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REACTIONS OF LOW VALENT TRANSITION-METAL COMPLEXES WITH HYDROGEN PEROXIDE. ARE THEY "FENTON-LIKE" OR NOT? 3. THE CASE OF $Fe(II)\{N(CH_2CO_2)_3\}(H_2O)_2^-$

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The reaction of $Fe(II)\{N(CH_2CO_2)_3\}(H_2O)_2^-$ with H_2O_2 in neutral and slightly acidic solutions was studied. The results indicate that the transient complex formed between these reagents, $(nta)(H_2O)$-$Fe^{2+}\cdot O_2H^-$, (where nta = $N(CH_2CO_2^-)_3$) reacts either directly with $\geqslant 0.175$ M 2-propanol or 2-methyl-2-propanol, or decomposes into the corresponding tetra-valent iron complex which then reacts with these alcohols. The nature of the final products in this system containing iron ions and nta depends on the pH, thus indicating that the nature of the transient complexes formed, or their relative yields, depend on the pH. The results prove that free hydroxyl radicals are not the major product of this "Fenton like" reaction under the experimental conditions. The implications of these results on the understanding of biological processes is discussed.

KEY WORDS: Fenton, iron, nitrilotriacetate, hydrogen-peroxide, hydroxyl free radical, alcohols.

INTRODUCTION

The oxidation of a variety of organic substrates by a mixture of a low-valent transition-metal complex and hydrogen-peroxide is commonly attributed to a "Fenton-like" mechanism,[1-4] i.e.

$$M^nL_m + H_2O_2 \rightarrow M^{n+1}L_m + \cdot OH + + OH^- \qquad (1)$$

followed by equation (2) or (3).

$$\cdot OH + RH \rightarrow \cdot R + H_2O \qquad (2)$$

$$\cdot OH + R_1R_2C{=}CR_3R_4 \rightarrow \cdot CR_1R_2CR_3R_4(OH) \qquad (3)$$

This mechanism is of major importance owing to its role in many catalytic oxidations,[5,6] and its suggested role in many deleterious biological processes.[7-9] The fact that relatively high concentrations of hydroxyl radical scavengers do not always protect the system has been attributed to a "site specific" mechanism, i.e. the metal ion is bound near the biological target and the damage is caused by the hydroxyl free radical immediately after its formation.[10-12]

Recent studies of the reactions of H_2O_2 with Cu_{aq}^+,[13-14] $Cu(phen)_2^+$,[15] $Cu(bpy)_2^+$,[16] polyaminocarboxylate complexes of iron(II),[17-18] $U(IV)_{aq}$[19] and $Ru(Hedta)(H_2O)$[20] indicate that at least under some conditions free hydroxyl radicals are not formed and that reaction (1) does not represent correctly the chemistry involved. It has therefore

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been proposed that complexes with higher oxidation states, possible forms of these include ML_m^{n+2}, $L_mM^n = 0$, $L_mM^n(H_2O_2)$ between which one cannot distinguish in many cases,[21] and not $\cdot OH$ radicals are formed in reaction (1). On the other hand other studies indicate that $\cdot OH$ free redicals are formed in the same reactions.[21,22] It has thus been pointed out that: "...different patterns of scavenger inhibition arise in the different assays because scavengers can react with intermediates in the detection reactions, all of which are multistep chains."[23]

In a recent study[14] it was shown that a thermodynamic analysis of the Fenton reaction and the "Fenton-like" reactions points out that their detailed mechanisms involve the formation of a transient complex between the low-valent cation, M^nL_m, and hydrogen peroxide of the type $M^nL_{m-1}O_2H^-$.

