The Fenton Reaction. Dependence of the Rate on pH

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The pH dependence of the evolution of O_2 in the Fenton reaction has been studied by using an indirect method for measuring $[O_2]$. The results confirmed observations of previous workers, namely, that the evolution of O_2 diminished as the pH was lowered. A quantitative analysis of the dependence of $[O_2]$ and $[Fe^{2+}]$ during the reaction as a function of time showed that the pH dependence of the course of the reaction can be accounted for by assuming an acid base reaction of the active intermediate: $FeO^{2+} + H^+ \rightleftharpoons FeOH^{3+}$. $FeOH^{3+}$ is the active entity in the reaction with Fe^{2+} to produce Fe^{3+} ions, while the other form FeO^{2+} is involved in reactions leading to O_2 evolution.

Introduction

The course of the reaction between Fe^{2+} ions and H_2O_2 (the Fenton reaction) depends on the pH. At pH < 1, the reaction is restricted to the oxidation of Fe^{2+} ions by H_2O_2

$$2Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + 2OH^- \qquad (a)$$
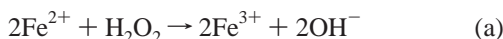
while above pH = 1, when an excess of H_2O_2 is present, part of the H_2O_2 is decomposed to O_2 and H_2O.

$$2H_2O_2 \rightarrow O_2 + 2H_2O \qquad (b)$$

This fact has been known for a very long time.[1,2] However, because of the lack of a method for following the evolution of O_2 during the reaction, no quantitative study of this change of the course of the reaction with pH has been made. Recently, a spectrophotometric method has been used to measure the amount of O_2 formed during the reaction as a function of time.[3] In this method, the reaction mixture is quenched with an excess of a strongly acidic solution of Fe^{2+} ions. From the moment of quenching on, the reaction becomes an oxidation of Fe^{2+} ions by H_2O_2 in the molar ratio of 2:1. If up to the moment of quenching there was an evolution of n_{O_2} moles of O_2 in the system, then, because of the stoichiometric relations in reactions a and b, the number of moles of Fe^{3+} formed in the quenched solution will be $2n_o - 4n_{O_2}$. n_o is number of moles of H_2O_2 present initially in the reaction mixture. Converting moles to concentrations, the absorbance A of the quenched reaction mixture, after the completion of the reaction of the residual H_2O_2 with excess Fe^{2+}, will be

$$A = A_o - 4\epsilon_{Fe^{3+}}[O_2]l \qquad (1)$$

$\epsilon_{Fe^{3+}}$ is the molar absorptivity of Fe^{3+} ions, l is the path length of light in the cell, and $A_o = 2\epsilon_{Fe^{3+}}[H_2O_2]_o l$ is the absorbance of the reaction mixture when quenched at $t = 0$. From eq 1, $[O_2]$ can be calculated.

It is the purpose of the present investigation to extend the use of this method to study the effect of pH on the course of the Fenton reaction.

Experimental Section

Iron powder puriss. of Fluka and H_2O_2 30%, unstabilized, Selectipur grade of Merck, were used. Deionized water was further purified in a Milli Q reagent water system apparatus.

The specific resistance measured was >10 MΩ cm. Other reagents used were of analytical grade.

Preparation of Fe(ClO$_4$)$_2$. The mode of preparation of Fe-(ClO$_4$)$_2$, free from Fe^{3+} ions, has been described earlier.[3] The only modification used was to raise the bath temperature from 27 to 30 °C in order to facilitate the dissolution of the Fe powder overnight when lower acid concentrations were used for the preparation of the reagent.

Determination of Fe^{2+} Ions. $[Fe^{2+}]$ was determined with *o*-phenanthroline using Hardwick's method.[4] Since at higher acidities a fading of the ferrous-phenanthroline complex occurred and occasionally also some precipitate was formed in the solution, the pH and the buffering capacity of the reagent solution were increased. The following reagent composition was used: 1.5 mol dm^{-3} CH$_3$COONH$_4$, 1.5 mol dm^{-3} CH$_3$COONa, 0.2 mol dm^{-3} NH$_4$F, and 0.2% *o*-phenanthroline. Absorbance was measured at $l = 510$ nm using the molar absorptivity of $\epsilon = 1.141 \times 10^4$ mol^{-1} dm^3 cm^{-1} of the Fe^{2+}-phenanthroline complex.

Quenching of the Reaction Mixture with Acidic FeSO$_4$. In one series of experiments, the reaction mixture was quenched with an excess of Fe^{2+} ions in 1 mol dm^{-3} H$_2$SO$_4$. H_2O_2, present at the time of quenching in the reaction mixture, reacted quantitatively with Fe^{2+} ions producing Fe^{3+} ions. The reaction is rapid, although not instantaneous. To ensure the completion of the reaction, the quenched mixture was held in a water bath of 27 °C for 15 min. The ferric sulfate complexes (which did not yield reproducible absorbance readings) were converted to a well-defined ferric-dihydrogen-phosphate complex. To this end, 0.2 cm^3 of an 1 mol dm^{-3} solution of H$_3$PO$_4$ were added for every cm^3 of final mixture. The solution was then diluted to a standard final volume (25 or 50 cm^3), and its absorbance was measured at $\lambda = 222$ nm. Proportionality between the measured absorbance and known concentrations of H_2O_2 in calibration curves showed that, under the conditions of the procedure, (1) the reaction between H_2O_2 and Fe^{2+} ions was complete and (2) the conversion of the sulfate complex to the phosphate complex was quantitative. The constancy of the (apparent) molar absorptivity $\epsilon_{Fe^{3+}}$ in the last column in Table 1 illustrates this point. The application of the method required the use of an Fe^{2+} ion solution free from measurable traces of Fe^{3+} ions. First, a 5×10^{-3} mol dm^{-3} solution of Fe(NH$_4$)$_2$-(SO$_4$)$_2$·6H$_2$O in 1 mol dm^{-3} H$_2$SO$_4$ was prepared. To reduce the concentration of residual Fe^{3+} ions in the reagent, it was let

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TABLE 1: Determination of Fe^{3+} Formed in Various Ranges of $[H_2O_2]$

procedure	range of $[H_2O_2]$, mol dm^{-3}	final vol, cm^3	l cm	$\epsilon_{Fe^{3+}}(app)$, mol^{-1} dm^3 cm^{-1}
1	$1 \times 10^{-3}-2 \times 10^{-4}$	50	1	4.69×10^3
2	$5 \times 10^{-4}-1 \times 10^{-4}$	25	1	4.72×10^3
3	$2.5 \times 10^{-4}-5 \times 10^{-5}$	25	2	4.72×10^3

to pass a 20 cm high column of Cd under N_2 in a closed apparatus.[3] Several cycles of reduction were performed by forcing the reduced solution repeatedly on the top of the Cd column by applying a small overpressure of N_2 in the apparatus. Usually, 5 or 6 cycles were necessary to reduce $[Fe^{3+}]$ to an acceptable level (a blank absorption of not more than 0.015). A sample of 0.08 cm^3 of this reagent was used for every cm^3 of final volume.

