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Steric effects in the photoinduced electron transfer reactions of ruthenium(II)-polypyridine complexes with 2,6-disubstituted phenolate ions

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The rate constants (k_q) for the photoinduced electron transfer reactions of Ru(II)-polypyridyl complexes ($\text{Ru}(\text{NN})_3^{2+}$) with 2,6-disubstituted phenolate ions in aqueous acetonitrile are highly sensitive to change in the bulkiness of the ligand in $\text{Ru}(\text{NN})_3^{2+}$ as well as the phenolate ion. The decrease in k_q value with the increase in the size of the ligand in $\text{Ru}(\text{NN})_3^{2+}$ and the phenolate ion is ascribed to the decrease in the electronic coupling matrix element, $|H_{\text{DA}}|$, between the donor and acceptor with the increase in the electron transfer distance. The hydrophobic interaction or possible π - π stacking between the pyridine rings of $\text{Ru}(\text{NN})_3^{2+}$ and the aryl moiety of ArO^- leads to less steric effect.

1. Introduction

The oxidation of phenols is of great interest because of their involvement in important biochemical and industrial processes.^{1–5} At present, there is intense interest in phytophenols and polyphenols (e.g., flavonoids) from natural sources that appear to act as antioxidants or radical scavengers.^{1–6} On the other hand, phenols have also been implicated in problems associated with estrogenic toxicity.^{2–7} It is well established that one-electron oxidation of phenolic compounds by oxidative enzymes (peroxidases, tyrosinase, prostaglandin synthase) can lead to the generation of phenoxyl radical.^{7,8} Thus the metabolism of phenol has been shown to result in the formation of the phenoxyl radical and the enzyme derived phenoxyl radicals cannot be ruled out in damage to biomolecules. Some of the less reactive phenols are likely to serve as a 'ferry' carrying an unpaired electron to an accessible site where the oxidative damage is initiated.^{3–5} The stability of the phenoxyl radical and its hydrophobicity would aid in this endeavor. The latter property would enable it to move easily about the cell and through biomembranes.

It has been well established that phenoxyl radicals containing bulky alkyl groups in the *ortho*-position are comparatively stable.^{9,10} With the added hydrophobicity, these alkyl-substituted phenoxyl radicals may play an important role in the toxicity as well as the antioxidant property of phenols. It is well known that polyphenols are present in substantial amounts in epidermal plant cells and in plant-derived foods and beverages.¹¹ The generation of phenoxyl radical involves either H-atom or electron abstraction from phenol and phenolate ion respectively. Though a large amount of work has been done on the H-atom abstraction reaction of phenols little effort has been made so far to understand the effect of change in the structure of the phenolate ion on the electron abstraction particularly by excited state electron acceptors.

The study of the kinetic and thermodynamic aspects of electron transfer to generate phenoxyl radicals bearing bulky alkyl groups in the *ortho*-position may help to understand the different biological roles of phenols. We have already reported the importance of substituent effects by studying the electron transfer (ET) reactions of several *meta*- and *para*-substituted phenolate ions to the excited state ruthenium(II)-polypyridine complexes.^{12–15}

The rate of ET from a donor to an acceptor molecule is influenced by exothermicity, reorganization energy and distance.^{16–18} During the past two decades numerous theoretical and experimental studies have been directed towards understanding the above factors that affect the rates of photoinduced ET reactions of Ru(II) complexes.^{19–25} To a large extent the ligands of $\text{Ru}(\text{NN})_3^{2+}$ (NN being the polypyridine ligand) and the nature of the quencher determine the distance over which the ET occurs.^{26–28} The distance dependence of ET has become increasingly important as attempts are made to unravel the complexities of ET reactions in biological systems and in natural and synthetic solar energy conversion systems.^{29,30}

The introduction of bulky alkyl groups in the *ortho*-position of phenol alters the oxidation potential and size of the phenol. Thus the presence of alkyl groups will affect the rate of ET through changes in the exothermicity and distance of ET (steric effect). Steric interactions between two reactant molecules may become a dominant factor when large ligands and bulky quenchers are involved. Should this occur, the rate would be less than that predicted on the basis of energetic factors.^{31,32} Such sterically inhibited reactions fall within the framework of accepted models describing nonadiabatic ET. In contrast to what is known about how the reactants influence the energetic and distance factors associated with ET, relatively little is known about steric factors, especially for bimolecular reactions. One way that bulky reactants could

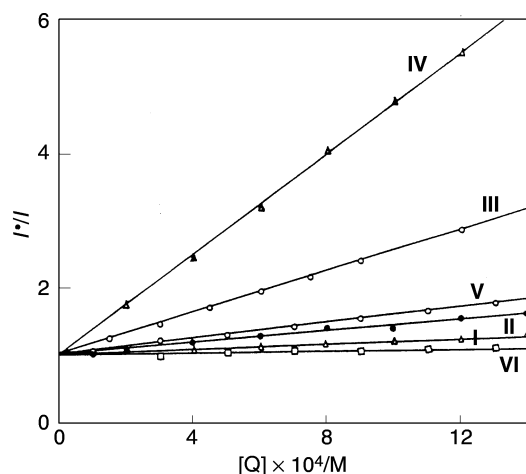


Fig. 1 Stern–Volmer plots for the luminescence quenching of $^*\text{Ru}(\text{dtbpy})_3^{2+}$ with ArO^- ions in AN : H_2O (80 : 20, v/v). I. Phenolate ion; II. 4-methylphenolate ion; III. 2-methylphenolate ion; IV. 2,6-dimethylphenolate ion; V. 2,6-diisopropylphenolate ion; VI. 2,6-di-*tert*-butylphenolate ion.

influence ET rates is to prevent a sufficient overlap between the donor and acceptor orbitals.

