Dissociation and Dioxygen Formation in Hydroxide Solutions of Tris(2,2′-bipyridyl)iron(III) and Tris(1,10-phenanthroline)iron(III): Rates and Stoichiometry

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Abstract: The fast redox reactions of the title Fe(III) complexes in basic solutions give the Fe(II) complexes and coordinated ligand *N*-oxide as primary products. Further reactions by parallel paths include dissociation to give the free ligand *N*-oxide and catalysis by hydroxy Fe(III) complexes leading to dioxygen. No O_2 is produced when dissociation of tris(2,2′-bipyridyl)iron(III) is suppressed by addition of excess ligand; the dependence of the O_2 yield on the degree of dissociation of this complex can be reproduced by using the rate constants for the parallel catalyzed and uncatalyzed decay of the first product.

The reduction of the mild one electron oxidants tris(1,10-phenanthroline)iron(III) and tris(2,2′-bipyridyl)iron(III) by hydroxide ion[2] gives the relatively long lived tris Fe(II) complexes and has long been of interest because it is fast and because dioxygen is one of the products.[3,4] Preliminary measurements of the O_2 yield suggests that this was a function both of the concentration of the complex and of the hydroxide concentration, and we report here the results of a further study of the stoichiometry of these reactions under conditions (complex, 2×10^{-3} to 1×10^{-5} M; OH^-, 0.2 to 5×10^{-5} M) where stopped-flow studies have shown that the rate of formation of $Fe(bpy)_3^{2+}$ and of $Fe(phen)_3^{2+}$ is first order both in Fe(III) complex and in OH^-.[3]

When the present work was initiated it was already known that $Fe(phen)_3^{3+}$ reacts much faster than $Fe(bpy)_3^{3+}$ and produces much less O_2. In both cases the O_2 yield is less than the yield of the tris Fe(II) complexes and no HO_2^- could be detected so that an oxidized ligand product is required. The reductions are too fast for outer-sphere charge transfer giving hydroxyl radicals, and it has been suggested[3,4] that the rate-determining step is addition of OH^- to a *carbon* atom of the ligand. However, it has also been pointed out[5] that a C–O bond, once formed, would be expected to persist in an oxidized ligand product so that such an intermediate is unlikely to produce dioxygen. We have now found and recently briefly reported[6] that $Fe(bpy)_3^{3+}$ and $Fe(phen)_3^{3+}$ are always significantly dissociated in solution and that it is the hydroxo complexes which form dioxygen. We report here the experimental work on which this conclusion was based together with that which leads us to conclude that ligand attack does occur during the rate-determining reduction but at a *nitrogen* atom of the diimine ligand.

The rate law for the Fe(III) systems also holds for $Os(bpy)_3^{3+}$, $Os(phen)_3^{3+}$, and $Ru(bpy)_3^{3+}$,[3,4] and for all three metals an intermediate, which absorbs at longer wavelengths than the tris divalent complexes, has been detected during the reduction.[4] Subsequent steps are however different. Thus, although the rates of reduction of the Os(III) complexes parallel those of the Fe(III) complexes, both with change of ligand (phen for bpy) and also with methyl substitution of the ligands,[3] no O_2 is produced and the rate-determining reduction is followed by oxidation both of the ligand and of the metal center.[7] The O_2 yield for the $Ru(bpy)_3^{3+}/OH^-$ system is very small when the kinetics are simple.[4]

Table I. Dissociation of $Fe(bpy)_3^{3+}$ in Acid Media 22 ± 1 °C

medium	$10^5 k_{d_3}$, s^{-1}
0.03 M HCl	8.0 ± 0.4[a]
0.0003 M HCl	45.8 ± 0.2[b]
0.03 M HCl + 0.002 M bpyHCl	8 ± 1[c]
0.10 M HCl	7.2 ± 0.3
0.03 M $HClO_4$	3.0
0.02 M H_2SO_4	8.1[d]
water	48 ± 1[b]

[a] $10^5 k_{d_3}$ for $Fe(phen)_3^{3+}$ in 0.03 M HCl is 4.6 s^{-1}. The products are Fe^{3+}, bpy, and $Fe(bpy)_3^{2+}$ (<2%). [b] The products also include the dimer $(H_2O(bpy)_2Fe)_2O^{4+}$. [c] Initial rate. [d] From ref 8.

The significantly greater lability of the Fe(III) and Fe(II) tris complexes over those of Ru and Os means that the overall reaction

$$Fe(bpy)_3^{3+} \xrightarrow{OH^-} Fe(bpy)_3^{2+} + \text{other products including } O_2$$

and the analogous reaction for $Fe(phen)_3^{3+}$ are complicated by dissociation and polymerization. We have chiefly studied $Fe(bpy)_3^{3+}$ because our interest in these systems was the mechanism of dioxygen formation and have found that it is possible to use $Fe(bpy)_3^{3+}$ and OH^- concentrations where the system is simplified in that successive reaction sequences effectively do not overlap and reduction is faster than both dissociation and polymerization. We use the data obtained under these conditions in an attempt to correlate the rates and stoichiometries at other concentrations.

Results

Dioxygen Yields from $Fe(bpy)_3^{3+}$. The O_2 produced on adding base to acid solutions of $Fe(bpy)_3^{3+}$ was found to be not only a function of the concentrations of complex and OH^- but also of the age of the acid solutions and the concentration and type of anion. The effect of changing complex concentration and of "aging" the reactant in 0.03 M HCl before addition of an equal volume of NaOH to $[OH^-] = 0.10$ M is illustrated for the most dilute and the most concentrated solutions in Figure 1.

The composition of the acid reactant solutions changes with time due to the first-order dissociation of $Fe(bpy)_3^{3+}$ and this is anion dependent (see Table I). Parallel reduction in these solutions is small; a correction for this was, however, significant in the most dissociated solutions when the $Fe(bpy)_3^{2+}$ yield of the reduction in base was calculated and is further discussed below. In Figure 2 the O_2 yield in 0.10 M OH^- is shown as a function of the degree of dissociation of the complex in different media.

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[2] 2,2′-Bipyridine and 1,10-phenanthroline are referred to as bpy and phen. The ligand *N*-oxides are referred to as bpyO and phenO.

[3] (a) G. Nord and O. Wernberg, *J. Chem. Soc., Dalton Trans.*, 866 (1972), and references therein; (b) G. Nord and O. Wernberg, *ibid.*, 845 (1975).

[4] C. Creutz and N. Sutin, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 2858 (1975).

[5] V. Ya. Shafirovich, A. P. Moravskii, T. S. *Dzhabiev*, and A. E. Shilov, *Kinet. Catal.* (*Engl. Transl.*), **18**, 427 (1977).

[6] B. Pedersen and G. Nord, Proceedings XXI Int. ICCC, Toulouse, France, p 198 (1980).

[7] B. Pedersen, Ph.D. Thesis, University of Copenhagen, in press (in English).

[8] F. Pantani and G. Ciantelli, *J. Electroanal. Chem.*, **14**, 423 (1967).