The absorbance of solutions was measured against identically treated blanks containing no H_2O_2. Separate calibration curves were run in three different and overlapping regions of $[H_2O_2]$, covering the range 1×10^{-3} mol dm^{-3}–5×10^{-5} mol dm^{-3}. The apparent molar absorptivity of Fe^{3+} ions $\epsilon_{Fe^{3+}}(app)$ was determined in each region and were used in the calculations. Details of the experimental procedure are summarized in Table 1.

Kinetic Measurements. A sample 0.0990 ± 0.0002 cm^3 (nominal volume 0.1 cm^3) of H_2O_2 was introduced in a series of reaction vessels and placed in a thermostat. $[H_2O_2]$ was determined with permanganate. The concentration was checked again upon the completion of all runs. The measured decrease of $[H_2O_2]$ in about 8 h was less than 1%. $[H_2O_2]_o$ in the reaction mixture was calculated using the known dilution ratio used during its preparation. (The subscript "o" denotes initial concentration.) Prior to initiating the reaction, 2.992 ± 0.002 cm^3 (nominal volume 3 cm^3) of a solution was added to the reaction vessel. This solution contained the necessary amounts of $HClO_4$ and $NaClO_4$ to give a required pH and ionic strength in the reaction mixture. The reaction was initiated by rapidly mixing in 0.0496 ± 0.0001 cm^3 (nominal volume 0.05 cm^3) of $Fe(ClO_4)_2$ placed on the flattened end of a small glass rod. The reaction was stopped by injecting the appropriate volume of the quenching solution: either *o*-phenanthroline in one series of experiments or acidic $FeSO_4$ in the other. In phenanthroline stopped runs, the reaction could be quenched 4 s after initiation. Time intervals were considerably longer in the O_2 evolution experiments. O_2 evolution was followed for about 45–60 min in different experiments. *o*-Phenanthroline quenched reaction mixtures were transferred quantitatively to a volumetric flask. They were filled up to mark and the absorbance was measured. In $FeSO_4$, stopped runs the quenched reaction mixtures were treated as described above. Optical absorbance was measured on a Beckman DU spectrophotometer upgraded by replacing its vacuum tubes by semiconductors and by attaching a digital readout to it.

Results

Experiments were performed at 25.0 °C at pH values of 1.20, 1.50, 1.80, 2.10, 2.30, 2.40, and 2.54. At each pH, two series of experiments were carried out: one quenched by *o*-phenanthroline, the other by acidic $FeSO_4$. In each series, $[H_2O_2]_o$ was varied, the values being approximately 1×10^{-3}, 7.5×10^{-4}, 5×10^{-4}, and 2×10^{-4} mol dm^{-3}. $[Fe^{2+}]_o$ was kept practically constant at 1×10^{-4} mol dm^{-3}. The ionic strength I was held constant at 0.400 mol dm^{-3}. Table 2 shows the results of two pairs of experiments run at pH = 1.20 and pH = 2.54, respectively. The results, together with the results of other

TABLE 2: Change of the Absorbance in Time in (a) $FeSO_4$ and (b) *o*-Phenanthroline Quenched Reactions at pH 1.20 and 2.54

	pH = 1.20				pH = 2.54		
	a		b		a		b
time s	A	time s	A	time s	A	time s	A
0	0.655	0	0.358	0	0.627	0	0.355
30	0.651	4	0.282	60	0.596	4	0.288
120	0.645	6	0.260	120	0.581	6	0.261
300	0.634	8	0.235	300	0.556	8	0.237
480	0.639	10	0.212	660	0.534	10	0.210
900	0.634	12	0.194	1080	0.520	12	0.196
1200	0.631	15	0.165	1260	0.513	15	0.173
1440	0.641	20	0.138	1560	0.502	20	0.150
1740	0.626	30	0.088	1860	0.496	30	0.113
2040	0.625	45	0.051	2460	0.490	45	0.078
2100	0.628	60	0.045	3000	0.473	70	0.054
2760	0.622			3780	0.452	130	0.034

	pH = 1.20		pH = 2.54	
	$[Fe^{2+}]_o$, mol dm^{-3}	$[H_2O_2]_o$, mol dm^{-3}	$[Fe^{2+}]_o$, mol dm^{-3}	$[H_2O_2]_o$, mol dm^{-3}
a	9.90×10^{-5}	5.09×10^{-4}	a 9.99×10^{-5}	4.98×10^{-4}
b	9.99×10^{-5}	5.08×10^{-4}	b 9.91×10^{-5}	4.98×10^{-4}

experiments at intermediate pH values, are plotted graphically in Figures 1a–d and 2a–d.

The data in Table 2 and in Figure 1a–d show a marked increase of the rate of formation of O_2 as the pH is increased. [The significance of the small increase of the solid (theoretical) lines in Figures 1a,b will be discussed in the Discussion section.] The amount of O_2 formed, calculated from the extent of decrease of the absorbance of the quenched reaction mixtures, is shown in Figure 3.

The $[Fe^{2+}]$ vs time curves show an opposite trend: the rate of disappearance of Fe^{2+} decreases as the pH is increased. These observations provide support to the suggestion that the evolution of O_2 is linked to the regeneration of Fe^{2+} in the system.[1,3]

Discussion

There exist two conceptually different theories of the mechanism of the Fenton reaction: one is based on the participation of free radicals, in the other, a compound formed between Fe^{2+} ion and an O atom (FeO^{2+}) is regarded as the active intermediate. Several review articles cover the subject which has been widened considerably by including also complexes of Fe^{2+} ions with organic ligands and by adding various oxidizable organic substrates to the system.[5-7] Some of these systems became quite complicated and controversy concerning the interpretation of the experimental results arose.[8-11] The present study and a previous one were restricted to the investigation of the reaction of uncomplexed Fe^{2+} ions and H_2O_2 in aqueous solutions, much as was done in the original investigation by Haber and Weiss and subsequently by Barb et al.[1,3,12] It was hoped to reduce in this manner the sources of ambiguities in the interpretation to a minimum.