The importance of electronic factors is revealed by the effect of *para*-substituents. The role of electronic effects on the rate of ET transfer reactions of phenolate ions with $^*\text{Ru}(\text{NN})_3^{2+}$,^{12–15} and the effects of introducing bulky substituents in the ligand, 2,2'-bipyridine of $\text{Ru}(\text{NN})_3^{2+}$ on the rate of photoinduced ET with aromatic amines,^{31,33} phenolate ions¹² and nitroaromatics³⁴ have already been reported from this laboratory. In the present study the bulkiness of the ligands, 2,2'-bipyridine and 1,10-phenanthroline of the $\text{Ru}(\text{II})$ complexes as well as the substituent in the *ortho*-position of the phenolate ion has been changed to provide sufficient steric hindrance in the ET process. The excited state ET reactions of five $\text{Ru}(\text{NN})_3^{2+}$ complexes with six phenolate ions have been studied with the aim of understanding the effect of changing the bulkiness of the ligand in $\text{Ru}(\text{NN})_3^{2+}$ and the quencher on the rate of ET. In this study a mixed solvent system is used because of the low solubility of some substituted phenolate ions in an aqueous medium.

2. Experimental

2.1. Materials

The five $\text{Ru}(\text{NN})_3^{2+}$ complexes {where NN = 2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine(dmbpy), 4,4'-di-*tert*-butyl-2,2'-bipyridine(dtbpy), 4-methyl-4'-neopentyl-2,2'-bipyridine(mnbpy) and 4,7-diphenyl-1,10-phenanthroline (dpphen)} were synthesized by known procedures. The phenols used in this study were obtained from Fluka and Aldrich and were purified by recrystallization or vacuum distillation. The solids were stored in a vacuum desiccator after purification. The solvents were purified by known methods.

2.2. Excited state lifetime measurements

The excited state lifetimes of the five $^*\text{Ru}(\text{NN})_3^{2+}$ complexes in $\text{CH}_3\text{CN-H}_2\text{O}$ (80 : 20, v/v) were measured using the laser flash photolysis technique, after purging the solutions with dry argon for 30 min. The details of the measurement of lifetime by the laser flash photolysis technique have already been described in our previous reports.^{12–15} The transient absorption decay of $\text{Ru}(\text{bpy})_3^{2+}$ observed after laser flash excitation (355 nm, 8 ns laser pulse) of a deoxygenated 20 μM solution of $\text{Ru}(\text{bpy})_3^{2+}$ containing 20 μM phenolate ion in aqueous acetonitrile (80% : 20%, v/v) at 298 K is shown in our previous reports.^{13,15}

2.3. Electrochemical measurements

The oxidation potentials of phenolate ions were determined by a cyclic voltammetric technique using a EG & G Princeton Applied Research Potentiostat/Galvanostat Model 273A and Model RE 0151 Recorder. The stock solutions of the phenolates for the electrochemical studies were prepared in $\text{CH}_3\text{CN-H}_2\text{O}$ (80 : 20, v/v). Potassium chloride was used as the supporting electrolyte. A glassy carbon electrode and a standard calomel reference electrode were used in the electrochemical measurements. Cyclic voltammograms were recorded after purging the solution with dry nitrogen gas for 30 min. All the phenolate ions exhibited quasireversible waves and our electrochemical results are in close agreement with the reported values in an aqueous medium.³⁵ However the redox potential values of phenolate ions measured in the present study differ systematically from the recently reported values in CH_3CN (Table 2, later) and this difference is explained later.¹⁰

2.4. Luminescence quenching measurements

The photochemical reduction of $^*\text{Ru}(\text{NN})_3^{2+}$ with phenolate ions was studied by a luminescence quenching technique. The sample solutions were purged carefully with dry nitrogen for 30 min to ensure that there was no change in volume of the solution. The steady state luminescence measurements were performed using a JASCO FP 770 spectrofluorometer. The quenching rate constant, k_q , values were determined from the Stern–Volmer equation and the details of obtaining k_q values from Stern–Volmer plots are given in our previous reports.^{12–15} A sample Stern–Volmer plot is shown in Fig. 1. Phenolate ion for quenching studies and electrochemical measurements was prepared by mixing the corresponding phenol with NaOH and the pH of the solution was maintained at 13 to confirm that the quencher was present as phenolate ion and not as phenol.

