JOURNAL OF CHEMICAL RESEARCH 2005 DECEMBER, 813–816 **RESEARCH PAPER** 813

Kinetics and mechanism of the oxidation of glyoxylic acid by peroxodisulfate induced by irradiation with visible light of aqueous solutions containing tris (2,2'-bypyridine)ruthenium(II) ion

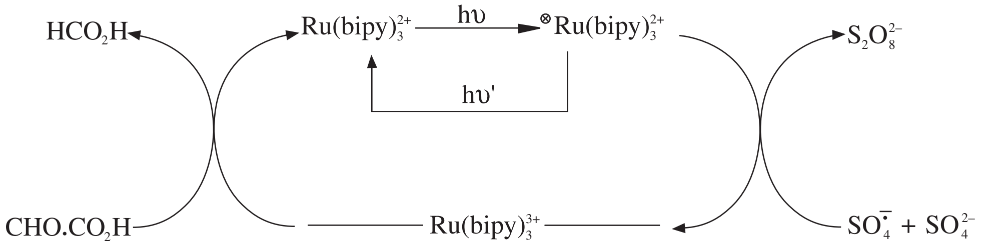
Namita Vijai, Suniti, C.L. Khandelwal and P.D. Sharma*

Department of Chemistry, University of Rajasthan, Jaipur-302004, India

The kinetics of light-induced oxidation of glyoxylic acid in the presence of $[Ru(bipy)_3^{2+}]$ as photo-catalyst have been studied. The observed kinetic rate law is given by

$$\frac{-d[S_2O_8^{2-}]}{dt} = \frac{k_q I_a \phi [S_2O_8^{2-}]}{k_0 + k_q[S_2O_8^{2-}]}$$

The reaction events are governed by the following scheme.



Keywords: kinetics, mechanism, light, photocatalyst sensitised

Peroxodisulfate is considered to be a strong oxidant both in aqueous and alkaline media.[1] Comparing peroxodisulfate and peroxomonosulfate, the reactions of the former are slower than the reactions of the latter, despite the fact that the potentials of the redox couples viz. $E_{SO_5^-/SO_4^{2-}}$ and $E_{S_2O_8^{2-}/SO_4^{2-}}$ are 1.84V,[3] and 2.01V,[2] respectively. These compounds are extensively used both in oxidation studies of organic/inorganic compounds as well as in reactions of synthetic[4] application. They are also efficient reagents in generating radicals by two successive one electron-transfer[5-7] steps. The reactions are activated by visible light and the photosplitting yields more powerful oxidising sulphate free radicals.[8-10]

$Ru(bipy)_3^{2+}$ has been considered in the role of solar photoharvesting units and its use is being explored in a large number of reactions.[11] It undergoes visible-light-induced photoredox reactions and, therefore, its polymer bound complexes are of much use and have been exploited for the conversion of light into electricity.[12] The photobleaching of the excited state of $Ru(bipy)_3^{2+}$ by peroxodisulfate in the presence of DNA and a series of mononucleotides has been studied.[13] These observations prompted us to undertake study of the title reaction with the sole aim of understanding the role of $[Ru(bipy)_3^{2+}]$ ion as a photocatalyst.

Experimental

$[Ru(bipy)_3]Cl_2.6H_2O$ was a sample from Aldrich and was employed as supplied. The solution of the catalyst was prepared in triply distilled water and was kept in bottles painted black from the outside to avoid photochemical decomposition. Potassium peroxodisulfate was of E. Merck grade and its solutions were also prepared in triply distilled water. Since trace metal ion catalysed decomposition of peroxodisulfate is already known, the solution of persulfate was prepared afresh each time for the kinetic studies. All other chemicals were of analytical reagent grade and were employed as supplied.

Triply distilled water was employed throughout the kinetic studies and the second distillation was from alkaline permanganate solution in an all glass assembly. The solutions were prepared in triply distilled water obtained by adding EDTA to ensure elimination of trace metal ions.

