Thermal and photoreactivities of oxalato*bis*(polypyridyl)chromium(III) complexes in aqueous media

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Abstract. The thermal and photochemistry of oxalato*bis*(polypyridyl)chromium(III) complexes have been studied. The rate constants for the thermal aquation reactions have been determined and the quantum yield for the photoaquation has been estimated as a function of excitation wavelength and pH of the solution. The quantum yield for photoaquation varies from 7×10^{-2} to 10^{-3} depending upon the pH of the solution and wavelength of excitation. The activation parameters for the thermal reactions have been estimated for the systems investigated.

Keywords. Photochemistry; chromium(III)–polypyridyl complexes.

1. Introduction

Over the past two decades the photochemistry of polypyridyl complexes of chromium(III) has been studied in detail, and provides some fundamental thermo-dynamic and spectroscopic details with reference to the use of these complexes for the solar energy conversion processes (Kemp 1980; Jamieson *et al* 1981; Kirk 1981) Chromium(III) complexes in general undergo photoaquation reactions on irradiation in the *d–d* bands which are assigned reasonably well based on theoretical models (Kemp 1980; Kirk 1981; Lilie and Waltz 1983; Lilie *et al* 1986; Perkovic and Endicott 1990). Earlier investigations (Broomhead *et al* 1971; Kane–Maguire and Langford 1972; Miyoshi *et al* 1982) on these complex ions are concerned with acid-catalysed exchange of oxalate oxygens with those in solvent water. A detailed study of thermal and photochemical reactions of the oxalato*bis*(polypyridyl)chromium(III) complexes is carried out in order to compare the properties of macromolecular chromium(III) complexes in the ground and excited states (Anbalagan and Natarajan 1991).

2. Experimental

$[Cr(bpy)_2(ox)]^+$ and $[Cr(phen)_2(ox)]^+$ were prepared by the literature method (Hancock *et al* 1976) with some modifications and the complexes characterized by elemental analysis and electronic spectra. The observed absorption bands are in good

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agreement with those reported in the literature; for $[Cr(bpy)_2(ox)]ClO_4$, the bands are seen at 497 ($\varepsilon = 66\cdot1\ M^{-1}\ cm^{-1}$), 464 ($\varepsilon = 49\cdot1\ M^{-1}\ cm^{-1}$), 448 ($\varepsilon = 90\cdot0\ M^{-1}\ cm^{-1}$), and 417 nm ($\varepsilon = 220\cdot1\ M^{-1}\ cm^{-1}$); analysis – calcd: C, 47·86; H, 2·90; N, 10·15; Cr, 9·45%. found: C, 46·73; H, 2·68; N, 10·47; Cr, 9·38%; and for $[Cr(phen)_2(ox)]NO_3\cdot H_2O$ analysis – calcd: C, 53·78; H, 3·10; N, 12·07; Cr, 8·98%. Found: C, 52·94; H, 3·23; N, 12·21; Cr, 8·91%. Chemicals used in the investigation were of analytical reagent grade. Details of the analytical techniques and the photolysis procedure are given elsewhere (Anbalagan and Natarajan 1991).

Thermal reaction kinetics was carried out with complex concentrations of $5 \times 10^{-3}\ M$ after adjusting the ionic strength with solutions of sodium perchlorate in the case of $[Cr(bpy)_2(ox)]^+$ and sodium nitrate in the case of $[Cr(phen)_2(ox)]^+$ (choice of sodium perchlorate was inconvenient for the latter because of the relative insolubility of the perchlorate salt of the phenanthroline complex). Water maintained at the required temperature was used to prepare fresh solutions for each experiment and the pH was adjusted to the desired value. The experimental solution was then transferred into a 1-cm spectrophotometer cell kept in the thermostatted cell holder. Reaction was followed spectrophotometrically by monitoring the decrease in absorbance over 5–7 half lives. Absorbance at infinite time was found to be constant and plots of $\log(A_t - A_\infty)$ vs. time were found to be linear. First order rate constants and Arrhenius parameters were evaluated and the reported rate constants are the mean of at least three runs. Spectra were repeatedly scanned between 700 and 400 nm to confirm the isosbestic point.

