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Journal of Photochemistry and Photobiology A: Chemistry 167 (2004) 101–109
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Redox chemistry of Ru(II) complexes of 6,7-dicyanodipyridoquinoxaline: a radiation chemical study

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Received 31 January 2004; received in revised form 29 March 2004; accepted 2 April 2004

Dedicated to the memory of the coauthor Prof. B.G. Maiya—who died when this publication has been in process.

Available online 28 July 2004

Abstract

The reactions of $^{\bullet}OH$, $O^{\bullet-}$, $SO_4^{\bullet-}$, $N_3^{\bullet}$ and e_{aq}^- with the ligands-1,10-phenanthroline (phen) and 6,7-dicyanodipyrido [2,2-d:2′,3′-f] quinoxaline (dicnq) and a series of their Ru(II) complexes ($[Ru(phen)_3]^{2+}$, $[Ru(phen)_2(dicnq)]^{2+}$, $[Ru(phen)(dicnq)_2]^{2+}$ and $[Ru(dicnq)_3]^{2+}$) have been studied by pulse radiolysis with optical detection. The $^{\bullet}OH$ and hydrated electron react with the ligands via adduct formation with diffusion controlled rates. The transient spectra obtained in the reactions of $^{\bullet}OH$ with phen has two peaks (350 and 430 nm) having nearly equal intensities and a broad maximum at 380 nm with dicnq. In the case of complexes, the rate constants for the reactions of $^{\bullet}OH$ and e_{aq}^- are in the range $(7.5–11.8) \times 10^9$ and $(1.6–3.1) \times 10^{10}$ $dm^3\,mol^{-1}\,s^{-1}$, respectively. The rate for the $^{\bullet}OH$ reaction increased with the dicnq content in the complex, whereas a reverse trend was seen in the hydrated electron reaction. Neither the ligand nor the Ru(II) complex except $[Ru(phen)_2(dicnq)]^{2+}$ is reactive toward the azide radical. In the reaction of $^{\bullet}OH$ with Ru(II) complexes, the transients have absorption maxima in the range of 380–435 nm whose intensity decreased with the dicnq content. The spectra measured in the reactions of $^{\bullet}OH$ and one electron oxidants ($Cl_2^{\bullet-}$, $SO_4^{\bullet-}$ or $N_3^{\bullet}$) with the complexes are not identical unlike with ligands. The reaction mechanism involves the addition of $^{\bullet}OH$ and e_{aq}^- to the ligands of the complexes and the conversion of Ru(II)–Ru(III) by the one electron oxidant.

Keywords: Pulse radiolysis; Ru(II) complex; Quinoxaline; Phenanthroline

1. Introduction

The radiation chemical techniques have been effectively applied to study the free radical chemistry of a variety of organic and biologically important molecules [1]. Water radiolysis is found to be the convenient way in the selective production of oxidising (e.g. $^{\bullet}OH$, $O^{\bullet-}$, $N_3^{\bullet}$) and reducing (e.g. e_{aq}^-, H and $CO_2^{\bullet-}$) radicals. In this technique, the radical yields are precisely known and the compounds with low solubility ($\leq 10^{-3}$ mol dm^{-3}) in water can be easily employed.

The radiation chemical studies are generally aimed at the evaluation of kinetics and the measurement of transient absorption spectra with a view to understand the mechanistic details. In the recent past, our group has carried out radiation chemical studies of a variety of substituted benzenes (halobenzenes [2], toluenes [2], cresols [3], benzaldehydes [4], anilines [5]) with a view to gain an insight into the structure-reactivity relationship and the nucleobases [6] for understanding the chemical basis of radiation induced DNA damage.

The redox chemistry of Ru(II) complexes is important because of their antitumour [7], anticancer [8] properties and application in solar cells [9]. The study of their absorption and luminescence spectra and properties like DNA binding has been well explored [10]. As pyridine-based ligands are preferred in such studies, the synthesis of the complexes with ligands having single charge transfer property is challenging and is, therefore, of current interest.

$[Ru(bpy)_3]^{2+}$ can be considered as a model to understand the reactions of various oxidizing and reducing radicals with such complexes by radiation chemical methods. It is re-

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doi:10.1016/j.jphotochem.2004.04.001

ported [11,12] that both $^{\bullet}OH$ and e_{aq}^- add to the aromatic ring without change in the oxidation state of ruthenium and the absorption maximum of the OH adduct is around 760 nm. The reaction of the oxidant, $Cl_2^{\bullet-}$, produced by pulse radiolysis [13] method causes the conversion of Ru(II) → Ru(III) as no characteristic peak was observed at this wavelength.

Rapid one electron reduction of the ruthenium complexes [14,15] was achieved in the aqueous solution by pulse radiolysis with conductivity and optical absorption detection. In some ruthenium complexes, protonation is observed in the non-coordinated nitrogen of the pyridine-based ligands and the relationship between pK_a and reduction potential was studied [14]. The reduction of Ru(II) complexes having ligands, 2,2′-bipyridine, 2,3-bis(2-pyridyl)quinoxaline, 2,3-bis(2-pyridyl)pyrazine, 2,3-bis(2-pyridyl)-5,6-dihydroxypyrazine, by e_{aq}^- has been reported [15] where the rates are diffusion controlled. Similar results were obtained from the pulse radiolysis of Ru(III, III) oxo aceto dinuclear complex [16] in acetonitrile saturated with oxygen. The transient absorption spectra have shown single charge transfer. The study of one electron oxidised Ru(II) dye [17] was done using $N_3^{\bullet}$ or $Br_2^{\bullet-}$ and its product distribution was studied by γ-radiolysis.

