



ISSN 2248-9649

International Journal of
Research in Chemistry and Environment

Available online at: www.ijrce.org



Research Paper

Effect of Oxygen on Photoinduced Electron Transfer Reactions of Ru(II) Polypyridyl Complex with Quinones in 50% Aqueous Acetonitrile and Aqueous Medium

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(Received 03rd December 2018, Accepted 25th December 2018)

Abstract: Photoinduced electron transfer reactions of $[Ru(dmbpy)_3]^{2+}$ complex with quinones in 50% acetonitrile and aqueous medium were studied. The complex shows an absorption maximum at 459 nm in 50% aqueous acetonitrile medium and an emission maximum at 605 nm. Emission spectrum were taken for aerated and deaerated sample solutions. The quenching rate constant k_q depends on the nature of the quencher, ligand and also on the nature of the solvent used. Stern-Volmer analysis has been used to find out the quenching rate constant. The results show that molecular oxygen plays an important role with the excited state of the $[Ru(dmbpy)_3]^{2+}$.

Keywords: quenchers, Stern-Volmer analysis, luminescence quenching, photophysics.

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Introduction

Luminescent d^6 transition metal complexes like Ru(II) complexes have been studied due to their photophysical and photochemical properties¹⁻⁷. The excited state properties of $[Ru(NN)_3]^{2+}$ complexes are dramatically affected by the introduction of electron-donating, and electron-withdrawing substituents in 4,4' position of 2,2' bipyridine⁸⁻¹². The rate of electron transfer (ET) from a donor to an acceptor is influenced by the ET distance¹³⁻¹⁵ reorganizational energy, nature of the quencher, ligand. Quinones are ubiquitous in nature and they act as good electron acceptors. Ru(II) complexes have been used to catalyze both oxidation and reduction processes under visible light irradiation. This light sensitizing nature of Ruthenium compounds have been used as chemosensors and they are used for the production of singlet molecular oxygen¹⁶. Many experiments have been carried out to understand the factors that affect the photoinduced electron transfer reactions. In particular the study of ET reaction from quinones (donor) to a d^6 metal complex (acceptor) is of great interest due to its wide application. The present study concentrates on the photoinduced electron transfer reaction of $[Ru(dmbpy)_3]^{2+}$ with different

quinones in the absence and presence of molecular oxygen in aqueous and 50% acetonitrile medium.

Material and Methods

All chemical $RuCl_3 \cdot 3H_2O$, 4,4'-dimethyl-2,2'-bipyridine and the quinones used in this present study were purchased from Sigma Aldrich and used as received. $[Ru(dmbpy)_3]^{2+}$ complex was synthesized from known procedure¹⁷. $RuCl_3 \cdot 3H_2O$ and 4,4'-dimethyl-2,2'-bipyridine were dissolved in 20 ml of ethylene glycol and refluxed for 4 h. The solution was allowed to cool at room temperature and filtered to remove insoluble impurities. A saturated solution of sodium tetrafluoroborate was then added drop wise into the filtrate until an orange precipitate formed. The product was filtered, washed with cold water and diethyl ether and further dried in a vacuum desiccator and characterized by IR, UV, ¹H NMR spectra.

Absorption and Emission spectral measurements

Sample solutions of $[Ru(dmbpy)_3]^{2+}$ and quinones were freshly prepared for each measurement. The $[Ru(dmbpy)_3]^{2+}$ concentration were taken as $2 \times 10^{-5}M$ and the concentration of quinones was varied between $4 \times 10^{-5}M$ and $2.8 \times 10^{-6}M$. Absorption and emission

studies were carried out using the samples of same concentration. Absorption spectrum was recorded using Systronics Double Beam UV Visible Spectrophotometer 2203. Emission Spectrum was carried out using JASCO FP 8600 Spectrofluorometer. All the sample solutions used for emission measurements were deaerated for approx 30 minutes using dry N₂ gas purging by keeping the solution in cold water, to ensure that there is no change in the volume of the solution. Emission measurements were also carried out for the sample in presence of oxygen (ie without passing N₂). All the measurements were carried out at room temperature.

