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THE CHEMISTRY AND PHOTOCHEMISTRY
OF RU(II) BIPYRIDYL CARBONYL COMPLEXES
INCORPORATED IN NAFION

by

Adrienne Jermyn

A Thesis presented to the University of Dublin
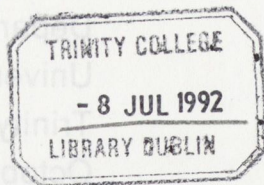for the degree of MSc.

Department of Chemistry,
University of Dublin,
Trinity College.
October 1991

Declaration

This thesis has not been submitted as an excercise for a degree at this or any other University. Except as otherwise indicated the work described herein was carried out by the author alone.

Adrienne Jermyn

Summary

The chemical reactions of bis(bpy)carbonylruthenium complexes, catalysts for the water gas shift reaction, have been investigated under mild conditions in Nafion, an ionic polymer. Chemical and photochemical reactions performed under alkaline, aqueous or atmospheric conditions were of particular interest.

A variety of techniques have been used to investigate the reactions occurring. These include Infra-red and Ultra-violet spectroscopy. The Nafion matrix is ideally suited to these techniques for bis(bpy)carbonyl complexes because of the absence of absorption bands in the UV/Vis spectrum and the carbonyl region of the IR spectrum. It is also chemically inert.

It is possible to prepare and incorporate the complexes into Nafion. Reactions are confined within an inert matrix and therefore the species involved in the water gas shift reaction catalysed by $[Ru(bpy)_2(CO)Cl]^+$ have been formed in-situ and subsequently characterised by spectroscopic methods. Nucleophilic attack of OH^- on $[Ru(bpy)_2(CO)_2]^{2+}$ affords $[Ru(bpy)_2(CO)(COOH)]^+$ which exists as an equilibrium mixture with $[Ru(bpy)_2(CO)_2]^{2+}$ and $[Ru(bpy)_2(CO)(COO^-)]^+$ in alkaline media depending on pH. This undergoes some decarboxylation to partially give the hydride $[Ru(bpy)_2(CO)H]^+$ which further reacts in water to afford $[Ru(bpy)_2(CO)(H_2O)]^{2+}$. This in turn exists in equilibrium with $[Ru(bpy)_2(CO)(OH)]^+$. The coordinated H_2O of $[Ru(bpy)_2(CO)(H_2O)]^{2+}$ readily undergoes substitution by CO to yield $[Ru(bpy)_2(CO)_2]^{2+}$. Bpy = 2,2'-Bipyridyl

Acknowledgements

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SECTION 1   Introduction

Methods of activating the reactions of carbon monoxide have long been a major area of catalysis research. Of particular interest is the water gas shift reaction. It is used extensively to increase the hydrogen content of water gas through the reaction of CO with steam to form hydrogen and CO_2 according to the reaction

$$CO_{(g)} + H_2O_{(g)} \longrightarrow H_{2(g)} + CO_{2(g)} \qquad (1)$$
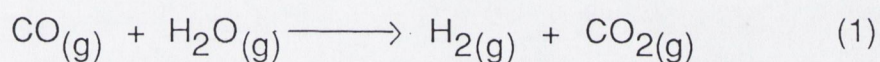
$$\Delta G_{298} = -28.16 kJmol^{-1}$$

$$\Delta H_{298} = -40.63 kJmol^{-1}$$

$$\Delta S_{298} = -42.25 Jmol^{-1}K^{-1}$$

By this process the reducing equivalents of CO can be converted to the more useable form of molecular hydrogen with relatively little loss in thermochemical potential.

This reaction is carried out over a wide range of pressures and gas compositions at temperatures in excess of $300^{\circ}C$ using heterogeneous catalysts consisting of iron oxides promoted by Cr_2O_3. Due to the exothermicity of this reaction industrial processes must be carried out in two or more stages with intermediate cooling.[1]

The same reaction can be carried out at lower temperatures with water being present as a liquid according to eqn.2

$$CO_{(g)} + H_2O_{(l)} \longrightarrow H_{2(g)} + CO_{2(g)} \qquad (2)$$
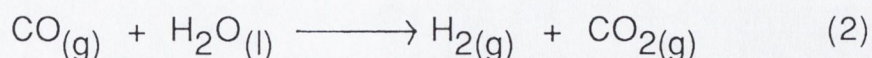
$$\Delta G_{298} = -19.41 \text{kJmol}^{-1}$$

$$\Delta H_{298} = +2.80 \text{kJmol}^{-1}$$

$$\Delta S_{298} = +76.5 \text{Jmol}^{-1}\text{K}^{-1}$$

Reaction 2 differs from reaction 1 in that it is slightly endothermic (ΔH^o differing from that of reaction 1 by the heat of vapourisation of water) and yet it is strongly favoured from the free-energy point. This is due to the large positive entropy change associated with reaction 2 .

The obvious benefit of carrying out the shift reaction at lower temperature is that the need to vapourise water is eliminated. In considering possible heterogeneous catalysts, metal carbonyl complexes are logical candidates given that certain coordinated carbonyls are activated towards nucleophilic attack of water[2]. Various metal carbonyls,including clusters, have also been used as homogeneous catalysts in the oxidation and /or reduction of carbon monoxide[3].

In the following sections the synthesis of metal carbonyls and the use of metal carbonyls as catalysts for the water gas shift reaction will be discussed. Particular attention will be focussed

on complexes of the type $[Ru(bpy)_2(CO)X]^{n+}$. These cationic complexes which are stable in water, have previously been used as homogeneous catalysts for the water gas shift reaction. The aim of this research has been to investigate the chemistry of these complexes further in a perfluorinated polymer, a medium which combines the advantages of both heterogeneous and homogeneous systems.

Classic synthesis of metal carbonyls

Metal carbonyl complexes were first reported in 1871 [4] with the isolation of $[(CO)PtCl_2]$, $[(CO)_2PtCl_2]$ and $[(CO)_3Pt_2Cl_4]$. Pullinger[5] followed this work by isolating the bromo derivative $[(CO)PtBr_2]$. Early attempts to prepare carbonyls of cobalt, iron, copper and platinum failed, even at temperatures up to $750^{o}C$ [6]. However two independent groups reported [7,8] in 1891 that the passage of CO over finely devided iron yielded a metal carbonyl initially thought to be $Fe(CO)_4$ but which was later correctly analysed as $Fe(CO)_5$. It was noticed that $Fe(CO)_5$ underwent photodecomposition[9]. In 1931 Pauling[10] predicted the existence of both $Ru(CO)_5$ and $Cs(CO)_5$ but it was not until 1936 that the synthesis of $Ru(CO)_5$ was reported[11]. This was found to deposit orange/red crystals upon exposure to light - these were thought to be $Ru_2(CO)_9$ but X-ray crystallographic data established the

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orange crystalline material as $Ru_3(CO)_{12}$[12]. Passing CO over RuX_3 yielded the first carbonyl halides of ruthenium, $RuX_2(CO)_2$. Chatt et al.[13] found that when CO is bubbled through a refluxing ethanolic solution of hydrated $RuCl_3$ a deep red carbonyl containing chlororuthenium solution is obtained. IR evidence[14] suggests that the major component is $[RuCl_2(CO)_2]_n$ but a monocarbonyl complex may also be present. At first it was thought that the polymeric carbonyl halides $[RuCl_2(CO)_2]_n$ were linear in structure with trans carbonyls and bridging chlorides, but in fact the structure has a cis carbonyl arrangement as shown by the existence of two strong carbonyl bands seen in the IR spectrum[15,16]. Since the first report of their synthesis in 1924[17] these polymers have been prepared by a variety of routes including passage of CO over RuX_3[15,18,19,20], oxidation of $Ru_3(CO)_{12}$ with halogens in inert solvent at temperatures in excess of $140^{\circ}C$[15,21] and by isolation from the yellow methoxyethanol carbonyl solution[22].

Polymeric carbonyl halides are very useful precursors to a wide variety of complexes containing a range of donor ligands including pyridine[18,19,20,23,24,25], amines[18,19,20,26] and other heterocyclic N donors[18,19,20,24,25,27], phosphines and phosphites. The red ethanolic solution was used in 1966 to prepare $Ru(py)_2(CO)_2Cl_2$[23]. It was noted that the red carbonyl solution became greenish-red on standing for 24 hours, it was thus recommended that the solution be used immediately upon preparation. Preparation of $Ru(bpy)(CO)_2Cl_2$ and the phen analogue

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by this method yielded red-brown crystals having cis-carbonyls. Even with an excess of bidentate ligand the cationic species $[Ru(bpy)_2(CO)_2]Cl_2$ and $[Ru(phen)_2(CO)_2]Cl_2$ were not obtained. In 1970 a configurational analysis of $[RuL_2(CO)_2]X_2$ compounds was published. These compounds were identified as the cis or trans dicarbonyl isomers by consideration of the intensity and number of CO stretching frequencies. The first monocarbonyl complex of Ru(II) with bipyridyl was reported in 1973[28]. The most common mononuclear complexes are neutral and have the general formula $[Ru(CO)_2(N-N)_2]X_2$ (N = bpy, phen). The carbonyl complexes are of interest because of their cationic water stable nature. The monocarbonyl complex $[Ru(bpy)_2(CO)Cl]^+$ was isolated as a secondary product in the known preparation[29,30] of $[Ru(bpy)_2Cl_2.2H_2O]$ which involves reaction of $RuCl_3.3H_2O$ with bpy in refluxing DMF. The hydride $[Ru(bpy)_2(CO)H]^+$ was prepared[31] by reacting the chlorocarbonyl and $NaBH_4$ in aqueous ethanol to give cis-$[Ru(bpy)_2(CO)H]^+$, the complex being isolated as the hexafluorophosphate derivative.

The chlorocarbonyl is a well characterised compound and may be used as the precursor for a large family of bis(bpy)Ru(II) complexes by both thermal and photochemical routes. The dicarbonyl complexes are generally prepared by reaction of $[RuX_2(CO)_2]_n$ with excess of nitrogen ligand. Upon reaction of this solution with N donors in EtOH compounds of the general formula $[Ru X_2(CO)_2L_2]$ [24] are formed where L_2 is one bidentate ligand or

two monodentate ligands. Reaction of bpy, in ethanol, with the red carbonyl solution yields a red/purple product as reported by Wilkinson[24] whereas aqueous ethanolic solution gives yellow crystals of [Ru(bpy)(CO)$_2$Cl$_2$]. Further reaction of [RuX$_2$(CO)$_2$L$_2$] with ligand L$_2$ in aqueous EtOH yields the cationic carbonyl complexes [Ru(L$_2$)$_2$(CO)$_2$]$^{2+}$ [24]. Other routes have also been proposed for the preparation of the dicarbonyl complexes. Deacon[32] suggests the more complicated route involving conversion of [Ru(bpy)(CO)$_2$Cl$_2$] into trifluoromethane sulphonate derivatives. [Ru(bpy)$_2$(CO)$_2$]$^{2+}$ may also be prepared by the reaction of [Ru(bpy)$_2$Cl$_2$] with AgSbF$_6$ and CO[33].

Water Gas Shift Reaction

To date much work has been carried out on various ruthenium carbonyl complexes, including those containing the halides, hydrides and hydroxides. The water gas shift reaction has previously been reported to have been successfully catalysed by carbonyl complexes. Classical carbonyl complexes, such as Fe(CO)$_5$[34,35] and [Ru$_3$(CO)$_{12}$][36] were the first metal carbonyl complexes to be used as catalysts. More recently, Ru(II)carbonylbipyridyl complexes[37] have been reported to effectively catalyse the photochemical water gas shift reaction.

King et al.[34,35] reported a series of studies involving Fe(CO)$_5$ as catalyst with reactions being carried out at elevated pressures

and temperatures ranging from 110 to $180^{\circ}C$. The following conclusions were reached:

1. The WGS reaction proceeds most rapidly in a moderately polar solvent system.

2. A rapid quantitative conversion of hydroxide ion to formate ion occurs prior to the onset of the WGS reaction so that formate is the dominant species of base present during the course of the WGS reaction.

3. Of the various derivatives possible from $Fe(CO)_5$ in base, only $HFe(CO)_4^-$ and the parent compound are present to any appreciable extent during the course of the WGS reaction.

4. The reaction proceeds at $130-180^{\circ}C$ which is relatively low for a WGS reaction

Yoshida et al[38] report a different approach based on the activation of the water molecule using low valent transition metal complexes capable of forming hydrido hydroxo species, trans H-M-OH. In view of the strong trans influence of hydride[39] an enhanced nucleophilic reactivity toward CO is expected for the hydroxo ligand in the H-M-OH species.

Ford and co. workers[36] reported the catalysis of the WGS reaction by metal carbonyl complexes under conditions where a homogeneous solution prepared from $[Ru_3(CO)_{12}]$ is an active catalyst under relatively mild conditions. The catalyst is also very active toward the decomposition of formate to H_2 and CO_2 under conditions active for the WGS reaction.

Choudhury et al.[37] have previously reported that [Ru(bpy)$_2$(CO)Cl]Cl and the phen equivalent catalyse the photochemical water gas shift reaction in aqueous solutions under mild conditions (20atm CO, 100-160°C). Tanaka et al.[40] however have found that [Ru(bpy)$_2$(CO)Cl][PF$_6$] is still active for the water gas shift reaction without irradiation in aqueous alkaline solutions.

Ruthenium carbonyl complexes have attracted much attention as very active catalysts for the WGS reaction[41]. The WGS reaction catalysed by transition metal complexes in alkaline media at elevated temperatures has been suggested to involve the following steps:

1. A nucleophilic attack of OH$^-$ or H$_2$O on the carbon atom of CO coordinated to transition metals, giving a hydroxycarbonyl complex (eqn.3).
2. A thermal decarboxylation of the hydroxycarbonyl complex to afford CO$_2$ and a metal hydride (eqn.4)

$$M\text{-}CO + OH^- \longrightarrow M\text{-}COOH \qquad\qquad eqn.3$$

$$M\text{-}COOH \longrightarrow M\text{-}H + CO_2 \qquad\qquad eqn.4$$
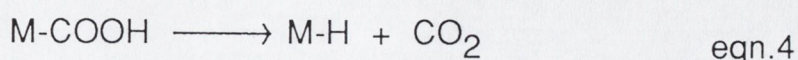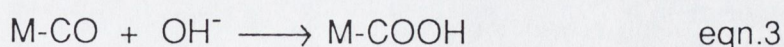
3. H$_2$ evolution by the reaction of the metal hydride with protons or water.

Table 1 shows typical values obtained by Tanaka. The discrepancy in the amounts of H_2 and CO_2 evolved in the gas phase probably results from the higher solubility of CO_2 than H_2 in addition to the formation of the carbonate ion in alkaline solutions as suggested by King[42]. In the absence of KOH the water gas shift reaction catalysed by $[Ru(bpy)_2(CO)Cl][PF_6]$ is slow. From the turnover numbers of $[Ru(bpy)_2(CO)Cl][PF_6]$ at 100 and 150°C, and the almost identical ones for $[Ru(bpy)_2(CO)_2][PF_6]_2$, it has been assumed that $[Ru(bpy)(CO)Cl]^+$ may be converted to $[Ru(bpy)_2(CO)_2]^{2+}$ under CO pressure in an alkaline solution.

Compound[a]	temp/$^\circ$C	atm	KOH[b]/mmol	gaseous product[c]	
				H_2	CO_2
$[Ru(bpy)_2(CO)Cl]^+$	100	2.9	3.2	3.8	—
$[Ru(bpy)_2(CO)Cl]^+$	100	9.6	3.2	165	95
$[Ru(bpy)_2(CO)Cl]^+$	150	4.8	3.2	112	46
$[Ru(bpy)_2(CO)Cl]^+$	150	9.6	3.2	197	75
$[Ru(bpy)_2(CO)Cl]^+$	150	19.2	3.2	502	203
$[Ru(bpy)_2(CO)Cl]^+$	150	9.6	0	1.1	0.7
$[Ru(bpy)_2(CO)_2]^{2+}$	70	9.6	3.2	4.1	1.1
$[Ru(bpy)_2(CO)_2]^{2+}$	100	2.9	3.2	10.8	0.4
$[Ru(bpy)_2(CO)_2]^{2+}$	100	9.6	3.2	147	82.7
$[Ru(bpy)_2(CO)_2]^{2+}$	150	9.6	3.2	198	75

a Pf_6 Salt 0.05 mmol in H_2O (15 cm^3).   b Quantity of KOH initially added
c Mol/(mol of catalyst 20 h).

Table 1 : Water Gas Shift catalysed by Ru(bpy)$_2$-carbonyl complexes [40]

It has been suggested that $[Ru(bpy)_2(CO)Cl]^+$ undergoes thermal and photochemical solvolyses in H_2O to give $[Ru(bpy)_2(CO)(H_2O)]^{2+}$ (eqn.5) and $[Ru(bpy)_2(H_2O)Cl]^+$ (eqn.6) respectively [29].

$$[Ru(bpy)_2(CO)Cl]^+ + H_2O \longrightarrow [Ru(bpy)_2(CO)(H_2O]^{2+} + Cl^- \quad eqn.5$$

$$[Ru(bpy)_2(CO)Cl]^+ + H_2O \xrightarrow{h\nu} [Ru(bpy)_2(H_2O)Cl]^+ + CO \quad eqn.6$$
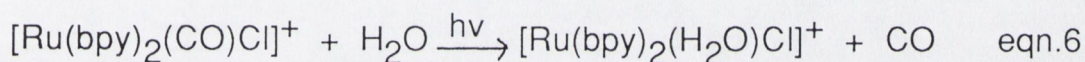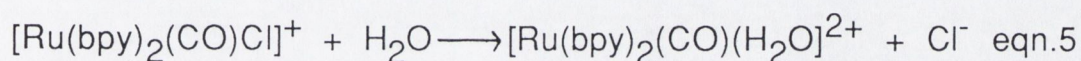
The addition of an aqueous KOH solution to a weakly acidic solution of $[Ru(bpy)_2(CO)(H_2O)]^{2+}$ results in the formation of $[Ru(bpy)_2(CO)(OH)]^+$ eqn.7[40]

$$[Ru(bpy)_2(CO)(H_2O)]^{2+} + OH^- \longrightarrow [Ru(bpy)_2(CO)(OH)]^+ + H_2O \quad eqn.7$$
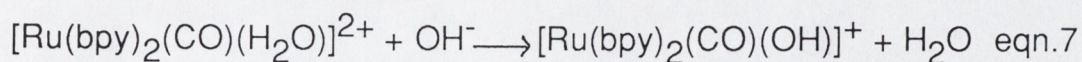
The pH dependence of the reaction is reversible, as shown by the UV/Vis spectra[40,53].

$[Ru(bpy)_2(CO)_2]^{2+}$ undergoes a nucleophilic attack of the coordinated CO by OH^- to give the Ruthenium hydroxycarbonyl

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complex $[Ru(bpy)_2(CO)(COOH)]^+$. Thus $[Ru(bpy)_2(CO)_2]^{2+}$ may exist as an equilibrium mixture with $[Ru(bpy)_2(CO)(COOH)]^+$ in weak alkaline solutions (eqn.8)

$$[Ru(bpy)_2(CO)_2]^{2+} + OH^- \longrightarrow [Ru(bpy)_2(CO)(COOH)]^+ \qquad \text{eqn.8}$$
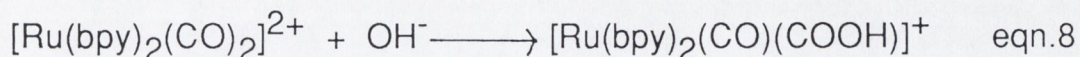
The hydroxycarbonyl complex formed in eqn.8 is known to undergo deprotonation reactions in strongly alkaline solutions[40]. Another equilibrium existing in alkaline solutions, therefore, may be expressed by eqn.9

$$[Ru(bpy)_2(CO)(COOH)]^+ + OH^- \longrightarrow [Ru(bpy)_2(CO)(COO^-)]^+ + H_2O$$

$$\text{eqn.9}$$
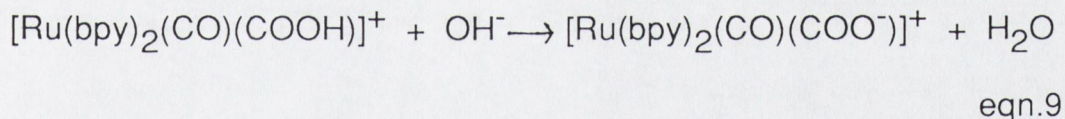
In the water gas shift reaction under aqueous alkaline conditions, CO readily reacts with OH^- quantitatively to form a formate ion, which may function as a buffer to some extent, adjusting the pH of the initial solution around 8.5 [40]. However, the pH value of the solution is lowered gradually to about 7.5 due to the formation of carbonate ion arising from CO_2 evolved in the course of the water gas shift reaction. Thus the reaction in alkaline media actually proceeds at pH 7.5 - 8.5. The distribution of several Ru(II) species at various pH's calculated from the equilibrium constants is shown in Fig.1.
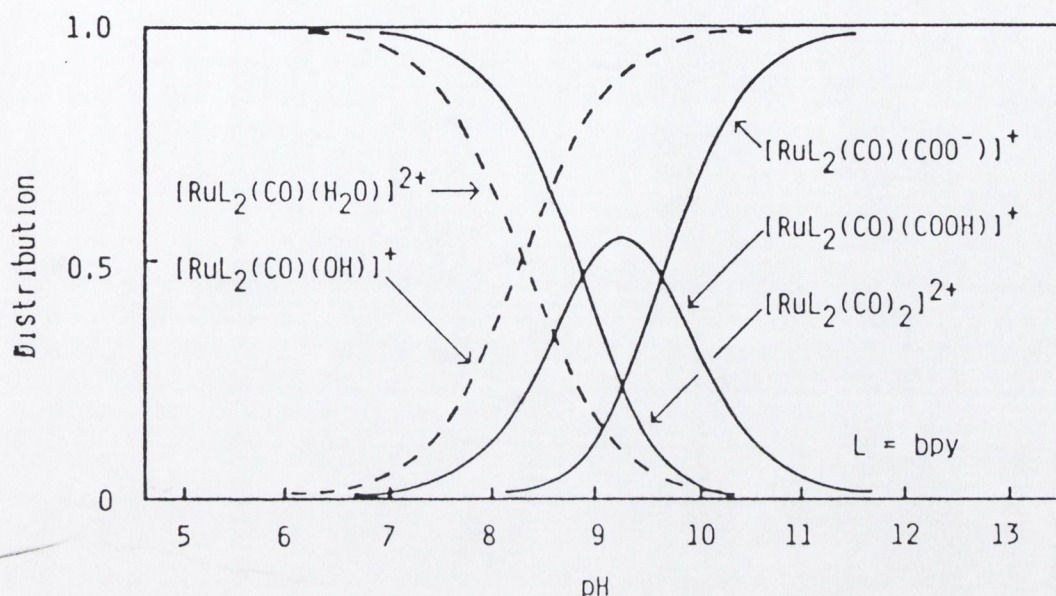
Fig.1 : The distribution of several Ru(II) species at various pH's[40]

The water gas shift reaction catalysed by some transition metal carbonyls, $M(CO)_6$ (M = Cr, Mo, W) in alkaline media has been reported to proceed preferentially by decomposition of the formate ion (eqn.10) which is produced at the beginning of the

$$HCOO^- + H_2O \xrightarrow{M(CO)6} H_2 + CO_2 + OH^- \qquad eqn.10$$
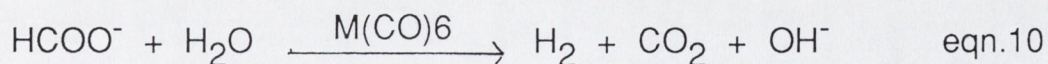
reaction[34,35,43]. For example, $HCOO^-$ reacts with $M(CO)_5$ resulting from the dissociation of a CO ligand of $M(CO)_6$ to afford $M(CO)_5OC(O)H^-$, which undergoes a decarboxylation to generate $M(CO)_5H^-$, as proposed by King et al.[35,44]. Tanaka[40]

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has examined the H_2 evolution arising from the decomposition of HCOOH in the presence of the Ru(II) complexes. The amount of H_2 evolved however was much smaller than that in the water gas shift reaction at $100^{\circ}C$ despite the presence of a large amount of $HCOO^-$ in the solution. Thus the decomposition of HCOOH may not be the main pathway for the H_2 evolution in the present water gas shift reaction.

A plausible catalytic cycle of the reaction is depicted in scheme 1 :[$Ru(bpy)_2Cl_2$] in an aqueous alkaline solution may be converted to $[Ru(bpy)_2(CO)_2]^{2+}$ probably through $[Ru(bpy)_2(CO)Cl]^+$ and $[Ru(bpy)_2(CO)(H_2O)]^{2+}$ successively, followed by the substitution reaction by CO. The nucleophilic attack of OH^- to one of the coordinated CO of $[Ru(bpy)_2(CO)_2]^{2+}$ at pH 8.0 - 9.0 gives $[Ru(bpy)_2(CO)(CO(OH)]^+$, which undergoes the decarboxylation to give $[Ru(bpy)_2(CO)H]^+$. The hydride thus formed reacts with H_3O^+ to evolve H_2 and also regenerates $[Ru(bpy)_2(CO)(H_2O)]^{2+}$. The different routes have been supported by the isolation and characterisation of the intermediates.

RuL_2CL_2

$\quad\quad | \quad - CO$

$CL^- \leftarrow |$

$\quad\quad \downarrow$

$[RuL_2(CO)CL]^+$

$\quad\quad | \quad - H_2O$

$CL^- \leftarrow |$

$H_2 \quad\quad\quad \downarrow$

$H_3O^+ \quad\quad \rightarrow [RuL_2(CO)(H_2O)]^{2+}$

$\quad\quad\quad CO \quad\quad H_2O$

$\quad\quad - OH^-$

$[RuL_2(CO)H]^+ \quad\quad H^+ \quad\quad \rightarrow H_2O \quad\quad [RuL_2(CO)_2]^{2+}$

$CO_2 \quad\quad [RuL_2(CO)(OH)]^+ \quad\quad OH^- \quad OH^-$

$[RuL_2(CO)(COOH)]^+$

$\quad\quad - OH^-$

$H^+ \quad\quad \rightarrow H_2O \quad\quad L=bpy$

$[RuL_2(CO)(COO^-)]^+$
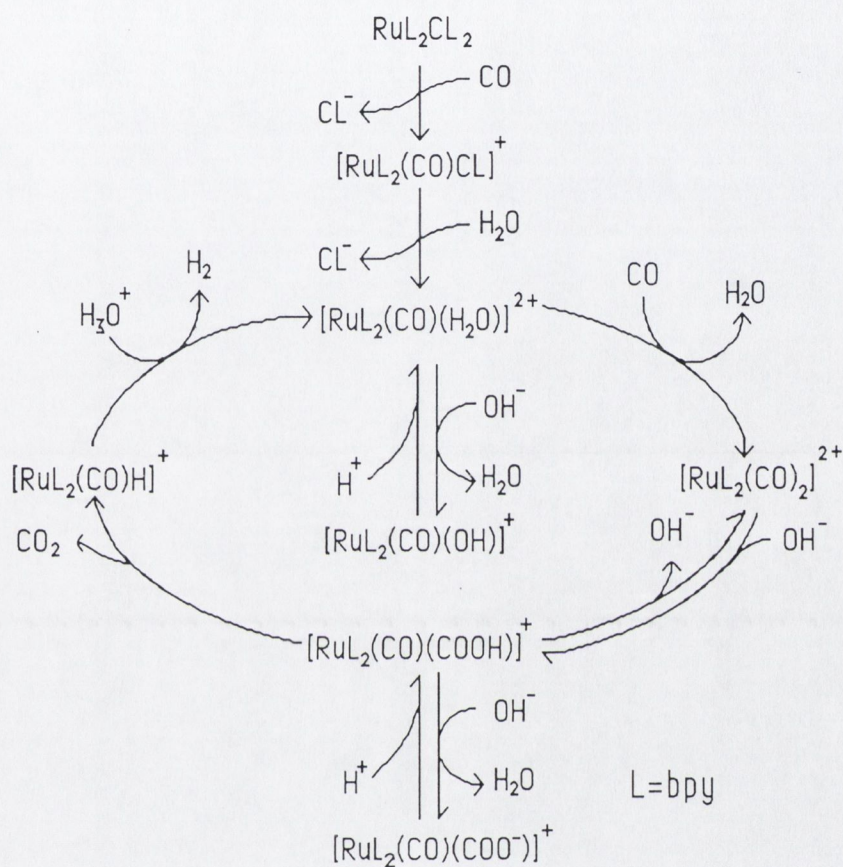
Scheme 1 : The water gas shift reaction catalysed by Ru(II) complexes[40]

As has been shown, Ru(II) carbonyl bipyridyl complexes are very active catalysts for the water gas shift reaction[37], especially when the reaction can be carried out under very mild aqueous alkaline conditions. The potential to perform the above catalytic cycle in-situ is very exciting, particularily as the

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intermediates could be isolated and examined spectroscopically in-situ. Therefore, it was decided to carry out all the reactions in Nafion, which is a commercial ionomer. Ionomers are polymers containing a low concentration of charged units along the chain and have been the subject of increasing interest during the past twenty five years. The presence of ionic groups in the polymer changes some of its properties dramatically. These changes are due primarily to the presence of reversible ionic crosslinks in these materials. Because of the low dielectric constant of most organic polymers, the ions or ionic dipoles tend to aggregate; this aggregation process, however, is limited because the ionic groups are covalently bonded to the organic chains[45].

Ionomers have shown themselves to be spectacularily useful as separators in the chlor-alkali industry, and as packaging materials because of their high strength and permeation properties.

