

PHOTORACEMIZATION OF $\text{Ru}(\text{BIPYRIDINE})_3^{2+}$

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Summary

$\text{Ru}(\text{bipyridine})_3^{2+}$ racemizes on irradiation with visible light in aqueous solution at neutral pH. The racemization, like the photodecomposition, has a small quantum yield and occurs via the phosphorescing state. Chiral effects are observed in the quenching reaction with $\text{Co}(\text{acetylacetonate})_3$.

1. Introduction

Over the last decade there has been a rapid increase in the literature published on the tris(bipyridine)ruthenium(II) ($\text{Ru}(\text{bipy})_3^{2+}$) ion because of its remarkable photochemistry. The absorption spectrum has intense bands ($\epsilon_{452} = 1.29 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and $\epsilon_{286} = 7.67 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) [1]. This characteristic absorption and the location of various excited states make $\text{Ru}(\text{bipy})_3^{2+}$ a good candidate for use in solar energy research [2 - 4]. Symmetry labels and multiplicities of the excited states have been given elsewhere [5].

Because this complex ion emits strongly and has a lifetime of approximately 0.6 μs [6], it is ideal for studying the quenching effects of other molecules on the luminescence [7 - 9].

In addition the excited state of $\text{Ru}(\text{bipy})_3^{2+}$ exhibits considerable photochemistry both of a permanent and of a transient nature. Examples of its transient photochemistry are the oxidation to $\text{Ru}(\text{bipy})_3^{3+}$ [10] and the reduction of the nitrogen-substituted 4,4'-bipyridine derivative in the absence of ethylenediaminetetraacetic acid [11]. The permanent photochemistry includes oxidation [12] and reduction [13] reactions as well as photosensitization [14], photoaquation [15] and photoanation [16, 17] processes.

In these reactions $\text{Ru}(\text{bipy})_3^{2+}$ is relatively inert and undergoes electron transfer [10, 13] without loss of the bipyridine ligands. The optical activity has been shown to have high thermal stability [18, 19]. Optical stability during (thermal) oxidation has also been demonstrated [20]. It has been

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suggested recently that $\text{Ru}(\text{bipy})_3^{2+}$ is chiroptically stable to excitation [21]. That this is not the case is shown by the results of the present work.

The absorption near 450 nm in the spectrum of $\text{Ru}(\text{bipy})_3^{2+}$ has been suggested to represent $d \rightarrow \pi^*$ transitions [5]. Intersystem crossing (ISC) to a nominal triplet state ^3CT occurs with unit efficiency [22].

^3CT can return to the ground state through a number of routes. These include phosphorescence, energy and/or electron transfer, the last being either to or from another molecule. Energy transfer processes can give rise to photochemistry of the quencher. An electron transfer quencher which is acting as an acceptor causes reductive quenching and ruthenium(III) is generated. Examples of such quenchers are $\text{Fe}(\text{CN})_6^{3-}$, Fe^{3+} , $\text{Co}(\text{acac})_3$, $\text{Co}(\text{phen})_3^{3+}$ and $\text{Eu}(\text{III})$ ($\text{acac} \equiv$ acetylacetonate, $\text{phen} \equiv$ 1,10-phenanthroline). Similarly ^3CT can gain an electron in oxidative quenching and ruthenium(I) is the product. Examples of this type of quencher include $\text{Fe}(\text{CN})_6^{4-}$, $\text{Eu}(\text{II})$ and $\text{Ru}(\text{NH}_3)_6^{2+}$ [7]. Quenching may lead either to a permanent change or to a transient change. The latter occurs if the electron transfer is rapidly followed by a thermal back electron transfer.