Photoexcitations were carried out in an air-equilibrated aqueous solution in the pH range 4–12 and the pH values of the solutions were adjusted with perchloric acid, nitric acid, and sodium hydroxide as required. Photolysis of the complexes were performed with concentrations generally in the range of $(3\cdot5-6\cdot8) \times 10^{-3}\ M$, $(0\cdot6-3\cdot1) \times 10^{-4}\ M$, and $(1\cdot1-1\cdot5) \times 10^{-4}\ M$ for 436, 330 and 254 nm irradiation experiments respectively at an ionic strength of the medium adjusted to 0·02 M with sodium perchlorate or sodium nitrate.

In a typical experiment, 15·5 ml of $3\cdot5 \times 10^{-3}\ M\ [Cr(bpy)_2(ox)]^+$ was photolyzed for 8 min and the photolyte was brought to pH 10. One ml of the solution was mixed with 5 ml of the solvent, n-heptane, and the mixture was shaken vigorously for 2 min. After 1 min, the organic layer was carefully transferred to a 1-cm cell and the solution absorbance at 282 nm was measured against the solvent as the reference. The same analytical procedure was carried out with a portion of the solution kept in the dark in order to determine the amount of bidentate ligand released in the thermal reaction. The quantum yields were calculated for the release of the polypyridyl ligand by means of calibration plots, after correcting for the thermal reaction.

3. Results

The absorption spectra of the freshly prepared solutions of the cations $[Cr(bpy)_2(ox)]^+$ and $[Cr(phen)_2(ox)]^+$ did not show any appreciable change for a few hours at 26°C in the pH range 4–9. At higher pH, however, the complexes exhibit gradual spectral changes, which are shown in figures 1a and 2a. The spectra show isosbestic points at 528 nm for $[Cr(bpy)_2(ox)]^+$ and at 529 nm for $[Cr(phen)_2(ox)]^+$ ion. The aquation reactions follow first-order kinetics as measured by spectrophotometric techniques

