AN INVESTIGATION OF THE REACTIVITY

AND CHROMATOGRAPHIC SEPARATION OF

SOME RUTHENIUM BIS (2,2'-BIPYRIDYL)

COMPOUNDS

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A Submission for the Degree of M.Sc.

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September 1988.

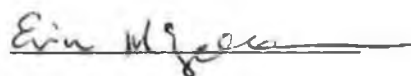This work is dedicated to the memory of my mother, Cecilia, and also to the rest of my family.

ACKNOWLEDGEMENTS

DECLARATION

I declare that the work described within this
thesis is all my own work.

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PREFACE

This thesis is divided into two distinct parts.
Part 1 concerns the synthesis of [Ru(bpy)$_2$(CO)H] PF$_6$
½C$_3$ H$_6$O. A brief examination of some of the reaction
chemistry of this complex is followed by a detailed
kinetic investigation into the reaction of [Ru(bpy)$_2$(CO)H]
PF$_6$. ½C$_3$ H$_6$O with benzaldehyde in acetonitrile with acetic
acid present as catalyst.

Part II is a high performance liquid chromatography
(HPLC), investigation of a number of cationic ruthenium
(II) bis(2,2'-bipyridine) complexes in particular
[Ru(bpy)$_2$ (HIm) Cl]$^+$, [Ru(bpy)$_2$(HIm)$_2$]$^{2+}$, [Ru(bpy)$_2$(VIm)Cl],$^+$
[Ru(bpy)$_2$(VIm)$_2$]$^{2+}$, [Ru(bpy)$_2$(CO)Cl]$^+$ and [Ru(bpy)$_2$(CO)H]$^+$,
(where HIm = imidazole ligand; VIm = vinylimidazole).
The photochemical reactions of some of these complexes are
investigated using HPLC, as a demonstration of the appli-
cations of the HPLC system developed.

The two parts are treated as completely separate
for the purposes of simplicity but where possible repetition
has been avoided. A number of the references are relevant
to both sections and these are listed separately in
each reference section.

PART I

A Kinetic investigation of the acid catalysed reaction
of [Ru(bpy)$_2$(CO)H] PF$_6$. $\frac{1}{2}$ acetone with Benzaldehyde
in acetonitrile.

INTRODUCTION

EXPERIMENTAL

PART II:

High Performance Liquid Chromatography (HPLC) of Cationic

Ruthenium (II) Bis (2,2' - bipyridine) compounds.

INTRODUCTION

AN INVESTIGATION OF THE REACTIVITY AND CHROMATOGRAPHIC SEPARATION OF SOME BIS (2,2'-BIPYRIDYL) COMPOUNDS

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ABSTRACT

The complex $[Ru(bpy)_2(CO)H]PF_6.1/2Acetone$ was synthesised in 50% yield. The reaction of this complex with a number of aldehydes, ketones and esters in buffered aqueous media and in an acidic acetonitrile environment revealed the reactivity to decrease in this order:

Aldehydes > Ketones > Esters

A kinetic study into the general acid catalysed reaction of this hydride complex with benzaldehyde was carried out and a rate coefficient of $1.3 \quad 10^{-2} mol^{-2} l^2 s^{-1}$ was calculated. An activation energy of $11.5 kJmol^{-1}$ was calculated. High Performance Liquid Chromatography (HPLC) was used to demonstrate the conversion of $[Ru(bpy)_2(CO)H]^+$ to $[Ru(bpy)_2(CO)Cl]^+$ in acetonitrile by addition of HCl.

Reverse phase ion pair chromatography (RP.IPC) and cation exchange chromatography were used for the analysis of ruthenium bis (2,2'-bipyridyl), (bpy), complexes using a range of mobile phases with lithium perchlorate, $(LiClO_4)$, as an additive. A C18 and a CN column were not suitable for the analysis due to peak distortion problems. A cation exchange, (CX), column provided a useful method for the separation of these compounds. Plots of %acetonitrile, (MeCN), vs. retention time at given $LiClO_4$ concentration suggested a change in the dominant retention mechanism, possibly from cation exchange to RP.IPC with increasing water content in the mobile phase. The presence of split peaks for the dicationic complexes at 80%MeCN : $20\%H_2O$; $0.1M$ $LiClO_4$ as mobile phase was attributed to competing retention mechanisms. The optimum system for the separation of the compounds examined was 80%MeCN : $20\%H_2O$; $0.08M$ $LiClO_4$ at a flow rate of 2.5ml/min.

The Photolyses of $[Ru(bpy)_2L_2]2+$ and $[Ru(bpy)_2(L)Cl]^+$, (L = imidazole / vinylimidazole), in MeCN was studied on an ODS and a CX column using the system developed. The ligand was replaced in these reactions to give $[Ru(bpy)_2(MeCN)_2]^{2+}$ for the dicationic compounds and $[Ru(bpy)_2(MeCN)Cl]^+$ for the monocationic compounds as the major final products. Other unidentified products were present in significant levels. The potential applications of HPLC in the study of ruthenium bis (2,2'-bipyridine) complexes were demonstrated by these experiments.

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<u>PART   I</u>

A Kinetic Investigation of the Acid
Catalysed Reaction of $[Ru(bpy)_2(CO)H]$ PF_6 .
½ Acetone with Benzaldehyde in Acetonitrile.

INTRODUCTION

A.   RUTHENIUM : PROPERTIES, APPLICATIONS AND CHEMISTRY

In 1804 Fourcray and Vauquelin, [1], observed that an azure blue solution was formed upon treatment of certain solutions of known platinum metals with zinc. This was due to ruthenium, Ru, but incorrectly ascribed as due to the presence of iridium, [2]. In the early 1840's Carl Ernst Claus isolated a new metal from residues being produced by the St. Petersburg refinery which treated platinum from the Urals, [3]. He named this new metal ruthenium.

Ruthenium is a rare earth metal with an abundance in the earths crust of ca.10^{-3} ppm. The main sources of the element along with other platinum metals are in native alloys. The principal use of ruthenium is for hardening alloys with palladium and platinum and alloys with platinum have use as electrical contacts. Ruthenium metal also has applications as a catalyst e.g. for the hydrogenation of alkenes and ketones, [4].

Numerous specific ruthenium complexes also have
applications as catalysts. There has been research
into the role of ruthenium complexes such as cis -
[Ru(dmso)$_4$Cl$_2$] into their possible role as anti-
tumour agents [5]. Ruthenium is a 2nd row transition
metal in group VIIIA of the periodic table under
iron and above osmium. It has an atomic number of
44, an atomic weight of 101.07 and an electronic
configuration of [Kr](4d)^7(5S)^1. It posseses seven
stable isotopes and melts at 2310°C. The chemistry
of ruthenium is particularly significant in view of
its ability to exist in a wide range of oxidation
states in complex, [Ru(0) to Ru (VIII)]. A review
by Griffiths covers the literature up to 1966 [6].
A comprhensive monograph on the chemistry of ruthenium
by Seddon and Seddon was published in 1984 [7].

The I oxidation state is of relatively little
importance for ruthenium but the chemistry of the 0
oxidation states is primarily of metal carbonyls.
For the II state an enormous number of complexes are
known, in particular those of π acid, chloro and
amine ligands. Extensive chemistry with both π acid

2.

and σ-donor ligands exist for the III state. The
chemistry of ruthenium IV and higher oxidation states
is mainly that of oxides such as ruthenium tetraoxide.
The general chemistry of ruthenium is described by
Cotton and Wilkinson [8].

B. RUTHENIUM (II) (2,2' - BIPYRIDINE) COMPLEXES

The study of ruthenium compounds had
traditionally related to their application as catalysts.
Recently interest has focussed on their involvement
in reactions which involve electron transfer.

Since 1976, ruthenium complexes of
2,2'-bipyridine, (bpy) and related ligands such as
1,10-phenanthroline, (phen), have attracted more
research than any other class of ruthenium complexes
[9,10]. This applies especially to tris (2,2'-
bipyridine) - ruthenium (II), ([Ru (bpy)$_3$]$^{2+}$) [Fig. 1.1.]
This was because of the unusual combination of photo-
chemistry, electrochemistry and chemical stability of
ruthenium 2,2'- bipyridyl complexes which led to
them being considered as potentially applicable as
photocatalysts for the photodissociation of water to
its elements by sunlight. The interest in these
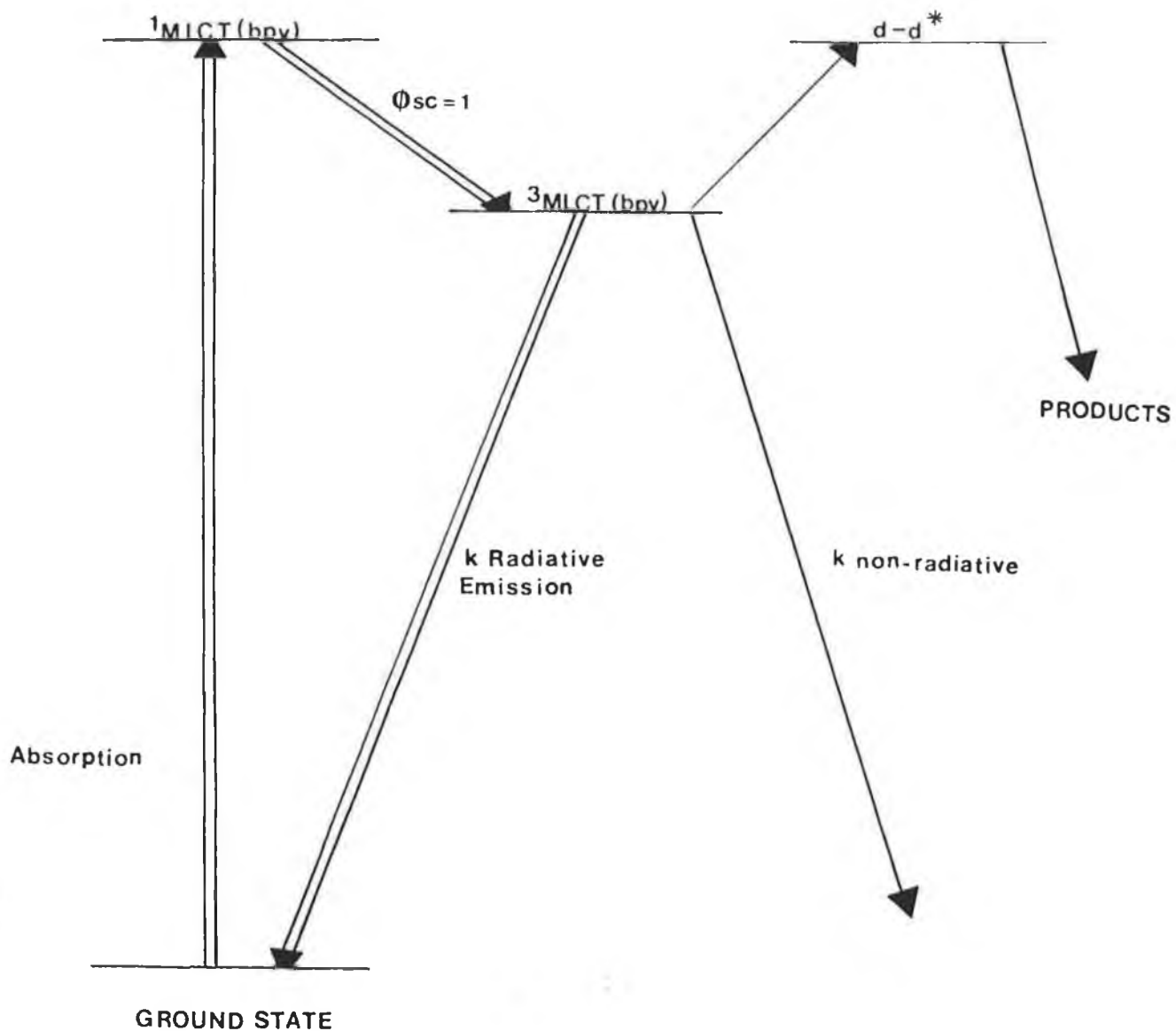
Fig. 1.1 The Excited State Manifold of $[Ru(bpy)_3]^{2+}$

studies was precipitated by the oil crisis in the
early seventies, as such a system would potentially
prove an extremely useful system for the storage of
solar energy.

In 1976 it was reported that $[Ru(bpy)_3]^{2+}$
did act as a photosensitiser for photodissociation of
water by sunlight [11].

$$2H_2O \xrightarrow[{[Ru(bpy)_3]^{2+}}]{Sunlight} 2H_2 + O_2 \qquad \text{Reaction 1.1}$$

However other laboratories and indeed the
authors themselves could not reproduce these results,
[12,13]. It was suggested that a bis-(2,2'-bipyridine)
ester derivative of $[Ru(bpy)_3]^{2+}$ present in the
surfactant monolayer as an impurity might have been
responsible [14] and these compounds received much
interest [15,16]. The focus of attention shifted
from $[Ru(bpy)_3]^{2+}$ to compounds of the general formula
$[Ru(bpy)_2 XY]^{n+}$ where X and Y may be a number of
different ligands. A great deal of information on
the reaction chemistry, electrochemistry and the
photochemistry of these complexes has been obtained,
[17], and the nature of the metal to ligand charge
transfer (MLCT), excited state is better understood [18].

Many of the new complexes of the structure $[Ru(bpy)_2 XY]^{n+}$ prepared in the search for an efficient photocatalyst to dissociate water have revealed interesting properties and applications in other areas apart from solar energy.

In recent years many ruthenium containing polymeric materials have been synthesised, [19], and their electrochemical, photochemical and photophysical properties examined. Very thin films of polymers such as these have been applied to the surface of solid electrodes to create a modified electrode, [20,21]. This enables the control of electrochemical processes at electrode surfaces. Polymer modified electrodes also have application in the storage of solar energy. Upon irradiation of the modified electrode with sunlight electron transfer produces an electric current.[20]

C. CARBONYL COMPOUNDS OF Bis (2,2' BIPYRIDINE) RUTHENIUM (II)

In the search for an efficient catalyst to achieve the photodissociation of water by solar energy many complexes of the general formula $[Ru(bpy)_2 XY]^{n+}$ were prepared. Some of these complexes were found to have interesting properties and applications in areas

other than solar energy. This is true in particular, for bis(2,2' - bipyridine) ruthenium (II) complexes containing a carbonyl group. Carbonyl halide derivatives of ruthenium (II) have received the bulk of this research [22 - 24]. One compound which has been used as a precursor for the synthesis of many ruthenium bis-2,2'-bipyridyl complexes is $[Ru(bpy)_2(CO)Cl]^+$ This complex was first reported in 1973 by Ruiz-Ramirez et al.[25].$[Ru(bpy)_2(CO)Cl]^+$ initially attracted interest as it was reported to be a side product in the synthesis of Ru $(bpy)_2Cl_2$. $2H_2O$ [26]. The method of preparation used to make the dichloride was that used to synthesise it as a starting material for the $[Ru(bpy)_3]^{2+}$ surfactant preparation by which the photo-dissociation of water by sunlight was achieved [11]. This led to speculation that it may have been present in the original surfactant layer of $[Ru(bpy)_3]^{2+}$ used.

Clear et al., prepared $[Ru(bpy)_2(CO)Cl]$ ClO_4 by synthesising $Ru(bpy)_2Cl_2 2H_2O$ from ruthenium trichloride and adding sodium perchlorate to the mother liquor after Ru $(bpy)_2$ Cl_2. $2H_2O$ had been removed, [26]. The final product was isolated in a 30-40% yield based on the ruthenium trichloride. The substitution of the carbonyl group by a solvent molecule, (e.g.

Methanol, (MeOH), or acetonitrile (MeCN)] when
irradiated with UV light and the substitution of the
chloride by a number of different molecules, (e.g.
MeCN, 4-Methylpyridine), when heated was also reported
in this paper.

In 1980 $[Ru(bpy)_2 (CO) Cl]^+$ was found to
photocatalyse the water-gas shift reaction, (WGSR), [27].

$$CO + H_2O \quad \underrightarrow{Catalyst} \quad H_2 + CO_2 \qquad \text{Reaction 1.2.}$$

Irradiation of aqueous solutions of
$[Ru(bpy)_2 (CO) Cl] Cl$ with visible light at 100°C in
the presence or absence of air produced hydrogen, but
no oxygen. CO and CO_2 were also products and therefore
this was a case of photochemical water-gas shift
reaction rather than a straight forward photodissociation
of water. Under 1 atmos. of carbon monoxide the reaction
was catalytic although slow. Detailed investigation
into the mechanism has been carried out. Choudhury
and Cole-Hamilton showed the reaction to be pH dependent
[28].   They concluded that CO_2 was produced thermally
while H_2 was photochemically produced in the rate
determining step. Tanaka et al., [29], proposed a
mechanism for this reaction at about 150°C which
included $[Ru(bpy)_2(CO)H]^+$ as an important intermediate

(RXN Scheme 1.3) Later work supported this as a likely

mechanism when the compound $[Rh(bpy)_2(CO)H]^+$ was

implicated as the catalyst in an investigation of

homogeneous catalysts of WGSR by (polypyridine)

rhodium complexes [30]. Kinetic investigations of

$[Ru(bpy)_2(CO)H]^+$ also supported this mechanism, [31].

Choudhury et al., synthesised a number of

cationic ruthenium carbonyl and dicarbonyl complexes

including $[Ru(bpy)_2(CO)Cl]^+$ and investigated the

spectroscopic properties of these compounds [32].

Kelly et al., used $[Ru(bpy)_2(CO)Cl]^+$ as a starting

material for the preparation of a wide range of

carbonyl

Reaction Scheme 1.3

Mechanism for the Water-Gas Shift Reaction

catalysed $[Ru(bpy)_2(CO)Cl]^+$ as proposed by

Tanaka et al [37]

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

CO

$[Ru(bpy)_2(CO)_2]^{2+}$ $\xrightarrow{OH^-}$ $[Ru(bpy)_2(CO)COOH]^+$ $\quad$ CO$_2$

OH$^-$

OH$^-$ $\quad$ H$^+$

$[Ru(bpy)_2(CO)(COO^-)]^+$

containing complexes of ruthenium (II) [33]. This
included [Ru(bpy)$_2$(CO) H$_2$O]$^{2+}$ which is believed to
be a key intermediate in the water-gas shift reaction
catalysed by [Ru(bpy)$_2$(CO)Cl]$^+$ [29]. The spectro-
scopic, electrochemical and photochemical properties
of the complexes are examined. Ishida et al., studied
electrochemical CO$_2$ reduction which is catalysed by
[Ru(bpy)$_2$ (CO)$_2$]$^{2+}$ and [Ru(bpy)$_2$(CO)Cl]$^+$ to assess
the pH dependence on the formation of CO and HCOO$^-$ [34].
Other carbonyl containing compounds which have attracted
research contain one bidentate ligand and two
carbonyl moieties bound to the ruthenium [35-37].

D.   HYDRIDO COMPLEXES OF RUTHENIUM (II)
     Bis (2,2' - BIPYRIDINE)

        The first fully authenticated transition
metal complex hydrides were the carbonyl hydrides
FeH$_2$CO$_4$ and CoHCO$_4$ [38,39]. There has been much
interest since then in transition metal hydrides
because of the catalytic applications of many of these
complexes [40]. The reduction of some ketones to the
corresponding alcohols using organotin hydrides is an
example, [43]. There are many examples of hydrido-

ruthenium complexes in particular ruthenium II

phosphine hydrides such as [Ru(PPH$_3$)$_5$H] PF$_6$, [42].

Of special interest are the cationic carbonyl hydrido

complexes of ruthenium and number of compounds of

the general formula [Ru(L-L)(CO)H]$^+$ have been

reported (e.g. L-L = 1,2, - bis (diphenylphosphino)

ethane [43] or 1,3 - bis (diphenylphosphino) propane

[44]. The dehydrogenation of aldehydes using

complexes of the type RuH$_2$(CO)(PPh$_3$)(L-L) was

described by Jung and Garrou [45]. Other ruthenium

(II) hydride complexes have also been shown to be

active for the hydrogenation of aldehydes and

ketones to alcohols [46,47].

In 1982 [Ru(bpy)$_2$(CO)H]$^+$ ClO$_4$ was prepared

by treating [Ru(bpy)$_2$(CO)Cl]$^+$ in aqueous ethanol

and was proposed as a possible intermediate in the

water gas shift reaction catalysed by [Ru(bpy)$_2$(CO)Cl]$^+$

[48]. The possibility of [Ru(bpy)$_2$(CO)H]$^+$ acting

as hydrogen producing centre arose from the

observation that it rapidly decomposed in weakly acidic

solution to produce molecular hydrogen. This resulted

in speculation that [Ru(bpy)$_2$(CO)H]$^+$ may have been

an active impurity in the monolayer assemblies of

surfactant [Ru(bpy)$_3$]$^{2+}$ type derivatives which were

initialy reported to cause photodissociation of water

[11], especially as its precursor [Ru(bpy)$_2$(CO)Cl]$^+$

is a major by product in the preparation of
Ru (bpy)$_2$Cl$_2$2H$_2$O.

The electrochemcial properties of
[Ru(bpy)$_2$(CO)H]$^+$ and its analogous compound
[Os(bpy)$_2$(CO)H]$^+$ have been investigated. [49].   It
also was noted that [Os(bpy)$_2$(CO)H]$^+$ reacted with
acid in acetonitrile to form molecular hydrogen and
with a solvent molecule substituted for the hydride.

[Os(bpy)$_2$(CO)H]$^+$ + H$^+$ $\xrightarrow{\text{MeCN}}$ [Os(bpy)$_2$(CO)(MeCN)]$^{2+}$ + H$_2$

Reaction 1.4.

Sullivan et al., explored several different
routes to produce hydridocarbonyl complexes of Os (II)
and Ru (II), containing polypyridine ligands [50].
They observed how the hydride ligand endowed the
metal to ligand charge transfer (MLCT) excited states
of some of the complexes with strong reducing properties,
including [Ru(bpy)$_2$(CO)H]$^+$.

[Ru(bpy)$_2$(CO)H]$^+$ is a relatively photostable
complex and unlike most other carbonyl complexes of
ruthenium bis bipyridyl is not efficiently
decarbobylated by UV radiation, [33] [Fig 1.2].   The

12.

Fig. 1.2 The Structure of $[Ru(bpy)_2(CO)H]^+$

Cis-
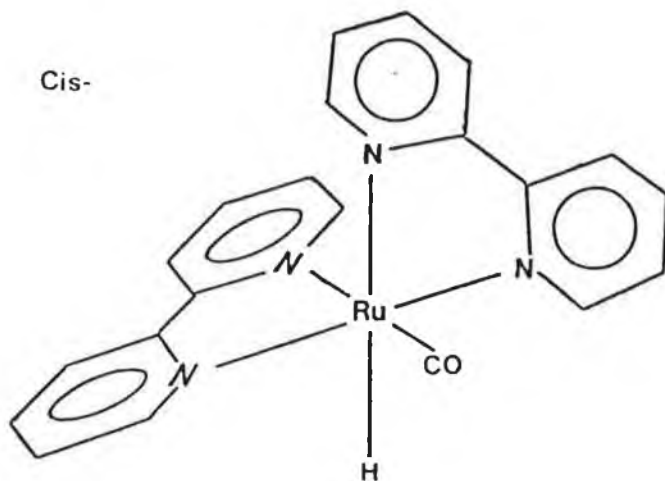
X-Ray Crystallograpghic Assignation

H on bpy
not shown
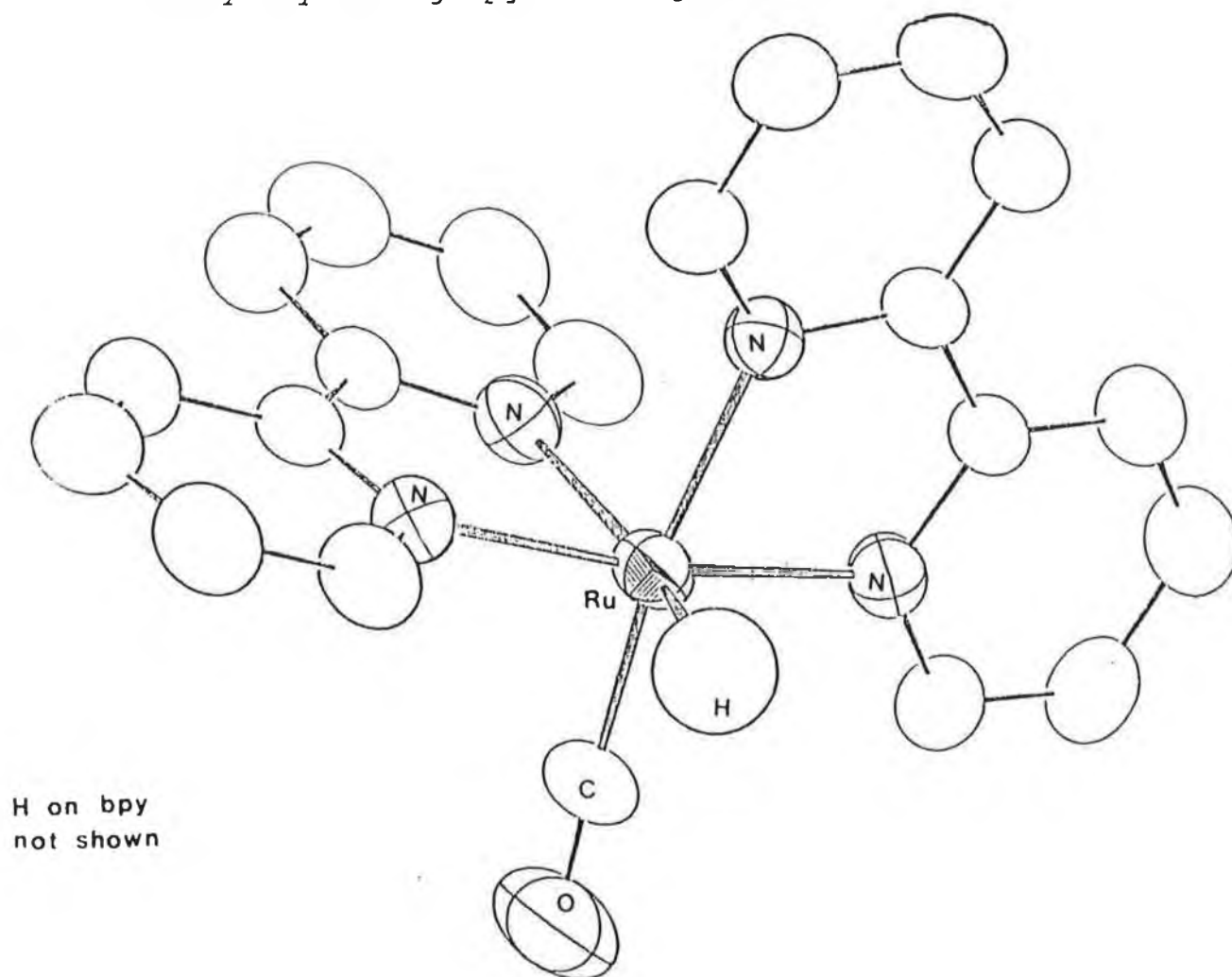
spectroscopic, electrochemical and photochemical properties of $[Ru(bpy)_2(CO)H]^+$ and other bis (2,2' - bipyridyl) - hydrido ruthenium complexes were investigated by Kelly and Vos. [51]. In aqueous acidic solution $[Ru(bpy)_2(CO)H_2O]^{2+}$ was produced.

$$[Ru(bpy)_2(CO)H]^+ + H^+ \xrightarrow{H_2O} [Ru(bpy)_2(CO)H_2O]^{2+} + H_2$$
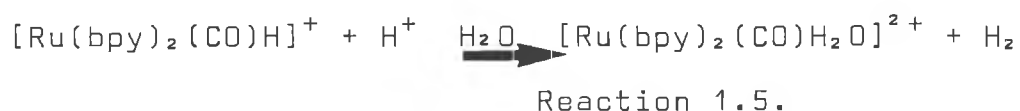
Reaction 1.5.

$[Ru(bpy)_2(CO)H]^+$ was also shown to decompose in a slightly acidic environment in the presence of acetone. The X-ray structure of $[Ru(bpy)_2(CO)H] PF_6 \cdot \frac{1}{2}C_3H_6O$ was elucidated and the kinetics for the reaction of $[Ru(bpy)_2(CO)H]^+$ (Reaction 1.5) in aqueous acid determined by Haasnoot et al., [31].

Recently a detailed kinetic investigation of the hydrogenation of acetone to propan-2-ol by $[Ru(bpy)_2(CO)H]^+$ in buffered aqueous solutions was undertaken [52]. The dependence of the pseudo-first order rate constant of the reaction, kobs, upon acetone, buffer concentration and pH was reported. A two step mechanism was proposed:-

14.

$(CH_3)_2$ CO + HA $\xrightarrow{\text{K}eq}$ $[(CH_3)_2CO \ldots\ldots HA)$ Reaction 1.6.
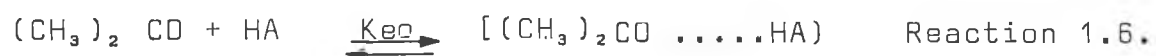
where HA = H_3O^+ and/or undissociated acid.

$[(CH_3)_2$ CO $\ldots$.HA] + $[Ru(bpy)_2(CO)H]^+$ $\xrightarrow[\text{K}]{H_2O}$

   $(CH_3)_2CHOH$ + $[Ru(bpy)_2(CO)H_2O]^{2+}$
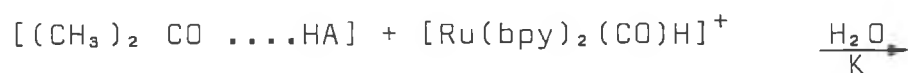
                                    Reaction 1.7.

No temperature dependence of the reaction was observed.

E. KINETIC STUDIES OF CHEMICAL REACTIONS

        Knowledge of the rate of a chemical reaction
is of fundamental importance to the understanding of
the nature of the reaction [53,54]. The rate of a
chemical reaction is governed by the reaction
conditions e.g. temperature, pressure, and species
present. The study of reaction rates may enable
optimization of conditions to exert control over the
progress of a reaction to its equilibrium state. The
reaction mechanisms may be revealed by studying reaction
rates. The rates may be measured by monitoring
pressure changes or using techniques such as
spectroscopy, electrochemical methods, polarimetry

and chromatography.

The rate of a chemical reaction may be expressed as the rate of change of any of the species. If this differs for different species in a reaction the species by which we define the rate of reaction must be stated. For a reaction in which

A + 2B $\longrightarrow$ 3C + D   Reaction 1.8.

the rates of each components are as follows:-
$-d[A]/dt = -\frac{1}{2}d[B]/dt = 1/3d[C]/dt = d[D]/dt$ Eqn 1.1.

The rate may be chosen as $d[A]/dt$ or $d[C]/dt$ etc and may relate to the concentration or a power of the concentration of one or more species. This is related to the rate by a factor known as the rate constant. For instance the rate of the above reaction might obey.

$-d[A]/dt = K[A][B]$ Eqn. 1.2.

or it might obey:

$-d[A]/dt = K[A][B]^2$ Eqn. 1.3.

This is the rate law for the reaction. Given
the experimental value of the rate constant and the
reaction conditions, the statement of the rate law
permits the prediction of the rate. It also aids
in the establishment of the mechanism which must
conform to the rate law. The rate law also allows
the classification of a reaction into its 'order'.

The order of a reaction is the power to which
the concentration of a species is raised in the rate
law. A reaction obeying the rate law given in Eqn 1.3.
is first order in A and second order in B. The
overall order for a reaction is the sum of the orders
for the individual components and hence the reaction
in this case is third order overall. The rate law
for a reaction can only be derived by experiment.

The rate law for the first order reaction

$$-d[A]/dt \quad = \quad K[A] \qquad\qquad \text{Eqn. 1.4.}$$

is the simplest rate law.
This can be rearranged to

$$-(1/[A]) \quad d[A] \quad = \quad K.dt \qquad\qquad \text{Eqn. 1.5.}$$

This can be integrated directly to result in the
equation:

$$[A]t \quad = \quad [A]o \quad \exp(-kt) \qquad\qquad \text{Eqn. 1.6.}$$

or,

$$\ln[[A]t \, / [A]o] \quad = \quad - kt \qquad\qquad \text{Eqn. 1.7.}$$

here, $[A]o$ is the initial concentration of A and
$[A]t$ is the concentration of A at time $= t$.

Measurement of the initial slopes of the
concentration of given components for a reaction
provides a direct method for the determination of the
rate law.   For a reaction between two compounds, A and
B, where there is known to be no other species involved
the rate law may be written as:-

$$- d[A]/dt \quad = \quad K \, [A]^a \, [B]^b \qquad\qquad \text{Eqn. 1.8.}$$

At the beginning of the reaction the rate is:-

$$- (d[A]/dt) \quad = \quad K \, [A]^a_o \, [B]^b_o \qquad\qquad \text{Eqn. 1.9.}$$

where $[A]o$ and $[B]o$ are the initial concentrations of
A and B respectively.   This may be written as:-

$$\lg[-[d[A]/dt] \, \text{init}] \quad = \quad \lg K + a\lg[A]o + b\lg[B]o \qquad \text{Eqn. 1.10.}$$

By plotting the slope of the tangent of the initial
change in concentration of A, $\lg[-(d[A]/dt)\text{init}]$,
against Ao and Bo the order of reaction can be calculated
from the initial slopes.   The intercept allows the
rate constant, k, to be calculated.

