Proton coupled electron transfer reaction of phenols with excited state ruthenium(II) – polypyridyl complexes

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INTRODUCTION

The conversion of phenol to phenoxyl radical is of interest to chemists because of its involvement in biologically important processes.  As oxidants, the ruthenium(II) – polypyridyl complexes, in the excited state, have favorable redox potentials and are chemically stable. Miedlar and Das presented a detailed report on the reductive quenching of *[Ru(bpy)3]2+ by several substituted phenolate ions. In the past decade, we have examined the efficiency of the photoexcited state of ruthenium(II) complexes containing electron-donating and -withdrawing groups in the 4,4′-position of 2,2′-bipyridine [Ru(NN)3]2−, to have electron transfer (ET) reactions with phenolate ions. These [Ru(NN)3]2− complexes in the excited state have not been used for the oxidation of neutral phenols because the reaction is endergonic. However, the intramolecular ET from phenol to Ru(III) generated from the oxidative quenching of excited state [Ru(NN)3]2+ with external electron acceptors has been reported recently from the laboratory of Hammastorm. Studies on systems with tyrosine appended to Ru(II) and Re(I) complexes showed pH-dependent rate constant for the proton coupled electron transfer (PCET) oxidation of tyrosine. The nature of this pH dependence has recently been of great interest and consensus that these reactions are subject to general base catalysis. Recently Yuasa and Fukuzumi reported interesting mechanistic borderline between one-step hydrogen transfer and sequential transfers of electron and proton in reactions of NADH analog with triplet excited states of tetrakis and [Ru(bpy)3]2+. The one-step hydrogen atom transfer pathway is completely changed to the rate-limiting ET followed by fast proton transfer (PT) when the phenyl group in tetrakis is replaced by pyridine. Ruthenium(II) complex of 4,4′-dicarboxy-2,2′-bipyridine (H2dcbpy), *[Ru(H2dcbpy)3]2+ has higher excited state reduction potential (1.55 V) compared to the parent complex *[Ru(bpy)3]2+ (0.76 V). In our recent report, we have shown that *[Ru(dcbpy)3]4− (reduction potential = 1.0 V) at high pH H2dcbpy is in the form of 2,2′-bipyridine 4,4′-dicarboxylate ion (dcbpy)) is a better oxidant than *[Ru(bpy)3]2+ in aqueous alkaline medium (pH 12.5) and the reaction is more exergonic by 0.2 eV. As far as H2dcbpy ligand is concerned, the interesting aspect is that it exists as an anion, CO2, in an alkaline medium but it is in neutral —CO2H(H2dcbpy) form in neutral and acidic medium. This aspect is significant here because —CO2H (Hammet α value = 0.40) is a better electron-withdrawing group than —CO2− (α = 0.11) which makes *[Ru(H2dcbpy)3]2+ (E0 1.55 V) a better oxidant than *[Ru(dcbpy)3]4− (E0 1.00 V). Because of its favorable reduction potential, we thought it would be interesting to study the luminescence quenching of *[Ru(H2dcbpy)3]2+ by neutral phenols in CH3CN. The photochemical conversion of PhOH → PhO• may take place in a single step (H atom transfer) or sequence of steps (ET followed by PT or vice versa). The mechanism of the photochemical conversion of PhOH → PhO• is a topic of recent interest because of its relevance to the oxidation of tyrosine in photosystem II. As far as the photochemical oxidation of PhO• → PhO• is concerned, ET is the rate controlling step which has been well established by us and others. On the other hand, the conversion of PhOH → PhO• involves H atom transfer i.e., ET accompanied by PT. In recent years, many group of
workers\(^{[22–48]}\) have made sincere attempts to understand whether these ET and PT processes take place in concerted transfer of electron and proton (CEPT) or in stepwise fashion (PCET).