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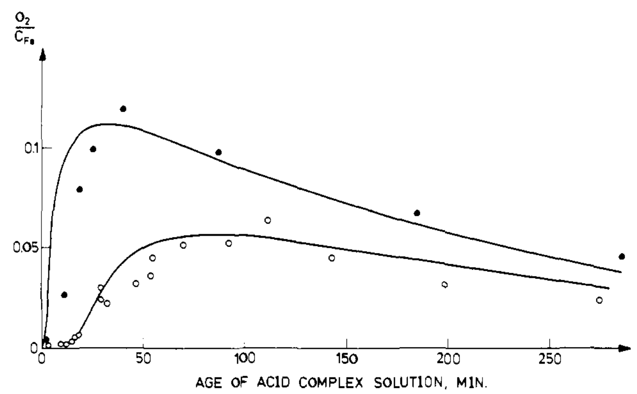

Figure 1. Variation of O_2 product concentration with the time for which solutions of $Fe(bpy)_3(ClO_4)_3$ in 0.03 M HCl were allowed to stand under He in the dark before addition of NaOH to give $[OH^-] = 0.10$ M and the complex concentrations c_{Fe}: (a) ● = 1×10^{-3} M; (b) ○ = 1×10^{-4} M. The full curves were calculated from eq 1 and 2 (see text).

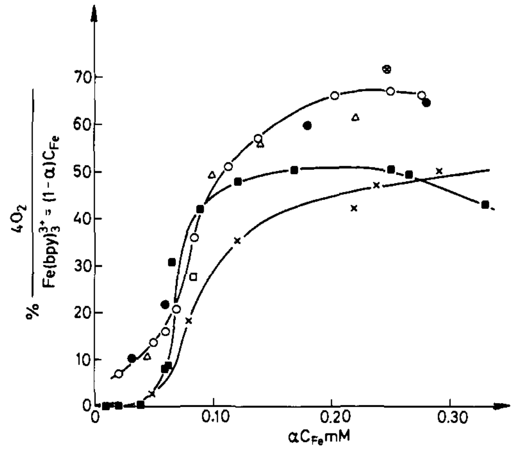

Figure 2. Illustration of change in O_2 yield with change in degree of dissociation (α) of $Fe(bpy)_3^{3+}$ in the acid solutions: (○) 0.03 M HCl, (⊗) 0.1 M HCl, (△) 0.02 M H_2SO_48 (■) 0.03 M HCl containing 0.02 M bpy, (□) 0.03 M HCl but 0.02 M bpy added with base, × 0.03 M $HClO_4$; $[OH^-] = 0.10$ M, $c_{Fe} = 1 \times 10^{-3}$ M.

The medium effect on the O_2 yield on changing HCl for H_2SO_4 is eliminated when solutions with the same degree of dissociation are compared, but $HClO_4$ solutions of $Fe(bpy)_3^{3+}$ dissociate more slowly and also produce less O_2 in base. The presence of dimers in the very dilute HCl solutions has no detectable effect in the O_2 yield. The presence of excess bpy eliminates O_2 formation at low degrees of dissociation of $Fe(bpy)_3^{3+}$. We also find that no O_2 is produced when the solid complex salt was dissolved directly on 0.10 M NaOH. The O_2 yield in more dilute OH^- solutions (0.01–0.001 M) was much greater than that calculated from the composition of the acid reactant together with the corresponding yield in 0.10 M NaOH. This increase is correlated in Table II with the extra dissociation of $Fe(bpy)_3^{3+}$ occurring during the slower reduction. From the data in the table we conclude that dissociation during reduction is negligible in 0.10 M OH^- and the further studies of O_2 yield reported below are for this concentration only.

The effect of $Fe(NO_3)_3$, added alone and together with bpy, is given in Table III. This concentration of $Fe(NO_3)_3$ had no detectable effect on the rate of dissociation of $Fe(bpy)_3^{3+}$ in acid solution. The O_2 yields are calculated as equivalents of O_2 per mole of undissociated $Fe(bpy)_3^{3+}$ as measured in the acid solutions with the appropriate dilution factor from addition of base and also a small correction for the O_2 used for the autoxidation oof $Fe(bpy)_3^{2+}$ during the 1 min before the O_2 was measured (see Experimental Section). In order to calculate this correction, we have measured both the rate of O_2 disappearance and of decrease in optical absorbance of $Fe(bpy)_3^{2+}$ in the product solutions and find this to be the same. We have confirmed that, as earlier reported,[9] the rate is first order in complex and in OH^- and also find that the pseudo-first-order rate constants in the product solutions, although not very different from those in solutions of $Fe(bpy)_3^{2+}$ alone, do show a small increase, Table IVA, which can be simulated by adding $Fe(NO_3)_3$, Table IVB.

Table II. Parallel Dissociation[a] and Reduction of $Fe(bpy)_3^{3+}$

$[OH^-]$, M	$(\alpha/(1-\alpha))_{average}$	10^6-$[O_2]$, M	ionic strength, M	k_{red}, s^{-1}
0.10	3×10^{-6}	4[b]	0.121	4.4
0.010	0.0038	17[c]	0.021	0.70[d]
0.0010	0.0096	48[c]	0.012	0.084[d]

[a] k_{d_3} is taken as 4.7×10^{-4} s^{-1} which is the experimental value at pH 4 to pH 6 (see Table I); k_{red} is the rate constant for the formation of $Fe(bpy)_3^{2+}$. [b] $c_{Fe} = 1 \times 10^{-3}$ M. [c] $c_{Fe} = 5 \times 10^{-4}$ M. [d] From ref 3. $(\alpha/(1-\alpha))_{average} = R$, refers to the reacting solution and is that calculated for six half-life intervals, using $R = (e^{kt} - 1)/(1 + k')$ where $k = k_{d_3} + k_{red}$ and $k' = k_{red}/k_{d_3}$.

Table III. Effect of $Fe(NO_3)_3$, Added Together with bpy to the Acid $Fe(bpy)_3^{3+}$ Solution, on the O_2 Yield in 0.10 M OH^-

soln no.	concn of dissoctd complex (αc_{Fe}),[a] mM	$[Fe(NO_3)_3]$, mM	[bpy], mM	% O_2 yield
1	0.009	0	0	~1
2	0.009	0.065	0	33 ± 2
3	0.009	0.061	0.122	66 ± 3
4	0.009	0.060	0.192	49 ± 2
5	0.25	0	0	67 ± 3
6	0.25	0.061	0.122	107 ± 4

[a] $c_{Fe} = 1 \times 10^{-3}$ M.

