Pulse-radiolytic Investigation of the Oxidation of Iron(II) and Iron(III) Complexes with 2,2′-Bipyridine

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The absorption spectra and decay kinetics of intermediates formed by the reaction of tris(2,2′-bipyridine) complexes of Fe^{II} and Fe^{III} with H atoms and OH radicals have been studied in aqueous solution using the pulse radiolysis technique. The product of the oxidation of $[Fe(bipy)_3]^{2+}$ with H atoms in acid solution is an $[Fe(bipy)_3H]^{2+}$ hydride intermediate which decomposes to give hydrogen and $[Fe(bipy)_3]^{3+}$. Intermediates formed by addition of OH to $[Fe(bipy)_3]^{2+}$ have complex kinetics probably indicating that a mixture of isomers is formed in the process. These OH adducts do not oxidize water to oxygen even in the presence of a catalyst such as colloidal RuO_2, Mn^{2+}, Co^{2+}, or Ni^{2+}. The OH adduct of $[Fe(bipy)_3]^{3+}$ also does not react with water to produce oxygen. Oxygen can be produced in stoicheiometric amounts by reaction of Br_2^- with $[Fe(bipy)_3]^{2+}$ catalyzed with RuO_2. The absorption spectra of OH adducts of $[Fe(bipy)_3]^{3+}$ and the kinetics of their reactions are reported and discussed.

The hydroxyl radical is a strong oxidizing agent [$E^\ominus(OH/OH^-) = 1.9$ V] and reacts with many metal complexes. In pulse radiolysis experiments.[1,2] it has been found that $[Ru(bipy)_3]^{2+}$ and $[Fe(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine) react very fast with the hydroxyl radical [equation (1)], and form

$$[M(bipy)_3]^{2+} + OH \longrightarrow [M(bipy)_3(OH)]^{2+} \quad (1)$$

intermediates which have absorption spectra between 650 and 800 nm.

In this work, pulse radiolysis was applied in the study of the kinetics and mechanism of the reaction of $[Fe(bipy)_3]^{2+}$ and $[Fe(bipy)_3]^{3+}$ with OH radicals and H atoms. The oxidation of $[Fe(bipy)_3]^{2+}$ to $[Fe(bipy)_3]^{3+}$ with Br_2^- was also observed. These studies are also expected to give more information about the reaction in which oxygen is produced from water since it is known that several strong oxidants such as Ru^{III}, Fe^{III}, and Os^{III} complexes with 2,2′-bipyridine or 1,10-phenanthroline are capable in the absence of light of oxidizing water to oxygen.[1–7] In addition, some steady-state γ-radiolysis studies were carried out in order to characterize the properties of the intermediate species formed in the $[Fe(bipy)_3]^{3+}$ reduction in aqueous solution.

Experimental

Materials.—The complexes $[Fe(bipy)_3]^{2+}$ and $[Fe(bipy)_3]^{3+}$ were synthesized as perchlorate salts according to literature procedures.[8] The solution pH was adjusted with H_2SO_4, NaOH, or phosphate buffers. The two types of RuO_2 catalysts used in this study were $RuO_2{\cdot}xH_2O$, a powder supplied from Alfa Inorganics and RuO_2 solution prepared according to a procedure described elsewhere.[6] Solutions were prepared from analytical grade chemicals (B.D.H. or Merck). Triply distilled water was used throughout.

Procedure.—The concentrations of $[Fe(bipy)_3]^{2+}$ were determined spectrophotometrically ($\varepsilon_{522} = 8\,650$ dm^3 mol^{-1} cm^{-1}). For hydrogen detection a Perkin-Elmer 154L gas chromatography instrument with a column of silica gel at 50 °C was used and for oxygen a molecular sieve column and a helium gas carrier.

Pulse radiolysis employed a Febetron 707 (Field Emission Corp.) electron accelerator with a pulse duration of 20 ns, the operating conditions being similar to those described previously.[9] The total light path through the cell was 5.1 cm. The absorbed doses were in the range 5—50 Gy per pulse measured by using a potassium hexacyanoferrate(III) dosimeter and taking $\varepsilon_{420}[Fe(CN)_6]^{3-}$ as 1 000 dm^3 mol^{-1} cm^{-1} and $G\{[Fe(CN)_6]^{3-}\} = 5.6$.[10]

Steady-state irradiations were performed with a ^{60}Co γ-source. The total absorbed doses were in the range 50—500 Gy and the dose rate was 100 Gy min^{-1}. The measurements were made at 20 ± 1 °C.