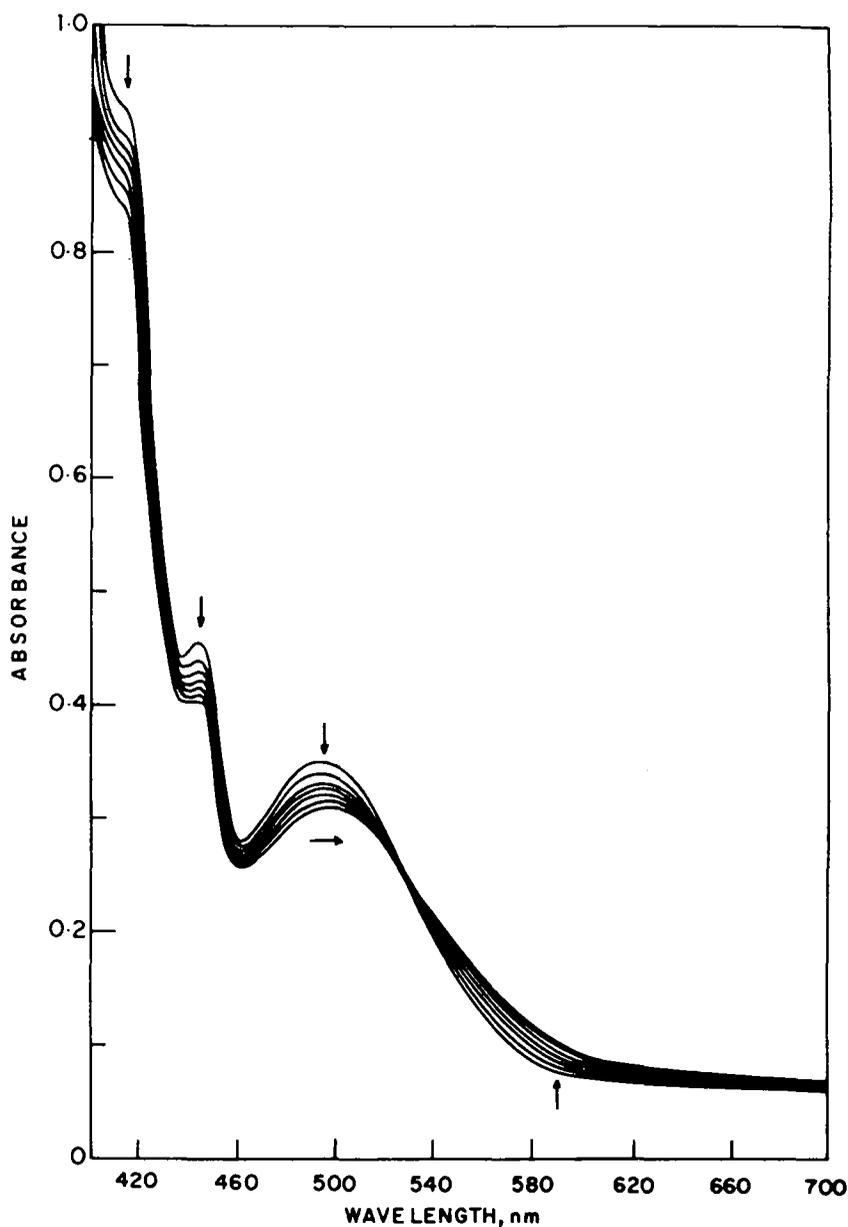**Figure 1.** (a) Thermal reaction of $[Cr(bpy)_2(ox)]^+$ in aqueous solution at 26°C, pH = 11·1 and 0·02 M ionic strength ($NaClO_4$). Spectra were recorded at intervals of 8 min. [Complex] = $4·8 \times 10^{-3}$ M.

