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Radiolytically-induced Outer-sphere Oxidation of Tris(2,2′-bipyridine)ruthenium(II) Ion in LiCl–H_2O Solutions

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The tris(2,2′-bipyridine)ruthenium(II) complex, $Ru(bpy)_3^{2+}$, has been the object of much attention as a prototype of a species that can mediate the conversion of light into chemical or electrical energy [1] (Light Absorption Sensitizer, LAS [2]), and the conversion of chemical or electrical energy into light [3] (Light Emission Sensitizer, LES [2]). The ability to engage in reversible one-electron oxidation and/or reduction is one of the fundamental requirements of an LAS or an LES. The redox behavior of a molecule can be conveniently studied by radiolysis. Under the usual radiolysis conditions of dilute aqueous solutions, it is easy to obtain the one-electron reduction product, $Ru(bpy)_3^{+}$, from $Ru(bpy)_3^{2+}$ [4]. In contrast, the one-electron oxidation product, $Ru(bpy)_3^{3+}$, has not been obtained in radiolysis [5] because the radiolytically-generated oxidative species in dilute aqueous solution (OH radical) adds to the aromatic ligands rather than oxidizing the metal center. We have found that one-electron oxidation of $Ru(bpy)_3^{2+}$ occurs upon the radiolysis of aqueous solutions that contain a large amount of LiCl. We report here a preliminary account of the results obtained on this system by continuous and pulse radiolysis experiments.

Experimental

$Ru(bpy)_3Cl_2 \cdot 5H_2O$ (C. Erba) was used as received. LiCl (Merck) was purified as follows. LiCl saturated aqueous solutions were refluxed in air for one day and, after cooling at room temperature, filtered with a Millipore apparatus (filter type HA, 0.45 μm). The middle 80% of the salt obtained by evaporation of these solutions ($LiCl \cdot H_2O$) was used. All other materials were analytical grade reagents.

Continuous radiolyses were performed using a ^{60}Co-Gammacell (Atomic Energy Canada, Ltd.) delivering a dose of *ca.* 8 Gy min^{-1}. Pulse radiolyses were performed using a 12 MeV linear accelerator coupled with an optical fast detection apparatus.

Results and Discussion

In agreement with Creutz and Sutin [5], we have found that irradiation of N_2O-saturated aqueous solutions of $Ru(bpy)_3^{2+}$ does not result in the oxidation of $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{3+}$, but leads, via OH attack, to Ru(II) species containing modified bpy ligands. The spectrum of the OH-adduct, determined by pulse radiolysis, is independent of pH (3–7) and shows a characteristic band at 760 nm ($\epsilon = 1800$ M^{-1} cm^{-1}) arising from the addition of OH to coordinated bipyridine [5]. The bimolecular rate constant for the formation of the OH-adduct is $k = (7.0 \pm 0.7) \times 10^9$ M^{-1} s^{-1}. In contrast, the continuous irradiation of a N_2O-saturated solution containing 8.0 M LiCl, 1.0 mM HCl, and 0.11 mM $Ru(bpy)_3^{2+}$, caused spectral changes clearly showing that the oxidation of $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{3+}$ took place. Specifically, the band at 450 nm was seen to decrease (Fig. 1) and the characteristic com-

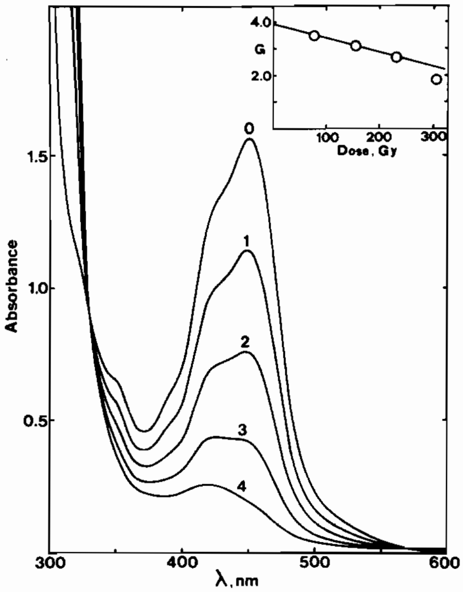

Fig. 1. Spectral changes observed in the continuous radiolysis of a N_2O-saturated solution containing 0.11 mM $Ru(bpy)_3^{2+}$, 1.0 mM HCl, and 8.0 M LiCl. Optical path = 1.0 cm; dose = 8.1 Gy min^{-1}. 0, spectrum of the unirradiated solution; 1–4, spectra obtained after successive 9.3 min irradiations. Inset shows, in terms of G-units, the yield of conversion of Ru(II) into Ru(III) (calculated assuming $\Delta\epsilon = 13\,000$ M^{-1} cm^{-1} at 450 nm) as a function of irradiation dose.