Results and Discussion

Oxidation of $[Fe(bipy)_3]^{2+}$ *with* OH *Radicals and* H *Atoms.*—An aqueous solution of $[Fe(bipy)_3]^{2+}$ is expected to undergo the following reactions after the pulse in the presence of N_2O [equations (2)—(4)].

$$H_2O \rightsquigarrow e^-(aq), H, OH, H_2O_2, H_2, H_3O^+, OH^- \quad (2)$$

$$e^-(aq) + N_2O \xrightarrow{H_2O} N_2 + OH + OH^- \quad (3)$$

$$OH + [Fe(bipy)_3]^{2+} \longrightarrow [Fe(bipy)_2(bipy\text{-}OH)]^{2+} \quad (4)$$

About 90% of the total primary radicals should react with $[Fe(bipy)_2]^{2+}$ to produce the OH adduct of $[Fe(bipy)_3]^{2+}$. Reaction (4) is very fast and we found $k_4 = 9 \times 10^9$ dm^3 mol^{-1} s^{-1}, following bleaching of the absorbance from 450 to 550 nm, for different $[Fe(bipy)_3]^{2+}$ concentrations (4×10^{-5}—5×10^{-5} mol dm^{-3}) for 8 Gy absorbed dose per pulse.

In this reaction outer-sphere electron transfer does not take place since bipy shows high reactivity towards the OH radical ($k_{OH+bipy} = 5.2 \times 10^9$ dm^3 mol^{-1} s^{-1} [11]). The OH is added to bipy to form a co-ordinate ligand radical. Electrophilic addition of a hydroxyl radical to $[Fe(bipy)_3]^{2+}$ should occur preferentially at the 4- and 6-positions of bipy.[12] The absorption spectrum and kinetics of the OH adduct has been observed previously in the 650—800 nm region and it has been found that the intermediate decays by a second-order process.[1] Absorption spectra obtained 15 μs after the pulse in the visible wavelength region are presented in Figure 1. The

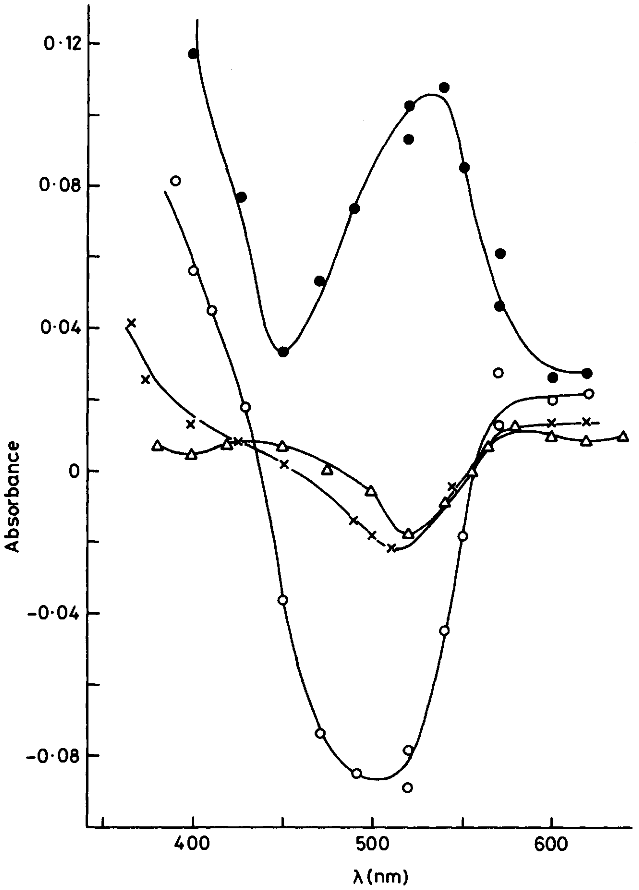

Figure 1. Absorption spectra of intermediates formed in aqueous $[Fe(bipy)_3]^{2+}$ solutions. N_2O-saturated solution of 1×10^{-5} mol dm^{-3} $[Fe(bipy)_3]^{2+}$, pH 7, measured at: 15 μs (○), 1 ms (×), and 500 ms (△) after pulse. Absorbed dose 10 Gy. (●) Spectrum 15 μs after pulse corrected for decreasing concentration of $[Fe(bipy)_3]^{2+}$ ($G = 5.4$) present initially in the solution

