THE PHOTOCHEMISTRY OF INORGANIC COMPLEXES

by

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SUMMARY

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The excited state of the tris bipyridyl ruthenium(II) ion, $Ru(bpy)_3^{2+}$, is known to be theoretically capable of both oxidising and reducing water to oxygen and hydrogen respectively. When this project was started, work had been published by Whitten et al (25) claiming that the photocleavage of water had been achieved by the irradiation of a surfactant derivative of $Ru(bpy)_3^{2+}$. Subsequently, these authors reported (26) that they could not reproduce their original findings. The intention of this research was to investigate what was happening in this system, trying especially to reproduce the photoproduction of hydrogen. Such an achievement where only water is broken down represents a potential means of conversion and storage of solar energy. It was suggested by various authors that this photocleavage of water reported by Whitten et al (25) was due to an impurity acting on its own or in conjunction with the main complex prepared. Several possible impurities were postulated and these compounds were synthesized for irradiation. These complexes were not irradiated as monolayers as in Whitten's arrangement, but were irradiated for the most part in micellar systems. Not all of these complexes were irradiated since attention was diverted towards the rôle of stearic acid used in the preparation of Whitten's monolayer assemblies. Stearic acid and other C_{18} compounds were irradiated with the water soluble as well as the surfactant ruthenium complexes and hydrogen evolution was observed in some cases. These experiments suggest that the hydrogen obtained might have been produced at the expense of the C_{18} compounds employed. By analogy, it may also be said that the hydrogen evolution observed by Whitten et al might have been derived from the stearic acid monolayers supporting the ruthenium complex.

More recently, work has been published claiming the photodissociation of water using microheterogeneous redox catalysts. A preliminary investigation of this system has been undertaken and the findings discussed.

Ru-bpy-complexes Water Photochemical Hydrogen Cleavage

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He is the image of the invisible God, the first-born of all creation; for in him all things were created, in heaven and on earth, visible and invisible . . . . . . all things were created through him and for him. He is before all things, and in him all things hold together.

The letter of Paul to the Colossians, Chap.1 vs 15-17
(R.S.V.)

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Experimental section:-

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FIGURES (cont'd)

ABBREVIATIONS

B.D.E.	The dioctadecyl ester of (4,4'-dicarboxy-2,2'-bpy)
5,5'-B.D.E.	The dioctadecyl ester of (5,5'-dicarboxy-2,2'-bpy)
bpy or 2,2'-bpy	2,2'-bipyridyl
4,4'-bpy	4,4'-bipyridyl
phen.	1,10-phenanthroline
5NP	5-nitro-1,10-phenanthroline
tpy	terpyridyl
py	pyridyl
diMe	dimethyl eg. diMebpy is dimethyl bipyridyl
diClbpy	dichlorobipyridyl
diNO_2bpy	dinitrobipyridyl
$\text{diNO}_2\text{bpyD.O.}$	dinitrobipyridyl dioxide
D.M.F.	dimethyl formamide
D.M.S.O.	dimethyl sulphoxide
E.D.T.A.	ethylenediamine tetra acetic acid
T.E.O.A.	triethanolamine
C.T.A.B.	cetyl trimethylammonium bromide
Fe.A.S.	ferrous ammonium sulphate
P.V.A.	polyvinyl alcohol
S.D.S.	sodium dodecyl sulphate
Pd-C	palladized charcoal
MV^{2+}	the oxidised form of methyl viologen
N.A.D.P.	nicotinamide adenine dinucleotide phosphate
S.C.E.	standard calomel electrode
B.S.A.	bis (trimethylsilyl) acetamide
ether	diethyl ether
2-phos	1,2-bis(diphenylphosphino)ethane
2=phos	cis 1,2-bis(diphenylphosphino)ethylene
V.P.O.	vapour pressure osmomometry
c.m.c.	critical micelle concentration
Ru(COOH)2	(4,4'-dicarboxy-2,2'-bpy)bis(2,2'-bpy) Ru(II)

CHAPTER 1 INTRODUCTION

INTRODUCTION

Solar power as an energy source is currently of great interest as an alternative to fossil fuels and the nuclear industry. Some of the reasons for this must surely be the political instability and the harmful effect on the environment of the energy sources used today. Although advocates of solar energy would not claim that it will be an adequate substitute for many years to come, its supporting rôle in the forms of tidal, wave, wind and geothermal energies could be of great value, especially in the long term.

A form of energy radiated by the sun which is not generally known to be commercially utilizable, is light. This is used by chlorophyll in plants to produce carbohydrates, the overall reaction being:-

$$2H_2O + CO_2 \xrightarrow[xh\nu]{\text{chlorophyll}} O_2 + \frac{1}{n}(CH_2O)_n + H_2O \qquad 1$$

where in green plants $x \simeq 8$ and n is in the region of 6.

In the primary photochemical process, water is split thus:-

$$H_2O \xrightarrow[h\nu]{\text{chlorophyll}} \frac{1}{2}O_2 + 2H^+ + 2e \qquad 2$$

Subsequently these hydrogen ions and electrons are incorporated by NADP to give $NADPH_2$ Efforts have been made by photobiologists to convert these hydrogen ions to hydrogen gas using ferredoxin and hydrogenase. The attempts have been successful to the extent of the production of 1L of H_2/hour/1g of chlorophyll but for only 6 hours (1).

This project is also concerned with the attempt to isolate hydrogen and oxygen from water by light but in this case using appropriate inorganic catalysts instead of chlorophyll. Hydrogen so produced would thus be chemically stored solar power. On combustion energy is released and since only water is produced the system is attractive from an environmental point of view.

PREREQUISITES FOR THE PHOTOCLEAVAGE OF WATER

Several prerequisites for the photocleavage of water have been outlined by Balzani et al (2). One of these is the need for the emission spectrum of the sun to overlap with the electronic absorption spectrum of water. The lowest energy for the unimolecular dissociation of water is 487kJ/mole and corresponds to the formation of molecular hydrogen and atomic oxygen. This energy is equivalent to 245 nm but there is virtually no solar radiation of this wavelength at sea level. Thus direct photodissociation cannot be achieved. On the other hand it is well known that the heat of dissociation of gaseous water into molecular hydrogen and molecular oxygen is only 243kJ/mole. This energy corresponds to a wavelength of 491nm and is in the region of maximum solar power output, (~17 watt m^{-2}. Thus this basic difficulty of the lack of overlap of the sun's emission spectrum with the absorption spectrum of water might be overcome by using properly devised systems in which transition metal complexes are used as catalysts. Many of these absorb in the visible and in various aqueous systems Balzani et al (2) propose four basic chemical cycles by which water may be photodissociated:-

CHEMICAL CYCLES FOR THE PHOTODISSOCIATION OF WATER.

C1 system.

$$X + H_2O \xrightarrow{h\nu} X^+ + H + OH^- \qquad 3$$

$$X^+ + \tfrac{1}{2}H_2O \longrightarrow X + H^+ + \tfrac{1}{4}O_2 \qquad 4$$

$$\tfrac{1}{2}H_2O \xrightarrow{h\nu} H + \tfrac{1}{4}O_2 \qquad \text{net reaction} \qquad 5$$

This cycle requires 361kJ/Nhν, where N is Avogadro's Number. A calculation based on the λ distribution of solar radiation shows that at most only about 1% of the solar energy would be stored. An example of this type of cycle would be the Ce^{4+} / Ce^{3+} couple where the practically determined situation is even worse, the quantum yield of the photoreaction being 10^{-3}. (3)

C2 system.

$$Y + H_2O \xrightarrow{h\nu} Y^- + H^+ + OH \qquad 6$$

$$Y^- + H_2O \longrightarrow Y + OH^- + \tfrac{1}{2}H_2 \qquad 7$$

$$H_2O \xrightarrow{h\nu} \tfrac{1}{2}H_2 + OH \qquad \text{net reaction} \qquad 8$$

The threshold energy for this process (328 kJ/Nhν ≡ 367 nm) is lower than that for the C1 system but is still too high for substantial solar energy conversion. Experiments on this cycle have been carried out using the Eu^{3+} / Eu^{2+} (4) and the Cr^{3+} /Cr^{2+} couples (5). The quantum yields were again found to be very low.

The formation of water derived radicals as in C1 and C2 not only imposes high threshold energies but is also very bad for the efficiency of the system. A hypothetical cycle which does not involve radicals is the C3 system.

$$Z + H_2O \xrightarrow{h\nu} ZO + H_2 \qquad 9$$

$$ZO \longrightarrow Z + \tfrac{1}{2}O_2 \qquad 10$$

$$H_2O \xrightarrow{h\nu} H_2 + \tfrac{1}{2}O_2 \qquad \text{net reaction} \qquad 11$$

The threshold energy for this cycle is 286 kJ/Nhν ≡ 420 nm and it can be shown theoretically that, 6% of the solar energy could be stored. In this case radicals are not formed so that back thermal reactions are much less important. However, a two electron transfer from a metal ion to water can hardly be caused by a photon having such a small amount of energy.

CYCLES INVOLVING BINUCLEAR COMPLEXES

It has been suggested (6) that if the catalyst and the substrate are arranged as in a binuclear co-ordination compound, molecular O_2, H_2O_2 or H_2 is possible in the excited atate without intermediate radical formation. In order to avoid breaking the molecular structure during photolysis, the two metal atoms should be linked together into a macrocyclic ligand. The di-μ-oxotetrakis (2 2' - bpy) di manganese (III,IV)complex has been discussed (7,8) as a possible oxygen generating catalyst in the photodecomposition of water but as can be seen from the equation the reaction is not cyclical:-

$$\left[(\mathrm{bpy})_2\ \mathrm{Mn}\ \mathrm{O}_2\ \mathrm{Mn}\ (\mathrm{bpy})_2\right]^{3+} \xrightarrow{h\nu} \mathrm{O}_2 + \text{unknown reduced products} \tag{12}$$

CYCLES INVOLVING HYDRIDO COMPLEXES

C3' system

$$\text{cis} - \mathrm{ML}_n\,\mathrm{H}_2^{z+} \xrightarrow{h\nu} \mathrm{ML}_n^{z+} + \mathrm{H}_2 \tag{13}$$

$$\mathrm{ML}_n^{z+} + \mathrm{H}_2\mathrm{O} \longrightarrow \mathrm{ML}_n^{(z-2)+} + 2\mathrm{H}^+ + \tfrac{1}{2}\mathrm{O}_2 \tag{14}$$

$$\mathrm{ML}_n^{(z-2)+} + 2\mathrm{H}^+ \longrightarrow \text{cis}\ \mathrm{ML}_n\,\mathrm{H}_2^{\ z+} \tag{15}$$

$$\mathrm{H}_2\mathrm{O} \xrightarrow{h\nu} \mathrm{H}_2 + \tfrac{1}{2}\mathrm{O}_2 \qquad \text{net reaction, } 286\text{kJ} / \mathrm{N}h\nu \equiv 420 \text{ nm} \tag{16}$$

Examples of the first reaction in this sequence have been discovered by G.L.Geoffroy et al (9). The complex cis $[\mathrm{H}_2\ \mathrm{Ir}\ \mathrm{Cl}\ (\mathrm{CO})(\mathrm{P\ Ph}_3)_2]$ is a stable compound but upon irradiation of an inert gas purged solution of the complex, hydrogen is liberated. The same was true of the thermally stable cis $[\mathrm{H}_2\ \mathrm{Ir}\ \mathrm{I}(\mathrm{CO})(\mathrm{P\ Ph}_3)_2]$. The slight modification of the ligands resulted in the hydrogen elimination from some square planar complexes as being very wavelength specific:-

$$\text{cis}\left[\mathrm{H}_2\ \mathrm{Ir}\ (2 - \text{phos})_2\right]^+ \xrightarrow{366\text{nm}} \mathrm{H}_2 \tag{17}$$

$$\begin{tikzcd} \text{cis}\left[\mathrm{H}_2\ \mathrm{Ir}\ (2{=}\ \text{phos})_2\right]^+ \arrow[r, "366\text{nm}"] \arrow[dr, "313/254\text{nm}"'] & \text{no } \mathrm{H}_2 \\ & \mathrm{H}_2 \end{tikzcd} \qquad 18$$

Subsequently, these authors reported (10) the photoinduced elimination of molecular hydrogen from $[\mathrm{Ir\ Cl\ H}_2\ (\mathrm{P\ Ph}_3)_3]$ and $[\mathrm{Ir\ H}_3\ (\mathrm{P\ Ph}_3)_3]$ which are stable under thermal conditions.

Another cycle involving hydrido complexes may be schematized as follows:-

C4 system.

$$\mathrm{ML}_n + \mathrm{H}^+ \xrightarrow{h\nu} \mathrm{ML}_n\ \mathrm{H}^+ \tag{19}$$

$$\mathrm{ML}_n\ \mathrm{H}^+ \longrightarrow \tfrac{1}{2}\left[\mathrm{ML}_n\right]_2^{z+} + \tfrac{1}{2}\mathrm{H}_2 \tag{20}$$

$$\tfrac{1}{2}\left[\mathrm{ML}_n\right]_2^{z+} + \tfrac{1}{2}\mathrm{H}_2\mathrm{O} \longrightarrow \mathrm{ML}_n + \mathrm{H}^+ + \tfrac{1}{4}\mathrm{O}_2 \tag{21}$$

$$\tfrac{1}{2}\mathrm{H}_2\mathrm{O} \xrightarrow{h\nu} \tfrac{1}{2}\mathrm{H}_2 + \tfrac{1}{4}\mathrm{O}_2 \qquad \text{net reaction} \tag{22}$$

Since two photons are used to split one water molecule, the threshold energy is only 143kJ/$Nh\nu$=841nm, so that theoretically, 40% of the solar energy could be stored. A photochemical version of reaction 20 has already been reported (11):-

$$2\left[H\ Ir\ (PF_3)_4\right] \xrightarrow{h\nu} H_2 + \left[(PF_3)_4Ir\text{-}Ir(PF_3)_4\right] \tag{23}$$

and the photochemical version of reaction 21, photoinduced metal-metal bond cleavage, has been obtained for several complexes (12).

TRIS BIPYRIDINE RUTHENIUM(II) $Ru(bpy)_3^{2+}$

Over the last few years this complex, $Ru(bpy)_3^{2+}$, has been intensively studied because of its potential application in the conversion and storage of solar energy. The electron transfer reactions of the excited state were first reported by Gafney and Adamson(13) while Creutz and Sutin (14) were the first to point out that complexes of this nature might be capable of effecting the decomposition of water induced by visible light. Studies have shown that the ground state complex absorbs visible light to form a $d\text{-}\pi^*$ charge transfer excited state which is relatively long lived, lifetime in water-0.6μs, and which undergoes facile electron transfer reactions:-

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu} \left[Ru^{III}(bpy^-)(bpy)_2\right]^{2+} \tag{24}$$

The formation of the excited state can be viewed as the creation of an electron-hole pair within the complex (equ.24) and as aconsequence the excited molecule is expected to be both a stronger reductant and a stronger oxidant than the ground state molecule. This is reflected in the redox potentials shown below:-

Table 1 Redox potentials of ruthenium polypyridine complexes at 25°C

Couple	E^o(V)	References
$Ru(bpy)_3^{3+}$ / $Ru(bpy)_3^{2+}$	+1.26	(15)
$^*Ru(bpy)_3^{2+}$ / $Ru(bpy)_3^{+}$	+0.84	(16,17)
$Ru(bpy)_3^{3+}$ / $^*Ru(bpy)_3^{2+}$	-0.84	(15)
$Ru(bpy)_3^{2+}$ / $Ru(bpy)_3^{+}$	-1.26	(18)

It should be noted from table 1 that ${}^{*}Ru(bpy)_3^{2+}$ is not as good a reductant as $Ru(bpy)_3^{+}$ nor as good an oxidant as $Ru(bpy)_3^{3+}$ but is thermodynamically less stable than either.

From the redox potentials given it can be seen that $Ru(bpy)_3^{3+}$ has the thermodynamic capability to oxidise water to oxygen whilst $Ru(bpy)_3^{+}$ has the capability to reduce hydrogen ions to hydrogen gas:-

$$2H_2O + 4Ru(bpy)_3^{3+} \longrightarrow O_2 + 4H^+ + 4Ru(bpy)_3^{2+} \quad E^o=0.03V, E(pH7)=0.44V \qquad 25$$

$$2H^+ + 2Ru(bpy)_3^{+} \longrightarrow H_2 + 2Ru(bpy)_3^{2+} \quad E^o=1.26V, E(pH7)=0.85V \qquad 26$$

The excited state, ${}^{*}Ru(bpy)_3^{2+}$, in principle, is also capable of reducing water and hydrogen ions to hydrogen gas:-

$$2H_2O + 2\,{}^{*}Ru(bpy)_3^{2+} \longrightarrow H_2 + 2OH^- + 2Ru(bpy)_3^{3+} \quad E^o=0.01V, E(pH7)=0.42V \qquad 27$$

$$2H^+ + 2\,{}^{*}Ru(bpy)_3^{2+} \longrightarrow H_2 + 2Ru(bpy)_3^{3+} \quad E^o=0.84V, E(pH7)=0.43V \qquad 28$$

It may also be seen that these four reactions are strongly pH dependent. In acid solution, irradiation of the complex might be expected to yield a cyclic system utilizing first equation 28 and then equation 25 where two complex molecules would be required to cleave one molecule i.e. a two photon process. Creutz and Sutin (19) found that $Ru(bpy)_3^{3+}$ would oxidise OH^- to O_2 as in equation 30 and proposed another cyclic system as follows:-

$${}^{*}Ru(bpy)_3^{2+} + H_2O \longrightarrow Ru(bpy)_3^{3+} + \tfrac{1}{2}H_2 + OH^- \qquad 29$$

$$Ru(bpy)_3^{3+} + OH^- \longrightarrow Ru(bpy)_3^{2+} + \tfrac{1}{4}O_2 + \tfrac{1}{2}H_2O \qquad 30$$

This again is a two photon process.

One of the main reasons why the above cycle and others have not been successful in obtaining gaseous hydrogen and oxygen is almost certainly that the very fast recombination reaction to water takes place. In addition the transfer of energy from the excited state molecule to a water molecule must compete with other fast quenching reactions e.g.

$${}^{*}Ru(bpy)_3^{2+} + Ru(bpy)_3^{3+} \qquad k=1x10^{8}M^{-1}s^{-1}\ (16) \qquad 31$$

As an example of competing reactions consider the following quenching mechanism:-

$$^{*}Ru(bpy)_3^{2+} + Fe_{aq}^{3+} \xrightarrow{k_q} Ru(bpy)_3^{3+} + Fe_{aq}^{2+} \qquad 32$$

$$Ru(bpy)_3^{3+} + Fe_{aq}^{2+} \xrightarrow{k_t} Ru(bpy)_3^{2+} + Fe_{aq}^{3+} \qquad 33$$

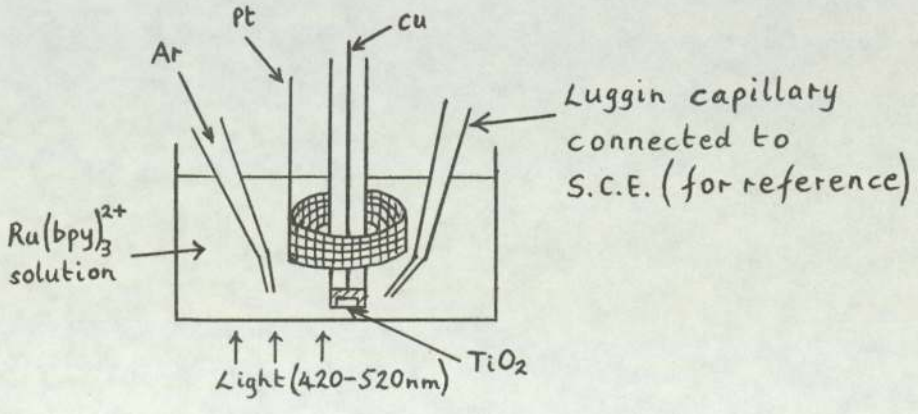
Here the back reaction is relatively slow ($k_t = 4.9 \times 10^6\ M^{-1}\ s^{-1}$) compared with the quenching reaction ($k_q = 2.9 \times 10^9\ M^{-1}\ s^{-1}$) (15). As a consequence appreciable steady state concentrations of $Ru(bpy)_3^{3+}$ and Fe_{aq}^{2+} are attained under continuous photolysis conditions. If, however, $Ru(bpy)_3^{2+}$ is substituted by $Ru(NH_3)_6^{2+}$, the following rate constants are obtained: $k_q = 2 \times 10^9\ M^{-1}\ s^{-1}$ and $k_t = 3.7 \times 10^9\ M^{-1}\ s^{-1}$. In this case steady state concentrations are not obtained. With regard to the back reaction , kinetic systems have been proposed where the gases should be prevented from recombination by generating the hydrogen and oxygen in separate parts of the photolysis vessel:-

PHOTOELECTROCHEMICAL CLEAVAGE OF WATER

a) <u>Semiconductor Electrodes</u>

The photodecomposition with the accompanying separation of hydrogen and oxygen produced might be accomplished in a cell proposed by Creutz and Sutin (19) as shown in figure 1.

Figure 1: Diagram of the electrochemical cell and the electrode arrangement employed by Clark and Sutin (22).



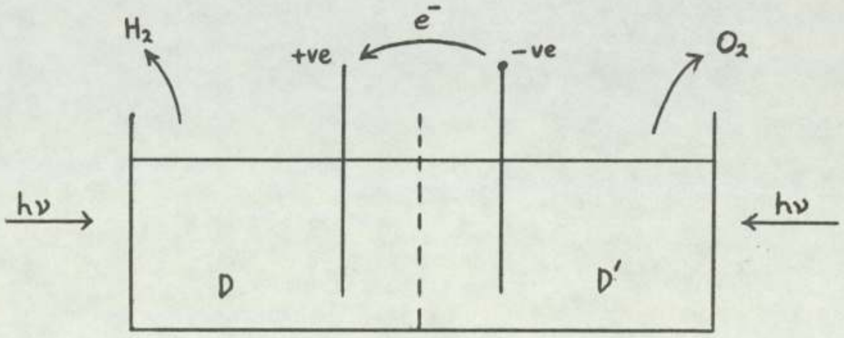
An n-type semiconductor electrode (20,21) is connected to a Pt electrode and both are immersed in a pH 9 buffer containing $Ru(bpy)_3^{2+}$. The semiconductor electrode is illuminated and the $^*Ru(bpy)_3^{2+}$ near the electrode surface injects an electron into the conduction band of the semiconductor. The $Ru(bpy)_3^{3+}$ resulting is then reduced by hydroxide ion to the starting complex with the production of oxygen. The electrons released by the $^*Ru(bpy)_3^{2+}$ flow from the semiconductor electrode through the external circuit to the Pt electrode where they effect the reduction of water (orH^+) to hydrogen. Thiscell was subsequently constructed by the authors and tested (22). They reported the photo-evolution of H_2 but regret that the characteristics of TiO_2 are unsuitable for a solar energy storage system. Other photo-electrode materials which may be satisfactory are $SrTiO_3$,$KTaO_3$ and $KTa_{0.77}Nb_{0.23}O_3$.

In another application, $Ru(bpy)_3^{2+}$ is oxidised by holes generated photochemically in the valence band of an MoS_2 electrode (23). The formation of oxygen then occurs by hydroxide reduction of $Ru(bpy)_3^{3+}$rather than by the oxidation of OH^- at the electrode surface.

b) Photogalvanic cells.

A cell of the type described below, proposed by Lepoutre et al (24) might be used for the photocleavage of water:-

Figure 2 : A photogalvanic cell for the conversion and storage of solar energy.



D and D' are two soluble dyes in solution in water. Both solutions are separated by a diaphragm (ion-selective membrane). Under the action of light, the excited form of D becomes a strong reducing agent capable of reducing water on one side, whilst on the other side, the excited form of D' is capable of oxidising water. If the two electrodes are connected via an external circuit, the current will flow in order to regenerate the oxidised and reduced forms of D and D' respectively. One can write the half reactions for the two processes:-

$$D \xrightarrow{h\nu} {}^{*}D \tag{34}$$

$${}^{*}D + H^{+} \longrightarrow D^{+} + \tfrac{1}{2}H_2 \tag{35}$$

$$D' \xrightarrow{h\nu} {}^{*}D' \tag{36}$$

$$D' + \tfrac{1}{2}H_2O \relbar\relbar D'^{-} + \tfrac{1}{4}O_2 + H^{+} \tag{37}$$

$$D^{+} + D'^{-} \relbar\relbar\relbar D + D' \tag{38}$$

In order to work, such a system requires that the regeneration reaction-38 is spontaneous. This can be obtained by careful selection of photosensitizers having the proper redox potentials, or alternatively by applying a small potential difference between the two electrodes. The authors showed that tetrasulphonated metal phthalocyanins were good photosensitizers for this kind of process. They were originally chosen because they have a structural resemblance to the chlorophyll molecule and they can be synthesized around most transition metals.

MONOLAYER ASSEMBLIES OF SURFACTANT Ru (bpy) $_3^{2+}$

The successful photodissociation of water was apparently realised by Whitten et al (25) who irradiated monolayers of the dioctadecyl ester of the 4,4$'$ dicarboxylic acid derivative of Ru (bpy) $_3^{2+}$ supported on microscope slides immersed in water. A synopsis of their technique is outlined here:-

The complex was dissolved to a known concentration in chloroform and injected onto the water surface in a Langmuir Trough. After the chloroform had evaporated, the complex was left as a monolayer on the water surface. This was compressed by a boom to a pressure of 30 dyn/cm to yield an area/

molecule of 40Å/molecule. The surfactant complex was then transferred onto glass slides coated with six layers of arachidic acid. These underlying arachidic acid monolayers were employed to facilitate the even deposition of the outermost ruthenium complex. The dried slides were mounted in a teflon holder submerged under water in the photolysis vessel and irradiated with a mercury lamp. A steady stream of gas was observed -0.5 cm^3 during a 24 hour period. Analysis of the gas by mass spectrometry and ignition indicated the presence of molecular hydrogen and oxygen.

It may be that by comparison with the water soluble parent complex electrostatic effects and the shielding of the ruthenium centre by the hydrophobic groups inhibited the back reaction:-

$$H_2 + \tfrac{1}{2}O_2 \longrightarrow H_2O \qquad 39$$

sufficiently for the gas to be collected. However the excitement due to this phenomenon was shortlived because soon afterwards these authors reported (26) that they were unable to reproduce their earlier work using a purified sample of their ruthenium complex. They suggested that this may be partially due to the photohydrolysis of the ester group. Several other workers (27, 28, 29, 30) have also tried to reproduce the work of Whitten et al using the same complex and analogues of the complex, but without success. Many reasons have been put forward to account for Whitten's observations, if they are accepted as being correct. Broadly, the discussion about this falls into two categories viz:-

(i) The photoreactivity with respect to hydrogen evolution is due in some way to the physical chemistry of the system. This aspect is primarily concerned with the orientation of the complex molecules on the glass slides and also their rôle in conjunction with the underlying fatty acid layers.

(ii) The photoreactivity with respect to hydrogen evolution is due to either an impurity or the effect of an impurity in conjunction with the main complex. - "the impurity theory". This view was amongst those put forward by Whitten et al and is shared by Creutz and Sutin (16). The reaction of an excited molecule with its parent ground state molecule generally does not proceed spontaneously:-

$$^{*}ML_3^{2+} + ML_3^{2+} \longrightarrow ML_3^{3+} + ML_3^{+} \qquad 40$$

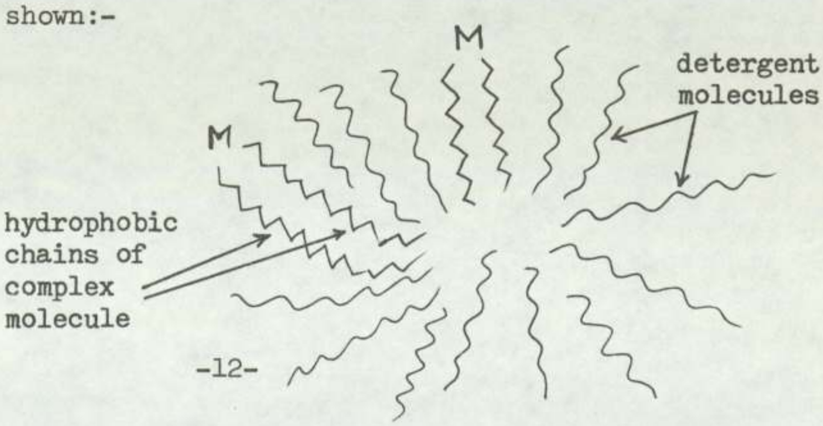
However, this type of reaction can occur if the ground and excited state molecules are different. Thus it has been proposed (16) that a reaction analogous to the above could account for the observations of Whitten et al (25). The presence of $RuL_3'^{2+}$ impurities in the original RuL_3^{2+} sample could have led to the formation of the +1 and +3 complexes which might have produced hydrogen and oxygen in subsequent reactions.

This work by Whitten et al provided a starting point for my research. Since work on surfactant ruthenium complexes using the Langmuir Trough in this department was already being carried out by Dr. Melvyn Cooke (65), it was envisaged that I be concerned with the "impurity theory". To this end, it was proposed that I prepare other ruthenium complexes which might have been formed inadvertently during the synthesis of "Whitten's Complex" and irradiate them in micellar systems. Since other metals (eg. Mn, Pd) were also involved in the preparation of this complex, B.D.E. complexes of these metals were to be made as well those of ruthenium.

MICELLAR SYSTEMS

As an alternative to monolayer assemblies, the irradiation of these B.D.E. complexes may be effected by incorporating the essentially water insoluble material in micelles where the metal ion head, M, is in contact with water and the hydrophobic chains radiate inwards alongside the solubilising detergent molecules. The complex may thus be held in a semi-rigid structure as shown:-

Figure 3:
Radial distribution
of molecules in a
spherical micelle.



The rigid structure of the monolayer assembly, thought to be important for the inhibition of the recombination reaction (eqn.39 on p.11), is thus partially maintained in the micelle. Furthermore it has been postulated (31) that as in monolayer assemblies, electrons can tunnel through micelles from the donor in the centre to the acceptor in the aqueous phase.

It has been shown by Whitten et al (32) that for a series of surfactant "spider complexes" containing three 4,4′- carboxy -2,2′-bpy ligands/Ru the excited state lifetime in acetonitrile is approximately 2μs which is greater than three times the excited state lifetime for Ru $(bpy)_3^{2+}$ - 0.6μs. It is presumed that the excited state of the dioctadecyl ester complex (25,26) also has a relatively long lifetime and may have been a major factor in the photoproduction of hydrogen and oxygen. The excited state lifetime of $Ru(bpy)_3^{2+}$ in aqueous solution (0.6μs) has been found to be increased in micellar solution (0.8μs) (33). In the search for systems in which a large fraction of the excited state energy is trapped and used before dissipation, it seems worthwhile to investigate micellar systems to this end.

Photoredox reactions of the surfactant $Ru(bpy)_3^{2+}$ in micellar solutions have been studied by Kalyanasundaram (34) who effected for the first time, a reaction between a donor-acceptor pair, neither of which absorb in the visible, by steady state irradiation. The reaction sequence is as follows:-

$$^{*}Ru\,L_3^{2+} + MV^{2+} \rightleftharpoons Ru\,L_3^{3+} + MV^{\dot{+}} \qquad 41$$

$$Ru\,L_3^{3+} + cysH \longrightarrow Ru\,L_3^{2+} + cysH^{\dot{+}} \qquad 42$$

$$cysH^{\dot{+}} \longrightarrow cys^{\cdot} + H^{+} \qquad 43$$

$$2cys^{\cdot} \longrightarrow cys - cys \qquad 44$$

where Ru L_3^{2+} is the surfactant derivative; MV^{2+} is methyl viologen, the electron acceptor; cysH is cysteine, the electron donor; and cys-cys is cystine, the final product.

It is unfortunate that he was unable to report the evolution of hydrogen and include the reaction:-

$$MV^{\dot{+}} + H^{+} \longrightarrow \tfrac{1}{2}H_2 \uparrow + MV^{2+} \qquad 45$$

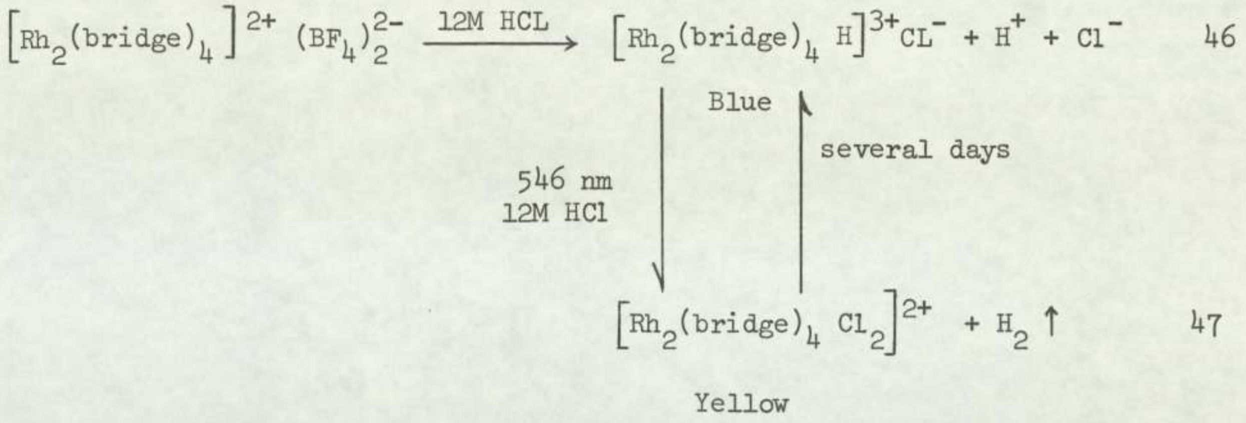
since this reaction is thermodynamically feasible and has been shown to be mediated by enzymes such as hydrogenase (35) and colloidal metals (36, 37).

In order to overcome the major limitation of the fast thermodynamically favourable back reactions of redox products, attention has been focused on the use of multiphase systems. As well as micelles, already mentioned, there include polyelectrolytes (38) lipid vesicles (39) and colloidal metal catalysts such as Pd or Pt. (36, 37).

HOMOGENEOUS SYSTEMS

Before this change of emphasis however, the photoproduction of hydrogen from aqueous homogeneous solutions had been reported for various systems. One of the earliest of these was the simultaneous oxidation and reduction of water to oxygen and hydrogen by Ce (IV) and Ce (III) perchlorates on irradiation with an U.V. lamp (40) and sunlight (41). The effective wavelength is thought to be 254nm for the reduction of water by Ce (III) perchlorate whilst the oxidation of water by Ce (IV) perchlorate is a dark reaction. The system is a Cl cycle as designated by Balzani et al (2)(mentioned earlier, P.3). Although the quantum yield of this reaction with respect to hydrogen evolution is only 0.0007, it was considered worthy of further investigation here from the point of view of increasing the quantum yield, particularly with the aid of tris bpy Ru (II)type complexes.

The photoevolution of hydrogen from a rhodium bridged dimer reported by H.B. Gray et al (42) received wide attention and even T.V. coverage! The reaction is shown below:-



$$\left[Rh_2(\mathrm{bridge})_4\right]^{2+}(BF_4)_2^{2-} \xrightarrow{\text{12M HCL}} \left[Rh_2(\mathrm{bridge})_4\ H\right]^{3+}CL^- + H^+ + Cl^- \qquad 46$$

$$\begin{tikzcd}[row sep=large] \left[Rh_2(\mathrm{bridge})_4\ H\right]^{3+} \text{ Blue} \arrow[d, shift right, "\substack{546\ nm \\ 12M\ HCl}"'] \\ \left[Rh_2(\mathrm{bridge})_4\ Cl_2\right]^{2+} + H_2\uparrow \arrow[u, shift right, "\text{several days}"'] \end{tikzcd} \qquad 47$$

Yellow

The photochemical step at 546nm is akin to the C3′ cycle for a hydrido complex as designated by Balzani et al (2)(mentioned earlier P.5):-

$$cis\text{-}ML_nH_2^{z+} \xrightarrow{h\nu} ML_n^{z+} + H_2 \qquad 13$$

Unfortunately,the subsequent steps of oxidation of water and the incorporation of H^+ to reform the complex are not reported. Instead,the complex is regenerated on standing in the presence of hydrogen.