and the rate constants and Arrhenius parameters for the complexes under investigation are summarized in table 1. It is clear from figures 1a and 2a that the lowest energy LF band shows a red shift during the reaction; in addition, a steady decrease in the solution pH is observed. Irradiation of the aqueous solutions of the complexes in the LF band shifts the absorption maxima to red, with a decrease in pH, and liberation of free heterocyclic ligand bpy or phen.
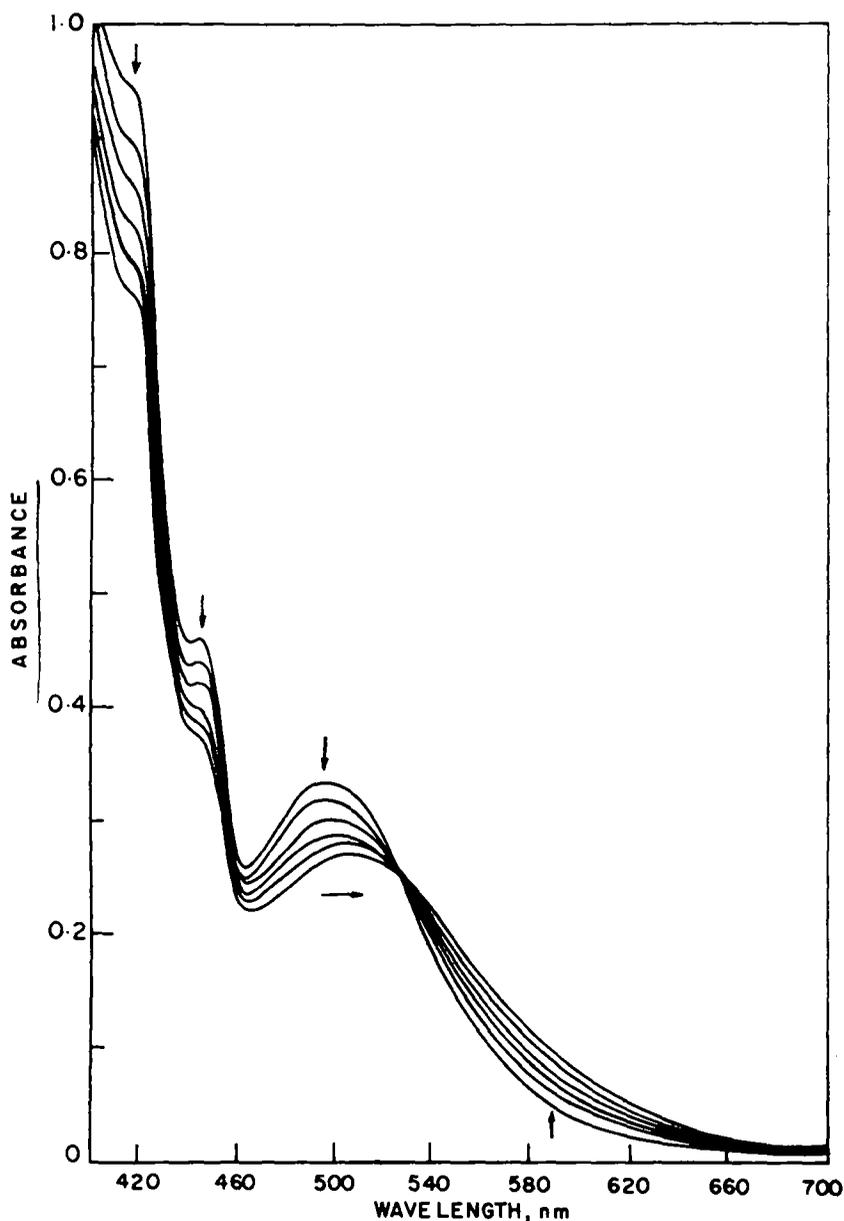
Figure 1. (b) Photolysis of $[Cr(bpy)_2(ox)]^+$ in aqueous solution at 26°C, pH = 9·1 and 0·02 M ionic strength (NaClO₄). Spectra were recorded at intervals of 10 min. Irradiation at $\lambda = 436$ nm.

