

Solvation effects on Kinetics and Charge Transfer

Spectroscopy of Transition Metal Compounds

A thesis presented for the Degree of  
Doctor of Philosophy, in the  
Faculty of Science, University of Leicester,  
by J. G. Chambers.

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THESIS

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STATEMENT

The work described in this thesis was carried out by the author in the Department of Chemistry of the University of Leicester between October 1973 and May 1976.

No part of this work has been submitted or is concurrently being submitted for any other degree.

Signed

*John G. Chambers.*

June 1976

J. G. Chambers

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*Basic research is when I'm doing  
what I don't know I'm doing.*

W. V. BRAUN.

## CONTENTS

### PAGE

<u>CHAPTER 1:</u>	Kinetics of reaction of the tris (2,2'-bipyridyl)-iron-(II) cation with cyanide and hydroxide anions along with acid aquation, in binary aqueous mixtures.	1
<u>CHAPTER 2:</u>	An investigation of solvent effects on visible and U.V. absorption spectra of transition metal compounds.	44
<u>CHAPTER 3:</u>	An investigation into the effects of micellar agents on a series of inorganic reactions in aqueous solution.	70
<u>CHAPTER 4:</u>	An investigation into organic-peroxide attack on some transition metal compounds.	89
<u>CHAPTER 5:</u>	An investigation of solvent effects on the Initial and Transition states for the reaction of (2,2'-bipyridyl)-dichloro-platinum-(II) in Aqueous Dioxan and Tetrahydrofuran with thiourea.	105
<u>CHAPTER 6:</u>	Solubilities of $\text{Fe}(\text{bipy})_2(\text{CN})_2$ and $\text{Fe}(\text{phen})_2(\text{CN})_2$ in binary aqueous mixtures.	116
<u>CHAPTER 7:</u>	A kinetic investigation of the isomerisation reactions of platinum olefin and $\Pi$ -bonded ketone compounds.	121
<u>APPENDIX:</u>	Computer programs and their descriptions.	A 1
	A description of activation parameters.	A23

## ABBREVIATIONS

bipy	2,2'-bipyridyl
phen	1,10-phenanthroline
5Cl-phen	5 chloro-1,10-phenanthroline
4,7 diMe-phen	4,7 dimethyl-1,10-phenanthroline
diaz	N,N' di-tert-butyl-1,4 diazabutadiene
dap	1,3 diamine-propane
Sb	Schiff-base
P	Triphenylphosphine
CTAB	Hexadecyl-trimethyl ammonium bromide (or cetyl trimethyl ammonium bromide.)
NaLS	Sodium dodecyl sulphate (or sodium lauryl sulphate.)
DMSO	Dimethyl sulphoxide
HMPA	Hexamethyl phosphoramide
DMF	Dimethyl formamide
THF	Tetrahydrofuran
DTBP	Di-tert-butyl peroxide
ButOH	Tert-butyl alcohol
D	Dielectric constant
nm	Nanometres
x <sub>2</sub>	Mole fraction of cosolvent

## CHAPTER 1

Title:    Kinetics of reaction of the tris (2,2'-bipyridyl)-iron-(II)  
          cation with cyanide and hydroxide anions along with acid  
          aquation, in binary aqueous mixtures.

## Introduction

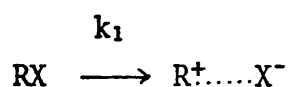
Many kinetic studies have been performed upon reactions of inorganic complexes in mixed aqueous solvents, both by physical and inorganic chemists.<sup>(101-103)</sup> In the majority of cases for the physical chemist, these reactions have been used to gain an insight into either solvent-solute or solvent-solvent interactions, the inorganic-complex reaction being used primarily as a tool for this purpose.<sup>(102)</sup> The opposite approach has generally been followed by inorganic chemists, using the known variations in solvent in conjunction with rate variation as a diagnosis of inorganic reaction mechanism. However, more recent work in inorganic reaction kinetics has brought these two approaches together. The fact that this has not happened before may at first appear strange, however this can be readily explained by the increase in availability of data, both kinetic and otherwise, and the recent advances in the understanding of kinetic and thermodynamic theories.

Examples of mechanistically orientated work are plentiful. The dependence of rate constants of an inorganic reaction upon solvent parameters has often been used to deduce mechanism, for instance, correlations between the dielectric constant of a particular mixed-solvent with the rate of reaction of an inorganic complex.<sup>(103)</sup> This type of study, although used as a sole proof of mechanism, usually requires some further supporting evidence (e.g. entropy of activation) since, in many cases, it tends to give ambiguous results. Such correlations usually involve plots of  $\log(k)$



against either  $1/D$  or  $(D-1)/(2D+1)$ , these give good linear relationships with large negative slopes for dissociative processes<sup>(103)</sup> (e.g. aquations of cobalt-(III)-amine-bromides and rhodium-(III)-chloride). However, in systems where the mechanism is not clearly dissociative, (i.e. where an associative contribution may be expected), the above plots tend to give a poorer correlation and either a small negative, or in some cases, a positive gradient. Hence poor correlation is often thought to be indicative of associative character. However, it is not possible to use the values of slope as an indication of the extent of associative character (i.e. increasing positive trend correlating with increasing associative character), due to the large standard deviations of the slope in these cases.

An example of another solvent parameter used in this type of approach is the well-established Y-parameter, introduced by Grunwald & Winstein.<sup>(104)</sup> This was originally used in the parallel field of organic reaction mechanisms. The above workers found certain reactivity trends in dissociative solvolysis reactions of species of the form  $RX$ , (where  $R$  = alkyl,  $X$  = halide) with solvent variation. They then pointed out that, solvolysis of an alkyl halide is not a single step process, but that it could be best viewed as involving a rate-determination step thus:-



giving initially a cationic intermediate.

Because this stage involves charge separation, it was pointed out that the above  $k_1$  would be dependent upon the so-called 'ionising power' of the solvent. Using this argument it was possible to arrange solvents in an order relative to their 'ionising power', and assign to each a number, 'Y', said to be a quantitative measure of this power. Hence using equation [1],

$$Y = \log k (\text{Bu}^t\text{Cl}) - \log k_o (\text{Bu}^t\text{Cl}) \quad \dots\dots [1]$$

[where  $k_o$  is the rate constant ( $k_1$ ) in 80% ethanol at 25°C (an arbitrary standard in this system), and  $k(\text{Bu}^t\text{Cl})$  is the same rate constant in another solvent at 25°C,] predictions of Y parameters for different solvents could be made. These calculated values could then be used in the following equation [2], where plots of  $\log k$  vs. Y, allowed rate constants (in any solvent whose Y-parameter was known) to be calculated:-

$$\log k = m \cdot Y + \log k_o \quad \dots\dots [2]$$

( $k$  and  $k_o$  defined as in [1]).

More important was that the value of the slope ( $m$ ) for a particular reaction gave an indication of the type of mechanism, (e.g. solvolysis of tert-Butyl chloride,  $m = 1.0$ , a purely dissociative process). However, when this approach was used in a bimolecular reaction it was found that no such similar rate predictions could be made. As an explanation for this, it was decided that the calculated Y-parameters did not take into account the nucleophilic power of the solvents, which should be important for a bimolecular process.

In the years following this interesting and useful piece of work, many reactions, not only organic, but also inorganic have used this approach to diagnose reaction mechanisms. Examples of the Grunwald-Winstein analysis in the field of inorganic reactions are plentiful if not always successful.<sup>(105)</sup> Langford used this approach in the aquation of cobalt-(III)-halides,<sup>(106)</sup> and although the agreement was not particularly good, an  $S_N1$  mechanism seemed to be implied by the results. The discrepancies in correlation were put down to two effects, one being that inorganic reactions were less sensitive to 'solvent ionising-power', hence giving small 'm' values, and the other

that the rate determination step was probably largely dependent upon solvation of the leaving anion. Other examples in similar reactions also exhibited the inadequacies of this approach. For instance the rates of aquation of chromium-(III)-halides<sup>(107)</sup> caused difficulties when relative solvation effects (similar to those used in tert-butyl chloride solvolysis) were used to explain the differences in solvolysis rates of cobalt-(III) and chromium-(III)-halides. The sole conclusion from the investigation was that the two metal complexes probably solvolysed via slightly different mechanisms. A similar result appeared when Y-parameters were used in the dissociative acid catalysed aquation of iron-(III)-phenanthroline complexes.<sup>(108)</sup> The problem in these reactions was that they required acid to be present to ensure complete reaction occurred, which would be expected to have a large structural effect on the solvent, thus possibly invalidating the use of this analysis. Also, the leaving group in these cases was not a halide anion, other investigations where the leaving group is a non-halogen have given similar results (i.e. a poor correlation with Y parameters) e.g. aquation of  $\text{Cr}(\text{NCS})_6^{3-}$ .<sup>(107)</sup>

Another reason for the inadequacy of applying the Grunwald-Winstein analysis to inorganic reactions is that in the original organic study, solvation effects at the R-group were small. However, in many inorganic studies, solvation at the inorganic cationic species (equivalent to the R-group) are relatively important. A modified form of equation [2] however, developed by Winstein et al.,<sup>(109)</sup> tried to bridge this gap, by introducing an extra term into the equation e.g:-

$$\log (k/k_o) = m.Y + l.N. \quad \dots\dots [3]$$

(where k,  $k_o$ , m and Y are as defined previously).

The variable 'N' in the above equation is said to represent the nucleo-

philicity of the solvent, and 'l' is a measure of the sensitivity of the substrate to changes in 'N'. This new model has been used in the investigation of aquation rates of  $\text{trans-}[\text{Co}(\text{dap})_2\text{Cl}_2]^+$ ,<sup>(105)</sup> and seems to account for the observed rate variations therein. However, this model still tends to neglect the effects of variation in the leaving anion solvation in favour of solvation changes at the larger cation.

As can be seen from the previous paragraphs, both 'D and Y' have been extensively used to diagnose inorganic reaction mechanisms. However, as expected, both of these have their faults, since both are based upon one unique system. 'D' is calculated from the pure mixed solvents, in the absence of any structural interference, such as would be caused by charged ions, and 'Y' parameters are specific to the tert-butyl chloride system. From these restrictions we can see that a more useful 'parameter' would be one which was inherent to each system under study. Such a parameter obviously would not be universally applicable to all systems, however recent advances in certain areas of thermodynamics allow us to attempt to calculate, (using various solvent models) a suitable entity. The one used in this work is the well-known 'chemical potential', or to be more accurate, the single ion value, defined as follows:-

$$\mu(\text{ION}) = \left( \frac{\partial G}{\partial n(\text{ION})} \right)_{P, T, (\text{other ions present}) = \text{constant}} \quad [4]$$

(i.e. chemical potential of an ion 'i' is equal to the changes in Gibbs free energy for the ion of species j while variations in pressure, temperature and all other ions in the system are kept constant.)

In many of the previously mentioned kinetic investigations, it has often been said that the rate determination step, (in dissociative aquation reactions) was probably largely dependent upon the leaving-anion solvation.

Using this piece of information linked with thermodynamic calculations based upon the chemical potential of the leaving group, we thought that it may be possible to make rate predictions for a particular reaction. Also by using these ideas in conjunction with the Grunwald-Winstein analysis a clearer picture of the system and mechanism as a whole might emerge.

We decided that the most appropriate reaction to examine would be one in which an associative pathway was followed. This would therefore test the Grunwald-Winstein analysis to beyond its limit, and hopefully, where this analysis proved unsatisfactory, our own analysis should take over. This should also show if the Grunwald-Winstein approach can, in fact, distinguish between dissociative and associative mechanisms.

