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Excited State Redox Chemistry of Polypyridyl Chromium(III) Complexes. A Determination of the Chromium(III)–(II) Self-Exchange Rate [1]

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Ultraviolet excitations of polypyridyl chromium(III) complexes in alcoholic or aqueous alkaline media have been found to result in formation of chromium(II) complexes apparently in competition with formation of the thermally equilibrated ^2E chromium(III) excited state. The upper state process probably involves oxidation of solvent species and can be used as a device for generating very reactive chromium(II) polypyridyl complexes. By selective excitation of one polypyridyl complex in the presence of a second, the $Cr(PP)_3^{3+,2+}$ self-exchange rate has been investigated and found to be approximately diffusion controlled. This is consistent with the self-exchange rate inferred from the very rapid reactions of other metal complexes with chromium polypyridyl species.

Introduction

The photochemistry of transition metal polypyridyl (PP) complexes has been rich and varied, owing largely to the relatively long excited state lifetimes and to the redox lability of these systems [2–7]. Such complexes have been the focus of recent interest because the lowest thermally equilibrated excited states are often 1–2 eV more powerful as oxidizing or/and reducing agents than the respective ground states. Thus the lowest energy excited states of $M(PP)_3^{n+}$ complexes have been used to oxidize or reduce a variety of organic and inorganic substrates, generally with a view of studying highly exergonic reactions or with attempting to make use of the chemical energy contained in displaced redox equilibria.

In the course of our studies of $Cr(PP)_3^{3+}$ complexes we have found that some of the redox behavior implicates solvent species. Thermal [8–10] and photochemical [11] oxidations of solvent species by polypyridyl and related complexes are often mechanistically complex, but reasonably comonplace [12]. In this note we report our investigations of this behavior and explore some of its implications.

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Experimental

The chromium(III) complexes were prepared by H_2O_2 oxidations of a mixture of Cr^{2+} and polypyridyl ligand in methanol in a minor variation of the literature procedure [13]. Most other complexes were available from previous studies at Wayne State University.

The $[Co(sep)]Cl_3$ [14] was prepared by a variation of the procedure of Sargeson and co-workers [15]. A solution of $[Co(en)_3]Cl_3$ in formalin was allowed to stand overnight, then concentrated at room temperature. When a precipitate began to form the mixture was cooled in an ice bath and the supernatant liquid was decanted. The residue was mixed with methanol, cooled in the ice bath, and ammonia gas was bubbled through the mixture for about half an hour. The crystalline product was separated by filtration and purified by recrystallization from water.

Flash photolysis systems and techniques were very similar to those described previously [16]. The pulse radiolysis system and techniques have also been described previously [17]. Rate constants based on absorbance decays were calculated from the slopes of first order plots where possible.

Stopped flow studies were performed using Aminco and Durrum apparatuses at Brookhaven National Laboratory.

Fischer Certified A.C.S. reagent grade 2-propanol and t-butanol were used in most of these experiments. In addition some flash photolysis experiments were carried out using purified alcohols. Fischer reagent grade 2-propanol was distilled and a sample with a boiling point of (82.29 ± 0.03) °C at 756 Torr

