Photoredox processes in coordination compounds

P NATARAJAN

Department of Inorganic Chemistry, University of Madras, Guindy Campus, Madras 600 025, India

Abstract. Transition metal complexes display a number of charge-transfer bands in the absorption spectra. Optical excitation of the metal complexes produces a variety of products depending upon the nature of the excited state. Cobalt(III) ammine complexes on excitation in the CTTM bands produce cobalt(II) and oxidised ligand. Ruthenium(II) complexes on excitation in the CTTL band leads to the oxidation of the metal centre. In certain reactions participation of the solvent in the primary photoredox reactions has also been reported. In recent years extensive investigations have been undertaken to utilize the photoredox systems of coordination compounds to convert solar energy to electricity or hydrogen.

1. Introduction

One of the most important reactions catalysed by light in natural systems namely photosynthesis involves electron transport *via* the excited chlorophyll molecules. In recent years, chemical reactions induced by light have been understood by directly investigating the nature of electronic excited states (Turro 1978). The primary reactions in photosynthetic systems are known to take place in picosecond time scale (Miller *et al* 1980). In this system and in other natural systems it is now well established that metal ions are involved in electron transfer reactions as mediators of charge transport (Elchhorn 1973). Biological electron transfer reactions are brought about by specific environment of the metal ion coordinated to the macromolecular ligands.

Electron transfer reactions of coordination compounds have been the subject of intense investigations by inorganic chemists both experimentally and theoretically for many years (Sutin 1968). Much of the earlier studies pioneered by Taube and coworkers (see Taube 1959) are concerned with the thermal electron transfer reactions and the theoretical framework was worked out by Marcus (1956), Hush (1967) and others (see Marcus and Sutin 1975). In recent years considerable amount of work has been done on excited state electron transfer processes of coordination compounds (Balzani *et al* 1979). Several attempts have been made to extend these studies to the photo-electrochemistry of liquid junction semiconductors. It looks promising that photo-induced redox reactions should serve to convert solar energy into fuels and electricity.

2. Excited states of coordination compounds

Reasonably good theoretical models (Figgis 1967) exist to understand electronic excited states of coordination compounds where the excitation is localised to metal centered orbitals and to derive the nature of the energy levels of the compounds. The electronic excited states of a typical octahedral coordination compound are schemati-
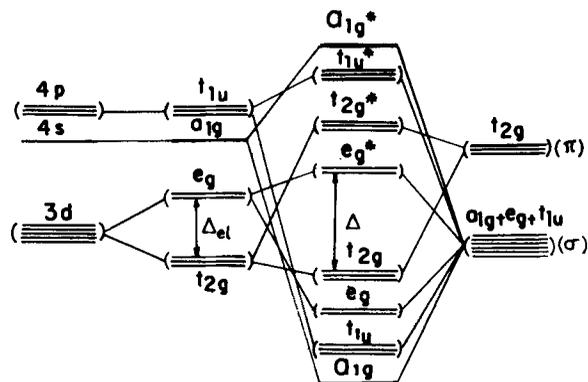
Figure 1. Electronic excited states for a coordination compound with O_h symmetry.

cally depicted in figure 1. The excited states in a transition metal compound are classified (Balzani and Carassiti 1970) into ligand-field bands and charge-transfer or electron transfer bands. In the latter category three types of transitions are assigned: metal-to-ligand charge-transfer transitions (MLCT); ligand-to-metal charge-transfer and charge-transfer-to-solvent transitions (SCT).

The charge transfer bands in the electronic spectra of coordination compounds have been identified and assigned based on experimental data. Jorgensen (1968) attempted to work out theoretical models to explain the electron transfer spectra of Werner type coordination compounds. As far as the ligand field transitions are concerned, the assignment could be done based on the ligand field model more successfully with first row transition metal compounds whereas in higher transition metals the theoretical model does not adequately interpret the absorption spectra. Emission spectral studies in organic systems have provided valuable information on the relaxation processes of excited states (Birks 1970). In fact many important excited state processes involving organic systems such as exciplex or excimer formation have been extensively investigated using emission spectroscopy. Comprehensive models proposed by Rehm and Weller (1969) on excited state electron transfer reactions are based on fluorescence studies. In transition metal complexes, room temperature emission has been observed only in a small number of compounds for these studies to be of much assistance in the understanding of electronic excited states (Fleisauer and Fleisauer 1970). In a few metal-complex systems where emission has been observed considerable information has been derived on the nature of excited states and their deactivation pathways.