3. Results and discussion

The structures of the ligands (NN) and quenchers (phenolates) used in the present study are shown in Fig. 2. The excited state lifetime (τ) of $^*\text{Ru}(\text{NN})_3^{2+}$ is highly sensitive to the change of medium.^{20,21} Though τ values of some $\text{Ru}(\text{II})$ complexes in pure solvents are available in the literature, the τ values of most complexes used in the present study in mixed solvents are not available. Therefore the τ values of the five $\text{Ru}(\text{II})$ complexes in acetonitrile–water (80 : 20 v/v) have been measured using laser flash photolysis technique and are given in Table 1 along with the τ values in CH_3CN . Addition of water to the organic solvent substantially decreases the τ value of $^*\text{Ru}(\text{NN})_3^{2+}$ and it has been established that non-radiative deactivation of $^*\text{Ru}(\text{NN})_3^{2+}$ is favorable in protic solvents leading to a decrease in τ value. Similar results have been reported on the τ values of $\text{Ru}(\text{II})$ complexes in mixed solvent systems.^{36,37}

Table 1 Excited state lifetimes of $^*\text{Ru}(\text{NN})_3^{2+}$ complexes in $\text{CH}_3\text{CN-H}_2\text{O}$ (80 : 20, v/v) at 298 K

$\text{Ru}(\text{NN})_3^{2+}$	Lifetime, τ/ns	
	$\text{CH}_3\text{CN-H}_2\text{O}$	CH_3CN^a
$\text{Ru}(\text{bpy})_3^{2+}$	684	850
$\text{Ru}(\text{dmbpy})_3^{2+}$	489	740
$\text{Ru}(\text{dtbpy})_3^{2+}$	728	1150
$\text{Ru}(\text{mnbpy})_3^{2+}$	626	850
$\text{Ru}(\text{dpphen})_3^{2+}$	4417	—

^a Taken from R. A. Krause, *Struct. Bonding*, 1987, **67**, 1; A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85.

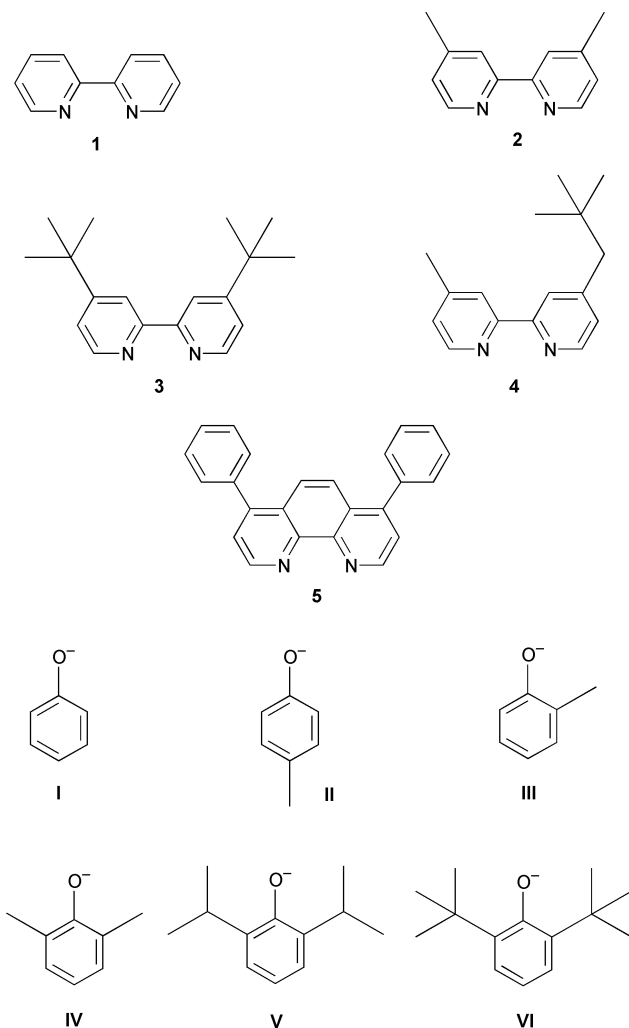


Fig. 2 The structures of the ligands (NN) and quenchers (phenolates) used in the study.

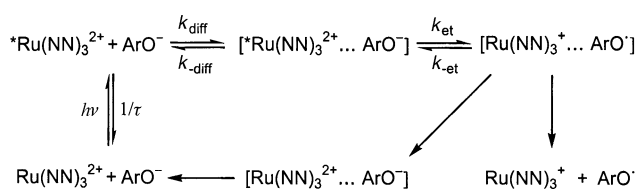
The oxidation potentials of ArO^- determined by the cyclic voltammetric technique are given in Table 2 along with the excited state reduction potentials of $\text{Ru}(\text{II})$ complexes. The oxidation potentials of substituted phenolate ions indicate that the values are influenced by the introduction of alkyl groups in the phenyl ring and by the change of alkyl group in 2 and 6 positions of phenolate ion. Similar results have been reported in the case of the phenols.³⁸ This is understandable, as isopropyl and *tert*-butyl groups are more electron releasing than methyl and thus 2,6-di-isopropylphenolate and 2,6-di-*tert*-butylphenolate ions are more easily oxidized than 2,6-dimethylphenolate ion at the electrode. The σ^* values (σ^* is

the Taft's polar substituent constant) for methyl, isopropyl and *tert*-butyl are 0.00, -0.19 and -0.30 respectively.^{39,40} The one-electron oxidation potentials of 2,6-dimethylphenolate and 2,6-di-*tert*-butylphenolate ions measured in acetonitrile are also given in Table 2. There is a constant difference of 0.320 V between the values in acetonitrile and aqueous acetonitrile. These redox potential values indicate that the phenolate ions are difficult to oxidize in aqueous acetonitrile compared to acetonitrile. This is reasonable as the added water hydrogen bonds with the O^- end of the phenolate ion thereby making the removal of an electron from ArO^- difficult. As the redox potentials of all phenolate ions used in the present study have been evaluated in a similar solvent system, the difference in E^0 values between the reported values in CH_3CN and the values measured in the present study (aqueous CH_3CN) will not affect the main aspects of our discussion. From the redox potential data in Table 1, the Gibbs energy changes, ΔG^0 , of the photoinduced ET reaction between $^*\text{Ru}(\text{NN})_3^{2+}$ and ArO^- can be estimated (*vide infra*) and are given in Table 3.