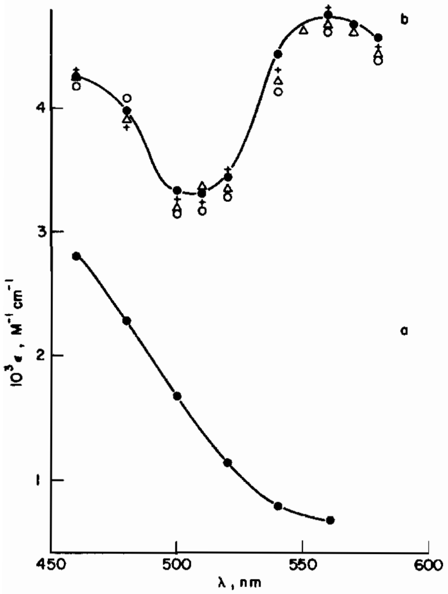

Fig. 1. Spectra of the transients obtained under different conditions: a) Spectra of the ^{2}E for $Cr(bpy)_3^{3+}$ in acid ($HClO_4$ 0.1 *M*) deaerated solutions. Photolysis cut off: $\lambda \geqslant$ 380 nm; $(r(bpy)_3^{3+}$: 5×10^{-5} *M*, energy/flash 250 Joule. Deaerated solution. Extinctions have been calculated from the initial absorbance and the initial concentration of ^{2}E. The initial concentration of ^{2}E was made equal to the initial concentration of $Cr(bpy)_3^{2+}$ obtained under the same conditions but from a total quenching of the excited state with Fe^{2+} (0.01 *M*). b) Spectra of the Species generated with various quenchers. • Fe^{2+}: 0.02 *M*; $HClO_4$: 0.1 *M*; deaerated; △ $Ru(NH_3)_6^{2+}$: 10^{-3} *M*; $HClO_4$: 0.1 *M*; deaerated; + NaOH: 0.16 *M*; aerated; ○ Neat methanol: deaerated; $Cr(bpy)_3^{3+}$: 5×10^{-5} *M* and energy/flash: 250 Joule in all these experiments. The spectra in methanol were obtained 500 μsec after the flash. Both the spectra obtained in NaOH and in MeOH have been normalized under the assumption that the extinction coefficient at 560 nm is 4786 M^{-1} cm^{-1}.

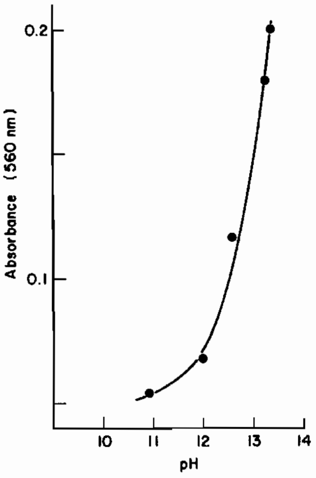

Fig. 2. Variations of the transient concentration with base. Absorptions at 560 nm were determined 300 μsec after the flash. $Cr(bpy)_3^{3+}$: 5×10^{-5} *M*; energy/flash: 250 Joule; [NaOH] + [$NaClO_4$] = 0.2 *M*; cut off filter transmitted $\lambda \geqslant 320$ nm.

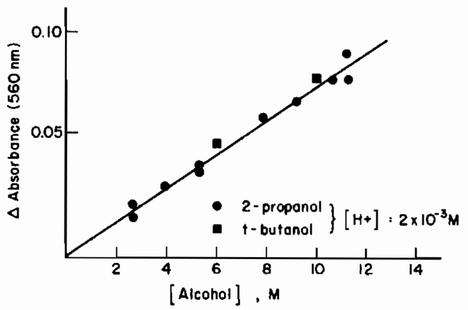

Fig. 3. Dependence of the Cr(II) yield on 2-propanol and t-butanol concentrations. Absorbance increase at 560 nm produced in flash photolyses of $Cr(bpy)_3^{3+}$ deaerated solutions containing 2×10^{-3} *M* $HClO_4$ and various alcohol concentrations. Cut off filters transmitted at $\lambda > 320$ nm. Absorbances were determined at about 300 μs after the photolysis flash; Cr(II) absorbancies were relatively stable in the alcoholic media.

was used for some experiments and t-butanol recrystallized three times by partial freezing was used in others. The results obtained were unaffected by these solvent purifications.

Solutions of $Co(sep)^{2+}$ were prepared by means of the zinc amalgam reduction of aqueous solutions of [Co(sep)] Cl_3 (0.09 *M* NaCl, 0.01 *M* HCl). All solutions were carefully deaerated, except where otherwise noted, by entrained, purified N_2 or Ar. In the flash photolysis studies of $Cr(bpy)_3^{2+}$ kinetics, optical monitoring was performed using a cutoff filter so that only light of $\lambda > 500$ nm traversed the sample cell. Cutoff filter solutions were also placed in the outer jacket of the sample cell as needed to isolate various optical regions.

Formaldehyde was determined with chromotropic acid [19].

