

Photoinduced inter- and intramolecular electron transfer reactions of carboxylatopentaamminecobalt(III) and excited state *tris*(2,2'-bipyridine) ruthenium(II) complexes

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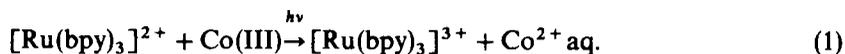
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Abstract. Carboxylatopentaamminecobalt(III) complexes were prepared and characterized. These cobalt(III) complexes were used to study the electron transfer mechanism involved in the photoredox system $\text{Ru}(\text{bpy})_3^{2+}$ – cobalt(III). The study shows that the electron transfer occurs from the excited state $\text{Ru}(\text{bpy})_3^{2+}$ to cobalt(III) complex through the intermediacy of the ligands.

Keywords. Photosensitization; electron transfer reaction; carboxylatopentaamminecobalt(III) complex.

1. Introduction

The photosensitizer, *tris*(2,2'-bipyridine) ruthenium(II) cation, has proved revolutionary and has attracted a great deal of attention due to its interesting and important features relevant to photophysics and photochemistry (Kalyanasundaram 1982; Graetzel 1983; Juris *et al* 1988; Norris and Meisel 1989). The quenching of the $^*[\text{Ru}(\text{bpy})_3]^{2+}$ luminescence by pentaammine complexes of cobalt(III) of the form $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ (X = Br^- , Cl^- , H_2O and NH_3) has been investigated by several workers (Gafney and Adamson 1972; Natarajan and Endicott 1973; Navon and Sutin 1974). Gafney and Adamson (1972) have proposed an electron transfer mechanism for this process



According to Natarajan and Endicott (1973), the mechanism involves triplet to triplet energy transfer followed by the intramolecular oxidation of one of the ligands of the cobalt(III) substrate. Navon and Sutin (1974) reinvestigated the reaction in an attempt to remove this controversy regarding the mechanism of this photoinduced redox reaction and they have come to the conclusion that it is the electron transfer mechanism which operates in this case. Bottcher and Haim (1980) have studied the quenching of the $^*[\text{Ru}(\text{bpy})_3]^{2+}$ by $[\text{Co}(\text{NH}_3)_5\text{L}]^{3+}$ (L = pyridines or carboxylates) and concluded that electron transfer occurs from the excited state $[\text{Ru}(\text{bpy})_3]^{2+}$ to cobalt(III) complex through the intermediacy of the ligands.

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In the present investigation, a number of carboxylatopentaamminecobalt(III) complexes have been used as quenchers for the quenching of the excited state $[\text{Ru}(\text{bpy})_3]^{2+}$ to understand the electron transfer mechanisms involved in these systems. The rate constants for the quenching of $^*[\text{Ru}(\text{bpy})_3]^{2+}$ by nitroaromatics is 100 times faster than the cobalt(III) complexes (Kalyanasundaram 1982). The present study shows that when one of the ligands of cobalt(III) complexes is a nitroaromatic ligand, the rate constant for quenching becomes 100 times higher than the other carboxylato ligands. The results are presented below.

2. Experimental methods

The carboxylatopentaamminecobalt(III) perchlorate complexes i.e. $[\text{Co}(\text{NH}_3)_5\text{L}]^{2+}$ (where L = carboxylato ligand; see table 1) were prepared and purified according to the reported procedure (Gould and Taube 1962) with modifications. Washing with ethanol or methanol was not employed in most cases since many of the complexes dissolved readily in alcohols when slightly damp. To remove the last traces of parent acid the complex was dissolved in hot water, saturated NaHCO_3 solution added dropwise to pH 8, and the solution quickly cooled; this procedure was not applicable to complexes of dibasic acids. Yields were generally low (often less than 20%). The method reported by Jackman *et al* (1968) was found to be the best method for the preparation of acetatopentaamminecobalt(III) complex. The $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ was prepared according to the reported procedure (Sprintschink *et al* 1977). Analar grade Na_2HPO_4 and $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ (E. Merck) were used in the preparation of the phosphate buffer. Water used in the studies was double distilled over alkaline potassium permanganate in an all-glass apparatus.

