Coordination Chemistry Reviews, 39 (1981) 121–179
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

ADVANCES IN THE PHOTOCHEMISTRY AND PHOTOPHYSICS OF CHROMIUM(III) POLYPYRIDYL COMPLEXES IN FLUID MEDIA

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(Received 16 September 1980)

CONTENTS

ABBREVIATIONS

bpy	2,2′-Bipyridyl
4,4′-Me_2bpy	4,4′-Dimethylbipyridyl
4,4′-Ph_2bpy	4,4′-Diphenylbipyridyl
phen	1,10-Phenanthroline
5-Clphen	5-Chloro-1,10-phenanthroline
5-Brphen	5-Bromo-1,10-phenanthroline
5-Mephen	5-Methyl-1,10-phenanthroline
4,7-Me_2phen	4,7-Dimethyl-1,10-phenanthroline
5,6-Me_2phen	5,6-Dimethyl-1,10-phenanthroline

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3,4,7,8-Me_4phen	3,4,7,8-Tetramethyl-1,10-phenanthroline
5-Phphen	5-Phenyl-1,10-phenanthroline
4,7-Ph_2phen	4,7-Diphenyl-1,10-phenanthroline
trpy	2,2′,2″-Terpyridine
en	Ethylenediamine
DMF	Dimethylformamide
CH_3CN	Acetonitrile
η_i	Efficiency of the i^{th} process
k_i	Rate constant for the i^{th} process
ϕ_i	Quantum yield for the i^{th} process
isc	Intersystem crossing process
rad	Radiative process
nr	Nonradiative process
rx	Reactive process
q	Quenching process
bet	Back-electron-transfer process
th	Thermal process
gsq	Ground-state quenching process

A. INTRODUCTION

Investigations in recent years have demonstrated that the excited states of transition metal complexes can engage in homogeneous electron- and energy -transfer reactions [1], and heterogeneous electron transfer at semiconductor electrodes [2]. Thus, the potential for the conversion of radiant (solar) energy to useful chemical and electrical energy by means of photochemical systems exists.

Recently, polypyridyl complexes of transition metals have been critically investigated as potential catalysts (photosensitizers) in photochemical systems for conversion and storage of solar energy. These investigations have focused predominantly on systems incorporating ruthenium(II) polypyridyl complexes, e.g. tris(2,2′-bipyridyl)ruthenium(II) [3].

Considerable attention has also been directed at the polypyridyl complexes of Cr(III), $Cr(NN)_3^{3+}$, where NN is 2,2′-bipyridine or 1,10-phenanthroline or some substituted analog of these two polypyridyl ligands [4]. The investigations have demonstrated that the metal-centered (MC) excited states of these chromium(III) complexes can engage in homogeneous energy and electron transfer, exhibit relatively long lifetimes [5,6] which can be prolonged by alterations of the solution medium [7,8] or ground-state concentration [9], and exhibit favourable redox properties [10]. The ground-state $Cr(NN)_3^{3+}$ complex shows absorption bands to ca. 450 nm [5], and is relatively inert in aqueous acidic media [7]. These and other photochemical and photophysical features of $Cr(NN)_3^{3+}$ complexes will be discussed in detail in Sections B–D in order to examine the potential viability of these complexes as photosensitizers for solar energy conversion and storage cycles. That these $Cr(NN)_3^{3+}$ complexes are feasible alternatives for such cycles is evidenced by observation of the generation of photocurrents in the visible region from $(^2MC)Cr(bpy)_3^{3+}$ [11], and the observations of hydrogen evolution from $Cr(bpy)_3^{3+}/Ru(bpy)_3^{2+}/EDTA/Pt(OH)_2$ and $Cr(4,4'\text{-}Me_2bpy)_3^{3+}/Ru(trpy)_2^{2+}/EDTA/Pt(OH)_2$ systems [12,13].

B. SPECTRAL CHARACTERIZATION OF $Cr(NN)_3^{3+}$ COMPLEXES

(i) The ground state of $Cr(NN)_3^{3+}$

Chromium(III) complexes possess a d^3 electronic configuration. The ground electronic state in octahedral microsymmetry is the quartet state $^4A_2$. Typically, absorption spectra of chromium(III) complexes reveal three weak absorption bands (quartet–quartet) in the ultraviolet and visible regions, and two very weak, spin-forbidden bands (quartet–doublet) in the red region. The quartet–quartet bands correspond to the spin-allowed transitions from the $^4A_2$ ground state to the excited quartet states $^4T_2$, a^4T_1, and b^4T_1. These transitions are shown in Fig. 1 for chromium(III) species of octahedral symmetry. Although the chromium(III) polypyridyl complexes possess dihedral (D_3) symmetry [14], they are often discussed in the context of octahedral microsymmetry. The features of Fig. 1 are applied to all the $Cr(NN)_3^{3+}$ complexes discussed herein.

König and Herzog [15] have thoroughly investigated the ground-state absorption spectrum of $Cr(bpy)_3^{3+}$ and, assuming octahedral microsymmetry, have assigned the three spin-allowed quartet bands at 23.4, 28.9 and 35.6×10^3 cm^{-1} to the $^4A_2 \rightarrow {}^4T_2$, $^4A_2 \rightarrow a^4T_1$, and $^2A_2 \rightarrow b^4T_1$ transitions, respectively. The three unresolved shoulders (centered at ca. 23.4×10^3 cm^{-1}) were assigned to vibrational co-excitation involving the coupling of electronic *d–d* transitions and vibrational transitions within the bipyridyl ligand. This coupling then results in some electron delocalization within the excited states. The bands at 32.7 and 42.1×10^3 cm^{-1} were interpreted as bipyridine ligand-centered transitions, $^1A_1 \rightarrow {}^1B_1$ and $^1A_1 \rightarrow {}^1A_1$, respectively.

The ground-state absorption spectra of several other chromium(III) polypyridyl complexes, $Cr(NN)_3^{3+}$, have been studied by Serpone and co-workers [5,6]. The spectra include those where NN is bpy, 4,4'-Me_2bpy, 4,4'-Ph_2bpy, phen, 5-Clphen, 5-Brphen, 5-Mephen, 5,6-Me_2phen, 4,7-Me_2phen, 3,4,7,8-Me_4phen, 5-Phphen and 4,7-Ph_2phen. For all of the spectra the lowest-energy multicomponent band was assigned [5] to the $^4A_2 \rightarrow {}^4T_2$ transition; this band yields the value of the ligand field splitting parameter Δ. The multi-

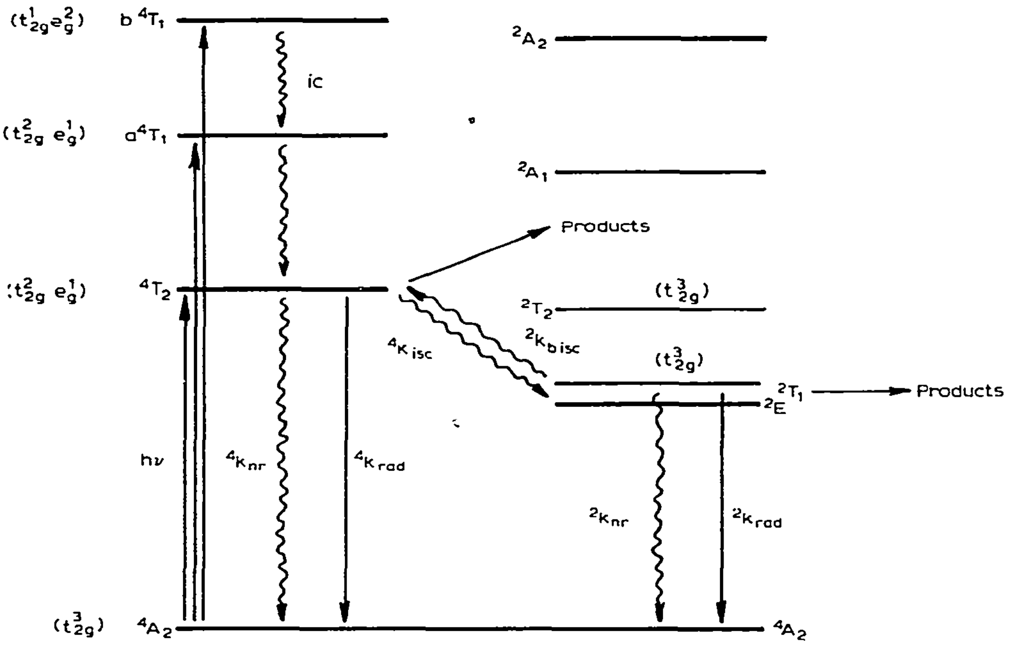


Fig. 1. Simplified energy level diagram of $Cr(NN)_3^{3+}$ complexes; $^4k_{nr}$, $^4k_{rad}$, and $^4k_{isc}$ are the rate constants of non-radiative, radiative, and intersystem crossing for the lowest excited quartet state, $^4T_2$; $^2k_{nr}$, $^2k_{rad}$, and $^2k_{bisc}$ are the corresponding rate constants for the thermally equilibrated ^2E and $^2T_1$ excited states; ic denotes internal conversion. The electron configuration of each state is also given.

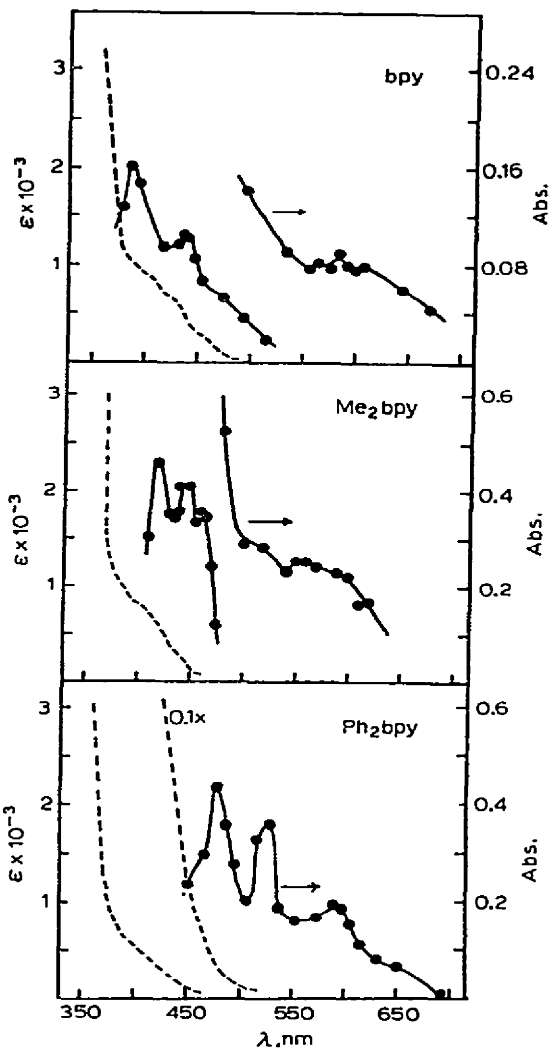
component nature of this band indicates some degree of synergism [5], suggesting that Δ comprises both σ and π contributions. The ground-state absorption spectra (dashed line) for $\lambda > 350$ nm of $Cr(bpy)_3^{3+}$, $Cr(4,4'\text{-}Me_2bpy)_3^{3+}$, and $Cr(4,4'\text{-}Ph_2bpy)_3^{3+}$ are presented in Fig. 2; those of $Cr(phen)_3^{3+}$, $Cr(5\text{-}Clphen)_3^{3+}$ and $Cr(3,4,7,8\text{-}Me_4phen)_3^{3+}$ are depicted in Fig. 3. A comparison of the centers of gravity of the lowest-energy bands of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ suggests that $\Delta_{bpy} \simeq \Delta_{phen}$. Spectral data obtained for other $Cr(NN)_3^{3+}$ complexes [5,6] have been used to approximate the relative values of Δ thus:

(a) $4,4'\text{-}Me_2bpy \geqslant 4,4'\text{-}Ph_2bpy \geqslant bpy$;

and

(b) $4,7\text{-}Ph_2phen \geqslant 5\text{-}Mephen \geqslant 5\text{-}Brphen \simeq 5\text{-}Clphen \geqslant phen \geqslant 3,4,7,8\text{-}Me_4phen \geqslant 5,6\text{-}Me_2phen \simeq 4,7\text{-}Me_2phen \geqslant 5\text{-}Phphen$.

The spectral results show that methyl or phenyl substitution at the 4,4′-positions of the bpy ligand causes a slight blue shift in the bands corresponding to the $^4A_2 \rightarrow {}^4T_2$ transition. Methyl substitution on the phen ligand



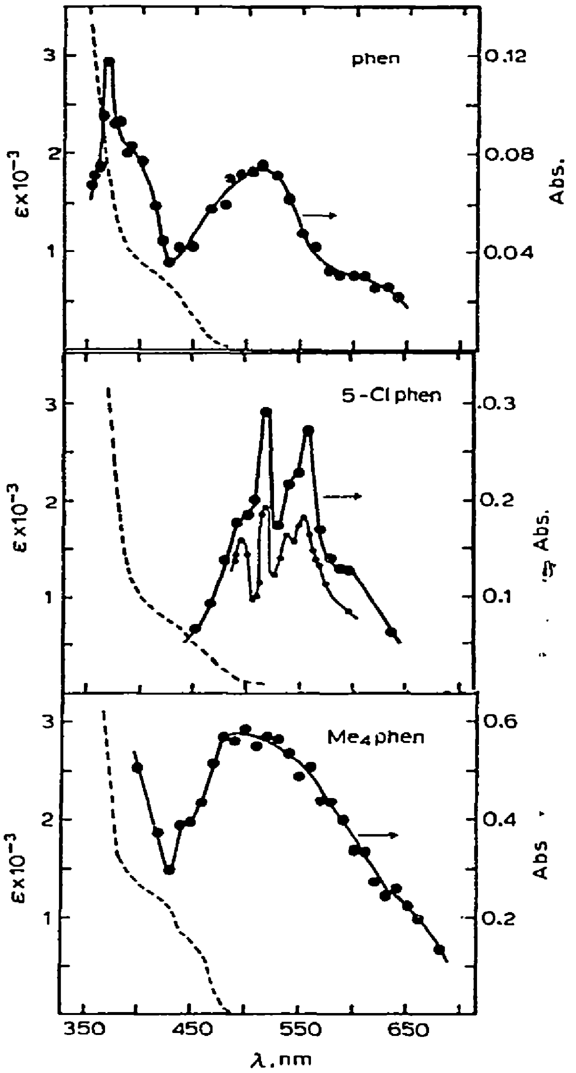


Fig. 2. Absorption spectra ($\lambda > 350$ nm) of the ground-state $Cr(NN)_3^{3+}$ complexes (dashed line), and of the primary transient species $(^2E)Cr(NN)_3^{3+}$ (solid line and points) where NN is bpy, 4,4′-Me_2bpy, and 4,4′-Ph_2bpy, obtained by flash photolysis absorption in N_2-purged acidic media (1 M HCl); concentration of complexes ca. $10^{-4}-10^{-6}$ M. Spectra were measured 40 μs after the flash except for the bpy complex, for which the spectrum was taken 150 μs after the flash [5].

Fig. 3. Absorption spectra ($\lambda > 350$ nm) of the ground-state $Cr(NN)_3^{3+}$ complexes (dashed line), and of the primary transient species $(^2E)Cr(NN)_3^{3+}$ (solid line and points) where NN is phen, 5-Clphen, and 3,4,7,8-Me_4phen, obtained by flash photolysis absorption in N_2-purged acidic media (1 M HCl); concentration of complexes ca. $10^{-4}-10^{-6}$ M. Spectra were taken 40 μs after the flash except for the phen complex, for which the spectrum was taken 150 μs after the flash [5].

blue-shifts this low-energy transition, while phenyl- and halo-substitution cause a red shift. Additionally, the values of the molar extinction coefficient are significantly increased upon phenyl substitution on both the bpy and phen frameworks [5,6]. This feature is analogous to that observed [16–20] for the effect of substitution on the absorption maxima of the metal-to-ligand-charge-transfer (MLCT) states of $\mathrm{Ru(NN)_3^{2+}}$ complexes. However, these do not show marked shifts in absorption maxima upon substitution [17], although the lifetimes of the emitting MLCT states and redox potentials of both ground and excited states appear to be somewhat sensitive to changes in ligand substituents.

(ii) *The nature of the excited states of* $Cr(NN)_3^{3+}$ *complexes*

Absorption of light into the first ligand-field band of a chromium(III) complex yields a vibrationally-excited Franck–Condon quartet state, which subsequently relaxes to a thermally-equilibrated ("thexi") [21] quartet state, ${}^4T_2^0$. This ${}^4T_2^0$ state is expected to be severely distorted with respect to the ${}^4A_2$ ground state. The distortion results from the promotion of an electron from a predominantly nonbonding $d\pi$ orbital (d_{xy}, d_{xz} and d_{yz}) to a formally σ^* antibonding orbital (d_{z^2} or $d_{x^2-y^2}$) and exemplifies itself in increased Cr–ligand bond lengths in the quartet state. In the solid state, fluorescence (${}^4T_2 \rightarrow {}^4A_2$) is expected to be broad and red-shifted with respect to the corresponding absorption band (${}^4A_2 \rightarrow {}^4T_2$). The energy of such distorted states will be sensitive to the nature of the coordinated ligands and the chromium–ligand bond strengths. Although fluorescence has been observed for some chromium(III) complexes at low temperature [22], only $\mathrm{Cr(urea)_6^{3+}}$ exhibits both room-temperature fluorescence and phosphorescence [23].

Adamson [24] originally proposed that the ${}^4T_2^0$ excited state was the direct precursor to the photochemical reactivity in chromium(III) species, on the basis of correlation of product yield with ligand field strength. Since then, the ${}^4T_2$ state has been implicated as the immediate precursor to photochemistry with the ${}^2E$ state being chemically inert except via the ${}^4T_2$ state attained through back intersystem crossing [23].

The lowest-energy doublet states, ${}^2E$ and ${}^2T_1$, are not expected to be greatly distorted with respect to the ${}^4A_2$ ground state since the ${}^4A_2 \rightarrow {}^2T_1/{}^2E$ transition involves no electron promotion to a σ^* antibonding orbital; rather electron spin-pairing or spin-flip occurs within the t_{2g} subshell. The bond lengths are thus expected to be very similar for the ${}^4A_2$ and ${}^2T_1/{}^2E$ states. Indeed, the nuclear equilibrium geometries of the ${}^4A_2$ and ${}^2T_1/{}^2E$ species are essentially identical inasmuch as the absorption (${}^4A_2 \rightarrow {}^2T_1/{}^2E$) and emission (${}^2T_1/{}^2E \rightarrow {}^4A_2$) maxima are coincident, there being no Stokes shift [22].

Definitive identification of the excited state(s) responsible for chromium(III) photoreactions remains somewhat elusive. Two principal pathways have been proposed to account for the photochemistry of these Cr(III) complexes. Both the lowest spin-forbidden doublet state [25,26], ^2E, and the lowest spin-allowed quartet, $^4T_2$ [24], have been implicated. In support of reactions originating from the quartet excited state, Chen and Porter [27] have noted that only 50% of the photolysis reaction of *trans*-$Cr(NH_3)_2(NCS)_4^-$ can be quenched by the doublet-quenching $Cr(CN)_6^{3-}$; this was taken as evidence that 50% of the thiocyanate loss occurs from the quartet excited state prior to intersystem crossing to the doublet excited state. Photosolvolysis of $Cr(NH_3)_6^{3+}$ must arise from the $^4T_2$ state [28] inasmuch as the phosphorescence is completely quenched by the doublet-quenching hydroxide ion. Furthermore, 40% of the photoreaction of $Cr(en)_3^{3+}$ in aqueous solution originates from the quartet state prior to intersystem crossing to the doublet state; the remaining 60% is quenched and this is believed to result from molecules passing through the doublet state [29]. Balzani et al. [29] have suggested that the quenchable portion of the photoreaction also comes from the quartet state, subsequent to back intersystem crossing from the doublet state. Further, Sabbatini and Balzani [30] and Wasgestian [31] have discounted the doublet mechanism in light of observations [30] that pyrazine and xanthone photosensitize the aquation of $Cr(CN)_6^{3-}$, while Michler's ketone and $Ru(bpy)_3^{2+}$ do not, although the latter two complexes do sensitize the phosphorescence emission.

Photoracemization studies of (+)-$Cr(en)_3^{3+}$ [22] and (+)-$Cr(phen)_3^{3+}$ [16,32] have shown that both the quartet and doublet excited states are implicated in the photoreactivity of these complexes. Investigation of (+)-$Cr(phen)_3^{3+}$ [16,32] has demonstrated that photoracemization is partially quenched by oxygen and iodide ion, with an unquenched residual yield which has been attributed [16] to a prompt reaction from the $^4T_2$ state prior to intersystem crossing to the quenchable ^2E state. Fourteen percent of the total photoracemization is not quenched by iodide ion, while 86% of the reaction occurs from excited-state species which have passed through equilibrated doublet states. Intersystem crossing ($^4T_2 \rightsquigarrow {}^2E$) appears to be a very rapid process in chromium(III) complexes, probably in the range of $10^{10}-10^{11}$ s^{-1} [33]. Further, intersystem crossing has been shown [32,34] to be wavelength-dependent, indicating that intersystem crossing and vibrational relaxation probably occur within similar time frames. Sasseville and Langford have recently observed [32] that the non-quenchable residual (14%) of the photoracemization reaction also exhibits a wavelength dependence, and the quantum yields for racemization increase (to some extent) with increasing initial vibronic excitation across the low-energy side of the first quartet band. The parallel between intersystem crossing and non-quenchable racemization in the $^4T_2$ state is credible since the efficiency of both processes increases with increasing vibronic excitation to an upper limit. The conclusion drawn is that there is a significant contribution from the vibrationally-equilibrated $^4T_2^0$ state to the non-quenchable reaction. As a result, reaction competes with vibrational relaxation.