In 1926 Guggenheim described a method where
the concentrations of the components is not necessary
for the elucidation of the rate constant [55]. The
course of the reaction may be followed by measurement
of some physical property of the system, $\emptyset$, which
varies with time according to the equation.

$$(\emptyset_{(\infty)} - \emptyset_{(t)}) = (\emptyset_{(\infty)} - \emptyset_{(o)}) \exp (-kt) \qquad \text{Eqn. 1.11.}$$

By plotting $\ln ((\emptyset_{(\infty)} - \emptyset_{(t)}) / (\emptyset_{(\infty)} - \emptyset_{(o)}))$
against time a slope of -k is obtained for a first
order reaction. However if the concentrations of all
the components are much greater than the species by
which the rate is defined the reaction behaves in
a pseudo first order manner. This is because the
other components are in large excess and so their
concentrations do not change significantly through
the course of the reaction. Using the same plot as
for a first order reaction yields a slope of -Kobs.
Kobs includes the concentration of the other components
in its value e.g. for Reaction 1.8.

$$\text{Kobs } [A] = K [B]^2 [A] \qquad \text{Eqn. 1.12.}$$

If the rate law stated in Eqn. 1.3 is correct by individually varying the concentration of the components in excess, in this case [B], and plotting against Kobs, the rate constant can be calculated, from the slope.

Arrhenius proposed an equation which describes the temperature dependence of a reaction:-

$$K_2 = A \exp (-Ea/RT) \qquad \text{Eqn. 1.13.}$$

where A = preexponential factor (independent of temperature).

$\qquad$ Ea = activation energy

$\qquad$ R = universal gas constant

rearranged this gives:-

$$\ln K_2 = \ln A - [Ea/RT] \qquad \text{Eqn. 1.14.}$$

A plot of $\ln K_2$ vs 1/T gives a slope of -Ea/R and an intercept of lnA. This is known as an Arrhenius plot and if a reaction yields a straight line graph it is said to exhibit Arrhenius type behaviour. [54].

EXPERIMENTAL

A. APPARATUS AND MATERIALS:

Previously described methods were used to synthesise $[Ru(bpy)_2(CO)Cl] ClO_4$ [26], and the precursor for the synthesis of $[Ru(bpy)_2(CO)H] PF_6$. $\frac{1}{2}C_3H_6O$; $Ru (bpy)_2Cl_2. 2H_2O$ [56]. All chemicals used were of analytical grade. All water used was passed through a millipore ion exchange system after distillation. The pH for kinetic studies in aqueous systems was controlled using Britton-Robinson buffer.

Kinetic data were obtained using computer linked UV/VIS spectrophotometry. Two spectrophotometers were used for this purpose. A Shimadzu UV-240 UV-visible recording spectrophotometer with a graphic printer PR-1 was interfaced to the computer by a Shimadzu option program/interface OPI-1. A Pye Unican SP8-100 UV/VIS spectrophotometer was interfaced to the computer by an 'ICI' Rexagan Interface system. A Commodore 8032-SK computer and Commodore CBM Model 8050 Dual Drive Floppy Disk was used and the results printed on a Commodore Tractor Printer 4022P. The temperature of the sample cells was controlled by a Heto water bath (±2°C).

Infrared spectra were obtained using a Perkin Elmer 983G infrared sepctrophometer. Gas chromatography was performed with a Pye Unican 4550 gas chromatograph and a Carlo Erba Stumentazione MEGA series integrator. The pH of aqueous solutions was monitored using a PTI-6 Universal Digital pH meter.

The equipment and materials used to perform HPLC analysis are described comprehensively in the experimental section of Section II.

A stock solution of $[Ru(bpy)_2(CO)H] PF_6$ in acetonitrile for kinetic studies was prepared by dissolving 15 mg of the complex in 10 mls of acetonitrile $(2\cdot43 \times 10^{-3}M)$. Stock solutions of acetic acid in acetonitrile of 0.14**M** to 0.84**M** were prepared by diluting the appropriate measure of glacial acetic acid with acetonitrile.

B. THE SYNTHESIS OF $[Ru(bpy)_2(CO)H]PF_6 \cdot \frac{1}{2}$ ACETONE

$[Ru(bpy)_2(CO)H] PF_6 \cdot \frac{1}{2} C_3H_6O$ was synthesised using $Ru(bpy)_2Cl_2 2H_2O$ as a precursor. The method used was a modification of a previously described method [51]. One gramme of $Ru(bpy)_2 Cl_2 2H_2O$ was

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refluxed in 100 ml of ethylene glycol and carbon monoxide bubbles through the solution until the solution turned yellow, after approximately $2\frac{1}{2}$ hours. Addition of excess NH_4PF_6 was used to crystallise out the $[Ru(bpy)_2(CO)Cl]PF_6$ product. 1.17 g of this product was obtained (93% yield). This was characterised by infrared spectroscopy. The dried crystals were redissolved in 150 ml of refluxing ethanol : water (2:1 v/v) and 1.4 g of $NaBH_4$ in 6.5 ml of water was added slowly to the solution while still hot. After twenty minutes to allow the reaction to go to completion 600 mg of NH_4PF_6 in 30 ml of water and was added to the solution, cooled to allow crystallization. The crystals were collected and washed with water to remove excess NH_4PF_6. The product was recrystallized from acetone-water by allowing the acetone to evaporate from the mix at room temperature over 3 days. 0.6 g of crystalline product were collected and dried, (yield = 50%) UV/Visible, infrared spectroscopy, and were used to characterise the product.

The purity and authenticity of synthesised complexes were further demonstrated using high performance liquid chromatography HPLC. The complexes were analysed using C_{18}, CX and CN columns. The mobile

phase consisted of MeCN : H_2O; $LiClO_4$. The methods used are described in Part II of this thesis. HPLC was used to determine the effect of the addition of 1 drop of concentrated HCl to 3 ml of 2.4×10^{-3} M $[Ru(bpy)_2(CO)H] PF_6 \frac{1}{2} C_3H_6O$ in acetonitrile using a CN cartridge column operating in the reverse phase mode and using a cation exchange, CX, column. The operating conditions were those used to achieve separation of $[Ru(bpy)_2(CO)H]$ and $[Ru(bpy)_2(CO)Cl]^+$ and other complexes as described in Part II of this thesis.

C. KINETIC STUDY OF THE REACTION OF $[Ru(bpy)_2(CO) H] PF_6 . \frac{1}{2}$ ACETONE WITH BENZALDEHYDE

A preliminary investigation of the reaction of $[Ru(bpy)_2(CO) H] PF_6 . \frac{1}{2} C_3H_6O$ with a selection of aldehydes, esters and ketones at given pH values **was** achieved by monitoring the decay in the absorbence of the ruthenium hydride complex at its λ max of 450 nm. 0.5 ml of stock $[Ru(bpy)_2(CO) H) PF_6 .$ $\frac{1}{2}C_3H_6O$ solution was placed in a quartz cuvette and 2.5 ml Britton-Robinson buffer of known pH added. 100 µl of the reactant compound was added. The cuvette was sealed and agitated to ensure homogeneity of the sample. This was then placed in the spectrophotometer and

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the absorbance decay recorded. The time span between
initiating the reaction by the addition of reactant
and commencing the absorbance measurements was kept
to approximately 5 seconds. The decay in the
absorbance was recorded until it became insignificant.
The reactant compounds studied using this method
were propanol, ethyl proprionate, ethyl benzoate,
acetone and benzaldehyde.

An organic system for the study of these
reactions was also devised. The Britton-Robinson
Buffer was replaced by 2.5 ml of known concentrations
of acetic acid in acetonitrile. These studies were
all performed at 20°C.

An in depth kinetic investigation of the acetic
acid catalysed reaction of $[Ru(bpy)_2(CO)H]PF_6$ with
benzaldehyde in acetonitrile was undertaken using
computer linked spectrophotometry.

The reaction was initiated as described for
the organic system used to study the other reactants.
However using the computer the absorbance value was
recorded at 50 second intervals until the absorbance
decay is undetectable between the sampling times.
A correlation coefficient is calculated for the plot of
absorbance versus time and a Kobs value was computed
from the slope of the plot of ln $[(OD_0-OD_\infty)/(OD_t-OD_\infty)]$

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vs time was completed for each set of data (OD_o, OD_t, OD_∞ is the absorbance of the solution at 450 nm at time =zero;t and infinity). The final point is then removed and the process repeated for the remaining set of points. This procedure is repeated until the calculations are performed for the first four points. The procedure then terminates. The set of points which yield the maximum correlation coefficient is taken as the maximum set of points over which linearity is maintained and the Kobs value for this set of data is the value taken for the Kobs for the given reaction conditions used. Results which did not give a maximum correlation coefficient of greater than 0.9999 were rejected and the reaction repeated.

The reaction was examined with respect to acetic acid concentration, benzaldehyde concentration and temperature. These parameters were varied individually to achieve this. The initial concentration of $[Ru(bpy)_2(CO)H]^+$ in the cuvette was 4×10^{-4}M for all conditions used. Each parameter is varied with all the other parameters at standard values. The standard concentration of acetic acid in the cuvette is 0.403 M, (2.5 ml of 0.5 M acetic acid in acetonitrile). The standard concentration

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of benzaldehyde in the cuvette was 0.318 M (100 µl)
and the standard temperature 25°C. Acetic acid was
varied between 0.113 M and 0.679 M in the cuvette
(2.5 ml of 0.140 M and 0.842 M acetic acid in
acetonitrile). Benzaldehyde concentration in the
system was varied between 0.16 M and 0.542 M, (50 µl
to 175 µl). Temperatures of 20°C to 55°C were used
to determine the temperature dependence of the reaction.
Each reaction was repeated three times and the average
Kobs values taken to calculate the reaction constants.
The entire process was repeated with fresh solutions
and the more linear set of values for the reaction
constants taken.

The reaction product was identified using
isothermal gas chromatography at 95°C. A packed glass
column with 15% SE30 was used with nitrogen as the
carrier gas at a flow of 39.0 mls/min. FID detection
was used.

RESULTS AND DISCUSSIONS

UV/Vis and IR spectroscopy was used to verify that
[Ru (bpy)$_2$(CO) H] PF$_6$. $\frac{1}{2}$ C$_3$H$_6$O, (RuH) was the product
formed by the synthesis described (Table 1.1.). The
intermediate product formed in step 1 of the synthesis
was identified as [Ru(bpy)$_2$(CO) Cl] PF$_6$ using
spectroscopy. The purity of these compounds were
demonstrated by HPLC with a CX column. The retention
times for these complexes matched those of authentic
complexes. The spectroscopic data agreed with that
obtained from the literature [3]

TABLE 1.1 DATA FOR SYNTHESIS OF [Ru(bpy)$_2$(CO)H]

PF$_6$. $\frac{1}{2}$ C$_3$H$_6$O

	IR	UV/VIS	HPLC	YIELD	COMPLEX
	ν(CO)/cm^{-1}	λ Max(logε) /nm[b]	Ret.time/ min[c]	%	
Step 1.	1961	415(3.3), 353(3.7)	2.8	93.1	[Ru(bpy)$_2$(CO)Cl] PF$_6$
Step 11.	1930	448(3.5), 353(3.7)	2.0	50.4	[Ru(bpy)$_2$(CO)H]PF$_6$.$\frac{1}{2}$ C$_3$H$_6$O

a KBr disc

b In acetonitrile

c Mobile phase - 80% MeCN; 20% H2O; 0.08 m LiClO$_4$ - Flow Rate 2.5mls/min.

By recording the decay in the absorbance of
an RuH solution at 450 nm the reaction of this
compound with various carbonyl containing compounds
was monitored. These reactions were performed in
both aqueous and organic systems. The pH was
controlled in the aqueous system and the acid
concentration in the organic system to control the
reaction rate and as such allow the reaction to go to
completion in a time span which allowed the half life
to be measured. The greater the acidity of the solution
the more rapid the reaction.

TABLE 1.2. HALF LIFES FOR REACTION OF [Ru(bpy)$_2$(CO)H]

PF$_6$.$\frac{1}{2}$C$_3$H$_6$O WITH CARBONYL COMPLEXES

	Aqueous System $t_{\frac{1}{2}}$ (pH)	Organic System $t_{\frac{1}{2}}$ [(CH$_3$COOH] M)
Acetone	90min (pH(6.0)	10min (1.61M)
Pentane-3-one	---	19min (1.61M)
Propanal	140sec, (pH(8.0)	80sec ,(0.403M), 500sec , (0.081M)
Benzaldehyde	Immiscible	270sec . (0.403M)
Ethyl Propionate	Negligibe reaction, (pH 4.0)	Negligible reaction, (4.03 M)
Ethyl Benzoate	Immiscible	Negligible reaction, (4.03 M).

a - all reactions measured at room temperature.(20°C)

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The reaction rates for these compounds with
RuH show that:-

aldehydes   >   Ketones   >   esters (R,R' = Organic
                                                                    Moieties)
$RC\lesssim_O^H$ $R-C\eqdef_O^R$ $R-C\eqdef_O^O - R$
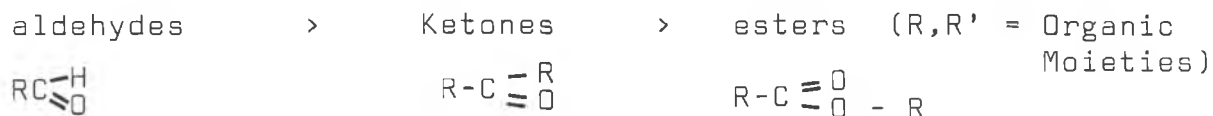
The larger more organic molecules show less
reactivity with RuH than the smaller molecules which
are less polar. This may be due to steric factors.
No reaction was seen to occur in the organic system
before addition of the reactant compound except at
very high acetic acid concentrations > 4 M. Even at
these high concentrations the reaction that occurs is
small.

HPLC showed that the reaction of
$[Ru(bpy)_2(CO)H]$ PF_6. $\frac{1}{2}$ C_3H_6O in acetonitrile with
concentrated HCl produced a product consistent with
$[Ru(bpy)_2(CO)Cl]^+$. Using both CN and CX columns and
a wide range of mobile phase the retention of the
acidified ruthenium hydride complex matched that
of a standard solution of $[Ru(bpy)_2(CO)]Cl^+$.
(Table 1.3.).

The reaction may be written:-
$[Ru(bpy)_2(CO)H]^+$ + HCL $\longrightarrow$ $[Ru(bpy)_2(CO)Cl]^+$ + H_2

Reaction 1.9.

30.
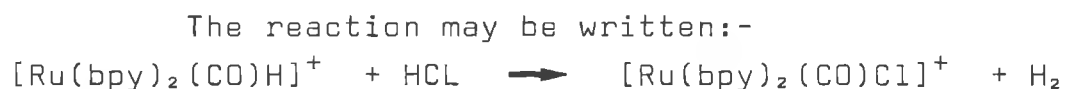
TABLE 1.3

Reaction of [Ru(bpy)$_2$(CO)H]$^+$ with HCl

HPLC Analysis: CX COLUMN   CN COLUMN
                              Detection = 254 nm   Detection = 254 nm
                              Flow Rate= 2.5 ml /min   Flow Rate= 1.5 ml /min

RETENTION TIMES (MINS)

Mobile Phases	[Ru(bpy)$_2$(CO)H]$^+$	[Ru(bpy)$_2$(CO)Cl]$^+$	Acid Treated [Ru(bpy)$_2$(CO)H]$^+$
CX COLUMN			
100% MeCN; 0.05 M LiClO$_4$	3.8	2.8	2.8
100% MeCN; 0.08 M LiClO$_4$	3.2	2.8	2.8
80% MeCN; 20% H$_2$O; 0.05 M LiClO$_4$	2.0	2.9	2.9
80% MeCN; 20% H$_2$O; 0.08 MLiClO$_4$	2.0	2.8	2.7
80% MeCN; 20% H$_2$O; 0.1 M LiClO$_4$	1.8	2.2	2.2
70% MeCN; 30% H$_2$O; 0.05 M LiClO$_4$	2.0	3.1	3.1
CN COLUMN			
100% MeOH; 0.1 M, LiClO$_4$	2.1	2.5	2.5
90% MeOH; 10% H$_2$O; 0.07 M LiClO$_4$	2.4	2.6	2.6
70% MeOH; 10% H$_2$O; 0.05 M LiClO$_4$	4.1	3.4	3.5
70% MeOH; 10% H$_2$O; 0.1 M LiClO$_4$	2.6	2.3	2.3

31.

KINETIC STUDY OF THE ACID CATALYSED REACTION OF

[Ru(bpy)$_2$(CO)H/PF$_6$. $\frac{1}{2}$ ACETONE WITH BENZALDEHYDE

IN ACETONITRILE

A large amount of kinetic data was generated
for the acid catalysed reaction of [Ru(bpy)$_2$(CO)H]
PF$_6$. $\frac{1}{2}$C$_3$H$_6$O, (RuH), with benzaldehyde, [phCHO] No
reaction occurs if the acid is not present in the
solution and insignficant reaction occurs when acid
is present and benzaldehyde is not. Each individual
reaction monitored contained phCHO and acetic acid,
HOAc, in large excess.with respect to RuH. As the
concentration of HOAc and phCHO do not change
signficantly during the course of the reaction, the
reaction may be deemed to behave in a pseudo first
order manner, i.e. the reaction rate depends entirely
on the concentration of RuH. Therefore the following
rate law holds:-

$$-d[RuH]/dt \quad = \quad Kobs \, [RuH] \qquad \text{Eqn. 1.4.}$$
$$\ln([RuH] \; /[RuH]0) \quad = \quad -Kobs.t \qquad \text{Eqn. 1.7.}$$

where [RuH]o is the initial RuH concentration
$(4\times10^{-4}M)$

[RuH]t is the RuH concentration at time t.

Using the Guggenheim method Kobs was calculated by plotting:-

$$\ln [(OD_0 - OD_\infty) / (OD_t - OD_\infty)] \quad vs \quad t \qquad \text{Eqn. 1.11.}$$

OD_0 = absorbance at t = 0 (@ 450 nm)

OD_∞ = absorbance at t = ∞ (@ 450 nm)

OD_t = absorbance at time = t (@ 450 mm)

The slope of this plot gives the value for Kobs.

The hydrogenation of acetone to propan-2-ol by RuH in buffered aqueous solutions has been investigated by Geraty et al., [52]. Using the same techniques (Guggenheim method), they showed Kobs to depend on buffer concentration as well as pH. This indicated that the reaction rate was a function of the concentrations of both dissociated and undissociated acid. The data they obtained agreed with a two step mechanism.

$$(CH_3)_2 CO + HA \xrightarrow{Keq} [(CH_3)_2 CO \dots HA] \qquad \text{Reaction 1.6.}$$

where HA stands for H_3O^+ and/or undissociated acids.
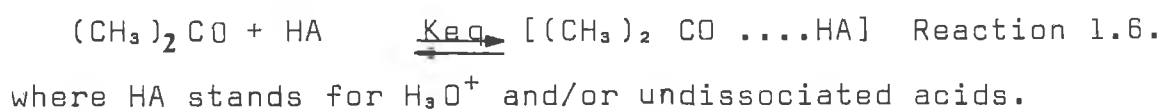
This last step is followed by a slow, rate determining, step.

$$[(CH_3)_2CO...HA] + [Ru(bpy)_2(CO)H]^+ \xrightarrow[k']{H_2O} (CH_3)_2CHOH + [Ru(bpy)_2(CO)H_2O]^{2+}$$
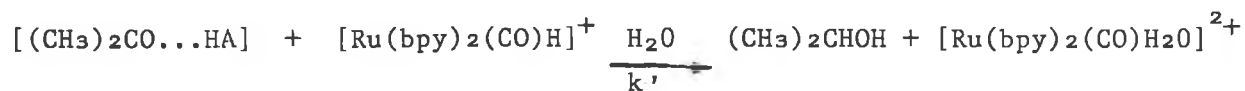
Reaction 1.7.

The reaction rate may be written as:-

rate : k' Keq $[(CH_3)_2CO]$ [HA] [RuH]   Eqn. 1.15

$= K[(CH_3)_2CO]$ [HA] [RuH]   Eqn. 1.16.

$=$ Kobs [RuH]   Eqn. 1.17.

The value of Keq was calculated from the pKa value for protonated acetone and this allowed calculation of k'.

For the purposes of this experiment, the acid-catalysed reaction of RuH with benzaldehyde in acetonitrile was assumed to follow a similar mechanism. No dissociation constant for acetic acid in acetonitrile is known to have been reported and so the dissociation is assumed to be negligible. It is also impossible to calculate a value of Keq as no value for pKa for protonated benzaldehyde in acetonitrile exists. The rate constant, **K** , calculable in this experiment is the value for the total reaction (i.e. the sum of the two steps - Keq. k').

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By plotting the Kobs values obtained at
different phCHO concentrations, Table 1.6., against
phCHO at given HOAc a slope of **K**[HOAc] is obtained.
Fig. 1.5.   This allows the calculation of the value of
K as 1.33×10^{-2} $mol^{-2} l^2 s^{-1}$. This method is similar
to those used by Allen et al., in their kinetic
studies of substitution reactions of ruthenium (II)
complexes containing 2,2' - bipyridine and 1,10 -
phenanthroline. [57].

The reaction studied here is analogous to the
reaction of $[Ru(bpy)_2(CO)H]^+$ with acetone in an acidic
environment which was maintained using Britton-
Robinson buffer [52]. GC chromatography showed that as
for the acetone reaction where the acetone was reduced
to propan-2-ol, the benzaldehyde (Ret time = 1.6 min)
in this reaction was also reduced to the corresponding
alcohol, benzyl alcohol. (Ret time = 1.4 min).
However there is no water present in this system the
ruthenium hydride is converted to $[Ru(bpy)_2(CO)MeCN]^{2+}$
rather than the H_2O containing equivalent. The overall
reaction may be written as

$$[Ru(bpy)_2(CO)H]^+ + phCHO \xrightarrow[\substack{HOAc \\ MeCN}]{K} [Ru(bpy)_2(CO)MeCN]^{2+} + phCHOH$$
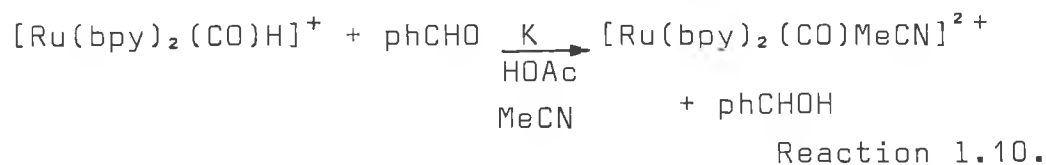
Reaction 1.10.

The rate is written as Kobs (RuH), but,

$$lg_{obs} [RuH] = K [RuH] [phCHO]^a [HOAc]^b \qquad Eqn. 1.18.$$

The initial slopes method was used to determine the order of reaction with respect to phCHO and HOAc. The following equation was used for given reaction.

$$lg[-(d[RuH]/dt)init) = lgK + alg[phCHO] + blg[HOAc]$$

Eqn. 1.10.

where, (d(RuH)/dt) unit is the slope of the initial decay of RuH.

and a and b are the orders with phCHO and HOAc respectively.

By plotting lg(-(d[RuH]/dt) init) against lg [phCHO] at a set [HOAc] concentration (Table 1.4.)[Fig. 1.3.] and against [HOAc] at a given [phCHO] concentration (Table 1.5.)[Fig. 1.4.] the values of a and b, (and thence the orders of the reaction for phCHO and HOAc), **are** obtained from the slope. The reaction is shown to be first order with respect to benzaldehyde. However, the results for HOAc yield an erratic curved plot and this suggests that the involvement of the acid in the

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reaction may be of a more complex nature. However,
assuming the reaction is in fact first order with
respect to HOAc, the following equation may be written:

$$d[RuH]/dt \quad = \quad K[RuH][PhCHO][HOAc] \qquad Eqn. \ 1.19.$$

$$= Kobs \ [RuH] \qquad Eqn. \ 1.20.$$

Determination of Order of Reaction by Initial Slopes Method
(T = 25°C).   **Table 1.4/1.5**

TABLE 1.4.   BENZALDEHYDE AT [HOAc] = 0.403**M**

[PhCHO]init M	lg[PhCHO]init	-[d(RuH)/dt)init Ms^{-1}	lg(-d(RuH)/dt)ini
0.162	- 0.790	5.7×10^{-3}	- 2.25
0.241	- 0.618	7.1×10^{-3}	- 2.15
0.318	- 0.498	9.5×10^{-3}	- 2.02
0.394	- 0.405	1.39×10^{-2}	- 1.86

For lg[PhCHO] init vs lg(-d[RuH]/dt) init)

slope = 1.03

Reaction is first order with respect to
Benzaldehyde.

TABLE 1.5. ACETIC ACID AT [PhCHO] = 0.318 m

[HOAc]init M	lg[HOAc]init	-(d[RuH]/dt)init Ms^{-1}	lg(-(d[RuH]/dt)init
0.1132	- 0.946	1.5×10^{-7}	- 6.82
0.2263	- 0.645	2.7×10^{-7}	- 6.57
0.2830	- 0.543	5.4×10^{-7}	- 6.27
0.3398	- 0.469	7.5×10^{-7}	- 6.13
0.3961	- 0.402	9.5×10^{-6}	- 6.02
0.4527	- 0.344	1.88×10^{-6}	- 5.74
0.5094	- 0.293	2.00×10^{-6}	- 5.70
0.5660	- 0.250	2.37×10^{-6}	- 5.63

For Plot of [H⁺] init vs lg (-(d[RuH]/dt) init

The results show a curved graph which is quite erratic. However a slope of **ca.**1 is obtained for the slope of the tangent at the lower concentrations of acid.

Fig. 1.3 The Determination of the Order of Reaction w.r.t. Benzaldehyde by Initial Slopes Method.

$-\lg([RuH]/dt)$init. vs. $-\lg[phCHO]$
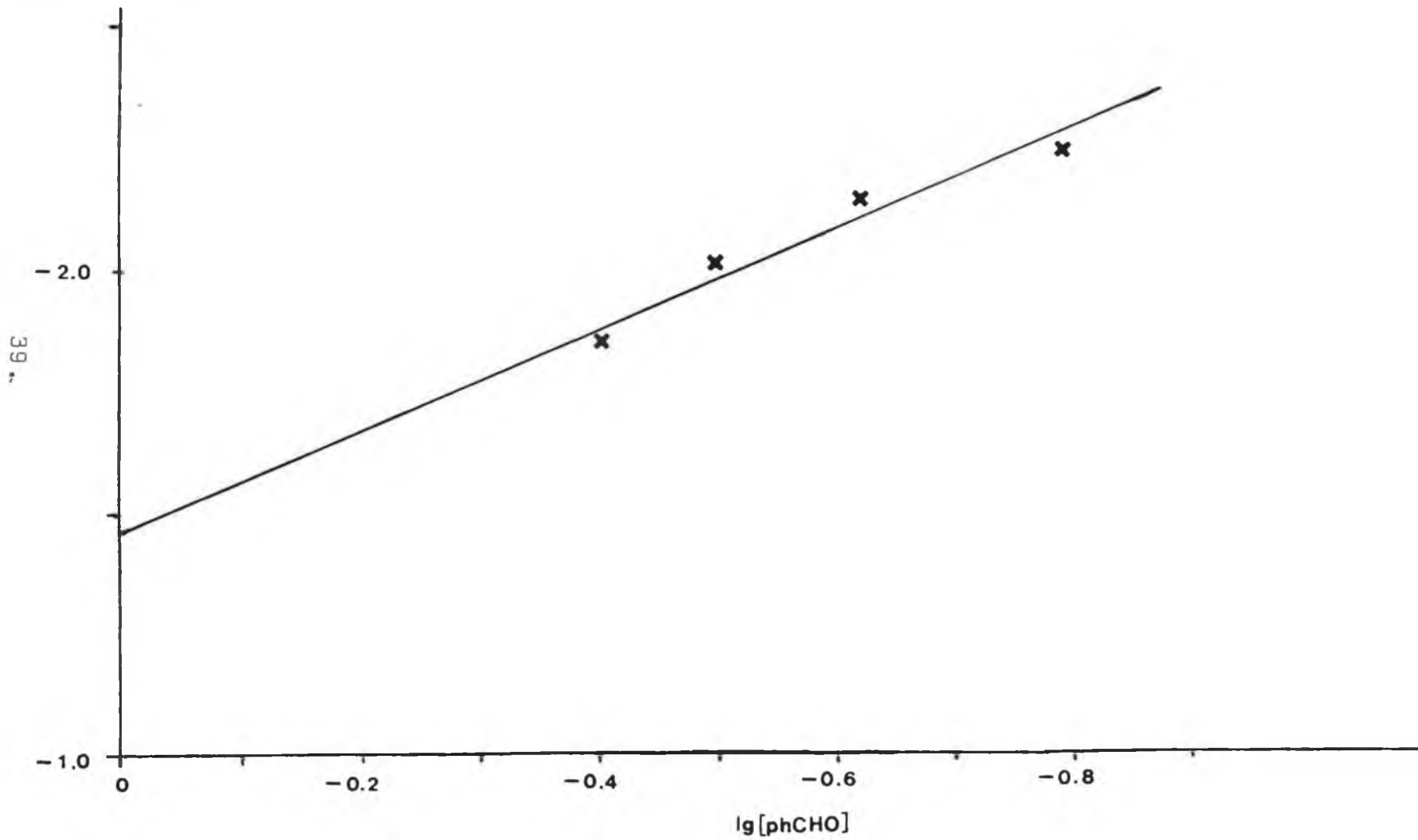
Fig. 1.4 The Determination of the Order of Reaction w.r.t. Acid
-lg([RuH]/dt)init. vs. -lg[HOAc]
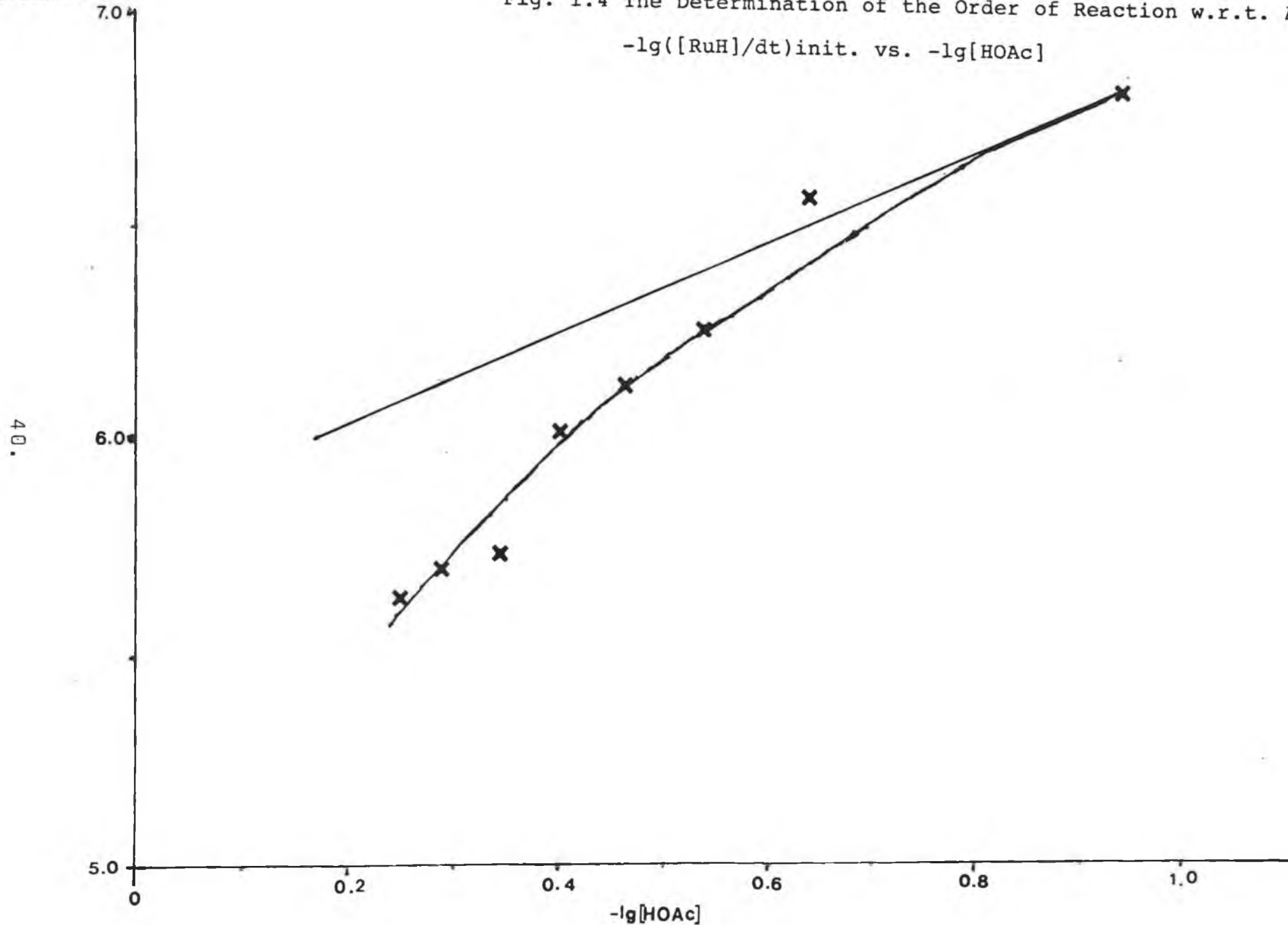
TABLE I.6.