Table 1. The quenching rate constants (k_q) for the reactions of $^*[\text{Ru}(\text{bpy})_3]^{2+}$ with cobalt(III) complexes $[\text{Co}(\text{NH}_3)_5(\text{OOCR})]^{2+}$ at 25°C, pH = 5.8 (phosphate buffer) and $\mu = 0.1 \text{ M}$ (NaClO_4)*.

RCOO^-	$10^{-9}, k_q (\text{M}^{-1} \text{s}^{-1})$
Formato	0.04
Acetato	0.05
Propionato	0.05
Butyrato	0.06
Cloroacetato	0.07
Benzoato	0.05
Pthalato	0.05
Phenylacetato	0.09
<i>o</i> -Chlorobenzoato	0.07
<i>p</i> -Chlorobenzoato	0.06
<i>o</i> -Toluato	0.10
<i>o</i> -Nitrobenzoato	1.72
<i>p</i> -Nitrobenzoato	2.27
<i>m</i> -Nitrobenzoato	3.63

* Error limits $k_q = \pm 20\%$

Absorption spectral measurements were carried out using a pye-Unicon 8800 UV-Vis spectrophotometer. IR spectra of the cobalt(III) complexes were recorded using a Perkin-Elmer 577 Infrared Spectrometer. Emission intensity measurements were carried out using JASCO FP-770 spectrofluorometer.

The sensitizer concentration was fixed at 5×10^{-6} M while the quencher concentration varied from 0.2 to 10×10^{-3} M. The pH was maintained at 5.8 and ionic strength at 0.1 M. All solutions were deaerated for 30 minutes by purging with pure nitrogen. The solutions were excited at the absorption maximum of $[\text{Ru}(\text{bpy})_3]^{2+}$ around 450 nm and the emission intensities were monitored at 600 nm. Since the cobalt(III) complexes absorb in the region of excitation it was necessary to introduce a correction. The correction was introduced using the following equation (Demas and Adamson 1973)

$$(I_0/I)_{\text{corr}} = (I_0/I)_{\text{app}} [(1 - 10^{-(A_D + A_Q)}) / (1 - 10^{-A_D})] [A_D / (A_D + A_Q)], \quad (2)$$

where $(I_0/I)_{\text{app}}$ is the observed ratio of emission intensity from an unquenched sample to that from a quenched one, and A_D and A_Q are the absorbance of the donor and quencher respectively at the excited wavelength.

3. Results and discussion

Carboxylatopentaamminecobalt(III) complexes, $[\text{Co}(\text{NH}_3)_5(\text{OOCR})]^{2+}$, were prepared and characterized. For cobalt(III) complexes containing NH_3 ligands the following IR bands are expected (Rao 1963); one or more bands in the range $3300\text{--}3200 \text{ cm}^{-1}$ (N-H stretching), a broad band around 1600 cm^{-1} (asymmetric NH_3 deformation), and a band in the range $850\text{--}800 \text{ cm}^{-1}$ (rocking). Carboxylate ions show a strong absorption in the region $1610\text{--}1550 \text{ cm}^{-1}$ (asymmetric O-C-O stretching) and another band around 1400 cm^{-1} (symmetric stretching). All these bands were found in the infrared spectra of the carboxylatopentaamminecobalt(III) complexes prepared. A bending motion of the H_2O ligand is usually found in the region of $800\text{--}1000 \text{ cm}^{-1}$ which is also the region where the rocking motion of the NH_3 ligand is found. The substitution of H_2O by the carboxylate ligand, which does not show any absorption in this range, is expected to decrease the intensity of the band around 800 cm^{-1} . Such a decrease in intensity was observed in the infrared spectra of the cobalt(III) complexes.

The cobalt(III) complexes used in the present study generally featured an absorption maximum (λ_{max}) around 500–504 nm. This is obviously due to the spin-allowed ligand field transition ${}^1A_{1g} \rightarrow {}^1T_{1g}$. This absorption maximum is considered to be typical of the carboxylatopentaamminecobalt(III) complexes (Gould and Taube 1962). The electronic absorption spectral properties of the carboxylatopentaamminecobalt(III) complexes are not affected significantly by changes in the acid ligands.

