cdot OH \rightarrow F e(OH)^{2+}$	$k=3 \times 10^8 M^{-1} s^{-1}$	33	M9
$H O_2 \cdot + H O_2 \cdot \rightarrow H_2 O_2 + O_2$	$k=8.3 \times 10^5 M^{-1} s^{-1}$	33	M10
$F e^{3+} + 2 H_2 O \rightleftharpoons F e(OH)_2^{+} + 2 H^{+}$	$K=1.6 \times 10^{-5} M^2$ $k_f=1.6 \times 10^5 s^{-1}$ $k_r=10^{10} M^{-2} s^{-1}$	33	M11
$2 F e^{3+} + 2 H_2 O \rightleftharpoons F e_2(OH)_2^{4+} + 2 H^{+}$	$K=7.9 \times 10^{-4} M$ (<i>kinetic steps</i> $\in$ M27 – M28)	33,40	M12
$F e(OH)^{2+} + H_2 O_2 \rightleftharpoons F e(OH)(H O_2)^{+} + H^{+}$	$K=2 \times 10^{-4}$ $k_f=2.8 \times 10^3 M^{-1} s^{-1}$ $k_r=1.4 \times 10^6 M^{-1} s^{-1}$	33,39†	M13
$F e(OH)(H O_2)^{+} \rightleftharpoons F e^{2+} + H_2 O_2$	$K=2.4 \times 10^{-11} M$ $k_f=2.4 \times 10^{-4} s^{-1}$ $k_r=10^7 M^{-1} s^{-1}$	33	M14
$F e(OH)_2^{+} + H_2 O_2 \rightleftharpoons F e^{2+} + H_2 O_2$	$K=1.2 \times 10^{-12}$ $k_f=1.2 \times 10^{-2} M^{-1} s^{-1}$ $k_r=10^{10} M^{-1} s^{-1}$	33*	M15
$H O_2 \cdot + O_2^{\cdot -} + H_2 O \rightarrow H_2 O_2 + O_2 + OH^{-}$	$k=9.7 \times 10^7 M^{-1} s^{-1}$	41	M16
$F e^{2+} + O_2^{\cdot -} + H_2 O \rightleftharpoons F e(OH)^{2+} + H_2 O_2$	$K=4.5 \times 10^2$ $k_f=1.3 \times 10^7 M^{-1} s^{-1}$ $k_r=2.9 \times 10^4 M^{-1} s^{-1}$	33,42	M17
$H_2 O_2 \rightleftharpoons H^{+} + H O_2^{\cdot -}$	$K=2.2 \times 10^{-12} M$ $k_f=2.2 \times 10^{-2} s^{-1}$ $k_r=10^{10} M^{-1} s^{-1}$	33,43	M18
$F e^{2+} + H_2 O \rightleftharpoons F e(OH)^{+} + H^{+}$	$K=7.9 \times 10^{-10} M$ $k_f=7.9 s^{-1}$ $k_r=10^{10} M^{-1} s^{-1}$	38	M19
$F e(OH)^{+} + H_2 O_2 \rightarrow F e^{IV} O^{2+} + H_2 O + OH^{-}$	$k=1 \times 10^6 M^{-1} s^{-1}$		M20
$F e^{IV} O^{2+} + H_2 O \rightarrow F e^{3+} + \cdot OH + OH^{-}$	$k=1.3 \times 10^{-2} s^{-1}$	44	M21
$F e^{IV} O^{2+} + \cdot OH \rightarrow F e^{3+} + H O_2 \cdot$	$k=1 \times 10^7 M^{-1} s^{-1}$	44	M22