Table IV

A. Pseudo-First-Order Constants for the Decay of $Fe(bpy)_3^{2+}$ in Product Solutions from $Fe(bpy)_3^{3+}$ ($[OH^-] = 0.10$ M) at 22 ± 1 °C

$10^4 c_{Fe}$, M	α	$10^4 k_{d_2}$, s^{-1}
1.00	0.03	8.3
1.00	0.25	9.6[a]
1.00	0.31	10.5
1.00	0.60	10.0

B. Effect of Added $Fe(NO_3)_3$ on the Pseudo-First-Order Dissociation of $Fe(bpy)_3^{2+}$ in Air-Saturated 0.10 M NaOH at 22 ± 1 °C

10^4·$[Fe(bpy)_3^{2+}]$, M	10^4·$[Fe(NO_3)_3]$, M	$10^4 k_{d_2}$, s^{-1}
1.00	0	7.7 ± 0.5[b]
0.92	0.20	7.3
0.92	0.40	9.6
0.92	0.60	11.2

[a] Rate of decrease in O_2 with time in helium-saturated product solution. [b] Agrees with ref 9.

Dioxygen Yields from $Fe(phen)_3^{3+}$. The O_2 yields were always very low for $Fe(phen)_3^{3+}$ and increased in an analogous way to that for $Fe(bpy)_3^{3+}$ with increasing degree of dissociation of the reactant. For a series of experiments analogous to those of Figure 1a, the O_2 yield increased from about 2% to a maximum value of 7%. This yield could be increased to 15% by adding $Fe(NO)_3$ under the conditions given in Table III.

Yields of $Fe(bpy)_3^{2+}$ and $Fe(phen)_3^{2+}$. These were determined by visible spectrophotometry a few seconds after adding base. Dissociation of the tris Fe(II) complexes is negligible during this time (cf Table IV), but correction is required for the small amount of tris Fe(II) complex produced by the parallel reduction which accompanies acid dissociation during the "aging" of the acid reactant solutions. In order to determine this, we have, in addition

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(9) G. Nord, *Acta Chem. Scand.*, **27**, 743 (1973) and references therein.

Table V. Calculated and Observed O_2 Yields from Partly Dissociated Fe(bpy)$_3{}^{3+}$ Solutions[a]

soln no.	$10^3(1 - \alpha)c_{Fe}$, M = [Fe(bpy)$_3{}^{3+}$], mM	$10^3\alpha c_{Fe}$, M	% O_2 yield	
			obsd	calcd
a_1	0.977	0.023	5.3 ± 0.5	33
a_2	0.861	0.139	57 ± 3	57
a_3	0.791	0.209	66 ± 3	60
a_4	0.724	0.276	66 ± 3	61
a_5	0.611	0.389	65 ± 3	63
a_6	0.557	0.443	67 ± 3	63
b_1	0.0953	0.0047	6.1 ± 0.5	0
b_2	0.0874	0.0126	10.2 ± 0.5	18
b_3	0.0708	0.0292	32 ± 1	37
b_4[b]	0.0655	0.0345	37 ± 2	39
b_5	0.0387	0.0613	37 ± 2	48
b_6[c]	0.0319	0.0681	39 ± 2	49

[a] Solutions as for Figure 1a,b. [b] Age of acid solution 88 min. [c] Age of acid solution 238 min.

to the change in concentration of Fe(bpy)$_3{}^{3+}$ = $(1 - \alpha)c_{Fe}$, with time (k_{d_3}, see Table I) also measured the concentration of Fe(bpy)$_3{}^{2+}$ formed.[10] In the acid medium used for Figure 1, (k_{d_3} = 8×10^{-5} s^{-1}) the concentration of Fe(bpy)$_3{}^{2+}$ was always 2.7% of αc_{Fe} so that the rate constant for reduction in these solutions is 2.2×10^{-6} s^{-1}. Subtraction of this from the concentration of Fe(bpy)$_3{}^{2+}$ formed in base allowed calculation of yield as moles of Fe(bpy)$_3{}^{2+}$ formed in base per mole of Fe(bpy)$_3{}^{3+}$ in acid.

The yield of Fe(bpy)$_3{}^{2+}$ varied from 83% to 86% for the series with $c_{Fe} = 1 \times 10^{-4}$ M as in Figure 1b and Table V, b_1–b_6. There was not detectable dependence on the composition of the solutions (and therefore on the O_2 yield). For $c_{Fe} = 1 \times 10^{-3}$ M (Figure 1a and Table V, a_1–a_6) the yield of Fe(bpy)$_3{}^{2+}$ increased from 84 ± 3% in the freshly prepared solutions to 95 ± 3% at the maximum O_2 yield of 67%.

These yields also include the Fe(bpy)$_3{}^{2+}$ formed during the decay of the intermediate, which was observed after the reduction of Fe(bpy)$_3{}^{3+}$ in base is complete, and this is discussed later in this paper.

The yield of Fe(phen)$_3{}^{2+}$ was found to be constant within the experimental repeatability and is 88 ± 3% for $c_{Fe} = 1 \times 10^{-3}$ M.

Oxidized Ligand Products. The product solutions were examined by NMR spectroscopy, by visible and UV spectrophotometry, and by mass spectrometry. For both the phen and the bpy systems several products were detected but only the mono-*N*-oxides of the two ligands were characterized together with the unchanged ligands. The uncomplexed ligands were extracted with chloroform from the aqueous reaction mixture for the NMR and mass spectrometry studies.

1,10-Phenanthroline *N*-Oxide (phenO). This was detected by ^{1}H NMR spectroscopy in chloroform extracts of solutions prepared by mixing acid Fe(phen)$_3{}^{3+}$ (~2 mM, <2% dissociated) with NaOH to [OH$^-$] = 0.10 M. The extraction was completed <15 sec after mixing. The spectrum of 1,10-phenanthroline *N*-oxide was clearly detected together with that of 1,10-phenanthroline; see Figure 3 and ref 13. No other species were present at concentrations high enough (~2%) to give detectable signals in this field range. The chloroform extracts were, however, bluish red and on dilution with chloroform gave the visible spectrum shown in Figure 4 and interpreted there to show that at least one complex (which is neither Fe(phen)$_3{}^{2+}$ nor Fe(phen)$_3{}^{3+}$) is present in these diluted extracts.

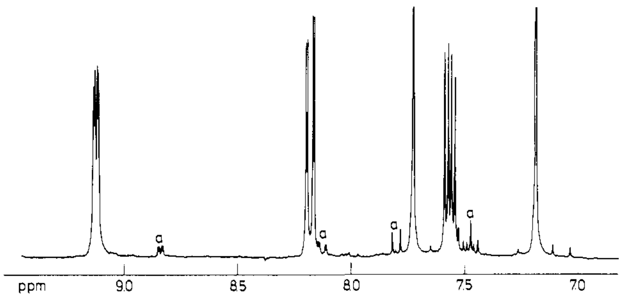

Figure 3. 270-MHz, ^{1}H NMR spectrum of $CDCl_3$ extract of the products of the Fe(phen)$_3{}^{3+}$ + OH$^-$ reaction. The peaks marked a are 1,10-phenanthroline *N*-oxide ppm vs. Me_4Si. The other peaks are 1,10-phenanthroline.