Determination of luminescence quenching constant k_q

The quenching rate constant k_q for the oxidative quenching of [Ru(dmbpy)₃]²⁺ with quinones was obtained from the Stern-Volmer plots using eq. (1)

$$\frac{I_0}{I} = 1 + k_{sv}[Q] \quad (1)$$

$$k_{sv} = k_q \tau_0$$

where K_{sv} , k_q , τ_0 are the Stern-Volmer constant, quenching constant and excited state lifetime respectively. The plot of I_0/I vs $[Q]$ is a straight line with an intercept of unity for all the quinones.

Results and Discussion

The structure of complex and quenchers used in the present study are shown in figure 1

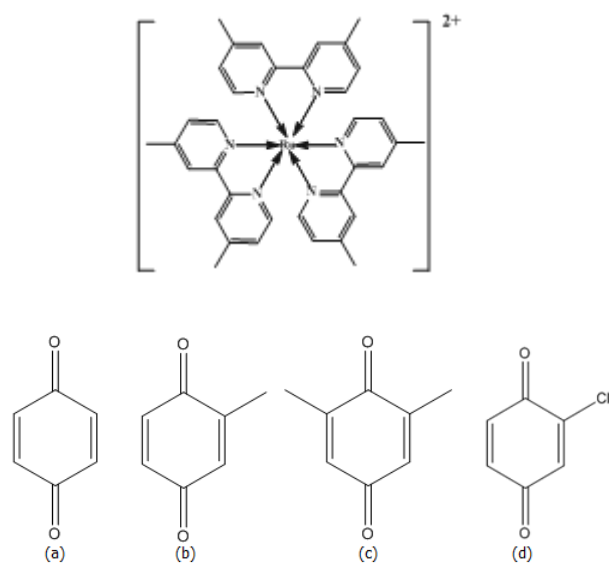


Figure 1: Structure of [Ru(dmbpy)₃]²⁺ complex and Quenchers (a) 1,4-benzoquinone (b) 2-methyl-1,4-benzoquinone (c) 2,6-dimethyl-1,4-benzoquinone (d) 2-chloro-1,4-benzoquinone

The absorption and emission spectrum of [Ru(dmbpy)₃]²⁺ complex in 50% acetonitrile and

aqueous medium were recorded and are summarized in Table 1. The complex shows a ligand Centred (LC) absorption peak of high energy at 284 nm which is due to the promotion of electron from π_L to π_L^* and a metal to ligand charge transfer (MLCT) peak at 458 nm. The weak shoulder around 324 nm corresponds to the metal centered (MC) transition from t_{2g} to e_g . The complex [Ru(bpy)₃]²⁺ has the emission maximum at 605 nm (Figure.3)

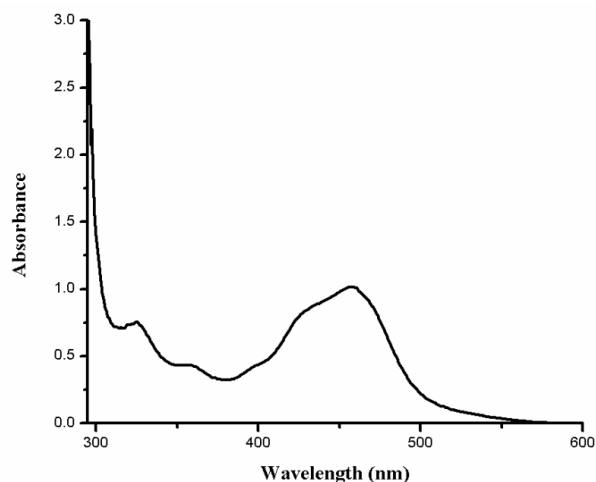


Figure 2: Absorption spectrum of [Ru(dmbpy)₃]²⁺ complex in 50% aqueous acetonitrile medium at room temperature

Table 1: Photophysical analytical data for [Ru(dmbpy)₃]²⁺ complex in 50% acetonitrile and aqueous medium