negative absorption is due to the decreased concentration of $[Fe(bipy)_3]^{2+}$ present initially in the solution. The spectrum corrected for the decreasing of the $[Fe(bipy)_3]^{2+}$ absorption is also presented. We were not able to compare the spectrum of the OH adduct of $[Fe(bipy)_3]^{2+}$ with that of the OH adduct to free bipy, since our detection system does not allow observation below 380 nm in $[Fe(bipy)_3]^{2+}$ solution where free bipy intermediates have maxima at 365 and 305 nm.[13]

It should be noted that the decay of the intermediate is not the same for all the wavelengths observed. The intermediate decay at 700—800 nm follows a second-order rate law.[1] At 520 nm the decay does not fit first or second order while at 400 nm the decay is clean first order with $k = (1.35 \pm 0.1) \times 10^3$ s^{-1} independent of initial radical concentration. Our kinetic data show that at least two isomeric intermediates are formed by addition of OH radical to the bipy complex of Fe^{II}. All rate constant data are summarized in the Table.

In N_2O-saturated $[Fe(bipy)_3]^{2+}$ at pH 7 we could not obtain oxygen formation by γ-radiolysis. The $[Fe(bipy)_3(OH)]^{2+}$ intermediates are not able to oxidize water to oxygen even in the presence of catalysts[5,6] such as colloidal RuO_2, Mn^{2+}, Ni^{2+}, Co^{2+}, and Fe^{3+}. The complex $[Fe(bipy)_3]^{2+}$ irreversibly decomposes in reaction with OH adduct. Some stable products with different absorption spectra between 400 and 350 nm are formed in this reaction. Absorption spectra of stable products after irradiation are presented in Figure 2 together with the spectra of $[Fe(bipy)_3]^{2+}$ and $[Fe(bipy)_3]^{3+}$. The spectra are not corrected for depletion of starting absorption. The complex $[Fe(bipy)_3]^{2+}$ reacts very fast with H atoms. Under the strongly acidic conditions (pH 1) hydrated electrons are rapidly converted into H atoms [equation (5)], therefore only H and OH

$$e^-(aq) + H^+ \longrightarrow H + H_2O \qquad (5)$$

radicals were considered as primary species in the radiolysis of the acidic solutions. In γ-irradiated solutions of $[Fe(bipy)_3]^{2+}$ (1×10^{-4} mol dm^{-3}) at pH 1 the value $G(H_2) = 3.0$ was obtained with 300 Gy at a dose rate of 100 Gy min^{-1}. The high yield of hydrogen is in agreement with the oxidation of $[Fe(bipy)_3]^{2+}$ to $[Fe(bipy)_3]^{3+}$ according to equations (6) and (7).

$$H + [Fe(bipy)_3]^{2+} \longrightarrow [Fe^{3+}(bipy)_3H^-] \qquad (6)$$

$$[Fe^{3+}(bipy)_3H^-] + H^+ \longrightarrow H_2 + [Fe(bipy)_3]^{3+} \qquad (7)$$

The hydrogen atom acts as an oxidizing agent and being itself converted to molecular hydrogen. In this reaction, a hydrido complex[14,15] is probably formed which reacts with oxonium ions by elimination of H^-.

Our results show that oxidation of $[Fe(bipy)_3]^{2+}$ with H atoms in the presence of catalyst can lead to formation of H_2 [equation (7)] and oxygen [equation (8)]. Oxygen was detected when an irradiated solution was neutralized in an argon atmosphere and then brought in contact with RuO_2 powder. Oxygen is formed according to equation (8). We found that

$$[Fe(bipy)_3]^{3+} + OH^- \xrightarrow[\text{catalyst}]{} [Fe(bipy)_3]^{2+} + \tfrac{1}{4}O_2 + \tfrac{1}{2}H_2O \qquad (8)$$

reaction (8) can be catalysed by RuO_2, TiO_2, or MnO_2. It is known[6] that the oxygen yield depends strongly on the pH, reaching a maximum between pH 7 and 8 where it corresponds to the stoicheiometry of the reaction (8).