In contrast to the organic molecules, coordination compounds which carry charge interact considerably strongly with the solvents or other environments. Interpretation of the excited processes becomes more complicated as the interaction between the solvent and the excited state is not understood well. In non-polar solvent most of the Werner type complexes are insoluble. In fact photochemical studies reveal information on the interaction of the excited states with solvent molecules.

The nature of excited states in organometallic systems (Geoffroy and Wrighton 1979) is not well understood as extensive pi-bonding occurs and most of the transitions seem to involve charge transfer processes. It is a long way before the excited state processes of organometallic complexes are understood based on the nature of the knowledge of the excited states.

3. Photochemical reactions of coordination compounds

In the ground state, coordination compounds give rise to either ligand labilisation reactions or redox reactions (Basolo and Pearson 1967). Ligand labilisation leads to aquation, anation or isomerisation reactions. Redox reactions lead to the oxidation or reduction of the metal centre with corresponding changes in the coordinating ligands. In general, photochemical reactions are different from the thermal reactions since the excited states have different electronic structure and as a consequence different geometry and other chemical properties from the ground state.

Absorption of light by ligand field bands produces excited states restricted to metal centred orbitals. From the emission spectral studies depending upon the nature of the transitions involved (for instance $t_{2g} \rightarrow t_{2g}$ or $t_{2g} \rightarrow e_g$ in the octahedral complexes) extent of distortion of the geometry of the excited states from the ground state could be determined. This is schematically illustrated in figure 2 for chromium(III) systems (Kirk 1981). Excitation of ligand field band produces thermal or antithermal products. Not much information is available on the rate of deactivation processes of ligand field excited states. For coordination compounds it appears that in the cases studied thus far the relaxation pathways and their characteristics differ markedly from those observed for organic systems (Porter 1975). Charge-transfer excitation of complexes leads to either ligand labilisation or redox reactions. (Endicott 1975).

4. Electron transfer reactions of metal complexes

Electron-transfer reactions mediated by metal ions have been recognised long ago. The importance of the electron transport in natural systems led Taube (1970) to investigate these reactions systematically. Depending upon the ligands coordinated, the redox potentials of metal complexes vary dramatically as shown in table 1. This property is found utilised in many biological reactions where the same metal ion brings about different types of redox reactions depending upon the nature of the coordinated ligands. Thus, copper or iron is found to undergo large number of enzymatic reactions involving number of metalloenzymes.

Using very simple systems electron-transfer reactions have been classified as inner-sphere or outer-sphere reactions (Reynolds and Lumry 1966):
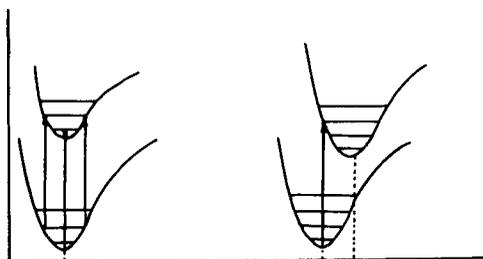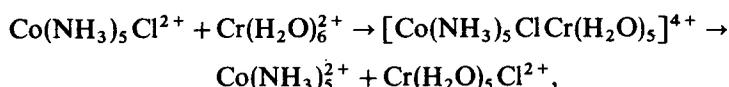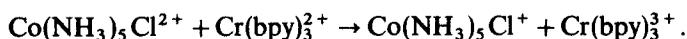
Figure 2. Geometry of the quartet and doublet excited states of chromium(III) complex.

Table 1. Redox potentials of metal complexes depending upon the coordinated ligand.

Couple	Redox potential V
$Fe(H_2O)_6^{3+} + e \text{———} Fe(H_2O)_6^{2+}$	0.77
$Cr(H_2O)_6^{3+} + e \text{———} Cr(H_2O)_6^{2+}$	-0.44
$Fe(bpy)_3^{3+} + e^- \text{———} Fe(bpy)_3^{2+}$	1.05
$Ru(bpy)_3^{3+} + e^- \text{———} Ru(bpy)_3^{2+}$	1.26