Kinetic procedure

The glass vessels of capacity of 500cm^3, diameter 70 mm, thickness 1 mm with a neck of 10mm were taken. 150 watt tungsten filament lamps were placed to right and left at equal distances from the centre of the reaction vessel. The reaction mixture was flushed with pure nitrogen gas for 15–20 min at least to ensure complete removal of the dissolved oxygen. Aliquot samples (5 cm^3) of the reaction mixture were withdrawn with the help of hypodermic syringes through the rubber septum caps tightened on the arm of the reaction vessel. This side arm was also used for pumping peroxodisulfate solution into the reaction mixture to initiate the reaction and the time was recorded when half of the syringe contents were released. The aliquot samples were added to KI solution employing Cu(II)–Fe(III) mixture as a mixed catalyst. The concentration of peroxodisulfate was calculated after accounting for the iodine liberated by the catalyst.

The rates in triplicate were reproducible to within ±5%. Initial rates were computed employing the plane mirror method.[14]

Results

The concentration of $[Ru(bipy)_3^{2+}]$ remains constant throughout the reaction conforming to the role of the complex ion as a photocatalyst in the reaction.

Stoichiometry

The reaction mixtures with variable concentrations of peroxodisulfate in excess over glyoxylic acid were allowed to react in a nitrogen atmosphere in the presence of tris(2,2'-bipyridine)ruthenium(II) as a photocatalyst. Oxidation of glyoxylic acid forms formic acid.[15]

These results roughly ascribe to the stoichiometry as represented by the Eqn(1)

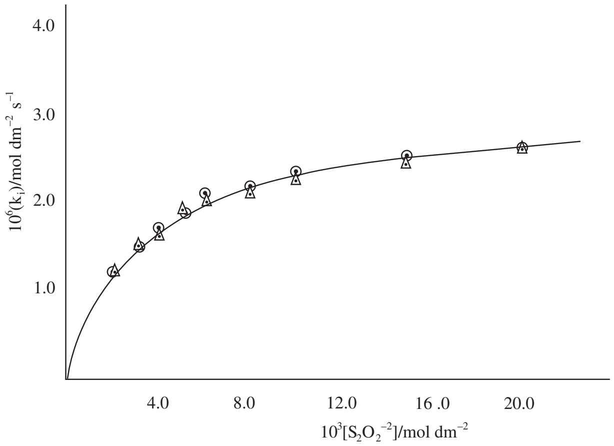
$$S_2O_8^{2-} + CHO\text{-}CO_2H \xrightarrow{[Ru(bipy)_3^{2+}]} 2SO_4^{2-} + HCOOH + CO_2 + 2H^+ \quad (1)$$

Peroxodisulfate dependence

The concentration of peroxodisulfate was varied in the range $(2.0–20.0) \times 10^{-3}$ mol dm^{-3} at fixed concentrations of other reaction ingredients *viz* $[GO_x] = 2.0 \times 10^{-3}$ and 3.0×10^{-3} mol dm^{-3} respectively, $[Ru(bipy)_3^{2+}] = 1.0 \times 10^{-6}$ mol dm^{-3} (glyoxylic acid has been written as GO_x for simplicity) and pH = 4.5. Initial rates (mol dm^{-3} s^{-1}) were calculated. A plot of intitial rate versus $[S_2O_8^{2-}]$ yielded a reactivity pattern as is given in Fig. 1.

---

* Correspondent.



$[GO_x]$ = ⊙ 2.0 × 10^{-3} mol dm^{-3} ; △ 3.0 × 10^{-3} mol dm^{-3} ;
[Ru(II)] = 1.0 × 10^{-6} mol dm^{-3}; pH = 4.5 ; light = 300 watt.

Fig. 1 Variation of ruthenium(II) concentration.

However, the rate dependence on the concentration of peroxodisulfate can be correlated by an emperical relationship as in Eqn(2).

$$\left[\frac{-d[S_2O_8^{2-}]}{dt}\right]^{-1} = A + B[S_2O_8^{2-}]^{-1} \qquad (2)$$