(a) Doublet state absorption spectra

In an effort to establish the identity of the photoreactive state(s) of $Cr(NN)_3^{3+}$ species, it has been necessary to characterize fully these complexes. The doublet state absorption spectra (Figs. 2 and 3) have been obtained by conventional microsecond flash photolysis [35]. The absorption spectrum of the ^2E state of $Cr(bpy)_3^{3+}$ exhibits bands at 590, 445 and 390 nm, with shoulders centered at ca. 650 and 475 nm. The entire spectrum decays via first-order kinetics in acidic, neutral and alkaline media, with $k = 1.6 \pm 0.3 \times 10^4$ s^{-1} at 22°C) [35] for the decay of the primary transient. This primary transient absorption is quenched by oxygen ($k_q = 1.7 \times 10^7$ M^{-1} s^{-1} at 22°C) [35], by iodide ion ($k_q = 1.2 \times 10^9$ M^{-1} s^{-1} at 22°C) [36], and by iron(II) ($k_q \sim 10^8$ M^{-1} s^{-1} at 22°C) [36]. Transient substrate bleaching is also observed upon flash excitation of $Cr(bpy)_3^{3+}$ in the pH range ca. 2–6 [35]. The rate of decay of this bleaching is pH-dependent, but remains unaffected by oxygen and iodide ion. The pH dependence follows the rate law $k_{obs} = k_0 + k_a[H^+]$ in the range $2.35 \geqslant pH \geqslant 5.35$ with $k_0 \sim 10$ s^{-1} and $k_a = 4 \times 10^5$ M^{-1} s^{-1}. Observation [35] that the decay of the primary transient is coincident with the decay of the phosphorescence ($^2E \rightarrow {}^4A_2$) has led to the identification of the primary transient as the ^2E excited state. This is further supported by the similar temperature dependencies exhibited by the primary transient and phosphorescence decays, and by oxygen and iodide ion quenching results.

The absorption spectra of the ^2E states of $Cr(4,4'\text{-}Me_2bpy)_3^{3+}$ and $Cr(4,4'\text{-}Ph_2bpy)_3^{3+}$ are very similar to that of $Cr(bpy)_3^{3+}$ [5]. Methyl substitution red-shifts the 390 nm band of $(^2E)Cr(bpy)_3^{3+}$, while phenyl substitution red-shifts both the 390 and 445 nm bands. The $(^2E)Cr(bpy)_3^{3+}$ absorption band at 590 nm remains virtually insensitive toward substitution at the 4,4′-positions of the bpy ligand, and has been assigned [5] to the $^2E \rightarrow b^2T_1$ transition (Fig. 1). Furthermore, the insensitivity of this band suggests that the doublet manifold b^2T_1 is predominantly metal-centered. The substituent-sensitive bands of $(^2E)Cr(bpy)_3^{3+}$ likely correspond to electronic transitions to doublet states possessing some ligand character, and may well be described as $^2E \rightarrow {}^2$(LMCT) transitions.

The $(^2E)Cr(phen)_3^{3+}$ absorption spectrum is characterized [5] by a broad band centered at 515 nm, which is insensitive toward methyl substitution at the 4,7- and 3,4,7,8-positions. However, 4,7-diphenyl and 5-halo-substitution on the phen ligand red-shifts the 515 nm band. This band was assigned to the $^2E \rightarrow b^2T_1$ transition.

(b) Doublet state lifetimes

The lifetimes of the states responsible for the two emission bands of $^*Cr(bpy)_3^{3+}$ (22°C, aqueous solution) are identical. These two bands have been assigned to the doublet $^2T_1$ and ^2E states [37]. That their lifetimes are identical is indicative of thermal equilibration of the two states. As a result, in the absence of environmental effects, the two states are taken as one. To the extent that the relative yield of ^2E phosphorescence from $^*Cr(bpy)_3^{3+}$ is the same for both ligand-centered (312 nm) and metal-centered (450 nm) excitation it is concluded that relaxation to the lowest quartet state (Fig. 1) occurs with unitary efficiency [35].

The observed lifetime of the ^2E state, $^2\tau_{obs}$, in the absence of quenchers is the reciprocal of the sum of all the rate constants k_i which depopulate the ^2E state [38], as given by eqn. (1) (cf. Fig. 1)

$$^2\tau_{obs} = 1/(^2k_{nr} + {^2k_{rx}} + {^2k_{rad}} + {^2k_{bisc}}) \qquad (1)$$

where the subscripts nr, rx, rad, and bisc refer to the nonradiative, reactive, radiative, and back intersystem crossing pathways, respectively. With reference to $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$, the ^2E state reacts with water ($^2k_{rx}$) in competition with radiative ($^2k_{rad}$) and nonradiative ($^2k_{nr}$) decay back to the $^4A_2$ ground state species; back intersystem crossing ($^2k_{bisc}$) to the $^4T_2$ excited state appears to be unimportant. For $Cr(bpy)_3^{3+}$, deactivation of the ^2E state via radiative decay is insignificant ($^2\eta_{rad} < 10^{-3}$) in comparison with the nonradiative ($^2\eta_{nr} = 1 - {^2\eta_{rx}} \simeq 0.8$) [8] and reactive ($^2\eta_{rx} \simeq 0.2$) decay modes [8]. Thus, the ^2E lifetimes can more aptly be defined by

$$^2\tau_{obs} = 1/(^2k_{nr} + {^2k_{rx}}) \qquad (2)$$

Inasmuch as $^2k_{nr} > (^2k_{rad} + {^2k_{rx}} + {^2k_{bisc}})$, the nonradiative decay mode ($^2k_{nr}$) of the ^2E state is the predominant factor responsible for the lifetime of the ^2E state [8]. Gutierrez and Adamson [39] on the other hand, have suggested that the emission lifetime of *trans*-$Cr(NH_3)_2(NCS)_4^-$ is determined primarily by the rate of chemical reaction ($^2k_{rx}$) from the doublet excited state.

The lifetimes of (^2E)$Cr(bpy)_3^{3+}$ and (^2E)$Cr(phen)_3^{3+}$ in deaerated neat water at 22°C are 0.068 and 0.25 ms, respectively [9]. With respect to the reported lifetime of (^2E)$Cr(en)_2(NCS)_2^+$ ($^2\tau \sim 10\ \mu s$) [40]; the (^2E)$Cr(NN)_3^{3+}$ complexes are surprisingly long-lived. The ^2E lifetimes of the various $Cr(NN)_3^{3+}$ complexes in deaerated 1 M HCl (22°C) at infinite substrate dilution are collected in Table 1.

Prolongation of the ^2E lifetime is an interesting phenomenon inasmuch as

TABLE 1

Lifetimes of $(^2E)Cr(NN)_3^{3+}$ and $(^3CT)Ru(NN)_3^{2+}$ complexes

NN	$^2\tau_0$ Cr(III)[a] (ms)	$^3\tau_0$ Ru(II)[b] (μs)
bpy	0.073[c]	0.060
4,4'-Me_2bpy	0.20[d]	0.33
4,4'-Ph_2bpy	0.17	0.67
5-Clphen	0.18	0.94
5-Brphen	0.18[d]	1.04
phen	0.33	0.92
5-Mephen	0.42	1.33
5,6-Me_2phen	0.42[d]	1.81
4,7-Me_2phen	0.57[d]	1.74
3,4,7,8-Me_4phen	0.64[d]	1.39
5-Phphen	0.22[d]	1.29
4,7-Ph_2phen	0.57[d]	4.68

[a] Extrapolated values to infinite substrate dilution in deaerated 1 M HCl at 22°C, see ref. 6. These τ are very sensitive to the composition of the solution medium (see text). [b] In deaerated H_2O at 25°C; ref. 17. [c] Ref. 9. [d] Solution also contains 4% v/v CH_3CN.

it enhances the potential reactivity of the excited states. As noted in Table 1, subtle modification of the polypyridyl ligand alters the lifetime of the ^2E state. It is observed that 4,4'-substitution on the bpy framework, and 4,7-dimethyl, 4,7-diphenyl, 5-methyl, 5,6-dimethyl, and 3,4,7,8-tetramethyl substitution on the phen framework cause an increase in the ^2E lifetime, while 5-bromo, 5-chloro and 5-phenyl substitution on the phen ligand decrease the ^2E lifetime. The variation in the lifetime can be rationalized in terms of the ligand acting as both an oscillating perturbation dipole and an energy acceptor. The more vibrationally rigid phen complexes would be expected to show a decreased rate of nonradiative decay ($^2k_{nr}$) in comparison with analogous bpy complexes, with a consequential increase in the ^2E lifetime. Indeed, this is observed (cf. Table 1), except in the cases of the 5-Clphen, 5-Brphen and 5-Phphen complexes where the lifetime decreases with respect to the unsubstituted complex. The halo substituents provide an increased dipole perturbation which would increase $^2k_{nr}$ and necessarily decrease the ^2E lifetime ($^2\tau_{obs} \sim 1/^2k_{nr}$). Phenyl and methyl substitution on the polypyridyl ligand decrease the perturbation dipole probably through their effect on the critical ligand vibrational modes.

In contrast to the effect of ligand substitution on the ^2E lifetime of the chromium(III) complexes, a thorough investigation of this effect on the charge-transfer excited-state lifetimes of $Ru(NN)_3^{2+}$ complexes reveals a somewhat different behavior. Crosby and co-workers [19,41,42] have studied the substituent effect on the properties of the charge-transfer excited state ($d\pi^*$) of substituted bpy and phen complexes of ruthenium(II) at 77 K. As a group, the phen complexes have smaller nonradiative rate constants than the bpy complexes, but the correspondingly substituted bpy and phen species have nearly identical radiative rate constants. Apparently, substituents do produce changes in the nonradiative rate constants, but reveal to be less effective than a change of bpy to phen. On the other hand, the radiative lifetimes of the levels in the $d\pi^*$ manifold appear to be less dependent on the details of the molecular framework of the ligand system than on the nature and positions of the substituents. Attachment of methyl groups at the 4,4′-positions of the bpy framework has no significant effect on any of the rate constants for deactivation of the excited state; however, phenyl substitution at these positions increases the radiative rate constants of all the levels in the manifold with a concomitant decrease in the nonradiative rate constants. The unusual sensitivity toward substitution at the 4,7-positions of the phen ligand appears to be relatively even more dramatic. Whereas 5,6-dimethyl substitution produces negligible changes in the rate constants compared to the unsubstituted phen complex, methyl and phenyl substitution at the 4,7-positions yield a sizeable increase in both the radiative and nonradiative rate constants of the A_1 level, with an observed decrease in the A_2 level. It would appear then that the electronic states are sensitive in a non-uniform way on both the nature of the substituents and on their positions on the phen and bpy frameworks.

In line with the above observations [19,41,42], Sutin and co-workers [17] have observed that in fluid media phenyl substitution at the 4,7-positions of the phen ligand and the 4,4′-positions of the bpy ligand effects an increase in the luminescence lifetime compared with that of the unsubstituted bpy or phen complexes. Otherwise, lifetimes do not appear to be especially sensitive toward substitution at the 4,7-positions of the phen ligand, inasmuch as the lifetimes of $Ru(4,7\text{-}Me_2phen)_3^{2+}$ and $Ru(5,6\text{-}Me_2phen)_3^{2+}$ are comparable (1.74 vs. 1.81 μs, respectively) [17]. In addition, attachment of methyl groups at the 4,4′-positions of the bpy ligand decreases the emission lifetime of the excited complex, while methyl substitution on the phen ligand nearly doubles the lifetime. The chloro and bromo substituents have no effect on the $^*Ru(NN)_3^{2+}$ lifetime in fluid media [17]. These effects of ligand substitution on the lifetimes of $^*Ru(NN)_3^{2+}$ complexes are apparent in Table 1.

At first glance, the variance in behavior between the lifetimes of the excited $^*Cr(NN)_3^{3+}$ and $^*Ru(NN)_3^{2+}$ complexes (cf. Table 1) might be attributed to the different orbital parentages of the respective excited states; that is, MLCT for the Ru(II) and MC for the Cr(III). However, it would be premature to attribute the difference solely to this.

Kane-Maguire et al. [43] and Henry [7] have observed no isotope effect on the ^2E lifetimes of either $Cr(bpy)_3^{3+}$ or $Cr(phen)_3^{3+}$ upon solvent deuteration (H_2O vs. D_2O). This was rationalized [43] on the basis that solvent deuteration has little or no effect on the intramolecular decay between two states which are relatively undistorted with respect to each other, as is the case for the ground $^4A_2$ and excited $^2E/^2T_1$ states. The lack of any solvent isotope effect on the ^2E lifetimes was taken [7] as evidence for the lack of direct vibrational coupling (e.g., through hydrogen-bonding) between $(^2E)Cr(NN)_3^{3+}$ and the bulk solvent. More recent studies [44] on this solvent isotope effect show that indeed the ^2E lifetimes remain unchanged with increasing D_2O concentration, and it appears that this medium change affects the efficiency of intersystem crossing between the quartet $^4T_2$ and doublet $^2E/^2T_1$ excited states (Section C(iii)). A similar lack of D_2O isotope effect has been reported for $Cr(CN)_6^{3-}$ [45].

In comparison with the chromium(III) systems, the lifetime and quantum yield for $Ru(bpy)_3^{2+}$ luminescence significantly increase upon solvent deuteration [46]. This observation was explained in terms of increased electron density in the solvent upon deuteration, and consequential increased interaction between the charge-transfer-to-solvent (CTTS) and metal-to-ligand-charge-transfer (MLCT) excited configurations.

Henry [7] has reported that there is no alteration of the $(^2E)Cr(bpy)_3^{3+}$ lifetime upon changes in solvent polarity. That the lifetime remained constant in water, acetonitrile, methanol, dimethylformamide and ethylene glycol would indicate that solvent polarity changes do not effect sufficient perturbation to alter the rate of nonradiative decay, within experimental uncertainty. However, Van Houten and Porter [47] report the $(^2E)Cr(bpy)_3^{3+}$ lifetime in dimethylformamide (DMF) to be 3 ± 1 μs (vs. 63 μs in H_2O). The ^2E lifetime decreased exponentially with increasing ratio of DMF/H_2O, in parallel with the emission intensity. This suggests that quenching by DMF must involve an increase in the nonradiative rate constant of ^2E while $^2k_{rad}$ remains constant [47].

In Henry's investigations [7,8] of the effects of nonaqueous solvents on the ^2E lifetimes of $Cr(bpy)_3^{3+}$, the observed decrease in emission intensity of $Cr(bpy)_3^{3+}$ in mixed solvent systems (CH_3CN/H_2O, DMF/H_2O and CH_3OH/H_2O) was taken as evidence for decreased efficiency of the population of the ^2E state. The ^2E lifetimes remain constant, and are sufficiently long-lived that the ^2E state can encounter nonaqueous solvent molecules. This would seem to suggest [8] that the presence of nonaqueous solvent in the first solvation sphere of the $(^2E)Cr(bpy)_3^{3+}$ species is not sufficient for reaction, with the result that the nonaqueous solvent does not introduce any static quenching process involving the ^2E excited state. The assumption that the $^4T_2$ excited state is the exclusive source of the ^2E excited state, and furthermore, that the $^4T_2$ state is the only precursor state interacting with the solvent is validated by the observation [8] that there is no change in the shape of the phosphorescence excitation spectrum with increasing amounts of nonaqueous solvent. A change in the shape of this spectrum would be expected if the solvent effect was caused by interception of some ^2E precursor state. Hence, the lowering of the population of the ^2E state in the presence of nonaqueous solvents results from a decrease in $^4T_2 \rightsquigarrow {}^2E/{}^2T_1$ intersystem crossing efficiency, which, in turn, arises from an increased rate in the non-radiative and/or reactive steps because of interaction of the $^4T_2$ state with the nonaqueous solvent.

In aqueous solution, high perchlorate anion concentrations ($[ClO_4^-] >$ 1 M) markedly increase the ^2E lifetimes and emission intensities, and decrease the quantum yields of photoaquation for both $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ [7]. The non-radiative ($^2k_{nr}$) and reactive ($^2k_{rx}$) pathways of the ^2E state are responsible for the observed lifetime increases, with $^2k_{rx}$ exhibiting a greater decrease than $^2k_{nr}$ in the presence of ClO_4^- [8]. The ^2E lifetime prolongation effected by high concentrations of anions appears to be a general phenomenon for $Cr(NN)_3^{3+}$ complexes [5,6,9]. In the presence of the ClO_4^- ion, it is expected that there will be extensive ion-pairing between the chromium(III) core and the anions in the interligand pockets as well as in the solvation sphere, thereby curbing access to the chromium(III) core by water molecule(s), resulting in a reduction in $^2k_{rx}$.

The large effect of anions on the ^2E lifetimes of $Cr(NN)_3^{3+}$ was rationalized [8] in a manner similar to that presented for the effect of substitution on the polypyridyl ligand; that is, that the ligand serves as both the oscillating dipole and the energy acceptor [48], thereby providing a pathway for electronic-to-vibrational energy transfer in the ^2E state. Thus, a decrease in $^2k_{nr}$ would arise if the vibrational freedom of the ligands was decreased, and also if the efficiency of the energy transfer was decreased. The vibrational freedom is expected to be reduced on going from the $Cr(bpy)_3^{3+}$ cation to the more vibrationally rigid $Cr(phen)_3^{3+}$ cation; also, a reduction in the energy transfer rate is expected in the presence of ion-pairing and occupation of the interligand pockets by the anions. Indeed, $(^2E)Cr(phen)_3^{3+}$ is longer-lived (0.25 ms) [9] than $(^2E)Cr(bpy)_3^{3+}$ (0.068 ms) [7] in O_2-free water at 22°C. It is also expected, and observed [7,9], that the lifetime effect of ClO_4^- anions is less pronounced for the phen complex in comparison to the bpy complex inasmuch as the more rigid phen complex is less prone to perturbation by the anions in the interligand pockets.

In addition to the lifetime prolongation effected by the perchlorate anion, a similar phenomenon has been observed for the $(^2E)Cr(NN)_3^{3+}$ lifetimes in the limit of infinite substrate dilution due to extensive ion-pairing between the chromium(III) core and chloride ion [9]. For the $Cr(phen)_3^{3+}$ complex in 1 M HCl at 22°C, ${}^2\tau_{obs}$ decreases by an order of magnitude (0.33 to 0.038 ms) as the chromium(III) substrate concentration is increased from 1×10^{-5} to 1×10^{-2} M, as illustrated in Fig. 4. The similar results obtained in 1 M NaCl [9] indicate that this phenomenon is caused by the chloride anion. In comparison, the marked diminution of the $({}^2E)Cr(bpy)_3^{3+}$ lifetime with increasing substrate concentration necessitates the use of 5 M HCl. The quenching phenomenon observed is adequately described by eqn. (3) where ${}^2k_0$ is the first-order rate constant for ${}^2E$ deactivation at infinite substrate

$$ {}^2k_{obs} = 1/{}^2\tau_{obs} = {}^2k_0 + {}^2k_g[Cr(NN)_3^{3+}] \qquad (3) $$

dilution, and ${}^2k_g$ is the second-order rate constant for the quenching of the ${}^2E$ state by a ground-state chromium(III) species (reaction (4)). For the

$$ ({}^2E)Cr(NN)_3^{3+} + ({}^4A_2)Cr(NN)_3^{3+} \xrightarrow[Cl^-]{{}^2k_{obs}} 2({}^4A_2)Cr(NN)_3^{3+} \qquad (4) $$

$Cr(phen)_3^{3+}$ cation in 1 M HCl at 22°C, ${}^2k_0 = 3.0 \times 10^3\ s^{-1}$ and ${}^2k_g = 2.3 \times 10^6\ M^{-1}\ s^{-1}$; while ${}^2k_0 = 1.0 \times 10^4\ s^{-1}$ and ${}^2k_g = 1.3 \times 10^6\ M^{-1}\ s^{-1}$ for $Cr(bpy)_3^{3+}$ in 5 M HCl at 22°C [9]. The ${}^2k_g$ rate constant reflects the encounter of ion-paired ground-state $[({}^4A_2)Cr(NN)_3^{3+} \ldots Cl^-]$ and excited-

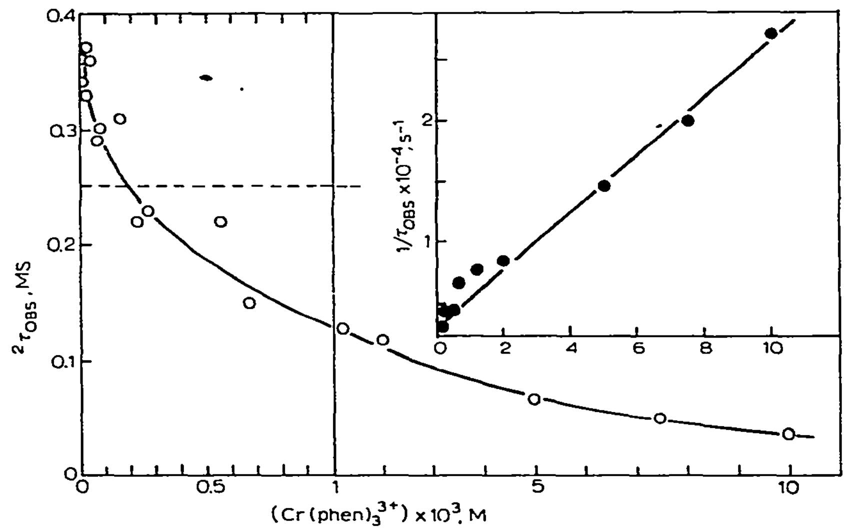


Fig. 4. Lifetime of $({}^2E)Cr(phen)_3^{3+}$ as a function of [substrate] in deaerated aqueous solutions at 22°C, O–, 1.0 M HCl; the dashed line, deaerated neat H_2O. Insert represents a plot of $1/{}^2\tau_{obs}$ for $Cr(phen)_3^{3+}$ as a function of [substrate] in deaerated 1.0 M HCl solution at 22°C [6].

state $[(^2E)Cr(NN)_3^{3+}\ldots Cl^-]$ species. The ground-state quenching reaction is then mediated by the chloride anion since concentration quenching is not observed in the absence of the anion; this is viewed [9] as arising from the interaction of ion-paired ground-state and ion-paired excited-state species to form an "ion-bridged excimer", $^*[Cr(NN)_3^{3+}\ldots Cl^-\ldots Cr(NN)_3^{3+}]$, which rapidly undergoes nonradiative decay via coupling of the vibrational modes in the aggregate. Excimer formation is not an unknown phenomenon for aromatic moieties and usually manifests itself in decreased excited-state lifetimes with increasing ground-state substrate concentrations [49]. Although the lifetime of the "ion-bridged excimer" could not be measured, as no emission attributable to its formation could be observed [9], it is most likely very short due to rapid nonradiative deactivation via coupling of the vibrational modes in the aggregate. Ground-state quenching of chromium(III) excited states in solid matrices has previously been attributed to the formation of such aggregates [50,51].

