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Thermal and Light-Induced Reduction of (+)-Tris(bipyridyl)ruthenium(III) in Aqueous Solution: Mechanistic Inferences from Optical Rotation Studies

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The thermal (pH 6.5) and light-induced (pH 2) reduction of (+)-$Ru(bpy)_3^{3+}$ (bpy = 2,2′-bipyridine) in aqueous solution proceeds with complete retention of optical activity. The present results, together with previous data on the stoichiometry and kinetics of these reactions, lend strong support to Creutz and Sutin's postulate of a pseudobase structure for the hydroxyl ion containing Ru(III) intermediate.

There is considerable interest in the reactivity of ML_3^{3+} (M = Fe, Ru, Ni; L = 2,2′-bipyridine, 1,10-phenanthroline) complexes in aqueous solution since oxidation of water to oxygen, with concomitant formation of ML_3^{2+}, is possible on the basis of energetic considerations.[1-4] The above reaction is crucial to the functioning of $ML_3^{3+/2+}$ as a catalyst in the light-driven conversion of water to hydrogen and oxygen. While simultaneous generation of H_2 and O_2 through such a process has so far not been possible—this is primarily due to mismatch of the various reaction rates——the application of this reaction to other photochemical systems of interest has been noted in the recent literature.[5-7]

The mechanism through which ML_3^{3+} reacts with water is also of some interest. In the absence of added catalysts, the reaction is complicated by the nonavailablity of a simple outer-sphere pathway for electron transfer from OH^-/H_2O to ML_3^{3+}. Formation of a reactive intermediate, resulting from the binding of OH^-/H_2O to the metal complex, is therefore implicated, but its exact identity has been the subject of much debate.[1,8-12] To a large extent, this controversy has arisen from the misplaced belief that the structure of this intermediate must be the same for all metal systems.[10] Such a belief has persisted despite the very different experimental observations reported by Ghosh et al.[8] and Nord et al.[9] for the RuL_3^{3+} and FeL_3^{3+} systems, respectively. We report here our optical rotation data on the uncatalyzed reduction of (+)-$Ru(bpy)_3^{3+}$ through thermal and photochemical routes. Our results provide further evidence in favor of the Ru(III) pseudobase formulation originally proposed by Creutz and Sutin[1] for this intermediate. We emphasize that our results and conclusions may not apply to the "analogous" FeL_3^{3+} system.

Experimental Section

$Ru(bpy)_3Cl_2{\cdot}2H_2O$ was synthesized from $RuCl_3$ and 2,2′-bipyridine (bpy). The enantiomers were resolved by the method of Dwyer and Gyarfas[13] and isolated as their perchlorate salts. All chemicals were of analytical grade, and triply distilled water was used throughout.

Optical rotation measurements on the hydroxyl ion induced reaction of (+)-$Ru(bpy)_3^{3+}$ were carried out as follows. A 65-mg sample of (+)-$Ru(bpy)_3(ClO_4)_2$ was dissolved in 40 mL of 0.01 M H_2SO_4. A portion of this solution served as control while the remaining amount (35 mL) was treated with PbO_2. Centrifugation of the product mixture yielded a clear green solution of $Ru(bpy)_3^{3+}$, equal volumes (5 mL) of which were then placed in each of six vials. Next, the spontaneous reaction of $Ru(bpy)_3^{3+}$ with OH^-/H_2O was carried out under thermal (pH 6.5, 9, 11, and 13) and photochemical (pH 2) conditions, while outer-sphere reduction of the complex was accomplished with Fe^{2+} ions as reductant (pH 2). The Ru concentration was the same in all solutions.

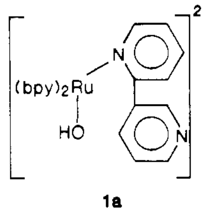
α (optical rotation) values of the above solutions were recorded at the sodium D line on a Model DIP-140 JASCO digital polarimeter, while UV–vis spectra were recorded on a Model SP8-100 Pye-Unicam spectrophotometer.