Table. Rate constants of the radicals produced on pulse radiolysis of aqueous solutions of iron(II) and iron(III) complexes with bipy

Reaction	Rate constant (dm^3 mol^{-1} s^{-1})	pH	Radical formed		
			Type	λ (nm)	Decay rate
$OH + [Fe(bipy)_3]^{2+}$	9×10^9	7	$[Fe(bipy)_3(OH)]^{2+}$	650—800	5×10^7 dm^3 mol^{-1} s^{-1} [a]
		7		400	1.3×10^3 s^{-1}
$Br_2^- + [Fe(bipy)_3]^{2+}$	1×10^8	7			
$OH + [Fe(bipy)_3]^{3+}$	$>1 \times 10^{10}$	3	$[Fe(bipy)_3(OH)]^{3+}$	400	8.6×10^2 s^{-1}
$H + [Fe(bipy)_3]^{3+}$	2.2×10^9 [b]	3	$[Fe(bipy)_3H]^{3+}$	400	6×10^4 s^{-1}

[a] Taken from ref. 1. [b] Taken from G. Navon and G. Stein, *J. Phys. Chem.*, 1966, **70**, 3630 (at pH = 1).

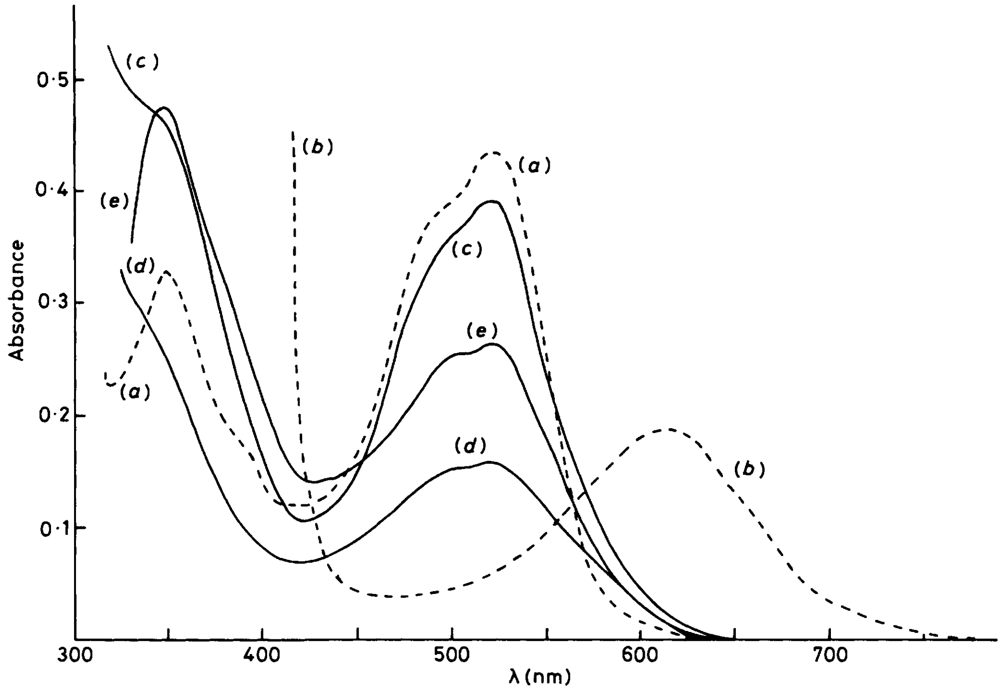

Figure 2. Absorption spectra of the stable products obtained in aqueous solutions (1 cm cell): (*a*) 5 × 10^{-5} mol dm^{-3} $[Fe(bipy)_3]^{2+}$ (pH 7) in the absence of irradiation (— — —), (*b*) 5 × 10^{-4} mol dm^{-3} $[Fe(bipy)_3]^{3+}$ (pH 0) in the absence of irradiation (— — —) (ε_{610} = 380 dm^3 mol^{-1} cm^{-1}), (*c*) after irradiation of 5 × 10^{-5} mol dm^{-3} $[Fe(bipy)_3]^{2+}$ with 70 Gy absorbed dose at pH 7, (*d*) after irradiation of 5 × 10^{-5} mol dm^{-3} $[Fe(bipy)_3]^{3+}$ with 70 Gy absorbed dose at pH 3 and correction for $[Fe(bipy)_3]^{2+}$ concentration present initially in solution, and (*e*) after irradiation of the same solution as in (*d*) with alkali added to pH 13