A similar prolongation of ^2E lifetimes mediated by the chloride ion has also been observed [6] for several $Cr(NN)_3^{3+}$ complexes, where NN is 4,4′-Me_2bpy, 4,4′-Ph_2bpy, 5-Mephen, 5,6-Me_2phen, 4,7-Me_2phen, 3,4,7,8-Me_4phen, 5-Clphen, 5-Brphen, 5-Phphen and 4,7-Ph_2phen. Again, the substituted bpy complexes require 5 M HCl to effect a significant lifetime prolongation, while the substituted phen complexes exhibit this phenomenon in 1 M HCl. Table 2 presents the applicable rate constants given by eqn. (3)

TABLE 2

First-order ($^2k_0$) and second-order (^2k_g) rate constants for ground-state quenching of $^*Cr(NN)_3^{3+}$ in the presence of chloride ion

NN	$^2k_0\,(s^{-1})$ [a]	$^2k_g\,(M^{-1}\,s^{-1})$ [a]	$^2k_0\,(s^{-1})$ [c]	$^2k_g\,(M^{-1}\,s^{-1})$ [c]
bpy	1.0×10^{4} [d]	1.3×10^{6} [d]	1.4×10^{4}	
4,4′-Me_2bpy [b]	3.2×10^{3} [d]	2.0×10^{6} [d]	5.6×10^{3}	
4,4′-Ph_2bpy	5.3×10^{3} [d]	1.0×10^{8} [d]	(1.9×10^{4}) [c]	6.0×10^{7} [c]
5-Clphen	5.5×10^{3}	1.7×10^{7}	6.8×10^{3}	3.5×10^{7}
5-Brphen [b]	5.7×10^{3}	5.4×10^{7}	$6\ \ \times10^{3}$	8.1×10^{7}
phen	3.0×10^{3}	2.3×10^{6}	4.3×10^{3}	6.1×10^{6}
5-Mephen	2.4×10^{3}	5.0×10^{6}	3.7×10^{3}	1.4×10^{7}
5,6-Me_2phen [b]	2.4×10^{3}	7.5×10^{6}	3.5×10^{3}	1.7×10^{7}
4,7-Me_2phen [b]	1.8×10^{3}	1.0×10^{7}	2.4×10^{3}	1.4×10^{7}
3,4,7,8-Me_4phen	1.5×10^{3}	1.5×10^{7}	1.6×10^{3}	3.9×10^{7}
5-Phphen [b]	4.5×10^{3}	5.7×10^{7}	5.6×10^{3}	9.3×10^{7}
4,7-Ph_2phen	1.8×10^{3} [b]	7.4×10^{7} [b]	(1.1×10^{4}) [e]	

[a] In argon-purged, 1 M HCl solutions at 22°C. [b] Solutions contain 4% v/v acetonitrile. [c] In argon-purged solutions containing 0.008 M Britton–Robinson buffer, 1.0 M NaCl, pH~9.4, at 22°C. [d] In 5 M HCl. [e] Solutions contain 40% v/v methanol.

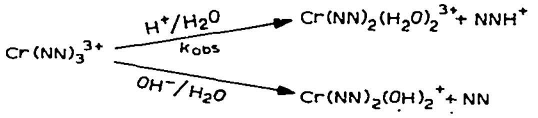
in order to compare the various $Cr(NN)_3^{3+}$ species. The data reveal that the observation of this phenomenon depends on low values of ${}^2k_0$ and high values of ${}^2k_g$. Table 2 also summarizes ${}^2k_0$ and ${}^2k_g$ values obtained under identical solution conditions as used to measure Φ_{obs} (Table 5), the quantum yield for the photoaquation reaction in alkaline solution. The pattern that emerges from these data is that the unsubstituted complexes have the lowest ${}^2k_g$ values, with ${}^2k_g$ increasing with increasing size of the chromium(III) cation. It would seem that the effect of phenyl substitution on the polypyridyl ligand is to provide a steric template for orbital overlap. With reference to the 5-halogen complexes, it is probably the electron-withdrawing capacity of the substituent which affects the ${}^2k_g$ value. The data show that, in addition to the solution medium, both the size of the cation and the nature of the ligand substituents have an effect on the value of ${}^2k_g$.

C. REACTIVITY OF $Cr(NN)_3^{3+}$ COMPLEXES

(i) *Thermal reactivity of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$*

Knowledge of the reactivity of ground-state $({}^4A_2)Cr(NN)_3^{3+}$ complexes aids in elucidating the photoreactivity of these complexes. To this extent, Maestri et al. [52] have shown that the thermal aquation of $Cr(bpy)_3^{3+}$ in the pH range 0–10.7 occurs via pH-dependent, first-order kinetics with k_{obs} = ca. 10^{-8} s^{-1} at $pH \leqslant 6$, and $4.7 \pm 0.4 \times 10^{-7}$ s^{-1} at pH 9–10.7 and 11°C. Arguments were presented against dissociative, ion-pair interchange, and Gillard-type [53] covalent-hydrate mechanisms for the aquation reaction (5). An associative mechanism, involving the formation of a seven-coordinate intermediate via nucleophilic attack of a water molecule at the chromium(III) center, was proposed [52,54] as the rate-determining step. The thermal aquation has been extended to include the pH range 10.7 to 14.0 for $Cr(bpy)_3^{3+}$ [54] and for $Cr(phen)_3^{3+}$ in the pH range 0 to 14 [55].

For both $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$, the stoichiometry of the solvolysis reaction is described by reaction (5), where NN refers to bpy or phen. At



$$Cr(NN)_3^{3+} \xrightarrow[k_{obs}]{H^+/H_2O} Cr(NN)_2(H_2O)_2^{3+} + NNH^+ \qquad Cr(NN)_3^{3+} \xrightarrow{OH^-/H_2O} Cr(NN)_2(OH)_2^{+} + NN \tag{5}$$

$pH \leqslant 6$, k_{obs} is very small and independent of solution pH. This has been rationalized in terms of relaxation of the initially-formed $Cr(NN)_3(H_2O)^{3+}$ intermediate back to $Cr(NN)_3^{3+}$ via acid-dependent and acid-independent pathways for the bpy complex (reaction (6)). The seven-coordinate inter-

$$Cr(NN)_3^{3+} + H_2O \underset{H^+}{\rightleftharpoons} Cr(NN)_3(H_2O)^{3+} \tag{6}$$

mediate, $Cr(NN)_3(H_2O)^{3+}$, subsequently undergoes deprotonation to form the short-lived $Cr(NN)_3(OH)^{2+}$ species. This step is revealed by the inflection point at pH 6–9 in plots of k_{obs} vs. pH (Fig. 5) for the $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ systems. The hydroxy intermediate subsequently undergoes ring-opening and, ultimately and irreversibly, loss of monodentate NN.

$$Cr(NN)_3(OH)^{2+} \rightarrow Cr(NN)_2(NN\text{-})(OH)^{2+} \tag{7}$$

$$Cr(NN)_2(NN\text{-})(OH)^{2+} \xrightarrow[OH^-]{} Cr(NN)_2(OH)_2^+ + NN \tag{8}$$

The existence of complexes containing monodentate bpy [56] and phen [57] ligands has been suggested. The pH region ca. 9–10.5 reflects the complete titration of $Cr(NN)_3(H_2O)^{3+}$, so that k_{obs} represents the rate constant for the rate-determining attack of H_2O on $Cr(NN)_3^{3+}$.

Above pH 10.7, k_{obs} is linearly dependent on $[OH^-]$ in the range $10.7 \leqslant pH \leqslant 12.2$; the slope of the line was identified with the rate constant for direct nucleophilic attack of OH^- on $Cr(NN)_3^{3+}$, followed by reactions (7) and (8). The first-order dependence of k_{obs} on $[OH^-]$ has not precluded a Gillard-type [53] covalent-hydrate mechanism in which the initial OH^- attack is at the C-6 position of the bpy ligand, or the C-2 (or C-9) position of the phen ligand. Subsequent deprotonation of the resulting quaternary

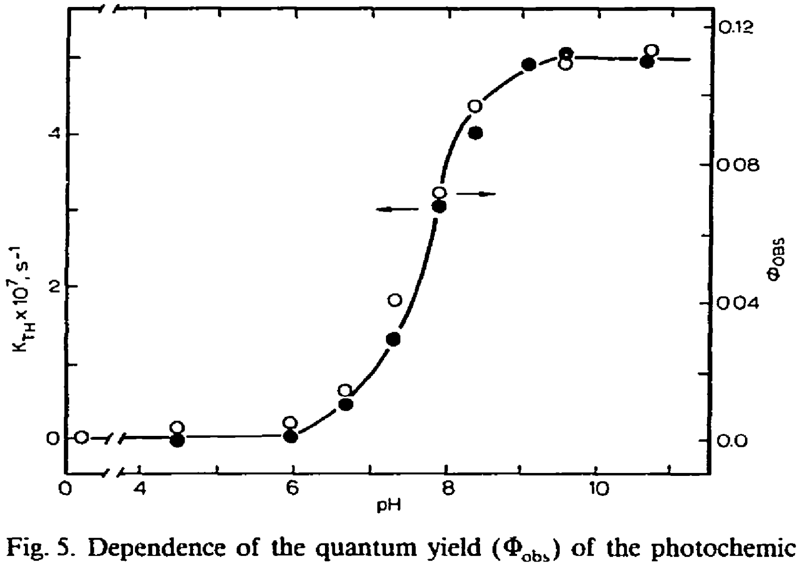


Fig. 5. Dependence of the quantum yield (Φ_{obs}) of the photochemical reaction (O) on pH, 11°C, air-equilibrated solutions, $\mu = 1.0$ M [35]. For comparison the dependence of the rate constant (k_{th}) of the thermal substitution reaction on pH is also indicated; 11°C, $\mu = 1.0$ M [52].

nitrogen followed by an intramolecular OH shift to the chromium(III) center would then lead to the same seven-coordinate intermediate $Cr(NN)_3(H_2O)^{3+}$. Inasmuch as no spectral variations in $Cr(NN)_3^{3+}$ solutions were observed even in very alkaline media, this mechanism was deemed unlikely. A Gillard-type mechanism has, however, been proposed for the OH^- reduction of $Ru(bpy)_3^{3+}$ [58], and of various polypyridyl and substituted polypyridyl complexes of iron(III) and osmium(III) [59].

Where $[OH^-] = 0.1-1.0$ M, k_{obs} linearly varies with $[OH^-]^2$ [54]. A plausible mechanism involves formation of ion-pairs between $Cr(NN)_3^{3+}$ and OH^-, followed by attack on the ion-pair by another OH^- to form some seven-coordinate intermediate which, also, ultimately and irreversibly leads to polypyridine release. Creutz and Sutin [58] have also observed a second-order $[OH^-]$-dependent path at $pH > 13$ in the reduction of $Ru(bpy)_3^{3+}$.

The rate constants and activation parameters for the thermal aquation of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ under identical experimental conditions are given in Table 3. The similarity in the activation parameters in the pH regimes > 6 supports a common mechanism for the two complexes inasmuch as similar intermediates are indicated.

(ii) *Photoreactivity of* $Cr(NN)_3^{3+}$

Continuous photolysis of $Cr(bpy)_3^{3+}$ or $Cr(phen)_3^{3+}$ in neutral or basic aqueous solution leads to substitution by two water (or hydroxy) molecules for one polypyridyl ligand [8,35]. The spectral changes and formation of free polypyridine mimic those observed for the corresponding thermal reactions [52,55]. For $Cr(bpy)_3^{3+}$ at pH 9.6, the absorption spectral changes of continuously photolysed [35], repeatedly flashed [35] and thermal solutions [52] were identical, with isosbestic points located at 306, 270, 262 and 254 nm [35]. Similar experiments on $Cr(phen)_3^{3+}$ locate the isosbestic points at ca. 235, 254, 287 and 304 nm [55]. The overall stoichiometric thermal and photochemical reactions are given in reactions (9) and (10), respectively, for

TABLE 3

Thermal activation parameters for $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ [a]

Activation parameter	pH ca. 10		pH ca. 12		0.50 M OH^-	
	bpy	phen	bpy	phen	bpy	phen
$\Delta H^{\ddagger}_{298}$ (kcal mole^{-1})	22.3	23.3	20.7	21.6	18.9	20.8
$\Delta S^{\ddagger}_{298}$ (eu)	−8.8	−8.4	−12.6	−11	−11	−5

[a] From refs. 6 and 35; in 0.008 M Britton–Robinson buffer, $\mu = 1.0$ M NaCl.

$Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ in basic aqueous solution, where Φ_{obs} is the observed quantum yield for polypyridine release. Both complexes are relatively inert toward thermal [52] and photosolvolysis [35] in acidic media. This observation, along with the observation that k_{obs} for the thermal reaction (9) and Φ_{obs} for the photoreaction (10) show identical dependencies on pH [35,52], suggest that the two reactions proceed through a common ground-state intermediate. The pH dependence is illustrated in Fig. 5 for $Cr(bpy)_3^{3+}$.

$$Cr(NN)_3^{3+} \underset{H_2O/OH^-}{\overset{k_{obs}}{\rightarrow}} Cr(NN)_2(OH)_2^+ + NN \tag{9}$$

$$Cr(NN)_3^{3+} \xrightarrow{h\nu} {}^*Cr(NN)_3^{3+} \underset{H_2O/OH^-}{\overset{\Phi_{obs}}{\rightarrow}} Cr(NN)_2(OH)_2^+ + NN \tag{10}$$

The associative mechanism outlined in the previous discussion is believed to be equally applicable to the photoreaction. That is, the same seven-coordinate intermediate $Cr(bpy)_3(H_2O)^{3+}$ generated via an associative pathway with the excited-state $^*Cr(bpy)_3^{3+}$ species is envisaged [8,35].

From the various extensive studies carried out by us and others, a general photochemical mechanism has evolved for the photoreactivity of $Cr(bpy)_3^{3+}$ in aqueous solution, and which can be extended to the other $Cr(NN)_3^{3+}$ complexes. This mechanism is presented in Scheme I.

The formation of the seven-coordinate intermediate (reactions (18) and (19)) is evidenced by transient bleaching in acidic media (secondary transient) [35]. Reformation of $(^4A_2)Cr(NN)_3^{3+}$ from the intermediate occurs via acid-dependent (reaction (22)) and acid-independent (reaction (21)) paths. The acid-dependent pathway involves Cr–O bond rupture, assisted by H^+; the acid-independent pathway reflects the relaxation of the intermediate to form $(^4A_2)Cr(NN)_3^{3+}$ via direct loss of coordinated water. The acid-dependent path is believed [60] to be the primary reaction leading to the relative stability, both photochemical [35] and thermal [52], of $Cr(bpy)_3^{3+}$ in acid solution. It has been shown [35] that the first-order rate constant for the recovery of ground-state absorption from the transient bleaching is linearly dependent on $[H^+]$ yielding $k_{obs} = k_{21} + k_{22}[H^+]$ where $k_{21} \leqslant 10\ s^{-1}$ and $k_{22} = 4 \times 10^5\ M^{-1}\ s^{-1}$. Both the acid-independent and -dependent paths are operable in the thermal reaction, for which the reverse of reaction (21) is the rate-determining step. Finally, deprotonation of the seven-coordinate intermediate (reaction (25)) leads, ultimately, quantitatively and irreversibly to ring-opening (reaction (26)) and to loss of NN (reaction (27)).

$$Cr(NN)_3(H_2O)^{3+} \rightleftharpoons Cr(NN)_3(OH)^{2+} + H^+ \tag{25}$$

$$Cr(NN)_3(OH)^{2+} \rightarrow Cr(NN)_2(NN\text{-})(OH)^{2+} \tag{26}$$

$$Cr(NN)_2(NN\text{-})(OH)^{2+} \xrightarrow{OH^-} Cr(NN)_2(OH)_2^+ + NN \tag{27}$$

SCHEME I

$$({}^4A_2)\mathrm{Cr(NN)}_3^{3+} \xrightarrow{h\nu} ({}^4T_2, a^4T_1, b^4T_1)\mathrm{Cr(NN)}_3^{3+} \quad \text{(Light absorption)} \tag{11}$$

$$({}^4T_2, a^4T_1, b^4T_1)\mathrm{Cr(NN)}_3^{3+} \rightarrow ({}^4T_2)\mathrm{Cr(NN)}_3^{3+} \quad \text{(Internal conversion)} \tag{12}$$

$$({}^4T_2)\mathrm{Cr(NN)}_3^{3+} \xrightarrow{{}^4k_{nr}} ({}^4A_2)\mathrm{Cr(NN)}_3^{3+} \quad \text{(Nonradiative decay)} \tag{13}$$

$$\xrightarrow{{}^4k_{isc}} ({}^2E)\mathrm{Cr(NN)}_3^{3+} \quad \text{(Intersystem crossing)} \tag{14}$$

$$\xrightarrow{{}^4k_{rx},\, \mathrm{H_2O}} \mathrm{Cr(NN)_3(H_2O)}^{3+} \quad \text{(Chemical reaction)} \tag{15}$$

$$({}^2E)\mathrm{Cr(NN)}_3^{3+} \xrightarrow{{}^2k_{nr}} ({}^4A_2)\mathrm{Cr(NN)}_3^{3+} \quad \text{(Nonradiative decay)} \tag{16}$$

$$\xrightarrow{{}^2k_{rad}} ({}^4A_2)\mathrm{Cr(NN)}_3^{3+} + h\nu' \quad \text{(Phosphorescence)} \tag{17}$$

$$\xrightarrow{{}^2k_{rx},\, \mathrm{H_2O}} \mathrm{Cr(NN)_3(H_2O)}^{3+} \quad \text{(Chemical reaction)} \tag{18}$$

$$({}^2E)\mathrm{Cr(NN)}_3^{3+} \xrightarrow{{}^2k_{rx},\, \mathrm{OH}} \mathrm{Cr(NN)_3(OH)}^{2+} \quad \text{(Chemical reaction)} \tag{19}$$

$$({}^2E)\mathrm{Cr(NN)}_3^{3+} + ({}^4A_2)\mathrm{Cr(NN)}_3^{3+} \xrightarrow{{}^2k_g,\, \mathrm{Cl}} 2({}^4A_2)\mathrm{Cr(NN)}_3^{3+} \quad \text{(Ground-state quenching)} \tag{20}$$

$$\mathrm{Cr(NN)_3(H_2O)}^{3+} \rightleftharpoons ({}^4A_2)\mathrm{Cr(NN)}_3^{3+} + \mathrm{H_2O} \quad \text{(Acid-independent decay of intermediate)} \tag{21}$$

$$\xrightarrow{\mathrm{H}^+} ({}^4A_2)\mathrm{Cr(NN)}_3^{3+} + \mathrm{H_2O} \quad \text{(Acid-dependent decay of intermediate)} \tag{22}$$

$$\xrightarrow[\mathrm{H_2O}]{\mathrm{H}^+} \mathrm{Cr(NN)_2(H_2O)}_2^{3+} + \mathrm{NNH}^+ \tag{23}$$

$$\mathrm{Cr(NN)_3(OH)}^{2+} \xrightarrow{\mathrm{OH}^-} \mathrm{Cr(NN)_2(OH)}_2^{+} + \mathrm{NN} \tag{24}$$

As discussed previously for the thermal reaction, a Gillard-type [53] covalent-hydrate mechanism is also plausible for the photoaquation of $Cr(NN)_3^{3+}$. A covalent-hydrate mechanism would be favored by ligand-to-metal-charge-transfer (LMCT) excited configurations as this mechanism involves nucleophilic attack on the polypyridine framework. On the other hand, an associative pathway incorporating nucleophilic attack at the chromium(III) core would be favored by metal-centered (MC) excited configurations; that is, by attack on the $^2E/^2T_1$ doublet species. Suggestions have been made [5,6,35,60] to the effect that the ^2E state is responsible for the photosolvolysis of the $Cr(NN)_3^{3+}$ complexes. Balzani and co-workers [40] have found evidence for direct reaction between the ^2E state and hydroxide ion for *trans*-$Cr(en)_2(NCS)_2^+$, a complex incapable of photosolvolysis via a covalent-hydrate pathway. For these reasons, a Gillard-type mechanism is also believed to be highly improbable for the $Cr(NN)_3^{3+}$ complexes.

The overall quantum yield, Φ_{obs}, for the photosolvolysis has been measured for several $Cr(NN)_3^{3+}$ complexes under a variety of experimental conditions. Figure 5 reveals, also, the dramatic change in Φ_{obs} over the pH range 0–10.7 for $Cr(bpy)_3^{3+}$ [35]. In air-equilibrated solutions, Φ_{obs} increases from 0.002 at pH 1.1 [60] to 0.11 at pH 9.6 for $Cr(bpy)_3^{3+}$ at 11°C [35]. In deaerated solutions, the Φ_{obs} values are somewhat larger, with Φ_{obs} increasing from 0.007 at pH 1.0 to 0.13 at pH 9.6 and 22°C for $Cr(bpy)_3^{3+}$ [35,60]. The increase in Φ_{obs} at pH ca. 1 in deaerated solution has been attributed [60] to the quenching of $(^2E)Cr(bpy)_3^{3+}$ by molecular oxygen. The values of Φ_{obs} in O_2-free, Britton–Robinson buffered solutions at 22°C have been measured [6] at various pH values for several $Cr(NN)_3^{3+}$ complexes. These are collected in Table 4. Table 5 summarizes the observed quantum yields, lifetimes and rate constants for the various $Cr(NN)_3^{3+}$ species under identical experimental conditions. Among the bpy complexes, the quantum yield for reaction decreases with increasing size of substituent on the bpy framework, as do the rate constants $^2k_{obs}$ and $^2k_{rx}$. Except for the 5-halo complexes, a similar trend is observed for the phen complexes. For the 5-halo species, the increase in Φ_{obs} is most likely due to the electron withdrawing nature of these chloro and bromo substituents and to an increase in the hydrophilic environment of the reaction site.