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posite band of $Ru(bpy)_3{}^{3+}$ in the 300–320 nm region (not shown in Fig. 1) was formed [6]. Under the experimental conditions used, $Ru(bpy)_3{}^{3+}$ was moderately stable; however, when the irradiated solution was made alkaline by the addition of NaOH, the absorption spectrum reproduced (within a few percent) that of the original $Ru(bpy)_3{}^{2+}$ solution. The yield of conversion of $Ru(bpy)_3{}^{2+}$ to $Ru(bpy)_3{}^{3+}$ was a function of the LiCl, $Ru(bpy)_3{}^{2+}$, and HCl concentrations and, as shown in the inset of Fig. 1, of irradiation dose.

In the pulse radiolysis experiments, the well known [7] absorption spectrum of the Cl_2^- radical ($\lambda = 340$ nm, $\epsilon = 8800\ M^{-1}\ cm^{-1}$) was obtained with N_2O-saturated aqueous solutions containing 1.0 mM HCl and 8.0 M LiCl. Under these conditions the disappearance of the Cl_2^- radical was second-order with $2k = (3.4 \pm 0.1) \times 10^9\ M^{-1}\ s^{-1}$. When $Ru(bpy)_3{}^{2+}$ was also present in the irradiated solution, the Cl_2^- absorption was again observed (note the window in the 350–400 nm region in the $Ru(bpy)_3{}^{2+}$ spectrum, Fig. 1); however, now the disappearance of the absorption at 340 nm was faster and essentially first-order with k_{obs} increasing linearly with increasing $[Ru(bpy)_3{}^{2+}]$ according to $k_{obs} = k_0 + k[Ru(bpy)_3{}^{2+}]$, where $k_0 = 6 \times 10^3\ s^{-1}$ and $k = 1.6 \times 10^9\ M^{-1}\ s^{-1}$. Bleaching of the 450 nm band of $Ru(bpy)_3{}^{2+}$ was also observed, and the values of k_{obs} thus obtained were similar to those obtained at 340 nm.

These results are consistent with the mechanism described by reactions 1–5, where the Cl_2^- radicals formed by oxidation of Cl^- by OH radicals (eqns. (1–3)) [7]* oxidize $Ru(bpy)_3{}^{2+}$ in an outer-sphere one-electron reaction (eqn. (4)) in competition with their disproportionation (eqn. (5)):

$$Cl^- + OH \rightleftharpoons ClOH^- \tag{1}$$

$$ClOH^- + H^+ \rightleftharpoons Cl + H_2O \tag{2}$$

$$Cl + Cl^- \rightleftharpoons Cl_2^- \tag{3}$$

$$Ru(bpy)_3{}^{2+} + Cl_2^- \longrightarrow Ru(bpy)_3{}^{3+} + 2Cl^- \tag{4}$$

$$Cl_2^- + Cl_2^- \longrightarrow Cl_2 + 2Cl^- \tag{5}$$

The decrease of the yield of $Ru(bpy)_3{}^{3+}$ with increasing irradiation dose indicates that $Ru(bpy)_3{}^{3+}$ competes with $Ru(bpy)_3{}^{2+}$ for Cl_2^- radicals (eqn. (6)). Reaction in eqns. (4) and (6) are in fact both thermodynamically allowed since $E^0(Ru(bpy)_3{}^{3+}/Ru(bpy)_3{}^{2+}) = 1.26$ V [1a], $E^0(Cl_2^-/2Cl^-) = 2.3$ V [9], and E^0-$Cl_2/Cl_2^-) = 0.6$ V [9]. An equivalent mechanism has been used to explain the reactions of the tris(2,2′-bipyridine) complexes of Os(II) and Os(III) with the I_2^- and $(SCN)_2^-$ anions [10].

$$Ru(bpy)_3{}^{3+} + Cl_2^- \longrightarrow Ru(bpy)_3{}^{2+} + Cl_2 \tag{6}$$

Preliminary experiments with solutions containing different concentrations of LiCl and HCl have shown that high LiCl concentrations are a strict requirement in order to obtain a high yield of conversion of $Ru(bpy)_3{}^{2+}$ to $Ru(bpy)_3{}^{3+}$ and that this system is very sensitive to the medium conditions. The details of the mechanism are under investigation and will be reported elsewhere.

The results obtained may open new perspectives in the study of redox processes of polypyridine-type complexes; they also confirm one of the mechanisms proposed to account for the enhancement of observed lyoluminescence when γ-irradiated alkali halides are dissolved in aqueous solutions containing $Ru(bpy)_3{}^{2+}$ [3c].

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*Cl_2^- radicals and related oxidizing species are also expected to be formed via direct effect of the ionizing radiation on LiCl [8].