Inner sphere

$$Co(NH_3)_5 Cl^{2+} + Cr(H_2O)_6^{2+} \rightarrow [Co(NH_3)_5 Cl Cr(H_2O)_5]^{4+} \rightarrow$$

$$Co(NH_3)_5^{2+} + Cr(H_2O)_5 Cl^{2+},$$

Outer sphere

$$Co(NH_3)_5 Cl^{2+} + Cr(bpy)_3^{2+} \rightarrow Co(NH_3)_5 Cl^+ + Cr(bpy)_3^{3+}.$$

For the same metal ions depending upon whether the reactions are innersphere or outersphere the reaction rate is changed. In the innersphere reactions formation of a bridge between the oxidant and reductant makes energetics of the reaction different from the outer sphere reactions where the electron transfer is not mediated through a bridging ligand. Marcus has proposed a theoretical model for explaining the electron transfer reactions and derived a simplified relationship $k_{12} = (k_{11} k_{22} K_2 f)^{1/2}$ relating the rate constant for the cross-reaction k_{12}, the equilibrium constant K_{12} and the self exchange rate constant k_{11} for the oxidant and k_{22} for the reductant respectively; f is a factor close to unity. For some ground state reactions the electron transfer rate constants are given in table 2.

Bimolecular electron transfer reactions occur in three steps (Chow *et al* 1977)

$$A + B = (AB),$$

$$(AB) = (A^+ B^-),$$

$$(AB) \rightarrow A^+ + B^-.$$
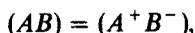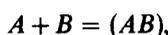
The first equilibrium involves the formation of the precursor complex where no strong interactions occur between the reactants. In the second step the coordination spheres of the reactants are altered to facilitate electron transfer. In the innersphere electron transfer reactions the bridge formation occurs in this step. In the outersphere electron transfer reactions the coordination environment including the solvent sphere around the reactants are altered appropriate to the formation of the activated complex.

5. Reactions from the charge-transfer-to-metal excited states

5.1 *Photochemistry of cobalt(III) complexes*

Cobalt(III) ion with nd^6 configuration forms low spin octahedral complexes which are kinetically inert. Cobalt(III) ammines have well separated charge-transfer and ligand

Table 2. Rate constants for electron transfer reactions in the ground state.

System	Rate constants $(M^{-1} sec^{-1})$
$Cr^{2+} + Cr(NH_3)_5 Br^{2+}$	$5\cdot1 \times 10^{-2}$
$Fe^{2+} + Fe(dipy)_3^{3+}$	2.7×10^4
$Fe(CN)_6^{4-} + IrCl_6^{2-}$	1.9×10^6
$Cr^{2+} + Co(NH_3)_6^{3+}$	$8\cdot9 \times 10^{-5}$
$V^{2+} + Co(NH_3)_5 Br^{2+}$	25
$Ru(NH_6)_6^{2+} + Co(NH_3)_5 Br^{2+}$	1.6×10^3
$Eu^{2+} + Co(NH_3)_5 OH_2^{3+}$	$0\cdot15$
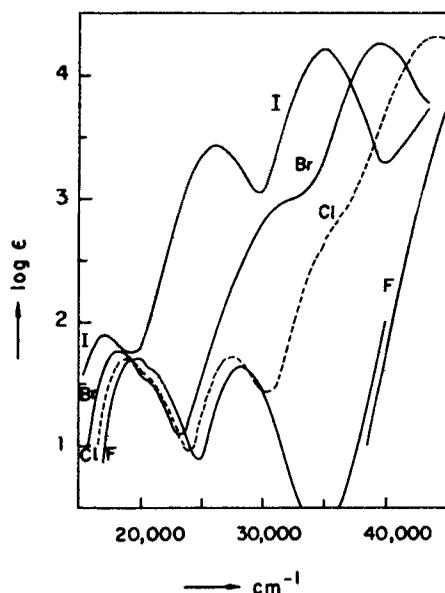
Figure 3. Charge-transfer transitions for $[Co(NH_3)_5 X]^{2+}$, $X = (Cl, Br, I)$ complexes.

field bands, these complexes do not show any emission. The photochemistry of the ammines and acidoammines of cobalt(III) ion has been extensively investigated (Ferraudi *et al* 1975). Depending upon the ease of oxidation of the ligand, CTTM transitions shift as shown in figure 3 for a series of acidoammine complexes. An empirical relationship is derived to relate the absorption band maximum and the electronegativity of the ligand (Jorgensen 1962). Irradiation in the CTTM band of the complex in aqueous solution in general results in the charge transfer to the metal centre which leads to the decomposition of the complex to give redox products. Quantum yields for cobalt(II) for the acidoammine complexes on irradiation at different wavelengths are given in table 3.

