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On the Reduction of Trivalent Metal–Polypyridine Complexes by OH^- Ion in Aqueous Solutions: an Alternative Pathway

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Previous studies on the reduction of trivalent metal–polypyridine complexes of the type $M^{III}(NN)_3{}^{3+}$, where NN is a polypyridyl ligand (2,2'-bipyridine, bpy, or 1,10-phenanthroline, phen; M = Fe, Ru, Os), have shown that these complexes are reduced by hydroxide ions to give the reduced product $M^{II}(NN)_3{}^{2+}$ and dioxygen (or hydrogen peroxide). These studies have indicated the formation of a precursor complex, $\{M^{III}(NN)_3OH\}^{2+}$, which has been suggested to be a 'Gillard-type' pseudo-base in which the OH^- has attacked a ring of the polypyridyl ligand. This formation of pseudo-base intermediate has recently been questioned, and here we present an alternative mechanism for the reduction reaction that is also consistent with the origin of chemiluminescence from the reduction reaction of $Ru^{III}(bpy)_3{}^{3+}$ by a base.

Introduction

The oxidation of water is an important element in cyclic schemes for the conversion and storage of solar energy. One such simple scheme [1] (reactions 1 and 2) involves the excited state of the $Ru^{II}(bpy)_3{}^{2+}$ cation (bpy = 2,2'-bipyridine) $^3(MLCT)Ru(bpy)_3{}^{2+}$, as one of the principal reagents capable, at least thermodynamically [$E^\circ(Ru(bpy)_3{}^{3+}/{}^*Ru(bpy)_3{}^{2+}) = -0.86$ V [2] and $E^\circ(H_2O/H_2) = -0.42$ V [3], of reducing water to dihydrogen. Reaction 2 represents the 'oxidation' step of

$$^*Ru(bpy)_3{}^{2+} + H_2O \longrightarrow Ru(bpy)_3{}^{3+} + \tfrac{1}{2}H_2 + OH^- \quad (1)$$

$$Ru(bpy)_3{}^{3+} + OH^- \longrightarrow Ru(bpy)_3{}^{2+} + \tfrac{1}{4}O_2 + \tfrac{1}{2}H_2O \quad (2)$$

water in the scheme which encompasses the net photosensitized decomposition of water. The iron(III)– and osmium(III)–tris(bipyridine) and tris(phenanthroline) derivatives also undergo hydroxide reduction [4–6] and it is on this reduction reaction that we focus our attention in this paper.

In an early publication, Nord and Wernberg [4] showed that the rate of reduction of $Fe(bpy)_3{}^{3+}$ and $Fe(phen)_3{}^{3+}$ is first order in [complex] and in $[OH^-]$. The same rate law obtained for OH^- reduction of several iron(III) and osmium(III) bipyridyl and phenanthroline (phen) complexes in the $[OH^-]$ range 0.005–0.075 *M* [5]. In more concentrated hydroxide ion solutions (0.01 to 0.5 *M*), a second order term in $[OH^-]$ also obtained for $Ru(bpy)_3{}^{3+}$: $k_{obs} = k_a[OH^-] + k_b[OH^-]^2$ [1]. Rate constants and activation parameters for $M^{III}(NN)_3{}^{3+}$ species are summarized in Table I [1, 5]. These data indicate that the bpy complexes are less reactive than the corresponding phen analogues, a problem not well understood [5]. The reactivity for the bpy complexes varies as Ru(III) > Fe(III) > Os(III) and this accords with the variation in the respective formal redox potentials: E° (Ru(III)/Ru(II)), 1.26 V [2]; E° (Fe(III)/Fe(II)), 0.98 V [5] and E° (Os(III)/Os(II)), 0.83 V [2]. Changes in k_a for the substituted polypyridyl complexes also parallel changes in the redox potentials of the M(III)/M(II) couples.

Postulated Mechanisms

That the enthalpy of activation, $\Delta H^\#$, for the reduction of $Fe(bpy)_3{}^{3+}$ is less than the enthalpy, ΔH°, for the previously suggested rate-determining step k_3, led Nord and Wernberg [5] to propose a