VARIATION OF Kobs WITH BENZALDEHYDE CONCENTRATION

[phCHO]	Kobs (x 10^3)	
(M)	(s^{-1})	[Kobs values - average for three readings]
0.162	1.35	
0.241	1.81	
0.318	2.23	
0.394	2.73	
0.470	2.95	
0.542	3.38	

Conditions   [RuH] = 4×10^{-4} M

                       [HOAc] = 0.403 M

                       T = 25°C   (298K)

Slope   = 5.35×10^{-3} mol^{-1} l s^{-1} =   k[HOAc]

       K   = 1.33×10^{-2} mol^{-2} l^2 s^{-1}

Fig. 1.5 Plot of Kobs vs. [phCHO]

42.
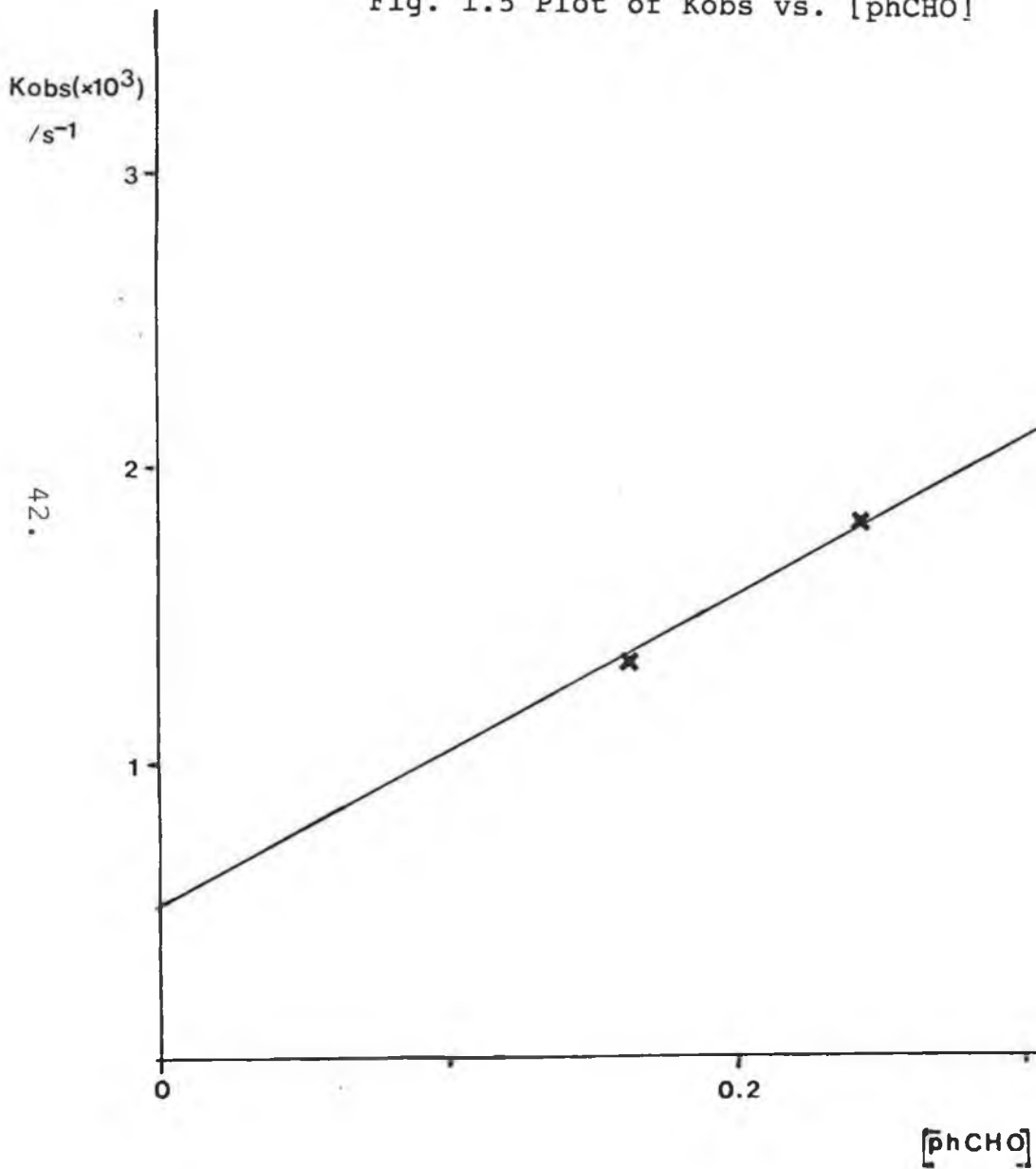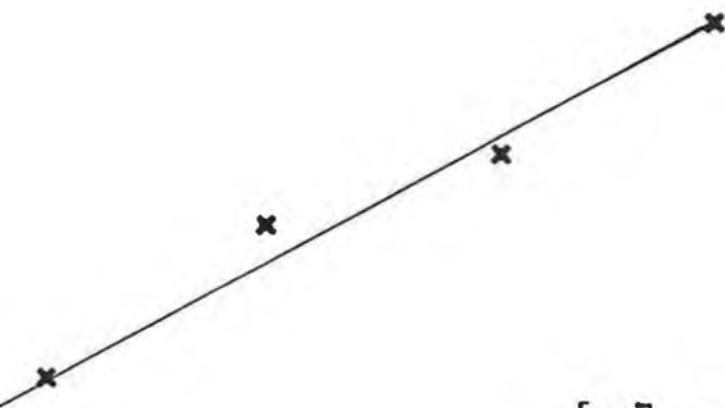
$[RuH]$ $= 4 \times 10^{-4}$ M

$[HOAc]$ $= 0.403$ M

T $= 25°C$

0.4

0.6

M

The acetone reaction with RuH was determined
to involve a fast pre-equilibrium which also holds
for the benzaldehyde reaction

$$phCHO + HOAc \xrightleftharpoons{Keq} [phCHO...HOAc] \quad \text{Reaction 1.11.}$$

This step is followed by a slower rate determining step.

$$[Ru(bpy)_2(CO)H]^+ + [phCHO...HOAc] \xrightarrow[MeCN]{k'} [Ru(bpy)_2(CO)MeCN]^{2+}$$
$$+ phCHOH$$

Reaction 1.12.
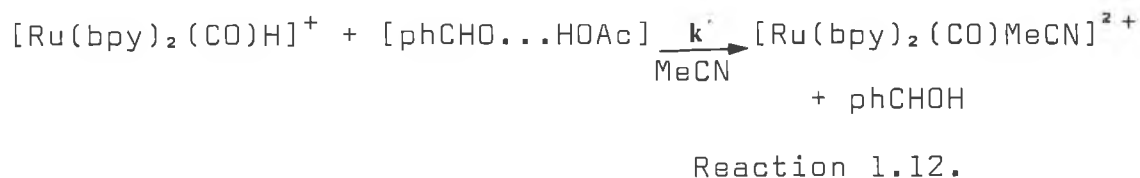
The high value obtained for **K** demonstrates
the ease with which the ruthenium complex will lose
its hydrogen to an aldehyde or ketone in acidic media.

By plotting Kobs against [HOAc] at given
[phCHO], K, can also be calculated Table 1.7, Fig. 1.6.
However the plot does not yield a linear graph. This
may be due to the fact that the reaction solution is
not sufficiently buffered for changing concentrations
of HOAc. However the initial slope does give a value
for K, 1.42×10^{-2} $mol^{-2}s^{-1}$, that corresponds well
with the value obtained for the Kobs vs [phCHO] plot.

43.

TABLE 1.7.

VARIATIONS OF KOBS WITH ACETIC ACID CONCENTRATION

[HOAc]	[Kobs] [X10^3]	
M	s^{-1}	
0.1132	0.302	Kobs values
0.2263	0.89	averaged over
0.2830	1.32	three readings
0.3398	1.80	
0.3961	2.44	
0.4527	3.58	
0.5094	4.60	
0.5660	5.71	
0.6220	7.83	
0.6791	9.21	

Conditions:-   [RuH]   = 4×10^{-4}M

[phCHO] = 0.318 M

T = 25°C (298 K)

Initial slope = 4.53×10^{-3} =   k[phCHO]

K = 1.42×10^{-2} $mol^{-2}l^2s^{-1}$

Fig. 1.6 Plot of Kobs vs.

[HOAc]

$[RuH] = 4 \times 10^{-4}$ M

$[phCHO] = 0.318$ M

T = 25°C

0.5

[HOAc]   M

Fig. 1.6B.   Plot of Kobs vs. $[HOAc]^2$

Slope=1.84 10^{-2} $mol^{-2}l^2s$

Fig 1.6C.   Plot of -log Kobs vs. -log [HOAc]

Slope = 2.1
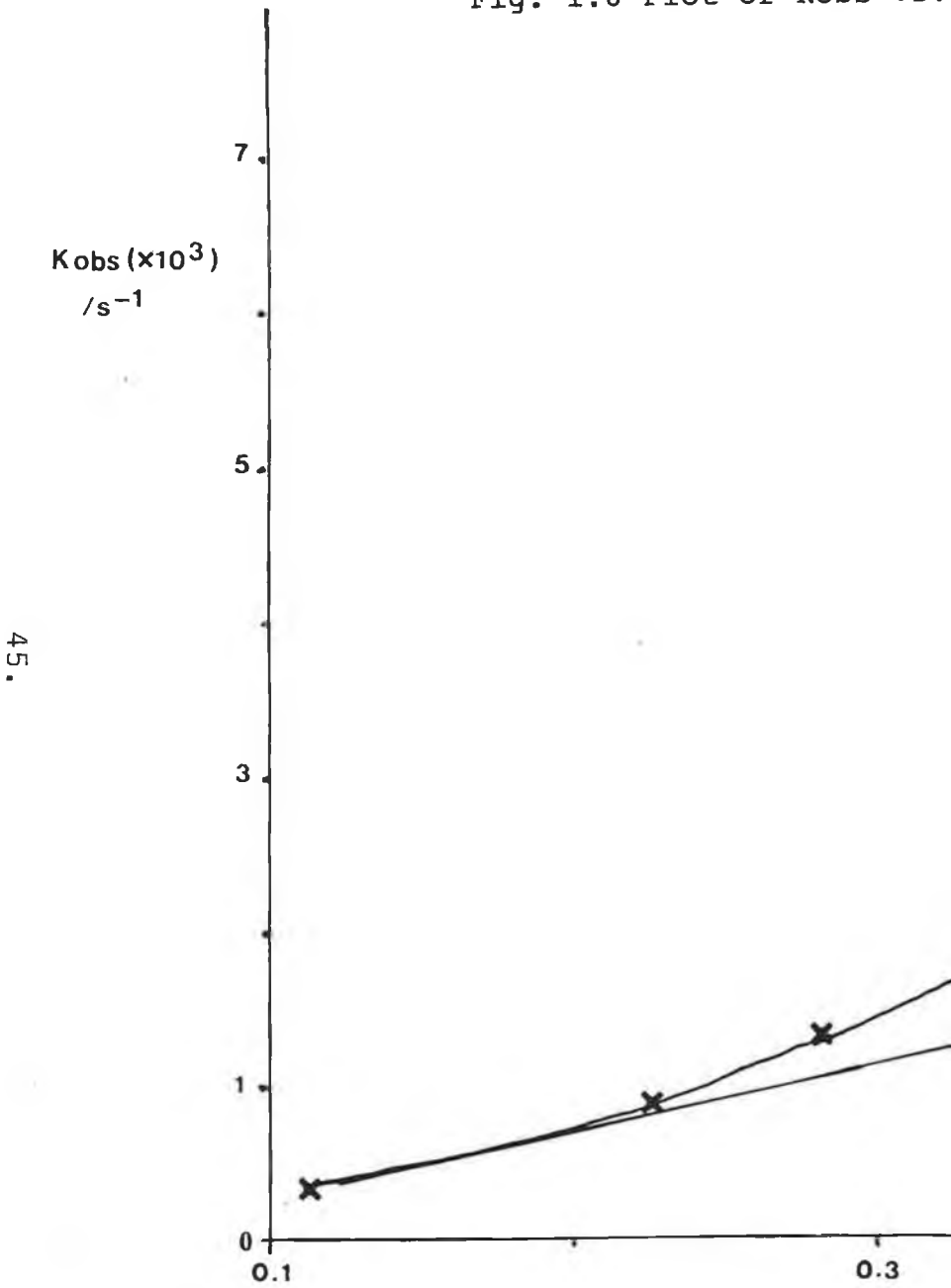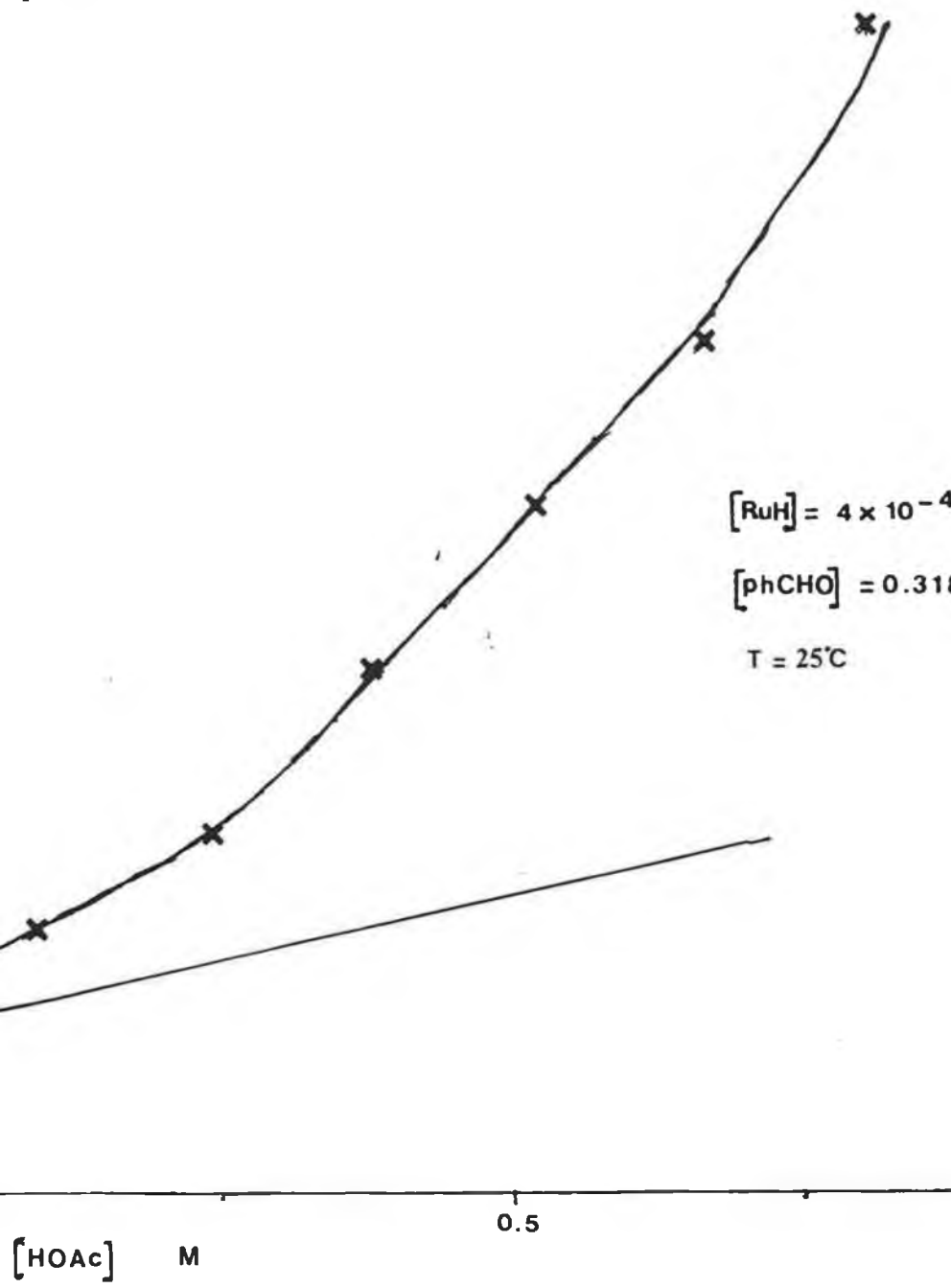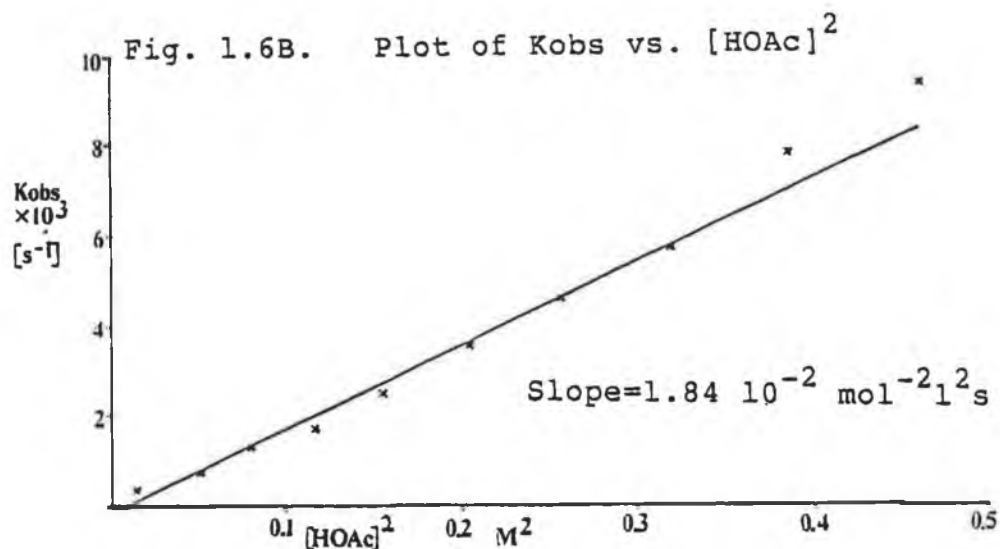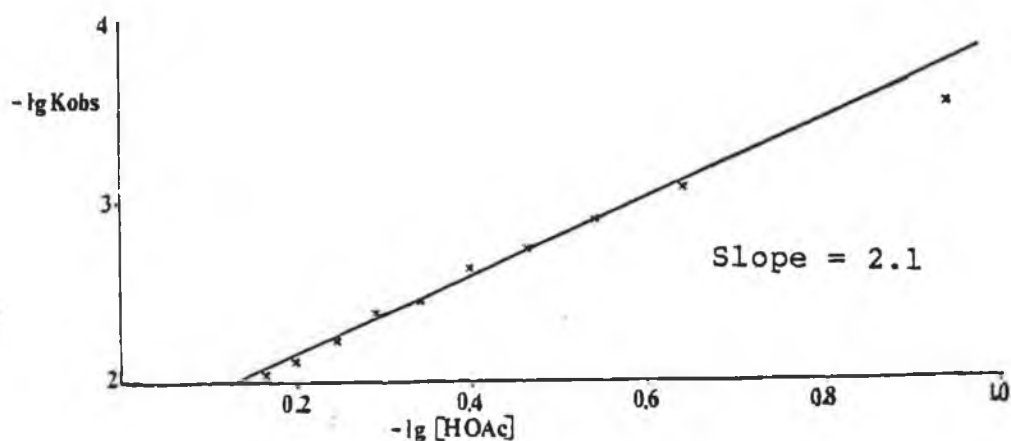
The plot of Kobs vs. $[HOAc]^2$ yields a graph close to a straight line fit,(fig. 1.6B). It is possible that two acetic acid molecules are necesary for the correct reaction stoichiometry. It may be that the acetic acid forms a dimer in the organic solution. If this is the case, then

Kobs =K[phCHO]$[HOAc]^2$ eqn. 1.18

and a plot of -log Kobs vs. -log[HOAc] should yield a slope of 2, (fig. 1.6C). This hypothesis is supported by the slope of 2.1 obtained for this plot.

TABLE 1.8.

VARIATION OF KOBS WITH TEMPERATURE

T	$(1/T) \times 10^3$	Kobs	ln Kobs
K	K^{-1}	s^{-1}	
294	3.401	1.73	- 6.360
298	3.355	1.78	- 6.331
302	3.311	1.95	- 6.240
308	3.246	2.09	- 6.171
313	3.195	2.32	- 6.066
318	3.145	2.55	- 5.972
323	3.096	2.71	- 5.912
328	3.059	2.80	- 5.878

Plot of i/T   vs   ln Kobs

Slope = - 1385 K^{-1} = -Ea R

R = 8.31441 $JK^{-1} mol^{-1}$

Ea = 11.5 kJ mol^{-1}

Intercept = 11.1

Fig 1.7 The Temperature Dependence of the Reaction of RuH with Benzaldehyde: Arrhenius Plot

$[RuH] = 4 \times 10^{-4}$ M

$[phCHO] = 0.318$ M

$[HOAc] = 0.403$ M

$-$ln Kobs

$1/T \times 10^3$ (K^{-1})

48.
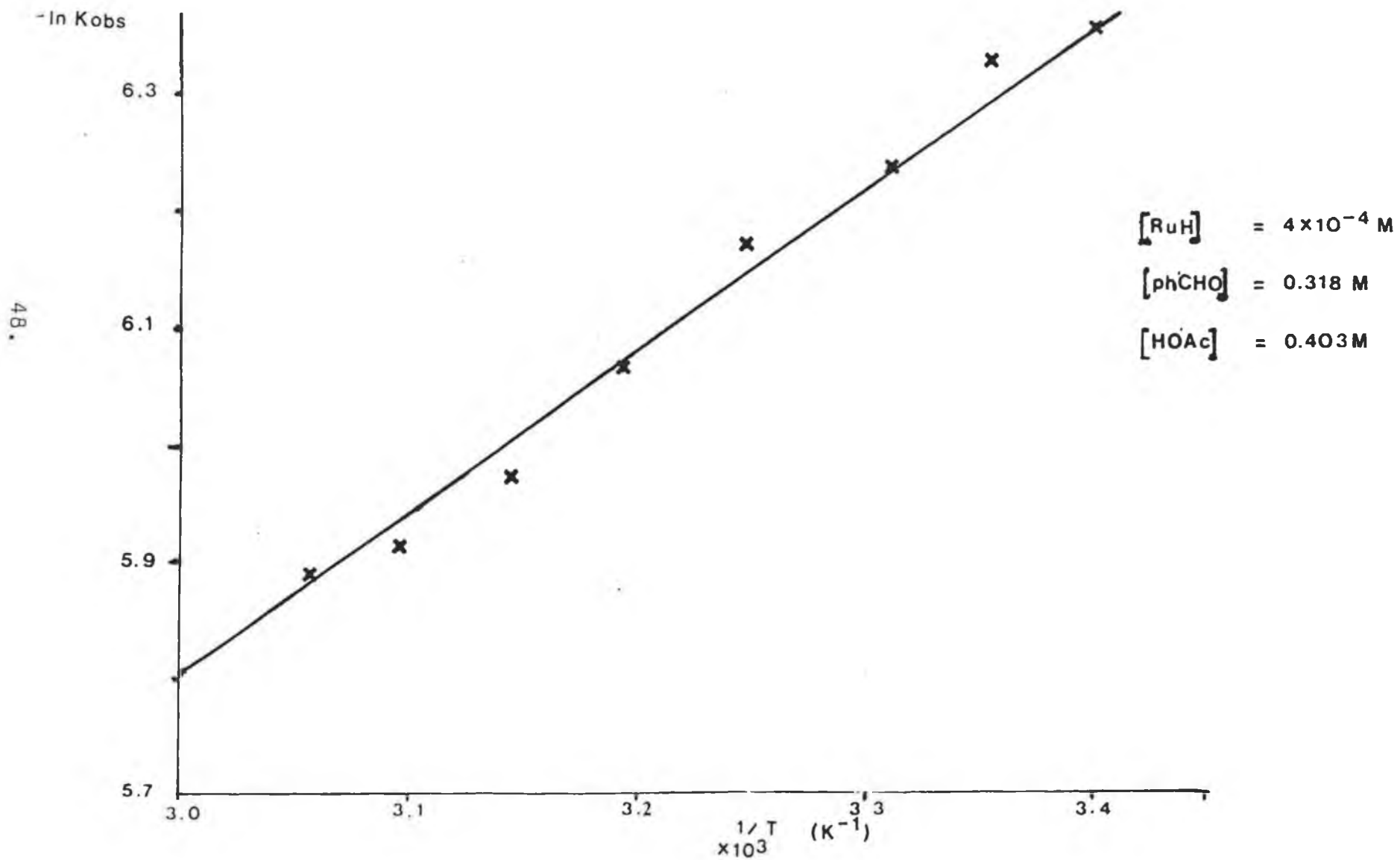
CONCLUSIONS

$[Ru(bpy)_2(CO)H]$ PF_6 . $\frac{1}{2}$ Acetone was synthesised from $Ru(bpy)_2$ Cl_2 $2H_2O$ by a method modified from one previously reported [63]. $[Ru(bpy)_2(CO)Cl]$ PF_6 is an intermediate product removed from solution and redissolved before reduction to the hydride using $NaBH_4$. The yield of 93% for $[Ru(bpy)_2(CO)Cl]$ PF_6 and 50% for the final product, $[Ru(bpy)_2(CO)H]PF_6.\frac{1}{2}$ C_3H_6O, is comparable to other methods. The hydride product was obtained as highly pure crystals.

The reaction of the hydrido ruthenium complex with a number of aldehydes, ketones and esters was monitored in acidic aqueous and organic environments. The aqueous system contained Britton-Robinson buffer and the organic system contained acetic acid in acetonitrile. For both systems the reaction with aldehydes was more efficient than with ketones and the reaction with esters was small. Within these classes the smaller compounds reacted at a faster rate with the hydride for both aqueous and organic systems.

The acid catalysed reaction of
$[Ru(bpy)_2(CO)H]$ PF_6 . $\frac{1}{2}$ C_3H_6O with benzaldehyde in
acetonitrile was studied under pseudo first order
conditions with benzaldehyde and acetic acid in large
excess. A plot of Kobs v Benzaldehyde concentration at
a given acetic acid concentration allowed the
determination of the rate constant, $(K = 1.33 \times 10^{-2}$
$mol^{-2} l^2 s^{-1})$, from the slope of the linear graph. The
graph of Kobs vs acetic acid concentration increased
in an exponential shape. This may be due to insufficient
buffering of the reaction solutions. However the initial
slope gave a value for K $(1.42 \times 10^{-2}$ $mol^{-2} l^2 s^{-1})$ which
corresponded to that obtained from the benzaldehyde
plot. The reaction products were identified as
benzyl alcohol and $[Ru(bpy)_2(CO)MeCN]^{2+}$

The reaction may be written

$[Ru(bpy)_2(CO)H]^+ + phCHO \xrightarrow[\substack{MeCN \\ HOAc}]{K} [Ru(bpy)_2(CO)(MeCN)]^{2+} + phCHOH$

Reaction 1.10.

This reaction is analogous to the acid
catalysed reaction of $[Ru(bpy)_2(CO)H]^+$ with acetone
previously studied [52]. The value of K is higher
for the benzaldehyde reaction however although it is of
the same order of magnitude.

The reaction of the hydride with benzaldehyde exhibits Arrhenius type behaviour and the activation energy; Ea, was calculated as 11.5 kJ mol^{-1} from an Arrhenius plot. This is a low activation energy demonstrating the ease by which the complex acts to hydrogenate aldehydes in acidic media. The results support the proposal $[Ru(bpy)_2(CO)H]^+$ acts as a hydrogen donating intermediate in the water gas shift reaction catalysed by $[Ru(bpy)_2(CO)Cl]^+$. The hydrido ruthenium complex is of interest also in that it is photostable unlike other ruthenium bis(bipyridyl) compounds containing carbonyl groups.

The intercept of ca. 0.55 s^{-1} for the graph of Kobs vs. benzaldehyde concentration may be the result of a side reaction,possibly involving the acid. However, the reason is not clear from these results.

A plot of Kobs vs. $[HOAc]^2$ demonstrated the possibility that two acetic acid molecules may be necessary to achieve the correct reaction stoichiometry. This suggests the possibility that acetic acid exists as a dimer in the organic reaction solution.

51.

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PART   II

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY
[HPLC], OF CATIONIC RUTHENIUM (II)
Bis (2,2' - Bipyridine) COMPOUNDS

INTRODUCTION

A. THEORETICAL CONSIDERATIONS OF HIGH PERFORMANCE
   LIQUID CHROMATOGRAPHY   (HPLC)

(I) INTRODUCTION

        Chromatography is a technique where by
substances can be separated by use of their differing
affinities for a stationary phase. This mobile phase
may be gaseous or liquid. The technique of liquid
chromatography may be divided into four basic types,
all of which have been applied under high pressure
as HPLC [1,2].

        Liquid-Solid Chromatography, [LSC], depends
on the absorption of the solute on polar absorbents.
In Partition Chromatography the solute is partitioned
between two immiscible solvents, one being stationary
and the other mobile. The stationary phase may be
coated onto an inert support, (Liquid - liquid
chromatography), or chemically bonded to the inert
support (Bonded phase chromatography). Bonded phase
chromatography is probably the most widely used form
of HPLC. It is termed "Normal Phase", if the
stationary phase is more polar than the mobile phase

and "reverse phase", if the opposite is true. Ion-
exchange chromatography involves the exchange of ions
between the mobile phase and the ionic sites of the
packing. Sulfonic acid functional groups bonded
to the packing are generally used for cation-exchange
resins and quaternary amines for anion-exchange.
Exclusion Chromatography, also known as Gel
Permeation and Gel Filtration, achieves separation
based on molecular size. A gel with an inert porous
surface is used as packing. Small molecules can enter
the porous network and are retained in the stagnant
mobile phase while large molecules pass unretained
through the column.

During the course of this project reverse
phase and cation-exchange HPLC were used. The vast
majority of complexes studied in this project were
charged so a technique known as Ion Pair Chromatography
(IPC), was used to effect separation. This technique
is generally used in the reverse phase mode and involves
adding a counter ion to the polar eluent. This
cointerion combines with the sample ion to form an
ion pair, which is retarded by the stationary phase
due to its increased lipophilic character.

This may be described from a practical stance by the equation:-

$$X^- \text{ aq } + Q^+ \rightleftharpoons [X^-Q^+] \text{ org}$$

However Ion Pair Chromatography involves much more complicated mechanisms than this simplified view suggests. This will be seen later.

(ii) COLUMN THEORY

It is necessary to compromise between resolution and column capacity in order to achieve an effective chromatographic system. The resolution, R, between two peaks can be quantatively measured using the following equation:-

$$R = \frac{2\triangle t}{W_2 + W_1} \qquad \text{Eqn. 2.1.}$$

where $\triangle t$ is the difference in time between the peak maxima and W_1 and W_2 are the peak widths at the base, by extrapolation of tangents, also measured in units of time [3].

61.

Resolution may be improved by varying the Column Selectivity, (α). This is a function of the thermodynamics of the exchange process, and is measured by the relative separation of the peaks:

$$\frac{t_{R_2} - t_0}{t_{R_1} - t_0} = \frac{t^1_{R_2}}{t^1_{R_1}} = \frac{K_2}{K_1}$$

where t_{R_1} and t_{R_2} are the retention times of components 1 and 2 respectively, t_0 is the retention time of unretained components, $t^1_{R_1}$ and $t^1_{R_2}$ are the adjusted retention times of components 1 and 2 and K_1 and K_2 are their distribution coefficients.

Resolution is also a function of the Capacity Factor, (k^1). This is an indication of the solute retention and is given:-

$$k^1 = \frac{t_r - t_0}{t_0} \qquad \text{Eqn. 2.5.}$$

Resolution can be achieved by varying column selectivity, capacity and efficiency. All three of these functions can be related to resolution by the following equation:-

$$R = 1/4 \quad \sqrt{N} \quad \times \quad \frac{\alpha - 1}{\alpha} \quad \times \quad \frac{k^1}{k^1 + 1} \qquad \text{Eqn. 2.6.}$$

62.

Column efficiency may be described as follows:-

$$N = \left|\frac{tr}{\sigma}\right|^2 = 16\left|\frac{tr}{W}\right|^2 = 5.5.\left|\frac{tr}{W\frac{1}{2}}\right|^2 \quad \text{Eqn. 2.2.}$$

where tr is the retention time, W is the peak width at
half the baseline and σ^2 is the band variance (in
terms of time). The value N is called the number of
theoretical plates. N is proportional to column
length so the preferred measure of column efficiency
is known as the height equivalent to theoretical
plate, H or HETP, as it is independent of column length.
H is related to N, as follows:;

$$H = L/N \qquad \text{Eqn. 2.3.}$$

where L is the column length.
The smaller the value of H the better the efficiency
of the column.

H is effected by band broadening and this results from
three main sources
(1)   Multiple paths of a solute through the
        column packing,
(2)   Molecular diffusion
(3)   Effects of mass transfer between the phases.
[4,5]

63.

Theoretically peaks should emerge from a
column displaying a Gaussian concentration profile.
However, this seldom occurs in practise and tailing
and the occurence of shoulders are often observed.
This is particularly true for ionic solutes. The
assymetry of a peak may be calculated as follows:-

$$A_s^2 = (\frac{b}{a})^2 \qquad\qquad \text{Eqn. 2.7.}$$

where b is the distance after peak centre and, a,
the distance before peak centre, both measured at
10% of the total peak height.

A good column will generally have an
assymetry value, As, of less than 2.5.

B.   THE HPLC ANALYSIS OF ORGANOMETALIC AND METAL
     CO-ORDINATION COMPLEXES

(I)   INTRODUCTION
      While there has been much study of the
applications of HPLC to organic and biochemically
active compounds it is only in recent years that the
HPLC of inorganic species has received much attention.

64.

Other methods of chromatography, such as gas
chromatography, (GC), thin layer chromatography, (TLC),
and column chromatography have been used for separation
and determination of inorganic compounds. The
applications of GC for the analysis of organometallic
and metal co-ordination compounds is severely limited
as in general they are relatively non-volatile. In
addition to this, many of these compounds are thermally
labile at the operating temperatures necessary to
achieve effective GC analysis. TLC and 'Classical'
colum chromatography, on the other hand, are cruder
analytical methods than HPLC and rarely offer an
acceptable level of accuracy or detection for sensitive
quantitative analyses. The separation of inorganic
species by classical chromatographic methods has been
reviewed by Michal, [6].

Metal-Organic systems may be divided into two
classes. These are: (i) organometallic compounds :
compounds which contain a carbon-metal bond, and,
(ii) metal co-ordination compounds : compounds which
do not contain a carbon-metal bond. Nitrogen-metal
bonds are common in these compounds. There have been
a number of reviews on HPLC of metal-organic compounds,
[7,10]. The first reported use of HPLC of metal chelates

65.

is generally credited to Huber et al., [II]. Rapid
improvement in HPLC methodology has been achieved
since then, significantly enhancing the potential of
HPLC for the separation of metal-organic species.