Perfluorinated ionomer membranes have been increasingly important since their introduction in the late 1960's. The first commercial example, Nafion, is manufactured by E. I. duPont de Nemours & Co. It is synthesised by the copolymerisation of tetraflouroethylene with a perfluorovinyl ether under the $-SO_2F$ form. Nafion has the structure shown in Fig.2

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$$-[(CF_2-CF_2)_m -CF-CF_2]_n -$$

$$\left[\begin{array}{c} O \\ | \\ CF_2 \\ | \\ CF-CF_3 \end{array}\right]_z$$

$$\begin{array}{c} O \\ | \\ CF_2 \\ | \\ CF_2 \\ | \\ SO_3H \end{array}$$

WHEN:
m = 5 to 13.5
n = ca 1,000
z = 1,2,3---
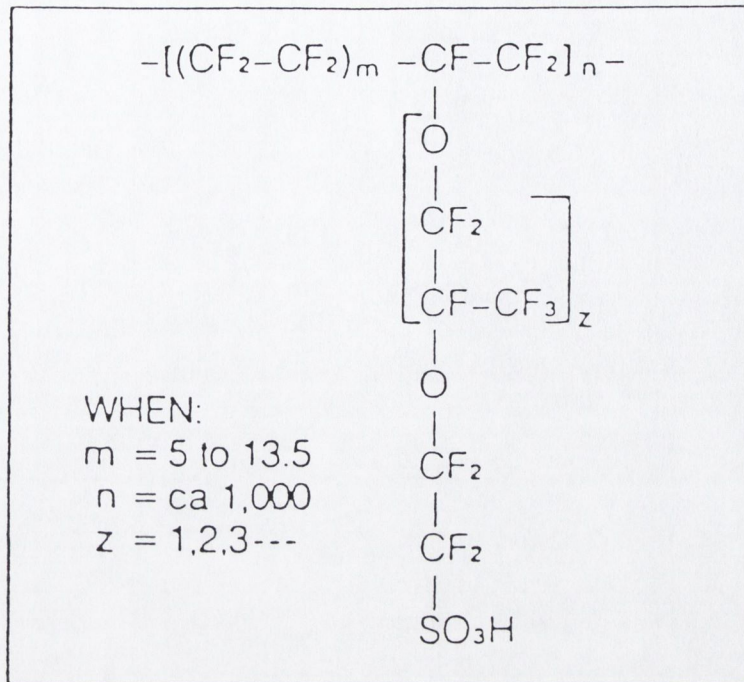
Fig.2 : Structure of Nafion

Variation in the value of m from 5 to 13.5 yields equivalent weight (EW) polymers from 950 to 1800. The EW is defined as the weight required of the acid form to neutralize one equivalent of base. It is this factor which has the greatest influence on membrane properties. Polymers with EW below 1000 experience excessive solvent swelling and dissolution occurs, whereas polymers with EW in the range 1000-1500g/mol are suitable as ion transport membranes.

Structurally the membranes are complex. In addition to some crystallinity, there are two distinct non-crystalline regions, the hydrophobic fluorocarbon phase and the hydrophilic ionic ares. Several structural models and variations on such models have over the years been proposed for Nafion. Eisenberg's[46] concept of cluster formation (1970) provides a reasonably general, molecular energetics-based theory of microphase

formation in ionomers. Certain assumptions can be challenged though, such as the degree of crystallinity not being accounted for. The cluster model of Hopfinger et al.[47] (ca.1976) may be considered to be a natural evolution from Eisenberg's concept but unfortunately it preceded the wealth of information from structural studies that appeared shortly afterwards. The most favoured model at present is that of a cluster-network arrangement developed by Hsu and Gierke[48]. The ionic clustering model is that of approximately spherical domains and the ion exchange sites are found near the interface, probably imbedded in the water phase. Such a structure satisfies the strong tendancy for the sulfonic acid sites to be hydrated and at the same time minimizes unfavourable interactions between water and the fluorocarbon matrix. The hydrated ionomer has spherical domains with an inverted micellar structure. The ionic clusters are assumed to be ~40Å in diameter and the channels ~10Å in length.(fig.3)
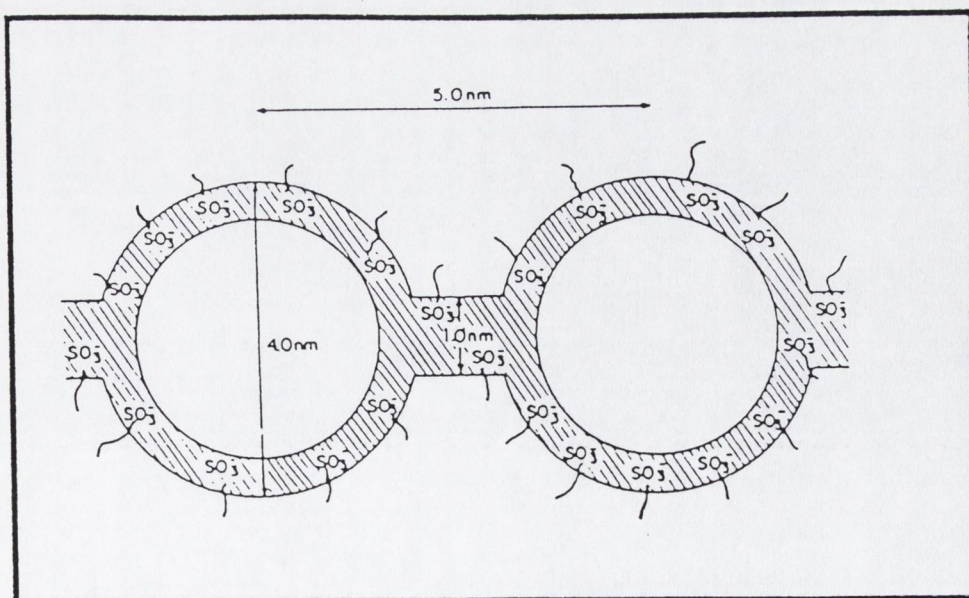
Fig.3 : Cluster network model developed by Gierke for Nafion perfluorinated membranes.

The perfluorosulfonic acid exchange site is a very strong acid as it is completely dissociated in water. This leads to the remarkably high degree of water uptake observed in the perfluorinated ionomer, as much as 50% by volume for 944 EW polymer. As the polymer absorbs more water the cluster diameter, exchange sites per cluster, and water molecules per exchange site all increase. The increase in the number of exchange sites per cluster with increasing water content is noteworthy because it suggests that cluster growth does not merely occur by an expansion of the dehydrated cluster. Rather, the growth of clusters appears to occur by a combination of this expansion and a continuous reorganization of exchange sites so there are actually fewer clusters in the fully hydrated sample (fig.4)[49].
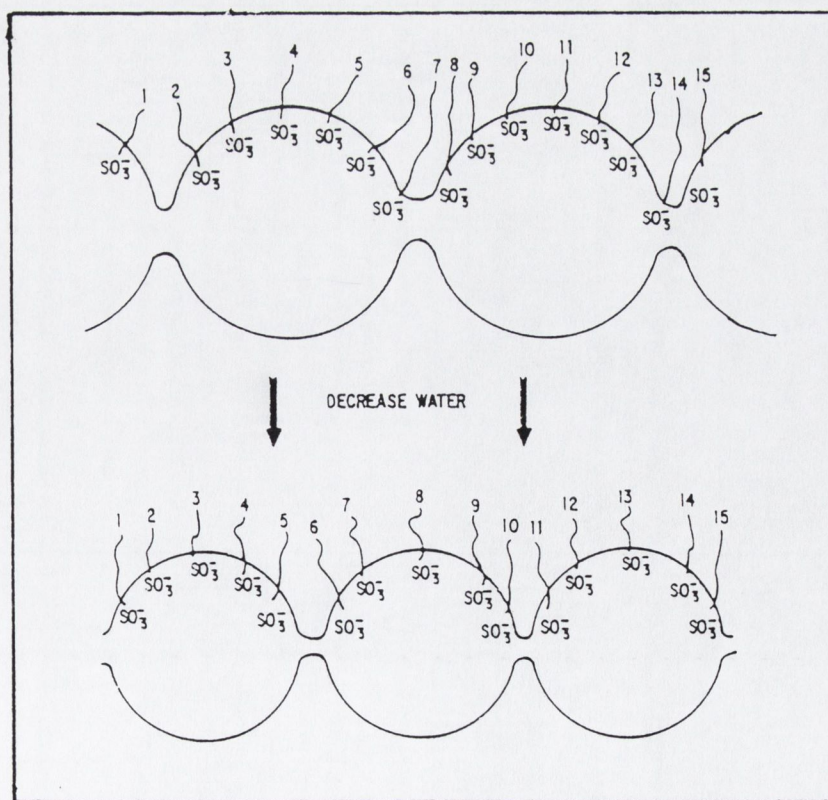
Fig.4 : Redistribution of ion exchange sites which occurs on dehydration of the polymer

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On dehydration the exchange sites from two clusters could be redistributed to form a third new cluster without significant spatial translation of polymer chains. The phenomenon of water absorption has been explained[49] in terms of the formation of the hydration shells around the ion dipoles.

Nafion was chosen as the supporting matrix because of its many useful properties. It is known to have the following advantages:

1. Good permiselectivity - This is commonly known as the Donnan Effect and is the difference resulting from the relative diffusion rates of cations and anions through the membrane. This difference is attributed to the Donnan potential which is produced by the tendancy of mobile counterions to diffuse out of the membrane. This produces a potential gradient at the polymer-solution interface. Therefore the equilibrium sorption of anions is suppressed. As a result the incorporation of neutral and positively charged species is facilitated.

2. Resistance towards chemical attack - Nafion has been shown to be extremely useful as a chemically inert supporting matrix into which cationic species can be incorporated. The Nafion is found to strongly retain these cationic species, even in the presence of aqueous, alkaline and alcoholic solution.

3. Nafion is a transparent material - therefore it is extremely useful for spectroscopic measurements. It has no absorption in the UV/Vis region or in the carbonyl region of the IR.

4. Nafion has the ability to exist in two forms, the acid or base form. This is simply done by exchanging the proton from the sulfonic acid moiety for a sodium ion. The pH can also be controlled by immersing the membrane in a buffer solution. The exchangability of the membrane is particularly useful when attempting to follow in-situ reactions by IR spectroscopy because of the complete absorption that occurs for acidic membranes.

5. Photochemical processes can be followed very easily. As a photochemical reaction is taking place the intermediates may be monitored in-situ by UV/Vis and IR spectroscopy. The Nafion itself is not altered during photochemistry.

6. Nafion has a cluster network structure - this means that it can be used to determine the size and distribution of the incorporated cations, being either homogeneously distributed or in close proximity to one or both surfaces of the membrane.

SECTION 2   RESULTS AND DISCUSSION

2.1 Introduction

An investigation of the chemistry and photochemistry of carbonyl complexes of Ru(II) incorporated in Nafion, and their subsequent reactivity, was carried out in this project, with the purpose of their exploitation in catalytic systems, especially the water gas shift reaction. The monocarbonyl complexes $[Ru(bpy)_2(CO)Cl]^+$ and $[Ru(bpy)_2(CO)H]^+$, and the dicarbonyl complex $[Ru(bpy)_2(CO)_2]^{2+}$ have been isolated and characterised (IR, UV/Vis spectroscopy). The chlorocarbonyl compound is an extremely useful starting material as it undergoes both thermal (loss of Cl^-) and photochemical (loss of CO) substitution. $[Ru(bpy)_2(CO)Cl]^+$ was reported[37] to be a catalyst for the photochemical water gas shift reaction - the chlorocompound, the aquacarbonyl or the dicarbonyl complex $[Ru(bpy)_2(CO)_2]^{2+}$ (previously prepared by Deacon[32] and Kelly et al.[50]) were thought to be the active species[37]. Hydride intermediates in the catalytic cycle were postulated[37] but no evidence for their existence during the cycle was obtained until Tanaka[40] reported the successful isolation of the hydride intermediate. Kelly and Vos[31] had prepared $[Ru(bpy)_2(CO)H]^+$ earlier (by reaction of $NaBH_4$ with $[Ru(bpy)_2(CO)Cl]^+$) and showed that it decomposed with evolution of hydrogen in the presence of acid to give the aquacarbonyl complex. Meyer[51] showed that the hydroxycarbonyl complex could be generated from the chlorocarbonyl

complex by reaction in alcoholic base. O'Connell [52] has shown that the chlorocarbonyl complex is attacked by base, resulting in the loss of CO_2 to give the diaqua complex $[Ru(bpy)_2(H_2O)_2]^{2+}$ and Cole-Hamilton [33,37] has reported that the aqua species will regenerate the chlorocarbonyl or aquacarbonyl moieties when light assisted reactions of CO are performed.

Therefore, it seemed possible that a catalytic scheme for the evolution of CO_2 and H_2 may involve some of the above processes. Tanaka et al. [40] systematically report the isolation of the possible intermediates in the water gas shift reaction catalysed by $[Ru(bpy)_2(CO)Cl]^+$ which is a catalyst precursor in weak aqueous alkaline solutions.

Consequently, it was considered possible that the water gas shift reaction could be carried out in Nafion. All reactions would be performed in-situ with the potential isolation of the intermediates in the membrane. The reactions would be monitored by Infra-red and Ultra-violet spectroscopy without altering any of the physical or chemical properties of the sample. The results are easily reproduced and the species are very stable in the membrane. It is interesting to compare the reactivity of the complexes in Nafion with their reactivity in solution.

Table 2 below gives spectroscopic data for each of the compounds involved in the catalytic cycle. Significant spectral changes are observed when the complexes are incorporated into Nafion. These changes will be discussed in later sections.

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$[Ru(bpy)_2(CO)_2]^{2+}$ was chosen as the initial entry point to the Tanaka cycle because the preparation was previously described[24] and the complex well characterised. Upon incorporation of the complex into Nafion it was believed that nucleophilic attack would lead to the evolution of CO_2 and H_2, and the subsequent formation in-situ of the complexes in the cycle. The preparation, incorporation and reactions performed on $[Ru(bpy)_2(CO)_2]^{2+}$ are described in the following section; the subsequent sections will describe $[Ru(bpy)_2(CO)H]^+$, $[Ru(bpy)_2(CO)Cl]^+$, $[Ru(bpy)_2(CO)(H_2O)]^{2+}$, $[Ru(bpy)_2(CO)(COO^-)]^+$ and finally $[Ru(bpy)(CO)_2Cl_2]$. The overall catalytic cycle in Nafion will then be reviewed.

Compound	I.R.(cm^{-1})		UV/Vis(nm)	
	Compound	Nafion	Compound	Nafion
$[Ru(bpy)_2(CO)_2]^{2+}$	2035 2084	2054 2104	316(Sh) 310(Sh) 302 248	316(Sh) 300 248
$[Ru(bpy)_2(CO)H]^+$	1930	1960	452 348 273	450 350 272
$[Ru(bpy)_2(CO)Cl]^+$	1966	2005	418(Sh) 353 313(Sh) 282 260(Sh)	415(Sh) 353(Sh) 264
$[Ru(bpy)(CO)_2Cl_2]$	2055 1997 330	2100 2038	354 313 305 286	306
$[Ru(bpy)_2(CO)(H_2O)]^{2+}$	——	2010	——	475 350 260
$[Ru(bpy)_2(CO)(OH)]^+$	——	1988	——	440 348 280 246
$[Ru(bpy)_2(CO)(COO^-)]^+$	——	1965	——	446 350 272
$[Ru(bpy)_2(CO)(COOH)]^+$	——	1970	——	——

Table 2 : Spectroscopic data

2.2 $[Ru(bpy)_2(CO)_2][PF_6]_2$

The route chosen for the preparation of the dicarbonyl complex involved the known reaction, in ethanol, of bpy with the red carbonyl solution $[Ru(CO)_2Cl_2]_n$ to yield $[Ru(bpy)(CO)_2Cl_2]$[24]. Reaction in ethanol yields a red/purple product as reported by Wilkinson[24] whereas aqueous ethanolic solution gives yellow crystals. $[Ru(bpy)(CO)_2Cl_2]$ and bpy were refluxed in ethanol/water for 24 hrs. Upon addition of a concentrated aqueous solution of NH_4PF_6 yellow crystals formed. These were recrystallised from ethanol/water.

The UV/Vis spectrum (CH_3CN) gives absorption maxima at 316(sh), 310(sh), 302 and 248nm. The Ir spectrum (KBr disc) has ν_{co} at 2035 and 2084cm^{-1}. Both spectra are in agreement with the literature[50]. The complex is insoluble in water but readily soluble in organic solvents.
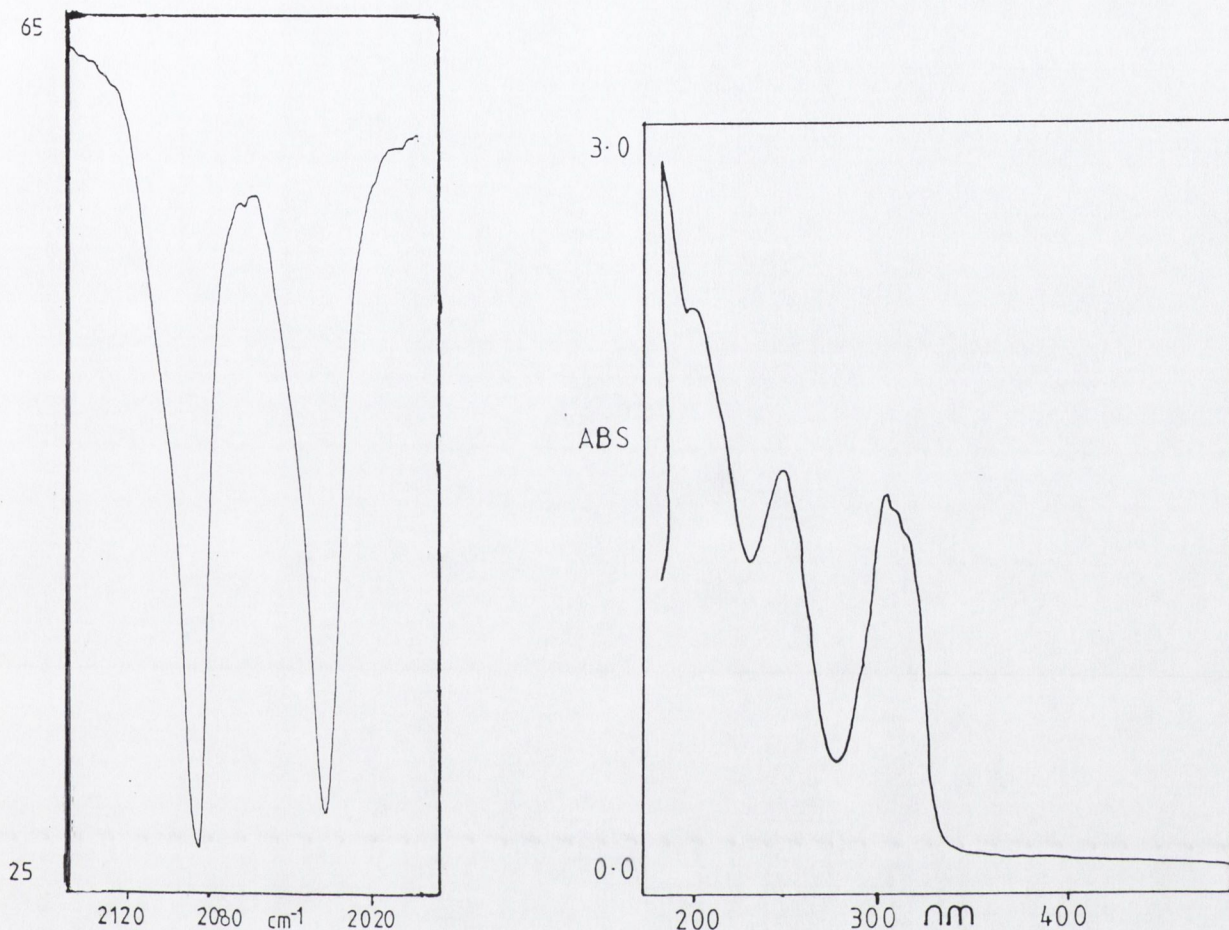
Fig.5 : IR(KBr) and UV/Vis(CH$_3$CN) spectra of [Ru(bpy)$_2$(CO)$_2$][PF$_6$]$_2$

The complex initially had to be incorporated into the Nafion membrane before experiments could be carried out. This was achieved by first dissolving the complex in a solution in which the Nafion sample would subsequently be stirred. Water was the desired solvent because of its unreactivity with Nafion but was unable to be used because of the insolubility of the complex. Alcohols were not desired for use because of their solvent swelling effect on Nafion. Therefore, it was decided to dissolve the complex in acetone and to subsequently evaporate off the acetone by swirling to leave a very fine deposit of the complex on the sides of the container. Pure water was then added and the mixture stirred for several minutes. Finally,

the Nafion sample was added to the suspension and stirred for a specified time. After removal of the sample from the solution the surface water was removed between sheets of tissue.

The UV/Vis and IR spectra were then recorded . The UV/Vis spectrum shows absorption maxima at 316(sh), 302 and 248nm while the IR spectrum shows ν_{CO} at 2104 and 2053cm^{-1}.
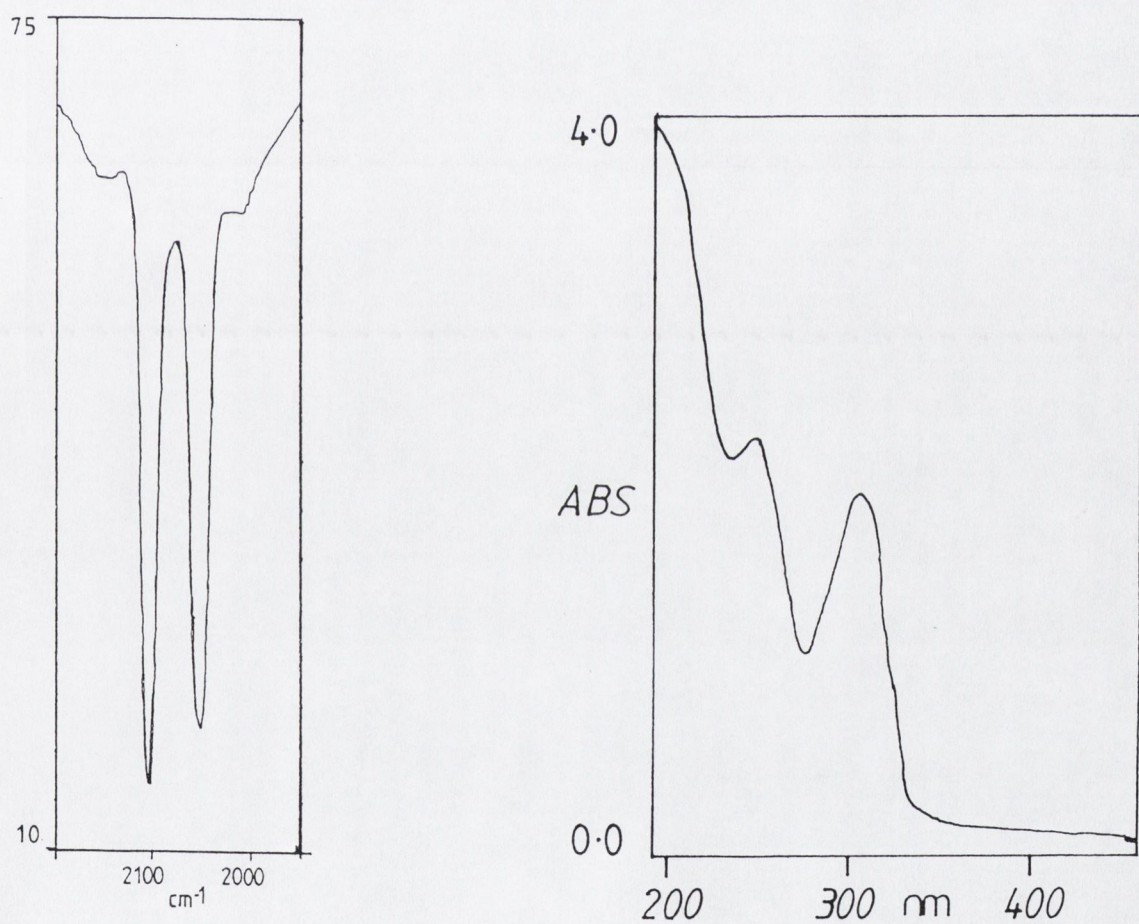
Fig.6 : IR and UV/Vis spectra of [Ru(bpy)$_2$(CO)$_2$][PF$_6$]$_2$ incorporated in Nafion

As can be seen, upon incorporation of the complex into Nafion the recorded IR spectrum shows a significant shift of the carbonyl bands to higher wavenumber. This shift in wavelength was consistent in

all samples prepared. Coordination of the complexes results in a decrease of the stretching frequency of free carbon monoxide ($2155 cm^{-1}$). All of the dicarbonyl complexes exhibit two strong carbonyl bands in the region $2000 - 2110 cm^{-1}$ indicative of cis stereochemistry. The replacement of a pi-donor ligand (Cl^-) with a pi-acceptor ligand (CO) to form the dicationic complex leads to a decrease in the M-C bond order, thus increasing the CO bond order and raising v_{CO} .The Nafion medium is also affecting the carbonyl position (section 2.8.6).

2.2.1 Treatment of $[Ru(bpy)_2(CO)_2][PF_6]_2$ with NaOH Solution

It is believed that there may be two successive equilibria in an aqueous alkaline solution of $[Ru(bpy)_2(CO)_2]^{2+}$ [40]. The species formed initially is thought to be the OH^- unstable (hydroxycarbonyl) complex which upon further OH^- treatment is deprotonated to give the (COO^-) species. Therefore, $[Ru(bpy)_2(CO)_2]^{2+}$ may exist as an equilibrium mixture with $[Ru(bpy)_2(CO)(COOH)]^+$ in weakly alkaline solutions as shown in eqn.8

$$[Ru(bpy)_2(CO)_2]^{2+} + OH^- \longrightarrow [Ru(bpy)_2(CO)(COOH)]^+ \qquad \text{eqn.8}$$

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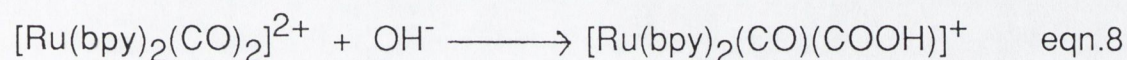
Another equilibrium existing in alkaline solution may be expressed by equation 9

$$[Ru(bpy)_2(CO)(COOH)]^+ + OH^- \longrightarrow [Ru(bpy)_2(CO)(COO^-)]^+ \quad eqn.9$$
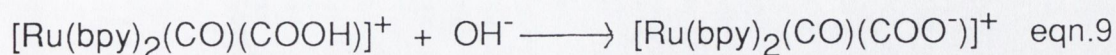
The formation of the mono(hydroxycarbonyl) complex from $[Ru(bpy)_2(CO)_2]^{2+}$ may be consistent with the fact that a similar equilibrium reaction is known to occur for $[Ru(bpy)_2(CO)_2][PF_6]_2$ with $NaOCH_3$ in dry CH_3OH giving $[Ru(bpy)_2(CO)C(O)OCH_3][PF_6]$.[40]

The nucleophilic attack of OH^- on $[Ru(bpy)_2(CO)_2]^{2+}$ incorporated in Nafion was monitored by IR and UV/Vis spectroscopy. Following treatment of the sample with 0.2M NaOH for 1min there is a significant change observed in the recorded IR spectrum : the two carbonyl peaks at 2054 and 2105cm^{-1} have decreased in intensity and a new band has grown in at ca. 1960cm^{-1}. With increased treatment time the carbonyl peaks are seen to disappear altogether while the ingrowing peak at ca. 1960cm^{-1} continues to increase in intensity; after 20mins the dicarbonyl complex is completely converted to the deprotonated (hydroxycarbonyl) and the peak remains unchanged. However, with 0.2M NaOH solution the overall reaction is rapid and it is difficult to monitor the intermediates spectroscopically.
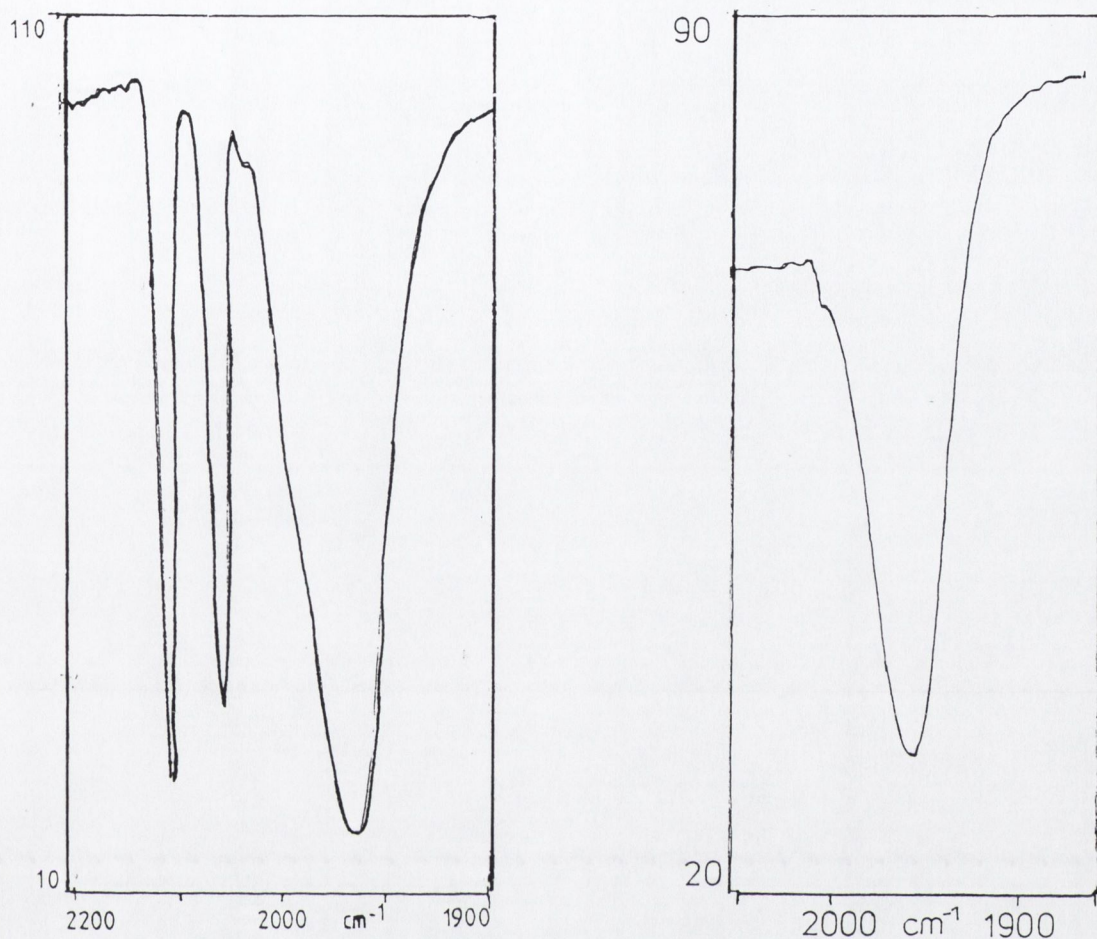
Fig.7 : IR spectra of a. $[Ru(bpy)_2(CO)(COOH)]^+$ and b. $[Ru(bpy)_2(CO)(COO^-)]^+$ in Nafion