$$M_{aq}^{n+} + H_2O_2 \leftrightharpoons M^nO_2H^{(n-1)+} + H_3O^+ \tag{4}$$

This complex might decompse *via*:

$$M^nO_2H^{(n-1)+} + H_3O^+ \rightarrow M_{aq}^{(n+1)+} + \cdot OH + OH^- \text{ or} \tag{5a}$$

$$M^nO_2H^{(n-1)+} + RH + H_3O^+ \rightarrow M_{aq}^{(n+1)+} + \cdot R + OH^- \text{ or} \tag{5b}$$

$$M^nO_2H^{(n-1)+} + H_3O^+ \rightarrow M_{aq}^{(n+2)+} + 2OH^- \tag{5c}$$

Furthermore a new and simple assay for the detection of free hydroxyl radicals was developed. Using this assay it was shown that in slightly acidic solutions and in the presence of 0.1 M ethanol for $M_{aq}^{n+} = Cr_{aq}^{2+}$ $k_{5a} \gg k_{5b}$[ethanol] whereas for $M_{aq}^{n+} = Cu_{aq}^{+}$ $k_{5a} \ll k_{5b}$[ethanol].[14]

It seemed of interest to use this new assay on a system of current interest. It was decided to study the reaction of $Fe(II)\{N(CH_2CO_2)_3\}(H_2O)_2^-$ with H_2O_2 due to the following reasons:

1. This is a simple iron complex which is soluble in neutral solutions.
2. It has been previously[24] been shown that the reaction:

$$Fe(II)(N\{CH_2CO_2\}_3)(H_2O)_2^- + \cdot CH_3 \rightarrow (N\{CH_2CO_2\}_3)(H_2O)Fe(III)\text{-}CH_3^- \tag{6}$$

is relatively fast. It was therefore reasonable to expect that the analogous reactions with the free radicals $\cdot CH_2CR_1R_2OH$, $R_i = H$ or CH_3, are also fast. This is an essential condition, see below, for the assay used.

3. The complex $(Fe(III)\{N(CH_2CO_2)_3\}(H_2O)_2$ has been used in a variety of biological studies.[25–30] These studies indicate that the deleterious effects caused by this complex are due to the products of the reaction of $Fe(II)\{N(CH_2CO_2)_3\}(H_2O)_2^-$ with H_2O_2.

4. This complex is very similar to Fe(II)(edta) the reaction of which with H_2O_2 is currently extensively being used for the determination of the structure of DNA.[31,32]

The results indicate that also in this system the oxidation of alcohols, > 0.1 M, is not caused by the formation of free $\cdot OH$ radicals.

EXPERIMENTAL

All chemicals were of analytical grade and were used without further purification. All solutions were prepared with heat-distilled water which was further purified by passing through a Millipore setup, the final resistance being > 10 MΩ/cm. The N_2O was purified from traces of dioxygen by bubbling it through two washing bottles containing VSO_4 in dilute H_2SO_4 over Zn amalgam, followed by two washing bottles containing pure water. pH was adjusted by $HClO_4$ and/or NaOH.

Solutions containing the required concentrations of nta and alcohols were deaerated using the syringe technique. The required amount of solid $FeSO_4$ was added while bubbling N_2O. The pH was adjusted by gradual addition of deaerated NaOH or $HClO_4$ while bubbling through the syringe into which the pH electrode was immersed. Solutions containing Cr^{2+}_{aq} were prepared as described earlier.[14]

A part of the solution thus prepared was irradiated in a ^{60}Co γ source with a dose rate of 3000 rad/min. A second part of the solution was mixed with a deaerated solution of H_2O_2. The gaseous products were analyzed using a Varian 3700 Chromatograph, calibrated with all the necessary standards.

The concentration of the stock H_2O_2 was determined by titration with $KMnO_4$.

The specific rate of the reaction of $Fe(II)\{N(CH_2CO_2)_3\}(H_2O)_2^-$ with H_2O_2 was measured using an Aminco-Marrow stopped-flow spectrophotometer.

RESULTS

N_2O saturated solutions containing 0.2 M $(CH_3)_3COH$ 1.0×10^{-3} M $FeSO_4$ and 2.0×10^{-3} M $N(CH_2CO_2H)_3$ at pH 7.0 were irradiated and the yield of 2-methyl-propene was determined to be ⩾ 90% of the yield of $\cdot CH_2C(CH_3)_2OH$ formed by the radiation. Similar results were obtained when the alcohol was replaced by $(CH_3)_2CHOH$ and the yield of propene was measured.