The separation of charged metal-organic compounds
poses a more difficult problem for HPLC. Ion-exchange
chromatography has been traditionally used, successfully,
for the separation of ionic metal chelates but more
recently the technique of ion chromatography,[12], has
showed great promise in this area.

(ii) THE HPLC ANALYSIS OF RUTHENIUM CONTAINING COMPOUNDS
There has been little research into the HPLC
of ruthenium compounds. In general, the HPLC of
ruthenium compounds is reported in a diversity of
journals with the emphasis rarely on the HPLC. For
this reason the separation mechanisms have not been
well investigated.

In 1979, Larsen reported the use of an ion-
exchange HPLC in the separation of neodymium from
solutions of spent nuclear fuel containing ruthenium
as a fission product, [13]. The reversed-phased
chromatographic behaviour of some trinuclear carbonyl

clusters of iron, ruthenium or osmium was studied by Mangia
et al., [14], using a Lichrosorb RP-18 column with
acetonitrile or acetonitrile/methanol as the mobile
phase. The HPLC of homo and hetero-tetrametalic iron,
ruthenium, osmium and nickel clusters was studied using
reverse phase chromatography also on an RP-18 column
by Casoli et al., [15].

In the reverse phase mode many of these compounds
were found to be susceptible to decomposition and a
normal phase mode using a silica column with a n-hexane
/THF mixtures proved to be more effective.

Gurira and Carr used reversed phased HPLC to
separate a range of acetylacetone (ACAC) metal chelates
including Ru(III)(ACAC)$_3$, [16]. An ultrasphere C18
column was used with a mobile phase of 40% acetonitrile
in water and a flow rate of 2 mL /min.

Wenclawiak and Bickman used a C18 column diluted
with methanol-buffer (pH4.6) - chloroform (57.5:30:12.5)
containing 2.5×10^{-4} m oxine to separate Ru(III) and
Os(IV), [17].

Ammine complexes of transition metals in the
platinum group including many ammine ruthenium (III)
complexes exhibit antitumour and mutagenic activities.
In order to gain some understanding of the mechanism
by which this operates, the hydrolysis reaction of
$[(dGuO)(NH_3)_5Ru]^{3+}$ (OGuO = deoxyguanosine) was
studied [18]. As this is a complex reaction it was
necessary to devise a HPLC system to follow the
reaction. Three methods were tried in order to achieve
an optimum system for the separation of these complexes.

(i)   Reverse phase Ion pair chromatography, (RP-IPC)
utilising alkylsulphonates in aqueous solution was
employed on Varian CH-10 and MCH-10 columns (polymeric
and monomeric octadecylsilane columns). However this
method yielded poorly resolved, broadly tailing peaks.

(ii)   Ion-exchange chromatography using an alkylsul-
phonate derivatized silica column (Vydax TP-401) diluted
with ammonium formate or ammonium acetate caused most
of the ruthenium-ammine complexes to be severely
retained even with high buffer concentrations.

(iii)   Isocratic elution with 0.2 M solutions of
ammonium formate, acetate, or proprionate, pH 5.5.,
on ODS columns at a flow rate of 1 ml/min. While the
ODS column yielded satisfactory results, optimal
results were achieved for this method with a C18
column.

(iii)   THE HPLC OF RUTHENIUM -(2,2' - Bipyridine)
        AND RUTHENIUM - 1,10 - Phenanthroline COMPLEXES

        The first detailed reported use of RP-IPC to
separate ionic metal chelates was by Valenty and Behnken
[19]. They used a μ Bondapak C18 column to determine
diester, monoester - monocarboxylate, and dicarboxylate
derivatives of $[Ru(bpy)_3]^{2+}$ [Fig. 2.1A.), which can
be distinguished on the basis of water solubility and
molecular charge. The mobile phase for the analysis
of compounds 1,III, and IV shown in Fig. 2.A, employed
a 20 min linear gradient, 50% THF in water to 100% THF
(both 0.015 M $MeSO_3H$, 0.5% (v/v) CH_3COOH] with a 2.0 ml/min
flow rate. The analysis of II, III and V [Fig. 2.1A],
employed a 10 min linear solvent gradient, 10% THF in
water to 40% THF in H_2O (both 0.005 M n-heptanesulphonic
acid, CH_3COOH, pH 3.5] with a flow rate of 2.0 ml /min.

This HPLC method provided satisfactory separation for the determination of these complexes, [Fig. 2.1B] .

Other workers have used this HPLC system in the subsequent detailed study of surfactant derivatives of $[Ru(bpy)_3]^{2+}$. Gaines and Valenty,[20], and Harriman, [21], used the system for this purpose and concluded that surfactant derivatives of $[Ru(bpy)_3]^{2+}$ do not sensitise the photodissociation of water into its elements as previously reported, [22]. However interest in surfactant ruthenium complexes remained and Gaines et al., continued to use HPLC to further their knowledge of the chemistry of $[Ru(bpy)_3]^{2+}$ and its monolayer films of surfactant derivatives, [23]. Emphasis then switched to an investigation of the variation of the monolayer composition and the identification of new products in the monolayer assemblies. Spectroscopic methods are not very suited to such analyses but HPLC is ideal for these studies. Valenty used the HPLC system to achieve this, [24]. Ghosh et al., also used the system to follow the spontaneous thermal and light-induced reduction of $[Ru(bpy)_3]^{3+}$ to $[Ru(bpy)_3]^{2+}$, [25]. They found the reaction to be accompanied by about 10% decomposition of the complex to minor products,which were separated by HPLC. [Fig. 2.2].
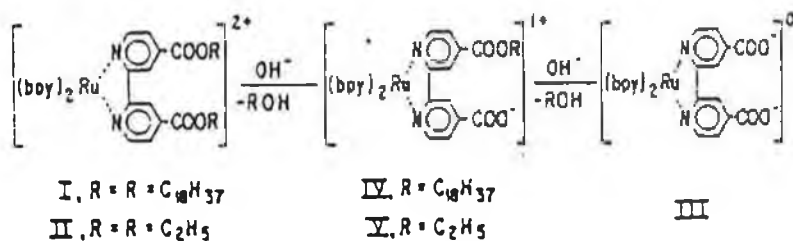
Fig. 2.1A [Ru(bpy)$_3$]$^{2+}$ Surfactant Derivatives
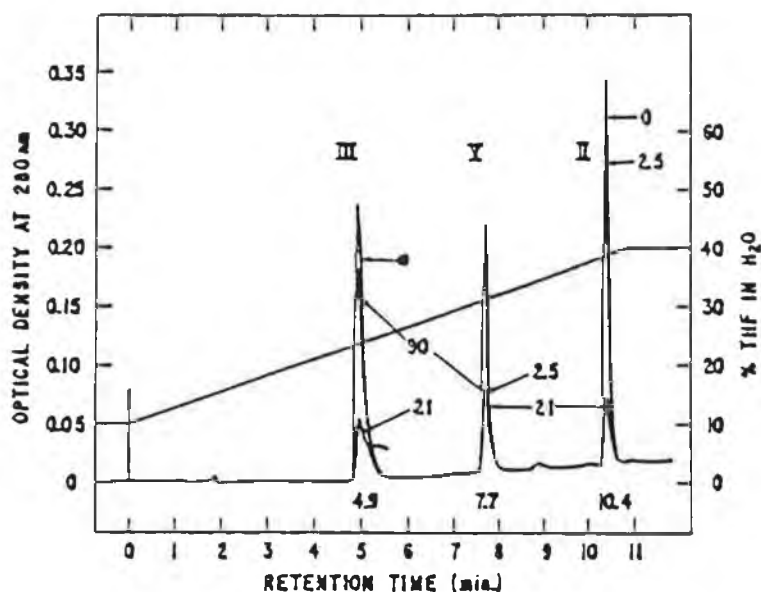
Fig. 2.1B HPLC of Hydolys s Reaction Shown in fig 2.1A at 0, 2.5, 21, 90 and   min Reaction Times. The Diagonal Line across the Figure shows the Composition of Mobile Phase with 0.005M n-Heptane-Sulphonic acid buffered to pH 3.5.   [Ref 19]
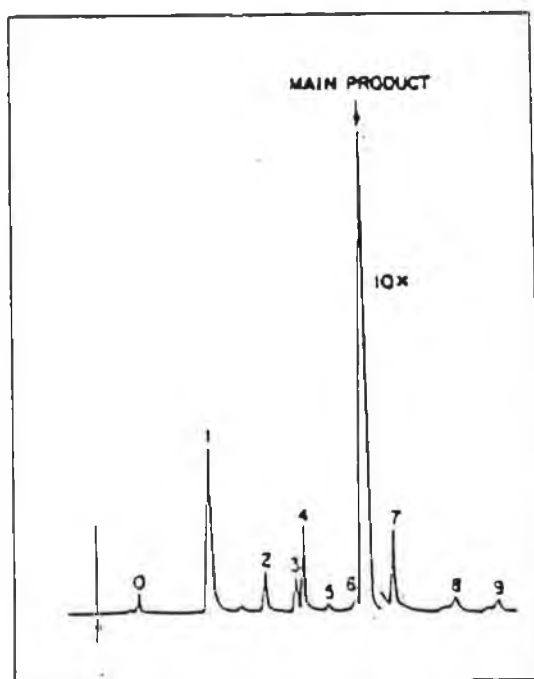
Fig. 2.2 HPLC Separation of the products of the Reduction of [Ru(bpy)$_3$]$^{3+}$ in 0.025M Phosphate Buffer, pH 7   [Ref 25]

71.

Poecker et al., used a similar HPLC system in the study of the reduction of Ru(IV) complexes. $[(bpy)_2(PY) Ru (O)]^{2+}$ and $[(trpy)(phen) Ru (O)]^{2+}$ (py = pyridine, trpy = 2,2',2" - terpyridine) in basic solution, [26]. They found that ca 80% of the reduced products that appear are the unmodified polypyridyl complexes of Ru(II), $[(bpy)_2(py) Ru (OH)]^{+}$ or $[(trpy) (phen) Ru (OH)]^{+}$. The HPLC system involved use of a partisil ODS-3 column. The mobile phases used consisted of various mixtures of solvent A (40% THF; 60% 0.2M acetate buffer, pH 3.6) and solvent B (5% THF; 60% 0.2 M acetate buffer, pH 3.6) or solvent C (40% THF; 60% 0.1 M trifluoromethane sulphonic acid, pH 2.6) and solvent D (5% THF; 95% 0.1M trifluoro methanesulphonic acid, pH 2.6). All solvents were 5 mM in sodium octanesulphonate.

O'Laughlin and Hansen used HPLC to effect the separation of $[Fe(Phen)_3]^{2+}$, $[Ni(Phen)_2]^{2+}$ and $[Ru(Phen)_3]^{2+}$ by RP-IPC on µBondapak CN columns [27]. Satisfactory separation was achieved using methanol-water or acetonitrile water mobile phases which were 0.015 M in methanesulphonic acid and 0.5% in acetic acid. pH was seen to have little effect over the range pH 2.9 to 6.0. n-Heptanesulphonate gave slightly better

better results when used as an ion-pair reagent rather than methanesulphonate. However tailing of peaks was a problem using this system.

O'Laughlin subsequently used a μ Partisil SCX column (cation exchange) and a Hamilton PRP-1 column (polystyrene - divinylbenzene (RP-IPC) to separate $[Ni(phen)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ from $[Fe(phen)_3]^{2+}$ [28]. Perchlorate ion was used as the pairing ion by using a mobile phase of 4:1 acetonitrile - water mixture 0.06 M perchloric acid as the mobile phase. The retention of the complexes on the cation exchange column was concluded not to be due to ion exchange. The distribution of the cationic chelates was shown to be due to the distribution of the chelate species paired with perchlorate ions between the mobile and stationary phases. This process is fundamentally different from the ion exchange separation of the metal cations by HPLC. It was also noted that the elution order of the complexes was different for the ion exchange and reverse phase columns with the same mobile phase.

A completely different perspective of $[Ru(phen)_3]^{2+}$ in HPLC is given by Tamagishi, [29]. Silica gel coated with racemic $[Ru(phen)_3]^{2+}$ - montmorillonite was used to resolve enantiomers having aromatic groups.

(iv)   THE HPLC OF OTHER METAL - 2,2' - Bipyridine and
       1,10 -Phenanthroline COMPLEXES

       Toneda et al., used an SP-Sephadex column to
separate $[Co(phen)_3]^{3+}$ and $[Ni(phen)_3]^{2+}$ using aqueous
KBr as eluent, [30].   An inversion of the elution
order was observed with increasing KBr concentration,
with $[Co(phen)_3]^{3+}$ eluting first at higher concentrations
of KBr.

       Lundgren and Schilt, [31], studied the
absorption of metal ions on Amberlite XAD-2
styrene-divinylbenzene resins coated with the ferroin
type ligand, 3-2-pyridyl -5,6 - diphenyl -1,2, 4 -
tramine (PDT) as a function of pH and anion.   They
attributed the absorption of this ligand and metal
complexes to Π-electron overlap between the styrene
moieties on the resin and adsorbate molecules.

       O'Laughlin reported the separation of
$[Fe(CN)_2(phen)_2]$ from $[Fe(phen)_3]^{2+}$ on both
μ Bondapak C18 and a PRP-1 column with an acetonitrile
water mobile phase containing 2.0g/1 $LiClO_4$.   [32].

74.

Mangia and Lugari resolved 2,2' - bipyridine
and the complexes $[Ni(bpy)_3]^{2+}$ and $[Fe(bpy)_3]^{2+}$ on a
μ Bondapak CN column using NCS^- as counter ion in
the methanol water mobile phases, [33]. The retention
volumes for $[Ni(bpy)_3]^{2+}$ were found to vary exponentially
with concentration of KNCS in the mobile phase.

A number of papers by Rigus and Pietzyte bear
relevance to this subject, [34,36]. In these papers
the separation of inorganic and organic anions is
studied using $[Fe(phen)_3]^{2+}$ as a mobile phase additive
rather than vice versa.

The HPLC of metal chelates is an extremely
complicated subject and as yet the actual retention
mechanisms little understood. However the applications
of HPLC in research in the chemistry of metal chelates
is widespread and its unique advantages in the study
of photochemical reactions of the compounds has been
demonstrated.

C. THE PHOTOCHEMISTRY OF RUTHENIUM (II) 2,2' BIPYRIDINE and 1,10 - PHENANTHROLINE COMPLEXES

The photochemistry of transition metal co-ordination compounds has been the subject of intense research, [37,38]. In particular the photochemistry of $[Ru(bpy)_3]^{2+}$ and its derivatives have attracted much attention. A large proportion of this work has concentrated on $[Ru(bpy)_3]^{2+}$ particularly because of its unusual photoredox properties and its potential for the storage of photochemical energy by the photodissociation of water, [22]. However, pure $[Ru(bpy)_3]^{2+}$ was shown not to catalyse this reaction, [20,21, 39], and much of the attention was focused on possible bis-bipyridyl complexes of ruthenium which may have been present as impurities in the initial surfactant layer used by Sprintschnik et al. As such the photochemistry of complexes of $[Ru(bpy)_2XY]^{n+}$ received much attention, [40]. In particular, the chemistry of $[Ru(bpy)_2(CO)Cl]^+$ was investigated, [41], as it was considered a likely impurity in the $[Ru(bpy)_3]^{2+}$ surfactant layer [42]. In addition Cole-Hamilton observed that $[Ru(bpy)_2(CO)Cl]^{+1}$ acted as a catalyst for the homogeneous water-gas shift reaction, [43,44].

The absorption of electromagnetic radiation is a quantized phenomenon and for radiation in the visible and U.V. regions sufficient energy is available to bring about change in the electronic state of a system. The relationship-between the energy of transition, E, and the frequency of the exciting radiation, ν , is given by the following equation:-

$$E = Nh\nu = Nhc/\lambda = (2.859 \times 10^4)/\lambda \text{ kcal mol}^{-1}$$

where N = Avagadro's number,

h = Planck's constant,

λ = wavelength of absorbed radiation in nanometres

c = velocity of light

This is the energy which is available for photochemical processes. For 200 nm to 800 nm the values for E are between ca. 143 and 36 kcal mol^{-1} respectively. For co-ordination compounds, sufficient energy is available to enable homolytic and heterolytic bond cleavage to occur and in some instances photo-ionisation. However, energetically enriched systems may have several modes of energy dissipation available to the system of which chemcial reaction is only one potential mode.

In principle there are three fundamental
types of photochemical reactions. These are
photosubstitution, photorearrangements and photoredox
reactions. In this project the identification of new
compounds formed by photosubstitution was of interest.

The absorption spectra of ruthenium (II)
polypyridyl complexes are dominated by metal-to-ligand-
charge transer, (MLCT). The nature of these transitions
governs the photoreactivity of these complexes. The
excited state manifold of $[Ru(bpy)_2XY]^{n+}$ compounds,
(X,Y, are monodentate ligands), has been carried out
[47,51] and this has led to a greater understanding
of the photochemistry of these complexes.

$[Ru(bpy)_3]^{2+}$ was considered photochemically
inert until Porter and Hoggard reported the photanation
of $[Ru(bpy)_3] Cl_2$ in DMF [52]. Durham et al., examined
the substitutional photochemistry in a variety of
different solvents and concluded that $[Ru(bpy)_3]^{2+}$
is essentially inert in such solvents as water,
acetone and acetonitrile in the absence of added
chloride ions [53]. Formation of $Ru(bpy)_2 Cl_2$ was
attributed to the presence of the counter anion.

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However, Jones and Cole-Hamilton observed that in the absence of oxygen $[Ru(bpy)_3]$ Cl_2 is photolabile in CH_2Cl_2 and acetone forming $Ru(bpy)_2Cl_2$ and in acetonitrile forms $[Ru(bpy)_2(MeCN) Cl]^+$ only [54].

Many authors have addressed the subject of photosubstitutional chemistry of compounds of the general formula $[Ru(bpy)_2 XY]^{n+}$ in acetonitrile. Brown et al., observed the substitution of the solvent ligand azido bis [2,2' - bipyridine] complexes of ruthenium (III) in acetonitrile [55]. Bonneson et al., demonstrated the formation of $[Ru(bpy)_2(MeCN)_2]^{2+}$ in two distinct steps upon irradiation of $[Ru(bpy)_2(OH_2)_2]^{2+}$ in acetonitrile. They also noted the occurence of photoisomerisation reactions [56]. Allen et al., [57] examined the substitutional reactions of compounds of the general formula $[Ru(bpy)_2(OH)X]^{n+}$. They calculated the second order rate constants for the thermal displacement of H_2O by a solvent molecule of acetonitrile and noted its dependence on the monodentate ligand.

D. THE CHEMISTRY AND PHOTOCHEMISTRY OF RUTHENIUM COMPLEXES
UNDERLINE CONTAINING IMIDAZOLE AND RELATED LIGANDS

The chemistry of imidazole and its derivatives
with transition metal ions have been the focus of
significant study. This is particularly because of
the prominence of the interactions of imidazole
derivatives such as histidine in biological reactions
where the imidazole moiety acts as a ligand towards
metals. [58]. Sundberg et al., made a number of
studies of complexes ruthenium ammines containing
histidine [59] and imidazole [60,61]. It was noted,
during these studies, that for the compound
$[Ru(NH_3)_5 (HIm)]^{2+}$ in aqueous solution of pH <2 the
N-bonded imidazole ligand is substituted for a water
molecule. A second reaction then occurs, where an
NH_3 is replaced by an imidazole which is C-bonded.
Boggess and Martin studied transition metal complexes
of 2-(2' - pyridyl) imidazole including Fe(II), [62].
Haga studied the synthesis, recation chemistry and
electrochemistry of ruthenium (II) bis (2,2' - bipyridine)
complexes containing 2,2'-bibenzimidazole and related
ligands, [63.64]. Dose and Wilson studied the
chemistry of ruthenium(II)complexes containing
2,2' biimidazole [65]. Long and Vos described the

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synthesis of [Ru(bpy)$_2$(HIm)$_2$] Cl$_2$.4H$_2$O and

[Ru(bpy)$_2$(VIm)$_2$](PF$_6$)$_2$ [66]. They also investigated

the acid/base chemistry and the emission spectroscopy

of the former complex. Buchanan et al., examined

the application of the HPLC method developed here

to a number of photochemical reactions of ruthenium (II)

bis-bipyridyl complexes including [Ru(bpy)$_2$(VIm)$_2$](PF$_6$)$_2$.

EXPERIMENTAL

A. APPARATUS AND MATERIALS

High Performance Liquid Chromatography was
performed using a Waters 6000 A Solvent Delivery
System and a Waters Model U6K injector. Detection
was achieved using a Waters Model 440 Absorbance
Detector at 254 nm and the resulting chromatograms
were recorded on a Phillips PM 8251 single Pen
Recorder. A selection of Radial Pak Cartridge
Columns were used with this system, within a radial
compression system. (Z - module). The cartridge
columns used were µBondapak C18 (8MBC1810µ),
µBondapak CN (5CN10µ), µBondapak-phenyl (8MPH10µ)
nad µBondapak CX (8PSCX10µ).

Isocratic liquid chromatography with
photodiode array detection was also performed. A
Waters 501 HPLC pump was used in conjunction with
a Waters 990 Photodiode Array Detector linked to an
NEC APC III computer. Chromatographic traces and
corresponding spectra were recorded with a Waters
990 Printer/Plotter. A Partisil 10-ODS steel
column was used.

All organic solvents used were of HPLC grade.
Water was passed through a millipore system to remove
organic impurities and metals, after distillation.
Ruthenium complexes previously synthesised were
dissolved in HPLC grade acetonitrile.

Photolysis of Ruthenium complexes in acetonitrile
was performed by irradiating a solution of complex in
HPLC grade acetonitrile with a Thorn Ultra Violet/
Visible Photolysis Lamp. The solution was contained
in a quartz cell of 1 cm length. The light was first
passed through a cell of 6 cm, internal length,
containing water, to remove thermal energy.

B.   TECHNIQUES

(i)   DEVELOPMENT OF GENERAL HPLC SYSTEM

a)   Sample Preparation

        $[Ru(bpy)_2(HIm)_2]$ Cl_2. $4H_2O$ was previously
prepared by Long and Vos [66]. $[Ru(bpy)_2(HIm)Cl]$ PF_6
and $[Ru(bpy)_2(HIm)_2]$ $(PF_6)_2$ were synthesised by the
same method used to synthesise the correspondining
Methylimidazole (MeIm) complexes [68]. $[Ru(bpy)_2(VIm)_2](PF_6)_2$
was synthesised by the method used for the preparation
of $[Ru(bpy)_2(Htrz)_2](PF_6)_2$,[Htrz = 1,2,4 - triazole]
[69].   Elemental analyses for these compounds were
obtained.

TABLE 2.1.   ELEMENTAL ANALYSIS OF RUTHENIUM COMPLEXES

	C	M	N	Cl	
$[Ru(bpy)_2(HIz)_2](PF_6)_2$	37.2%	2.9%	13.3%	-	calculated
	36.8%	2.9%	13.5%	-	Found
$[Ru(bpy)_2(HIm)Cl]PF_6H_2O$	41.7%	3.0%	12.7%	5.4%	Calculated
	40.6%	3.2%	12.4%	5.2%	Found
$[Ru(bpy)_2(VIm)_2](PF_6)_2$	40.4%	3.1%	12.6%	-	Calculated
	40.1%	3.0%	12.6%	-	Found
$[Ru(bpy)_2(VIm)Cl]PF_6$	43.6%	3.2%	12.2%	-	Calculated
	43.3%	3.1%	12.3%	-	Found
$[Ru(bpy)_2(HIm)_2]Cl_2.4H_2O$	45.1%	4.6%	16.2%	10.3%	Calculated
	44.3%	4.3%	16.2%	10.7%	Found

These samples were all shown to be pure by TLC tests.

$[Ru(bpy)_2(CO)Cl]$ ClO_4 was prepared as described by Clear et al. [42]. $[Ru(bpy)_2(CO)H]$ PF_6 . $\frac{1}{2}$ C_3H_6O was synthesised by a method described previously in this thesis, (cf. Section I), which is based on a method described by Kelly et al. [70].

All samples were made up to a concentration of approximately 10^{-2} M, in HPLC grade acetonitrile. Sample solutions are degassed with a sonic bath and filtered through an sartorius disposable 0.2 μ filter. In most cases approximately 5 μl of sample was injected onto the column. In addition to the samples mentioned 5 mls of the $[Ru(bpy)_2(CO)H]$ PF_6 . $\frac{1}{2}$ C_3H_6O sample was taken and 4 drops of concentrated hydrochloric acid were added to it. This solution was allowed to stand for over one hour before being injected onto the column.

b) Preparation of Mobile Phase and Chromatographic System

        A variety of solvent mixtures were used as
mobile phase in this study. All mobile phases contained
either acetonitrile or methanol as the main solvent
component. Analar grade Lithium Perchlorate was used
as the ion pair reagent and the effect of $LiClO_4$
concentration was studied. Brief studies were also
performed using SDS as the ion pair reagent with
a CN column.

        To prepare the mobile phase the necessary
volumes of HPLC grade solvent were mixed to give the
required volume : volume ratio, and filtered using
a Sartorius 0.45 µ disposable filter. The required
quantity of Analar Grade $LiClO_4$ was added and the
solution degassed for 30 minutes using a sonic bath.
This also ensured complete dissolution of the $LiClO_4$.
When performing isocratic studies, the mobile phase
was recycled to avoid unnecessary waste of expensive
solvents.

        Studies were made using C18, CN and CX radial
pak cartridge columns. The chromatographic system
was allowed to equilibrate for approximately one
hour prior to any sample injection. Detection was at
254 nm using a UV absorbance detector.

(ii) PHOTOLYSIS STUDY OF IMIDAZOLE AND VINYLIMIDAZOLE
      CONTAINING COMPLEXES BY HPLC

        1.0×10^{-3} m solutions of $[Ru(bpy)_2(VIm)_2](PF_6)_2$
and $[Ru(bpy)_2(VIm)Cl]PF_6$ in HPLC grade acetonitrile
were prepared. 7.8×10^{-4} M $[Ru(bpy)_2(HIm)_2](PF_6)_2$
and 9.7×10^{-4} M $[Ru(bpy)_2 (HIm)Cl] PF_6 H_2O$ in HPLC
grade acetonitrile also prepared. These solutions were
stored in the dark. Photolysis was performed on these
solutions by placing ca 3 ml in a Quartz cuvette and
placing this in the light beam, of wavelength range UV
to visible region for a measured time. A water bath
of 6 cm internal length was placed before the sample in
the light beam to reduce thermal energy.   10 µl of
sample was removed at recorded intervals and injected
onto the column.

        The reaction was followed by isocratic HPLC
with a CX cartridge column. The mobile phase used
was 80% acetonitrile : 20% water (v/v) with 0.05 M or
0.07 M $LiClO_4$ as the ion pairing agent. 2.5 ml /min
was the flow rate and detection was by UV absorbance
at 254 nm. The photolysis was also monitored using
a partisil ODS column and 80% acetonitrile : 20% water
(v/v) with 0.05 M or 0.08 M $LiClO_4$ as mobile phase.

Photodiode array detection enabled the absorbance spectra

of the individual peaks eluted to be obtained.

Photolyses of the imidazole and vinylimidazole complexes

of ruthenium were examined using the ODS column and

photodiode array detection.   Also chromatograms of

previously synthesised complexes of Ru(bpy)$_2$ Cl$_2$. 2H$_2$O,

[71,72], [Ru(bpy)$_2$(MeCN)Cl]PF$_6$ [14] were obtained for

reference.   [Ru(bpy)$_2$(4MIm)$_2$](PF$_6$)$_2$ and [Ru(bpy)$_2$(4MIm)H$_2$O]PF$_6$

complexes were synthesised by the same method as used

for the corresponding 1-methylimidazole complexes [68].

UV/Vis spectra were obtained for the solutions

of [Ru(bpy)$_2$(VIm)$_2$](PF$_6$)$_2$, [Ru(bpy)$_2$(VIm)Cl]PF$_6$,

[Ru(bpy)$_2$(HIm)Cl]PF$_6$, [Ru(bpy)$_2$(HIm)$_2$] (PF$_6$)$_2$ and

[Ru(bpy)$_2$(HIm)Cl]PF$_6$.H$_2$O in acetonitrile.

88.

RESULTS AND DISCUSSION

A. DEVELOPMENT OF METHOD FOR THE SEPARATION OF
   RUTHENIUM bis (2,2' - bipyridyl) COMPLEXES

REVERSE PHASE ION PAIR CHROMATOGRAPHY

ALthough reverse phase ion pair chromatography
(RP-IPC), is a widely practised technique, the exact
retention mechanism is still a controversial subject.
[74]. Several mechanisms have been proposed and retention
times have been used as evidence to support them in the
majority of cases. However, no one interpretation of
the mechanisms proposed suffices to explain all the
observations. The given experimental conditions for a
particular separation determines the retention mechanism
which will dominate.

The simplest postulate for the ion pair mechanism
describes the formation of an ion pair in the mobile
phase, prior to absorption onto the stationary phase.
This then behaves as a neutral molecule with the
polarity of the "ion pair" determining its retention [75,76].
An ion pair reagent which contains a longer alkyl chain
will form a less polar "ion pair" and as such have a
greater affinity for the stationary phase. Thus, this

compound should exhibit the greater retention.

An alternative hypothesis describes a dynamic
ion-exchange process [77,78]. The solvophobic centre
of the impaired ion pairing agent is absorbed to the
stationary phase resulting in the column behaving
as an ion exchanger. With increased length of the
alkyl chain on the ion pair reagent, surface coverage
is increased, resulting in greater retention of the
analyte.

These two mechanisms may be considered to be
extreme viewpoints. Many other mechanisms which are
compromises of these, or which encompass aspects of
either or both, have been proposed. These include a
dynamic complex exchange model [79] a combined
desolvation and ion exchange mechanism [80] and a more
plausible ion-interaction model (IIC) [81,82]. All
of these mechanisms have been supported by retention
data. However, Knox and Hartwick [83], questioned the
validity of this as these mechanisms involve kinetic
processes and retention data result from thermodynamic
equilibria. They suggest that study of peak shape
may provide insight into the mechanisms involved as
this is governed by kinetic processes.

The IIC model is broader in scope than the "ion pair" and 'dynamic ion exchange' models. The model does not require ion pair formation in either phase and is not based on classical ion exchange. The model assumes dynamic equilibrium of the lipophilic ion resulting in the formation of an electrical double layer on the surface. Sample retention results from an electrostatic force due to the surface charge density provided by the reagent ion and from an additional sorption effect onto the non-polar surface. The net result is that a pair of ions, (not necessarily an ion pair) has been absorbed onto the stationary phase. [Fig.2.3.]

RP-IPC was originally used for the separation of organic anions [76,84] but rapidly adapted for the separation of inorganic anions [85,86,87]. This was generally achieved using a solvophobic cation such as tetralkylammonium salts as ion pair reagents [88]. With the use of solvent only mobile phases (i.e. containing no ion pair reagents), the anions elute with little or no retention.

The results for the separation of the ruthenium model complexes, using the µBondapak C18 cartridge column show the reverse of this effect. Table 2.2.

TABLE 2.2.

RETENTION DATA FOR RUTHENIUM COMPLEXES SEPARATED ON A C18 COLUMNS FOR A SELECTION OF MOBILE PHASES

Ret. Time (Min)	0.05M LiClO$_4$	0.05M LiClO$_4$		0.075M LiClO$_4$	0.1M LiClO$_4$
	0.05M LiClO$_4$ 100% MeCN	50% MeCN 50% CH$_3$Cl$_3$	0.05M LiClO$_4$ 100% MeOH	70% MeCN 30% H$_2$O	70%MeOH 30% H$_2$O
$[Ru(bpy)_2(HIm)_2]^{2+}$	3.1	3.0	7.1	4.2	3.9
$[Ru(bpy)_2(HIm)Cl]^{+}$	3.1	3.0	4.1	3.7	3.9
$[Ru(bpy)_2(VIm)_2]^{2+}$	3.2	2.9	6.3	5.3	4.8
$[Ru(bpy)_2(VIm)Cl]^{+}$	3.2	2.9	4.4	4.4	4.4
$[Ru(bpy)_2(CO)H]^{+}$	3.2	2.8	4.4	6.7	6.8

ASSYMETRY VALUES FOR SOME OF THE MOBILE PHASES

	0.075 M LiClO$_4$ 70% MeOH : 30% H$_2$O	0.1M LiClO$_4$ 70% MeOH : 30% H$_2$O
$[Ru(bpy)_2(HIm)_2]^{2+}$	3.0	1.9
$[Ru(bpy)_2(HIm)Cl]^{+}$	2.0	1.5
$[Ru(bpy)_2(VIm)_2]^{2+}$	3.4	1.9
$[Ru(bpy)_2(VIm)_2Cl]^{+}$	2.0	2.0
$[Ru(bpy)_2(CO)H]^{+}$	3.5	2.5

Fig. 2.3 Model of Proposed Mechanism for Ion Interaction
Chromatography. [Ref 81]
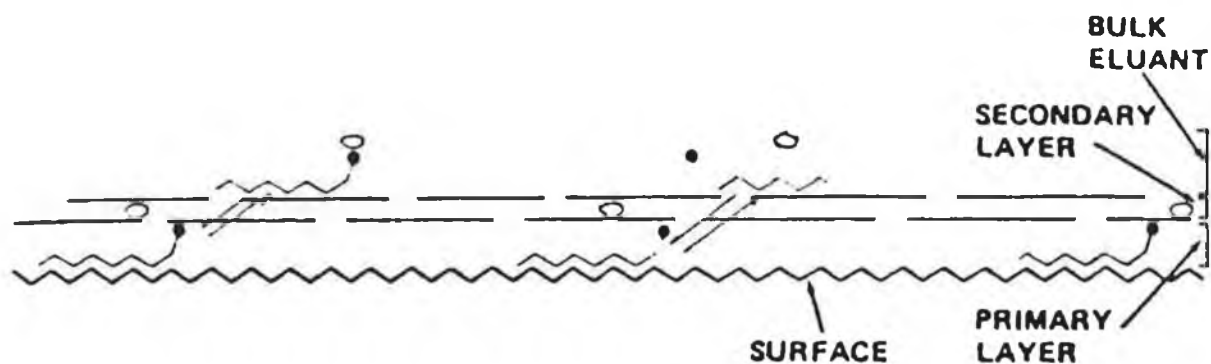
**The Ion-Interaction modal. The reagent ions (solid circles
with alkyl tails) ($\wedge\wedge\wedge^{\mathcal{J}}$) are adsorbed and create a charged primary ion
layer and an oppositely charged secondary ion layer. See text for
additional details. ●: ion of positive charge; ○: ion of negative**

Very large retention is observed when a mobile phase
containing no ion pair reagent is used. A more rapid
elution is induced by added $LiClO_4$ as an ion pair
reagent to the mobile phase.   At a flow rate of
1.5 ml /min of 100% MeCN mobile phase, at ambient
temperatures, all the ruthenium model complexes showed
excessively large retention times (i.e. > 20 mins)
with severe distortion of peak shape. However when a
mobile phase of 0.05 M $LiClO_4$ in MeCN was used greatly
reduced retention times were observed but little
separation occurred, with all the compounds eluting
at approximately 3 minutes retention time. However,
the peak shape was also significantly improved, with
tailing being reduced to an acceptable level. Mobile
phases of 0.05 M $LiClO_4$ in MeCN plus a less polar
solvent such as chloroform, dichloromethane and ethylacetate,
showed a further, though very small, reduction in
retention and also a slight decrease in separation.
However use of a more polar solvent in the mobile
phase serves to increase the retention of the complexes
and some separation may then be seen to occur. However
as the retention time increases distortion of peak
shape also increases with tailing becoming more
apparent.