Photoracemizations of metal chelate complexes are not common. Four racemizations of this kind which are known occur for $\text{Co}(\text{ox})_3^{3-}$ [23], $\text{Cr}(\text{phen})_3^{3+}$ [24, 25], $\text{Co}(\text{phen})_3^{3+}$ [26] and $\text{Cr}(\text{en})_3^{3+}$ [27] ($\text{ox} \equiv$ oxalato, $\text{en} \equiv$ ethylenediamine). Although luminescence, rate and quenching studies have been carried out on the racemization of $\text{Cr}(\text{phen})_3^{3+}$ [24, 25], the mechanism has not been elucidated. $\text{Co}(\text{phen})_3^{3+}$ becomes $\text{Co}(\text{phen})_3^{2+}$ in the presence of light and the labile $\text{Co}(\text{II})$ racemizes by a dissociative mechanism [26]. The mechanism for the racemization of $\text{Cr}(\text{en})_3^{3+}$ is also not known [27].

There is therefore little background information to suggest what mechanism the photochemical racemization of $\text{Ru}(\text{bipy})_3^{2+}$ follows. The evidence from our studies favours a common dissociative mechanism involving photoaquation and photoracemization.

2. Experimental

Tris(bipyridine)ruthenium(II) dichloride hexahydrate was used and had been previously recrystallized. For the resolution of $\text{Ru}(\text{bipy})_3^{2+}$ the method of Burstall [18] gave a low yield. A method similar to that of Dwyer and Gyarfás [20] gave the best results. A mixture of 0.296 g (3.96×10^{-4} mol) of $\text{Ru}(\text{bipy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ and 0.131 g (4.03×10^{-4} mol) of potassium antimony tartrate was dissolved in 5 ml of hot water. On slow cooling to ice temperature dark-orange crystals of approximate dimension 1 mm were formed. The solution was vacuum filtered and the crystals were recrystallized in the dark from 2.5 ml of water to give 85.4 mg of $[(\text{SbO})(\text{C}_4\text{H}_4\text{O}_6)]_2 \cdot \text{Ru}(\text{bipy})_3$. Subsequent procedures were carried out either under red light or in the dark. The product was dissolved in 20 ml of 10% NaOH and the $\text{Ru}(\text{bipy})_3\text{Br}_2$ was precipitated on addition to a solution of KBr. This mixture

was heated until dissolution was complete and was then cooled slowly to give flakey orange crystals which were filtered by suction. These were recrystallized from a KBr solution. A 5.47×10^{-4} M solution of $\text{Ru}(\text{bipy})_3\text{Br}_2$ gave a value for $[\alpha]_D^{20}$ of $-793 \pm 80^\circ$. $\text{Co}(\text{acac})_3$ was prepared by the method of Bryant and Fernelius [28]. The preparation of $\text{Co}(\text{phen})_3\text{Cl}_3$ followed that of Pfeiffer and Werdelmann [29].

Isotropic spectra were obtained with a Cary 11 spectrophotometer. Circular dichroism (CD) spectra were run on a Jasco J20 spectrometer.

The apparatus used for lifetime measurements was similar to that described by Demas and Flynn [30]. The nitrogen gas laser tube, about 50 cm long, was run at pressures between 110 and 125 Torr with the flow of nitrogen (grade G Canadian Liquid Air) being controlled by a needle valve on the nitrogen tank and being removed from the other end of the laser tube with a rotary vacuum pump. The discharge was controlled by an external spark gap and thyration. The nitrogen plasma produced an emission at 337 nm. The capacitors were charged to 12 kV by a Spellman model PN-15 0 - 15 kV high voltage power supply. The laser was housed in an aluminum screen cage which was situated about 3 m from the detection apparatus to reduce electrical noise. The detection system comprised a B&L monochromator, with 5.36 mm slits and set at 600 nm, and an RCA 8645 photomultiplier. The signal from the multiplier was taken through a low capacitance coaxial cable system with an effective resistance of 46.5Ω . The signal was amplified through a 7A16 plug-in unit and displayed on a Tektronics model 7904 oscilloscope and photographed. This system shows that the decay of Rhodamine 6G in ethanol occurs in less than 10 ns.

Potassium ferrioxalate actinometry was carried out as described by Calvert and Pitts [31].