N_2O saturated solutions containing a 1:1 mixture of $(CH_3)_3COH$ and of $(CH_3)_2CHOH$ at different concentrations and pH's and different concentrations of $FeSO_4$, $Fe_2(SO_4)_3$ and $N(CH_2CO_2H)_3$ were either irradiated in the ^{60}Co γ source or mixed with a deaerated solution of H_2O_2 and the relative yields of 2-methyl-propene and propene was determined. The results are summed up in Table I and Figure 1. The lowest alcohol concentration used was 0.175 M in order to avoid a competition between the reaction of $\cdot OH$ radicals with the alcohols with their reaction with nta.[36] Identical experiments with solutions which contained 1.0×10^{-3} M $Cr(H_2O)_6^{2+}$ instead of the iron salts and the nta were carried out. The ratio $[C_4H_8]/[C_3H_6]$ equals 1.70 ± 0.17 in the irradiated solutions and 1.78 ± 0.18 when H_2O_2 was added to the solutions.

The specific rate of reaction of $Fe(II)\{N(CH_2CO_2)_3\}(H_2O)_2^-$ with H_2O_2 increases with pH up to pH 3.8 where it reaches a plateau value of $(1.1 \pm 0.15) \times 10^4 M^{-1}s^{-1}$, $\Delta H^{\#} = 9.3 \pm 1.0$ Kcal/mol; $\Delta S^{\#} = -17 \pm 6$ e.u. These values are in reasonable agreement with the literature.[33,34]

DISCUSSION

The assay used

The assay used is based on the measurement of the relative yields of two free redicals of the type $\cdot CH_2CR_1R_2OH$, R_1 = H or CH_3, formed in solutions containing a 1:1 mixture of two alcohols of the type $CH_3CR_1R_2OH$. The advantage of this approach

TABLE I
The relative yields of 2-methyl-propene and propene

$^{2+}_{aq}$] × 10^3	$[Fe^{3+}_{aq}]$ × 10^3 M	[nta] × 10^3 M	$[ROH]_T^{(b)}$ M	$[H_2O_2]$ × 10^3 M	pH	$[C_4H_8]/[C_3H_6]$	
						Fenton	Radiat
	–	6.0	0.675	1.2	7.0	4.62	1.95
	–	6.0	0.675	1.2	7.0	4.28	2.01
	–	6.0	0.675	1.2	7.0	4.03	1.61
	–	6.0	0.675	1.2	7.0	4.31	1.87
	0.5	6.0	0.675	1.2	7.0	4.03	1.70
	1.0	6.0	0.675	1.2	7.0	4.23	1.72
	2.0	6.0	0.675	1.2	7.0	3.90	1.68
	–	6.0	0.675	0.6	7.0	4.01	
	–	6.0	0.675	2.4	7.0	4.48	
	–	6.0	0.675	4.8	7.0	4.60	
	–	4.0	0.675	1.2	7.0	4.03	1.86
	–	5.0	0.675	1.2	7.0	4.11	1.68
	–	10.0	0.675	1.2	7.0	3.91	1.80
	–	6.0	0.170	1.2	7.0	4.43	1.75
	–	6.0	0.338	1.2	7.0	4.29	1.85
	–	6.0	1.350	1.2	7.0	3.95	1.87
	–	6.0	0.170	1.2	4.3	2.85	
	–	6.0	0.338	1.2	4.3	2.95	
	–	6.0	0.675	1.2	4.3	2.95	1.72
	–	6.0	1.350	1.2	4.3	2.95	
	–	6.0	0.675	1.2	7.0	no products	
	–	6.0	0.675	1.2	4.0	no products	
	–	6.0	0.675	1.2	2.0	small yield of products.	