Recent measurements of the absorbance of quenched reaction mixtures (quenching by Fe^{2+}) when the starting concentration of H_2O_2 was $<10^{-4}$ mol dm^{-3}, indicated the formation of a binuclear species which could easily be formed from FeO^{2+} but not in an obvious way from the radical $^{\bullet}OH$. FeO^{2+} as the active intermediate in the Fenton reaction has been first proposed by Bray and Gorin in 1932.[13] Recent molecular dynamics simulations of the $Fe^{2+} + H_2O_2$ system have also indicated that FeO^{2+} rather than the $^{\bullet}OH$ radical is the transient species in the reaction.[14] Following a different line of research, the formation
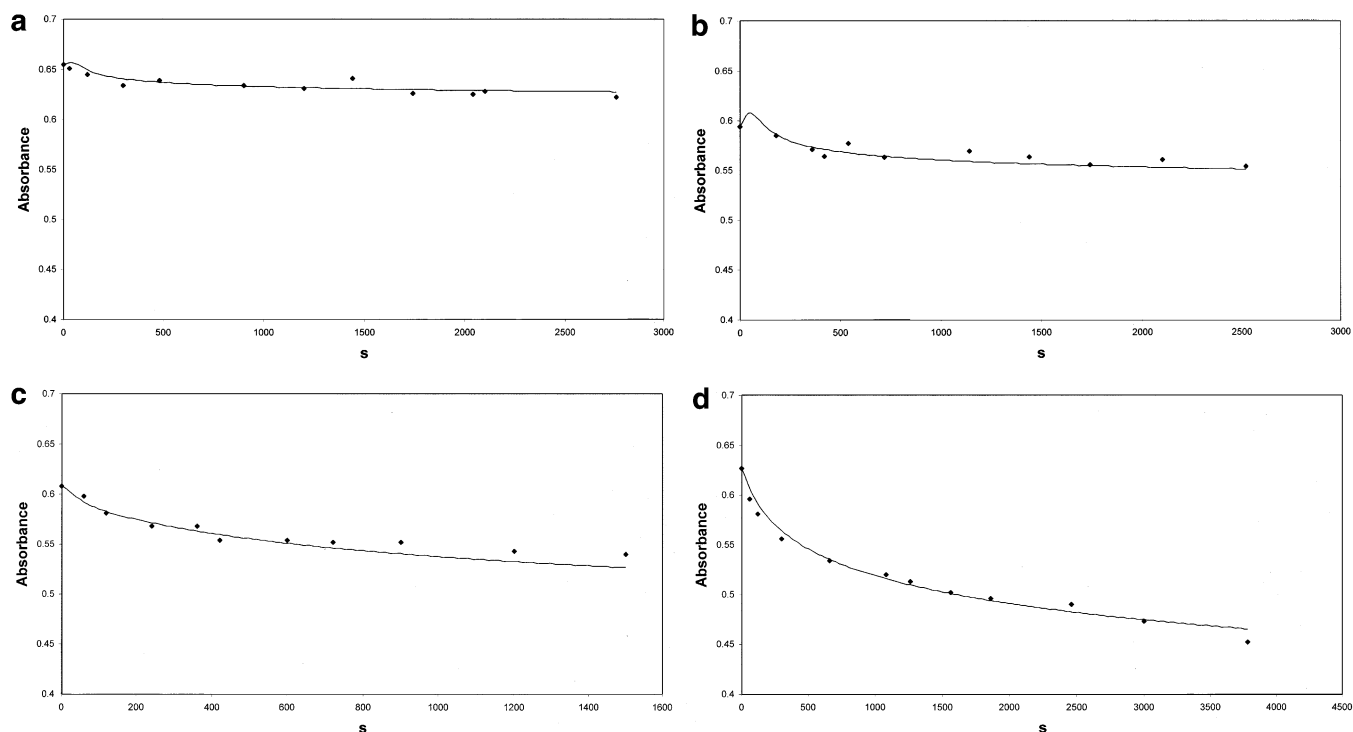
Figure 1. Decrease of the absorbance due to O_2 evolution at different pH values. $t = 25.0$ °C. $I = 0.400$ mol dm^{-3}. $\lambda = 222$ nm.

	pH	$[Fe^{2+}]_o$, mol dm^{-3}	$[H_2O_2]_o$, mol dm^{-3}
a	1.20	9.90×10^{-5}	5.09×10^{-4}
b	1.50	1.01×10^{-4}	5.01×10^{-4}
c	2.10	1.01×10^{-4}	5.14×10^{-4}
d	2.54	9.99×10^{-5}	4.98×10^{-4}

of FeO^{2+} in the reaction between O_3 and Fe^{2+} has been reported by Sehested and co-workers (see Appendix 1).[15,16] On the basis of this idea, the following mechanism was proposed for the Fenton reaction (Scheme 1).[3] The scheme accounted for the basic features of the reaction as observed at a constant pH:

(1) There is no evolution of O_2 at low $[H_2O_2]/[Fe^{2+}]$.

(2) O_2 is evolved at high $[H_2O_2]/[Fe^{2+}]$ (at pH above 1). There is a regeneration of Fe^{2+} in the system coupled to the formation of O_2.

(3) Addition of Fe^{3+} increases the rate of evolution of O_2; addition of F^- ions reverses the effect.

According to Scheme 1, the intermediate FeO^{2+} can react in several ways. It can react (a) with H_2O_2 in step 4 to produce O_2 and regenerate Fe^{2+} ions, (b) with Fe^{2+} in step 5 and produce two Fe^{3+} ions, or (c) with Fe^{3+} ions in step 6 and produce a binuclear complex $\{FeOFe\}^{5+}$. $\{FeOFe\}^{5+}$ can then further react with another molecule of H_2O_2 in step 7, providing a second path for the evolution of O_2.

At high $[Fe^{2+}]/[H_2O_2]$, step 5 suppresses step 4 and the sequence 6−7: there is no evolution of O_2. At high $[H_2O_2]/[Fe^{2+}]$, step 4 and the reaction sequence 6−7 become significant

SCHEME 1
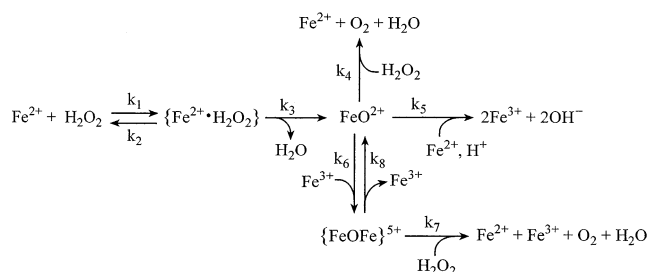
with the appearance of O_2 among the products and with the concomitant regeneration of Fe^{2+}. The addition of Fe^{3+} ions increases the rate of evolution of O_2 (step 6). The addition of F^- ions reverses the effect by binding Fe^{3+} ions.

All these effects are observed at a constant pH. Results in the present work show, in accordance with the observations of previous workers, that increasing the pH increases the rate of evolution of O_2.[1] There are a number of ways, in the framework of Scheme 1, in which H^+ ions can influence the course of the reaction. The assumption of an acid−base equilibrium involving FeO^{2+} accounts for most of the experimental observations.

$$FeO^{2+} + H^+ \overset{1/K}{\rightleftharpoons} FeOH^{3+}$$
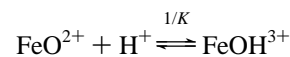
K is defined as the dissociation constant of $FeOH^{3+}$. The effect of the pH on the course of the reaction can be explained, if we make the following assumptions:

(a) The protonated state $FeOH^{3+}$ is the active form oxidizing Fe^{2+}

$$FeOH^{3+} + Fe^{2+} \rightarrow FeOH^{2+} + Fe^{3+} \qquad \text{(step 5)}$$

It is a one-electron transfer from Fe^{2+} to $FeOH^{3+}$ (viewed differently, it is the simultaneous transfer of two oxidation equivalents from O to two Fe^{2+} ions).