The optimum conditions for separation of these
complexes on this column were found to be with a mobile

phase of **0.075** M LiClO$_4$ in a solution of 70% MeOH and
30% H$_2$O at a flow rate of 1.5 ml /min. This system
allowed for the separation of the corresponding
mono- and dication complexes and also the two dication
complexes containing different ligands, i.e.

[Ru(bpy)$_2$(HIm)Cl]$^+$ and   [Ru(bpy)$_2$(HIm)$_2$]$^{2+}$

[Ru(bpy)$_2$(VIm)Cl]$^+$ and   [Ru(bpy)$_2$(VIm)$_2$]$^{2+}$

and [Ru(bpy)$_2$(HIm)$_2$]   and   [Ru(bpy)$_2$(VIm)$_2$]$^{2+}$
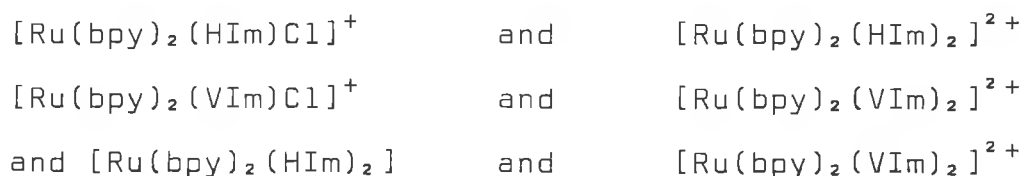
[Table 2.2.] However poor peak shapes with severe
tailing were observed for these separations, [Fig.2.4.].
Calculated assymetry values showed this system to have
extremely limited practical applications.

The fact that the analyte cations studied
exhibit very large retention times when there is no
couterion in the mobile phase,and that the retention
is decreased upon addition of the counterion is easily
explained, despite this being the reverse of what is
observed for classical RP-IPC. All of the model
compounds contain a ruthenium atom at the core of each
molecule surrounded by a number of ligands. Two
2,2'-bipyridine,(bpy), ligands are present in all
the complexes taking up four of the six co-ordination
sites around the ruthenium. It is in the remaining

Fig. 2.4   Separation of Ruthenium Compounds on C18 Column

HPLC
   Mobile Phase: 70% MeOH ; 0.075M LiClO$_4$
   Flow Rate: 1.5 ml /min

$[Ru(bpy)_2(HIm)Cl]^+$

$[Ru(bpy)_2(HIm)_2]^{2+}$

0   2   4   6   8   10

Retention Time(min)
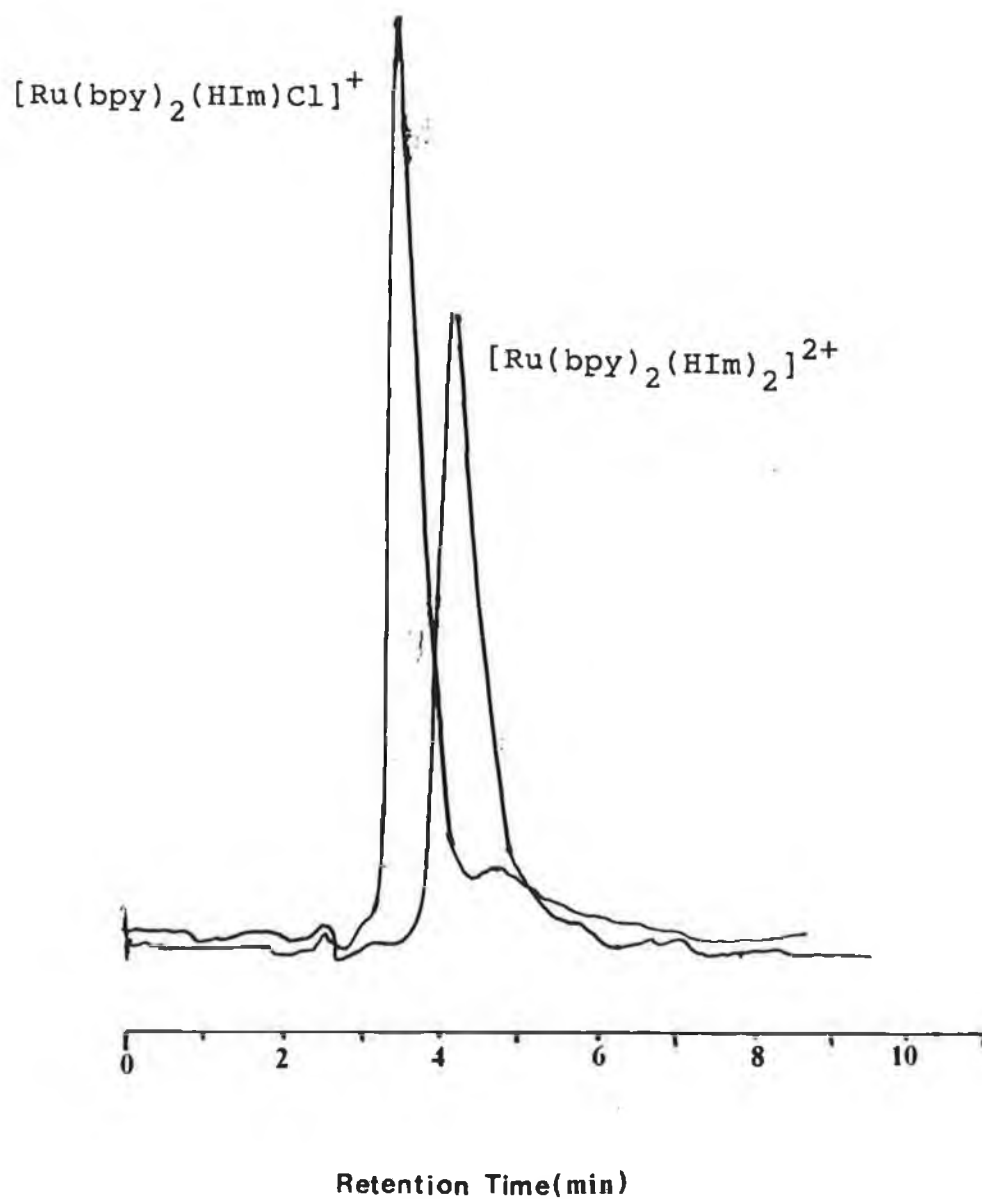
two sites that the ligands differ in each complex.
The two dication complexes contain two imidazole, [HIm],
ligands in one case and two vinylimidazole, [VIm],
ligands in the other. The monocations contain a
chlorine atom at one co-ordination site and a HIm,
VIm, or CO ligand at the final site. One monocation
complex contained hydrogen instead of a chlorine atom
at one site and a CO at the other. The bpy, HIm and
VIm ligands serve to increase the solvophobic nature
of these complexes and the complexes behave as such.

They exhibit high affinity for the stationary
phase and little for the polar mobile phase. However
the chlorate counterion is solvophilic and the
interaction between this and the cation results in
reduced retention. In many respects the ruthenium
cation complexes can be considered similar to the
ion pair reagents in classical RP-IPC in that they
behave as hydrophobic ions.

Very little study has been done on the
separation mechanism for metal chelate cations
containing 2,2' - bipyridyl or 1,10-phenanthroline
ligands.

However, Rigas and Pietrzyk [34], have used
RP-IPC on PRP-1 and Zorbax C18 columns to effect
the separation of inorganic anions, including the
ClO_4 anion, using $[Fe(phen)_3]^{2+}$ as the ion pair
reagent. The retention was found to be consistent
with the ion-interaction mechanism. Detection was
by UV absorbance at 510 nm where $[Fe(phen)_3]^{2+}$
absorbs. The absorbance was offset after
equilibration of the column. An increase in the
absorbance occured when the analyte peak eluted due
to the increase in $[Fe(phen)_3]^{2+}$ in this band. Hence
the presence of an anion e.g. ClO_4^- is seen to increase
the concentration of $[Fe(phen)_3]^{2+}$ in the mobile
phase. The system studied for the separation of our
model complexes is simply a converse of this system
studied by Rigas and Pietzyk. The metal chelate
is the analyte and the chlorate is the ion pair
reagent rather than vice versa. The mechanism governing
the systems should be similar, and thus an ion inter-
action process should dominate the separation of the
model complexes. Rigas and Pietzyk have also used
$[Fe(phen)_3]^{2+}$ as ion pair reagent in the separation
of organic anions on PRP-1 [35].

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The use of RP-IPC to separate these model complexes on a C18 column is a technique with severe limitations. This is due to the considerable tailing effects. All of the complexes studied showed peak distortion to a great degree if the retention time exceeded five minutes. This phenomenon is probably due to the interaction of the analyte with unreacted silanol groups on the column. [90]. Poor peak shapes and excessive retentions are the result. This is particularly evident with the C18 column as opposed to other columns investigated. However severe the conditions, none of the complexes could be induced to elute with a retention time of less than 2.8 mins and with these conditions separation was minimal. The interaction of the cationic complexes with the silanol sites may be due to adsorption by hydrogen bonding or cation exchange [89]. Cation exchange is less likely to be reversible as the molecule is eliminated as a cation source available for bonding with the ClO_4^- ion. Rigas and Pietrzyk noted that retention of $[Fe(phen)_3]^{2+}$ was less reversible on Zorbax C18 columns than PRP-1 columns (reverse phase) [34]. Earlier studies [90] had indicated that this was due to cation exchange activity by the free

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silanol sites on the C18 column. Thus it would seem
probable that this is also the reason for the
excessive retention and tailing of peaks in these
studies. This would also curtail any quantative
applications of the technique. The use of end capped
columns would serve to greatly reduce these effects
and result in increased resolution and efficiency,
decreased retention times and more symmetrical peak
shapes. An alternative method to reduce peak tailing
could involve the use of a competing cation such as
n-nonyl amine. This might be preferentially adsorbed
onto the free silanol sites making them unavailable
to the complex ions. However, this would be a change
in the equilibrium of the system and it would be very
difficult to predict the effect this might have.

Other parameters which have an effect on the
system equilibrium are the counteranion of the
complexes and the Li^+ ion in the mobile phase.
Furthermore, the analyte bands would be expected to
be broader than for neutral compounds as the cations
adsorbed onto the stationary phase will repel each
other and therefore space themselves further apart.

100.

A CN column was used in the reversed phase mode. With a 100% MeOH mobile phase containing $LiClO_4$ to a concentration of 0.05 M the ruthenium model complexes all eluted at significantly lower retention and also demonstrated better resolution than for those conditions on the C18 column. [Table 2.3.] (Fig. 2.5.). The optimum conditions for separation used a mobile phase of 0.08 M $LiClO_4$; 70% MeOH : 30% H_2O at a flow rate of 1.5 ml /min. Other mobile phases used contained acetonitrile and water with $LiClO_4$.

Although peak tailing was still evident, especially at the longer retention times, it was considerably less a problem for this column than for the C18 Column. However an added complication occured when using optimum separation conditions and conditions close to the optimum, in that some of the complexes exhibited splitting effects.

Peak splitting is a phenomenon associated with ion-pair chromatography which is not well understood. A pure sample may appear as a severely distorted peak or as two discrete peaks. Low and Haddad [91] proposed that this was the result of a composite interplay of two retention mechanisms, such as ion pairing and dynamic ion exchange which are

TABLE 2.3.

RETENTION DATA FOR RUTHENIUM COMPLEXES SEPARATED ON A CN COLUMN FOR A SELECTION

OF MOBILE PHASES

Ret. Time (min)	0.05 M $LiClO_4$ 100% MeOH	0.1 M $LiClO_4$ 100% MeOH	0.08 M $LiClO_4$ 70% MeOH 30% H_2O	0.1 M $LiClO_4$ 70% MeOH 30 H_2O
$[Ru(bpy)_2(HIm)_2]^{2+}$	3.7	2.6	2.5	1.9
$[Ru(bpy)_2(HIm)Cl]^+$	1.7	1.6	1.6	1.5
$[Ru(bpy)_2(VIm)_2]^{2+}$	3.7	3.6	3.2	2.4
$[Ru(bpy)_2(VIm)Cl]^+$	1.9	1.8	1.9	1.6
$[Ru(bpy)_2(CO)H]^+$	2.2	2.4	2.6	1.9

ASSYMETRY VALUES

	0.08 M $LiClO_4$ 70% MeOH : 30% H_2O	0.1 M $LiClO_4$ 70% MeOH : 30% H_2O
$[Ru(bpy)_2(HIm)_2]^{2+}$	1.8	2.0
$[Ru(bpy)_2(HIm)Cl]^+$	1.7	1.3
$[Ru(bpy)_2(VIm)_2]^{2+}$	6.3	1.8
$[Ru(bpy)_2(VIm)Cl]^+$	1.3	1.0
$[Ru(bpy)_2(CO)H]^+$	2.0	1.5

Fig. 2.5   Separation of Ruthenium Compounds on CN Column

HPLC
   Mobile Phase: 70% MeOH ; 0.075M LiClO$_4$
   Flow Rate: 1.5 ml /min

$[Ru(bpy)_2(HIm)Cl]^+$

$[Ru(bpy)_2(VIm)Cl]^+$

$[Ru(bpy)_2(HIm)_2]^{2+}$

$[Ru(bpy)_2(VIm)_2]^{2+}$

0   2   4   8   0   2   4   6   8

Retention Time (min)
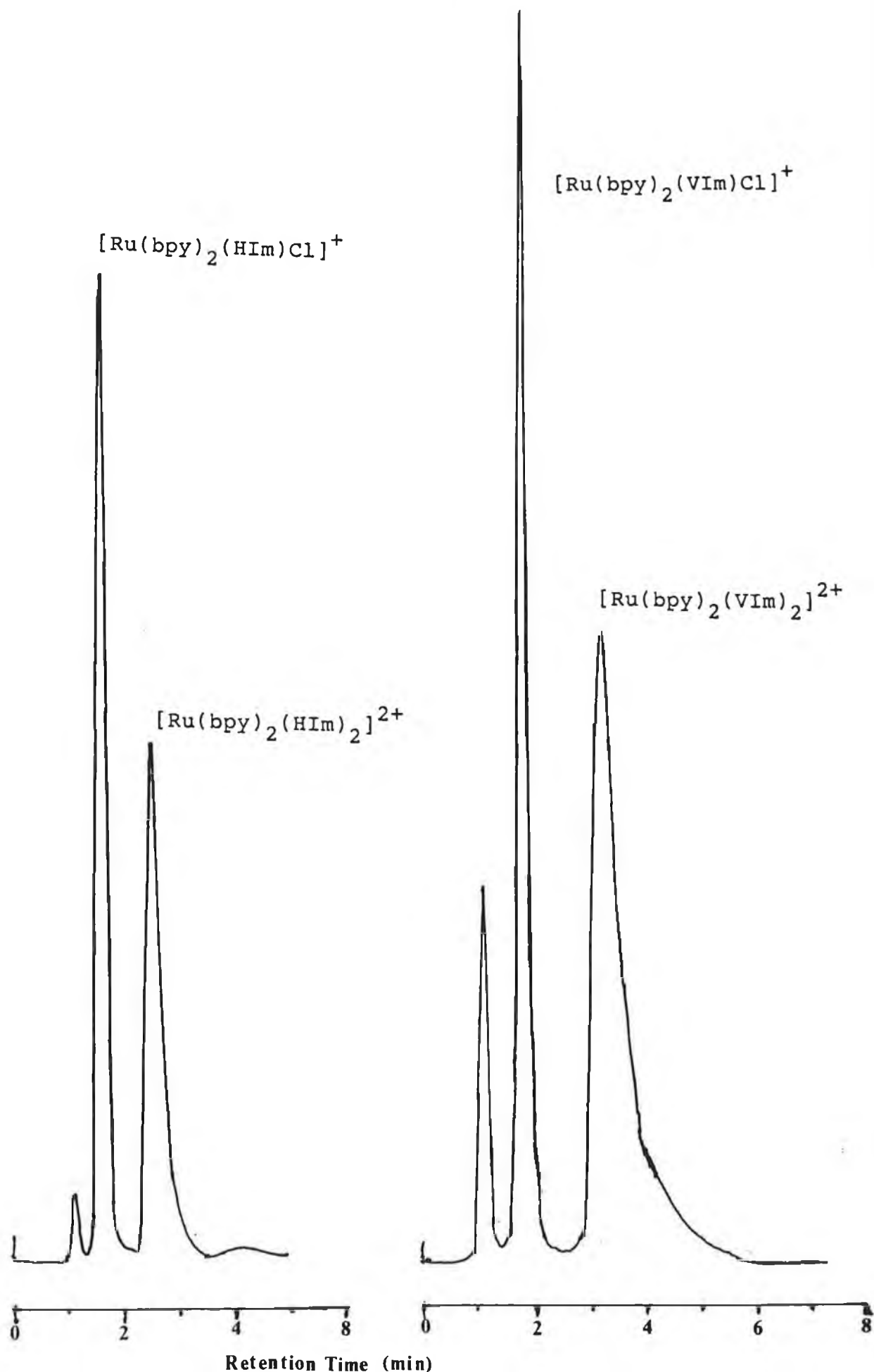
competitive under certain conditions. At 70% MeOH :
30% H_2O, 0.08 M $LiClO_4$ with a 1:5 ml /min flow rate,
$[Ru(bpy)_2(HIm)Cl]PF_6$ and $[Ru(bpy)_2(VIm)Cl]PF_6$ gave two
distinct peaks. For $[Ru(bpy)_2(HIm)Cl]PF_6$ a major peak
eluted after 1.6 mins with a minor peak, approximately
one tenth of the height eluting at 1.2 mins. For
$[Ru(bpy)_2(VIm)Cl]PF_6$ the major peak at 1.9 mins
was approximately three times the height of the minor
peak at 1.2 mins. None of the other complexes studied
demonstrated evidence of the occurence of this phenomenon.
The complexes which were split were shown to be
chromatographically pure. The absorbance ratios at
two different detection wavelengths, 254 nm and 280 nm
for the split peaks were similar, suggesting that they
consisted of the same compound.

Hanson and O'Laughlin [27] used a μBondapak
CN column to achieve the separation of $[Ru(phen)_3]^{2+}$
and $[Fe(phen)_3]^{2+}$. With a mobile phase of 50%
MeCN 50% H_2O; 0.5% acetic acid and 0.015 M methane-
sulphonic acid at 1.0 ml/min flow rate, they observed
that the $[Ru(Phen)_3]^{2+}$ peak was split. However they
made no attempt to explain this observation. At the
present time, Low and Haddad's model remains the most
plausible explanation of the phenomenon of peak
splitting [91].

Studies using sodium dodecyl sulphate, (SDS),
as the ion pair reagent instead of $LiClO_4$ were
performed on the CN column [Table 2.4.]. Retention
was seen to be very large with much tailing particularly
for the dication complexes. This is because the ion
pair reagent contains a large C12, alkyl group.
Therefore the "ion-pair" shows a greater affinity
for the stationary phase compared with the Ru complex
ClO_4 "ion pair" as there are solvophobic contributions
from the counterion as well as from the Ru complex.
Classical alkyl group containing ion pair reagents,
such as SDS, would therefore appear to have little or
no value as counterions for the separation of these
model complexes. In general however CN columns might
prove more useful for these separations than C18
columns if peak splitting could be eliminated. The
use of end capped columns would be advisable so as to
reduce tailing effects.

(ii) Cation Exchange Chromatography

As with the CN and C18 columns, the retention
mechanism that operates for the Ru model complexes on
a cation exchange (CX) column are extremely complicated.
[Table 2.5.] Many of the problems encountered with
the RP-IPC technique were also prevalent with this
system. MeCN was found to be a more suitable solvent

TABLE 2.4.

RETENTION DATA FOR RUTHENIUM COMPLEXES ON A CN COLUMN

USING SDS AS MOBILE PHASE ADDITIVE

RET. TIME (Min)	0.03 M SDS 100% MeOH	0.05 M SDS 100% MeOH
$[Ru(bpy)_2(HIm)_2]^{2+}$	6.4 [ST]	3.2 [ST]
$[Ru(bpy)_2(HIm)Cl]^+$	1.4	1.2
$[Ru(bpy)_2(VIm)_2]^{2+}$	10.6 [ST]	5.0 [ST]
$[Ru(bpy)_2(VIm)Cl]^+$	1.7	1.5
$[Ru(bpy)_2(CO)H]^+$	2.0	1.4
$[Ru(bpy)_2(CO)Cl]$	2.9 [T]	2.0

T   =   Tailing

ST   =   Severe Tailing

TABLE 2.5.

RETENTION DATA FOR CX COLUMN FOR A SELECTION OF

MOBILE PHASES   (FLOW RATE = 2.5 ml /min)

Ret. Time (Min)	100% MeCN		
	0.05M LiClO$_4$	0.08M LiClO$_4$	0.1M LiClO$_4$
[Ru(bpy)$_2$(HIm)$_2$]$^{2+}$	6.7	4.4	4.3
[Ru(bpy)$_2$(HIm)Cl]$^+$	4.0	3.0	3.0
[Ru(bpy)$_2$(VIm)$_2$]$^{2+}$	4.1	3.0	2.8
[Ru(bpy)$_2$(VIm)Cl]$^+$	3.5	2.8	2.7
[Ru(bpy)$_2$(CO)H]$^+$	3.8	3.2	2.3
[Ru(bpy)$_2$(CO)Cl]$^+$	2.8	2.9	2.7

	80% MeCN : 20% H$_2$O		
	0.05M LiClO$_4$	0.08M LiClO$_4$	0.1M LiClO$_4$
[Ru(bpy)$_2$(HIm)$_2$]$^{2+}$	8.5	6.0	3.1
[Ru(bpy)$_2$(HIm)Cl]$^+$	2.5	2.3	2.1
[Ru(bpy)$_2$(VIm)$_2$]$^{2+}$	5.0	3.8	2.3
[Ru(bpy)$_2$(VIm)Cl]$^+$	2.2	2.2	2.0
[Ru(bpy)$_2$(CO)H]$^+$	2.0	2.0	1.8
[Ru(bpy)$_2$(CO)Cl]$^+$	2.9	2.8	2.2

	70% MeCN : 30% H$_2$O		
	0.05M LiClO$_4$	0.08M LiClO$_4$	0.1M LiClO$_4$
[Ru(bpy)$_2$(HIm)$_2$]$^{2+}$	14.8	6.3	4.6
[Ru(bpy)$_2$(HIm)Cl]$^+$	2.4	2.2	2.0
[Ru(bpy)$_2$(VIm)$_2$]$^{2+}$	8.5	4.1	3.1
[Ru(bpy)$_2$(VIm)Cl]$^+$	2.2	2.0	1.9
[Ru(bpy)$_2$(CO)H]$^+$	2.0	2.5	1.8
[Ru(bpy)$_2$(CO)Cl]$^+$	3.1	2.4	2.3

for the mobile phase than MeOH as the latter resulted
in long retentions. LiClO$_4$ was used in the mobile
phase to provide the counteranion. A flow rate of
2.5 ml /min was used. Although this is quite a high
flow rate which shortens the column lifetime it has
two advantages. Firstly, elution of the compounds
is achieved in a smaller time span resulting in less
broadening and tailing for the later eluting complexes,
and secondly, it reduces the risk of precipitation
of LiClO$_4$ in the pump, which causes blockage.

Peak tailing, though still a major problem
with this system, is not as severe as with the RP-IPC
systems. As with the reverse phase systems, the use
of end capped columns should rectify this. However,
the aim of this study was to achieve the best
separation for the model complexes with the minimum of
peak distortion. The complexes were injected onto the
column with MeCN/H$_2$O mobile phases containing LiClO$_4$.
Retention times were plotted against % MeCN at given
LiClO$_4$ concentrations [Fig. 2.6 A/B/C] and against
concentration of LiClO$_4$ at given MeCN : H$_2$O ratios.
[Fig. 2.7. A/B/C]. These graphs demonstrate the
complexity of the mechanisms involved.

0.05M LiClO4 \ %MeCN

%MeCN vs. retention time

%MeCN (v/v) in H2O

Ret. time [min]

+ [Ru(bpy)2(HIm)Cl]+   ◇ [Ru(bpy)2(VIm)2]2+
✕ **[Ru(bpy)2(CO)H]+**   ▽ [Ru(bpy)2(CO)Cl]+

□ **[Ru(bpy)2(HIm)2]2+**
△ **[Ru(bpy)2(VIm)Cl]+**

Fig. 2.6B   The Effect of Acetonitrile Variation in the Mobile
            Phase at 0.08M LiClO$_4$

0.08M LiClO4 \ %MeCN

%MeCN vs. retention time

%MeCN (v/v) in H2O

+ [Ru(bpy)2(HIm)Cl]+   ◇ [Ru(bpy)2(VIm)2]2+
× **[Ru(bpy)2(CO)H]+**   ▽ **[Ru(bpy)2(CO)Cl]+**

□ [Ru(bpy)2(HIm)2]2+
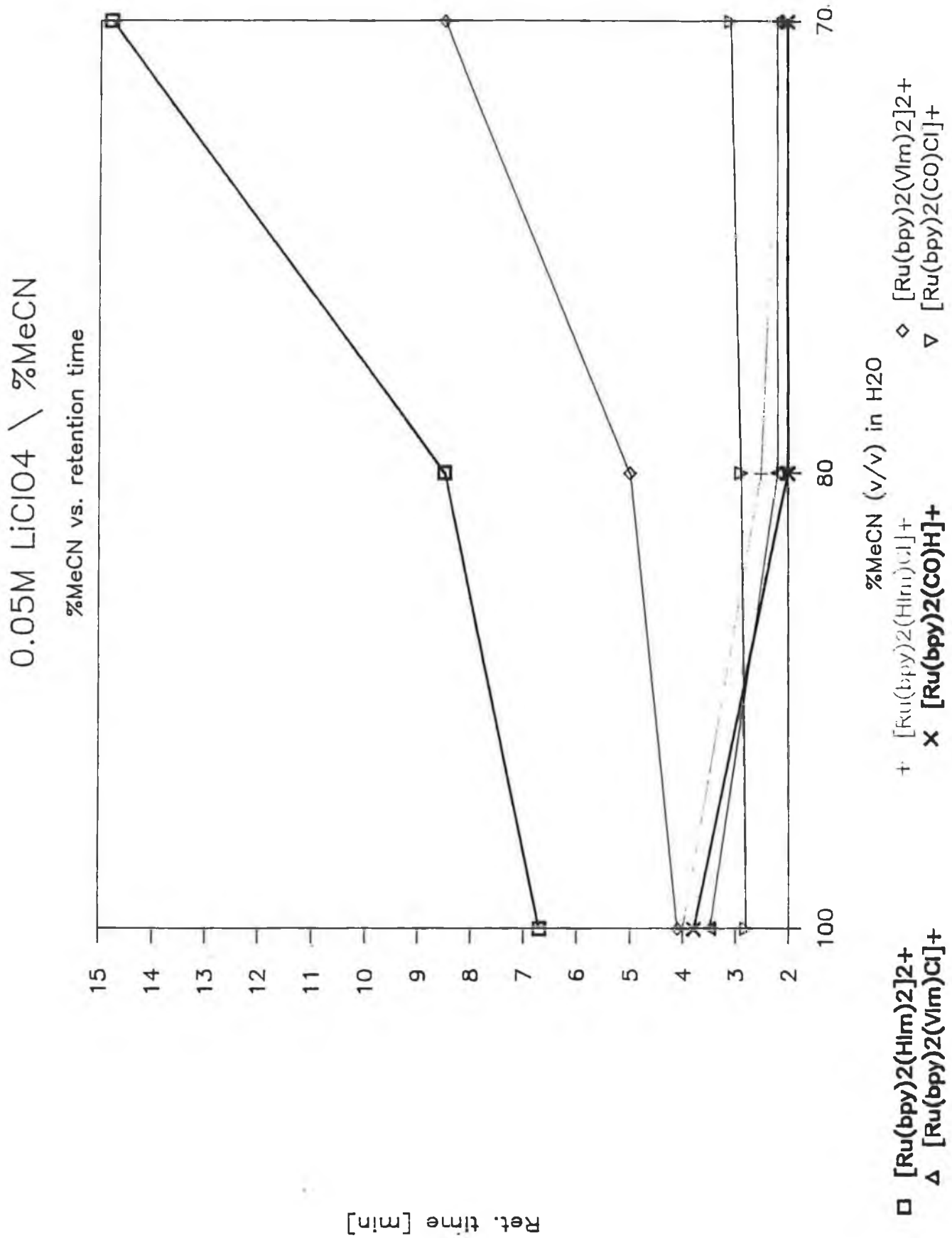▲ [Ru(bpy)2(VIm)Cl]+

Ret. time [min]
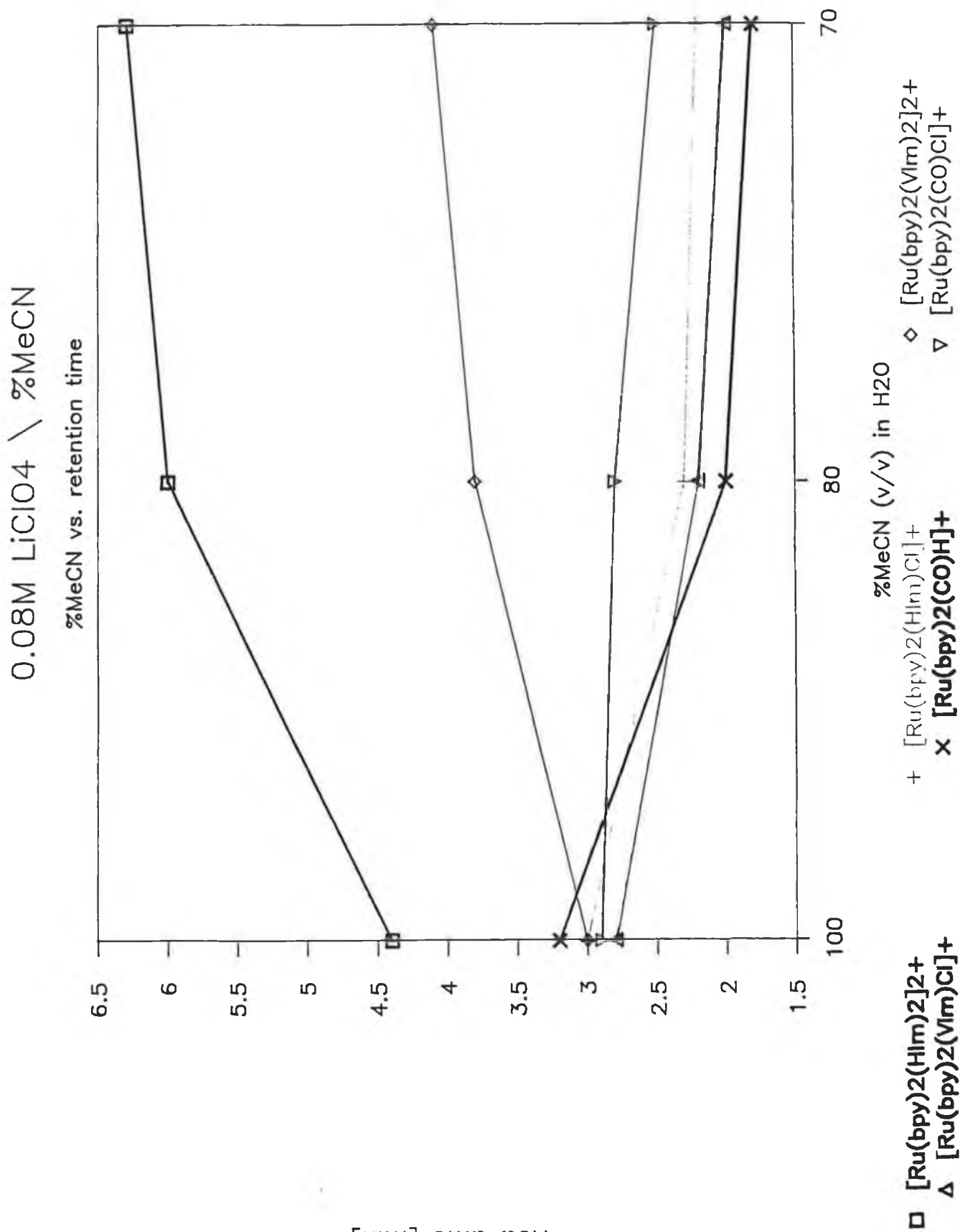
Fig 2.6C The Effect of Acetonitrile Variation in the Mobile
Phase at 0.1M LiClO$_4$