For the choice of reaction, we found that there were two well-investigated types of reaction, both equally suitable for our work. The first is substitution at a square planar  $d^8$  complex.<sup>(110)</sup> Such a process is almost invariably associative due to both steric (two vacant axial positions) and electronic (an empty  $p(z)$  orbital) reasons, being both low spin and having a low co-ordination number. The second choice is (more specifically) cyanide attack at a low spin iron-(II) compound.<sup>(111,112)</sup> As has been stated above, much work has already been done in this area, particularly with tris-bidentate-iron-(II) species. Schilt performed much of the original preparative work which was allowed to stand unchallenged until renewed interest in this area (both preparative and kinetic) brought forth both new ideas and corrected some of the earlier work. The reaction studied in this Chapter (among others) is, in fact, one of the many that Schilt investigated in the 1950's<sup>(113)</sup> and later the first kinetic study was performed by Margerum et al., (i.e. the attack of cyanide anion on the tris-bipyridyl-iron-(II) species). Originally the reaction was believed to yield the tetracyano-product,  $Fe(bipy)(CN)_4^{2-}$ . However, this has been found not

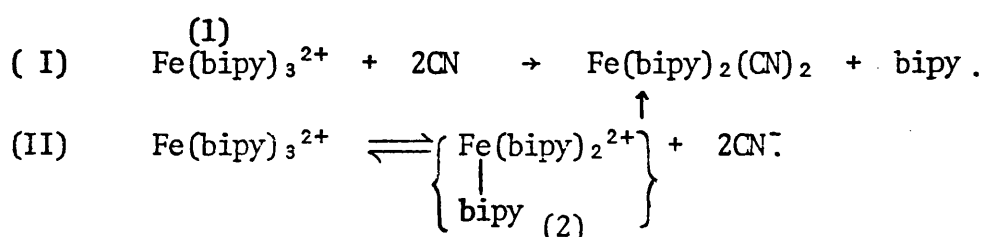
to be the case, the reaction proceeding only to the neutral dicyano-species  $\text{Fe}(\text{bipy})_2(\text{CN})_2$ , identified by both preparative and spectrophotometric means.<sup>(113)</sup> This neutral compound does react further with cyanide to give the above tetracyano-compound (and, presumably, eventually the hexacyano-ferrate-(II) compound), but this process was found to be extremely slow by comparison with the first stage.

A later kinetic investigation found that the reaction was made up of a two term rate law<sup>(112)</sup> as is found for the analogous hydroxide attack at this compound<sup>(111)</sup>:-

$$k_{\text{OBS}} = k_1 + k_2 \cdot [\text{CN}^-] \quad \dots\dots [5]$$

$$\text{and for the hydroxide, } k_{\text{OBS}} = k_1 + k_2 \cdot [\text{OH}^-]$$

again no evidence for the formation of the tetra-cyano-species was found, the two term rate law indicating that both associative and dissociative pathways were operating in parallel. This investigation compared the rates for cyanide and hydroxide attacks and acid aquation, assigning the  $k_1$  term to a dissociative process, and  $k_2$  to an associative one. The actual mechanism of cyanide attack was also established, although not without some uncertainty, by the following arguments. The bimolecular reaction could, in fact, be occurring via two independent mechanisms, the one by direct attack of cyanide anion at the cationic species (I) or, secondly, by attack of cyanide after one of the bidentate groups has undergone iron-nitrogen bond breaking (II) to give a unidentate ligand, (i.e. bipyridyl bonding via only one nitrogen atom) e.g:-



If (II) was the correct mechanism, then at high cyanide concentrations a tailing off of rate would be expected, in fact this was found not to occur, hence suggesting (I) as the more likely route. Comparisons of these results with those for the analogous reaction with the phenanthroline compound,  $(\text{Fe}(\text{phen})_3^{2+})$  gave similar rate profiles. However in this case the bidentate group is too rigid for route (II) to be feasible, hence again giving support to route (I).

Recent work by Gillard<sup>(114)</sup> has postulated that the mechanism of the actual way in which cyanide anion bonds to the complex cation may not be via direct attack at the central ion (iron-(II)), but may be instead at the bipyridyl ligands. This does not detract from the above route (I), since that was only concerned with the actual state of the cation when the cyanide attack occurs, (i.e. species 1 or 2), and not with the position of that attack.

The following work in this Chapter is a report of the associative reaction of cyanide and hydroxide ions with the tris-(2,2'-bipyridyl)-iron-(II) cation. Rate constants have been obtained for the cyanide reaction in several mixed aqueous solvents, (and have been compared with rate predictions from thermodynamic calculations) and also for aqueous solutions containing different salts. Acid aquation of the complex in the same mixed solvents (as used in the above investigation) has also been carried out, and the dependence of the rate constants upon solvent composition for both cyanide and acid reactions is discussed. Comparisons of the two sets of rate constants, one associative and the other dissociative, are also made.

#### EXPERIMENTAL SECTION:-

##### for cyanide attack at the compound.

A stock solution of the tris-(2,2'-bipyridyl)-iron-(II) cation was made

up in a minimum volume of 100% water, using AnalaR iron-(II) ammonium sulphate and a slight excess of the required stoichiometric quantity of 2,2'-bipyridyl (i.e. Fe(II):bipy = 1: >3<3½). After shaking, any excess of ligand was removed by filtration. The potassium cyanide and potassium chloride solutions were made up by direct weighing from the AnalaR materials. Fresh solutions of these were used for each solvent mixture, the concentration of the stock solutions being 0.3 mol. dm<sup>-3</sup>. All the solvent mixtures used were made up from deionised water and the best available commercial grade of organic co-solvents, the percentage volumes quoted are by volume before mixing, (i.e. 30% Methanol means 30 ml. methanol + 70 ml. water) since in many cases contraction occurs on mixing the organic solvent and water. The cells used in the kinetic runs contained a total volume of 3 ml., 2.0 ml. of this was occupied by the iron-(II) species stock solution giving the cell concentration of iron-(II) as  $2 \times 10^{-4}$  mol. dm<sup>-3</sup>. The remaining volume in the cell was occupied by potassium cyanide and potassium chloride. A typical set of four cell mixtures for a particular solvent mixture is shown here:-

CELL:-	1	2	3	4
	(ml)	(ml)	(ml)	(ml)
Fe(bipy) <sub>3</sub> <sup>2+</sup> ( $3 \times 10^{-4}$ mol. dm <sup>-3</sup> )	2.0	2.0	2.0	2.0
KCN (0.3 mol. dm <sup>-3</sup> )	0.25	0.5	0.75	1.0
KCl (0.3 mol. dm <sup>-3</sup> )	0.75	0.5	0.25	0.0
∴ [KCN] =	0.025	0.05	0.075	0.1
/mol. dm <sup>-3</sup>				

The potassium chloride present in all but one of the above cells is necessary to maintain the total ionic strength of the cell at 0.1 mol. dm<sup>-3</sup> (ignoring the contribution from the iron-(II) species due to its low con-



centration). The potassium chloride does not take part in this (or any other) reaction and this type of compound is often referred to as an 'inert salt' under the conditions of the reaction. The reason that it is necessary to keep the ionic strength constant is that many reactions, particularly those where charged ions are involved, show large rate variations with ionic strength.

Kinetic runs were carried out in the thermostatted cell compartment of a Unicam SP800 recording spectrophotometer fitted with an SP825 clock attachment. Optical density values were monitored at or near 520 nm, approximately the wavelength of maximum absorption (in the visible region) of the starting material. Neither potassium cyanide nor potassium chloride showed any absorption at this wavelength as was the case for all the solvent mixtures used. Duplicate kinetic runs were carried out for each solvent mixture, the listed observed rate constants being a mean of these. The temperature of the reactions was maintained at 308.2 K except for the tert-butyl alcohol-water mixtures which were carried out at 298.2 K. (The reason for this being that the effects of tert-butyl alcohol on water structure are maximised at lower temperatures<sup>(115)</sup>).

In all kinetic runs, the final optical density (followed to over 3 half-lives) was found to be non-zero as expected, since one of the products of the reaction absorbs at approximately the same wavelength as the starting material. Kinetic results ( $k_{OBS}$ ) were obtained from the raw data by use of Programs 1 and 8, (as listed in the Appendix) each of these employing a 'guessed-infinity' routine. The composite rate constants, ( $k_1$  and  $k_2$  terms) were obtained by a standard linear least mean squares analysis of these previously determined  $k_{OBS}$  values and the appropriate potassium cyanide concentrations. Results for the hydroxide reactions were obtained by similar methods; the experimental techniques used were analogous to those

used for the above cyanide reactions.

### Results:-

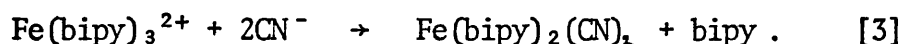
The product of the reaction was confirmed by visible spectrophotometry,<sup>(113)</sup> the lowest energy absorption bands being in good agreement with the values reported previously. First order rate constants,  $k_{OBS}$ , for the reaction of the  $Fe(bipy)_3^{2+}$  cation with cyanide anion in various binary aqueous mixtures are listed in Tables 1, 2 and 4. Under the conditions of the reactions, (i.e. a large excess of cyanide anion as compared with the concentration of the iron compound) first order kinetics were observed in all cases. Plots of  $k_{OBS}$  against cyanide concentration were linear, the value of the slope being assigned to  $k_2$ , (described below). All of these plots gave near-zero intercepts, these values being assigned to the  $k_1$  term in the following rate law, [1] as has been previously described by J. Burgess<sup>(112)</sup> e.g:-

$$k_{OBS} = k_1 + k_2 \cdot [CN^-] \quad \dots \quad [1]$$

leading to [2],

$$\frac{-d [Fe(bipy)_3^{2+}]}{dt} = k_{OBS} \cdot [Fe(bipy)_3^{2+}] \quad \dots \quad [2]$$

As was stated above, the  $k_1$  term was small under the conditions used in our reactions, hence the reaction of primary interest taking place is shown here, [3]:-



No evidence for the subsequent reaction with excess cyanide to yield the tetracyano-iron-(II) product was found, final visible absorption spectra

TABLE 1

First order rate constants ( $k_{\text{OBS}}$ ) and derived second order rate constants ( $k_2$ ) for the reaction between  $\text{Fe}(\text{bipy})_3^{2+}$  and cyanide anion in binary aqueous mixtures; at 308.2 K and an ionic strength of  $0.1 \text{ mol. dm}^{-3}$ , maintained with potassium chloride. Solvent compositions are by volume before mixing.

[KCN]/mol. $\text{dm}^{-3}$	$10^3 k_{\text{OBS}}/\text{s}^{-1}$				$k_2$
	0.025	0.050	0.075	0.100	mol $^{-1}$ $\text{dm}^3 \text{ s}^{-1}$
WATER:					0.028 A
METHANOL:					
10%	1.47	2.6	3.8	5.1	0.044
20%	1.75	3.2	4.6	6.2	0.058
30%	2.1	3.9	6.5	8.6	0.090
ETHANOL:					
10%	1.54	2.8	3.9	4.2	0.040
20%	1.6	3.6	4.7	6.2	0.061
30%	3.0	6.4	8.1	8.6	0.080
1,4 DIOXAN:					
10%	1.68	2.9	4.6	5.8	0.058
20%	2.3	4.5	6.8	9.1	0.090
30%	3.6	7.1	10.6	14.0	0.125
ACETONE:					
10%	1.15	2.3	3.3	4.5	0.042
20%	1.55	3.0	4.6	6.1	0.059
30%	3.5	6.6	8.7	9.8	0.084
GLYCEROL:					
50%	1.8	3.5	5.4	6.2	0.061

(A:- from reference 112)

TABLE 2

First order rate constants ( $k_{\text{OBS}}$ ) and derived second order rate constants ( $k_2$ ) for the reaction between  $\text{Fe}(\text{bipy})_3^{2+}$  and cyanide anion in binary aqueous mixtures; at 298.2 K and an ionic strength of  $0.1 \text{ mol. dm}^{-3}$ , maintained with potassium chloride. Solvent compositions are by volume before mixing.

[KCN]/mol. $\text{dm}^{-3}$	$10^3 k_{\text{OBS}}/\text{s}^{-1}$				$k_2$
	0.025	0.050	0.075	0.100	mol $^{-1}$ $\text{dm}^3 \text{ s}^{-1}$
WATER:					0.0077 <sup>B</sup>
t-BUTYL ALCOHOL:					
9.74%	0.9	1.4	1.7	2.0	0.011
18.0%	0.9	1.5	2.0	3.0	0.028
28.4%	1.5	2.5	4.1	5.3	0.054
36.9%	2.1	4.4	6.1	7.5	0.072
43.0%	2.3	5.3	8.6	11.6	0.120
48.2%	3.1	6.3	10.0	12.0	0.130
ETHYLENE GLYCOL:					
10%				1.2	0.012
20%				1.7	0.017
30%				2.1	0.021
ACETONITRILE:					
10%				1.57	0.0157
20%				2.2	0.022
30%				2.9	0.029
D.M.S.O:					
10%				1.4	0.014
20%				1.9	0.019
30%				3.8	0.038

(B:- from reference 112)

remaining unchanged over an extended period of time.