$Fe^{IV}O^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO_2 + OH^+$	$k = 1 \times 10^4 M^{-1} s^{-1}$	44	M23
$Fe^{IV}O^{2+} + HO_2 \rightarrow Fe^{3+} + O_2 + OH^+$	$k = 2 \times 10^6 M^{-1} s^{-1}$	44	M24
$Fe^{2+} + Fe^{IV}O^{2+} + H_2O \rightarrow 2Fe^{3+} + 2OH^+$	$k = 7.2 \times 10^4 M^{-1} s^{-1}$	44	M25
$Fe^{2+} + Fe^{IV}O^{2+} + H_2O \rightarrow Fe_2(OH)_2^{4+}$	$k = 1.8 \times 10^4 M^{-1} s^{-1}$	44	M26
$Fe_2(OH)_2^{4+} \rightleftharpoons 2Fe(OH)^{2+}$	$K = \frac{K_{M2}^2}{K_{M12}} = 2.03 \times 10^{-2} M$ $k_f = 0.35 s^{-1}$ $k_r = 17$	45	M27
$Fe_2(OH)_2^{4+} + H^+ \rightleftharpoons Fe(OH)^{2+} + Fe^{3+} + H_2O$	$K = \frac{K_{M2}}{K_{M12}} = 5.06$ $k_f = 3.5 M^{-1} s^{-1}$ $k_r = 0.691 M^{-1}$	45	M28
$Fe_2(OH)_2^{4+} + H_2O \rightleftharpoons Fe(OH)^{2+} + Fe(OH)_2^{+} + H^+$	$K = \frac{K_{M2} K_{M11}}{K_{M12}} = 8.1 \times 10^{-5} M^2$ $k_f = \frac{3.6 \times 10^{-3}}{[H^+]}$	45	M29

^aFor simplicity, the iron species appear without water coordination, *i.e.* Fe^{2+} represents $Fe(H_2O)_6^{2+}$ and $Fe(OH)^{+}$ represents $Fe(H_2O)_5OH^+$. Reactions M19, M6, M20, and M25 or M26 in Table 1 are analogous to R3, R4, R7, and R9, respectively, in Bataineh *et al.* kinetic model or reconstructed kinetic model. ^{*}Modified from Ref. ³³. ^{*}Forward rate constant for Fe(III) substitution estimated for neutral ligand (acetic acid). Equilibrium constants K are shown in SI units with concentrations given in moles per liter (M). Water is assumed to have an activity of 1, rather than a concentration of 55M. The rate constants for the forward and reverse reactions are denoted by k_f and k_r , respectively.

Reactions M1-M10 are adapted from Scheme 3 in Stanbury,³³ while reactions M11-M19 extend the model to include additional speciation or radical reactivity relevant at higher pH. The equilibrium constants for M2 and M15 are noted with an asterisk since they are modified from Ref. ³³ to ensure compliance with Wegscheider's condition and internal consistency of the model reaction loops (Supplementary Information Section S5). Rate constants for the reactions of Fe(IV) in M21-M26 are taken from Jacobsen *et al.*⁴⁴, which characterized ferryl ion reactivity in acidic solutions. The Fe(III) hydroxo dimer ($Fe_2(OH)_2^{4+}$) is described with three kinetic steps (M27 to M29): spontaneous, acid-catalyzed, and base-catalyzed. These steps are parameterized to satisfy detailed balance with M2, M11, and M12. In the base-catalyzed channel (M29), rapid deprotonation of the dimer precedes cleavage, which yields the characteristic $1/[H^+]$ dependence while remaining consistent with mass action kinetics. The only *unknown* irreversible rate constant

in the model is M20; the rate of Fe(IV) formation. This rate constant is set to $k_{M20}=1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, since our analysis above using the iron speciated reconstructed kinetic model suggests a rate constant on this order is required. Furthermore, k_{M20} is of similar magnitude to the formation rate of Fe(IV) in the reaction of Fe(II) with ozone ($8.5 \pm 0.9 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$)⁴⁴.

To implement the propagation of reactions in a kinetic scheme, we assume that equilibrium is maintained using diffusion-limited kinetics in cases where no explicit slower forward or reverse rate constants are available. This is achieved by using a diffusion limit of $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for reactions M1-M2, M15, M18, M19, and a termolecular limit of $10^7 \text{ M}^{-2} \text{ s}^{-1}$ for reaction M14. An exception was applied to M11; although three species are involved in the reverse reaction, a bimolecular limit is assumed since equilibrium replenishing at pH=7 was shown to proceed on a time scale of minutes. Changing this rate had little to no effect on the overall observed rate but influenced Fe(III) speciation above pH = 4 (Supplementary Information Section S6).

Our unified kinetic model predictions for buffered pH conditions are presented in Figure 4. The model replicates the experimental results and captures the pH-dependent transition of the Fenton reaction rate $k_{Fe}(\text{M}^{-1} \text{ s}^{-1})$, in the presence of excess of H_2O_2 . It reproduces the flat kinetic dependence at acidic pH (pH<3), followed by a pronounced rate acceleration as the system approaches near-neutral pH. In contrast, the radical only oxidation pathway, *i.e.* disabling Fe(IV) formation in the unified kinetic framework, shows minimal pH sensitivity with some increase in the observed kinetics at pH>4. This weaker pH dependence suggests that the radical mechanism alone cannot account for the substantial increase in Fe(II) oxidation rate at higher pH, underscoring the importance of including Fe(IV)-mediated pathways and pH-sensitive iron speciation in kinetic models seeking to accurately represent Fenton chemistry. Comparison of the model to experimental

data recorded in seawater⁴⁶ is shown in Figure S16. Although exhibiting faster overall kinetics across the pH range, the seawater data has similar shape to our unified kinetic model predictions for pure water.