The ΔG^0 data given in Table 3 indicate that all reactions are exoergic and may proceed by rates close to the diffusion controlled rate if the reaction is controlled by exoergicity alone. The excited state redox reactions of five $\text{Ru}(\text{II})$ complexes with six substituted phenolate ions have been studied in acetonitrile–water (80 : 20 v/v) by a luminescence quenching technique and the observed quenching rate constants, k_q , are presented in Table 3.

The luminescence quenching of the excited state $\text{Ru}(\text{NN})_3^{2+}$ by phenolate ion, a reduction process, is established from the spectroscopic identification of the photo-products, phenoxyl radicals (ArO^\bullet) and $\text{Ru}(\text{NN})_3^+$ (spectra are given in our previous reports^{13,15}) and from the linear variation of $RT \ln k_q$ with the redox potentials of the phenolate ions.^{12,41} Thus the behavior of these redox systems can be discussed by a common mechanism depicted in Scheme 1.⁴²

The reactants diffuse together to form the encounter complex at the closest distance of approach. The ET occurs in this association complex [$^*\text{Ru}(\text{NN})_3^{2+} \cdots \text{ArO}^-$] resulting in the formation of a caged pair of radicals or radical ions. These in turn, either escape from the solvent cage to give the redox



Scheme 1

Table 2 Redox potentials and radii of $\text{Ru}(\text{NN})_3^{2+}$ and phenolate ions

$\text{Ru}(\text{NN})_3^{2+}$	Excited state reduction potentials ^a /V	$r_R/\text{\AA}$	Quencher	Oxidation potentials ^b /V	$r_Q/\text{\AA}$
$\text{Ru}(\text{bpy})_3^{2+}$	0.75	7.1	Phenolate	0.350	3.8
$\text{Ru}(\text{dmbpy})_3^{2+}$	0.64	7.9	4-Methylphenolate	0.275	4.0
$\text{Ru}(\text{dtbpy})_3^{2+}$	0.72	9.2	2-Methylphenolate	0.270	4.0
$\text{Ru}(\text{mnbpy})_3^{2+}$	0.65	8.9	2,6-Dimethylphenolate	0.250 (-0.07) ^c	4.2
			2,6-Diisopropylphenolate	0.210	4.6
$\text{Ru}(\text{dpphen})_3^{2+}$	0.65	10.7	2,6-Di- <i>tert</i> -butylphenolate	0.130 (-0.19) ^c	5.0

^a Values in CH_3CN vs. SCE taken from ref. 20 and 31. Addition of 20% H_2O did not affect the values appreciably. ^b Measured in the present study using KCl as the supporting electrolyte and SCE as the reference electrode in 80% acetonitrile–20% water (v/v) medium. The electrochemical cell contained a three-electrode arrangement, a saturated calomel electrode (SCE), a Pt counter electrode and a glassy carbon working electrode. A 0.01 M solution of recrystallized KCl in the same solvent was used as electrolyte. ^c Values in CH_3CN taken from ref. 10.

Table 3 Quenching rate constants, $k_q/\text{M}^{-1} \text{s}^{-1}$ for $^*\text{Ru}(\text{NN})_3^{2+}$ in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (80 : 20, v/v) at 298 K

Quencher	$\text{Ru}(\text{bpy})_3^{2+}$			$\text{Ru}(\text{dmbpy})_3^{2+}$			$\text{Ru}(\text{dtbpy})_3^{2+}$			$\text{Ru}(\text{mnbp})_3^{2+}$			$\text{Ru}(\text{dpphen})_3^{2+}$		
	Calc.	Obs.	$-\Delta G^\circ/\text{eV}$	Calc.	Obs.	$-\Delta G^\circ/\text{eV}$	Calc.	Obs.	$-\Delta G^\circ/\text{eV}$	Calc.	Obs.	$-\Delta G^\circ/\text{eV}$	Calc.	Obs.	$-\Delta G^\circ/\text{eV}$
Phenolate	7.2×10^9		0.40	2.5×10^9		0.29	5.9×10^9		0.37	2.9×10^9		0.30	2.8×10^9		0.30
4-Methylphenolate	7.2×10^9			2.1×10^9			4.3×10^8			7.8×10^8			7.7×10^8		
	1.2×10^{10}	0.48		5.8×10^9	0.37		9.8×10^9	0.44		6.4×10^9	0.38		6.3×10^9	0.38	
	9.8×10^9			6.8×10^9			7.7×10^8			3.1×10^9			1.7×10^9		
2-Methylphenolate	1.2×10^{10}	0.48		5.8×10^9	0.37		1.0×10^{10}	0.45		6.4×10^9	0.38		6.3×10^9	0.38	
	9.7×10^9			6.8×10^9			2.3×10^9			3.2×10^9			1.6×10^9		
2,6-Dimethylphenolate	1.3×10^{10}	0.50		6.8×10^9	0.39		1.1×10^{10}	0.47		7.5×10^9	0.40		7.4×10^9	0.40	
	1.6×10^{10}			1.5×10^{10}			5.3×10^9			7.7×10^9			2.8×10^9		
2,6-Diisopropylphenolate	1.8×10^{10}	0.54		1.5×10^{10}	0.43		1.8×10^{10}	0.51		1.6×10^{10}	0.44		1.6×10^{10}	0.44	
	1.8×10^{10}			1.7×10^{10}			9.8×10^8			8.3×10^8			4.5×10^8		
2,6-Di-tert-butylphenolate	1.9×10^{10}	0.62		1.7×10^{10}	0.51		1.9×10^{10}	0.59		1.8×10^{10}	0.52		1.8×10^{10}	0.52	
	7.3×10^9			5.6×10^9			2.3×10^8			3.2×10^8			1.8×10^8		