The observed quantum yield Φ_{obs} is also affected by the presence of anions, revealing marked decrease with increasing anion concentration [8]: $\Phi_{obs} = 0.16$, 0.08 and 0.009 for $Cr(bpy)_3^{3+}$ in air-equilibrated aqueous solutions (pH 9.8) containing 1 M NaCl, 5 M NaCl and 5 M $NaClO_4$, respectively. Nonaqueous solvents also affect the observed quantum yield of $Cr(bpy)_3^{3+}$. In comparison to that in water ($\Phi_{obs} = 0.16$), $\Phi_{obs} = 0.02$ in dimethylformamide and $\leqslant 10^{-3}$ in acetonitrile at 22°C (air-equilibrated) [8].

The temperature dependence of Φ_{obs} for the photosolvolysis of $Cr(bpy)_3^{3+}$

TABLE 4

Observed quantum yields (Φ_{obs}) for polypyridine release from $Cr(NN)_3^{3+}$ complexes [a]

NN	[Cr(III)] (mM)	Φ_{obs} (pH) [b]
bpy	1.0	0.13 (9.3)
4,4'-Me_2bpy [c]	0.12	0.002 (5.1) 0.06 (9–10.5)
4,4'-Ph_2bpy [d]	0.048	0.011 (5.1) 0.02 (9–10.5)
5-Clphen	0.14	0.002 (5.1) 0.011 (9–10.5)
5-Brphen [c]	0.12	0.006 (5.1) 0.008 (9–10.5)
phen	1.5	0.0005 (5.1) 0.006 (9–10.5)
5-Mephen	0.12	0.004 (5.1) 0.012 (9–10.5)
5,6-Me_2phen	0.11	0.005 (5.1) 0.007 (9–10.5)
4,7-Me_2phen [c]	0.11	0.0003 (5.1) 0.004 (9–10.5)
3,4,7,8-Me_4phen [c]	0.084	0.0002 (5.1) 0.002 (9–10.5)
5-Phphen [c]	0.072	0.003 (5.1) 0.006 (9–10.5)
4,7-Ph_2phen [d]	0.034	0.0012 (5.1) 0.0014 (9–10.5)

[a] Ref. 6. [b] In argon-purged solutions containing 0.008 M Britton–Robinson buffer, 1.0 M NaCl, at 22°C. [c] Solution contains 4% v/v acetonitrile. [d] Solution contains 40% v/v methanol.

TABLE 5

Photochemical and photophysical characteristics of $Cr(NN)_3^{3+}$ at pH 9–10.5 and 22°C [a]

NN	$^2k_{obs}$ (s^{-1})	$^2k_{rx} = \Phi_{obs}\,{}^2k_{obs}$ (s^{-1})
bpy	1.41×10^4	1.6×10^3
4,4'-Me_2bpy [b]	5.67×10^3	3.5×10^2
4,4'-Ph_2bpy [c]	2.00×10^4	4.2×10^2
5-Clphen	1.17×10^4	1.3×10^2
5-Brphen [b]	1.57×10^4	1.3×10^2
phen	1.35×10^4	0.8×10^2
5-Mephen	5.56×10^3	6.7×10^1
5,6-Me_2phen	5.26×10^3	3.4×10^1
4,7-Me_2phen [b]	4.00×10^3	1.4×10^1
3,4,7,8-Me_4phen [b]	4.76×10^3	0.8×10^1
5-Phphen [b]	1.23×10^4	0.7×10^2
4,7-Ph_2phen [c]	1.35×10^4	1.9×10^1

[a] Ref. 6. [b] Solution contains 4% v/v acetonitrile. [c] Solution contains 40% v/v methanol.

in O_2-free, alkaline solution has been measured in the temperature range 279.5–309.5 K [61]. Φ_{obs} increases from 0.14 at 279.5 K to 0.19 at 309.5 K at pH 9.8. The excited state responsible for the photoreactivity of $\mathrm{Cr(bpy)_3^{3+}}$ had been suggested as being the metal-centered ^2E state, although the $^2T_1$ state could also play a role [35]. Recent studies [61] on the temperature-dependence of the photoaquation of $\mathrm{Cr(bpy)_3^{3+}}$ reveal that the enthalpy of activation, $\Delta H^{\dagger}$, of the reaction from the $^2E/^2T_1$ states is considerably less (by ca. 13 kcal mole^{-1}) than the comparable reaction from the $^4A_2$ ground state. This observation lends credence to the view that the $^2T_1$ state is responsible for the photoreaction since a vacant t_{2g} orbital would result in less reorganizational energy being required to form the activated complex. Reaction from the doublet arises from interaction of the thermally-equilibrated $^2T_1^0$ state with solvent. To the extent that the $^2T_1$ state has an unoccupied t_{2g} orbital, a solvent molecule can be accommodated between the bpy ligands. A comparison of the activation parameters for the thermal [52] and photo-aquation [61] reactions reveals that for $\mathrm{Cr(bpy)_3^{3+}}$ the photoreaction is faster by ten orders of magnitude than, necessitates less activation enthalpy than, and shows a parallel decrease in activation entropy with the thermal reaction. These activation parameters are $\Delta H^{\ddagger}_{298} = 9.6 \pm 0.4$ kcal mole^{-1} and $\Delta S^{\ddagger}_{298} = -10.0 \pm 1.4$ eu (Britton–Robinson buffered solutions, pH 9.8, $\mu = 1.0$ M NaCl).

Porter and Van Houten [47,62] have investigated the photolytic behavior of $\mathrm{Cr(bpy)_3^{3+}}$ in DMF at room temperature, and found evidence for a chromium(II) intermediate. Irradiation of O_2-free solutions of $\mathrm{Cr(bpy)_3^{3+}}$ in neat DMF at room temperature yields observations different from those in aqueous solutions. The luminescence lifetime and quantum yield of $\mathrm{Cr(bpy)_3^{3+}}$ in DMF are a factor of 15 smaller than they are in water, while the photochemical quantum yield for the disappearance of $\mathrm{Cr(bpy)_3^{3+}}$ in DMF is orders of magnitude larger than in water. The overall quantum yield for the photosolvolysis of $\mathrm{Cr(bpy)_3^{3+}}$ in O_2-free DMF was estimated to be of the order of unity [62].

Absorption of radiation ($\lambda = 442$ nm) by $\mathrm{Cr(bpy)_3^{3+}}$ in neat DMF populates the $^4T_2$ state (reaction (28)) with subsequent intersystem crossing to the ^2E state (reaction (29)), presumably also with unitary efficiency, (η_{isc} = ca. 1) [62]. Since $\mathrm{Cr(bpy)_3^{2+}}$ has been observed during photolysis and $(^2E)\mathrm{Cr(bpy)_3^{3+}}$

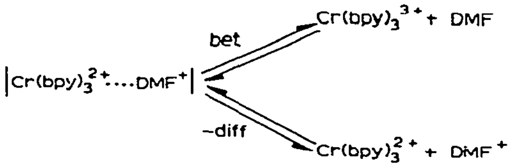
$$(^4A_2)\mathrm{Cr(bpy)_3^{3+}} \xrightarrow[\mathrm{DMF}]{h\nu\,(442\,\mathrm{nm})} (^4T_2)\mathrm{Cr(bpy)_3^{3+}} \qquad (28)$$

$$(^4T_2)\mathrm{Cr(bpy)_3^{3+}} \overset{\mathrm{isc}}{\rightsquigarrow} (^2E)\mathrm{Cr(bpy)_3^{3+}} \qquad (29)$$

is known to be a strong oxidizing agent [36], the ^2E species undergoes reduction to form a cage pair (reaction (30)).

$$({}^2E)\mathrm{Cr(bpy)}_3^{3+} + \mathrm{DMF} \rightleftharpoons |\mathrm{Cr(bpy)}_3^{2+} \ldots \mathrm{DMF}^+| \qquad (30)$$

It may well be that DMF itself serves as the electron donor, though this remains uncertain. Subsequently, back-electron transfer (bet) results in overall quenching which occurs in competition with diffusion out (−diff) of the cage pair. To the extent that the entire reaction is completed in a short time,



(31)

reaction of $\mathrm{Cr(bpy)}_3^{2+}$ with DMF^+ does not appear to be important [62]. The quantum yield for $\mathrm{Cr(bpy)}_3^{2+}$ formation was estimated to be ca. 0.006. Subsequent solvolysis leads to ligand substitution of one bpy ligand (reaction (32)), and further reaction with $\mathrm{Cr(bpy)}_3^{3+}$ yields $\mathrm{Cr(bpy)_2(DMF)}_2^{3+}$ and $\mathrm{Cr(bpy)}_3^{2+}$ (reaction (33)).

$$\mathrm{Cr(bpy)}_3^{2+} + 2\mathrm{DMF} \rightleftharpoons \mathrm{Cr(bpy)_2(DMF)}_2^{2+} + \mathrm{bpy} \qquad (32)$$

$$\mathrm{Cr(bpy)_2(DMF)}_2^{2+} + \mathrm{Cr(bpy)}_3^{3+} \rightleftharpoons \mathrm{Cr(bpy)_2(DMF)}_2^{3+} + \mathrm{Cr(bpy)}_3^{2+} \qquad (33)$$

It was further noted that if some $\mathrm{Cr(bpy)}_3^{3+}$ remains in the reaction solution, the reverse of reaction (32) cannot occur because of competition with reaction (33). The equilibrium in reaction (32) is established when all the $\mathrm{Cr(bpy)}_3^{3+}$ is consumed.

The implication of a chromium(II) species in DMF was rationalized [62] in terms of the formation of a radical ion via oxidation of a DMF molecule in the inner solvation sphere. This radical ion can then escape from the cage pair by self-exchange with molecules in the outer solvent sphere, and ultimately with the bulk solvent via transfer of an electron from the bulk solvent into the inner solvent sphere. Although $\mathrm{Cr(bpy)}_3^{3+}$ can be reduced to $\mathrm{Cr(bpy)}_3^{2+}$ in DMF and in water [62], the fate of the chromium(II) species appears different in the two solvents. Porter and Van Houten [62] attribute this difference to the fact that a solvent molecule such as DMF can more efficiently undergo oxidation and escape from the cage pair than could a solute in low concentration as it would be in aqueous solutions.

It is possible to estimate some of the photophysical parameters with the presently available data. Using Scheme I, various parameters may be defined. Equation (2) defines the observed lifetime of the ${}^2E$ state, while eqn. (34) defines the intrinsic ${}^2E$ lifetime, ${}^2\tau_0$. The reciprocal of ${}^2\tau_0$ represents the intrinsic decay of the ^2E state.

$$^2\tau_0 = 1/(^2k_{\mathrm{rad}} + {}^2k_{\mathrm{nr}} + {}^2k_{\mathrm{rx}}) \tag{34}$$

The efficiencies of the various steps in Scheme I can also be defined: (a) the efficiency for the formation of the ^2E state

$$^2\eta = {}^2\eta_{\mathrm{isc}}(1 - {}^2\eta_{\mathrm{gsq}}) \tag{35}$$

(b) the efficiency for intersystem crossing between the $^4T_2$ and ^2E excited states

$$^4\eta_{\mathrm{isc}} = {}^4k_{\mathrm{isc}}/(^4k_{\mathrm{isc}} + {}^4k_{\mathrm{nr}}) \tag{36}$$

(c) the efficiency of the ground-state quenching process

$$^2\eta_{\mathrm{gsq}} = {}^2k_{\mathrm{g}}[\mathrm{Cr}^{3+}]/{}^2k_{\mathrm{obs}} = 1 - (^2k_0/{}^2k_{\mathrm{obs}}) \tag{37}$$

(d) the efficiency for radiative decay of the ^2E state

$$^2\eta_{\mathrm{rad}} = {}^2k_{\mathrm{rad}}/{}^2k_0 \tag{38}$$

(e) the efficiency for the reactive decay of the ^2E state

$$^2\eta_{\mathrm{rx}} = {}^2k_{\mathrm{rx}}/{}^2k_0 = \Phi_{\mathrm{obs}}/{}^2\eta \tag{39}$$

Since $^2k_{\mathrm{rad}}$ is very small, $^2k_0$ is approximately equal to $^2k_{\mathrm{nr}} + {}^2k_{\mathrm{rx}}$; and thus $^2k_{\mathrm{nr}}$ and $^2k_{\mathrm{rx}}$ can be described by eqns. (40) and (41), respectively.

$$^2k_{\mathrm{nr}} = {}^2k_0 - {}^2k_{\mathrm{rx}} \tag{40}$$

$$^2k_{\mathrm{rx}} = {}^2k_0 - {}^2k_{\mathrm{nr}} = {}^2\eta_{\mathrm{rx}}\,{}^2k_0 = \Phi_{\mathrm{obs}}\,{}^2k_0/{}^2\eta \tag{41}$$

Since $^2\eta$ is ca. 1 [63,64], $^2k_{\mathrm{rx}} = \Phi_{\mathrm{obs}}\,{}^2k_{\mathrm{obs}}$; the values of $^2k_{\mathrm{rx}}$ are collected in Table 5. The $^2k_{\mathrm{rx}}$ values reflect the ease with which the seven-coordinate intermediate, $\mathrm{Cr(NN)_3(H_2O)^{3+}}$, is formed subsequent to interaction of the solvent with $^2E/^2T_1$. It appears that the flexibility of the ligand framework and degree of hydrophilicity in the interligand pocket site dictate the magnitude of $^2k_{\mathrm{rx}}$. The electronegative halo substituents facilitate entry of H_2O into these pockets, increasing $^2k_{\mathrm{rx}}$ over the unsubstituted phen complex. Moreover, methyl and phenyl substitution on the polypyridyl ligand create favorable orbital overlap, and increase the hydrophobic environment about the chromium(III) core, decreasing $^2k_{\mathrm{rx}}$. $^2k_{\mathrm{rx}}$ is greater for the more flexible bpy complex as compared to the more rigid phen complex.

It is noteworthy that $^{4\to2}\Phi_{\mathrm{rx}}$ (quantum yield of product formation upon irradiating into the $^4T_2$ state) for the $\mathrm{Cr(phen)_3^{3+}}$ complex is $0.05(^{4\to2}\Phi_{\mathrm{rx}})$ of $\mathrm{Cr(bpy)_3^{3+}}$ [64]. Two factors may be responsible for this: (a) ground-state concentration quenching of $\mathrm{Cr(phen)_3^{3+}}$ in 1 M $\mathrm{Cl^-}$ media, and (b) the greater rigidity of the phen vs. the bpy ligand framework.

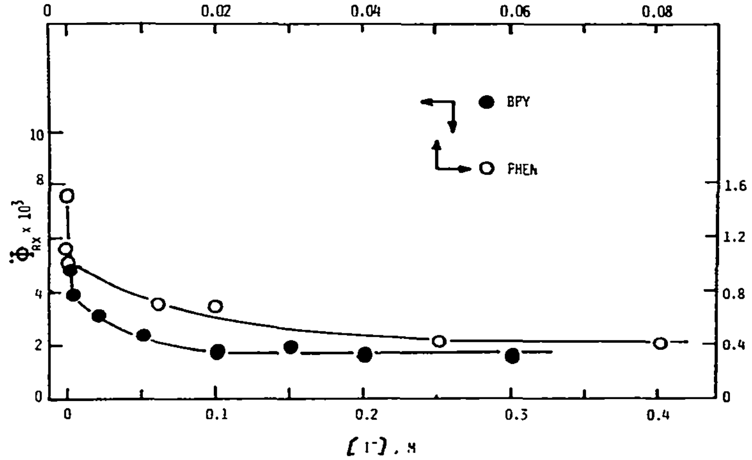


Fig. 6. Dependence of the quantum yield (Φ_{rx}) for the photoaquation of $Cr(bpy)_3^{3+}$ (●) and $Cr(phen)_3^{3+}$ (○) complexes on I^- concentration; 22°C, $\mu = 1.0$ M; deaerated buffered solutions, pH 9–10 [65].

Inasmuch as iodide ion quenches the photoreaction from $^2E/^2T_1$ with $^2k_q \sim 10^9$ M^{-1} s^{-1} [35] for the various $Cr(NN)_3^{3+}$, any nonquenchable portion of the observed quantum yield for reaction (Φ_{rx}) must arise directly from the $^4T_2$ state. The total quantum yield for release of NN is given by eqn. (42), where $^4\eta_{rx}$ is the efficiency of reaction from the $^4T_2$ state, and $^2\eta_{rx}(= {}^2k_{rx}\,{}^2\tau)$ is the efficiency of reaction from $^2E/^2T_1$.

$$\Phi_{obs} = \Phi_{rx} = \left({}^2\eta_{rx}\,{}^4\eta_{isc}\right) + {}^4\eta_{rx} \tag{42}$$

The plot of Fig. 6 reveals that with increasing concentration of I^-, the value of Φ_{rx} reaches a plateau in alkaline solution (pH = 9.3) for both $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ [65]. These plateau values reflect the efficiency of reaction from the $^4T_2$ state, $^4\eta_{rx}$. For $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ at pH 9.3, $\mu = 1.0$ and 22°C, $^4\eta_{rx} = 2 \times 10^{-3}$ and 7×10^{-4}, respectively. The lower value of $^4\eta_{rx}$ for the phen complex may be attributed to the $^4T_2$ state of this complex being less distorted than that of the bpy complex, owing to the greater rigidity of the phen framework. These results suggest that the $^4T_2$ state is the immediate precursor to reaction from the $^2E/^2T_1$ manifold, and that there is reaction from the quartet state of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$, albeit a small fraction of the overall quantum yield.

(iii) Quartet ⇝ doublet intersystem crossing in $Cr(NN)_3^{3+}$ complexes

The nature and extent of participation of the quartet $^4T_2$ and doublet $^2E/^2T_1$ excited configurations in the photochemistry of $Cr(NN)_3^{3+}$ complexes has stimulated increased interest since the initial report by Bolletta et al. [63] that the intersystem crossing efficiencies (${}^4\eta_{\rm isc}$) for $\rm Cr(bpy)_3^{3+}$ and $\rm Cr(phen)_3^{3+}$ were 0.94 and 0.21, respectively. The method used to determine ${}^4\eta_{\rm isc}$ in this study was based on electronic energy transfer from an emitting donor species (D) to an emitting acceptor species (A). For the two donor/acceptor couples biacetyl/$\rm Cr(bpy)_3^{3+}$ in H_2O and $\rm Cr(phen)_3^{3+}$/$\rm Cr(CN)_6^{3-}$ in H_2O/DMF, a representative energy level diagram given in Fig. 7 was used as the basis for determining ${}^4\eta_{\rm isc}$. For both couples, excitation of the donor species D causes a sensitized emission from the acceptor species A. According to Fig. 7, the emission intensity of the acceptor, E_A^0, and the sensitized emission intensity, E_A^s, of the acceptor are given by eqns. (43) and (44), respectively

$$E_A^0 \propto I_A^0 \eta_i^A \eta_2^A \tag{43}$$

$$E_A^s \propto I_D \eta_i^D \eta'_{ct} \eta_2^A \tag{44}$$

where I_A^0 is the light intensity absorbed by the acceptor solution, and I_D is the light intensity absorbed by the donor in a solution containing known amounts of donor and acceptor species. The efficiency of the intersystem crossing step (η_i) from the spin-allowed state to the spin-forbidden state for

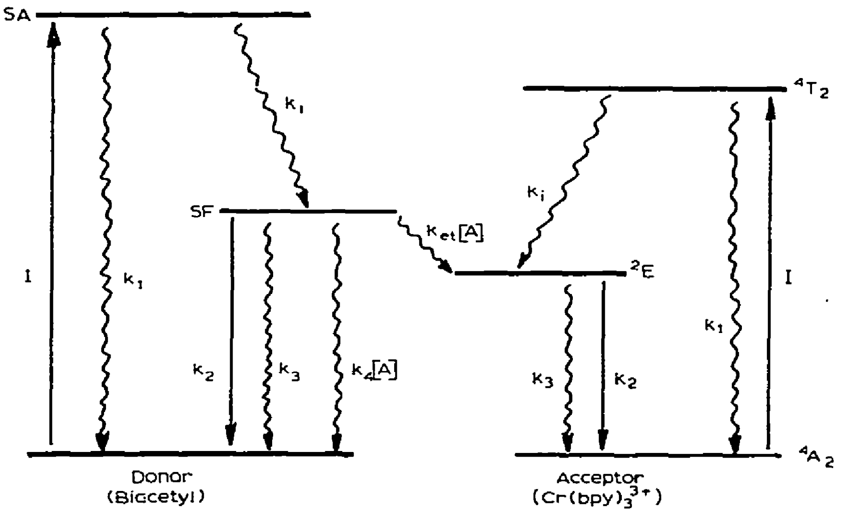


Fig. 7. Simplified energy level diagram of the couple Biacetyl/$\rm Cr(bpy)_3^{3+}$ used in the determination of the intersystem crossing efficiency in $\rm Cr(bpy)_3^{3+}$. SA denotes a spin allowed state and SF a spin forbidden state; k_1, k_2, k_3, k_4, k_i and k_{ct} refer to the rate constants of nonradiative, radiative, nonradiative, quenching, intersystem crossing, and energy transfer processes; I refers to the intensity of the exciting light.