The redox reaction occurs exclusively on irradiation in the charge-transfer band; irradiations in the ligand field bands do not produce cobalt(II). The proposed

Table 3. Quantum yield for the reduction of cobalt III amine complexes.

Complex	(nm) of excitation	Quantum yield
$Co(NH_3)_6^{3+}$	254	0·16
$Co(en)_3^{3+}$	254	0·13
$Co(dien)_2^{3+}$	254	0·03
$Co(NH_3)_5Cl^{2+}$	254	0·25
$Cis\ Co(en)_2Cl_2^{+}$	254	0.06
$Co(NH_3)_5N_3^{+}$	254	0·20
$Co(EDTA)^{-}$	254	0.06

mechanism for the photoreduction of cobalt(III) ammines is given by the following scheme (Simic and Lilie 1974):

$$[Co^{III}(NH_3)_5x]^{2+} \xrightarrow{hv} {}^{*}(Co^{III}(NH_3)_5x)^{2+} \ (\text{CTTM})$$

$$\text{CTTM} \longrightarrow (Co^{II}(NH_3)_5 \cdot x),$$

$$(Co^{II}(NH_3)_5 \cdot x) \longrightarrow Co^{II}(NH_3)_5^{2+} + \cdot x,$$

$$Co^{II}(NH_3)_5^{2+} \xrightarrow{H^+} Co(NH_3)_2^{2+} + 3NH_4^+, \ k > 10^6 \ \text{sec}^{-1},$$

$$Co(NH_3)_2^{2+} \to Co(II) + 2NH_4^+.$$
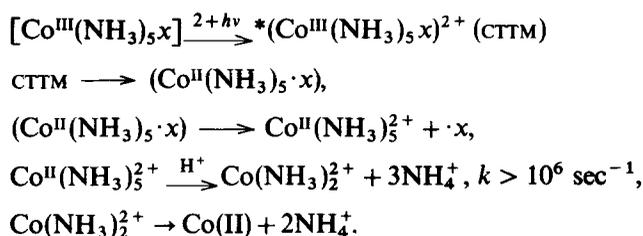
It has also been observed that with polydentate ligands the redox quantum yield decreases compared to the monodentate complexes (Natarajan and Endicott 1973).

One of the important reactions occurring from the charge transfer excited states of cobalt(III) complex is the linkage isomerization reaction. For instance $(Co(NH_3)_5NO_2)^{2+}$ ion on irradiation in the CTTM band produces cobalt(II) and the linkage isomer, (Balzani et al 1968).

$$(Co(NH_3)_5 NO_2)^{2+} \longrightarrow Co(II) + (Co(NH_3)_5ONO)^{2+}.$$

Considerable interest was shown to understand the process by which the nitrite isomer was formed. Scandola et al (1973) carried out the irradiation of the complex in water-glycerol mixtures and suggested that the increased formation of the linkage isomer with the concomitant decrease in cobalt(II) yield as the viscosity of the irradiated solution is due to the geminate radical recombination.

$$((NH_3)_5 Co^{II} \cdot NO_2),$$
$$\downarrow$$
$$(NH_3)_5 Co^{III} - NO_2).$$
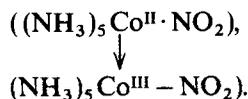
However investigations on the photochemical behaviour of $Co(NH_3)_5 N_3^{2+}$ ion and cis $Co(en)_2 (NO_2)_2^{+}$ ion in highly viscous solutions containing synthetic high polymers or other alcohols did not show evidence for radical recombinations. It was suggested (Natarajan 1977; Arunachalam and Natarajan 1983) that the excited state relaxation process itself is affected by the nature of the medium which affects the quantum yields for products. More recently Natarajan and Radhakrishnan (1982) have studied the photoreaction of the complex cis-$Co(en)_2 (NO_2)_2^{+}$ in neat acetonitrile and compared
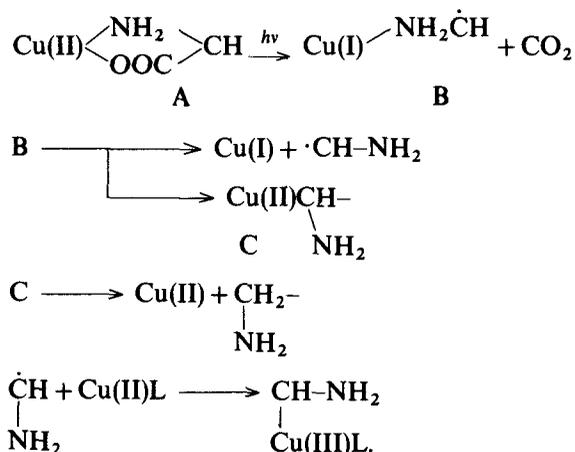
the behaviour with that in aqueous solution. It is indicated that more the hydrophylic environment of the excited state of cobalt(III) complex, cobaltous ion formation is facilitated.