The dependence of the second order rate constants,  $k_2$ , for the aforementioned attack of cyanide anion at the iron compound, (to be found in Tables 1, 2 and 4) in mixed aqueous solvents has been plotted against several solvent parameters, namely  $E_T$ ,  $Y$  and  $1/D$ . The first of these, the  $E_T$  scale is dealt with more thoroughly in Chapter 2. All that needs to be said here is that it is not a kinetic parameter and as such did not give a good correlation with our reactivity trends. Logarithmic plots of rate constants against  $Y$ ,  $x_2$  and  $1/D$  (where values of these parameters were available) can be found in Figures 1, 2, 3 and 4, and further discussion of their meaning will be dealt with in the relevant section.

The investigation carried out in several aqueous-tert-butyl alcohol mixtures was done at the lower temperature, 298.2 K, for the reason described in the experimental section. Previous work done on several dissociative reactions in these mixtures at this temperature (e.g. the acid aquation of the  $\text{Fe}(\text{5NO}_2\text{-phen})_3^{2+}$  cation<sup>(115)</sup>) produced some interesting results at certain tert-butyl alcohol mole fractions. Thus we thought that it would be interesting to see if these structural (solvent) effects became apparent in a bimolecular reaction system. A logarithmic plot of the second order rate constants for our reaction against mole fraction of tert-butyl alcohol is displayed in Figure 4. Also displayed here are results pertaining to several other binary aqueous mixtures, also at 298.2 K for comparative purposes.

#### EXPERIMENTAL SECTION:-

##### for the acid aquation of $\text{Fe}(\text{bipy})_3^{2+}$ .

The reaction cells were made up in a similar way to those described for the previous cyanide kinetics, the iron-(II) compound occupying two-thirds of the cell volume in the appropriate binary aqueous mixture. The remaining

FIGURE 1

A logarithmic plot of derived second order rate constants ( $k_2$ ) for the attack of cyanide anion at the  $\text{Fe}(\text{bipy})_3^{2+}$  cation against the solvent Y-parameter in several binary aqueous mixtures at 308.2 K.

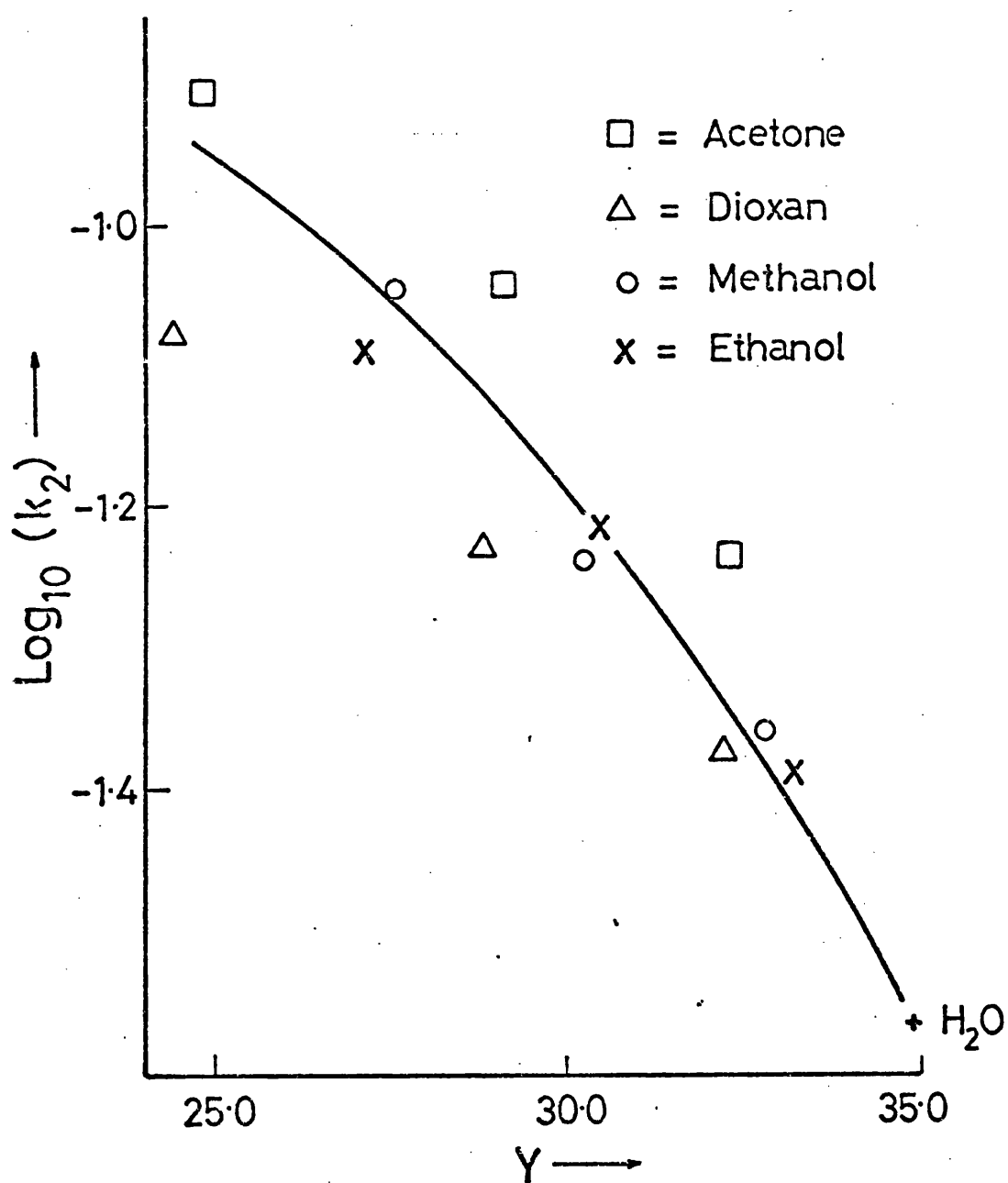
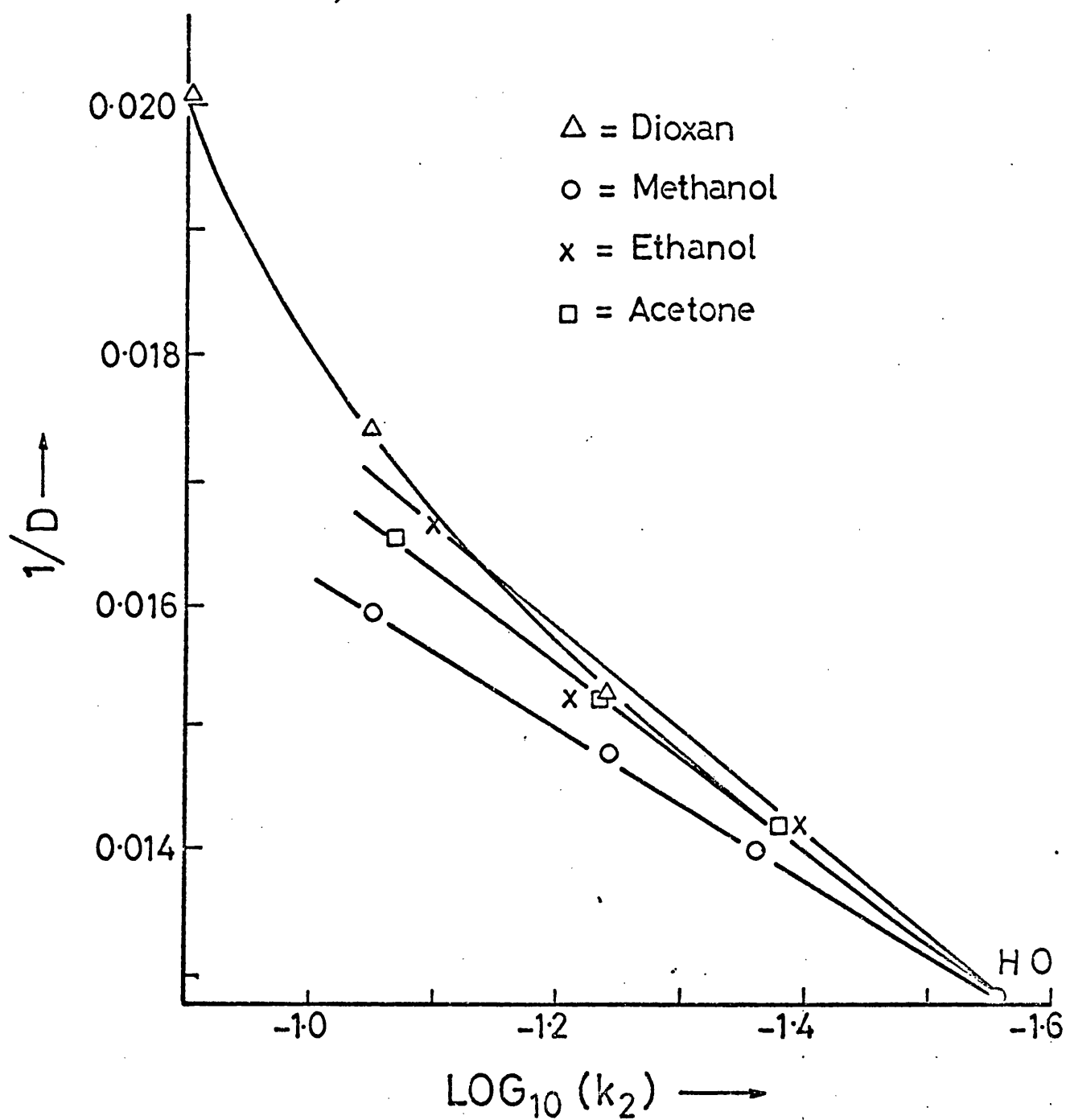


FIGURE 2

A logarithmic plot of the derived second order rate constants ( $k_2$ ) for the attack of cyanide anion at the  $\text{Fe}(\text{bipy})_3^{2+}$  cation against a function of the solvent dielectric constant in several binary aqueous mixtures at 308.2 K.



**FIGURE 3**

A logarithmic plot of the derived second order rate constants ( $k_2$ ) for the attack of cyanide anion on the  $\text{Fe}(\text{bipy})_3^{2+}$  cation against mole fraction of organic cosolvent ( $x_2$ ) for a series of binary aqueous mixtures at 308.2 K.