Medium	Absorption (nm)	Emission (nm)	Lifetime (ns)*
50% acetonitrile	458	605	580
aqueous	458	605	380

*taken from the published report¹⁸

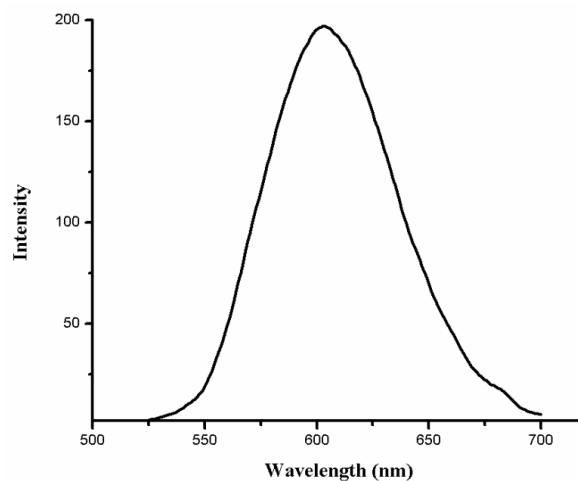


Figure 3: Emission spectrum of [Ru(dmbpy)₃]²⁺ with 2-methyl-1,4-benzoquinone in 50% aqueous acetonitrile medium

The change in the luminescence intensity of the excited state of $[\text{Ru}(\text{dmbpy})_3]^{2+}$ with incremental addition of 2-chloro-1,4-benzoquinone in 50% acetonitrile is shown in figure 3.

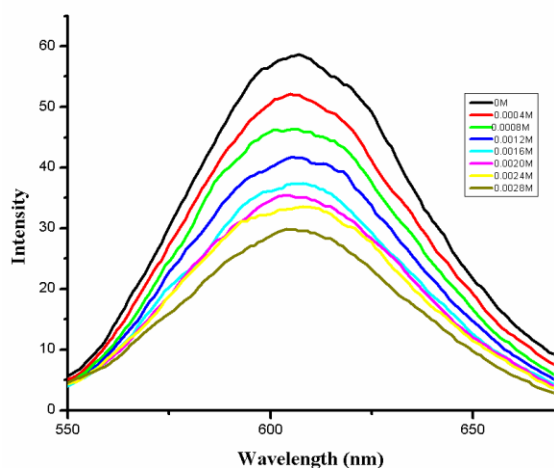


Figure 4: Emission spectrum of $[\text{Ru}(\text{dmbpy})_3]^{2+}$ with incremental addition of chloro 1,4-benzoquinone

The Stern-Volmer plot of $[\text{Ru}(\text{dmbpy})_3]^{2+}$ with different concentrations of chloro-1,4-benzoquinone in aerated aqueous solution at 298K is shown in Figure 5.

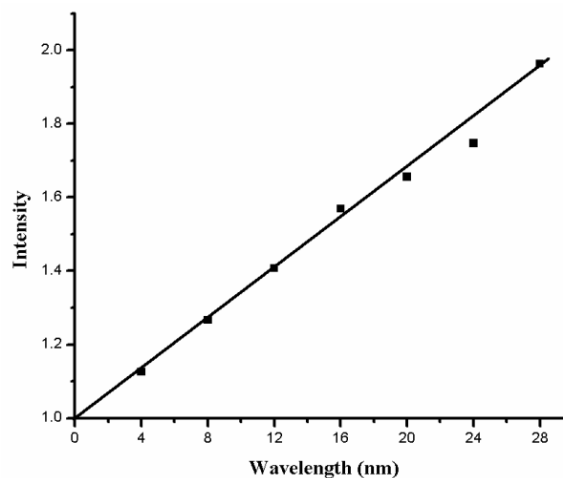


Figure 5: Stern-Volmer plot of $[\text{Ru}(\text{dmbpy})_3]^{2+}$ with different concentrations of 2-chloro-1,4-benzoquinone in aerated aqueous solution at 298K

Table 2: Rate constants for the oxidative quenching of $^*[\text{Ru}(\text{dmbpy})_3]^{2+}$ in aerated and deaerated 50% aqueous acetonitrile and aqueous medium (9:1 water: acetonitrile v/v)