The spectral changes accompanying 436 nm photolysis of monomer complexes in basic solution are shown in figures 1b and 2b. The isosbestic point obtained in each complex is in good agreement with that observed for the thermal reaction. The final spectra remained unchanged for more than an hour. The quantum yields of the
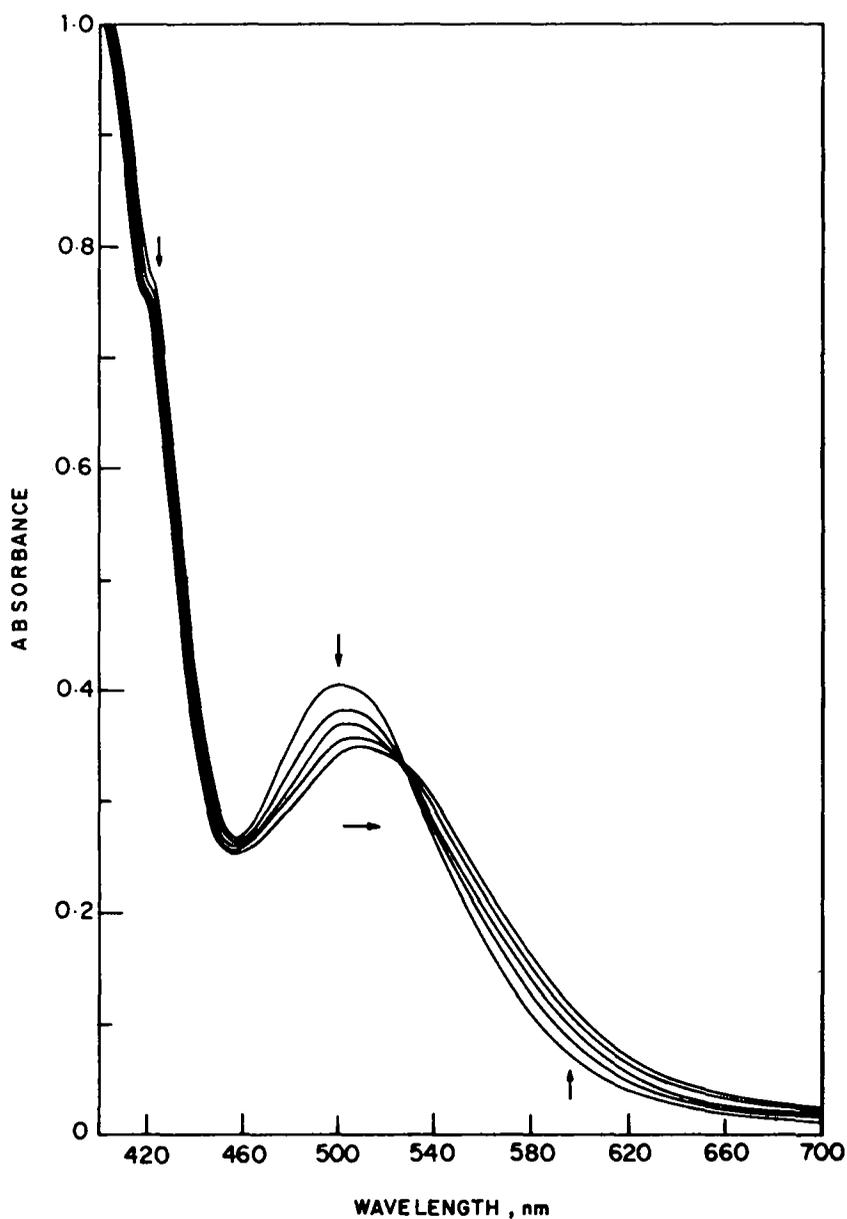
Figure 2. (a) Thermal reaction of $[Cr(phen)_2(ox)]^+$ in aqueous solution at 26°C, pH = 11·2 and 0·02 M ionic strength (NaNO$_3$). Spectra were recorded at an interval of 8 min. [complex] = 6·4 × 10^{-3} M.