Fig. 2.7A The Effect of LiClO$_4$ Variation in the Mobile Phase at 70% MeCN

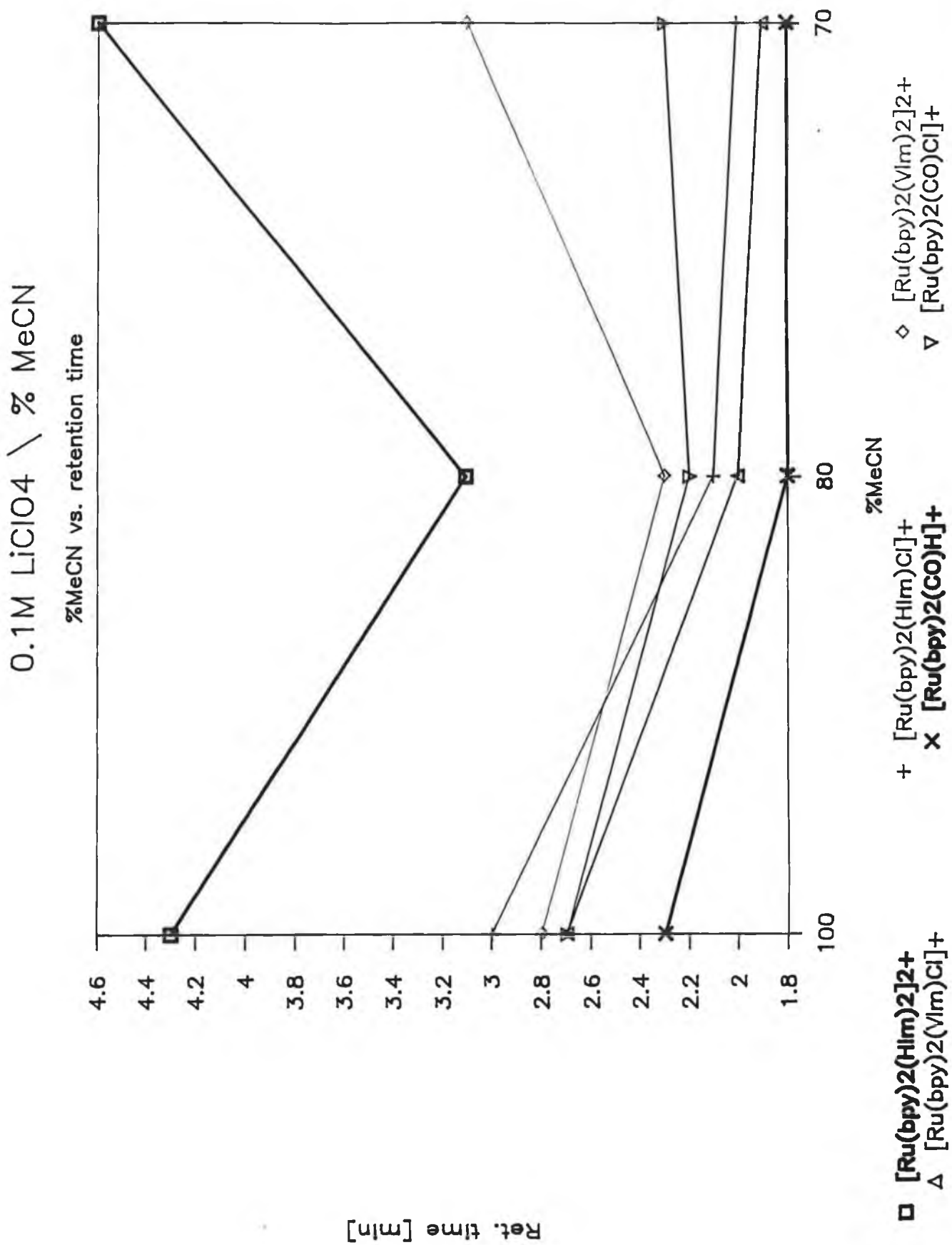

70% MeCN \ LiClO4

LiClO4 vs. retention time

Ret. time [min]

LiClO4 conc. [M]

+ [Ru(bpy)2(HIm)Cl]+   ◇ [Ru(bpy)2(VIm)2]2+
✕ **[Ru(bpy)2(CO)H]+**   ▽ [Ru(bpy)2(CO)Cl]+

□ [Ru(bpy)2(HIm)2]2+
△ [Ru(bpy)2(VIm)Cl]+
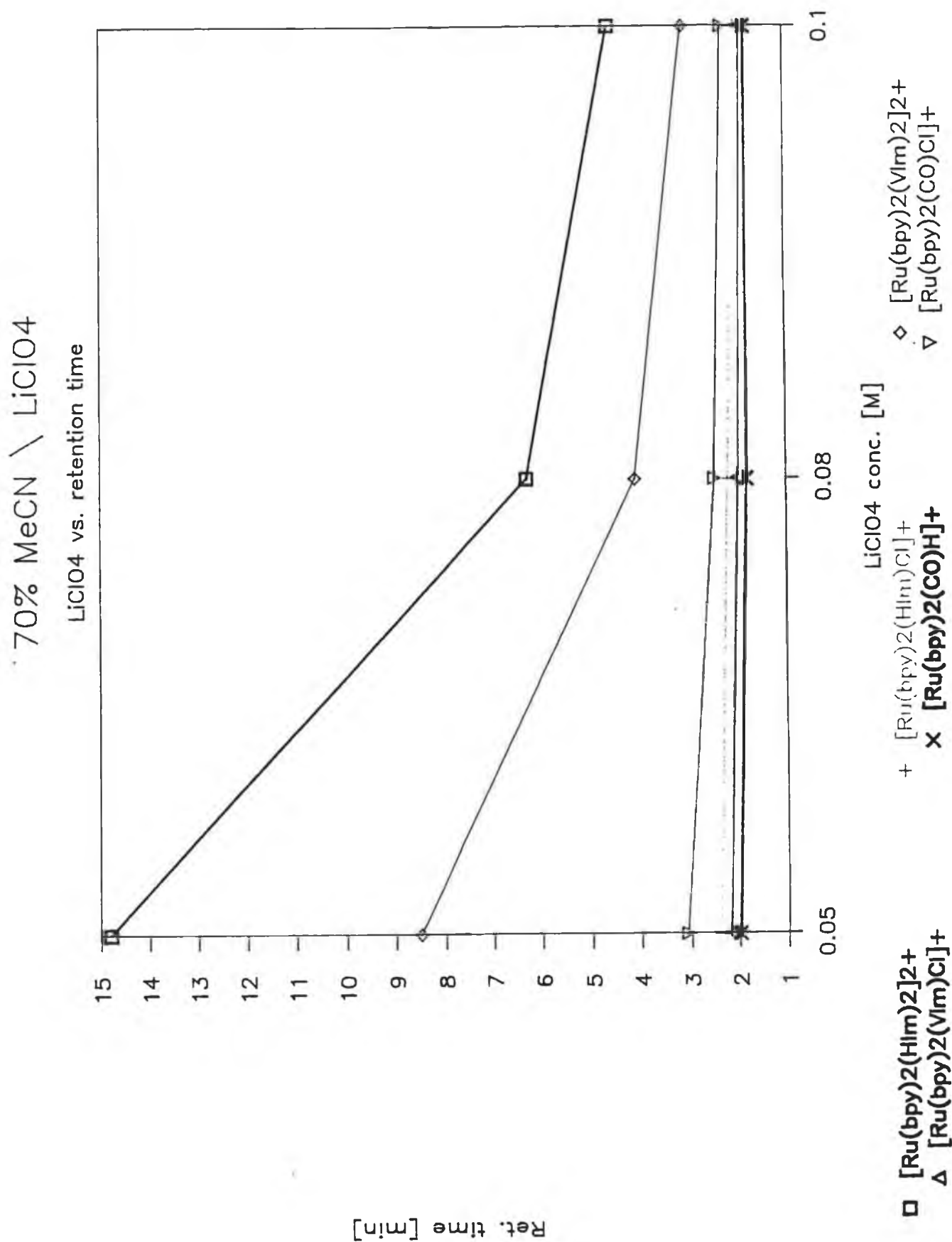
Fig. 2.7B The Effect of LiClO$_4$ Variation in the Mobile Phase at 80% MeCN

80% MeCN \ LiClO4

LiClO4 vs. retention time

Ret.time [min]

LiClO4 conc. [M]

+ [Ru(bpy)2(HIm)Cl]+   ◇ [Ru(bpy)2(VIm)2]2+
✕ **[Ru(bpy)2(CO)H]+**   ▽ [Ru(bpy)2(CO)Cl]+
□ **[Ru(bpy)2(HIm)2]2+**
△ **[Ru(bpy)2(VIm)Cl]+**
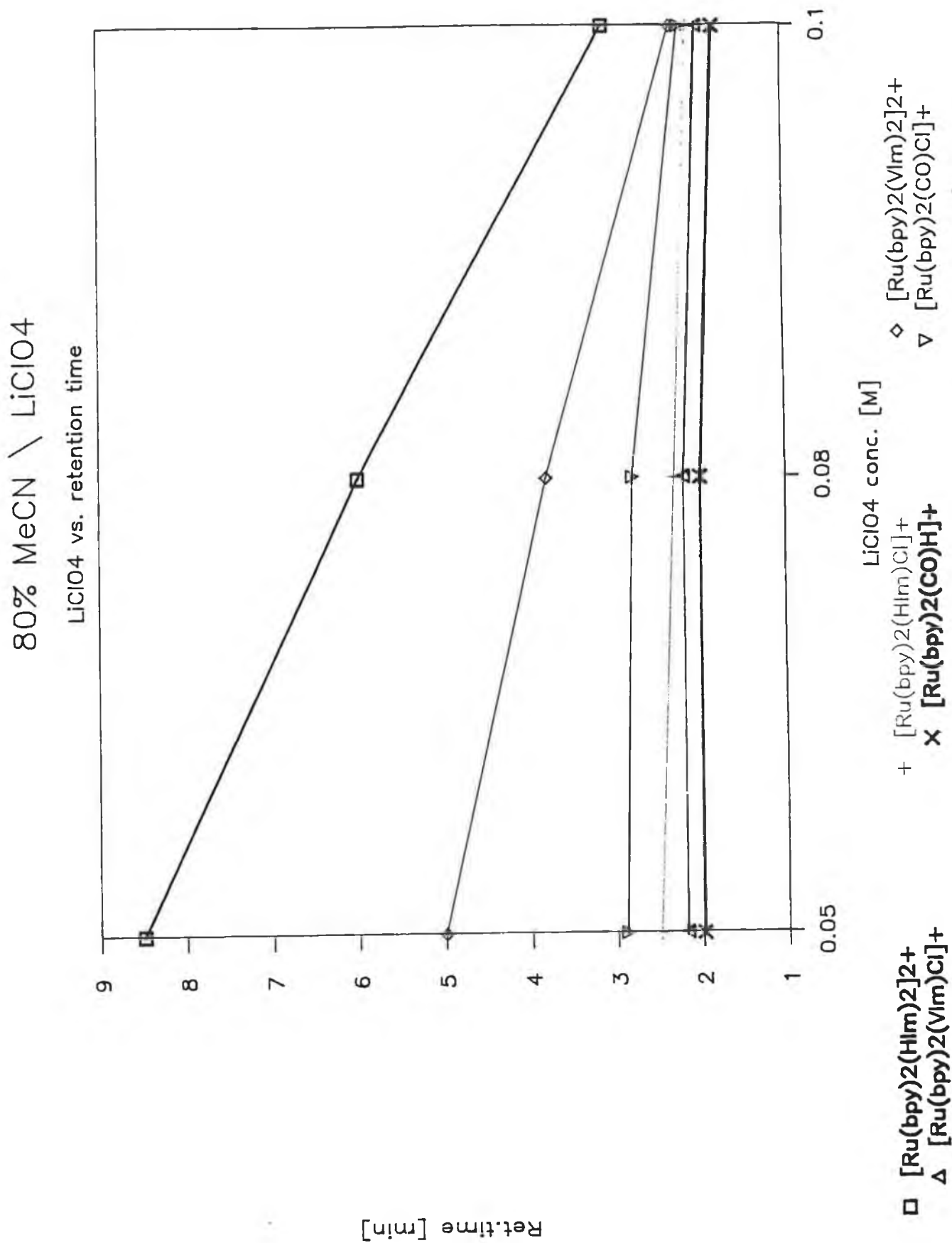
Fig. 2.7C   The Effect of LiClO$_4$ Variation in the Mobile Phase at
at 100% MeCN

100% MeCN \ LiClO4

LiClO4 vs. retention time

LiClO4 conc. [M]

Ret time [min]

+ [Ru(bpy)2(HIm)Cl]+   ◇ [Ru(bpy)2(VIm)2]2+
✕ **[Ru(bpy)2(CO)H]+**   ▽ [Ru(bpy)2(CO)Cl]+

□ **[Ru(bpy)2(HIm)2]2+**
▲ **[Ru(bpy)2(VIm)Cl]+**

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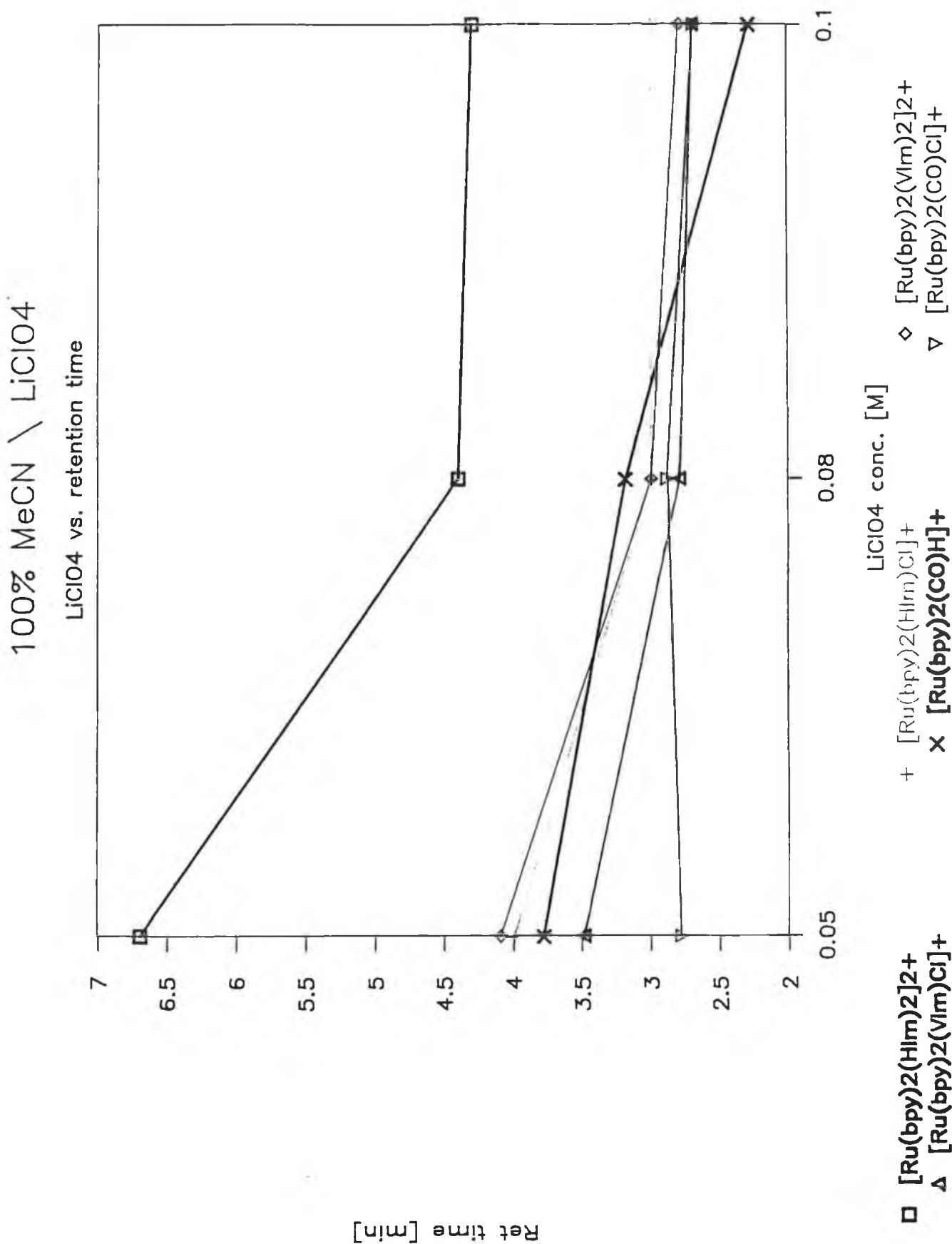
The retention times for the dicationic compounds increase exponentially with increasing water content at 0.05 M $LiClO_4$. The retention times for the monocationic compounds, excluding $[Ru(bpy)_2(CO)Cl]^+$, decreases at the same conditions. This suggests that the retention mechanism which operates at these conditions is probably due to the distribution of the compounds between the mobile and stationary phases rather than classical ion exchange. Support for this explanation is provided by O'Laughlin, [28]. In performing a separation of a selection of $[M(phen)_3]^{2+}$ compounds, (M = Ni, Ru, Fe), on an SCX column using an MeCN = H_2O : $HClO_4$ mobile phase. He concluded that the retention was not due to ion exchange but a distribution of the chelate species, paired with ClO_4 ions, between the mobile and stationary phases.

For the corresponding plot at 0.09**M** $LiClO_4$ [Fig. 2.6.] the same trend is observed. However, the curves for the dicationic complexes no longer exhibit an exponential shape. At 0.1 M $LiClO_4$ a different phenomenon is observed. The monocationic complexes, excluding $[Ru(bpy)_2CO\ Cl]^+$, exhibit small decreases in retention whereas the dicationic

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complexes decrease in retention and then increase again. This would suggest the possibility of a change in the dominant retention mechanism for the dicationic complexes. At high acetonitrile water ratios the dominant retention mechanism is possibly due to cation exchange. As the water content is increased in the mobile phase the distribution mechanism becomes the dominant form. The fact that with an 80% MeCN : 20% H_2O, 0.1 M $LiClO_4$, mobile phase the peaks for the dicationic complexes demonstrate splitting effects particularly those containing imidazole ligands, provides evidence for this suggestion.

Plots of retention time versus concentration of $LiClO_4$ at given MeCN : H_2O ratios showed the retention time for all complexes studied to reduce with increasing $LiClO_4$ concentration [Fig. 2.7.]. However the graph shapes are not uniform for the different MeCN : H_2O ratios. A possibility is that the competing retention mechanisms contribute to this effect.

Extensive further rate work is needed to provide a conclusive explanation, for the on-column phenomena present in this system.

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It should be noted that there is a reversal
of the elution order for the CX column as opposed to
the C18/CN columns. The monocationic complexes still
elute before the dications but within these groups
the elution order was different, the vinylimidazole
complexes eluting before their corresponding imidazole
complexes. The ruthenium hydride complex studied has
the shortest retention on the CX column but is quite
strongly retained on the reverse phase columns, eluting
last of the monocations. Similar observations were made
by O'Laughlin [28] when studying the separation of
$[M(Phen)_3]^{2+}$ (M = Ni,Ru,Fe), complexes in an MeCN : H_2O
$HClO_4$ mobile phase. He observed the order of elution
for these complexes to be reversed when using an SCX
column as opposed to a reversed phase PRP-1 column.

An advantage of the systems described is that
as they are isocratic the mobile phase can be recycled
and thence the running costs of the system are very
small.

The use of HPLC in this form of chemistry is
demonstrated by following photolysis reactions of
some of the ruthenium complexes. This is described
in the next section. The most suitable system chosen
to monitor these reactions was using the CX column with

mobile phase of 80% MeCN : 20% H_2O , 0.08 M $LiClO_4$ or
0.05 M $LiClO_4$. [Fig. 2.8.]. These systems can be
easily modified to suit the immediate requirements
of an experiment.

B. THE PHOTOLYSIS IN ACETONITRILE OF IMIDAZOLE AND
   VINYLIMIDAZOLE CONTAINING COMPLEXES OF RUTHENIUM
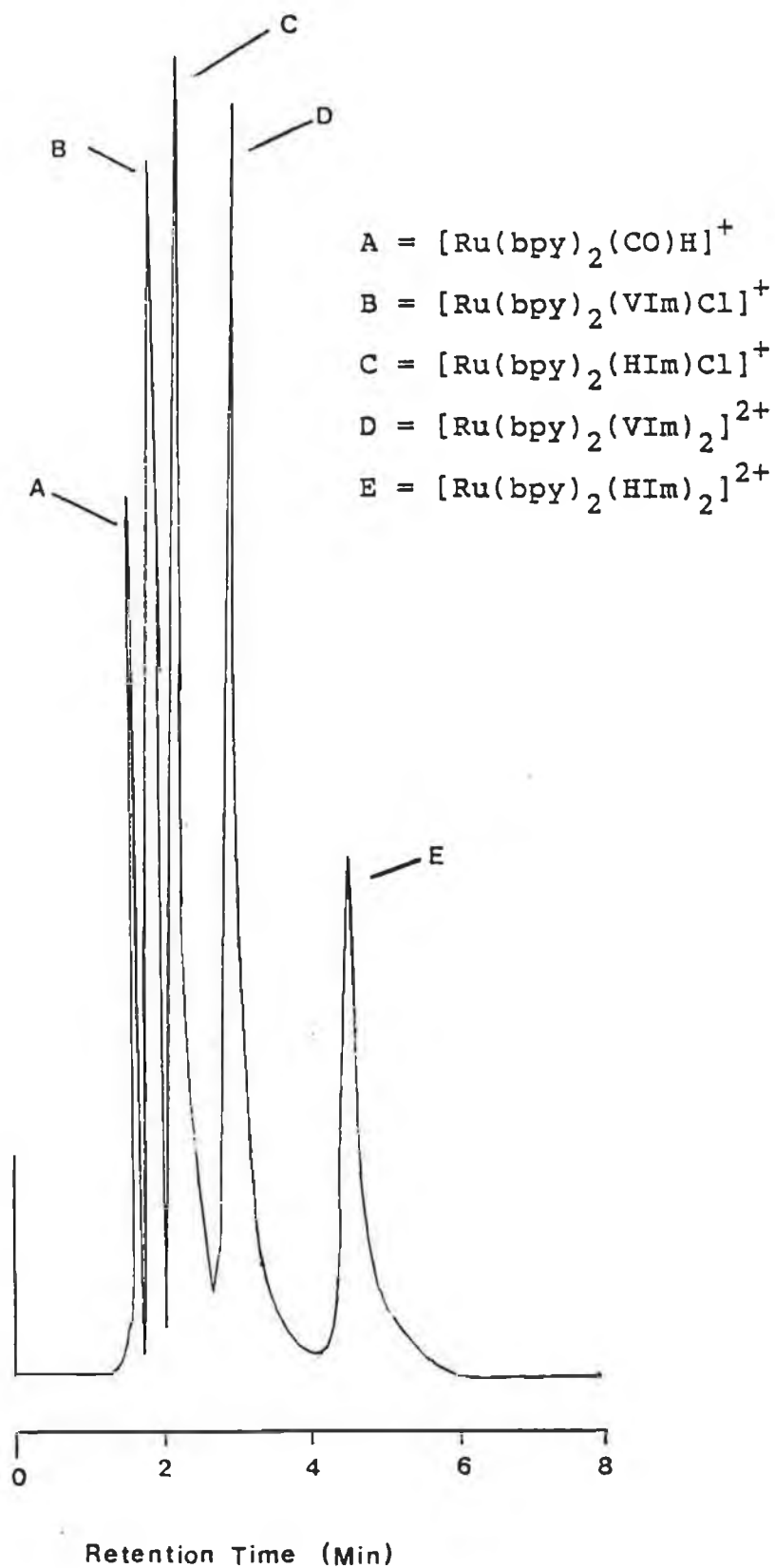   bis (2,2'-bipyridine)

   (i) An Application of the HPLC System

       The chemical and photochemical properties of
ruthenium bis(bipyridyl) complexes have been studied in
great detail in recent years [37,38,40,43,44].
Photochemical studies have been carried out, generally
using spectroscopic or electrochemical techniques.
However minor products and impurities are masked by
greater quantities of major products and often the
only indication of complex reactions is shown by poor
isosbestic points. For this reason HPLC has a
distinct advantage over other methods in that it allows
for the separation of the different products, and
indeed intermediates, involved in a reaction. Used
in conjunction with spectroscopic and/or electrochemical
techniques, HPLC offers an approach to studies of
reactions such as these which can greatly enhance our
understanding of these reactions. For example in

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Fig. 2.8 The Separation of Ruthenium Compounds on a CX Column

HPLC
   Mobile Phase: 80% MeCN ; 0.08M LiClO$_4$
   Flow Rate: 2.5 ml /min

$A = [Ru(bpy)_2(CO)H]^+$

$B = [Ru(bpy)_2(VIm)Cl]^+$

$C = [Ru(bpy)_2(HIm)Cl]^+$

$D = [Ru(bpy)_2(VIm)_2]^{2+}$

$E = [Ru(bpy)_2(HIm)_2]^{2+}$

Retention Time (Min)

this case a photodiode array detector enabled the UV/Vis
spectra of the separated intermediates and products to
be obtained. Along with retention time, this provided
a powerful method of peak indentification.

The compounds studied were [Ru(bpy)$_2$(HIm)Cl]PF$_6$,
[Ru(bpy)$_2$(HIm)$_2$](PF$_6$)$_2$, [Ru(bpy)$_2$(VIm)Cl]PF$_6$ and
[Ru(bpy)$_2$(VIm)$_2$](PF$_6$)$_2$. Photolysis of these complexes
in acetonitrile was induced by irradiation with light
in the ultra violet/visible range. The photolysis
reaction under these conditions were seen to be of a
more complicated nature than at first imagined.

While a CX column produced more efficient
chromatography, peak identification could only be
achieved by use of retention times. A more thorough
study of the reactions was achieved with a photodiode
array detector using an ODS column although the
chromatography was poorer. The ideal system would be
the use of the CX column system in conjunction with
the photodiode array detector but limited resources
made this impossible.

(ii)   The Photolysis of [Ru(bpy)$_2$(HIm)Cl]PF$_6$

       and [Ru(bpy)$_2$(HIm)$_2$] (PF$_6$)$_2$

Note: All Retention Times quoted are for Mobile Phases
        containing 0.08 **M** LiClO$_4$ (ODS Column) and
        containing 0.07**M** LiClO$_4$ (CX Column) unless stated.

        For the photolysis in acetonitrile of the
complex [Ru(bpy)$_2$(HIm)$_2$](PF$_6$) [Fig. 2.9 - 11], the
final product is the solvent substituted complex.
[Ru(bpy)$_2$(MeCN)$_2$]$^{2+}$. This was verified by comparison
of the retention times with authentic bis-acetonitrile
complex and comparison of spectra (λmax. ca. 420 nm,
Rt = 6.0 min [CX]/6.2 min (ODS). This complex is
strongly retained by both the CX and ODS columns.
No formation of [Ru(bpy)$_2$(MeCN)$_2$]$^{2+}$ is observed for
the photolysis of [Ru(bpy)$_2$(HIm)Cl]PF$_6$ in acetonitrile
[Fig. 2.12-14].

        The photolysis of [Ru(bpy)$_2$(HIm)$_2$]$^{2+}$ when
monitored by HPLC shows the occurence of the
intermediate [Ru(bpy)$_2$(HIm)(MeCN)]$^{2+}$, (λmax ca. 444nm,
Rt = 3.9 min [CX]/4.0 min [ODS]. The formation of
this compound takes place relatively quickly but the
level present subsides as [Ru(bpy)$_2$(MeCN)$_2$]$^{2+}$ begins

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TABLE 2.6.

PHOTOLYSIS OF $[Ru(bpy)_2(HIm)_2]^{2+}$ AND $[Ru(bpy)_2(HIm)Cl]^+$

IN ACETONITRILE

Mobile Phase : 0.08M $LiClO_4$; 80% MeCN : 20% H_2O

Column : ODS   Flow Rate : 2.5 ml /min

Detection: Photodiode Array   [Monitor   : 254 nm]

Photolysis Time = 15 min $[Ru(bpy)_2(HIm)_2]^{2+}$

Retention Time (Mins)	Identification	λ Max (nm)
1.2. (V.S)	- - - - -	- - -
2.0 (V.S.)	- - - - -	- - -
3.2	$[Ru(bpy)_2(HIm)_2]^{2+}$	489
3.8	- - - - -	439
4.0	$[Ru(bpy)_2(MeCN)(HIm)]^{2+}$	444
6.2	$[Ru(bpy)_2(MeCN)_2]^{2+}$	422

Photolysis Time = 165 min $[Ru(bpy)_2(HIm)Cl]^+$

Retention Time (Mins)	Identification	λ Max (nm)
1.2 (V.S.)	- - - - -	- - -
1.9	$(Ru(bpy)_2(HIm)Cl)$	510 nm
2.2	- - - - -	485 nm
2.51	$[Ru(bpy)_2(MeCN)Cl]^+$	470 nm
3.7	- - - - -	438 nm

(V.S.) = Very small peaks

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PHOTOLYSIS of [Ru(bpy)$_2$(HIm)$_2$](PF$_6$)$_2$

COLUMN: CX

MOBILE PHASE:

80% CH$_3$CN:20% H$_2$O; 0·05m LiClO$_4$
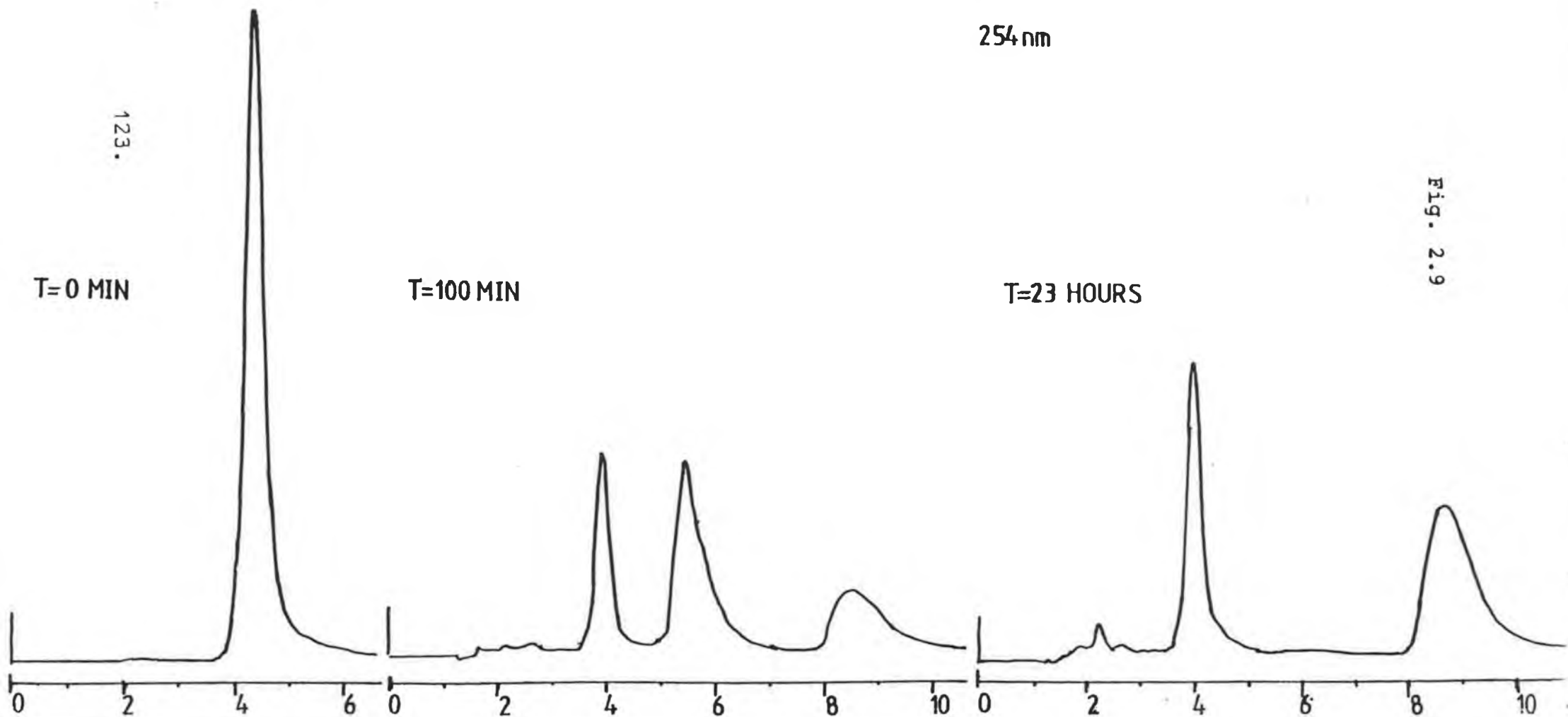
UV DETECTION:

254 nm

123.