Quencher	50% aqueous acetonitrile		Aqueous (9:1 water: acetonitrile (v/v))	
	k_q ($\text{M}^{-1}\text{s}^{-1}$)			
	deaerated	aerated	deaerated	aerated
1,4-benzoquinone	1.229×10^{10}	2.908×10^9	1.45×10^{10}	5.22×10^9
2-methyl-1,4-benzoquinone	1.113×10^{10}	2.831×10^9	1.56×10^{10}	5.657×10^9
2,6-dimethyl-1,4-benzoquinone	6.917×10^9	3.756×10^9	1.171×10^{10}	9.565×10^9
2-chloro-1,4-benzoquinone	1.077×10^{10}	1.427×10^9	5.55×10^9	9.230×10^9

The quenching rate constant, k_q for the excited state electron transfer reaction of $[\text{Ru}(\text{dmbpy})_3]^{2+}$ with various quinones have been tabulated in table 2 in presence and absence of dissolved oxygen. From the table we infer that all the quinones quench the excited state of $[\text{Ru}(\text{dmbpy})_3]^{2+}$ efficiently. Dissolved oxygen quenches the excited state complex effectively. In presence of molecular oxygen, the intensity of quenching decreases widely. The k_q value varies from $1.427 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ to $3.756 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ in 50% aqueous acetonitrile in presence of dissolved oxygen. In aerated aqueous solution the k_q value varies from $5.22 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ to $9.595 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$.

The quenching rate can be explained in terms of the potential of the quinones. Both electronic and steric effect plays an important role in the oxidative quenching of the excited state of $[\text{Ru}(\text{dmbpy})_3]^{2+}$. The quenching rate constant also depend on the electron transfer distance between the luminophore and the

quencher. Quenching rate constant decreases with the increase in size of the quencher.

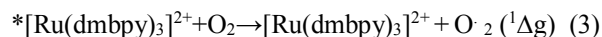
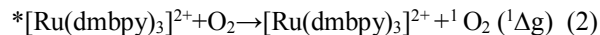
Comparing the k_q value, 2-methyl-1,4-benzoquinone has $1.113 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ whereas the bulkier quencher 2,6-dimethyl-1,4-benzoquinone has a value of $6.917 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. The quenching rate constant value increases in aqueous aerated sample compared to the sample in 50% aqueous acetonitrile.

A close scrutiny of the table 2 shows that the k_q value for the excited state electron transfer between $[\text{Ru}(\text{dmbpy})_3]^{2+}$ and quinones in deaerated sample prove the efficient interacting mechanism of oxygen with the excited state of $[\text{Ru}(\text{dmbpy})_3]^{2+}$.

Photochemical oxidation of $[\text{Ru}(\text{dmbpy})_3]^{2+}$ using molecular oxygen

Molecular oxygen exhibits a high efficiency towards the quenching of the excited state of the complex*

[Ru(dmbpy)₃]²⁺ in aqueous solution. The quenching of *[Ru(dmbpy)₃]²⁺ by molecular oxygen occurs by two mechanisms. One is energy transfer (eq. 2) quenching generating the ground state sensitizer and singlet oxygen. The other mechanism is electron transfer (ET) quenching (eq. 3) generating the oxidized Ru complex and super oxide radical anion.



These data show that energy transfer is thermodynamically the preferred pathway¹⁹. A similar trend occurs in our case also. The variations in quenching rate constant prove the effective role of molecular oxygen in quenching pathway. In all the experiments molecular oxygen is not purged into the

samples as molecular nitrogen. The dissolved oxygen itself was more sufficient to quench the excited states of the Ru polypyridyl complex.

Conclusion

The ruthenium polypyridyl complex has been prepared from the literature. They were characterized by both UV-Vis and fluorescence techniques. The excited state behavior of the complex were studied in presence and absence of molecular oxygen. The quenching of the excited state was finely enhanced by the presence of molecular oxygen. The role of oxygen in this quenching may be due to the production of either singlet oxygen or superoxide radical anion.

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