

## Diffusive and Non-diffusive Luminescence Quenching Via Electron - Transfer from $\text{Ru}(\text{bpy})_3^{2+*}$ to $\text{Fe}^{3+}$ in Fluid Media

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**Summary:** Luminescence of  $\text{Ru}(\text{bpy})_3^{2+*}$  in 1-alkanols is quenched via electron-transfer to the added quencher,  $\text{Fe}^{3+}$ . In lower alcohols (methanol to 1-propanol) quenching is diffusive with respect to the reactants mobility. In higher alcohols quenching measurements are interpreted as indicating non-diffusive electron-transfer over distances up to  $30 \text{ \AA}$ .

### Introduction

This communication reports the luminescence quenching of  $\text{Ru}(\text{bpy})_3^{2+*}$  via electron transfer to  $\text{Fe}^{3+}$  in normal alcohols (1-alkanols). In alcohols higher than 1-propanol our results indicate long-range ( $30 \text{ \AA}$ ) electron-transfers which are non-diffusive in so far as kinetic mobility of the reaction is concerned (Fig. 1). In addition, photoinduced electron transfer involving diffusive encounters between redox partners in lower alcohols (methanol to 1-propanol) are also reported (Fig. 2).

Thermally activated electron transfers (ET) over long distances are well characterized [1,2]. However, only a few reports concerning the photoinduced long-range electron transfer (PILRET) in rigid media are available [3-5]. Importantly, to the best of our knowledge PILRET in fluid media are as yet unknown and are the subject of this report.

The electron-transfer quenching (eq. 1) of the luminescent state of  $\text{Ru}(\text{bpy})_3^{2+*}$  is well known [6].



We used 1-alkanols to study the environmental effects on this reaction. Procurement and purification of 1-alkanols is reported elsewhere [7].  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  (Strem Chemicals) and Ferric perchlorate (K & K Chemicals) were used as received.

In alcohols higher than 1-propanol  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  dissolves rather very slowly over a period of a week to give a clear solution. We

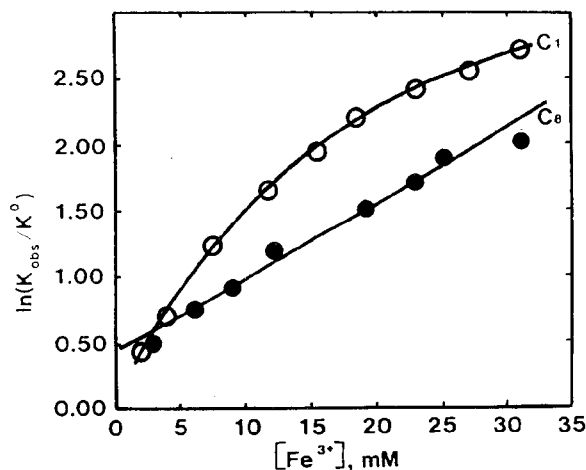


Fig. 1: Variation of  $\ln(k_{\text{obs}}/k^0)$  of the emission quenching of  $\text{Ru}(\text{bpy})_3^{2+*}$  by  $\text{Fe}^{3+}$  in 1-octanol (C8) and methanol (C1) at room temperature ( $22^\circ\text{C}$ ). In 1-butanol and 1-hexanol plots similar to C8 are obtained.

preferred slow dissolution in the dark and opted not to hasten this process by heating. On the other hand solubility of ferric perchlorate does not pose any problems and it is easily soluble in all the alcohols. Solutions of  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  ( $\approx 5 \times 10^{-5} \text{ M}$ ) were used to prepare 0.1 M stocks of the quencher. In each alcohol about 8-10 sample solutions of the quencher were prepared. In a particular alcohol the samples were prepared by diluting an appropriate volume of the quencher stock to 5 ml using a  $5 \times 10^{-5} \text{ M}$   $\text{Ru}(\text{bpy})_3\text{Cl}_2$  solution in that alcohol as dilution medium. Samples were *in situ* deaerated using high purity nitrogen. All solutions containing quencher were prepared just prior to their use in kinetic studies.

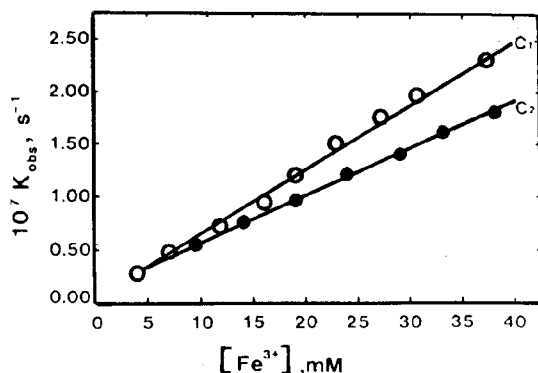


Fig. 2: Variation of  $k_{\text{obs}}$  with  $\text{Fe}^{3+}$  in methanol (C1) and in ethanol (C2) at room temperature. Similar plots are obtained in other alcohols.