Results and Discussion

Flash photolyses of $Cr(bpy)_3^{3+}$ in aqueous solutions produce a strongly absorbing transient whose spectra, lifetime, and identification as the thermally equilibrated ^{2}E excited state have been previously discussed by other authors [5e, 5f, 6]. In deaerated basic aqueous media and in deaerated alcoholic media we have found flash photolyses to produce a different, strongly absorbing, and very reactive species, with an absorbance maximum at about 560 nm (Fig. 1). This species was frequently produced together with the ^{2}E transient during the photolysis flash. The yield of this second species was dependent on the solution pH (Fig. 2), the excitation wavelength

TABLE I. Relative Yields of $Cr(bpy)_3^{2+}$ Produced in Flash Photolyses of $Cr(bpy)_3^{3+}$ in Neat Methanol.

Wavelength Region Irradiated, nm	ΔA_{560} nm	Excitation Range, nm	ΔA_{560}(corr)[a]
>200	0.30	200–260	0.57
>260	0.20	260–320	0.40
>320	0.06	320–430	0.09
>430	0.02	>430	0.02

[a]Values corrected for an approximate light distribution using $Co(NH_3)_5Br^{2+}$; $[\overline{Br_2}]$ was measured for excitation in the same regions, see ref. 21a. Substrate absorbance was effectively zero at 560 nm.

(Table I), and alcohol concentration (Fig. 3). This chemical species had absorption spectra and the chemical reactivity characteristic of $Cr(bpy)_3^{2+}$ [13, 18]. We have made direct comparisons of reactivity and spectra under our experimental conditions by generating $Cr(bpy)_3^{2+}$ in reductive quenching of (^{2}E)-$Cr(bpy)_3^{3+}$ with Fe^{2+}, $Ru(NH_3)_6^{2+}$, *etc.* (Fig. 1). Under conditions of moderate pH or concentration of alcohol we have been able to detect both the (^{2}E)-$Cr(bpy)_3^{3+}$ transient and $Cr(bpy)_3^{2+}$. Other polypyridyl complexes of chromium (III) behave similarly, and we have found that the (^{2}E)$Cr(PP)_3^{3+}$ *lifetime* is not strongly medium dependent under such conditions (refs. 53, 5f, 6b and Table II); however the ^{2}E *yield* is medium dependent under these conditions. These observations indicate that the chromium(II) complex is produced from relatively high energy excited states, *not from the* (^{2}E)$Cr(PP)_3^{3+}$ *state.* By analogy with previous studies [11, 16, 20] it seems plausible that the solvent dependent process leading to $Cr(bpy)_3^{2+}$ is a prompt, upper state process which occurs in competition with excited state relaxation to form the (^{2}E)$Cr(bpy)_3^{3+}$ transient, as in eqns. (1)–(5)* [21]:

$$Cr(bpy)_3^{3+} + h\nu \rightarrow {}^*[Cr(bpy)_3^{3+}] \tag{1}$$

$$^*[Cr(bpy)_3^{3+}] + RCH_2OH \rightarrow Cr(bpy)_3^{2+} + RCH_2OH^+ \tag{2}$$

$$^*[Cr(bpy)_3^{3+}] \rightarrow {}^2E \tag{3}$$

$$^2E \rightarrow Cr(bpy)_3^{3+} \tag{4}$$

$$2RCH_2OH^+ \rightarrow RCH_2OH + RCO + 2H^+ \tag{5}$$

The alcohol radicals (written as ROH^+ in eqn. (2)) could in principle be involved in attack on the substrate; however, no spectroscopic anomalies such as shifted absorbance maxima or very short lived transient absorbance changes were observed which would require such reactions. In anaerobic methanol solutions we found the $Cr(bpy)_3^{2+}$ yield to be (2.1 ± 0.3) of the yield of CH_2O as required by (1)–(5).

Reaction (2) provides a device for investigating the $Cr(bpy)_3^{3+}/Cr(bpy)_3^{2+}$ self-exchange reaction. Deaerated methanolic solutions 1.0×10^{-4} *M* in $Cr(bpy)_3^{3+}$ were flash photolyzed with the flash adjusted so that 10^{-6} $M \leqslant [Cr(bpy)_3^{2+}] \leqslant 5 \times 10^{-6}$ *M*. The $Cr(bpy)_3^{2+}$ produced in this manner was found to exhibit stable absorbances for periods of several

*An alternative mechanism might be H-atom abstraction from the solvent such as has recently been reported for the 1,10-phenanthroline $n\pi^*$ excited state oxidations of organic solvents and water [22]. However this process has not been observed for coordinated polypyridyls where the nitrogen atom is relatively inaccessible.