In CH\(_2\)CN, ArOH exists predominantly as the ArOH/CH\(_2\)CN hydrogen-bond complex, with only minor amounts of the ‘free’ ArOH being present. Thus, the efficiency of the reaction ArOH → ArO\(^*\) is determined by the strength of the interaction between ArOH and CH\(_2\)CN. If the conversion takes place by single step, hydrogen atom abstraction, the rate of reaction is usually related to the bond dissociation energy of phenol. If the phenol is in the form of hydrogen-bonded complex with solvent, the conversion of ArOH → ArO\(^*\) is unlikely to proceed through H-atom transfer reaction. Alternatively the reaction may take place by rate controlling ET followed by fast PT.

A concerted transfer of electron and proton (CEPT) facilitates a low energy pathway for the ET process by avoiding the charged intermediates, PhO\(^*\)H\(^+\) and PhO\(^-\), of the stepwise mechanism. The CEP mechanism need not be the fastest one, because the transition state configuration may be more constrained that would increase the activation free energy. This means that the reactant nuclei have to distort into a position where the reactant and product free energy surfaces for CEP are isoenergetic. These geometrical changes involved in the formation of transition state correspond to high reorganization energy (\(\lambda\)). The concerted mechanism is favored energetically and stepwise mechanism has low \(\lambda\) value. These arguments point out that though CEP is a low energy pathway it involves large \(\lambda\) value. Though these views have been considered in detail in recent years on the intramolecular ET from tyrosine to Ru(III), no attempt has been made so far on the bimolecular photoinduced ET reactions of Ru(II) complexes with phenols.\(^{[20–22,30–36]}\) To address this problem we have studied the reaction of several phenols with excited state \([\text{Ru(H}_2\text{dcbpy)}_3]^{2+}\) and \([\text{Ru(bpy)}_3]^{2+}\) in CH\(_2\)CN by luminescence quenching technique. As the rate of ET from 4-methoxy phenol to \([\text{Ru(H}_2\text{dcbpy)}_3]^{2+}\) is facile in a wide pH range and the reaction can be studied by luminescence quenching technique, we are able to address the mechanism of the reaction, concerted electron and proton transfer or stepwise here. To confirm that the quenching process proceeds through the formation of phenoxy radical we have recorded the spectrum of the transients by laser flash photolysis technique. This study indicates the formation of phenoxy radical as a transient during the course of the reaction.

**EXPERIMENTAL SECTION**

**Materials**

Chloride salts of \([\text{Ru(NN)}_3]^2+\) (NN = 2,2’-bipyridine, 4,4’-dicarboxyl-2,2’-bipyridine) complexes were prepared by reacting RuCl\(_3\)3H\(_2\)O (Aldrich) with the corresponding ligands according to the procedures previously described\(^{[26,49,50]}\). Then the complexes were treated with ammonium hexafluorophosphate to get the PF\(_6^−\) salts \([\text{Ru(NN)}_3][\text{PF}_6]_2^{[49,50]}\). Phenol and its derivatives were purchased from Fluka and Aldrich; phenol was further purified by distillation. HPLC grade solvents were used in all experiments. Buffer solutions were prepared by known literature procedure.\(^{[51]}\)

**Equipment**

The absorption and emission spectral studies were made with SPECORD S100 diode-array spectrophotometer and JASCO FP 6300 spectrofluorometer, respectively. Excited state lifetime and transient absorption measurements were made with laser flash photolysis technique using an Applied Photophysics SP-Quanta Ray GCR-2(10) Nd:YAG laser as the excitation source.\(^{[52]}\) The time dependence of the luminescence decay is observed using a Czerny–Turner monochromator with a stepper motor control and a Hamamatsu R-928 photomultiplier tube. The production of the excited state on exposure to 355 nm was measured by monitoring (pulsed Xenon lamp of 250 W) the absorbance change. The change in the absorbance of the sample in laser irradiation was used to calculate the rate constant as well as the time-resolved absorption transient spectrum. The change in the absorbance on flash photolysis was calculated using the expression

\[
\Delta A = \log\left(\frac{I_0}{I_0 - I_1}\right)
\]

\[
\Delta I = (I_1 - I_0)
\]

where \(\Delta A\) is the change in the absorbance at time \(t\), \(I_0\) is the voltage after flash, \(I\) is the pretrigger voltage and \(I_0\) is the voltage at particular time. A plot of ln \((\Delta A - \Delta A_{\infty})\) versus time gives a straight line. The slope of the straight line gave the rate constant for the decay. The reciprocal of these values gave the lifetime of the triplet. The time-resolved transient absorption spectrum was recorded by plotting the change in absorbance at a particular time versus wavelength.