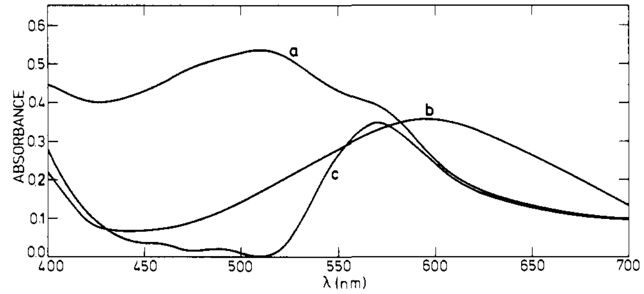

Figure 4. Visible absorbance of a chloroform extract of the products of the Fe(phen)$_3{}^{3+}$ + OH$^-$ reaction (a), including Fe(phen)$_3{}^{3+}$ for comparison (b), and after subtraction of Fe(phen)$_3{}^{2+}$ (c).

A similar chloroform extract gave an ion of mass 196 in a mass spectrograph, as also did a chloroform solution of the pure crystalline phenO.

2,2-Bipyridine *N*-Oxide (bpyO). We are unable to identify this in chloroform extracts. The ^{1}H NMR spectra contained many peaks which were also present in the reaction mixture used to prepare the monoxide. The composition of the aqueous product solutions was therefore studied. When these are allowed to decay in air, all complexed Fe(III) and Fe(II) is converted to hydrated Fe(III) oxide and in such solutions we detected 2,2′-bipyridine *N*-oxide by its UV absorption. The following dilute reaction mixture containing 1.23×10^{-4} M Fe(bpy)$_3{}^{3+}$ (age ~2 min) and 0.10 M OH$^-$ allowed quantitative determination of bpy and bpyO in the final products because the absorption of Fe(OH)$_3$ was small and could be reproduced by using Fe(NO$_3$)$_3$. After subtraction of this the spectrum from 220 and 350 nm corresponded (±1%) to a mixture of 3.30×10^{-4} bpy ((λ nm, ϵ M^{-1} cm^{-1}): (280, 1.40×10^4), (251, 0.44×10^4), and (233, 1.10×10^4)) and 0.32×10^{-4} M bpyO ((260, 1.43×10^4), (247, 1.06×10^4), and (232, 1.95×10^4)). Unlike the chloroform extracts of concentrated solutions the final aqueous product solutions therefore only contain bpy, bpyO, and possibly traces (≲2%) of other organic products.

Stopped-Flow Study of the Primary Products. We have remeasured the rate of increase of optical absorbance at a maximum of Fe(bpy)$_3{}^{2+}$ (λ 520 nm (ϵ 0.84×10^4)) and of Fe(phen)$_3{}^{2+}$ (λ 510 nm (ϵ 1.13×10^4)) in the more dilute[14] complex solutions ($c_{Fe} = 2 \times 10^{-4}$ M) and in agreement with our earlier work[3] find that in excess base (0.10 M) the reactions are first order in complex with $t_{1/2}$ = 158 ms for Fe(bpy)$_3{}^{2+}$ formation and 1.8 ms for Fe(phen)$_3{}^{2+}$ formation and independent of the O_2 yields and of added ligand. An extra feature that we did not previously observe (but which was reported for the Ru system)[4] was a small increase of absorbance after the first-order formation of the Fe(II) tris complexes was essentially complete. This increase was found from ~1.2 to ~6 s and was so small that accurate trace reading was difficult. There was, however, a detectable increase with aging of the solutions, e.g., in 3×10^{-5} M Fe(bpy)$_3{}^{3+}$ ([OH$^-$] = 0.10

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[10] The rate constants for the dissociation of Fe(bpy)$_3{}^{2+}$ and Fe(phen)$_3{}^{2+}$ in HCl[11] are similar to those for Fe(bpy)$_3{}^{3+}$ and Fe(phen)$_3{}^{3+}$. However, the reactions Fe(bpy)$_3{}^{3+}$ + Fe^{2+} → Fe(bpy)$_3{}^{2+}$ + Fe^{3+} and the corresponding phen reaction are fast[12] so that it is the total concentration of Fe(bpy)$_3{}^{2+}$ or Fe(phen)$_3{}^{2+}$, formed by parallel reduction during the dissociation of Fe(bpy)$_3{}^{3+}$, or Fe(phen)$_3{}^{3+}$, which is measured.

[11] J. E. Dickens, F. Basolo, and H. M. Neumann, *J. Am. Chem. Soc.*, **79**, 1286 (1957) and references therein.

[12] M. H. Ford-Smith and N. Sutin, *J. Am. Chem. Soc.*, **83**, 1078 (1961).

[13] S. Ogawa and N. Gotoh, *Kogyo Kagaku Zasski*, **74**, 2127 (1971).

[14] With the apparatus at our disposal, it was not possible to measure the complete time dependence of the high optical absorbances at λ 520 nm of more concentrated solutions than this.

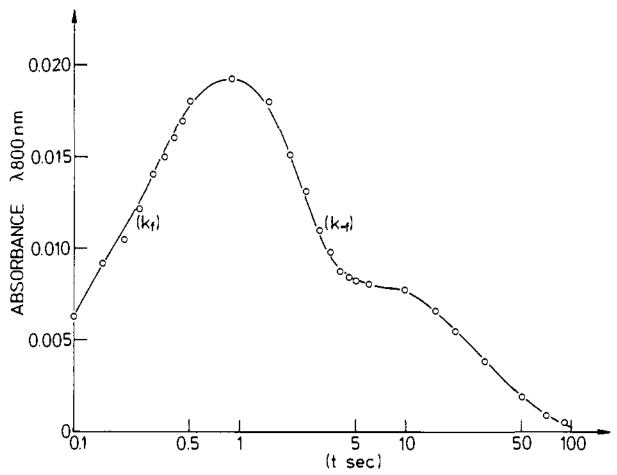


Figure 5. Change in absorbance (2-cm cell) with time at λ 800 nm for solution b_4 in Table V.

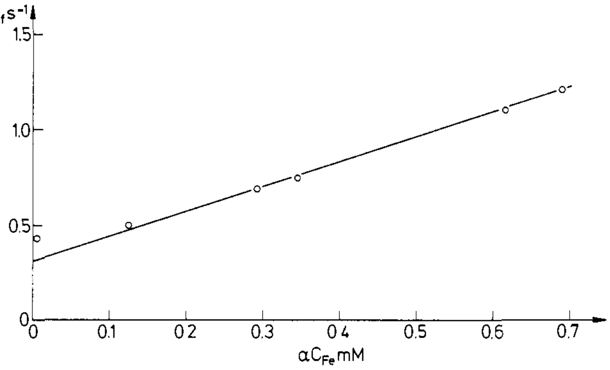


Figure 6. Pseudo-first-order decay constant of primary product vs. concentration of dissociated reactant at $c_{Fe} = 1 \times 10^{-4}$ M, $[OH^-] = 0.10$ M.

M) which was 8% dissociated this increase was 1.7% of the total absorbance, while in a similar solution which was 20% dissociated it was 2.3%. After ~6 s the absorance decreased in a way which quantitatively accorded with the rate of dissociation of the tris Fe(II) complex.