In an attempt to isolate the (hydroxycarbonyl) intermediate the reaction was performed using weaker alkaline conditions than previously. Upon incorporation of the dicarbonyl into Nafion the membranes were treated with one of 0.01, 0.02, 0.05, 0.1 and 0.2M NaOH solutions. Complete conversion of the dicarbonyl complex to the carboxylate complex ($1965cm^{-1}$, 446, 350 and 272nm) occurs readily with all but 0.01M NaOH solution. Upon addition of the 0.01M NaOH solution continuous scanning in the UV/Vis region of the spectrum shows an immediate significant increase in intensity at 350 and 450nm. This trend continues for 90 mins after which time the spectra begin to superimpose themselves and a stable species is

obtained. The IR region was also monitored for a membrane containing a strong concentration of the dicarbonyl complex (Fig.8). Following 1 mins treatment in 0.01M NaOH solution the bands at 2105 and 2054cm^{-1} remain intense but a very weak stretch is appearing at 2005cm^{-1} (a). As treatment time is increased the 2005cm^{-1} band increases in intensity and moves to lower wavenumber (b) - it subsequently splits slightly indicating that there are two species present, presumably the (hydroxycarbonyl) (1970cm^{-1}) and the deprotonated (hydroxycarbonyl) (1960cm^{-1}) (c). As the treatment is continued the (hydroxycarbonyl) peak decreases in intensity as the carboxylate peak increases (d). This trend is resulting from the deprotonation reaction. There is still substantial evidence for the dicarbonyl species, conversion to the deprotonated (hydroxycarbonyl) is not complete and an intermediate species is present, presumably the (hydroxycarbonyl).
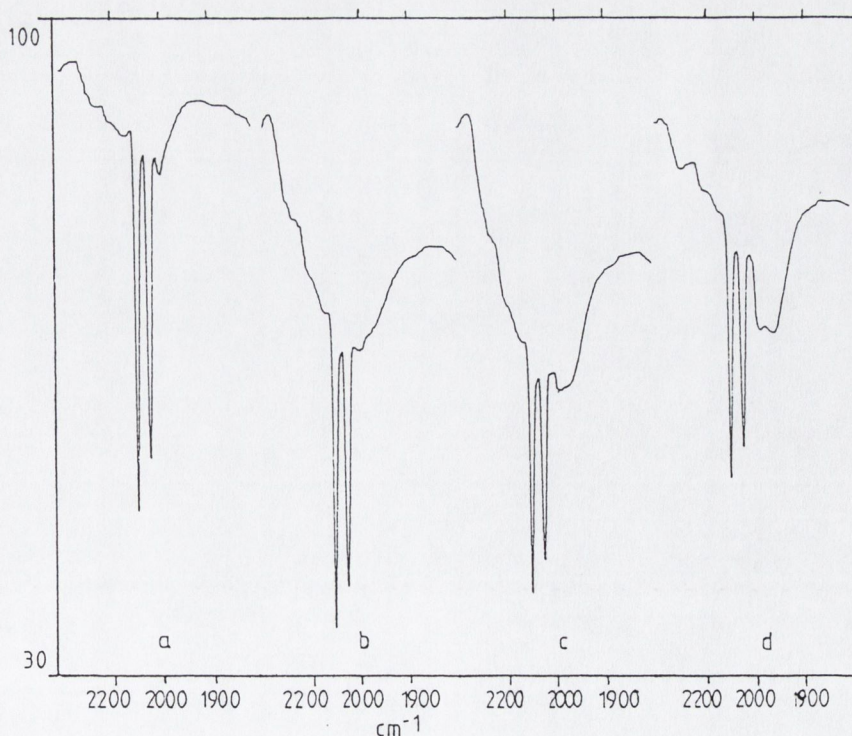
Fig.8 : IR spectra of [Ru(bpy)$_2$(CO)$_2$][PF$_6$]$_2$ following treatment with 0.01M NaOH solution for a. 1, b. 5, c. 10 and d. 40mins

Upon treating the incorporated sample with 0.2M NaOH solution at room temperature the UV/Vis spectra subsequently recorded show noticeable changes as the treatment is continued, with the gradual growth of new absorption bands at 446, 350 and 272nm. When the dicarbonyl complex has been completely converted there is no further change in the spectrum.
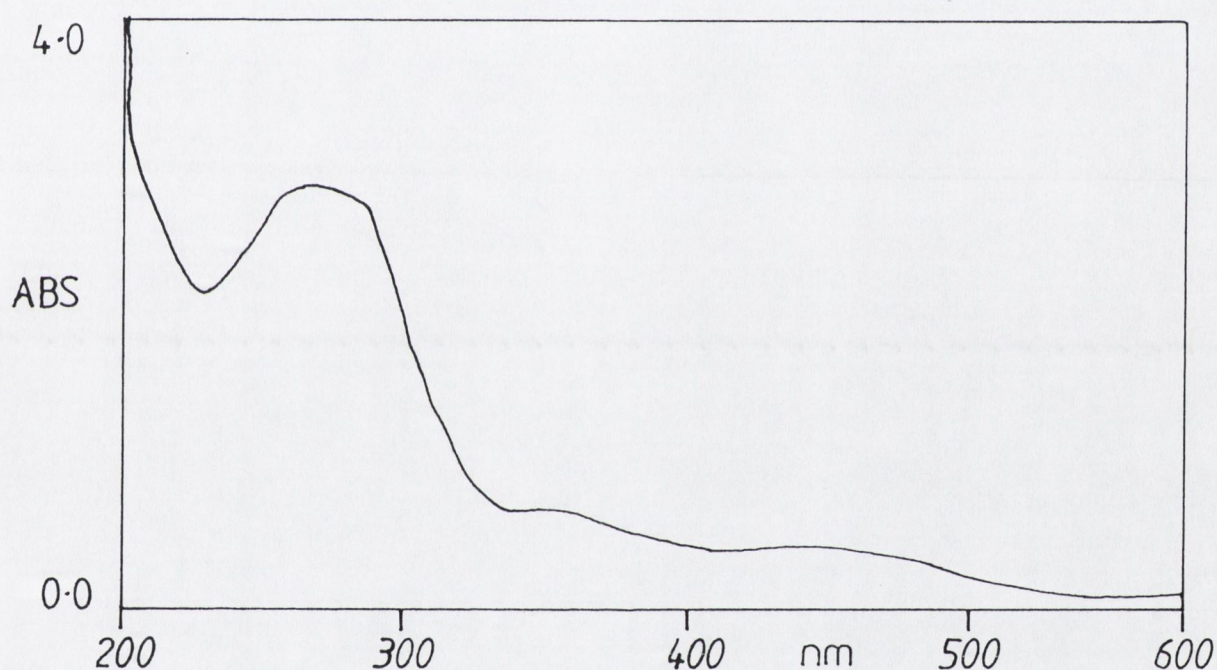
Fig.9 : UV/Vis absorption spectrum of $[Ru(bpy)_2(CO)_2][PF_6]_2$ after 5 mins treatment with 0.2M NaOH solution.

Although the above treatment was repeated for other samples using the same materials, the UV/Vis spectra are identical but there is some shifting of the carbonyl band occurring in the IR spectra. The ingrowing carbonyl band is found between 1958 and 1965cm^{-1} after 10 mins treatment with 0.2M NaOH solution. This effect is thought to be due to the medium effects of the Nafion membrane (section 2.8.6)

Tanaka[40] suggests that the free (hydroxycarbonyl) is found at $1960cm^{-1}$. In the experiments carried out in Nafion it was initially thought that the species formed at $1960cm^{-1}$ was the (hydroxycarbonyl), but this was found not to be the case when the reaction was performed under very mild alkaline conditions - it is thought that the Nafion is causing a shift of v_{CO} to occur during the reactions of the complexes, further to the shift upon incorporation of the complexes, giving higher v_{CO} values for the complexes formed in Nafion.

It is possible in weakly alkaline solutions that the time required for the diffusion of OH^- into the membrane is affecting the overall reaction, producing the unstable (hydroxycarbonyl) which upon further treatment in OH^- undergoes a rapid deprotonation to give the deprotonated (hydroxycarbonyl). In Nafion the (hydroxycarbonyl) is thought to be the ca.$1970cm^{-1}$ species. The deprotonated (hydroxycarbonyl) $[Ru(bpy)_2(CO)(COO^-)]^+$ is found at $1960cm^{-1}$ in Nafion, similar to that of the free (hydroxycarbonyl).

The equilibrium reaction was also monitored by preparing a dicarbonyl sample in Nafion and subsequently treating it in 0.2M NaOH solution as before to give the deprotonated (hydroxycarbonyl). This was followed by treatment in 0.01M NaOH solution and subsequently in increasingly stronger concentrations of NaOH solutions. IR spectral results indicate that in 0.01 and 0.02M NaOH solution the dicarbonyl is still strongly present even after 90 mins treatment shown by the presence of two intense stretches at 2105 and $2054cm^{-1}$ - however with the stronger concentrations of base

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the equilibrium lies on the side of the deprotonated (hydroxycarbonyl), shown by the presence of only one stretch at $1960cm^{-1}$.

It is interesting to note at this point that the $1960cm^{-1}$ species, attributed to the deprotonated, carboxylate species, appears to produce the same UV/Vis and IR spectra as the prepared hydride, $[Ru(bpy)_2(CO)H]^+$, when this complex is incorporated into Nafion. The hydride gives ν_{CO} at $1960cm^{-1}$ and UV/Vis absorption maxima at 450, 350 and 272nm (section 2.3). Therefore, the question arose as to whether a possibly new and effective pathway to the hydride had been discovered. This idea led to the decision to carry out heat and photolysis experiments on the two species in question. The results will be discussed in section 2.7. However, the most important method of differentiating between the hydride and the deprotonated (hydroxycarbonyl) is to consider the reactions of the species in water. The hydride should give the aquacarbonyl complex whereas the deprotonated (hydroxycarbonyl) should revert to the dicarbonyl complex.

2.2.2 Heat treatment of $[Ru(bpy)_2(CO)_2][PF_6]_2$ in Nafion with NaOH Solution

Several experiments were carried out to determine the effects of both temperature and duration of treatment in NaOH solution on the dicarbonyl complex incorporated in Nafion.

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a. Temperature studies : The temperatures of the 0.2M NaOH solutions examined ranged from $25^{\circ}C$ to $100^{\circ}C$. Nafion samples which had previously been incorporated with $[Ru(bpy)_2(CO)_2][PF_6]_2$ were stirred in the NaOH solutions of varying temperature. The effects of temperature were monitored by UV/Vis and IR spectroscopy at room temperature after removal of the samples from solution.

Results obtained indicate that the higher the NaOH solution temperature the higher the wavenumber of the ingrowing peak in the IR, which is found between $1955 cm^{-1}$ (for a sample treated at room temperature) to $2000 cm^{-1}$ (for a sample treated at $100^{\circ}C$). Obviously the temperature of reaction is having a large effect on the position of the ingrowing peaks; it appears probable that increasing temperature causes a significant swelling of the membrane, as a result the medium of the membrane is altered considerably, causing the shift in wavelength of the carbonyl peak. It is also possible that the species being formed at the different temperatures are not the same ; this fact has not been determined conclusively as yet because although the UV/Vis spectra recorded are the same (the absorption maxima are seen to occur at 448, 350 and 272nm) the IR spectra exhibit very marked differences in the position of the carbonyl peak. However, the peak is very sharp in all cases with no evidence of an intermediate species in the form of a split carbonyl peak.
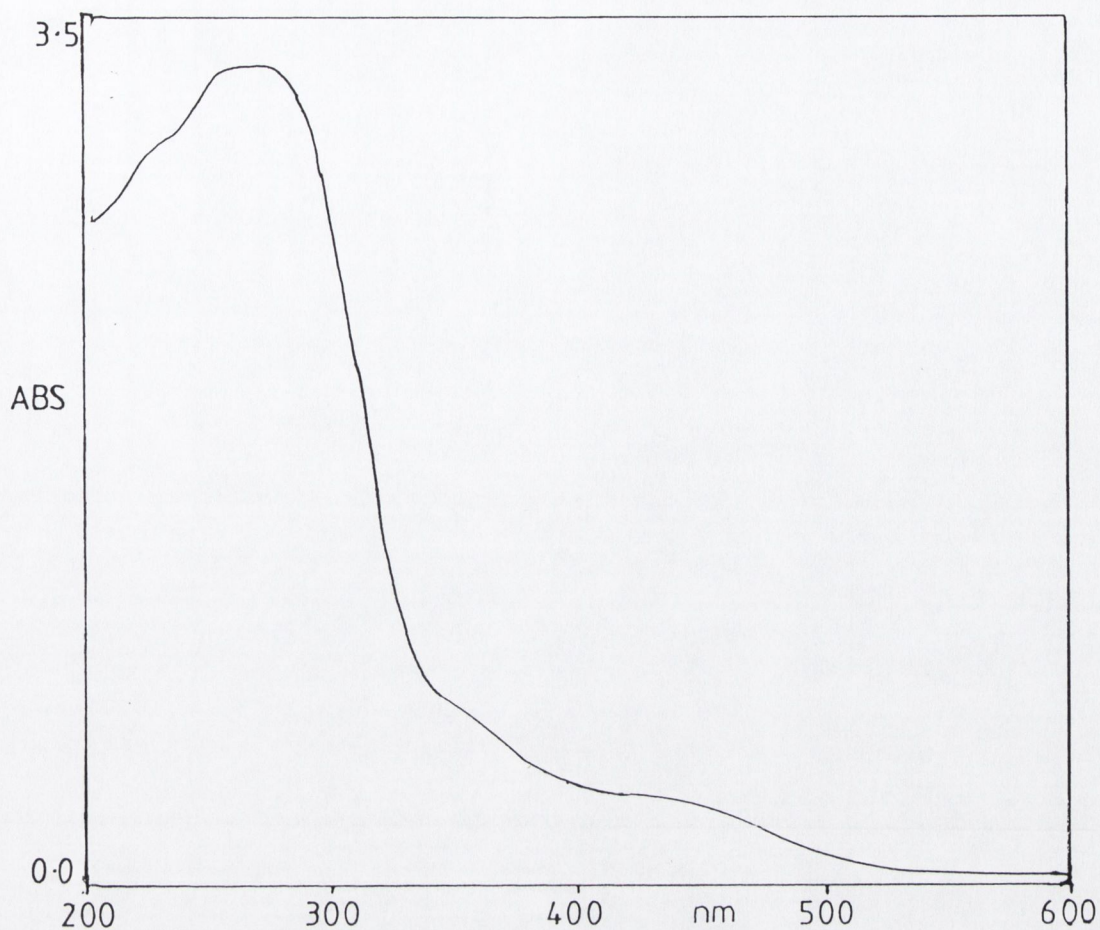
Fig.10 : UV/Vis spectrum of $[Ru(bpy)_2(CO)_2][PF_6]_2$ in Nafion following treatment with 0.2M NaOH
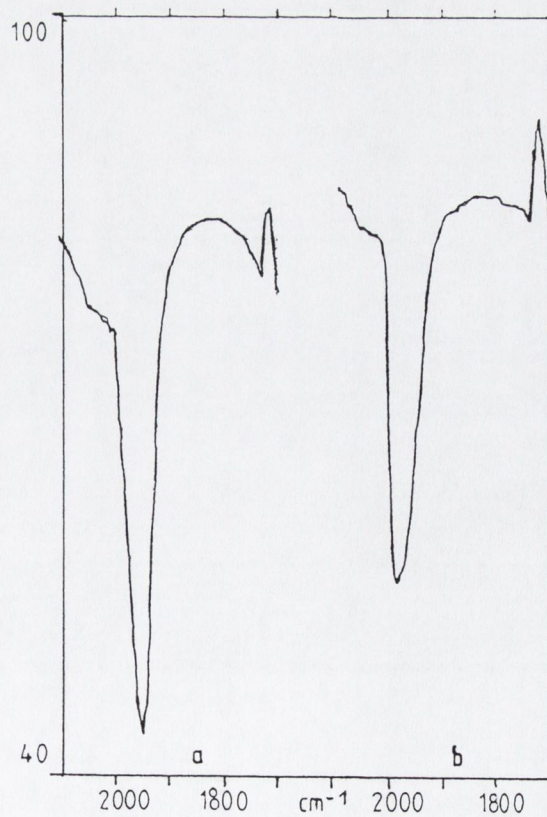
Fig.11 : IR spectra of $[Ru(bpy)_2(CO)_2][PF_6]_2$ in Nafion following treatment in 0.2M NaOH solution at a. 25°C and b. 75°C

b. Time studies : Apart from the variation in reaction temperature the duration of treatment was also varied. Upon treating the sample with 0.2M NaOH solution the carbonyl peaks decreased in intensity while a new peak grew in the region 1955-2000cm^{-1}, the position of the stretch being dependent upon the reaction temperature as shown above. With the higher temperatures, a faster reaction was expected because excessive swelling of the membrane should allow for easier diffusion of the NaOH but in fact no differentiation could be made between the rates of reaction over the temperature range 25 - 100°C of 0.2M NaOH solution.

2.2.3   Photolysis of [Ru(bpy)$_2$(CO)$_2$][PF$_6$]$_2$ in Nafion

Photolysis was carried out using a medium pressure Hg lamp, a quartz water bath, quartz lens and quartz cuvette. The complex was first incorporated into Nafion by the method previously described, the sample was then placed in the quartz cuvette containing the required solvent and photolysis carried out for the desired times. The lamp used irradiates at ca. 254, 313, 365 and 436nm.

2.2.3.1 Photolysis of $[Ru(bpy)_2(CO)_2][PF_6]_2$ in Nafion immersed in H_2O

Photolysis was initially for periods of 10secs but was gradually increased to periods of 10mins. The subsequent reactions were monitored by UV/Vis and IR spectroscopy: as with previous experiments these techniques are very useful for the recording of in-situ species. The percent of decarbonylation resulting from the photolysis can be easily obtained from the IR spectra.

After 10secs photolysis there is substantial evidence for decarbonylation; in fact decarbonylation at this early stage is most rapid. The intensity of the carbonyl stretches at 2105 and 2054cm^{-1} are reduced by 50% within the first 30secs. Apart from this there is the growth of a new stretch at 2010cm^{-1}. After only 95secs photolysis the three stretches are equally intense, but even after 30mins irradiation there is still significant evidence for the dicarbonyl complex with the existence of two minor peaks at 2054 and 2105cm^{-1}. The intense stretch at 2011cm^{-1} is characteristic of the aquacarbonyl complex.
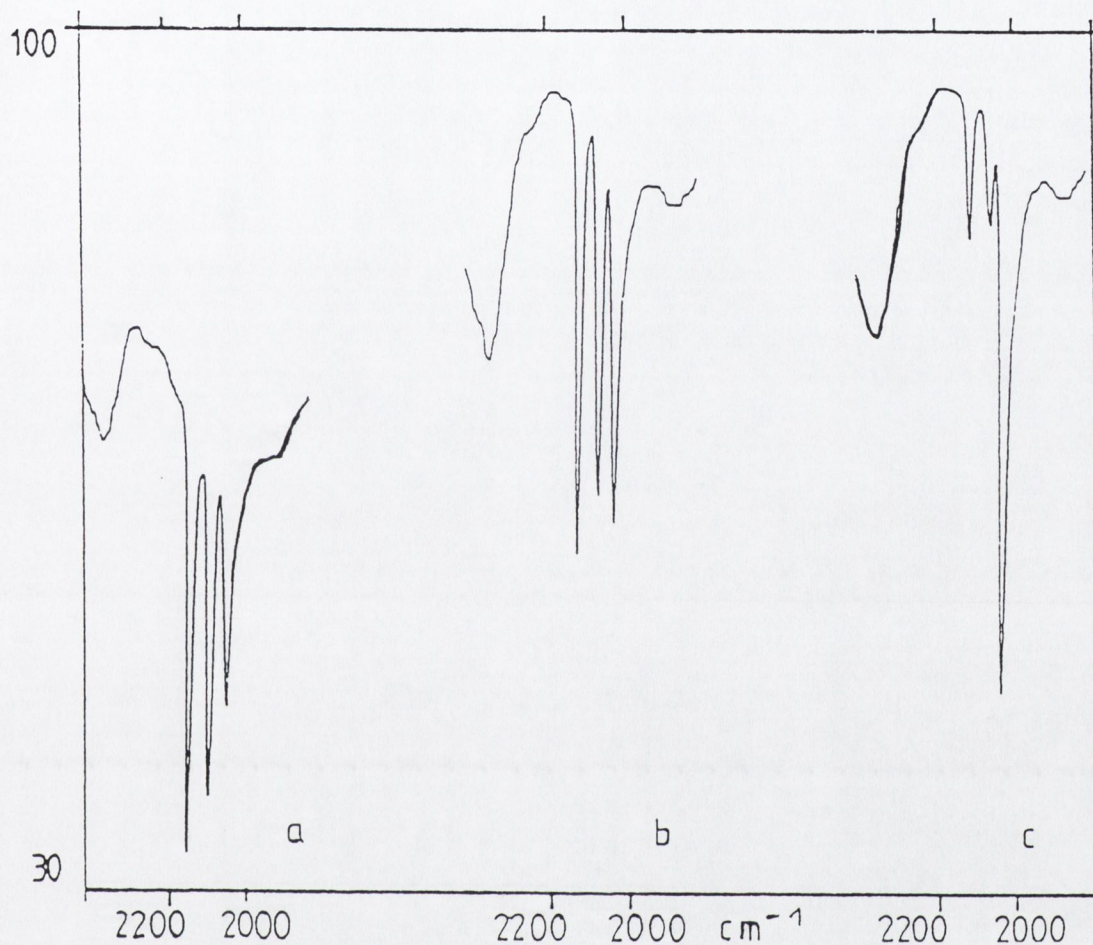
Fig.12 : IR spectra of [Ru(bpy)$_2$(CO)$_2$][PF$_6$] in Nafion following photolysis in H$_2$O for a. 10 secs b. 1.5 mins and c. 30 mins

There is also an appreciable change in the recorded UV/Vis absorption spectra following irradiation. After originally incorporating the complex the UV/Vis spectra shows absorption maxima at 316(sh), 310(sh), 303 and 249nm. However, upon prolonged photolysis (30mins) the spectrum has altered considerably to show new maxima at 330(sh) and 480nm. During further photolysis, these absorption maxima continue to increase in intensity but remain at the same wavenumber.
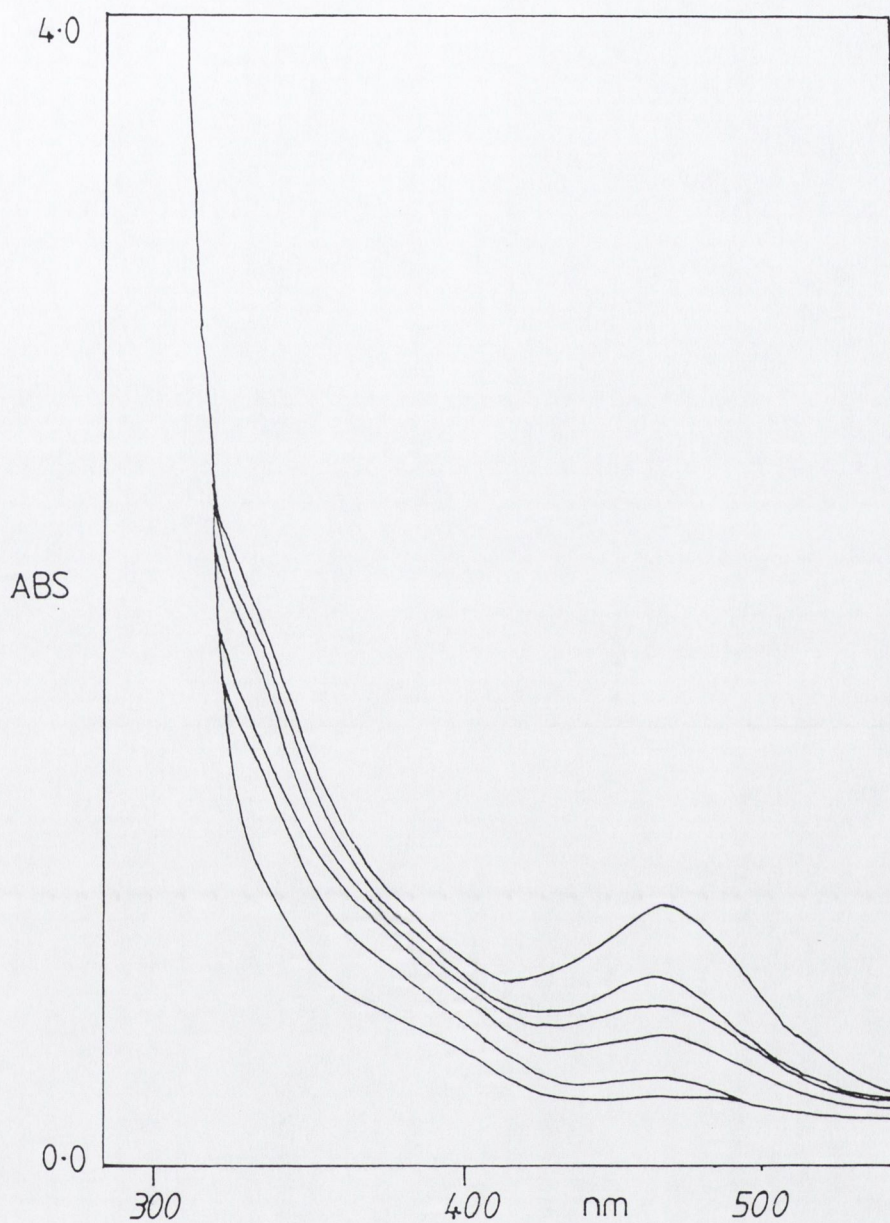
Fig.13 : UV/Vis spectrum of [Ru(bpy)$_2$(CO)$_2$][PF$_6$]$_2$ in Nafion following photolysis in H$_2$O for 1, 5, 10, 15, 20, 30 mins

It is thought probable that the dicarbonyl complex is initially converted to the aquacarbonyl complex, [Ru(bpy)$_2$CO(H$_2$O)]$^{2+}$ which in turn is converted to the diaqua complex cis-[Ru(bpy)$_2$(H$_2$O)$_2$]$^{2+}$ seen by the existence of the band at 480nm (the trans isomer is found at 492nm)[52]. Therefore these species exist in the Nafion, giving rise to the stretches in the IR spectrum. The overall reaction

is best explained by considering the photolysis process - the sample is irradiated at 436nm and initially all the energy is absorbed by the dicarbonyl complex, therefore conversion to the aquacarbonyl takes place readily. However, the aquacarbonyl absorbs energy as the photolysis process is continued and conversion to the diaqua complex occurs easily. The remainder of the light energy is absorbed by the dicarbonyl but conversion to the aquacarbonyl is slower than previously because of the reduced available energy.

Although photolysis was carried out for a total of 30mins there is evidence in the spectra that the dicarbonyl complex has not completely converted to the diaqua complex because of the existence in the IR spectrum of the two weak bands at 2054 and 2104cm^{-1}. Equation 11 shows the conversion of the dicarbonyl to the aquacarbonyl and hence to the diaqua complex. This same result is obtained when the reaction is carried out using MeOH as solvent. In this instance the aquacarbonyl is primarily formed followed by the conversion into the diaqua complex.

$$[Ru(bpy)_2(CO)_2]^{2+} \xrightarrow[hv]{H_2O} [Ru(bpy)_2(CO)(H_2O)]^{2+}$$

$$\Big\downarrow\, H_2O \quad hv$$

$$[Ru(bpy)_2(H_2O)_2]^{2+} \qquad \text{eqn.11}$$
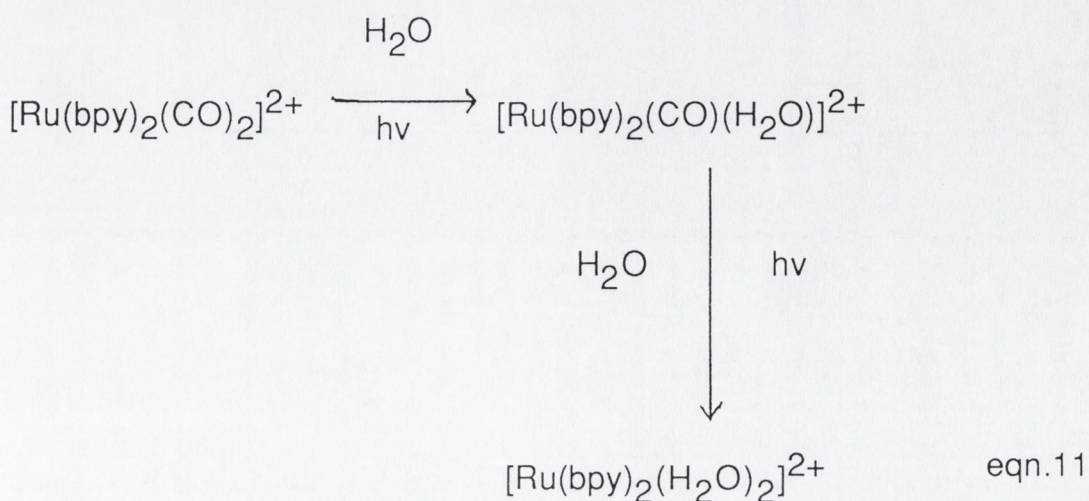
2.2.3.2 Photolysis of [Ru(bpy)$_2$(CO)$_2$][PF$_6$]$_2$ in Nafion immersed in 0.2M NaOH solution

The photolysis apparatus was as before. The cuvette was filled with 0.2M NaOH in which photolysis of the sample was performed. Once again the reaction was followed by UV/Vis and IR spectroscopy. After incorporating the [Ru(bpy)$_2$(CO)$_2$][PF$_6$]$_2$ complex the sample was irradiated in the NaOH solution initially for 1min, and then for increasing lengths of time.