The photoproduction of hydrogen has been reported from aqueous solutions at the expense of the consumption of various organic molecules.

Brandys and Stein (43) reported the evolution of hydrogen from aqueous solutions of europium ions. This reaction is designated as a C2 cycle by Balzani et al (2) (mentioned earlier P.4).

$$Eu^{3+}(H_2O) \underset{}{\overset{h\nu}{\rightleftharpoons}} Eu^{2+}(H_2O)_{n-1} + H^+ + {}^{\bullet}OH \qquad 48$$

$${}^{\bullet}OH + RH_2 \longrightarrow H_2O + {}^{\bullet}RH \qquad 49$$

$$Eu^{2+}(H_2O) \xrightarrow{h\nu} Eu^{3+} + OH^- + {}^{\bullet}H \qquad 50$$

$${}^{\bullet}H + RH_2 \longrightarrow H_2\uparrow + {}^{\bullet}RH \qquad 51$$

$${}^{\bullet}RH + Eu^{3+} \longrightarrow Eu^{2+} + H^+ + R \qquad 52$$

The hydrogen originates partly in the water and partly in the solute but the net result is:-

$$RH_2 \xrightarrow{Eu^{2+}\ h\nu} R + H_2\uparrow \qquad 53$$

where RH_2 is 2-propanol and R is acetone. The wavelengths of light used here are in the region 200-400 nm and therefore restrict the cycle's utilization as a solar energy storage system.

HETEROGENEOUS SYSTEMS

The transition from homogeneous to heterogeneous processes centres on the evolution of hydrogen at the expense of organic molecules such as T.E.O.A. and E.D.T.A. These reductants react rapidly with $Ru(bpy)_3^{3+}$ but do not quench $*Ru(bpy)_3^{2+}$ significantly. In one system the photolyte is homogeneous before irradiation but hetereogeneous after irradiation. Here it was reported (44) that hydrogen is produced when a mixture of $Ru(bpy)_3^{2+}$, $Rh(bpy)_3^{3+}$ or $Rh(bpy)_2(H_2O)_2^{3+}$, T.E.O.A. and chloroplatinate (IV) is irradiated with visible light. Evidence was presented that the formation of hydrogen occurs via a Rh(III) hydride, $[Rh(bpy)_2H(H_2O)]^{2+}$ which is decomposed by the colloidal Pt formed during the photochemical decomposition of the chloroplatinate (IV). Moradpour et al (45) observed hydrogen evolution from the irradiation of $Ru(bpy)_3^{2+}$, MV^{2+} and E.D.T.A. in the presence of a Pt catalyst. Similar experiments were carried out by Grätzel et al who reported hydrogen production from a homogeneous solution free of Pt (46) and also from a microhetrogeneous solution containing either powdered or colloidal metal catalyst (36). Hydrogen production was considerably greater from colloidal Pd, Ru and Pt than from powdered PdO_2, IrO_2 and Ru. Yields up to 12 litres/day/litre of solution with the colloidal Pt catalyst were obtained. Further to this the same authors published work claiming the cyclic cleavage of water into oxygen and hydrogen, using colloidal RuO_2 (37):-

$$Ru(bpy)_3^{2+} + MV^{2+} \xrightarrow{h\nu} Ru(bpy)_3^{3+} + MV^{+} \qquad 54$$

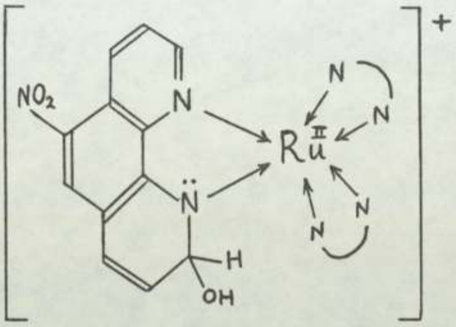
$$Ru(bpy)_3^{3+} + \tfrac{1}{2}H_2O \xrightarrow{\text{colloidal } RuO_2} \tfrac{1}{4}O_2 + H^{+} + Ru(bpy)_3^{2+} \qquad 55$$

$$MV^{+} + H_2O \xrightarrow{\text{colloidal Pt}} \tfrac{1}{2}H_2 + OH^{-} + MV^{2+} \qquad 56$$

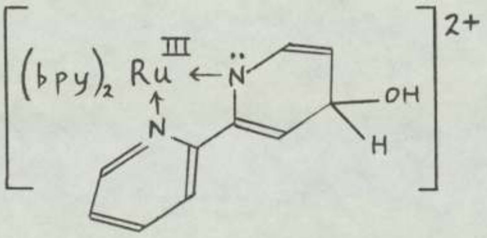
In the 4-quantum process proposed above, the cleavage of water by visible light appears to have been achieved although the authors report a depletion of $Ru(bpy)_3^{2+}$ (<5%) during 3 hours irradiation.

LIGAND AND METAL CO-ORDINATION OF WATER AND HYDROXIDE ION

It has been found that nucleophiles such as CN^- and OH^- can attack co-ordinated ligands (47).Of particular interest is the reversible reaction of tris (5-NO_2-1,10-phen) Ru (II)with hydroxide ion in which a mono-hydroxy compound was shown to be initially formed by addition of OH^- at the 9 position:-

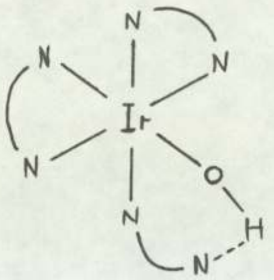


Similar species were proposed by Creutz and Sutin (19) as intermediates in their observation of the oxidation of OH^- to O_2 by $Ru(bpy)_3^{3+}$:-



There is currently widespread debate about the generality of this phenomenon. Several of the earlier claims of such processes made by Gillard's group seem to have been refuted. The relevant data have not yet appeared in print but were presented at the Chemical Society Inorganic Mechanisms Group meeting in December 1980 (Cardiff). Evidence interpreted as showing the formation of a monodentate bpy complex as an intermediate in the photolysis of $Ru(bpy)_3^{2+}$ in aqueous acid solution has been presented by Van Houten and Watts (48). They suggest that a species of this nature, $\left[Ru(bpy)_2\ H_2O\,(bpy)\right]^{2+}$ may provide a mechanism to account for production of hydrogen and oxygen by excitation of monolayer bound $Ru(bpy)_3^{2+}$ reported by Whitten et al (25). Watts et al (49) have also studied an analogous Ir-monodentate -bpy complex:-

They claim that this is also thermodynamically capable of effecting the photochemical cleavage of water:-



$$* \left[Ir(bpy)_2\ OH\ (bpy)\right]^{2+} + H_2O \longrightarrow \left[Ir(bpy)_2\ OH\ (bpy)\right]^{+} + \tfrac{1}{2}H_2O_2 + H^{+} \qquad 57$$

$$\left[Ir(bpy)_2\ OH\ (bpy)\right]^{+} + H^{+} \longrightarrow \left[Ir(bpy)_2\ OH\ (bpy)\right]^{2+} + \tfrac{1}{2}H_2 \qquad 58$$

$$* \left[Ir(bpy)_2\ OH\ (bpy)\right]^{2+} \Big/ \left[Ir(bpy)_2\ OH\ (bpy)\right]^{+} \quad E^{o} = + 1.84V$$

PROPOSALS FOR RESEARCH

Initially it was planned to investigate the work of Whitten et al to find out why their observations were irreproducible. This investigation was to take the form of studies of the irradiation of their surfactant complex in micellar systems, together with the irradiation of other surfactant Ru-bpy and M-B.D.E. complexes (where M = eg Mn, Pd). At the same time, interest was being shown in the rôle of the arachidic acid and cadmium arachidate underlying the surfactant $Ru(bpy)_3^{2+}$ in the monolayer assemblies. This led to the preparation and micellar irradiation of a series of metal stearates with the "Whitten Complex". Success in this area led Dr. Cooke to irradiate dispersions of stearic acid with this complex and the water soluble (4,4′-dicarboxy -2,2′-bpy) bis (2,2′-bpy) Ru (II) complex -Ru(COOH)2. In his work hydrogen and a peak due to an unidentified product were observed from the G.C. analysis. Since there are similarities between the compounds used in this system and one of the polymers used by Grätzel et al (37), it was proposed that attempts be made to reproduce the Grätzel system not only to confirm their photoproduction of hydrogen but more particularly to see whether the G.C. revealed any further peaks which might indicate the breakdown of starting materials.

At one point, the unassigned peak found for the stearic acid/Ru(COOH)2 system was thought to be due to carbon monoxide released from carboxyl group(s) on either stearic acid and/or the diacid-Ru complex. To eliminate the latter possibility an attempt was made to prepare the analogous dinitro complex, because of the similarity between the electron withdrawing properties of these two substituted bpy ligands.

Further, it was proposed that attempts be made to reproduce and even improve on the quantum yield of hydrogen photoproduction from the irradiation of Ce(III) perchlorate reported by Heidt & McMillan (40, 41). It was envisaged that Ru-bpy complexes might be used to achieve this.

Interest has been shown in monodentate — bpy complexes (49,50) from the solar energy conversion point of view. This is probably because it may be advantageous to obtain co-ordination of OH^- or H_2O directly to the central transition metal ion. As a result of this interest, it was proposed that both water soluble and surfactant $[Ru^{II}\ tpybpy\ X]$ complexes be prepared. (X = OH or H_2O). In this way energy-transfer or electron-transfer between co-ordinated OH^- or H_2O and the metal might be achieved, and might then facilitate the photodissociation of water.

CHAPTER 2 DISCUSSION OF THE PREPARATION OF THE COMPLEXES

DISCUSSION OF THE PREPARATION OF THE COMPLEXES

In addition to the discussion of the syntheses of the complexes, the reasons why many of them were prepared is also included.

A. WATER SOLUBLE RUTHENIUM COMPLEXES

a) Tris bipyridyl ruthenium (II) perchlorate

The photochemistry of this complex has been studied intensively for reasons outlined in the Introduction. Accordingly, it was prepared with a view to continuing the study of its photochemistry in various systems (see chapters 3 and 4).

The preparation of this complex and others using ethanol as solvent, is based upon that given by Rose and Wilkinson (51) and Klassen (52) in which the reduction of $RuCl_3 \cdot H_2O$ in alcoholic solution with hydrogen (~2 atm.), in the presence of platinum black is followed by reaction with excess ligand. Here however, and also in the preparation of $[Ru^{II}(5NP)_3](ClO_4)_2$ hydrogen and platinum black were not used. This less vigorous reducing environment might have been responsible for the formation of the presumed Ru(III) species, $[Ru^{III}Cl_4(bpy)]$ (bpyH) and consequently prevented a higher yield of $[Ru^{II}(bpy)_3](ClO_4)_2$ from being obtained. The synthetic route via the reduction of $RuCl_3 \cdot H_2O$ or $K_2[RuCl_5(H_2O)]$ with hypophosphorous acid in the presence of excess ligand (53) was avoided since it has been shown (54) that the product, even after recrystallization, contains ~0.7% of phosphorus impurity, corresponding to a phosphate content of ~0.2%. Whilst this may not be a serious impurity in studying the photochemistry of these complexes, it cannot be neglected in studying their electrochemistry, especially in the presence of semiconductor electrodes (55).

The explosive decomposition of the complex, $[Ru^{II}(bpy)_3](ClO_4)_2$, on heating, precluded its submission for chlorine analysis. This applied to all other perchlorate complexes prepared subsequently.

b) Tris (5-nitro-1,10-phen) ruthenium (II) perchlorate

The complex was prepared in moderate yield with the formation of an additional brown complex analogous to that formed in the preparation of

$Ru(bpy)_3^{2+}$, the C.H.N. of which suggested a Ru(III) species.

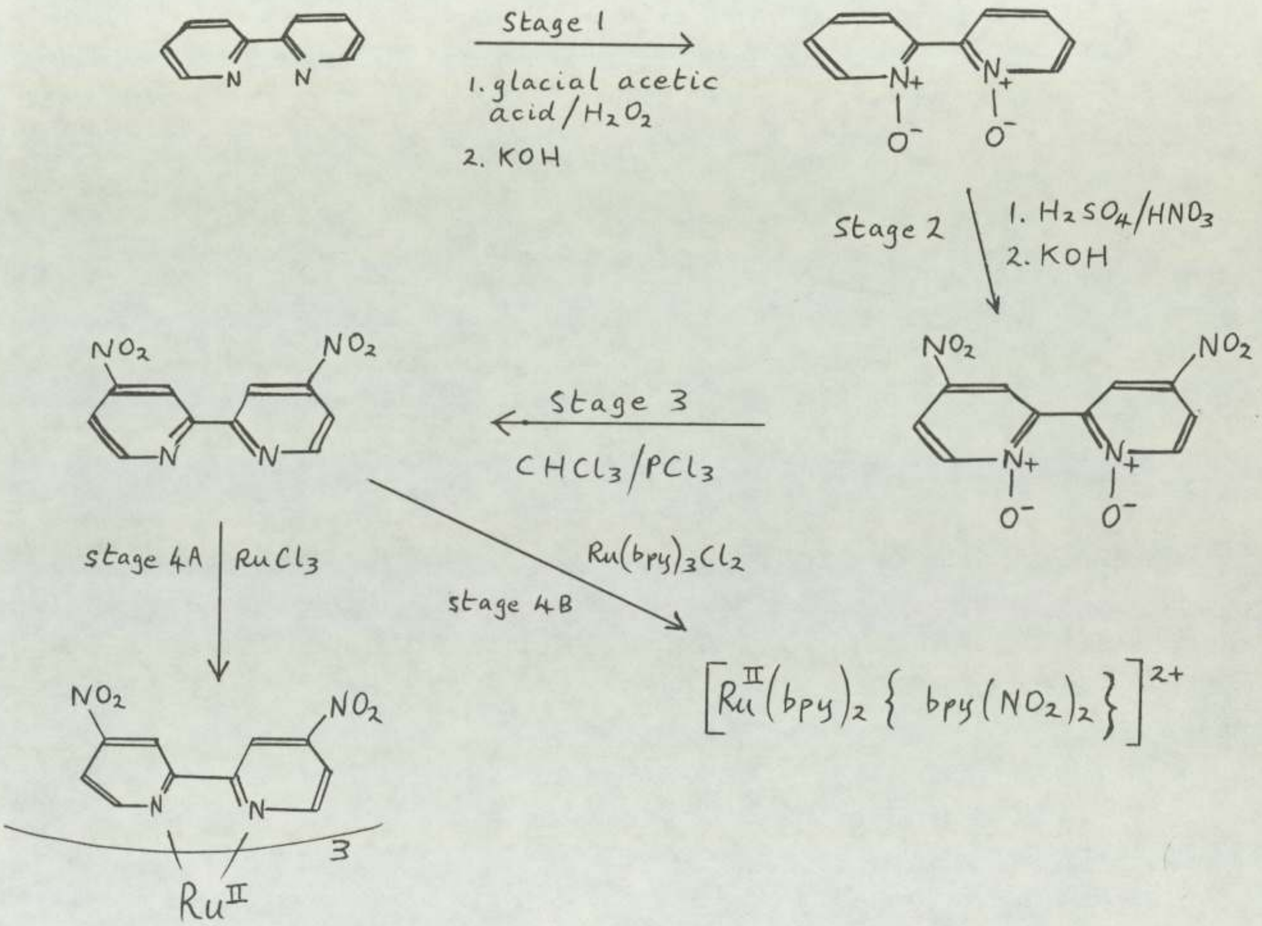
c) (4,4'-dicarboxy-2,2'bipyridyl) bis (2,2'-bipyridyl) ruthenium(II) perchlorate - Ru(COOH)2

Although the yield obtained for the recrystallized complex was only 16.2%, much of the crude complex was available for recrystallization if necessary. The weight of crystalline material obtained, 0.06g, was sufficient for the photochemical experiments carried out. The interesting feature of this perchlorate complex is its high solubility in water. This makes it impossible to precipitate the Ru(II) cation by the addition of ClO_4^-. This is strange because Whitten et al (26) report the precipitation of the Ru(II) cation with PF_6^- . For this reason,as much of the water as possible had to be removed. This was achieved on the rotary evaporator at low temperature by the addition of ethanol to form an azeotropic mixture. Some of the red crystals,which had formed from a concentrated solution of the complex,on standing redissolved! This is almost certainly due to the uptake of moisture from the atmosphere to give an aqueous ethanolic mixture in which the complex is then soluble. The visible spectra of the $-COO^-$ and -COOH species is in accordance with the literature (26) and t.l.c. suggested the complex was pure although the nitrogen analysis could have been better.

Dinitro bipyridyl ruthenium complexes

This section comprises the attempted preparation of $\left[Ru^{II}(bpy)_2\{bpy(NO_2)_2\}\right](ClO_4)_2$ and $\left[Ru^{II}\{bpy(NO_2)_2\}_3\right](ClO_4)_2$. In the last section the preparation of the $\left[Ru^{II}(bpy)_2\{bpy(COOH)_2\}\right](ClO_4)_2$ complex, -Ru(COOH)2, was discussed. This complex in admixture with stearic acid under both U.V. and visible irradiation yielded hydrogen together with one or more unidentified peaks eluted after nitrogen. One of these was thought to be carbon monoxide resulting from the breakdown of one or more carboxyl groups from either the ruthenium complex and/or the stearic acid. To confirm or otherwise the splitting of carbon monoxide from the Ru diacid complex, -Ru(COOH)2, it was proposed that the analogous $diNO_2$ complex be prepared. This complex may react in similar ways to Ru(COOH)2 because of the similarity of the electron withdrawing effects of the two substituted bpy ligands. If the electron withdrawing properties of the bpy ligands is important then it may be worthwhile to prepare the tris diNO_2Ru complex also. The synthetic routes to the two complexes is outlined in fig. 4

Figure 4 The synthetic routes to two diNO_2bpy-Ru complexes



2,2'-bipyridyl-1,1'-dioxide (STAGE 1)

This preparation is based on that given by **Haginawa** (56a) and the product was obtained in good yield and purity.

4,4'-dinitro-2,2'-bipyridyl-1,1'-dioxide (STAGE 2)

On addition of the cooled nitrated mixture to ice, the solution turned green. This has been observed before (57) and may be due to ligand complexation to metal impurities in the ice obtained from tap water. Continued basification with KOH yielded three yellow products designated diNO$_2$bpy D.O. ①, ② and ③ at different pH's. The m.pts. or decomposition points of these compounds was 20-30°C lower than the literature value of 274°C (56a). Nevertheless, all three products were used for the next stage. The isolation of the product was hampered by the co-precipitation of presumably KNO_3 and/or K_2SO_4. It may have been better to use NaOH to basify since $NaNO_3$ is very much more soluble in water than KNO_3. However, anhydrous and hydrated Na_2SO_4 salts exist in four forms some of which being more and some less soluble than K_2SO_4.

4,4'-dinitro-2,2'-bipyridyl (STAGE 3)

The PCl_3 used was yellow and did not fume on exposure to air. Furthermore, on addition to the $CHCl_3$ suspension,since two liquid phases resulted, it was suspected that the PCl_3 was partially hydrolysed. Nevertheless, some of the desired product was obtained, having a decomposition point slightly higher than that quoted in the literature (56b).
The reaction was repeated using recovered material, assumed to be diNO$_2$bpyD.O., and treating with fuming colourless PCl_3 and $CHCl_3$ but no more diNO$_2$bpy was obtained. This indicates that the recovered material might not have been diNO$_2$bpyD.O. after all. In addition to the orange needles of diNO$_2$bpy, some yellow cystals were also obtained. Although the m.pt. for this yellow product is ~30°C lower than for the literature value of 4,4'-dichloro-bpy, 143°C (56a) it is reasonable to suppose that some of this compound would be formed since it is prepared by the action of neat PCl_3 (without $CHCl_3$) on diNO$_2$bpy D.O. The C.H.N.Cl results for the presumed diClbpy obtained are peculiar since the C.H.N. and Cl analyses result from two separate techniques (found C.H.N., <1.0 and Cl, 7.4 whereas cald. Cl, 31.6). There have been compounds for which C.H.N.Cl analyses have been unsuccessful probably due to incomplete vapourization/combustion. A t.l.c. analysis of the presumed diClbpy would have been valuable since one of the three components shown on the

thin layer chromatogram of $diNO_2bpy$ may have been identified as diClbpy. Neither of these two compounds obtained (diClbpy or $diNO_2bpy$) are likely to be dioxides because of the much higher m.pt./decomposition pt. of the latter:-

$$\left.\begin{array}{ll} \text{di Cl bpy 1,1'-dioxide} & 261^{\circ}C \\ \text{di } NO_2 \text{ bpy 1,1'-dioxide} & 274^{\circ}C \end{array}\right\} \quad (56a)$$

d) Tris (4,4'-dinitro-2,2'-bipyridyl) ruthenium(II) perchlorate (STAGE 4A)

The black solid produced during the refluxing of $RuCl_3$ and $diNO_2bpy$ is analogous to the proposed Ru(III) complexes formed during the preparations of $Ru(bpy)_3^{2+}$ and $Ru(5NP)_3^{2+}$ (already mentioned). After thorough washing, the complex analyses to $\left[Ru^{III}Cl_4(diNO_2bpy)\right]$ (diClbpyH). The inclusion of a diClbpy ligand in this complex was considered because of the low % nitrogen found on analysis and the likelihood of the nominally assigned $diNO_2bpy$, containing impurities of diClbpy.

The blue filtrate shown to contain at least 2 components by t.l.c. was eluted through an alumina column using an acetone 50%/water 50% solvent. The purple and blue components were separated and the latter diluted to a volume large enough for visible irradiation in the silica reactor. The homogeneous solution appeared to be $\sim 10^{-6}M$ and no hydrogen was obtained from its irradiation. In retrospect, since the quantity of material was too small to allow more than one irradiation the addition of a dispersion of stearic acid may have been more successful.

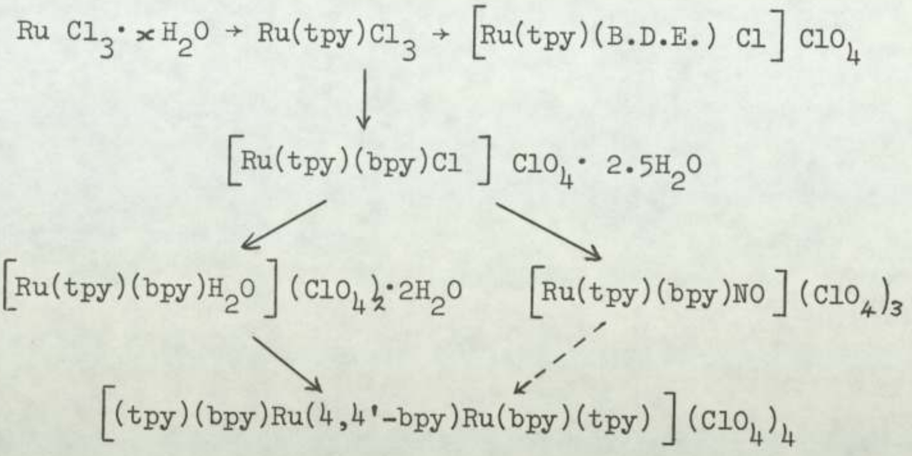
e) (4,4'-dinitro-2,2'-bipyridyl) bis (2,2'-bipyridyl) ruthenium (II) perchlorate

This complex was prepared with little difficulty in reasonable yield and purity.

Ruthenium-Terpyridyl Complexes

In the discussion in the Introduction (P.19), it was suggested that energy or electron transport between co-ordinated OH or H_2O and the central metal ion might be important in achieving the photocleavage of water. To this end, the preparation of a family of complexes having the general formula $[Ru(tpy)(bpy)X]$ was attempted (where X = OH or H_2O). The synthetic routes of these complexes is shown in fig. 5

Figure 5 : The synthetic routes of some Ru-tpy complexes



Trichloroterpyridyl ruthenium (III)

This preparation was carried out several times as more of the complex was required. It appeared that the yield of Rutpy ②, $Ru(tpy)Cl_3$ increased whereas the yield of Rutpy ① decreased the longer the time the $RuCl_3 \cdot xH_2O$/tpy/HCl mixture was allowed to stand. The black water insoluble Rutpy ① was unidentified but may be an oxo-bridged polymeric type of complex: Ru....O....Ru.

f) The dioctadecyl ester of chloroterpyridyl (4,4'-dicarboxy-2,2'-bipyridyl) ruthenium(II) perchlorate

Instead of bpy, B.D.E. was tried in order to make a surfactant Ru-tpy complex for micellar irradiation. Extensive solubility tests were carried out to find a mutual solvent for the refluxing of $Ru(tpy)Cl_3$ and B.D.E. The best appeared to be formalin! Although the B.D.E. is soluble in hot alcohol and $Ru(tpy)Cl_3$ in hot water, the formaldehyde has the effect of reducing the Ru to the Ru(II) state, as indicated by the pink colour of the resulting solution, facilitating the complexation of the bpy type ligand. The C.H.N. of the presumed Ru-tpy-B.D.E. complex is not very convincing particularly with respect to the nitrogen figure. However, the carbon figure is tolerable and as expected is between the experimental values of the starting materials:-

	C%
B.D.E.	77.0
$\left[Ru(tpy)(B.D.E.)\,Cl\right]^+$	58.9
$Ru(tpy)\,Cl_3$	37.3

In addition, the complex was neither soluble nor did it decompose in water. Unfortunately due to interest in other systems this complex was not irradiated.

Chloro terpyridyl bipyridyl ruthenium(II) perchlorate

This complex was prepared as a precursor to both the nitroso and aquo complexes without much difficulty. The C.H.N. figures seem to fit best when assuming 2.5 water molecules of crystallization as proposed by Dwyer et al (59).

Aquo terpyridyl bipyridyl ruthenium(II) perchlorate

This complex was prepared both for irradiation and as a precursor to the bridged dimer. After the removal of the aqueous ethanolic solution on a rotary evaporator, the residual brown complex was taken up in acetone. This red —brown solution was assumed to contain $\left[Ru^{II}(tpy)(bpy)H_2O\right]^{2+}$ and was used without further treatment for the preparation of the bridged dimer. The residual black solid which may have been soluble in a larger volume of acetone, partially dissolved to yield a green solution. Thus the black solid was either a Ru(III) species or the effect of heating with acetone in air converted it to a Ru(III) species. The C.H.N. of the black solid fits well for the Ru(II) complex having two water molecules of crystallization as proposed by Dwyer et al (59). Nevertheless the Ru(III) complex, $\left[Ru^{III}(tpy)(bpy)OH\right](ClO_4)_2\cdot 2H_2O$ would fit equally as well.

Terpyridyl bipyridyl nitroso ruthenium (II) perchlorate

This complex was prepared as a precursor to the bridged dimer.

The preparation of this complex was based on that given by Godwin and Meyer (60).

for the $\left[Ru^{II}(bpy)_2py(NO)\right](PF_6)_3$ complex. Their starting material was $\left[Ru^{II}(bpy)_2(py)_2\right](PF_6)_2$ which was hydrolysed to presumably the $\left[Ru(py)(bpy)_2(H_2O)\right]^{2+}$ complex by refluxing in water. The Ru-tpy-bpy complex used here and treated with $NaNO_2/HCl$ was the unhydrolysed $\left[Ru^{II}(tpy)(bpy)Cl\right]^+$. Indications that the synthesis was going wrong were that the addition of $NaNO_2$ did not turn the solution from red to yellow and the subsequent addition of $NaClO_4$ did not yield golden yellow crystals. Although a tpy rather than a bpy complex was being attempted the colours of the complexes are likely to be similar. A small amount of a yellow compound precipitated during the recrystallization of the crude brown perchlorate complex with ether and acetone was hopeful. However, separation of this yellow component by column chromatography yielded a complex with peculiar CHN results. The red component also separated was probably unreacted or regenerated starting material $\left[Ru(tpy)(bpy)Cl\right]^+$. More success may have been achieved using $\left[Ru^{II}(tpy)(bpy)H_2O\right]^{2+}$ as the starting material which is analogous to $\left[Ru(bpy)_2\ py\ H_2O\right]^{2+}$ used by Godwin and Meyer (60).

The C.H.N. figures for the yellow component are considerably lower than expected for $\left[Ru^{II}tpy\ bpy\ NO\right](ClO_4)_3$ (cald: C,36.6; H,2.3; N,10.3 - found: C, 4.4; H,1.2; N,2.9). Nevertheless, a consideration of the C/H and C/N ratios suggests that the complex may still contain bpy or tpy - possibly just one bpy ligand:-

	cald.	found
C/H	15.9	12.0
C/N	3.6	5.0

g) μ-4,4'-bipyridyl-bis[terpyridyl bipyridyl ruthenium(II)]perchlorate - bridged dimer

The bridged dimer $\left[(bpy)_2(py)Ru(4,4'\text{-}bpy)Ru(py)(bpy)_2\right]^{x+}$ prepared by Powers and Meyer (61) exhibited interesting spectral changes on oxidation of the 4+ complex to the mixed valence 5+ complex. The photochemistry of this type of system may be of interest and it was proposed that the preparation of the analogous $\left[(tpy)(bpy)Ru\ (4,4'\text{-}bpy)Ru(bpy)(tpy)\right]^+$

complex be attempted for such a study. Since the preparation of the nitroso complex had proved unsuccessful, a solution of $[Ru(tpy)(bpy)H_2O]^{2+}$ was used. The desired complex is orange and a very small amount of an orange solid had formed after the reflux but was insufficient to be dealt with further. At this stage additional ClO_4^- was added to ensure electrical neutrality and to effect the precipitation of more of the orange solid.

The aquo complex used, assumed to be $[Ru(tpy)(bpy)H_2O]^{2+}$, was prepared from $[Ru(tpy)(bpy)Cl]ClO_4$ but hydrolysis of the latter to yield an electrically neutral Ru(II) complex would have to be $[Ru^{II}\ tpy\ bpy\ OH]ClO_4$. Hence for a dimer, $[Ru^{II}\text{-bridge-}Ru^{II}]^{4+}$, additional ClO_4^- is required. After tituration with ether, a brown hygroscopic solid rather than a bright orange complex was obtained. Since it was unlikely that this was the desired complex, further purification by column chromatography was not carried out. Although only 1/3 of the refluxed solution was subsequently treated, more success for the preparation of the bridged dimer would probably be achieved by starting again with the nitroso complex prepared from the aquo complex.

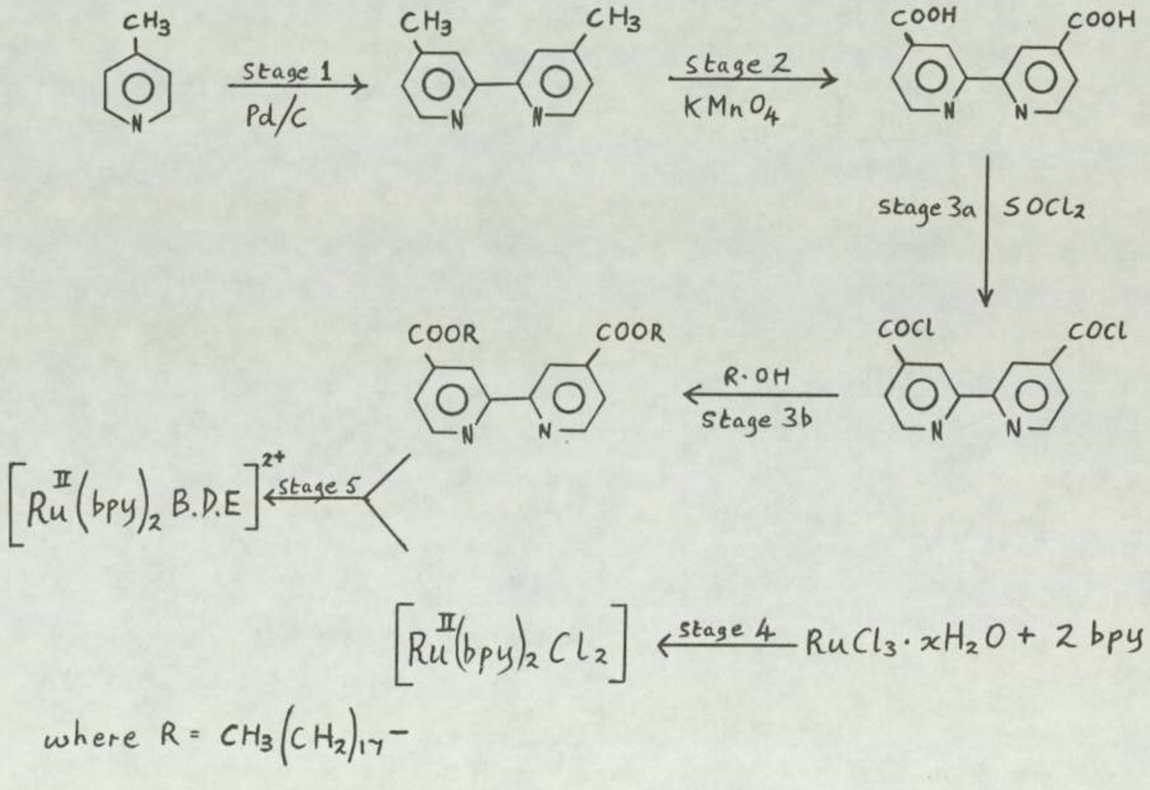
WATER INSOLUBLE RUTHENIUM COMPLEXES

The reasons for the preparation of these complexes have been outlined in the Introduction. The preparation of some of the complexes was attempted because they were thought to be possible impurities in "Whitten's Complex" (26) whilst others were prepared simply as Ru-B.D.E. complexes which might have interesting photochemistry. The $[Ru(tpy)(B.D.E.)Cl]ClO_4$ complex which would normally be included in this section has been discussed in the Ru-tpy section.

a) The dioctadecyl ester of (4,4'-dicarboxy-2,2'-bipyridyl) bis (2,2'-bipyridyl) ruthenium (II) perchlorate - "Whitten's Complex"

The synthetic route is based upon that given by Whitten et al (26) and is shown in fig. 6 .

Figure 6 : The synthetic route of "Whitten's complex"



4,4'-dimethyl-2,2'-bipyridyl (STAGE 1)

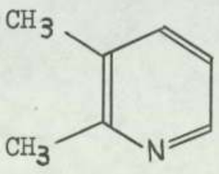
After the dimerisation of γ-picoline a large volume of benzene was added and the reflux continued for a short period. This increase in volume was probably carried out in order to inhibit the crystallization of the product during filtration. The disadvantage of using benzene however is that during the reduction to ~1/3 volume, much of the unreacted γ-picoline available for recovery is distilled over as an azeotrope with benzene. If this is the reason for the use of benzene then another solvent which does not form an azeotrope with γ-picoline ought to be used: e.g. γ-picoline ! Although a filter paper pulp was successful in removing the catalyst under vacuum a straightforward gravity filtration proved effective if carried out at least twice (57) ! Although the recrystallized diMebpy was obtained in low yield (5.1% cf Whitten et al (26) 6.1%) the purity of the compound was high as indicated by the crystallization of a colourless product even before recrystallization. This is in comparison with the larger yields and lower purity obtained using Raney Nickel (62).