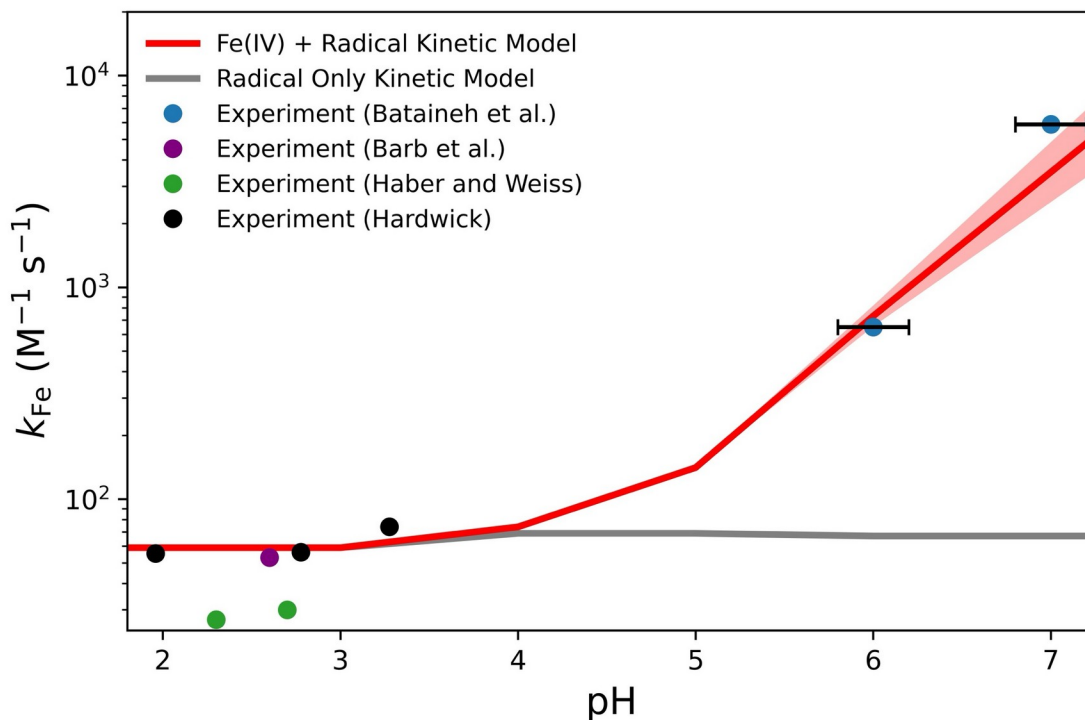


Figure 4 – The pseudo second order rate constant for the Fenton reaction $k_{Fe} (M^{-1} S^{-1})$ for conditions with excess H_2O_2 is plotted against buffered pH. Experimental results are shown with circle markers from Bataineh et al.²² (blue) in non-coordinating buffers: MES for pH=6 and MOPS for pH=7, the uncertainty in pH measurements is as horizontal error bar, in acidic conditions experimental results are from Barb et al.⁴⁷ (purple), Haber and Weiss¹² (green – underpredicted, prior to development of rapid mixing techniques), and Hardwick⁴⁸ (black). Kinetic model predictions are shown for the unified model in red with a red shaded area describing the uncertainty in estimating the exponential fit and k_{Fe} from the model kinetic traces. Predictions for the radical only oxidation pathway are shown in grey. A line to guide the eye is shown connecting model predictions.

To the best of our knowledge, the unified model presented above and shown in Figure 4 is the first framework for Fenton chemistry that uses physically realistic iron speciation and correctly describes the pH dependence of the reaction. This framework is proposed as a base kinetic model

that establishes a mechanistic foundation for describing Fenton chemistry across a pH range important for biology and the environment. However, it does not capture all the complexities that can arise from ionic strength, photo-Fenton reactions, ligand coordination, and complexation. These factors are all known to significantly influence Fenton chemistry in complex ways.^{6,19,21,23,44,46,47,49–59} Thus a more complex model would be required to begin incorporating these additional factors.