The intramolecular electron transfer reactions in a related series of ruthenium modified proteins [18] were studied by reductive pulse radiolysis. It was shown that 2,2′-bipyridine and 4,4′-diamino-2,2′-bipyridine facilitate one electron reduction, whereas intramolecular oxidation was seen in cytochrome *c*. It was concluded that the nature and number of ligands act as a driving force for the reaction.

Recently, the synthesis of a new ligand 6,7-dicyanodipyrido[2,2-d:2′,3′-f] quinoxaline (dicnq) for ruthenium complexes having better 'molecular light switch' effect, i.e. charge transfer property due to cyano groups is reported [19]. These complexes have been well characterised and their absorption as well as emission spectra are studied. Therefore, it is interesting to study the redox chemistry of its ruthenium complexes. The present work is a comprehensive study of reactions of $^{\bullet}OH$, $O^{\bullet-}$, $SO_4^{\bullet-}$, $N_3^{\bullet}$ and e_{aq}^- with a series of ruthenium complexes having the general formula $[Ru(phen)_n(dicnq)_{3-n}]^{2+}$ ($n = 0, 1, 2, 3$) where phen is 1,10-phenanthroline and the structures of the ligands are shown in Fig. 1.

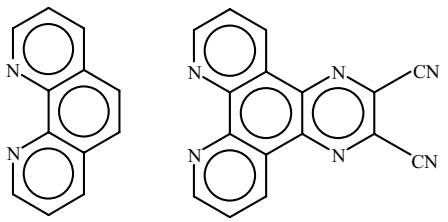


Fig. 1. Ligands used in this study. 1,10-phenanthroline (phen) and 6,7-dicyanodipyrido[2,2-d:2′,3′-f]quinoxaline (dicnq).

The results from kinetics and spectral studies of the oxidised and reduced species of the phen and dicnq ligands and their complexes with Ru(II) by pulse radiolysis technique are presented.

2. Experimental

2.1. Chemicals

The ligand dicnq and the complexes $[Ru(phen)_3]^{2+}$, $[Ru(phen)_2(dicnq)]^{2+}$, $[Ru(phen)(dicnq)_2]^{2+}$ and $[Ru(dicnq)_3]^{2+}$ were synthesised, purified and characterised as reported earlier [19]. All other chemicals used were of AR grade. The solutions were freshly prepared in water purified by Millipore Milli-Q system. The pH was adjusted by phosphate buffer (pH 7) or 0.1 mol dm^{-3} NaOH (pH ∼ 13). The ground state spectra were taken just before the irradiation.

2.2. Irradiations

The LINAC facility (7 MeV, 50 ns) at BARC, Mumbai, was used to measure the kinetics and transient absorption spectra. The detailed description of the facility has been already reported [20]. The dose rate was determined using the KSCN dosimetry where $(SCN)_2^{\bullet-}$ has absorption maxima at 480 nm with a molar absorptivity of 7600 dm^3 mol^{-1} cm^{-1}. The dose rate was usually kept at 7 Gy per pulse.

γ-Radiolysis of aqueous solutions of the ligands and the complexes were performed in a ^{60}Co source at the Department of Chemistry, University of Pune, with a dose rate of 11 Gy min^{-1}. The chemical oxidation was carried out by gradual addition of ceric ammonium sulphate and the spectral changes were measured. The concentration of the complex was kept around 20×10^{-6} mol dm^{-3} and the amount of Ce(IV) was varied from 0.12×10^{-3} to 2.0×10^{-3} mol dm^{-3}.

The high energy radiation leads to the generation of following radiolytic products:

$$H_2O \rightsquigarrow H, H_2, e_{aq}^-, {}^{\bullet}OH, H_2O_2, H_3O^+$$

e_{aq}^- was converted into $^{\bullet}OH$ by saturating the aqueous solution with N_2O gas:

$$e_{aq}^- + N_2O \rightarrow N_2 + {}^{\bullet}OH + OH^-,$$

$$k = 8.7 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

In strongly alkaline medium, $^{\bullet}OH$ is rapidly converted into its conjugate base form:

$$^{\bullet}OH + OH^- \overset{pK_a=11.9}{\rightleftharpoons} O^{\bullet-} + H_2O$$

The sulphate radical anion was produced from the reaction of e_{aq}^- and $H^{\bullet}$ with $S_2O_8^{2-}$ (0.015 mol dm^{-3}) in the presence of inert gas and 0.2 mol dm^{-3} *t*-butanol by following reaction:

$$S_2O_8^{2-} + e_{aq}^-(H) \rightarrow SO_4^{\bullet-} + SO_4^{2-}(HSO_4^-)$$

The secondary radical $N_3^{\bullet}$ was generated in N_2O saturated solution containing 0.015 mol dm^{-3} NaN_3 where $^{\bullet}OH$ is converted to $N_3^{\bullet}$:

$$^{\bullet}OH + N_3^- \rightarrow N_3^{\bullet} + OH^-, \quad k = 1.2 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}\ at\ pH\ 7$$

For the study of the reaction of e_{aq}^-, the solutions were saturated with N_2 containing *t*-butanol (0.2 mol dm^{-3}) as a scavenger:

$$^{\bullet}OH + (CH_3)_3COH \xrightarrow{N_2} {}^{\bullet}CH_2C(CH_3)_2OH + H_2O, \quad k = 7.6 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$$

The $Cl_2^{\bullet -}$ was produced by pulse radiolysis of the N_2O saturated solution containing 0.05 mol dm^{-3} LiCl and 1×10^{-4} mol dm^{-3} HCl.