Several attempts to photosensitize cobalt(III) complexes have been made (Gafney and Adamson 1972; Natarajan and Endicott 1973; Navon and Sutin 1974; Demas 1973; Berkoff *et al* 1980). Photosensitization of cobalt(III) complexes gives rise to cobalt(II) ions. However, the mechanism of photosensitization is still ambiguous. Although many early results have indicated that the photosensitization occurs by an energy transfer mechanism later it turned out that reexamination of the systems has shown that the quenching is due to a chemical mechanism in some cases and in other cases both physical and chemical mechanisms of sensitization take place (Kalyanasundaram 1982; Balzani *et al* 1978).

It is also of interest to investigate the extent of communication between different types of excited states. On irradiation in the ligand field bands the quantum yield for redox decomposition is negligibly small (10^{-3}) whereas excitation in the charge transfer region does not lead to aquation or photoanation reactions. It thus appears that higher energy charge transfer excited states do not relax passing through the low lying d–d excited states. The surfaces of the d–d and CTTM states do not seem to cross each other (Ferraudi *et al* 1976).

5.2 *Photoredox reactivity of* CTTM *states of the complexes of* Cu(II) *and other metal ions*

Copper(II) forms kinetically labile complexes which on irradiation in aqueous solution produces copper(I) and ligand radical. The secondary reactions and the lability of copper(II) complexes make the systems more difficult to understand. Copper(II) acetate on irradiation in aqueous solution produces copper(I) and methyl radical (Ferraudi 1978). Flash photolysis studies indicate the formation of methyl radicals. Recently the photochemistry of copper(II) aminoacid complexes has been investigated using flash photolysis technique (Namasivayam and Natarajan 1983; Natarajan and Ferraudi 1981). The primary photochemical reaction involves the formation of copper(I) coordinated to the free radical. The copper I radical species are shown to initiate vinyl polymerisation reactions and steps involved in the photochemistry of copper(II)-aminoacid are shown below.

$$Cu(II){<}{\overset{NH_2}{\underset{OOC}{}}}{>}CH \xrightarrow{h\nu} Cu(I){\nearrow}^{NH_2\dot{C}H} + CO_2$$

$$\quad\quad\quad\quad A \quad\quad\quad\quad\quad\quad\quad\quad B$$

$$B \xrightarrow{} Cu(I) + \cdot CH{-}NH_2$$
$$\quad\quad\quad\quad\longrightarrow Cu(II)\underset{C}{\underset{}{CH-}}{\overset{}{\underset{NH_2}{}}}$$

$$C \longrightarrow Cu(II) + \underset{NH_2}{CH_2-}$$

$$\underset{NH_2}{\dot{C}H} + Cu(II)L \longrightarrow \underset{Cu(III)L.}{CH-NH_2}$$

Studies of polymerisation kinetics have led to the calculation of primary quantum yields for the formation of the copper I coordinated free radical which is difficult to measure directly since secondary reactions enhance the extent of formation of copper(I). Copper(II) complexes with polypyridyl ligands undergo photoreactions to produce copper(I) with low quantum yields (Ferraudi and Muralidharan 1981).

6. Photochemistry from CTTL states

In the case of metal complexes in which the metal is present in low oxidation states and the ligand electron-deficient or aromatic systems intense charge-transfer to ligand transitions have been observed in the visible or near UV region. Excitation of CTTL bands of metal complexes produces CTTL excite states and the photochemistry of these systems has been of much interest in recent years.

Ruthenium(II) ammines form complexes with pyridine and substituted pyridines. $Ru(NH_3)_5 py^{2+}$ (py = pyridine) has absorption maximum in the visible region at 407 nm with molar absorptivity of 7500. The transition is assigned as MLCT and the peak shifts depending upon the substituents on pyridine (Ford 1978). Corresponding ruthenium(III) complexes do not show this band supporting the MLCT assignment for the ruthenium(II) systems.