Initially, after 1mins photolysis the UV/Vis spectrum shows the growth of new absorption maxima at 490, 350 and 295nm and the absorption at 300nm has been shifted to almost 350nm. As photolysis time is increased (20mins) the bands at 490 and 295 continue to increase in intensity while the 256nm absorption is gradually lowered in intensity.

The IR spectrum, after 15mins irradiation, shows the disappearance of the carbonyl peaks at 2105 and 2054cm^{-1} and a new peak has grown in at 1960cm^{-1}. When the sample is irradiated for another 15mins the 1960cm^{-1} peak has been shifted to 1983cm^{-1}. From previous experiments[52] it is thought probable that this species is the deprotonated aquacarbonyl. Later experiments involving the hydride complex in Nafion give similar results for a deprotonated aquacarbonyl.
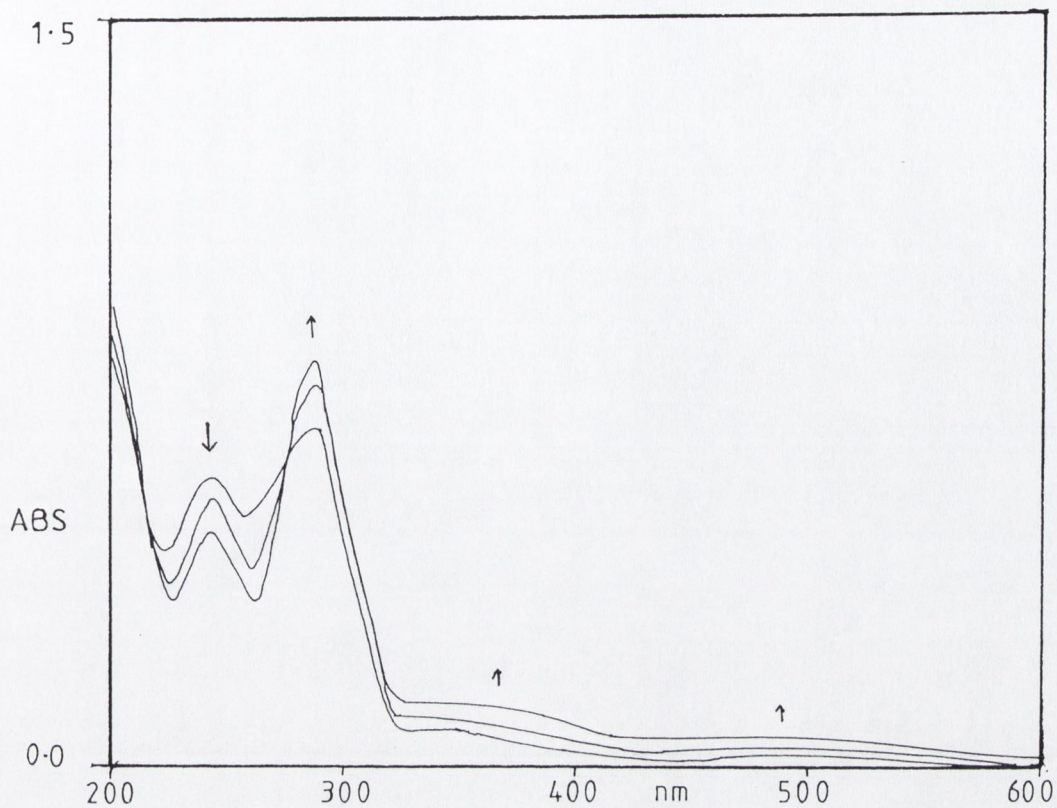
Fig.14 : UV/Vis spectrum of $[Ru(bpy)_2(CO)_2][PF_6]_2$ in Nafion following photolysis in 0.2M NaOH solution
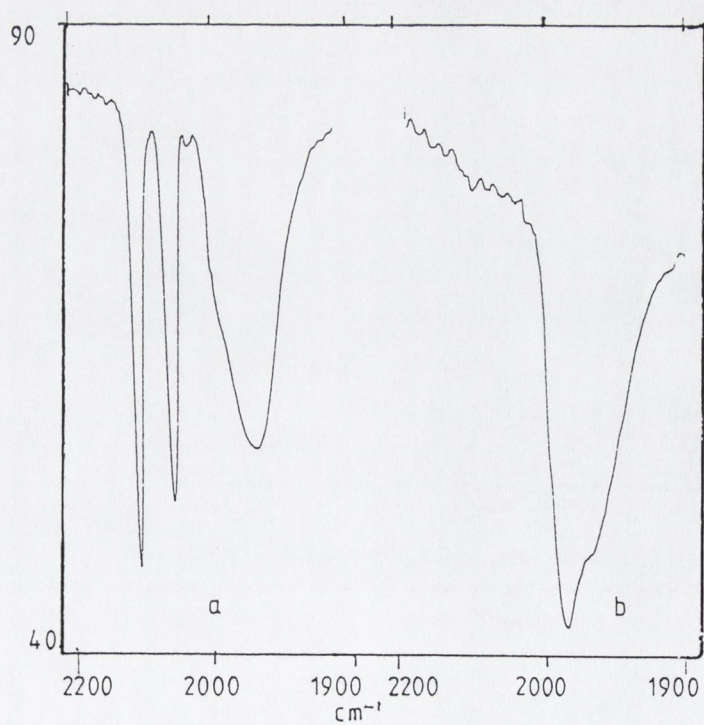
Fig.15 : IR spectra of $[Ru(bpy)_2(CO)_2][PF_6]_2$ in Nafion following photolysis in 0.2M NaOH solution for a. 0.5 mins and b. 30 mins

The overall reaction takes place as in equation 12.

$$[Ru(bpy)_2(CO)_2]^{2+} \xrightarrow{\text{NaOH/h}\nu} [Ru(bpy)_2(CO)(COOH)]^+$$

$$\text{NaOH} \Big| \text{h}\nu$$

$$[Ru(bpy)_2(CO)(OH)]^+ \qquad\qquad \text{eqn.12}$$
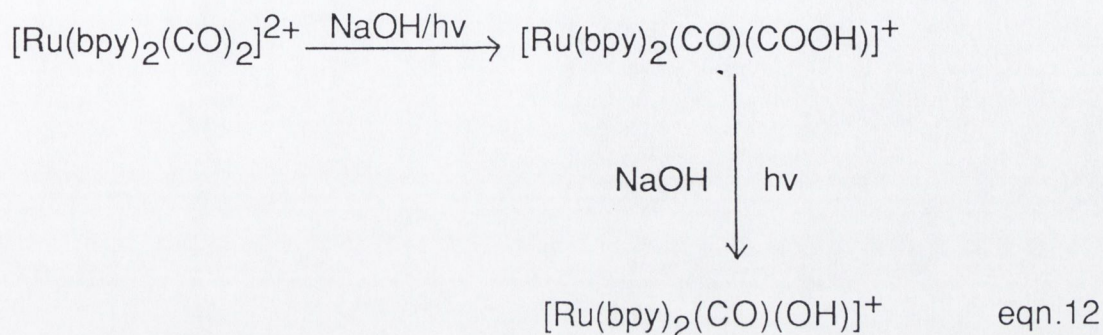
2.2.4 Conversion of $[Ru(bpy)_2(CO)(COO^-)]^+$ to $[Ru(bpy)_2(CO)_2]^{2+}$ upon treatment with water

A Nafion sample containing $[Ru(bpy)_2(CO)(COO^-)]^+$ was stirred in water for a total of 10 hours after which time IR and UV/Vis absorption spectra were recorded. ν_{CO} was found at 2105 and $2053cm^{-1}$ while the absorption spectrum showed maxima at 316(sh), 302 and 248nm. These results indicate the regeneration of the dicarbonyl complex and not the generation of the aquacarbonyl complex indicating that the $1960cm^{-1}$ product is indeed the deprotonated (hydroxycarbonyl) and not the hydride.

44
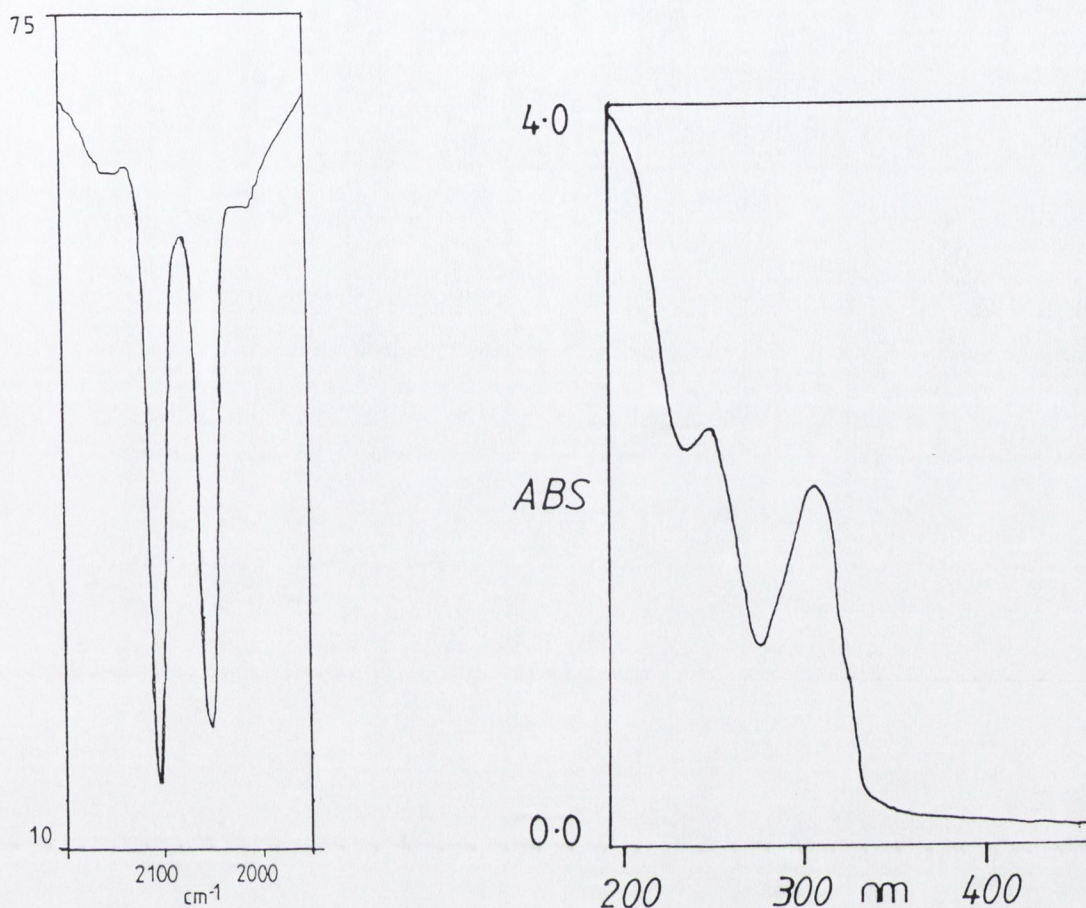
Fig. 16 : IR and UV/Vis spectra of $[Ru(bpy)_2(CO)_2]^{2+}$ following treatment of $[Ru(bpy)_2(CO)(COO^-)]^+$ in Nafion with water

2.2.5 Effects of buffer solutions on $[Ru(bpy)_2(CO)(COOH)]^+$

The carboxylate species was first prepared by treating a dicarbonyl sample with 0.2M NaOH solution for an hour. A sodium borate buffer solution pH 10.7 was prepared and the carboxylate sample stirred in it for 30, 60, 120 mins and finally overnight to

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obtain an equilibrated sample. IR spectra were run after each treatment. The spectrum for the equilibrated sample exhibited two peaks at 2104 and 2053cm^{-1} assignable to the dicarbonyl and also a stretch at 1971cm^{-1} which was assigned to the (hydroxycarbonyl). It appears that at pH 10.7 the two species are in equilibrium. The spectrum is identical to that obtained when the dicarbonyl is treated with the same buffer solution indicating that a reversible equilibrium exists.

Further experiments were carried out to determine more fully the effects of subsequently increasing and decreasing the pH of the buffer solution used with the dicarbonyl sample. The sample was first stirred in sodium borate buffer solutions of pH 10.09, 10.41, 10.71, 11.02, 11.40, 11.68 and 12.02 for 4 hours. The pH of the buffer was then decreased and finally the sample was stirred in pure water. IR spectra were run after each treatment.

At pH'^{S} 10.09, 10.41 and 10.71 the intensity of the peak growing at 1970cm^{-1} is very weak and only increases very slightly as the pH is increased. The dicarbonyl stretches decrease slightly. However, when the pH is raised to 11.02 there is considerable alteration in the intensities of the stretches and at pH 11.40 the three stretches at 1970, 2105 and 2054cm^{-1} are of equal intensity. It appears that the dicarbonyl and the (hydroxycarbonyl) are in equilibrium.

46
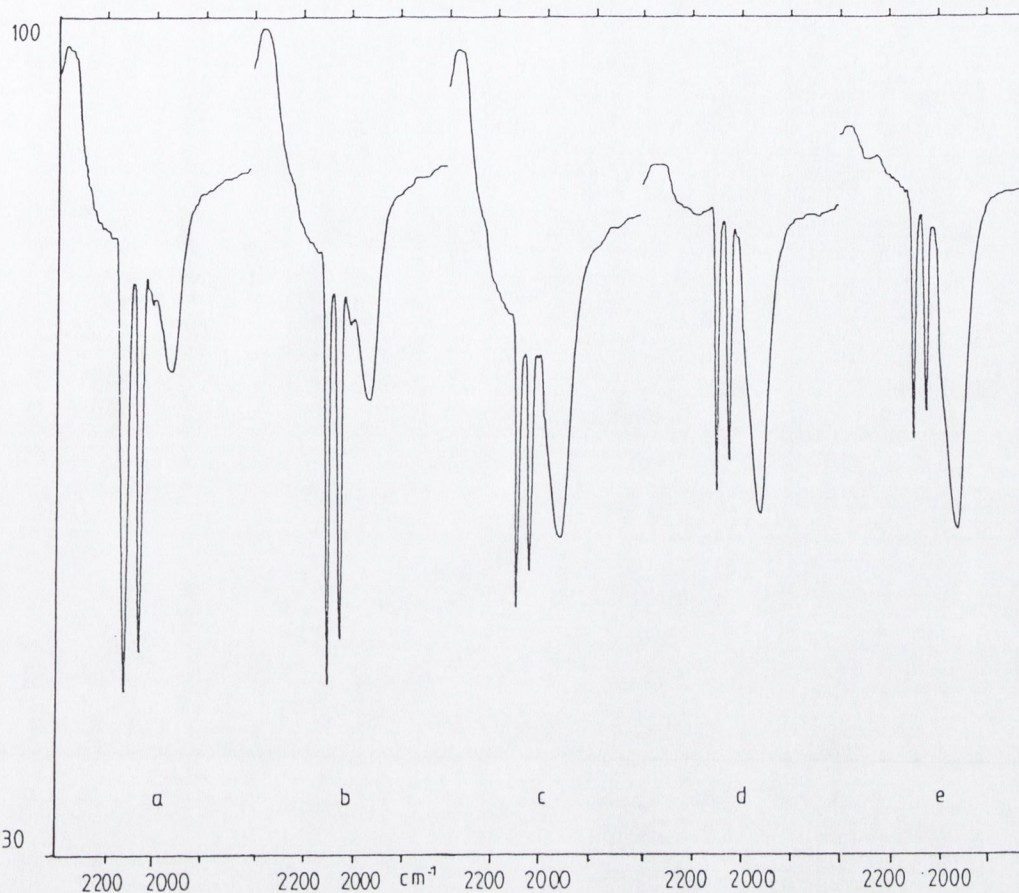
Fig. 17.1 : Treatment of $[Ru(bpy)_2(CO)(COOH)]^+$ consecutively with buffer solution at pH. a. 10.41, b. 10.71, c. 11.02, d. 11.40, e. 11.72

As the pH of the buffer solution is increased the dicarbonyl stretches become significantly reduced in intensity and at pH 12.02 conversion is almost complete with only very weak dicarbonyl stretches visible in the IR region. It was interesting to observe that when the sample is treated in buffer pH 10.7 instead of recovering the species formed previously the IR spectrum now exhibits three stretches of equal intensity; the two dicarbonyl peaks are present at 2104 and 2053cm^{-1} while the (hydroxycarbonyl) species is at 1969cm^{-1}. The sample was subsequently stirred in pure water overnight to give three stretches at 2104, 2053 and 2012cm^{-1}. The stretch at 2012cm^{-1}

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is indicative of the aquacarbonyl species. The UV/Vis absorption maxima occur at 380 and 475nm, also in agreement with data for the aquacarbonyl complex.
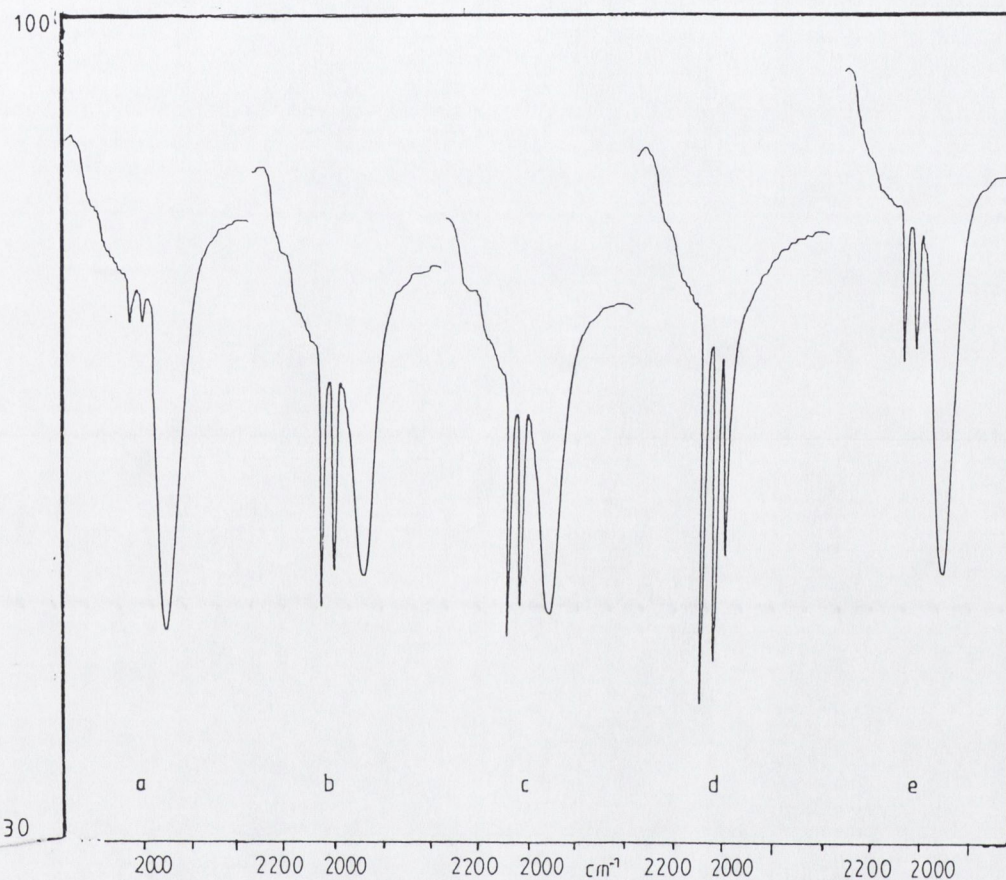
Fig.17.2: Treatment of [Ru(bpy)$_2$(CO)(COOH)]$^+$ consecutively with Buffer solution pH : a. 12.02, b. 10.70, c. 10.72, d. treated in pure water overnight, e. pH 10.70

It is possible that at pH 10.70 there is some hydroxycarbonyl present, the broad stretch at 1970cm^{-1} could be obscuring it. Therefore, by treating the formed aquacarbonyl(d) in pH 10.70 the hydroxycarbonyl stretch, if present, may not be obscured. However, upon treatment of the aquacarbonyl sample with buffer solution pH 10.70 three stretches are present at 2105, 2054 and 1969cm^{-1}. There is still no evidence for the hydroxycarbonyl. Further treatment in water regenerates the aquacarbonyl.

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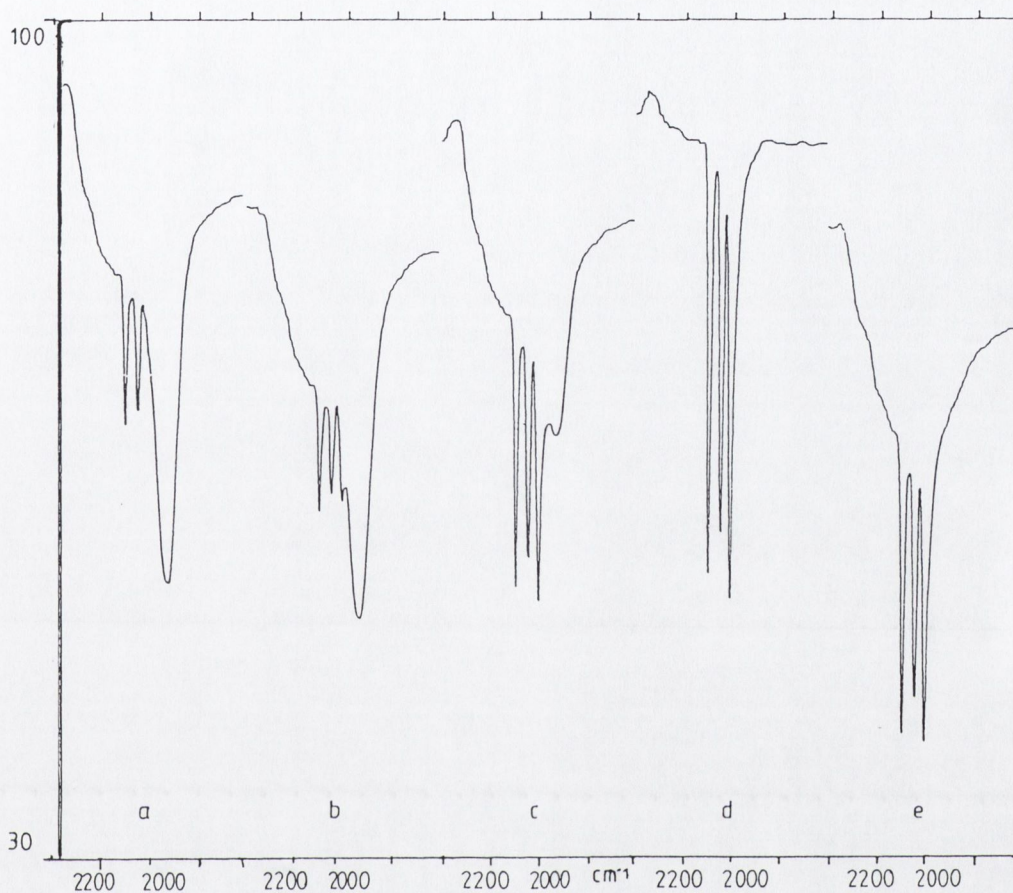
Fig.17.3 : Treatment of $[Ru(bpy)_2(CO)(COOH)]^+$ consecutively in Buffer solution. a & b. pH 10.70, c, d & e. pure water

It is obvious from the spectra recorded that the medium surrounding the complex is affecting the rate of reaction of the buffer solutions on the species formed - different spectra have been recorded when using the same buffer solution. This is due to the time taken for the ions to diffuse through the membrane and will be discussed later (Sec. 2.8.3).

2.2.6 Attempted conversion of $[Ru(bpy)_2(CO)(COOH)]^+$ to $[Ru(bpy)_2(CO)H]^+$

In order to obtain the hydrido carbonyl complex the (hydroxycarbonyl) had first to be prepared. This was achieved by first incorporating the dicarbonyl into Nafion and treating with sodium borate buffer pH 11.91 for 12 hours. The IR spectrum recorded shows three stretches at 2105, 2052 and 1957cm^{-1}. In order to attempt to convert the (hydroxycarbonyl) to the hydride the sample was then placed on the vac line and heated at 100°C for 12 hours. An IR spectrum was then run and exhibited three stretches at 2105, 2053 and 1962 cm^{-1}. The stretch at 1962cm^{-1} is indicative of the hydride. The UV/Vis spectrum gives two absorption maxima at 350 and 450nm. These values are in agreement with those recorded when the prepared hydride is incorporated into Nafion (Table 2). The hydride is known to convert to the aquacarbonyl when treated with acidic or aqueous solutions. Therefore the sample was stirred in pure water overnight giving IR stretches at 2104, 2053 and 2012cm^{-1} and UV/Vis absorption maxima at 380 and 475nm, these data are indicative of the aquacarbonyl. It should be noted, however, that there is also a substantial increase in the dicarbonyl absorption indicating a significant reverse to this compound.

50
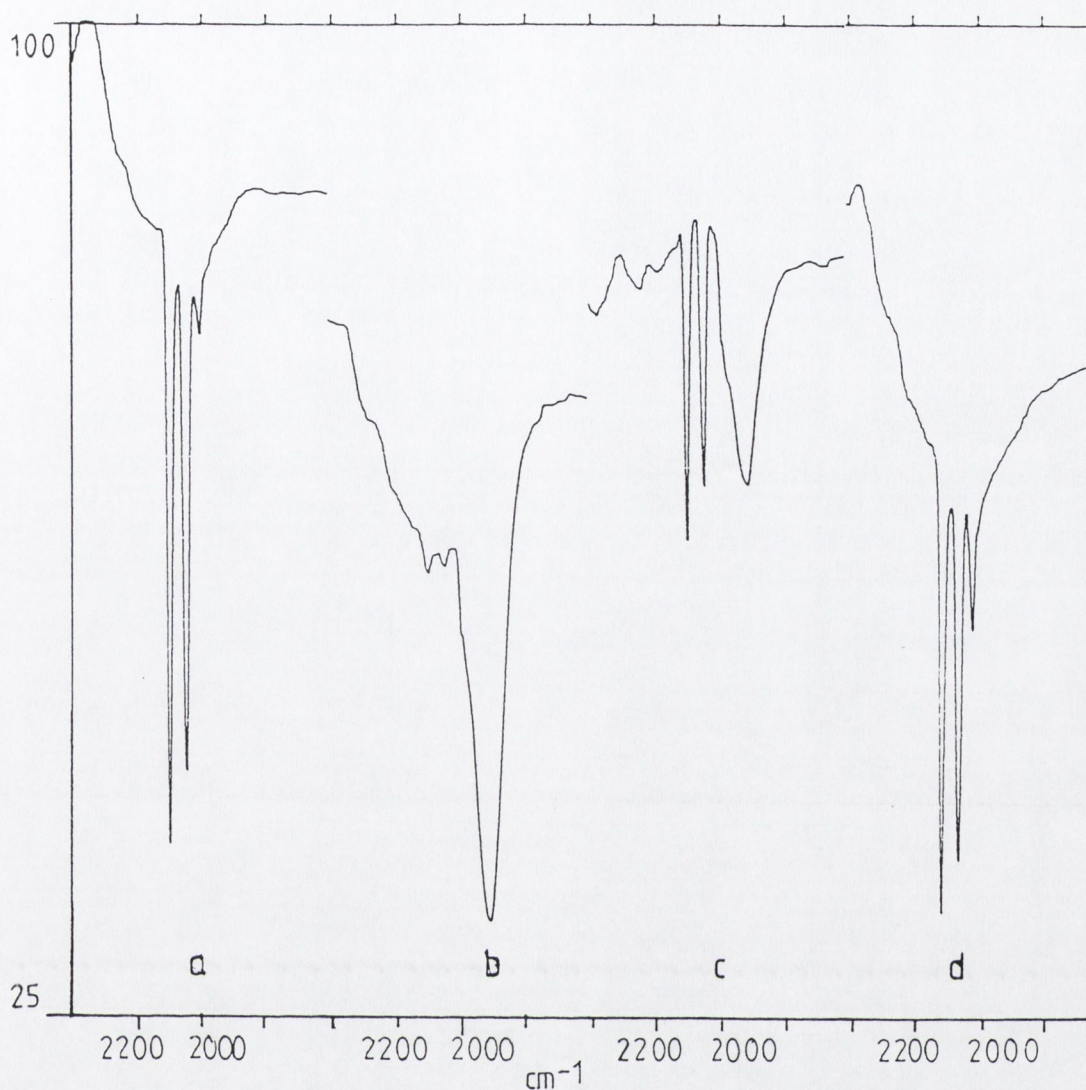
Fig.18 : IR spectra of $[Ru(bpy)_2(CO)(COOH)]^+$ undergoing conversion to $[Ru(bpy)_2(CO)(H_2O)]^{2+}$. a. dicarbonyl, b. buffer pH 11.91, c. vacuum heated, d. pure water

2.2.7 Photolysis of $[Ru(bpy)_2(CO)(COOH)]^+$ in Nafion

The samples were prepared by treating the dicarbonyl sample in sodium borate buffer solution pH 11.7 for 3-4 hours giving an IR stretch at $1953cm^{-1}$. Photolysis was carried out as usual but a glass filter (cutting off irradiation below ~300nm) was placed in front of the sample to prevent irradiation of any dicarbonyl present. The influence of the following was examined.