Accuracy ± 10%
Total alcohol concentration. $[(CH_3)_3COH]/[(CH_3)_2CHOH] = 1.0$
No H_2O_2

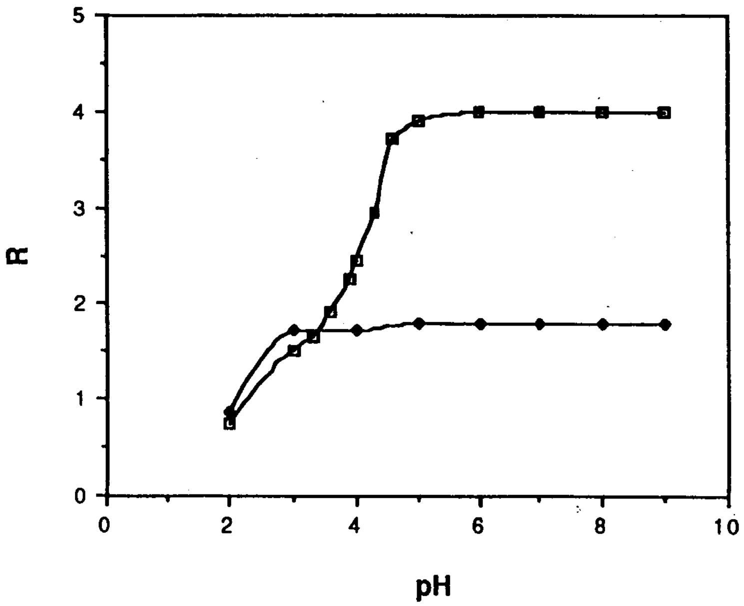

FIGURE 1 The relative yields of 2-methyl-propene and propene, R, as a function of pH. Solution composition: N_2O saturated, 1:1 mixture of $(CH_3)_3COH$ and of $(CH_3)_2CHOH$ total alcohol concentration 0.675 M, 1.0×10^3 M $FeSO_4$, and 6.0×10^{-3} M $N(CH_2CO_2H)_3$. Open squares: 1.2×10^{-3} M H_2O_2; Full squares: irradiated samples.

over that of measuring the relative yields of the radicals $\cdot CH_2CHR_1OH$ and $\cdot CR_1(CH_3)OH$ formed in a solution containing $CHR_1(CH_3)OH$ is due to the fact that the radicals $\cdot CH_2CR_1R_2OH$ have very similar chemical properties whereas the radicals $\cdot CH_2CHR_1OH$ and $\cdot CR_1(CH_3)OH$ differ considerably in their chemical properties. Therefore slight changes in the composition of the system during the reaction are not expected to affect the results in contrast to observations in assays based on the comparison of the yeilds of $\cdot CH_2CHR_1OH$ and $\cdot CR_1(CH_3)OH$.[3]

The standard used to calibrate the assay are $\cdot OH$ radicals formed in the radiolysis of aqueous solutions via the reactions.[35]

$$H_2O \xrightarrow{\gamma} e^-_{aq}\ (2.65),\ H\ (0.60),\ OH\ (2.65),\ H_2\ (0.45),\ H_2O_2\ (0.75) \qquad (7)$$

where the values in parenthesis give the relative yeilds of the primary products.[35] In N_2O saturated solutions the following reaction occurs:

$$e^-_{aq} + N_2O \rightarrow N_2 + \cdot OH + OH^- \qquad k = 8.7 \times 10^9 M^{-1}s^{-1}\,[36] \qquad (8)$$

Thus over 90% of the primary free radicals are transformed into $\cdot OH$ radicals, the rest being hydrogen atoms. In the present study the alcohols used were $CH(CH_3)_2OH$ and $C(CH_3)_3OH$ which react with $\cdot OH$ radicals via the reactions:

$$\cdot OH + CH(CH_3)_2OH \rightarrow \cdot C(CH_3)_2OH(85.5\%) + \cdot CH_2CH(CH_3)OH\ (13.3\%)$$