product formation on excitations at different wavelengths for the complexes are presented in tables 2 and 3. The complexes show low reactivities at low pH and hence the reaction was studied in a relatively alkaline medium to get appreciable absorption spectral changes.
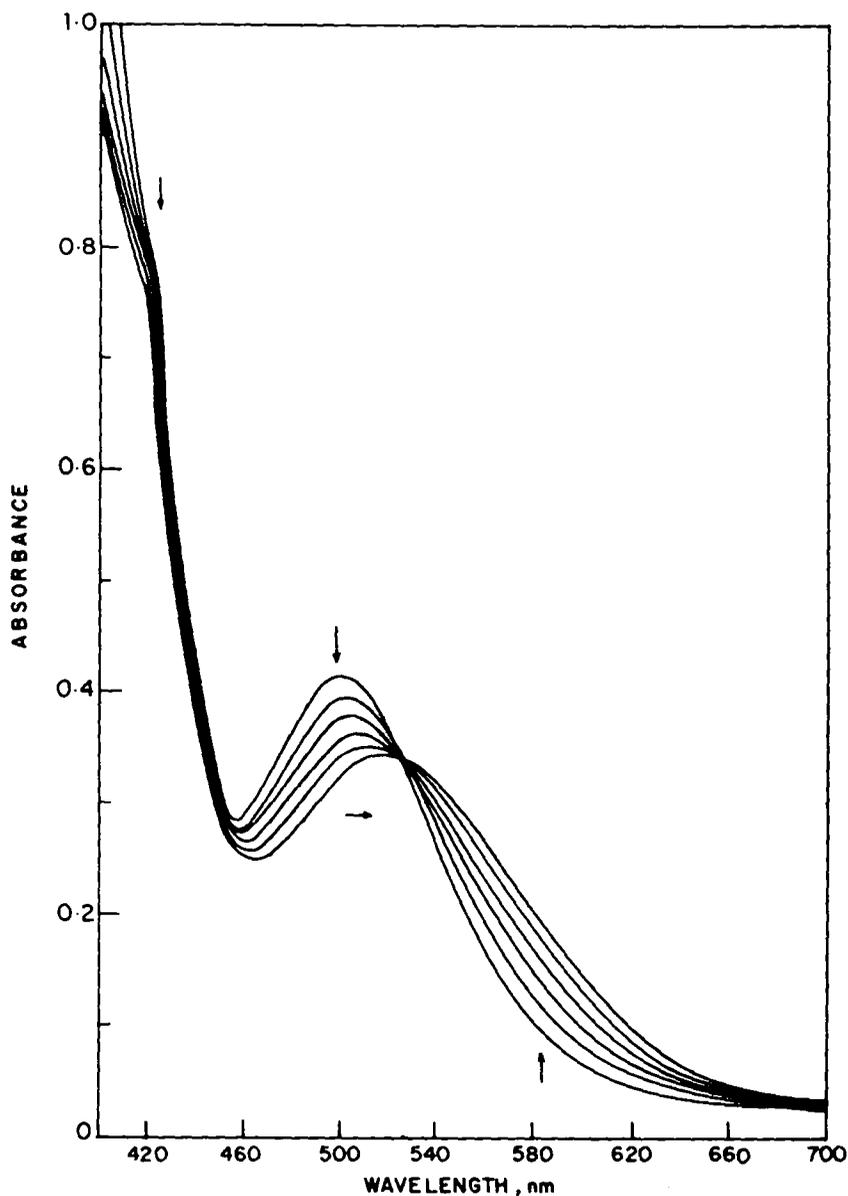
Figure 2. (b) Photolysis of $[Cr(phen)_2(ox)]^+$ in aqueous solution at 26°C, pH = 9·1 and 0·02 M ionic strength ($NaNO_3$). Spectra were recorded at an interval of 10 min. Irradiation at $\lambda = 436$ nm.

Table 1. First-order rate constants and activation parameters for the hydrolysis of chromium(III) complexes in aqueous solution at 45°C, pH = 12. Ionic strength adjusted to 0·02 M with $NaClO_4$ or $NaNO_3$.

Complex	[Complex] (mM)	$10^7 k_{obs}$, (s^{-1})	E_a (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (eu)
$[Cr(bpy)_2(ox)]^+$	5·71	114·7	103·8	101·3	−15·9
$[Cr(phen)_2(ox)]^+$	5·57	163·6	95·9	92·9	−38·1

Table 2. Quantum yields for the photo-substitution of $[Cr(bpy)_2(ox)]^+$ complex in air-equilibrated aqueous solution at 27°C.

pH	At irradiation wavelength (nm)		
	436	330	254
4·0	< 0·002	0·001	< 0·001
5·0	0·02	0·005	0·001
6·0	0·04	0·01	0·001
7·1	0·04	0·01	0·002
8·0	0·05	0·02	0·002
9·0	0·06	0·02	0·002
10·0	0·06	0·02	0·003
11·0	0·06	0·02	0·003
12·0	0·07	0·03	0·005

Table 3. Quantum yields for the photosubstitution of $[Cr(phen)_2(ox)]^+$ complex in air-equilibrated aqueous solution at 27°C.

pH	At irradiation wavelength (nm)		
	436	330	254
4·0	$< 10^{-4}$	$< 10^{-4}$	$< 10^{-4}$
5·0	$< 10^{-4}$	$< 10^{-4}$	$< 10^{-4}$
6·0	$< 10^{-4}$	$< 10^{-4}$	$< 10^{-4}$
7·0	$< 10^{-4}$	$< 10^{-4}$	0·001
8·0	0·002	0·001	0·001
9·0	0·002	0·002	0·001
10·0	0·003	0·002	0·001
11·0	0·004	0·002	0·001
12·0	0·004	0·003	0·001