The redox potentials of \([\text{Ru(NN)}_3]^2+\) complexes in an acetonitrile medium were determined by cyclic voltammetric technique using EG & G Princeton Applied Research Potentiostat/Galvanostat Model 273A. A glassy carbon (working electrode) and a standard (Ag/Ag\(^+\)) electrode (reference electrode) were used for the electrochemical measurements and tetrabutylammonium perchlorate (0.1 M) was the supporting electrolyte.

**Quenching studies**

Freshly prepared solutions were used for the spectral measurements. The solutions used for the excited state lifetime and emission measurements were deaerated by dry argon and N\(_2\) gas respectively for 20 min. The change of emission intensity of \([\text{Ru(NN)}_3]^2+\) with change of \([Q]\) measured at 298 K is shown in Fig. 1. The quenching rate constant, \(k_q\), for the reaction was
determined by the luminescence-quenching technique from the Stern–Volmer equation using emission intensity data:[53]

\[
\frac{I_0}{I} = 1 + k_q \tau_0 [Q]
\]  

(3)

where \(I_0\) and \(I\) are the emission intensities in the absence and presence of the quencher respectively and \(\tau_0\) is the emission lifetime of Ru(II) complexes in the absence of the quencher. A sample Stern–Volmer plot for the luminescence quenching of \(*[Ru(NN)3]^2+\) with phenol is shown in Fig. 2.

**RESULTS AND DISCUSSION**

The structures of the ligands of \([Ru(NN)3]^2+\) complexes used in the present study are shown in Chart 1. The absorption and emission spectral data and the excited state lifetimes and the redox potentials of \([Ru(NN)3]^2+\) complexes used in the present study are collected in Table 1. These values are close to the already reported values.[8–10,25–30] The bimolecular quenching rate constant, \(k_q\), values for the reductive quenching of two Ru(II) complexes \(*[Ru(bpy)3]^2+\) and \(*[Ru(H2dcbpy)3]^2+\) with various phenols measured from the Stern–Volmer plots along with the values for the quenching on \(*[Ru(dcbpy)3]^4-\) with phenolate ions are given in Table 2. The free energy change (\(\Delta G^0\)) values calculated from the reduction potentials of \([Ru(NN)3]^2+\) and oxidation potentials of phenols/phenolate ions are collected in Table 3. The reductive quenching of \(*[Ru(bpy)3]^2+\) and \(*[Ru(H2dcbpy)3]^2+\) with \(p\)-methoxy-phenol has been studied

![Figure 2. Stern–Volmer plot for the reductive quenching of \(*[Ru(H2dcbpy)3]^2+\) with 2,6-di-tert-butyl phenol](image)

**Chart 1. Structure of the ligands and the quenchers**

**Table 1.** Absorption and emission spectral data, excited state lifetime (in ns), and redox properties of \([Ru(NN)3]^2+\) complexes in acetonitrile medium at 298 K

<table>
<thead>
<tr>
<th>Photophysical data</th>
<th>([Ru(bpy)3]^2+)</th>
<th>([Ru(H2dcbpy)3]^2+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption maximum, (\lambda_{abs,\text{max}}) nm ((c_{\text{max}}), M(^{-1}) cm(^{-1}))</td>
<td>452(14 500)</td>
<td>467(11 600)</td>
</tr>
<tr>
<td>Emission maximum</td>
<td>612</td>
<td>636</td>
</tr>
<tr>
<td>Life time (ns)</td>
<td>850</td>
<td>1080</td>
</tr>
<tr>
<td>(E_{\text{em}}) (eV)</td>
<td>2.12</td>
<td>2.1</td>
</tr>
<tr>
<td>(E^0\text{2+/+}) (V) vs. SCE</td>
<td>0.76</td>
<td>1.55</td>
</tr>
</tbody>
</table>