At λ 800 nm the absorbance of the tris(bpy) and -(phen) complexes of both Fe(II) and Fe(III) is negligible but intermediates absorb.[4] In all cases at this wavelength the absorbance was found to increase to a maximum and then decay. We report here details for some of the two series of $Fe(bpy)_3^{3+}$ solutions used to construct Figure 1a,b; the compositions of these solutions are given in Table V. For the dilute series (b) the maximum in absorbance was not attained until the first-order $Fe(bpy)_3^{2+}$ formation was essentially complete (~1s) and the rate of decrease in absorbance (unit the plateau, ~5 s in Figure 5) is first order in the absorbing species for at least three half-lives (k_{-f} path in Figure 5). In freshly prepared solutions both the change in absorbance (Δ(absorbance) = maximum absorbance − plateau absorbance) and the rate of decay were not detectably altered by addition of 0.01 M bpy. The decay rate changes with the degree of dissociation (α) of $Fe(bpy)_3^{3+}$ in the acid solutions, as illustrated in Figure 6, which leads to

$$k_{-f} = k_o + k_1 \alpha c_{Fe} = 0.31 + (1.31 \times 10^4)\alpha c_{Fe} \quad (1)$$

In the more concentrated solutions, a_1–a_6 in Table V, the maximum absorbance is found before the reduction of $Fe(bpy)_3^{3+}$ is complete. For solutions a_2–a_6 the whole curves can be reproduced with one absorbing intermediate which is formed at the same rate as $Fe(bpy)_3^{2+}$ and decays according to eq 1. The change in absorbance (Δ) for these solutions is linear with the calculated maximum concentration of the intermediate (I), as demonstrated in Figure 7. For the other solutions the time at which the maximum in absorbance occurs is much longer than that calculated for the maximum concentration of I, and the rate of increase in absorbance due to this intermediate is masked by the absorbance of at least one other species. In these solutions, however, the concentration of intermediate at the observed time of maximum absorbance, calculated under the assumption that it is formed with $k_f = 4.4$ s^{-1}, is also the same linear function of Δ(absorbance), see Figure 7. The apparent extinction coefficient (per mole of $Fe(bpy)_3^{3+}$) is 170 ± 10 M^{-1} cm^{-1}. The system can therefore be understood if a highly absorbing species is rapidly formed in very small concentration and has decayed when the maximum in absorbance is observed. After the decay of the main intermediate, the absorbance remains constant until about 6 s, when another small much slower decrease occurs, so that an additional product that is relatively long lived is also required before all Fe(III) is converted to $Fe(OH)_3$.

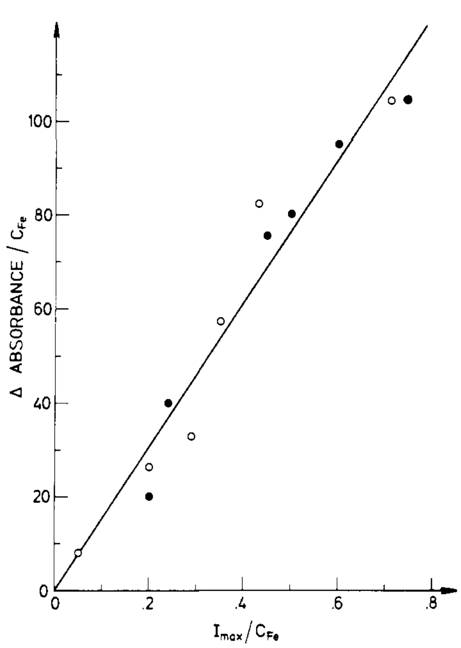


Figure 7. Absorbance of intermediate at λ 800 nm vs. concentration intermediate (I)

$$I_{max} = \frac{k_f(1-\alpha)c_{Fe}}{(k_{-f} - k_f)}(e^{-k_f t_{max}} - e^{-k_{-f} t_{max}})$$

$k_f = 4.4$ s^{-1}, k_{-f} from eq 1. t_{max} = observed time of maximum absorbance. (○) $c_{Fe} = 1 \times 10^{-3}$ M; (●) $c_{Fe} = 1 \times 10^{-4}$ M.

Discussion

Correlation of Rates and Stoichiometries. These can be correlated by using the simplified reaction sequence (seen in Scheme I). The rate constants included in the Scheme I are for 0.10 M OH^- and the Cl^- medium used for Figure 1 and the tables.

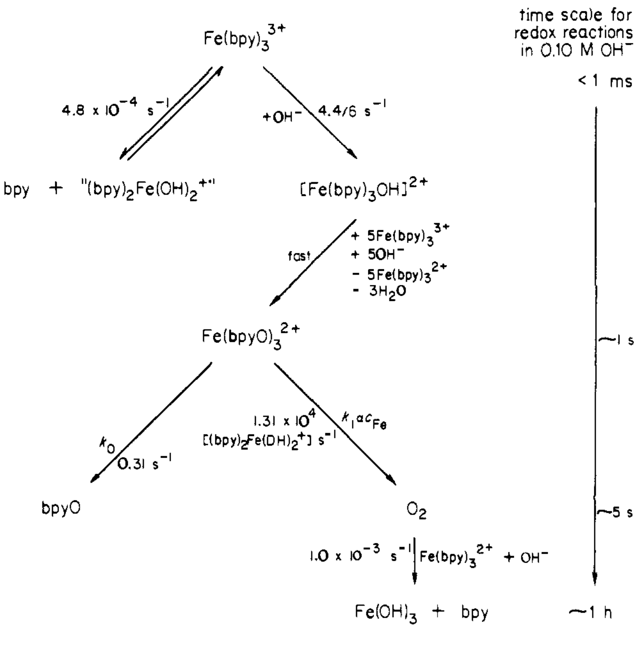
The O_2 yields can be well reproduced according to Scheme I, which leads to

$$\text{yield of } O_2 = \frac{4O_2}{c_{Fe}(1-\alpha)} = \frac{\tfrac{2}{3} k_1 \alpha c_{Fe}}{k_o + k_1 \alpha c_{Fe}} \quad (2)$$

The catalyst concentration, αc_{Fe}, is the concentration of dissociated Fe(III) complex and, when OH^- is 0.10 M and neither bpy nor $Fe(NO_3)_3$ is added, this is also the concentration of dissociated reactant measured in the acid solutions. The calculated O_2 yields given in Table V were obtained by using eq 2 as also were the full curves drawn in Figure 1. In the latter the small concentration of O_2 used during the 1 min before it was measured was subtracted for direct comparison with the measured O_2 product concentrations. For the ClO_4^- solutions used in Figure 2 the variation of O_2 yield can be reproduced by using $k_1/k_o = 1.04 \times 10^4$ M^{-1}.

For the $Fe(phen)_3^{3+}/OH^-$ system in a series analogous to those of Figure 1a, a comparable plot to Figure 6 leads to $k_o = 39$ s^{-1} and $k_1 = 1.6 \times 10^4$ M^{-1} s^{-1}, and these values also reproduce the O_2 yields.

