

Complete suppression of back-reaction in strongly acidic media for photochemically active Ru(bp)₃²⁺-O₂ system

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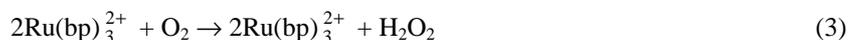
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Oxygen is one of the few molecules which effectively quench Ru(bp)₃²⁺ (bp: 2,2'-bipyridyl; $k_q = 3.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} = k_{CT} + k_{eT}$ where CT is charge transfer and eT is energy transfer). In this paper, we describe a non-sacrificial system, Ru(bp)₃²⁺ and H₂O₂ formation. This is achieved by efficient suppression of the back reaction between Ru(bp)₃³⁺ and O₂^{*-}, using a proton trap for O₂^{*-}-Ru(bp)₃²⁺-Ru(bp)₃³⁺ cycle in 7 or 9 M H₂SO₄, which is found to be completely reversible when photooxidation is followed by electrolytic reduction. Luminescence studies show that presence of O₂ causes 30% quenching of luminescence intensity in 9M H₂SO₄. Quantum yield measurements reveal that ~27 molecules of Ru(bp)₃²⁺ are formed for every 100 photons absorbed. This suggests that almost 100% of the forward reaction leads to irreversible product formation, i.e. Ru(bp)₃²⁺ and H₂O₂, following the mechanistic path 1 and 2.



Transient difference absorption spectra were also recorded for this system and the results correspond nicely to our steady-state luminescence data, i.e. disappearance of ^{*}Ru(bp)₃²⁺ is practically equal to the chemical quantum yield for Ru(bp)₃³⁺ formation. The back reaction for this system was also studied in dark and the equilibrium constant for (3) was calculated to be 0.21 in 7 M H₂SO₄.



This equilibrium is shifted entirely to the left at pH 7, suggestive of very pronounced cell potential change at low pH which remains to be fully understood.