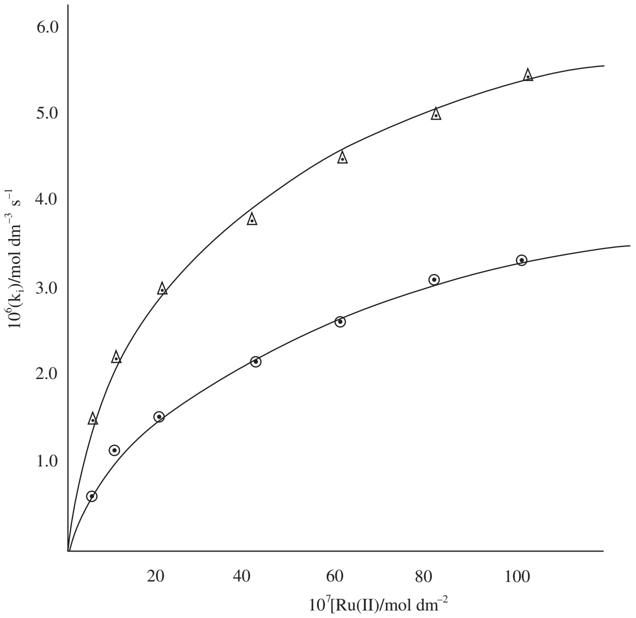
where A and B are empirical rate constants.

Glyoxylic acid (GO_x) dependence

The concentration of glyoxylic acid was varied in the range (2.0–10.0) × 10^{-3} mol dm^{-3} at constant concentrations of other reaction ingredients *viz* $[S_2O_8^{2-}]$ = 4.0 × 10^{-3} mol dm^{-3}, $[\mathrm{Ru(bipy)}_3^{2+}]$ = 1.0 × 10^{-6} mol dm^{-3} and pH = 4.5. Initial rates were calculated and these were found to be independent of the concentration of substrate ascribing zero order dependence with respect to the substrate.

Hydrogen ion concentration dependence

The effect of hydrogen ion concentration on the rate of the reaction was studied in the pH range 4–6. The rate of the reaction was also found to be independent of pH.



$[S_2O_8^{2-}]$ = ⊙ ,2.0 × 10^{-3} mol dm^{-3} ; △ ,4.0 × 10^{-3} mol dm^{-3} ;
$[GO_x]$ = 2.0 × 10^{-3} mol dm^{-3}; pH = 4.5 ; light = 300 watt.

Fig. 2 Variation of ruthenium (II) concentration.

Effect of catalyst concentraction

The catalyst concentration was varied in the range (0.5–1.0) × 10^{-5} mol dm^{-3} keeping constant concentrations of other reaction ingredients *viz* $[S_2O_8^{2-}]$ = 2.0 × 10^{-3} and 3.0 × 10^{-3} mol dm^{-3} respectively, $[GO_x]$ = 2.0 × 10^{-3} mol dm^{-3} and pH, 4.5. Initial rates were calculated and a plot of initial rate (mol dm^{-3} s^{-1}) against the concentration of $[\mathrm{Ru(bipy)}_3^{2+}]$ initially increases in a first order manner and then tends towards a limiting rate. Such a behaviour of the rate is accounted for the equation as follows.

$$I_a = I_o \{1\text{–}\exp(-A[\mathrm{Ru(bipy)}_3^{2+}])\} \qquad (3)$$

Where I_a is amount of light that is being absorbed, A is an empirical constant for such a complex for the length of the light path and molar extinction coefficient of $[\mathrm{Ru(bipy)}_3^{2+}]$ (Fig. 2).

Such a behaviour[15] of the catalyst has also been reported for the variation of catalyst concentration in other studies. This trend can be accounted[16] for by the changes in the concentration of photocatalyst on absorption of light. Since the rate is proportional to I_a, the curve as is obtained in (Fig. 2) appears to be in perfect agreement with Eqn(3).