Distilled water or a solution of the appropriate quencher of known ionic strength was placed in a 1 cm spectrometer cell and the solid chiral $\text{Ru}(\text{bipy})_3^{2+}$ as the dibromide salt was added. It was dissolved until the optical density at 450 nm of the solution was near to but did not exceed 1.2. The solution was then placed in a Zwickle flask and was degassed with purified argon. The solution was delivered into the spectrometer cell which contained a small magnetic stir bar and which had been swept out with flowing argon. The isotropic and CD spectra were recorded after the cell had been sealed by closing the stopcocks. Successive values of the CD absorption were taken after irradiation at 458 nm to determine the rate of racemization. After significant racemization had occurred the isotropic spectrum was again recorded. The same solution was then used where possible for lifetime studies in a front surface arrangement.

3. Results

3.1. Photoracemization

Irradiation of 5.5×10^{-5} M Δ - $\text{Ru}(\text{bipy})_3^{2+}$ in neutral aqueous solution at 458 nm resulted in a regular decrease in the intensity of the CD spectrum,

with no change in the isotropic absorption intensity or spectrum. The racemization was followed quantitatively using the linear relation

$$\ln \delta A / \delta A_0 = kt \quad (1)$$

where $\delta A (= A_R - A_L)$ is the differential absorption for right- and left-handed polarized light, and k is a constant for any determination mode at constant intensity of the exciting light. The constant k can be related to the quantum yield ϕ_{rac} for racemization, values of which are given in Table 1 as a function of temperature. We also remeasured the phosphorescence decay lifetimes over the same temperature range; these are also presented in Table 1. All of these results were obtained in thoroughly deoxygenated solutions.

Both lifetimes and photoracemization quantum yields were measured in D_2O . They are larger in D_2O by factors of 1.77 and 1.83 respectively.

3.2. Quenching

In order to study their effect on the photoracemization, several quenchers of $\text{Ru}(\text{bipy})_3^{2+}$ luminescence were selected. These included $\text{Co}(\text{phen})_3^{3+}$, Fe^{3+} (aqueous) and $\text{Fe}(\text{CN})_6^{4-}$ which were used under the conditions cited in the literature. As shown by the results in Table 2, however, the literature quenching data could not be reproduced, possibly because of the extremely large ionic strength effects associated with highly charged donor-acceptor pairs. The data for the quenching of the photoracemization together with those for the quenching of the lifetime are given in Table 2 in the form of quenching rate constants k_q defined by the usual Stern-Volmer expression (2)

$$k_q = \frac{1}{\tau_0[\text{Q}]} \left(\frac{\phi_0}{\phi} - 1 \right) = \frac{1}{[\text{Q}]} \left(\frac{1}{\tau} - \frac{1}{\tau_0} \right) \quad (2)$$

where τ_0 and ϕ_0 are the lifetime and quantum yield in the absence of quencher.

Data are also given in Table 2 for the neutral quencher, the racemic form of $\text{Co}(\text{acac})_3$. Since the solubility of $\text{Co}(\text{acac})_3$ in water is small, only partial quenching of the $\text{Ru}(\text{bipy})_3^{2+}$ luminescence could be achieved and corrections had to be made for the fact that $\text{Co}(\text{acac})_3$ absorbs light appre-

TABLE 1

Racemization quantum yields of $\Delta\text{-Ru}(\text{bipy})_3^{2+}$ in deoxygenated aqueous solution

T (K)	$10^4 \phi$	τ (ns)
276	0.52	—
284	—	690
289	—	677
296	2.88	657
310	—	507
313	9.33	—

TABLE 2

Quenching constants for racemization and for luminescence of Δ -Ru(bipy) $_3^{2+}$

Quencher	k_q (rac) ($M^{-1} s^{-1}$)	k_q (lum) ($M^{-1} s^{-1}$)
Fe $^{3+}$ ^a	1.3×10^8	8.3×10^8
Co(phen) $_3^{3+}$ ^b	3.5×10^8	6.8×10^8
Fe(CN) $_6^{4-}$ ^b	3.3×10^8	1.14×10^9
Co(acac) $_3$ ^c	5.7×10^8	9.0×10^8

^aIn 0.1 M NaClO $_4$ and 0.01 M HClO $_4$.