**Table 2.** Rate constant, \(k_q\), values for the reductive quenching of \(*[Ru(NN)3]^2+\) with phenols in acetonitrile at 298 K

<table>
<thead>
<tr>
<th>Quencher</th>
<th>([Ru(bpy)3]^2+)</th>
<th>([Ru(H2dcbpy)3]^2+)</th>
<th>(*[Ru(dcbpy)3]^4-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>—</td>
<td>—</td>
<td>5.2 \times 10^8</td>
</tr>
<tr>
<td>4-Methyl phenol</td>
<td>4.2 \times 10^6</td>
<td>9.2 \times 10^6</td>
<td>1.3 \times 10^8</td>
</tr>
<tr>
<td>4-Methoxy phenol</td>
<td>3.8 \times 10^7</td>
<td>7.6 \times 10^8</td>
<td>1.2 \times 10^9</td>
</tr>
<tr>
<td>2,6-Dimethyl phenol</td>
<td>7.3 \times 10^6</td>
<td>2.0 \times 10^7</td>
<td>2.2 \times 10^9</td>
</tr>
<tr>
<td>2,6-Di-tert-butyl phenol</td>
<td>1.0 \times 10^7</td>
<td>1.3 \times 10^6</td>
<td>—</td>
</tr>
</tbody>
</table>

\(^a\) As the reaction has been carried out at pH = 12.5 all phenols present in the form of phenolate ions.
at different acid concentrations using trichloroacetic acid and the $k_q$ values are given in Table 4.

**Luminescence quenching rate constants**

The Stern–Volmer plots from the emission intensity data (Fig. 2) are linear for all photoredox systems, indicating that dynamic quenching is the predominant process and the contribution from static quenching is negligible here (Fig. 3). At this juncture it is relevant to mention that though Hoffman et al. [6, 17, 19] have reported that the quenching rate constant for the photoreduction of $^*$[Ru(NN)$_3$]$_2^{2+}$ with 4-methoxy phenol is $1.8 \times 10^7$ M$^{-1}$ s$^{-1}$ in aqueous solution at pH 7. On the other hand, it is found from the present study that for the same reaction in acetonitrile, the $k_q$ value is $3.8 \times 10^7$ M$^{-1}$ s$^{-1}$. When we use $^*$[Ru(H$_2$dcbpy)$_3$]$_2^{2+}$ as the photosensitizer, the quenching rate constant becomes $7.6 \times 10^9$ M$^{-1}$ s$^{-1}$, i.e., when the ligand bipyridine is replaced by 4,4′-dicarboxyl-2,2′-bipyridine, the $k_q$ value increases by more than one order (20 times). If $\Delta G^0$ is the only important parameter and the reaction proceeds through the rate controlling ET process then the difference should be still higher because $\Delta G^0$ values differ by $\sim 0.8$ eV. These results seem to point out that other factors also play a role and the reaction is unlikely to proceed through simple ET mechanism. In order to understand the role of other factors like the steric effect on the rate of the reaction, quenching reaction has been studied using phenols with bulky substituents such as methyl and tert-butyl groups on the 2- and 6-positions. Interestingly, the quenching rate constant value is varied slightly when we introduce methyl in the 2,6-positions compared to 4-methyl phenol (Table 2). On the other hand, substantial decrease in $k_q$ value is observed when tert-butyl group is introduced in the 2, 6-positions of phenol. In our recent reports, we have unequivocally established that steric effect is predominant only if both reactants, $^*$[Ru(NN)$_3$]$_2^{2+}$ and phenolate ions, carry bulky groups. We have shown previously that though we could observe noticeable steric effect (30 times) when tert-butylphenol as the reactants. This steric effect can be ascribed to the increase of ET distance when the reaction occurs between two reactants carrying bulky groups. It is important to mention that though tert-butyl group is bulky it is an electron donating group and has negative Hammett $\sigma$ values. The