Effect of incident light

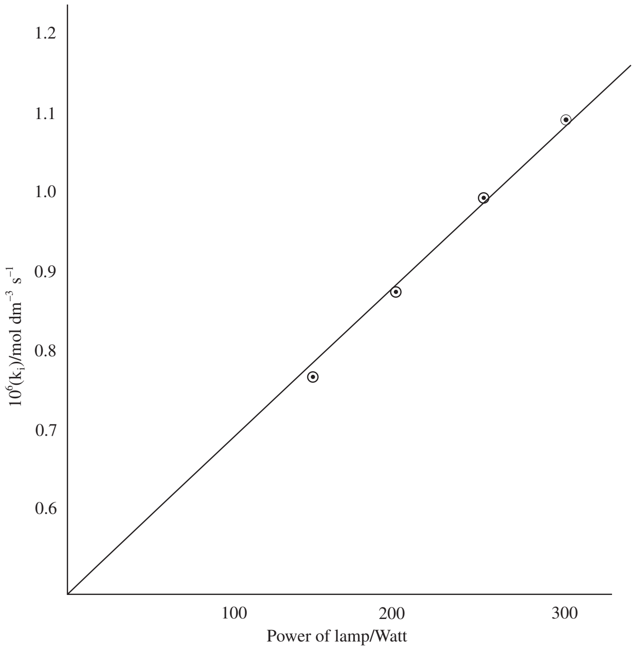
It is worth mentioning that there is very slow reaction of peroxodisulfate and glyoxylic acid in absence of photocatalyst. However, the intensity of the incident light was varied by changing the intensity of lamps and a proportionality between initial rates and intensity of the lamps was observed. This shows that a proportional change in the rate is observed with the change in light intensity (Fig. 3) (measured by power of the lamp).

Effect of salts

The effect of salts such as lithium perchlorate was studied at contant concentrations of other reaction ingredients *vis* $[S_2O_8^{2-}]$ = 2.0 × 10^{-3} mol dm^{-3}, $[GO_x]$ = 2.0 × 10^{-3}, $[\mathrm{Ru(bipy)}_3^{2+}]$ = 1.0 × 10^{-6} mol dm^{-3} and pH, 4.5 employing photolight lamps of intensity of 300 watts. The initial rate decreases with increasing concentration of lithium perchlorate accounting with the fact that the reaction is between an ion and a molecule.

Discussion

$\mathrm{Ru(bipy)}_3^{2+}$ photoluminescence[17-19] provides information both about quencher molecules and also even microenvironment as O_2 is considered to be an efficient quencher for ruthenium complexes.[11,20] The $\mathrm{Ru(bipy)}_3^{2+}$ complex is easily reduced and oxidised[21,22]



$[S_2O_8^{2-}]$ = 2.0 × 10^{-3} mol dm^{-3} ; $[GO_x]$ = 2.0 × 10^{-3} mol dm^{-3} ;
[Ru(II)] = 1.0 × 10^{-6} mol dm^{-3}; pH = 4.5.

Fig. 3 Variation of light.

and acts as a chromophore of choice in solar energy conversion,[23,24] and photoinduced electron transfer reactions.[24,25-27] The photoinduced reaction occurs from the lowest excited state and electron transfer reactions of this species exhibit either oxidation or reduction depending upon oxidation potentials[16] of the $\mathrm{Ru(bipy)}_3^{2+}$/$\mathrm{Ru(bipy)}_3^{2+}$ and $\mathrm{Ru(bipy)}_3^{2+}$/$\mathrm{Ru(bipy)}_3^{+}$ couples. However, peroxodisulfate is an oxidative quencher[28,29] of $\mathrm{Ru(bipy)}_3^{2+}$ as the former decomposes on photoreduction into two ions and this also checks the back electron transfer. $\mathrm{Ru(bipy)}_3^{2+}$, $\mathrm{SO_4{\bullet}^-}$ and $\mathrm{SO_4^{2-}}$ are generated on quenching of $\otimes\mathrm{Ru(bipy)}_3^{2+}$ by peroxodisulfate, and $\mathrm{Ru(bipy)}_3^{3+}$ and $\mathrm{SO_4{\bullet}^-}$ are strong oxidants[30,31] for the oxidation of glyoxylic acid.