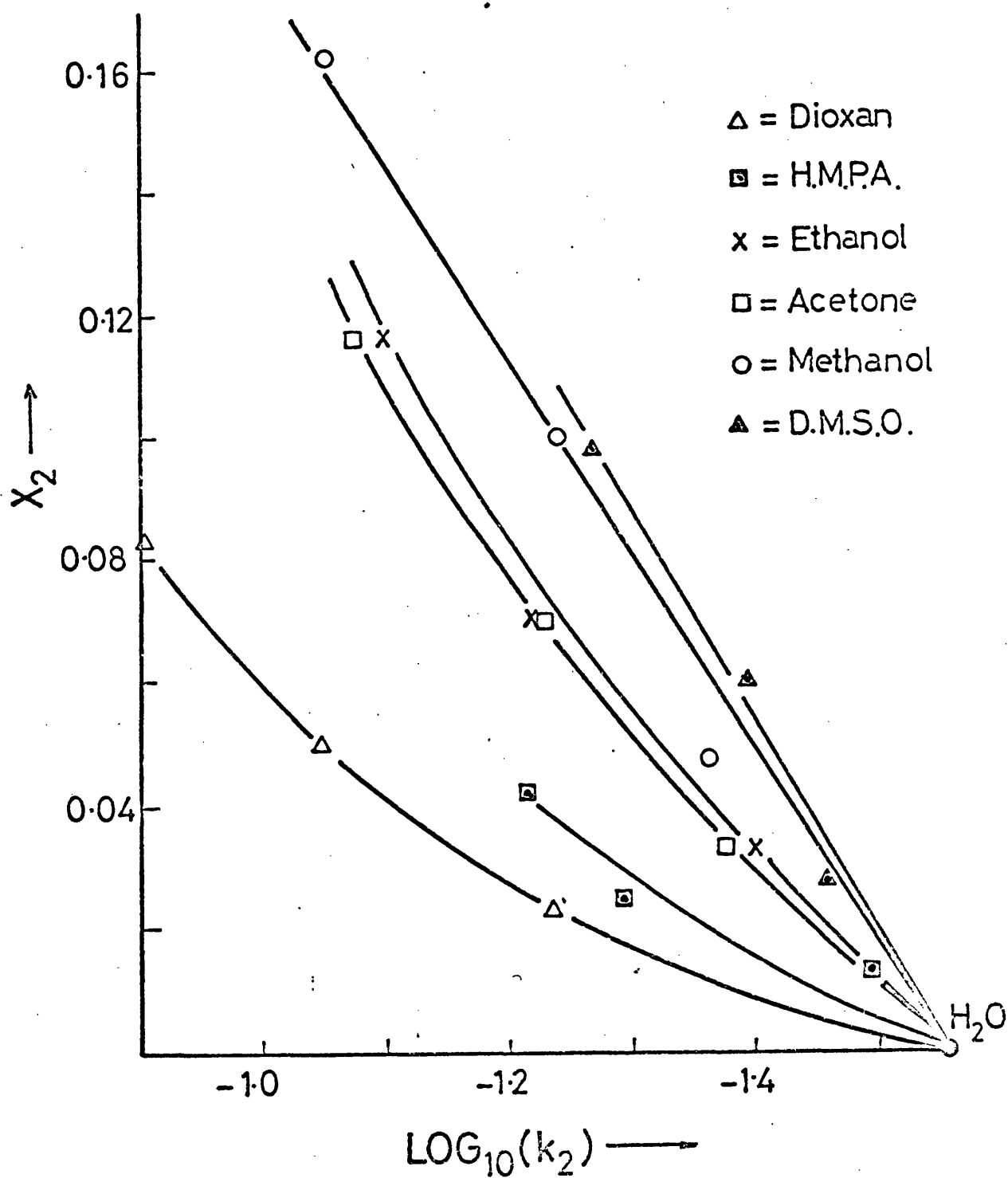
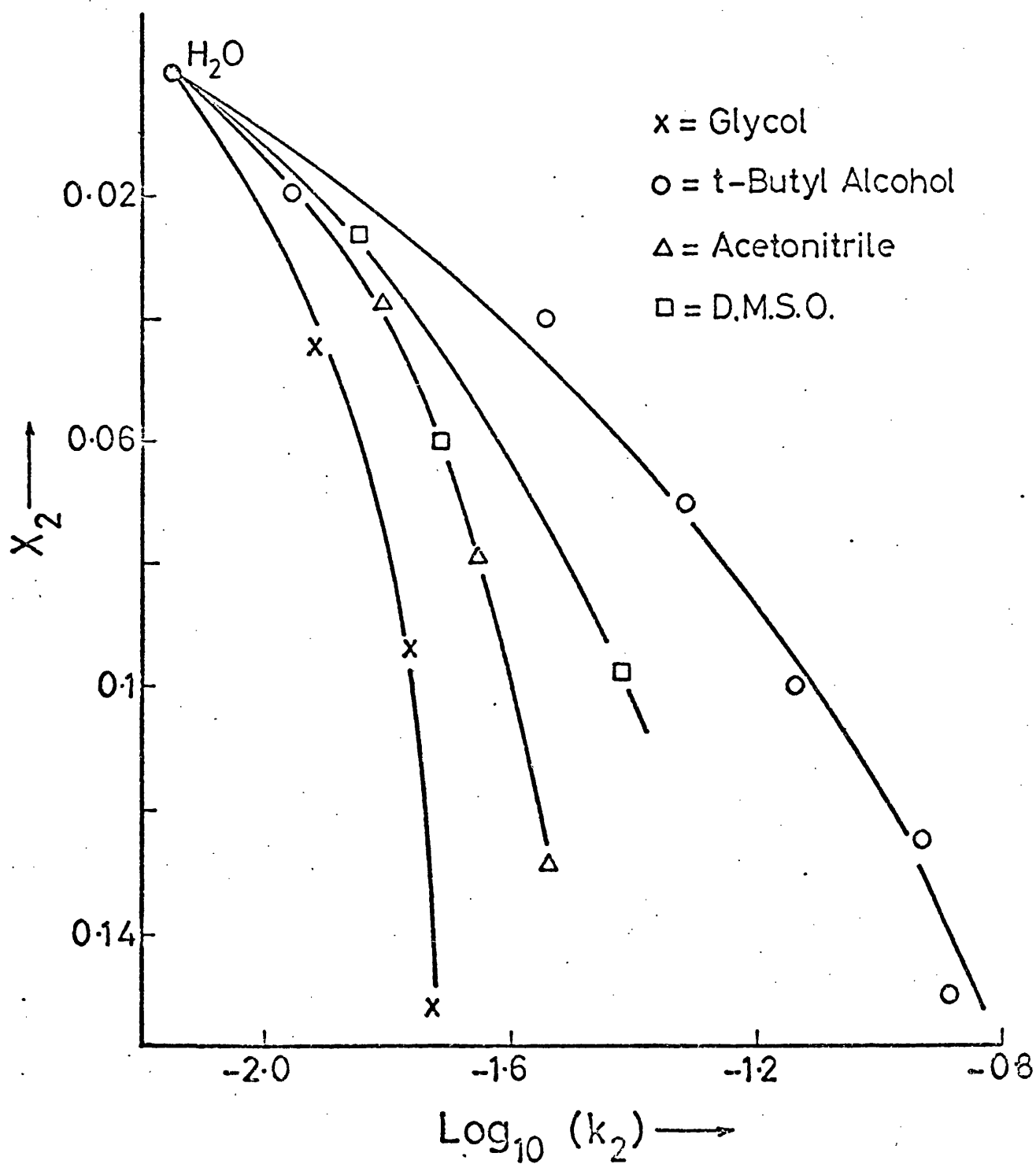




FIGURE 4

A logarithmic plot of the derived second order rate constants ( $k_2$ ) for the attack of cyanide anion on the  $\text{Fe}(\text{bipy})_3^{2+}$  cation against mole fraction of organic cosolvent ( $x_2$ ) for a series of binary aqueous mixtures at 298.2 K.



section of the cells contained a known concentration of sulphuric acid, (assessed by titration against standard alkali) in the same aqueous mixture. A range of acid concentrations,  $0.67\text{--}4.81 \text{ mol. dm}^{-3}$  was used for each mixture to enable the maximum (limiting) rate to be calculated. All runs were carried out at  $308.2 \text{ K}$ ; in each case the final recorded optical density (at  $520 \text{ nm}$ ) value was found to be approximately zero, thus indicating that all reactions proceeded to completion. The initial concentration of the iron-(II) compound was  $2 \times 10^{-4} \text{ mol. dm}^{-3}$  in all kinetic runs. The aqueous mixtures containing methanol, ethanol or 1,4 dioxan were made up by volume before mixing as described previously. [N.B. Satisfactory reproducible results could not be obtained for acetone-water mixtures.]

#### Results:-

The dependence of first order rate constants, ( $k_{AQ}$ ) for the aquation of the  $\text{Fe}(\text{bipy})_3^{2+}$  cation on acid concentration has been established for the afore-mentioned binary aqueous mixtures,<sup>(116)</sup> and is described in equation [4]:-

$$\frac{-d [\text{Fe}(\text{bipy})_3^{2+}]}{dt} = k_{AQ} \cdot [\text{Fe}(\text{bipy})_3^{2+}] \dots\dots [4]^{\ddagger}$$

The results obtained for the various solvent mixtures are shown along with acid concentrations in Table 3. Plots of  $k_{AQ}$  against acid concentration for the three sets of solvent mixtures have also been drawn and are displayed in Figure 5. A similar logarithmic plot against mole fraction of co-solvent is also to be found in Figure 6, and this will be compared with the

[ $\ddagger$  It should be noted that  $k_{AQ}$  is an acid dependant rate constant, and so this equation is not quite so straightforward.]

TABLE 3

First order rate constants ( $k_{OBS}$ ) for aquation of the  $Fe(bipy)_3^{2+}$  ion in acidic binary aqueous mixtures at 308.2 K. Values of the limiting rate constant ( $k_{AQ(LIM)}$ ) were estimated graphically from the  $k_{OBS}$  values listed herein. Solvent compositions quoted are those before mixing.

	$10^3 k_{OBS}/s^{-1}$				
$[H_2SO_4]/mol. dm^{-3}$	0.67	1.35	2.71	3.76	4.81
(SOLVENT)					
WATER:					3.35 °C
METHANOL:					
10%	2.0	2.5	2.7	2.5	2.48
20%	1.7	2.2	2.3	2.2	2.1
30%	1.4	2.0	2.0	1.9	1.75
ETHANOL:					
10%	1.8	2.3	2.3	2.2	2.15
20%	1.4	1.8	1.9	1.7	1.6
30%	1.3	1.5	1.5	1.42	1.4
1,4 DIOXAN:					
10%	2.1	2.7	2.8	2.4	2.4
20%	1.8	2.4	2.4	1.9	1.9
30%	1.7	2.1	2.1	1.7	1.7

(C:- from reference 116)

FIGURE 5

A plot of the dependence of the rate of aquation of the  $\text{Fe}(\text{bipy})_3^{2+}$  cation on concentration of sulphuric acid in several binary aqueous mixtures at 308.2 K.