Data were acquired using the laser-flash photolysis facility at the Center for Fast Kinetics Research at the University of Texas at Austin. Details of this facility are available elsewhere [8]. Briefly, a 532 nm (300 mJ) second harmonic pulse (11ns) from a Quantel YG418 Nd:YAG Q - Switched laser was used to excite samples contained in a 5 mm fluorimetry cuvette positioned in the spectrometer. Laser beam was attenuated prior to its use as an excitation source and this was achieved using a metal gauze screen. Each sample was given five laser shots and the subsequent luminescence decay at 650 nm was analyzed using an averaging program. All decays were exponential and were analyzed for first-order kinetics to obtain the observed first-order rate constants,  $k_{\text{obs}}$ ,  $\text{s}^{-1}$ . Variation of  $k_{\text{obs}}$  with quencher concentration, C (in  $\text{mole l}^{-1}$ ), in all 1-alkanols was linear as demanded by the Stern-Volmer equation:

$$k_{\text{obs}} = k^{\circ} + k_{\text{m}} C \quad (2)$$

where,  $k^{\circ}$  is the natural decay rate of the luminescence and  $k_{\text{m}}$  (in  $\text{M}^{-1} \text{s}^{-1}$ ) is the measured second-order specific rate of the electron-transfer process, eq. 1.

Values of  $k_{\text{m}}$  for reaction 1 in a number of alkanols are reported in Table 1. Two salient features of these  $k_{\text{m}}$  data are the followings. Firstly, in lower alcohols (C1-C3)  $k_{\text{m}}$  decreases with increasing viscosity of the medium and this trend is entirely consistent with a bimolecular mechanistic model involving collision encounters. Secondly and more im-

Table 1: Measured second-order specific rates,  $k_{\text{m}}$ , of the quenching of the luminescent state of  $\text{Ru}(\text{bpy})_3^{2+}$  by  $\text{Fe}^{3+}$  in 1-alkanols, effective electron-transfer distances, R, and the viscosity,  $\eta$ , of 1-alkanols.

Solvent	$k_{\text{m}} \times 10^{-8}$	$\eta^{b,c}$	$R^d$
Methanol	$6.2 \pm 0.8$	0.54	--
Ethanol	$4.4 \pm 0.5$	1.08	--
1-Propanol	$3.3 \pm 0.5$	1.99	--
1-Butanol	$2.6 \pm 0.4$	2.64	$28 \pm 2$
1-Hexanol	$2.7 \pm 0.4$	4.59	$28 \pm 2$
1-Octanol	$2.5 \pm 0.4$	7.21	$32 \pm 2$

<sup>a</sup>Units,  $\text{M}^{-1} \text{s}^{-1}$ . <sup>b</sup>Units, cP.

<sup>c</sup>Rauf, M.A.; Stewart, G.H.; Farhatziz. *J. Chem. Eng. Data*, **28**, 324 (1983).

<sup>d</sup>Units, Angstrom.

portantly, in alcohols higher than C3 the solvent viscosity appears to be totally ineffective in altering  $k_{\text{m}}$ . This surprising insensitivity of  $k_{\text{m}}$  to viscosity changes clearly indicates that the non-diffusive mechanisms of electron-transfers are operative. Collisionless PILRET has recently been reported in rigid media [3,4] with viscosity as high as  $10^5$  cP in some cases [4]. Rigidity (high viscosity) of reaction medium appears to hold the reactants apart at fixed (statistically averaged) distances  $\sim 25 \text{ \AA}$ . These center to center effective electron-transfer distances, R, were calculated using Perrin equation [9]:

$$(k_{\text{obs}}/k^{\circ}) = \exp(4\pi N_A R^3 C/3000) \quad (3)$$

where,  $N_A$  is the Avogadro's number. It is instructive to note that our data in alcohols higher than C3 also obey the Perrin equation (Fig. 1). On the contrary, in  $(k_{\text{obs}}/k^{\circ})$  versus C plots in lower alcohols are curved (Fig. 1) indicating the inapplicability of eq. 3 to data in these alcohols.

Values of R that fit our data on luminescence quenching to eq. 3 are given in Table 1. Clearly, these R values indicate efficient PILRET in fluid media. These R values are consistent with long-range tunneling mechanisms [1,2]. Solvation of electrons in 1-alkanols is well known [10] and it is

quite conceivable that  $\text{Fe}^{3+}$  ions are similarly solvated. Additionally, emission maxima of  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  in higher alcohols are red shifted compared to their values in lower alcohols indicating that the luminescent state is strongly solvated [11]. Thus it is likely that in these media electron donating and electron accepting centers are held apart by two layers of carbon chains of alcohols. However, it is highly unlikely that these saturated chains act as conductive wires passing the electron along from source to sink.

In summary, we have demonstrated efficient PILRET in fluid media. These electron-transfers are non-diffusive and are associated with higher alcohols only. Mechanism of electron-transfer switches from non-diffusive in higher alcohols over to diffusive in lower alcohols. Our work largely differs from that of others [3,4] in that our media are fluid. This type of systems offer great advantages in modeling biologically important ET, PILRET, and the distance dependence of PILRET, owing to their simplicity and ease of handling.

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