Considering all these experimental observations including the complex dependence on peroxodisulfate concentration, the lack of dependence on glyoxylic acid concentration and the first order dependence on the photocatalyst concentration, the following reaction mechanism can be envisaged:

$$[\mathrm{Ru(bipy)}_3^{2+}] + h\nu \xrightarrow{I_a} [\otimes\mathrm{Ru(bipy)}_3^{2+}] \qquad (4)$$

$$[\otimes\mathrm{Ru(bipy)}_3^{2+}] \xrightarrow{k_o} \begin{cases} [\mathrm{Ru(bipy)}_3^{2+}] + h\nu' \\ \mathrm{Ru(bipy)}_3^{2+} + \Delta \end{cases} \qquad (5)$$

$$[\otimes\mathrm{Ru(bipy)}_3^{2+}] + \mathrm{S_2O)_8^{2-}} \xrightarrow{k_q} [\mathrm{Ru(bipy)}_3^{3+}] + \mathrm{SO_4{\bullet}^-} + \mathrm{SO_4^{2-}} \qquad (6)$$

$$[\mathrm{Ru(bipy)}_3^{2+}] + \mathrm{SO_4{\bullet}^-} \xrightarrow{k_1} [\mathrm{Ru(bipy)}_3^{3+}] + \mathrm{SO_4^{2-}} \qquad (7)$$

$$\mathrm{O = CH\text{-}CO_2H} + \mathrm{SO_4{\bullet}^-} \xrightarrow{k_2} \mathrm{O = CH\text{-}CO_2^{\bullet}} + \mathrm{SO_4^{2-}} + \mathrm{H^+} \qquad (8)$$

$$\mathrm{O = CH\text{-}CO_2^{\bullet}} + \mathrm{SO_4{\bullet}^-} \xrightarrow[\mathrm{H_2O}]{} \mathrm{HCO_2H} + \mathrm{CO_2} + \mathrm{SO)_4^{2-}} + \mathrm{H^+} \qquad (9)$$

$$\mathrm{O = CH\text{-}CO_2H} + [\mathrm{Ru(bipy)}_3^{3+}] \longrightarrow \mathrm{O = CH\text{-}CO_2^{\bullet}} + [\mathrm{Ru(bipy)}_3^{2+}] + \mathrm{H^+} \qquad (10)$$

$$\mathrm{O = CH\text{-}CO_2^{\bullet}} + [\mathrm{Ru(bipy)}_3^{3+}] \xrightarrow[\text{Fast}]{\mathrm{H_2O}} \mathrm{HCOOH} + [\mathrm{Ru(bipy)}_3^{2+}] + \mathrm{H^+} + \mathrm{CO_2} \qquad (11)$$

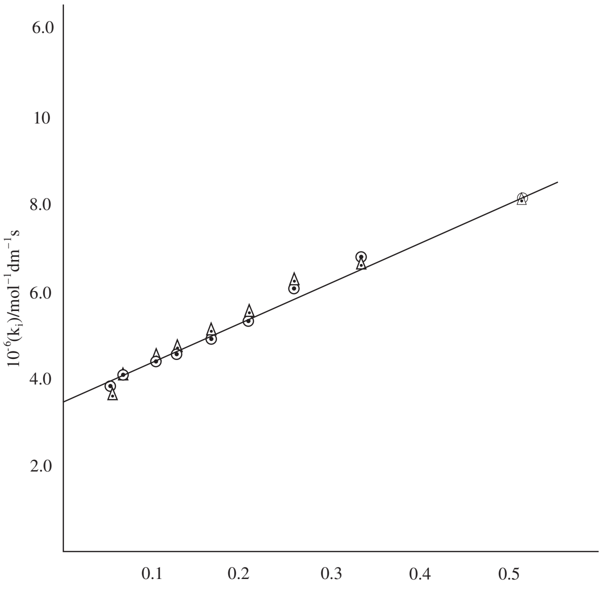
There is little possibility of distinguishing the reactions represented by Eqns (9) to (11). Such a mechanism, however, leads to the rate law (12).

$$\frac{-d[\mathrm{S_2O_8^{2-}}]}{dt} = \frac{k_q I_a \phi [\mathrm{S_2O_8^{2-}}]}{k_0 + k_q[\mathrm{S_2O_8^{2-}}]} \qquad (12)$$

where ϕ is the efficiency of formation of the excited species, I_a is the amount of light absorbed by $[\mathrm{Ru(bipy)}_3^{2+}]$ and $I_a\,\phi$ is the light used for excitation of $[\mathrm{Ru(bipy)}_3^{2+}]$.