2.3. Ground state correction

The absorption spectra of the transient and their molar absorptivity values at λ_{max} are important for the characterisation of the transient species. After subjecting the parent to the electron beam pulse, a fraction of the parent molecules may be lost due to the chemical reaction. Bleaching signals are obtained where the parent and transient absorbance overlap and the spectrum does not represent the true characteristic of the transient species. Therefore, a correction term representing the amount of parent depleted has to be incorporated in the measurement. If it is assumed that the entire radicals generated react with the complex, then $\Delta A = \Delta\varepsilon l[R]$, where [R] is the concentration of the radical produced and $\Delta\varepsilon = \varepsilon_r - \varepsilon_p$. The ε_r and ε_p refer to the molar absorptivities of the transient and parent, respectively. A knowledge of the dose per pulse, ΔA and ε_p leads to the determination of ε_r as shown in the following equation:

$$\varepsilon_r = \varepsilon_p + \frac{A_p G_d \varepsilon_d}{G_r A_d} \quad (1)$$

The symbols have their usual meaning and the subscript d corresponds to the KSCN dosimeter solution.

3. Results and discussion

3.1. Kinetics

3.1.1. Reactions of $^{\bullet}OH$ and $O^{\bullet -}$

The reactions of the OH radical with the ligands (phen and dicnq) as well as their complexes with ruthenium were carried out in N_2O saturated aqueous solution at pH 7 and the rates of formation of the transients were determined at their respective absorption maxima in the wavelength region 340–430 nm. The concentration of ligands phen and dicnq was maintained between (0.2–1.0) $\times 10^{-3}$ and (0.2–1.0) $\times 10^{-4}$ mol dm^{-3}, respectively. The concentration range for $[Ru(phen)_3]^{2+}$ is (1.0–5.0) $\times 10^{-4}$ and (1.0–5.0) $\times 10^{-5}$ mol dm^{-3} for $[Ru(phen)_2(dicnq)]^{2+}$. For the rest of the complexes, it is (0.2–1.0) $\times 10^{-4}$ mol dm^{-3}. The rates have shown a linear dependence with [solute]. The measured *k* values in this work are accurate to within 10%.

The second order rate constant measured with phen (430 nm) was found to be 5×10^9 dm^3 mol^{-1} s^{-1} which is in reasonable agreement with that reported earlier by Teply et al. [21a] ($k = 7.0 \times 10^9$ dm^3 mol^{-1} s^{-1}). Due to the poor signal/noise ratio, in the case of dicnq, the rate was measured using a single concentration (10^{-4} mol^{-1} dm^3) and $k = 1.2 \times 10^9$ dm^3 mol^{-1} s^{-1} was obtained. Our *k* values for the ligands are similar to those reported [21] earlier for bipyridine ($k = 6.2 \times 10^9$ dm^3 mol^{-1} s^{-1}) and for the substituted quinoxalines like bpq^+ and Me_2bpq^+ ligands.

The absorption buildup in the case of Ru(II) complexed with phen and dicnq ligands nearly corresponded to the bleaching of the ground state absorption at 450 nm and the relevant traces in the case of $[Ru(phen)_2(dicnq)]^{2+}$ for 5.0×10^{-5} mol dm^{-3}, as an example, are shown in Fig. 2. The formation trace recorded at 350 nm shows two processes: a major process involving the addition of the OH radical to the ligand as well documented in [22] and an additional minor process. However, the nature of the latter transient species is not yet clear.

The rate constants measured for the OH radical reaction with Ru(II) complexes, tabulated in Table 1, are in the order (0.7–1.1) $\times 10^{10}$ dm^3 mol^{-1} s^{-1}. The values are in agreement with those measured when ruthenium is complexed with other pyridine-based ligands [11,22] (e.g. $k = 7 \times 10^9$ dm^3 mol^{-1} s^{-1} for $[Ru(bpy)_3]^{2+}$ at pH 7). Furthermore, the rate constants have shown an increase when phen was completely replaced by dicnq (Table 1). For example, the rate constant measured with $[Ru(phen)_3]^{2+}$ is 7.5×10^9 dm^3 mol^{-1} s^{-1}, whereas the *k* value for $[Ru(dicnq)_3]^{2+}$ is 11.8×10^9 dm^3 mol^{-1} s^{-1}. Despite the presence of electron withdrawing cyano groups, the increasing aromaticity of the ligands seems to be the determining factor for the observed increase in the rates.

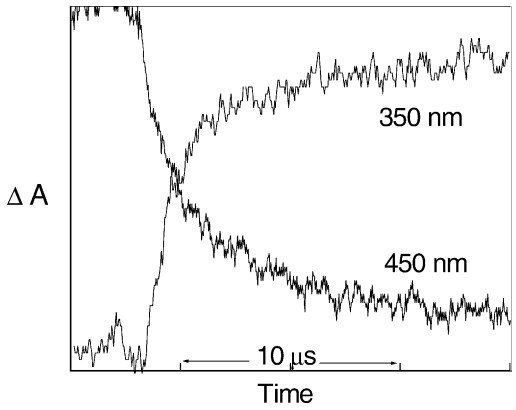


Fig. 2. The time-dependent absorption buildup at 350 nm and the corresponding bleaching at 450 nm recorded after the pulse in N_2O saturated neutral solution of $[Ru(phen)_2(dicnq)]^{2+}$, dose per pulse ~7 Gy.