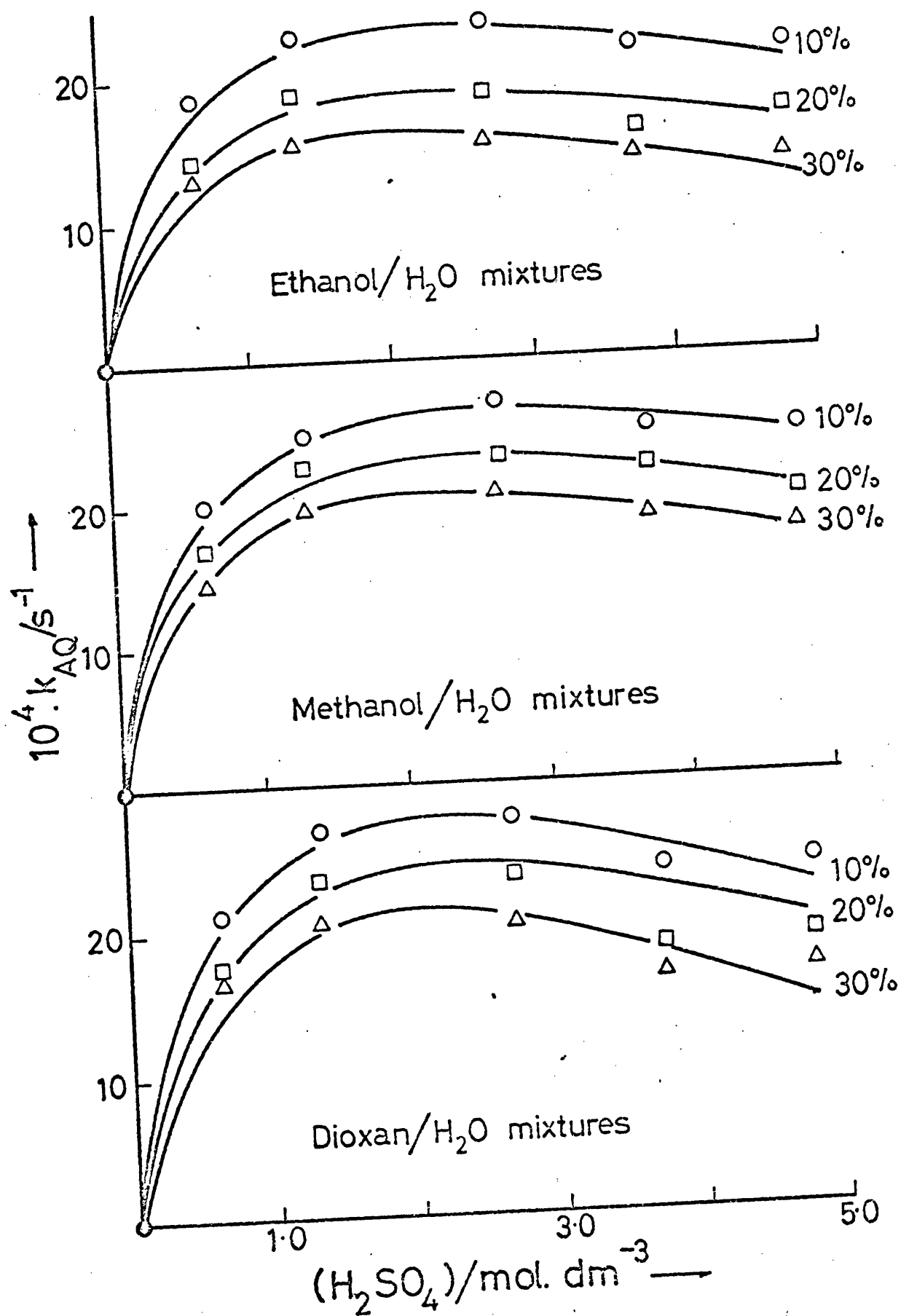
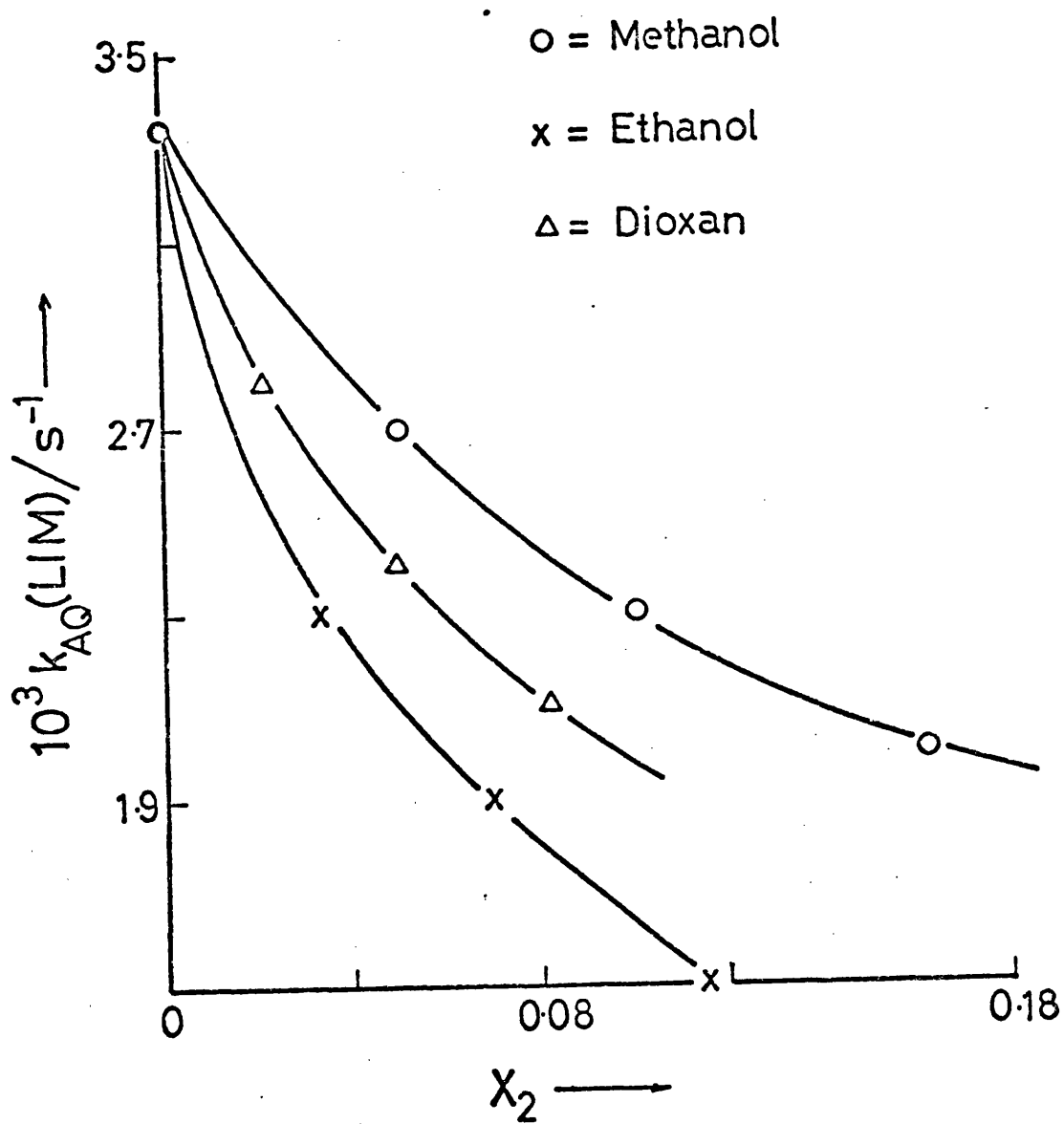


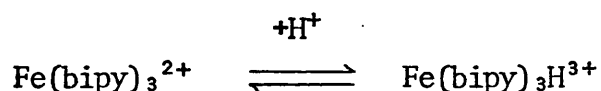
FIGURE 6

A plot of the limiting aquation rates  $[k_{AQ}(LIM)]$  for the aquation of the  $Fe(bipy)_3^{2+}$  cation against the mole fraction of organic cosolvent ( $x_2$ ) in a series of binary aqueous mixtures at 308.2 K.



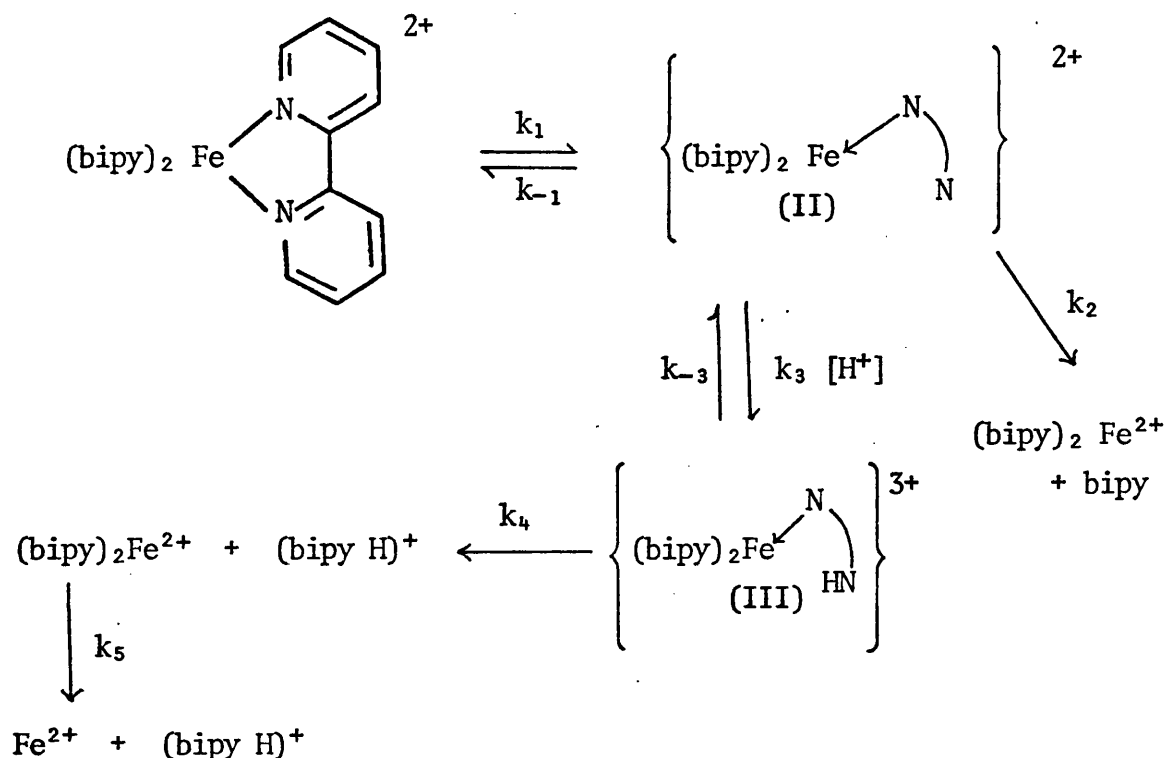
analogous plot for cyanide attack at the iron-(II) compound in the later discussion section.

The dependence of  $k_{AQ}$  on acid concentration in these mixed solvents is very similar to that established by other workers,<sup>(116,117)</sup> in pure aqueous solution. The first mechanistic explanation of this behaviour, (i.e. a limiting rate occurring at high acid concentration) came from Baxendale & George in 1950,<sup>(118)</sup> who decided that the  $\text{Fe}(\text{bipy})_3^{2+}$  cation must react more slowly than its protonated form,  $\text{Fe}(\text{bipy})_3\text{H}^{3+}$ , then the following equilibrium,



would give the observed limiting rate effect. However this argument was soon dismissed for several good reasons. Firstly, since the unprotonated species is a weak base, it is unlikely that large quantities of the protonated species would be formed. Also, one would expect these two species to exhibit different spectral characteristics, but this was not observed to be so.

The mechanism, proposed by Basolo et al.,<sup>(119)</sup> shortly after the above workers in 1953 is still accepted today as the most likely mechanistic explanation, although it has been slightly modified over the years. The reaction scheme is shown here:-



(N.B. In (II), bipy is represented simply as  $\text{N} \text{---} \text{N}$ , and in (III), the protonated form is drawn as  $\text{N} \text{---} \text{NH}$ .)

This mechanism has been suggested for many acid dependent aquations where the bidentate groups are not necessarily bipyridyl groups. However, if the bipy groups are replaced by rigid groups, (e.g. phen) the initial reaction to give a unidentate bidentate-group becomes impossible. This may be why the aquation of the  $\text{Fe}(\text{phen})_3^{2+}$  cation shows an absence of a similar acid dependence.

If we apply a steady state approximation for the concentrations of the partially dissociated species, the observed rate constant is given by:-

$$k_{\text{OBS}} = \frac{k_1 (k_2 + k_3 [\text{H}^+])}{k_{-1} + k_2 + k_3 [\text{H}^+]} \quad \dots\dots [5]$$

(see ref. 116)

A recent simplification by Sykes et al.,<sup>(120)</sup> included a  $K_3$  term, defined as the protonation equilibrium of species (II) in the previous reac-

tion scheme. Thus,  $K_3 = k_3/k_{-3}$ . Again applying steady state approximations to the species labelled (II) and (III), the following rate law is arrived at:-

$$k_{OBS} = \frac{k_1 (k_2 + K_3 k_4 [H^+])}{k_1 + k_2 + K_3 k_4 [H^+]} \quad \dots [6]$$

Both [5] and [6] give the desired limiting rate at high  $[H^+]$  as follows. The consequences of equations [5] and [6] are obvious; at low  $[H^+]$ , if we were to extrapolate to  $[H^+] = 0$ , we would arrive at equation [7]:-

$$k_{OBS} = \frac{k_1 \cdot k_2}{(k_{-1} + k_2)} \quad \dots [7]$$

At high  $[H^+]$ , the terms  $k_{-1}$  and  $k_2$  disappear (i.e. they are small enough to be ignored) enabling us to cancel the  $K_3 k_4 [H^+]$  terms (and the corresponding terms in [5]) leaving us with the limiting rate equation as shown in equation [8]:-

$$k_{OBS} = k_1 \quad \dots [8]$$

The graphical representation of this is shown here in Diagram A, between  $[H^+] = 0$  and a suitably large value:-

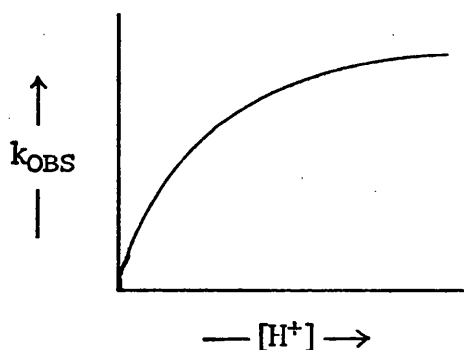


DIAGRAM A.