$$+ H_2O \qquad k = 2 \times 10^9 M^{-1}s^{-1}\,[36] \qquad (9)$$

$$\cdot OH + C(CH_3)_3OH \rightarrow \cdot CH_2C(CH_3)_2OH + H_2O$$

$$k = 4.2 \times 10^{8}\,\mathrm{M}^{-1}\mathrm{s}^{-1\,36} \tag{10}$$

The measurement of the relative yields of the radicals $\cdot CH_2C(CH_3)_2OH$ and $\cdot CH_2CH(CH_3)OH$ is performed via the reaction sequence:

$$\begin{aligned}&\cdot CH_2C(CH_3)_2OH/\cdot CH_2CH(CH_3)OH + M^{(n)}L_m \rightarrow L_{m-1}M^{(n+1)}\text{-}\\ &\qquad CH_2C(CH_3)_2OH/L_{m-1}M^{(n+1)}\text{-}CH_2CH(CH_3)OH + L\end{aligned} \tag{11}$$

followed by:

$$\begin{aligned}&L_{m-1}M^{(n+1)}\text{-}CH_2C(CH_3)_2OH/L_{m-1}M^{(n+1)}\text{-}CH_2CH(CH_3)OH + L \rightarrow\\ &\qquad M^{(n+1)}L_m + CH_2{=}C(CH_3)_2/CH_2{=}CHCH_3 + OH^-\end{aligned} \tag{12}$$

Where n and $(n + 1)$ are the formal oxidation states of the central cation and L are the non participating ligands. In the present study ($M^{(n)}L_m$ = $Fe(II)\{N(CH_2CO_2)_3\}(H_2O)_2^-$ or $Cr(H_2O)_6^{2+}$.

Equation (11) described the reaction of aliphatic free radicals with many low velent transition metal complexes[37] and especially with $Fe(II)\{N(CH_2CO_2)_3\}(H_2O)_2^-$ [23,38] or $Cr(H_2O)_6^{2+}$.[39] The β elimination step, reaction (12), is a relatively fast step in most systems studied.[39-43] The free radical $\cdot C(CH_3)_2OH$ oxidizes $Cr(H_2O)_6^{2+}$ to $Cr(H_2O)_6^{3+}$ [38] and reduces $Fe(III)\{N(CH_2CO_2)_3\}(H_2O)_2$ to $Fe(II)\{N(CH_2CO_2)_3\}(H_2O)_2^-$ [44], in none of these reactions is an olefin being formed. Thus the measurement of the relative yields of the olefins $CH_2{=}C(CH_3)_2$ and $CH_2{=}CHCH_3$ gives the relative yield of the free radicals $\cdot CH_2C(CH_3)_2OH$ and $\cdot CH_2CH(CH_3)OH$. Naturally it has to be shown that all the β free radicals react via reactions (11) and (12). Therefore the ratio of the olefins formed has to be independent of the concentrations of $M^{(n)}L_m$, $M^{(n+1)}L_m$, alcohols, the ligand L and the hydrogen peroxide added in the Fenton like reaction. The choice of the alcohols, which differ from those used in the earlier study,[14] is due to the easier analysis of the heavier olefins in the presence of N_2O.

The $Cr(H_2O)_6^{2+}$ system

The results clearly point out that the ratio of the yields of the two olefins, $[C_4H_8]/[C_3H_6]$, is the same for the irradiated samples and those to which H_2O_2 was added. This result, which corroborates the results obtained with other alcohols,[14] proves that even in the presence of >0.1 M alcohols the transient complex $(H_2O)_5Cr^{III}O_2H^+$ decomposes into $Cr(H_2O)_6^{3+} + \cdot OH$ prior to its reaction with the alcohols.The ratio also equals, within the experimental accuracy, the ratio of the yields of the corresponding free radicals calculated from the specific rates of reactions (9) and (10).