4. Discussion

4.1 *Thermal reaction mode*

Spectral changes observed for the $[Cr(NN)_2(ox)]^+$ complexes indicate that the ions underwent exclusively substitution reactions (figures 1 and 2). The occurrence of the aquation reaction (1) was confirmed by noting the decrease in pH and by characterizing the release of the heterochelate ligand.

$$[Cr(NN)_2(ox)]^+ + 2OH^- \rightarrow [Cr(NN)(OH)_2(ox)]^- + NN. \tag{1}$$

After the completion of the reaction, extraction in organic solvents shows the presence of free bpy (or phen) ligand as the reaction product. Moreover, the observed spectral changes accompanying the thermal reaction are not due to oxalate ligand substitution in the case of $[Cr(NN)_2(ox)]^+$ complexes, since a shift of the ligand field bands to shorter wavelengths would be expected if oxalate is replaced by water during reaction. An important spectral difference between the oxalato and aquo complexes of

chromium(III) is indicated by a progressive shift of the wavelength maxima of the former to higher wavelengths, relative to the latter. Likewise, replacement of oxalate ligand by hydroxide ion in alkaline medium is expected to show a peak at 517 nm. This behaviour is not observed and hence, the replacement of oxalate by OH^- or water is not proposed in the complex cations $[Cr(NN)_2(ox)]^+$. Thermal aquation of $[Cr(NH_3)_4(ox)]^+$ and $[Cr(en)_2(ox)]^+$ has already been investigated (Kirk *et al* 1971; House 1972). Both the complexes hydrolyse in acid solution via Cr–N bond breaking and no free oxalate was observed in these reactions also.

The rate constants and the activation parameters determined for the aquation reaction as presented in table 1 reveal that the rate of the thermal reaction is sufficiently slow. Further, the aquation of $[Cr(NN)_3]^{3+}$ complexes show (Soignet and Hargis 1972; Maestri *et al* 1976) a pH dependent first-order kinetics and an associative mechanism was proposed, involving the formation of a seven-coordinate intermediate for both $[Cr(bpy)_3]^{3+}$ and $[Cr(phen)_3]^{3+}$ ions at pH 6, with k_{obs} being very small and independent of pH. This has been rationalized in terms of relaxation of the heptacoordinate intermediate, that is, initially formed $[Cr(NN)_3(H_2O)]^{3+}$ undergoes ring opening, leading to reversible loss of monodentate NN ligand. At higher pH, k_{obs} for $[Cr(NN)_3]^{3+}$ is linearly dependent on the pH of the medium and is due to the direct nucleophilic attack of the OH^- ion at the metal centre.

It is known that hydroxide ion has the greater nucleophilicity than water and its attack on Cr(III) results in a stronger Cr–OH bond formation in the transition state, which is evident from the observed negative entropy values suggesting an associative mechanism. Therefore the rate-determining step would involve direct nucleophilic attack of the OH^- ion at the Cr(III) centre and subsequent release of NN ligand. The reaction pathways are represented by (2) and (3)

$$[Cr(NN)_2(ox)]^+ + OH^- \rightarrow [Cr(NN)_2(ox)(OH)], \tag{2}$$

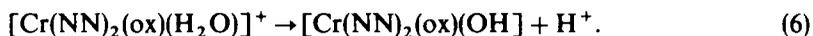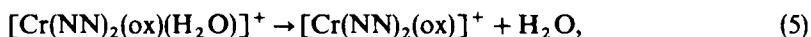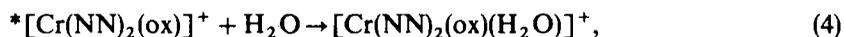$$[Cr(NN)_2(ox)(OH)] + OH^- \rightarrow [Cr(NN)(ox)(OH)_2]^- + NN. \tag{3}$$