Thus equation [8] implies that the observed limiting rate refers to the fission of the first iron-nitrogen bond.

Applying the previous mechanistic analysis to our work in mixed aqueous solvents gives good agreement. However, although a limiting rate does occur at high acid concentration, further increase in this acid concentration tends to produce a slight decrease in reaction rate. For this reason, in Table 3 the values for the limiting rate constants,  $k_{AQ}(LIM)$  were taken as the maximum observed values of the  $k_{AQ}$  values listed. The actual reasons for this anomalous behaviour are not obvious, however in view of the large structural changes on going from pure water to these mixed aqueous solvents these observations do not seem too distressing.

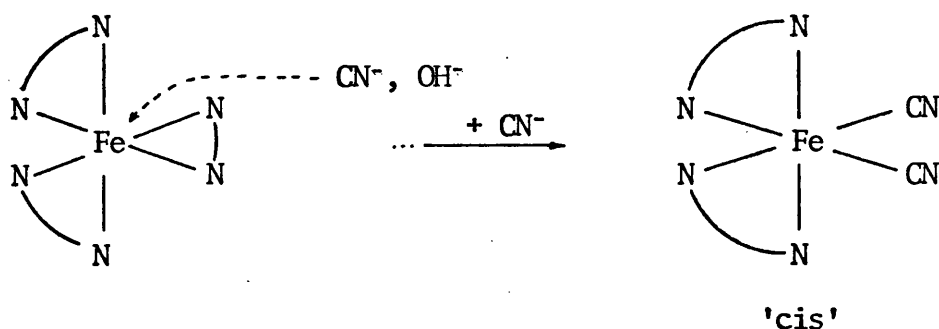
#### Discussion:-

##### for the cyanide reaction.

The rate laws previously described in equations 1 and 2 indicate that this reaction proceeds via parallel first- and second-order pathways. The former corresponds to a dissociative process, the rate determining step being the first iron-nitrogen bond breaking,<sup>(112)</sup> as is observed in the limiting rate for the acid aquation reaction, followed by loss of the bipy ligand. However, as we have stated earlier, the  $k_1$  terms were small in all of our reactions.

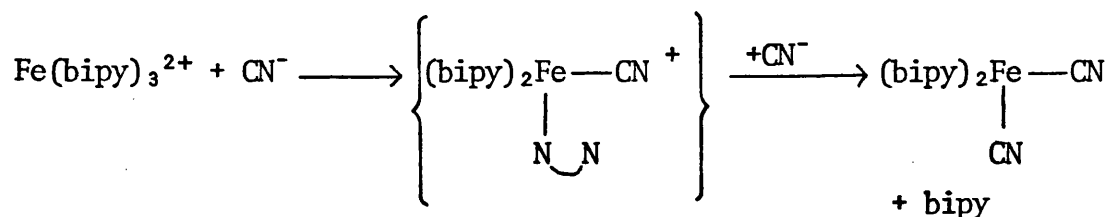
The  $k_2 [CN^-]$  term of equation 1 has been taken to indicate a bimolecular attack of cyanide at the iron-(II) compound.<sup>(111,112)</sup> Until recently only one of the proposed mechanisms<sup>(112)</sup> seemed to be capable of explaining the observed kinetic parameters. This mechanism viewed the reaction as being due to direct attack of cyanide anion at the central iron-(II) nucleus. This achieved support from evidence relating to substituent effects;<sup>(112)</sup> since the central nucleus of a tris-bidentate complex will be surrounded by

a high electron density in the  $t_{2g}$  orbital, the incoming negative ion will have to push through this. Hence if electron withdrawing groups are situated on the ligands, they would be expected to reduce the electron density at the central ion, thus making nucleophilic attack a more viable process, (i.e. and vice versa for electron donating substituents). This type of behaviour has been demonstrated using substituted bipy and phen on iron-(II) tris-bidentate species in the past, with both cyanide and hydroxide as the nucleophilic incoming groups<sup>(112)</sup>:- e.g.



[N.B.  $\text{N} \curvearrowright \text{N}$  represents a bidentate group such as bipy or phen.]

The only product formed is the cis-isomer, shown in the previous diagram. This result can be explained by either the observation that a trans-product would be sterically strained (from molecular model building observations) and/or that the complete reaction scheme involves a monodentate bidentate-group, (as has previously been postulated for the acid aquation reaction) formed after the initial attack by cyanide anion, e.g:-

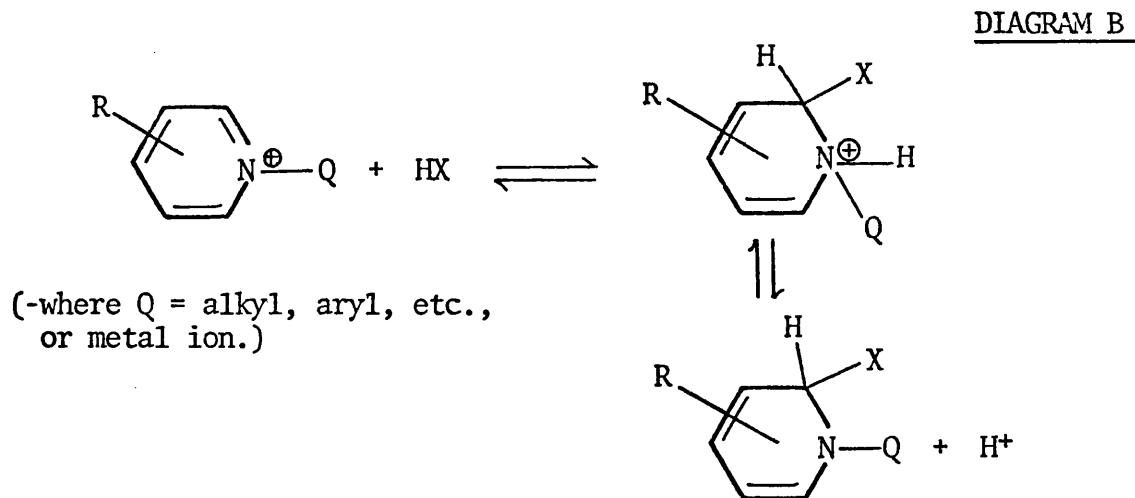


Thus the two cyanide groups would occupy the same geometric positions

as were occupied by the displaced bipy group. Either or both of these two explanations may be responsible for the observed product identity, although no direct positive evidence is available to support the latter of these.

In the last few years an alternative to the previous direct-attack mechanism for both hydroxide and cyanide at this type of compound has been proposed.<sup>(114)</sup> This mechanism, (see Diagram B) is based upon observations of reaction studies of quaternised pyridines, especially those relating to the increased electrophilicity of the 2-position (adjacent to the nitrogen) as compared with the non-quaternised pyridine. The connection between, say, an alkyl group and a metal ion, although possessing seemingly unrelated properties, can be in certain cases quite real.

The argument is as follows. Any quaternised N-heterocycle, no matter what the nature of the quaternising agent (Q), may participate in the equilibria shown here:-

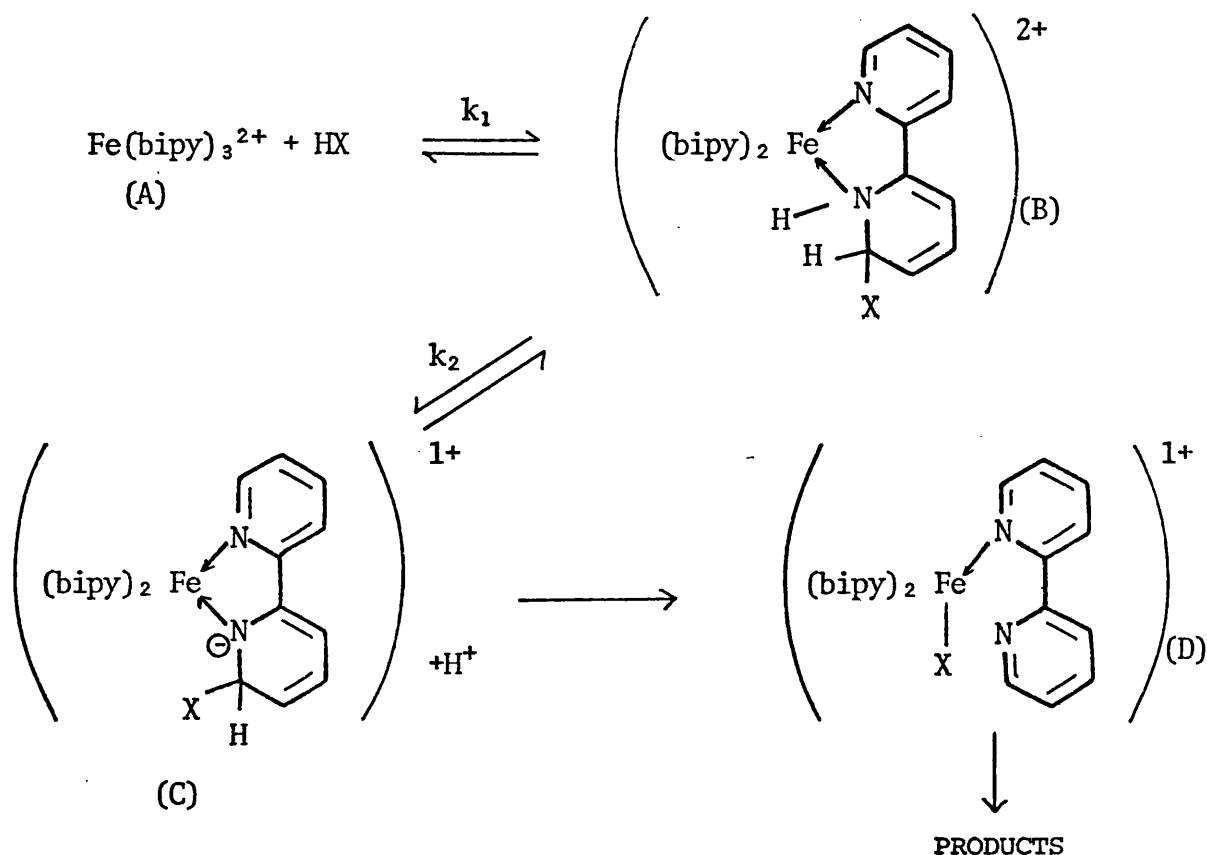


Hence if we apply this argument in the case of Q = metal ion, we arrive at Diagram C, which represents an alternative reaction scheme for substitution at  $\text{Fe}(\text{bipy})_3^{2+}$  species, and is described as follows. The initial step is attack by X ( $\text{X} = \text{OH}^-$  or  $\text{CN}^-$ ) on one of the bipy groups at the 6-position of one of the rings, the nitrogen atom being simultaneously protonated to yield

species (B).<sup>‡</sup> This then loses this proton to give species (C), which then undergoes an intramolecular shift to form (D) and thence to products.

Support for this type of mechanism, where  $X = OH^-$  is quite strong, mainly due to work on the  $Pt(bipy)_2^{2+} + OH^-$  system,<sup>(121)</sup> where substitution of hydroxide at this cationic species seems to be reversible.

DIAGRAM C.



Spectroscopic changes observed when the two ( $OH^- + Pt(bipy)_2^{2+}$ ) are mixed are said to be best explained by substitution of  $OH^-$  at either the 6 or 6' position on one of the pyridine rings. Hydrolysis has been discounted, since the observed changes were much too fast for this, and also the spectral changes are completely reversed upon acidification. By use of N.M.R.

[<sup>‡</sup> For  $X = CN^-$  this step is thought not to occur, rather  $A \rightleftharpoons C$ .]

spectroscopy it has been possible for the workers concerned to establish the product as that expected from substitution at the 6- (6'-) position.