Table 1
The second order rate constants ($k/10^9$ dm^3 mol^{-1} s^{-1}) and their respective absorption maxima (λ_{max} (nm)) measured in the study

Compound	$^{\bullet}OH$		$O^{\bullet-}$		$SO_4^{\bullet-}$	e^-_{aq}	
	λ_{max}	k	λ_{max}	k	λ_{max}	λ_{max}	k
Phen	350 430	5.0	340 440	0.8	430	325 360 490	8.8
Dicnq	380	(1.2)	380 450	1.5	380	310 380	(6.5)
$[Ru(phen)_3]^{2+}$	435 500	7.5	420	2.4	430	435 500	31.3
$[Ru(phen)_2(dicnq)]^{2+}$	425	8.2	420	(3.7)	n.d.	440	25.7
$[Ru(phen)(dicnq)_2]^{2+}$	420	8.7	420	(2.4)	n.d.	440	21.9
$[Ru(dicnq)_3]^{2+}$	380	(11.8)	400	(1.0)	n.d.	440	(16.0)

The values in the parenthesis are calculated from a single trace.

The reaction of $O^{\bullet-}$ was carried out in N_2O saturated basic solutions (pH ∼ 13) of phen and dicnq where the reacting species is mainly $O^{\bullet-}$ and the second order rate constant with dicnq was found to be 1.5×10^9 dm^3 mol^{-1} s^{-1}, i.e. nearly doubled compared to phen (0.8×10^9 dm^3 mol^{-1} s^{-1}). This is in contrast to the trend observed in the $^{\bullet}OH$ reaction and since $O^{\bullet-}$ is a nucleophile; the electron deficient dicnq ligand is more reactive.

The second order rates constants measured in the $O^{\bullet-}$ reaction with the Ru(II) complexes are in the range (1.0–3.7) $\times 10^9$ dm^3 mol^{-1} s^{-1} (Table 1) and the rate in $[Ru(phen)_2(dicnq)]^{2+}$ was found to be the highest. In contrast to the behaviour with the $^{\bullet}OH$ reaction, a decrease in the rates was observed on going from $[Ru(phen)_2(dicnq)]^{2+}$ to $[Ru(dicnq)_3]^{2+}$.

3.1.2. Reactions of $N_3^{\bullet}$ and $SO_4^{\bullet-}$

No predominant signal was observed in the reaction of the azide radical ($E^0 = 1.33$ V) reaction even on a 1 ms scale for both the ligands and with the complexes (10^{-4} mol dm^{-3}). The exception is $[Ru(phen)_2(dicnq)]^{2+}$ where the absorption spectrum could be recorded. Thus, the rates of oxidation of the ligands and the other ruthenium complexes by the azide radical are $\leq 10^7$ dm^3 mol^{-1} s^{-1}.

The lack of oxidation by $N_3^{\bullet}$ is in accord with the oxidation potentials reported [19] for the complexes by cyclic voltammetry in CH_3CN. No oxidation was observed for both phen and dicnq when the potential was scanned up to +1.8 V. However, the complexes have shown lower oxidation potential values in the range 1.26–1.51 V for $[Ru(phen)_3]^{2+}$ to $[Ru(dicnq)_3]^{2+}$, respectively.

When a stronger oxidant such as $SO_4^{\bullet-}$ ($E^0 = 2.45$ V) was used, the oxidation of the ruthenium centre in $[Ru(phen)_3]^{2+}$ was found to be diffusion controlled (>10^9 dm^3 mol^{-1} s^{-1}). Due to the thermal reaction of $S_2O_8^{2-}$ with $Ru(phen)_2(dicnq)]^{2+}$ $[Ru(phen)(dicnq)_2]^{2+}$ and $[Ru(dicnq)_3]^{2+}$, the reaction of $SO_4^{\bullet-}$ could not be studied.

3.1.3. Reactions of e^-_{aq}

The rate constants for the e^-_{aq} reaction were determined in N_2 saturated solutions containing 0.2 mol dm^{-3} *t*-butanol at pH 7 and the rate was monitored from the decay of e^-_{aq} at 700 nm.

Both the ligands and the complexes were found to be highly reactive toward e^-_{aq}. The k values are 6.5×10^9 for dicnq and 8.8×10^9 dm^3 mol^{-1} s^{-1} in the case of phen. This is in accord with the values observed in other pyridine-based ligands [21] and unsubstituted quinoxaline [23]. A decrease in the rates (k = (3.1–1.6) $\times 10^{10}$ dm^3 mol^{-1} s^{-1}) was seen while going from $[Ru(phen)_3]^{2+}$ to $[Ru(dicnq)_3]^{2+}$. This is in contrast to the trend observed in the $^{\bullet}OH$ reaction.

The rate constants for ruthenium complexes [12,15] having pyridine-based ligands (e.g. bpy, dpq, dpp, dhp) are also $\sim 10^{10}$ dm^3 mol^{-1} s^{-1}. However, the metal atom does seem to affect the reaction rates [24–26] as can be seen from the doubling of the k value in $[Co(phen)_3]^{2+}$, $[Cr(phen)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ complexes as compared to $[Ru(phen)_3]^{2+}$.

3.2. Absorption spectra of the parent compounds

The ground state spectrum of the parent compounds, i.e. the ligands and ruthenium complexes were recorded in the region 200–800 nm at pH 7 in aqueous medium. The molar absorptivities at the respective absorption maxima are shown in Table 2.