Scheme I

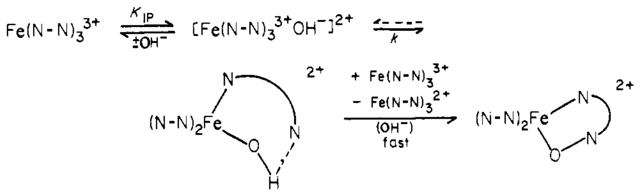


Scheme I will account for the O_2 yields in the presence of added excess bpy if dissociation is reversed during the addition of base. In this case the high *yields* given in Figure 2 become spurious and substitution of the observed O_2 *concentrations* in eq 2 requires αc_{Fe} not only to be negligible at low values of αc_{Fe} in acid but also to be very small throughout the series. For the data given in the figure and also an extended series (α acid up to 0.49), we find that the concentration of O_2 measured never requires the degree of dissociation in basic 0.01 M bpy to be greater than 7%.

The O_2 yields given in Table III also accord with Scheme I. Thus, if the bpy added in solution 6 completely converts an equivalent concentration of catalyst to $Fe(bpy)_3^{3+}$, the concentration of this would increase to 1.12 mM and the O_2 yield therefore be decreased to 67%. On the other hand, an explanation of the increased O_2 "yield" in solution 2 over solution 1 would require the added Fe(III) to catalyze the rate of dissociation of $Fe(bpy)_3^{3+}$ in base (cf. Table IV for $Fe(bpy)_3^{2+}$ in base): the O_2 concentration corresponds to a catalyst concentration of 0.074 mM and 0.926 mM $Fe(bpy)_3^{3+}$. For solutions 3 and 4 in the table, both catalyst and $Fe(bpy)_3^{3+}$ concentrations are required to be adjusted. The fact that the data in the table can be reasonably correlated with change in the degree of dissociation of $Fe(bpy)_3^{3+}$ means that the increase of O_2 concentration on addition of $Fe(NO_3)_3$ does not necessarily require an extra catalytic path and that neither this nor the data for addition of bpy in the table give information about the formula of the catalyst. However, it presumably contains bpy and is required to contain at least one OH^- which is in a cis position to either a second coordinated OH^- or to a coordinated water molecule.

Apart from the fact that the highly absorbing trace intermediates have been omitted, the main assumption made in Scheme I is that the composition of the *N*-oxide and O_2-producing first product is that of the known tris *N*-oxide and O_2-producing first product is that of the known tris *N*-oxide complex of Fe(II). The mechanistic significance of the detection of *N*-oxide as a product and the formulation of the main intermediate in O_2 formation as containing coordinated *N*-oxide is discussed later in this paper. This intermediate requires an $Fe(bpy)_3^{2+}$ yield of 83%, and we have assumed that the increase in the observed total yield over this amount is due to the production of $Fe(bpy)_3^{2+}$, or of a similarly absorbing species, from the products of the O_2 decay path. The concentration of free bpy parallels that of catalyst and therefore increases with increase in O_2 yield. However, as stated earlier in this paper, it was only experimentally feasible to measure the time dependence of the absorbance at λ 520 nm in the more dilute solutions.

Scheme II



The rate of dissociation in base given in Scheme I is that measured in neutral and dilute acid solutions (see also Tables I and II).

The higher rates in Cl^- and SO_4^{2-} over ClO_4^- parallel those known for both dissociation and racemization of $Fe(phen)_3^{3+}$ and attributed to ion-pair formation.[11] When this effect is included, Scheme I applies to all the systems we have studied.

Mechanisms. The Rate-Determining Step. The new experimental fact which is mechanistically significant for the rate-determining reduction of OH^- is the detection of the ligand *N*-oxide. This must be a primary product because such compounds slowly rearrange to give stable products containing C–O bonds. The rate law requires the first formed reactive intermediate to have the composition $Fe(N{-}N)_3OH^{2+}$ where N–N is bpy or phen. We suggest that this and also *N*-oxide are formed according to Scheme II, where the reactant is depicted as an ion pair and the energy of activation chiefly arises from the breaking of one Fe–N bond.

"Half-bonded" structures have earlier been suggested to explain the increase of the rate of dissociation of $Fe(bpy)_3^{2+}$ with increasing H^+ concentration.[15] The fact that the dissociation of $Fe(phen)_3^{2+}$ is not strongly acid dependent was attributed to stabilization of coordinated $bpyH^+$ in the trans N–N configuration which is energetically favored by the free ligand. In the above scheme, however, bpy is required to remain in the cis configuration in the expanded coordination sphere of the reactive intermediate. This is, of course, the only configuration available to phen. It is relevant that similar complexes containing unidentate phen have recently been identified[16] and that an analogous bpy complex was invoked to explain the NMR spectra of $Pt(bpy)_2^{2+}$ in basic solution.[17] It seems possible that such structures are a general feature of the reactions of bpy and phen complexes because the substitution reactions of $Fe(bpy)_3^{2+}$ and $Fe(phen)_3^{2+}$ with OH^- and CN^-, although first order in both complex and nucleophile, have recently been found to have similar activation volumes as required for a rate-determining dissociation.[18] These latter rates are, however, very similar for both the phen and the bpy complexes and complete dissociation of a ligand has in both cases occurred in the products. The much slower rate of reduction by OH^- of $Fe(bpy)_3^{3+}$ than of $Fe(phen)_3^{3+}$, could arise from a smaller contribution of cis half-bonded ligand to a reactive intermediate of the correct configuration for coordinated *N*-oxide to be formed after further oxidation accompanied by proton loss. This scheme is equally applicable to the Ru and Os reactions and therefore could account for the common rate law.

O_2 Formation. Previous mechanisms do not allow for the fact that no O_2 is produced in basic solutions of the tris Fe(III) chelates alone. The main intermediate which produces O_2 by the catalyzed path is formulated in the above scheme as a tris *N*-oxide of Fe(II) and this is required to be rapidly formed from $Fe(bpy)_2bpyO^{2+}$ either by rapid disproportionation, which would involve O transfer,[19] or by OH^- addition to the metal center and further

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(15) "Mechanisms of Inorganic Reactions", 2nd ed., F. Basolo and R. G. Pearson, Eds., Wiley, New York, 1967, p 218.

(16) O. Wernberg and A. J. Hazell, *J. Chem. Soc., Dalton Trans.*, 973 (1980).

(17) O. Farver, O. Mønsted, and G. Nord, *J. Am. Chem. Soc.*, **101**, 6118 (1979).

(18) G. A. Lawrance, D. R. Stranks, and S. Suvachittanont, *Inorg. Chem.*, **18**, 82 (1979).

(19) O transfer from *N*-oxides to coordinated carbonmonoxide to give CO_2 is known to occur. Private communication from Dr. Bernard Shaw to G. Nord.

oxidation. Both mechanisms involve the successive breaking of single Fe–N bonds.