Oxidation of $[Fe(bipy)_3]^{3+}$.—Oxidation of $[Fe(bipy)_3]^{3+}$ with OH radicals was observed in solutions at pH 3 in the presence of 1 mol dm^{-3} Na_2SO_4. The $[Fe(bipy)_3]^{3+}$ is not a thermally stable complex and it also slowly dimerises even in neutral or acid solution with formation of $[Fe_2(bipy)_4(OH)_2]^{4+}$ or $[Fe_2O(bipy)_4]^{4+}$ dimers.[5,16,17] We used fresh solutions prepared before irradiation. However, in experiments with $[Fe(bipy)_3]^{3+}$ reactions with dimers are not excluded. In these solutions *ca.* 10% of $[Fe(bipy)_3]^{3+}$ was spontaneously reduced to $[Fe(bipy)_3]^{2+}$ in the absence of irradiation. This spontaneous reduction does not lead to the formation of molecular oxygen. The rate of reduction increased with increasing pH, and O_2 can be observed for pH > 9.[6] Oxidation of $[Fe(bipy)_3]^{3+}$ by OH [equation (9)] is very fast and $k_9 > 1 \times 10^{10}$ dm^3 mol^{-1} s^{-1}

$$[Fe(bipy)_3]^{3+} + OH \longrightarrow [Fe(bipy)_3(OH)]^{3+} \quad (9)$$

was determined from transient absorbance formation in 1 × 10^{-4} mol dm^{-3} $[Fe(bipy)_3]^{3+}$ at pH 3. The rate constant is approximately the same as that for the reaction of $[Fe(bipy)_3]^{2+}$ with OH [equation (4)]. In N_2O-saturated solution the reaction (9) is dominant and to a small extent equation (10) takes place.

$$[Fe(bipy)_3]^{3+} + H \longrightarrow [Fe(bipy)_3H]^{3+} \longrightarrow H^+ + [Fe(bipy)_3]^{2+} \quad (10)$$

This reaction was observed in a solution of $[Fe(bipy)_3]^{3+}$ (1 × 10^{-4} mol dm^{-3}) containing Bu^{t}OH (0.5 mol dm^{-3}), alcohol being added to scavenge OH radicals. The reaction is not a simple electron transfer and we found that the transient is formed [Figure 3(*b*)] which decays with first-order kinetics ($k = 6 \times 10^4$ s^{-1}). We assumed that the Bu^{t}OH radical produced does not influence decay rates. We corrected the observed absorption in N_2O-saturated solution for the contribution of $[Fe(bipy)_3H]^{3+}$ [Figure 3(*b*)] using G(H) = 0.6 and for the same absorbed dose the $[Fe(bipy)_3H]^{3+}$ concentration was calculated. The spectrum of the OH adduct is given by the full line in Figure 3(*a*). The absorption of the OH adduct changes with time. It should be noted that there is bleaching of the absorption after 20 μs in the wavelength region 450—580 nm where $[Fe(bipy)_3]^{2+}$ absorbs. This means that $[Fe(bipy)_3]^{2+}$ reacts with the $[Fe(bipy)_3(OH)]^{3+}$ intermediate and $G\{-[Fe(bipy)_3]^{2+}\} \sim 1$ was found. However, since the transient absorption up to 500 nm is very weak, the procedure in this study does not permit an unequivocal identification of the secondary intermediates and observation of their kinetics. The decay of the OH adduct observed at 400 nm followed a first-order rate law with $k = 8.6 \times 10^{-2}$ s^{-1}.