Although no similar spectral changes were observed by us when either hydroxide or cyanide were added to solutions containing  $\text{Fe}(\text{bipy})_3^{2+}$ , this step could be hidden by subsequent fast intramolecular rearrangement followed by further reaction giving the observed products. However analogous experiments with  $\text{Ru}(\text{bipy})_3^{2+}$  in solutions containing cyanide showed no evidence for the reversible or irreversible addition of cyanide to the co-ordinated ligands. A similar set of investigations using several different ions (e.g. azide, cyanate, thiocyanate and fluoride) with  $\text{Fe}(\text{bipy})_3^{2+}$  performed by ourselves produced some interesting results. A spectral change was observed for all of these mixtures, however after purification of these salts followed by adjusting the pH of their solutions to +7, a change was observed only for azide ion. The lowest energy absorption in the visible region for the  $\text{Fe}(\text{bipy})_3^{2+}$  species was found to change shape (over ~10 minutes) on addition of a solution of sodium azide, (pH = 7), no subsequent changes being observed over several hours. Attempts to ascertain whether this process was reversible were not successful. However, this would seem to indicate that a reaction similar to that proposed above may be occurring here. It should be noted however that in the case of cyanide attack at the  $\text{Fe}(\text{bipy})_3^{2+}$  cation, there is no need to invoke indirect attack at the ligand rather than direct attack at the metal, since cyanide ion has a greater affinity for iron-(II) than, say, 4-bipy. This is not however the case for hydroxide ion attack at this ion, and it may be that the difference observed between the reactivity trends of these two nucleophiles (see Figure 8) is due to their different modes of attack.

### Kinetic trends:-

The reactivity trends for the reaction between  $\text{Fe}(\text{bipy})_3^{2+}$  and  $\text{CN}^-$  are both obvious, and quite large, by comparison with the same trend exhibited for the analogous acid aquation reactions.

As long ago as 1930, Hughes, Ingold and their associates had formulated a basis for predicting solvent effects on reactivities of organic compounds involving various combinations of charged and uncharged substrates.<sup>(122)</sup> For bimolecular reactions involving species of opposite charge, in their case  $\text{Me}_3\text{S}^+ + \text{OH}^-$  and in our case  $\text{Fe}(\text{bipy})_3^{2+} + \text{CN}^-$ , one would predict, (from the results of the afore-mentioned workers) a marked increase in rate on going from pure water to an aqueous mixture, containing for example methanol.

Such predictions follow in a quite straightforward manner from simple assumptions made by the previous workers. Their key proposal was that solvation would be treated as a purely electrostatic phenomenon. From this, assuming that solvation changes will dominate a reaction, it was possible to treat any reaction solely in terms of the electrostatic interactions concerned. For instance a polar solvent would be expected to accelerate or retard a reaction depending upon whether the transition state is more, or less polar than the initial state respectively, (i.e. a polar molecule will prefer a polar solvent to a non-polar solvent by virtue of its increased solvation or, from a different viewpoint; the polar molecule will attract the polar solvent, thus doing work, and hence lowering the energy of the system).

Applying these ideas to our reaction, from the electrostatic point of view, we have the system:-



The transition state will obviously have an overall charge equal to +1, (i.e. a cationic species) hence using the previous arguments we would expect an increase in rate as the solvent polarity drops. This is in fact observed, (see Tables 1 and 2) the rates increasing in each solvent mixture as the proportion of non-aqueous solvent is increased.<sup>†</sup>

Applying this treatment to the analogous acid aquation reaction in a series of mixed aqueous solvents also gives the correct prediction. The overall rate variation here (at the limiting acid aquation rate) with solvent mixture is much smaller than was the case for the previously described reaction (see Figure 6). The initial and transition states in this reaction are both di-positively charged (as shown in the reaction scheme earlier in this Chapter) hence one would expect solvation changes to favour neither one nor the other of these as the proportion of organic-co-solvent is increased.

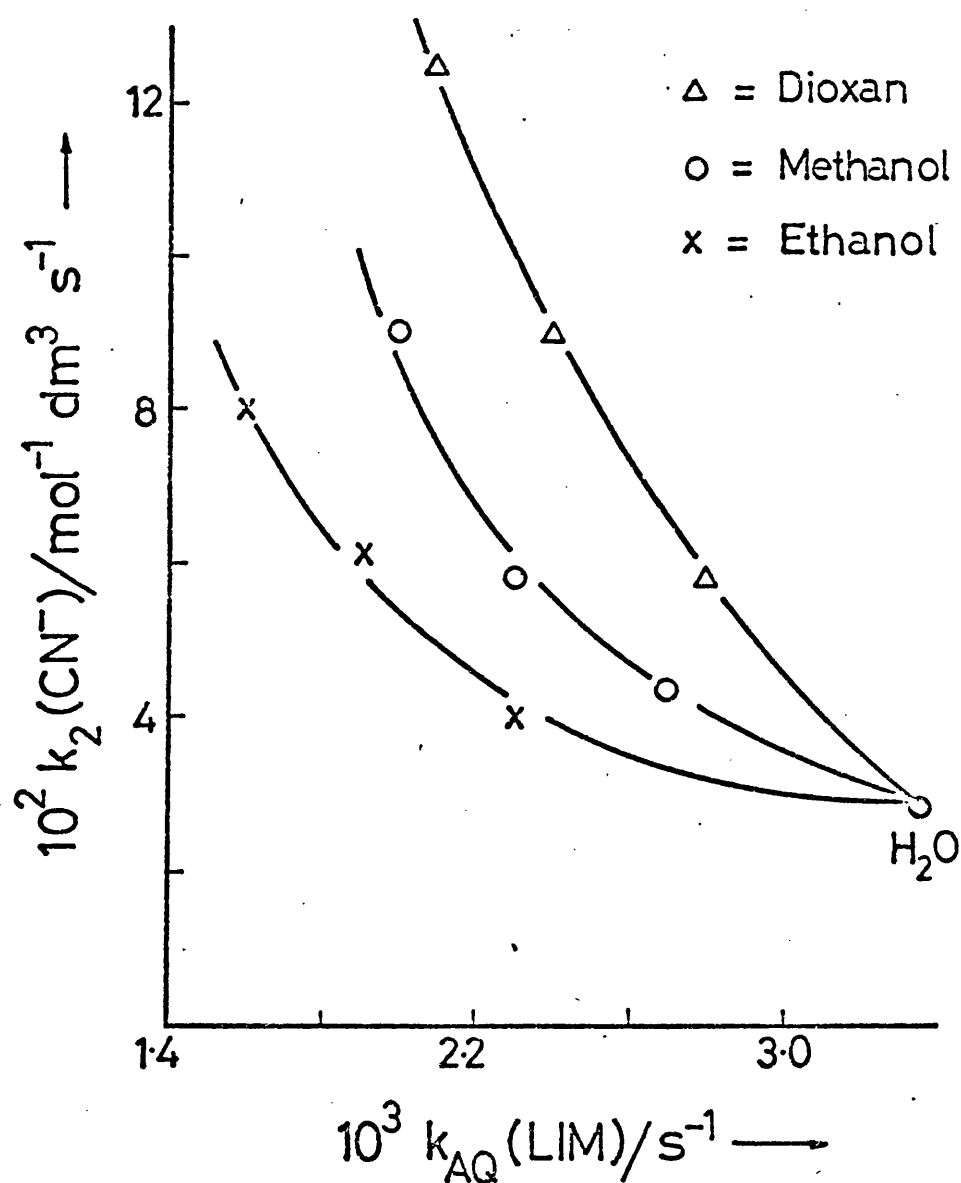
Similar predictions can also be arrived at by use of the so-called 'Absolute theory of rates',<sup>(123)</sup> where the arguments used entail a more mathematical approach, (i.e. and hence less qualitative than the previously cited arguments). The most important assumption here is however the same as was described in the previous analysis:- that the electrostatic interactions are of utmost importance.

The relationship between the second order rate constants for cyanide attack at  $\text{Fe}(\text{bipy})_3^{2+}$  and the corresponding values for the limiting acid aquation rate is illustrated in Figure 7. The marked difference in the size of the rate variations with solvent composition for the two reactions is evident in this plot if one examines the scales used on the two axes. The scale used on the  $k_2$  axis is a factor of ten greater than that for the

[<sup>†</sup> As is the case for the hydroxide reaction with  $\text{Fe}(\text{bipy})_3^{2+}$ .]

FIGURE 7

A plot of the derived second order rate constant  $[k_2(\text{CN}^-)]$  for the attack of cyanide anion at the  $\text{Fe}(\text{bipy})_3^{2+}$  cation against the limiting aquation rate  $[k_{\text{AQ}}(\text{LIM})]$  for the same cationic species in a series of binary aqueous mixtures at 308.2 K.





aquation rate axis. This difference can be seen more clearly perhaps on comparing Figures 3 and 6, where the logarithms of the rate constants are both plotted against  $x_2$ .

This greater sensitivity for the bimolecular attack of cyanide at the iron-(II) compound cannot be explained purely in terms of solvation changes at the transition state as it is formed, insofar as iron-nitrogen bond-stretching is a contributor to the formation of this transition state. Thus this would not be expected to have a large effect on reactivity variation with solvent composition. Instead the controlling factor in this reaction seems to be the variation in solvation characteristics of the cyanide anion with solvent composition. This would seem to be quite consistent in terms of the relative solvation of the ions concerned with the observed reaction. The  $\text{Fe}(\text{bipy})_3^{2+}$  cation and the transition state species are both very large in contrast to the small cyanide anion, thus the latter ion will be more strongly solvated by solvent-water by virtue of its high charge/size ratio. Solvation at the two larger species will be weaker and hence the effect of replacing solvent water by organic-co-solvent will be much less than the effects at cyanide for the equivalent change. Hence although the reaction is bimolecular, we would expect reactivity trends to be mainly a reflection of solvation changes at the cyanide anions alone. Thus in our solvent mixtures, as the solvent-water is replaced the overall solvent becomes less polar, hence the solvation of the cyanide anions decreases. This allows the cyanide anions to move more freely through the solvent, facilitating bimolecular attack at the  $\text{Fe}(\text{bipy})_3^{2+}$  cations. Thus the reaction rate increases as the proportion of organic co-solvent is increased.

This may explain the apparent lack of any anomalous behaviour in the aqueous-tert-butyl alcohol results in contrast to the results obtained in the investigation of the aquation of the related  $\text{Fe}(\text{5NO}_2\text{-phen})_3^{2+}$  cation in

the same solvent mixtures.<sup>(115)</sup> The results obtained in this system were probably connected with solvation changes at this large iron-(II) cation and its subsequent transition state. Thus a connection between this work and ours would not be expected in the light of the recent discussions.

A thermodynamic investigation of our reaction, involving attempts to gain an indication of the magnitude of the solvation changes at the cyanide anions by measuring a quantity known as the 'chemical potential' of that ion is described later in this Chapter. Correlations between these values and the reactivity trends are discussed along with rate predictions based solely on these changes. Before this however, application of the previously described Grunwald-Winstein analysis<sup>(104)</sup> to both our cyanide and acid aquation might be of interest, especially since one of these reactions is associative and the other dissociative in character.

#### Grunwald-Winstein analysis:-

In the original application of this analysis for  $S_N1$  solvolysis of an organic chloride, a plot of rate constant against solvent  $Y$  values (calculated from the model  $S_N1$  solvolysis of tert-butyl chloride)<sup>†</sup> was expected to be linear with a slope ( $m$ ) = 1.0.<sup>(104)</sup> As the reactions studied became more distant, (i.e. the ratio of  $S_N1/S_N2$  decreasing) both in terms of mechanism and the identity of the leaving group<sup>†</sup> so as one would expect the slopes of the above-mentioned plots differ markedly from unity, some becoming non linear. In the case of  $S_N2$  reactions, where the nucleophilicity of the solvent/ligand becomes important one would expect not a single line for all co-solvents (as is observed in the model reaction) but instead one

[ ‡ Defined as in the introduction to this Chapter. The rate determining step is loss of the chloride anion followed by attack of solvent.]

[ † When the solvolysis of the analogous tert-butyl bromide was treated by the  $Y$ -parameter analysis, it did not give a slope of unity!]

for each co-solvent, and all with a slope considerably less than unity.