the donor and acceptor, respectively, is given by eqns. (45) and (46)

$$\eta_i^{\mathrm{D}} = k_i^{\mathrm{D}}/\left(k_i^{\mathrm{D}} + k_1^{\mathrm{D}}\right) \tag{45}$$

$$\eta_i^{\mathrm{A}} = k_i^{\mathrm{A}}/\left(k_i^{\mathrm{A}} + k_1^{\mathrm{A}}\right) \tag{46}$$

and the efficiency of the emission from the spin-forbidden state of the acceptor is given in eqn. (47), while the energy transfer efficiency from the spin-forbidden donor state to the spin-forbidden acceptor state is given by eqn. (48)

$$\eta_2^{\mathrm{A}} = k_2^{\mathrm{A}}/\left(k_2^{\mathrm{A}} + k_3^{\mathrm{A}}\right) \tag{47}$$

$$\eta'_{\mathrm{et}} = \frac{k_{\mathrm{et}}^{\mathrm{D}}[\mathrm{A}]}{k_2^{\mathrm{D}} + k_3^{\mathrm{D}} + \left(k_{\mathrm{et}}^{\mathrm{D}} + k_4^{\mathrm{D}}\right)[\mathrm{A}]} \tag{48}$$

Taking $(k_{\mathrm{et}}^{\mathrm{D}} + k_4^{\mathrm{D}})$ in eqn. (48) as equal to $k_{\mathrm{q}}^{\mathrm{D}}$, eqn. (48) becomes

$$\eta'_{\mathrm{et}} = \eta_{\mathrm{q}}\eta_{\mathrm{et}}\frac{k_{\mathrm{q}}^{\mathrm{D}}[\mathrm{A}]}{k_2^{\mathrm{D}} + k_3^{\mathrm{D}} + k_{\mathrm{q}}^{\mathrm{D}}[\mathrm{A}]}\cdot\frac{k_{\mathrm{et}}^{\mathrm{D}}}{k_{\mathrm{q}}^{\mathrm{D}}} \tag{49}$$

where η_{q} represents the quenching efficiency of the spin-forbidden donor state by the ground-state acceptor species, and η_{et} refers to the fraction of quenching events that cause formation of the excited acceptor species. Carrying out the emission intensity measurements under the same instrumental conditions, eqns. (43) and (44) may be combined to yield

$$\frac{E_{\mathrm{A}}^{0}}{E_{\mathrm{A}}^{\mathrm{s}}} = \frac{I_{\mathrm{A}}^{0}\eta_i^{\mathrm{A}}}{I_{\mathrm{D}}\eta_i^{\mathrm{D}}\eta_{\mathrm{q}}\eta_{\mathrm{et}}} \tag{50}$$

From the above analysis

$$E_{\mathrm{A}}^{\mathrm{s}} = E'_{\mathrm{A}} - \alpha_{\mathrm{A}}E_{\mathrm{A}}^{0} \tag{51}$$

$$I_{\mathrm{D}} = \alpha_{\mathrm{D}}I_{\mathrm{A}}^{0} \tag{52}$$

$$\eta_{\mathrm{q}} = 1 - \left(E'_{\mathrm{D}}/\alpha_{\mathrm{D}}E_{\mathrm{D}}^{0}\right) \tag{53}$$

and

$$\frac{\eta_i^{\mathrm{A}}}{\eta_i^{\mathrm{D}}\eta_{\mathrm{et}}} = \frac{E_{\mathrm{A}}^{0}}{E_{\mathrm{A}}^{\mathrm{s}} - \alpha_{\mathrm{A}}E_{\mathrm{A}}^{0}}\left(\alpha_{\mathrm{D}} - \frac{E'_{\mathrm{D}}}{E_{\mathrm{D}}^{0}}\right) = R \tag{54}$$

Since R is an experimentally-determined quantity in eqn. (54), the ratio $(\eta_i^{\mathrm{A}}/\eta_i^{\mathrm{D}}\eta_{\mathrm{et}})$ can be obtained. Thus, η_i^{A} can be determined if η_i^{D}, η_{et}, and R are known. η_i^{D} for biacetyl in aqueous solution at room temperature was taken as 0.86 and $\eta_{\mathrm{et}} = 1$; the efficiency for intersystem crossing η_i^{A} for $\mathrm{Cr(bpy)_3^{3+}}$ in the biacetyl/$\mathrm{Cr(bpy)_3^{3+}}$ couple is 0.94 in water [63]. A similar analysis on the

$Cr(phen)_3^{3+}/Cr(CN)_6^{3-}$ couple gave $\eta_i^D = 0.21$ in $H_2O/DMF(1/3\ v/v)$ media at room temperature.

Recently, alteration of solution medium has been shown to have profound effects on the various photochemical and photophysical parameters of the $Cr(NN)_3^{3+}$ systems. These include concentration quenching in the presence of anions [7 − 9] and the diminution of the ^2E lifetimes in DMF [47,62]. As a result, additional experiments have been performed in an effort to determine the intersystem crossing efficiency, $^4\eta_{isc}$.

Serpone et al. [64] have attempted to determine the intersystem crossing yield $^4\eta_{isc}$, as given by eqn. (55) for $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ under identical experimental and instrumental conditions.

$$^4\eta_{isc} = {}^4k_{isc}/({}^4k_{isc} + {}^4k_{nr} + {}^4k_{rx}) \tag{55}$$

From the energy state diagram for $Cr(NN)_3^{3-}$ given in Fig. 1, it can readily be shown that for direct excitation into the doublet $^2E/^2T_1$ manifold, the quantum yield for photoaquation from the doublet is $^2\Phi_{rx} = {}^2k_{rx}\,{}^2\tau$; and for excitation into the quartet $^4T_2$ manifolds, the quantum yield is $^{4\rightarrow 2}\Phi_{rx} = {}^4\eta_{isc}\,{}^2k_{rx}\,{}^2\tau$. Because the quantum yield of reaction directly from the quartet is less than 10% of $^{4\rightarrow 2}\Phi_{rx}$, its contribution was ignored. Therefore, $^{4\rightarrow 2}\Phi_{rx} = {}^2\Phi_{rx}\,{}^4\eta_{isc}$. Comparison of $^{4\rightarrow 2}\Phi_{rx}$ for the $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3-}$ complexes leads to

$$\frac{^{4\rightarrow 2}\Phi_{rx}^{P}}{^{4\rightarrow 2}\Phi_{rx}^{B}} = \frac{^{2}\Phi_{rx}^{P}}{^{2}\Phi_{rx}^{B}} \cdot \frac{^{4}\eta_{isc}^{P}}{^{4}\eta_{isc}^{B}} \tag{56}$$

where B and P refer to the bpy and phen complexes, respectively: $^{4\rightarrow 2}\Phi_{rx}^{P} = 0.010$ [6], $^{4\rightarrow 2}\Phi_{rx}^{B} = 0.18$ [61] and $^4\eta_{isc}^{B} \sim 1$ [63]. Then $^4\eta_{isc}^{P}$ can be estimated if the ratio $(^2\Phi_{rx}^{P}/^2\Phi_{rx}^{B})$ is determined under identical photochemical and solution medium conditions as used to determine the $^{4\rightarrow 2}\Phi_{rx}$ values. Direct excitation ($\lambda_{exc(max)} = 692$ nm) into the doublet manifold of $Cr(bpy)_3^{3-}$ and $Cr(phen)_3^{3-}$ in deaerated buffered alkaline solutions (pH = 9.26, $\mu = 1.0$ M NaCl, 22°C), and subsequent determination of free polypyridine released gave $^4\eta_{isc}^{P} \sim {}^4\eta_{isc}^{B} \sim 1$ [64]. This result is in accord with the value of 0.95 suggested by Kane-Maguire and Langford [66] from oxygen quenching studies of the photoracemization of (−)-$Cr(phen)_3^{3-}$.

More recent investigations [44] on solvent isotope effects on the photophysical behavior of $Cr(bpy)_3^{3-}$ and $Cr(phen)_3^{3-}$ have demonstrated that the medium composition affects the efficiency of intersystem crossing between the quartet and doublet manifolds. It was observed [44] that the luminescence intensity from the ^2E state of $Cr(bpy)_3^{3-}$ decreases with increasing mole fraction of D_2O vs. H_2O. Since the luminescence intensity reflects the population of the ^2E state, the observed effect reveals that the

$^4T_2$ state (the precursor to ^2E) is sensitive to the isotopic nature of the solvent. On the other hand, the $(^2E)\mathrm{Cr(bpy)}_3^{3+}$ lifetime remains unchanged with increasing amounts of D_2O vs. H_2O; this observation reflects the independence of the nonradiative rate constant, $^2k_{nr}$, for the $^2E \rightarrow {}^4A_2$ decay mode. Similar lifetime behavior is exhibited by $\mathrm{Cr(phen)}_3^{3+}$; however, the luminescence intensity of $\mathrm{Cr(phen)}_3^{3+}$ also remains unchanged as the D_2O/H_2O ratio is increased [44]. The results of this investigation are collected in Table 6. The radiative quantum yield, Φ_{rad}, proportional to the luminescence intensity, decreases with increasing mole fraction of D_2O for $\mathrm{Cr(bpy)}_3^{3+}$: $\Phi_{rad} = {}^4\eta_{isc}({}^2k_{rad}/{}^2k_0)$. Since the indices of refraction for H_2O and D_2O are essentially the same and Φ_{rad} is independent of solvent composition for the $\mathrm{Cr(phen)}_3^{3+}$ cation, it was not expected that $^2k_{rad}$ would be responsible for the observed diminution of Φ_{rad} for the bpy complex. Rather, $^4\eta_{isc}$ decreases with increasing amounts of D_2O for $\mathrm{Cr(bpy)}_3^{3+}$ and remains constant for the $\mathrm{Cr(phen)}_3^{3+}$ complex.

The explanation for these observations emanates from several factors [44]. Firstly, in the $^4T_2$ state, distorted with respect to the $^4A_2$ state, there are probably solvent molecules occupying the opened interligand pockets and which exhibit weak electronic interactions between the lone electron pairs and the vacant t_{2g} orbital that points into the pockets. The direction and magnitude of the solvent isotope effect argues against coupling of the vibrational levels of $^4T_2$ and $^4A_2$ by the solvent; the lower vibrational frequencies of D_2O relative to H_2O suggests that D_2O is less efficient in its coupling and would favor a modest hydrogen-favored effect. The solvent involvement in the nonradiative process could arise from the microstructure

TABLE 6

Emission intensities, lifetimes and relative values of Φ_{rad} for $\mathrm{Cr(bpy)}_3^{3+}$ and $\mathrm{Cr(phen)}_3^{3+}$ in deaerated H_2O/D_2O mixtures at 22°C [a]

Complex	χ_D	Intensity	$^2\tau$ (ms)	Φ_{rad} (rel)
$\mathrm{Cr(bpy)}_3^{3+}$	0.00	60.5	0.066	1.00
	0.20	46.6	0.067	0.77
	0.40	37.3	0.066	0.62
	0.60	26.5	0.066	0.44
	0.80	18.0	0.063	0.32
	0.99	12.6	0.061	0.23
$\mathrm{Cr(phen)}_3^{3+}$	0.00	53.0	0.23	1.00
	0.50	45.5	0.20	0.99
	0.99	45.0	0.19	1.00

[a] Ref. 44.

of the solvent in the immediate vicinity of the complex ion; D_2O is a more structured solvent than is H_2O [67]. If the nonradiative process were entropically more favorable in D_2O than in H_2O with little or no enthalpic difference, then ${}^4k_{nr}^{H} < {}^4k_{nr}^{D}$ [44]. The significance of this entropic effect is supported by our recent observations that in D_2O, ${}^4\eta_{isc}$ increases in the presence of salts in a manner similar to the ability of these salts to modify solvent structure [67].

The invariance of Φ_{rad} with solvent isotope composition for the $Cr(phen)_3^{3+}$ cation (Table 6) was explained [44] in terms of both the rate of intersystem crossing (${}^4k_{isc}$) and the rate of nonradiative decay (${}^4k_{nr}$) being less sensitive to the solvent isotope substitution in the phen system than in the bpy system. If the $({}^4T_2)Cr(phen)_3^{3+}$ species were less distorted than the $({}^4T_2)Cr(bpy)_3^{3+}$ species because of the greater rigidity of the phen framework, then the interligand solvent molecules would be less strongly bound, resulting in a lessened sensitivity toward vibronic coupling in the intersystem crossing decay mode and a lessened contribution of the entropic effect in the nonradiative decay mode.

In light of reports that both *trans*-$Cr(en)_2(NCS)_2^+$ [68] and $Cr(en)_3^{3+}$ [34] show a decrease in population of the doublet state in the long wavelength tail of the quartet band, it has been suggested [34] that these observations are due to quartet population at some vibrational energy level lower than the "crossover point" between the quartet and doublet potential energy surfaces, and that the photoreaction originates from the quartet state [68]. Although ${}^4\eta_{isc}$ is believed to be near unity for $Cr(bpy)_3^{3+}$ [63,64], Langford and Sasseville have recently indicated [69] that there is a "crossover point" for $Cr(bpy)_3^{3+}$ at ca. 590 nm whereupon ${}^4\eta_{isc}$ decreases. This seems to suggest that the unitary value for ${}^4\eta_{isc}$ for $Cr(bpy)_3^{3+}$ is only valid for quartet excitation well above the 0–0 band energy, and that intersystem crossing occurs in competition with vibrational relaxation in the quartet manifold.

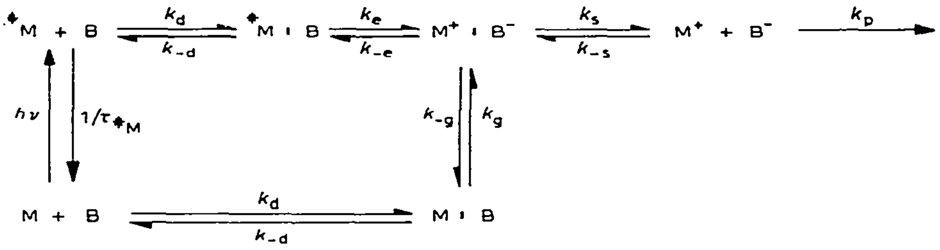
D. BIMOLECULAR QUENCHING OF CHROMIUM(III) EXCITED STATES

Excited-state quenching provides a unique method for obtaining photochemical and photophysical information and for elucidating the roles of the various excited-state deactivation pathways. With respect to chromium(III) polypyridyl complexes, the object is to ascertain the relative importance of the quartet ${}^4T_2$ and doublet ${}^2E/{}^2T_1$ excited states, and the importance of each deactivation pathway within each excited-state configuration. Balzani et al. [1] have thoroughly reviewed the available data up to 1975 and more recently [70] have included a detailed kinetic analysis of the quenching processes of excited states of transition metal complexes.

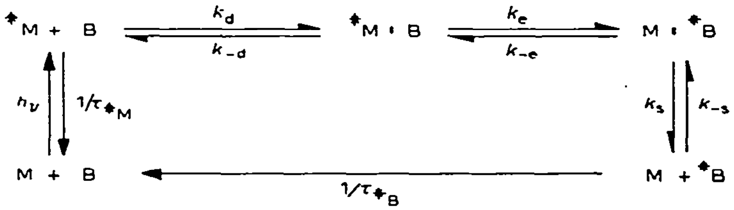
When spin and energy requirements are satisfied, excited-state quenching processes between organic species are usually diffusion-controlled [71–73]. This generality, however, is not applicable to transition metal complexes, for which quenching efficiency in the collision encounter is strongly affected by the nature of the ligands [74–78] and by the charge and geometry of the complex [74,79–83]. Studies of quenching processes of excited-state polypyridyl transition metal complexes have lent insight into the excited-state reactivities of these complexes.

Several distinct mechanisms exist for the bimolecular quenching of excited -state molecules [49,71,72], of which the most relevant to transition metal complexes are the following: electronic energy transfer, electron transfer, spin-catalyzed deactivation, excimer or exciplex formation, and external heavy atom effect. These processes are noted in Fig. 8. The participation of each of these pathways in the quenching process has been discussed [1] with particular emphasis on the various factors which determine their occurrence and relative importance. The most common quenching pathways for polypyridyl transition metal complexes are the electron and energy transfer paths; these are depicted in Schemes II and III, respectively.

SCHEME II



SCHEME III



Since excited-state lifetimes in fluid media are usually short, bimolecular processes involving these excited states must be near the diffusion-controlled limit so that they can compete with intramolecular deactivations. However, it is unlikely that either ligand substitution or inner-sphere electron transfer reactions could occur at a rate competitive with the deactivation of the

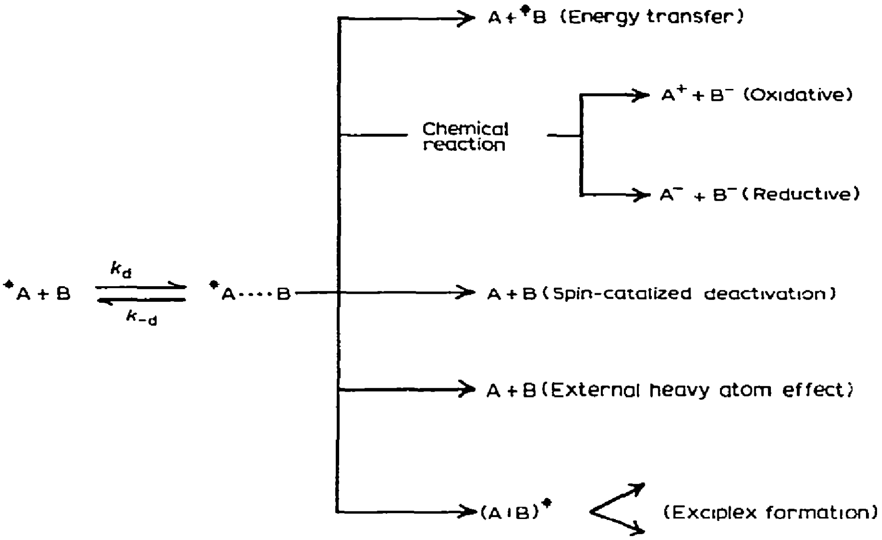


Fig. 8. Selected bimolecular quenching pathways of an excited-state species.

excited state. On the other hand, outer-sphere electron transfer and energy- and spin-allowed electronic energy transfer quenching pathways are rapid enough to successfully compete with intramolecular deactivation.

The nature of the polypyridyl chromium(III) complexes will undoubtedly have an effect on these quenching processes. Shielding of the chromium(III) core by the hydrophobic ligand sphere, for example, should affect the interaction of the MC states with the quenchers. Also, since the energy of the ^2E state varies only slightly with changes in the ligand field strength, the effect of structure on the quenching process can be examined by varying the ligand sphere.

(i) Bimolecular electron transfer

Transition metal complexes can undergo redox reactions via either outer-sphere or inner-sphere pathways. Inner-sphere redox reactions are not expected to occur within the lifetime of the excited-state species since ligand substitution processes are generally slow and therefore cannot compete with excited-state decay. On the other hand, an outer-sphere redox pathway forms an activated complex in which the number and type of ligands on the two reactants remain unchanged. This pathway may be very fast, and can thereby compete with deactivation of an excited-state species. The quenching rates are governed by "intrinsic" (self-exchange rates of the reactants) as well as "extrinsic" (overall free energy change of the reaction) factors [1].

Excitation of an electron from a low-energy (bonding) orbital to a higher-energy (antibonding) orbital reduces the ionization potential and increases the electron affinity of a molecule. Thus, it is expected that an electronically-excited species, *M, will be both a better reductant and a better oxidant than its corresponding ground state M. The rate constant for the quenching process, shown in Scheme II, can be determined using steady-state approximations, as has been shown by various workers [10,84–91].

Often an electron transfer process does not yield products different from the reactants; this is usually indicative of rapid, reverse thermal electron transfer. The rate constant for the quenching process, k_q, is given by eqns. (57) and (58), with the latter relating k_q to the free energy of activation $\Delta G_e^\dagger$ [70].

$$k_q = \frac{k_d}{1 + \frac{k_{-d}}{k_e} + \frac{k_{-d}k_{-e}}{k_{-g}k_e}} \tag{57}$$

$$k_q = \frac{k_d}{1 + \frac{k_{-d}}{Z}\left[\exp\frac{\Delta G_e^\dagger}{RT} + \exp\frac{\Delta G_e^0}{RT}\right]} \tag{58}$$

Equation (58) can be used to estimate the dependence of k_q on the overall free energy change ΔG_e^0, if the free energy of activation for the electron transfer step, $\Delta G_e^\dagger$, can be related to ΔG_e^0.

Marcus [84,85] has provided the classical relationship (59) to relate $\Delta G_e^\dagger$ to ΔG_e^0; Rehm and Weller [86,87] have proposed the empirical relationship (60).

$$\Delta G_e^\dagger = \frac{\lambda}{4}\left(1 + \frac{\Delta G_e^0}{\lambda}\right)^2 \tag{59}$$

$$\Delta G_e^\dagger = \left[\left(\frac{\Delta G_e^0}{2}\right)^2 + \left(\frac{\lambda}{4}\right)^2\right]^{1/2} \tag{60}$$

A detailed kinetic analysis and critical review of these two relationships has been presented by Balzani et al. [1,70].

The dependence of k_q on ΔG_e^0 (eqn. (58)) as predicted by the Marcus and Rehm-Weller theories is illustrated in Fig. 9. It is clear that for positive and slightly negative values of ΔG_e^0 the dependence of log k_q on ΔG_e^0 is virtually identical. However, in the region where ΔG_e^0 becomes increasingly more negative, the Marcus theory reveals a dramatic decrease in k_q (commonly referred to as the Marcus inverted region); in contrast, the Rehm-Weller

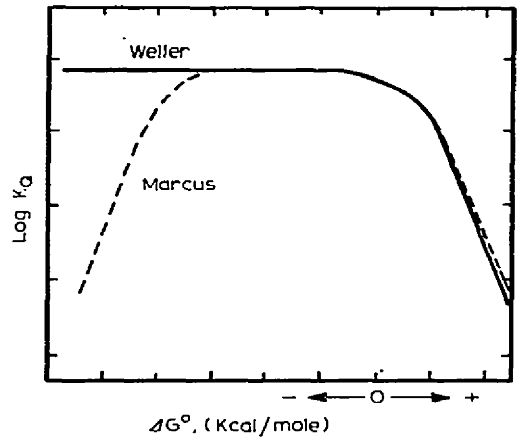


Fig. 9. Dependence of log k_q on ΔG_e^0 calculated from eqn. (58) (see text) where ΔG_e^0 is given by the Marcus and Rehm–Weller relationships.

empirical relationship predicts that k_q reaches a plateau value under these conditions. Evidence for adherence to the Marcus behavior has only been found in the quenching of $(^3CT)\mathrm{Ru(bpy)}_3^{2+}$ for which there is a small decrease in k_q with increasing endoergic character of the quenching reaction (increasing negativity of ΔG_e^0) [88].