4.2 *Photochemical reaction mode*

Irradiation of the complexes in the ligand field bands shows a shift of the absorption maxima to longer wavelengths during photoreaction. Photolysis in aqueous solution gives rise to an increase in the pH of the solution. The isosbestic points observed and qualitative identification of free bpy (or phen) ligand on irradiation again confirm that the photoreaction is similar to the thermal reaction. A number of mixed ligand complexes, *cis*-$[Cr(N)_4Cl_2]^+$ ($N_4 = (NH_3)_4$, $(en)_2$ or trien) undergo aquation of amine *trans* to a chloride ligand and chloride release dominates in the case of trien complex only due to steric factors (Kirk *et al* 1971b; Thomson and Sheridan 1979). Similar situation is found in $[Cr(NN)_2(ox)]^+$ complexes, where oxalate release is not observed. It has been observed from the tables 2 and 3 that quantum yields of the complexes are dependent on the pH of the medium and also wavelength of excitation. The photolysis behaviour of the complexes, $[Cr(NN)_2(ox)]^+$ show properties similar to those for the complexes $[Cr(NN)_3]^{3+}$ and $[Cr(en)_2(ox)]^+$. Hoffman and coworkers (Henry and Hoffman 1978; Maestri *et al* 1978; Bolletta *et al* 1983) have observed that continuous photolysis of $[Cr(NN)_3]^{3+}$ ion in neutral (or basic) aqueous solution

leads to the substitution of the polypyridyl ligand by two molecules of water (or hydroxide ion). Photochemical and thermal reactivities of these complexes are qualitatively same in acidic and basic media (Maestri *et al* 1978; Serpone *et al* 1981). For the compounds $[Cr(NN)_2(ox)]^+$, the thermal reaction is a close parallel to the behaviour of photoreaction mode and suggests a common mechanism. Although, similarities are observed between the overall properties of oxalato*bis*(polypyridyl) chromium(III) and *tris*(polypyridyl)chromium(III) as delineated above, significant differences in the details of kinetic behaviour are observed.

The overall photochemical reaction scheme of the complexes under investigation shows a primary Cr–N bond cleavage, which ultimately undergoes loss of the bidentate ligand. The inactivity of the complexes in acidic solutions appears to be due to the fact that the seven-coordinate intermediate is in competition with the relaxation path as given in (5) along with other relaxation pathways. A slow increase in ϕ values in the pH range 6–8 shows that the seven-coordinate intermediate undergoes deprotonation as represented in (6)

$$*[Cr(NN)_2(ox)]^+ + H_2O \rightarrow [Cr(NN)_2(ox)(H_2O)]^+, \tag{4}$$

$$[Cr(NN)_2(ox)(H_2O)]^+ \rightarrow [Cr(NN)_2(ox)]^+ + H_2O, \tag{5}$$

$$[Cr(NN)_2(ox)(H_2O)]^+ \rightarrow [Cr(NN)_2(ox)(OH)] + H^+. \tag{6}$$

Subsequently, the intermediate species undergoes a ring opening and irreversible loss of the bidentate ligand,

$$[Cr(NN)_2(ox)(OH)] \rightarrow [Cr(NN)(ox)(OH)(H_2O)] + NN. \tag{7}$$

On the other hand, at pH > 9, the quantum yield steadily increases which represents direct nucleophilic attack of the hydroxide ion at the excited Cr(III) centre as given in (8)

$$*[Cr(NN)_2(ox)]^+ + OH^- \rightarrow [Cr(NN)_2(ox)(OH)], \tag{8}$$

$$[Cr(NN)_2(ox)(OH)] + OH^- \rightarrow [Cr(NN)(ox)(OH)_2]^- + NN. \tag{9}$$

Hence, pathways (4)–(7) account for the lower quantum yields in acidic, neutral or mildly alkaline solutions.

The photochemical behaviour of polypyridyl chromium(III) complexes appears to contrast with that of the amine complexes of chromium(III) which are generally found (Sandrini *et al* 1977, 1978; Maestri *et al* 1978; Kirk 1981) to be more reactive towards photosubstitution in acidic solutions.

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