4,4'-dicarboxy-2,2-bipyridyl (STAGE 2)

As the diMebpy is oxidised, the $KMnO_4$ is reduced to MnO_2. This latter in turn promotes the autodecomposition of $KMnO_4$ with the corresponding oxidation of water:

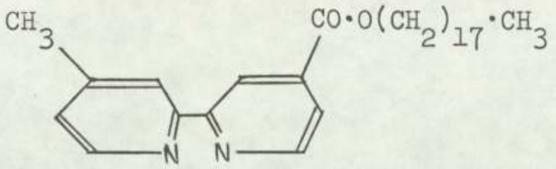
$$H_2O \longrightarrow \tfrac{1}{2}\, O_2 + 2H^+ + 2e \qquad 59$$

The ammonia, noted to be present, almost certainly arises from ring fracture and the high pH observed (pH10) may result from $NH_4 \cdot OH$: the hydrogen ions incorporated for the formation of $NH_4 \cdot OH$ being made available from the oxidation of water (eqn. 59). This ring cleavage has also been observed (63) for the oxidation of 2,3-dimethylpyridine:



$$\xrightarrow{O_3} CH_3\cdot CO\cdot CO\cdot CH_3 + CH_3\cdot CO\cdot CHO + CHO\cdot CHO + NH_3$$

It has been stressed in the Introduction that any impurities in the final Ru-di-ester complex may be important. One of these, already identified by Whitten et al (26) using H.P.L.C., is the Ru-mono-ester complex where the bpy-ester ligand would be:-



The reason for this, suggested by Seddon (64) is undoubtedly the partial oxidation of 4,4'-diMe bpy to give a mixture of the "monoacid" and the "diacid". For this reason the nominally assigned 4,4'-dicarboxy-2,2'-bpy was analysed for the presence of "monoacid". Carboxylic acids are difficult to analyse because of their low volatility, lack of solubility in organic solvents and extensive hydrogen bonding in aqueous solution. Accordingly, it was proposed that the silylated derivative be prepared in order to eliminate these factors. However, on analysis, the presumed silylated compound was discovered to be a mixture of acetamide, formed from the hydrolysis of B.S.A., and the unreacted starting material, the bipyridine-carboxylic acid. Several unsuccessful silylation attempts were made. One reason for this failure may have been the use of insufficiently dry ether, the moisture from which would hydrolyse the B.S.A.

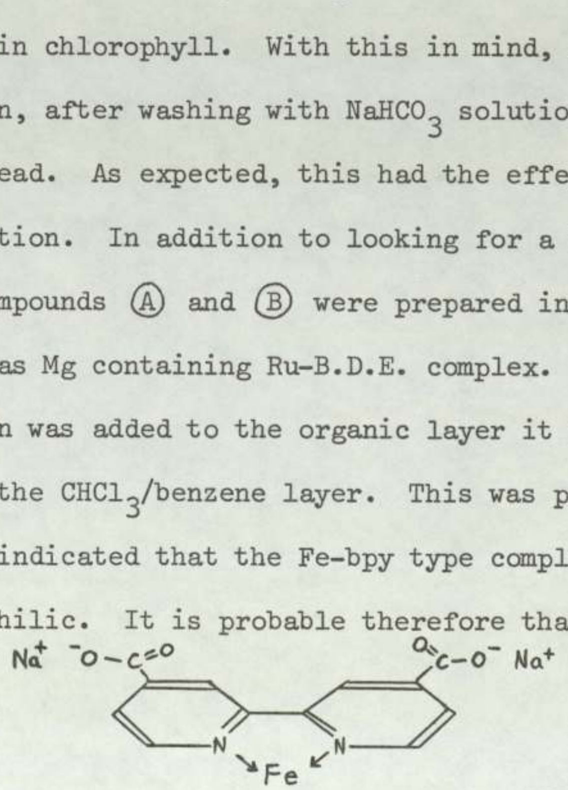
Concurrent with the preparation and analysis of the presumed silylated derivative was the analysis of the bipyridine-carboxylic acid itself. Much conflicting evidence was found at first e.g. for the presumed silylated compound, the mass spectrum suggested the "monoacid" whilst the CHN analysis tallied, very nearly with the "diacid". However, the molecular ion peak of 214 obtained for the presumed silylated derivative can be explained; in that the "monoacid" only appears because it is predictably more volatile than the "diacid". That the compound is mainly "diacid" has been substantiated by titration and n.m.r. analysis of the sodium salt. Both of these giving an average M.Wt. of ~240: this is equivalent to a mixture of the "diacid" (86%) and the "monoacid" (14%). Furthermore, t.l.c. analysis showed the compound to be a mixture of two bipyridine derivatives.

The dioctadecyl ester of 4,4'-dicarboxy-2,2'-bipyridyl (STAGE 3)

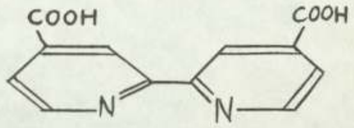
On addition of chloroform to the refluxed solution in a separating funnel, a cloudy solution was obtained. This may have been due to traces of unreacted bpy-diacid insoluble in the chloroform or the precipitation of a small amount of B.D.E., its reduced solubility being due to the presence of traces of water in the chloroform.

This latter idea was tested in the following way:- B.D.E. and octadecanol were dissolved in dry chloroform and traces of water added to the clear solutions. On shaking,the octadecanol solution remained clear whilst the B.D.E. solution became cloudy. Thus, this indicated that the cloudiness of the organic solution prior to extraction with aqueous $NaHCO_3$ was due to B.D.E. although it is likely that there would have been traces of bpy-diacid present as well. After washing with aqueous $NaHCO_3$ the organic layer is obviously saturated with water and therefore the organic solution is predictably cloudy with colloidal B.D.E. The solution was treated with $MgSO_4$ and after shaking and standing filtered to remove suspended $MgSO_4$. But in doing so,much of the B.D.E. also in suspension is lost. It has been shown that $CaCl_2$ used as a drying agent co-ordinates with bpy compounds and is therefore unsuitable. This may also be the case for $MgSO_4$ and it is possible that after filtering off the $MgSO_4$, the organic filtrate may contain traces of Mg-B.D.E. chelate complexes. This may be significant when one considers the key rôle played by Mg in chlorophyll. With this in mind, solution B, half of the organic portion, after washing with $NaHCO_3$ solution,was dried with molecular sieves instead. As expected, this had the effect of reducing the cloudiness of the solution. In addition to looking for a better drying reagent, the two B.D.E. compounds Ⓐ and Ⓑ were prepared in order to provide a Mg free as well as Mg containing Ru-B.D.E. complex.

When the $NaHCO_3$ solution was added to the organic layer it turned pink and considerably more so than the $CHCl_3$/benzene layer. This was presumably due to impurities of iron and indicated that the Fe-bpy type complex formed was more hydrophilic than lyophilic. It is probable therefore that the pink colouration was due to



where the carboxylate ion has the tendency to donate electrons into the ring, increasing the electron density on the Natoms and so facilitating complexation. Acidification of the pink $NaHCO_3$ solution yielded a white precipitate of presumably bpydiacid, after the neutralisation of $HCO_3^{\ominus}$. In this case, the carbox lic acid group has the opposite effect. The tendency to withdraw electrons inhibits complexation and hence the white uncomplexed compound is formed.



T.l.c. of B.D.E. revealed three bpy type compounds of which the component at Rf 0.60 is probably B.D.E., the component at Rf 0.28 probably the monoester and the component left on the base-line is probably a trace of unreacted bpydiacid.

Cis dichlorobis (2,2'-bipyridyl) ruthenium(II) (STAGE 4)

In this preparation an excess of $RuCl_3$ was used to prevent the formation of the tris complex. Ethanol was used as the refluxing solvent instead of D.M.F. reported by Whitten et al (26) because of the difficulty in distilling off the latter after the reflux (b.pt.D.M.F. = 152°C). The orange crystals first formed are presumably $[Ru^{II}(bpy)_2(H_2O)_2]Cl_2$ which on treatment with lithium chloride are converted to the desired purple complex $Ru(bpy)_2Cl_2$. The λmaxima in methanol of 518nm and 360nm appear to be shifted somewhat from those quoted by Whitten et al (26) of 550nm and 375nm in ethanol. This may be due to the presence of the diaquo precursor as an impurity.

a) The dioctadecyl ester of (4,4'-dicarboxy-2,2'-bipyridyl) bis (2,2'-bipyridyl) ruthenium(II) perchlorate (STAGE 5)

The preparation of this complex using B.D.E. Ⓐ (dried with $MgSO_4$) presented no problems and was obtained in good yield and purity. The corresponding Mg free "Whitten Complex" prepared from B.D.E. Ⓑ (dried by molecular sieves) was not in fact carried out.

A surface pressure isotherm for the complex prepared here was obtained (65) giving a value of 82Å^2/molecule. This figure is of the same order as for Whitten's purified perchlorate complex and those quoted by other workers. The isotherm of the original preparation of Whitten et al, which gave H_2 and O_2, yielded a surprisingly low area of ~40Å^2/molecule. In contrast, their perchlorate complex purified by repeated recrystallization gave a value of 85Å^2/molecule, also at 30 dyn/cm. No other group has been able to reproduce the 40Å^2/molecule, the area thought to be critical for water photocleavage.

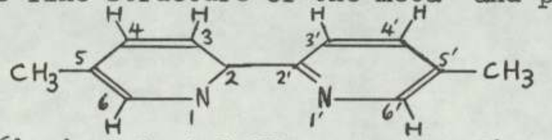
b) The dioctadecyl ester of (5,5'-dicarboxy-2,2'-bipyridyl) bis (2,2'-bipyridyl) ruthenium (II) hexafluorophosphate

A diagram of the synthetic route of this complex can be imagined from that given for the 4,4' analogue on P.**31**. β-picoline is known to be an impurity in γ-picoline and if used as the starting material instead of γ-picoline, the 5,5'-complex would result. This is therefore a possible impurity in "Whitten's Complex" and for this reason it was synthesized.

5,5'-dimethyl-2,2'-bipyridyl (STAGE 1)

This dimerisation was based on that given by Sasse (**66**) using Raney-Nickel. A larger if less pure yield was obtained using this method by comparison with palladized charcoal but a direct comparison cannot be made of the two catalysts because the compounds themselves are different. Indeed, the m.pt. of the 5,5'-diMebpy (111°C) was considerably lower than that obtained for the 4,4'-diMebpy (163°C).

The n.m.r. spectrum is consistent with the product being 5,5'-diMebpy. The splitting of the peaks as recorded represent ortho-interactions although the fine structure of the meta- and para-interactions can just be seen on an expanded spectrum.



6,6'-singlet at 1.55 τ corresponding to 2 protons - no ortho protons.

3,3'-doublet at 1.76 τ corresponding to 2 protons - each of the 3,3' protons having 1 ortho proton.

4,4'-doublet at 2.46 τ corresponding to 2 protons - each of the 4,4' protons having 1 ortho proton.

5,5'-singlet at 7.69 τ corresponding to 6 methyl protons.

5,5'-dicarboxy-2,2'-bipyridyl (STAGE 2)

The preparation of this compound presented no problems and was obtained in very much greater yield (79%) than the corresponding 4,4'-compound (only 10%).

The dioctadecyl ester of (5,5' dicarboxy-2,2'-bipyridyl) STAGE 3

In this case the intermediate compound, the diacyl halide was isolated, m.pt.188°C, before the preparation of the 5,5'-B.D.E. The m.pt. of the latter, 109°C was somewhat higher than that of the corresponding 4,4'-B.D.E., 86°C.

From the n.m.r. spectrum, the integral of the peaks in the region 0.7 - 1.5 τ and the broad peak at 5.6 τ is very small by comparison with that of the singlet at 8.7 τ. Because of this the 6 bpy protons in the region 0.7 - 1.5 τ cannot be used to determine the number of protons responsible for the large singlet at 8.7 τ. The spectrum of this compound is similar to that recorded by Whitten et al (26) for the 4,4'-B.D.E. where they quote 70 protons as being responsible for this large singlet. Using this assignment, the peaks in the region 0.7 - 1.5 τ approximate to 6 and 4 protons respectively which also follow the Whitten et al (26) quotation for the 4,4'-B.D.E. The interesting feature here is the separation of the methylene-groups, α to the carbonyl group at 5.6 τ, from the rest of the aliphatic chain appearing as a single peak at 8.7 τ.

Cis dichlorobis (2,2'-bipyridyl) ruthenium (II) (STAGE 4)

This stage is identical to that for the 4,4' complex and is discussed on P.35.

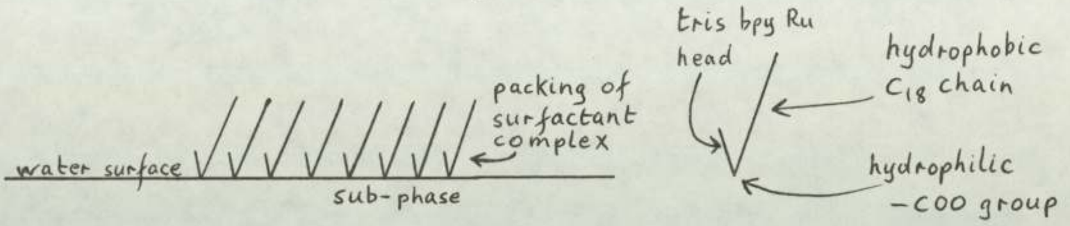
b) The dioctadecyl ester of (5,5'-dicarboxy-2,2'-bipyridyl) bis (2,2'-bipyridyl) ruthenium(II) hexaflurophosphate (STAGE 5)

The hexaflurophosphate complex was prepared in lower yield (43%) than the 4,4'-perchlorate complex (74%) and from the C.H.N. figures it ought to have been recrystallized. Nevertheless, the complex was submitted to Dr.Cooke for photochemical study. Monolayer assemblies on microscope slides were prepared and irradiated following the procedure of Whitten et al (26) in two reactors. In one, irradiation was with visible light and no hydrogen was produced whereas in the other, U.V. irradiation resulted in the evolution of a small amount of hydrogen. This result was inconclusive however because it was later discovered that the photolyte from the UV reactor had previously yielded hydrogen from another set of slides irradiated beforehand.

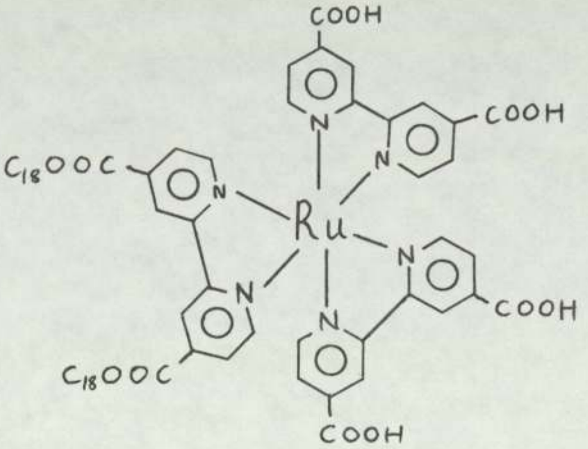
c) The dioctadecyl ester of (4,4'-dicarboxy-2,2'bipyridyl) bis (4,4'-dicarboxy-2,2'bipyridyl) ruthenium(II) hexafluorophosphate

It has been suggested that the monolayer arrangement of the "Whitten Complex" on the water surface in the Langmuir Trough can be visualised as a cluster of ticks ! (✓) :-

Figure 7 : The proposed packing arrangement in a monolayer of "Whitten's Complex"

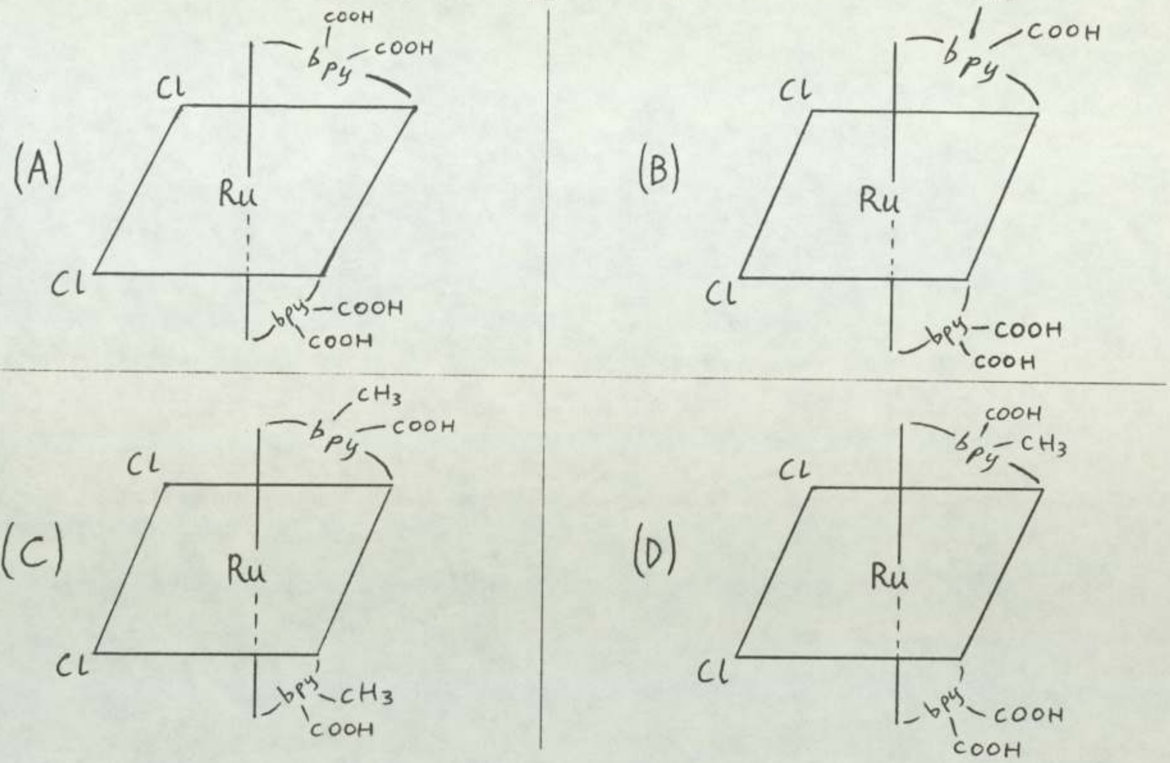


In the search for a monolayer giving an isotherm approximating to 40Å^2/ molecule it was questioned whether the lowering of the tris-bpy-Ru head and the -COO group into the sub-phase would facilitate a closer packing. To this end, it was proposed that the tris-bpy-Ru head be made more hydrophilic by using the bpydiacid instead of bpy. By so doing, the following complex would result:-



The cisdichloro bis (4,4'-dicarboxy-2,2'-bpy) Ru(II) prepared in the 1st stage revealed four spots on t.l.c. analysis. Bearing in mind the probable impurity of the "monoacid" in the "diacid" it can be seen that a sample of the complex (A) might contain:-

Figure 8 A possible composition of a sample of cis dichloro bis (4,4'-dicarboxy-2,2'-bpy) Ru(II).

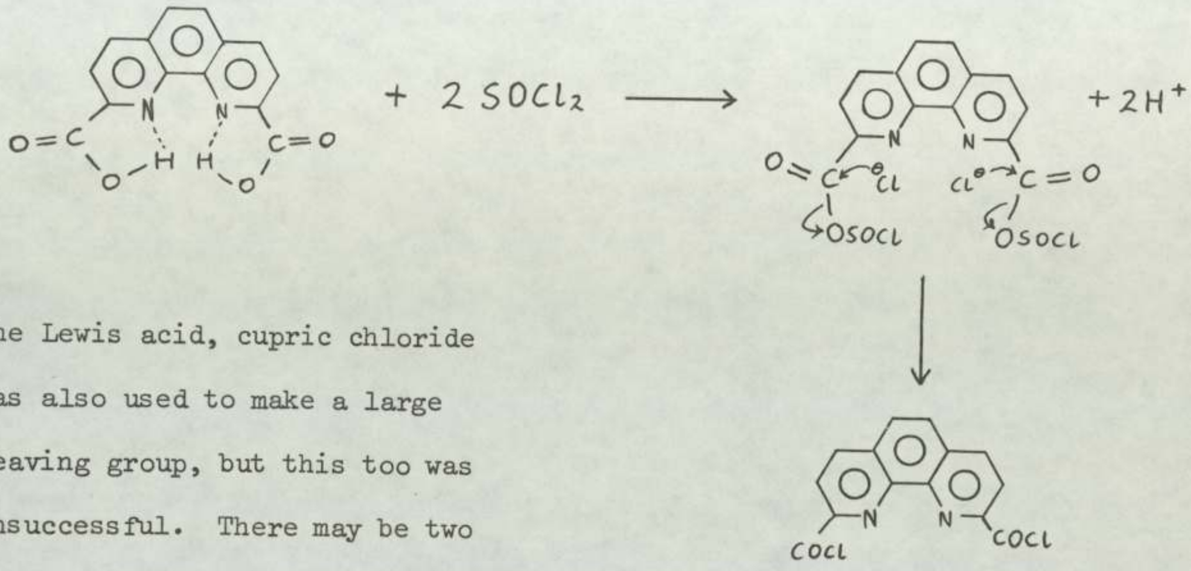


The realisation that (B) is different from (D) leads to the possibility of several more different structures, each of which has an optical isomer. This problem is, of course, also true of the esterified ruthenium complex. T.l.c. analysis was also carried out on the final complex at different stages in its purification. Results of this have not been presented due to the complexity of the analysis and the Rf values were difficult to estimate due to the extensive tailing of the spots. This tailing is characteristic of the t.l.c. of carboxylic acids which exhibit extensive hydrogen bonding with the developing solvent. Furthermore, the carboxyl groups may render some of these complexes soluble in water and therefore impossible to study by surface chemistry. Nevertheless, even after the removal of the water soluble components, a small amount of a water insoluble complex was left and a surface pressure isotherm gave an area of 44Å^2/molecule. Therefore, although the complex had not been characterised, the desired isotherm had been achieved.

d) A dioctadecyl ester of a bis (2,9 -dicarboxy-1,10 -phen) ruthenium complex

The preparation of the diacid of 2,9-diMe-1,10-phen was carried out without any difficulty and obtained in good yield (54%); better than the 4,4'-bpy-diacid (10%) but poorer than the 5,5'-bpy-diacid (79%).

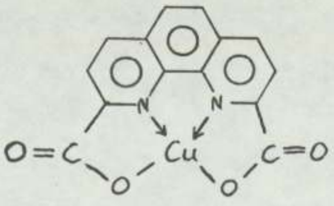
The difficulty encountered was the acylation step. Thionyl chloride is used in order to make the large leaving group - OSOCl :-



The Lewis acid, cupric chloride was also used to make a large leaving group, but this too was unsuccessful. There may be two reasons for this lack of success:

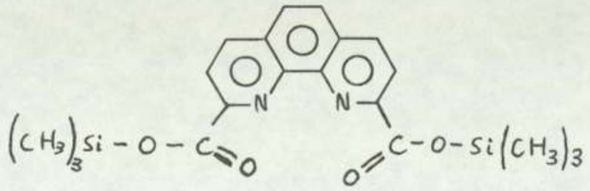
(i) The carboxylic acid groups in positions 2 and 9 on the phenanthroline ring are so placed as to facilitate hydrogen bonding giving rise to a resistant five-membered structure.

(ii) When copper is used, it may be co-ordinated to form a triple ring system:-



In both of these cases, any such ring structures formed will be stable because of the rigidity of the phenanthroline molecule. This would not be the case for the corresponding bipyridine derivative.

A possible route to the diester which has not yet been tried is via the disilylated derivative:-



This would obviate the need for an acylation step.

e) The diocadecyl ester of cis dichloro diaquo (5,5'-dicarboxy-2,2' bipyridyl) ruthenium (II)

The CHN analysis of the complex indicates that only one of the esterified - bpy groups had chelated to ruthenium. Nevertheless, its lack of solubility in water suggests that the compound is an esterified - bpy - ruthenium complex which could be used in surface chemistry studies and micellar systems. Unfortunately, this was not pursued and was not, therefore, subjected to photochemistry.

C. THE ATTEMPTED PREPARATION OF OTHER TRANSITION METAL B.D.E. COMPLEXES

The likelihood of other metal - B.D.E. complexes being present as impurities in the final "Whitten Complex" has already been discussed in the Introduction. Metals which are involved in the preparation are Ni, Pd, Mn and Mg. Palladized charcoal was used for the dimerization of γ-picoline to diMebpy and although not reported it is likely that Raney-Nickel would be employed for the preparation of commercial bpy. Raney-Nickel was used here for the preparation of the 5,5'-diMebpy following the method for the dimerisation of pyridine outlined by Sasse (66) who reported the formation of a petroleum insoluble Ni(II) complex containing 2,2'-bpy and 2,2'-pyrrolylpyridine. $KMnO_4$ was used for the oxidation of diMebpy to the "bpy diacid" whilst $MgSO_4$ was employed as a drying agent in the preparation of B.D.E. Of these only the B.D.E. complexes of Pd and Mn were attempted, Mn being of interest because of its rôle in conjunction with Mg in photosynthesis.

In addition, B.D.E. complexes of Co and Fe were attempted but neither these nor the B.D.E. complexes of Mn and Pd were in fact irradiated due to more pressing avenues of research.

a) PREPARATION OF Mn-B.D.E. COMPLEXES

$[\mathrm{Mn(B.D.E.)_2Cl_2}]\mathrm{Cl}$

For this preparation, water was used in addition to ethanol in order to dissolve the $MnCl_2.4H_2O$ but its presence appeared to inhibit the coordination of B.D.E. to Mn causing the precipitation of unreacted B.D.E. in the cooled solution. Nevertheless, the yellow colour of the solution and solid indicated the formation of a Mn-B.D.E. complex which could be separated from the white B.D.E. on the basis of its different density and by fractional crystallization. The yellow product analyses well for $[\mathrm{Mn^{III}(B.D.E.)_2Cl_2}]\mathrm{Cl}$. The simple $\mathrm{Mn^{3+}_{aq}}$ ion disproportionates in aqueous solution but this oxidation state is stabilised to some extent by complexation. This is exemplified by the acetylacetonate, $\mathrm{Mn(acac)_3}$. However, the complex was prepared under reducing conditions (in ethanol) and analyses well for $[\mathrm{Mn^{II}(B.D.E.)_2Cl_2}]$ or $[\mathrm{Mn^{II}(B.D.E.)_2}]\mathrm{C}$ except for the chlorine figure, (Cl, cald: 4.4%, found: 6.2%).

Tetrahedral complexes of Mn(II) are usually yellow and are unstable in water. The complex prepared here is also kinetically labile with respect to water and as such is therefore unsuitable for aqueous photochemistry.

b) PREPARATION OF Fe-B.D.E. COMPLEXES

$[Fe\ B.D.E.\ (H_2O)_2Cl_2]$

Initially an excess of Fe(III) was used in order to prepare a 1:1 Fe(III)-B.D.E. type complex. Such a case has been observed when $FeCl_3$ is reacted with phenanthroline in glacial acetic acid (67). A yellow complex $Fe(phen)Cl_3$ formulated to contain hexa-coordinate Fe(III), possibly $Fe_2(phen)_2Cl_6$ is obtained. However the direct reaction between aquo-ferric ions and phen. gives a brown material containing two Fe atoms per molecule. In the preparation of a Fe-B.D.E. complex recorded here (P.104) a red solid was precipitated (Fe-B.D.E. ①) which may have been a Fe(III) complex or alternatively a Fe(II) complex since a reducing solvent, Et OH, was used for the reflux. A reasonable fit to the experimental C.H.N. values would be the partially hydrolysed complex, $[Fe\{bpy\ (COO.Et)_2\}(H_2O)_2\ Cl_2]$, but unfortunately, however, the chlorine figures do not tally (Cl, cald: 11.4%, found: 19.9%). This is probably due to the presence of impurities of $Fe\ Cl_3$ in the complex. It is also unlikely to be a B.D.E. complex because of its high solubility in water. The slight solubility of Fe-B.D.E. ②, thought to be $[Fe(B.D.E.)(H_2O)_4](ClO_4)_2$, in water suggests that this is not a B.D.E. complex either. Although the C.H.N. fit for FeB.D.E. ② is not very good it is much better than would be the perchlorate analogue of the $bpy(COOEt)_2$ complex proposed for Fe-B.D.E.-① ....30.8% Carbon. However, even though this ligand does not fit the experimental C.H.N. figures for Fe.B.D.E.-② , there is a remarkable similarity between the C/H and C/N ratios of FeB.D.E. ① and ②:-

	C/H	C/N
FeB.D.E. ①	11.8	7.8
FeB.D.E. ②	11.4	7.7
B.D.E.	7.2	20.6

This indicates that the same ligand is present in both complexes.

The treatment of bpy type ligands in Et OH with Fe(II) resulted in the formation of red complexes of presumably $Fe(bpy/B.D.E.)_3$ for three of the cases tried whereas an excess of Fe(II) reacting with B.D.E. resulted in a purple coloration. This may be due to the formation of a <3:1 ratio of B.D.E.:Fe - possibly a 1:1 ratio. The co-ordination of bpy to a metal is likely to be easier than for B.D.E. because, in concentrated solution, the long hydrocarbon chains on the latter will hinder the 180° rotation about the inter-annular bond necessary to achieve the conformation required for chelation.

c) PREPARATION OF Co-B.D.E. COMPLEXES

(i) $[Co(bpy)_2B.D.E.](NO_3)_3$

Stage 1 Preparation of $[Co(bpy)_2Cl_2]Cl\cdot 3H_2O$

This preparation is based upon that given by Vlček (68), in which during the evaporation of ethanol on a water bath, green needles were supposed to be formed. Instead, an amorphous green flocculent solid was precipitated which is probably the same material. Although this has been designated as the "trans" complex, a violet complex $[Co(bpy)_2Cl_2]Cl.7H_2O$ also designated as trans (69) has now been suggested to be $[Co(bpy)_2(CO_3)]Cl$ (70). According to Vlček (68), after the decantation of the mother liquor from the green needles, slow evaporation should result in the formation of the violet cis isomer. A similar result is reported here and I would suggest that the ethanolic solution of the chlorine precipitated solid be left to evaporate slowly at room temperature rather than on a water bath. In this way, the precipitation of the green complex would probably be avoided so increasing the yield of the desired cis isomer.

Stage 2 Preparation of $[Co(bpy)_2\ B.D.E.](NO_3)_3$

In order to facilitate the co-ordination of B.D.E. to the Co(III) ion, the co-ordinated and counterion chloride was removed by precipitation with $AgNO_3$. The red solution which resulted was probably of the type $[Co^{III}(bpy)_2X]Y$ where either X and Y are both NO_3^- or X is OH^- and Y is NO_3^-. The change in colour of the solution from red to orange is brought about by the expulsion of X and the introduction of B.D.E. The water soluble yellow crystals also formed at this stage analyse well for $\left[Co^{III}(bpy)_2(H_2O)_2\right](NO_3)_3$. The stability of the CoB.D.E. complexes ① and ② in water was much improved upon previously prepared samples whose colour disappeared on standing in the aqueous medium. This is a good indication that a Co-B.D.E. complex had been prepared although the C.H.N. results indicate that the purity, especially of CoB.D.E. ②, could have been considerably better. Clearly, from the method it can be seen that there will be impurities of B.D.E. although the C figures for the calculated value and the experimental value for CoB.D.E. ① are very close (B.D.E. C% = 77.0). After the filtration of CoB.D.E. ①, the resulting yellow solution should only have been partially evaporated. This would have given a far purer product. Why CoB.D.E. ② is soluble in acetone but CoB.D.E. ① is not is difficult to tell.

(ii) $\left[Co^{III}B.D.E.Cl_3H_2O\right]$

Another approach towards the preparation of a Co(III)-B.D.E. complex was via the formation of a Co(II) complex, since chelating ligands give strong M-L bonds facilitating the oxidation to Co(III). Co(II) in ethanolic solution was blue due to the tetrahedral species whereas on treatment with water the octahedral aquo complex is obtained with the precipitation of B.D.E. ie B.D.E. not co-ordinated in aqueous solution. The green -blue solid formed was probably a crude Co(II)-B.D.E. complex which gradually turned orange -brown - indicative of the formation of a Co(III)-B.D.E. complex. Indeed elemental analysis is reasonable for $\left[Co^{III}(B.D.E.)Cl_3(H_2O)\right]$.

d) PREPARATION OF Pd-B.D.E. COMPLEXES

(i) $\left[Pd(bpy)\ B.D.E.\right]Cl_2$

Stage 1 Preparation of $PdbpyCl_2$

In this preparation two complexes were formed having the same C.H.N.Cl analysis yet visibly quite different. It may be that one is indeed $Pd^{II}(bpy)Cl_2$ whilst the other is $\left[Pd^{II}(bpy)_2\right]^{2+}(Pd^{II}Cl_4)^{2-}$, this latter having the same empirical formula. The I.R. spectrum of Pdbpy ① reveals aromatic character and therefore the presence of bipyridyl.

Stage 2 Preparation of $[Pd(bpy)B.D.E.]Cl_2$

The greenish-grey Pd bpy ①, after extraction with acetonitrile, now designated Pd bpy ③, had a similar elemental analysis, ie having slightly low values compared with the calculated value for $Pd(bpy)Cl_2$. This suggests that Pd bpy ① was not a mixture containing a CH_3CN soluble component but a single substance which was partially soluble in CH_3CN. The yellow solution was assumed to contain $[Pd(bpy)\ (CH_3CN)_2]Cl_2$. During the reflux of this with B.D.E., a yellow solid was precipitated from the acetonitrile solution. Since B.D.E. is soluble in hot acetonitrile, neither of the Pd-B.D.E. complexes ① and ② derived from this yellow solid could have been impure B.D.E. Elemental analysis reveals that co-ordinated B.D.E. is absent from Pd B.D.E. ① and indicates that the latter may be unreacted $Pd(bpy)Cl_2$ and since it is relatively insoluble in hot acetonitrile may be akin to Pd bpy ①. The elemental analysis for Pd B.D.E. ② indicates that it is a B.D.E. complex, yet as previously stated it is insoluble in hot acetonitrile. It may be $[Pd\ (B.D.E.)_2]Cl_2$ containing B.D.E. as impurity.

(ii) $Pd\ (B.D.E.)\ Cl_2$

This is another attempt at the co-ordination of B.D.E. to Pd by the replacement of Cl by CH_3CN, and is based upon a method for the analogous Pt complex (71). The reaction of $Pd(CH_3CN)_2Cl_2$ with B.D.E. in $CHCl_3$/acetone in the cold gave a product which after recrystallization analysed well for $Pd\ B.D.E.Cl_2$. This is a more convincing Pd-B.D.E. complex (Pd B.D.E. ③) than Pd B.D.E. ② purporting to be $[Pd\ bpy\ B.D.E.]Cl_2$.

D. THE PREPARATION OF CERIUM, BARIUM, CADMIUM AND MAGNESIUM STEARATES

The preparation of the monolayer assemblies of Ru complexes described by Whitten et al (26) involved the deposition of several layers of arachidic acid on the microscope slide prior to the coating of the outer monolayer of the Ru complex. Arachidic acid was spread on the surface of the water containing Cd ions in the Langmuir Trough. By so doing, much of the arachidic acid was converted to Cd arachidate and the resulting mixture taken up as an arachidic acid/Cd-arachidate monolayer onto the microscope slide. Interest in these fatty acid layers has been shown by Dr.Cooke who irradiated slides prepared by using stearic acid instead of arachidic acid and Ba ions instead of Cd ions in the sub-phase. Such experiments were more successful with respect to the photoproduction of H_2 and O_2 than those with Cd ions. Thus the stearates of Cd and Ba were prepared for both monolayer and micellar irradiation.

Some interesting aspects of Ce/Ru mixtures will be discussed in chap.4. Cerous stearate was prepared in order to extend the photochemical study into micellar systems. It was envisaged that this compound be irradiated with both water soluble and surfactant complexes.