The emission intensity measurements give excellent Stern-Volmer plots (figure 1). The quenching rate constants calculated from these plots are summarized in tables 1 and 2. The values of the quenching rate constants (k_q) for the reaction of $*[\text{Ru}(\text{bpy})_3]^{2+}$ with *o*-, *p*- and *m*-nitrobenzoates along with the ΔG_{23} (free energy change for the electron transfer step) (Marcus 1965; Meites and Zuman 1972; Bock *et al* 1979) are given in table 2.

Photolysis of a mixture of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Co}(\text{NH}_3)_5\text{X}]^{3+}$ yields $[\text{Ru}(\text{bpy})_3]^{3+}$

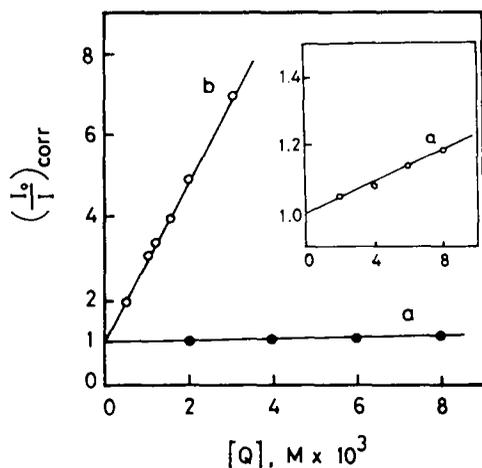


Figure 1. Stern-Volmer plot for the quenching of $^*[\text{Ru}(\text{bpy})_3]^{2+}$ by (a) $[\text{Co}(\text{NH}_3)_5(\text{OCC}_6\text{H}_5)]^{2+}$ and (b) $[\text{Co}(\text{NH}_3)_5(\text{OCC}_6\text{H}_4\text{NO}_2\text{-}m)]^{2+}$.

Table 2. The quenching rate constants (k_q) and ΔG_{23} for the reactions of $^*[\text{Ru}(\text{bpy})_3]^{2+}$ with *o*-, *m*-, and *p*-nitrobenzoates at 25°C, pH = 5.8 (phosphate buffer) and $\mu = 0.1 \text{ M}$ (NaClO_4)^a.

RCOO^-	$10^{-9}, k_q (\text{M}^{-1} \text{s}^{-1})$	$\Delta G_{23} (\text{kcal/mol})$
<i>o</i> -Nitrobenzoate	3.63	-17.98
<i>p</i> -Nitrobenzoate	6.06	-13.14
<i>m</i> -Nitrobenzoate	6.66	-4.60

^a Error limits $k_q = \pm 20\%$

and Co^{2+} aquo complexes. The latter is produced in yields close to 100% for all cobalt(III) complexes (Navon and Sutin 1974). They showed that the photosensitized decomposition occurs via direct electron transfer as outlined in (1). The data showed that the rate constants for the quenching of excited state $[\text{Ru}(\text{bpy})_3]^{2+}$ by cobalt(III) complexes increase in the order $\text{NH}_3 < \text{H}_2\text{O} < \text{Cl}^- < \text{Br}^-$ with the rate constant for $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$ quenching being diffusion controlled or very close to the diffusion controlled limit.

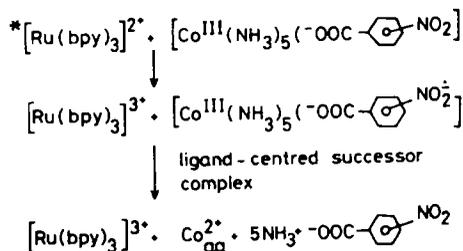
In the present study, when the carboxylato group in the cobalt(III) complex is aliphatic, the k_q values are found to be almost the same, the values being $(0.05 \pm 0.01) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. For aromatic carboxylato complexes in which the benzene ring has a substituent other than the nitro group (like $-\text{CH}_3$, $-\text{Cl}$ and $-\text{COOH}$) also, the k_q values are almost constant, the values being $(0.07 \pm 0.01) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. These observations show that the rates of outer-sphere electron transfer reactions of these carboxylatopentaamminecobalt(III) complexes with $^*[\text{Ru}(\text{bpy})_3]^{2+}$ are quite insensitive to the nature of the carboxylate ligand.