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a. Buffer solution : The sample was photolysed in sodium borate buffer solution pH 11.7 . After 1 min there is only a slight change recorded in the IR spectrum with the $1953cm^{-1}$ stretch shifting to $1956cm^{-1}$. As photolysis is continued for periods of 5, 10 and 30mins the stretch is recorded at 1957, 1957 and $1959cm^{-1}$ respectively. However, after a further five hours treatment the stretch has shifted to $1965cm^{-1}$. As well as the shifting of the (hydroxycarbonyl) stretch the dicarbonyl stretches are decreased in intensity, even though the glass filter should cut off irradiation below 350nm (below which the dicarbonyl absorbs light in the UV). Following treatment in pure water for several hours the aquacarbonyl is generated $(2012cm^{-1})$ in equilibrium with the dicarbonyl (2015, $2054cm^{-1}$).
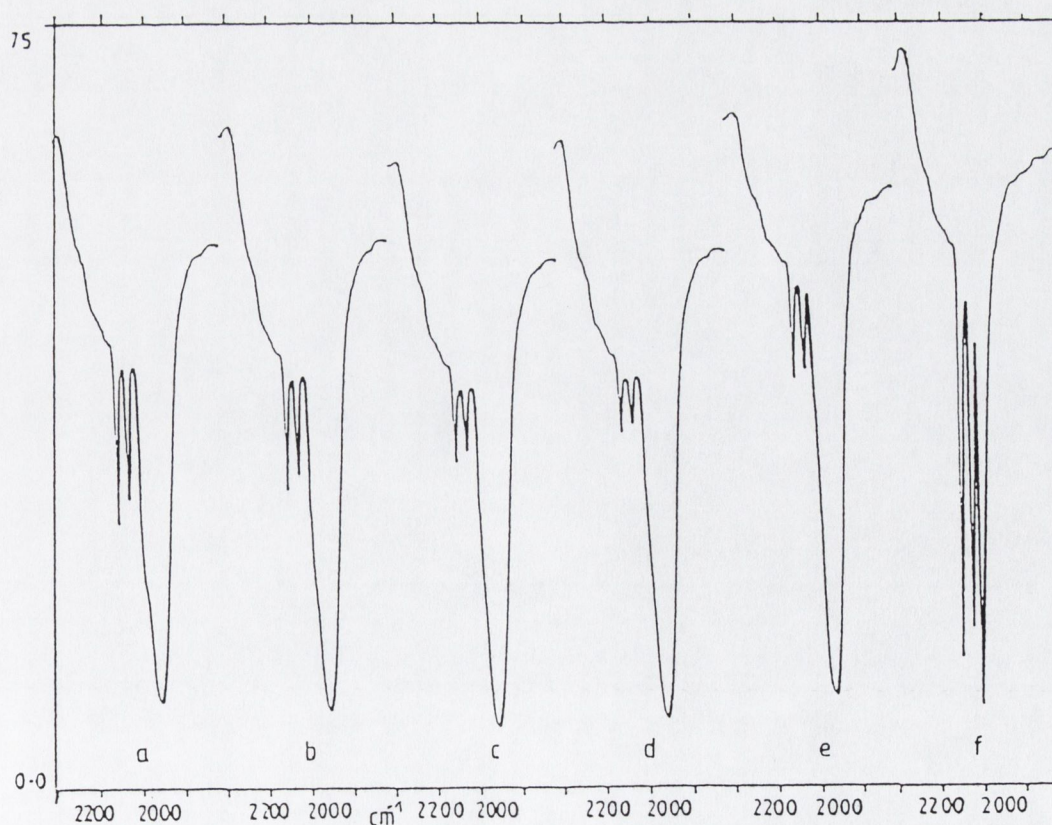
Fig. 19: Photolysis of $[Ru(bpy)_2(CO)(COOH)]^+$ in buffer solution pH 11.70 for a. 1, b. 5, c. 10, d. 30 mins, e. 5 hours. f. treated in pure water for 3 hours

b. Dry conditions : The prepared sample was dried on the vac line for approx. 10 hours leading to stretches in the IR region at 2105, 2054 and 1953cm^{-1}. Following photolysis for 5 mins two stretches were observed at 1993 and 1947cm^{-1} - the 1993cm^{-1} stretch is possibly due to [Ru(bpy)$_2$(CO)OH]$^+$ produced in the reaction, the 1947cm^{-1} stretch has not been assigned. As photolysis is continued after two hours the 1947 and 1993cm^{-1} stretches are no longer seen but a stretch at 1965cm^{-1} with a shoulder at 1990cm^{-1} is present. At this stage of the process there is no significant change in the intensities of the dicarbonyl stretches. However, after a further two hours photolysis there is a very noticeable decrease in the intensity of the dicarbonyl stretches and an increase in the stretch at 1965cm^{-1}. This is probably best explained by considering the nature of the reaction. Initially the decarbonylation reaction is slow, possibly due to reaction of some OH$^-$ present in the membrane giving [Ru(bpy)$_2$(CO)OH]$^+$ which explains the stretch at 1993cm^{-1}. As photolysis is continued the hydride is formed with a stretch at 1965cm^{-1}. Only when this complex is formed can photolysis cause the decarbonylation reaction to occur. Finally, treatment in water causes formation of the aquacarbonyl.
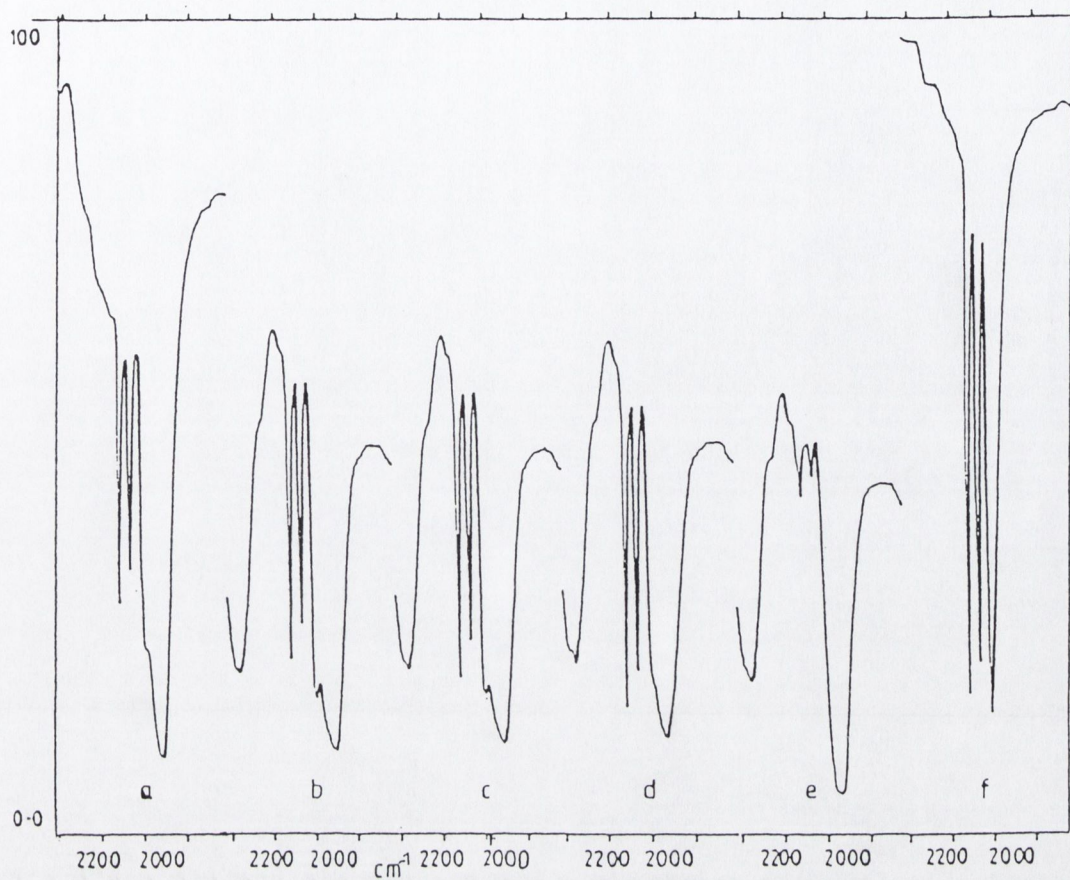
Fig. 20 : Photolysis of [Ru(bpy)$_2$(CO)(COOH)]$^+$ under dry conditions for a. 1, b. 5, c. 20 mins, d. 2, e. 4 hours. f. treated in pure water for 3 hours.

2.3 $[Ru(bpy)_2(CO)H][PF_6]$

Cis-$[Ru(bpy)_2(CO)Cl]^+$ and $NaBH_4$ were allowed to react in aqueous ethanol to give cis-$[Ru(bpy)_2(CO)H]^+$, the complex being isolated as the hexafluorophosphate derivative[31]. The carbonyl stretch (KBr disc) occurs at $1930cm^{-1}$ which is at a considerably lower wavenumber than that for the other carbonyl complexes prepared - this is due to the electron donating ability of the hydride ion. The UV/Vis (CH_3CN) spectrum shows absorption maxima at 452, 348 and 273nm. The hydride complex is known to be stable to organic and weak aqueous alkaline solutions but to be unstable to acid, decomposing to give the aquacarbonyl complex.[31]

$$[Ru(bpy)_2(CO)H]^+ + H_3O^+ \longrightarrow [Ru(bpy)_2(CO)(H_2O)]^{2+} + H_2$$

eqn.13
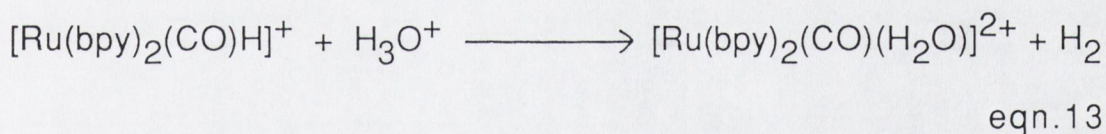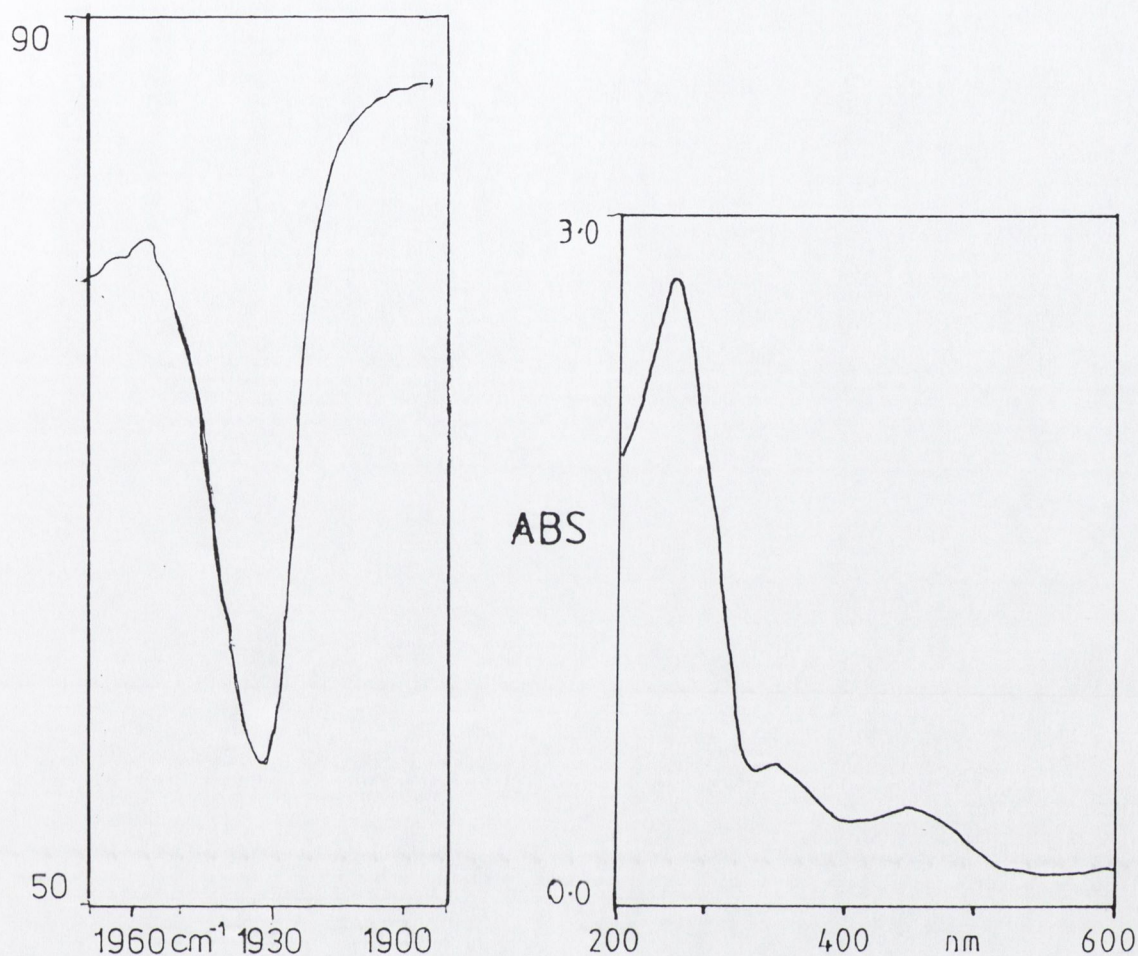
Fig.21 : IR(KBr) and UV/Vis(CH_3CN) of $[Ru(bpy)_2(CO)H][PF_6]$

All samples were prepared by first incorporating the hydride into the Nafion membrane. As with the dicarbonyl complex the hydride is insoluble in water, it also decomposes rapidly in weakly acidic solution to give H_2 and the aquacarbonyl. As a result a mixture of solvents was required : the system used was acetonitrile/ 0.2M sodium hydroxide solution/ water (equal volumes). The acetonitrile dissolves the hydride while the water removes any traces of the acetonitrile from the membrane, thus preventing any undesired reactions taking place. The NaOH solution was used to keep the solution and membrane basic and thus prevent conversion to the aquacarbonyl.

The hydride was incorporated by stirring a Nafion strip in the solution to give the required concentration of sample. A low concentration sample was prepared in order to be able to record a UV/Vis spectrum. As a result the IR bands are necessarily weak in intensity. The UV/Vis spectra recorded show absorption maxima at 270, 350 and 450nm. As with the dicarbonyl, upon incorporation into Nafion of the hydride there is little change in the recorded UV/Vis spectrum.

The IR spectrum shows a significant shift for the carbonyl stretch of ca.30cm^{-1} to give a peak at 1960cm^{-1}. The incorporated samples show only a weak absorption in the IR spectrum and bands are quite broad.
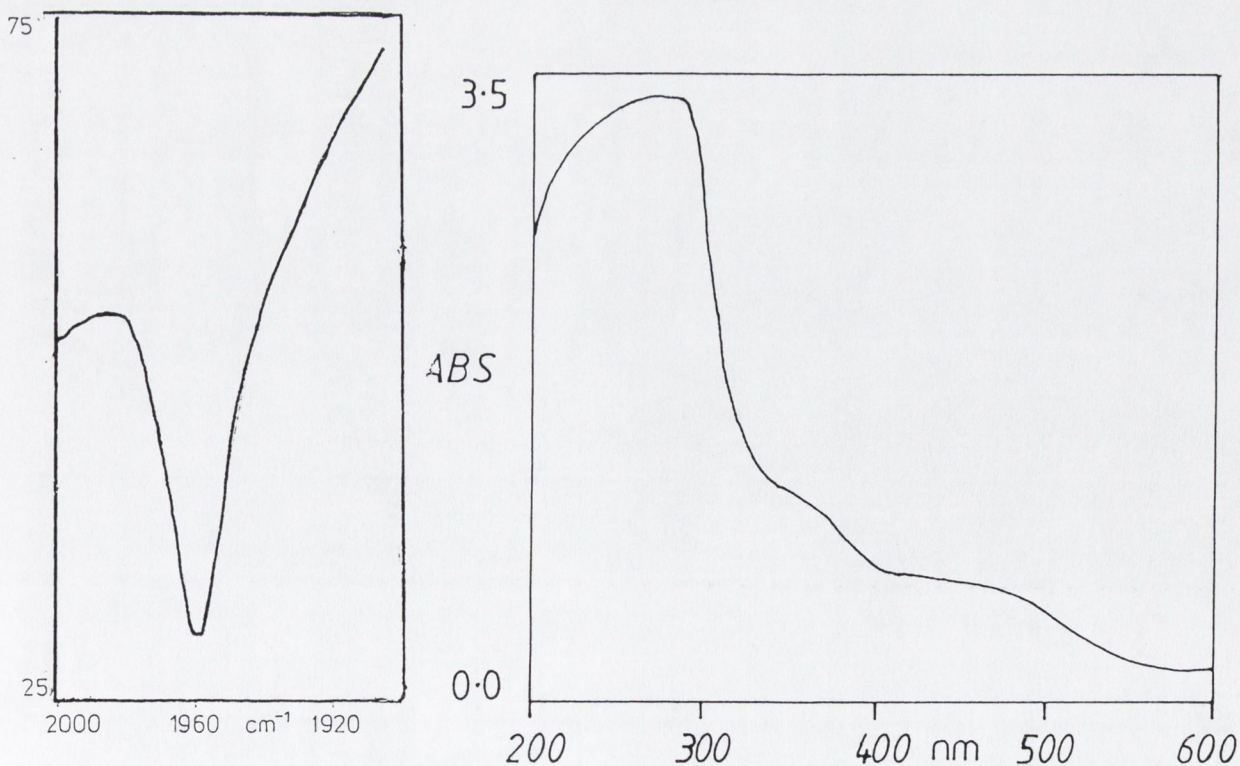
Fig.22 : IR and UV/Vis spectra of [Ru(bpy)$_2$(CO)H][PF$_6$] in Nafion

2.3.1   Heat treatment of $[Ru(bpy)_2(CO)H]^+$ in Nafion

The effects of heat were examined by stirring a hydride incorporated Nafion in either boiling aqueous NaOH solution or in a heated, dry, sealed flask.

a. NaOH Solution : The hydride was first incorporated into Nafion by the method previously described to give UV/Vis absorption maxima at 272, 350 and 452nm and an IR stretch at $1960cm^{-1}$. The sample was then stirred in boiling 0.2M NaOH for 20mins and spectra recorded. The UV/Vis spectrum shows no change in the position of the absorption maxima but there is a slight decrease in the intensity of the band. This trend continues as the sample is treated for increasing periods of time. The IR spectrum recorded after 20mins shows a carbonyl stretch at $1962cm^{-1}$: as the treatment is continued there is no change in the position of the carbonyl peak.

Dry Thermolysis : As above, the hydride was incorporated into the Nafion, the sample was then placed in a stoppered round bottomed flask and immersed in an oil bath at $120^{o}C$ for 20mins. After being removed from the flask IR and UV/Vis spectra were recorded. The UV/Vis absorption maxima are at 270, 350 and 450nm while the IR carbonyl stretch occurs at $1960cm^{-1}$. Both spectra appear to be unaltered to any appreciable extent. The sample was reheated as before for a further 30mins but no change was recorded in the spectra.

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2.3.2 Photolysis of [Ru(bpy)$_2$(CO)H]$^+$ incorporated in Nafion

The hydride was incorporated into the Nafion by the method described previously. Photolysis was carried out using a Hg lamp, a quartz lens and water bath, and a quartz cuvette containing the sample. Samples were selectively photolysed in either NaOH solution or under atmospheric conditions. Photolysis reactions were monitored by IR and UV/Vis spectroscopy.

a. Photolysis in NaOH solution : After incorporation of the hydride into Nafion the carbonyl stretch occurs at 1963cm^{-1} in the IR spectrum while the UV/Vis spectrum exhibits absorption maxima at 272, 350 and 450nm. Upon photolysis of the sample in 0.2M NaOH for 30secs the UV/Vis spectrum begins to show an increase in the absorption intensity at 270nm but this absorption maxima has at the same time been shifted to 278nm. The 354 and 450nm absorptions have also grown considerably with the 450nm absorption growing more rapidly.

The sample was further photolysed for periods of 1, 3 and 5mins. The UV/Vis spectra continue to exhibit a pattern of increasing absorption with the 272nm band being shifted eventually to 286nm and the 350 and 450nm absorptions being shifted to 356 and 480nm respectively. The corresponding IR spectra exhibit carbonyl stretches at 1963cm^{-1} which decrease in intensity with each successive photolysis period until after 20mins irradiation there is no evidence for the carbonyl stretch; indicating that the decarbonylation reaction is complete - it is

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probable that the cis-diaqua complex has been formed as indicated by the UV/Vis absorption at 480nm, in agreement with the literature[52].
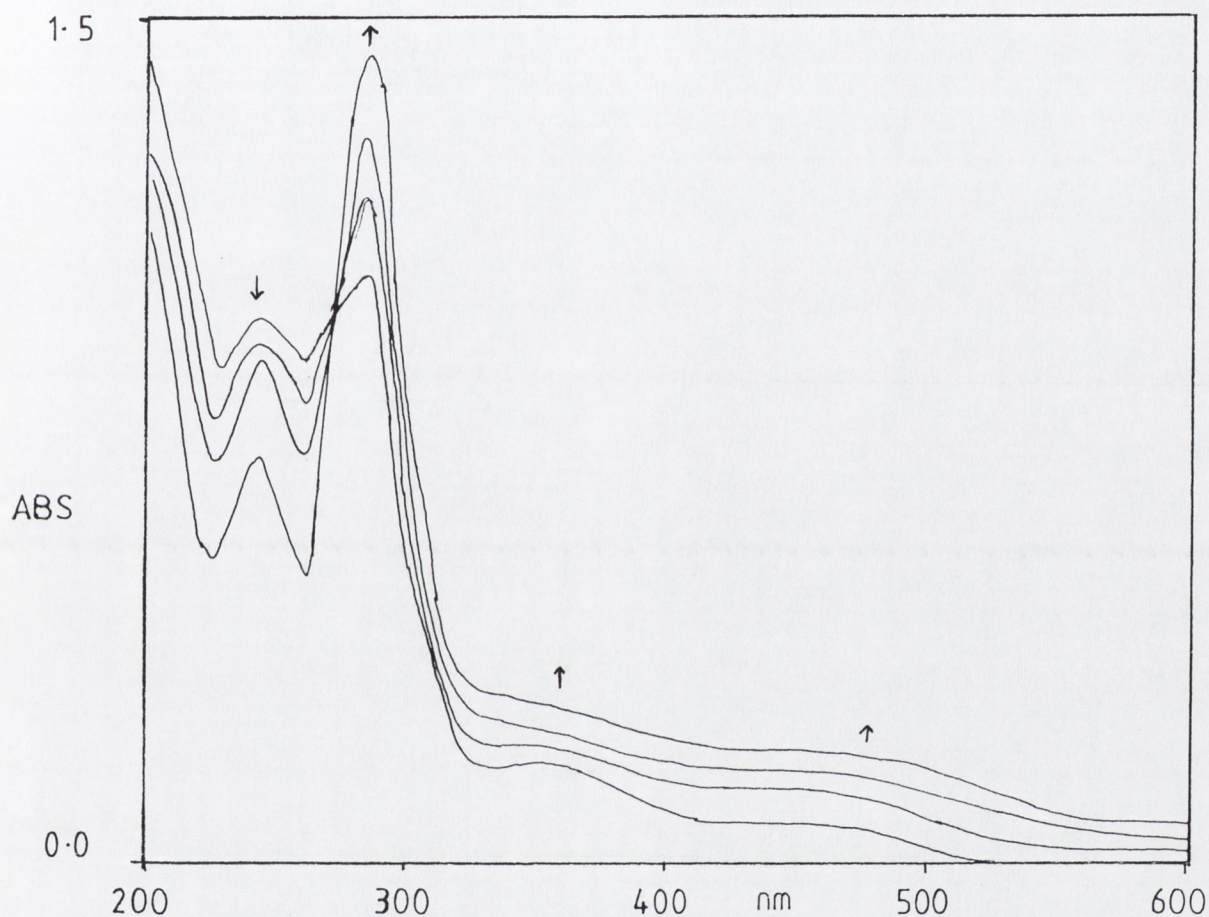
Fig.23 : UV/Vis spectra of [Ru(bpy)$_2$(CO)H][PF$_6$] in Nafion after photolysis in 0.2M NaOH solution

b. Atmospheric photolysis: The hydride was incorporated into Nafion in the usual manner with the result that the membrane contains water. The sample was placed in a dry quartz cell exposed to the atmosphere and irradiated for 0.5, 1, 3, 5 and 10mins. After 0.5mins irradiation there were noticeable changes

in the UV/Vis spectrum with a marked increase in intensity of the absorptions at 272 and 452nm, a decrease in intensity of the 248nm absorption whereas the 348nm absorption remains unaltered. The single change occurring in the IR spectrum is the decrease in intensity of the carbonyl stretch which is still found at 1963cm^{-1}. Following 20mins photolysis the UV/Vis absorption maxima are to be found at 248, 282, 348 and 454nm with a continuous growth in intensity observed for all but the 248nm absorption maximum. The IR spectra shows the gradual decrease in intensity of the 1963cm^{-1} carbonyl stretch until after 20mins it has completely disappeared.
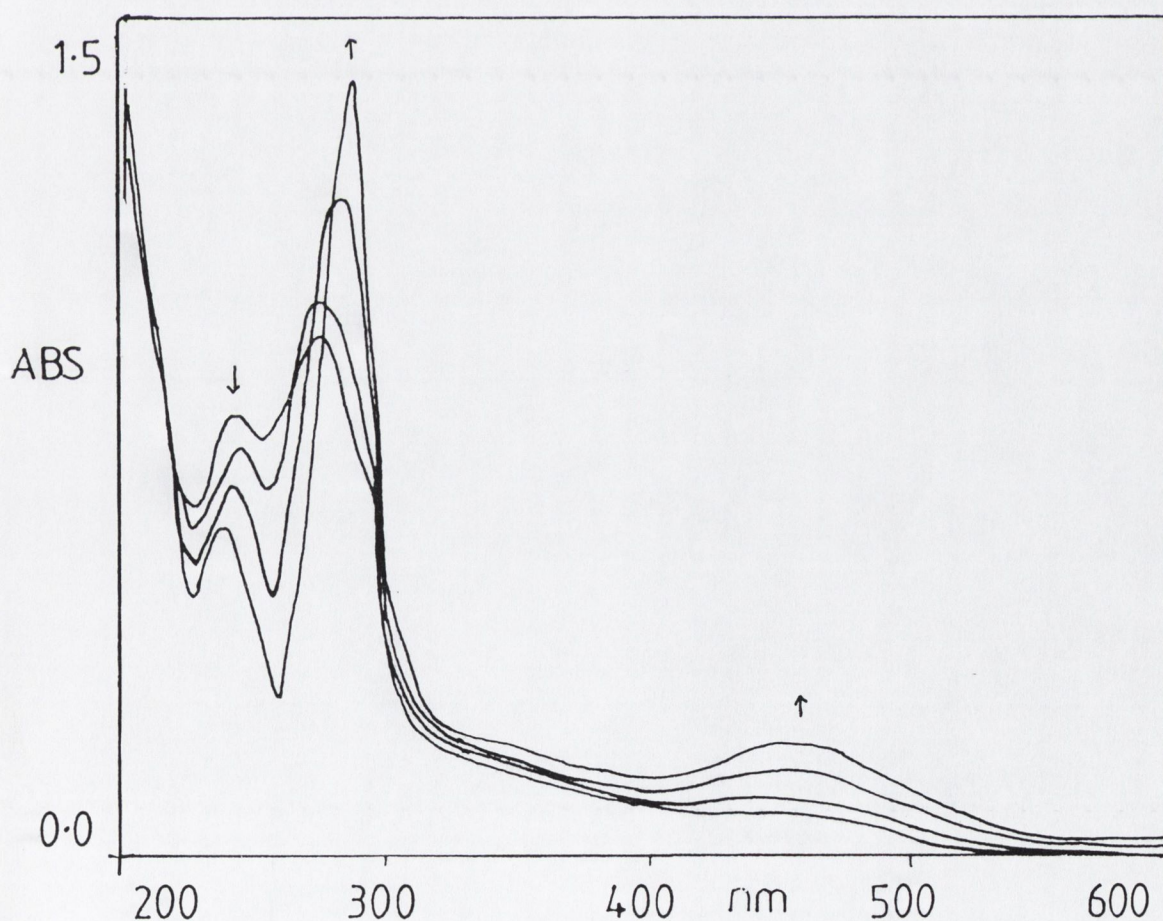
Fig.24 : UV/Vis spectra of [Ru(bpy)$_2$(CO)H][PF$_6$] in Nafion after photolysis under atmospheric conditions

2.3.3   Treatment of $[Ru(bpy)_2(CO)H]^+$ in Nafion with H_2O

Following incorporation of the hydride into Nafion the sample was stirred in pure water for selected periods of time. After one hours treatment the UV/Vis spectrum shows absorption maxima at 275, 352 and 452nm which is very similar to that observed for the hydride incorporated in Nafion. In the IR spectrum, there is a slight shift of the carbonyl peak from 1960 to $1965cm^{-1}$.