During the preparation of B.D.E., the drying of the product was carried out using both Mg-containing and Mg-free materials because of the possible rôle of Mg in the form a Mg-B.D.E. type compound as an impurity in the final Ru complex. This has already been mentioned with reference to the function of Mg in chlorophyll (P.42). For similar reasons Mg-stearate was prepared.

Unfortunately, of the four stearates prepared, only barium stearate was irradiated.

The preparation of these stearates was straightforward although for two of them, Ce(III) and Mg(II), the yields are too high. The metal salt ought not be an impurity because this would have been dissolved out when the crude stearate was washed. In the case of cerous stearate,if incomplete substitution took place,yielding $Ce(C_{17}H_{35}.COO)_2NO_3$ then the % age yield would be 90%. However, this is not allowed since the compound on analysis revealed no nitrogen. An improvement upon the preparative method would be the washing of the crude and still wettable stearate with hot rather than cold water since although sodium stearate is soluble in cold water it is not wetted at first and therefore dissolves slowly. If sodium stearate is present as a major impurity it may be difficult to leach out because of the mutual attraction of the hydrophobic chains in the sodium and crude stearates.

E. PREPARATION OF HYDROLYSED MALEIC ANHYDRIDE/STYRENE COPOLYMER

It was proposed that an investigation be made into certain aspects of the work of Grätzel and Kalyanasundaram (37) who reported the photocleavage of water using redox catalysts. In their method,they employed the hydrolysed maleic anhydride/styrene copolymer for the stabilisation of a RuO_2 colloid. It was for this reason that the hydrolysed copolymer was prepared.

STAGE 1 PREPARATION OF MALEIC ANHYDRIDE/STYRENE COPOLYMER

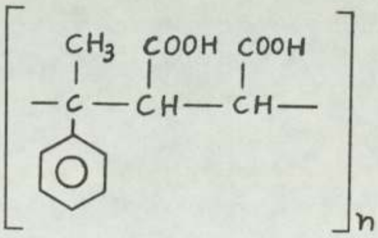
After the violent reaction had taken place, toluene was used mistakenly to dissolve the product. Solubility tests revealed that, in fact, all the starting materials except $ZnCl_2$ were soluble in toluene and benzene but the copolymer was not. Thus the solid mass after the reaction was extracted with benzene. The colloidal nature of the resulting solution may have been due to a small amount of the copolymer or possibly to the partial dissolution of traces of maleic acid resulting from the hydrolysis of any unreacted maleic anhydride present. Any maleic acid left after the Soxhlet extraction would have been dissolved out at the same time as $ZnCl_2$ during the washing with water.

The resulting product is clearly a new material having a m.pt. (310°C - decomposition) considerably higher than any of the organic starting materials. In the I.R., a peak at 3,040cm^{-1} and a sharp peak at 1500cm^{-1} are indicative of aromaticity. Absorptions at 1,720 and 1,785cm^{-1} are expected for two carbonyl groups but the broad absorption in the region 2,300-3,700cm^{-1} indicates the presence of a carboxylic acid. This may be due to some already hydrolysed copolymer or to the presence of a carboxylic acid impurity. This would account for the low percentage of carbon in the C.H.N. analysis. The method of preparation is based upon that given by Breitenbach and Renner (72) who report that the copolymer is soluble in butanone. This was not observed here but it was soluble in dilute alkali and could therefore be hydrolysed.

STAGE 2 PREPARATION OF HYDROLYSED MALEIC ANHYDRIDE/STYRENE COPOLYMER

After the precipitation of the hydrolysed copolymer it was added to water to remove any residual HCl. However, this was not possible since by so doing the hydrolysed polymer partially dissolved to form a sludge which could not be filtered. Thus the mixture was re-acidified and the reprecipitated free acid polymer filtered off.

The percentage of carbon in the product shown by C.H.N. analysis is still low and there is little solubility in 1,4-dioxan. This is contrary to the solubility studies reported by Breitenbach and Renner (72). Nevertheless, V.P.O. confirms the product as a polymer having a M.Wt.of $\sim$7,000. N.m.r. analysis indicates the product to be aromatic from the multiplet centred at $\sim 2.8\tau$. The only aromatic peak shown in the I.R. is at 1500cm^{-1}. The expected peak just above 3,000cm^{-1} appears to have been obscured by the strong broad absorption due to the carboxylic acid groups in the region 2,300-3,700cm^{-1}. Thus it appears that the hydrolysed maleic anhydride/styrene copolymer has been prepared:-

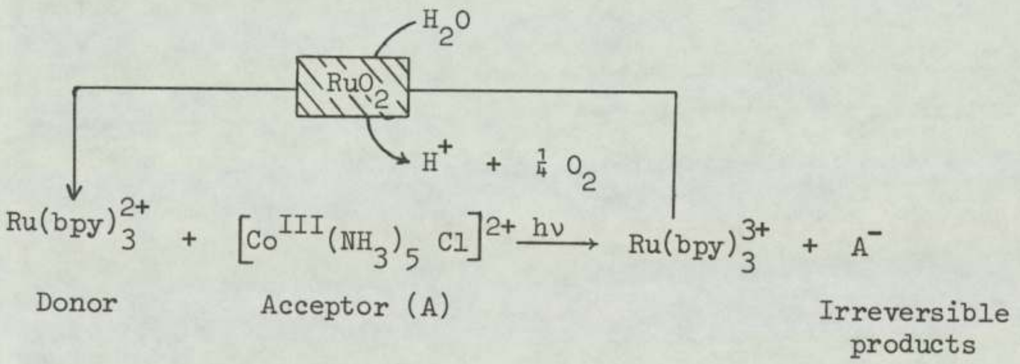


CHAPTER 3 THE IRRADIATION OF WATER SOLUBLE RUTHENIUM COMPLEXES

THE IRRADIATION OF WATER SOLUBLE RUTHENIUM COMPLEXES

A. TRIS BIPYRIDYL RUTHENIUM (II)

The reasons for the choice of $Ru(bpy)_3^{2+}$ for photochemical study have been elaborated in the Introduction. In this work the complex has been irradiated in several systems of which only two were in purely homogeneous media. One of these was essentially a **blank**, the U.V. irradiation of a 10^{-4}M aqueous solution of $Ru(bpy)_3^{2+}$. As expected no changes were observed. However, the U.V. irradiation of the same solution containing additionally cis-$[Co^{III}(bpy)_2Cl_2]Cl$ caused a significant drop in pH from 5.6 → 2.8. A pH change has also been reported (37) for the irradiation of $Ru(bpy)_3^{2+}/[Co^{III}(NH_3)_5Cl]^{2+}/RuO_2$ colloid but in this case the pH increased. This was probably due to the formation of $NH_4.OH$ although it was proposed that H^+ is produced as shown:-



The fate of A^- has also been discussed (13,79) in terms of the following two competing reactions:-

$$Ru(bpy)_3^{3+} + [Co^{II}(NH_3)_5Cl]^+ \longrightarrow Ru(bpy)_3^{2+} + [Co(NH_3)_5Cl]^{2+} \text{ ....the back reaction}$$

$$[Co(NH_3)_5Cl]^+ \xrightarrow{H+} Co^{2+}aq + 5NH_4^+ + Cl^-$$

A similar system may have been achieved for $[Co(bpy)_2Cl_2]Cl$ where there are no NH_3 ligands available to cause an increase in pH. Furthermore, the reduced form of $[Co^{III}(bpy)_2Cl_2]Cl$ is likely to be $Co^{II}(bpy)_2X_2$ (where X is Cl^-, OH^- or H_2O) which would be readily oxidised back to the original Co(III) complex. Since a reduction in pH was observed during the irradiation, presumably due to the formation of H^+, it is not inconceivable that oxygen was produced as well. It may be possible to enhance the effect by the inclusion of a microhetrogeneouscatalyst. A study of the photochemistry of $Ru(bpy)_3^{2+}$ in conjunction with the chelate complex, $CoL(H_2O)_2^{2+}$ in the presence of either ascorbate or Eu_{aq}^{2+} has shown that the photoproduction of hydrogen has also been achieved. (74,75).

Irradiation of heterogenous systems

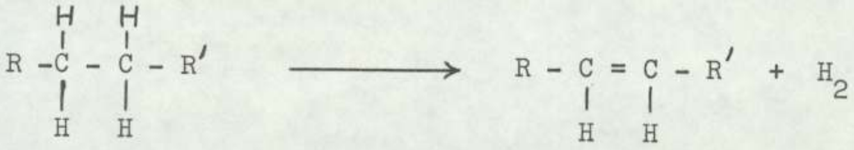
$Ru(bpy)_3^{2+}$ was irradiated with palladised charcoal but no gas was evolved or changes in the solution observed except a slight increase in the absorbance at 224nm. This would normally have been overlooked were it not for the fact that this same observation was noted for the irradiation of a micellar solution of the "Whitten Complex" and palladised charcoal (P.138). Since absorptions in this region are due to the bpy ligands it is possible that they have been affected in some way during the irradiation as a result of the presence of the palladised charcoal. No such differences were observed for the irradiation of aqueous $Ru(bpy)_3^{2+}$ or micellar "Whitten Complex" in the absence of palladised charcoal.

A freeze-thawed sample of an irradiated micellar solution of $Ru(bpy)_3^{2+}$ and barium stearate with U.V. gave a deflection on the G.C. baseline where hydrogen is expected to appear. This would normally have been overlooked were it not for the fact that this was also observed for the irradiation of a micellar solution of the "Whitten Complex" and barium stearate (P.140). This latter solution on standing overnight yielded 7 μL of hydrogen. Unfortunately, the micellar solution of $Ru(bpy)_3^{2+}$ and barium stearate did not produce any hydrogen on standing.

Some of the reasons for irradiating barium stearate and stearic acid have already been mentioned in the Introduction (P.18) and in chap.2 (P.47). Initially a dispersion of stearic acid was irradiated with Ru(COOH)2 by Dr. Cooke using U.V.light. In addition to the production of hydrogen, a peak thought to be carbon monoxide was also observed. It was postulated that this gas was formed from the carboxylic acid groups of either the stearic acid or Ru(COOH)2 or both. To test this, stearic acid was irradiated with $Ru(bpy)_3^{2+}$ in the silica reactor with visible light (P.126) and 0.2μL of hydrogen was produced before degassing. Thus the hydrogen produced here may arise from either a chemical reaction at room temperature, or is solely photochemical or both. The hydrogen produced on hot water degassing this solution was either the release of dissolved hydrogen formed during irradiation or the formation of hydrogen from a chemical reaction enhanced by elevated temperature. The same solution was irradiated and degassed several times with varying amounts of hydrogen produced. The solution was then irradiated at the temperature normally used for degassing. At first a large increase in hydrogen was observed which on further irradiation under the same conditions decreased. The same solution was irradiated several times over a long period in order to either achieve a turnover number of 1 or exhaust the solution. The indications were that the latter was the case particularly because of the continued decrease in hydrogen production. In addition, for the elevated temperature irradiations, an undesignated peak, originally thought to be carbon monoxide was observed. Although this gas has not been identified it is probable that it is a breakdown product of the starting materials. There were other evidences that both $Ru(bpy)_3^{2+}$ and stearic acid were affected. During the irradiation and/or heating an insoluble green material had formed. This is probably a Ru^{3+}-stearate type of complex. Also the cloudy dispersion after the prolonged irradiation was completely clear indicating the breakdown of stearic acid into water soluble components. The drop in pH over the prolonged irradiation does not necessarily indicate the breakdown of starting materials and it is to be noted that the sharpest drop in pH occurred when the most hydrogen was produced.

The above experiment has shown that if the undesignated peak is due to an oxygen containing gas then it must either be derived from the carboxylic acid group in stearic acid or from a carbon fragment and dissolved oxygen. For this reason, $Ru(bpy)_3^{2+}$ was irradiated with octadecane with visible light. Here again hydrogen was produced but without the formation of the insoluble green material as for stearic acid. Thus the carboxyl group is probably involved in the formation of this compound. The release of hydrogen from this system, if not from water, must surely be concomitant with the formation of centres of unsaturation or ring compounds,

eg.



$$R-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-R' \longrightarrow R-\underset{H}{C}=\underset{H}{C}-R' + H_2$$

Conversely, the cleavage of a C-C bond would require the uptake of hydrogen. However, situations may be envisaged for the above two cases where, if oxygen is involved, this need not be so. Octadecane without $Ru(bpy)_3^{2+}$ upon visible irradiation yielded a small amount of hydrogen. This was unexpected and since the amount of hydrogen produced was less than in the previous experiment, one would like to think that this was a spurious result or at best due to traces of $Ru(bpy)_3^{2+}$ adsorbed onto the reactor walls from the previous solution. This $Ru(bpy)_3^{2+}$ free octadecane solution was not hot-water degassed for fear of affecting it adversely prior to the addition of solid $Ru(bpy)_3^{2+}$. Upon irradiation, the resulting solution now containing $Ru(bpy)_3^{2+}$ gave little hydrogen which may have been due to the fact that the octadecane concentration had been increased by a factor of ten. The octadecane concentration was increased in the hope of increasing the hydrogen production but the thicker dispersion which resulted may have been counterproductive, especially if the particle size is important. The solution was maintained at a temperature (35°C) just above that of the m.pt. of octadecane (30°C) such that an emulsion was formed. The irradiation of a particulate dispersion at eg. 20°C however, might have been of value. Although no undesignated peaks, eluting after nitrogen, were observed for octadecane irradiations, further experiments would be required for confirmation.

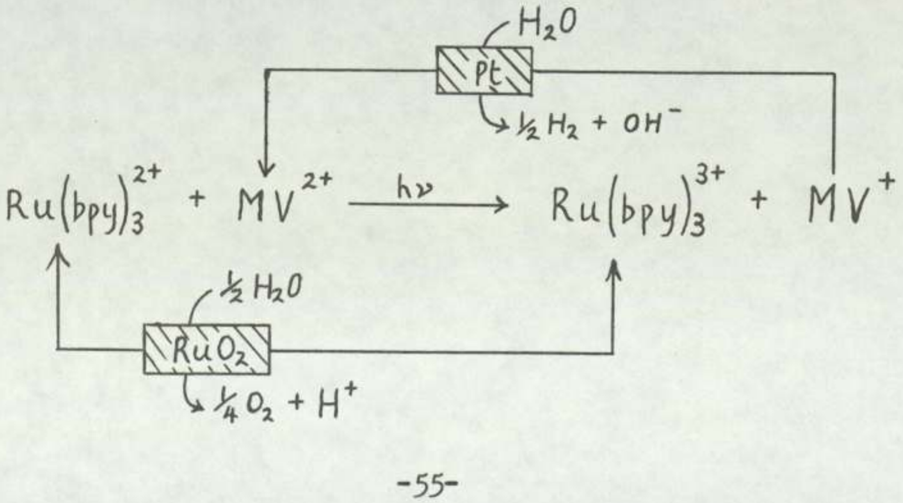
Irradiations with finely divided metal catalysts

This section is concerned with an investigation into the work of Grätzel and Kalyanasundaram (37) who reported the photocleavage of water with redox catalysts. In their photolyte they employed a hydrolysed maleic anhydride/

styrene copolymer for the stabilisation of a RuO_2 colloid. This copolymer contains carboxyl groups and it was suggested by us that during irradiation, in addition to the evolution of hydrogen some gas, tentatively designated as carbon monoxide, might have been produced. Because of its long retention time on the G.C. and since it would not be expected, it was not reported.

Several preliminary experiments were carried out before Grätzel and Kalyanasundarams' photolyte could be reproduced as nearly as possible. The visible irradiation of a dispersion of $Ru(bpy)_3^{2+}$, stearic acid and the solid hydrolysed copolymer produced a trace of hydrogen and a small peak eluted after nitrogen as expected for a $Ru(bpy)_3^{2+}$ /stearic acid mixture. In addition, however, we noted that after degassing there was an increased N_2:O_2 ratio. This reduction in oxygen content had not been observed for $Ru(bpy)_3^{2+}$/stearic acid mixture alone. Also, the photolyte, on standing and/or irradiation became much lighter in colour with the precipitation of an orange solid. This precipitation reaction was reproduced when solid copolymer was added to a solution of $Ru(bpy)_3^{2+}$ which, after centrifugation, was virtually colourless. This did not occur when the hydrolysed copolymer was first dissolved in hot water and then added to the $Ru(bpy)_3^{2+}$ solution. The colloidal orange solution was virtually unchanged after centrifugation. This latter technique appears to have been the one adopted by Grätzel and Kalyanasundaram, but nevertheless, the use of this copolymer might explain their reported depletion of $Ru(bpy)_3^{2+}$ during irradiation.

The components used by Grätzel and Kalyanasundaram and the mechanism they propose for the photocleavage of water are shown below:-



where the Pt exists as a colloid stabilised by P.V.A. and the RuO_2 exists as a colloid stabilised by a hydrolysed maleic anhydride/styrene copolymer.

In the present study $Ru(bpy)_3^{2+}$, MV^{2+}, RuO_2 and Pt were irradiated with visible light giving a small amount of hydrogen and possibly oxygen. This illustrated the feasibility of the reaction without using polymeric materials. From the diagram above it can be seen that all four components are mandatory for the continuous evolution of either hydrogen or oxygen. The continuous evolution of one gas determines the continuous evolution of the other. Some unirradiated solution from this last experiment was filtered and made up such that a mixture of $Ru(bpy)_3^{2+}$, MV^{2+}, RuO_2 and hydrolysed copolymer was irradiated. Surprisingly, a small amount of hydrogen was observed. This may have been due to the inclusion of traces of finely divided Pt carried through during the filtration.

Before the irradiation of this solution, it was degassed with argon. A deliberate bubble of gas was left above the solution and was analysed before and after irradiation. It was hoped that, from a comparison of $N_2:O_2$ ratios, this would give a better indication as to whether oxygen was being produced photochemically. Unfortunately, the analysis of the deliberate bubble yielded a large increase in nitrogen as well as oxygen indicating the outgassing of more dissolved air from the solution. Clearly, this technique could not be adopted if the deaeration were carried out with "white spot" nitrogen which is in any case unsuitable since it was found to contain $0.26\mu L\ H_2/1cm^3$ (260p.p.m.).

Grätzel and Kalyanasundaram reported the production of $0.3cm^3$ of oxygen and $0.6cm^3$ of hydrogen after 3 hours illumination. The present work conducted so far in no way approached these quantities! This was almost certainly due to the way in which the metal catalysts had been prepared. These authors prepared their hydrated RuO_2 colloid from RuO_4. This was probably important since they report that the unhydrated RuO_2 failed to give oxygen. RuO_4 could not be supplied to me because of its high toxicity. Also the Pt colloid they prepared was derived from H_2PtCl_6. In a previous publication (36) they report hydrogen photoproduction from other metal colloids as well as Pt eg.Pd,Ru. Thus since H_2PtCl_6 was unavailable K_2PdCl_6 was used in conjunction with P.V.A. to prepare a Pd sol. A large quantity of hydrogen was used to effect the reduction to metallic Pd. A beam of light was passed through the solution but it was not certain whether a colloid had been formed. Nevertheless, a portion of this solution was taken together with colloidal RuO_2, $Ru(bpy)_3^{2+}$ and MV^{2+} and irradiated but no hydrogen was observed. During the preparation of the colloidal Pt or Pd catalyst hydrogen would be dissolved in the solution and adsorbed onto the particles of metal so produced. Is it to be assumed that the deaeration with nitrogen by Grätzel and Kalyanasundaram prior to irradiation, included the colloidal Pt catalyst and if so would the adsorbed hydrogen be released at this point rather than 3 hours later when the gas above the solution was analysed ?

The reproduction of this system for the photoproduction of hydrogen and oxygen was, for the most part, unrealized. Furthermore, no peak eluted after nitrogen, originally designated as carbon monoxide, was observed. However,if large quantities of hydrogen had been produced, it might have been, since Dr.Cooke has shown that this undesignated peak is more likely to be observed the larger the peak of hydrogen.

B. (4,4'-DICARBOXY-2,2'-BPY)BIS(2,2'-BPY) RUTHENIUM (II) - Ru(COOH)2

The hexafluorophosphate complex of Ru(COOH)2 was prepared by Dr.Cooke who irradiated it with a dispersion of stearic acid and $BaCl_2$ using U.V.light. He obtained hydrogen and an undesignated peak, originally assigned as carbon monoxide. More discussion relating to this is to be found on P.52.
Monolayer assemblies of the "Whitten Complex" deposited on layers of stearic acid where the latter had been taken up from water containing Ba^{2+} ions were found to be successful with respect to the photoproduction of hydrogen (P.47). This interest in the rôle of Ba^{2+} was increased when micellar solutions of the "Whitten Complex" and barium stearate also yielded hydrogen upon irradiation (chap. 5, P.79). For these reasons $BaCl_2$ was included in our irradiations of Ru(COOH)2. The composition of the solution made up by Dr. Cooke, which

yielded hydrogen was reproduced as nearly as possible and irradiated in the silica reactor with visible light. This solution containing Ru(COOH)2, $BaCl_2$, stearic acid, $KHCO_3$ and NH_4 OH gave H_2. The above solution was made up again and the hydrogen photoproduction reproduced. A solution with the above composition was irradiated under reduced pressure in the hope that any hydrogen produced would be liberated from the solution as it was formed. This was unsuccessful as was the irradiation at atmospheric pressure in the absence of a deliberate bubble. Since these systems were producing only very small quantities of hydrogen, deliberate bubbles of air were injected above the photolyte since the hydrogen evolved will be partitioned in favour of the gas rather than the liquid phase. Experiments carried out by Dr. Cooke suggested that the evolution of hydrogen was maximal within the pH range 6.0-6.5. Thus two identical solutions of stearic acid, $KHCO_3$ and the perchlorate complex of Ru(COOH)2 were irradiated at pH6.4 and pH6.3 (Table 15 solutions 9 and 10-P.131),but no hydrogen was observed. However, a trace of hydrogen was obtained for a $BaCl_2$, stearic acid, $KHCO_3$ and Ru(COOH)2 solution buffered with phosphate at 6.7 and also for a homogeneous solution of $BaCl_2$ and Ru(COOH)2 at pH3.2 (Table15 solution 1-P.131).Variations of this last solution (Table 15 solutions 2→7-P.131)including the attempted reproducibility of the $BaCl_2$/Ru(COOH)2 solution (Table 15, solution 8-P.131) all failed to liberate hydrogen upon irradiation.

From these results no clear pattern emerged to indicate which factors were necessary for the photoproduction of hydrogen although the following points may be worthy of consideration. More hydrogen appears to have been evolved where the Ru(COOH)2 is at least 10^{-4}M and also where the volume of photolyte is relatively large i.e. when there is a large quantity of Ru(COOH)2 irradiated. Therefore,the negative result for Ru(COOH)2, stearic acid and $KHCO_3$ (Table15 , solutions 9 and 10-P.131)is probably due to the concentration of Ru(COOH)2 being too low. In addition, it has been suggested that the presence of stearic acid is important, as it is for the irradiation with $Ru(bpy)_3^{2+}$ (P.52), especially since the evolution of hydrogen from solution 1 (Table15 -

P.131) was irreproducible. It is uncertain whether Ba^{2+} is necessary in this system or not. Certainly in the $Ru(bpy)_3^{2+}$/stearic acid system (P.52) it is not.

None of the above irradiations with visible light gave rise to an undesignated peak eluted after nitrogen during G.C. analysis as was the case for the U.V. irradiations of this system carried out by Dr.Cooke. Furthermore, none of these solutions were subject to heating at 70°C for prolonged periods as was the case for the $Ru(bpy)_3^{2+}$/stearic acid system (P.52). Therefore, it is possible that heating at 70°C has a similar effect upon the solution as U.V.light.

C. (4,4'-DINITRO-2,2'-BPY)BIS(2,2'-BPY) RUTHENIUM (II)

As well as extending this study from Ru(COOH)2 to $Ru(bpy)_3^{2+}$ as discussed on P. 52 it was proposed that the analogous dinitro complex be prepared for irradiation with stearic acid. The advantage of this complex is that the electron withdrawing-COOH groups are replaced by the carbon free electron withdrawing - NO_2 groups,thus eliminating the possibility of carbon monoxide formation from the Ru complex. The irradiation of this complex at sufficient concentration (10^{-4}M) with stearic acid yielded a small amount of hydrogen and an undesignated peak eluted after nitrogen,illustrating, in common with $Ru(bpy)_3^{2+}$, that the undesignated gas is probably not derived from the Ru complex but is a breakdown product of stearic acid. However, pyridine is cleaved by ultrasonic waves giving acetylene and hydrogen cyanide, and it is possible that during the preparation of the photolyte, some breakdown of the bpy rings occurred giving rise to the production of small molecules, later seen on the G.C.

D. RUTHENIUM TERPYRIDYL COMPLEXES

The reasons for the preparation and irradiation of these complexes have been discussed in the Introduction (P.19) and chap.2 (P.26). The complexes irradiated were $[Ru(tpy)(bpy)Cl]^+$, $[Ru(tpy)(bpy)H_2O]^{2+}$ and $[Ru(tpy)(bpy)OH]$ in both aqueous and micellar solutions as shown in table 16 on P. 133 but no hydrogen was produced. The irradiation of some of these complexes with stearic acid might have been more successful giving rise to interesting variations of Ru complex/stearic acid phenomena. The most interesting feature of the Ru-tpy complexes is the discovery of the following acid base equilibrium:-

$$\underset{\text{yellow}}{\left[Ru^{II}(tpy)(bpy)H_2O\right]^{2+}} + OH^- \longrightarrow \underset{\text{violet}}{\left[Ru^{II}(tpy)(bpy)OH\right]^{+}} + H_2O$$

CHAPTER 4 IRRADIATION OF SOLUTIONS CONTAINING CERIUM IONS

IRRADIATION OF SOLUTIONS CONTAINING CERIUM IONS

INTRODUCTION

Solutions of cerium ions were irradiated in order to reproduce and possibly improve upon the findings of Heidt and McMillan (41) who claimed to have successfully produced hydrogen and oxygen from the photocleavage of water using both U.V. and sunlight to irradiate Ce(III) and Ce(IV) perchlorates in $HClO_4$. The reactions postulated are shown below in shortened form:-

$$4Ce(IV) + 2H_2O \longrightarrow 4Ce(III) + 4H^+ + O_2 \quad \text{dark reaction} \quad \ldots\ldots\ldots\ldots\ldots 60$$

$$2(Ce^{III} \cdot H_2O)^{3+} \xrightarrow{H^+ / h\nu} 2(Ce^{IV}OH)^{3+} + H_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 61$$

Since Ce(III) and Ce(IV) perchlorates are not commercially available, other Ce(III) and Ce(IV) salts were used. Consider the following redox potentials for Ce(IV)/(III):-

Table 2 : Some redox potentials of the Ce(IV)/(III) couple.

media	E^o(V)
2M $HClO_4$	1.71
1M HNO_3	1.61
1M H_2SO_4	1.44
2M HCl	1.28

The perchlorate acid medium gives the highest E^o for Ce(IV)/(III) but the other acid media are also capable of oxidising water to oxygen:-

$$O_2 + 4H^+ + 4e \longrightarrow 2H_2O \qquad E^o = 1.23v \quad \ldots\ldots\ldots\ldots 62$$

The observation that these Ce(IV)/(III) redox potentials are more positive than the E^o for the reduction of $O_2 \rightarrow H_2O$ may be important with respect to the photocleavage of water by Ce(IV)/(III). Thus H_2SO_4 and HCl were also used in addition to perchloric acid. In addition to the E^o conferred on the Ce(IV)/(III) couple by the acid chosen, the Ce(IV) ion is stabilised in some acid solutions. H_2SO_4 is often used for $Ce(SO_4)_2$ where sulphatoceric acid, $H_2Ce(SO_4)_3$ is said to be formed. Similar complexes are formed in HCl, HNO_3 and $HClO_4$ media although there are some differences of opinion on this theory (76). Ce(IV)-perchloric acid solutions however decompose slowly whereas Ce(IV) in sulphuric acid is stable over long periods and need not be protected from light. Since Ce(IV) in neutral solution is reduced comparatively very quickly, even in the dark, sulphuric acid media was used for the photochemistry of Ce(IV) in admixture with ruthenium complexes. The majority of the results relating to the irradiation of cerium solutions are to be found in tabular form at the end of this chapter.

REACTIONS IN THE GLASS REACTOR

No hydrogen was observed from any of the irradiated cerium solutions but interesting colour changes indicating redox reactions during irradiation are worthy of comment. The experiments are shown in table 3 on P. 69. It was observed that $Ce(SO_4)_2$ oxidised $Ru(bpy)_3^{2+}$ as indicated by the change in colour from orange to green. On irradiation of this green solution, where an excess of Ce(IV) was used, comprising Ce(IV), Ce(III) and Ru(III) the original orange $Ru(bpy)_3^{2+}$ colour was restored. This observation prompted further investigation to establish the phenomenon as being genuinely photochemical.

AN INVESTIGATION INTO THE POSSIBLE PHOTOCHEMICAL REDUCTION OF Ce(IV) BY Ru(II) IN SULPHURIC ACID

The first experiment, (i), employing only two solutions and a 10 fold excess of Ce:Ru was considerably improved upon in experiment (ii)-table 4 , P. 70 , by having solutions in the light and the dark, and by reducing the Ru concentration such that Ce:Ru was 100:1. This experiment showed that the increased reduction of Ce(IV) in flask D as compared with flasks C, E and F is due to both irradiation with visible light and the presence of $Ru(bpy)_3$ species. This experiment was varied further by investigating the rôle of dissolved oxygen and, in addition, the effect of temperature was eliminated by keeping the solutions at 32°C during the irradiation - experiment (iii)-table 5 , P. 71 . Here again, as in experiment (ii), considerably more reduction of Ce(IV) occurred in the presence of both $Ru(bpy)_3$ species and light - flask J than in the other flasks I, K and L. However, the reduction of Ce(IV) was greatly increased when, in addition, much of the oxygen was removed by degassing with nitrogen. This is as expected since inspection of the reaction of the oxidation of water by Ce(IV):-

$$4Ce^{4+} + 2H_2O \rightarrow 4Ce^{3+} + 4H^+ + O_2 \qquad \text{.........................63}$$

shows that if the dissolved oxygen is removed either before or during the reaction, whether completely or partially, then the position of equilibrium will be displaced from left to right, i.e. there will be an increase in the reduction of Ce(IV). This theory is in keeping with the work of Grant (77) who found that oxygen bubbled into Ce(IV) solutions inhibited the reduction. However, he suggests that this is due to the deactivation of the surface which acts as a catalyst. This explanation also fits these observations. Although oxygen is released in this reaction its evolution was not verified by an oxygen meter. The pH was not monitored either, since at low pH a considerable change in $[H^+]$ would be necessary for a significant pH deflection to be observed. If the H_2SO_4 concentration were reduced such that small changes in pH could be measured (i.e. as the solution approached neutrality) the E^o for the Ce(IV)/(III) couple might be affected. A consideration of the concentrations and stability constants involved would enable the determination of the Ce(IV)/(III) E^o at higher pH and thus indicate the degree to which Ce(IV) could oxidise $H_2O \rightarrow O_2$ and Ru(II) → Ru(III). The increased reduction of Ce(IV) in the deaerated and irradiated flask H, containing Ru(II), (21.7×10^{-6} moles Ce(IV) reduced), is particularly significant in comparison with the deaerated and irradiated solution G containing no Ru(II), (6.9×10^{-6} moles Ce(IV) reduced), this latter solution G being little different from the non-deaerated and irradiated solution I containing no Ru(II). However, in solution L containing Ru(II), which was not irradiated, more Ce(IV) was reduced (7.7×10^{-6} moles Ce(IV) reduced) than in any of the solutions without Ru(II). A similar result was also observed in experiment (ii) where in the unirradiated solutions slightly more Ce(IV) was reduced in solution F containing Ru(II) than in solution E without Ru(II). This suggests that either a photochemical reaction had started after the mixing of the components in ambient light but before being wrapped in aluminium foil and then continued in the dark or more likely, the $Ru(bpy)_3$ species catalysed the reduction of Ce(IV) by a non-photochemical process. To investigate this further two follow-up experiments might be carried out. Experiment (iii) could be extended to involve, in addition, two more solutions in the dark made up as for K and L but deaerated. Instead of the photochemically active $Ru(bpy)_3$ species, a similar complex e.g. $Os(bpy)_3^{2+}$ might be used to compare the reduction of Ce(IV) in the light and in the dark. $Os(bpy)_3^{2+}$ is chosen in preference to $Fe(bpy)_3^{2+}$ since the latter dissociates in acid media. The thermal instability of Ce(IV) in sulphuric acid solutions has been studied by Grant (77) who showed that this reduction occurs above 40°C in the presence of a glass surface which acts as a catalyst. The reaction, which is approximately zero order, stops when the products of the reaction deactivate the catalyst surface.

Ag(I) and Hg(II) also catalyse the reaction.

This appears to be the rôle of $Ru(5NP)_3^{2+}$ where the Ce(IV) was found to have been reduced completely in both irradiated and non-irradiated solutions - tables 7 and 8, Page 73. In this experiment also, $Ru(bpy)_3^{2+}$ was used, giving the same result as before. Thus a direct comparison of $Ru(bpy)_3^{2+}$ and $Ru(5NP)_3^{2+}$ was made, the photochemistry of the latter, if any, being completely masked by its thermal catalytic effect. A small amount of perchloric acid was added to one of the solutions in this experiment to assess its effect, if any, since both ruthenium complexes were prepared with perchlorate counterions. As far as I am aware, there are no reports in the literature of the $Ru(bpy)_3^{2+}$ photocatalysed reduction of Ce(IV) although Grätzel and Kalyanasundaram (37) have reported the reduction with hydrated RuO_2 powder in the dark producing oxygen. Unhydrated RuO_2 failed to give O_2.

It was hoped that, in addition to the oxidation of water to oxygen by the reduction of Ce(IV), the reduction of water to hydrogen by the oxidation of Ce(III) might be accomplished, mediated by $Ru(bpy)_3^{2+}$. In this proposal, the effective wavelength of photocleavage reported by Heidt and McMillan (41) of 254nm might be considerably increased by using visible light harvested by $Ru(bpy)_3^{2+}$ at ~ 450nm. The reverse appeared to take place. The redox potentials of the couples involved not only indicate whether the redox reactions will take place but also enable the position of equilibrium to be calculated. Thus, we would expect the presence of some $Ru(bpy)_3^{2+}$ even after the treatment of a large excess of Ce(IV). This is indicated by the green colour of the solution as opposed to the true blue colour of $Ru(bpy)_3^{3+}$. The colour would also be affected by the pale green of Ce(IV). After the addition of Ce(IV) to Ru(II) we would therefore expect the solution to contain Ce(IV), Ce(III), Ru(III) and Ru(II). If the photochemical reaction proceeds via *Ru(II) this might be oxidatively quenched to Ru(III) by Ce(IV) which in turn is reduced to Ce(III). The Ru(III) then oxidises H_2O or OH^- to O_2 and is reduced back to Ru(II) whereupon the cycle continues until all the Ce(IV) has been reduced to Ce(III) and finally all the Ru(III) has been reduced to Ru(II):-

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu} {}^*Ru(bpy)_3^{2+} \quad \ldots\ldots 64$$

$$^*Ru(bpy)_3^{2+} + Ce(IV) \rightarrow Ru(bpy)_3^{3+} + Ce(III) \quad \ldots\ldots 65$$

$$2Ru(bpy)_3^{3+} + 2OH^- \rightarrow 2Ru(bpy)_3^{2+} + \tfrac{1}{2}O_2 + H_2O \quad \ldots\ldots 66$$

In this mechanism OH^- is oxidised to O_2 by Ru(III) and not by Ce(IV). In this argument, it is assumed that the reaction between $^*Ru(bpy)_3^{2+}$ and Ce(IV) (eqn. 65) is very much faster than the thermal counterpart of $Ru(bpy)_3^{2+}$ and Ce(IV). However, this latter reaction has been shown (78) to be very fast ($k = 8.82 \pm 0.12 \times 10^3$ $l.mole^{-1}$ sec^{-1}) and one would expect very little difference in the time taken for the reduction of all the Ce(IV) between $Ru(bpy)_3^{2+}$ and $^*Ru(bpy)_3^{2+}$ assuming that the $Ru(bpy)_3^{3+}$ so produced is converted back to $Ru(bpy)_3^{2+}$ via the oxidation of hydroxyl ions (eqn. 66). The rôle of $^*Ru(bpy)_3^{2+}$ in this scheme could be investigated further by slowing down the thermal reaction. This might be achieved by the application of the Marcus Theory (79) which states that, for this system, as E^o ($Ru\ L_3^{3+}/Ru\ L_3^{2+}$) approaches E^o (Ce(IV)/(III)), (i.e. $\Delta\ E^o$ approaches zero), k becomes smaller. This has been demonstrated by Miller and Prince (78) for the oxidation of a series of substituted tris 1,10-phen and 2,2'-bpy ruthenium (II) complexes by cerium (IV). Thus, the thermal reaction of RuL_3^{2+} with Ce(IV) would be slowed down if a ruthenium complex having an E^o (RuL_3^{3+}/RuL_3^{2+}) approaching 1.44V (E^o for Ce(IV)/(III) in $1MH_2SO_4$) could be found. Alternatively, the E^o for Ce(IV)/(III) could be reduced by using HCl as the acid media. The discussion of this system is to be found in the next section.