products or undergo back ET leading to the formation of the original reactants.

According to the semiclassical formulation of Marcus theory, the rate constant (k_{et}) for the photoinduced ET from ArO^- to $^*\text{Ru}(\text{NN})_3^{2+}$ is given by eqn. (1).

$$k_{\text{et}} = 4\pi^2 |H_{\text{DA}}|^2 / h(4\pi\lambda RT)^{1/2} \exp(-\Delta G^\ddagger/RT) \quad (1)$$

where $|H_{\text{DA}}|$ is the electronic coupling coefficient, λ is the reorganization energy and ΔG^\ddagger , the Gibbs energy of activation. Marcus eqn. (2) relates ΔG^\ddagger with the Gibbs energy change ΔG^0 and the reorganization energy (λ).

$$\Delta G^\ddagger = (\lambda + \Delta G^0)^2 / 4\lambda \quad (2)$$

The value of ΔG^0 can be calculated from the redox potentials of $^*\text{Ru}(\text{NN})_3^{2+}$ and the phenolate ions using eqn. (3).

$$\Delta G^0 = E^0(\text{Q}^{\cdot-}/\text{Q}) - E^0(^*\text{Ru}(\text{NN})_3^{2+}/\text{Ru}(\text{NN})_3^+) + w_{\text{p}} - w_{\text{r}} \quad (3)$$

In eqn. (3), w_{p} and w_{r} represent the electrostatic work required to bring two photoproducts ($\text{Ru}(\text{NN})_3^+$ and ArO^\cdot) or two initial reactants ($\text{Ru}(\text{NN})_3^{2+}$ and ArO^-) together to the close contact distance to form the ion pair and the encounter complex respectively. The values of the work terms can be calculated from the Debye equation⁴³ and used in the estimation of the ΔG^0 values. The reorganization energy (λ) is the sum of two contributions, $\lambda = \lambda_{\text{out}} + \lambda_{\text{in}}$, where λ_{in} represents the activation of the vibrational modes of the reactants and λ_{out} represents changes in the solvent structure around the reactants, which is strongly dependent on the solution medium. The value of λ_{out} can be estimated from eqn. (4).

$$\lambda_{\text{out}} = (\Delta e)^2 (1/2r_{\text{R}} + 1/2r_{\text{Q}} - 1/d)(1/\epsilon_{\text{op}} - 1/\epsilon_{\text{s}}) \quad (4)$$

where Δe , D_{op} and D_{s} are the charge transferred, the optical and static dielectric constants respectively. The radii of $\text{Ru}(\text{NN})_3^{2+}$ and ArO^- are represented by r_{R} and r_{Q} respectively and are given in Table 2 and d is the sum of the radii, $r_{\text{R}} + r_{\text{Q}}$. The values of λ_{out} calculated from eqn. (4) are in the range 0.63–0.84 eV. In the calculation of λ_{out} the static dielectric constant (ϵ_{s}) and refractive index $\epsilon_{\text{op}} = n^2$, n is the refractive index (ϵ_{op}) of CH_3CN are used. Though the presence of 20% H_2O changes the values of ϵ_{s} and ϵ_{op} of the medium slightly, the small change in λ_{out} due to this will not affect the discussion as the same ϵ_{s} and ϵ_{op} values have been used for all redox systems. It is pertinent to point out that λ_{out} is distance (d) dependent and the variation of λ_{out} with distance is taken care of in its calculation. There is no significant change in the Ru–N bond distance when $\text{Ru}(\text{NN})_3^+$ is formed after electron transfer from ArO^- to $\text{Ru}(\text{NN})_3^{2+}$. But a difference of 0.13 Å

is noticed in the C–O bond distance when phenoxyl radical is formed from phenolate ion after ET.⁴⁴ The delocalization of the unpaired electron onto the aromatic ring causes this difference between the structures of the phenoxyl radical and phenolate ion. The C–O bond length in the phenoxyl radical is 1.23 Å while the value in the phenolate ion is 1.36 Å. Experimental verification of these structural differences comes from IR data. The experimental vibrational frequency for the C–O stretch of $\text{C}_6\text{H}_5\text{O}^\cdot$ at 1505 cm^{-1} is 240 cm^{-1} larger than in $\text{C}_6\text{H}_5\text{O}^-$.⁴⁵ This leads to the λ_{in} value of 0.2 eV.^{16,19} Thus the total reorganization energy, λ , value for this redox system is in the range 0.83–1.04 eV.