An advantage of using a kinetic framework for Fenton chemistry that includes detailed iron speciation is that further complexities can be evaluated through their direct effect on a specific species or equilibrium constants. Further constraining rate constants for forward and reverse equilibrium reactions, applying corrections to equilibrium constants and irreversible reactions based on ionic strength and temperature, and additional experimental data for Fe(IV) reactivity and speciation, will all increase the kinetic model accuracy and its utility in describing Fenton chemistry. This framework enables targeted exploration of specific systems, experimentally or computationally, by tuning rate constants, modifying equilibria, or introducing new elementary steps to represent ligand binding or competitive complexation that are relevant to the system of interest. This framework lays the groundwork to promote a shift from isolated system-specific studies toward a transferable and mechanistically consistent understanding of Fenton chemistry.

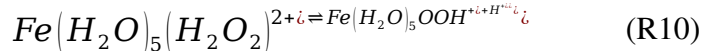
Beyond its application to canonical Fenton systems, it is also possible to use this framework to describe “Fenton-like” reactions starting from Fe(III) oxidation. However, a more rigorous treatment of iron precipitation would be required. For Fenton reaction timescales on the order of seconds to minutes, such as those plotted in Figure 4, little to no precipitation of newly formed Fe(III) hydroxide is expected to occur or significantly impact the kinetic results.⁶⁰ In contrast, starting from a solution of fully equilibrated Fe(III) involves solid precipitates. Accurately

modeling “Fenton-like” systems or very slow Fenton chemistry within this framework is feasible, provided that solid-phase equilibria are incorporated to account for precipitation effects on iron speciation and reactivity. This example highlights a specific opportunity to broaden the framework's application to address more complex chemical systems that include solid-phase interactions or additional equilibrium constraints.

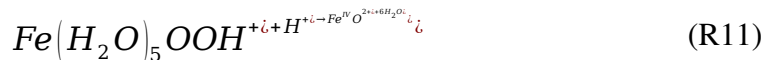
A significant advantage of a robust kinetic model is that it can be used to test the “kinetic viability” of theoretical predictions. For example, theoretical work by Lu *et al.*⁶¹ reported evidence that Fe(IV) is formed after complexation of Fe(III) with hydrogen peroxide. Specifically, at pH < 7.7, Fe(IV) was proposed to form via the reaction of OH radical with water coordinated $Fe(OH)^{2+}$, i.e. $(H_2O)_5Fe^{III}(OH)^{2+}$. To evaluate this mechanism, we replaced the Fe(IV) formation step (M20) in our model with that proposed by Lu *et al.*⁶¹: $Fe(OH)^{2+} + OH \rightarrow FeO^{2+} + H_2O$. The resulting predictions at pH 6 are too slow to reproduce the experimental data (Supplementary Information Section S9). While this reaction pathway may be energetically favorable, our model suggests that its overall contribution to the Fenton reaction rate is kinetically insignificant. Thermodynamic favorability alone does not translate to kinetic relevance in this case, as assigning the reaction a diffusion-limited rate constant, pushing to a kinetic upper limit, still results in Fe(IV) formation rate that is too low to account for the acceleration observed in near-neutral pH. No fitting parameters were used to evaluate the validity of the Fe(IV) formation pathway proposed by Lu *et al.*⁶¹ within the framework, since the only fit parameter (the reaction rate of M20) was removed from the analysis. This ensures an unbiased comparison between the kinetic validity of that pathway vs. reaction M20, already included in the model. Evidently, our model indicates that the primary mechanism for an accelerated rate in the transition from acidic to neutral pH is the Fe(IV)

formation pathway through the reaction of $Fe(OH)^{+2.66}$ with hydrogen peroxide (M20). This pathway was also supported in *ab-initio* molecular dynamics simulations conducted by Ensing et al.²⁸

A second example where our framework can be used to assess kinetic viability comes from a recently proposed mechanism for the formation of Fe(IV) by Koppenol²⁴. In this mechanism, proposed in 2022, the forming reagent is not $Fe(OH)^{+2.66}$ (M20), but rather hydrogen peroxide coordinated Fe(II), *i.e.* $Fe(H_2O)_5(H_2O_2)^{2+2.66}$. The acid-base equilibrium of this species governs the pH dependence of the Fenton reaction by,