Taking the reciprocal of the Eqn (12), and then re-arranging, Eqn (13) is obtained.

$$\frac{-d[\mathrm{S_2O_8^{2-}}]}{dt} = \frac{1}{I_a\phi} + \frac{k_0}{k_q I_a \phi [\mathrm{S_2O_8^{2-}}]} \qquad (13)$$



$[\mathrm{GO}_x]$ = ⦿,2.0×10^{-3}mol dm^{-3}; ◬ ,3.0×10^{-3}mol dm^{-3};
$[\mathrm{Ru(II)}] = 2.0 \times 10^{-3}$ mol dm^{-3}; pH = 4.5 ; light = 300 watt.

Fig. 4 A plot of $(k_i)^{-1}$ versus $[\mathrm{S_2O_8}^{-2}]^{-1}$.

A plot of $1/k_i$ versus $1/[\mathrm{S_2O_8^{2-}}]$ was made that yielded a straight line with non-zero intercept (Fig. 4).

If we compare the rate Eqn (13) with that of the empirical rate Eqn(2).

$$A = (I_a\phi)^{-1} \text{ and } B = \frac{k_0}{k_q I_a \phi}$$

The ratio of intercept and slope of the line gives k_q/k_0 where k_q is the quenching rate constant. Since intercept and slopes are 3.34×10^6 and 1.0×10^4 respectively their ratio will come out to be 3.34×10^2. Further, it is reported radiative processes that t_0 is 660 nanosecond[16] and thus

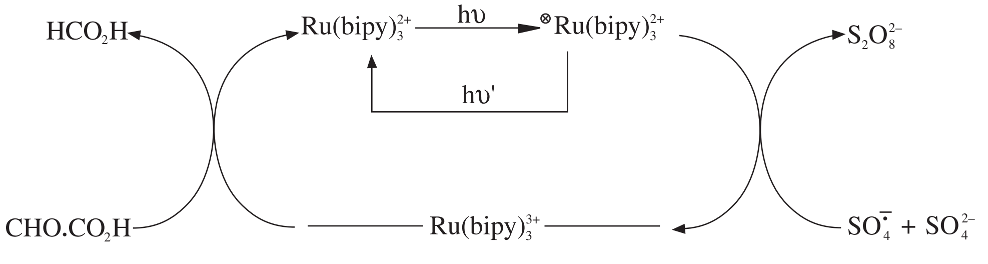
$$k_0 = 1.52 \times 10^{-6}\ \mathrm{s^{-1}} \qquad (14)$$

The value of k_q was, therefore calculated to be 5.1×10^8 dm^3 mol^{-1} s^{-1}, which is in good agreement with the earlier reported values.[32,33]

The rates of light induced reactions normally do not exhibit temperature dependence (<40°C) and thus the activation energy of quenching reaction is close to that of the non-radiative quenching of the photoexcited species.[17]

Thus in conformity of these observations Scheme 1 appears to be attractice to define the reaction events in the oxidation of glyoxylic acid by peroxodisulfate in an environment of nitrogen in the presence of $[\mathrm{Ru(bipy)}_3^{2+}]$ as a photocatalyst.

Received 13 October 2004; accepted 4 May 2005
Paper 04/2812



Scheme 1

References

1 L. Venkatasubramanian, P. Dharamlingam and P. Maruthamuthu, *Int. J. Chem. Kinet.*, 1990, **22**, 69.

2 M.M. Latimer, (ed), *The Oxidation States of Elements and their Potentials in Aqueous Solution*; Prentice Hall, Englewood Clipps, New Jersey, 1952, p. 78.

3 *Technical Data on Peroxodiphosphate*, FMC Corporation, New Jersey, 1970.

4 D.A. House *Chem. Rev.*, 1962, **62**, 185.

5 G. Manivannam and P. Maruthamuthu, *J. Polym. Sci. Polym. Chem.*, 1986, *24*, 3393; G. Bida, R. Gurci and J.O. Edwards, *Int. J. Chem. Kinet.*, 1973, **5**, 859; M. Maruthamuthu and P. Neta, *J. Phys. Chem.*, 1978, **82**, 710; S.S. Hariharan and P. Maruthamuthu, *Macromol. Chem.*, 2091, **181**, 1980; P. Maruthamuthu, *Curr. Sci.*, 1980, **49**, 591.