^bIn 0.5 M NaCl.

^cIn H $_2$ O.

ciably at 458 nm. The quantum yields reported are those based on light absorbed by the Ru(bipy) $_3^{2+}$ only. This correction is difficult to make accurately because the concentration of Co(acac) $_3$ decreases continuously during the run. It is found, however, that both the initial lifetime and the racemization quantum yield are decreased proportionately by quenching.

The effects of relatively high concentrations of perchlorate ion were also tested. Although the lifetime was virtually unaffected by the presence of 0.20 M NaClO $_4$, the racemization quantum yield was increased by a factor of 1.46.

3.3. Induced optical activity

In the quenching of the luminescence and the photoracemization of Δ -Ru(bipy) $_3^{2+}$ by racemic Co(acac) $_3$, the CD spectrum characteristic of Δ -Co(acac) $_3$ appeared, grew and, as the reaction neared completion, decreased again. The behavior of δA for the wavelength 470 nm and for the difference 640/580 nm (the maximum and minimum of the Co(acac) $_3$ CD spectrum) is represented in Fig. 1, together with the isotropic absorbance of Co(acac) $_3$,

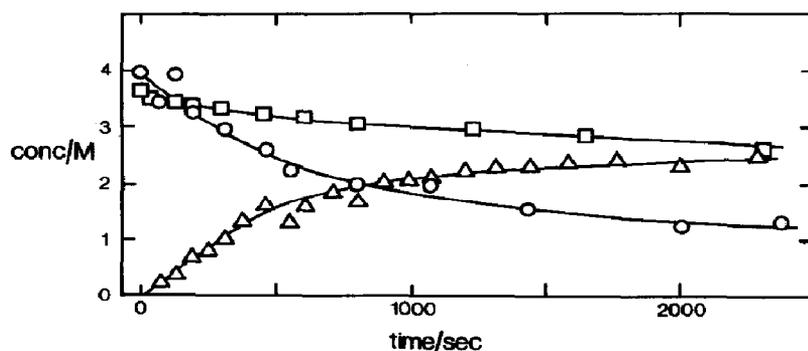


Fig. 1. Concentration changes during photolysis: ○, [Δ -Ru(bipy) $_3^{2+}$] - [Λ -Ru(bipy) $_3^{2+}$] ($\times 10^5$); △, [Δ -Co(acac) $_3$] - [Λ -Co(acac) $_3$] ($\times 10^5$); □, [Co(acac) $_3$] ($\times 10^3$).

as a function of irradiation time. The CD spectrum beyond 550 nm is just that of $\text{Co}(\text{acac})_3$ itself with $\delta A = 0$ at 622 nm [32]. The isotropic spectrum in this region remains that of $\text{Co}(\text{acac})_3$. Hence the cobalt product of the reaction is optically inactive and does not absorb appreciably above 550 nm.

4. Discussion

The photophysical processes for $\text{Ru}(\text{bipy})_3^{2+}$ are now well established. Intersystem crossing to the phosphorescent charge transfer state ^3CT occurs rapidly and with unit quantum efficiency. Although this is nominally a triplet state, because of the large spin-orbit coupling there is considerable mixing of the singlet and triplet states and spin is no longer a good quantum number. The lifetime of the state in deoxygenated aqueous solution at room temperature (22 °C) is 650 ± 50 ns but is markedly temperature and oxygen dependent. Van Houten and Watts [33] have analyzed this temperature dependence in terms of two states as

$$\tau^{-1} = 1.3 \times 10^6 + 10^{13} e^{-5250/T} \quad (3)$$

Our data, derived from a limited range of studies, are in good agreement with this equation.

The ratio ϕ/τ for the luminescence is independent of temperature and, with $\phi_{\text{ISC}} = 1$, represents the radiative rate constant of the emitting state.