Fig. 2.9

T= 0 MIN

T=100 MIN

T=23 HOURS

Fig. 2.10   HPLC Analysis of the Photolysis of $[Ru(bpy)_2(HIm)_2]^{2+}$
in MeCN: Photolysis Time = 15 mins

HPLC

Mobile phase: 80% MeCN ; 0.08M $LiClO_4$
Column: ODS
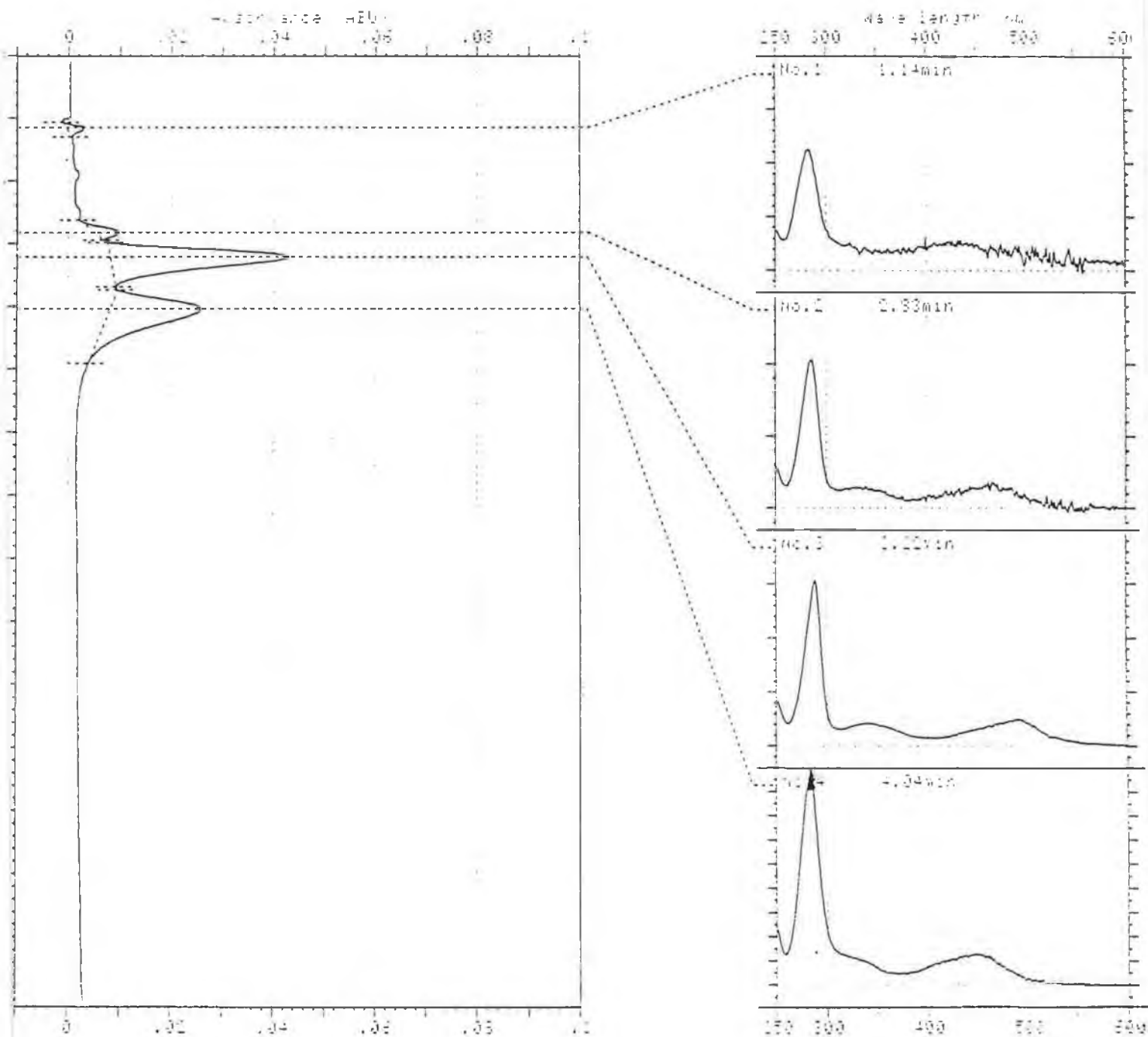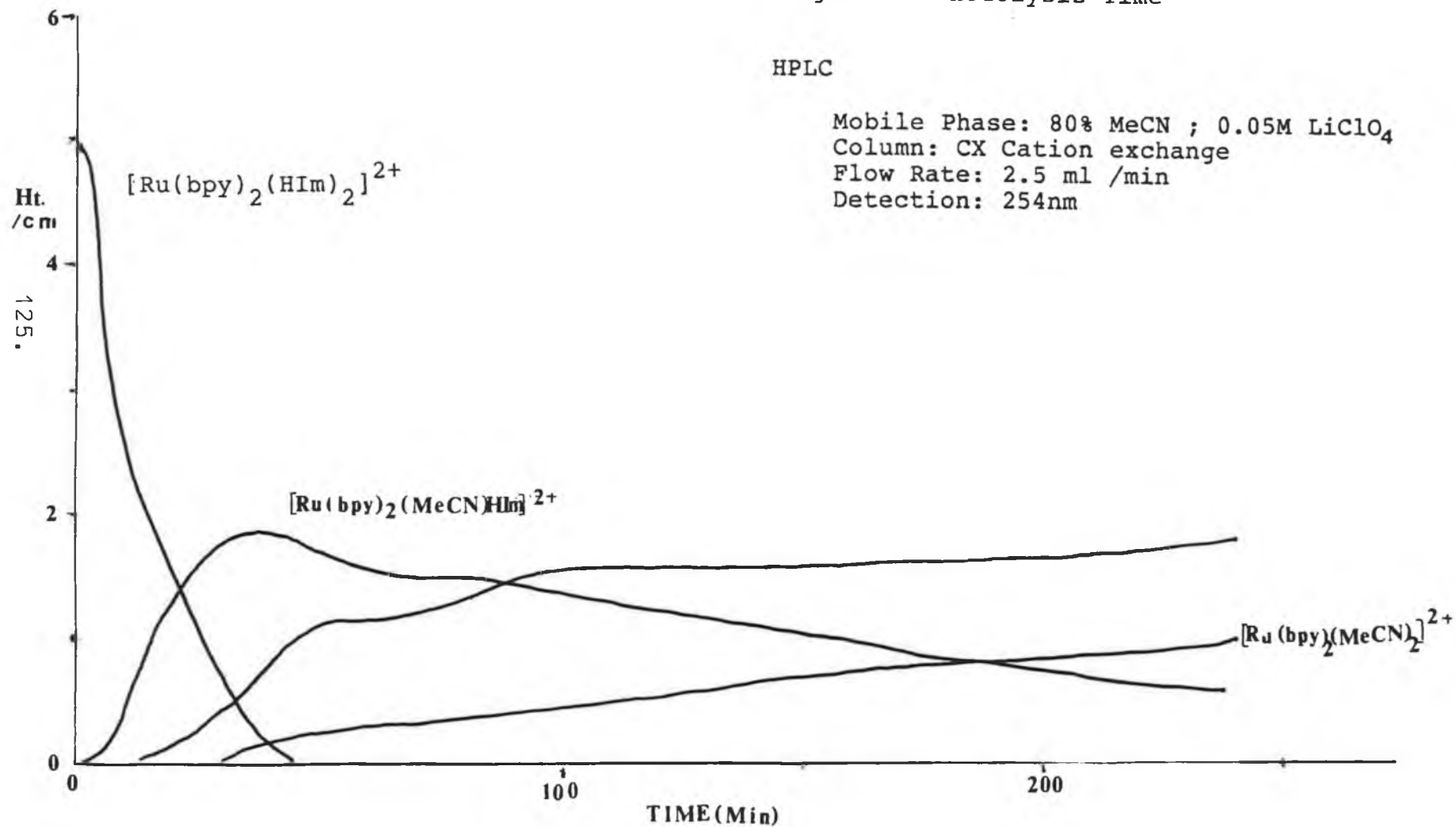Flow Rate: 2.5 ml /min
Detection: Photodiode Array/254nm

Fig. 2.11 HPLC Analysis of the Photolysis of $[Ru(bpy)_2(HIm)_2]^{2+}$ in MeCN

Peak Height vs. Photolysis Time

HPLC

Mobile Phase: 80% MeCN ; 0.05M LiClO$_4$
Column: CX Cation exchange
Flow Rate: 2.5 ml /min
Detection: 254nm

$[Ru(bpy)_2(HIm)_2]^{2+}$

$[Ru(bpy)_2(MeCN)HIm]^{2+}$

$[Ru(bpy)_2(MeCN)_2]^{2+}$

Ht. /cm

125.

TIME(Min)

to form. However a second peak occurs in parallel with $[Ru(bpy)_2(HIm)(MeCN)]^{2+}$ and this has not been identified as yet. For the CX column analyses with 0.07 M $LiClO_4$ in the mobile phase, this peak was seen to appear at the retention time where the pure starting material had diminished. With the ODS column this peak can be partially resolved enabling the spectrum to be obtained. This revealed a λmax of ca. 438 nm. This peak also appears for photolysis of $[Ru(bpy)_2(HIm)Cl]^+$ in acetonitrile as a minor product but has not been identified as yet. A possibility is that this peak is due to a trans isomer, such as trans $[Ru(bpy)_2(MeCN)_2]^{2+}$. Indeed this compound does have a λ max of ca. 440 nm.[73]

The main product for the photochemical reaction of the imidazole chloro containing complex is $[Ru(bpy)_2(MeCN)Cl]^+$, (λMax ca. 338, 471 nm, [54], Rt = 2.2 min [CX]/2.5 min [ODS]).

Numerous other minor products are visible for both compounds particularly after prolonged exposure to the beam. This may be due to thermal degradation of the complexes. A notable occurence is the formation of very small levels of Ru $(bpy)_2Cl_2$, (λmax = 362, 523 nm, Rt = 1.7 min [ODS] for the monoimidazole complexes. This indicates that the Cl is liberated

126.

PHOTOLYSIS of [Ru(bpy)$_2$(HIm)Cl]PF$_6$

COLUMN: CX
MOBILE PHASE:
80% CH$_3$CN:20% H$_2$O;0·05m LiClO$_4$
UV DETECTION:
254 nm

T=0 MIN

T=25 MIN

T=300 MIN

T=24 HOURS

MIN

127.
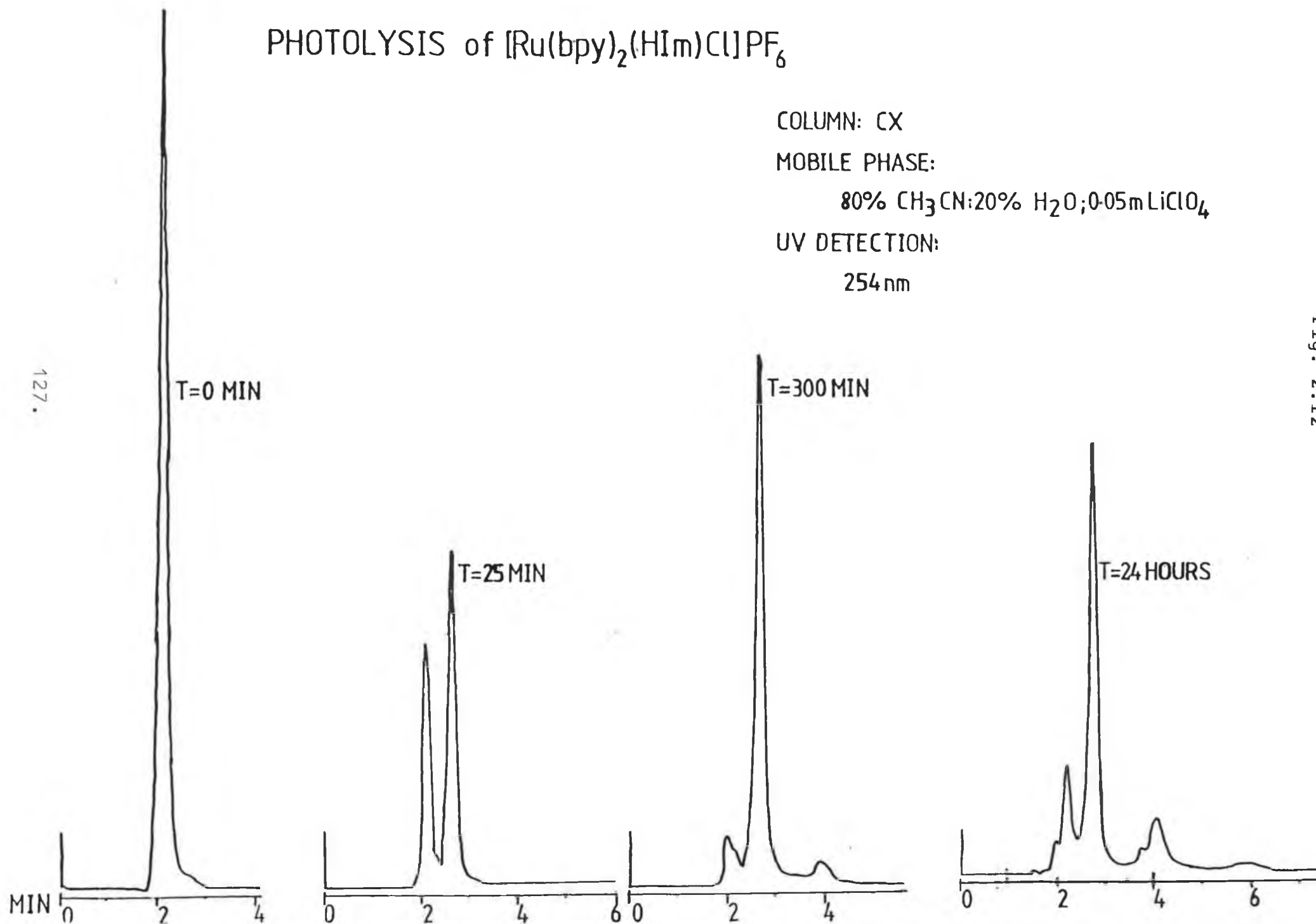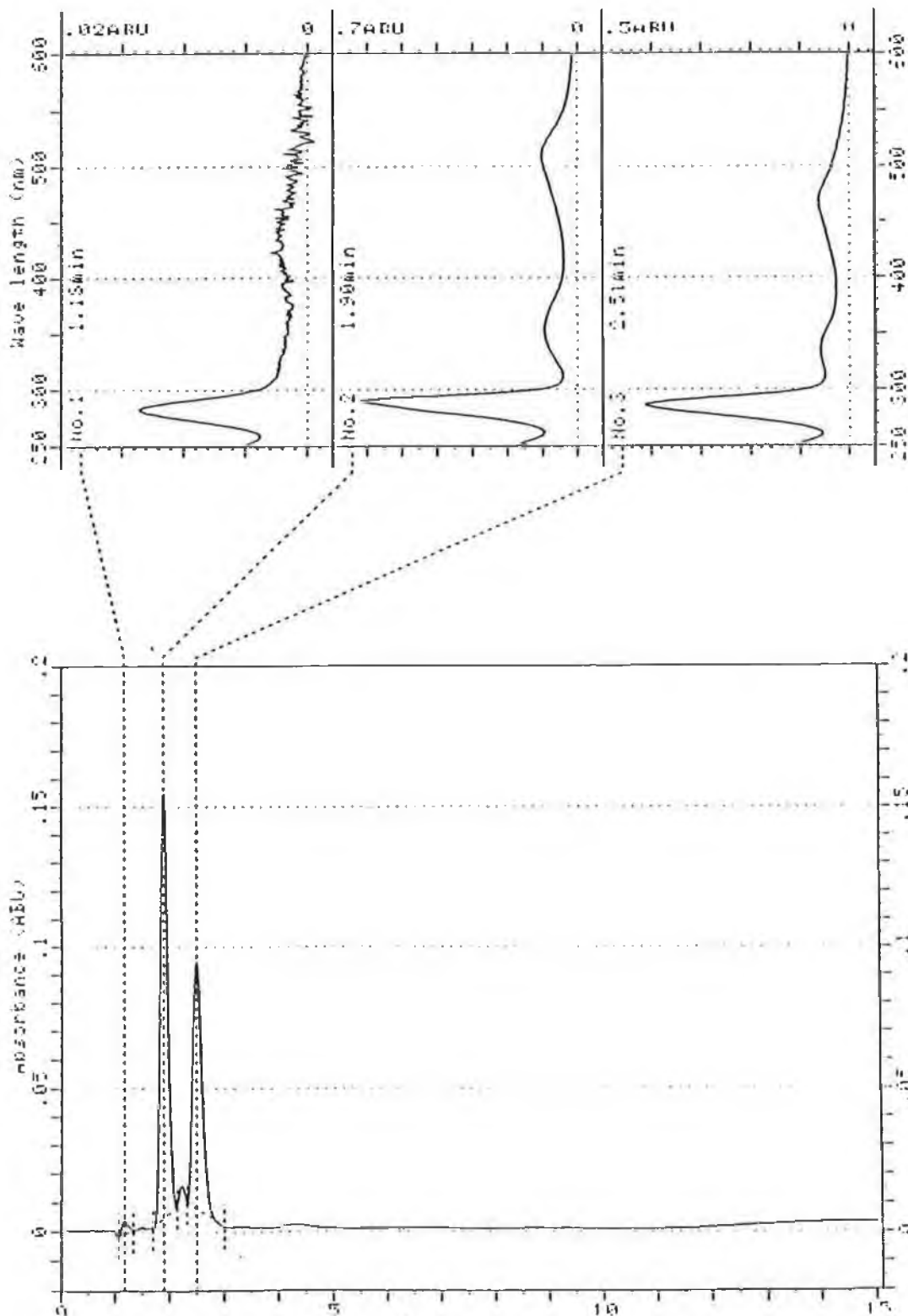
Fig. 2.12

Fig. 2.13 HPLC Analysis of the Photolysis of $[Ru(bpy)_2(HIm)Cl]^+$
in MeCN; Photolysis Time = 30 mins

HPLC

Mobile Phase: 80% MeCN; 0.08M LiClO$_4$
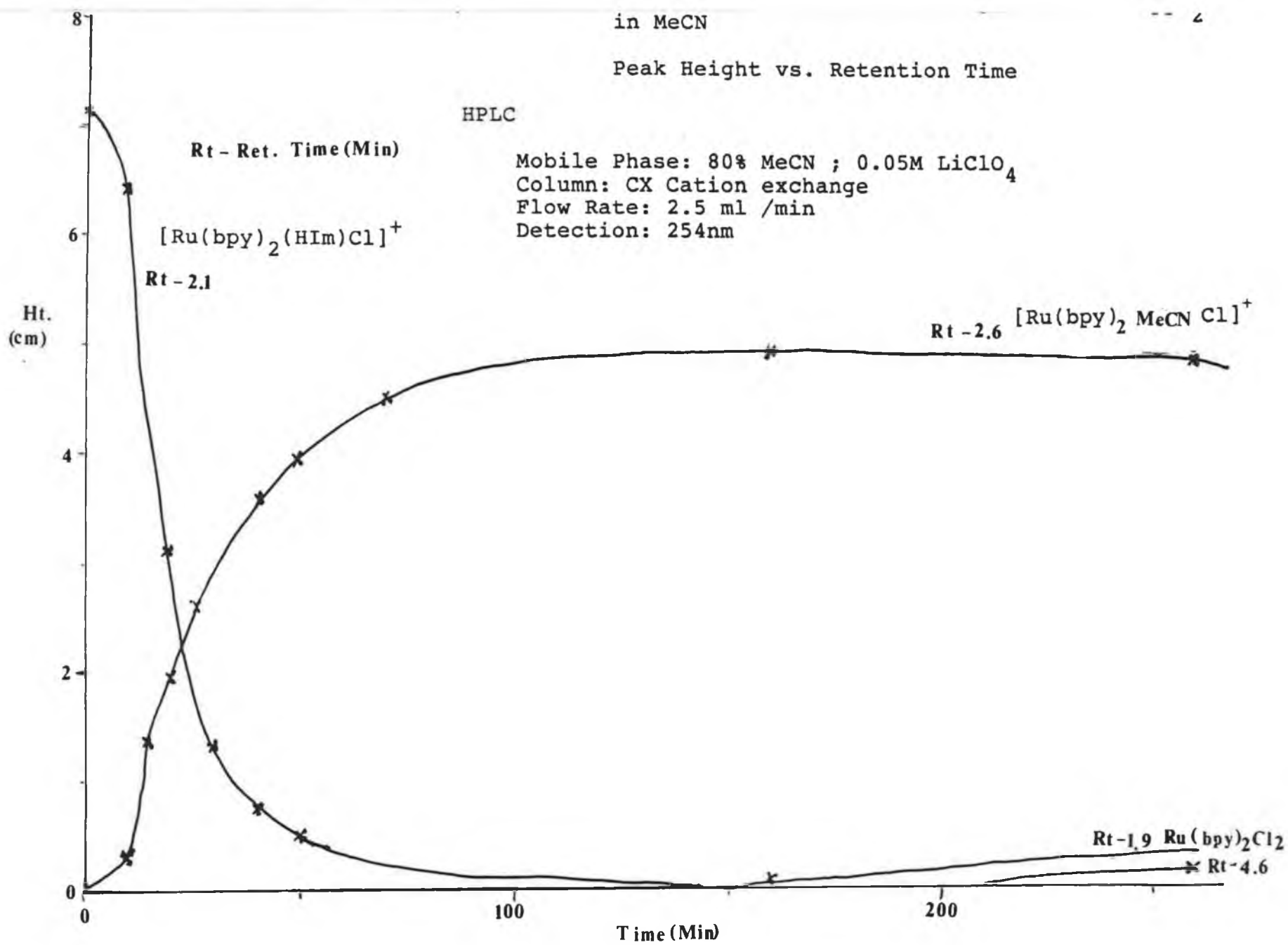Column: ODS Reverse Phase
Flow Rate: 2.5 ml /min
Detection: 254nm

Peak Height vs. Retention Time

in MeCN

HPLC

Mobile Phase: 80% MeCN ; 0.05M LiClO$_4$
Column: CX Cation exchange
Flow Rate: 2.5 ml /min
Detection: 254nm

Rt – Ret. Time (Min)

[Ru(bpy)$_2$(HIm)Cl]$^+$

Rt – 2.1

Ht.
(cm)

Rt –2.6 [Ru(bpy)$_2$ MeCN Cl]$^+$

Rt –1.9 Ru(bpy)$_2$Cl$_2$
Rt –4.6

Time (Min)

129.

from the complex to allow the production of Ru(bpy)$_2$Cl$_2$
This probably occurs in the formation of the unknown
species.

(iii)   The Photolysis of [Ru(bpy)$_2$(VIm)Cl]PF$_6$ and
        [Ru(bpy)$_2$(VIm)$_2$](PF$_6$)$_2$

        The photochemical reactions of the vinylimidazole
containing complexes in acetonitrile follow the same
pattern as that of the imidazole complexes. The final
product of the photolysis of [Ru(bpy)$_2$(VIm)$_2$]$^{2+}$ is
[Ru(bpy)$_2$(MeCN)$_2$]$^{2+}$, (λmax ca. 420 nm, Rt = 6.0 min [CX]/
6.2 min [ODS]] (Fig. 2 15-17). The intermediate
product, [Ru(bpy)$_2$(VIm)(MeCN)]$^{2+}$ is also observed
(λmax ca. 441 nm, Rt = 3.3 min [CX]/3.9 min (ODS)].
The expected equivalent of the relatively large
unidentified peak observed for the bis-vinylimidazole
complex is not observed. However this may mean that
its presence is masked by another peak, although it
is possible that this peak does not occur for this
compound. This compound is present in small levels
for the mono-vinylimidazole complex. (λmax ca.
435 nm, Rt = 3.2 [CX]/3.7 nm (ODS)].

TABLE 2.7.

PHOTOLYSIS OF $[Ru(bpy)_2(VIm)_2]^{2+}$ AND $[Ru(bpy)_2(VIm)Cl]^+$

IN ACETONITRILE

Mobile Phase : 0.08 M $LiClO_4$; 80% MeCN : 20% H_2O

Column : ODS   Flow Rate : 2.5 ml /min

Detection : Photodiode Array   [Monitor   254 nm]

Photolysis Time = 45 min $[Ru(bpy)_2(VIm)_2]^{2+}$

Retention Time (Mins)	Identification	λ Max (nm)
1.2 (V.S.)	-----	---
2.9	$[Ru(bpy)_2(VIm)_2]^{2+}$	478
3.8	$[Ru(bpy)_2(VIm)(MeCN)]^{2+}$	441
6.2	$[Ru(bpy)_2(MeCN)_2]^{2+}$	420

Photolysis Time = 90 min $[Ru(bpy)_2(VIm)Cl]^+$

Retention Time (Mins)	Identification	λ Max (nm)
1.2. (V.S.)	-----	---
1.5 (V.S.)	$Ru(bpy)_2Cl_2$	523
2.0	$[Ru(bpy)_2(VIm)Cl]^+$	505
2.5	$[Ru(bpy)_2(MeCN)Cl]^+$	468

(V.S.) = Very Small

131.

Fig. 2.15   HPLC Analysis of the Photolysis of
            $[Ru(bpy)_2(VIm)_2]^{2+}$ in MeCN and MeOH

HPLC: Column: CX
      Flow Rate: 2-4 ml /min
      Mobile Phase: 80% MeCN; 0.08M $LiClO_4$
      Detection: 254nm

MeOH

MeCN

min

132.
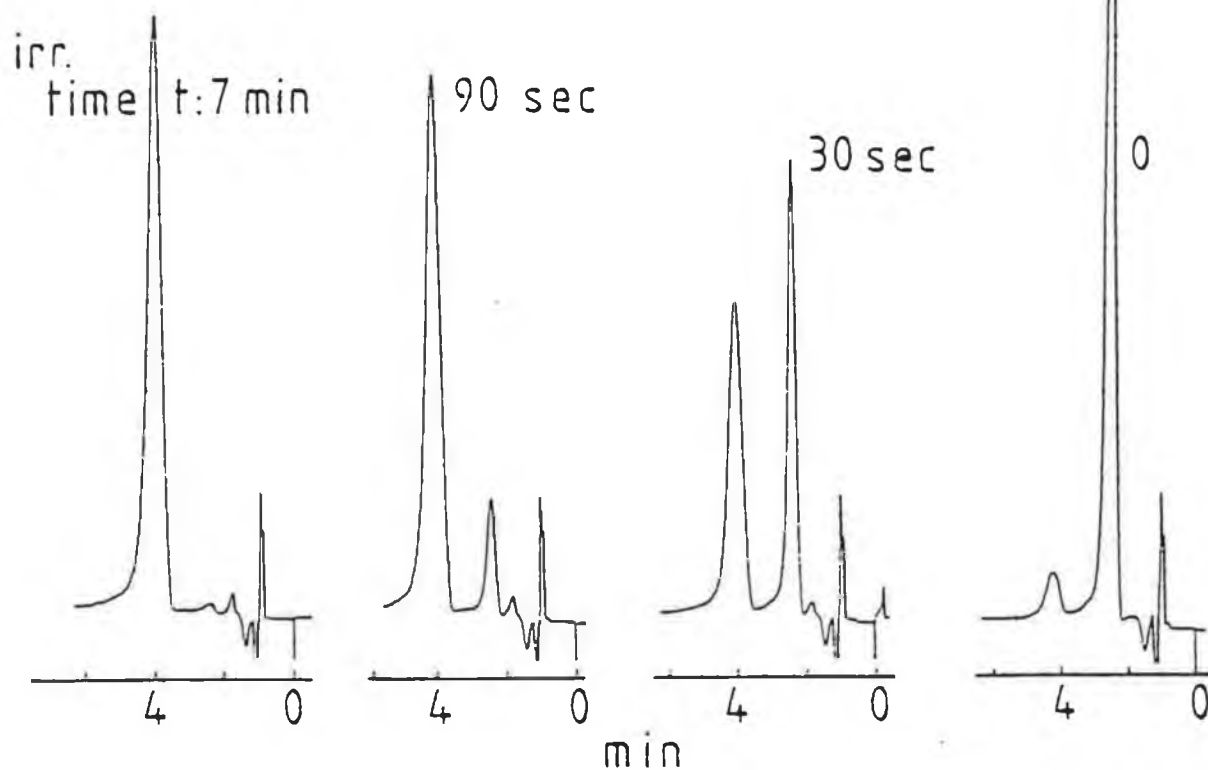
Fig. 2.16   HPLC Analysis of the Photolysis of $[Ru(bpy)_2(VIm)_2]^{2+}$
            in MeCN: Photolysis Time = 230 mins

            HPLC

                Mobile Phase: 80% MeCN; 0.08M LiClO$_4$
                Column: ODS Reverse Phase
                Flow Rate: 2.5 ml /min
                Detection: 254nm

133.

Fig. 2.17 HPLC Analysis of the Photolysis of $[Ru(bpy)_2(VIm)_2]^{2+}$ in MeCN

Peak Height vs. Photolysis Time

HPLC

Mobile Phase: 80% MeCN; 0.07M $LiClO_4$
Column: CX Cation Exchange
Flow Rate: 2.5 ml /min
Detection: 254nm
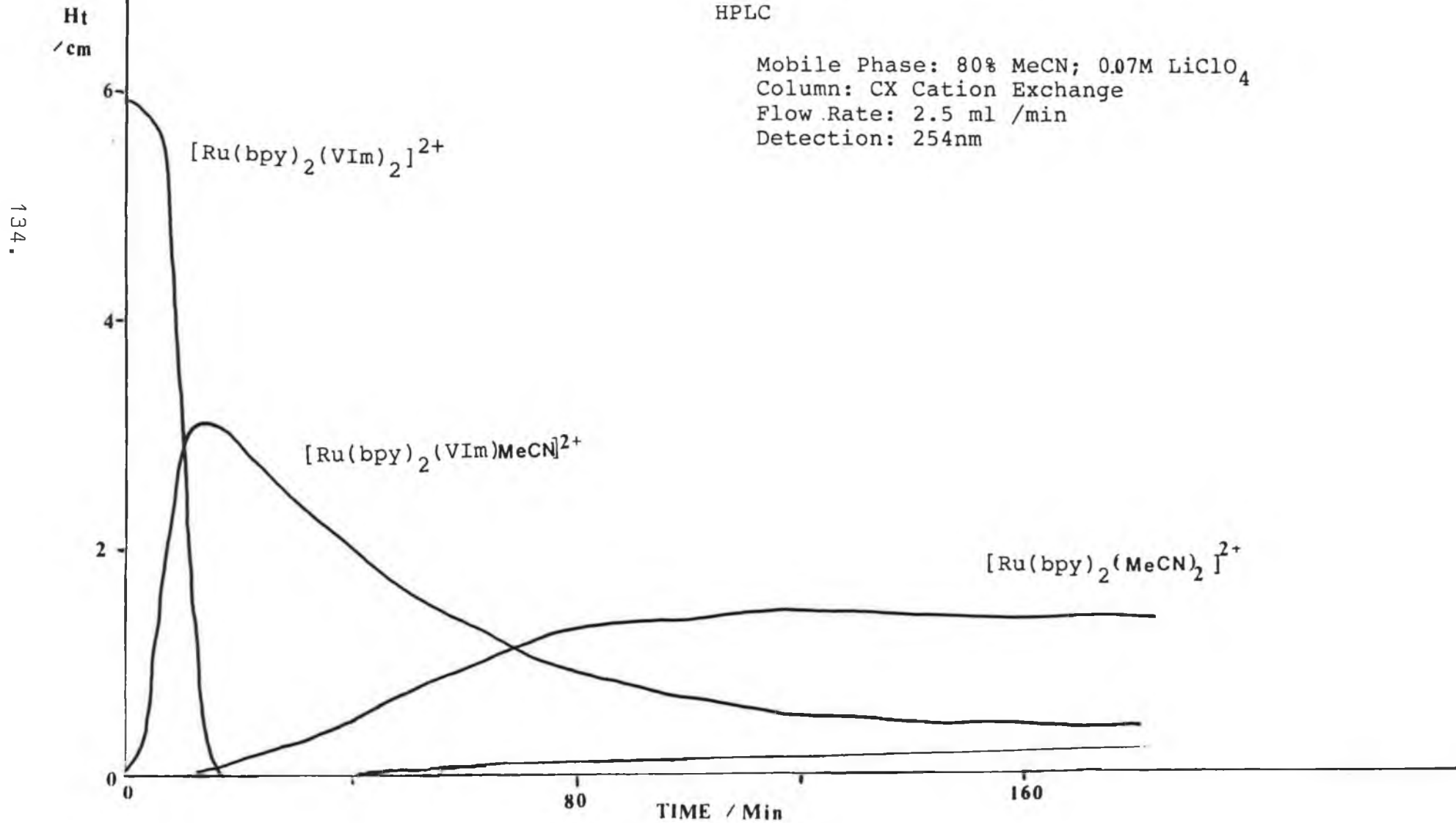
The major product for the photolysis of $[Ru(bpy)_2(VIm)Cl]^+$ in acetonitrile [Fig. 2 18-20], is $[Ru(bpy)_2(MeCN)Cl]^+$ (λmax ca. 469 nm, Rt = 2.2 min (CX)/2.5 min [ODS]). Also seen for this reaction, as with that for the mono-imidazole complex, is the occurence of $Ru(bpy)_2Cl_2$.

For both the bis- and mono- complexes studies were carried out with the CX column demonstrating the presence of free vinylimidazole after prolonged photolysis time. As with the imidazole complexes the reactions were seen to be extremely complicated with the formation of many minor unidentified products, particularly after lengthy exposures.

(iv) General considerations for these Photochemical
      Reactions

The reactions studied can be summarised simply. For the complexes of the structure $[Ru(bpy)_2(X)_2]^{2+}$, where X = VIm or HIm, the compound $[Ru(bpy)_2(MeCN)X]^{2+}$ is formed as an intermediate. The amount of this product decreases as $[Ru(bpy)_2(MeCN)_2]^{2+}$ is formed as the major final product. [Reaction Scheme 2.1].

135.