TABLE II. Lifetime of the ^{2}E Excited State of $Cr(PP)_3^{3+}$.

$t_{1/2}$[a] (μsec)	Medium Conditions[b]
60 ± 5	6.6 *M* 2-propanol; 2.5×10^{-3} *M* $HClO_4$
65 ± 5	6.6 *M* 2-propanol; 2.5×10^{-3} *M* $HClO_4$; 3 *M* $NaClO_4$
70 ± 5	6.6 *M* 2-propanol; 2.5×10^{-3} *M* $HClO_4$; 6 *M* $NaClO_4$
60 ± 5	———————; 2.5×10^{-3} *M* $HClO_4$; ———————
120 ± 6	———————; 2.5×10^{-3} *M* $HClO_4$; 6 *M* $NaClO_4$
120 ± 5[c]	0.05 *M* H_2SO_4
120 ± 5[c]	10^{-5} *M* H_2SO_4
118 ± 5[c]	pH 6.5
100 ± 10[c]	0.1 *M* NaOH

[a]Average over 5 determinations; for (^{2}E)$Cr(bipy)_3^{3+}$ except as indicated. [b]Solutions deaerated with Ar. [c]For (^{2}E)Cr(5-Cl-phen)$_3^{3+}$; decay rates were independent of wavelength of observation (460 nm < λ < 580 nm). Half-lives based on observations of the decay of the 520 nm absorbance.

TABLE III. Rate Constants for Oxidation–Reduction Reactions of Polypyridyl–Chromium(III) Complexes.

Oxidant	Medium	10^6 [Reductant]$_o$	k_I, s^{-1} [a]	k_{II}, M^{-1} s^{-1}
$Cr(Me_2phen)_3^{3+}$	Methanol (~99%)	1.6[b]	1.0 ± 0.3	6.2×10^5
		2.5[b]	1.7 ± 0.3	6.8×10^5
		4.3[b]	3.0 ± 0.2	7.0×10^5
	7×10^{-3} M HCl; ~95% Methanol	~2[b]	$(1.4 \pm 0.4) \times 10^2$	$(7.0 \pm 0.5) \times 10^7$
	0.05 M HCl; ~95% Methanol	~2[b]	$(7.1 \pm 0.8) \times 10^2$	$(3.5 \pm 0.3) \times 10^8$
	0.1 M HCl; ~90% Methanol	~2[b]	$(1.9 \pm 0.1) \times 10^2$	$(9.6 \pm 0.3) \times 10^8$
$Ru(NH_3)_6^{3+}$ [d]	0.1 M $HClO_4$			$(1.4 \pm 0.4) \times 10^9$
	0.03 M H_3SO_4	~2[c]		$(0.7 \pm 0.07) \times 10^9$[d]
$Cr(Mephen)_3^{3+}$	0.09 M NaCl; 0.01 M HCl	(~30)[e]	$(1.1 \pm 0.1) \times 10^2$ [f]	$(2.2 \pm 0.2) \times 10^5$
	0.09 M NaCl; 0.01 M HCl	(~30)[e]	$(4 \pm 1) \times 10^2$ [g]	$(3 \pm 1) \times 10^5$

[a]Average and average deviation of 3–6 determinations. [b]Initial concentration of $Cr(bpy)_3^{2+}$ produced in each flash from selective excitation and photoredox of $Cr(bpy)_3^{3+}$ in methanol. [c]Generated in the $Ru(NH_3)_6^{2+}$ quenching of $(^2E)Cr(bpy)_3^{3+}$ in flash photolysis experiments; second order decay conditions. Rate constants estimated using extinction coefficients for $Cr(PP)_3^{2+}$ (*e.g.*, see Fig. 1). [d]For reaction of $Ru(NH_3)_6^{3+}$ with $Cr(Me_2phen)_3^{2+}$. [e]$Co(sep)^{2+}$ reactions determined by stopped flow techniques. [f]$[Cr(Mephen)_3^{3+}]_o = 0.5 \times 10^{-3}$ M. [g]$[Cr(Mephen)_3^{3+}]_o = 1.4 \times 10^{-3}$ M.