The spectrum measured with phen has two peaks at 228 and 265 nm where the intensity of the former is higher ($\varepsilon_{228} = 5.0 \times 10^4$ dm^3 mol^{-1} cm^{-1} and $\varepsilon_{265} = 3.6 \times 10^4$ dm^3 mol^{-1} cm^{-1}). The aqueous dicnq spectrum with major peaks at 265, 306 and weak absorption maxima at 230, 346 and 365 nm which are similar to that recorded [19] in CH_3CN but the additional shoulder at 230 nm is absent in the latter. The common peak at 265 nm in both the phen and dicnq is due to the phen structure and the

Table 2
The absorption maxima and molar absorptivities measured in the UV-Vis spectra of phen, dicnq and their ruthenium complexes

Compound	λ_{max} (log ε)
Phen	228 (4.70), 265 (4.56)
Dicnq	230 (4.16), 265 (4.41), 306 (4.16), 347 (3.68), 362 (3.57)
$[Ru(phen)_3]^{2+}$	223 (4.91), 263 (5.13), 421(4.21), 447 (4.23)
$[Ru(phen)_2(dicnq)]^{2+}$	223 (4.81), 265 (4.92), 443 (4.17)
$[Ru(phen)(dicnq)_2]^{2+}$	223 (4.68), 265 (4.84), 443
γ-irradiation, dose = 1.4 kGy	(4.05) 365 (3.8),440 (3.98)
$[Ru(dicnq)_3]^{2+}$	205 (4.72), 265 (4.94), 300 (4.70), 443 (4.03)

other peaks of dicnq (230 and 306 nm) correspond to the transitions from quinoxaline portion of the ligand [27].

All the spectra of Ru(II) complexes ($[Ru(phen)_3]^{2+}$ to $[Ru(dicnq)_3]^{2+}$) used in this study are similar exhibiting peaks at 223, 265 nm and a broad band centred around 440 nm. Furthermore, a shoulder around 300 nm grows while the peak at 223 nm loses its intensity with the replacement of phen by dicnq in the complexes (Table 2). The intensities of the peaks are dependent on the nature of the ligand attached to it. Similar spectra were observed in acetonitrile [19]. However, the peak at 223 nm is absent and the molar absorptivities are higher.

The UV region of the spectra is dominated by the transitions due to both phen and dicnq. Moreover, the MLCT transitions: Ru(dπ) → phen(π∗) and Ru(dπ) → dicnq(π∗) are located in the visible region.

In order to examine the spectral changes under γ-radiolysis, N_2O saturated solution of $[Ru(phen)(dicnq)_2]^{2+}$ was irradiated in a ^{60}Co-gamma source to a dose of about 1.4 kGy and spectrum shows a reduction in the trough at 350 nm along with the broadening and reduction in the intensity of the peak at 450 nm as compared to its ground spectrum. The peak intensities are shown in Table 2.

3.3. Transient absorption spectra

3.3.1. Reactions of $^{\bullet}OH$ and $O^{\bullet-}$

3.3.1.1. Ligands. The transient absorption spectra recorded in the reaction of $^{\bullet}OH$ with phen ($\times 10^{-3}$ mol dm^{-3}) after the completion of the reaction (3 μs) exhibited two prominent peaks at 350 and 430 nm of nearly equal intensity (Fig. 3).

The molar absorptivities calculated, taking G_{OH} = 5.6, are ε_{350} = 3100 dm^3 mol^{-1} cm^{-1} and ε_{430} = 2980 dm^3 mol^{-1} cm^{-1}. The spectrum, reported earlier [21a] by Janovsky and Teply, has a single peak at 435 nm (ε = 2400 dm^3 mol^{-1} cm^{-1}) but their measurement was carried out beyond 350 nm. As is evident from the spectrum recorded at 40 μs, no further changes were observed (inset Fig. 3) except the usual bimolecular decay.

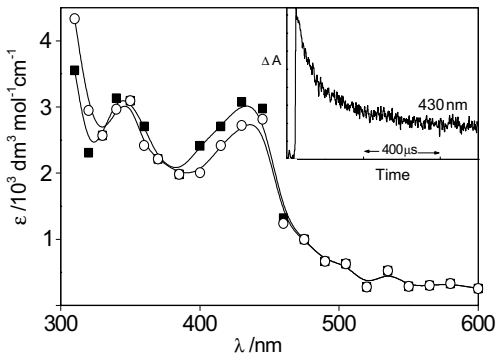


Fig. 3. The time resolved absorption spectra observed in the reaction of $^{\bullet}OH$ with phen, 3 μs (■) and 40 μs (○) after the pulse, at pH 7; inset: decay at 430 nm [phen] = 1 × 10^3 mol dm^{-3}, dose per pulse ∼7 Gy.

The transient absorption spectrum obtained in the $^{\bullet}OH$ reaction with dicnq was measured at 40 μs and has a broad maximum centred around 380 nm but the signal intensities are low (ε_{380} = 1200 dm^3 mol^{-1} cm^{-1}) as shown in Fig. 4.

The spectrum measured on pulse radiolysis of N_2O saturated basic solutions of phen, where $O^{\bullet-}$ is the reacting species, is similar to that measured in the $^{\bullet}OH$ reaction. However, the peaks are less intense and are broadened.

In contrast, the transient spectrum in the case of dicnq is different from the measured $^{\bullet}OH$ reaction spectrum. It has a very intense peak at 380 nm (ε_{380} = 2880 dm^3 mol^{-1} cm^{-1}) and an additional weak peak at 450 nm.