One method utilized to confirm the existence of an electron transfer quenching pathway emanates from the relationship (61) given by Marcus [89,90] for electron transfer reactions.

$$k_q = k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \tag{61}$$

where $\log f_{12} = (\log K_{12})^2/4 \log(k_{11}k_{22}/Z^2)$, and k_{11} and k_{22} are the rate constants for the self-exchange reactions (62) and (63), respectively; K_{12} is the equilibrium constant for the cross-reaction (64), and Z is the collision number usually taken as 10^{11} M^{-1} s^{-1}.

$$Q + \mathrm{Q}^+ \overset{k_{11}}{\rightleftharpoons} Q^+ + \mathrm{Q} \tag{62}$$

$$^*Cr(\mathrm{NN})_3^{3+} + \mathrm{Cr(NN)}_3^{2+} \overset{k_{22}}{\rightleftharpoons} Cr(\mathrm{NN})_3^{2+} + {}^*\mathrm{Cr(NN)}_3^{3+} \tag{63}$$

$$^*\mathrm{Cr(NN)}_3^{3+} + \mathrm{Q} \overset{K_{12}}{\rightleftharpoons} \mathrm{Cr(NN)}_3^{2+} + \mathrm{Q}^+ \tag{64}$$

Also

$$\log k_{12} = 0.5 \log k_{11}k_{22} + 0.5(1 + \alpha) \log K_{12} \tag{65}$$

where $\alpha = (\log K_{12})/4 \log(k_{11}k_{22}/Z^2)$. A linear relationship between log

$k_q(=\log k_{12})$ vs. $(1+\alpha)\log K_{12}$ suggests electron transfer quenching; if k_{11} is known, the value of k_{22} can be estimated by fitting the experimental data assuming various values of k_{22}. Log K_{12} is a measure of the driving force for electron transfer and varies as ΔE^0. The effect of driving force on electron transfer reactions has recently come under critical scrutiny [92,93]. Creutz and Sutin [88] have predicted that electron transfer rates should begin to decrease at high enough driving forces; concrete evidence is, however, still lacking.

Turning now to the actual investigations of excited-state electron transfer quenching, it is evident that polypyridyl transition metal complexes are suitable candidates as they provide a wide range of excited state properties. These properties can be varied by altering the metal center, altering the type of ligand, or simply by adding substituents to the polypyridyl ligand framework. It is this "excited-state tuning" which allows the complex to serve as both a reductant and an oxidant, an attribute not possible for the metal ion or the free polypyridine molecule alone.

Where the Stokes shift between the ground-state absorption and excited-state emission is very small, and the changes in shape, size and solvation between the two states are also small, the entropy differences between the ground and excited states may be neglected. Whence the redox potentials of the excited state can be estimated from eqns. (66) and (67) for chromium(III) polypyridyl species

$$E^0(\mathrm{Cr}^{4+}/{}^*\mathrm{Cr}^{3+}) = E^0(\mathrm{Cr}^{4+}/\mathrm{Cr}^{3+}) - E_{0\text{-}0}(\mathrm{Cr}^{3+}/{}^*\mathrm{Cr}^{3+}) \qquad (66)$$

$$E^0({}^*\mathrm{Cr}^{3+}/\mathrm{Cr}^{2+}) = E^0(\mathrm{Cr}^{3+}/\mathrm{Cr}^{2+}) - E_{0\text{-}0}(\mathrm{Cr}^{3+}/{}^*\mathrm{Cr}^{3+}) \qquad (67)$$

where $E_{0\text{-}0}(\mathrm{Cr}^{3+}/{}^*\mathrm{Cr}^{3+})$ is the one-electron potential corresponding to the zero–zero spectroscopic energy of the excited state. The reduction potentials of the ^2E states of $\mathrm{Cr(NN)}_3^{3+}$ complexes have been evaluated [5,10] from the excitation energy ($\Delta G^* \sim 1.7$ eV) and ground-state reduction potentials [91,93–96]. These excited-state redox potentials, along with the corresponding ground-state potentials, are summarized in Table 7. The validity of this procedure has been verified in the case of the MLCT state of $\mathrm{Ru(bpy)}_3^{2+}$ [97], for which the estimated value of -0.84 V for $E^0(\mathrm{Ru}^{3+}/{}^*\mathrm{Ru}^{2+})$ [17] is in accord with the value of -0.81 V for the $\mathrm{Ru(bpy)}_3^{3+}/{}^*\mathrm{Ru(bpy)}_3^{2+}$ couple in acetonitrile [98]; this was taken [97] as good evidence that the entropy difference between the ground state and the luminescent state of $\mathrm{Ru(bpy)}_3^{2+}$ is small. For some of the $\mathrm{Cr(NN)}_3^{3+}$ complexes cited in Table 7, Balzani and co-workers [92] have experimentally verified the estimation of the redox potentials of the various polypyridyl complexes using a series of quenchers of graded potential. A comparison of the ground- and excited-state redox potentials in Table 7 reveals that the latter states are indeed better oxidants

TABLE 7

Formal reduction potentials of $Cr(NN)_3^{n+}$ complexes at 25°C [a]

NN	$E^0(Cr^{3+}/Cr^{2+})$ (V)	$E^0(^*Cr^{3+}/Cr^{2+})$ (V)
bpy	−0.26	+1.44
4,4′-Me_2bpy	−0.45	+1.25
4,4′-Ph_2bpy	(−0.28) [b]	(+1.39) [c]
5-Clphen	−0.17	+1.53
5-Brphen	−0.15	+1.55
phen	−0.28	+1.42
5-Mephen	−0.30	+1.39
5,6-Me_2phen	−0.29 [d]	+1.40 [c]
4,7-Me_2phen	−0.45	+1.23
3,4,7,8-Me_4phen	(−0.57) [b]	(1.11) [c]
5-Phphen	−0.21 [d]	+1.49 [c]
4,7-Ph_2phen	(−0.26) [b]	(+1.41) [c]

[a] Vs. NHE, in 1.0 M LiCl at 25°C. Ref. 91, unless otherwise noted. [b] Ref. 10; calculated by interpolation from log k_{12} obtained from plots of log k_q vs. log K_{12}. [c] Ref. 10. [d] Vs. NHE, calculated taking E^0 of $Cr(phen)_3^{3+/2+}$ as −0.28 V, and using E^f values for the appropriate $Cr^{3+/2+}$ couple in Table IV of ref. 96.

than their respective ground states. The reduction potentials of the chromium(III) complexes parallel those of the corresponding Ru(III) complexes [17], with the chromium potentials ca. 1.5 V more negative. The potentials for reduction of the ^2E excited states are also about 1.7 V more positive than the corresponding ground-state reduction potentials. This uniform shift of the excited-state reduction potential is due to the similarity in the wavelengths for maximum emission in the $Cr(NN)_3^{3+}$ complexes.

$Cr(bpy)_3^{3+}$ would appear to be a good candidate for studies in bimolecular excited-state redox reactions inasmuch as the lowest excited state, $^2E/^2T_1$, is relatively long-lived in aqueous media ($^2\tau = 0.063$ ms) [9], is photostable in acidic media [8] and exhibits an efficient emission [37] which can be easily monitored. Balzani and co-workers [36,99] have shown that $Ru(bpy)_3^{2-}$ quenches the emission of $(^2E)Cr(bpy)_3^{3+}$ via electron transfer. An energy transfer pathway was discarded inasmuch as the energies of the lowest excited states of $Cr(bpy)_3^{3+}$ and $Ru(bpy)_3^{2+}$ are 13,800 and 17,100 cm⁻¹, respectively [36]. Flash photolysis experiments carried out in the presence of iodide ion, which selectively quenches the ^2E state of $Cr(bpy)_3^{3+}$, have unequivocally demonstrated that reductive electron transfer occurs via reactions (68)–(71) [36]

$$Cr(bpy)_3^{3+} \xrightarrow{h\nu} \rightarrow (^2E)Cr(bpy)_3^{3+} \qquad (68)$$

$$({}^2E)\mathrm{Cr(bpy)}_3^{3+} + I^- \xrightarrow{k_{69}} \mathrm{Cr(bpy)}_3^{2+} + \mathrm{I}\cdot \qquad (69)$$

$$({}^2E)\mathrm{Cr(bpy)}_3^{3+} + \mathrm{Ru(bpy)}_3^{2+} \xrightarrow{k_{70}} \mathrm{Cr(bpy)}_3^{2+} + \mathrm{Ru(bpy)}_3^{3+} \qquad (70)$$

$$\mathrm{Ru(bpy)}_3^{3+} + \mathrm{Cr(bpy)}_3^{2+} \xrightarrow{k_{71}} \mathrm{Ru(bpy)}_3^{2+} + \mathrm{Cr(bpy)}_3^{3+} \qquad (71)$$

where $k_{69} = 1.4 \times 10^9$ M^{-1} s^{-1} [5], $k_{70} = 4.0 \times 10^8$ M^{-1} s^{-1} [99] and $k_{71} = 2.6 \times 10^9$ M^{-1} s^{-1} [36]. The products of reaction (70) are not observed because of the fast thermal back-electron transfer reaction (71). Reactions (69) and (70) demonstrate that the ${}^2E$ state of Cr(bpy)$_3^{3+}$ is a strong oxidizing agent.

The quenching of $({}^2E)$Cr(bpy)$_3^{3+}$ by a series of aliphatic and aromatic amines and methoxybenzenes has been investigated by flash photolysis techniques; these studies have shown that the quenching results in the formation of a one-electron oxidation product of the quencher [92]. The quenchers examined and the corresponding k_q values obtained are given in Table 8. Plots of log k_q vs. ΔG_e^0 show no decrease in k_q as predicted by the Marcus theory (eqn. (58)). A comparison of the relationships between k_q and ΔG_e^0 for aliphatic and aromatic amines reveals that the reorganizational energy λ is greater for the aliphatic amines since the electron to be transferred is more localized in the aliphatic amine, thereby requiring a greater geometrical perturbation upon oxidation. As well, owing to this greater electron localization, steric factors should cause a decrease in the quenching rate constant of the aliphatic amines compared to that for the aromatic amines.

Luminescence quenching of $({}^2E)$Cr(bpy)$_3^{3+}$ by various transition metal cyanide complexes has been studied by Juris et al. [100]. As is apparent from Tables 8 and 10, quenching of $({}^2E)$Cr(bpy)$_3^{3+}$ occurs via reductive electron transfer with Mo(CN)$_8^{4-}$, Fe(CN)$_6^{4-}$, Ru(CN)$_6^{4-}$, and Ni(CN)$_4^{2-}$; via oxidative electron transfer with Fe(CN)$_6^{3-}$ and Co(CN)$_6^{3-}$; and via energy transfer with Cr(CN)$_6^{3-}$. Discrimination between the possible quenching pathways cannot be based solely on the observations of reduced or oxidized products, since a reverse electron-transfer reaction so often occurs (vide infra), nor can it be based solely on the k_q values experimentally obtained. However, the relationship between the k_q values and the redox potentials of the excited-state $({}^2E)$Cr(bpy)$_3^{3+}$ and quencher species provide some insight into the thermodynamic favorability of either a reductive or oxidative electron transfer pathway. The quenching rate constants k_q obtained in this investigation [100] of the cyanide complexes show no Marcus inverted region; that is, there is no decrease in k_q at the larger negative values of ΔG_e^0.

Cr(bpy)$_3^{2+}$ and Fe$_{aq}^{3+}$ result from quenching of $({}^2E)$Cr(bpy)$_3^{3+}$ by Fe$_{aq}^{2+}$ at

TABLE 8

Electron transfer rate constants (k_q) for quenching of $Cr(NN)_3^{3+}$ complexes

NN	Quencher	k_q ($M^{-1} s^{-1}$)	Electron transfer mechanism	Ref.
bpy	Fe^{2+}	1.6×10^{7}[a]	Reductive	91
bpy	Fe^{2+}	3.7×10^{7}[b]	Reductive	5
4,4′-Me_2bpy	Fe^{2+}	0.082×10^{7}[a]	Reductive	91
4,4′-Me_2bpy	Fe^{2+}	0.22×10^{7}[b]	Reductive	5
4,4′-Ph_2bpy	Fe^{2+}	2.0×10^{7}[b]	Reductive	5
5-Clphen	Fe^{2+}	4.8×10^{7}[a]	Reductive	91
5-Clphen	Fe^{2+}	1.2×10^{8}[b]	Reductive	5
5-Brphen	Fe^{2+}	8.4×10^{7}[b]	Reductive	10
phen	Fe^{2+}	1.5×10^{7}[a]	Reductive	91
phen	Fe^{2+}	3.2×10^{7}[b]	Reductive	5
5-Mephen	Fe^{2+}	1.0×10^{7}[a]	Reductive	91
5-Mephen	Fe^{2+}	3.4×10^{7}[b]	Reductive	10
5,6-Me_2phen	Fe^{2+}	2.6×10^{7}[b]	Reductive	10
4,7-Me_2phen	Fe^{2+}	0.089×10^{7}[a]	Reductive	91
4,7-Me_2phen	Fe^{2+}	0.60×10^{7}[a]	Reductive	5
3,4,7,8-Me_4phen	Fe^{2+}	0.092×10^{7}[b]	Reductive	5
5-Phphen	Fe^{2+}	4.5×10^{7}[b]	Reductive	10
4,7-Ph_2phen	Fe^{2+}	2.5×10^{7}[b]	Reductive	5
bpy	4-aminodiphenylamine	9.4×10^{9}[c]	Reductive	92
bpy	*N,N,N′,N′*-tetramethylbenzidine	10.5×10^{9}[c]	Reductive	92
bpy	*N,N′*-diphenyl-*p*-phenylenediamine	7.2×10^{9}[c]	Reductive	92
bpy	Benzidine	8.7×10^{9}[c]	Reductive	92
bpy	α-Naphthylamine	7.2×10^{9}[c]	Reductive	92
bpy	β-Naphthylamine	8.2×10^{9}[c]	Reductive	92
bpy	*N,N′*-diethylaniline	6.4×10^{9}[c]	Reductive	92
bpy	Diphenylamine	9.1×10^{9}[c]	Reductive	92
bpy	Triphenylamine	7.3×10^{9}[c]	Reductive	92

TABLE 8 (continued)

NN	Quencher	k_q (M^{-1} s^{-1})	Electron transfer mechanism	Ref.
bpy	Tributylamine	0.69×10^{9}[c]	Reductive	92
bpy	Triethylamine	0.74×10^{9}[c]	Reductive	92
bpy	*N*,*N'*-Me_2-benzylamine	0.25×10^{9}[c]	Reductive	92
bpy	*N*-methylaniline	11×10^{9}[c]	Reductive	92
bpy	Dicyclohexylamine	0.20×10^{9}[c]	Reductive	92
bpy	1,2,4-$(OMe)_3$benzene	2.8×10^{9}[c]	Reductive	92
bpy	Dibutylamine	0.16×10^{9}[c]	Reductive	92
bpy	Dipropylamine	0.15×10^{9}[c]	Reductive	92
bpy	Aniline	9.90×10^{9}[c]	Reductive	92
bpy	Diethylamine	0.089×10^{9}[c]	Reductive	92
bpy	1,4-$(OMe)_2$benzene	1.1×10^{9}[c]	Reductive	92
bpy	Dibenzylamine	0.010×10^{9}[c]	Reductive	92
bpy	1,2,3-$(OMe)_3$benzene	0.043×10^{9}[c]	Reductive	92
bpy	1,2-$(OMe)_2$benzene	0.24×10^{9}[c]	Reductive	92
bpy	*tert*-butylamine	0.014×10^{9}[c]	Reductive	92
bpy	1,3,5-$(OMe)_3$benzene	0.019×10^{9}[c]	Reductive	92
bpy	Iodide ion	14×10^{8}[b]	Reductive	5
4,4'-Me_2bpy	Iodide ion	0.40×10^{8}[b]	Reductive	5
4,4'-Ph_2bpy	Iodide ion	22×10^{8}[b]	Reductive	5
5-Clphen	Iodide ion	80×10^{8}[b]	Reductive	5
phen	Iodide ion	21×10^{8}[b]	Reductive	5
4,7-Me_2phen	Iodide ion	1.5×10^{8}[b]	Reductive	5
3,4,7,8-Me_4phen	Iodide ion	0.47×10^{8}[b]	Reductive	5
4,7-Ph_2phen	Iodide ion	59×10^{8}[b]	Reductive	5
bpy	$Mo(CN)_8^{4-}$	52×10^{8}[d]	Reductive	100
bpy	$Fe(CN)_6^{4-}$	49×10^{8}[d]	Reductive	100
bpy	$Ru(CN)_6^{4-}$	55×10^{8}[d]	Reductive	100
bpy	$Ni(CN)_4^{2-}$	14×10^{8}[d]	Reductive	100
bpy	$Ru(bpy)_3^{2+}$	6.1×10^{8}[a]	Reductive	91
bpy	$Ru(bpy)_3^{2+}$	4.0×10^{8}[c]	Reductive	99
4,4'-Me_2bpy	$Ru(bpy)_3^{2+}$	2.0×10^{8}[a]	Reductive	91
phen	$Ru(bpy)_3^{2+}$	8.3×10^{8}[a]	Reductive	91

bpy	$Ru(4,4'\text{-}Me_2bpy)_3^{2+}$	11	$\times 10^{8\,a}$	Reductive	91
bpy	$Ru(3,4,7,8\text{-}Me_4phen)_3^{2+}$	~13	$\times 10^{8\,a}$	Reductive	91
bpy	$Ru(4,7\text{-}Me_2phen)_3^{2+}$	11	$\times 10^{8\,a}$	Reductive	91
phen	$Ru(4,7\text{-}Me_2phen)_3^{2+}$	14	$\times 10^{8\,a}$	Reductive	91
bpy	$Ru(5\text{-}Mephen)_3^{2+}$	9.9	$\times 10^{8\,a}$	Reductive	91
4,7-Me_2phen	$Ru(5\text{-}Mephen)_3^{2+}$	11	$\times 10^{8\,a}$	Reductive	91
bpy	$Ru(phen)_3^{2+}$	9.1	$\times 10^{8\,a}$	Reductive	91
bpy	$Ru(5\text{-}Clphen)_3^{2+}$	6.1	$\times 10^{8\,a}$	Reductive	91
phen	$Ru(5\text{-}Clphen)_3^{2+}$	8.1	$\times 10^{8\,a}$	Reductive	91
5-Mephen	$Ru(5\text{-}Clphen)_3^{2+}$	8.4	$\times 10^{8\,a}$	Reductive	91
bpy	$Ru(5\text{-}NO_2phen)_3^{2+}$	1.8	$\times 10^{8\,a}$	Reductive	91
phen	$Ru(5\text{-}NO_2phen)_3^{2+}$	2.6	$\times 10^{8\,a}$	Reductive	91
bpy	$Os(bpy)_3^{2+}$	15	$\times 10^{8\,a}$	Reductive	91
phen	$Os(bpy)_3^{2+}$	15	$\times 10^{8\,a}$	Reductive	91
bpy	$Ru(bpy)_3^{3+}$	0.06	$\times 10^{8\,a}$	Oxidative ?	91
bpy	$Os(bpy)_3^{3+}$	<0.01	$\times 10^{8\,a}$	Oxidative ?	91
bpy	$Fe(CN)_6^{3-}$	2.6	$\times 10^{8\,d}$	Oxidative ?	100
bpy	$Co(CN)_6^{3-}$	<0.002	$\times 10^{8\,d}$	Oxidative ?	100

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[a] 1 M H_2SO_4, at 25°C. [b] 1 M HCl, at 25°C. [c] 0.02 M TEAP in acetonitrile, at 22°C. [d] Water, $\mu=0.5$(NaCl), at ca. 20°C. [e] Water, $\mu=0.2$, at 25°C.

pH 3 [10,36]; quenching proceeds via reductive electron transfer [91]. Brunschwig and Sutin [91] have advanced the possibility that the observed electron transfer products could be produced if an energy transfer step occurred prior to the electron transfer step, as depicted in eqns. (72) and (73).

$$({}^2E)\mathrm{Cr(NN)}_3^{3+} + \mathrm{Fe}_{\mathrm{aq}}^{2+} \rightarrow {}^*\mathrm{Fe}^{2+}|\mathrm{Cr(NN)}_3^{3+} \tag{72}$$

$${}^*\mathrm{Fe}^{2+}|\mathrm{Cr(NN)}_3^{3+} \rightarrow \mathrm{Fe}^{3+}|\mathrm{Cr(NN)}_3^{2+} \tag{73}$$

For such a pathway to be feasible, reaction (73) would necessarily have to be faster than an electron transfer process involving the encounter complex from reaction (72); that is, faster than reaction (74).

$$\mathrm{Fe}_{\mathrm{aq}}^{2+}|{}^*\mathrm{Cr(NN)}_3^{3+} \rightarrow \mathrm{Fe}^{3+}|\mathrm{Cr(NN)}_3^{2+} \tag{74}$$

The involvement of energy transfer was deemed [91] improbable inasmuch as reaction (73) would likely require more reorganizational energy than reaction (74); and also, the orbital symmetry for reaction (73) is less favorable than for reaction (74). Other studies [10,36] have been in agreement with a reductive electron transfer mechanism for quenching of $^*\mathrm{Cr(NN)}_3^{3+}$ by $\mathrm{Fe}_{\mathrm{aq}}^{2+}$. Table 9 summarizes the values of k_q so obtained. Also, Fe^{2+} has available low-lying excited states at 10.4×10^3 cm^{-1} and ca. 14.4×10^3 cm^{-1} above the ground state [101], thus making energy transfer energetically

TABLE 9

Electron transfer rate constants (k_q) and thermal back electron transfer rate constants (k_{bet}) for the $\mathrm{Cr(NN)}_3^{3+}/\mathrm{Fe}_{\mathrm{aq}}^{2+}$ systems at 22–24°C [a]

NN	$k_q \times 10^{-7}$ ($\mathrm{M^{-1}\,s^{-1}}$)	$k_{\mathrm{bet}} \times 10^{-9}$ ($\mathrm{M^{-1}\,s^{-1}}$)
bpy	3.7	1.44 ± 0.04
4,4′-Me$_2$bpy	0.22	10.6 ± 0.6
4,4′-Ph$_2$bpy	2.0	1.6 ± 0.2
5-Clphen	12	0.61 ± 0.08
5-Brphen	8.4	1.4 ± 0.4
phen	3.2	1.3 ± 0.3
5-Mephen	3.4	2.0 ± 0.7
5,6-Me$_2$phen	2.6	2.7 ± 1.0
4,7-Me$_2$phen	0.60	(7)
3,4,7,8-Me$_4$phen	0.092	(18)
5-Phphen	4.5	1.9 ± 0.6
4,7-Ph$_2$phen	2.5	1.4 ± 0.4

[a] Refs. 5,10; in 1 M HCl, 22–24°C.

feasible. An oxidative path was discounted since $E^0 > 1.6$ V vs. NHE for the $Cr(NN)_3^{4+}/Cr(NN)_3^{3+}$ couple and $E^0 > -0.1$ V for the $Cr(NN)_3^{4+}/(^2E)Cr(NN)_3^{3+}$ couple [5]. The rate constants (k_{bct}) have also been measured for the thermal back-electron transfer reaction [10]

$$Fe_{aq}^{3+} + Cr(NN)_3^{2+} \xrightarrow{k_{bct}} Fe_{aq}^{2+} + Cr(NN)_3^{3+} \tag{75}$$

and are collected in Table 9 along with the corresponding k_q values. It is evident that the slowest rate of the thermal back reaction (75) is provided by the 5-Clphen complex, while the fastest rate is exemplified by the 3,4,7,8-Me_4phen complex.