On irradiation, the complex ion does not undergo redox reaction. On the other hand aquation of pyridine ligand takes place. Flash photolysis of the complex ion produces (Natarajan and Endicott 1972) a transient and the transient has been proposed to have the structure.

$$(NH_3)_5\, Ru\, N\langle\ominus\rangle$$

The intermediate rearranges to assume a π-bonded pyridine with the metal which eventually is replaced by water.

In the polypyridyl complexes of ruthenium(II), osmium(II) and iron(II) charge-transfer-to-ligand transitions have been observed in the visible region. In recent years the photochemistry of these complexes has been investigated in great detail (Sutin 1979). *Tris*(2,2'-dipyridine) ruthenium(II) complex, $Ru(bpy)_3^{2+}$ is a well-known compound which on excitation in the CTTL band produces an excited state with a lifetime of $0.5\,\mu sec$ and whose thermodynamic properties are quite different from those of the ground state. The excited state, $Ru(bpy)_3^{2+}$ serves as a good reducing agent.

7. Photochemistry from the charge-transfer to solvent excited states

Excited states of molecules which involve the surrounding medium have been studied in detail. In particular interactions between the solute and solvents are more in polar solvents and depending upon the polarity of the solvent changes in absorption spectra are observed. One of the well-known systems in which photochemistry from the CTTS excited state occurs is potassium hexacyanoferrite(II) (Matheson 1963). The photochemical reaction is given by

$$Fe(CN)_6^{4-} \xrightarrow[H_2O]{h\nu} Fe(CN)_6^{3-} + e^- (H_2O)$$
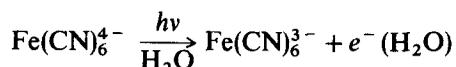
and hydrated electron has been detected by scavenging experiments and in absorption spectra.

8. Excited states as electron transfer reagents

While the redox reactions have been studied extensively the excited state electron transfer reactions have been discovered only in recent years. Pioneering work on excited state electron transfer reactions has been carried out by Weller (1968) and his coworkers in the case of organic molecules. Electron transfer reactions of excited states of transition metal complexes are of particular interest since they are promising for solar energy conversion to fuels or electricity and also for the production of metal ions in unusual oxidation states. In general, excited state electron transfer reactions with a quencher may be given by the scheme.

$$*A + B \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} *A \cdot B \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} [A^+ B^-]$$

$$h^\nu \Big\updownarrow r_0$$

$$A + B \longleftarrow A \cdot B \qquad A^+ + B^-.$$

The rate constant for the excited state electron transfer reaction is given by

$$kq^{\mathrm{obs}} = \frac{k_{12}}{1 + \dfrac{k_{12}}{\Delta v \cdot k_{30}} \exp\left(G_{23}^*/RT\right) + \exp\left(\Delta G_{23}/RT\right)}.$$

One of the most important bimolecular redox reactions involving an excited state of a coordination compound is (Bock 1974)

$$*\mathrm{Ru(bpy)}_3^{2+} + \mathrm{Fe(III)} \rightarrow \mathrm{Fe(II)} + \mathrm{Ru(bpy)}_3^{3+}.$$

The rate constant for the reaction is determined to be 10^9 M^{-1} sec^{-1} in aqueous acidic solution at 25°C. The reaction products are of high energy and they recombine to produce the ground states of the starting materials. The energetics of the $\mathrm{Ru(bpy)}_3^{2+} - \mathrm{Fe(II)}$ system in different oxidation states is given in figure 4. When

Figure 4. Redox potentials (Volts) of the ground and excited states of $\mathrm{Ru(bpy)}_3^{2+}$ ion.

methylviolegen (Whitten 1980) is used as a quencher of $*Ru(bpy)_3^{2+}$ the following reactions take place

$$*Ru(bpy)_3^{2+} + PQ^{2+} \xrightarrow{k_q} Ru(bpy)_3^{3+} + PQ^+,$$

$$PQ^+ + Ru(bpy)_3^{3+} \rightarrow PQ^{2+} + Ru(bpy)_3^{2+}.$$
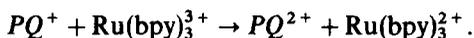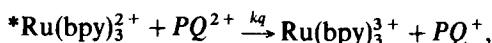
A plot of the electron transfer quenching constant versus reduction potential of the quenchers clearly shows the point at which electron transfer quenching becomes endothermic. From the ground state potential in the same medium, ($E_{1/2}$ for $Ru(bpy)_3^{3+}/Ru(bpy)_3^{2+} = 1\cdot29$ V) it can be seen that photoexcitation increases the oxidising power by $2\cdot10$ V, a value very close to the spectroscopic excited state energy ($2\cdot18$ V) of $*Ru(bpy)_3^{2+}$.