A careful analysis of the k_{q} data in Table 3 reveals that the quenching rate constants are influenced by the introduction of alkyl and phenyl groups in the ligands, 2,2'-bipyridine and 1,10-phenanthroline and also by the substituents in the phenolate ion. To understand the effect of ΔG^0 on the k_{q} of the reaction, $\log k_{\text{q}}$ is plotted against ΔG^0 and the plot is shown in Fig. 3. The shape of the plot is interesting. With an increase in the exothermicity of the reaction ($-\Delta G^0$), the k_{q} value increases, reaches a maximum but then further increase in $-\Delta G^0$ leads to a decrease in the k_{q} value. The appearance of this plot may tempt one to postulate that the Marcus inverted region has been observed in this photoinduced ET reaction but careful scrutiny of the data reveals that the low k_{q} value observed for the phenolate ions containing isopropyl and *tert*-butyl groups is due to the steric effect of these bulky groups. It is to be

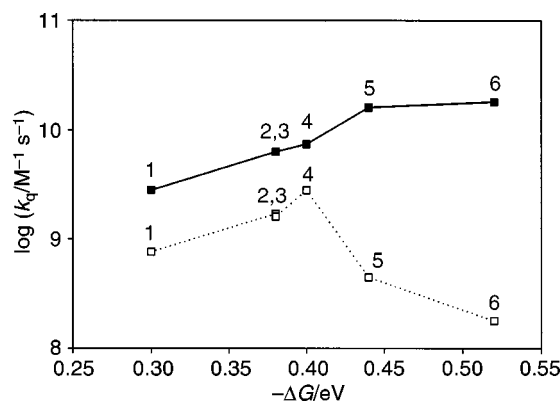


Fig. 3 The $\log k_{\text{q}}$ vs. ΔG° plot for different phenolate ions with $\text{Ru}(\text{dpphen})_3^{2+}$ (solid line: calculated; dotted line: observed) 1. Phenolate ion; 2. 4-methylphenolate ion; 3. 2-methylphenolate ion; 4. 2,6-dimethylphenolate ion; 5. 2,6-diisopropylphenolate ion; 6. 2,6-di-*tert*-butylphenolate ion.

noted that the Marcus inverted region can be observed only if the condition $-\Delta G^0 > \lambda$ is satisfied, which is not the case in this reaction. The value of λ is in the range 0.83–1.04 eV. Thus only if the $-\Delta G^0$ value exceeds 0.85 eV can one check for observation of the Marcus inverted region. Thus the low k_q value observed with PhO^- carrying bulky isopropyl and *tert*-butyl groups at high exoergicity confirms the important role of the steric effect. In order to understand the role of the steric effect in depth, the effect of changing ΔG^0 and the electron transfer distance, d , on the quenching rate constant of the reaction, must be considered separately *i.e.*, one parameter must be maintained constant when the other one varies with the nature of the reactant. We want to emphasize the point that we could see the role of the steric effect only when both reactants carry bulky groups. Since the aim of our present study is to look at the effect of introducing bulky alkyl groups in the *ortho*-position of the phenolate ion, further discussion is centered on the reaction of 2,6-disubstituted phenolate ions. If we look at the ΔG^0 data given in Table 3, it remains almost constant for the complexes Ru(dmbpy)_3^{2+} , Ru(mnbpy)_3^{2+} and Ru(dpphen)_3^{2+} but d varies. Thus the decrease in k_q values in the order $\text{Ru(dmbpy)}_3^{2+} > \text{Ru(mnbpy)}_3^{2+} > \text{Ru(dpphen)}_3^{2+}$ (with phenolate ion as the quencher $\text{Ru(mnbpy)}_3^{2+} \simeq \text{Ru(dpphen)}_3^{2+}$) may be attributed to the increase in the electron transfer distance. If we take other redox systems with same driving force, for example Ru(bpy)_3^{2+} -2,6-dimethylphenolate, Ru(dtbp)_3^{2+} -2,6-diisopropylphenolate, Ru(mnbpy)_3^{2+} -2,6-di-*tert*-butylphenolate and Ru(dpphen)_3^{2+} -2,6-di-*tert*-butylphenolate, though ΔG^0 is almost constant, the k_q value decreases with increase in the bulkiness of the system. To understand the real role of the steric effect in these photoredox reactions, these data should be analyzed by taking into account the change in the ΔG^0 values given in Table 3. This can actually be done by calculating the rate constants for ET (k_{et}) theoretically by applying Marcus theory to these photoinduced redox reactions (using eqn. (1)–(4)). The k_q data can be calculated by substituting the value of k_{et} derived from Marcus theory in eqn. (5)

$$k_q = k_{\text{et}} k_{\text{diff}}/k_{\text{et}} + k_{\text{diff}} \quad (5)$$