For the *o*-, *p*- and *m*-nitrobenzoate complexes the k_q values are much higher, the values being 1.72×10^9 , 2.27×10^9 and $3.63 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ respectively (table 1). These values are about two orders of magnitude greater than those of the cobalt(III)

complexes having aliphatic or aromatic acids with a substituent other than nitro group, as one of the ligands.

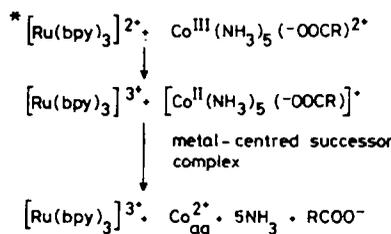
When the free ligands *o*-, *p*- and *m*-nitrobenzoates are used as quenchers the k_q values are found to be even higher than those of the corresponding cobalt(III) complexes (table 2). The k_q values are 3.69×10^9 , 6.06×10^9 and $6.66 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ respectively for *o*-, *p*- and *m*-nitrobenzoates as against the values of 1.72×10^9 , 2.27×10^9 and $3.63 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the corresponding cobalt(III) complexes. This is attributed to the difference in the rates of diffusion of the free ligands and the corresponding cobalt(III) complexes and also to the steric hindrance imposed on the nitrobenzoato complexes.

The higher values of the quenching rate constants for the nitrobenzoatopentaamminecobalt(III) complexes when compared with those of the other carboxylato complexes (tables 1 and 2) clearly indicate that the electron from the excited state $[\text{Ru}(\text{bpy})_3]^{2+}$ complex is transferred first to the easily reducible nitro group to form the ligand-centred successor complex which further undergoes subsequent intramolecular electron transfer leading to the reduction of cobalt(III) center (scheme 1). When



Scheme 1.

carboxylatopentaamminecobalt(III) complexes other than the nitrobenzoato complexes are used as quenchers, the electron transfer occurs directly from the excited state $[\text{Ru}(\text{bpy})_3]^{2+}$ complex to the less reactive cobalt(III) center and it is reflected in the low value for the quenching rate constants (scheme 2).



Scheme 2.

The k_q values obtained for *o*-, *p*- and *m*-nitrobenzoates as quenchers suggest that the quenching efficiency is in the order *m*-nitrobenzoate > *p*-nitrobenzoate > *o*-nitrobenzoate. But the ΔG_{23} values suggest the reverse trend i.e. *o*-nitrobenzoate > *p*-nitrobenzoate > *m*-nitrobenzoate (table 2). This reversal of trend in the quenching efficiency may be attributed to steric reasons. In *o*- and *p*-nitrobenzoates the polar and resonance effects are almost equal (Chapman and Shorter 1972). But in the *o*-nitrobenzoate the steric hindrance imposed by the $-\text{COOH}$ group reduces the ease of formation of the encounter complex. The k_q values are almost identical for

m- and *p*-nitrobenzoates since the electron transfer process is diffusion controlled as suggested by the observed quenching rate constants.

4. Conclusion

From the observed quenching rate constants the following conclusions have been made.

- (1) In the case of $[\text{Co}(\text{NH}_3)_5\text{OOCR}]^{2+}$ where R is a aliphatic or aromatic group with any substituent other than $-\text{NO}_2$, direct electron transfer occurs from $^*[\text{Ru}(\text{bpy})_3]^{2+}$ to the less reactive cobalt(III) center.
- (2) The higher values of the quenching rate constants for the nitrobenzoatopentaamminecobalt(III) complexes when compared with those of the other carboxylatopentaamminecobalt(III) complexes indicate that with the former, the electron from the $^*[\text{Ru}(\text{bpy})_3]^{2+}$ complex is transferred first to the easily reducible $-\text{NO}_2$ group to form the ligand-centered successor complex which then undergoes subsequent intramolecular electron transfer leading to the reduction of cobalt(III) centre.

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