Europium(II) aquo ions (Creutz and Sutin 1976) can reduce the excited state of $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{3+}$ to produce europium(III) ions.

9. Application of photoredox processes in solar energy conversion

Conversion of sunlight to fuel or electricity has received wide attention in recent years (Anon 1981). Much of the activity is related to the photoexcitation of charge-transfer electronic excited states of coordination compounds. Homogeneous photoreactions containing transition metal compounds produce energy-rich compounds. However these products readily recombine in homogeneous solution to give back the starting materials. Research interest in the conversion of solar energy to fuel or electricity centres around the photoredox reactions of the type

$$A + D \rightleftharpoons A^- + D^+,$$

in which $A + D$ are solutes of which one is exited by light. Major problems to overcome before these systems are put to practical use are concerned with the retardation of the back thermal reaction and the production of fuel or electricity using A^- and D^+. Attempts have been made in recent years (Kiwi *et al* 1982) through judicious choice of molecular systems in particular the use of functional electron relays to effect separation of A^- and D^+.
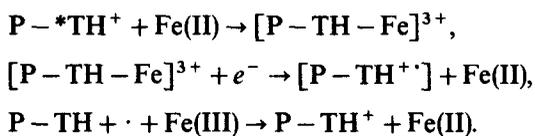
A system which is known for a considerable amount of time is the iron-thionine photogalvanic cell (Wildes *et al* 1977). In this cell moderate photopotential is known to be generated in a homogeneous solution containing iron(II) and thionine on absorption of visible photons. However the efficiency of the cell is very low due to competing energy wasting back reactions shown below.

$$Fe(II) + Th \underset{Fe(III)}{\overset{h\nu}{\rightleftharpoons}} S \rightarrow L.$$
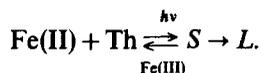
In addition, the solubility of the dye was low in water to use a thin cell which to some extent overcomes the thermal recombination reactions. More soluble thiazine dye derivatives have been shown to increase the efficiency of this photogalvanic cell (Albery 1982).

A different approach was made to condense the thionine dye with a macromolecule and use the macromolecular dye in the photogalvanic cell (Tamilarasan and Natarajan

1981). In homogeneous cell the efficiency did not improve. On the other hand when the polymeric dye was coated to an inert electrode a new type of electrode reaction occurred with appreciable current flow even in fairly thick $(10\,\mu)$ polymer-dye coated electrodes. The following electrode reactions are proposed for the polymer-dye coated electrode (Tamilarasan and Natarajan 1984).

$$P - {}^{*}TH^{+} + Fe(II) \rightarrow [P - TH - Fe]^{3+},$$

$$[P - TH - Fe]^{3+} + e^{-} \rightarrow [P - TH^{+\cdot}] + Fe(II),$$

$$P - TH + \cdot + Fe(III) \rightarrow P - TH^{+} + Fe(II).$$

Photogalvanic cells using $Ru(bpy)_3^{2+}$-iron(III) have also been reported (Lin and Sutin 1976). In homogeneous solution thermal back reactions effectively reduce the efficiency of the cells to very low levels. The knowledge that the excited state of $Ru(bpy)_3^{2+}$ ion can absorb visible light and almost quantitively transfer its excitation energy in a redox reaction has induced enormous activity to use this ion for the development of electrochemical cells to produce electricity or hydrogen splitting water. In recent years Kiwi and Gratzel (1979) have used colloidal catalysts to bring about hydrogen and oxygen formation from water.

$$A^{-} + H_2O \xrightarrow{Pt} \tfrac{1}{2}H_2 + OH^{-} + A$$

$$2D^{+} + H_2O \xrightarrow{RuO_2} 2H^{+} + \tfrac{1}{2}O_2 + D$$
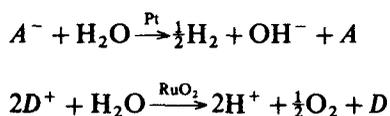
A^{-} and D^{+} were produced in a photochemical reaction.

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