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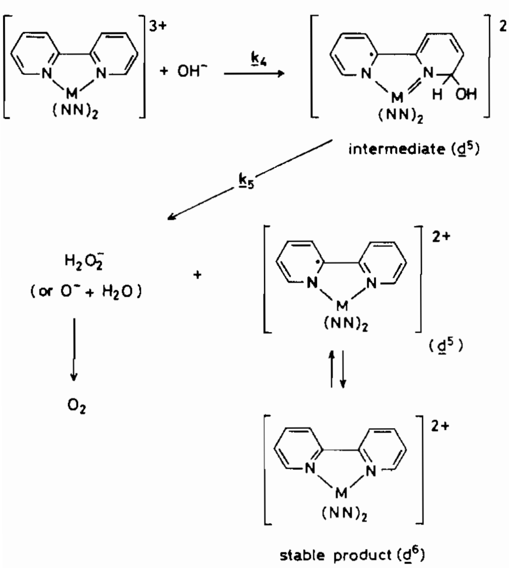
TABLE I. Rate Constants and Activation Parameters at 25 °C and $\mu = 1.0\,M$ in the Hydroxide Ion Reduction of $M^{III}(NN)_3^{3+}$.[a]

Complex	$\Delta G^{\#}$ (kcal/mol)	$\Delta H^{\#}$ (kcal/mol)	$\Delta S^{\#}$ (e.u.)	k_a (M^{-1} s^{-1})
$Fe(phen)_3^{3+}$	13.8	11.1	−10	421
$Fe(5\text{-}Mephen)_3^{3+}$	14.3	–	–	191
$Fe(5,6\text{-}Me_2phen)_3^{3+}$	14.6	9.1	−19	117
$Fe(4,7\text{-}Me_2phen)_3^{3+}$	15.3	10.3	−17	35
$Fe(3,4,7,8\text{-}Me_4phen)_3^{3+}$	16	15	−3	17
$Fe(bpy)_3^{3+}$	15.8	14.9	−4	16
$Fe(4,4'\text{-}Me_2bpy)_3^{3+}$	17.2	13	−14	1.7
$Os(phen)_3^{3+}$	14.5	12	−8	156
$Os(5\text{-}Mephen)_3^{3+}$	14.8	8.6	−19	93
$Os(bpy)_3^{3+}$	16.5	15.6	−3	4.7
$Os(4,4'\text{-}Me_2bpy)_3^{3+}$	18.1	15.3	−11	0.32
$Ru(bpy)_3^{3+}$ [b]	–	15.3	+7	148[c]

[a]Reference 5. [b]Reference 1. [c]$k_b = 138\,M^{-2}$ s^{-1}.

$$Fe(bpy)_3^{3+} + OH^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Fe(bpy)_3^{2+} + \cdot OH \qquad (3)$$

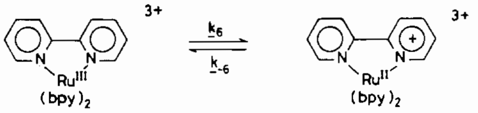
precursor intermediate as the product of reaction 3, $[Fe(bpy)_3OH]^{2+}$. The nature of this species is depicted in the following scheme; this was based on the available data [5]. Attack by OH^- ions occurs on the polypyridyl rings to form a pseudo-base radical species; no radicals were detected in the reacting solutions, but Gusenius [7] earlier reported unidentified radicals.



(4)

(5)

Independently, Creutz and Sutin [1] also proposed analogous pseudo-base species in the OH^--reduction of $Ru(bpy)_3^{3+}$ (species *3* and *3′* in reactions 6–10) in which formation of the reduced product $Ru(bpy)_3^{2+}$ was predominantly first order over the entire pH range, and added bromide or t-butanol had no effect. Thus the presence of free·OH radicals or O^- in the reaction was ruled out. The rate-determining step k_6 (low pH) depicts an intramolecular



(6)

1 2

$$\begin{array}{llll} 2 + H_2O \searrow & & & (7) \\ 2 + OH^- \longrightarrow & Ru^{II}(bpy)_3OH^{2+} + [Ru^{II}(bpy)_3OH^{2+}]' & & (8) \\ 1 + OH^- \nearrow & 3 \qquad\qquad\qquad 3' & & (9) \end{array}$$

$$Ru(bpy)_3^{3+} + \left\{\begin{matrix} Ru^{II}(bpy)_3OH^{2+} \\ [Ru^{II}(bpy)_3OH^{2+}]' \end{matrix}\right\} \longrightarrow \left\{\begin{matrix} Ru^{III}(bpy)_3OH^{3+} \\ [Ru^{III}(bpy)_3OH^{3+}]' \end{matrix}\right\} \qquad (10)$$

$$Ru(bpy)_3OH^{3+} \underset{\text{fast}}{\overset{K_{11}}{\rightleftharpoons}} Ru(bpy)_3O^{2+} + H^+ \qquad (11)$$

$$Ru(bpy)_3O^{2+} \xrightarrow[\text{slow}]{OH^-} Ru(bpy)_3^{2+} + HO_2^- \qquad (12)$$

$$Ru(bpy)_3OH^{3+} + Ru(bpy)_3O^{2+} \longrightarrow 2\ Ru(bpy)_3{}^{2+} + O_2 + H^+ \qquad (13)$$