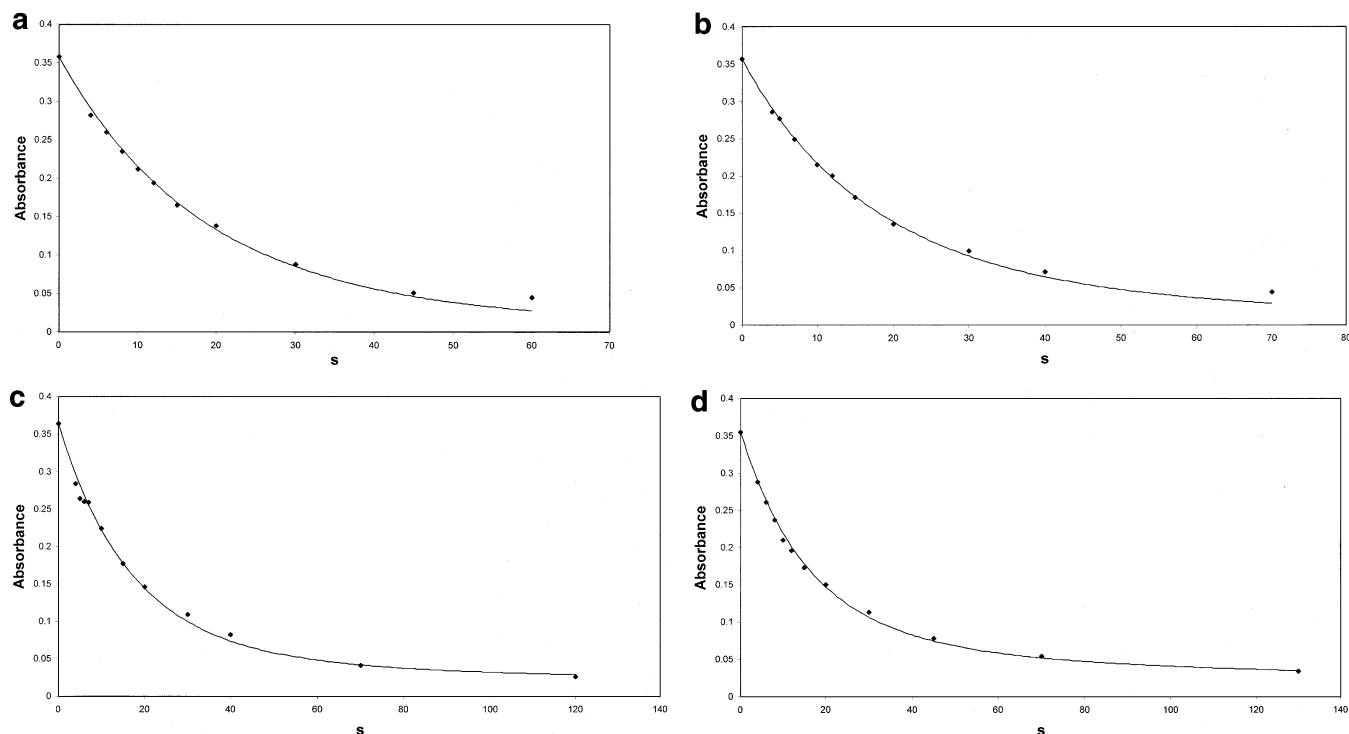(b) The basic form, FeO^{2+} is involved in the evolution of O_2.

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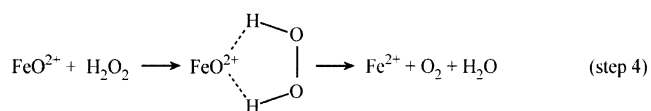
Figure 2. Decrease of the absorbance due to the disappearance of Fe^{2+} ions at different pH values. $t = 25.0$ °C. $I = 0.400$ mol dm^{-3}. $\lambda = 510$ nm.

	pH	$[Fe^{2+}]_o$, mol dm^{-3}	$[H_2O_2]_o$, mol dm^{-3}
a	1.20	9.99×10^{-5}	5.08×10^{-4}
b	1.50	9.96×10^{-5}	5.05×10^{-4}
c	2.10	1.02×10^{-4}	5.02×10^{-4}
d	2.54	9.91×10^{-5}	4.98×10^{-4}
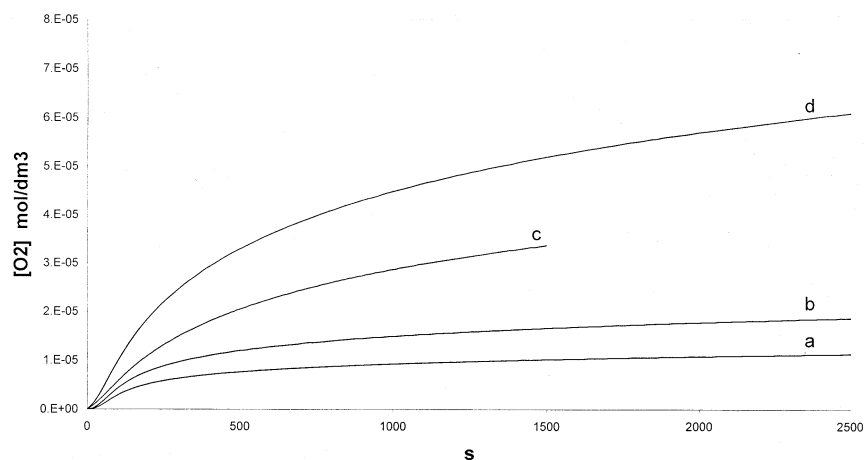
Figure 3. Calculated $[O_2]$ vs time curves. (Data identical with those of Figure 1.)

(c) The formation of the binuclear complex $\{FeOFe\}^{5+}$ also requires the participation of FeO^{2+}

$$FeO^{2+} + Fe^{3+} \rightarrow \{FeOFe\}^{5+} \qquad \text{(step 6)}$$

As the result of these reactions, an increase in the acidity will favor the oxidation of Fe^{2+} ions, while a decrease will promote O_2 evolution. The modified scheme, including the acid−base equilibrium, is shown in Scheme 2. A computer simulation of the reaction, using Scheme 2 as a basis, was performed. The calculations showed that five rate parameters were sufficient to determine the course of the reaction. It was equivalent to assuming the existence of the following equilibria and steady states in the system: (1) a steady state in regard of $[Fe^{2+} \cdot H_2O_2]$, (2) equilibrium between FeO^{2+} and $FeOH^{3+}$ and (3) steady state

SCHEME 2
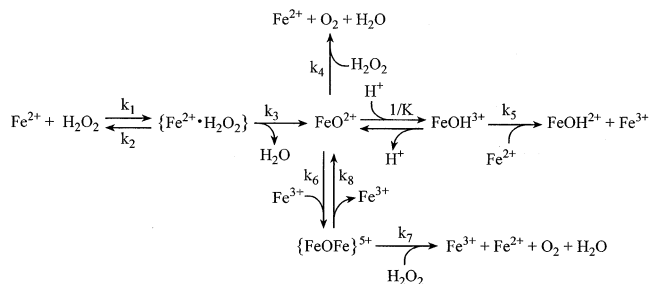
in regard of the sum of the concentrations of FeO^{2+} and $FeOH^{3+}$. There were three independent concentration variables: $[O_2]$, $[FeOFe^{5+}]$, and $[Fe^{2+}]$. {There was some freedom in choosing independent concentration variables. For example,