The $Fe(II)\{NCH_2CO_2)_3\}(H_2O)_2^-$ system

The ratio $[C_4H_8]/[C_3H_6]$ obtained in the irradiated samples, Table I, is equal, within the experimental accuracy, to that obtained in the chromous system. This result proves that indeed reactions (11) and (12) occur also in this system. This result is further corroborated by the observation that the absolute yields of the olefins in solutions containing only one alcohol equals to the calculated yield of the corresponding free radicals in these solutions. A different ratio is obtained at pH 2.0, Figure 1, but at this pH the yield of the olefins is very small, probably due to the fact that the concentration $(Fe(II)\{N(CH_2CO_2)_3\}(H_2O)_2^-$ is very small at this pH and the rate of the reaction of $Fe(H_2O)_6^{2+}$ with aliphatic free radicals is low.[45] Thus the results at pH 2.0 are meaningless as an assay for $\cdot OH$ radicals.

The results obtained when H_2O_2 is added to the solutions, Table 1 and Figure 1, clearly indicate that the ratio $[C_4H_8]/[C_3H_6]$ formed under these conditions differs considerably from that obtained in the irradiated solutions. Furthermore the results are independent of the concentrations of Fe_{aq}^{2+}, Fe_{aq}^{3+}, nta, H_2O_2 and the alcohols. These results indicate that the assay is indeed valid. Thus we have to conclude that at least in solutions containing > 0.17 M alcohols the major pathway to the oxidation of the alcohols in this system does not involve free $\cdot OH$ radicals.

In principle the ratio $[C_4H_8]/[C_3H_6]$ observed does not rule out participation of some free $\cdot OH$ radicals in the reaction sequence. If the alcohols are oxidized by a mixture of $\cdot OH$ radicals and another transient then the ratio of $[C_4H_8]/[C_3H_6]$ produced by the transient has to be higher than 4.2, the average of the experimental values in Table 1. The larger the contribution of free $\cdot OH$ radicals the larger this ratio has to be so that the weighed average of the ratios due to the two processes will give the experimental result. In principle two reaction schemes can be envisaged:

a. A competition between the reactions:

$$M^nO_2H^{(n-1)+} + H_3O^+ \rightarrow M_{aq}^{(n+1)+} + \cdot OH + OH^- \tag{5a}$$

$$M^nO_2H^{(n-1)+} + RH + H_3O^+ \rightarrow M_{aq}^{(n+1)+} + \cdot R + OH \tag{5b}$$

This scheme does not fit the results as it predicts that the observed ratio of $[C_4H_8]/[C_3H_6]$ will depend on the alcohol concentration, whereas the results clearly rule out such a dependence. The same conclusions hold for any other plausible competing reactions of an intermediate complex to form an $\cdot OH$ radical and the $\cdot R$ radicals, e.g. between reactions (13) and (14).

$$M_{aq}^{(n+2)+} + H_2O \rightarrow M_{aq}^{(n+1)+} + \cdot OH + H_3O^+ \tag{13}$$

$$M_{aq}^{(n+2)+} + RH + H_2O \rightarrow M_{aq}^{(n+1)+} + \cdot R + H_3O^+ \tag{14}$$

b. A competition between the reactions:

$$M^nO_2H^{(n-1)+} + H_3O^+ \rightarrow M_{aq}^{(n+1)+} + \cdot OH + OH^- \tag{5a}$$

$$M^nO_2H^{(n-1)+} + H_3O^+ \rightarrow M_{aq}^{(n+2)} + 2OH^- \tag{5c}$$

followed by reaction (14). This reaction sequence is in accord with the results if the ratio of the radicals $\cdot CH_2C(CH_3)_2OH$ and $\cdot CH_2CH(CH_3)OH$ formed in reaction (14) is considerably higher than that due to the competition between reactions (9) and (10). It should be stressed that the results do not indicate that reaction (5a) contributes to the reaction sequence but they also do not rule it out. The same conclusions hold for any other plausible competing reactions of an intermediate complex to form an $\cdot OH$ radical and another intermediate complex which then oxidizes the alcohols to the corresponding free radicals.