It is worth noting that the increase of the absorption with a maximum of 520 nm takes place at times longer than 10 s. However, because of the smallness of transient absorbance [Figure 3(*a*)] and instability of the analytical light source on the time scale of minutes, a systematic study of $[Fe(bipy)_3]^{2+}$ formation was impractical by pulse radiolysis. We obtained by γ-radiolysis an increase of absorption with a maximum at 520 nm which could correspond to $[Fe(bipy)_3]^{2+}$ formation. However, we were not able to be certain that this was a $[Fe(bipy)_3]^{2+}$ absorption since the spectrum obtained after irradiation (Figure 2) below 400 nm differs from that of $[Fe(bipy)_3]^{2+}$ indicating formation of some other stable products. Addition of alkali after irradiation to solution at pH 3 shows that initial $[Fe(bipy)_3]^{3+}$ irreversibly decomposes during irradiation by reaction with OH radicals. The same results were found when RuO_2 was added after irradiation in neutral solutions.

Formation of Molecular Oxygen.—We expected that one or all isomers of the OH adducts may react with OH^- in a two-

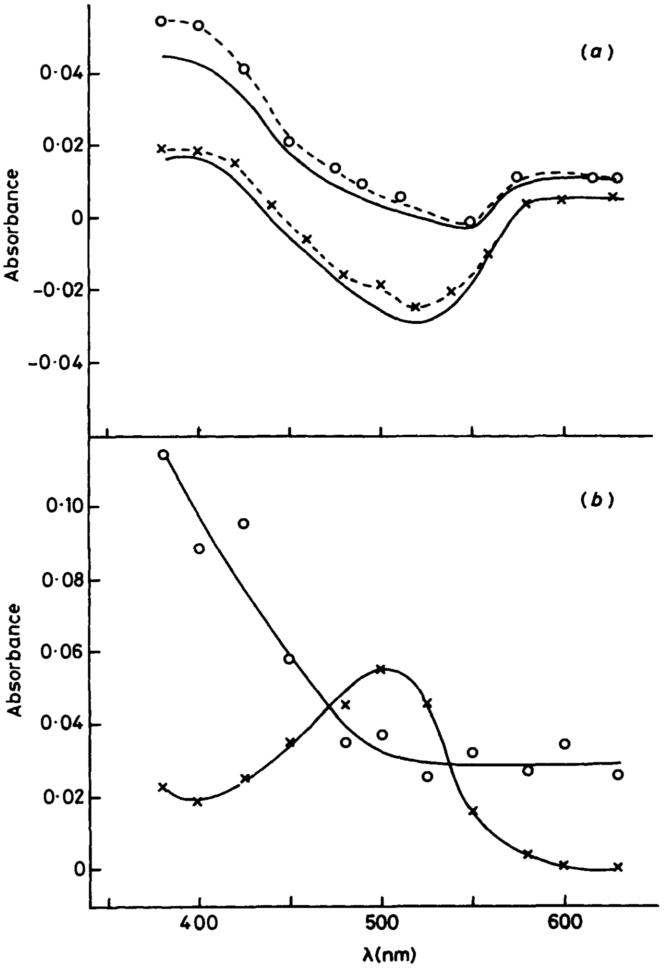

Figure 3. Absorption spectra of intermediates formed in aqueous $[Fe(bipy)_3]^{3+}$ solution. (*a*) N_2O-saturated solution of 1×10^{-4} mol dm^{-3} $[Fe(bipy)_3]^{3+}$, pH 3 measured at 15 μs (○) and 1 ms (×) after pulse. The full line represents the spectrum after corrections for $[Fe(bipy)H]^{3+}$ ($G = 0.6$) absorption. Absorbed dose 10 Gy. (*b*) Ar-saturated solution of 1×10^{-4} mol dm^{-3} $[Fe(biby)_3]^{3+}$ and 0.5 mol dm^{-3} Bu^tOH, pH 3 measured at 15 μs (○) and 1 ms (×) after pulse. Absorbed dose 25 Gy

electron process resulting in the formation of H_2O_2. The same equations (11) and (12) have been proposed for the oxidation

$$[Fe(bipy)_3(OH)]^{3+} + OH^- \longrightarrow [Fe(bipy)_3]^{2+} + H_2O_2 \quad (11)$$

$$H_2O_2 + 2[Fe(bipy)_3]^{3+} + 2OH^- \longrightarrow O_2 + 2\,[Fe(bipy)_3]^{2+} + 2H_2O \quad (12)$$