TABLE 3: Convergence Limits of Parameters at pH = 2.40[a]

	k_1', mol^{-1} dm^3 s^{-1}	$(k_4/k_5)K$, mol dm^{-3}	$(k_6/k_5)K$, mol dm^{-3}	k_7, mol^{-1} dm^3 s^{-1}	k_8, s^{-1}	ϵ_{FeOFe}, mol^{-1} dm^3 cm^{-1}	σ_A
	53.2	3.7×10^{-5}	6.8×10^{-4}	45	9.7×10^{-3}	2.4×10^4	7.2×10^{-3}
s^+	6.5	0.28	1.3	0.13	0.18	0.0	
s^-	6.4	0.26	1.4	0.16	0.18	0.0	

[a] $t = 25.0$ °C. $I = 0.400$ mol dm^{-3}. $\lambda = 222$ nm.

$[H_2O_2]$ and $[Fe^{3+}]$ could have been chosen instead of the pair $[O_2]$ and $[Fe^{2+}]$.}

The relevant rate equations were

$$d[O_2]/dt = \{(v_1 + k_8[FeOFe^{5+}])(k_4/k_5)(K/[H^+])[H_2O_2]/$$
$$DENOM\} + k_7[FeOFe^{5+}][H_2O_2] \quad (2)$$

$$d[FeOFe^{5+}]/dt = \{(v_1 + k_8[FeOFe^{5+}])(k_6/k_5)(K/[H^+]) \times$$
$$[Fe^{3+}]/DENOM\} - (k_7[H_2O_2] + k_8)[FeOFe^{5+}] \quad (3)$$

$$d[Fe^{2+}]/dt = -\{(v_1 + k_8[FeOFe^{5+}])(2[Fe^{2+}] + (k_6/k_5) \times$$
$$(K/[H^+])[Fe^{3+}])/DENOM\} + (k_7[H_2O_2] + k_8)[FeOFe^{5+}]$$
$$(4)$$

$$DENOM = (k_4/k_5)(K/[H^+])[H_2O_2] +$$
$$[Fe^{2+}] + (k_6/k_5)(K/[H^+])[Fe^{3+}]$$
$$v_1 = k_1'[Fe^{2+}][H_2O_2]$$

where $k_1' = k_1k_3/(k_2 + k_3)$.

The simultaneous differential equations were integrated numerically using the material balance equations

$$[Fe^{2+}]_o = [Fe^{2+}] + [Fe^{3+}] + 2[FeOFe^{5+}] \quad (5)$$

$$[H_2O_2]_o = [H_2O_2] + 2[O_2] + 0.5[Fe^{3+}] + 1.5[FeOFe^{5+}] \quad (6)$$

Theoretical absorbance vs time curves were calculated and fitted to the experimentally measured values. All the data obtained at a given pH served as the basis for the fitting procedure (80–90 data). They belonged to a series of four double runs (one quenched with *o*-phenanthroline, the other with acidic FeSO$_4$) in which $[H_2O_2]_o$ was varied. $[Fe^{2+}]_o$ was kept constant in all experiments.

The five parameters varied in the fitting procedure were k_1', $(k_4/k_5)K$, $(k_6/k_5)K$, k_7, and k_8.[3] (Note that the parameters $(k_4/k_5)K$ and $(k_6/k_5)K$ replace (k_4/k_5) and (k_6/k_5), appearing in the rate equations when no distinction is made between the reactions of FeO^{2+} and of its protonated form FeOH^{3+}.[3] By denoting the former rate constants as "old", the following correspondences exist between the old and new rate constants: (k_4/k_5)(old) = $(k_4/k_5)(K/[H^+])$ and (k_6/k_5)(old) = $(k_6/k_5)(K/[H^+])$.)

It was assumed in the calculations, as in a previous study, that both free Fe^{2+} ions and {FeOFe}$^{5+}$ are able to react with *o*-phenanthroline.[3] In the simulation of runs quenched by excess Fe^{2+} ions, a minor correction term $(\epsilon_{FeOFe} - 3\epsilon_{Fe^{3+}}$(app))$[FeOFe^{5+}]l$ was introduced in the expression for the calculation of the absorbance. It accounted for the absorbance of {FeOFe}$^{5+}$ in the system. (This term becomes substantial only in experiments using $[H_2O_2]_o < 10^{-4}$ mol dm^{-3}). The addition of the correction term required the inclusion of a sixth parameter ϵ_{FeOFe} in the calculations. (K appears in the rate equations only in combination with rate constants. Using the present analysis, its absolute value cannot be determined.)

The measure of agreement between the theoretical curves and the experimental data is shown in Figures 1a–d and 2a–d. The theoretical curves are presented as solid lines, the experimentally measured absorbances as points. The small initial rise (at 1–2 min) in the theoretical curves in Figure 1a,b is due to the formation of {FeOFe}$^{5+}$ in the system. (This rise is not reflected in the limited number of experimental points which were spread to cover a time interval of about 60 min.) The effect disappears at higher pH (Figure 1c,d) where the decrease of the absorbance due to the increased rate of formation of O$_2$ outweighs the initial increase.

The values of the best fitting parameters in experiments at pH 2.40 are shown in Table 3.

The last column lists the standard deviation σ_A of the experimentally measured absorbance values from those calculated from the model. s_i^+ and s_i^- are sensitivity indices. s_i^+ is defined as $1000\{\Sigma(\Delta A_i^+)^2 - \Sigma(\Delta A)^2\}/\Sigma(\Delta A)^2$ where $\Sigma(\Delta A)^2$ is the residual sum of squares of deviations of the absorbance measured experimentally from the calculated ones. $\Sigma(\Delta A_i^+)^2$ is the same quantity when the ith parameter is increased by 1%. s_i^- is defined in an analogous manner when the ith parameter is decreased by 1%. A higher sensitivity index indicates better accuracy of the value of the parameter in question.