Fig. 2.18   HPLC Analysis of the Photolysis of
             [Ru(bpy)$_2$(VIm)Cl]$^+$ in MeCN and MeOH

HPLC: Mobile Phase: 80% MeCN; 0.08M LiClO$_4$
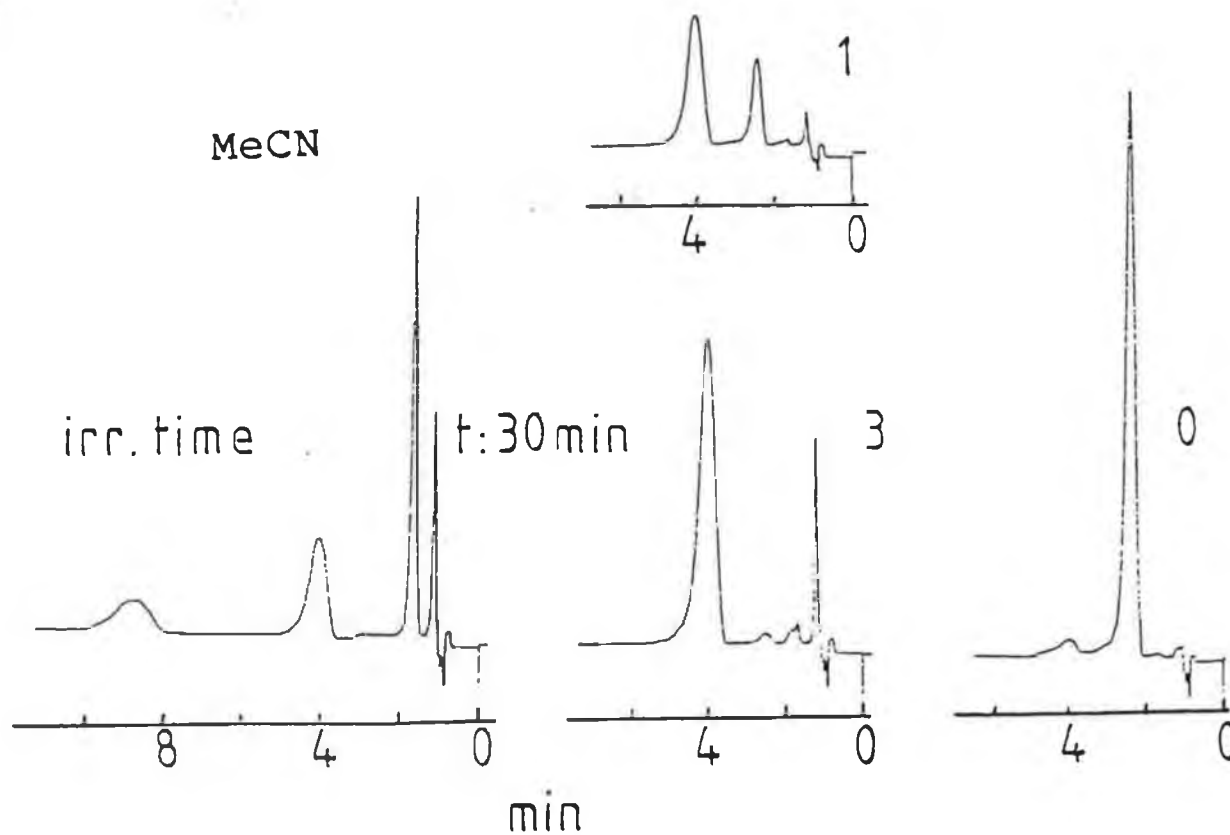   Column: CX
       Flow Rate: 2-4 ml /min
       Detection: 254nm
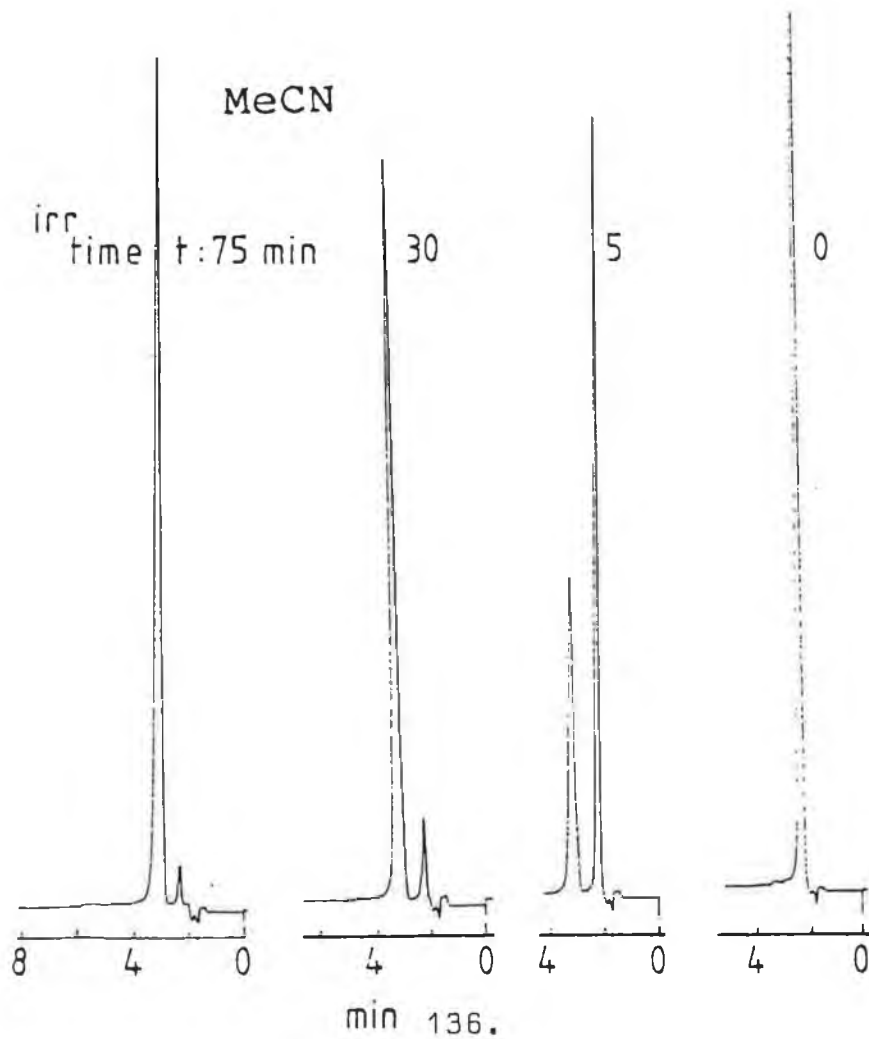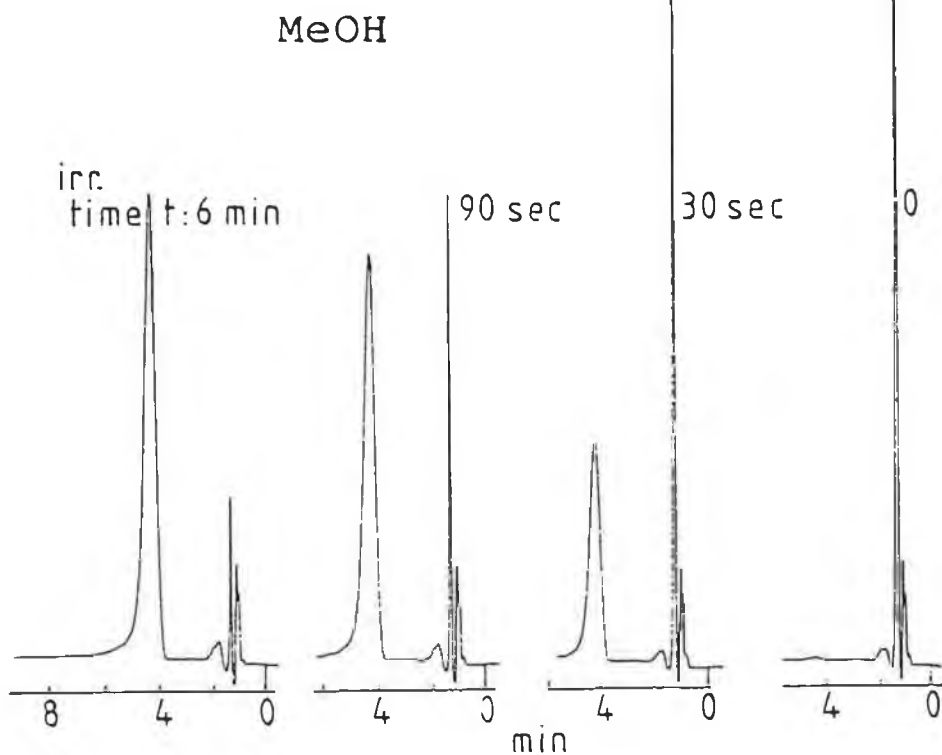
Fig. 2.19 HPLC Analysis of the Photolysis of $[Ru(bpy)_2(VIm)Cl]^+$
in MeCN: Photolysis time = 15 mins

HPLC

Mobile Phase: 80% MeCN; 0.08M $LiClO_4$
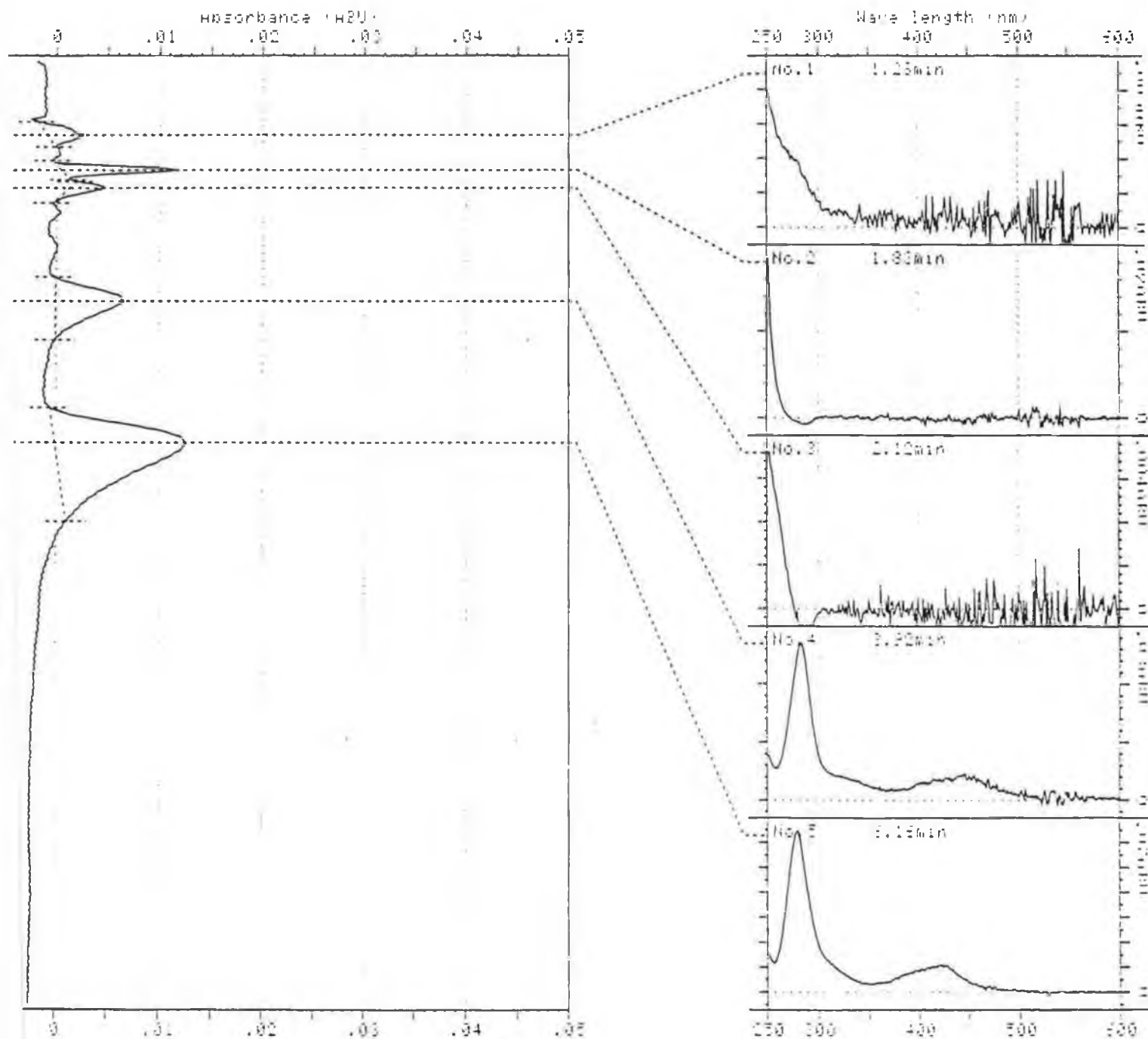Column: ODS Reverse Phase
Flow Rate: 2.5 ml /min
Detection: 254nm
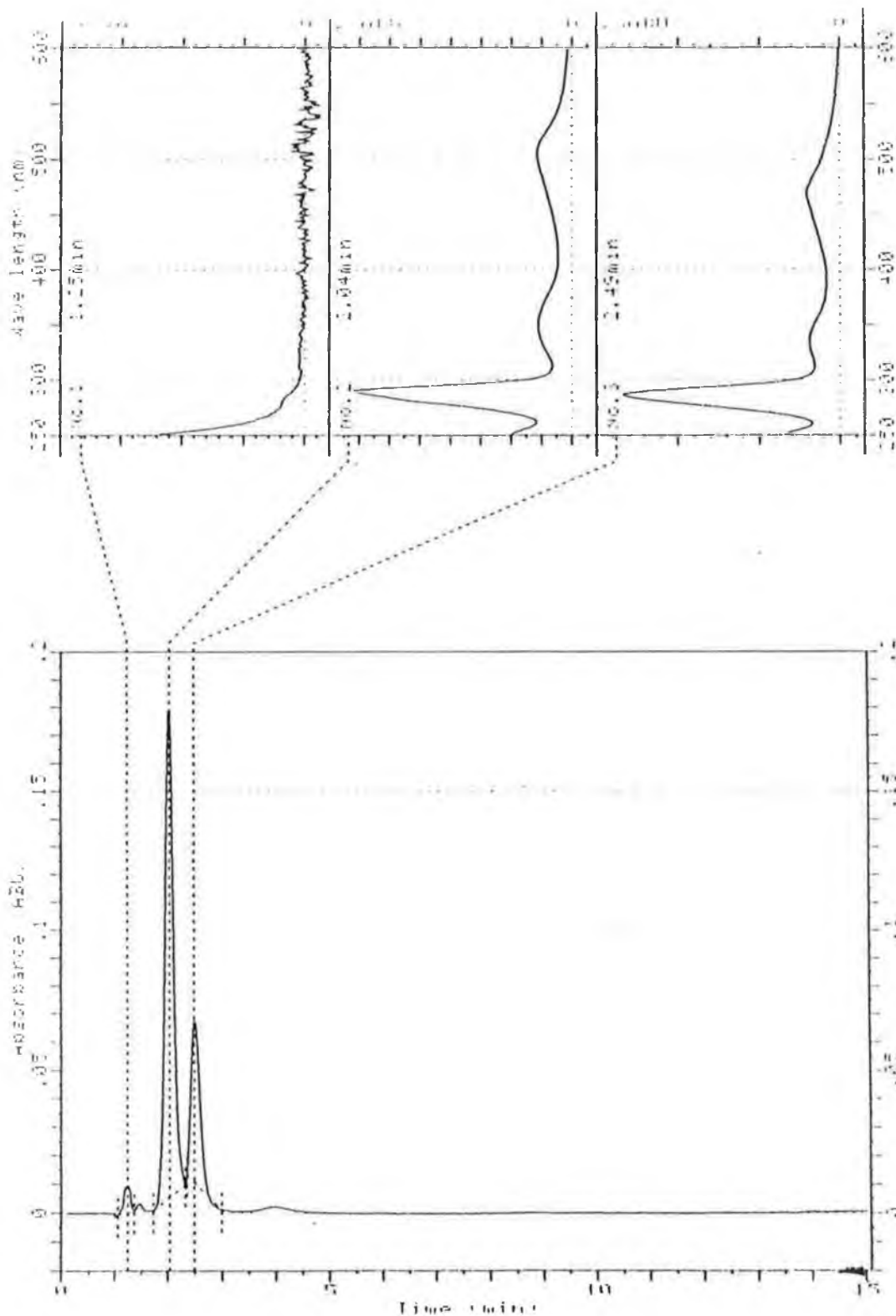
Fig 2.19B HPLC Analysis of the Photolysis of $[Ru(bpy)_2(VIm)Cl]^+$ in MeCN

HPLC

    Mobile Phase: 80% MeCN ; 0.1M LiClO$_4$
    Column: ODS Reverse Phase
    Flow Rate: 2.5 ml /min
    Detection: Photodiode Array fast UV/Vis scan
    Photolysis Time: 5 Mins

λ 300 – 800 nm

min
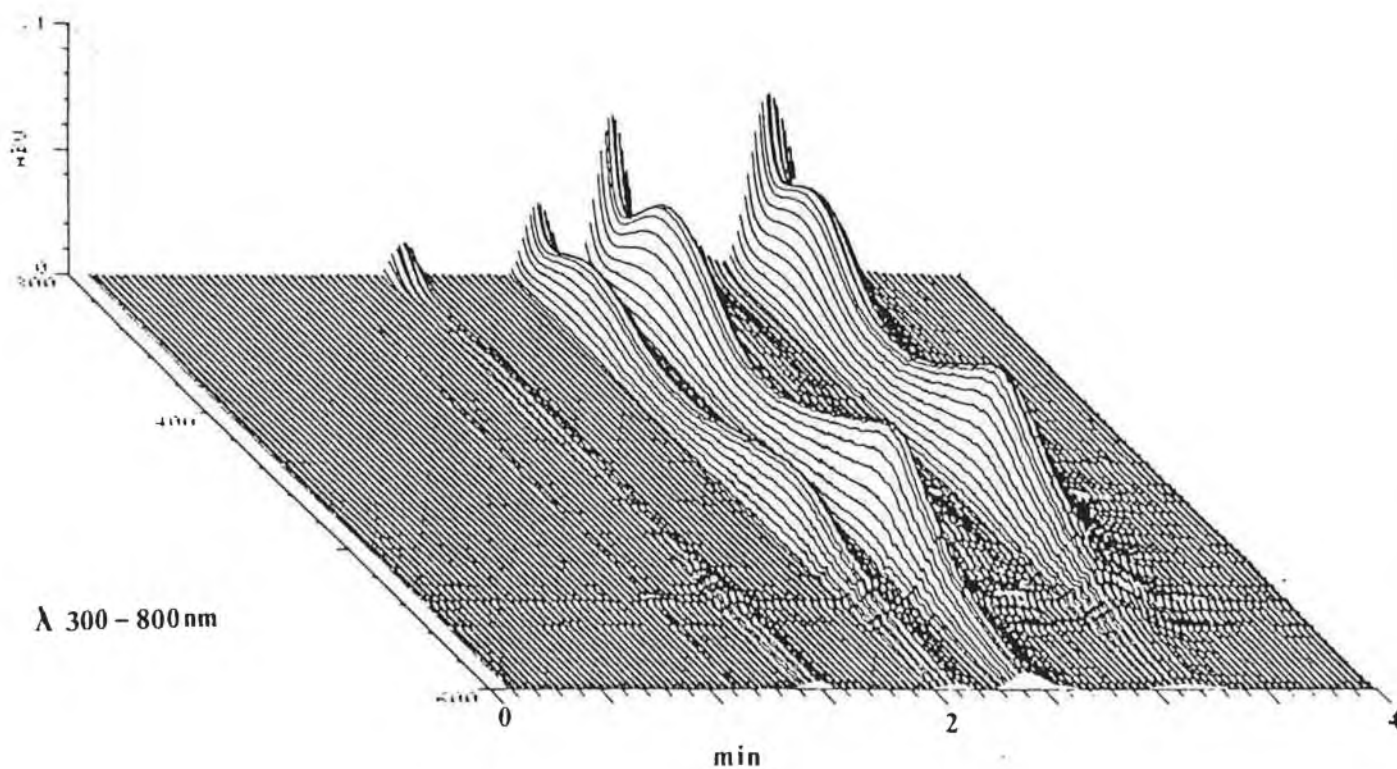
Fig. 2.20   HPLC Analysis of the Photolysis of $[Ru(bpy)_2(VIm)Cl]^+$ in MeCN

Peak Height vs. Photoysis Time

HPLC

Mobile Phase: 80% MeCN; 0.07M $LiClO_4$
Column: CX Cation Exchange
Flow Rate: 2.5 ml /min
Detection: 254nm
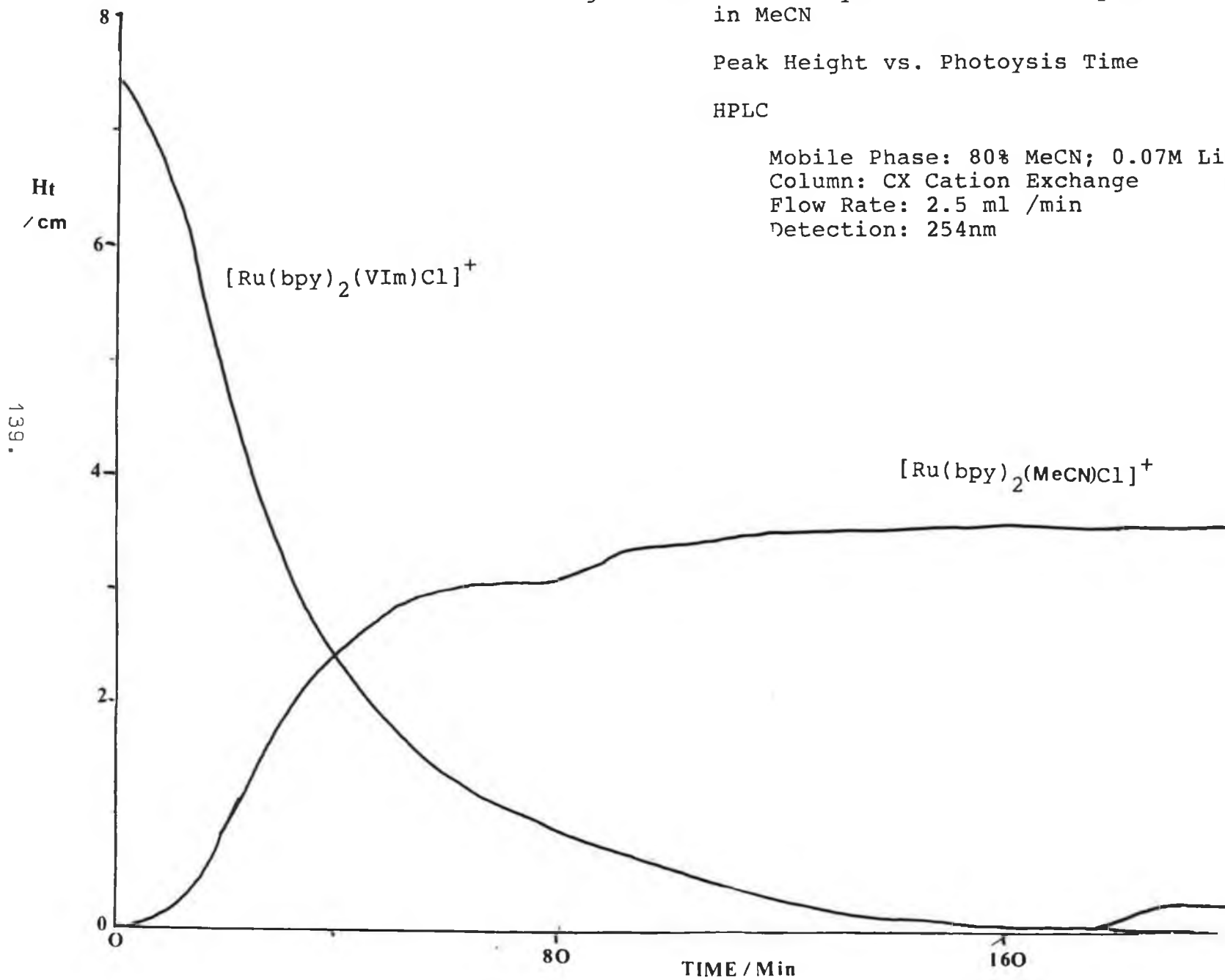
Many minor peaks were observed after
prolonged exposure and most of these were not
identified. All the photolysis were carried out
with a glass water bath between the source and
the sample to remove infrared and ultra violet
radiation and so reduce thermal effects. However
subsequent photolyses performed without the water
bath resulted in very clean reactions with only
major products observed. These reactions went to
completion rapidly. The probable reason for this
is that the glass water bath reduces the wavelength
range impingent on the sample cell. This results
in much slower reaction rates. Due to much
longer exposure times necessary to induce complete
or near complete reactions, heat builds up in the
cell resulting in significant thermal degradation.
In effect, the water bath serves to increase thermal
degradation rather than decrease it. The reactions
were followed using the CX column system with a
gradient flow rate. Excellent chromatograpjy
was achieved for this system with little peak
distortion.

Subsequent studies were also done by others
analysing the photolysis of $[Ru(bpy)_2(VIm)_2](PF_6)_2$
in acetonitrile/LiCl   using this HPLC System. [67].

140.

REACTION SCHEME:

Scheme 2.1:   Photochemical reactions of dicationic complexes of ruthenium (II)
              bis (2,2' - bipyridine) in acetonitrile

cis[Ru(bpy)$_2$L$_2$]$^{2+}$ $\xrightarrow[\text{h}\nu]{\text{MeCn}}$ cis[Ru(bpy)$_2$(MeCN)L]$^{2+}$ $\xrightarrow[\text{}]{\text{MeCn}}$ cis[Ru(bpy)$_2$MeCN)$_2$]$^{2+}$

hν↓

Other minor
  Products

MeCN
hν hν

?   trans.[Ru(bpy)$_2$(MeCN)$_2$]$^{2+}$

hν↓?

?
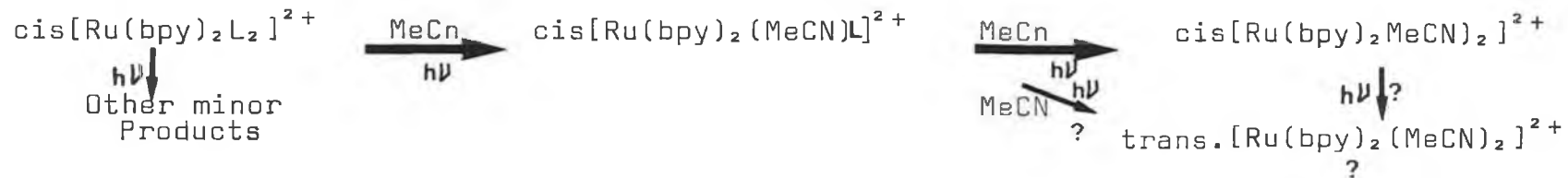
Scheme 2.2:   Photochemical reactions of monocationic complexes of ruthenium (II)
              bis (2,2' bipyridine) in acetonitrile.

cis[Ru(bpy)$_2$(L)Cl]$^{+}$ $\xrightarrow[\text{h}\nu]{\text{MeCn}}$ cis[Ru(bpy)$_2$(MeCN)Cl]$^{-}$ $\xrightarrow[\text{}]{\text{h}\nu}$ cis[Ru(bpy)$_2$MeCN]$_2$]$^{2+}$

hν↓

Minor
Products

hν│Cl

cis- Ru(bpy)$_2$Cl$_2$

MeCN/ hν↘?
trans[Ru(bpy)$_2$(MeCN)$_2$]$^{2+}$
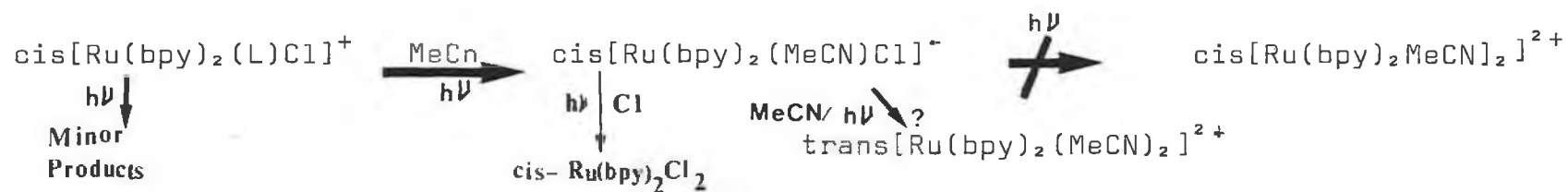
L = HIm or VIm

This indicated that $[Ru(bpy)_2(VIm)Cl]^+$ and $[Ru(bpy)_2(MeCN)_2]^{2+}$ are formed simultaneously before $[Ru(bpy)_2(MeCN)Cl]^+$ is formed as the major final product. These results agree with those given here in that $[Ru(bpy)_2(MeCN)Cl]^+$ did not form $[Ru(bpy)_2(MeCN)_2]^{2+}$ with further photolysis.

(v)   An Appraisal of the HPLC System for the Study of these Photochemical Reactions.

The HPLC system proved to be very useful for following the reactions. It demonstrated the range of minor products formed which were hitherto unknown. It also demonstrated the effect the presence of the water bath had on the photolyses. Combining the HPLC system with photodiode array detection in particular proved a very powerful technique. The best system for studying these reactions would encompass a gradient elution system for flow rate or $LiClO_4$ concentration, a CX column and photodiode array detection. The mobile phase for the system would be 0.05 M - 0.08 M $LiClO_4$; 80% MeCN : 20% H_2O.

CONCLUSIONS:

As a technique for the study of Ruthenium (II) bis (bipyridyl) complexes and their rections. HPLC has great potential. A general system was developed to achieve effective separation of many of these complexes using a selection of model compleses. The model compounds used were $[Ru(bpy)_2(HIm)Cl]PF_6$, $[Ru(bpy)_2(HIm)_2](PF_6)_2$, $[Ru(bpy)_2(VIm)Cl]PF_6$, $[Ru(bpy)_2(VIm)_2](PF_6)_2$, $[Ru(bpy)_2(CO)H]PF_6$, $[Ru(bpy)_2(CO)Cl] ClO_4$. The optimum system discovered involved the use of a CX cartridge column which was found to be more satisfactory than reverse phase columns such as ODS, CN and C18 columns. The mobile phase used consisted of $0.08M$ $LiClO_4$ in 4:1 (v/v) acetonitrile-water and a flow rate of 2.5 ml /min. The mobile phase, and in particular the $LiClO_4$ concentration, may be modified to suit a given analysis. The CX column provided a more efficient separation with tailing than the reverse phase columns. Although its retention mechanism is not clear, the results suggests that it operates on a mixed retention system where both reverse phase and cation exchange mechanisms play a part. The dominant mechanism is dependent on the chromatographical conditions.

This system is suitable for the separation of monocationic from dicationic ruthenium (II) bis(bipyridyl) complexes and for the separation of more than one dicationic complex. However, it does not provide good separation for more than one monocationic complex. Low $LiClO_4$ concentrations are necessary to achieve the longer retention times necessary to enable separation.

Based on these results the best system for the HPLC analysis of ruthenium (II) bis (bipyridyl) complexes would use a CX stationary phase cation exchange, and a mobile phase of 4:1 (v/v) acetonitrile, water, and a $LiClO_4$ concentration gradient. Alternatively the $LiClO_4$ concentration may be set and a flow rate gradient used. Peak shape may be improved by the use of end capped columns.

This sytem proves very useful for tasks such as determining compound purity and reaction studies of ruthenium (II) bis (bipyridyl). This was demonstrated by the study of the photolyses reactions of $[Ru(bpy)_2(X)_2]^{2+}$ and $[Ru(bpy)_2(X)Cl]^+$, (X = VIm or HIm), complexes in acetonitrile. This showed the final product for the photolyses of the $[Ru(bpy)_2(X)_2]^{2+}$ complexes in acetonitrile to be $[Ru(bpy)_2(MeCN)_2]^{2+}$, with $[Ru(bpy)_2(X)(MeCN)]^{2+}$ as an intermediate.

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The final product for the photolyses of
the $[Ru(bpy)_2(X)Cl]^+$ complexes is $[Ru(bpy)_2(MeCN)Cl]^+$.
It must be noted that many other minor products
were formed also. Some of these could be attributed
to thermal degradation associated with the long
exposure times. The long exposure times necessary
appeared to be a result of a glass water bath in
the light path which removes much of the radiation
below 230 nm resulting in slower reaction rates.

HPLC was seen to be an excellent method for
studying complex reactions of ruthenium (II)
bis (bipyridyl) complexes as, unlike conventional
methods, it allowed separation of minor products
to be obtained. When used in conjunction with
conventional methods for the study of such reactions,
such UV/Vis spectrophotometry by using a photodiode
array detector, it proved to be a very powerful
technique. However, much care must be taken to
avoid mistaking artifactual peaks for actual peaks.
Artifactual peaks may be caused by a variety of
phenomena. The compounds present on the column are
dependent on column and mobile phase conditions
and problems may occur with ligand substitution on
column for labile complexes e.g. ligand exchange for
mobile phase solvent molecule. Retention mechanism
phenomena such as peak splitting can also create

145.

problems. In general, however, this system has many
applications for the study of ruthenium (II) bis
(bipyridyl) complexes and their reactions and it may
be that in these studies, our understanding of
reversed phase ion pair and cation exchange
chromatography will be enhanced.

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GLOSSARY

Ru	Ruthenium
bpy	2,2' - Bipyridine
phen	1,10-Phenanthroline
CO	Carbonyl
HIm	Imidazole
VIm	Vinylimidazole
C_3H_6O	Acetone
RuH	$[Ru(bpy)_2(CO)H]PF_6 \cdot \frac{1}{2}C_3H_6O$
MeCN	Acetonitrile
MeOH	Methanol
PhCHO	Benzaldehyde
HOAc	Acetic acid
L	Ligand
$LiClO_4$	Lithiumperchlorate
HPLC	High Performance Liquid Chromatography
GC	Gas Chromatography
UV	Ultra Violet (Radiation)
IR	Infra Red (Radiation)
MLCT	Metal to Ligand Change Transfer
RP-IPC	Reverse Phase Ion Pair Chromatography
IIC	Ion Interaction Chromatography
As	Assymetry Value for HPLC Peak