After a further 30mins treatment in H_2O the UV/Vis spectrum showed absorption maxima at 260, 356 and 468nm. The IR spectrum is considerably altered with the $1965cm^{-1}$ peak being shifted to higher wavenumber at $2012cm^{-1}$. Upon further treatment in water (1hr) there is no change observed in either the IR or UV/Vis spectra indicating that a stable species has been formed; this species is assumed to be the aquacarbonyl complex.

Fig.25 : IR spectra of $[Ru(bpy)_2(CO)H][PF_6]$ in Nafion after treatment in H_2O for

a. 30 mins and b. 90 mins

2.4 [Ru(bpy)$_2$(CO)Cl][PF$_6$]

[Ru(bpy)$_2$(CO)Cl]$^+$ was reported[37] to be a catalyst for the photochemical water gas shift reaction. The complex was isolated as a secondary reaction product in the known preparation[29,30] of [Ru(bpy)$_2$Cl$_2$.2H$_2$O] which involves reaction of[RuCl$_3$.3H$_2$O] with bpy in refluxing DMF. The chlorocarbonyl is a well characterised compound and may be used as the precursor for a large family of bis(bpy)Ru(II) complexes by both thermal and photochemical routes. Following preparation of the chlorocarbonyl complex spectra were recorded. The UV/Vis (CH$_3$CN) spectra shows absorption maxima at 262, 282, 313, 352 and 415nm. The IR spectrum shows a carbonyl stretch at 1966cm^{-1}.
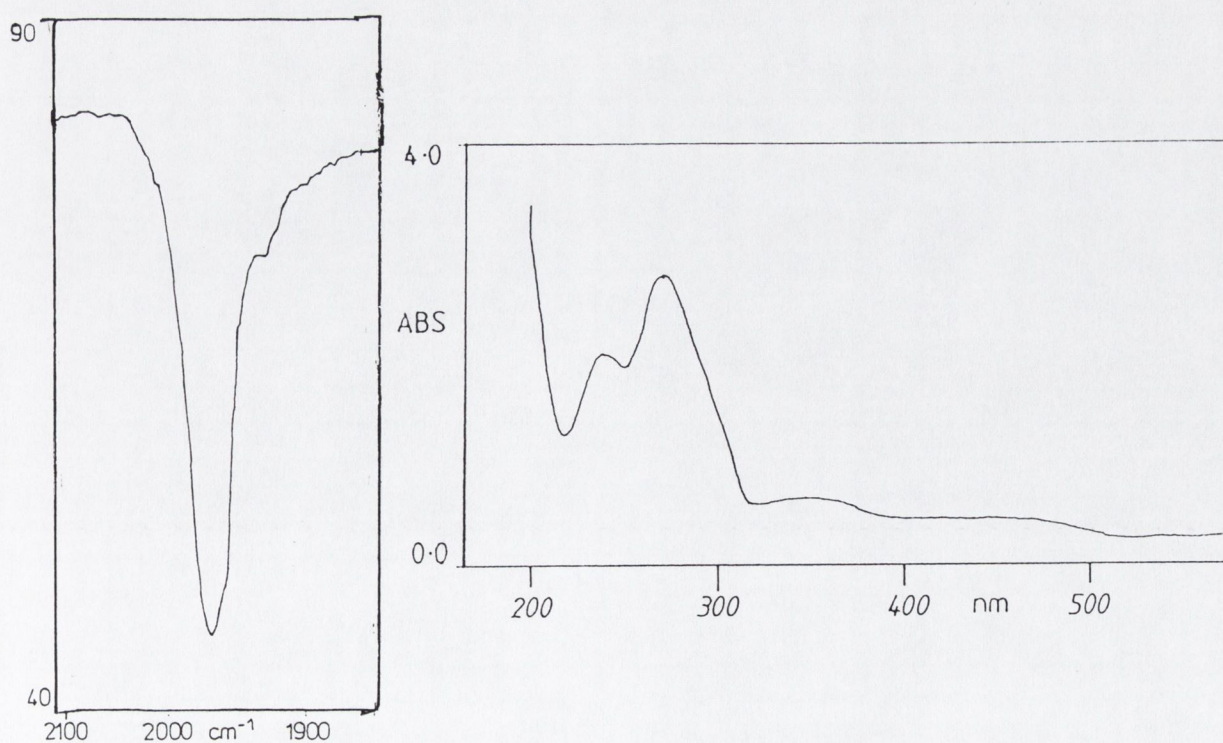
Fig.26 : IR(KBr) and UV/Vis(CH$_3$CN) spectra of [Ru(bpy)$_2$(CO)Cl][PF$_6$]

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It was found that $[Ru(bpy)_2(CO)Cl][ClO_4]$ is readily soluble in acetonitrile but not in water. Therefore, in order to incorporate the complex it was initially dissolved in acetonitrile which was subsequently evaporated off. Pure water was added to give a desired concentration and the Nafion strip was then stirred in this mixture. The IR spectrum shows the carbonyl stretch to have shifted from $1966cm^{-1}$ in the free compound to $2005cm^{-1}$ in the incorporated sample and similarly the UV/Vis spectrum shows a shift from having absorption maxima at 262, 282, 313, 352 and 415nm to having absorptions at 264, 353(sh) and 415(sh)nm.
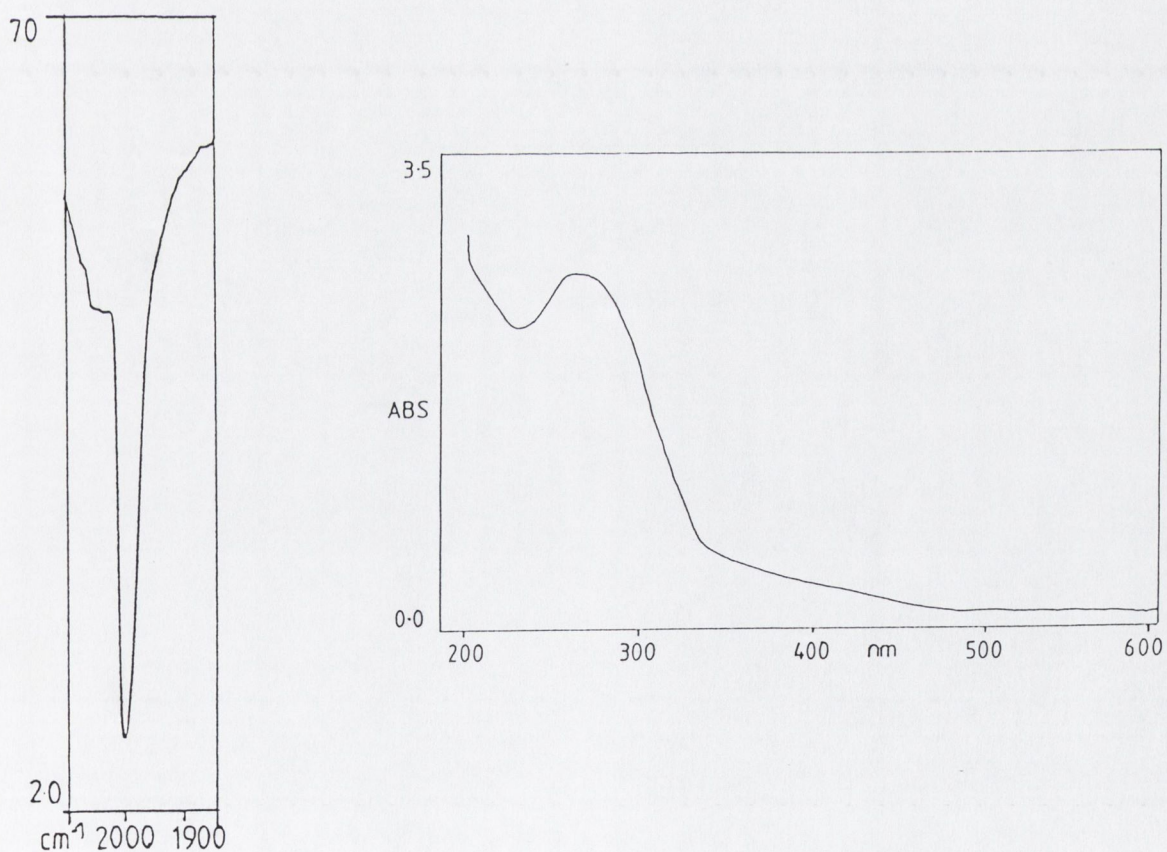
Fig.27 : IR and UV/Vis spectra of $[Ru(bpy)_2(CO)Cl][PF_6]$ incorporated in Nafion

2.4.1   Treatment of [Ru(bpy)$_2$(CO)Cl][PF$_6$] in Nafion with H$_2$O

Following incorporation of the complex into Nafion the membrane was stirred in pure water at 25°C for 20mins after which time the UV/Vis and IR spectra were recorded. The IR spectrum still exhibited a peak at 2005cm^{-1} and the UV/Vis absorption maxima occurred at 264nm. No change in either spectra was observed. The membrane was stirred in pure water for a further hour but again no change was recorded in either the UV/Vis or IR spectra. However [Ru(bpy)$_2$(CO)Cl]$^+$ undergoes a thermal solvolysis in water to give [Ru(bpy)$_2$(CO)(H$_2$O)]$^{2+}$ according to the equation

$$[Ru(bpy)_2(CO)Cl]^+ + H_2O \longrightarrow [Ru(bpy)_2(CO)(H_2O)]^{2+} + Cl^-$$
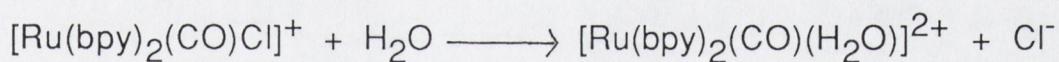
The IR spectrum shows ν_{CO} at 2010cm^{-1} and UV/Vis absorption maxima occur at 475, 350 and 260nm. These values are in close agreement with those for the aquacarbonyl formed from the hydride complex. When a Nafion strip containing [Ru(bpy)$_2$(CO)Cl]$^+$ was immersed in water and photolysed, photolabilisation of CO initially yielded [Ru(bpy)(H$_2$O)Cl]$^+$. The absorption maxima occur at 345 and 505nm. On prolonged photolysis [Ru(bpy)$_2$(H$_2$O)$_2$]$^{2+}$ is formed with absorption maxima at 342 and 486nm. It is probable that the labilised chloride ions

are ejected from the hydrated clusters of the Nafion due to the negative potential in the inter cluster channels (Donnan Effect)[45].
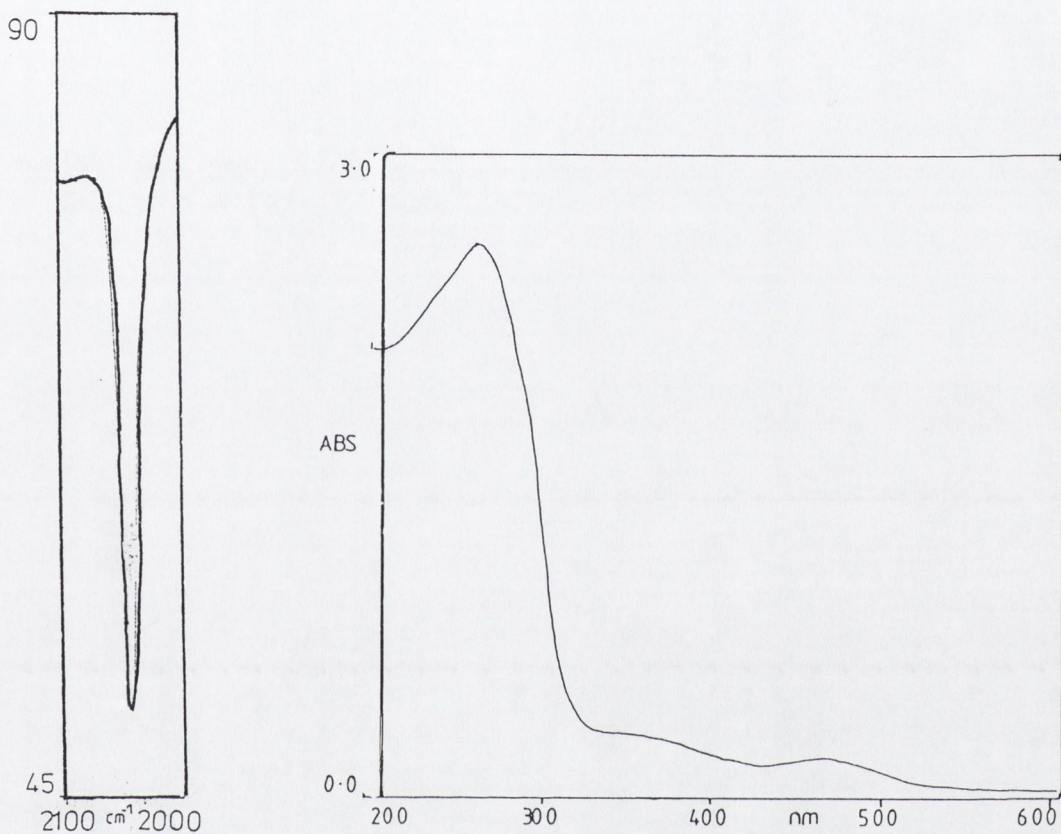
Fig.28 : IR and UV/Vis spectra of $[Ru(bpy)_2(CO)(H_2O)]^{2+}$ in Nafion

2.5 $[Ru(bpy)_2(CO)(H_2O)]^{2+}$

The aquacarbonyl in Nafion was prepared by treating the hydride in Nafion in water overnight. Conversion of the aquacarbonyl to the dicarbonyl was then attempted by irradiation of the sample under varying conditions. The aquacarbonyl was first photolysed under ambient conditions in a quartz cell with a 0.75cm glass plate filter to prevent irradiation of the dicarbonyl as it was

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formed. Photolysis produces the growth of a new absorption maximum at 480nm while a simultaneous increase in intensity at 340 and 390nm also occurs. However, after 4 hrs irradiation the shoulder at 395nm has completely disappeared. The spectra indicate the formation of the diaqua complex. This is further shown to be the case by the gradual decrease in intensity of the stretches at 2104 and $2053cm^{-1}$ in the IR region. However, in order to convert the aquacarbonyl to the dicarbonyl the CO groups must not be labilised. The irradiation was therefore carried out under an atmosphere of CO but the results were as before.

The aquacarbonyl was also treated in alkaline solutions of concentrations ranging from 0.01M to 0.2M NaOH. By monitoring the carbonyl region of the IR the position of equilibrium can be determined. In weakly basic solutions equilibrium lies on the side of the aquacarbonyl but for samples treated in bases of 0.05M or greater the equilibrium favours the hydroxycarbonyl.

2.5.1 Conversion of $[Ru(bpy)_2(CO)(H_2O)]^{2+}$ to $[Ru(bpy)_2(CO)_2]^{2+}$

The aquacarbonyl species was obtained by treating the hydride in Nafion in water overnight to obtain complete conversion. The sample was then placed in a Bomb calorimeter at 30atm CO and heated at $120^{o}C$ for 12 hours. Initially experiments were carried out where the bomb also contained a sodium borate buffer

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solution of pH 12.4 or 9.01. After removal of the sample from the bomb the IR spectra exhibit four stretches in the carbonyl region at 2104, 2084, 2054 and 2039cm^{-1}. These were assigned to the free dicarbonyl and the incorporated dicarbonyl. It appears that the reaction in the bomb is causing some of the formed dicarbonyl complex to be released from the Nafion medium. The free dicarbonyl complex is soluble in acetone and was removed from the sample by washing in acetone leaving only a pure incorporated dicarbonyl sample.
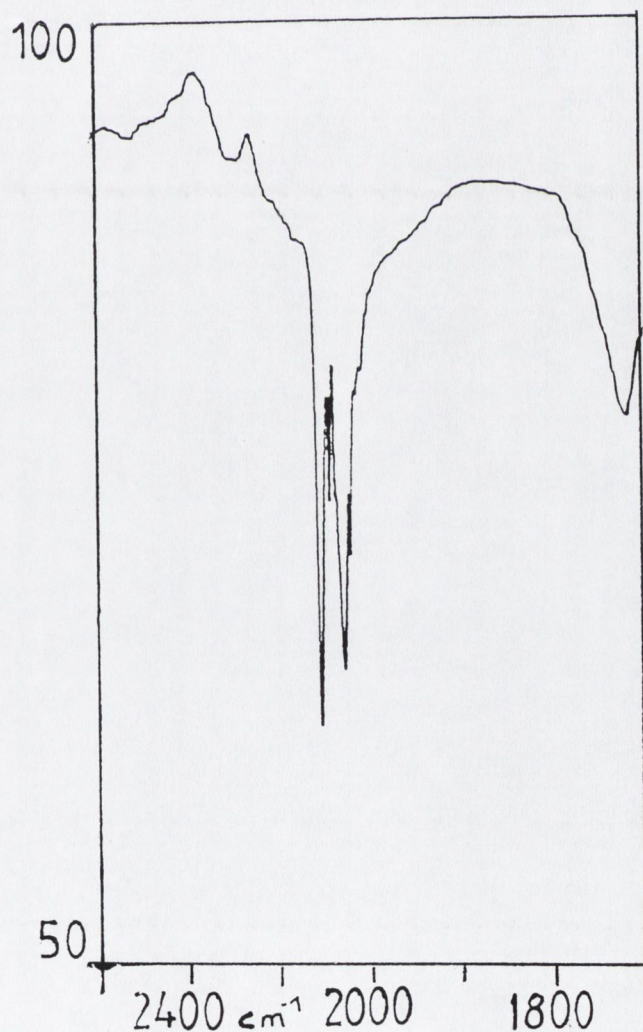
Fig.29 : IR spectrum following treatment of [Ru(bpy)$_2$(CO)(H$_2$O)]$^{2+}$ in a bomb calorimeter with buffer solution pH 12·4

The above reaction was also performed using water instead of the aqueous alkaline solution - reaction proceeded cleanly to give only the incorporated dicarbonyl sample.

If, indeed, the aquacarbonyl complex had not been converted to the dicarbonyl complex as expected, then on treating the sample with an aqueous alkaline solution the deprotonated species, $[Ru(bpy)_2(CO)(OH)]^+$, should be formed. Therefore, the above, water treated hydride sample, thought to be the aquacarbonyl, was stirred in 0.2M NaOH solution for 30mins. The UV/Vis absorption maxima occur at 275, 350 and 450nm while the IR spectrum shows carbonyl peaks at 2011 and 1988cm^{-1}. The 2011cm^{-1} stretch is assigned to the aquacarbonyl species while the 1988cm^{-1} stretch is thought to be the deprotonated, hydroxycarbonyl species. The sample was stirred again in 0.2M NaOH solution for a further 20mins. The UV/Vis spectrum shows little change with absorption maxima at 246, 280, 348 and 440nm. The IR spectrum only exhibits one carbonyl stretch at 1989cm^{-1}. At this stage the aquacarbonyl has been fully converted to the deprotonated, hydroxycarbonyl species. If this sample is subsequently treated with water it should return to the aquacarbonyl as in eqn.14. This is indeed found to be the case.

$$[Ru(bpy)_2(CO)(OH)]^+ + H_2O \longrightarrow [Ru(bpy)_2(CO)(H_2O)]^{2+} \qquad eqn.14$$
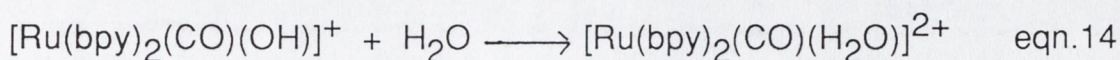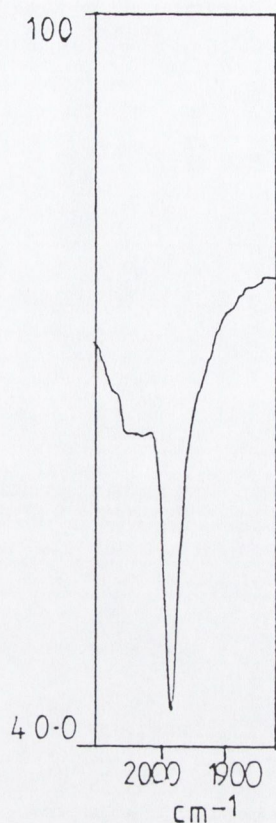
Fig.30 : IR spectrum of $[Ru(bpy)_2(CO)OH]^+$ in Nafion

2.6   Comparison   of $[Ru(bpy)_2(CO)H][PF_6]$ and $[Ru(bpy)_2(CO)(COO^-)][PF_6]$ incorporated in Nafion

When $[Ru(bpy)_2(CO)_2]^{2+}$ was treated with 0.2M NaOH solution the expected reaction was the formation of the (hydroxycarbonyl) species, $[Ru(bpy)_2(CO)(COOH)]^+$, but instead spectra were recorded which were in very close agreement with those recorded for the incorporated hydride. Therefore a series of experiments were necessary to discover if the formed species was the same as the incorporated hydride. Photolysis and heat experiments were performed on the hydride in Nafion and also on the species formed when the dicarbonyl was treated with NaOH solution.

As previously explained, upon treating a $[Ru(bpy)_2(CO)_2][PF_6]_2$

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incorporated Nafion with an aqueous 0.2M NaOH solution a marked change could be observed in the UV/Vis and IR spectra. The absorption spectra of $[Ru(bpy)_2(CO)_2][PF_6]_2$ in Nafion shows two absorption maxima at 248 and 302nm which gradually disappear upon the addition of aqueous NaOH solution; instead three new bands at 272, 350 and 446nm appear. In the IR spectrum there is a noticeable change as the stretches at 2053 and $2105cm^{-1}$ disappear completely and a peak grows in at $1960cm^{-1}$. These spectra are obtained after only three minutes treatment with NaOH solution and are stable thereafter to further NaOH treatment. These spectra are in close agreement with those obtained upon incorporation of the hydride into Nafion. Although It was thought that the (hydroxycarbonyl) species should be formed by the above procedure because of the use of such mild conditions[40], further investigations were carried out to assure the identity of the above formed species and to prove that it was not the hydrido carbonyl. The reversibility of the deprotonated species to give the dicarbonyl complex has previously been discussed in section 2.2.4.

Photolysis and heat studies in both NaOH solution and atmospheric conditions were performed on the hydride and the new formed unknown species. These experiments for the hydride have been discussed previously in section 2.3. Following the experiments on the unknown species (described below) it was finally thought to be the deprotonated (hydroxycarbonyl) species $[Ru(bpy)_2(CO)(COO^-)][PF_6]$ which is in equilibrium with $[Ru(bpy)_2(CO)(COOH)][PF_6]$

2.6.1 Thermolysis of $[Ru(bpy)_2(CO)(COO^-)]^+$ in Nafion in a. NaOH solution

All the samples were prepared by first incorporating $[Ru(bpy)_2(CO)_2]^{2+}$ into Nafion and treating with 0.2M NaOH solution. This gave UV/Vis spectra with absorption maxima at 272, 350 and 450nm while v_{CO} appears at 1960cm^{-1} (section 2.2.1).

a. NaOH solution : Heat studies were carried out by placing the Nafion sample in boiling 0.2M NaOH solution for consecutive periods of 20, 30 and 30 mins. Initially, following treatment of $[Ru(bpy)_2(CO)_2]^{2+}$ with NaOH solution at room temperature the IR carbonyl stretch occurred at 1960cm^{-1} and the UV/Vis absorption maxima were observed at 272, 350 and 450nm. After stirring the sample in boiling NaOH for 20mins the 1960cm^{-1} peak had shifted to 1958cm^{-1} and the UV/Vis absorption maxima were at 275,348 and 440nm. When the sample was further treated for 30mins in boiling NaOH solution the 1958cm^{-1} stretch had shifted noticeably to 1985cm^{-1} but no change was apparent in the UV/Vis spectrum. Following a further treatment of 30mins the IR stretch remained at 1986cm^{-1} and the UV/Vis absorption maxima appeared at 275, 350 and 450nm.
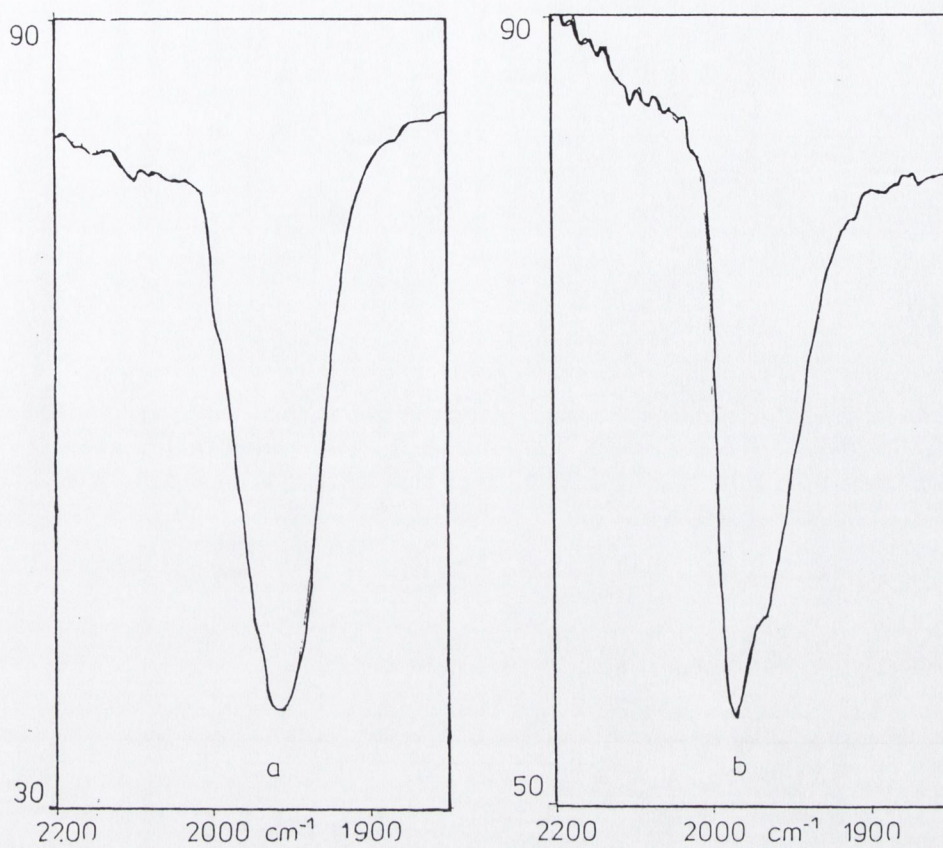
Fig.31 : IR spectra of [Ru(bpy)$_2$(CO)(COO$^-$)][PF$_6$] in Nafion after treatment with boiling 0.2M NaOH solution for a. 20 mins and b. 50mins.
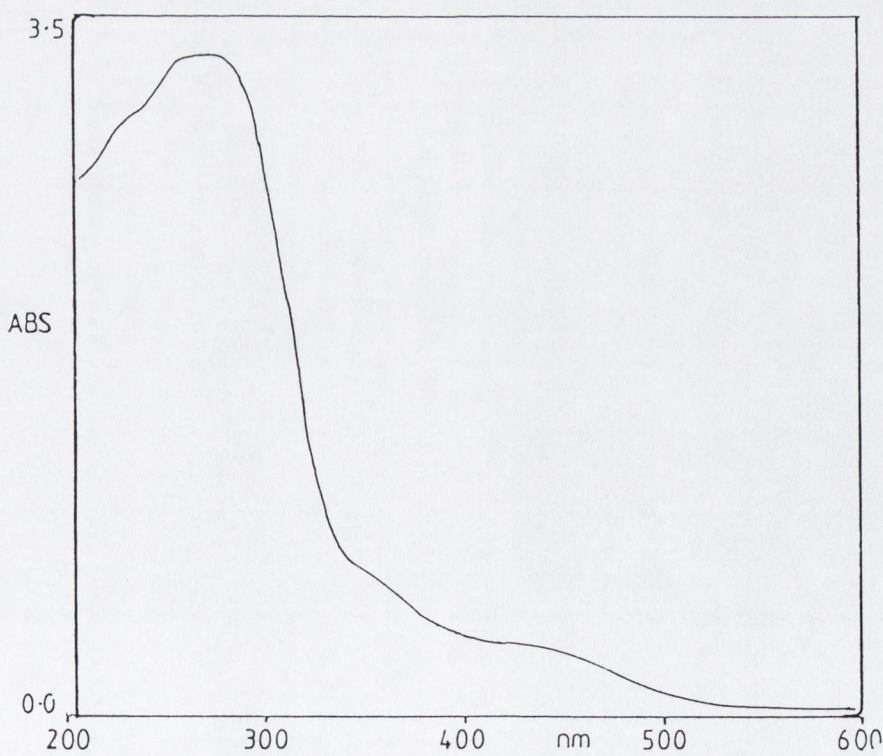
Fig.32 : UV/Vis spectrum of [Ru(bpy)$_2$(CO)(COO$^-$)][PF$_6$] in Nafion after treatment with boiling 0.2M NaOH for 50 mins

As can be seen from the above results, by comparison with those obtained for the hydride where no change was observed (section 2.3.1), there is a very marked dissimilarity in the IR spectra obtained; a clear indication that two different species are being formed.