3.3.1.2. Ru(II) complexes. The measurement of the transient absorption spectra in the $^{\bullet}OH$ reaction with the Ru(II) complexes was limited to the region 300–850 nm due to the strong absorption of the parent below 300 nm (Table 2). The difference spectra recorded for the $^{\bullet}OH$ reaction with Ru(II) complexes containing phen at pH 7 have shown peaks around 350 nm and bleaching around 450 nm. The corrected spectrum for $[Ru(phen)_3]^{2+}$ has a broad band centred around 435 nm and a shoulder at 500 nm which is similar to its parent spectrum with a slight blue shift and a low inten-

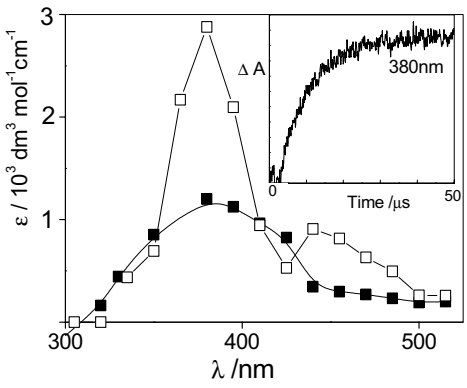


Fig. 4. The transient absorption spectra observed in the reactions of $^{\bullet}OH$ (■) and $O^{\bullet-}$ (○) with dicnq at 40 μs after the pulse at pH 7; inset: absorption build up at 380 nm [dicnq] = 1 × 10^{-4} dm^3 mol^{-1}, dose per pulse ∼7 Gy.

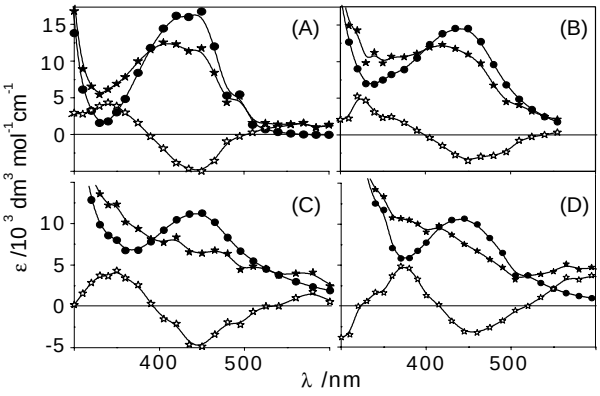


Fig. 5. The difference (☆) and corrected (★) transient absorption spectra measured after the completion of the •OH reaction with the corresponding parent (●) absorption spectra: (A) $[Ru(phen)_3]^{2+}$; (B) $[Ru(phen)_2(dicnq)]^{2+}$; (C) $[Ru(phen)(dicnq)_2]^{2+}$; (D) $[Ru(dicnq)_3]^{2+}$ at pH 7, dose per pulse ∼7 Gy.

sity broad band around 760 nm. Such a type of the spectrum was reported [11] earlier in the case of $[Ru(bpy)_3]^{2+}$ with a characteristic peak at 760 nm.

Furthermore, in the spectra obtained with the mixed ligand complexes, there is a loss of the characteristic peaks around 420 and 760 nm with the increasing dicnq content in the complex (Fig. 5).

The difference spectra obtained in the reaction of $O^{\bullet-}$ with the complexes are similar in nature to that found in the •OH reaction i.e. a peak around 350 nm followed by the bleaching around 450 nm. In the corrected spectra in the reaction of $O^{\bullet-}$ with $[Ru(phen)_3]^{2+}$, $[Ru(phen)_2(dicnq)]^{2+}$, $[Ru(phen)(dicnq)_2]^{2+}$ and $[Ru(dicnq)_3]^{2+}$; the product spectra have broad absorption bands similar to those obtained with other oxidising radicals.

3.3.2. Reactions of $N_3^{\bullet}$ or $SO_4^{\bullet-}$

The azide radical was found to be unreactive toward the ligands (phen and dicnq) and the complexes except $[Ru(phen)_2(dicnq)]^{2+}$. This spectrum has shown a blue shift (λ_{max} = 390 nm) from that obtained in the •OH reaction. The species formed in the reaction of $SO_4^{\bullet-}$ with $[Ru(phen)_3]^{2+}$ has absorption maxima centred around 440 nm. The spectra obtained in the reactions of $[Ru(phen)_3]^{2+}$ and $[Ru(phen)_2(dicnq)]^{2+}$ with $Cl_2^{\bullet-}$ are similar to those obtained with the other one electron oxidant ($SO_4^{\bullet-}$ or $N_3^{\bullet}$).

3.3.3. Reaction of e^-_{aq}

The transient absorption spectra in the e^-_{aq} reaction were obtained in N_2 saturated solutions containing 0.2 mol dm^{-3} *t*-butanol. Absorption maxima at 310 and 375 nm were seen in the transient spectrum of dicnq. Similar spectrum was also seen in phen with an additional peak at 490 nm (Fig. 6).

In the case of ruthenium complexes, the difference spectra have shown major peaks around 350 and 500 nm (Fig. 7). Bleaching was found only in $[Ru(phen)_3]^{2+}$. The

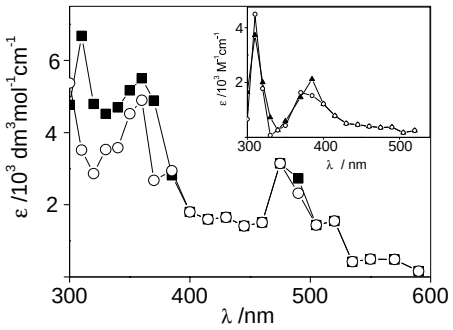


Fig. 6. The corrected time resolved spectra of the one electron reduced species of phen: 3 μs (■) and 40 μs (○) and dicnq (inset) 10 μs (▲) and 40 μs (○), after the pulse, pH 7, dose per pulse ∼7 Gy.

corrected spectra exhibit a major broad peak centred around 440 nm similar to its parent with a minor red shift. In $[Ru(phen)_3]^{2+}$, an additional peak at 500 nm was seen. The peak at 380 nm was also found in the transient spectrum of 2,3-bis(2-pyridyl)-quinoxaline [15] following the reaction of e^-_{aq}.