The convergence limits of the parameters obtained at different pH are summarized in Table 4. The data in Tables 3 and 4 show that the rate parameter most accurately determined in the experiments is k_1', the rate constant of formation of FeO^{2+} from Fe^{2+} and H$_2$O$_2$ via the precursor complex {Fe^{2+}·H$_2$O$_2$}. (Because of the FeOH$^{3+} \rightleftharpoons$ FeO^{2+} + H$^+$ equilibrium, it is not possible to decide, whether step 3 represents the loss of a H$_2$O molecule with the production of FeO^{2+} or rather the loss of an OH$^-$ ion and the production of FeOH^{3+}.) The rate of this step determines to a large extent the rates of the subsequent stages of the reaction involved in the oxidation of Fe^{2+} ions and in the evolution of O$_2$. It implies that the rate constants of the subsequent steps have much smaller influence on the rate. As a consequence, they can be determined with lesser accuracy. By averaging the values of k_1' listed in Table 4 we obtain $k_1' = 52.4 \pm 0.9$ mol^{-1} dm^3 s^{-1}. This value is in good agreement with the previously determined value of $k_1' = 55.4 \pm 0.4$ mol^{-1} dm^3 s^{-1} at pH = 2.43 and $I = 0.05$M.[3] It is also in excellent agreement with Barb et al.'s value of $k_o = 53.0 \pm 0.7$ mol^{-1} dm^3 s^{-1} at 24.6 °C.[1] k_o plays an analogous role in the free radical mechanism as k_1' in the present one: both are second-order rate constants of formation of the active intermediate, be it the •OH radical or FeO^{2+}. It should be pointed out that Barb et al.'s value was obtained under the restrictive condition of no O$_2$ evolution. In the present work, k_1' was determined in a much wider range of experimental conditions. Barb et al. reported an anomalous variation of k_o in experiments using low reagent concentrations. They attributed it to the presence of "nonremovable impurities" in the distilled water used by them. No such effect was observed in the present work nor in an earlier work of Rigg et al.[17] Wells and Salam report a value of $k_o = 50$ mol^{-1} dm^3 s^{-1} ($t = 25$ °C; $I = 1.0$ mol dm^{-3}) and claim

Fenton Reaction

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TABLE 4: Convergence Limits of Parameters at Various pH Values

pH	k_1', mol^{-1} dm^3 s^{-1}	$(k_4/k_5)K$, mol dm^{-3}	$(k_6/k_5)K$, mol dm^{-3}	k_7, mol^{-1} dm^3 s^{-1}	k_8, s^{-1}	ϵ_{FeOFe}, mol^{-1} dm^3 cm^{-1}
1.20	51.8		2.0×10^{-3}	87	9.9×10^{-3}	5.1×10^4
1.50	51.8	4.4×10^{-6}	3.0×10^{-3}	53	3.2×10^{-2}	7.7×10^4
1.80	50.9	3.6×10^{-5}	1.3×10^{-3}	35	7.9×10^{-3}	6.1×10^3
2.10	53.0	2.6×10^{-5}	7.9×10^{-4}	21	3.9×10^{-3}	
2.30	52.5		9.8×10^{-4}	49	6.7×10^{-3}	
2.40	53.2	3.7×10^{-5}	6.8×10^{-4}	45	9.7×10^{-3}	2.4×10^4
2.54	53.4	1.3×10^{-5}	4.9×10^{-4}	37	1.6×10^{-3}	3.3×10^3

^{a} $t = 25.0$ °C. $I = 0.400$ mol dm^{-3}. $\lambda = 222$ nm.

that it is constant up to pH 3.[18] Hardwick obtained a constant value of $k_o = 43 \pm 1$ mol^{-1} dm^3 s^{-1} in the pH range of 1−2.8 at a somewhat lower temperature of 20 °C.

The computer simulations indicated that step 4 is a minor pathway for the production of O_2, especially at low pH. As a consequence, values of $(k_4/k_5)K$ became uncertain at the acidic end of the pH range under investigation (pH 1.20 and 1.50). Probably due to experimental errors, the computer program assigned a very low value to $(k_4/k_5)K$ also at pH 2.30. Taking the values of $(k_4/k_5)K$ at 1.80, 2.10, 2.40, and 2.54 as a basis, we obtain $(k_4/k_5)K = (3 \pm 1) \times 10^{-5}$ mol dm^{-3}. Using this value, (k_4/k_5)(old) at pH 2.43 is calculated to be 8×10^{-3}, compared with 7.5×10^{-3} found previously. The calculations indicated constant if not very accurate values for k_7 and k_8. The average value of k_7 (not including the value at pH 1.20) is $(4 \pm 1) \times 10$ mol^{-1} dm^3 s^{-1}. The best value for k_8 becomes $(7 \pm 3) \times 10^{-3}$ s^{-1}. (Here the value at pH 1.50 was not included in the average. Its inclusion would have increased k_8 to 1×10^{-2} s^{-1} with a large increase of the standard deviation.)

There is a marked decrease of $(k_6/k_5)K$ with the increase of the pH. This phenomenon is attributed to the hydrolysis of Fe^{3+} ions

$$Fe^{3+}(H_2O) \overset{K_{Fe}}{\rightleftharpoons} Fe^{3+}OH^- + H^+$$
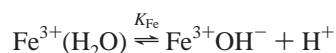
and assuming that only Fe^{3+} ions can react with FeO^{2+} in step 6. If this interpretation is correct, then by denoting the total concentration of Fe^{3+} ions by T, and the second-order rate constant of reaction of Fe^{3+} with FeO^{2+} by k_6', we obtain

$$v_6 = k_6'[Fe^{3+}][FeO^{2+}] = k_6'\{[H^+]/([H^+] + K_{Fe})\}T[FeO^{2+}] \quad (7)$$

and

$$k_6 \equiv v_6/(T[FeO^{2+}]) = k_6'[H^+]/([H^+] + K_{Fe}) \quad (8)$$

K_{Fe} is the acid dissociation constant of $Fe^{3+}(H_2O)$: $K_{Fe} = [FeOH^{2+}][H^+]/[Fe^{3+}]$ From here

$$\{(k_6/k_5)K\}^{-1} = \{(k_6'/k_5)K\}^{-1}\{1 + (K_{Fe}/[H^+])\} \quad (9)$$

In Figure 3 the inverse of $(k_6/k_5)K$ is plotted as a function of $1/[H^+]$. The extrapolation of the straight line to $1/[H^+] = 0$ gives $(k_6'/k_5)K = 2.5 \times 10^{-3}$ mol dm^{-3}. From the slope of the straight line, $K_{Fe}\{(k_6'/k_5)K\}^{-1} = 4.50$. We calculate that for pH = 2.43, $(k_6/k_5)K = 6.24 \times 10^{-4}$ mol dm^{-3} and $(k_6/k_5)(K/[H^+]) = 0.17$, compared to (0.24 ± 0.04) obtained previously at 25.0 °C and $I = 0.05$ mol dm^{-3}. The ratio of slope and intercept should give the dissociation constant of K_{Fe}. From the data, $K_{Fe} = 1.1 \times 10^{-2}$ M. This value is very high and indicates a less than equilibrium concentration of free Fe^{3+} ions in the system. [Using

the empirical equations of Milburn and Vosburgh for the dependence of K_{Fe} on the ionic strength (ref 19), the value of Knight and Sylva for K_{Fe} becomes 2.0×10^{-3} mol dm^{-3} (ref 20). The measurements of Byrne and Kester yield $K_{Fe} = 2.2 \times 10^{-3}$ mol dm^{-3} (ref 21). All values refer to $t = 25$ °C and $I = 0.400$ mol dm^{-3}.] One possible explanation is that step 5 is not a simple electron transfer process but involves the transient formation of a dimer of partially hydrolyzed Fe^{3+} ions.

$$FeOH^{3+} + Fe^{2+} \rightarrow \{FeOHFe\}^{5+} \rightarrow FeOH^{2+} + Fe^{3+} \quad (10)$$

This interpretation implies that the oxidation of Fe^{2+} by $FeOH^{3+}$ is an inner-sphere electron-transfer process. Sutin and co-workers found that the dissociation of the hydrolyzed dimer of ferric ions (which they write as $\{Fe(OH)_2Fe\}^{4+}$) is relatively slow and dependent on the pH.[22,23] The formation of the dimer can explain the lower than equilibrium concentration of Fe^{3+} in the system. The limited accuracy of the data does not make a more quantitative investigation of this aspect of the mechanism possible. No satisfactory estimation of ϵ_{FeOFe} can be made from the data.