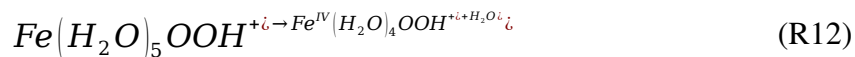


Followed by formation of Fe(IV) by,



R10 and R11 are analogous to Eq. 12 and Eq. 13 in Koppenol.²⁴ By setting the equilibrium of R10 to $pKa=5$, Koppenol²⁴ argues that this reaction will be kinetically equivalent to M20 and thermodynamically preferred. As we have no kinetic information for R10 or R11, nor the intrinsic pH dependence of R11, we can only examine if this mechanism is kinetically viable by checking a kinetic upper bound in which the intermediate $Fe(H_2O)_5OOH^{+2.66}$ is assumed to convert to $Fe^{IV}O^{2+2.66}$ instantaneously. Kinetic modeling of this scenario, implemented by replacing M20 with R10 and R11, is shown in Figure S18. The overall kinetics are faster than the experimental results or our unified kinetic model, pointing to an overall kinetic viability of this mechanism. A better agreement between the experimental results and this mechanism can be achieved by either shifting the pKa of R10 to a higher value or reducing the rate of R11. In 2024, Meyerstein and coworkers⁵⁸ presented a similar mechanism linking the pH dependence to

$Fe(H_2O)_5(H_2O_2)^{2+\ddot{O}\ddot{O}}$ through R10. Using DFT calculations, they determine the pKa of R10 to be 7.2 and propose Fe(IV) formation by,



Since we have no kinetic information for reactions involving $Fe^{IV}(H_2O)_4OOH^{+\ddot{O}\ddot{O}}$, we refrain from making a quantitative prediction regarding the feasibility of this mechanism. Taken together, the proposals of Koppenol²⁴ and Meyerstein *et. al.*⁵⁸ motivate targeted experimental studies to constrain the rate constants of R10 and R11/R12. To avoid introducing multiple free parameters, and until such rates are available and $Fe(H_2O)_5OOH^{+\ddot{O}\ddot{O}}$ or $Fe^{IV}(H_2O)_4OOH^{+\ddot{O}\ddot{O}}$ are experimentally confirmed, M20 remains the Fe(IV) formation mechanism included in our model.

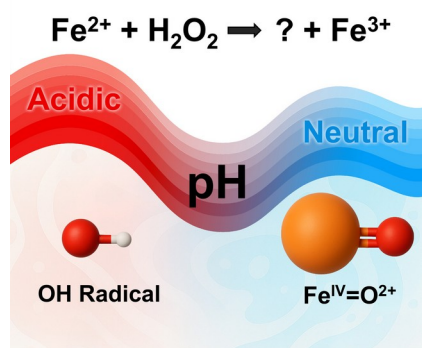
Conclusion

To conclude, we developed a unified kinetic model for Fenton Chemistry that includes both OH radical and Fe(IV) formation pathways. To our best knowledge, this is the first kinetic model that is able to quantitatively reproduce the pH dependence of the Fenton reaction while incorporating valid iron speciation. Since the model treats speciation explicitly, further complexities can be added as influencing a single species or through their effect on thermodynamic equilibria. The model provides a flexible kinetic framework that opens up opportunities for both experiment and theory to challenge assumptions and iterate on its current formulation. This framework advances our fundamental understanding of Fenton chemistry, a mechanism debated in the literature for over a hundred years.

Acknowledgements

This work was supported by the Condensed Phase and Interfacial Molecular Science Program (CPIMS), in the Chemical Sciences Geosciences and Biosciences Division of the Office of Basic Energy Sciences of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. We thank Dr. Ryan S. Reynolds (UC Irvine), Dr. Alexander M. Prophet (LBNL and UC Berkeley), Prof. Rebecca J. Rapf (Trinity University), Emily K. Brown (LBNL and UC Berkeley), Dr. Grazia Rovelli (Italfarmaco), Prof. David Limmer (LBNL and UC Berkeley) and Prof. Meirong Zeng (Shanghai Jiao Tong University) for helpful discussions.

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A new kinetic framework captures the long-debated pH dependent mechanism of the Fenton reaction. By incorporating iron speciation, the model quantitatively explains the shift from OH radical oxidation in acidic conditions to Fe(IV) formation near neutral pH. This framework corrects prior underestimations of rate constants and accurately reproduces the acceleration in iron oxidation by hydrogen peroxide.

Keywords

Fenton Chemistry, Kinetic Modeling, Reaction Mechanism, pH, Speciation

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