Brunschwig and Sutin [91] have shown that quenching of various $^*Cr(NN)_3^{3+}$ complexes by $Ru(NN)_3^{2+}$ proceeds via reductive electron transfer and also that the quenching rate is dependent on the driving force for electron transfer, ΔE^0. The $(^3CT)Ru(NN)_3^{2+}$ state is at higher energy than the $(^2E)Cr(NN)_3^{3+}$ state (2.1 eV vs. 1.7 eV) [91], thus ruling out an energy transfer quenching pathway. The quenching rate constants k_q are summarized in Table 8 for the generalized reaction (76).

$$^*Cr(NN)_3^{3+} + Ru(NN')_3^{2+} \xrightarrow{k_q} Cr(NN)_3^{2+} + Ru(NN')_3^{3+} \tag{76}$$

Using the relationships between k_q and ΔG_e^0, it was demonstrated that the values of k_q increase with increasing driving force of the reaction, ΔE^0, but much less dramatically than predicted by the Marcus model [89,90].

Quenching of $Cr(bpy)_3^{3+}$ excited states by quencher species capable of oxidizing chromium(III) to chromium(IV) has revealed some inconclusive results regarding the operable quenching mechanism [91]. The quenchers examined were $Ru(bpy)_3^{3+}$ and $Os(bpy)_3^{3+}$. Of these two quenchers, $Ru(bpy)_3^{3+}$ was expected to quench more efficiently than the Os(III) analog if oxidative electron transfer occurred since the driving force ΔE^0 for the Ru(III) reaction is more favorable (1.25 vs. 0.82) [91]. Indeed, $Os(bpy)_3^{3+}$ is an inefficient quencher compared with $Ru(bpy)_3^{3+}$, allowing only an upper limit of k_q (ca. 1×10^6 M^{-1} s^{-1}) to be formulated [91]. The quenching rate constant for the $Ru(bpy)_3^{3+}$ reaction was determined to be 6×10^6 M^{-1} s^{-1}, both values being determined in 1 M H_2SO_4 at 25°C. An energy transfer pathway cannot be discounted for these two M(III) polypyridyl quenchers inasmuch as the Ru(III) complex has an absorption band at 674 nm [98] which is in close proximity to the emission band at 695 nm [14] of $^*Cr(bpy)_3^{3+}$; and both the Ru(III) and Os(III) complexes have spin-forbidden bands at longer wavelengths, which may be close to, or overlap with, the 728 nm emission of $^*Cr(bpy)_3^{3+}$ [5]. Inconclusive results were also obtained upon using $Fe(CN)_6^{3-}$ and $Co(CN)_6^{3-}$ as possible oxidative quenchers of the $(^2E)Cr(bpy)_3^{3+}$ species [100].

Utilization of the Marcus theory for outer-sphere electron transfer reactions in the form of reactions (61) and (65) has afforded the estimation of self-exchange rate constants k_{22} for the couples involved in reaction (63). Determination of these self-exchange rate constants permits comparison of the excited-state reaction with the corresponding ground-state reaction in reactions (63) and (77), respectively, inasmuch as the excited and ground states may differ in shape, size and/or dipole moment.

$$\mathit{Cr}(\mathrm{bpy})_3^{3+} + \mathrm{Cr}(\mathrm{bpy})_3^{2+} \rightleftharpoons \mathit{Cr}(\mathrm{bpy})_3^{2+} + \mathrm{Cr}(\mathrm{bpy})_3^{3+} \tag{77}$$

This difference should be reflected in the reorganizational parameter λ (see eqns. (59) and (60)) for the ground-state and excited-state reactions. Since the Stokes shift between the ground-state absorption and excited-state emission is related to nuclear coordinates of these states, one also expects the Stokes shift to be related to the difference in λ of the ground and excited states. Hence, an observed Stokes shift of zero would necessarily imply similar reorganizational parameters for the two states.

Several groups [10,91,102] have investigated the $^*\mathrm{Cr(NN)}_3^{3+}/\mathrm{Cr(NN)}_3^{2+}$ excited-state self-exchange reaction in reductive electron transfer quenching experiments. Both Brunschwig and Sutin [91] and Serpone et al. [10] have determined the self-exchange rate using $\mathrm{Fe}_{\mathrm{aq}}^{2+}$ as the quencher species, as per reaction (78).

$$^*\mathrm{Cr(NN)}_3^{3+} + \mathrm{Fe}_{\mathrm{aq}}^{2+} \xrightarrow{k_q} \mathrm{Cr(NN)}_3^{2+} + \mathrm{Fe}_{\mathrm{aq}}^{3+} \tag{78}$$

The self-exchange reactions corresponding to this cross-reaction are noted as reactions (79) and (63), with k_{11} and k_{22} as the self-exchange rate constants, respectively.

$$\mathit{Fe}_{\mathrm{aq}}^{2+} + \mathrm{Fe}_{\mathrm{aq}}^{3+} \rightleftharpoons \mathit{Fe}_{\mathrm{aq}}^{3+} + \mathrm{Fe}_{\mathrm{aq}}^{2+} \tag{79}$$

For the $\mathrm{Fe}^{2+}/\mathrm{Fe}^{3+}$ couple, $k_{11} = 4.0\ \mathrm{M^{-1}\ s^{-1}}$ [103]. Serpone et al. [10] have obtained an "apparent" k_{22} of ca. $10^5\ \mathrm{M^{-1}\ s^{-1}}$ from the intercept of a log k_{12} vs. log K_{12} plot. Endicott and Ferraudi [104] have estimated k_{22} for the $^*\mathrm{Cr(bpy)}_3^{3+}/\mathrm{Cr(bpy)}_3^{2+}$ couple to be ca. $3 \times 10^5\ \mathrm{M^{-1}\ s^{-1}}$, based on data for the $\mathrm{Ru(bpy)}_3^{2+}/^*\mathrm{Cr(bpy)}_3^{3+}$ cross-reaction and employing a self-exchange rate constant of ca. $4 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$ [17,88] for the $\mathrm{Ru(bpy)}_3^{3+}/\mathrm{Ru(bpy)}_3^{2+}$ couple. On the other hand, Brunschwig and Sutin [91] estimated $k_{22} \sim 1 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$ from a series of $\mathrm{Ru(NN)}_3^{2+}/^*\mathrm{Cr(NN)}_3^{3+}$ reactions (reaction (63)) in 1 M $\mathrm{H_2SO_4}$ at 25°C. However, an experimental value of $k_{\mathrm{ex}} \sim 600\ \mathrm{M^{-1}\ s^{-1}}$ was obtained based on $\mathrm{Fe}^{2+}/^*\mathrm{Cr(NN)}_3^{3+}$ reactions. The discrepancy between the experimental and theoretical estimations of k_{22} was explained in terms of nonadiabaticity of the cross-reaction (78) while the self-exchange reactions (79) and (63) are probably adiabatic. If the Marcus relationship (61) is modified to include a term for the probability of electron transfer in the activated complex, eqn. (61) becomes

$$k_{12} = p_{12}(k_{11}k_{22}K_{12}f_{12}/p_{11}p_{22})^{1/2} \tag{80}$$

where p terms are the probabilities of electron transfer in the respective activated complexes. In the adiabatic limit, $p_{12} = p_{11} = p_{22} = 1$, and eqn. (80) reduces to (61). However, if the cross-reaction (78) is non-adiabatic and the self-exchange reactions (79) and (63) are adiabatic, then $p_{11} = p_{22} = 1$ and $p_{12} << 1$; the intercept of a log k_{12} vs. $(1 + \alpha)$ log K_{12} plot will yield $k_{22}p_{12}$ [2], and not simply k_{22}. Since $p_{12} << 1$, k_{22} for reaction (63) will be $> 10^{5}$ M^{-1} s^{-1}, the "apparent" value determined by Serpone et al. [10], and is probably ca. $10^8 - 10^9$ M^{-1} s^{-1} [91]. The rate constant for the self-exchange reaction (77) was also estimated to be ca. $10^8 - 10^9$ M^{-1} s^{-1} [10]. Ferraudi and Endicott [102] have reported $k_{ex} \sim 4 \times 10^9$ M^{-1} s^{-1} for reaction (81) from flash photolysis studies of $Cr(bpy)_3^{3+}$ in the presence of $Cr(Me_2phen)_3^{3+}$ in methanolic solution (25°C, $\mu = 0.1$ M).

$$(^4A_2)Cr(bpy)_3^{3+} + Cr(bpy)_3^{2+} \rightarrow Cr(bpy)_3^{2+} + (^4A_2)Cr(bpy)_3^{3+} \tag{81}$$

These above results demonstrate the similarities in the excited-state (63) and ground-state (81) self-exchange reactions. This is not unexpected in view of the fact that the reactants in both reactions have the same charges, and the $^4A_2$ and ^2E states are virtually undistorted with respect to each other. These similarities suggest that the ground- and excited-state reactions can only differ with respect to their inner-sphere barriers, $\Delta G^{\dagger}_{in}$ [91], taking both reactions as adiabatic. For metal-centered states, the differences in these barriers for the ground-state, $\Delta G^{\dagger}_{in}$, and excited-state, $^*\Delta G^{\dagger}_{in}$, exchange reactions have been approximated [91] by eqn. (82), where f is a breathing force constant, a is the Cr–N bond distance and subscripts 2 and 3 denote the charge on the complex.

$$\begin{aligned}\Delta(\Delta G^{\dagger}_{in}) &= {}^*\Delta G^{\dagger}_{in} - \Delta G^{\dagger}_{in} \\ &= \frac{3f_2}{f_2 + f_3}\left[(f_3^* - f_3)a_2^2 + \frac{E_s}{6} \cdot \frac{(a_3^* + a_3 + 2a_2)}{(a_3^* + a_3)}\right]\end{aligned} \tag{82}$$

The $3f_2/(f_2 + f_3)$ term is expected [105] to be small inasmuch as the $^4A_2$ and ^2E states have the same electron configuration. The second term in eqn. (82) has five possible fates, as discussed by Brunschwig and Sutin [91] and Serpone et al. [10]. To the extent that the t_{2g} orbitals in both the $^4A_2$ and ^2E states are equally occupied, $a_3^* = a_3$, and $E_s = 0$; thus, $\Delta(\Delta G^{\dagger}_{in})$ would necessarily be zero, and the inner-sphere barriers for the ground- and excited-state reactions would be identical. This reasoning suggests that the exchange rate for the two reactions should be nearly identical, as is observed.

The remaining possibilities for the second term in eqn. (82) imply excited-state Cr–N bond distances that are either longer or shorter than in the ground state, and are not applicable here.

The lifetime of the $^4T_2$ state of $Cr(bpy)_3^{3+}$ has been estimated to be of the order of 10^{-11} s [106]. This state cannot be involved in reaction (63) since $a_3^* > a_3$, and because its lifetime is too short to be involved in bimolecular reactions. The other possibility is the $^2T_1$ state, in thermal equilibrium with the ^2E state. These latter two states differ only in the t_{2g} orbital population: $(\underline{\alpha}, \underline{\alpha}, \beta)$ for the ^2E state and $(\underline{\alpha}, \underline{\alpha}\beta, \underline{\quad})$ for the $^2T_1$ state. Unfortunately, the available data and the uncertainties inherent in the Marcus relationships precluded a delineation as to the reactive state in the self-exchange reactions involving the $^2E/^2T_1$ pair.

It is interesting to note that the ^2E state does not appear to be implicated in the reductive quenching of $^*Cr(bpy)_3^{3+}$ in alcoholic media [102].

$$^*Cr(bpy)_3^{3+} + ROH \rightarrow Cr(bpy)_3^{2+} + ROH^+ \tag{83}$$

This suggestion was based on observations that both the $(^2E)Cr(bpy)_3^{3+}$ transient and $Cr(bpy)_3^{2+}$ were detected in aqueous alkaline and alcoholic media, and that the $(^2E)Cr(bpy)_3^{3+}$ lifetime is relatively independent of solution media while the $(^2E)Cr(bpy)_3^{3+}$ yield $(^4\eta_{isc})$ is medium-dependent. It was suggested [102] that the solvent-dependent process leading to the chromium(II) species is a prompt, upper-state process that occurs in competition with excited-state relaxation to form the ^2E transient. The investigation of Ferraudi and Endicott implies [102] the involvement of either the $^4T_2$, or $^2T_2$, or some higher excited state.

The importance of electron transfer quenching studies lies therefore in the identification of products of the process, the identity and characterization of the excited state which gives rise to the oxidized or reduced species, the fate of the excited-state electron transfer products, and the comparison of the corresponding excited-state and ground-state exchange reactions. Reductive electron transfer studies have shown that $Cr(NN)_3^{2+}$ is produced, and these species are potential charge carriers in photogalvanic systems. In Section E the $Cr(NN)_3^{2+}$ species are shown to be capable of reducing water to hydrogen in the presence of a catalyst.

(ii) Bimolecular energy transfer

Energy transfer occurs via two types of interactions: (i) A dipole–dipole interaction which takes place over an intermolecular distance much larger than the molecular diameter. This type of interaction is important only for spin- and symmetry-allowed transitions in the donor and quencher species. Thus, in transition metal complexes which exhibit relatively weak, low-energy spin-forbidden absorption bands, the dipole–dipole interaction does not significantly contribute to excited-state energy transfer. (ii) An exchange interaction, on the other hand, requires a collisional encounter, and thus, is dependent on the energy of the excited-state species. The kinetic scheme presented in Scheme III is that for a collisional energy transfer process.

Using Scheme III and analogous assumptions in deriving expression (57) for electron transfer quenching, Balzani and Bolletta [107] have shown that k_q for energy transfer quenching is given by eqn. (84) and that k_q can be related to free energy changes and free energy of activation by the equivalent of eqn. (58).

$$k_q = \frac{k_d}{1 + \frac{k_{-d}}{k_c} + \frac{k_{-d}k_{-c}}{k_s k_c}} \tag{84}$$

The overall free energy change for the energy transfer process is given by eqn. (85)

$$\Delta G_c^0 = -E_{0\text{-}0}(^*\text{M,M}) + E_{0\text{-}0}(^*\text{B,B}) + \text{constant} \tag{85}$$

wherein $E_{0\text{-}0}$ refers to the zero–zero excited-state energy, and the constant term accounts for differences in partition functions and in the entropies of the ground and excited states. This constant is usually small and is considered negligible in most cases. When a homogeneous series of donors (*M) is quenched by a single quencher, eqn. (85) reduces to

$$\Delta G_c^0 = -E_{0\text{-}0}(^*\text{M,M}) + \text{constant} \tag{86}$$

At low values of $E_{0\text{-}0}(^*\text{M,M})$, eqns. (58) and (86) predict that log k_q will increase linearly with $E_{0\text{-}0}$ with a slope $1/2.303RT$; at high $E_{0\text{-}0}(^*\text{M,M})$ values, log k_q becomes equal to log k_d (plateau) as depicted in Fig. 10.

To ascertain that quenching occurs via energy transfer from the donor to the acceptor species, there must be some experimental or theoretical evidence to support this contention. Luminescence from the excited-state acceptor species (*B) is evidence for energy transfer; however, if the acceptor species undergoes a sensitized chemical reaction, it cannot be automatically assumed that energy transfer has occurred as the observed phenomenon may well be due to chemical interaction between the donor excited state (*M) and the acceptor ground state (B), or to a catalytic effect on the reactivity of the acceptor ground state. Clear-cut evidence (i.e., sensitized emission) for an energy transfer pathway is seldom encountered with transition metal complexes. However, such a pathway has often been proposed on the basis of various tenets such as: (i) the magnitude of k_q values relative to the diffusion-controlled rate constant k_d [108]; (ii) correlation of the k_q values with the energies of the excited-state species [100,108]; (iii) comparison of

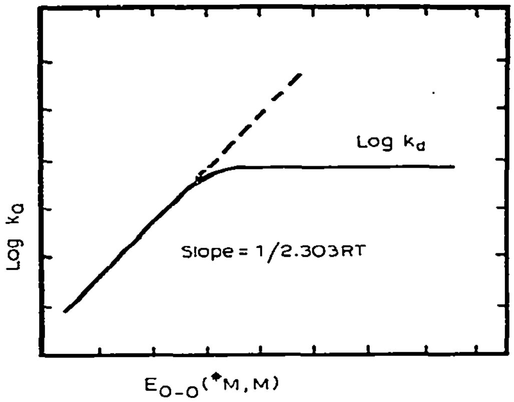

Fig. 10. Dependence of log k_q on the excited-state energy E_{0-0}(M*,M) (see text).

analogous ground-state reactions [17]; (iv) the sensitivity of k_q towards excited-state redox potentials [17,100]; and (v) comparison of the spectroscopic energies and redox potentials of the donor and quencher species. The important feature of intermolecular energy transfer in photoreactive systems is the selective population (or depopulation) of a specific excited-state species.

Sensitized emission has been observed for the $^*Cr(bpy)_3^{3+}/Cr(CN)_6^{3-}$ and $^*Cr(phen)_3^{3+}/Cr(CN)_6^{3-}$ donor/acceptor couples in H_2O/DMF solutions [64]. Energy transfer for these two couples is both spin- and thermodynamically-allowed, while an electron transfer pathway is thermodynamically unfavorable. A subsequent investigation on the $^*Cr(bpy)_3^{3+}/Cr(CN)_6^{3-}$ couple confirms an energy transfer path [100]. A comparison of the k_q values for $^*M(bpy)_3^{n+}/Cr(CN)_6^{3-}$ couples (where M = Ru(II), Os(II) and Cr(III)) reveals that k_q increases in the order Ru(II) < Os(II) < Cr(III) [100]. An energy transfer path should be more favorable for the Cr(III) ion owing to its higher ionic charge and to the absence of excited-state distortion relative to the Os(II) and Ru(II) analogs. However, the metal-centered nature of $(^2E)Cr(bpy)_3^{3+}$, which is expected to cause a less favorable overlap between donor and quencher orbitals [109], does not favor an energy transfer pathway. The greater value of k_q for the Cr(III) complex suggests that ionic charge and/or excited-state distortion play major roles in energy transfer processes.

The quenching of the ^2E states of several $Cr(NN)_3^{3+}$ complexes by molecular oxygen in 1 M HCl has been investigated [91,108], and is believed to proceed via energy transfer. Both the results of Brunschwig and Sutin [91] and Serpone et al. [108] indicate that the k_q values are considerably slower than the diffusion-controlled limit by 2–3 orders of magnitude, and are slower than the k_q values obtained for organic triplet states. That energy transfer is energetically favorable is revealed by comparison of the $({}^2E)\mathrm{Cr(NN)}_3^{3+}$ energy (ca. 13.7 kK) [108] and $({}^1\Sigma_g^+)\mathrm{O}_2$ and $({}^1\Delta_g)\mathrm{O}_2$ (ca. 12.9 and 7.9 kK) [110] energies. The k_q values are collected in Table 10, and it is clear that they are sensitive to the energies of the ${}^2E$ donor states. These results suggest that the operable reaction is

$$({}^2E)\mathrm{Cr(NN)}_3^{3+} + ({}^3\Sigma_g^-)\mathrm{O}_2 \rightarrow ({}^4A_2)\mathrm{Cr(NN)}_3^{3+} + ({}^1\Delta_g)\mathrm{O}_2 \qquad (87)$$

Brunschwig and Sutin [91] have suggested that the ${}^1\Sigma_g^+$ state of oxygen is populated in the process, rather than the ${}^1\Delta_g$ state, from the observation that the k_q values for oxygen quenching of organic triplet states and

TABLE 10

Energy transfer rate constants (k_q) for quenching of $({}^2E)\mathrm{Cr(NN)}_3^{3+}$ complexes

NN	Quencher	$k_q \times 10^{-7}$ $(\mathrm{M}^{-1}\,\mathrm{s}^{-1})$ [a]	Ref.
bpy	$\mathrm{Cr(CN)}_6^{3-}$	4.1 [b]	100
bpy	$\mathrm{Cr(CN)}_6^{3-}$	[c]	63
phen	$\mathrm{Cr(CN)}_6^{3-}$	[c]	63
bpy	Oxygen	1.7	5, 108
bpy	Oxygen	2.6	91
bpy	Oxygen	2.7 [d]	91
bpy	Oxygen	2.9 [e]	91
4,4′-Me$_2$bpy	Oxygen	3.4	5, 108
4,4′-Me$_2$bpy	Oxygen	4.2	91
4,4′-Ph$_2$bpy	Oxygen	17	5, 108
5-Clphen	Oxygen	3.7	5, 108
5-Clphen	Oxygen	3.7	91
5-Brphen	Oxygen	3.5	6
5-Brphen	Oxygen	4.0	91
phen	Oxygen	2.7	5, 108
phen	Oxygen	4.9	91
phen	Oxygen	5.0 [e]	91
phen	Oxygen	4.4 [f]	91
5-Mephen	Oxygen	5.7	6
5-Mephen	Oxygen	6.4	91
5,6-Me$_2$phen	Oxygen	8.5	6
4,7-Me$_2$phen	Oxygen	19.0	5, 108
4,7-Me$_2$phen	Oxygen	8.8	91
3,4,7,8-Me$_4$phen	Oxygen	15.0	5, 108
5-Phphen	Oxygen	5.5	6
4,7-Ph$_2$phen	Oxygen	31.0	5, 108

[a] In 1 M HCl at 25°C, unless otherwise noted. [b] In water, 0.5 M NaCl, at ca. 20°C. [c] In $\mathrm{H_2O}$/DMF solutions, at ca. 20°C. [d] In 1 M DCl, at 25°C. [e] In $\mathrm{D_2O}$, at 25°C. [f] In water, at 25°C.