2.6.2 Photolysis of $[Ru(bpy)_2(CO)(COO^-)]^+$ in Nafion in a. NaOH solution and b. Atmosphere

Samples were prepared by first incorporating $[Ru(bpy)_2(CO)_2]^{2+}$ into Nafion and treating with 0.2M NaOH solution. Photolysis was carried out as before. The samples were selectively photolysed in either NaOH solution or under atmospheric conditions. UV/Vis and IR spectra were recorded after each irradiation period.

a. NaOH solution: The sample was photolysed originally for a period of 30secs after which time the IR spectrum remained unchanged with v_{CO} at 1960cm^{-1}. After a further 3mins photolysis v_{CO} was found at higher wavenumber, this increase in wavenumber continued as photolysis was continued until after 20mins v_{CO} had shifted to 1984cm^{-1}.
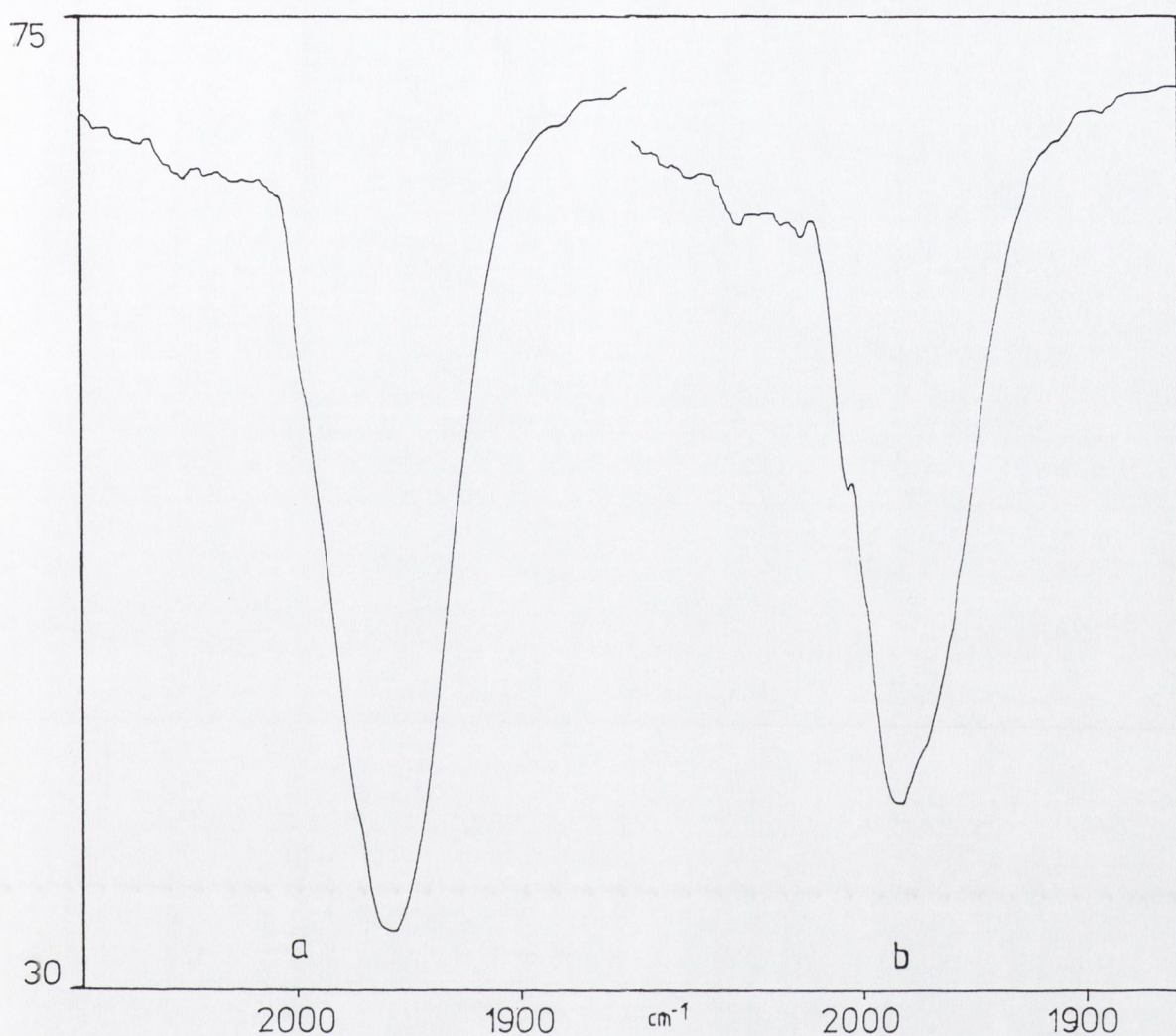
Fig.33: IR spectra of $[Ru(bpy)_2(CO)(COO^-)][PF_6]$ in Nafion after photolysis in 0.2M NaOH solution for a. 3 mins and b. 20 mins

The reaction was also monitored by UV/Vis spectroscopy - an absorption maximum began to grow in at 490nm while the maxima at 350 and 275nm increased in intensity. There is a simultaneous decrease in the intensity of the 248nm absorption. It was also observed that the 275nm absorption shifts to longer wavelength as photolysis is carried out - after 20mins total irradiation it is found at 286nm.
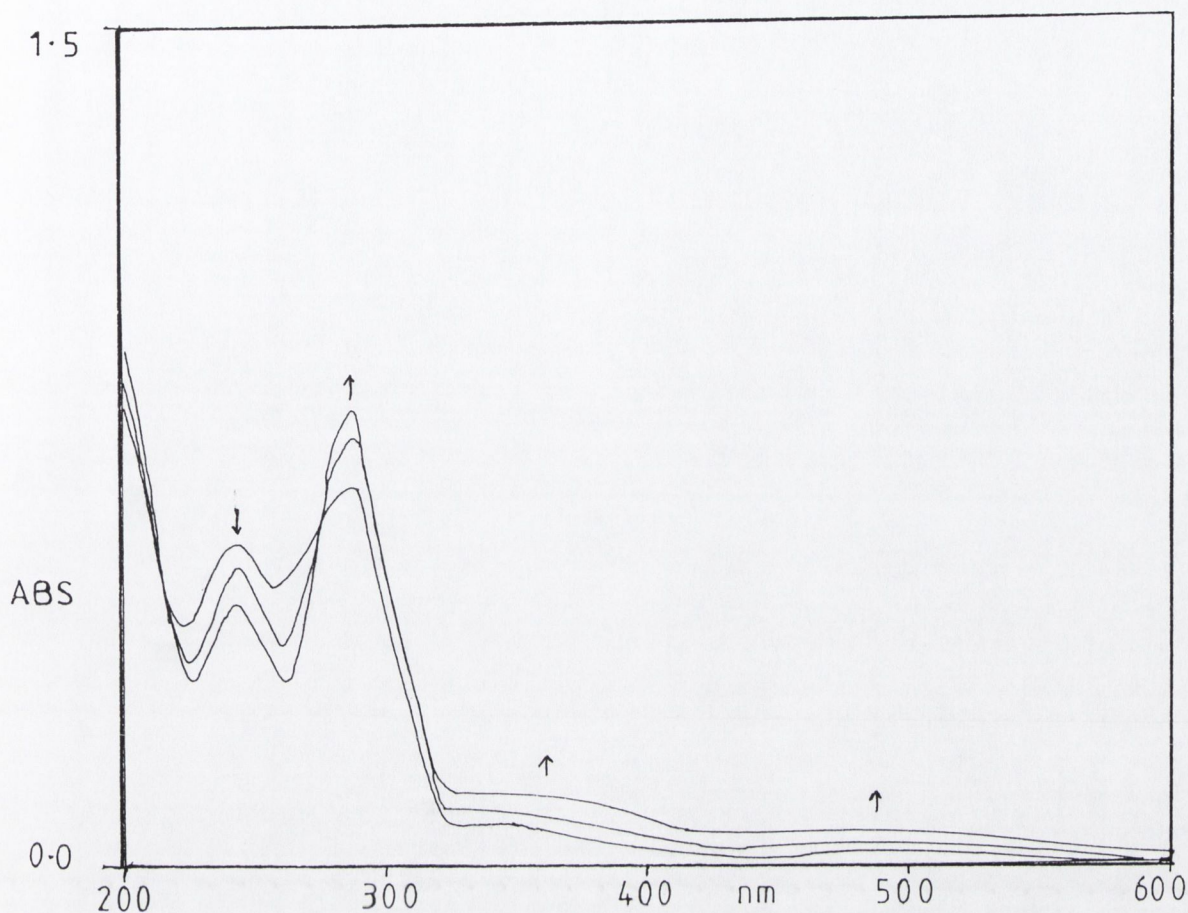
Fig.34 : UV/Vis spectra of [Ru(bpy)$_2$(CO)(COO$^-$)][PF$_6$] in Nafion after photolysis in 0.2M NaOH

b. Atmosphere : The sample was placed in a dry quartz cuvette exposed only to the atmosphere. Following photolysis for 20mins the IR spectrum shows v_{co} at 1966cm^{-1} - the position is unchanged during photolysis although there is a decrease in the intensity of the 1966cm^{-1} peak. The UV/Vis spectra exhibit a marked increase in intensity at 486 and 350nm while there is a gradual decrease in intensity at 242nm. It is interesting to note that the 272nm absorption is shifted to 288nm after 30secs photolysis whereas in the samples photolysed in 0.2M NaOH solution the shift is much more gradual.
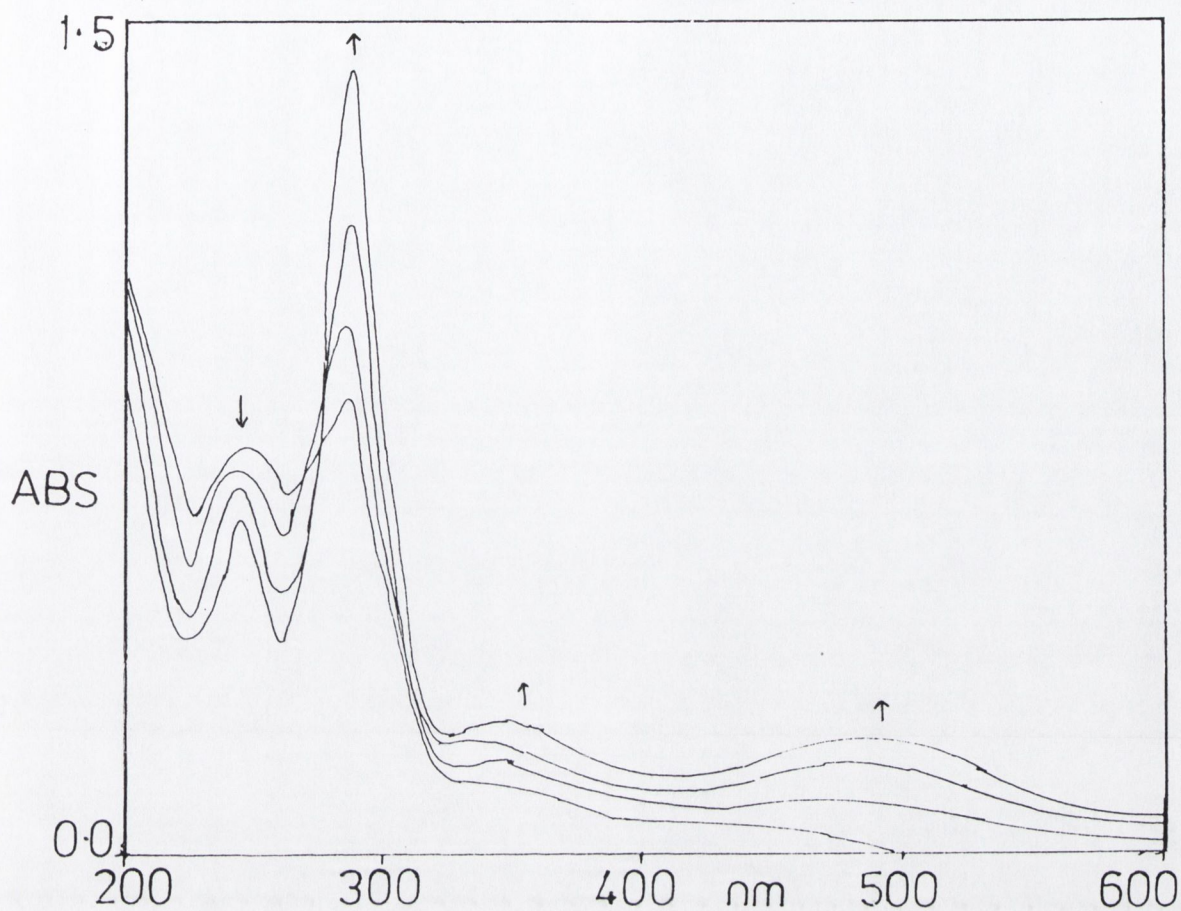
Fig.35: UV/Vis spectra of $[Ru(bpy)_2(CO)(COO^-)][PF_6]$ in Nafion after photolysis under atmospheric conditions

2.7 $Ru(bpy)(CO)_2Cl_2$

The compound was prepared according to the known preparation by refluxing the red carbonyl solution[13] $[Ru(CO)_2Cl_2]_n$ with excess bpy in aqueous ethanolic solution giving v_{CO} (KBr) = 1997 and 2055cm^{-1} while the absorption maxima occur at 354, 305

and 286nm. Incorporation into Nafion was achieved by dissolving the compound in acetone which was then evaporated off. Water was added and the mixture boiled. The Nafion strip was then stirred in this solution for an hour. ν_{CO} = 2040, 2100cm^{-1}. UV/Vis = 306nm.
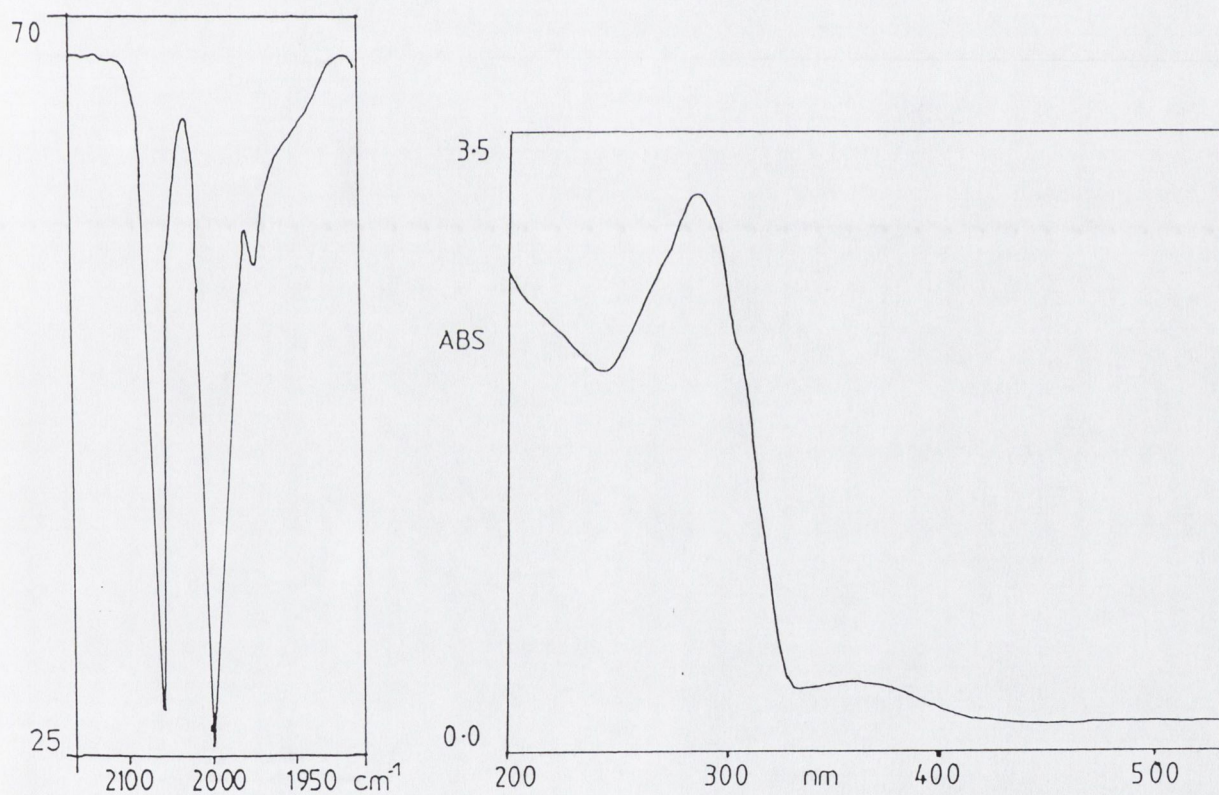
Fig.36 : IR(KBr disc) and UV/Vis(CH$_3$CN) spectra of [Ru(bpy)(CO)$_2$Cl$_2$]
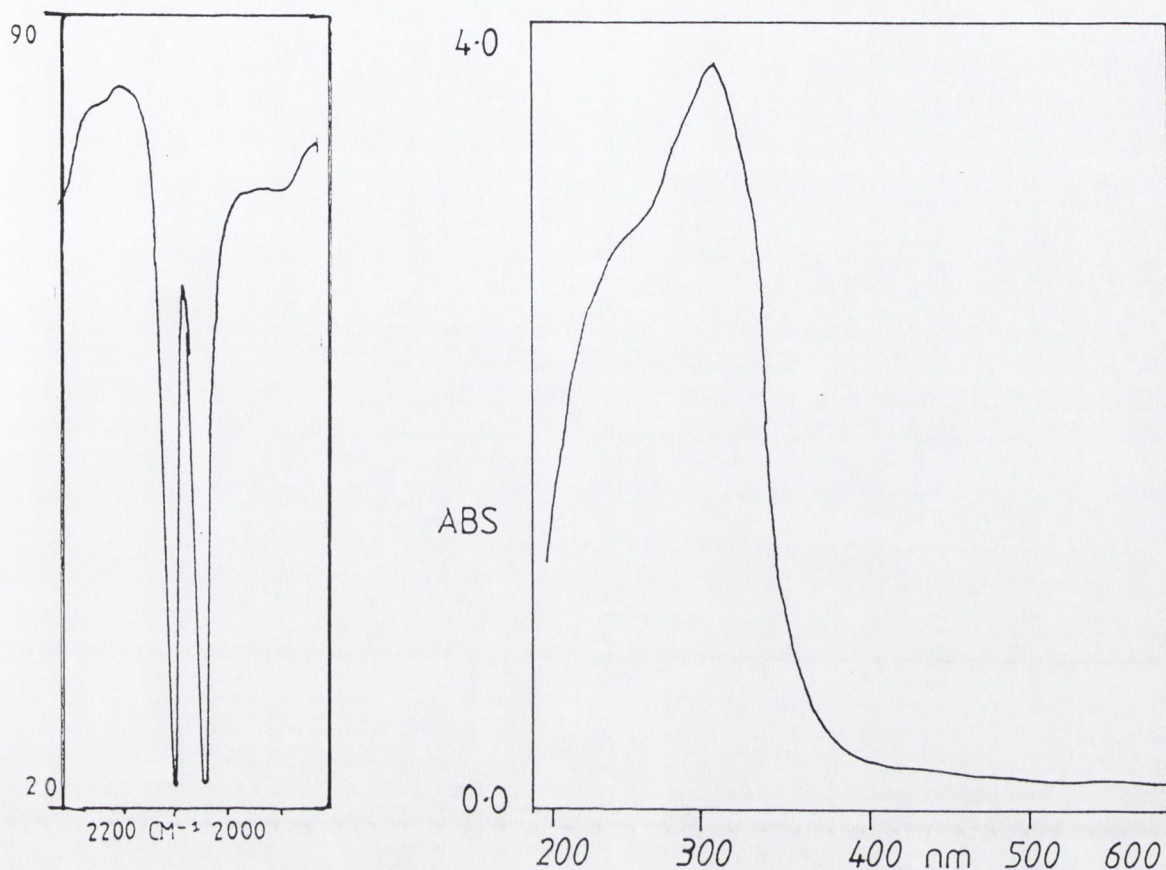
Fig.37 : IR and UV/Vis spectra of [Ru(bpy)(CO)₂Cl₂] incorporated in Nafion

2.7.1 Photolysis of Ru(bpy)(CO)$_2$Cl$_2$ in Nafion immersed in H$_2$O

The photolysis apparatus was as before - the cuvette was filled with water into which the sample was placed. The sample was photolysed initially for 15secs, irradiation was for a total of 20mins. After only 15secs irradiation a noticeable shift had occured in the UV/Vis spectrum with the growth of a new band at

625nm. As photolysis is prolonged the 625nm absorption increases in intensity and a new absorption maxima at 490nm grows in. This trend continues as photolysis is prolonged.

The reaction was also monitored by IR spectroscopy - as photolysis time is increased the v_{CO} peaks at 2040 and $2100cm^{-1}$ decrease in intensity while a new peak grows in at $1995cm^{-1}$.
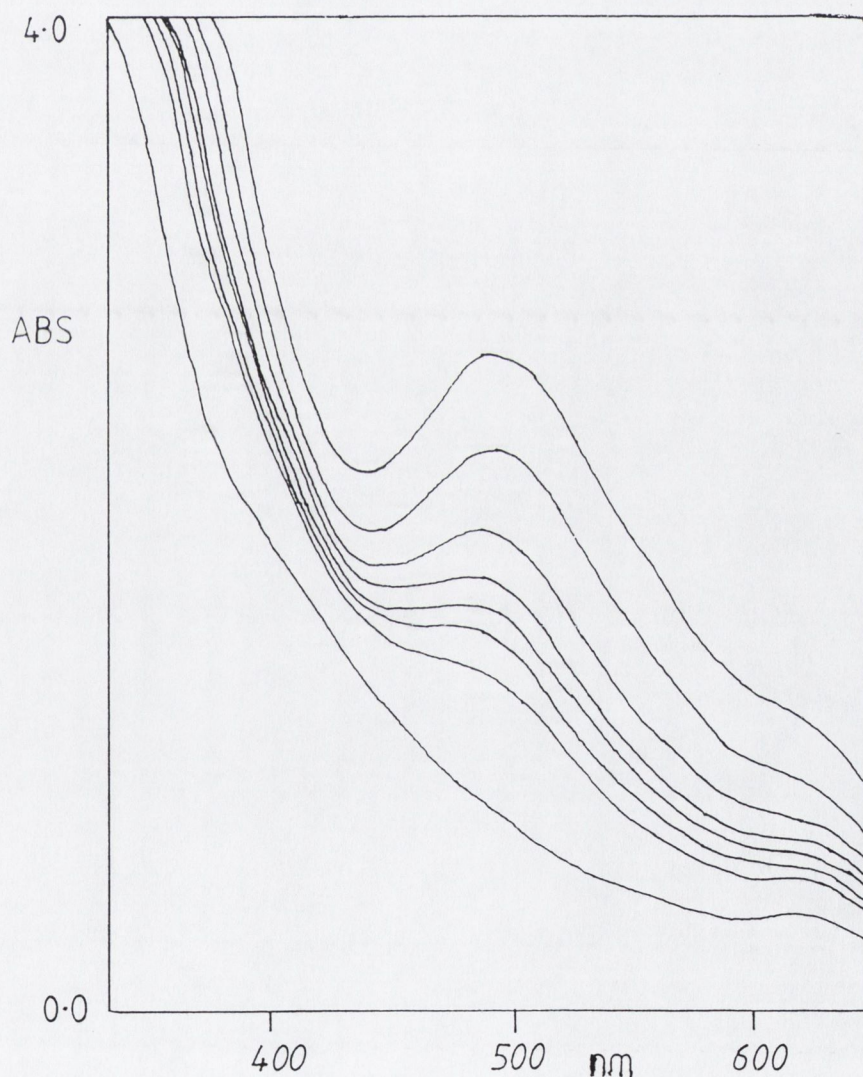
Fig.38 : UV/Vis spectrum of $[Ru(bpy)(CO)_2Cl_2]$ in Nafion after photolysis in H_2O

2.8 DISCUSSION

2.8.1 Infra-red Spectroscopy

Carbon monoxide is known to form complexes with almost every transition element as well as with the metals of Group 1B. The bonding in these complexes consists of two components, a forward sigma bond and a backward pi bond. The sigma bond is formed by the overlap of the highest filled orbital of CO (5σ) with empty orbitals of the metal, while the pi bond is formed by overlap of formally full d-orbitals of the correct symmetry with the lowest empty orbital of CO(2π). Both the 5σ and 2π orbitals are localised mainly on the carbon atom so metal-carbon multiple bonding is occurring. The two components of the bonding are synergic - pi donation by the metal makes it a better sigma acceptor and causes the CO group to become a better sigma donor. This affects electron and orbital availability at both the carbon and metal, stabilising metals in low oxidation states.

The vibrational spectra of metal carbonyls are particularly informative - they are sharp, sensitive to their environment and are often quite intense, The number and pattern of the bands gives information about the molecular symmetry and geometry, while the position of the bands relate to the bonding.

Metal complexes containing one or more CO ligands bound to a single metal atom show one or more intense bands between 1800

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and 2200cm^{-1} - these are assigned to the carbon-oxygen stretch of the coordinated CO. The CO stretches are highly sensitive to the environment and exhibit large interactions[58].

Upon coordination of 2,2'-bpy to a metal slight modification of the spectrum occurs[59] - in particular the ring frequencies (1600-1000cm^{-1}) undergo slight but observable shifts to higher wavenumber. The bands at 995 and 759cm^{-1} (free ligand) are those which have been suggested to be most useful for diagnosis of coordination of bpy to a metal[60]. Upon coordination the former shifts to 1010cm^{-1} while the latter often shifts by as much as 10-20cm^{-1} to higher wavelength.

It has previously been suggested that cis-bis(bpy)Ru(II) complexes have spectra which are more complex in the region 700-800cm^{-1} than those for the trans complexes[61]. The bands near 760 and 730cm^{-1} are characteristic of vibrations of the pyridine conjugated rings.

All of the bis(bpy) complexes show bands at 1600cm^{-1} and at approx. 730 and 770cm^{-1} due to the bpy ring vibrations. Two sharp bands at 1245 and 1315cm^{-1} are due to aromatic C-N stretching[62]. C-H bending modes were observed at 1450 and 1470cm^{-1} [63].

Free carbon monoxide exhibits a stretching frequency at 2155cm^{-1}. Upon coordination to Ruthenium a decrease in bond order results for CO with a decrease in v_{CO}. The monomeric carbonyl complexes [Ru(bpy)$_2$(CO)L]$^{n+}$ exhibit a strong band in the

range 1950-2020cm^{-1}, this is indicative of cis stereochemistry. The position of this band is directly related to the pi acceptor properties of the sixth ligand and the overall charge on the complex. The monomeric dicarbonyl complexes exhibit two intense bands in the region 1980-2100cm^{-1}. v_{CO} is greater for the dicationic species because reduced electron density results in a decrease of Ru-CO back bonding which increases the CO bond order and raises v_{CO}. Similar effects were reported by Meyer[54] for the isoelectronic bis(bpy) complexes of NO^{+}. [RuL$_2$(CO)Cl$_2$] compounds exhibited a single stretch at 330cm^{-1}, required for a trans chloride configuration.

The above features were common for all the spectra recorded. However, additional features were observed in the spectra of the individual complexes.

Upon coordination of the complexes into Nafion significant changes occur in the spectra. In all of the complexes a large red shift is observed for the carbonyl groups. It is not possible to examine the effects on the bpy absorptions because the Nafion absorptions occur in the same region. In general the carbonyl peaks are shifted by ~30cm^{-1} - too substantial a shift to be due solely to backbonding. Therefore the Nafion environment must be greatly influencing the absorption of the complexes. In all of the complexes v_{CO} is found at 1960-2155cm^{-1}, the dicarbonyl complexes being at highest wavenumber. As before two carbonyl peaks are observed for the bis(carbonyl) complexes, indicative of cis stereochemistry.

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2.8.2   UV/Vis Spectroscopy

All transition metal carbonyl complexes known contain electrons assignable to the outermost d subshell of the metal atom, in fact, the availability of such electrons for pi backbonding appears to play an essential role in stabilising such carbonyls. With the exception of d^{10} complexes metal carbonyls are therefore expected to show d-d transitions, though these are often obscured by bands of other kinds. This is because d-d transitions are between orbitals of the same parity and are forbidden, thus resulting in very weak intensities.

The UV/Vis spectrum of free bipyridyl consists of absorption maxima at 226 and 282nm $(\varepsilon 1.02*10^4)$[64] assigned as $\pi-\pi*$ transitions. The n-$\pi*$ transitions are thought to lie under the long wavelength tail of the bpy spectrum. The spectrum of free bipyridyl is relatively unaffected by complex formation[58]. On coordination to a metal these internal ligand bands are red shifted and lie at ~245 and 300nm.[55,64]. The visible spectra for such complexes consists of two metal to bipyridyl charge transfer transitions at ~370 and 500nm. In most cases the other coordinated ligands, while affecting transitions involving bipyridyl, do not display CT transitions of their own, these may be hidden by transitions involving bipyridyl.

For the bis(bpy) monocarbonyl complexes the bpy intraligand transitions were observed in the regions 260 and 300nm, the latter being split in some cases by interactions with the metal

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d-orbitals[58]. Two weaker shoulders are seen on the low energy side of the $\pi-\pi*$ transitions. These were assigned as $d\pi-\pi^*$ MLCT transitions having undergone a substantial hypsochromic shift because of the presence of the carbonyl ligand. CO has extensive π- acceptor properties which strongly stabilise the $d\pi$ levels and hence increase the energy of the $d\pi-\pi^*$ transitions. However Cl⁻ is a π-donor and so has the opposite effect so that in $[Ru(bpy)_2(CO)Cl]^+$ for example, the influence of CO stabilising the $d\pi$ orbitals is reduced significantly. Similar effects were reported by Meyer[54] for bis(bpy)Ru(II)nitrosyl complexes. In addition to the above features an intense sharp peak was observed in all cases at ~305nm having the following properties

1. The band is observed for mono and dicarbonyl Ru(II)bipyridyl complexes. It is possible that this absorption band is due to an intraligand $\pi-\pi*$ transition centred at the dicarbonyl ligand.

2. The band is relatively sensitive to the sixth ligand.

For the dicarbonyl complexes $\pi-\pi*$ transitions were observed in the regions 260 and 300nm, the latter was split in some cases by interactions with the metal $d\pi$ orbitals. The low energy shoulder was seen as a sharp band at 315nm. A weak shoulder in the region 320 - 360nm for $[RuL_2(CO)_2Cl_2]$ complexes was assigned as a MLCT transition having undergone a substantial hypsochromic shift due to the π-acceptor properties of the carbonyl ligands. The shift is less pronounced for the monocarbonyl complexes. For complexes with strong acceptor

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ligands in all six coordination sites ie. $[Ru(bpy)_2(CO)_2]^{2+}$ the stabilisation and subsequent blue shift were such that no transitions were observed in the visible region.