Van Houten and Watts [15] have also demonstrated that $\text{Ru}(\text{bipy})_3^{2+}$ at above room temperature is subject to irreversible photodecomposition in aqueous acidic solution. The reaction has only a small quantum yield in 0.1 M HCl, but this yield increases with temperature faster than does the reciprocal lifetime of the phosphorescing state. Using eqn. (3) and the quantum yield data they derive the following for the rate constant k_p of the photoreaction:

$$k_p = \phi_p/\tau = 1.9 \times 10^{13} e^{-8030/T} \quad (4)$$

Although their data with 1 M HCl are limited, they give approximately the same temperature coefficient as those derived in 0.1 M HCl. Van Houten and Watts [15] have suggested that this reaction occurs via a ligand field state lying 10.4 kcal mol⁻¹ above the lowest level of the "triplet" charge transfer state, which together with a further activation energy of 5.5 kcal mol⁻¹ gives a total apparent activation energy of 15.9 kcal mol⁻¹. However, the mechanism in which reaction occurs via the "triplet" CT state with an activation energy of 15.9 kcal mol⁻¹ is kinetically indistinguishable from that which involves the ligand field state. Further evidence for the participation of a second state in the luminescence spectrum has been presented by other workers [34].

4.1. Photoracemization

The quantum yield for photoracemization is small but is readily observable even at below room temperature. Our evidence supports a mechanism

in which the "triplet" state, or some other state in thermal equilibrium with it, is responsible for the photoracemization. The substitution of D₂O for H₂O as the solvent nearly doubles the lifetime of the emitting state and also doubles the racemization quantum yield. Thus solvent deuteration has no apparent effect on the racemization rate constant itself.

One reason for examining the quenching of photoracemization by electron transfer quenchers was to determine the possible intermediacy of either Ru(I) or Ru(III) in the racemization pathway. There is a considerable difference in the rate of quenching of the racemization compared with that of emission, which may indicate some involvement of other oxidation states of ruthenium in the racemization. The data obtained using Co(acac)₃ as quencher, which we consider the more reliable because of the absence of ionic strength effects, give comparable values of the quenching constant for racemization and of lifetimes (Table 2).

The temperature dependence of the racemization was analyzed by formulating its rate constant k_{rac} as

$$k_{\text{rac}} = \phi_{\text{rac}}/\tau \quad (5)$$

When $\ln k_{\text{rac}}$ is plotted against $1/T$, the straight line obtained gives

$$k_{\text{rac}} = 2.0 \times 10^{14} e^{-7960/T} \quad (6)$$

The activation energy is thus 15.8 kcal mol⁻¹ which is, within experimental error, the same as that in eqn. (4) for the photochemical reaction, but having a pre-exponential factor larger by one order of magnitude.

Since the product identified by Van Houten and Watts [15] contains a one-ended bipyridyl, and since we find the same activation energy for racemization as they find for the reaction, a mechanism involving a five-coordinate intermediate would seem to be appropriate for both systems. Such an intermediate could be achiral or could rapidly undergo inversion between the two enantiomeric forms. In the absence of an appreciable H⁺ concentration and at temperatures below 50 °C, the one-ended bipyridyl in the five-coordinate intermediate would simply re-coordinate and racemization would be the only process observed. At low pH, however, the one-ended bipyridyl would be sufficiently stabilized by protonation to allow a counter-ion such as Cl⁻ or a solvent molecule to enter the sixth position, leading to a stable six-coordinate species but still retaining a one-ended bipyridyl.

With this mechanism in mind, *i.e.* taking into account an achiral intermediate in both the racemization and photodecomposition pathways, we then studied the racemization in ethanol. In this case photodecomposition occurred with substitution of the counter-ion into the coordination sphere [17, 35]. The sample photoracemized and photodecomposed in a ratio of about 10:1. During the racemization and decomposition the CD spectrum observed, as δA (see eqn. (1)), remained that of Ru(bipy)₃²⁺ and δA was zero for wavelengths beyond 575 nm. We conclude from the latter data that the decomposition product, *i.e.* Ru(bipy)₂Br₂ since the chiral bromide salt

was used, is completely racemic. This result supports the suggestion that decomposition and racemization have a common achiral intermediate which is formed from the ^3CT state of $\text{Ru}(\text{bipy})_3^{2+}$.