and the calculated and experimental values obtained for Ru(dpphen)_3^{2+} are given in Fig. 3 and for all Ru(II) complexes in Table 3. In eqn. (5) k_{diff} is the rate constant for the process of diffusion to form the encounter complex. The value of k_{diff} has been calculated using the Debye–Smoluchowski equation.⁴⁶ Scrutiny of the data in Fig. 3 reveals that there is an appreciable difference in the quenching rate constants between the calculated and experimental values for the system $^*\text{Ru}(\text{NN})_3^{2+}$ - ArO^- . The difference between k_q^{obs} and k_q^{cal} increases with the increase in the bulkiness of the quencher *i.e.*, with phenolate ions containing isopropyl and *tert*-butyl groups, the difference is very large. Thus the large difference between the calculated and experimental k_q values in the case of phenolate ions carrying bulky alkyl groups in the 2,6-positions may be attributed to the steric effect. Though steric effects have been observed in several previous investigations on intermolecular ET reactions, systematic analysis of the results has been carried out in only a few cases.^{32,47,48} In our previous study³¹ on the ligand-induced steric effect in the reactions of $\text{Ru}(\text{NN})_3^{2+}$ with aromatic amines, the steric effect was explained by correlating the k_q data to the change in the ET distance. In most of the studies, the increase in the ET distance with the increase in the bulkiness of the reactants was considered as the major reason for the decrease in the electronic coupling matrix element (H_{DA}) thereby rendering the ET reaction nonadiabatic. The data obtained for the quenching of Eosin Y dye with sterically hindered phenols are similar to our results; k_q values for the quenching of Eosin Y dye by 2-methylphenol, 2,4,6-trimethylphenol and 2,6-di-*tert*-

butyl-4-methylphenol are 7.7 (0.85 V), 5.2 (0.78 V) and 0.45 (0.66 V) $\times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ respectively.⁴⁷ The values in parentheses are the oxidation potentials of the phenols. If one compares the k_q values obtained for 2,4,6-trimethylphenol and 2,6-di-*tert*-butyl-4-methylphenol, the latter is 11 times smaller than the former though the latter has a more favorable redox potential value. In the present study also if we compare the k_q data observed for 2,6-dimethylphenolate and 2,6-di-*tert*-butylphenolate ions, the difference is in the range 15–24 times, particularly with Ru(II) complexes containing bulky ligands.

The k_q values obtained for different substituted phenolates collected in Table 3 and the arguments presented above qualitatively explain the importance of the change in size of the alkyl group in ArO^- on the ET reaction of phenolates with $^*\text{Ru}(\text{NN})_3^{2+}$. The change in the structure of the alkyl group in close proximity to the reaction center alters the polar as well as the steric effects. To treat quantitatively the effect of the change of alkyl groups in ArO^- on the reactivity of phenolate ions with $\text{Ru}(\text{NN})_3^{2+}$ the observed k_q data may be analyzed in terms of Taft's empirical eqn. (6) and (7).^{39,40}

$$\log k_q = \log k_0 + \rho^* \sigma^* \quad (6)$$

$$\log k_q = \log k_0 + \delta E_s \quad (7)$$

where σ^* and E_s are the Taft's polar and steric substituent constants and ρ^* and δ are the corresponding susceptibility constants. If the polar effect of the alkyl group alone is the predominant factor in this reaction, then the change of alkyl group should increase the k_q value in the order methyl < isopropyl < *tert*-butyl. But the k_q data given in Table 3 are in the opposite order. It is important to mention that the change of polar effect with the change in the structure of the substrate will be clearly felt in the redox potential value (*cf.* Table 2). The electrochemical data of alkyl-substituted phenolate ions indicate that the oxidation potential is not very sensitive to the bulkiness of the alkyl group in the *ortho*-position. On the other hand the ET reaction of ArO^- to $\text{Ru}(\text{NN})_3^{2+}$ is sensitive to the steric nature of the phenolate ion. Thus from this analysis we realize that, in addition to the polar effect, the steric effect also plays an important role in the reaction of phenolate ions. An increase in the size of the alkyl group may bring in the importance of the steric effect and thereby the decrease in the k_q value. As the observed k_q value decreases with the increase in the bulkiness of the alkyl group in the phenolate ions, k_q values have been correlated with the Taft's steric substituent constant, E_s . The correlation is satisfactory in all five complexes (slope = 0.25; $r = 0.98$). As the introduction of the alkyl groups leads to a change in both polar and steric effects, the single parameter equation may not be sufficient to account for the observed effect. Since there is little available data, the application of the multiparameter equation involving the polar and steric components is not relevant statistically and thus not attempted here.