Another explanation which might account for the enhanced reduction of Ce(IV) in irradiated solutions containing $Ru(bpy)_3^{2+}$ is that $^*Ru(bpy)_3^{2+}$ transfers its energy to Ce(IV) which in turn oxidises water to oxygen:

$$^*Ru(bpy)_3^{2+} + Ce(IV) \rightarrow Ru(bpy)_3^{2+} + {}^*Ce(IV) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ 67$$

$$4^*Ce(IV) + 2H_2O \rightarrow 4Ce(III) + 4H^+ + O_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ 68$$

Here again this assumes that reaction 68 is faster than the thermal reaction (eqn. 60).

REACTIONS OF Ce(IV) AND $Ru(bpy)_3^{2+}$ IN HYDROCHLORIC ACID

The colour changes observed in this experiment (table 6, P.72) serve to indicate the redox reactions taking place. Ce(IV) in solution A, containing Ru(II) and H_2SO_4 was stable for 90 minutes, whereas, in solution B, containing Ru(II) and HCl some reduction was evident after 90 minutes. The fastest reduction of Ce(IV) was observed from solution D containing HCl but without Ru(II) i.e. more reduction than solution B containing Ru(II). Thus, either Ru(II) is inhibiting the reduction or HCl is promoting it. This latter is observed by comparison of solutions C and D. After the addition of Ru(II) to solutions C and D after 90 minutes, solution C remained unchanged whereas for solution D the characteristic orange of $Ru(bpy)_3^{2+}$ turned a yellowy-green like solution B after 90 minutes. At this point solutions B and D were of identical composition (initially-

Ce(IV), Ru(II) and HCl). Clearly, the Ru(II) in solution D was reoxidised to Ru(III), either by reformed Ce(IV) or some other species possibly Cl_2. A small amount of the latter is allowed on consideration of its redox potential ($Cl_{2(g)}/2Cl^-$ + 1.36V) compared with those of $Ru(bpy)_3^{3+}/^{2+}$.... 1.26V and Ce(IV)/(III) .... 1.28V(2MHCl). The removal of the flask stopper allows the escape of Cl_2 (or O_2) and the solution reverts to the characteristic $Ru(bpy)_3^{2+}$ orange colour.

OTHER IRRADIATIONS OF CERIUM SOLUTIONS WITH AND WITHOUT $Ru(bpy)_3^{2+}$ and $Ru(5NP)_3^{2+}$

In this section (table 9 , P.74) traces of hydrogen were only observed from the visible irradiation of micellar $Ru(5NP)_3^{2+}$ in the absence of cerium (solutions 1 and 2). This does not indicate a negative effect from cerium since micellar irradiations with cerium were not carried out. This result may be compared with that of the irradiation of another microheterogeneous system comprised of $\left[Ru(bpy)_2\ (diNO_2bpy)\right]^{2+}$ and stearic acid where a trace of hydrogen was also obtained. The common feature is the $-NO_2$ group which may be important. In solution 6 the orange solid formed is almost certainly the perchlorate complex precipitated by the addition of the common ion ClO_4^- in perchloric acid. The result of the irradiation of solution 9 where the irradiated solution became colourless leaving the unirradiated solution in the reservoir green has already been discussed at length.

TABLE 3 Reactions of Ce(III) and Ce(IV) with $Ru(bpy)_3^{2+}$ in the glass (1st) reactor

Components	concn.(M)	pH	reactor	irradn. time	observation
$Ru(bpy)_3^{2+}$ $Ce_2(SO_4)_3$ H_2SO_4	10^{-4} $2x10^{-4}$ 1	1.2	1st	2 days	1cm^3 of gas obtained → no H_2
Above soln. reirrad.			1st+glass wool	3 days	no gas produced
$Ru(bpy)_3^{2+}$ $Ce(SO_4)_2$ H_2SO_4	10^{-4} 10^{-4} 10^{-1}	1.7	1st +glass wool	2 days	*1cm^3 $\xrightarrow{\text{degassed}}$ 2cm^3
Above soln.oxidised by xs $Ce(SO_4)_2$ (10^{-3} moles)-soln.turns from orange (RuII) to green (RuIII)			1st	17 hours	during irradn.soln. turned from green back to orange $\xrightarrow{\text{degassing}}$ No H_2
$Ce(SO_4)_2$ H_2SO_4	10^{-4} 10^{-1}	1.7	1st	1 day	1cm^3 $\xrightarrow{\text{degassed}}$ 3cm^3 No H_2.No change in colour

TABLE 4 Reactions of Ce(IV) with $Ru(bpy)_3^{2+}$ in H_2SO_4 - expt.(ii)

No. of moles of Ce(IV) reduced in 50·5cm^3 during irradn.	Solution	Volumes of reagents taken	Concentrations	Light or Dark	Titres for 10cm^3 aliquot			Average titre corrected for 50·5cm^3
					1st	2nd	Average	
6.42×10^{-6}	C	25cm^3 of 2×10^{-3}M Ce(IV) 25cm^3 of 0.1M H_2SO_4 0.5cm^3 of water	10^{-3}M Ce(IV)	LIGHT	8.55	8.70	8.63	43.58
14.75×10^{-6}	D	25cm^3 of 2×10^{-3}M Ce(IV) 0.5cm^3 of 10^{-3}M Ru(II) 25cm^3 of 0.1M H_2SO_4	10^{-3}M Ce(IV) 10^{-5}M Ru(II)		6.85	7.10	6.98	35.25
5.05×10^{-6}	E	25cm^3 of 2×10^{-3}M Ce(IV) 25cm^3 of 0.1M H_2SO_4 0.5cm^3 of water	10^{-3}M Ce(IV)	DARK	8.80	9.00	8.90	44.95
6.32×10^{-6}	F	25cm^3 of 2×10^{-3}M Ce(IV) 0.5cm^3 of 10^{-3}M Ru(II) 25cm^3 of 0.1M H_2SO_4	10^{-3}M Ce(IV) 10^{-5}M Ru(II)		8.70	8.60	8.65	43.68

TABLE 5 : Reactions of Ce(IV) with $Ru(bpy)_3^{2+}$ in H_2SO_4 - expt. (iii)

Volumes of reagents taken	Concentration	Light Deaerated	Light	Dark	
$15cm^3$ of $2x10^{-3}M$ Ce(IV)	$6.0x10^{-4}M$ Ce(IV)	G 23.1	I 23.5	K 25.3	Titre corrected for $50cm^3$ of soln.
containing H_2SO_4	0.03M H_2SO_4				
Made up to $50cm^3$ - water		6.9	6.5	4.7	No.of moles of Ce(IV) reduced ($x10^{-6}$)
$15cm^3$ of $2x10^{-3}M$ Ce(IV)	$6.0x10^{-4}M$ Ce(IV)	H 8.3	J 19.3	L 22.3	Titre corrected for $50cm^3$ of soln.
containing H_2SO_4	0.03M H_2SO_4				
$0.3cm^3$ of $10^{-3}M$ $Ru(bpy)_3^{2+}$	$6.0x10^{-6}M$ Ru(II)				
Made up to 50 cm^3 - water		21.7	10.7	7.7	No.of moles of Ce(IV) reduced ($x10^{-6}$)

Initial number of moles of Ce(IV) before irradiation in each flask = 30×10^{-6}.

TABLE 6 : Reactions of Ce(IV) with $Ru(bpy)_3^{2+}$ in HCl

Solution	A		B		C		D	
		concn. in photolyte		concn. in photolyte		concn. in photolyte		concn. in photolyte
Composition	11mgCe(IV)	8.0×10^{-4}MCe(IV)	11mgCe(IV)	8.0×10^{-4}MCe(IV)	11mgCe(IV)	8.0×10^{-4}MCe(IV)	11mgCe(IV)	8.0×10^{-4}MCe(IV)
	2cm 10^{-3}MRu(II)	8.0×10^{-5}MRu(II)	$2cm^3 10^{-3}$MRu(II)	8.0×10^{-5}MRu(II)	$3cm^3 2 \times 10^{-3}$M$HClO_4$	2.4×10^{-4}MClO_4^-	$3cm^3 2 \times 10^{-3}$M$HClO_4$	2.4×10^{-4}MClO_4^-
	$20cm^3$1MH_2SO_4	1.6MH^+	$20cm^3$2MHCl	1.6MH^+	-	-	$20cm^3$2MHCl	1.6MH^+
	$3cm^3 H_2O$	-	$3cm^3 H_2O$	-	$22cm^3 H_2O$	-	$2cm^3 H_2O$	-
Time, t (mins)	Colour of soln.		Colour of soln.		Colour of soln.		Colour of soln.	
0	Green		Pale green		v. pale green		v.pale green	
3½	Green		Pale green		v. pale green		colourless	
10	Green		Pale green		nearly colourless (red to ferroin)		colourless (red to ferroin)	
90	Green		Yellowy-green*		colourless		colourless	
(after 90mins) Addition of ferroin to $10cm^3$ aliquot of soln.	Bluey-green		Yellow		Would have been red if added		Would have been red if added.	
Addition of $2cm^3$ of 10^{-3}MRu(II) (after 90 mins)					characteristic orange colour of Ru(II) which on standing for ½ hour remained unchanged		characteristic orange colour of Ru(II) which on standing for ½ hour turned yellowy-green (cf.soln.B > 90 mins *)	

TABLE 7 : The concentrations of the reagents in table 8

Reagent	Concentration in 50cm^3 of photolyte (M)
$(NH_4)_2\left[Ce^{(IV)}(NO_3)_6\right]$	9.4×10^{-4}
$Ce^{(III)}(NO_3)_3 \cdot 6H_2O$	1.88×10^{-4}
$Ru(5NP)_3^{2+}$	3.44×10^{-5}
$Ru(bpy)_3^{2+}$	3.0×10^{-5}
$HClO_4$	8.0×10^{-5}
H_2SO_4	6.0×10^{-2}

TABLE 8 : Reactions of Ce(III) and Ce(IV) with $Ru(bpy)_3^{2+}$ and $Ru(5NP)_3^{2+}$ in H_2SO_4

Photolyte composition	Titres of FeAS for 20cm^3 aliquots			
	↓ light		↓ dark	
Ce(IV), Ce(III), $Ru(5NP)_3^{2+}$, H_2SO_4	0.0	47	0.0	47
Ce(IV), Ce(III), $Ru(bpy)_3^{2+}$, H_2SO_4	5.5	33.25	15.3	8.7
Ce(IV), Ce(III), $HClO_4$, H_2SO_4	16.3	6.25	17.35	3.63
Ce(IV), Ce(III), H_2SO_4	15.65	7.88	17.35	3.63
		↑		↑
	No.of moles of Ce(IV) reduced during irradn. adjusted to 50cm^3 of photolyte (x10^{-6})			

No. of moles of Ce(IV) before irradiation ..... 47×10^{-6}

TABLE 9 : Reactions of cerium ions with $Ru(bpy)_3^{2+}$ and $Ru(5NP)_3^{2+}$ in the silica reactor

			H_2 obtained		
Solution composition	UV or Vis (100W)	Irradn. time	delib. bubble	hot water jacket	Other observations
1. $Ru(5NP)_3^{2+}$ 5×10^{-5}M S.D.S. 1.4×10^{-2}M	vis	3 days	trace	trace	pH 7.4 before and after irradn.
2. Soln. 1 reirrad., aerated for one day	vis	2 days	X	trace	
3. $Ru(5NP)_3^{2+}$ 10^{-5}M S.D.S. 1.4×10^{-2}M Ba Stearate 2.2×10^{-5}M	vis	19 hours	X	X	pH 6.9 before and after irradn.
4. $Ru(5NP)_3^{2+}$ 2.6×10^{-5}M $Ce(NO_3)_3$ 2.5×10^{-2}M H_2SO_4 2.5×10^{-2}M	UV	17½ hours	-	X	
5. $Ce(NO_3)_3$ 1.8×10^{-2}M $HClO_4$ 1.0×10^{-1}M	UV	22 hours	-	X	
6. $Ce(NO_3)_3$ 1.35×10^{-2}M $HClO_4$ 7.5×10^{-2}M $Ru(5NP)_3^{2+}$ 3.0×10^{-4}M	UV	3 days	-	X	initially orange soln., after irradn. or standing became nearly colourless with pptn. of orange solid.
7. $Ce(NO_3)_3$ 6.7×10^{-2}M $HClO_4$ 1.75M	UV	25½ hours	-	X	no differences in pH (0.4) or UV spectra before & after irradn.
8. Soln. 7 reirrad.	UV	18 hours	-	-	No H_2 revealed on freeze-thawing soln.
9. $Ru(bpy)_3^{2+}$ 10^{-5}M $(NH_4)_2Ce(NO_3)_6$ 1.1×10^{-3}M H_2SO_4 10^{-1}M	UV	17½ hours	-	X	After irradn., soln. in reactor colourless whilst soln. in reservoir still green.

CHAPTER 5 THE IRRADIATION OF THE DIOCTADECYL ESTER OF (4,4'-DICARBOXY-2,2'-BPY)BIS(2,2'-BPY) RUTHENIUM (II) PERCHLORATE....... "THE WHITTEN COMPLEX"

THE IRRADIATION OF THE DIOCTADECYL ESTER OF (4,4'-DICARBOXY-2,2'-BPY)BIS (2,2'-BPY) RUTHENIUM(II)PERCHLORATE - "THE WHITTEN COMPLEX"

Introduction

Irradiation experiments on this complex were almost entirely carried out in micellar solution using S.D.S., where the concentration of the latter was usually $1.4\text{x}10^{-2}$M. Since solubilisation of the "Whitten Complex" was to be effected in micelles, a concentration of S.D.S. just above its C.M.C. was employed. Fluorimetry (80) and conductiometry (81) give values for the C.M.C. of S.D.S. as $6.6\text{x}10^{-3}$M and $8.1\text{x}10^{-3}$M respectively. The reasons for the irradiation of Ru complexes in micellar solution and a diagram of the "Whitten Complex" in an anionic micelle made with S.D.S. are given in the Introduction. A cationic micellar solution of the "Whitten Complex" was also prepared using cetyl trimethylammonium bromide (C.T.A.B.) - $CH_3(CH_2)_{15}\ N(CH_3)_3^+\ \ Br^-$ and irradiated with visible light. There were no changes in the solution nor was the evolution of hydrogen observed.

AN "INVERTED" MICELLAR SYSTEM

In addition to the S.D.S. micellar "Whitten Complex" solutions irradiated, discussed in the next two sections, it was proposed that an inverted micellar system be attempted. In micelles of this kind, the polar heads of the surfactant molecules are attracted to one another in the centre of the micelle with the hydrophobic, hydrocarbon chains radiating out in the solution,which in this case is an organic solvent:-

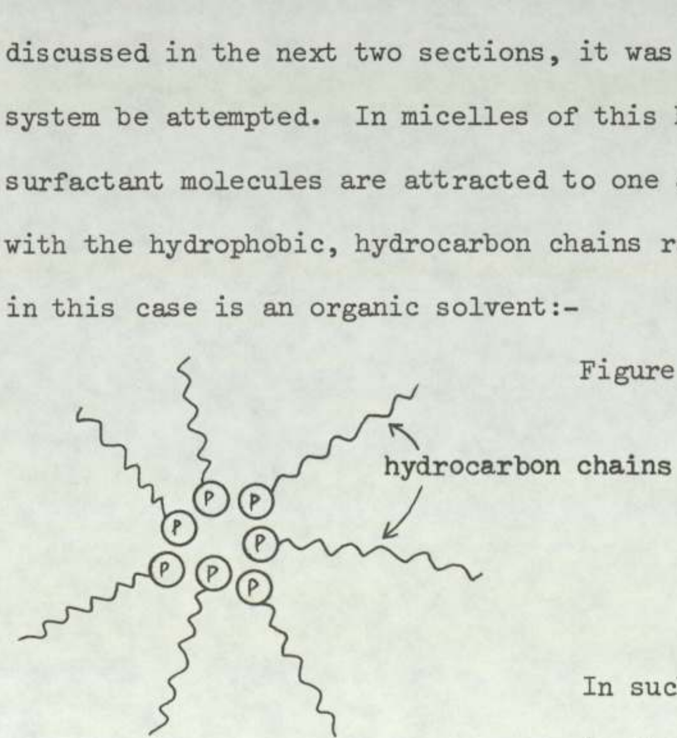


Figure 9 Inverted micelle in organic solution

Ⓟ = polar head

In such systems water has been sequestered in these micelles and has been shown to undergo interesting reactions (82). If an "inverted" micellar solution is prepared, containing a small amount of water, and incorporating the "Whitten Complex" then the Ru-bpy heads will be concentrated in the centre of the micelle. They will thus be held in a semi-rigid structure in close contact with the sequestered water molecules affording possible interesting photochemical behaviour. In order to prepare such a solution, the following constraints need to be borne in mind:-

(i) the organic solvent chosen must be immiscible with water at low concentrations of water.

(ii) the detergent chosen must form micelles in the organic solvent.

(iii) the "Whitten Complex" must be insoluble in the organic solvent except in the micellar solution.

(iv) the organic solvent chosen must not dissociate into harmful gases upon irradiation. [An organic solvent to meet these criteria was not discovered although more work could be done towards this goal.]

IRRADIATIONS IN ACETONE

During this search it was realised that irradiation could be carried out in acetone in which the "Whitten Complex" is soluble. In practice, the irradiation was carried out in a 5% solution of acetone in water. Although it was doubtful whether hydrogen had been produced in this visible irradiation, the U.V. irradiation reported by Dr.Cooke gave significant quantities of hydrogen. Although it seems probable that this is derived from the acetone used, there is some evidence to suggest that this is not so: the irradiation of deuterated acetone yielded less than the expected amount of deuterium. In any labelling experiment using D_2O, care needs to be taken when interpreting the results because of the fast exchange reaction between hydrogen and deuterium. In this study, for example, a deuterated compound on dissolving in water might exchange some deuterium for hydrogen so that after irradiation, any D_2 or HD obtained could have resulted from D_2O or HDO.

IRRADIATION IN S.D.S. MICELLAR SOLUTION

The U.V. irradiation of the "Whitten Complex" alone in S.D.S.micellar solution yielded no hydrogen nor were there any changes in the U.V. spectra. However a considerable pH drop had occurred, 5.1→2.8. A photochemical interpretation of pH changes in micellar solutions is difficult. The cooling of S.D.S. solutions in the reactor from the circulating water resulted in an increase in turbidity. This change in the micellization of the solution was also reflected in a change in pH. Furthermore, a hot solution of S.D.S. on cooling to room temperature remained virtually clear for several days. Micellar solutions of the "Whitten Complex" and barium stearate (discussed in the next section) were facilitated by heating. Now if the degree of aggregation of the molecules is important, then from the point of view of reproducibility, these solutions should have been left for the same length of time to equilibrate before irradiation. In practice, this is impossible, but serves to illustrate that changes in turbidity, as well as pH, during irradiation, give no reliable indication to genuine photochemical behaviour.

The U.V. irradiation of a micellar solution of the "Whitten Complex" containing palladised charcoal produced a slight increase in the solution absorbance at 225nm. This would normally have been overlooked were it not for the fact that this same observation was noted for the irradiation of a micellar solution of $Ru(bpy)_3^{2+}$ and palladised charcoal (P.124) and is discussed in chap.3.P52.

The first irradiation of a micellar solution of the "Whitten Complex" containing $BaCl_2$ with visible light resulted in the formation of an orange colloid which aggregated further to a precipitate. This precipitation reaction appeared to start when the micellar solution was added to the relatively concentrated $BaCl_2$ solution (10^{-2}M) prior to appropriate dilution for irradiation. This orange colloid obviously contained "Whitten Complex" and its formation was probably responsible for the fact that no hydrogen was observed. The solution was made up again containing ten times less $BaCl_2$ which upon irradiation yielded a trace of hydrogen without the formation of an orange colloid. In addition, a white "scum" formed on the surface of the solution which may have been barium stearate or a long hydrocarbon chain fragment resulting from the breakdown of the "Whitten Complex". This may have been partly responsible for the trace of hydrogen observed since this situation resembles the irradiation of micellar "Whitten Complex" where barium stearate was added deliberately to effect the evolution of hydrogen. This is discussed in chap.3 on P.52 and in the next section:-

IRRADIATION WITH BARIUM STEARATE IN S.D.S.MICELLES

The first irradiation of the above mixture (M.W.Ba 1) with U.V.gave on analysis of the freeze-thawed solution, only a trace of hydrogen. This was in fact registered as a stepping on the baseline yet the withdrawal and analysis of a sample of the same gas the following day revealed 7μL of hydrogen! These observations were reproduced with a fresh solution (M.W.Ba2) made up from the solid materials irradiating again with U.V.light except that very much less hydrogen was detected. In view of this, continued efforts were made to reproduce, as far as possible, the procedure carried out in the first experiment. Particular care was taken in making up the solutions in the same way, to the same concentrations. The difficulties encountered in reproducing micellar solutions have been discussed in the last section. One of the problems was that solution(M.W.Ba 1)was made up in part from a micellar solution of barium stearate. Not all of the solid barium stearate added to the micellar solution dissolved, therefore the true concentration was unknown.

Solutions were made up and treated in various ways, irradiating with visible light, but only small peaks of hydrogen were observed. One of these solutions,(M.W.Ba3), for which small peaks of hydrogen were obtained, subsequently yielded a peak equivalent to 2.8μL hydrogen. This represented the largest amount of hydrogen relative to Ru complex produced so far (1 mole H_2 $\equiv$ 5.2 moles Ru complex). It was considered, however, that the hydrogen produced in this case did not result from the visible irradiation but from heating during the thawing of the frozen solution. At first, thawed solutions were only heated to ~40°C whereas temperatures of 70°C and above were used later on. To test this, more of the above solution (M.W.Ba3) was poured into the reactor and left to stand in the dark before freeze-thaw-G.C.testing. A small peak of hydrogen was obtained. Leaving this freeze-thawed solution to stand for 3 days in the dark with a deliberate bubble of air (~1cm^3) again yielded a small amount of hydrogen. Thus, it appeared that irradiation with visible light was unnecessary for the production of small quantities of hydrogen. Since the solutions were handled in subdued light, the possible rôle of light in this reaction cannot be ruled out. Strictly, the experiment should be conducted in a photographic darkroom using only the safety light for the preparation and handling of the solutions.

More solutions were prepared including one containing a large excess of barium stearate and irradiated under various conditions, as reported. Several parameters were investigated which were thought to be influential. These included pressure, heating, nitrogen deaeration, silicone grease and the time the solutions were left to stand between different procedures. The details of many of these experiments have not been included because of their complexity.

From these results no clear pattern emerged to indicate which factors were necessary for the production of hydrogen. The first irradiations employed U.V. light and this it seems was successful in producing hydrogen without undue heating of the thawed solution (~40°C). In subsequent irradiations with visible light, heating the thawed solution seems to have been a major factor. This idea that heating has a similar effect upon the solution as U.V. light has already been proposed for the $Ru(bpy)_3^{2+}$/stearic acid system (P.59). It is perhaps unfortunate that more U.V. irradiations were not carried out. The main reason for the change to visible light was the realisation that the solar spectrum at sea level contains very little U.V. and therefore for a solar energy storage system to be of value a photochemical reaction in the visible needs to be employed. Moreover, Dr. Cooke, whose work was complementary to mine, used U.V.light almost exclusively. In addition, pyridine is slowly cleaved by U.V. light giving glutaconic aldehyde derivatives. It is conceivable, therefore, that these bpy complexes may be broken down by U.V. especially at the intensities employed.

Although it is felt that heating the solution was important, it appeared that certain specific solutions were more successful than others indicating that the way the micellar systems were prepared is critical. This difficulty is in common with attempts by Dr.Cooke to reproduce monolayers of Ru complexes capable of the photodissociation of water.

The leaving to stand for a day or more of the freeze-thawed solution after initial sampling and testing was also important either because the reaction initiated by U.V. or heating was a slow one or the solution continued outgassing even at room temperature.

There may have been quenching of the Ru complex excited state by oxygen but experiments with nitrogen degassed solutions and irradiations under reduced pressure produced no marked effect.

The only variation in the composition of the solution was the trial of an excess of barium stearate since the emphasis was upon the reproduction of the first observed evolution of hydrogen. It is possible that stearic acid would have been just as efficient as in the case of $Ru(bpy)_3^{2+}$.

EXPERIMENTAL SECTION

CHAPTER 6 THE PREPARATION OF THE COMPLEXES

A. WATER SOLUBLE RUTHENIUM COMPLEXES

a) Tris bpy ruthenium(II)perchlorate

The synthesis of the complex and others using ethanol as solvent are based upon those given by Rose and Wilkinson(51) and Klassen(52).

Commercial $RuCl_3 xH_2O$ (0.64g, 2.65×10^{-3} moles of Ru) was refluxed with 2,2'-bipyridyl(1.3g, 8.40×10^{-3} moles) in ethanol for 13 hours. A dark brown solid, Rubpy①, was formed which was filtered off, 0.27g, leaving a brownish-red filtrate to which was added a concentrated solution of $NaClO_4 \cdot H_2O$(0.94g, 6.7×10^{-3} moles) in water($4cm^3$). On cooling and standing overnight a bright red solid was precipitated. Yield of crude product, 1.44g, 71%. This was recrystallised from water($125cm^3$) to give 0.96g, 47% Rubpy②.

ANALYSIS

Rubpy①

The complex is moderately soluble in water to give a yellowy-brown solution.

C.H.N.for $(bpyH)[Ru^{III}Cl_4(bpy)]$

cald: C,43.2; H,3.1; N,10.1; Cl,25.5.

found: C,40.0; H,2.7; N,9.1; Cl,24.5.

Rubpy②

The complex dissoves slowly in water to give an orange solution having λ maxima at 243nm(shoulder at 253nm), 286nm and 451nm(shoulder at 424nm)

C.H.Nfor $[Ru^{II}(bpy)_3](ClO_4)_2$

cald: C,46.9; H,3.1; N,10.9.

found: C,46.2; H,3.1; N,10.8.

Percussion of a small amount of the sample had no effect but on heating, it decomposed explosively leaving a black deposit of presumably metallic ruthenium.

b) Tris (5-nitro-1,10-phen) ruthenium(II)perchlorate

Commercial $RuCl_3 xH_2O$ (0.15g, 6.01×10^{-4} moles) was refluxed in ethanol ($30\ cm^3$) for 1 hour during which time the solution changed colour from brown (RuIV) to green (Ru III). 5-nitro-1,10-phen (0.42g, 1.84×10^{-3} moles) (83), dissolved in ethanol (10 cm^3) was added to the green solution and the reflux continued for a further 23 hours. A brown solid was produced which was filtered off and weighed, 0.17g - Ru5NP ①. To the red -brown filtrate was added a concentrated solution of $NaClO_4 \cdot H_2O$ (0.27g, 1.92 x 10^{-3} moles) in water (2 cm^3) and an immediate orange -brown precipitate was produced. After cooling and standing it was filtered off and weighed. Yield of crude $[Ru^{II} (5NP)_3](ClO_4)_2$, 0.34g (57.4%). The crude product was recrystallized from water (150 cm^3) to give a crop of dark red crystals. Recrystallized yield, 0.12g, (20.5%) - Ru 5NP ②.

ANALYSIS

Ru 5NP ①

Solubility: Complex dissolves sparingly or slowly in water and acetone.

C.H.N.Cl for complex:

cald. for $[Ru^{III} Cl_4(5NP)]$ (5NPH): C,41.6; H,2.0; N,12.1; Cl, 20.5.

cald. for $|Ru^{III} (5NP)_2 Cl_2]Cl$: C,43.8; H,2.1; N,12.8; Cl. 16.2.

found : C,40.3; H,2.1; N,12.8; Cl. 17.2.

Ru 5NP ②

Solubility: Complex dissolves slowly in water.

C.H.N. for complex:

cald. for $[Ru^{II} (5NP)_3](ClO_4)_2$: C,44.3; H,2.2; N,12.9.

found : C,43.7; H,2.0; N,12.8.

I.R. analysis, Nujol Mull, of both Ru 5NP ① and ② shows - NO_2 group peaks at 1350cm^{-1} due to symm. N ═ O str. and peaks at 1515cm^{-1} and 1540cm^{-1} due to asymm. N ═ O str. These peaks are absent from the I.R. spectrum of $[Ru(bpy)_3](ClO_4)_2$.

c) <u>(4,4' - dicarboxy - 2,2' - bpy) bis (2,2' - bpy) ruthenium(II) perchlorate - Ru(COOH)2.</u>

This synthesis is based upon that given by Whitten et al (26) for the hexafluorophosphate complex.

$[Ru(bpy)_2 Cl_2]\cdot 2H_2O$ already prepared (P.99), (0.52g,10^{-3} moles), $NaHCO_3$ (0.30g, 3.57×10^{-3} moles) and 4,4'-dicarboxy - 2,2' - bpy (0.10g, $4.1\text{x}10^{-4}$ moles) were refluxed together in a solution of water (15cm^3) and methanol (10cm^2) for 2 hours. After which time $NaHCO_3$ was filtered off and saturated $NaClO_4$ solution (25cm^3) was added to the methanolic solution. After refrigeration overnight, no perchlorate complex was produced. As much of the solvent as possible was removed on a rotary evaporator. Ethanol (20cm^3) was added and the resulting mixture swirled and filtered to give a brown solid comprising a mixture of presumably a ruthenium complex and $NaClO_4$. This mixture was washed again with ethanol to dissolve the $NaClO_4$. To the remaining crude orange product, 0.44g, was added more ethanol (100cm^3) and the mixture heated. Most of the complex did not dissolve in this volume of hot ethanol (100cm^3). However, the mixture was filtered and the filtrate containing that which did dissolve was reduced to 75cm^3. This solution was transferred to a clean unscratched beaker and left to evaporate for 4 days. After which time a crop of red needle-like crystals were produced which were filtered off and dried in a vacuum desiccator. Yield,0.06g,(16.2%). The filtrate was allowed to evaporate further when more product was formed. On leaving to stand for a longer period this solid redissolved!

ANALYSIS

The complex is insoluble in acetone and choloroform, partially soluble in ethanol but very soluble in water. The visible absorption of the aqueous solution of the complex varied according to pH as follows:-

Table 10 The variation of the absorption spectrum of Ru(COOH)2 with pH

pH	above sample-nm	lit.(26)-nm
0.6	419 478	420 475
12.5	456	455

C.H.N. for $[Ru^{II}(bpy)_2(\text{4,4'-dicarboxy-bpy})](ClO_4)_2$

cald: C,44.9 ; H,2.8 ; N, 9.8.

found: C,45.6 ; H,3.2 ; N,12.0

T.l.c. analysis of the sample dissolved in ethanol on an alumina plate developed in a solution of ethanol 40% and water 60% gave only one spot, Rf = 0.44. This single orange spot fluoresced brightly in U.V. light which revealed no further components.

d) Tris (4,4'-dinitro-2,2'-bpy) ruthenium(II) perchlorate

The synthesis of this complex was attempted in four stages of which three were necessary for the preparation of the (4,4'-diNO_2-2,2'-bpy) ligand.

STAGE 1: 2,2'-bipyridyl - 1,1' - dioxide

This preparation follows the method given by **Haginawa** (56a).

Bipyridyl (10g, 6.41×10^{-2} moles) was dissolved in glacial acetic acid ($50cm^3$) and heated at 70°C for 8½ hours during which time hydrogen peroxide (30%, $25cm^3$) was added in three portions. The solution was allowed to cool and then basified with KOH solution. Precipitation of the crude product started to take place at pH7 and was complete at pH12. The precipitate was filtered off and washed with cold water at pH8. The filtrate was tested for complete precipitation. The crude bpy-dioxide was recrystallised from hot water to give a crop of colourless crystals, yield, 7.3g, 61%. M.pt: decomposition at ~290°C; lit. (56a) decomposition at 310°C.

ANALYSIS

C.H.N. for $C_{10}H_8N_2O_2$

cald: C,63.8 ; H,4.3 ; N,14.9.

found: C,60.9 ; H,4.6 ; N,14.8.

STAGE 2: 4,4'-dinitro-2,2'-bpy-1,1'-dioxide

This preparation is based upon that given by Sasse et al (58).

Bpy-1,1'-dioxide (5.8g, 3.1×10^{-2} moles) was dissolved in concentrated H_2SO_4 (14 cm^3), the mixture being cooled in an ice bath. To this viscous solution, a mixture of conc. H_2SO_4($14cm^3$) and conc. HNO_3($20cm^3$) was added cautiously over a period of 5 minutes. The solution was refluxed for $1\frac{1}{2}$ hours during which the flask contents turned brown as nitrogen dioxide was released. The cooled solution was added to crushed ice (100g). The resulting green solution was basified slightly with KOH solution and left to stand at pH2 overnight. On standing the solution had turned yellow with the precipitation of some yellow crystals, diNO$_2$bpyD.O. ①. These were filtered off, 0.79g, and the filtrate basified further with KOH solution when more yellow product was precipitated from pH2→pH5.5. In addition, colourless crystals of presumably KNO_3 or K_2SO_4 were also precipitated. The total precipitate was filtered off, washed with water to dissolve out the potassium salts, and then filtered again to give a second yellow product kept as diNO$_2$bpy D.O.②, 0.34g. Further basification with KOH solution of the mother liquor yielded a brown solid and in strongly alkaline solution a yellow solid, presumed to be the dipotassium salt of the desired compound. The total precipitate was filtered off, washed with water in which the latter is soluble and the brown solid filtered off, dried and kept as diNO$_2$bpy D.O.③, 0.28g. The diNO$_2$bpy D.O. compounds ①, ② and ③ were treated with hot ethanol independently to remove any mono-nitro compound formed. The results are tabulated below:-

Table 11 M.pts and ethanol treatment of dinitrobipyridyldioxide compounds

compound	m.pt°C	effect of treatment with hot Et-OH
diNO$_2$bpy D.O. ①	243	insoluble - ethanol remains colourless
diNO$_2$bpy D.O. ②	decomposes at ∿ 250	partially soluble to give a yellow solution which on cooling produced yellow crystals of presumably the mono-nitro compound.
diNO$_2$bpy D.O. ③	decomposes explosively at 255	
literature (56a)	274	

After washing diNO$_2$bpy D.O. ①, ② and ③ with hot ethanol, the total yield was 1.30g, 15.2%. The resulting diNO$_2$bpy D.O. was insoluble in water.