Figure 5 shows a presentation of the time variation of the major components during the Fenton reaction. The bulk of Fe^{2+} ions disappears in the initial phase of the reaction (curve a) with the concomitant rise of $[Fe^{3+}]$ (both hydrolyzed and unhydrolyzed forms of Fe^{3+}, curve b). Fe^{3+} ions react with the active intermediate FeO^{2+}, present in the system at a low steady-state concentration, giving rise to the binuclear mixed valence species $\{FeOFe\}^{5+}$ (curve c). The increase of $\{FeOFe\}^{5+}$ increases the rate of formation O_2 (another way of formation of O_2 is through the direct reaction of FeO^{2+} with H_2O_2). The maximum of $[FeOFe^{5+}]$ causes the appearance of an inflection in the $[O_2]$ vs time curve (curve e). H_2O_2 decreases during the reaction (curve d). For the given initial conditions, 9.8% of the initial amount of H_2O_2 has been used up at 1500 s in the oxidation of Fe^{2+} ions, and 20.9% in the production of O_2 and 69.1% are still unreacted. Any remaining H_2O_2 at the end of the Fenton reaction will disappear ultimately in the ensuing catalytic decomposition by Fe^{3+} ions.[24,25]

A final point concerns the oxidation of substrates, like alcohols by Fenton's reagent.[26−28] Since these reactions were performed in moderately to strongly acidic solutions, it seems probable that the acidic form of the active intermediate $FeOH^{3+}$ is involved in them. Both one-equivalent and two-equivalent oxidations of substrates by $FeOH^{3+}$ are possible by reducing it either to $FeOH^{2+}$ or to Fe^{2+}. Both one equivalent and two equivalent oxidations by Fenton's reagent have been reported in the literature.[26−29]

In conclusion, this study shows that the model of the Fenton reaction based on the intermediacy of FeO^{2+}, accounts satisfactorily for the supression of O_2 evolution at low pH, if an acid−base equilibrium involving FeO^{2+} is introduced in the mechanism and different reactivities of the acidic and basic
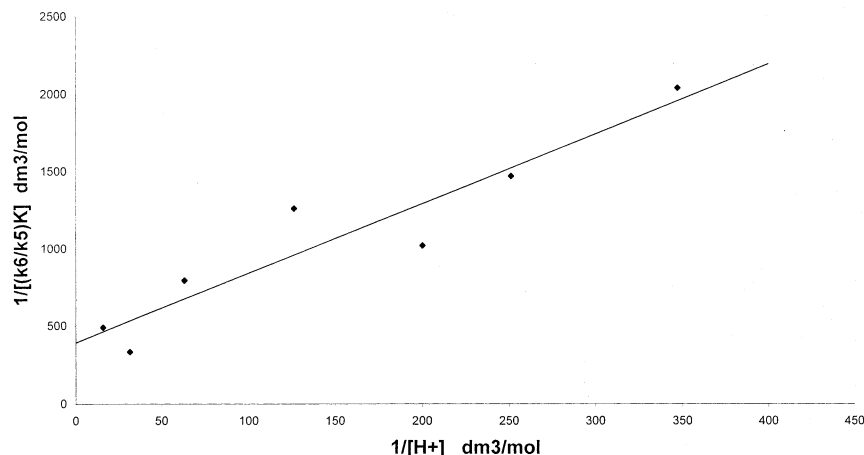
Figure 4. $[(k_6/k_5)K]^{-1}$ as a function of $[H^+]^{-1}$. $t = 25.0\ °C$. $I = 0.400\ mol\ dm^{-3}$.
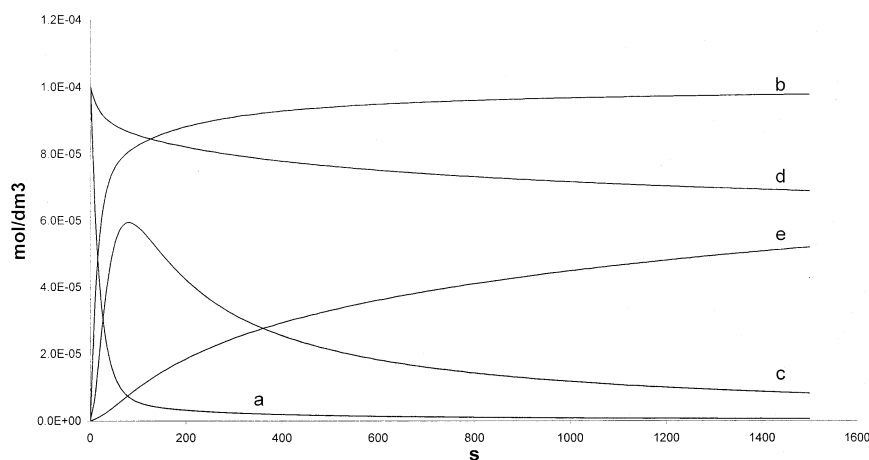

Figure 5. Concentration vs time curves of major components in the Fenton reaction. a. $[Fe^{2+}]$ b. $[Fe^{3+}]$ c. $[FeOFe^{5+}]$ d. $[H_2O_2]$ e. $[O_2]$. $[Fe^{2+}]_o = 9.99 \times 10^{-5}\ mol\ dm^{-3}$. $[H_2O_2]_o = 4.98 \times 10^{-4}\ mol\ dm^{-3}$. pH = 2.54. The rate parameters are given in Table 4. In the plot, the concentration of $\{FeOFe\}^{5+}$ has been multiplied by 10, that of H_2O_2 has been divided by 5. $[Fe^{3+}]$ represents all forms of Fe^{3+}, hydrolyzed and unhydrolyzed.

forms are assumed toward Fe^{2+} on one hand, and toward H_2O_2 and Fe^{3+} on the other. The scheme proposed here is a minimal scheme. Further observations may lead to more elaborate schemes revealing finer details of the mechanism.