4.2. Induced optical activity

The quenching of $\text{Ru}(\text{bipy})_3^{2+}$ luminescence by $\text{Co}(\text{acac})_3$ leads to reduction of the cobalt to a $\text{Co}(\text{II})$ species and presumably to oxidation of the acetylacetonate [36]. Excited $\text{Ru}(\text{bipy})_3^{2+}$ acts as an electron donor in the quenching reaction to form $\text{Ru}(\text{bipy})_3^{3+}$. This is a transient ion since there is no permanent decrease in the $\text{Ru}(\text{bipy})_3^{2+}$ concentration.

Our experiments demonstrate clearly that the quenching reaction leads to the generation of optical activity in the initially racemic $\text{Co}(\text{acac})_3$ quencher [37]. Thus the two stereoisomers of $\text{Co}(\text{acac})_3$ interact with $\Delta\text{-Ru}(\text{bipy})_3^{2+}$ at different rates. The $\text{Co}(\text{acac})_3$ isomer which is in excess is shown by its CD spectrum and by the assignment of Jonas and Norden [32] to be the Δ isomer. Therefore the interaction of excited $\Delta\text{-Ru}(\text{bipy})_3^{2+}$ with $\Lambda\text{-Co}(\text{acac})_3$ has a larger rate constant than that from reaction with the Δ isomer.

From an analysis of the data in Fig. 1, the efficiencies of various processes for the $\text{Ru}(\text{bipy})_3^{2+}\text{-Co}(\text{acac})_3$ system can be estimated. The quenching rate constant is $(7.1 \pm 1.8) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. A fraction (0.04) of the quenching leads to disappearance of $\text{Co}(\text{acac})_3$, in agreement with the literature value for ϕ of 0.02 [34]. Nevertheless this obviously accounts for only a small fraction of the total quenching that is occurring. From work with potassium poly(vinyl sulfate) in solution [36], the major part of the quenching occurs by an electron transfer from $\text{Co}(\text{acac})_3$ to $^*\text{Ru}(\text{bipy})_3^{2+}$, followed by a reverse electron transfer within the solvent cage to give the reactant species in their ground states [36]. Since no result except quenching is obtained, we can only conjecture what the role of the chirality of the donor and the acceptor is on the bulk of the quenching reaction.

For that part of the reaction which leads to $\text{Co}(\text{II})$, however, we have a quantitative measure of this effect. It is small and amounts to a ratio of the rate constant of $\Delta\text{-Ru}(\text{bipy})_3^{2+}\text{-}\Delta\text{-Co}(\text{acac})_3$ to that of $\Delta\text{-Ru}(\text{bipy})_3^{2+}\text{-}\Lambda\text{-Co}(\text{acac})_3$ of 1.03. In this case any attempt to measure the chiral influence on quenching by comparing the rate constants of the resolved stereoisomers would not succeed.

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References

- 1 J. D. Miller and R. H. Prince, *J. Chem. Soc. A*, (1966) 1048.
- 2 S. Markiewicz, M. S. Chan, R. H. Sparks, C. A. Evans and J. R. Boulton, *Int. Conf. on the Photochemical Conversion and Storage of Solar Energy*, London, Ontario, 1976, E7.