STAGE 3: 4,4'-dinitro-2,2'-bipyridyl

This preparation was based upon that given by Maerker & Case (56b).

Dinitrobpydioxide (1.3g, 4.68×10^{-3} moles) was added to dry chloroform (25cm^3, distilled from calcium chloride) and the suspension cooled to 0°C before the addition of phosphorus trichloride (3cm^3). The two liquid phases were heated to reflux for one hour during which time, some solid appeared in the PCl_3 layer and the $CHCl_3$ layer became clearer. The mixture was poured onto crushed ice (50g) which after melting yielded a brown solid and a yellow solid in addition to the organic and aqueous phases. The mixture was filtered, the solid material washed with chloroform and the chloroform washings added to the filtrate. This was then basified with conc. NaOH solution and the resulting precipitate of unreacted dinitro-bpy-dioxide filtered off. The aqueous layer was separated from the organic layer and washed with several portions of chloroform (total volume 210 cm^3). These chloroform washings were added to the organic layer and the total chloroform solution evaporated to dryness. The resulting yellow solid was fractionally recrystallised from 95% ethanol to give some pale yellow crystals, yield, 0.1g, m.pt., 109°C(literature (56a)for 4,4' dichloro-2,2'-bpy = 143°C) and some orange needles, yield, 0.07g, 6.1%, m.pt.= 205°C (decomposition) (literature (56b) for 4,4'-dinitro-2,2'-bpy = 195-197°C).

ANALYSIS

C.H.N.Cl. for yellow crystals - $C_{10} H_6 N_2 Cl_2$

cald. : C,53.3 ; H,2.7 ; N,12.4 ; Cl,31.6.

found : C,<1.0 ; H,<1.0; N,<1.0 ; Cl, 7.4.

T.l.c. of the orange needles (the presumed dinitro-bpy) on an alumina plate, using chloroform as the eluting solvent, gave a chromatogram as follows:-

Table 12 The t.l.c. analysis of dinitrobipyridyl

Rf	Observations
0.11	orange spot visible in daylight
0.28	very faint spot visible in UV only
0.83	visible in the UV only

STAGE 4: Tris (4,4'-dinitro-2,2'-bpy) ruthenium (II) perchlorate

Commercial $RuCl_3 \cdot \chi H_2O$ (0.01g, 4.74×10^{-5} moles of Ru) was refluxed in ethanol ($15cm^3$) for 1 hour to facilitate the reduction of ruthenium (Ru(IV) → Ru(III)) yielding a green solution. Dinitrobpy (0.03g, 1.22×10^{-4} moles) was added and the reflux continued for a further 3½ hours. The solution was then filtered to give a black crystalline solid $RudiNO_2$ ①, 0.02g, and a blue filtrate. This solution was evaporated to $2cm^3$ and spotted on an alumina t.l.c. plate and developed in acetone 50%/water 50% producing a blue spot at Rf = 0.92 and a purple spot at Rf = 0.61. The black crystalline solid, $RudiNO_2$ ① was refluxed in hot water ($15cm^3$) for 45 minutes. The undissolved solid was filtered from the pale blue solution and refluxed again with a further portion of water ($15cm^3$) for a further 5 hours. The undissolved solid was again filtered from the now colourless solution, dried and submitted for CHN analysis:-

C.H.N. cald. for $\left[Ru^{II}(diNO_2bpy)_3\right]Cl_2$: C,39.6 ; H,2.0 ; N,18.5.

cald. for $\left[Ru^{III}Cl_4(diNO_2bpy)\right]$ (diClbpyH):C,33.6 ; H,1.7 ; N,11.8.

found :C,33.6 ; H,2.4 ; N,12.7.

The complex is insoluble in either cold or hot water, acetone, chloroform or ethanol.

e) (4,4'-dinitro-2,2'-bpyridyl) bis (2,2'-bpy) ruthenium(II) perchlorate

The method outlined here represents the fourth stage in the preparation of this complex. The first three stages for the preparation of dinitrobpy are given on pages 86-89.

$[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (0.15g, $2.93\text{x}10^{-4}$ moles, already prepared P.99) and dinitro-bpy (0.07g, $2.85\text{x}10^{-4}$ moles, already prepared) were refluxed together in ethanol ($15cm^3$) and water ($5cm^3$) for 24 hours. The resulting "ruthenium red" solution was filtered to remove a small amount of undissolved solid and the filtrate, evaporated to 1/3 of the volume, was added to a concentrated solution of sodium perchlorate in ethanol ($1cm^3$). After standing and some evaporation for five days, a black solid was precipitated, 0.07g, (27.3%).

ANALYSIS

T.l.c. of the product, alongside $Ru(bpy)_2Cl_2$ as blank, developed in ethanol on an alumina plate showed no traces of $Ru(bpy)_2Cl_2$.

C.H.N. for $[Ru(bpy)_2(diNO_2bpy)]\ (ClO_4)_2$

cald. : C,42.0 ; H,2.6 ; N,13.1.

found : C,43.1 ; H,2.9 ; N,13.5.

f) The dioctadecyl ester of chloro terpyridyl(4,4'-dicarboxy-2,2'-bipyridyl) ruthenium(II)perchlorate

STAGE 1: Trichloro terpyridyl ruthenium(III)

The method is based on one given by Krause(84) using tpy instead of bpy.

Commercial $RuCl_3 \cdot H_2O$ (0.26g, $1.08\text{x}10^{-3}$ moles Ru) and terpyridyl (0.26g, $1.11\text{x}10^{-3}$ moles) were mixed together in MHCl ($9cm^3$) and left to stand for 16 days. After which time, the solution was less coloured with the deposition of a brown solid. This was filtered off, 0.47g, and refluxed with water ($60cm^3$). The mixture was filtered giving a small amount of black solid, 0.09g Rutpy① and the green filtrate taken to dryness on a rotary evaporator, 0.38g, (78.3%). - Rutpy②.

ANALYSIS

C.H.N.Cl. for Rutpy① yielded strange results. In particular, the incomplete combustion and the irregular colour change during the oxygen flask titration yielded a very low chlorine content.

C.H.N.Cl. for $[Ru^{III}\ tpyCl_3]$ - Rutpy②

cald: C,40.8 ; H,2.5 ; N,9.5 ; Cl. 24.1.

found: C,37.3 ; H,2.8 ; N,14.1 ; Cl, 26.6.

Visible spectrophotometry of the complex dissolved in water gave λ maxima of 475 and 692 nm.

I.R: By comparison with a spectrum of terpyridyl, Rutypy ② is clearly a Ru-tpy complex whereas Rutpy ① is not.

STAGE 2: The dioctadecyl ester of chloro terpyridyl (4,4'-dicarboxy-2,2'-bipyridyl) ruthenium(II) perchlorate

$\left[\text{Rutpy Cl}_3\right]$ (0.13g, 3.01×10^{-4} moles) was refluxed with B.D.E. (0.23g, 3.01×10^{-4} moles) (already prepared P. 90), for 7 hours in formalin! After which time a purple solid was formed which was filtered off. This appeared to be a mixture of the starting materials. The resulting dark reddy-brown filtrate was added to an excess of $NaClO_4$ dissolved in a minimum volume of water. After standing for 3 days the precipitated brown perchlorate salt was filtered off and dissolved in chloroform. After filtration to a clear solution, the chloroform extract was taken to dryness on a rotary evaporator giving a purpley-brown water insoluble solid, 0.02g (5.5%).

ANALYSIS

C.H.N. for $\left[\text{Ru}^{II}(\text{tpy})(\text{B.D.E.})\,\text{Cl}\right]\text{ClO}_4$ cald. values

require: C,62.1 ; H,7.5 ; N,5.7.

found: C, 58.9 ; H, 8.7 ; N, 1.6.

UV and visible spectrophotometry of the complex in chloroform gave λ maxima of 255,318,410 and 532nm.

g) <u>μ-4,4'-bipyridyl-bis [terpyridyl bipyridyl ruthenium (II)] perchlorate (bridged dimer)</u>

STAGE 1: Chloro terpyridyl bipyridyl ruthenium (II) perchlorate - 2.5-hydrate

RutpyCl_3 (0.26g, 5.87×10^{-4} moles), already prepared, P. 90, and bipyridyl (0.12g, 7.45×10^{-4} moles) were refluxed together in a mixture of ethanol 25% and water 75% ($20cm^3$) for 5 hours during which time the solution changed from green, due to Ru(III), to the characteristic reddy-brown of Ru(II). The pH of the solution was 2.8. To half the solution ** was added an excess of sodium perchlorate dissolved in water ($1cm^3$) and refrigerated for 3 weeks. A crystalline brown perchlorate complex was filtered off, dried and weighed. Yield of crude product was 0.07g (38.2%). This was recrystallized from water giving a crop of black crystals which were submitted for CHN analysis. A small amount of the recrystallised complex dissolved in hot water produced no turbidity with a solution of $AgNO_3$.

ANALYSIS

C.H.N. for $[Ru^{II}tpybpyCl]\,ClO_4.2.5H_2O$

cald : C,44.7 ; H,3.6 ; N,10.4.

found : C,45.0 ; H,3.0 ; N,10.9.

STAGE 2A: Aquo terpyridyl bipyridyl ruthenium (II) perchlorate -2- hydrate

$[Ru^{II}tpybpyCl]\,ClO_4$ (0.45g, $7.2x10^{-4}$ moles was dissolved in hot water ($150cm^3$) to which was added an excess of freshly prepared Ag_2O. After standing, the resulting white precipitate of AgCl was filtered off and the resulting red filtrate taken to dryness on a rotary evaporator using ethanol to facilitate the removal of water as an azeotropic mixture. Sufficient acetone ($20cm^3$) was added to dissolve the majority of the dark brown solid to be used for the preparation of the bridged dimer *P.94 That which was not dissolved was submitted for analysis.

ANALYSIS

C.H.N. for $[Ru^{II}\,tpybpyH_2O](ClO_4)_2\cdot 2H_2O$

cald: C,40.4 ; H,3.4 ; N,9.4.

found: C,40.7 ; H,2.7 ; N,9.5.

To the residual black solid, was added a further portion of acetone and the mixture heated. A pale green solution was formed,indicative of the presence of Ru(III).

STAGE 2B: Terpyridyl bipyridyl nitroso ruthenium(II) perchlorate

The preparation of this complex was attempted as another precursor to the bridged dimer basing the method on that given by Godwin and Meyer (60) using the other half of the $[\mathrm{RutpybpyCl}]^+$ solution - see P. 92** To this solution ($12cm^3$) containing 2.93×10^{-4} moles of Ru complex was added 2MHCl ($2cm^3$) and the solution heated to 50°C. A solution of $NaNO_2$(0.06g, 9.23×10^{-4} moles) in water ($4cm^3$) was added but the expected colour change from red to yellow did not take place. Furthermore, on addition of an excess of $NaClO_4$ dissolved in water ($1cm^3$) a brown rather than the expected golden yellow solid was precipitated, 0.08g. The complex was partially soluble in cold but much more soluble in hot water. Recrystallization of a small portion of the perchlorate complex by the addition of ether to an acetone solution of the complex produced a brown solid followed by the deposition of a small amount of yellow compound on standing. Rather than separate the bulk of the complex by fractional crystallization, column chromatography was used after preliminary t.l.c. tests on the acetone solution of the complex. Thus the complex was dissolved in hot acetone and the cooled solution transferred to an alumina column, 15cm x 1.3 cm(i.d.) and eluted with 2% H_2O : 98% acetone. A red component was eluted first followed by a yellow component, this latter being eluted with 20%H_2O : 80% acetone to facilitate speedy removal from the column. The yellow solution was taken to dryness and the resulting brown solid, 0.05g, submitted for C.H.N.:-

ANALYSIS

C.H.N. for $[\mathrm{RutpybpyNO}](ClO_4)_3$

cald.: C,36.6 ; H,2.3 ; N,10.3.

found: C,14.4!; H,1.2 ; N,2.9!

STAGE 3: The bridged dimer

The method of preparation is based upon that given by Powers and Meyer (61).

To the solution from P92 * ($20cm^3$) containing $7.2x10^{-4}$ moles of $[RutpybpyH_2O]^{2+}$ was added NaN_3 (0.07g, $1.08x10^{-3}$ moles) dissolved in methanol and the solution left to stand for 10 minutes. 4,4' bpy (0.07g, $4.49x10^{-4}$ moles) dissolved in acetone ($5cm^3$) was added and the solution refluxed in an argon atmosphere for 22 hours. A small amount of orange solid had formed which was filtered off but was insufficient to be dealt with further. An excess of $NaClO_4$ dissolved in acetone ($2cm^3$) was added to 1/3 of the filtrate but no precipitation took place even after 2 days refrigeration. The solution was taken to a viscous liquid by evaporation and added to diethyl ether ($50cm^3$). After a short time of stirring,a brown solid was obtained which was filtered off, washed again in diethyl ether and allowed to dry in air. The product, however, did not dry but appeared to be hygroscopic.

B. WATER INSOLUBLE RUTHENIUM COMPLEXES

a) The dioctadecyl ester of (4,4'-dicarboxy - 2,2'-bipyridyl) bis (2,2'-bipyridyl) ruthenium (II) perchlorate

The synthetic route is based upon that given by Whitten et al (26).

STAGE 1: 4,4-dimethyl-2,2'-bipyridyl

Freshly distilled γ-picoline (600cm^3, 570g, 6·12 moles) was refluxed with palladised charcoal (24g, 10% Pd on C) for four days. Benzene (210cm^3) was then added and the reflux continued for a further hour. The hot solution was filtered several times until reasonably clear and visibly free from colloidal palladized charcoal. An effective filter was prepared as follows. Small pieces of filter paper were added to some water and shaken vigorously until a pulp was obtained. This was transferred to a sintered glass funnel and pressed to remove the surplus water. After washing with acetone and then benzene, the filter was ready for use. The yellow filtrate on standing yielded a crop of crystals which were filtered off. The resulting filtrate was reduced to ∿1/3 of its volume (∿250cm^3) by distillation, cooled and seeded to produce a further crop of colourless crystals. After refrigeration of the solution overnight these were filtered off and the total of crude material recrystallized from ethyl acetate, yield 28.7g, 5.1%, m.p.t.162-164°C (lit value (26) 175-179°C).

ANALYSIS

C.H.N. for $C_{12}H_{12}N_2$

cald.: C,78.2 ; H,6.6 ; N, 15.2.

found: C,78.1 ; H,6.6 ; N, 15.3.

STAGE 2: 4,4'-dicarboxy -2,2'-dipyridyl

Powdered 4,4'-diMe-bpy (26.4g, 0.14 moles) was added to a solution of $KMnO_4$ (82.5g, 0.52 moles) in water (700cm^3) and refluxed with stirring for 22 hours. The MnO_2 which had been produced was filtered off giving a clear pale yellow solution (800cm^3) of pH10 and smelling of ammonia. This filtrate was washed with 3 portions of ether (total volume 600cm^3) in order to recover unreacted 4,4'-diMe-bpy and then treated with HCl (25cm^3) to precipitate the diacid. After settling, a portion of the supernatant suspension was centrifuged and tested for complete precipitation. The amorphous diacid was filtered-off and washed with acetone and then ether to facilitate drying, yield 3.4g, 9.7%. The compound decomposed at ∿310°C. The MnO_2 filtrand was seen to contain crystals of unreacted 4,4'-diMe-bpy. This was recovered by Soxhlet extraction using ether as solvent. The recovery of unreacted 4,4'-diMe-bpy was particularly necessary because of the need to repeat the reaction several times due to the low percentage yields obtained.

ANALYSIS

(i) The I.R. spectrum showed the characteristic broad absorption for carboxylic acids between 3000-2100cm^{-1}. A peak at 1710cm^{-1} due to the carbonyl group(s) was also observed.

(ii) CHN for $C_{12} H_8 N_2 O_4$.

cald : C,59.0 ; H,3.3 ; N,11.5.

found: C,56.9 ; H,3.5 ; N,10.9.

(iii) T.l.c. analysis on silica using pyridine as solvent showed two spots of Rf values 0.55 and 0.31. The spray reagent was an aqueous solution of $FeCl_3$, revealing the two bpy derivatives as pink spots.

(iv) An alkaline solution of the sodium salt of the acid was titrated with hydrochloric acid using phenolphthalein as indicator. This led to the calculation of the M.Wt. as 239.9.

(v) N.m.r. of the sodium salt in D_2O : d at 1.33(2), s at 1.74(2), d at 2.2(2) and s at 7.73(0.43) τ. The integration of the peaks suggest a mixture of the "diacid", 85.7%, and the "monoacid", 14.3%, yielding an average M.Wt. of 239.7.

Silylation of 4,4'-dicarboxy -2,2'-bipyridine

The silylation followed the method given by J.F.Klebe et al (85). A slurry of the carboxylic acid in ether was treated with a large excess of bis (trimethylsilyl) acetamide (B.S.A.) at ∿30°C for 15 mins. The slightly cloudy solution which resulted was filtered to remove acetamide. The filtrate was evaporated to dryness under vacuum to remove ether and unreacted B.S.A. The resulting dry solid, presumed to be the silylated derivative was then analysed.

ANALYSIS

(i) The product on heating changed state slightly at 76°C, corresponding to the m.pt.of acetamide, but did not melt on further heating. At ~310°C charring took place.

(ii) T.l.c. and I.R. observations were the same as for the carboxylic acid except that in addition, acetamide was deduced to be present in some samples.

(iii) C.H.N. analysis calculated for $C_{18}H_{24}N_2O_4Si_2$: C,55.7 ; H,6.2 ; N,7.2.

calculated for acetamide, C_2H_5NO : C,40.6 ; H,8.5 ; N,23.7.

found: C,39.8 ; H,9.3 ; N,24.0.

(iv) Mass spectral analysis yielded a molecular ion peak of 214, equivalent to the M.Wt. of the "monoacid".

Since several attempts were made at the silylation with slightly different conditions, some of these analyses above were carried out on different samples.

STAGE 3: The dioctadecyl ester of 4,4'-dicarboxy -2,2'-bipyridyl

4,4'-dicarboxy-2,2'-bpy was refluxed with an excess of thionyl chloride for 3 hours. The resulting yellow solution was evaporated to dryness under vacuum to remove excess $SOCl_2$ and the residue left in a vacuum desiccator overnight. To the completely dry diacyl halide,was added a slight excess of octadecanol and refluxed for 5 hours in benzene which had been dried over sodium and distilled from $LiAlH_4$. The resulting cloudy yellowish solution was transferred, unfiltered, to a separating funnel and chloroform added. The organic solution still cloudy was filtered and the clear filtrate washed with two portions of filtered, saturated sodium bicarbonate solution. During this washing to remove unreacted diacyl halide, (hydrolysed to the diacid), the aqueous phase turned pink. The organic layer, also slightly pink, was then washed with water and after standing, as much water as possible was separated from the now cloudy chloroform/benzene solution. The organic phase was divided into two equal portions A and B which were dried differently.

To solution A was added powdered anhydrous $MgSO_4$. The solution, after shaking and standing was filtered and much of the solvent taken off the filtrate on a rotary evaporator. Acetone was then added to the residue to precipitate the crude B.D.E. Recrystallisation from acetone/chloroform gave a product of m.pt.84-86°C - B.D.E. Ⓐ.

Instead of $MgSO_4$, solution B was treated with molecular sieves to give a product, after recrystallization, of m.pt.82-84°C - B.D.E. Ⓑ.

The sodium bicarbonate washings contained a considerable quantity of insoluble material which was revealed to be B.D.E. This was recovered and recrystallized. The total yield of recrystallized B.D.E. was 5.4g, 41.4% (based on 4,4'-dicarboxy-2,2'-bpy).

ANALYSIS

Solubility: The product was insoluble in ethanol, acetone and water but soluble in acetonitrile and chloroform.

	m.pt. °C
C.H.N. for B.D.E., $C_{48}H_{80}N_2O_4$	
cald: C,77.0 ; H,10.7 ; N,3.7.	87 lit.(26)
B.D.E. Ⓐ: C,72.8 ; H,10.7 ; N,3.8.	84-86
B.D.E. Ⓑ: C,75.8 ; H,11.0 ; N,3.7.	82-84
B.D.E. Ⓑ after two further recrystallations with Et.OH	
: C,77.1 ; H,11.0 ; N,3.8.	86

T.l.c. analysis: B.D.E. dissolved in $CHCl_3$ was spotted onto an alumina plate and developed in benzene. The developed and dried plate was sprayed with a 2% solution of ferric nitrate in 65% HNO_3 to reveal a large pink spot at Rf = 0.60, a very faint pink spot at Rf = 0.28 and a small pink spot at Rf = 0.0 (baseline).

STAGE 4: Cis dichloro bis (2,2'-bpy) Ru (II)

Commercial ruthenium chloride (1.7g, 7.06×10^{-3} moles Ru) was refluxed with bipyridine (2.0g, 1.28×10^{-2} moles) in ethanol (100 cm^3) for 12 hours. The purple solution was then reduced to 1/3 bulk by solvent evaporation, treated with acetone and refrigerated overnight. A crop of orange crystals were produced which were filtered off, washed with distilled water and then suspended in an ethanol/water (50:50, $140cm^3/140cm^3$) solution. This resulting suspension was refluxed for an hour, filtered and then treated cautiously with lithium chloride (34g, 0.8 moles). Ethanol was distilled off and the resulting aqueous solution cooled in an ice bath to form a crop of dark purple crystals; weight 0.9g, yield 28%.

ANALYSIS

The absorption spectrum in spectroscopic methanol gave λ maxima of 518 and 360 nm (lit.(26) in Et-OH→550nm and 375nm) for $Ru(bpy)_2Cl_2 \cdot x\, H_2O$.

C.H.N.cald.for $x = 0$ $C_{20}H_{16}N_4Cl_2Ru$: C,49.58 ; H,3.31 ; N,11.57.

cald.for $x = 1$ $C_{20}H_{18}N_4O\,Cl_2Ru$: C,47.80 ; H,3.58 ; N,11.15.

Found: C,47.89 ; H,3.08 ; N,10.34.

N.m.r. in D.M.S.O. gave a series of irregular peaks due to aromatic bpy protons in the region 1-3 τ.

STAGE 5: Dioctadecyl ester of (4,4'- dicarboxy-2,2'-bpy)bis (2,2'-bpy) Ru(II) perchlorate

B.D.E. Ⓐ (0.37g, 5.0×10^{-4} moles) was refluxed with $[Ru(bpy)_2Cl_2]$ (0.25g, 4.56×10^{-4} moles) in ethanol under nitrogen for 5½ hours. After which time $NaClO_4 \cdot H_2O$ (0.29g, 2.07×10^{-3} moles) dissolved in water ($20cm^3$) was added and the red solution refrigerated overnight. The brown solid which formed was filtered off. The complex was dissolved in acetone ($270cm^3$), in which the unreacted B.D.E. is insoluble, filtered and the solution evaporated to dryness on a rotary evaporator. It was then washed with water and pentane, yield, 0.46g (74.1%).

ANALYSIS

Solubility: The complex is insoluble in water and pentane but soluble in acetone and chloroform.

C.H.N. for $\left[Ru^{II}(bpy)_2\ B.D.E.\right](ClO_4)_2$

cald: C,59.9 ; H,7.1 ; N,6.2

found: C,58.6 ; H,7.8 ; N,6.0.

A surface pressure isotherm for the complex, gives a value of 82Å^2/molecule at 30 dyn/cm.

b) The dioctadecyl ester of (5,5'-dicarboxy-2,2'-bpy) bis (2,2'-bpy) Ru(II) hexafluorophosphate

The method of preparation of this complex is based upon that given for the 4,4'-analogue(Pages 95-100)the essential difference here being the use of β-picoline instead of γ-picoline for the preparation of the dioctadecyl ester ligand.

STAGE 1: 5,5'-dimethyl-2,2'-bipyridyl

The procedure carried out was one based on the dimerisation of pyridine by W.H. Sasse (66). β-picoline (75cm^3) was refluxed for 30 hours with previously prepared degassed nickel, prepared from Raney-nickel (31g). Unreacted β-picoline was distilled off under vacuum to leave a brown solid from which the crude dimethyl-bpy was extracted with boiling 60/80 petroleum ether. Three recrystallizations yielded a product of m.pt.111°C; weight 11.9g ; yield 17%.

ANALYSIS

T.l.c. on alumina showed only one spot; Rf = 0.62; solvent, toluene 90%, pyridine 10%. Revelation was by 254/366nm U.V.light. N.m.r. in $CDCl_3$:s at 1.55(2), d at 1.76(2), d at 2.46(2) and s at 7.69(6) τ.

STAGE 2: 5,5'-dicarboxy-2,2'-bipyridine

5,5'-dimethyl-2,2'-bpy (3g) was swirled with potassium permanganate

(9.5g) in water and refluxed for 3 hours. On cooling, the solution was filtered. The filtrate was washed with ether (2x20cm^3) to extract unreacted starting material and then treated with concentrated hydrochloric acid to precipitate the carboxylic acid. This was filtered off and washed with acetone to give a white powder of m.pt. >312°C (charring takes place); weight 3.2g; yield 79%. The manganese dioxide from the first filtration was also washed with ether and all the ethereal washings were evaporated to dryness to recover the unreacted starting material.

ANALYSIS

I.R. spectral analysis of the product showed a broad peak absorbing in the region 3140-1900cm^{-1}, characteristic of carboxylic acids. Absorption due to the carbonyl group appeared at 1710cm^{-1}.

STAGE 3: The dioctadecyl ester of (5,5'-dicarboxy-2,2'-bpy)→5,5'-B.D.E.

5,5'-dicarboxy-2,2'-bpy (1.2g) was refluxed with thionyl chloride (24cm^3) for 7 hours. On cooling a light yellow product crystallized out as the diacyl chloride and was filtered off; m.pt.188°C; weight 0.75g; yield 54%. This was then refluxed with octadecyl alcohol (0.55g) for 3½ hours in dry benzene (20cm^3). After refluxing, chloroform (25cm^3) was added and the mixture washed with a cold aqueous saturated solution of sodium bicarbonate (60cm^3). The organic phase was dried over anhydrous magnesium sulphate and evaporated to dryness. Recrystallization from acetone/chloroform gave a white powder of m.pt.109°C; weight 0.08g; yield 12%.

ANALYSIS

N.m.r. in $CDCl_3$ showed peaks in the region 0.7-1.5τ(6), a broad peak at 5.6τ(4) and a s at 8.7τ(70). I.R. spectral analysis showed absorption due to the long aliphatic chains (C-Hstr.) at 2850 and 2920cm^{-1} and due to the carbonyl group at 1710cm^{-1}.

STAGE 4: Cis dichloro bis (2,2'-bpy) ruthenium (II)

The preparation of this complex has already been described on P.99

STAGE 5: The dioctadecyl ester of (5,5'-dicarboxy-2,2'-bpy) bis (2,2'-bpy) ruthenium (II) hexafluorophosphate

5,5'-B.D.E. (0.14g) was refluxed with $Ru(bpy)_2Cl_2$ (0.09g) for 14 hours in ethanol ($25cm^3$). Water ($20cm^3$) and ammonium hexafluorophosphate (0.07g) were added and the mixture refrigerated overnight. The brown solid which formed was collected by filtration. In order to remove unreacted 5,5'-B.D.E., the complex was dissolved in acetone in which 5,5'-B.D.E. is insoluble. The brown acetone solution was evaporated to dryness and the resulting solid washed with water and pentane to yield the hexafluorophosphate complex; weight 0.12g; yield 43%.

ANALYSIS

C.H.N. for $\left[Ru^{II}(bpy)_2\ (5,5'\text{-B.D.E.})\right]\ (PF_6)_2$ **cald. values**

require: C,56.2 ; H,6.6 ; N,5.8.

found: C,65.7 ; H,10.9; N,3.4.

c) The dioctadecyl ester of (4,4'-dicarboxy-2,2'-bpy) bis (4,4'-dicarboxy-2,2'-bpy) ruthenium (II) hexafluorophosphate

STAGE 1: Cis dichloro bis (4,4'-dicarboxy-2,2'-bpy) ruthenium (II)

4,4'-dicarboxy-2,2'-bpy was refluxed with commercial $RuCl_3.{\times}H_2O$ in ethanol ($30cm^3$) for 11 hours. Half the solvent was removed on a rotary evaporator and acetone ($10cm^3$) added. The solution, left in a refrigerator overnight, produced a light brown solid which was filtered off to give a purple solution. This solution was taken to dryness on a rotary evaporator to yield a crop of dark purple crystals, yield 92%.

ANALYSIS

I.R. spectral analysis showed the characteristic broad absorption of carboxylic acids between 3600-2400cm^{-1}. A carbonyl peak was also present at 1710cm^{-1}. T.l.c. analysis on alumina gave four spots of Rf values 0.69, 0.62, 0.53 and 0.23, using the solvent system:benzene 80%/methanol 13%/ acetic acid 7%. The ruthenium compounds were coloured and therefore needed no spray reagent for revelation.

STAGE 2: The dioctadecyl ester of (4,4'-dicarboxy-2,2'-bpy) bis (4,4'-dicarboxy-2,2'-bpy) Ru(II) hexafluorophosphate

This synthesis was carried out as for the Whitten complex P.99 (26). However, the original product, yield 61%, required several stages of purification before all the water soluble components were removed. Further analysis of the product was not possible since after this exhaustive purification only sufficient material was available for surface chemistry study (65).

d) A dioctadecyl ester of a bis (2,9-dicarboxy-1,10-phenanthroline) ruthenium complex

2,9-dimethyl-1,10- phen was oxidised by $KMnO_4$ to the corresponding diacid by the procedure already described (P. 95), yield 54%, m.pt.>312°C-decomposition. The diacyl derivative was attempted using the same procedure already described (P. 97), but this was unsuccessful even with using a large excess of thionyl chloride and cupric chloride as a Lewis acid.

e) The dioctadecyl ester of cis dichloro diaquo (5,5'-dicarboxy-2,2'-bpy) - ruthenium (II)

An excess of commercial ruthenium trichloride (0.01g) was refluxed with 5,5'-B.D.E. (0.02g) in ethanol ($10cm^3$) for 26 hours. After refluxing and then standing for some time a brown solid separated out which was filtered off and weighed, yield 0.01g (25.2%).

ANALYSIS

C.H.N. for $\left[Ru^{II}(5,5'\text{-B.D.E.})\ (H_2O)_2\ Cl_2\right]$-$C_{48}H_{84}N_2O_6Cl_2Ru$

cald : C,60.2 ; H,8.8 ; N,2.9.

found: C,58.7 ; H,8.9 ; N,2.6.

T.l.c. on alumina using the solvent system: benzene 80%/methanol 13%/ acetic acid 7%, showed spots of Rf values 0.85, 0.52 and 0.0. The ruthenium compounds were coloured and therefore needed no spray reagent for revelation.

C. THE ATTEMPTED PREPARATION OF OTHER TRANSITION METAL B.D.E. COMPLEXES

a) PREPARATION OF Mn-B.D.E. COMPLEXES

$\left[Mn^{III}(B.D.E.)_2\ Cl_2\right]Cl$

B.D.E. (0.29g, 3.87 X 10^{-4} moles) and $MnCl_2.4H_2O$ (0.19g, 9.6 X 10^{-4} moles) were refluxed together in a mixture of Et OH(50cm^3) and water (3cm^3) for 4 hours. On cooling the yellow solution, a white solid, presumably B.D.E., was precipitated. The solution was taken to dryness on a rotary evaporator, rectified spirit (dry ethanol-30cm^3) added and the solution refluxed for a few minutes. The resulting yellow solution was allowed to cool. A yellow solid was precipitated in admixture with a white solid. The contents of the flask were reheated and the resulting yellow solution allowed to cool more slowly. On cooling, less white precipitate was formed with the yellow precipitate. The mixture was swirled such that the majority of the white precipitate could be decanted without much loss of yellow precipitate. This left a small volume of solution containing most of the precipitated yellow compound. This residual solution was heated to boiling and rectified spirit added until all the yellow precipitate had redissolved. The solution was allowed to cool slowly to yield the yellow product which was filtered off, dried and weighed. Yield=0.1g.

ANALYSIS: On addition to water the yellow product turned white.

Elemental analysis

found: C, 70.3; H, 10.0; N, 3.7; Cl, 6.2.

$\left[Mn^{III}(B.D.E.)_2Cl_2\right]Cl$ requires: C, 69.5; H, 9.7; N, 3.4; Cl, 6.4

b) PREPARATION OF Fe-B.D.E. COMPLEXES $\left[Fe^{II}(B.D.E.)(H_2O)_2Cl_2\right]$

B.D.E. (0.3g, 4.07X10^{-4} moles) and $FeCl_3.6H_2O$(0.17g, 6.29X10^{-4}moles) were refluxed together in Et-OH (20cm^3) for 4 hours producing a red solution. On cooling and standing overnight, a red solid was precipitated which was filtered off and dried in air. Yield of 1st Fe-B.D.E. complex, Fe B.D.E.①, 0.04g. To the red filtrate was added an ethanolic solution of an excess of $NaClO_4.H_2O$ (0.5g, 4.2X10^{-3} moles) and the solution allowed to stand for two weeks. After which time, a red solid was precipitated which was filtered off, washed with water to remove $NaClO_4$ and dried in air. Yield of 2nd Fe-B.D.E. complex, Fe B.D.E.②, 0.084g.

ANALYSIS

Fe B.D.E.①

Solubility:- readily soluble in acetone and water to give deep red solutions.

Elemental analysis

found: C,41.2; H,3.5; N, 5.3; Cl,19.9.

$[Fe^{II}(B.D.E.)\ (H_2O)_2\ Cl_2]$ requires: C,63.2; H,9.2; N,3.1; Cl,4.3.

$[Fe\{bpy\ (COOEt)_2\}(H_2O)_2\ Cl_2]$ requires: C,41.5; H,4.3; N,6.1; Cl,11.4.

Fe B.D.E.②

Solubility: readily soluble in acetone and chloroform to give red solutions and slightly soluble in water.

Elemental analysis

found: C,46.7; H,4.1; N,6.1.

$[Fe^{II}(B.D.E.)\ (H_2O)_4](ClO_4)_2$ requires: C,53.6; H,8.2; N,2.6.

A test was carried out to see the effect of relative ligand and cation concentration upon the colour and therefore the nature of the complex formed. $Fe^{II}SO_4$ was added to some ligand in Et.OH and warmed:-

Bpy	colour	B.D.E.	colour
Fe^{II} in excess →	red	Fe^{II} in excess →	purple
bpy in excess →	red	B.D.E. in excess →	red

c) PREPARATION OF Co-B.D.E. COMPLEXES

(i) $[Co^{III}(bpy)_2\ B.D.E.]\ (NO_3)_3$

Stage 1 Preparation of cis $[Co^{III}(bpy)_2\ Cl_2]Cl.3H_2O$

The preparation of this complex is based upon that given by **Vlček** (68).

$CoCl_2.6H_2O$(1g, $4.2X10^{-3}$ moles), LiCl(1g, $2.4X10^{-2}$ moles) and bpy (1.6g, $10.3X10^{-3}$ moles) were successively dissolved in 50cm^3 of dry MeOH under nitrogen. Gaseous Cl_2 was then slowly bubbled into this solution under cooling for 15 minutes during which time a grey solid was precipitated.

The solution was allowed to stand overnight, during which time purple crystals had also formed. The grey and purple solids were filtered off, redissolved in hot Et OH and the solution allowed to evaporate on a water bath. A small amount of a green flocculent precipitate was formed which was filtered from the hot purple solution. This latter was allowed to evaporate at room temperature overnight when a crop of purple crystals was produced. These were filtered off and the purple filtrate subject to evaporation on the water bath again. More green flocculent precipitate was produced which was filtered from the hot purple solution and this latter allowed to evaporate at room temperature overnight to give a further crop of purple crystals as before. Total yield of purple crystals, the cis complex, 1.1g, 54.7%.