The pH dependence of the ratio $[C_4H_8]/[C_3H_6]$, Figure 1, might in principle be due to the following causes:

a. At the lower pH's the complex $Fe(II)\{N(CH_2CO_2)_3\}(H_2O)_2^-$ dissociates into $Fe(H_2O)_6^{2+}$ and nta, and not all the free radicals $\cdot R$ are scavenged by the remaining $Fe(II)\{N(CH_2CO_2)_3\}(H_2O)_2^-$ and the $Fe(H_2O)_6^{2+}$ formed. A calculation using the known pK_a's of nitrilotriacetic acid[46] and the stability constant of the complex $Fe(II)\{N(CH_2CO_2)_3\}(H_2O)_2^-$[46] indicates that 93.7%, 86.4%, 77.3%, 64.9%, 60.2%, 44.8%, 29.4% and 16.4% of the iron ions in the solution are present as $Fe(II)\{N(CH_2CO_2)_3\}(H_2O)_2^-$ at pH's 5.0, 4.6, 4.3, 4.0, 3.9, 3.6, 3.3 and 3.0 respectively. As the iron concentration in these experiments was 3×10^{-3}M and as 1×10^{-3}M $Fe(II)\{N(CH_2CO_2)_3\}(H_2O)_2^-$ is sufficient to scavenge all the free radicals $\cdot R$ clearly the observed effect is not due to this cause. This conclusion is corroborated by the observation that the pH has no effect on the results in the irradiated samples at $pH > 3.0$.

b. At the lower pH's the complex $Fe(II)\{N(CH_2CO_2)_3\}(H_2O)_2^-$ dissociates into $Fe(H_2O)_6^{2+}$ and the product of the reaction of the latter complex with H_2O_2 oxidizes the alcohols with a different selectivity. This mechanism can be ruled out as $Fe(H_2O)_6^{2+}$ reacts much slower than $Fe(II)\{N(CH_2CO_2)_3\}(H_2O)_2^-$ with H_2O_2 and therefore all the radicals formed above pH 3.0 are formed via reactions of the latter complex.

c. The intermediate complex formed has a pK_a in the pH range studied and the acidic form reacts relatively faster with $CH(CH_3)_2OH$ than with $C(CH_3)_3OH$. However if the two forms of the intermediate complex are in a fast equilibrium with each other one would expect that the results will depend on the alcohols concentrations in the pH range were the results change with pH, and this is not observed, Table 1. Thus this mechanism is ruled out.

d. The intermediate complex formed decomposes in two competing reactions into two other intermediates which then oxidize the alcohols. The specific rates of these two competing reactions depend on the pH and thus the nature of the final products depends on the pH. Two plausible such reactions could be:

$$M^nO_2H^{(n-1)+} + H_3O^+ \rightarrow M_{aq}^{(n+1)+} + \cdot OH + OH^- \qquad (5a)$$

$$M^nO_2H^{(n-1)+} + H_3O^+ \rightarrow M_{aq}^{(n+2)+} + 2OH^- \qquad (5c)$$

It should be pointed out, as above, that the results do not prove that these reactions occur, but they are a reasonable explanation of all the observed results.

CONCLUDING REMARKS

The results obtained in this study point out that the oxidation of alcohols at concentrations larger than 0.175 M by the reaction mixture of $Fe(II)\{N(CH_2CO_2)_3\}(H_2O)_2^-$ and H_2O_2 does not occur via free $\cdot OH$ radicals only. Some participation of these radicals can not be ruled out. The results do not enable to distinguish between the possibilities that the oxidizing agent is $Fe(II)\{N(CH_2CO_2)_3\}(H_2O)(O_2H)^-$ or $Fe(IV)\{N(CH_2CO_2)_3\}(H_2O)_2$, the latter complex is probably better described by $Fe(IV)\{N(CH_2CO_2)_3\}(H_2O)(O)^-$, as we have no indpendent information on the chemical properties of these complexes. However arguments raised support the idea that Fe(IV) complexes are formed in the reaction sequence.

These results thus point out that deleterious processes in biological processes which are attributed to the formation of free $\cdot OH$ radicals via "Fenton like" reactions might occur via other intermediates which are formed via single electron oxidizing agents.

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