- 3 G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsh and D. G. Whitten, *J. Am. Chem. Soc.*, **98** (1977) 2337.
- 4 M. Kirch, J.-M. Lehn and J.-P. Sauvage, *Helv. Chim. Acta*, **62** (1979) 1345.
- 5 R. W. Harrigan and G. A. Crosby, *J. Chem. Phys.*, **59** (1973) 3468.
- 6 J. N. Demas and G. A. Crosby, *J. Mol. Spectrosc.*, **26** (1968) 72.
- 7 C. Creutz and N. Sutin, *Inorg. Chem.*, **15** (1976) 499.
- 8 J. N. Demas and J. W. Addington, *J. Am. Chem. Soc.*, **98** (1976) 5800.
- 9 C. J. Lin and N. Sutin, *J. Phys. Chem.*, **80** (1976) 97.
- 10 P. Natarajan and J. F. Endicott, *J. Am. Chem. Soc.*, **94** (1972) 5909.
- 11 K. Takuma, Y. Shuto and T. Matsuo, *Chem. Lett.*, (1978) 983.
- 12 J. S. Winterle, D. S. Kliger and G. S. Hammond, *J. Am. Chem. Soc.*, **98** (1976) 3719.
- 13 H. D. Gafney and A. W. Adamson, *J. Am. Chem. Soc.*, **94** (1972) 8238.
- 14 J. N. Demas and A. W. Adamson, *J. Am. Chem. Soc.*, **93** (1971) 1800.
- 15 J. Van Houten and R. J. Watts, *Inorg. Chem.*, **17** (1978) 3381.
- 16 M. Gleria, F. Minto, G. Beggiano and P. Bortolus, *Chem. Commun.*, (1978) 285.
- 17 P. E. Hoggard and G. B. Porter, *J. Am. Chem. Soc.*, **100** (1978) 1457.
- 18 F. H. Burstall, *J. Chem. Soc.*, (1936) 173.
- 19 W. W. Brandt, F. P. Dwyer and E. C. Gyarfas, *Chem. Rev.*, **54** (1954) 954.
- 20 F. P. Dwyer and E. C. Gyarfas, *Proc. R. Soc., N.S.W.*, **83** (1949) 170.
- 21 A. Gafni and I. Z. Steinberg, *Isr. J. Chem.*, **15** (1977) 102.
- 22 F. Bolletta, M. Maestri and V. Balzani, *J. Phys. Chem.*, **80** (1976) 2499.
- 23 S. T. Spees, Jr., and A. W. Adamson, *Inorg. Chem.*, **1** (1962) 531.
- 24 N. A. P. Kane-Maguire and C. H. Langford, *J. Am. Chem. Soc.*, **94** (1972) 2125.
- 25 N. A. P. Kane-Maguire and C. H. Langford, *Inorg. Chem.*, **15** (1976) 464.
- 26 M. Yamamoto and Y. Yamamoto, *Inorg. Nucl. Chem. Lett.*, **10** (1976) 691.
- 27 N. A. P. Kane-Maguire, J. E. Phifer and C. G. Toney, *Inorg. Chem.*, **15** (1976) 593.
- 28 B. E. Bryant and W. C. Fernelius, *Inorg. Synth.*, **5** (1957) 188.
- 29 P. Pfeiffer and B. Werdelmann, *Z. Anorg. Chem.*, **261** (1950) 197.
- 30 J. N. Demas and C. M. Flynn, Jr., *Anal. Chem.*, **48** (1976) 353.
- 31 J. G. Calvert and J. N. Pitts, Jr., *Photochemistry*, Wiley, New York, 1966.
- 32 I. Jonas and B. Norden, *Inorg. Nucl. Chem. Lett.*, **12** (1976) 43.
- 33 J. Van Houten and R. J. Watts, *J. Am. Chem. Soc.*, **98** (1976) 4853.
- 34 R. J. Watts, J. S. Harrington and J. Van Houten, *Adv. Chem. Ser.*, **168** (1978) 57.
- 35 W. M. Wallace and P. E. Hoggard, *Inorg. Chem.*, **18** (1979) 2934.
- 36 D. Meyerstein, J. Rabani, M. S. Matheson and D. Meisel, *J. Phys. Chem.*, **82** (1978) 1879.
- 37 G. B. Porter and R. H. Sparks, *J. Chem. Soc., Chem. Commun.*, (1979) 1094.