seconds [22]. When the flash photolyses were performed in the presnece of 5×10^{-8} M to 10^{-7} M $Cr(Me_2phen)_3^{3+}$, we observed a pseudo first order transient decay of $Cr(bpy)_3^{2+}$ absorbance at 560 nm. In separate experiments we have found $Cr(Me_2phen)_3^{2+}$ to have an absorption maximum at about 470 nm and in the near red, with an absorption minimum at ~560 nm. Consequently, the transient absorbance in these experiments is attributed to $Cr(bpy)_3^{2+}$ and its decay is attributed to reaction (6). There is a –0.08 V difference in the $Cr(bpy)_3^{3+,2+}$ and $Cr(Me_2phen)_3^{3+,2+}$ electrode potentials [23], so that $K_5 = 0.044$ for eq. (6):

$$Cr(bpy)_3^{2+} + Cr(Me_2phen)_3^{3+} \rightarrow Cr(bpy)_3^{3+} + Cr(Me_2phen)_3^{2+} \quad (6)$$

Our observations, summarized in Table III, demonstrate that the rate of reaction (6) increases as expected with ionic strength in methanol, and that $k_5 = (9.6 \pm 0.3) \times 10^8$ M^{-1} s^{-1} or (for $\Delta G^o \cong 0$) [24, 25] $k_{ex} \cong (4 \pm 1) \times 10^9$ M^{-1} s^{-1} (methanolic solution, 25 °C, $\mu = 0.1$). This is close to the diffusional limit expected [26] in this medium. It is in very good agreement with the value of $k_{ex} \cong (2 \pm 1) \times 10^9$ M^{-1} s^{-1}** based on the $Co(sep)^{2+}$ reduction of $Cr(Mephen)_3^{3+}$ [24, 25], and in reasonable agreement with the nearly diffusion controlled $Ru(NH_3)_6^{3+}$/$Cr(bpy)_3^{2+}$ reaction [27].

**For this reaction in aqueous solutions: $K_{12} \cong 15 \pm 4$ (based on a value of $\Delta E^o = +0.07$ v; potentials determined at Brookhaven National Laboratory by B. Brunschwig and by G. M. Brown), $f_{12} = 0.93$ and $k_{Co} = k_{11} = 2.8 \pm 0.8$ M^{-1} s^{-1} (at $\mu = 0.1$, based on the value of $k_{11} = 5.2 \pm 0.3$ M^{-1} s^{-1} at $\mu = 0.2$ reported in ref. 16). We would estimate $k_{ex} > 10^9$ M^{-1} s^{-1} using $k_{Ru} = k_{22} = 4.3 \times 10^3$ M^{-1} s^{-1}.

Reaction (6) was also studied by pulse radiolysis. Solutions of $Cr(bpy)_3^{3+}$ (5×10^{-3} M) in 1 M t-butanol and 10^{-4} M $HClO_4$ were deaerated with nitrogen. Various concentrations of $Cr(Me_2phen)_3^{3+}$ were used in order to see the previous reaction. A rate constant $k = 3 \times 10^3$ sec^{-1} was obtained with $Cr(Me_2phen)_3^{3+} = 10^{-3}$ M; thus $k_5 \cong 3 \times 10^6$ M^{-1} s^{-1} and $k_{ex} \cong 7 \times 10^7$ M^{-1} sec^{-1} (aqueous medium, 25 °C, $\mu \cong 0.01$). However attempts to use higher concentrations of $Cr(Me_2phen)_3^{3+}$ produced new transients whose origin is probably in secondary Cr(III)–ligand–radical reactions.

Conclusions

(a) High energy excitations of $Cr(PP)_3^{3+}$ complexes can lead to chromium(II) species in basic and alcoholic media. This kind of solvent dependent photoredox process has now been found for a variety of coordination complexes [12, 13, 18] and may be a contributing factor to excited state quenching by solvolytic species, especially at large excitation energies.

(b) The $Cr(bpy)_3^{3+,2+}$ self-exchange (electron transfer) rate is very nearly diffusion limited.

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