Comparison of the rate constants obtained from the Marcus theory and the experimental values has led us to conclude that photoinduced ET reactions of Ru(II) complexes with sterically hindered phenolate ions may be nonadiabatic. According to the semiclassical theory of ET, the rate constant for a nonadiabatic ET reaction is given by eqn. (1). The electronic coupling matrix element, $|H_{\text{DA}}|$, is a measure of the coupling between the orbitals of the donor and the acceptor. The distance dependence of $|H_{\text{DA}}|$ is given by eqn. (8).

$$|H_{\text{DA}}|^2 = |H_{\text{DA}}|_0^2 \exp[-\beta(d - d_0)] \quad (8)$$

where $|H_{\text{DA}}|_0$ is the value of the matrix element when the reaction is adiabatic at van der Waals contact distance (d_0) and β is the attenuation factor. The value of $|H_{\text{DA}}|$ is taken to be 200 cm^{-1} when $d = 3 \text{ \AA}$ and it decreases with distance by the factor 1.0 \AA^{-1} .⁴⁹ The minimum and maximum d values in the present study are 10.9 and 15.7 \AA respectively. The value

of d is calculated by simply adding the radii of $\text{Ru}(\text{NN})_3^{2+}$ and ArO^- . If we substitute these values in eqn. (8) the value of $|H_{\text{DA}}|$ becomes 3.9 and 0.35 cm^{-1} respectively. Thus the increase in d by 4.8 \AA leads to a decrease in k_{et} by a factor of ~ 10 which is similar to the decrease in the observed quenching rate constants with increase in the size of the reactants. Thus the inference is that with the introduction of bulky substituents in the reactants the ET reaction becomes more non-adiabatic. According to Sutin *et al.* if $H_{\text{DA}} < 10 \text{ cm}^{-1}$ the reaction is nonadiabatic.¹⁶ It is interesting to recall that it has now been established that the great majority of ET reactions studied so far are nonadiabatic.⁵⁰

In earlier studies the observed steric effect has been explained in terms of the increase in the ET distance with the introduction of bulky substituents in the reactants. Thus if the change in the distance is the major factor responsible for the observed steric effect, then the value of k_{et} should decrease exponentially with the increase in the ET distance (d) (eqn. (9)).

$$k_{\text{et}} = k_{\text{et}}^0 \exp[-\beta(d - d_0)] \quad (9)$$

where k_{et}^0 is the rate constant of ET at contact distance (d_0). Since ΔG^0 and λ are distance-dependent parameters, to evaluate the variation of $|H_{\text{DA}}|$ with distance, eqn. (1) is used to calculate $|H_{\text{DA}}|^2$. Since eqn. (1) contains ΔG^0 and λ terms, the variation of these parameters with distance is taken care of when we substitute the values for the different reactants in this equation. Now the values of $|H_{\text{DA}}|^2$ calculated from eqn. (1) for the reaction of different $\text{Ru}(\text{NN})_3^{2+}$ with 2,6-di-*tert*-butylphenolate ion are plotted against the electron transfer distance, $d (= r_{\text{R}} + r_{\text{Q}})$. The plot is nonlinear and most of the points deviate from the linear plot. This deviation from linearity may be attributed to the value of d different from the sum of the radii of the reactants *i.e.*, $d \neq r_{\text{R}} + r_{\text{Q}}$. Even in the case of intramolecular ET reactions, the actual ET distance is shorter than the distance between the electron donor and acceptor.⁵¹ When we look at the reactants, both $\text{Ru}(\text{NN})_3^{2+}$ and ArO^- carry hydrophobic aryl moieties and opposite charges. It is pertinent to point out that Hoffmann *et al.*⁵² have reported from NMR spectral data the importance of π -stacking between the phenyl ring of phenol and the pyridine rings of $\text{Ru}(\text{bpy})_3^{2+}$. NMR spectral studies of $\text{Ru}(\text{bpy})_3^{2+}$ in the presence of phenols indicate face-to-face (parallel) π -stacking interaction rather than edge-to-edge (T-shape) orientations. A face-to-face orientation is expected to minimize the steric effect when $\text{Ru}(\text{bpy})_3^{2+}$ and phenol stack. The π - π stacking may facilitate orbital overlap of the reactants whereas the bulky groups disfavor it. Shetty *et al.*⁵³ have shown that the sensitivity of the system to the steric environment may provide insight on the geometry of π - π stacking. The presence of bulky *tert*-butyl groups prevents the molecules from closely approaching each other, thereby hindering π - π interactions. The steric effect observed in the present study supports the notion that the π - π interaction involves a face-to-face stacking rather than an edge-to-face orientation which may lead to a more predominant steric effect. Thus we presume that one of the reasons for the smaller steric effect in the present system is the π -stacking between the ligand of the metal complex and the phenyl ring of the electron donor, ArO^- . In order to check the ground state complex formation between $\text{Ru}(\text{NN})_3^{2+}$ and ArO^- we have recorded the absorption spectrum of the mixture of $\text{Ru}(\text{bpy})_3^{2+}$ and PhO^- using concentrations of reactants similar to those used for the quenching studies. No evidence is obtained for ground state complex formation between $\text{Ru}(\text{NN})_3^{2+}$ and ArO^- from absorption spectral studies.

It is interesting to compare the present results with the steric effect observed on the reaction of *ortho*-substituted phenols with alkyl radicals.⁵⁴ The rate constants for the unsubstituted, methyl and *tert*-butyl substituted phenols are

5.3, 6.4 and $0.48 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ respectively, confirming the known fact that steric factors have a significant influence on the reactivity of phenols.

In summary, the present study and previous studies confirm the point that the steric crowding about the hydroxy group in phenol is very important in decreasing the reactivity of phenols. However, the reactivity of phenolate ions carrying bulky alkyl groups, apart from the steric effect, is affected by hydrophobic interactions and π - π stacking between the reactants. Thus these factors should be taken into account when we want to use these phenols as inhibitors of radical chain reactions and to test their toxicity.

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