![Table 3. $\Delta G^0$ (eV) values for the reductive quenching of $^*$[Ru(NN)$_3$]$_2^{2+}$ with phenols in acetonitrile at 298 K](image)

<table>
<thead>
<tr>
<th>Quencher</th>
<th>$E^0_{\text{oxd}}$ (V) vs. SCE</th>
<th>$[\text{Ru(bpy)}_3]^{2+}$</th>
<th>$[\text{Ru(H}_2\text{dcbpy)}_3]^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>1.69 (0.86)</td>
<td>0.93</td>
<td>0.14</td>
</tr>
<tr>
<td>4-Methyl phenol</td>
<td>1.67 (0.71)</td>
<td>0.91</td>
<td>0.12</td>
</tr>
<tr>
<td>4-Methoxy phenol</td>
<td>1.30 (0.58)</td>
<td>0.54</td>
<td>-0.25</td>
</tr>
<tr>
<td>2,6-Dimethyl phenol</td>
<td>1.81 (0.50)</td>
<td>1.05</td>
<td>0.26</td>
</tr>
<tr>
<td>2,6-Di-tert-butyl phenol</td>
<td>1.86</td>
<td>1.10</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Values in the parenthesis are the oxidation potentials of phenols versus NHE in aqueous medium. [68]

![Figure 3. Absorption spectra of $[\text{Ru(H}_2\text{dcbpy)}_3]^{2+}$ in the presence of 2,6-di-tert-butyl phenol in acetonitrile medium at the concentrations of (a) 0, (b) 0.001, (c) 0.002, (d) 0.003, and (e) 0.004 M. (Inset:Subtracted spectra of Ru(II) complex and Phenol from the reaction mixture)](image)
predominant steric effect observed here seems to point out PCET rather than simple ET from phenol to the sensitizer in the rate controlling step.

**Effect of pH on the rate of luminescence quenching reaction**

In recent years, much importance is given to understand the correct mechanism for the conversion of Tyr$_z$→ Tyr$^*$ in photosystem II.[20–22,55–57] To get an idea on this problem, model systems have been designed involving [Ru(NN)$_3$]$^{2+}$ as photosensitizers. The excited state [Ru(NN)$_3$]$^{2+}$ complex is oxidized by external electron acceptors, MV$_2^+$ or Co$_3^{4+}$ to generate [Ru(NN)$_3$]$^{3+}$. This tripositive ion abstracts H atom from tyrosine to generate tyrosyl radical. Based on the pH dependence of this process, the authors concluded that if the reaction is pH dependent it proceeds through PCET mechanism. If the reaction is pH independent the reaction proceeds through H-atom transfer mechanism. Thus to get a clue on the mechanism of the reaction the quenching of [Ru(bpy)$_3$]$^{2+}$ has been studied at different pH and the $k_q$ values are given in Table 4. Interestingly, the quenching of [Ru(NN)$_3$]$^{2+}$ and [Ru(H$_2$dcbbpy)$_3$]$^{2+}$ has been observed at different pH and the $k_q$ values are given in Table 4. Interestingly, the quenching of [Ru(bpy)$_3$]$^{2+}$ has been observed at different pH and the $k_q$ values are given in Table 4. Interestingly, the quenching of [Ru(NN)$_3$]$^{2+}$ with 4-methoxy phenol is highly sensitive to pH and thus the reaction is likely to proceed through PCET mechanism particularly at pH < $pK_a$ of phenol. At pH $>$ $pK_a$, the reaction proceeds through ET mechanism.