The Ru(II) complexes [15] while reacting with hydrated electron have only a single absorption maxima at 440 nm in their transient spectra. Further, the one electron reduced species of binuclear complexes higher molar absorptiviteis than the mononuclear complexes.

4. Discussion

4.1. Ligands

In both phen and dicnq, the •OH forms an adduct since the OH radical is known to react by addition to the aromatic ring. The observed transient spectrum is a mixture of its different isomeric OH adducts (reaction (1), Scheme 1). The radical cation formed in the reaction of $SO_4^{\bullet-}$ on hydrolysis

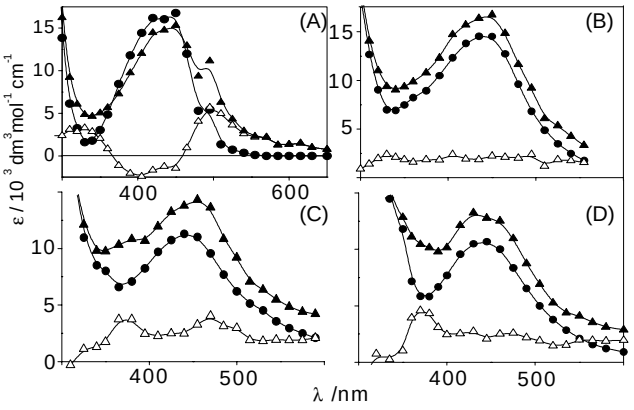
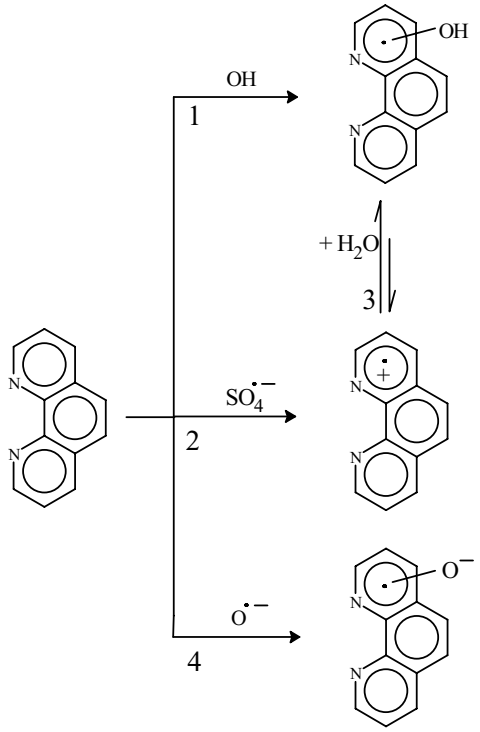
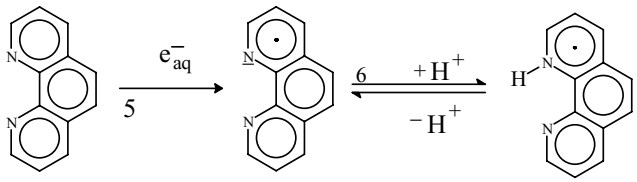


Fig. 7. The difference (△) and corrected (▲) absorption spectra following the reaction of hydrated electron with the complexes and the respective parent spectrum (●): (A) $[Ru(phen)_3]^{2+}$, 2 μs; (B) $[Ru(phen)_2(dicnq)]^{2+}$, 2 μs; (C) $[Ru(phen)(dicnq)_2]^{2+}$, 3 μs; (D) $[Ru(dicnq)_3]^{2+}$, 4 μs, after the pulse, pH 7, dose per pulse ∼7 Gy.



Scheme 1. Reactions of •OH, O•−, $SO_4^{\bullet-}$ with the ligands considering phen as an example.



Scheme 2. Reaction of e^-_{aq} with phen.

forms OH adduct (reaction (3)). Such a mechanism was also proposed in the case of substituted benzenes [2], pyridines [21b] and quinoxalines [21c]. This reaction is base catalysed and the stabilisation of the radical cation is not likely at pH 7 used in our experiments. The O•− radical also reacts by addition, as H abstraction from the ring is unlikely (reaction (4), Scheme 1).

The addition of e^-_{aq} takes place at the N atom and it abstracts a proton from the aqueous medium resulting in the formation of the pyridinyl radical as observed [21] in the pyridine-based compounds (Scheme 2).

In the case of dicnq, e^-_{aq} is likely to add to the pyrazine ring since it is more electron deficient due the cyano groups, followed by its immediate protonation (Scheme 3). Such a mechanism was also reported [23] in the case of unsubstituted quinoxalines.

4.1.1. Ru(II) complexes

In order to understand the reaction mechanism of reaction of oxidizing radicals with Ru(II) complexes, the reaction of $Cl_2^{\bullet-}$ by pulse radiolysis and chemical oxidation by Ce(IV) of $[Ru(phen)_3]^{2+}$ and $[Ru(phen)_2(dicnq)]^{2+}$ were carried out.

The corrected transient spectra recorded in the case of $[Ru(phen)_2(dicnq)]^{2+}$ are shown in Fig. 8A. It can be seen that the spectra recorded in the case of •OH reactions are not identical to that recorded in the reaction of one electron oxidant $Cl_2^{\bullet-}$ or $N_3^{\bullet}$ suggesting that the intermediate formed is different in both the cases. The OH radical reaction involves its addition to the ligand having highly conjugated aromatic ring structure. Further, in mixed ligand complexes, phen, being relatively electron rich, is the preferred site of •OH attack.