6 P. Muruthamuthu, L. Venkatasubramanian and P. Dharamlingam, *J. Chem. Soc. Faraday Trans I*, 1986, **82**, 359.

7 L. Venkatasubramanian and P. Maruthamuthu, *Int. J. Chem. Kinet.*, 1990, **22**, 69.

8 W.K. Wilmarth and A. Haim, In *Peroxide Reaction Mechanism* J.O. Edwards (Ed), Wiley-Interscience, New Jersey, 1962, p. 177.

9 P. Maruthamuthu and H. Taniguchi, *J. Phys. Chem.*, 1977, **81**, 194.

10 R.J. Lussier, W.M. Risen and J.O. Edwards, *J. Phys. Chem.*, 1970, **74**, 4039.

11 K. Kalyansundaram, *Co-ord. Chem. Rev.*, 1982, **46**, 159 and refs cited therein.

12 M. Kaneko, S. Nemoto, A. Yamada and Y. Kurimura, *Inorg. Chim., Acta*, 1980, **44**, L-289.

13 H. Gorner, C. Stradowski and D. Schulte Frohlinde, *J. Photochem. Photobiol.*, 1988, **47**, 15.

14 M. Latshaw, *J. Am. Chem. Soc.*, 1925, **47**, 793.

15 H.A. Sokel, *Anal. Chim. Acta.*, 1977, **89**, 407; P. Gupta, P.D. Sharma and Y.K. Gupta, *J. Chem. Soc., Dalton Trans.*, 1984, 1867.

16 S. Nishida and M. Kimura, *Bull Chem. Soc. Jpn.*, 1987, **10**, 2367; *Bull. Chem. Soc. Jpn.*, 1991, **64(4)**, 1840; *Inorg. Chim. Acta.*, 1990, **174(2)**, 231.

17 A. Juris and V. Balzani, *Coord. Chem. Rev.*, 1988, **84**, 85.

18 E. Krausz and J. Ferguson, *Prog. Inorg. Chem.*, 1989, **37**, 293.

19 T.J. Kemp, *Prog. React. Kinet.*, 1980, **10**, 301.

20 M. Kaneko, S. Ivahata and T. Asakura, *Photochem. Photobiol.*, 1992, **55**, 505.

21 R.S. Lumpkin, E.M. Kober, L.A. Worl, Z. Murtaza and T.J Meyer, *J. Phys. Chem.*, 1990, **94**, 239.

22 V. Bazani, F. Bolleta, M.T. Gandolfi and M. Maestri, *Top. Curr. Chem.*, 1978, **75**, 1.

23 T.J. Meyer, *Acc. Chem. Res.,* 1989, **22**, 164.

24 H.A. Garrera, H.E. Osponer, N.A. Garcia, J.L. Cosa and C.M. Previtali, *J. Photochem.*, 1986, **33**, 257.

25 V. Balzani, F. Scandola, G. Orlandi, N. Sabbatini and M.T. Indelli, *J. Am. Chem. Soc.*, 1981, **105**, 3370.

26 R.A. Marcus and N. Sutin, *Biochem. Biophys. Acta.*, 1985, **811**, 265.

27 T. Minisci, A. Citterio and C. Giordano, *Acc. Chem. Res.*, 1983, **16**, 27.

28 H.S. White and A.J. Bard, *J. Am. Chem. Soc.*, 1982, **104**, 6891.

29 S. Nishida and M. Kimura, *J. Chem. Res.*, 1986, 336; *Inorg. Chim. Acta.*, 1990, **174**, 231; *Bull. Chem. Soc. Jpn.*, 1991, **64**, 1840.

30 F. Bolletta, M. Giano, V. Balzani and N. Serpone, *Inorg. Chim. Acta.*, 1982, **62**, 207.

31 U. Furholz and A. Haim, *Inorg. Chem.*, 1987, **26** 3243.

32 J.N. Demas and A.W. Adamson, *J. Am. Chem. Soc.*, 1973, **95**, 5159.

33 F.E. Lyttle and D.H. Hercules, *J. Am. Chem. Soc.*, 1969, **91**, 253.