The $k_q$ data collected in Table 4 show that the $k_q$ value for [Ru(H$_2$dcbbpy)$_3$]$^{2+}$ is little sensitive to the change of pH when pH < $pK_a$; the $k_q$ value is high at pH > $pK_a$ compared to the values at low pH. As far as [Ru(H$_2$dcbbpy)$_3$]$^{2+}$ ion is concerned at low pH H$_2$dcbbpy is in the form of undissociated acid but it gets dissociated when pH > 7. In between pH 2 and 7 the extent of dissociation may vary depending on the pH of the medium. As already pointed out in the introduction, the reduction potential of [Ru(H$_2$dcbbpy)$_3$]$^{2+}$ is high (1.55 V) if H$_2$dcbbpy is in the undissociated form. When it is in the form of dianion at high pH the reduction potential of [Ru(dcbbpy)$_3$]$^{3-}$ is low(1.0 V) (*vide infra*). However, the $k_q$ data collected on the quenching of [Ru(bpy)$_3$]$^{2+}$ with 4-methoxy phenol help us to conclude that the reaction proceeds through PCET mechanism when phenol is in neutral form.

**Driving force dependence of the quenching rate constants**

The rate of ET from a donor molecule to an acceptor in a solvent is controlled by free energy change of the reaction ($\Delta G^\circ$), the reorganization energy ($\lambda$), and the electronic coupling between the reactant and product states (Eqn (4)).[58–60]

$$k_q = \frac{2\pi h^2}{\hbar(4\pi\lambda k_BT)^{1/2}} \exp\left(-\frac{\Delta G^\circ + \lambda^2}{4\lambda k_BT}\right)$$

The free energy change ($\Delta G^\circ$) of ET reaction can be calculated by the following expression:

$$\Delta G^\circ = E_{A(OH)/A} - E_{D^{2+/+}} + w_D - w_T$$

and $\lambda$, the solvational reorganization energy is given by

$$\lambda = (e\Delta e)^2/4\pi\epsilon_0 \int_{1/2t:a + 1/2t:b - 1/2t:a}/1/D_{o-p} - 1/D_{s}$$

In Eqn (5) and (6), $E_{A(OH)/A}$ and $E_{D^{2+/+}}$ are the oxidation potential of phenol and excited state reduction potential of [Ru(NN)$_3$]$^{2+}$, $w_D$ and $w_T$ are the work terms accounting for the work required to bring the products and reactants together, $D_{o-p}$ and $D_s$ are the optical and static dielectric constants of the solvent, respectively, and $t:a$ and $t:b$ are the radii of the reactants.[15,16,61] The value of $\lambda$ calculated from Eqn (6) was found to be 0.83 eV at this pH. The $\Delta G^\circ$ values calculated using Eqn (6) are given in Table 3.

It is important to point out that the oxidation potential of ArOH is pH dependent and the variation of $E_{A(OH)/A}$ with pH is given by the following equation for pH $<$ $pK_a$.

$$E_{A(OH)} = \left(E_{A(OH)/A} - (RT \ln 10 x \text{pH})/F\right)$$

Recently Hammarstro¨ m and co-workers[31–39] have demonstrated that the driving force ($-\Delta G^\circ$) for the reaction of phenol with Ru(III) (both inter- and intramolecular processes) increases with pH as represented by Eqn (8) for the intramolecular process in the Ru–Tyr complex.

$$\Delta G^\circ = F_{o-x} - 0.059 \times (\text{pH} + 2) V$$

The data collected in Table 4 show that the luminescence quenching of [Ru(bpy)$_3$]$^{2+}$ with 4-methoxyphenol is pH dependent and it varies from 2.2 $\times$ 10$^7$ at pH = 8 to 3.3 $\times$ 10$^8$ at pH = 12.5. On the other hand at acidic pH (pH 4 and 6) no quenching is possible. At low pH, the reaction is endergonic and thus the quenching process is slow.