Elemental analysis

for $[Co^{III}(bpy)_2Cl_2]Cl.3H_2O$

calcd. C,45.6; H,4.1; N,10.5; Cl,20.0.

found. C,47.7; H,3.7; N,11.2; Cl,20.3.

Stage 2 Preparation of $[Co^{III}(bpy)_2\text{ B.D.E.}](NO_3)_3$

$[Co(bpy)_2Cl_2]Cl.3H_2O$ (0.2g, 3.8×10^{-4} moles) and $AgNO_3$ (0.2g, 14.1×10^{-4} moles) were refluxed in water (25cm^3) for 1 hour. The precipitated AgCl was filtered off into a preweighed sintered glass crucible and was equivalent to 3.01 atoms of Cl/molecule of $[Co(bpy)_2Cl_2]Cl\cdot3H_2O$. The red filtrate was evaporated down to ~10cm^3, B.D.E. (0.27g, 3.6×10^{-4} moles) added and the reflux continued with an additional 40cm^3 of Et.OH for 20 hours. During this time the solution had become gradually orange and after cooling a brown precipitate had formed. The solution was filtered to yield a yellowish - pink filtrate which on standing produced a crop of yellow crystals, Co bpy①. The brown solid, which appeared to be a mixture of four components was washed with $CHCl_3$ to dissolve B.D.E. and any Co-B.D.E. complex. The solution was filtered and the filtrate on evaporation yielded a mixture of yellow and white solids. This mixture was such that the white solid, presumably B.D.E., could be removed physically with a spatula. The residual yellow solid was partially soluble in acetone to give a yellow solution. Filtration of the mixture gave a yellow solid, Co B.D.E. ①, yield 0.18g, and a yellow solution which on evaporating to dryness yielded a light brown solid, Co B.D.E. ②.

ANALYSIS

Co bpy ①

Solubility: insoluble in acetone and $CHCl_3$ but readily soluble in water.

C.H.N. for $[Co^{III}(bpy)_2(H_2O)_2](NO_3)_3$

cald. C,40.7; H,3.4; N,16.6.

found. C,41.2; H,3.3; N,14.8.

Co B.D.E. ① and ②

The solubility of the Co B.D.E. complexes is shown below:-

	①	②
$CHCl_3$	✓	✓
acetone	X	✓
water	X	X

✓ soluble

X insoluble

The solids ① and ② on standing in water were not discoloured even after several days. This is in contrast to previously prepared presumed Co-B.D.E. complexes whose yellow colour disappeared on standing in water.

Elemental analysis

found.	Co B.D.E. ①	C,63.2; H,9.1; N,4.7.
"	Co.B.D.E. ②	C,55.3; H,8.5; N,4.2.
$[Co^{III}(bpy)_2B.D.E.](NO_3)_3$	requires	C,62.7; H,7.4; N,7.5.

(ii) Preparation of $[Co^{III}(B.D.E.)Cl_3(H_2O)]$

B.D.E. (0.29g, $3.8X10^{-4}$ moles) and $CoCl_2.6H_2O$ (0.14g, $5.9X10^{-4}$ moles) were refluxed together in Et.OH ($20cm^3$) for 4 hours. A small portion of the hot blue solution which resulted was added to water. An immediate precipitate of a pink -orange solid was formed. After centrifugation and removal of the supernatant pink solution more water was added. After shaking and centrifugation both the sediment and supernatant solution lost most of their colour. The rest of the blue solution which had not changed colour during the reflux, was evaporated down to 5cm^3 to yield on cooling and standing a green—blue solid.

This was filtered off and redissolved in hot Et-OH (4cm^3) and allowed to stand for 4 days. After which time an orange -brown solid was precipitated and the deep blue solution had turned a very pale purple. The orange -brown precipitate was filtered off and dried in air, yield, 0.03g (8.5%).

ANALYSIS:

Solubility: soluble in $CHCl_3$ but insoluble in water. The colour of the complex is retained after standing in water, in the same way as for the complexes Co B.D.E. ① and ②.

Elemental analysis

found: C,66.2; H,9.5; N,3.4; Cl,9.5

$[Co (B.D.E.) Cl_3 (H_2O)]$ requires: C,62.0; H,8.6; N,3.0; Cl,11.5.

d) PREPARATION OF Pd-B.D.E. COMPLEXES

(i) $[Pd (bpy) B.D.E.] Cl_2$

Stage 1 Preparation of $Pd (bpy) Cl_2$

$PdCl_2$ (0.9g, $5.21X10^{-3}$ moles) and bipyridyl (1.0g, $6.41X10^{-3}$moles) were mixed together in a 50:50 ethanol/water mixture (20cm^3) and refluxed for 3 hours. After which time a precipitate was formed which appeared to be a mixture of a green —grey solid and a yellow solid. The total precipitate was filtered from the red solution and on the basis of solubility tests, was added to CH_2Cl_2 (50cm^3) in which the yellow component was soluble. The solution was heated to boiling and filtered to yield a green —grey solid. Pd bpy ①, yield 1.2g (70%) and a yellow filtrate which on evaporation to dryness produced a yellow solid, Pd bpy ②, yield 0.02g (1.2%).

ANALYSIS

The solubilities of the two complexes are shown in table 13 .

Table 13 The solubilities of Pd-bpy ① and Pd-bpy ②

	Pd-bpy①		Pd bpy②	
solvent	cold	hot	cold	hot
$CHCl_3$	X	X	X	X
CH_2Cl_2	X	X	X	✓
$(CH_3)_2CO$	X	X	X	X
H_2O	X	X		
Et-OH	X	X		
Et.O.Et	X	X		
HCl	✓	✓✓		
HNO_3	✓	✓✓		
CH_3CN	✓	✓✓ *		

X .... insoluble

✓ .... soluble

✓✓... increase in solubility

* On cooling, yellow needles are formed.

Elemental analysis

Pd bpy① found: C,32.9; H,2.2; N,7.9; Cl,19.6.

Pd bpy② found: C,36.4; H,2.5; N,8.5; Cl,20.8.

Pd bpy Cl_2 requires: C,36.0; H,2.4; N,8.4; Cl,21.3.

I.R. analysis of Pd bpy ① - KBr disc, gave a peak at 3,050cm^{-1}, and five peaks between 1450cm^{-1} and 1,600cm^{-1} - indicative of aromaticity. There was insufficient Pd bpy② for I.R. analysis.

Stage 2 Preparation of $\left[Pd(bpy)\ B.D.E.\right]Cl_2$

Pd bpy①was extracted with acetonitrile in a Soxhlet extractor for 5 hours to produce a yellow solution of the soluble component and leaving some greenish-grey material in the Soxhlet thimble, Pd bpy③. The yellow solution was taken to dryness on a rotary evaporator. The resulting browny-yellow solid which was insoluble in cold alcohol, water or chloroform, Pd bpy④ (0.14g, $4.20X10^{-4}$ moles) was refluxed in acetonitrile (50cm^3) with B.D.E. (0.35g,

4.68×10^{-4} moles) for 13 hours. After which time, a yellow solid precipitated from a yellow solution. This latter was decanted off, the precipitate washed with hot acetonitrile and the mixture filtered. The yellow solid was then washed with hot chloroform and filtered to give a yellow solid, Pd B.D.E. ①, yield 0.05g, and a yellow solution which on evaporating to dryness gave another yellow solid, Pd B.D.E. ②, yield 0.16g.

Elemental analysis

Pd bpy ③ found: C, 32.1; H,2.0; N,7.7; Cl,17.7.
Pd bpy Cl_2 requires: C, 36.0; H,2.4; N,8.4; Cl,21.3.

Pd B.D.E. ① found:C,36.8; H,2.6; N,5.6.
Pd B.D.E. ② found:C,77.6; H,11.0; N,4.4; Cl,4.1.
$[Pd(bpy)(B.D.E.)]Cl_2$ requires:C,64.4; H,8.1; N,5.2; Cl,6.6.

(ii) $Pd(B.D.E.)Cl_2$

Stage 1 Preparation of $Pd(CH_3CN)_2Cl_2$

K_2PdCl_4(1g, 3.06×10^{-3} moles) was dissolved in a large excess of acetonitrile (2cm^3, 3.62×10^{-2} moles) and water (20cm^3) and left to stand for 3 days. After which time a crop of yellow-green crystals had formed. The red supernatant liquid was decanted off and the crystals, which were more soluble in acetone than in chloroform, were dissolved in a hot solution of chloroform and acetone using a minimum of acetone - total volume of cooled stock solution was 50cm^3. Visible spectroscopy at 420nm of the red supernatant liquid initially decanted from the crystals indicated that ~86% of the K_2PdCl_4 had reacted to form $Pd(CH_3CN)_2Cl_2$. Therefore stock solution (50cm^3) contained ~2.63×10^{-3} moles of $Pd(CH_3CN)_2Cl_2$.

Stage 2 Preparation of Pd B.D.E. Cl_2

Into 7.5cm^3 of the stock solution (~4.0×10^{-4} moles of $Pd(CH_3CN)_2Cl_2$)was dissolved B.D.E. (0.09g, 1.20×10^{-4} moles) and the resulting solution left to stand overnight. After which time, a small amount of brown solid amongst a yellow,partially crystalline,solid came down. The precipitate was filtered off and recrystallized from an acetone/chloroform mixture, yield of Pd B.D.E. ③, 0.09g (81% based on B.D.E.).

Elemental analysis

Pd B.D.E. ③ found: C,60.9; H,8.6; N,2.5; Cl,12.8.
Pd (B.D.E.) Cl_2 requires: C,62.2; H,8.6; N,3.0; Cl,7.7.

D. PREPARATION OF CERIUM, BARIUM, CADMIUM AND MAGNESIUM STEARATES

Sodium stearate was dissolved in hot water ($100cm^3$) to which was added a hot solution of a slight excess of the appropriate molar quantity of the metal ion in water ($\sim 20cm^3$). An immediate white precipitate was formed which after cooling was filtered off. The filtrate was tested with a solution of the metal ion to ensure complete precipitation. The crude stearate was then transferred to a beaker, washed with water ($\sim 200cm^3$), filtered again, pressed between filter papers and finally dried in a vacuum desiccator.

Yields:			
	Cerous stearate	6.0g	105%
	Barium stearate	7.0g	92%
	Cadmium stearate	3.2g	94%
	Magnesium stearate	3.8g	102%

ANALYSIS

Solubility: The dry stearate is not only insoluble in water but is not even wetted by it on stirring or prolonged standing. With acetone and chloroform the stearates produce cloudy solutions.

Elemental analyses

found: C,61.2; H,10.6; N,0.0.

$Ce(C_{17}H_{35}COO)_3$ requires: C,65.4; H,10.6; N,0.0.

found: C,60.5; H,10.2; N,0.0.

$Ba(C_{17}H_{35}COO)_2$ requires: C,61.4; H,9.9; N,0.0.

found: C,61.1; H,10.4; N,0.0.

$Cd(C_{17}H_{35}COO)_2$ requires: C,63.6; H,10.3; N,0.0.

found: C,80.6; H,11.7; N,0.0.

$Mg(C_{17}H_{35}COO)_2$ requires: C,73.1; H,11.8; N,0.0.

E. PREPARATION OF HYDROLYSED MALEIC ANHYDRIDE/STYRENE COPOLYMER

STAGE 1 PREPARATION OF MALEIC ANHYDRIDE/STYRENE COPOLYMER

a) Purification of starting materials

Most of the starting materials for this preparation had to be especially purified before use:-

1. Zinc Chloride

The anhydrous $ZnCl_2$ bottle was kept in a polythene bag, containing desiccant in a dry box until it was needed.

2. Styrene

Styrene was washed twice with sodium hydroxide solution (10%) to remove t-butyl catechol and then three times with water. The resulting yellowish cloudy styrene was allowed to stand, becoming clear as droplets of water separated out. The clear styrene was distilled under nitrogen to reduce polymerisation. Even though the temperature was allowed to reach 120°C, sufficient styrene came over before the rest of the styrene in the distillation flask began to polymerise.

3. Benzoyl Peroxide

Benzoyl Peroxide was dissolved in chloroform and the cloudy solution left to stand in a separating funnel overnight. After which time, the organic solution had cleared and was run-off from the small amount of water which had separated out above it. The chloroform solution was heated to 40°C and methanol added. Crystals of benzoyl peroxide started to precipitate almost immediately. After cooling and standing a crop of colourless crystals were formed which were filtered off, washed with methanol and dried in vacuo. The dry benzoyl peroxide was kept under vacuum until needed.

4. Maleic Anhydride

The maleic anhydride was purified by "cold finger" sublimation to remove impurities of maleic acid.

b) Preparation of the unhydrolysed copolymer

To a slurry of maleic anhydride (3.39g, $3.46X10^{-2}$ moles) in styrene ($4cm^3$, 3.60g, $3.46X10^{-2}$ moles) was added anhydrous $ZnCl_2$(4.72g, $3.46X10^2$ moles) and benzoyl peroxide (0.08g, 3.31×10^{-4} moles) under nitrogen. The mixture was swirled and heated gently when a violent reaction took place. White smoke was evolved and the mixture became extremely hot eventually resulting in a solid mass. Since this could not be dissolved or slurried out using toluene the flask was smashed and the solid ground in a pestel and mortar. The resulting powder was transferred to a Soxhlet thimble and extracted overnight using benzene as solvent to remove all unreacted starting materials except $ZnCl_2$. After the Soxhlet extraction, the benzene solvent was slightly cloudy due to the formation of a colloidal solution of the copolymer. This was considered unworthy of recovery. The solid material left in the Soxhlet thimble was turned out onto a watch glass. After the surplus benzene had evaporated, the crude copolymer appeared to gradually increase in weight. Since this was presumably due to the absorption of atmospheric moisture by $ZnCl_2$, the crude copolymer (~7.9g) was washed in water (100cm^3) to give ~4.2g of water insoluble copolymer, m.pt. ~310°C (decomposition).

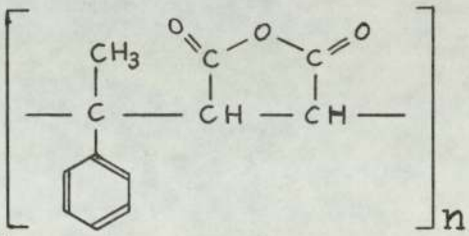
ANALYSIS

Solubility: the unhydrolysed copolymer was insoluble in hot or cold acetone, butanone, benzene, toluene and water but soluble in alkaline solution.

Elemental analysis

found: C,61.1; H,5.6; N,0.0.

$C_{12}H_{10}O_3$ requires: C,71.3; H,5.0; N,0.0.



I.R. analysis - KBr disc.

Absorption in the region 2,300-3,700cm^{-1} was indicative of a carboxylic acid. Absorptions at 1720 and 1785cm^{-1} probably due to two carbonyl groups. Small peaks just above 3,000cm^{-1} and a peak at 1500cm^{-1} suggestive of an aromatic group.

STAGE 2 PREPARATION OF THE HYDROLYSED COPOLYMER

The unhydrolysed copolymer (4.1g) was swirled with ~0.5M KOH solution (150cm^3) and heated to 80°C overnight. The resulting dense milky colloidal solution was acidified with HCl to precipitate the free-acid. This was filtered off to give a white filtrand and a clear filtrate of pH3. This latter was tested with HCl for complete precipitation. After the removal of as much water as possible in the Büchner funnel, the hydrolysed copolymer was transferred to a watch glass and eventually dried to a hard product in a vacuum desiccator. This was ground to a powder in a pestel and mortar and weighed off, yield 1.4g, m.pt. ~310°C - decomposition.

ANALYSIS

Solubility: the hydrolysed copolymer was insoluble in hot or cold acetone, chloroform, benzene, toluene and 1,4 -dioxan but soluble especially in the hot in water, ethanol and T.H.F. to give cloudy solutions.

N.m.r.

A concentrated solution of the hydrolysed copolymer was made up in T.H.F. and run on a 30MHz instrument. A faint but genuine multiplet was observed centred at $\sim 2.8\tau$, away from solvent peaks upfield.

Vapour Phase Osmometry was carried out on the product using T.H.F. as solvent and benzil as calibrant to give an approximate M.Wt. of 7,000.

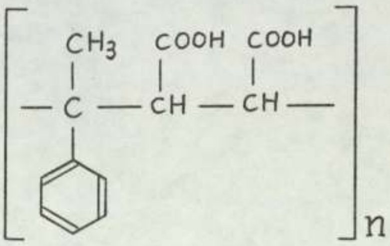
I.R. analysis - KBr disc and hexachlorobutadiene mull.

Broad absorption between 2,300-3,700 cm^{-1} was indicative of a carboxylic acid. A broad peak at 1720cm^{-1} probably due to carbonyl group(s). A sharp peak at 1500cm^{-1} is suggestive of aromaticity but no peak was seen just above 3,000cm^{-1}, possibly obscured by broad carboxylic acid absorption.

Elemental analysis

found: C,59.9; H,5.9; N,0.0.

$C_{12}H_{12}O_4$ requires: C,65.4; H,5.5; N,0.0.



CHAPTER 7 IRRADIATION OF THE COMPLEXES

THE IRRADIATION OF THE COMPLEXES

THE APPARATUS USED

The complexes prepared were irradiated in both homogeneous and heterogeneous systems. These latter included a) micellar solutions, b) dispersions of virtually insoluble materials prepared using an ultrasonic bath and c) metal catalysts on charcoal and as microheterogeneous colloidal sols.

The solutions of the complexes were irradiated, for the most part, in a glass reactor for visible photochemistry or in a smaller silica reactor suitable for both visible and U.V. irradiation. These are described and shown in figures 10 and11. Other photochemical reaction vessels used are described later on in the text.

The use of the silica reactor

Arrangement 1

This is shown in fig. 10 on P. 119. The solution ($\sim 120 cm^3$ required) to be irradiated is poured into the reactor and is filled by means of the separating funnel R, which is used as a levelling device. All the air may be removed by inverting the reactor before inserting subaseal 1 . A volume of air (usually $1-2 cm^3$) may be addedto the top of the gas collection head if required using a syringe injected through the subaseal 1 with taps C, D and E open to maintain at atmospheric pressure. The water jacket system was arranged such that the reactor could be cooled during irradiation with tap water and if required subsequently, heated with hot water at 70°C by the use of two3way taps. In addition to the water jacket, a fan was also used for cooling. The irradiating source was either a tungsten bulb or a medium pressure mercury U.V. lamp housed with the fan and reactor under a large wooden box. With the taps C, D and E closed, the cooling water running, and the wooden box in position, the lamp and fan were switched on. After irradiation, photolyte may be sampled from the 3-way tap C using the levelling reservoir, R, for testing pH or spectrophotometric analysis. Any gas produced in the collection head may be sampled using a syringe through subaseal 1 with taps D and E open.

Fig.10 The Silica Reactor
Arrangement 1

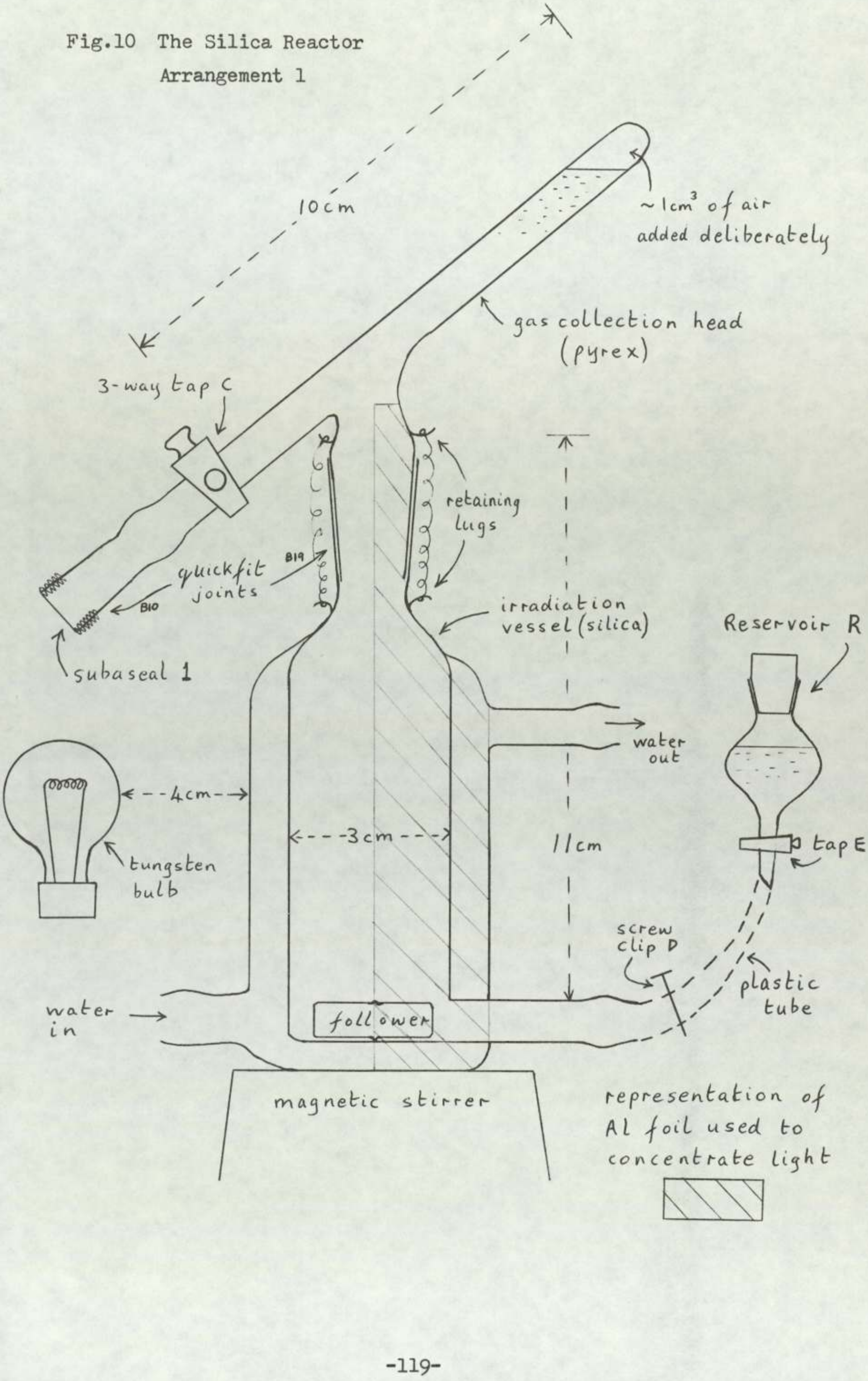
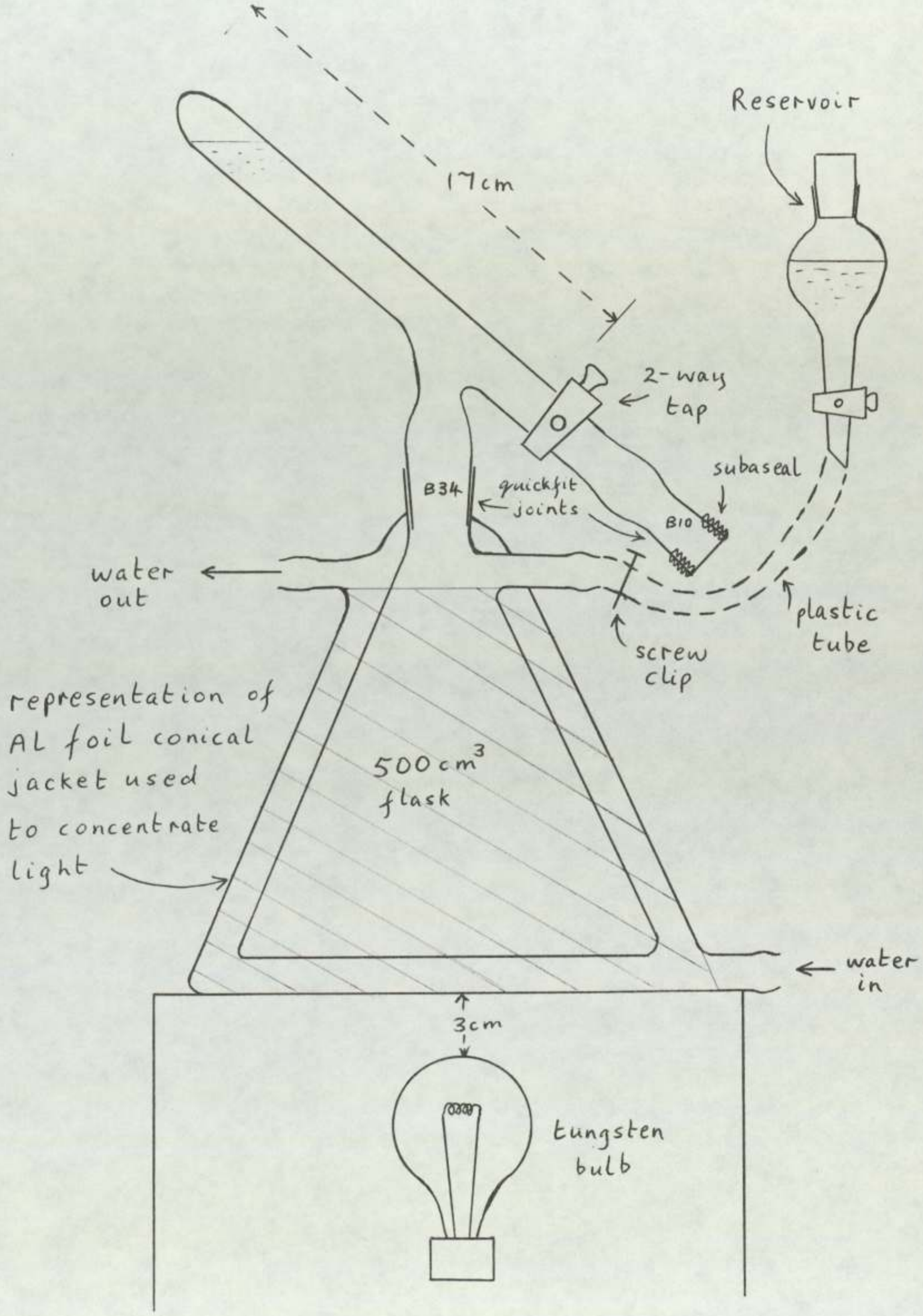


Fig. 11 The Glass Reactor



Use of U.V. lamp

When the U.V. lamp was used it was held touching the reactor and bound to it with copper wire. The fan was unnecessary for the U.V. lamp since it has its own cooling water jacket.

Arrangement 2

This differs from arrangement 1 in so far as the gas collection head is replaced by a glass stopper and the plastic tube and reservoir R are replaced by subaseal 2 . By so doing, the photolyte volume is reduced to 65cm^3. Exclusion of all the air or the inclusion of a known volume of gas may be effected using syringes injected through the subaseal 2 . Similarly after irradiation, gas may be withdrawn.

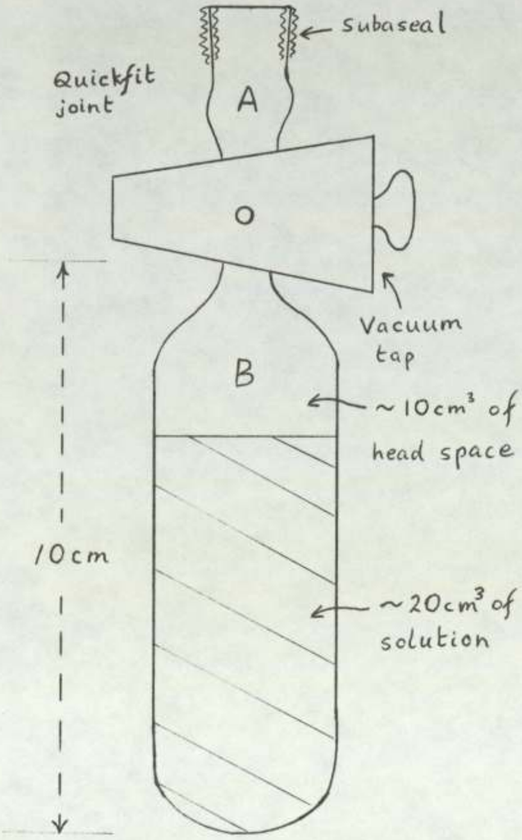
The use of the glass reactor

This is shown in fig.11on P.120. As can be seen from the diagram the mode of operation is similar to that of the silica reactor.

Irradiation is from a tungsten lamp beneath the flask and the light is concentrated by an aluminium foil jacket.

The use of the freeze-thaw (F.T.) tube

Fig12 The freeze-thaw tube



(i) For freeze-thawing

After irradiation in say the silica reactor, 20cm^3 of the solution may be injected into the F.T.-tube through the vacuum tap using a 25cm^3 syringe (fig.12). The solution is then frozen in a bath of CO_2/acetone with the tap open and keeping the solution agitated to avoid cracking the tube during the expansion of freezing. With the tube still in the CO_2/acetone bath the air space above the liquid is evacuated to <5mm Hg. The tap is then closed and unirradiated solution poured into section A. The solution is then thawed gradually by placing the tube in warm water. Solution from A is let in gradually, care being taken not to allow in any air until the system is at atmospheric pressure. Section A is replenished and a subaseal placed in position such that no air is entrained. The tube is inverted and the tap opened. The dissolved gas so produced may now be sampled by using two syringes: one withdrawing the gas as unirradiated solution is injected in from the other. In this way air may be prevented from being sucked into the tube.

In addition, some solutions, so treated, were left standing in the dark or irradiated further. For this, ~1-2cm^3 of solution was withdrawn by syringe from section B such that an equal volume of air was allowed in. The tap was closed, the solution replenished in section A and the subaseal replaced.

(ii) For irradiation

The F.T.-tube was also used for irradiation. Solution was injected into the tube leaving ~1cm^3 of air beneath the tap which was then closed. Section A was filled up and the subaseal replaced. After irradiation, the deliberate bubble is sampledas already described in section (i) ~10cm^3 of solution may then be withdrawn leaving ~20cm^3 for freeze-thaw treatment as already described in section (i).

Some irradiations were carried out under reduced pressure; ~20cm^3 of solution is used to allow sufficient head space for the frothing due to escaping air during the reduction in pressure. After irradiation the system is equilibrated to atmos.press. with unirradiated solution and the gas sampled as described in section (i). Irradiation was with a 100W bulb 8cm away and cooling was by fan only.

The use of the freeze-thaw flask

This is shown in fig.13 and its mode of operation is analogous to that of the F.T.-tube described above.

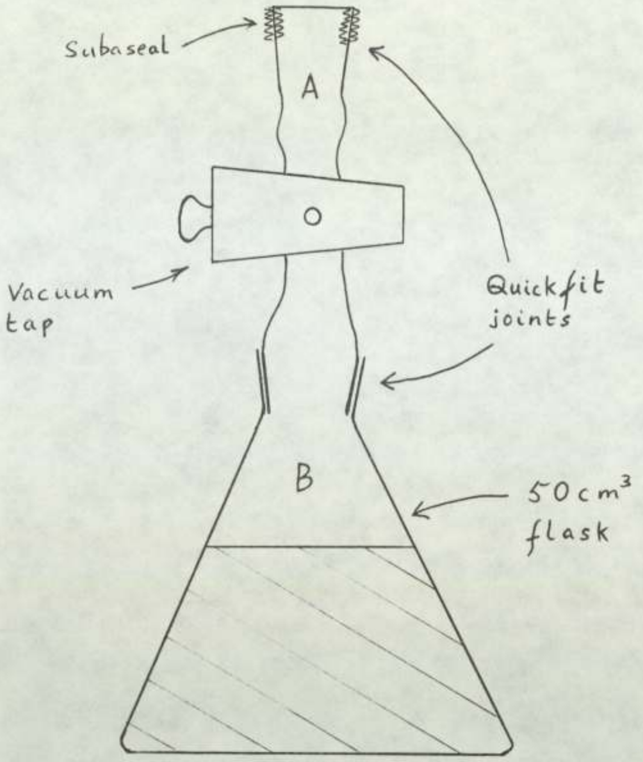


Fig. 13

The freeze-thaw flask

Gas Chromatographic Analyses

These were carried out on a PYE UNICAM Series 104 instrument with the following conditions:-

Carrier gas	Argon
Carrier gas flow rate	10cm^3/min.
Column packing	5 Å molecular sieves
Column temperature	80°C

IRRADIATION OF WATER SOLUBLE RUTHENIUM COMPEXES

A. TRIS BIPYRIDYL RUTHENIUM (II)

Irradiation of $Ru^{II}(bpy)_3^{2+}$ and cis $[Co^{III}(bpy)_2Cl_2]Cl$

A solution containing $Ru(bpy)_3^{2+}$ (10^{-4}M) and cis $[Co^{III}(bpy)_2Cl_2]Cl$(10^{-4}M) was irradiated by U.V. for 18 hours in the silica reactor (arrangement 1 P. 118) After degassing with hot water, the resulting gas bubble was withdrawn and sampled by G.C.- no hydrogen. The same solution was irradiated again for a further 3 days. After which time no gas had been produced. Some of the irradiated solution ($50cm^3$) was quickly decanted into a $50cm^3$ conical flask and freeze-thawed as described on P. 122. G.C. analysis of the dissolved gas revealed no hydrogen. No apparent differences in the UV-Vis spectra of the solutions before and after irradiation were observed but the pH had dropped from 5.6 to 2.8.

Irradiation of $Ru(bpy)_3^{2+}$

A solution of $Ru(bpy)_3^{2+}$ (10^{-4}M) was irradiated with U.V. for 24 hours in the silica reactor (arrangement 2 P. 121).After which time there was no change in either the pH, 4.2 or the U.V.-Vis spectra of the solutions before and after irradiation. Some of the irradiated solution ($50cm^3$) was quickly decanted into a $50cm^3$ conical flask and freeze-thawed as described on P. 122. G.C. analysis of the dissolved gas revealed no hydrogen.

Irradiation of a suspension of palladised charcoal in $Ru(bpy)_3^{2+}$

Palladised charcoal (0.11g) was added to $Ru(bpy)_3^{2+}$ solution (10^{-4}M, $100\ cm^3$). A portion of this mixture ($65cm^3$) was irradiated with U.V. for 4 days in the silica reactor (arrangement 2 P.121).The palladised charcoal was kept mixed by using a magnetic stirrer. Because of this the U.V. lamp was held $8cm^3$ away from the reactor. After irradiation no gas had been produced, the pH remained unchanged, 6.1,and no hydrogen was found from the freeze-thawing of the solution ($50cm^3$). However slight differences in the U.V.spectra of the filtered solutions were observed viz: At 224nm;irradiated solution absorbance, 0.70,unirradiated solution absorbance, 0.52.

Irradiation of a micellar solution of $Ru(bpy)_3^{2+}$

A solution containing $Ru(bpy)_3^{2+}$ (10^{-5}M) and S.D.S. (1.4×10^{-2}M) was irradiated in the glass reactor P.121for 5 days with a 150W bulb. After which time ~1cm^3 of gas had been produced which was withdrawn and tested by G.C. analysis, no hydrogen. The pH increased slightly during irradiation from 8.8 to 9.5.

Irradiation of a micellar solution of $Ru(bpy)_3^{2+}$ and barium stearate

A solution containing $Ru(bpy)_3^{2+}$ (10^{-4}M), S.D.S. (1.4×10^{-2}M) and barium stearate ($\leq 2.7\times10^{-5}$M,P.139)was irradiated in the silica reactor (arrangement 2 P.121)with U.V. for 17 hours. After irradiation no gas had been produced, the pH remained unchanged, 6.6, and there were no differences in the U.V.-Vis spectra of the solution before and after irradiation. Some of the solution (50cm^3) was freeze-thawed and the liberated dissolved gas analysed by G.C. A deflection of the baseline where hydrogen appears was observed.