$Fe(bpyO)_3^{2+}$ and $Fe(phenO)_3^{2+}$ have been prepared as solids and their electronic spectra found to be very different in Nujol mulls and in nonaqueous solutions.[20] The compounds are not stable in aqueous solution. The spectrum of $Fe(bpyO)_3^{2+}$ in nitromethane is reported to have a shoulder at λ 505 nm (ϵ 1684 M^{-1} cm^{-1}) and at maximum at λ 862 (ϵ 48 M^{-1} cm^{-1}). This latter band is assigned by the authors to d-d transitions in the metal center. The present intermediate, when formulated as $Fe(bpyO)_3^{2+}$ has a molar extinction coefficient in aqueous 0.10 M hydroxide of $\sim 10^3$ M^{-1} cm^{-1} at λ 800 nm and this is more reasonably attributable to a charge-transfer band.

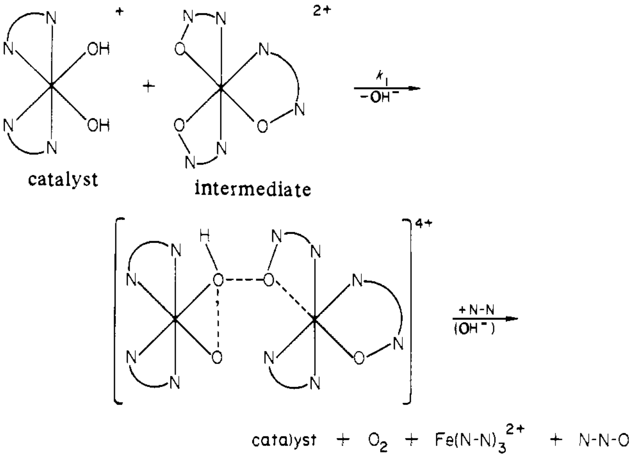
The significance of the earlier work on the $Ru(bpy)_3^{3+}/OH^-$ system[4] in the deduction of the structure of this main intermediate is difficult to assess because of the fact that at least two intermediates absorb at λ 800 nm. The intensely absorbing trace intermediate which we find in the most dilute Fe solutions could well correspond to one of the intermediates in the $Ru(bpy)_3^{3+}/OH^-$ system and would be therefore analogously formulated as containing a coordinated bpyOH radical.[4] The 800-nm absorbance in solution a_1 in Table V attains its maximum when the reduction of $Fe(bpy)_3^{3+}$ is about 90% complete, and this is also the behavior reported for the $Ru(bpy)_3^{3+}/OH^-$ reaction. The rate of disappearance of the trace intermediate $Fe(bpy)_2bpyOH^{3+}$ is required to be increased either by reaction with the Fe(III) catalyst or by a product of the O_2 formation reaction, because it was not detectable in solutions a_2–a_6 in Table V. The absorbance of these latter solutions accords with the formation of one intermediate which can carry the whole $Fe(bpy)_3^{3+}/OH^-$ reaction.

In spite of the fact that it was not feasible for us to confirm that the main intermediate is $Fe(bpyO)_3^{2+}$, we have used this formulation because not only will it account for the stoichiometry but also because the catalyst has the required configuration to accept O from such a compound and form dioxygen. It was pointed out by Dwyer and co-workers[21] that one of the necessary requisites for a metal complex to catalyze the rearrangement of trimethylamine *N*-oxide was the ability to bind the *N*-oxide through its oxygen and also to provide a hydroxyl group in the neighboring (cis) coordination position. The transfer of O to the metal center of the catalyst in this reaction is the step which we consider relevant to O_2 production in our system because the intermediate so formed has also been suggested as the first stage in the catalyzed disproportionation of HO_2^-. Many examples of the catalysis of HO_2^- by Fe(III) chelates containing adjacent OH^- groups have appeared in the literature,[22] and the occurrence of an intermediate containing metal-bound O appears in an early example[23] where the other four coordination positions are occupied by the tetradentate ligand triethylenetetramine. In the catalyzed HO_2^- disproportionation, the O–O bond in the product O_2 is supposed to be formed by reaction of a second molecule of HO_2^- with this Fe–O intermediate.

For the $Fe(N\text{-}N)_3^{3+}/OH^-$ system the O transfer step and the succeeding O–O bond formation can be combined in one reactive intermediate,[24] as in Scheme III.

The composition of the longer lived intermediate formed from the uncatalyzed (k_O) path is not known; polymeric species which contain bridging peroxo groups would, however, accord with the general chemistry of such solutions.

Scheme III



Recent work on these systems has concentrated on changes in the O_2 yield from the $Fe(bpy)_3^{3+}/OH^-$ and $Ru(bpy)_3^{3+}/OH^-$ systems with changes in the pH of the solutions[4,5] and also with addition of RuO_2 as catalyst. In the absence of added catalyst the increase in O_2 yield with decreasing OH^- concentration reported in ref 5 probably has no extra significance because the authors were not then aware of the necessity of using fresh solutions, and even if they have done so, the increase of O_2 yield could be explained as arising from parallel dissociation and reduction as in Table II of the present paper. The Ru work was, however, carried out with fresh solutions, and also $Ru(bpy)_3^{3+}$ is not labile so that the sharp increase in O_2 yield at pH 9 is worthy of further discussion. It is significant that this occurs when the reduction is slow and the kinetics are no longer simple. We find[7] that the $Os(bpy)_3^{3+}/OH^-$ system exhibits similar deviations from the simple rate law, the reaction sequence involving the stepwise formation of several intermediates which contain bpy and finally forming $Os^{VIII}O_4(OH)_2^{2-}$, bpyO, $Os(bpy)_3^{2+}$ and bpy as products. The requirement, without added catalyst, in the $Ru(bpy)_3^{3+}/OH^-$ system for a *dual mechanism* for O_2 formation through analogous partly dissociated complexes containing Ru in higher oxidation states than 4+, is that reduction of $Ru(bpy)_3^{3+}$ by OH^- is slow enough for dissociation of the intermediate Ru(II) tris *N*-oxide to occur when unreacted $Ru(bpy)_3^{3+}$ is still present to further oxidize the dissociated product, and at pH 9 this requirement is satisfied. Thus, for example, stepwise oxidation of Ru to the known $(bpy)RuO_2\cdot(OH)_2$ compound could be possible, but on further oxidation this would not produce a stable Ru(VIII) product but O_2 and Ru(IV) which could be reoxidized by $Ru(bpy)_3^{3+}$. This alternative O_2-producing mechanism is attractive because of the possibility that O_2 can be produced in a homogeneous system of $Ru(bpy)_3^{3+}$, Ru(IV), and bpy under conditions where consumption of the ligand as bpyO and other oxidized products is negligible. It is relevant that RuO_2 does produce O_2 in weakly basic buffered solutions[25] of $Fe(bpy)_3^{3+}$ and that these would contain free bpy. Neither for this nor for the $Ru(bpy)_3^{3+}/OH$ system has the possibility that the function of RuO_2 is to produce a homogeneous catalytic sequence previously been suggested.