As far as p-methoxyphenol is concerned $E = 1.30$ V when it is in the unionized form and the value is 0.58 V when it is in the form of phenolate ion. The $pK_a$ value of 4-methoxy phenol is 10.2. Thus from the pH dependence of $k_q$ values we realize that at pH $<$ $pK_a$ the $k_q$ value is largely pH dependent and at pH values more than $pK_a$, $k_q$ value is little sensitive to the change of pH of the medium. When we look at the $k_q$ values obtained for the quenching of [Ru(bpy)$_3$]$^{2+}$ with 4-methoxyphenol at different pH there is no quenching at pH < 8. At pH 8, the $k_q$ value is 2.2 $\times$ 10$^7$ and at pH = 10, the value becomes 1.2 $\times$ 10$^9$ M$^{-1}$ s$^{-1}$ and at pH > 10 the change in $k_q$ value is small. These data clearly point out that the quenching process is highly sensitive to pH and the change of oxidation potential of phenol with pH should be considered to account for the effect. Using a pH-dependent driving force (Eqn (8)) in the Marcus equation (Eqn (4)), it is possible to derive an expression for the pH dependence of the ET rate constant. When the phenol is in the unionized form, the electron and proton transfer occur simultaneously in one reaction step, with one common transition state. For PCET, the reaction coordinate region must be where the free energy surfaces for the reactant and product state cross (the transition state). Since the O–H bond is broken in the reactions, the product free energy surface is repulsive in the O–H coordinate, and the transition state involves an elongated O–H bond and leads to large $\lambda$ at pH < 10. With an increase in pH, the entropy of mixing due to protonation increases, whereas the free energy of the product state decreases (Fig. 4). These arguments indicate that $\Delta G^\circ$ for the proton coupled ET reaction decreases with pH thus accounting for the increase in $k_q$ values with pH for the quenching of [Ru(bpy)$_3$]$^{2+}$ with 4-methoxy phenol. The marked increase (> 100 fold) in the rate constant going from the protonated form of phenol to the unprotonated form is mainly due to the decrease in $\lambda$. At low pH $\lambda = 2.0$ eV compared to 0.9 eV at high pH. The large $\lambda$ value at low pH is probably an effect of large inner-sphere reorganization, possibly characteristic for the proton coupled ET bond-breaking reaction.

On the other hand, if we look at the $k_q$ values obtained for the quenching of [Ru(H$_2$dcbbpy)$_3$]$^{2+}$ with 4-methoxy phenol as a
function of pH though the $k_q$ value is high at pH > $pK_{ar}$, there is no clear trend when pH < $pK_{ar}$. It is important to remember that apart from ArOH, the nature of the ligand in $[\text{Ru(H}_2\text{dcbpy)}_3]^{2+}$ depends on the pH of the medium i.e. in the form of $-\text{CO}_2\text{H}$ at low pH and $-\text{CO}_2^-$ at high pH. The reduction potential of $[\text{Ru(H}_2\text{dcbpy)}_3]^{2+}$ varies substantially with the change of pH of the medium. If the ligand is in the form of $-\text{CO}_2\text{H}$, the $E^0_{\text{Ru}^{2+}/\text{Ru}}$ is 1.55 V and if it is in the $-\text{CO}_2^-$ form the reduction potential is 1.0 V. Thus, the increase of pH facilitates the oxidation of phenol but retards the reduction potential of $[\text{Ru(NN)}_3]^{2+}$ when NN is 4,4-$\text{dicarboxyl-2,2}$-$\text{bipyridine. This opposing trend observed with the electron donor and acceptor with the change of pH is responsible for the absence of clear trend in the $k_q$ values observed with } [\text{Ru(H}_2\text{dcbpy)}_3]^{2+}$.