Results and Discussion

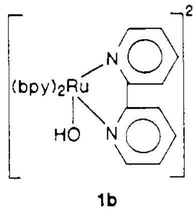
The reduction of $Ru(bpy)_3^{3+}$ in water is a complex reaction, as has been shown recently by Ghosh et al.[8] Neither H_2O_2 nor O_2 is produced in the absence of added catalysts. Instead, reaction of $Ru(bpy)_3^{3+}$ over the entire pH range (0–12) yields predominantly $Ru(bpy)_3^{2+}$, traces of CO_2, and small amounts of Ru(II) complexes containing bpy and oxidized bpy. The product profile is similar for the photochemical pathway, for which an accelerated reduction rate is observed upon excitation of the ligand-to-metal charge-transfer transition (LMCT) of $Ru(bpy)_3^{3+}$. The stoichiometry for both processes, i.e. thermal and photochemical, can be approximately represented by eq 1, where n = 15–20 and m < 1. $Ru(bpy)_2(bpy')^{2+}$ represents all Ru(II)-containing degradation products, comprising 5–8% of initial Ru(III). Equation 1 can be viewed as a disproportionation reaction, wherein 5–8% of the Ru(III) complex ions—which are initially converted to the reactive intermediate **1**—undergo extensive oxidative degradation, thereby providing the electrons necessary to reduce the remaining fraction (92–95%) of $Ru(bpy)_3^{3+}$. Such a process can occur through a series of energetically favorable, hydroxyl ion induced outer-sphere reactions as outlined in the paper by Ghosh et al.[8]

$$\underset{\mathbf{1}}{Ru(bpy)_3OH^{2+}} + nRu(bpy)_3^{3+} \xrightarrow{OH^-} nRu(bpy)_3^{2+} + mCO_2 + Ru(bpy)_2(bpy')^{2+} \quad (1)$$

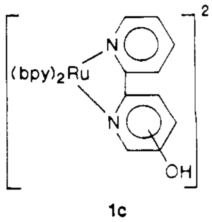
Three possible structures (**1a–c**) can be proposed for the intermediate **1**. **1a** corresponds to –OH coordination at the metal



1a



1b



1c

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center following cleavage of a Ru–N bond. The seven-coordinate intermediate **1b** is formed through OH^- attack at the metal center of $Ru(bpy)_3^{3+}$.[10] In contrast, the metal coordination sphere remains unperturbed in **1c**, the site of OH^- coordination being a bipyridine carbon. Previous studies indicate that 5- and 7-coordinate complexes undergo facile racemization. For example, Porter has observed that $Ru(bpy)_3^{2+}$ photoracemizes in acidic solution following cleavage of a Ru–N bond,[14,15] while Kepert has noted that such compounds can also racemize readily through solvent coordination at the metal center,[16] since the activation energy for racemization of such a species is less than 2% of that computed for the Bailar twist. Kepert's theoretical results are borne out by the work of Busch and co-workers,[17] who have reported the base-catalyzed racemization of $Co(edta)^-$, a process presumably involving a 7-coordinate intermediate formed as a result of OH^- attack on Co(III). Thus, while in acid solution at 100 °C the rate constant for racemization is 4.2×10^{-6} s^{-1}, the second-order rate constant for racemization in basic solution (first-order dependence on OH^-) at 35 °C is 0.53 M^{-1} s^{-1}. Further, it may be noted that the above racemization rate is limited by the rate of the first step, namely OH^- attack on Co(III). The above results therefore suggest that formation of **1a** or **1b** may lead to significant racemization of the complex. Evidence for such racemization may be sought in the Ru(II)-containing side products derived from **1**.

From eq 1, and the discussion above, it is evident that 92–95% of $Ru(bpy)_3^{3+}$ is reduced to Ru(II) through outer-sphere electron-transfer reactions. Since such processes involve no racemization of the metal center, it is anticipated that this fraction of $Ru(bpy)_3^{3+}$ would retain its stereochemistry at the end of the reaction.[18] Consequently, for experiments with optically active $Ru(bpy)_3^{3+}$, a minimum of 92–95% of the initial optical activity would be retained in the product mixture, irrespective of the nature of **1**. However, retention of optical activity beyond this value would shed light on the structure of the Ru(II)-containing side products formed in this reaction. For example, complete retention of optical activity in the product mixture would imply that the stereochemistry of the side products, and by inference **1**, is fully conserved in this reaction. Such an observation would lend strong support to the pseudobase formulation for **1** proposed by Creutz and Sutin.[1] It is with this objective in view that we have carried out the optical rotation studies outlined below. We note that the complex stoichiometry of this reaction was not taken into account in the previous work by Gillard and co-workers on the reduction of optically active RuL_3^{3+}.[19] These authors had assumed that reduction of RuL_3^{3+} proceeds with concomitant formation of H_2O_2. Accordingly, an oversimplistic mechanism for this reaction was proposed.