of water by $[Fe(bipy)_3]^{3+}$ in alkaline solutions.[1-4] We found the total product yield, $G(O_2) = 0.4 \pm 0.1$ in solution at pH 3 and 7 which corresponds to O_2 formation in reaction of primary radiolytic H_2O_2 with $[Fe(bipy)_3]^{3+}$ [equation (12)], $G(O_2) = \frac{1}{2}G_{H_2O_2} = 0.35$. If the reactions (8), (11), and (12) take place, then $G(O_2)$ should be $\frac{1}{2}G_{H_2O_2}{}^{+}\ \frac{1}{4}[G_{e^-(aq)} + G_{OH}] \sim 3$, where $G_{subscript}$ is the primary product yield. Our results show that the oxygen yield is 10 times lower. Since formation of $[Fe(bipy)_3]^{2+}$ is much higher than O_2 it seems that reduction to $[Fe(bipy)_3]^{2+}$ goes without formation of O_2. Most likely, decomposition of $[Fe(bipy)_3(OH)]^{3+}$ culminates in degradation of the ligand with no net water oxidation.

We compared oxygen yield obtained with oxygen formation in the reaction of Br_2^- ions with $[Fe(bipy)_3]^{2+}$ where $[Fe(bipy)_3]^{3+}$ is formed and reacts with water in the presence of catalyst. In an γ-irradiated solution of Br^- (0.1 mol dm^{-3}) and $[Fe(bipy)_3]^{2+}$ (1×10^{-4} mol dm^{-3}) saturated with N_2O in the presence of RuO_2 (3 mg powder in 10 cm^3 solution) at pH 7 the evolution of O_2 was observed with $G(O_2) = 2$. This oxygen yield is in good agreement with the value calculated when the following reactions [equations (13) and (14)] occur, and

$$Br_2^- + [Fe(bipy)_3]^{2+} \longrightarrow [Fe(bipy)_3]^{3+} + 2Br^- \quad (13)$$

$$4[Fe(bipy)_3]^{3+} + 2H_2O \xrightarrow{RuO_2} 4[Fe(bipy)_3]^{2+} + O_2 + 4H^+ \quad (14)$$

$G(O_2) = \frac{1}{2}G_{H_2O} + \frac{1}{4}[G_{OH} + G_{e^-(aq)} + G_H] = 1.9$. In the same solution in the absence of $[Fe(bipy)_3]^{2+}$ $G(O_2) = 0.3$ was obtained.

Our results show that OH adducts of $[Fe(bipy)_3]^{3+}$ do not oxidize water to oxygen. We have no evidence on whether RuO_2 or some other catalysts can mediate in the reaction of $[Fe(bipy)_3(OH)]^{3+}$ with water since in these experiments $[Fe(bipy)_3]^{3+}$ present in solution as initial reactant could also oxidize water.

The OH radicals react very fast with $[Fe(bipy)_3]^{2+}$ and form intermediates which have spectra very different from that of $[Fe(bipy)_3]^{3+}$; they do not react by a simple charge-transfer mechanism and OH is added to bipy. The complex $[Fe(bipy)_3]^{2+}$ behaves very similarly to tris(1,10-phenanthroline)iron(II) which also reacts very fast with OH and forms intermediates by addition of OH to the ligand.[2,18,19] According to our results, isomeric intermediates are produced by reaction of OH radicals which irreversibly decompose most probably by degradation of the ligand. None of these intermediates oxidizes water to oxygen in neutral and acid solution. The OH reacts with $[Fe(bipy)_3]^{3+}$ and forms isomers, although this study is more complex since $[Fe(bipy)_3]^{3+}$ is not a thermally stable complex and has a tendency to dimerize.

The complex $[Fe(bipy)_3]^{2+}$ can be oxidized to $[Fe(bipy)_3]^{3+}$ with H atoms and Br_2^-. Hydrogen atoms in acid solution probably produce $[Fe(bipy)_3H]^{2+}$, a hydride intermediate which gives hydrogen and $[Fe(bipy)_3]^{3+}$. Oxygen production can be observed in irradiated solutions of Br^- and $[Fe(bipy)_3]^{2+}$ at pH 7 where the oxygen yield reaches stoicheiometric proportions.

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Received 31*st December* 1981; *Paper* 1/2010