

# Kinetics and mechanism of the photooxidation of bis(bipyridine)dichlororuthenium(II) and the photoreduction of bis(bipyridine)dichlororuthenium(III) in chloroform

Sathiyabalar, S.<sup>ab</sup> and Hoggard, P.E.<sup>ac</sup>

<sup>a</sup> Department of Chemistry, North Dakota State University, Fargo, ND 58105, United States

<sup>b</sup> Department of Chemistry, University of Jaffna, Jaffna, Sri Lanka

<sup>c</sup> Department of Chemistry, Santa Clara University, Santa Clara, CA 95053, United States

## Abstract

In air-saturated  $\text{CHCl}_3$  irradiation of  $[\text{Ru}(\text{bpy})_2\text{Cl}_2]^{0/+}$  (bpy = 2,2'-bipyridine) with the full UV output of a 200-W mercury lamp converted the Ru(II) complex completely to Ru(III) at or below  $58^\circ\text{C}$ , and converted the Ru(III) complex completely to Ru(II) at or above  $60^\circ\text{C}$ . No thermal reaction occurred in either direction. The photooxidation takes place through a radical chain mechanism initiated by absorption of light by chloroform followed by C-Cl bond homolysis. This leads to the formation of trichloromethylperoxy radicals, each of which can cause the oxidation of two molecules of  $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ . The mechanism proposed is consistent with the experimental rate law,  $d[\text{Ru}(\text{III})]/dt = a[\text{Ru}(\text{II})]^{1/2}$ . The photoreduction in deoxygenated solution takes place through direct excitation of  $[\text{Ru}(\text{bpy})_2\text{Cl}_2]^+$ , which then oxidizes  $\text{Cl}^-$  to Cl atoms. Because of its short lifetime, only the Ru(III) complexes that are ion-paired with chloride ion can react.