Table I lists α (optical rotation) values recorded for (+)-$Ru(bpy)_3^{2+}$ and for product mixtures formed from the reaction of (+)-$Ru(bpy)_3^{3+}$ with (i) Fe^{2+} and (ii) OH^-/H_2O (note that the Ru(II) concentration is the same in all solutions and that the maximum error in the α values is ±0.002°). Reduction of (+)-$Ru(bpy)_3^{3+}$ via the photochemical pathway was carried out at pH 2 while the base-induced thermal reduction was studied over the range pH 6–13. It can be seen from the table that reduction of $Ru(bpy)_3^{3+}$ with Fe^{2+} regenerates $Ru(bpy)_3^{2+}$, with complete retention of stereochemistry (compare entries 1 and 2). Thus no racemization of (+)-$Ru(bpy)_3^{3+}$ (in 0.01 M H_2SO_4) is observed during the time period (~30 min) required to conduct the above set of experiments.[20] More importantly however, the thermal and light-induced reactions of (+)-$Ru(bpy)_3^{3+}$ at pH 6.5 and 2, respectively, also proceed with complete retention of optical activity (entries 3 and 4). However, ~3% loss of optical activity is observed for reactions carried out at pH 9, 11, and 13 (entries 5, 6, and 7). While interpretation of the high-pH results is more complex,[21] the data for photochemical reduction at pH 2 and thermal reduction at pH 6.5 indicates that the Ru(II)-containing side products are not racemized during the reaction. Furthermore, the specific rotation of these products must also be similar to that of (+)-$Ru(bpy)_3^{2+}$. The important point that emerges from this study is that the Ru coordination sphere remains unperturbed in **1**, and in products derived from **1**. Thus we assign **1c** as the most reasonable structure for the intermediate **1**.

Table I. α (Optical Rotation) Values of Product Mixtures Formed from the Reduction of (+)-$Ru(bpy)_3^{3+}$ in Aqueous Solution[a]

no.	reductant	final pH	α,[b] deg	% retention[c]
1		2	0.410[d]	
2	Fe^{2+}	2	0.409	99.7
3	OH^-/H_2O	2	0.407[e]	99.2
4	OH^-/H_2O	6.5	0.410	100.0
5	OH^-/H_2O	9	0.397	96.8
6	OH^-/H_2O	11	0.400	97.5
7	OH^-/H_2O	13	0.398	97.0

[a] The Ru concentration is the same in all solutions. [b] The maximum error in α values is ±0.002°. [c] The maximum error in the computed values is ±0.5%. [d] (+)-$Ru(bpy)_3^{3+}$ not subjected to any redox transformation. [e] Light-induced reduction.

While the present results argue in support of **1c** as the structure of the primary intermediate, the other possible structures, in particular **1b**,[10] cannot be ruled out on the basis of this evidence alone. However, when taken together with the previous data,[8] the arguments in favor of the pseudobase formulation[1,8] are indeed compelling. We reiterate here the other evidences in its favor. First, the rate enhancement observed upon excitation of the LMCT mode suggests that the site of nucleophilic OH^-/H_2O attack is most likely a bipyridine carbon, and *not* the metal center.[22] Second, unlike the FeL_3^{3+} case,[9] neither any free bpyO (bpyO = bipyridine *N*-oxide) nor any Ru-coordinated bpyO is found in the product mixture. Third, the spectroscopic and electrochemical properties of some side products are virtually the same as those of $Ru(bpy)_3^{2+}$, and the few differences observed reflect minor modifications of the bipyridine rings in these products. Fourth, $Ru(bpy)_3^{3+}$ reduction at high pH leads to weak chemiluminescence, presumably arising from OH^- attack at a coordinated bpy followed by intramolecular electron transfer from ligand to metal.

Conclusion

Optical rotation data for (+)-$Ru(bpy)_3^{3+}$ reduction in aqueous solution indicates that the product mixtures retain complete optical activity when the reactions are carried out thermally at pH 6.5 and photochemically at pH 2. These results can be best understood in terms of a pseudobase formulation for the intermediate **1**. Finally, we note that optical rotation studies on the analogous $Ru(phen)_3^{3+}$ (phen = 1,10-phenanthroline) system yielded similar results.

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(21) Loss of optical activity in the high-pH experiments could arise from partial racemization of intermediates and/or formation of heavily degraded side products.

(22) Intermediate **1b** has been recently proposed by Lay and Sasse.[10] We note, however, that the reversibility, and kinetic implications, of the hydroxide addition step (to yield **1b**), have not been adequately considered by these authors.