Experimental Section

Electronic absorption spectra were measured with either a Cary Model 118, or a Model 14 UV–visible spectrophotometer. Nuclear magnetic resonance spectra were measured with a Bruker HX-270 instrument in the Fourier transform mode. The rate of dissociation of $Fe(bpy)_3^{3+}$ in acid solutions was measured both by optical spectrophotometry and by ^1H NMR spectroscopy. In the former method the rate of decrease of absorbance of $Fe(bpy)_3^{3+}$ was measured at two of the following wavelengths (λ nm, ϵ M^{-1} cm^{-1}): (610, 300), (520, 108), (390, 1210), (218, 6.9×10^4). The decrease of absorbance of $Fe(phen)_3^{3+}$ was measured

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[20] A. N. Speca, N. M. Karayannis, and L. L. Pytlewski, *Inorg. Chim. Acta*, **9**, 87 (1974).

[21] J. C. Craig, F. P. Dwyer, A. N. Glazer, and E. C. Horning, *J. Am. Chem. Soc.*, **83**, 1871 (1961).

[22] References to early work including catalysis by mono and bis bpy and phen complexes of Fe(III) are given in Chum and de Castro (H. L. Chum and M. L. de Castro, *J. Am. Chem. Soc.*, **96**, 5278 (1974)). These latter authors were, however, interested in the inhibition by a tris Fe(II) complex.

[23] R. C. Jarnagin and J. H. Wang, *J. Am. Chem. Soc.*, **77**, 822 (1955).

[24] The catalyst is formulated for simplicity as a bis chelate. The intimate mechanism for the formation and decay of the depicted reactive intermediate may be a series of fast reactions involving Fe(IV) and the radicals OH and O_2H as discussed in the above references. The only experimental evidence for radical formation is the detection of the intermediate which is highly absorbing at λ 800 nm and which we have suggested may contain a bpyOH radical. This is formed, however, in a side reaction.

[25] K. Kalyanasundaram, O. Mičić, E. Pramauro, and M. Grätzel, *Helv. Chim. Acta*, **62**, 2432 (1979).

at (590, 820) and (510, 370). In the NMR study the rate of increase of the heights of the peaks due to H's (3 and 4) of the free bpy was measured because these were well separated from those of the coordinated ligand. The system of numbering is given in ref 17. Mass spectra were obtained on a Varian MAT CH 50 instrument equipped with a combined EI/FI/FD ion source.

Dioxygen was measured on a Beckman GC 5 gas chromatograph, with a He ionization detector, used in combination with a Van Slyke apparatus as described in ref 26. The error in the measured O_2 given in Table V chiefly arises from the variation in the volume of solutions delivered from the syringes used for mixing. The concentrations of O_2 were measured 1 min after rapidly adding excess base to acid solutions of $Fe(bpy)_3{}^{3+}$ and of $Fe(phen)_3{}^{3+}$ which had been allowed to partly dissociate under He in the dark.

Stopped-flow measurements were made in a Durrum apparatus which is the property of the University of Lund. Absorbance changes were read from photographs of oscilliscope traces. Figure 5 is a combination of three traces at different time scales.

All solutions and reagents were of AnalaR grade. Triply distilled water was used for the O_2 determination measurements and doubly distilled water for the other measurements.

The Fe(III) and Fe(II) complexes were prepared, purified, and analyzed by published methods[3,9] as also were 1,10-phenanthroline *N*-oxide (phenO) and 2,2′-bipyridine *N*-oxide (bpyO).[27,28] PhenO was prepared as light brown crystals. BpyO is hygroscopic and difficult to prepare free from bpy. Our best product contained 2.1% bpy, as determined from both the ^1H NMR spectrum and also the UV spectrum of the mixture.

Registry No. Ferrin, 13479-49-7; tris(2,2′-bipyridyl)iron(III), 18661-69-3; oxygen, 7782-44-7; hydroxide, 14280-30-9; phenanthroline *N*-oxide, 1891-19-6; bipyridine *N*-oxide, 33421-43-1.

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(26) "Measurement of Oxygen", H. Degn, I. Balslev, and R. Brook, Eds., Elsevier, Amsterdasm, 1976, p 1.

(27) E. J. Corey, A. L. Borror, and T. Foglia, *J. Org. Chem.*, **30**, 288 (1965).

(28) I. Murase, *Nippon Kagaku Zassaki*, **77**, 682 (1956); *Chem. Abstr.*, **52**, 9100*a* (1958).

An X-ray Absorption Study of the Binuclear Iron Center in Deoxyhemerythrin

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Abstract: New EXAFS data at 80 K obtained on deoxyhemerythrin in solution reveal an iron–iron peak at a separation of 3.13 ± 0.03 Å. A repeat of measurements at 300 K shows the iron–iron peak greatly reduced, confirming the hyopthesis of increased relative thermal motion of the two iron atoms from the loss of the μ-oxo bridge. The signal from the first shell of ligands around the iron atoms was analyzed by using a difference spectrum vs. oxyhemerythrin, since rearrangements were expected in only a few ligands. The results of this analysis show that the nine ligands between the irons and the protein remain unchanged, the bound dioxygen is replaced by hydroxide, and the short bond to the bridging oxygen is broken, leaving it bound to one iron. Thus, one iron becomes five-coordinate while the other remains six-coordinate. Details of this analysis are given and the results discussed in light of the information available form other sources.

The respiratory protein hemerythrin contains a pair of nonheme iron atoms which are responsible for the reversible binding of molecular oxygen. Reaction of deoxyhemerythrin with oxygen is known to result in the oxidation of the iron atoms from ferrous to ferric, with the concomitant reduction of dioxygen to peroxide.[2,3] In a recent X-ray absorption spectroscopic investigation,[4] we determined that the binuclear iron center in oxyhemerythrin has the same structure as in metazido- and methydroxohemerythrins, in which the bound peroxide has been replaced by azide and hydroxide, respectively. EXAFS data showed consistently that in all three oxidized forms each iron atom is coordinated to a total of five nitrogen and oxygen ligands at an average distance of 2.15–2.16 Å and an additional oxygen at a distance of 1.80–1.83 Å. This analysis agreed well with the proposed X-ray crystal structure for metazidohemerythrin[5] in which the two iron atoms are bridged by two protein carboxylates and an oxo group from solvent; one iron is coordinated to three additional protein imidazoles while the other is coordinated to two protein imidazoles and one azide ion. Furthermore, the short iron–oxygen distance of 1.80–1.83 Å for the bridging oxo group determined by EXAFS was in agreement with the proposed role of this group in mediating the strong antiferromagnetic coupling of the iron atoms.[2] Finally, the close similarity of the X-ray absorption properties of oxyhemerythrin and metazidohemerythrin indicated that the two forms must have the same active site structure except that oxyhemerythin has a peroxide ion in place of the azide ion.

Previous EXAFS measurements[4] performed at room temperature indicated that the geometry of the active site of deoxyhemerythrin is distinctly different from that of the oxidized forms. The first-shell peak showed a rearrangement of the ligands, and the peak from the iron–iron spacing that was obvious in the oxidized forms had disappeared. The most likely explanation is that a μ-oxo bridge present in the oxidized forms had been lost upon reduction and that the disappearance of the iron–iron peak was due to increased thermal motion of the two iron atoms relative to one another once this bridging atom had been removed. It is known that thermal motion can cause a decrease in the EXAFS amplitude via a Debye–Waller type factor.[6] This mechanism

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