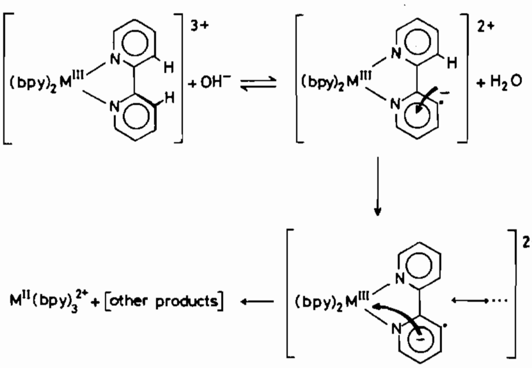
electron transfer from a bound bipyridine in $Ru(bpy)_3{}^{3+}$ to the metal centre, while direct OH^- attack on *1* is rate-determining in the first-order kinetics at high pH [1]. The dioxygen yield was a sharp function of pH, attaining its maximum value (0.8) at pH 9 (reactions 11–13) but here the kinetics were very complicated [1]. The nature of $Ru(bpy)_3O^{2+}$ and how dioxygen forms in reaction 13 with $Ru(bpy)_3OH^{3+}$ are not clear. It was also suggested that unimolecular or bimolecular decomposition of oxidized *3* and *3′* at low pH leads to degradation of ligand with no net water oxidation, and that at high pH, decomposition of $Ru(bpy)_3O^{2+}$ also effects ligand degradation with formation of some peroxide. The latter suggestion has also been proposed in more recent work on dioxygen formation from the $Fe(bpy)_3{}^{3+}$–OH^- reaction [8]. However, the nature of the degraded 'oxidized' ligand is not known.

Recently, Pedersen and Nord [8] have suggested that O_2 evolution occurs only when $Fe(bpy)_3{}^{3+}$ is partly dissociated and contains coordinated hydroxide. No O_2 appears to form when solid $[(bpy)_3Fe](ClO_4)_3$ is dissolved in 0.1 *M* NaOH or when $Os(bpy)_3{}^{3+}$ is the reactant. Reduction of $Fe(bpy)_3{}^{3+}$ with OH^- was faster ($t_{1/2} < 1$ s) than subsequent dissociation and re-oxidation of $Fe(bpy)_3{}^{2+}$ ($t_{1/2} \geqslant 15$ min). They concluded that formation of the O–O bond involves oxygen atom transfer to the coordinated hydroxide and that evolution of O_2 is no evidence for the occurrence of *reversible* nucleophilic attack on the coordinated polypyridyl ligand (*i.e.* formation of species *3* and *3′*). A recent critical review [9] of the 'evidence' available on the existence of covalent hydrates and pseudo-bases in polypyridyl–metal complexes has questioned the presence of such species.

Alternative Pathways

We begin by considering the recent work of Constable and Seddon [10] who demonstrated that the 3,3′-protons on the bpy ligand of $Ru(bpy)_3{}^{2+}$ are acidic. Reaction of $Ru(bpy)_3{}^{2+}$ in $(CD_3)_2SO$ with $Na[OCD_3]$ also in $(CD_3)_2SO$ yielded $Ru(3,3'-{}^2H_2bpy)_3{}^{2+}$; deuterium–hydrogen exchange occurs at all six 3,3′-positions of bpy. No further exchange at any other position was observed once exchange at the 3,3′-positions was complete. These observations favour a mechanism involving initial deprotonation of the complex in a conventional acid–base reaction. The suggestions above [1, 5] of nucleophilic attack by OH^- at the C-4 or C-4′ positions [1] to give the pseudo-base species *3* or *3′* do not accord with these observations, as attack at C-4 or C-4′ would also have led to complete deuterium– hydrogen exchange of the 5,5′-protons [10]. Interestingly, $Ru(phen)_3{}^{2+}$ and $Ru(4,4'-Me_2bpy)_3{}^{2+}$ undergo no H/D exchange under the conditions where $Ru(bpy)_3{}^{2+}$ undergoes exchange. Similar observations were reported earlier by Nord and Wernberg [5] on $Fe(phen)_3{}^{2+}$ in NaOD solutions. The effect of increased charge from M(II) to M(III) on these bpy and phen complexes is not known, but it is expected that $M(bpy)_3{}^{3+}$ and substituted derivatives show a greater reactivity towards deprotonation.