In order to understand the driving force dependence of the photooxidation of phenols using $[\text{Ru(bpy)}_3]^{2+}$ and $[\text{Ru(H}_2\text{dcbpy)}_3]^{2+}$ as the photosensitizers, the values of log $k_{et}$ are plotted against the $\Delta G^0$ values (Fig. 5). The values of $k_{et}$ were determined from the experimentally observed $k_q$ values using the relation shown below.

$$k_q = \frac{k_d}{1 + (k_d k_{et} K_{eq})}$$

where $k_d$ is the diffusion-controlled rate constant, $K_{eq}$ is the equilibrium constant for the formation of the encounter complex, and $k_{et}$ is the forward ET rate constant. Recently Mayer and co-workers\cite{62} have established that despite its simplifications, the adiabatic Marcus equation is still the logical starting point for the proton coupled ET reactions of phenols. It is important to point out that the inner-sphere reorganization for phenol is unusual because it involves not only small shifts in equilibrium bond distances, as in the standard Marcus model, but also movement of a proton across an OH—oxidant bond. The proton can be thought of as transferring ~0.7 Å between two minima on an adiabatic potential energy surface. This would not seem to fit easily into the standard Marcus model, where a single parabolic surface, defined by the reorganization energy $\lambda$, describes all of the solvent and inner-sphere reorganizations. When Mayer\cite{62}
applied Marcus theory for the PCET reaction of phenols with iron(III)-polypyridine complexes he observed log $k_{et}$ versus $\Delta G^0$ plot similar to Fig.5 shown here. Thus, the reaction of $[\text{Ru(NN)}_3]^{2+}$ with neutral phenols is not likely to proceed through proton coupled ET mechanism not by ET. Thus the plot of log $k_{et}$ versus $\Delta G^0$ also supports the operation of PCET at low pH. In sum, the dependence of quenching rate constants on the driving force, effect of pH, and transient spectrum are consistent with the PCET mechanism. These conclusions are consistent with the findings of Hammarstrom and co-workers\cite{31-33} for their system.

**Absorption spectrum of transient formed from the reaction of $[\text{Ru(H}_2\text{dcbpy)}_3]^{2+}$ with 4-methoxy phenol**

The ground-state absorption spectrum of $[\text{Ru(H}_2\text{dcbpy)}_3]^{2+}$ is shown in Fig. 1. The strong absorption in the 300 nm corresponds to the $\pi-\pi^*$ (LC) transition and the low energy absorption at 467 nm is assigned to the $d_{\pi}-\pi^*$ (MLCT) transition. We have recorded the excited-state absorption for $[\text{Ru(H}_2\text{dcbpy)}_3]^{2+}$ in an acetonitrile medium. In Figs 6(a) and (b), $\Delta \lambda$ is proportional to $e^*=e^0$, where $e^*$ and $e^0$ are the extinction coefficients of Ru(II) complex in the excited and ground states, respectively, at the particular wavelength. Figures 6(a) and (b) are the absorption spectra of $[\text{Ru(H}_2\text{dcbpy)}_3]^{2+}$ recorded in the absence and presence of 0.05 M 4-methoxy phenol. The band decay at 467 and 600 nm corresponds to the $[\text{Ru(H}_2\text{dcbpy)}_3]^{2+}$ with 4-methoxy phenol is facile in a wide pH range, these data are not of much value to decide on the nature of the mechanism because of the nature of the $H_2$dcbbpy at different pH. On the other hand, the reaction of $[\text{Ru(bpy)}_3]^{2+}$ with 4-methoxyphenol at different pH clearly shows that reaction at low pH proceeds through PCET mechanism. The reaction of $[\text{Ru(H}_2\text{dcbpy)}_3]^{2+}$ with 2,6-disubstituted phenols entails large steric effect in the wide pH range. These results on model reactions help us to propose the formation of phenoxyl radical from phenol in photosystem II may occur by PCET mechanism at pH < $pK_a$ and by ET at pH > $pK_a$.

**REFERENCES**


**CONCLUSION**

The photoinduced reaction of $[\text{Ru(NN)}_3]^{2+}$ with neutral phenols in CH$_3$CN proceeds through PCET mechanism. However, when the reaction is carried out at pH > $pK_a$, the reaction occurs via simple ET mechanism. Though the reaction of $[\text{Ru(H}_2\text{dcbpy)}_3]^{2+}$ with 4-methoxy phenol is facile in a wide pH range, these data are not of much value to decide on the nature of the mechanism because of the nature of the $H_2$dcbbpy at different pH.