$(^2E)Cr(NN)_3^{3+}$ both begin to decrease at similar energies. Others suggested [108] that the magnitude of k_q, relative to the diffusion-controlled limit, may arise from the insulating effect of the solvation spheres which would slow down the penetration of oxygen to the distance necessary for effective quenching. The variation in k_q was neither attributed to Franck–Condon factors [111], nor solely to the insulating effect of tight solvation spheres [74] about the highly-charged Cr(III) cation. Quenching by molecular oxygen via energy transfer has also been suggested for $^*Cr(acac)_3$, $^*Cr(NCS)_6^{3-}$, **trans*-$Cr(NH_3)_2(NCS)_4^-$ and $^*Cr(CN)_6^{3-}$, wherein the energy transfer process should be promoted by "conducting" ligands like CN^- and NCS^-, and hindered by "insulating" ligands like $NH_2CH_2CH_2NH_2$ and NH_3 [74].

The dependence of k_q on ΔG_e^0, as revealed by a plot of log k_q vs. ΔG_e^0, shows that oxygen quenching of $(^2E)Cr(NN)_3^{3+}$ follows a Marcus inverted behavior [108]. This behavior is analogous to the electron transfer quenching of the MLCT states of Ru(II) polypyridyl complexes in which "vestiges" of the inverted Marcus region have been reported [88]. In addition, it must be noted that the k_q values for oxygen quenching of $(^2E)Cr(NN)_3^{3+}$ are somewhat sensitive toward the redox potentials of the polypyridyl complexes; a plot of log k_q vs. ΔE^f, (where ΔE^f is the difference in the formal reduction potentials, E^f, of the $Cr(NN)_3^{3+}$ species and E^f of the $Cr(phen)_3^{3+}$ [96]), shown in Fig. 11 for various phen complexes, reveals a small but definite dependence on redox potentials. However, this dependence is nowhere near as dramatic as that exhibited by the $(^2E)Cr(NN)_3^{3+}/Fe_{aq}^{2+}$ systems for which

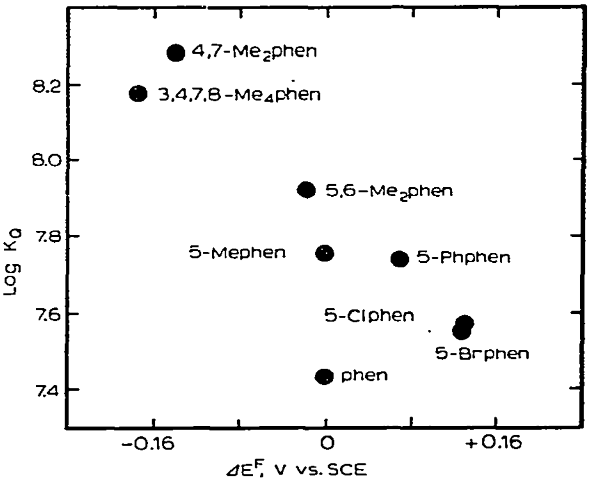

Fig. 11. Dependence of log k_q on ΔE^f for oxygen quenching of $^*Cr(NN)_3^{3+}$ species; ΔE^f is the difference between the formal reduction potentials E^f of the $Cr(NN)_3^{3+}$ complexes and that of $Cr(phen)_3^{3+}$ (see e.g. ref. 96).

quenching does proceed via electron transfer. Variations of k_q with ΔE^f potentials (Fig. 11) are suggestive of an oxidative electron transfer path, even though formation of $Cr(NN)_3^{4+}$ and HO_2 radicals would be endoergic ($\Delta G > 0.2$ eV) [108]. A reductive electron transfer pathway is unlikely in light of the strongest oxidants $(^2E)Cr(5\text{-Clphen})_3^{3+}$ and $(^2E)Cr(5\text{-Brphen})_3^{3+}$ having the smaller k_q values.

E. UTILIZATION OF $Cr(NN)_3^{3+}$ IN SOLAR ENERGY CONVERSION SCHEMES

Any endoergic photoreaction is capable of converting light energy into chemical energy. If the products of such a reaction are kinetically stable, they are potential "fuels" that can be stored, transported, and converted to the original or other chemical species with evolution of energy.

As noted earlier, absorption of light provides a method by which excitation of an electron from a low-energy to a high-energy orbital increases the electron affinity and decreases the ionization potential of a molecule. Thus, an electronically-excited state is both a better reductant and a better oxidant than its corresponding ground state. If the lifetime of the excited-state species is sufficiently long, the species can engage in bimolecular reactions involving encounter and transfer (electron and energy) with another species. Electronic excitation increases the oxidation and reduction potentials of a molecule. Thus, absorption of light is capable of driving a redox reaction in the non-spontaneous direction, and any excited-state energy can thus be converted to chemical energy in some outer-sphere reaction of the excited state. A redox scheme utilizing radiant energy has great potential, if back-electron-transfer reactions can be minimized such that the build-up of high-energy products is maximized. To accomplish these rate requirements, various alterations to systems involving polypyridyl complexes have been investigated, including modification of the reactants and incorporation of synthetic membranes to separate the high-energy products from any undesired energy-wasting reactions.

To date, the vast majority of work incorporating polypyridyl complexes has focused on ruthenium(II) complexes. Lin and Sutin [97] have observed a rather large photogalvanic potential (ca. 0.18 V) for the $Ru(bpy)_3^{2+}/Fe_{aq}^{3+}$ system. However, the more attractive way to utilize solar energy is the photocatalyzed splitting of water to yield hydrogen and oxygen. The reaction is highly endoergic ($\Delta H^0 = 295$ kJ mole^{-1}, $\Delta G^0 = 237$ kJ mole^{-1}).

$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2 \qquad (88)$$

Water is transparent to solar radiation in the visible and ultraviolet regions and does not begin to absorb until below 200 nm. Therefore, direct photolysis of water with solar radiation is not possible, and the reaction must be sensitized by redox catalysts in some cyclic scheme. A multistep process involving two or more quanta of light is required to make efficient use of the radiant energy, as a single quantum process would require energy of $\lambda < 400$ nm; > 237 kJ mole^{-1}. Several investigations involving ruthenium(II) polypyridyl complexes have shown that hydrogen is indeed produced.

Visible irradiation of deaerated or aerated aqueous solutions (pH 4–5) of $Ru(bpy)_3^{2+}$, EDTA, methylviologen (MV^{2+}), and a colloidal platinum catalyst leads to oxidative quenching of $Ru(bpy)_3^{2+}$ by MV^{2+} followed by reduction of the oxidized complexes by the electron donating EDTA; in the presence of the catalyst the process affords hydrogen, with yields of hydrogen vs. EDTA of about unity [113]. A similar system has been investigated by Graetzel and co-workers [112] wherein triethanolamine (TEOA) serves as the electron donor and PtO_2 as the catalyst. The overall mechanism induced by light absorption is the reduction of water and oxidation of TEOA. Kalyanasundaram and Graetzel [114] have also shown that visible irradiation of aqueous solutions (pH 4.7) containing $Ru(bpy)_3^{2+}$ and MV^{2+} in the presence of RuO_2 and colloidal platinum yields simultaneous evolution of hydrogen and oxygen in a 2 : 1 ratio.

Kirsch et al. [115] and Sutin and co-workers [116] have observed hydrogen evolution from a system incorporating $Ru(bpy)_3^{2+}$, $Rh(bpy)_3^{3+}$, triethanolamine, and some platinum catalyst. Kirsch et al. [115] suggested that a rhodium hydride complex serves as the precursor in the formation of hydrogen.

In view of the observation that the short-lived reductant $^*Ru(bpy)_3^{2+}$ can be reduced to the longer-lived, more strongly reducing $Ru(bpy)_3^{+}$ species, Sutin and co-workers [117] have shown that $Ru(bpy)_3^{+}$ can reduce the metal complex $[Co^{II}(Me_6[16]dieneN_4)]^{2+}$ to the corresponding cobalt(I) complex. This cobalt(I) species subsequently reacts with H^+ to form a metal hydride, which eventually leads to hydrogen production. Europium(II) is used to reduce $^*Ru(bpy)_3^{2+}$, and the overall quantum yield for hydrogen production was reported to be 0.05 [117].

Miller and McLendon [12] have observed hydrogen evolution from systems incorporating chromium(III) polypyridyl complexes (reactions (89)–(92)). An aqueous solution (pH 4.0) containing $Cr(bpy)_3^{3+}$, $Ru(bpy)_3^{2+}$, EDTA and $Pt(OH)_2$ was irradiated (410–500 nm) to produce hydrogen with a quantum yield $\geqslant 0.002$ based on $Cr(bpy)_3^{3+}$.

$$Cr(bpy)_3^{3+} \xrightarrow{h\nu} {}^*Cr(bpy)_3^{3+} \tag{89}$$

$$^*Cr(bpy)_3^{3+} + Ru(bpy)_3^{2+} \rightarrow Cr(bpy)_3^{2+} + Ru(bpy)_3^{3+} \tag{90}$$

$$Ru(bpy)_3^{3+} + EDTA \rightarrow Ru(bpy)_3^{2+} + ED3A + CO_2 + CH_2O \tag{91}$$

$$Cr(bpy)_3^{2+} \xrightarrow[Pt(OH)_2]{H^+} \tfrac{1}{2}H_2 + Cr(bpy)_3^{3+} \tag{92}$$

In this particular system, $Ru(bpy)_3^{2+}$ is also capable of acting as the photocatalyst inasmuch as $*Ru(bpy)_3^{2+}$ is efficiently quenched by $Cr(bpy)_3^{3+}$ to yield $Ru(bpy)_3^{3+}$ and $Cr(bpy)_3^{2+}$, the same species as those obtained in reaction (90). Iodide ion selectively quenches $*Cr(bpy)_3^{3+}$; thus addition of iodide ion to the $Cr^{3+}/Ru^{2+}/EDTA/Pt(OH)_2$ solution virtually negates hydrogen production [13]. This result indicates that $Cr(bpy)_3^{3+}$, and not $Ru(bpy)_3^{2+}$, serves as the photocatalyst in this system.

Hydrogen production was also observed [12] (quantum yield of ca. 0.003) in aqueous solutions (pH 4.9) containing $Cr(4,4'\text{-}Me_2bpy)_3^{3+}$, $Ru(trpy)_2^{2+}$, EDTA and a $Pt(OH)_2$ catalyst. The short-lived $Ru(trpy)_2^{2+}$ ($\tau < 5$ ns) [118] is capable of quenching (via electron transfer) $*Cr(NN)_3^{3+}$.

$$*Cr(NN)_3^{3+} + Ru(trpy)_2^{2+} \rightarrow Cr(NN)_3^{2+} + Ru(trpy)_2^{3+} \qquad (93)$$

The advantages of the substituted chromium(III) complex $Cr(4,4'\text{-}Me_2bpy)_3^{3+}$ over the $Cr(bpy)_3^{3+}$ species include a longer ^2E lifetime (0.23 ms vs. 0.073 ms) [5] for the former complex. Also, the substituted complex is a stronger reductant, with $E^0(Cr^{3+}/Cr^{2+}) = -0.45$ V vs. NHE; the corresponding parent complex has $E^0 = -0.26$ V [91]. The substituted complex is less reactive toward photosolvolysis than the unsubstituted bpy complex, probably the result of steric inhibition imposed by the methyl groups at the 4,4'-positions such that attack by water molecules at the chromium(III) center is impaired.

Recently, Balzani and co-workers [13] have reported hydrogen production from aqueous solutions using $Cr(NN)_3^{3+}$ complexes as photosensitizers (reactions (94)–(97))

$$Cr(NN)_3^{3+} \xrightarrow{h\nu} *Cr(NN)_3^{3+} \qquad (94)$$

$$*Cr(NN)_3^{3+} + EDTA \rightarrow Cr(NN)_3^{2+} + EDTA^+ \qquad (95)$$

$$Cr(NN)_3^{2+} + H^+ \xrightarrow[\text{Pt cat.}]{} Cr(NN)_3^{3+} + \tfrac{1}{2}H_2 \qquad (96)$$

$$EDTA^+ \rightarrow \text{irreversible decomposition} \qquad (97)$$

Their studies demonstrated that only $Cr(NN)_3^{3+}$ complexes possessing a sufficiently negative reduction potential capable of reducing H^+ at pH 4.8 were able to photosensitize hydrogen production. Hydrogen evolution was observed when NN = phen, $4,4'\text{-}Me_2bpy$, and $4,7\text{-}Me_2phen$; yields were < 0.001, 0.025, and 0.035 ml min^{-1} of irradiation, respectively. The low turnover numbers of these Cr(III) systems (TN = 4 for the Me_2bpy complex) compared to that of the $Ru(bpy)_3^{2+}/MV^{2+}/EDTA$ system (TN > 120) was attributed [13] to formation of catalytic amounts of $Cr(NN)_2(H_2O)_2^{2+}$, which catalyses the rapid degradative aquation of the Cr(III) complexes. On the other hand, one of the advantages of the chromium(III) system is that only Cr(II) is formed; whereas in the cycle involving $Rh(bpy)_3^{3+}$ [115] one- and two-electron reduction is thought to occur. Furthermore, no "relay" species is required for the chromium systems, as is the case for the $Ru(bpy)_3^{2+}$ cycles [113].

Creutz and Sutin [58] have shown that the luminescent state of $Ru(bpy)_3^{2+}$ is, in principle, capable ($E^0(Ru^{3+}/{}^*Ru^{2+}) = -0.84$ V) of reducing water to hydrogen ($E^0(H_2O/H_2) = -0.83$ V) in the pH region 0–14 according to reactions (98) and (99)

$$^*Ru(bpy)_3^{2+} + H_2O \rightarrow Ru(bpy)_3^{3+} + \tfrac{1}{2}H_2 \tag{98}$$

$$Ru(bpy)_3^{3+} + OH^- \rightarrow Ru(bpy)_3^{2+} + \tfrac{1}{4}O_2 + \tfrac{1}{2}H_2O \tag{99}$$

in which the $Ru(bpy)_3^{3+}$ formed in the first reaction is reduced by OH^- in the second reaction to give oxygen since $E^0(Ru^{3+}/Ru^{2+}) = 1.26$ V and $E^0(O_2/OH^-) = +0.4$ V. Kinetic reasons ($\tau \sim 0.6$ μs), however, prevent the reduction of water. Further, it was proposed [58] to effect the photodecomposition of water by visible irradiation using an appropriate electrochemical cell consisting of a $Ru(bpy)_3^{2+}$-sensitized semiconductor TiO_2 electrode connected to a platinum electrode. Irradiation of the transparent semiconductor electrode and formation of $^*Ru(bpy)_3^{2+}$ lead to injection of an electron into the conduction band of TiO_2. The resulting $Ru(bpy)_3^{3+}$ species is subsequently reduced by OH^-, yielding oxygen. Simultaneously, H_2O is reduced to hydrogen at the counter platinum electrode. One advantage of such a TiO_2/Pt cell arrangement is the regeneration of the photochemically active substrate in the visible region via oxidation of water.

A cathodic photocurrent has been observed by Langford and co-workers [11] in a photoelectrochemical cell ($\lambda_{irr} = 457$–514 nm) consisting of 10^{-4} M $Cr(bpy)_3^{3+}$ in deaerated 0.1 M H_2SO_4, a transparent SnO_2 n-doped semiconductor electrode, and a platinum counter electrode. Addition of a reducing scavenger (Fe^{II}EDTA) to the solution causes the photocurrent to become anodic with adjustment of the potential. Adjustment of the potential allows for competition between reaction (102) and the reverse of reaction (101), since the Cr(II) species will be rapidly oxidized at the platinum electrode

$$Cr(bpy)_3^{3+} \underset{k_{-100}}{\overset{h\nu}{\rightleftharpoons}} {}^*Cr(bpy)_3^{3+} \tag{100}$$

$$^*Cr(bpy)_3^{3+} + Fe(II) \underset{k_{-101}}{\overset{k_{101}}{\rightleftharpoons}} Cr(bpy)_3^{2+} + Fe(III) \tag{101}$$

$$Cr(bpy)_3^{2+} \underset{\text{Pt electrode}}{\overset{k_{102}}{\longrightarrow}} Cr(bpy)_3^{3+} \tag{102}$$

surface. The rate constant $k_{101} = 3.6 \times 10^7$ M^{-1} s^{-1} [11]. This value and that (k_{-100}/k_{101}) obtained for a plot of the reciprocal of anodic photocurrent vs. 1/[Fe(II)] yield a lifetime for the photoreactive state equal to $1/k_{-100} = {}^2\tau = 0.063$ ms, identical to that found by other methods for the ^2E state of Cr(bpy)$_3^{3+}$ [5]. This confirms the capability of the ^2E state to undergo reduction. A catalytic cycle for the photosensitized electrolysis of water can be envisaged if some modification of the system can be accomplished in which the lability of the chromium(II) species is minimized. To this end, various polypyridyl ligands were investigated [5,10] with data showing that the slowest rate of back-electron transfer (reaction (102)) was afforded by the Cr(5-Clphen)$_3^{3+}$ complex.

The requirements cited by Balzani et al. [119] for efficient solar energy storage and conversion cycles might be applicable to chromium(III) polypyridyl complexes, Cr(NN)$_3^{3+}$. We have already shown that the $^4A_2 \rightarrow {}^4T_2$ absorption band of Cr(NN)$_3^{3+}$ complexes does extend into the visible to ca. 450 nm [5]; there is some overlap of the electronic absorption spectrum of these complexes with that of the solar emission spectrum. The ^2E states of the various Cr(NN)$_3^{3+}$ species are sufficiently long lived (Table 1) that these excited-state species can participate in bimolecular reactions, e.g., ground-state, and electron and energy transfer quenching reactions. The ideal system for storage and conversion of solar energy incorporating chromium(III) complexes will be one in which the following criteria are met: (1) The lowest excited state should be formed with unitary efficiency; that is, $^4\eta_{isc} = 1$. Of those complexes investigated thus far, Cr(bpy)$_3^{3+}$ and Cr(phen)$_3^{3+}$ appear to satisfy this requirement inasmuch as the ^2E state of the former complex is populated with an efficiency of ca. 1 [63,64]. (2) The lifetime of the ^2E state should be maximized so that bimolecular electron and energy transfer reactions can occur with a variety of quencher species, but without requiring abnormally large quencher concentrations. The (^2E)Cr(3,4,7,8-Me$_4$phen)$_3^{3+}$ exhibits a lifetime of 0.64 ms in 1 M HCl at 22°C at infinite substrate dilution, which is ca. nine times that observed for (^2E)Cr(bpy)$_3^{3+}$ under identical experimental conditions (Table 1). (3) The redox potential of the excited state, E^0(*Cr^{3+}/Cr^{2+}), should be as large as possible in order to efficiently oxidize the quencher. This redox potential is equal to +1.53 V for the (^2E)Cr(5-Clphen)$_3^{3+}$ complex [5], compared with +1.11 V for the (^2E)Cr(3,4,7,8-Me$_4$phen)$_3^{3+}$ complex [10]. (4) It has been shown that the photochemistry and photophysics of Cr(NN)$_3^{3+}$ complexes are affected by modification of the environment [8,9]; hence, the ground-state quenching observed [9] for *Cr(bpy)$_3^{3+}$ and *Cr(phen)$_3^{3+}$ must be minimized. Similar observations were made for the substituted polypyridyl complexes [6]; the bpy complexes require 5 M HCl for this quenching phenomenon to be observed. Thus, it would appear that the bpy and 4,4′-Me$_2$bpy complexes are better candidates for conversion schemes inasmuch as ground-state quenching is minimized for these complexes compared to the phen complexes.

In the various investigations and analyses discussed heretofore, it is evident that chromium(III) polypyridyl complexes are also potential photosensitizers in the search for feasible cycles for solar energy conversion and storage. Studies directed at unraveling the photochemical and photophysical behavior of these complexes should aid in elucidating their potential use in conversion cycles.

Clearly, what must be stressed is that future studies of all the systems mentioned here in this section be focused towards identifying and understanding the various molecular processes taking place in the several suggested schemes for harnessing solar energy. Only then will photochemists contribute significantly towards this goal.

ACKNOWLEDGEMENTS

We greatly appreciate support of this work by the Natural Sciences and Engineering Research Council of Canada (A-5443), Formation de Chercheurs et d'Action Concertée du Québec, The National Science Foundation (CHE79-18013), and the North Atlantic Treaty Organization (No. 658). We also thank Prof. V. Balzani and his associates for their continued interest in this work, and Prof. C.H. Langford for many useful discussions.

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