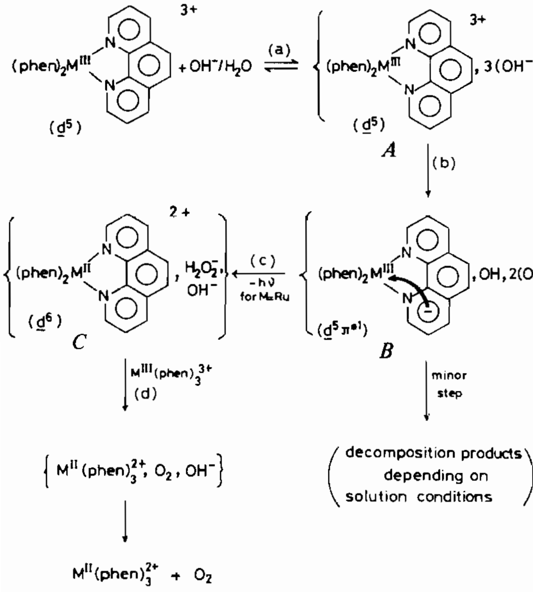
On this basis, reduction of $M(bpy)_3{}^{3+}$ (M = Ru, Fe, Os) by OH^- ions may occur (scheme 14) *via* initial deprotonation followed by formation of a bound ligand–anion radical (electron on ligand π^* orbitals) eventually collapsing to yield the reduced products $M(bpy)_3{}^{2+}$ and chemiluminescence for M = Ru. While scheme 14 has appeal, it fails to explain the greater reactivity of the phenanthroline complexes [5, 11] (Table I), and the existence of various species depending on pH [1] including degraded ligands [1, 8]. It must be remembered that, in contrast to bpy complexes in which the 3,3′-positions are positions of steric strain, the phen complexes are devoid of such positions.



(14)

We next consider a pathway involving outer-sphere complexes. The importance of this type of complexes as precursors in the reduction of $Ru(NN)_3{}^{3+}$ by $Fe(H_2O)_6{}^{2+}$ has been noted [12]. In this regard, iron(II)–polypyridine complexes are known to form strong, stable outer-sphere species with ClO_4^-, Cl^-, Br^-, I^-, and NO_3^-; iodide forms the complexes $(phen)_3Fe^{II}(I^-)_n$ for n = 1–4, while for the other anions n = 1–3 [13, 14]. Stability constants range from 2 M^{-1} for β_1 to 70 M^{-4} for β_4 [14], and appear to be dependent on ionic strength [15]. The greater charge in $M^{III}(NN)_3{}^{3+}$ should give stronger, more stable outer-sphere complexes. No doubt some of the unidentified substances reported by Creutz and Sutin [1] may be one or more of these complexes when the anion is OH^-. Our alternative pathway (scheme 15) for OH^- reduction of $M(NN)_3{}^{3+}$

is based on these outer-sphere complexes with hydroxide, and we assume that all events take place amonst the species within the solvent cage { }. This would preclude *free* radicals. For scheme 15, we use a phen complex and take it that the predominant outer-sphere complex is the neutral species in cage {*A*}, reminiscent of our findings in the system $Cr(terpy)_2^{3+}$–perchlorate anion [16] (terpy = 2,2′,2″-terpyridine), in which the three anions are wedged inside the interligand pockets. Johansson [14] has recognized that the phen complexes form stronger outer-sphere complexes with certain anions, and attributed this to stronger interactions between the anions and the π-electronic system of the phen ligand framework. In other words, OH^- and the phen π-electron system form a 'charge transfer species' which in step (b) gives a reduced phen ligand and a coupled •OH radical still interacting with the π system. The species in cage {*B*} is analogous to the metal-to-ligand-charge-transfer, MLCT, excited states ($d^5\pi^{*1}$) of $M(NN)_3^{2+}$ complexes which give chemiluminescence ($d^5\pi^{*1} \rightarrow d^6$) and the reduced product; in concert, •OH may also interact with OH^- ions



(15)

to give $H_2O_2^-$ (or $O^- + H_2O$ in cage {*C*}). Formation of dioxygen ensues [17]; decomposition products result from OH radical interactions with the polypyridine complex in {*B*}. Some aspects of scheme 15 are similar to reactions 11–13 but differ in detail. This pathway helps to understand the greater reactivity of $M(phen)_3^{3+}$ over $M(bpy)_3^{3+}$ complexes. Scheme 14 helps explain some recent findings [18] in the photochemistry of $Cr(bpy)_3^{3+}$ in 1.0 *M* OH^- aqueous media. Under certain conditions of light intensity, the quantum yield for the formation of $Cr(bpy)_2(OH)_2^+$ is >1, possibly implicating a labile chromium(II) species. It must be noted that the differences in reactivity of the phen complexes over the bpy complexes may also be explained by noting the possibility that the two different complexes react *via* different pathways.

Acknowledgements

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