Irradiation of $Ru(bpy)_3^{2+}$, stearic acid and hydrolysed maleic anhydride-styrene copolymer

Stearic acid (0.07g) and copolymer (0.05g) were added to $Ru(bpy)_3^{2+}$ (134cm^3, 5×10^{-5}M) and the solution placed in an ultrasonic bath for ~5 mins. The pH, 4, was adjusted to 6 to increase the solubility of the copolymer and the flask replaced in the ultrasonic bath. The small amount of still undispersed copolymer (now orange) and stearic acid were removed in a separating funnel. The solution was then irradiated in the silica reactor (arrangement 1 P.118)with visible light (150W bulb) for 19 hours with ~1cm^3 of air deliberately added into the gas collection head.

After irradiation the deliberately added air bubble was withdrawn and analysed by G.C. revealing a trace of hydrogen and a very small peak eluted after nitrogen. During irradiation the pH had dropped slightly from 5.6 → 5.4. Hot water at 70°C was passed through jacket for ~3 hours after which time the resulting gas, 0.5cm^3 was G.C. analysed to reveal a small peak of hydrogen, an undesignated peak eluted after nitrogen and an increased N_2:O_2 ratio.

The photolyte, as a result of standing and/or irradiation became much lighter in colour with the precipitation of an orange solid.

Irradiation of $Ru(bpy)_3^{2+}$ and stearic acid

Stearic acid (0.09g) was dispersed in $Ru(bpy)_3^{2+}$ solution ($165cm^3$, $10^{-4}M$) using an ultrasonic bath and the resulting solution irradiated in the silica reactor (arrangement 1 P.118)with visible light (150W bulb) for 17½ hours with ~$1cm^3$ of air added deliberately into the gas collection head. After irradiation,the deliberately added bubble was withdrawn and G.C. tested giving a large peak of hydrogen, no peaks eluted after nitrogen and a N_2:O_2 ratio as normal (as for air). The pH remained unchanged at 4.9. The solution was degassed by passing hot water at 70°C through the jacket and the resulting gas produced,tested,giving a large peak of hydrogen, no peaks eluted after nitrogen and N_2:O_2 ratio as normal (for dissolved air). During degassing,a small amount of a green material soluble in acetone, was deposited on the reactor walls. The above procedure of irradiation and degassing was repeated to give a total of 7 irradiations of the same solution. The experiment is summarised in table14.

After the degassed solution from the first irradiation had cooled, the stearic acid was reduced in solubility to give some precipitation and a cloudy solution but after the 7th irradiation the solution remained clear after cooling and standing.

Irradiation of $Ru(bpy)_3^{2+}$ and octadecane

Octadecane (0.02g) (mpt=30°C) was melted in a beaker and the molten material injected with a preheated syringe into $Ru(bpy)_3^{2+}$ solution ($138cm^3$,$10^{-4}M$) at 40°C in an ultrasonic bath. The resulting emulsion was adjusted to pH 8.3 and irradiated in the silica reactor (arrangement 1 P.118)with visible light (150W bulb) for 20 hours with ~$1cm^3$ of air deliberately added. The emulsion was maintained by circulating water at 35°C through the jacket. After irradiation, the deliberate bubble was tested,giving a small peak of hydrogen. The solution was degassed at 70°C for 3½ hrs. to produce a volume of gas which on G.C. analysis contained 1.3 μL hydrogen. Another deliberate bubble of air

TABLE 14 Hydrogen evolution from $Ru(bpy)_3^{2+}$ and stearic acid

Irradiation No.	Irradiation time	µL of H_2 obtained from		undesignated peak eluted after N_2 *3	pH before & after		temp. during irradiation (°C)
		delib. bubble	degassing				
1	17½hours	0.2	4.6	X	4.9	4.9	20
2	3 days	3.5	1.9	X	4.9	4.8	
3	2 days	3.6	0.6	X	4.8	4.8	
4	2 days	2.4	1.3	X	4.8	4.8	
5	3 days	11.7		✓	4.8	4.4	70 *2
*1 6	23 hours	2.5		✓	4.4	4.4	
7	23 hours	1.6		✓	4.4	4.4	
		total vol.of H_2 obtained, 33.9 µL					

*1 Solution not irradiated but left in the dark.

*2 Hot water at 70°C was passed through the jacket during irradiation.

*3 A diluted sample of natural gas was analysed by G.C. but the methane peak appeared at 19.8cm as compared with the undesignated peak elution of 17.4 cm.

(~1cm^3) was injected into the gas collection head and the solution maintained at 70°C in the dark for 19 hours. Subsequent G.C. analysis of this gas revealed a small peak of hydrogen. No green deposit was seen in the reactor after irradiation and/or degassing.

Irradiation of octadecane with and without $Ru(bpy)_3^{2+}$

Octadecane (0.20g) was emulsified in water (200cm^3) according to the method outlined on P.126and the resulting dispersion, irradiated as for the previous $Ru(bpy)_3^{2+}$ octadecane emulsion,for 3 days. G.C. analysis of the deliberate bubble revealed a very small peak of hydrogen. The pH of the solution remained unchanged, 5.5. The solution was then drained from the reactor and $Ru(bpy)_3^{2+}$ added to give a concentration of 10^{-4}M. This was irradiated again under the same conditions as above for 19 hours. The pH of the solution remained unchanged, 5.1. G.C. analysis of the deliberate bubble revealed only a very small peak of hydrogen.

Irradiation of $Ru(bpy)_3^{2+}$, MV^{2+}, RuO_2 and Pt

To a solution ($145cm^3$) containing $Ru(bpy)_3^{2+}$(10^{-4}M) and MV^{2+}($2x10^{-3}$M), was added wet RuO_2 (~0.05g) and Pt powder (0.01g). The Pt powder was ground in a pestel and mortar with a small volume of the solution (~$10cm^3$) prior to addition. The RuO_2 and Pt were dispersed in the solution by placing in an ultrasonic bath and the resulting mixture irradiated in the silica reactor (arrangement 1 P.118)with visible light (150W bulb) for 19 hours with the addition of ~$1cm^3$ of air injected into the gas collection head. A magnetic stirrer was employed. After irradiation,the pH of the filtered solution was unchanged, 6.0, and G.C. analysis of the deliberate bubble revealed a small peak of hydrogen and a slight increase in oxygen. This was indicated by a reduction of the N_2:O_2 pk.height ratio of 2.35 for air to 2.19.

Irradiation of $Ru(bpy)_3^{2+}$, MV^{2+}, RuO_2 and hydrolysed maleic anhydride/ styrene copolymer

The copolymer (0.13g) was dissolved in hot water ($25cm^3$) and the cloudy solution added to a dispersion of wet RuO_2 (0.08g) in water ($25cm^3$). The pH was adjusted to 7.9 and the solution stirred for 1 hour. A $2cm^3$ portion of this colloid ($53cm^3$) was added to $57cm^3$ of filtered unirradiated solution containing $Ru(bpy)_3^{2+}$(10^{-4}M) and MV^{2+} ($2x10^{-3}$M) from the previous experiment.

The resulting solution was degassed in the silica reactor with argon for ~½ hour, towards the end of which,a sample of gas was taken from the outlet of the sintered bubbler and G.C. analysed. No hydrogen was present and as expected the O_2 and N_2 concentrations were much reduced. The sintered bubbler was carefully withdrawn and replaced by a glass stopper leaving ~$1.5cm^3$ of argon above the solution which was then irradiated according to arrangement 2 P.121with visible light (150W bulb) for 18 hours. G.C.analysis of the deliberately left argon bubble revealed a small peak of hydrogen and an increase in both O_2 and N_2.

"White spot" nitrogen was found to be unsuitable for deaerating since it contains 0.26μL H_2/1cm^3 (260 p.p.m.)

Irradiation of $Ru(bpy)_3^{2+}$, MV^{2+}, RuO_2/hydrolysed maleic anhydride-styrene copolymer and Pd/polyvinyl alcohol

Preparation of colloidal palladium:

P.V.A. (0.38 g) was dissolved in a hot solution of K_2PdCl_6(0.04g) dissolved in water (20cm^3) and the pH,3.5 adjusted to 8.1. The solution was heated on a water bath,90°C, for ½hour after which hydrogen was bubbled through the solution, maintained at between 60°C and 90°C, for ~ 3½ hours. The solution, appropriately diluted, was viewed with a beam of light incident upon it to assess whether a colloid had been formed. This test was inconclusive but the solution was used nevertheless.

The irradiation:

To this colloidal Pd solution (3cm^3) was added 10cm^3 of previously prepared colloidal RuO_2(P.128)and 98cm^3 of filtered unirradiated solution containing $Ru(bpy)_3^{2+}$ (10^{-4}M) and MV^{2+} from the experiment described on P.128. The resulting solution was degassed and irradiated as for the previous experiment (P.128) for 23 hours. G.C. analysis of the deliberately added argon bubble revealed no hydrogen but a large increase in both O_2 and N_2 was observed. A slight reduction in the pH from 6.9 → 6.5 during irradiation was noted.

The effect of the hydrolysed maleic anhydride-styrene copolymer upon $Ru(bpy)_3^{2+}$

a) The hydrolysed copolymer (0.10g) was dissolved in hot water (10cm^3) and the solution added to $Ru(bpy)_3^{2+}$ (10^{-4}M). After centrifugation of the cloudy orange solution for 10 mins a small amount of the copolymer was precipitated but the supernatant solution was still colloidal and orange.

b) The solid hydrolysed copolymer was then added to $Ru(bpy)_3^{2+}$(10^{-4}M) and the mixture shaken and contrifuged. All of the copolymer was precipitated as an orange solid leaving the supernatant solution clear and virtually colourless.

B. (4,4'-DICARBOXY-2,2'-BPY)BIS(2,2'-BPY)RUTHENIUM(II)-Ru(COOH)2

Irradiation of $BaCl_2$, $KHCO_3$, Stearic acid and Ru(COOH)2-hexafluorophosphate complex

A solution containing $BaCl_2$($8x10^{-5}$M), $KHCO_3$(10^{-3}M), Ru(COOH)2($8x10^{-6}$M) and stearic acid (80mg dispersed in $130cm^3$ using an ultrasonic bath) was adjusted to pH7.2 with NH_4.OH and irradiated in the silica reactor, arrangement 2 (P.121)for 20 hours with a deliberate bubble of air (~$1cm^3$) using a 100W bulb. G.C. analysis of the deliberately added bubble after irradiation yielded a small peak of hydrogen. Freeze thaw treatment of $20cm^3$ of solution in a FT-tube (P.121)yielded no further hydrogen nor did leaving the freeze thawed solution to stand for a day with $0.5cm^3$ air. The pH of the solution remained virtually unchanged, 7.0. The experiment was repeated with a fresh solution of the above and a small peak of hydrogen was reproduced.

A portion of the fresh solution $20cm^3$ was irradiated in a freeze thaw tube (P.121)under reduced pressure for 17 hours with a 100W bulb. After bringing to atmos.press. by letting in unirradiated solution the residual bubble was G.C. tested ... no hydrogen.

A further portion of this solution was irradiated in the silica reactor (arrangement 1 P.118),100W bulb, for 18 hours without a deliberate bubble. G.C. analysis of the gas produced by degassing with a hot water jacket (70°C) yielded no hydrogen.

A fresh solution of $BaCl_2$, stearic acid, $KHCO_3$ and Ru(COOH)2 was made up containing NaH_2PO_4(10^{-2}M) and Na_2HPO_4(10^{-2}M) of which $30cm^3$ was irradiated in a F.T.-tube for 17 hours at atmos.press. with a 100W bulb. After irradiation, G.C. analysis of the $1cm^3$ left in the F.T.-tube revealed a trace of hydrogen. The pH of the buffered solution remained at 6.7. After the withdrawal of $10cm^3$ of solution, freeze thawing of the 20 cm^3 left, revealed no hydrogen.

Further irradiations of both the hexafluorophosphate and perchlorate complexes are shown in TABLE 15. The solutions were irradiated in the silica reactor (arrangement 1 P.118)but no hydrogen was observed either from the deliberate bubbles injected, from hot water jacket degassing or from freeze-thawing except in the case of solution 1. No undesignated peaks eluting after nitrogen were observed.

TABLE 15 Further irradiations of Ru(COOH)2

Soln.No.		Solution Composition	Irradiation time	pH	
				before	after
PF_6^-	1	$BaCl_2$ 10^{-3}M Ru(COOH)2 10^{-4}M	20 hours	3.2	3.2
	2	$BaCl_2$ 10^{-3}M	20 hours	5.0	4.9
	3	Ru(COOH)2 10^{-4}M	20 hours	3.3	3.3
	4	$BaCl_2$ 10^{-4}M Ru(COOH)2 10^{-5}M	18½hours	4.0	4.0
	5	Soln.4reirradiated	3¼hours	8.6	6.6
	6	Soln.5reirradiated	18 hours	8.7	8.6
	7	$BaCl_2$ 10^{-4}M Ru(COOH)2 10^{-5}M S.D.S.1.4×10^{-2}M	3 days	7.5	7.5
	8	$BaCl_2$ 10^{-3}M Ru(COOH)2 10^{-4}M	18 hours	3.7	3.7
ClO_4^-	9	Ru(COOH)2 10^{-5}M Stearic acid,80mg dispersed in 200 cm^3 of soln., $KHCO_3$ soln.added to adjust pH.	14 hours	6.4	6.4
	10	Fresh soln. of 9	41 hours	6.3	6.3

C. (4,4'-DINITRO-2,2'-BPY)BIS(2,2'-BPY) RUTHENIUM (II)

Irradiation of $[Ru(bpy)_2(diNO_2bpy)]^{2+}$

A solution of $[Ru(bpy)_2(diNO_2bpy)]^{2+}$ (10^{-4}M) was irradiated in the silica reactor (arrangement 1 P.118)with visible light (150W bulb) for 26 hours with ~1cm^3 of air injected into the gas collection head. After irradiation,G.C. analysis revealed no hydrogen and the pH of the solution remained unchanged, 5.1.

Irradiation of $[Ru(bpy)_2(diNO_2bpy)]^{2+}$ and stearic acid

Stearic acid (0.07g) was dispersed into a solution containing $[Ru(bpy)(diNO_2bpy)]^{2+}$($10^{-4}$M) by means of an ultrasonic bath and the resulting solution irradiated in the silica reactor (arrangement 1 P.118) with visible light (150W bulb) for 20 hours with ~1cm^3 of air injected into the gas collection head. After irradiation,the pH remained unchanged,4.0, and G.C. analysis revealed a trace of hydrogen and an undesignated peak eluted after nitrogen. The solution was degassed with hot water at 70°C for ~3½ hours and the resulting bubble tested. A trace of hydrogen and an undesignated peak with the same elution time (18.6cm) as before were again observed. Methane from a sample of natural gas eluted at 20.3cm.

The experiment was repeated using 10^{-5}M $[Ru(bpy)_2(diNO_2bpy)]^{2+}$, irradiating for 2 days but no hydrogen or undesignated peaks were observed.

D. RUTHENIUM TERPYRIDYL COMPLEXES

The following Ru-tpy-bpy perchlorate complexes shown in table 16, ($4x10^{-5}$M) were irradiated in the silica reactor (arrangement 1 P. 118), with visible light (100W bulb) incorporating a deliberate volume of air ~1cm^3. After irradiation and testing of the deliberate bubble, the solution was degassed with hot water (~70°C) and the resulting gas G.C. analysed. No hydrogen was observed for any of the complexes nor were there any changes in pH during irradiation.

Table 16 The irradiation of Ru-tpy complexes

Soln.no.	Complex	pH	irradiation time
* 1	$[Ru^{II}(tpy)(bpy)Cl]^+$	4.4	25 hours
2	$[Ru^{II}(tpy)(bpy)H_2O]^{2+}$	5.2	20 hours
3	$[Ru^{II}(tpy)(bpy)H_2O]^{2+}$ + S.D.S. (1.4×10^{-2}M)	7.7	3 days
4	$[Ru^{II}(tpy)(bpy)OH]^+$	10.8	16 hours
5	$[Ru^{II}(tpy)(bpy)OH]^+$ + S.D.S.(1.4×10^{-2}M)	-	1 day
6	Fresh solution of 5	10.8	19 hours

Solutions of $[Ru^{II}(tpy)(bpy)OH]^+$ (violet) were prepared by basifying $[Ru^{II}(tpy)(bpy)H_2O]^{2+}$ (yellow) with KOH.

*Arrangement 2 P.121

IRRADIATION OF SOLUTIONS CONTAINING CERIUM IONS

Solutions of salts of Ce(IV) and Ce(III) were irradiated with and without RuL_3^{2+} (where L = bipyridyl or 5 -nitro-1,10-phenanthroline) in homogeneous systems. Those results which are in tabular form are to be found at the end of Chapter 4 on Pages 69-74.

The first set of experiments in which Ce(III) and Ce(IV) sulphates are irradiated with $Ru(bpy)_3^{2+}$ in the glass reactor is summarised in table 3 on P. 69.

Notes accompanying table 3 :-

1st reactor mode of operation and diagram on Pages 120 and 121.

No significant changes in pH were observed during irradiation unless stated.

* $1cm^3 \xrightarrow{degassed} 2cm^3$ means $1cm^3$ initially produced which increased to $2cm^3$ after degassing.

Degassing of solutions was effected either by simply leaving to stand or passing hot water through the jacket.

A TEST TO ESTABLISH THE $Ru(bpy)_3^{2+}$ CATALYSED PHOTOCHEMICAL REDUCTION OF Ce(IV) → Ce(III) IN AQUEOUS SOLUTION:

(i) A ten fold excess of Ce : Ru

Two solutions were made up as follows:-

Solution A: without $Ru(bpy)_3^{2+}$

$25cm^3$ of $2x10^{-3}M$ ‡Ce(IV)

$5cm^3$ of $1M\ H_2SO_4$

- made up to $50cm^3$ with water-solution pale green due to Ce(IV).

Solution B: containing $Ru(bpy)_3^{2+}$

$25cm^3$ of $2x10^{-3}M$ Ce(IV)

$5cm^3$ of $1M\ H_2SO_4$

$5cm^3$ of $10^{-3}M\ Ru(bpy)_3^{2+}$

- made up to $50cm^3$ with water-solution dark green due to $Ru(bpy)_3^{3+}$

The solutions were transferred to two $50cm^3$ conical flasks and stoppered leaving an air space of about 2cm^3 above each solution. The flasks were placed in a large petrie dish containing water and the solutions irradiated from beneath with a 100 W tungsten bulb. After 6½ hours irradiation solution A was the same pale green Ce(IV) colour whilst solution B had turned yellow. The water surrounding the flasks to prevent overheating had risen in temperature to approximately 32°C.

‡ Ce(IV) used here and subsequently was A.R. $(NH_4)_2\left[Ce^{(IV)}(NO_3)_6\right]$ unless stated otherwise.

25cm^3 aliquots of the solutions were analysed quantitatively for Ce(IV) using ferrous ammonium sulphate,(Fe.A.S.) 10^{-3}M, as titrant and ferroin as indicator.

The following titres were obtained:-		colour change after addition of ferroin
Solution A	19.00 cm^3	bluey-green → orange
Solution B	2.00 cm^3	pale yellow → orange

In order to compensate for the difference in colour change during titration due to the presence of $Ru(bpy)_3^{2+}$, 10cm^3 aliquots of the irradiated solutions were taken for titration,to which was added :-

1cm^3 of 10^{-3} $Ru(bpy)_3^{2+}$	to solution A
1cm^3 of water	to solution B

The following titres for 11cm^3 aliquots were obtained:-

Solution A	7.50cm^3 (titre adjusted for 25cm^3 aliquot=7.5x2.5=18.75cm^3)
Solution B	0.00cm^3

Moles of Ce(IV) in solutions A & B before irradiation=$5.0\text{x}10^{-5}$moles

Moles of Ce(IV) reduced in 50cm^3 of solution A = $1.2\text{x}10^{-5}$ moles

" " " " " " " " B = $4.6\text{x}10^{-5}$ moles

(ii) A hundred fold excess of Ce : Ru (first experiment)

The previous experiment,(i),was repeated but with two major variations namely (a) the $Ru(bpy)_3^{2+}$ concentration was reduced such that the Ce:Ru ratio was 100:1 and (b) in addition, two more solutions were made up, one with and one without $Ru(bpy)_3^{2+}$ which were kept in the dark. The results from this experiment are shown in table 4 on P. 70

The solutions were made up as shown in table 4 , two being irradiated for 5 hours whilst the other two were kept in the dark by being wrapped up in aluminium foil. All four stoppered flasks were placed in the apparatus described on P. 135. After irradiation, $10cm^3$ aliquots were titrated against $10^{-3}M$ Fe.A.S. using ferroin as indicator. The titres are also shown in table 4.

Since a reduced amount of $Ru(bpy)_3^{2+}$ was used in this experiment, the colours of the solutions before irradiation were virtually the same pale yellowy-green. After irradiation, little change in colour was observed; nevertheless $0.1cm^3$ of 10^{-3} Ru(II) was added to the $10cm^3$ aliquots of solutions C and E before titration.

After the withdrawal of aliquots for analysis the two irradiated solutions (C and D) were left in ambient light and the two unirradiated solutions (E and F) were rewrapped in Al foil. The four stoppered flasks were left to stand for a week after which time solutions C,E,F were still green whilst solution D was nearly colourless.

(iii) A hundred fold excess of Ce:Ru (second experiment)

The previous experiment, (ii), was repeated but with the variation that in addition, two more solutions were made up, one with and one without $Ru(bpy)_3^{2+}$ which were both deaerated for 1 hour with nitrogen prior to irradiation.

The solutions were made up and irradiated for 7 hours. The temperature of the water in the petrie dish was maintained at 32°C. After irradiation, $20cm^3$ aliquots were titrated against $10^{-3}M$ Fe.A.S. The results are shown in table 5, P. 71.

REACTIONS OF Ce(IV) AND $Ru(bpy)_3^{2+}$ in HCl

Solutions of $(NH_4)_2\left[Ce^{(IV)}(NO_3)_6\right]$, $Ru(bpy)_3^{2+}$, H_2SO_4 and HCl were made up, left to stand in ambient light at room temperature and any changes in colour noted at different time intervals:-

The experiment is summarized in table 6 on P. 72.

A TEST TO COMPARE THE EFFECT OF $Ru(bpy)_3^{2+}$ and $Ru(5NP)_3^{2+}$ UPON THE REDUCTION OF Ce(IV)

Eight solutions were made up as shown in tables 7 and 8 on Page 73 of which four were kept in the dark and four irradiated for 17 hours under the conditions outlined on P.135, the temperature being maintained at 30°C. After irradiation, $20cm^3$ aliquots of the photolytes ($50cm^3$) were titrated against Fe.A.S.(10^{-3}M). The results are recorded in table 8 on P.73.

THE IRRADIATION OF CERIUM IONS WITH $Ru(bpy)_3^{2+}$ AND $Ru(5NP)_3^{2+}$ IN THE SILICA REACTOR

Other irradiations of cerium solutions with and without $Ru(bpy)_3^{2+}$ and $Ru(5NP)_3^{2+}$ were carried out in the silica reactor (arrangement ① P.118), the results of which are shown in table 9 on P.74.

THE IRRADIATION OF THE DIOCTADECYL ESTER OF (4,4'-DICARBOXY-2,2'-BPY)BIS (2,2'-BPY) RUTHENIUM (II) PERCHLORATE .... "THE WHITTEN COMPLEX"

Irradiation of "Whitten's Complex" and S.D.S.

A solution containing "Whitten's Complex" ($1.84x10^{-5}M$) and S.D.S. ($7x10^{-4}M$) was irradiated in the silica reactor (arrangement 1 P.118) for 3 days with U.V. during which time no hydrogen was observed (freeze-thaw technique P.121) nor were there any differences in the U.V.-Vis spectra of the solutions before and after irradiation. However the pH dropped from 5.1 to 2.8.

A solution of S.D.S. ($1.4x10^{-2}M$) only was irradiated in the glass reactor with a 150W bulb for 14 hours, again with no hydrogen observed.

Irradiation of "Whitten's Complex", S.D.S. and $BaCl_2$

(i) A solution containing "Whitten's Complex" ($1.8x10^{-5}M$), S.D.S. ($1.4x10^{-2}M$) and $BaCl_2$($10^{-3}M$) was irradiated in the silica reactor (arrangement 1 P.118) for 19½ hours with a 100W bulb. No hydrogen was obtained from either the deliberate bubble or hot water jacket (70°c) degassing. The pH remained virtually unchanged 6.0→5.8. Addition of the micellar "Whitten Complex" solution ($1.8x10^{-4}M$) to the $BaCl_2$ solution ($10^{-2}M$) before appropriate dilution for irradiation produced an orange colloidal solution which after irradiation and/or standing aggregated to form a precipitate.

(ii) A fresh solution of the above was made up containing "Whitten Complex" ($1.8x10^{-5}M$), S.D.S. ($1.4x10^{-2}M$) and $BaCl_2$($10^{-4}M$) which was irradiated as above for 18 hours during which the pH remained virtually unchanged, 5.5→5.3. G.C. analysis of the deliberate bubble revealed a trace of hydrogen but none was observed from hot water degassing (70°C). The turbid solution during irradiation produced a small amount of white precipitate or "scum" seen mostly on the surface of the solution.

Irradiation of a suspension of palladised charcoal in a micellar solution of "Whitten's Complex"

Palladised charcoal (0.06g) was added to a solution ($100cm^3$) containing "Whitten's Complex" ($10^{-5}M$) and S.D.S. ($1.4x10^{-2}M$) and shaken. On standing, much of the palladised charcoal remained in suspension. As a result, this suspension was decanted from the settled Pd-C into the silica reactor and irradiated under the conditions of arrangement 2 (P.121)with U.V. for 2 days. After which time the pH was unchanged, 6.8 and 50cm^{3}of solution freeze-thawed (P.122)yielded no hydrogen (G.C. analysis). Slight differences in the U.V. spectra of the filtered solutions were observed viz: At 225nm;irradiated solution absorbance,1.12; unirradiated solution absorbance,0.87.

Irradiation of a C.T.A.B. micellar solution of "Whitten's Complex"

A solution containing "Whitten's Complex (10^{-5}M) and C.T.A.B. (10^{-3}M) was irradiated in the silica reactor (arrangement 1 P.118)for 17½ hours with a 100W bulb. The pH remained virtually unchanged 4.2→4.0. No hydrogen from either the deliberate bubble or hot water degassing (70°C) was observed.

Irradiation of an aqueous acetone solution of "Whitten's Complex"

"The Whitten Complex" (0.006g) was dissolved in hot acetone (5cm^3) and the solution diluted to 100cm^3 with water (complex concentration-4×10^{-5}M). 30cm^3 of the solution was transferred to a F.T.-tube and irradiated with a deliberate bubble at atmospheric pressure. 20cm^3 of the solution was transferred to another F.T.-tube and irradiated at reduced pressure (25mm Hg). Irradiation was for 17 hours with a 100W bulb during which time the pH had dropped from 5.9→5.5. The observation of traces of hydrogen was doubtful. The G.C. was not sensitive to acetone.

IRRADIATION OF MICELLAR SOLUTIONS OF BARIUM STEARATE AND "WHITTEN'S COMPLEX"

Preparation and irradiation of micellar barium stearate

Barium stearate (0.014g) was added to S.D.S. solution (750cm^3, 1.4×10^{-2}M) and stirred for ~3 hours at 65°C. After which time some undissolved particles of barium stearate were filtered off. A portion of the resulting clear filtrate (Ba-S-1), being $<2.7\times10^{-5}$M in barium stearate, was irradiated in the silica reactor (arrangement 1 P.118)with U.V. for 3 days. Some of the solution (50cm^3) was freeze-thawed (F.T.-flask, P.122)but no hydrogen was observed.

Irradiation of mixtures of micellar barium stearate and "Whitten's Complex"

9cm^3 of a stock solution of "Whitten's Complex" (3.7x10^{-4}M) was added to 91cm^3 of the stock solution of barium stearate (Ba-S-1) such that the resulting solution (M.W.Ba.1) contained the "Whitten Complex" (3.3x10^{-5}M), barium stearate (<2.5x10^{-5}M) and S.D.S. (1.4x10^{-2}M). This was irradiated in the silica reactor (arrangement 2 P.121) with U.V. for 18 hours. After which time freeze thawing of 50cm^3 in the F.T.-flask (P.122) gave 1.5cm^3 of gas. G.C. analysis of 1cm^3 of this gas revealed only a trace of hydrogen but the withdrawal of the residual 0.5cm^3 the following day gave 7μL of hydrogen! No differences in the U.V.-Vis spectra of the solutions before and after irradiation was noted.

The solution left in the reactor was supplemented with fresh solution and irradiated under the conditions above for a further 23 hours. The solution was freeze-thawed (F.T.-flask 50cm^3 P.122) and the resulting gas tested on the 1st day ... trace of hydrogen
2nd day ... no hydrogen
5th day ... small peak of hydrogen

A fresh solution of the above was made up (M.W.Ba.2) from stock solutions of barium stearate (Ba-S-2) and "Whitten's Complex" starting from the solid materials. Thus "Whitten's Complex" (10^{-4}M), barium stearate (10^{-4}M) and S.D.S. (10^{-2}M) photolyte was irradiated in the silica reactor (arrangement 2 P.121) with U.V. for 4 days. The solution was freeze-thawed (F.T.-flask 50cm^3 P.122) and the resulting gas tested on the 1st day ... no hydrogen
2nd day ... trace of hydrogen
4th day ... small peak of hydrogen

The F.T.-flask and contents were freeze-thawed again and the solution irradiated at atmos.press.with 150W bulb (8cm away) for 18 hours. G.C. analysis of the deliberate bubble revealed a small peak of hydrogen.

A mixture of U.V., visible irradiated and unirradiated solution (M.W.Ba 2) was aerated by pouring into a large petrie dish and subsequently treated in various ways before and during further irradiation, including nitrogen degassing, freeze-thawing and leaving to stand in the dark. Only traces of hydrogen were observed.

Another fresh solution of the above was made up (M.W.Ba 3) from stock solutions of barium stearate (Ba-S-3) and "Whitten Complex" starting from the solid materials. Thus "Whitten Complex" ($3.2x10^{-5}$M), barium stearate ($<2.2x10^{-5}$M) and S.D.S. ($1.4x10^{-2}$M) photolyte was irradiated in the silica reactor (arrangement 2 , P.121)with a 150W bulb for 17 hours. No hydrogen was observed from the deliberate bubble injected. The reactor and solution was left to stand for a day before 40cm^3 was transferred to the F.T.-flask and 20cm^3 to the F.T.-tube. After freeze-thawing, G.C. analysis of both tube and flask revealed traces of hydrogen. The F.T.-tube and flask were then left to stand with ~1cm^3 of air added for a day and tested again: no hydrogen from the F.T.-flask but a small peak of hydrogen from the F.T.-tube.

The experiment was repeated with solution M.W.Ba3 irradiated in the silica reactor (arrangement 2 P.121) for 17 hours with a 150W bulb. A trace of hydrogen was observed from the deliberate bubble. 2x20cm^3 of solution were transferred to two F.T.-tubes and freeze-thawed yielding traces of hydrogen in both cases. Immediately after the withdrawal of the gas samples, ~1cm^3 of hot solution was displaced by the injection of air. After leaving the tubes to stand in the dark overnight, G.C. analysis revealed peaks of hydrogen from both tubes, one of which being equivalent to 2.8μL hydrogen where 1 mole $H_2 \equiv$ 5.2 moles of Ru complex. The F.T.-tubes were allowed to stand for a further day under the same conditions with peaks of hydrogen again being observed.

More solution (M.W. Ba 3) was poured into the silica reactor (arrangement 2 , P.121) and kept in the dark for 17 hours. No hydrogen was obtained from the deliberate bubble but freeze-thawing of the solution (F.T.-tube) gave a small peak of hydrogen. ~1cm^3 of air was left to stand over the hot solution for 3 days in the dark again yielding a small peak of hydrogen.

More fresh solutions were made up in daylight and in subdued light in a way as closely as possible resembling previous solutions which gave hydrogen. Also used,wasastock solution of barium stearate containing a large excess of barium stearate and one which had been left to stand for several months. These solutions and the unmixed stock solutions of barium stearate and "Whitten's Complex" and ones which had already yielded hydrogen, were irradiated in the silica reactor, F.T.-flask and F.T.-tube under various conditions:- a) under atmospheric or reduced pressure b) whilst hot c) already freeze-thawed d) nitrogen degassed. The solutions were then freeze-thawed in the F.T.-tubes with the temperature during thawing being allowed to rise to ~90°C. The solutions were left to stand with deliberate air bubbles under various conditions as for the irradiations given above,for several days,during and after which, samples were taken for analysis ..... very little or no hydrogen was observed.

CONCLUSIONS

The aim of this project was to investigate routes to the photocleavage of water into gaseous hydrogen and oxygen. This work commenced five years ago and at that time there appeared to be one successful route already available. In this, Whitten et al (25) claimed to have obtained hydrogen and oxygen from water as a result of irradiating monolayers of a surfactant $Ru(bpy)_3^{2+}$ complex,but were unable to reproduce their earlier findings (26). The obvious place to start was to reinvestigate the Whitten system and subsequently to proceed by modifying it.

Two basic theories, elaborated in the Introduction, have been proposed to account for Whitten's failure to reproduce the photocleavage of water. The phenomenon was due to:-

(i) a unique orientational effect of the complex molecules which because of the difficulties encountered in the assembly of monolayers could not be repeated.

(ii) impurities in the complex which were absent from purified samples used subsequently - "the impurity theory".

For this reason, several complexes were synthesised for irradiation but interest in the rôle of stearic acid/arachidic acid meant that many of these complexes were not irradiated. Micellar systems were employed for the most part for those complexes which were irradiated,where the semi-rigid structure is analogous to the monolayer architecture used by Whitten et al.

The fact that these B.D.E. complexes of Ru, Mn, Co and Pd have been prepared illustrates the possibility that impurities of this nature could have been formed during the original preparation of "Whitten's Complex" and adds credence to the "Impurity Theory".

For a solar-energy storage system of this kind to be truly catalytic, the turnover of hydrogen: Ru complex needs to be >1:1. In this work, the turnovers achieved were ~1:11 for the $Ru(bpy)_3^{2+}$/stearic acid dispersion and ~1:5 for the S.D.S. micellar "Whitten Complex"/barium stearate system. Because of this, only small volumes of hydrogen were obtained from the small quantities of materials used and it was therefore difficult to use the mass spectrometer to confirm or otherwise the origin of the hydrogen from water. The most promising and most reproducible system of the two just mentioned, from a hydrogen evolution point of view, is the $Ru(bpy)_3^{2+}$/stearic acid dispersion. I believe more work could be done on this system, to establish the identity of the unassigned peak eluting after nitrogen on the G.C., and related to this, an analysis of the photolyte before and after irradiation. It is possible that this unidentified gas, and may be the hydrogen as well, originates from the stearic acid, and might be the explanation of the hydrogen evolution observed by Whitten et al (25) who used several layers of arachidic acid for the construction of their monolayer assemblies.

The investigation into the work of Grätzel and Kalyanasundaram (37), primarily to assess the effect upon the maleic anhydride-styrene copolymer during irradiation was inconclusive. This was because we were unable to reproduce his conditions exactly. Nevertheless, the work which was carried out does offer an explanation as to why the $Ru(bpy)_3^{2+}$ concentration was depleted after irradiation viz. the possible formation of a maleic anhydride-$Ru(bpy)_3^{2+}$ compound.

Another system which is worthy of further study is the $Ru(bpy)_3^{2+}$/Ce(IV) system. Here it was discovered that $Ru(bpy)_3^{2+}$ effected the photochemical reduction of Ce(IV) to Ce(III) although the mechanisms by which this takes place is not understood. This photochemical reduction is not observed, however for the analogous $Ru(5NP)_3^{2+}$ complex where the reduction of Ce(IV) to Ce(III) is a thermal one and takes place in the absence of light.

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