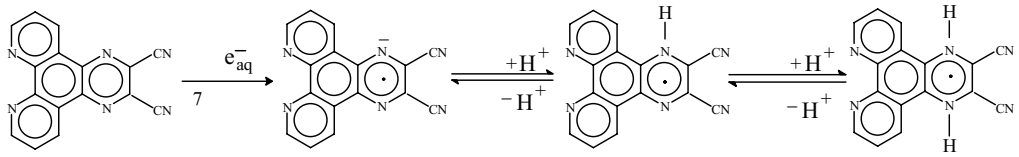
In contrast, the one electron oxidation of Ru(II) by $Cl_2^{\bullet-}$ leads to Ru(III):

$$[Ru^{II}(phen)_n(dicnq)_{3-n}]^{2+} \xrightarrow{Cl_2^{\bullet-}} [Ru^{III}(phen)_n(dicnq)_{3-n}]^{3+} \quad (2)$$

Such oxidation of Ru(II) in the reaction of $Cl_2^{\bullet-}$ was reported [13] in the case of $[Ru(bpy)_3]^{2+}$. Similarly, the oxidation by the azide radical also occurs in $[Ru(phen)_2(dicnq)]^{2+}$ as reported by Das and Kamat [17] in Ru(II) dye and Luo et al. [18] in the case of $[Ru^{II}(bpy)_2imidazole,H_2O]$-His33$(cytc^{III})$. This is confirmed by the chemical oxidation of Ru(II) complexes by Ce(IV) in $[Ru(phen)_2(dicnq)]^{2+}$ (Fig. 8B).

The spectra of Ru(III) complexes are broadly divided into three regions: The UV region (≤350 nm) mainly consists of a very intense interligand $\pi \rightarrow \pi*$ transition band which is similar to that observed in Ru(II) complexes. The region 350–500 nm is dominated by MLCT involving $d\pi_{t2g} \rightarrow \pi^*_{LL}$ transition ($\varepsilon \leq 15\,000\ M^{-1}\ cm^{-1}$). A weak LMCT band was seen only in $[Ru(phen)_3]^{2+}$, at $\lambda \geq 500$ nm. This observation is in accord with the earlier work of Nazeeruddin et al. [28] on the chemical oxidation of Ru(II) complexes of 2,2′-bipyridine carrying electron-donating substituents.

The reduction of Ru(II) complexes by e^-_{aq} occurs at the ligand as is evident from the similarity in the spectra measured in the reaction of hydrated electron with the ligands and the complexes. In the case of the complexes containing



Scheme 3. Reaction of e^-_{aq} with dicnq.

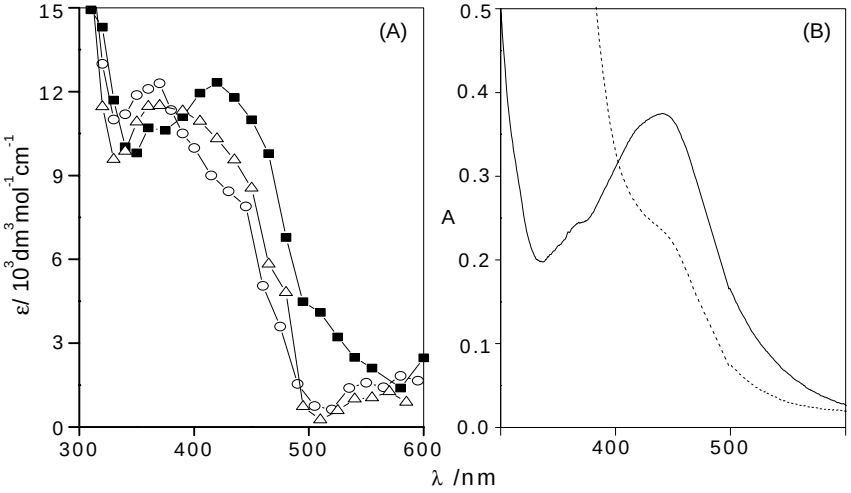
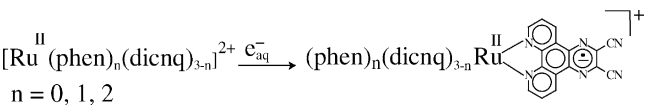


Fig. 8. The corrected spectra recorded in the reactions of $[Ru(phen)_2(dicnq)]^{2+}$ with (A) •OH (■), $Cl_2^{\bullet -}$ (△) and $N_3^{\bullet}$ (○) at 40 μs after the pulse, dose rate 7 Gy per pulse; (B) Ce^{4+} oxidation 1.18×10^{-3} mol dm^{-3} [Ce^{4+}] (- - -) and without Ce^{4+} (—).

dicnq, the preferred site for reduction is dicnq due to the presence of electron withdrawing cyano groups:



As the amount of dicnq increases, the major transient species, dicnq$^{\bullet -}$, has peaks below 380 nm where the absorption of the complexes is minimum and therefore, no bleaching at 440 nm was noticed in the spectra of $[Ru(phen)_2(dicnq)]^{\bullet +}$, $[Ru(phen)(dicnq)_2]^{\bullet +}$ and $[Ru(dicnq)_3]^{\bullet +}$ in contrast to $[Ru(phen)_3]^{\bullet +}$.

5. Conclusions

The kinetics and the spectral nature of the one electron oxidised and reduced forms of Ru(II) complexes of 6,7-dicyanodipyrido quinoxaline were studied using radiation chemical techniques. The compounds are reactive to both the oxidizing and reducing radicals ($k = 10^9$ to 10^{10} M^{-1} s^{-1}). •OH forms an adduct with the aromatic ring of the ligand. The radiation chemical oxidation of Ru(II) → Ru(III) is confirmed by the chemical oxidation of the complexes by Ce(IV).

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