Appendix 1

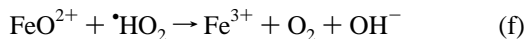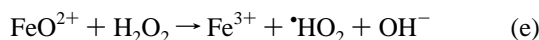Logager et al. produced FeO^{2+} through the ozonization of Fe^{2+}.

$$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2 \qquad (c)$$
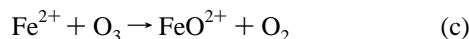
It was found that FeO^{2+} is able to react with both Fe^{2+} and H_2O_2.[15,16a] It was suggested that the reaction of FeO^{2+} with Fe^{2+} produces both Fe^{3+} and $Fe(OH)_2Fe^{4+}$ with subsequent dissociation of the latter to produce also monomeric Fe^{3+}.

$$Fe(OH)_2Fe^{4+} \rightarrow 2Fe^{3+} + 2OH^- \qquad (d)$$
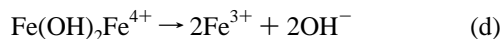
This pathway of Fe^{3+} ion formation corresponds to step 10 in the present work.

In the reaction of FeO^{2+} with H_2O_2, Jacobsen et al. assume the formation of free radicals

$$FeO^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^\bullet HO_2 + OH^- \qquad (e)$$

$$FeO^{2+} + {}^\bullet HO_2 \rightarrow Fe^{3+} + O_2 + OH^- \qquad (f)$$

Since the rate constant k_f given by them ($2 \times 10^6\ mol^{-1}\ dm^3\ s^{-1}$) is much larger than k_e ($1 \times 10^4\ mol^{-1}\ dm^3\ s^{-1}$), the set e−f is kinetically indistinguishable from step 4 of Scheme 2, in which no radicals are produced. The pair e−f differs from step 4 in the respect that they yield Fe^{3+} ions, while in step 4 Fe^{2+} ions are formed. Since it has been established that in the Fenton reaction the production of O_2 is coupled with the regeneration of Fe^{2+}, step 4 seems to be the more proper representation of the O_2 producing step.[1,3]

Jacobsen et al. report that in the absence of Fe^{2+} and H_2O_2, FeO^{2+} is unstable and decays spontaneously to yield Fe^{3+} in a first-order reaction.[16b] The rate constant k_{decomp} was found to be dependent on pH. A plot of k_{decomp} as a function of pH had a sigmoidal shape from which an approximate value of 2 has been obtained for pK_a of the equilibrium $FeOH^{3+} \rightleftharpoons FeO^{2+} + H^+$ (the equilibrium is written by the authors in a slightly different form). Jacobsen et al. account for the decay in terms of reactions which involve ${}^\bullet OH$ and ${}^\bullet HO_2$ radicals. It is, however, possible to account for the decay of FeO^{2+} also on the basis of Scheme 2. The decay of FeO^{2+} can be attributed to the reversal of its reaction of formation:

$$FeO^{2+} + H_2O \rightarrow Fe^{2+} + H_2O_2 \qquad (g)$$

$$FeOH^{3+} + H_2O \rightarrow Fe^{2+} + H_2O_2 + H^+ \qquad (h)$$
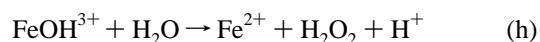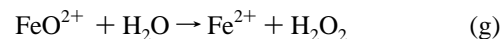
(Note that at the start of the decay experiments, there were practically no Fe^{2+} and H_2O_2 present in the system.) Fe^{2+} ions

thus formed will react in a rapid reaction with ferryl ions producing Fe^{3+} ions (step 5). The occurrence of both reactions g and h, involving both protolytic states of FeO^{2+}, can explain the sigmoidal form of dependence of k_{decomp} on the pH.

Jacobsen et al.[16] report that the rate constant of the reaction between FeO^{2+} and Fe^{2+} decreases with increasing pH, if the corresponding decrease of the ionic strength is not compensated for by adding an inert electrolyte, but remains constant, if the ionic strength is held constant. No systematic study of the reaction of FeO^{2+} with H_2O_2 has been made as a function of pH. It is, therefore, not possible to compare at present quantitatively $(k_4/k_5)K$ of this work with the corresponding quantity (k_5/k_3) of Logager et al.[15] If the value $pK_a = 2$ is used, k_4/k_5 becomes 3×10^{-3}, but this result requires further confirmation.
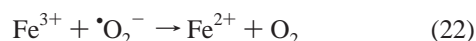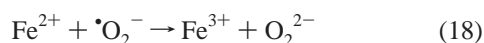
Appendix 2

The Free Radical Mechanism. In the free radical mechanism, postulated originally by Haber and Weiss[12] and elaborated subsequently by Barb et al.,[24] the change of course of the reaction as a function of pH has been attributed to the acid–base equilibrium involving the $^{\bullet}HO_2$ radical[1,2,12,30,31]

$$^{\bullet}HO_2 = H^+ + {^{\bullet}O_2}^-$$
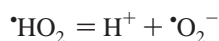
The acid dissociation constant of radiolytically produced $^{\bullet}HO_2$ K_{HO_2} has been determined as 1.6×10^{-5} mol dm^{-3}.[30,31]

Using the method of pulse radiolysis, Rush and Bielski studied the reactions of the two forms of $^{\bullet}HO_2$ with Fe^{2+} and Fe^{3+} ions, respectively. They reported the occurrence of the following reactions

$$Fe^{2+} + {^{\bullet}HO_2} \rightarrow Fe^{3+} + HO_2^- \qquad (17)$$

$$Fe^{2+} + {^{\bullet}O_2}^- \rightarrow Fe^{3+} + O_2^{2-} \qquad (18)$$

$$Fe^{3+} + {^{\bullet}O_2}^- \rightarrow Fe^{2+} + O_2 \qquad (22)$$

(The numbering of reactions in this section follows that of Rush and Bielski.[31]) $^{\bullet}HO_2$ has been found to be unreactive toward Fe^{3+}. By denoting by R the ratio of rate constants of reactions of all forms of $^{\bullet}HO_2$ with Fe^{2+} and Fe^{3+}, respectively, we obtain

$$R = (k_{18}/k_{22}) + [k_{17}/(k_{22}K_{HO_2})][H^+] \qquad (A1)$$

R is equivalent to the ratio of k_3/k_4 of Barb et al.[1] By studying the Fenton reaction, Barb et al.[1] reported a linear dependence of R on $[H^+]$ (Figure 17 in ref 1). At 24.6 °C, the straight line intersected the $[H^+]$ axis at $[H^+]_{int} = -5 \times 10^{-3}$ mol dm^{-3}. Using eq A1, we obtain

$$K_{HO_2} = -(k_{17}/k_{18}) [H^+]_{int} \qquad (A2)$$

Inserting Rush and Bielski's[31] values of $k_{17} = 1.2 \times 10^6$ mol^{-1} dm^3 s^{-1} and $k_{18} = 1 \times 10^7$ mol^{-1} dm^3 s^{-1}, we obtain $K_{HO_2} = 6 \times 10^{-4}$ mol dm^{-3}. This value is 40 times higher than that obtained in the radiolysis study.[31]

Thus, by adhering to the free radical formulation, the variation of R with the pH in the Fenton reaction does follow the pattern predicted on the basis of radiolytic results. There is, however, a disagreement between the best values of K_{HO_2} fitting the experimental results in the two domains.

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