Upon incorporation of the complexes into Nafion noticeable changes are observed in the absorption spectra. In general the spectra become simpler in appearance, sometimes with only one absorption maxima. However, CO is a very good π-acceptor and so strongly stabilises the $d\pi$-levels - therefore the bis carbonyl complexes show little change upon incorporation. The spectrum for the hydride is also unchanged upon incorporation. Slight changes occur for the chlorocarbonyl complex, with the disappearance of the shoulders at 282 and 313nm absorption, and for $[Ru(bpy)(CO)_2Cl_2]$, with the disappearance of the shoulder at 284nm. These effects are probably due in part to the reduced polarity of the Na^+ form Nafion compared with aqueous solution. The more hydrated the membrane the more likely it is that the Ru complex is interacting with the fluorocarbon chain[49]. Particularly strong changes in absorption spectra may result when chemical bonds are formed between a metal ion and the ionic group of the membrane. It is also possible that the chlorocomplexes are decomposing to some extent in Nafion due to the possible coordination of the complex with the sulfonic acid group giving for example $[Ru(bpy)(CO)_2(CF_3SO_2)_2]$[27]

2.8.3   Correlation of results to Tanaka cycle

A plausible catalytic cycle for the water gas shift reaction was proposed by Tanaka[40] and is depicted in Scheme 1 (See Introduction) . We decided to enter the cycle at three different places by first preparing the required compounds - the chlorocarbonyl, the dicarbonyl and the hydrido complexes - according to the known preparations. They were characterised by IR and UV/Vis spectroscopy and are in agreement with those obtained by Tanaka[40]. As explained in the previous sections, significant changes occurred in the recorded spectra upon incorporation of the compounds into Nafion and new spectral data is to be expected when carrying out the Tanaka[40] cycle in Nafion. Spectral data was therefore compiled for the complexes prepared and incorporated into Nafion and it was this data which was used to identify species formed in-situ in reactions. The data obtained from species formed by different routes in the cycle was compared and found to be identical to that already compiled from the incorporated complexes. It is possible to perform the catalytic cycle in Nafion as shown by the scheme outlined below (Fig.39).
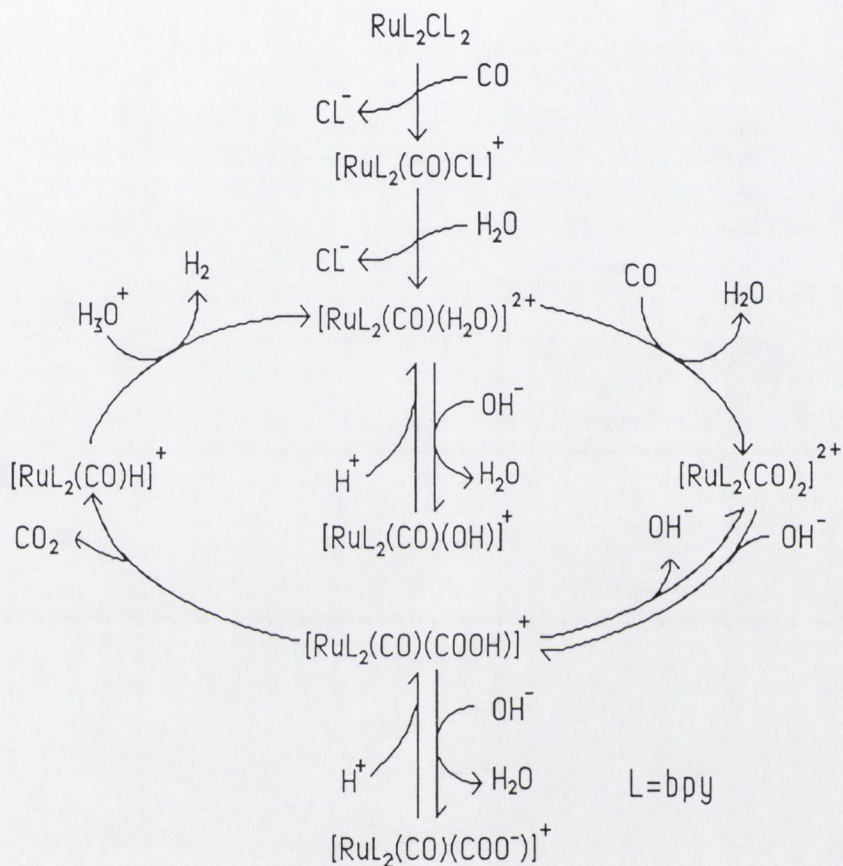
Fig.39 : Catalytic cycle as observed in Nafion.

Upon incorporation of the complexes into Nafion significant spectral changes occur. This implied that there could possibly be changes in the reactivity of the complexes in Nafion. Upon treatment of the incorporated dicarbonyl complex with 0.2M NaOH solution the (hydroxycarbonyl) complex is initially formed

but is rapidly deprotonated to give the carboxylate species. It is very difficult to isolate the (hydroxycarbonyl) using 0.2M NaOH solution because the deprotonation occurs rapidly. However, if a sodium borate buffer solution of approx. pH 10.7 is used the (hydroxycarbonyl) is formed in equilibrium with the dicarbonyl and can be isolated in-situ. The production of the (hydroxycarbonyl) is initially very slow. This is best explained by considering the manner in which the complexes are incorporated into the Nafion; the complex is taken up from solution and becomes distributed throughout the membrane, however the complex is somewhat more concentrated at the surfaces. At the start of the reaction only the surface complex is able to react and the amount of conversion is small as a direct result. However, as the reaction proceeds, more of the complex becomes accessible to the buffer solution as diffusion takes place and the reaction rate is significantly increased. It is possible that the initial small spectral changes are due to reaction of the buffer solution itself- the negativity of the ions make them slow to penetrate into the membrane, explained by the Donnan effect. Equilibration of the sample occurs after several hours treatment with the buffer solution. We have monitored spectroscopically the treatment of $[Ru(bpy)_2(CO)_2]^{2+}$ with NaOH solutions of varying pH's.

We have also shown that the temperature of reaction has a substantial effect on the position of the ingrowing stretch in the IR region. With higher temperature the stretch is shifted to higher wavenumber - shifts of $\sim 30 cm^{-1}$ have been seen to occur. This is probably due to solvent swelling effects resulting in

considerable alteration of the membrane medium. It is also possible that the species being formed at the different temperatures are not the same but this has not been proven.

Photolysis of the dicarbonyl complex results in the loss of the carbonyl groups as expected - in water the aquacarbonyl is initially formed which upon continued photolysis is converted to the diaqua complex. The reaction is clean with no secondary products formed. However, the photolysis reaction in 0.2M NaOH leads to the hydroxycarbonyl species formed from the aquacarbonyl. rather than the above conversion to the diaqua camplex.

Tanaka[40] has previously examined the reaction of the free dicarbonyl in a bomb calorimeter with aqueous alkaline solutions leading to the formation of the hydride among other products. We examined a similar reaction in Nafion to produce the hydride from the (hydroxycarbonyl). The (hydroxycarbonyl) sample was placed on the vacuum line at 100°C for 12 hours after which time a shifting of the stretch in the IR region from $1970cm^{-1}$ to $1962cm^{-1}$ had occurred. However, the $1962cm^{-1}$ stretch was very weak and in order to confirm its identity as the hydride the sample was treated in water overnight to convert it to the aquacarbonyl. The conversion occurred readily giving a stretch at $2012cm^{-1}$ in the IR region, leading to the conclusion that the hydride had been successfully formed.

The free hydride is also easily incorporated into Nafion and is the most useful precursor to the aquacarbonyl by treatment in

water. The aquacarbonyl can then be converted to the hydroxycarbonyl in aqueous alkaline solution. Photolysis of the hydride in NaOH solution leads to decarbonylation and the subsequent formation of the diaqua complex. Treatment of the aquacarbonyl, formed from the hydride, in a bomb calorimeter with CO leads to the dicarbonyl complex.

2.8.4   Identification of Species

The spectroscopic data obtained for the complexes incorporated in Nafion show very noticeable differences when compared with those obtained for the free complexes. As a result the identities of the incorporated species were reviewed. Both the data obtained from the IR and UV/Vis spectra was considered.   The most useful results are from the IR spectra - the bands are sharp and intense and therefore the wavenumbers are very accurate, more so than in the absorption spectra where the bands are generally broad. Also, the wavenumber shifts were much greater in the IR spectra.

For all the complexes incorporated into Nafion the IR spectra show a shift of the carbonyl bands to higher wavenumber of $\sim 30 cm^{-1}$. These shifts are of significant importance because of the potential use of the complexes as probes. Similar shifts

occurring in the UV/Vis region have previously been reported upon incorporation of such complexes into micelles and clays[54,55,56,57]. Hence uncertainty arose as to whether the species in Nafion were the same as the free complexes, or had incorporation caused a reaction to occur. However, we have now successfully performed the catalytic cycle in Nafion although the spectral data is significantly altered from that obtained for the reaction of the free complex. This is to be expected due to the sensitive nature of IR and UV/Vis spectroscopy to the environment of the complex. From the different starting points in the cycle reactions were performed to ultimately give the same product. Spectral data obtained for the various products was the same regardless of the route chosen. The data also corresponded to that obtained when the free complex was incorporated into Nafion. This is significant because it showed that it is the Nafion medium which is affecting the spectra obtained. It was thus concluded that the complexes are unaltered upon incorporation into Nafion and reactions proceed to the same products as with the free complexes.

2.8.5   Modification of reactions in Nafion

Upon incorporation of the complexes into Nafion reactions are not greatly modified compared to solution. In some cases reactions can occur readily which must be assisted in solution[45]. The reasons

for this have not been proved conclusively because of the complexity of the ionomer. Thus, the isolation of complexes in ionomers, sometimes in formed domains into which they have been ion exchanged at low temperature, can place them in a physical environment in which they have become particularily reactive. This reactivity plus the containment of the species which diffuse to them lead to the ability of the ionomers to undergo reactions under mild conditions which are analogous to those which otherwise require higher pressures, temperatures or forcing conditions. Moreover, the diffusion limitations imposed by the ionomer can influence rates of reactions to a degree that indicates that product or reactant separation is feasible.

We have shown that the rates of some reactions are initially slow - this is due to the fact that although the complex is more concentrated at the surface than in the centre of the membrane only a small amount of the complex can react until the solvent diffuses through the membrane. However the Donnan Effect plays an important role in the rate of diffusion of the solvent. The Donnan potential is caused by a build up of negative charge at the membrane surface as anions try to penetrate the embrane in order to compensate for the weak concentration of mobile anions in this phase. This sets up an electric field which counterbalances the tendancy of the ions to equilibrate in the two phases (membrane and solution).

2.8.6 Discussion

As can be seen throughout the results there is a considerable change in the spectra when the complexes are incorporated into Nafion. A good deal of work has been done on the nature and extent of the solvent shifts shown by carbonyl groups. Much evidence has been accumulated in favour of the view that the shifts arise entirely from interaction effects. In extreme cases these would be hydrogen bonds. It seems likely that as the Nafion becomes increasingly hydrated hydrogen bonding between the carbonyl group and the water molecules has a significant effect on the environment of the complexes resulting in the shifts observed in the spectra. It is also possible that hydration of the Nafion is playing a large role - it is reported[49] that a membrane of equivalent weight 1100 having been boiled in water has a cluster diameter of ~4.7nm with ~80 ion exchange sites per cluster. Because of the low concentrations of complex in the membrane it is unlikely that any cluster contains more than one complex ion. The complexes have relative freedom of motion within ion clusters, enlarged due to the degree of hydration. It appears that in hydrated Nafion[65] the spectral shifts result from the interaction of the Ru complex with the fluorocarbon chain rather than the sulfonate head groups. As the clusters contract on dehydration there is significant interaction between the sulphonate head groups and the metal centre via the labile ligand sites. Thus the blue shift is resulting from the formation of a sulphonate-type complex $Ru<-O-(SO)_2-CF_2-$. Meisel[55] and Lee[56] have reported similar observations in UV/Vis spectral data for Nafion films and perfluoroctanoate micelles respectively.

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Fripiat[57] studied Ru(II) complexes in negatively charged clays and observed shifts of absorption maxima to longer wavelength than in aqueous solution, the more hydrated samples being at the highest wavelength. He took this as evidence for covalent bonded or distorted bpy ligands as a result of adsorption.

2.8.7   Conclusion

We have shown that it is possible to carry out a variety of chemical and photochemical reactions within the Nafion environment. By spectroscopic monitoring we have observed the effects of pH, concentration and degree of hydration on such reactions. However, if Nafion is to be successfully used as a medium for the water gas shift reaction it will be necessary to achieve the following : control of pH and reaction conditions, and degree of hydration. We have successfully controlled and monitored the pH in Nafion with relative ease. However, control of reactant concentrations is more difficult. Since uptake depends on pH, nature of buffer used, ionic strength, soak duration, concentration of soaking solution, presoaking (whether

in water, buffer or a non-aqueous system), degree of hydration, whether the Nafion is in the acidic or basic form, temperature of solvent control of such a system is difficult.

However, the above difficulties are presently under review. Future work will involve a more detailed look at the kinetics of the reactions taking place in the Nafion - flash photolysis and transient IR spectroscopy will be the main techniques employed.

SECTION 3   EXPERIMENTAL SECTION

3.1   Instrumentation

Infra-red spectra were recorded on a Perkin-Elmer 883 IR spectrophotometer. Samples were either KBr discs for the free compounds or, for the incorporated complexes, the Nafion strip was taped to the sample holder and the spectrum run as usual. $\%T \; v \; CM^{-1}$

Ultraviolet/Visible spectra were recorded on a Pye Unicam PU8800 UV/Vis spectrophotometer using matched 2mm quartz cells for Nafion samples and 1cm matched quartz cells for all solutions.

All Nafion samples, both in the IR and UV/Vis region, were run against a clean reference Nafion strip. The Nafion was considered to be clean when it no longer had an optical density >0.5 above 200nm in the UV/Vis region.

3.2   Materials

$[Ru(bpy)_2(CO)Cl]^+$ as the perchlorate or hexafluorophosphate salt was prepared according to Kelly and Vos[29,53] and purified by column chromatography on neutral alumina using 50/50 benzene/acetonitrile as eluant to yield yellow crystals. $[RuCl_2(CO)_2]_n$ was prepared by the method of Chatt[13] and used

immediately. Hydrated ruthenium trichloride (Johnson & Matthey) and 2,2'-bipyridyl (Aldrich) were used as purchased. Solvents were purified by distillation before use.

3.3 NAFION

The Nafion 1170 membranes which were obtained from E. I. duPont de Nemours & Co. and initially very brown in colour, were cut into strips approx. 8*30mm. Cleaning is effected by treatment with 0.2M KOH (1-1.5hrs), rinsing in pure water, then placing in 50:50(v/v) EtOH:H_2O in an ultrasonic bath for 2hrs. The membranes were then soaked in pure water overnight followed by stirring in 1M H_2SO_4. Finally, they were ultrasonically rinsed in pure water for 20mins before allowing to dry at ambient temperature and pressure. The above process was repeated if necessary to ensure the Nafion is thoroughly cleaned (i.e. no absorption in the UV/Vis spectrum above 200nm). If the Nafion still proves unclean the remaining impurities can be removed by boiling the Nafion in 0.2M KOH for 2 hours.

The mass of the membrane, both hydrated and dehydrated, is easily determined. It has been found[66] for H^+ form Nafion that completely hydrated samples contain 28.4wt% water, the ambiently hydrated samples contain 6.7wt% water whereas the ambiently rehydrated samples contain 3.3wt% water. However different values were obtained for the Na^+ form Nafion used in

the experiments. Completely hydrated samples contain 33.1wt% water, the ambiently hydrated samples contain 24.1wt% water whereas the ambiently rehydrated samples contain 12.6wt% water. Knowing the dry mass of each membrane it is possible to calculate the number of SO_3^- groups present. Hence, one is able to control the degree of exchange by assuming that all the ruthenium complex added to an aqueous exchanging solution will be incorporated into the membrane.

3.4   Preparation

$[Ru(CO)_2Cl_2]_n$: 2.018g of $RuCl_3.3H_2O$ was heated at reflux in EtOH ($50cm^3$) for 7 hours while bubbling carbon monoxide through, resulting in a blood red solution (A). This was used immediately[13].

$[Ru(bpy)(CO)_2Cl_2]$: To $30cm^3$ (4.97mmol) of the above prepared $[Ru(CO)_2Cl_2]_n$ solution (A) was added bpy (3.8904g, 25mmol) and followed by the addition of $15cm^3$ of EtOH and $45cm^3$ of H_2O. The mixture was refluxed for two hours after which time a yellow/red solid formed. The solution was suction filtered and the resulting yellow solid washed with ether. Yield : 2.055g.   UV/Vis(MeOH): 354, 313, 305, 286nm.   IR(KBr): 2055, 1997, 330cm^{-1}

[Ru(bpy)$_2$(CO)$_2$][PF$_6$]$_2$: The complex [Ru(bpy)(CO)$_2$Cl$_2$] (0.4952g, 1.28mmol) and bpy (0.2876g, 1.84mmol) were refluxed in EtOH/H$_2$O (33:67 v:v, 375cm^3) for 24 hours. The solution was left to cool overnight. A concentrated aqueous NH$_4$PF$_6$ solution yielded yellow crystals which were recrystallised from EtOH/H$_2$O. Yield = 0.4512g, 65%. UV/Vis (CH$_3$CN) = 316(sh), 310(sh), 302, 248nm. IR (KBr) V$_{CO}$ = 2035, 2084cm^{-1}.

[Ru(bpy)$_2$(CO)Cl][ClO$_4$] : The compound was obtained as a secondary product of the literature synthesis of [Ru(bpy)$_2$Cl$_2$].2H$_2$O[30]. RuCl$_3$.xH$_2$O (10.7g, 41mmol) and bpy (12.5g, 80mmol) were heated at reflux in DMF for 8hrs. The solution was reduced to a volume of 30cm^3 and an equivalent volume of acetone added. Upon standing overnight purple [Ru(bpy)$_2$Cl$_2$].2H$_2$O crystals were obtained and filtered off. Yield = 7.91g. This crude material was further purified by column chromatography using neutral alumina and acetonitrile/benzene (50:50) as eluant. The solution obtained was concentrated to a volume of approx. 50cm^3 and benzene added. On standing yellow crystals were formed, these were filtered off, washed with benzene and filtered dry. 1g of crude material gave 860mg of pure compound with an overall yield of 33%. UV/Vis (CH$_3$CN) 260(sh), 282, 313(sh), 353(sh), 418(sh)nm. IR(KBr) = 1966cm^{-1}

[Ru(bpy)$_2$(CO)H][PF$_6$] : [Ru(bpy)$_2$(CO)Cl][ClO$_4$] (0.9539g, 1.65mmol) in refluxing ethanol/water (2:3 v/v, 150cm^3) were treated with NaBH$_4$ (1.184g,31mmol) dissolved in minimum water and the mixture was refluxed for 30 mins. An excess of aqueous NH$_4$PF$_6$ was added and the mixture left to cool overnight. Upon standing yellow/orange crystals formed in the solution which were then filtered off (0.6631g, 68%). The crude material was recrystallised from acetone/water mixtures. The orange crystals obtained were filtered dry (0.484g, 50%).

UV/Vis (CH$_3$CN) = 452, 348, 273nm ; IR (KBr) = 1930cm^{-1}

3.5   Incorporation of compounds into Nafion

All Nafion samples were prepared in the Na$^+$ form.

[Ru(bpy)$_2$(CO)$_2$][PF$_6$]$_2$: A solution was prepared by dissolving [Ru(bpy)$_2$(CO)$_2$][PF$_6$]$_2$ (0.0029g) in distilled acetone (10cm^3). The acetone was evaporated off by swirling and water (10cm^3) added. The solution was stirred for 5 mins before a Nafion strip was added and the mixture stirred for 90 mins.   UV/Vis = 316(sh), 300, 248nm.   IR = 2105, 2054cm^{-1}

[Ru(bpy)$_2$(CO)Cl][ClO$_4$] : A solution was prepared by dissolving [Ru(bpy)$_2$(CO)Cl][ClO$_4$] (0.0021g) in acetonitrile (10cm^3) which was evaporated off. H$_2$O (10cm^3) was added and the Nafion strip stirred for 90 mins. IR = 2005cm^{-1}. UV/Vis = 264, 353(sh), 415(sh)nm

[Ru(bpy)$_2$(CO)H][PF$_6$] : [Ru(bpy)$_2$(CO)H][PF$_6$] (0.0026g) was dissolved in H$_2$O/ 0.2M NaOH/ CH$_3$CN (v/v:30cm^3) and the solution stirred for 5 mins. A Nafion strip was stirred in this solution for 90 mins. IR = 1960cm^{-1}. UV/Vis = 450, 350, 272nm

[Ru(bpy)(CO)$_2$Cl$_2$] : [Ru(bpy)(CO)$_2$Cl$_2$] (0.0022g) was heated in boiling water (50cm^3) for 10 mins. A Nafion strip was added and stirred for 2 hrs. IR = 2100, 2038cm^{-1}. UV/Vis = 306nm

3.6 Photolysis

All irradiation was carried out using a 250W medium pressure mercury lamp. The apparatus was set up to include a quartz water bath as filter. Samples were placed in a quartz cuvette which contained the required photolysis solvent.

REFERENCES

1. C. L Thomas " Catalytic processes and proven catalysts".
    Academic Press, New York 1970.

2. E. L. Mutterties, Inorg. Chem., 1965, 4, 1841

3. M. G. Thomas, B. F. Beier, E. L. Mutterties, J. Am. Chem. Soc.,
    1976, 98, 1296

4. P. Schutzenberger, J. Chem. Soc., 1871, 1009

5. W. Pullinger, J. Chem, Soc., 1891, 598

6. L. Mond, H. Hirtz and M. Cowap, J. Chem. Soc., 1910, 798

7. L. Mond and F. Quincke, J. Chem. Soc., 1891, 604

8. M. Berthelot, Compt. rend., 1891, 112, 1343

9. L. Mond and C. Langer, J. Chem. Soc., 1891, 1342

10. L. Pauling, J. Am. Chem. Soc., 1931, 53, 1367

11. W. Manchot and W. J. Manchot, J. Anorg. Allg. Chem., 1936, 226,
    385

12. E. R. Corey and L. F. Dahl, J. Am. Chem. Soc., 1961, 83, 2203

13. J. Chatt, B. L. Shaw and A. E. Field, J. Chem. Soc., 1964, 3466

14. M. L. Berch and A. Davison, J. Inorg. Nucl. Chem., 1973, 35, 3763

15. B. F. G. Johnson, R. D. Johnston and J. Lewis, J.Chem. Soc., 1969,
    792

16. F. A. Cotton and B. F. G. Johnson, Inorg. Chem., 1964, 3, 1609

17. W. Manchot and J. Koenig, Chem. Ber., 1924, 57B, 2130

18. R. J. Irving, J. Chem. Soc., 1956, 2879

19. W. Hieber and H. Heusinger, J. Inorg. Nucl. Chem., 1957, 4, 179

20. W. Hieber and P. John, Chem. Ber., 1970, 103, 2161

21. B. F. G. Johnson, R. D. Johnston, P. L. Josty, J. Lewis and I. C.
    Williams, Nature, 1967, 213, 901

22. S. C. Grocott and S. B. Wild, Inorg. Chem., 1982, 21, 3535

23. T. A. Stephenson and G. Wilkinson, J. Inorg. Nucl. Chem.,1966, <u>28</u>, 945

24. J. V. Kingston, J. W. S. Jamieson and G. Wilkinson, J. Inorg. Nucl. Chem., 1967, <u>29</u>, 133

25. M. I. Bruce and F. G. A. Stone, J. Chem. Soc.(A)., 1967, 1238

26. B. F. G. Johnson, J. Lewis and I. E. Ryder, J. Chem. Soc. Dalton Trans., 1977, 719

27 D. St. C. Black, G. B. Deacon and N. C. Thomas, Aust. J. Chem., 1982, <u>35</u>, 2445

28. L. Ruiz-Ramirez, T. A. Stephenson and E. S. Switkes, J. Organomet. Chem., 1973, <u>49</u>, C77

29. J. M. Clear, J. M. Kelly, C. M. O'Connell, J. G. Vos, C. J. Cardin, S. R. Costa and A. J. Edwards, J. Chem. Soc. Comm., 1980, 750

30. G. Sprintschnik, W. K. Sprintschnik, P. P. Kirsch and D. G. Whitten, J. Am. Chem. Soc., 1977, <u>99</u>, 4947

31. J. M. Kelly and J. G. Vos, Angew, Chem. Int. Ed. Eng., 1982, <u>21</u>, 628

32. D. St. C. Black, G. B. Deacon and N. C. Thomas, Trans. Met. Chem., 1980, <u>5</u>, 317

33. D. Choudhury, R. F. Jones, G. Smith and D. J. Cole Hamilton, J. Chem. Soc. Dalton Trans., 1982, 1143

34. A. D. King, Jr, R. B. King and D. B. Yang, J. Am. Chem. Soc., 1981, <u>103</u>, 2699

35. A. D. King, Jr, R. B. King and E. L. Sailers, J. Am. Chem. Soc., 1981, <u>103</u>,1867

36. R. M. Laine, R. G. Reinker and P. C. Ford, J. Am. Chem. Soc., 1977, <u>99</u>, 252.

37. D. J. Cole Hamilton, J. Chem. Soc. Chem. Comm, 1980, 1213
D. Choudhury and D. J. Cole Hamilton, J. Chem. Soc. Dalton Trans., 1982, 1885

38. T. Yoshida, Y. Ueda and S. Otsuka, J. Am. Chem. Soc., 1973, 100, 3941

39. T. G. Appleton, H. C. Clark and L. E. Menzer, Coord. Chem. Rev., 1973, 10, 335

40. H. Ishida, K. Tanaka, M. Morimoto and T. Tanaka, Organometallics, 1986, 5, 724

41. K. E. Inkrott and S. G. Shore, J. Am. Chem. Soc., 1978, 100, 3954

P. C. Ford, R. G. Rinker, C. Ungerman, R. M. Lain, V. Landis and S. A. Moya, J. Am. Chem. Soc., 1978, 100, 459

K. E. Inkrott and S. G. Shore, Inorg.Chem., 1979, 18, 281

D. C. Gross and P. C. Ford, J. Am. Chem. Soc. 1985, 107, 585

J. C. Bricker, C. C. Nagel, A. A. Bhattacharyya and S. G. Shore, J. Am. Chem. Soc., 1985, 107, 377

42. A. D. King, Jr, R. B. King and D. B. Yang, J. Am. Chem. Soc., 1980, 102, 1028

43. B. H. Weiller, J. P. Liu and E. Grant, J. Am. Chem. Soc., 1985, 107, 1595

44. W. A. R. Sleigeir, R. S. Sapierza, R. Rayford and L. Lam, Organometallics, 1982, 1, 1728

D. J. Darensbourg, M. B. Fiocher, R. E. Schmidt, Jr and B. J. Baldwin, J. Am. Chem. Soc., 1981, 103, 1297

D. J. Darensbourg and D. Drew, J. Am. Chem. Soc., 1976, 98, 275

45. M. Pineri and A. Eisenberg "Structure and Properties of Ionemers", Nato, ASI Series C, No.198, (Reidel) (1987)

46. A. Eisenberg, Macromolecules, 1970, 3, 147

47. "Ions in polymers" ACS Symposium Series No.187, Ed. by A. Eisenberg (Am. Chem. Soc.) 1982

48. W. Y. Hsu and T. D. Gierke, Macromolecules, 1982, 15, 101

49. H. L. Yeager and A. Eisenberg, Eds., "Perfluorinated Ionomer Membrane Adv. Chem. Ser. No. 180", Amer, Chem, Soc., Washington D.C, 1981, 283

50. J. M. Kelly, C. M. O'Connell and J. G. Vos, Inorg. Chim. Acta, 1982, 64, L75

51. T. R. Weaver, T. J. Meyer, S. A. Adayemi, G. M. Brown, R. P. Eckberg, W. E. Hatfield, E. C. Johnson, R. W. Murray and D. J. Unterecker, J. Am. Chem. Soc., 1975, 97, 2039

52. C. M. O'Connell, PhD Thesis, Dublin

53. J. M. Kelly, C. M. O'Connell and J. G. Vos, J. Chem. Soc. Dalton Trans., 1986, 253

54. R. W. Callahan and T. J. Meyer, Inorg. Chem., 1977, 16, 574

55. P. C. Lee and D. Meisel, J. Am. Chem. Soc., 1980, 102, 5477

56. N. J. Turro and P. C. Lee, J. Phys. Chem., 1982, 86, 17

57. D. Krenska, S. Abdo, H. Van Damme, M. Cruz and J. J. Fripiat, J. Phys. Chem., 1980, 84, 2447

58. P. S. Braterman Ed., "Metal Carbonyl Spectra", Academic Press, 1975

59. S. Wajda and K. Rachlewicz, Inorg. Chim. Acta., 1977, 16, 574

60. B. Durham, S. R. Wilson, D. J. Hodgson and T. J. Meyer, J. Am. Chem. Soc., 1980, 102 , 600

61. R. A. Krause, Inorg. Chim. Acta., 1977, 22, 209

62. W. M. Wallace and P. E. Haggard, Inorg. Chem., 1979, 18, 2934

63. M. Muniz-Miranda, E. Castellucci, N. Neto and G. Sbrana, Spectrochim. Acta., 1983, 39A, 107

64. G. M. Bryant, J. E. Fergusson and H. K. J. Powell, Aust. J. Chem., 1971, 24, 257

65. D. A. Buttry and F. C. Anson, J. Am. Chem. Soc., 1983, 105, 685

66. D. McCormack, PhD. Thesis, Dublin