Application of this type of analysis with our acid aquation reaction gave the non-linear plot displayed in Figure 10. The slope ( $m$ ) for this plot is 0.2–0.3 implying that the rate is very much less sensitive to solvent nature than is the case for the solvolysis of tert-butyl chloride. This is to be expected since in our reaction there is no charge separation on forming the transition state. Examples of some other ' $m$ ' values for aquation and other reactions of transition metal compounds are listed here:-

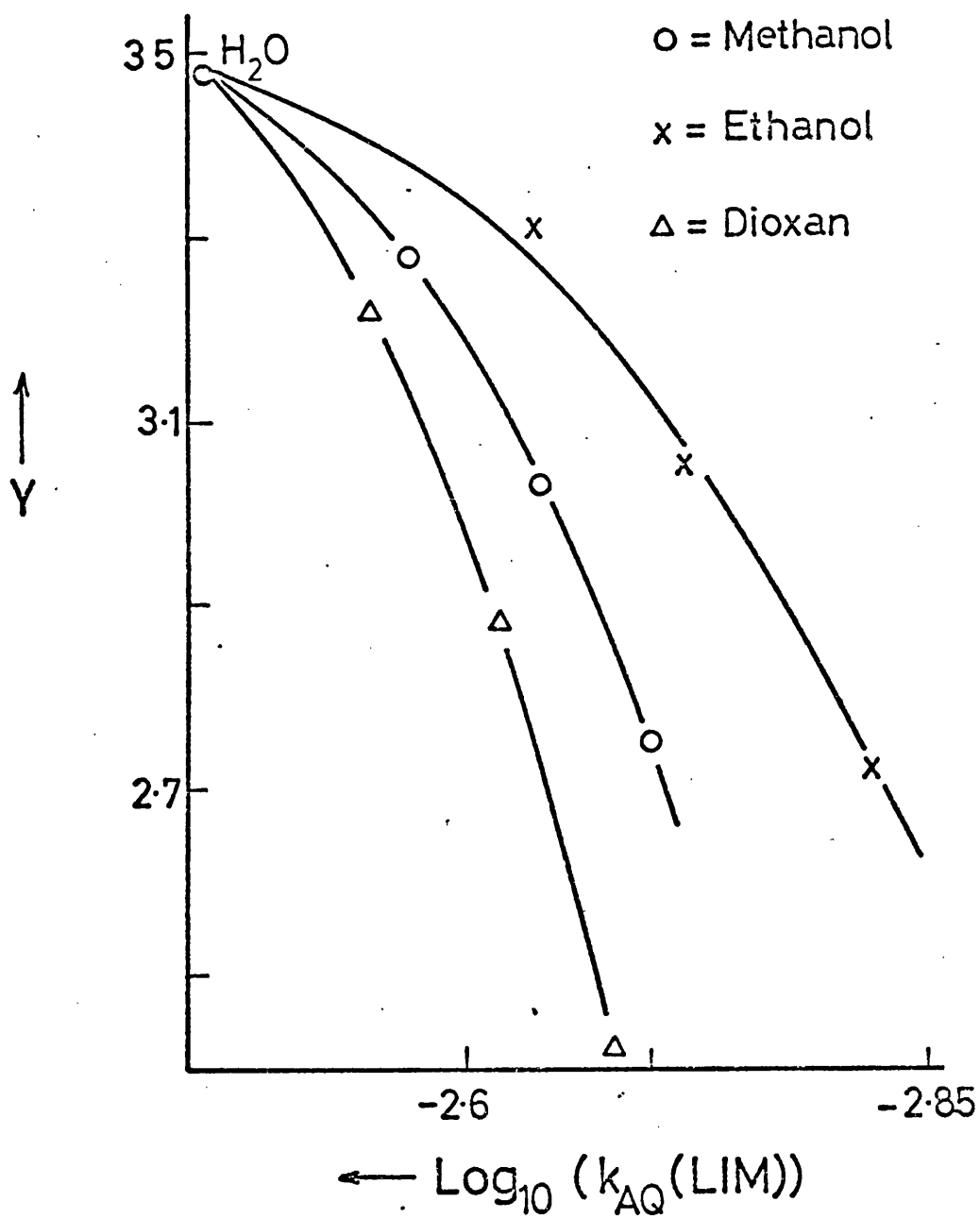
COMPOUND	SLOPE ( $m$ )	REFERENCE
cis-Coen <sub>2</sub> Cl <sub>2</sub> <sup>+</sup>	0.25 – 0.3	(124)
Cr(NCS) <sub>6</sub> <sup>3-</sup>	0.08	(107)
Fe(bipy) <sub>2</sub> (CN) <sub>2</sub> + phen	0.2	(125).

As we can see, all of these ' $m$ ' values are very small; the similar value obtained for this reaction and of Fe(bipy)<sub>2</sub>(CN)<sub>2</sub> may be a reflection of the fact that both this reaction and ours involve a common leaving group (i.e. bipy). This is a large hydrophobic group and so one would expect only a small degree of solvation of this group and of the moiety remaining. Thus only a small solvent dependence of aquation rate is observed.

Application of this analysis to the associative cyanide reaction with Fe(bipy)<sub>3</sub><sup>2+</sup> is demonstrated in Figure 1. As in the previous reaction a family of curves rather than a single linear solvent dependence occurs, reminiscent of bimolecular solvolysis. The limiting ' $m$ ' value estimated from this plot for the water-rich mixtures is -1.0 to -1.1. Similar values for other bimolecular aquation reactions have also been found by

**FIGURE 10**

A logarithmic plot of the limiting rates of aquation ( $k_{\text{LIM}}$ ) for the  $\text{Fe}(\text{bipy})_3^{2+}$  cation against the solvent Y-parameter in a series of binary aqueous mixtures at 308.2 K.



other workers and are listed here:-

COMPOUND	SLOPE (m)	REFERENCE
$\text{Hg}^{2+} + \text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$	-0.35	(126)
$\text{Hg}^{2+} + \text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$	-0.25	(126)
$\text{Hg}^{2+} + \text{ReCl}_6^{2-}$	-1.7	(127).

The sign and magnitude of these 'm' values must be related to the associative character of these reactions. However, their analysis in terms of a comparison with the model solvolysis of tert-butyl chloride would seem to suggest that in the above systems (including ours) the solvent sensitivity is extremely large. This may be explained partly for our reaction by the solvation changes at the small cyanide anion, and possibly in some of the previously listed reactions by similar changes at the  $\text{Hg}^{2+}$  ion. Both of these are small highly charged ions and hence would be expected to be extremely sensitive to solvation changes.

A comparison between  $\text{OH}^-$  and  $\text{CN}^-$  as nucleophiles with the  $\text{Fe}(\text{bipy})_3^{2+}$  cation in two series of mixed aqueous solvents has also been carried out. The results are listed in Table 4, and plotted in Figure 8. As expected the hydroxide reaction seems to be more sensitive than the cyanide to solvent structure changes. If we assume that in both reactions it is the solvation changes at the nucleophile which are primarily responsible for the observed reactivity trends, as was outlined earlier, thus the observed reactivity comparison is as expected, since the hydroxide ion is smaller than the cyanide ion and so solvation changes will be larger for this ion. It is interesting to note that in Figure 3, plots of  $\log(k_2)$  vs.  $x_2$  for the solvent mixtures for the cyanide reaction are very different; however both of the co-solvents (HMPA and DMSO) are reported as being similarly

TABLE 4

First order rate constants ( $k_{\text{OBS}}$ ) and derived second order rate constants ( $k_2$ ) for attack of hydroxide and cyanide ions at the  $\text{Fe}(\text{bipy})_3^{2+}$  ion in two sets of binary aqueous mixtures at 308.2 K, and an ionic strength of 0.1 mol.  $\text{dm}^{-3}$  maintained with potassium chloride. Solvent compositions are by volume before mixing.

HYDROXIDE RESULTS:-

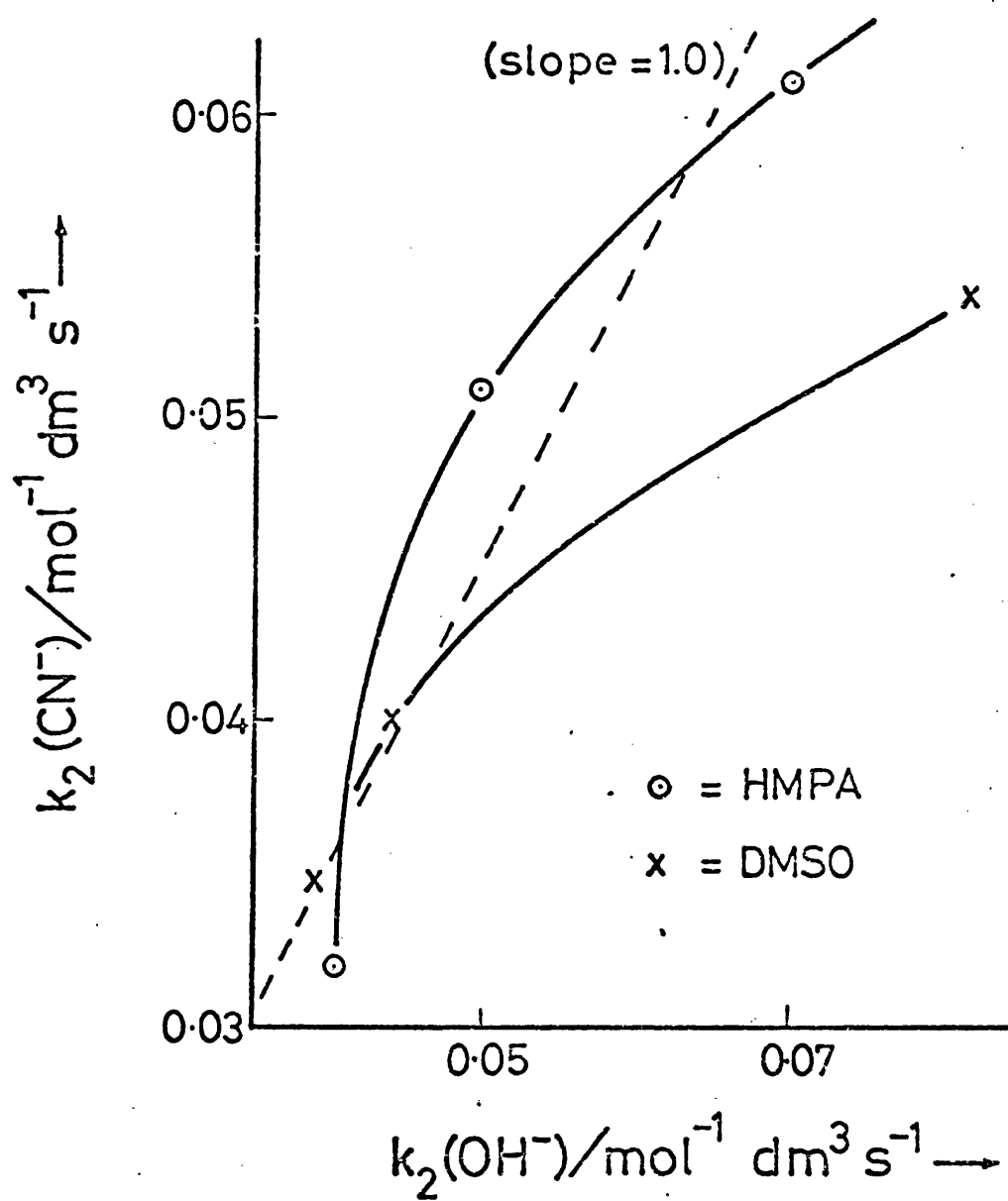
	$10^3 k_{\text{OBS}}/\text{s}^{-1}$				$10^3 k_1/\text{s}^{-1}$	$k_2$ $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$
[KOH]	0.025	0.050	0.075	0.100		
HPMA:						
10%	1.22	2.4	3.4	4.3	0.27	0.041
20%	1.56	2.7	3.9	5.3	0.26	0.050
30%	2.2	3.6	5.8	7.3	0.35	0.070
DMSO:						
10%	1.26	2.3	3.2	4.1	0.36	0.038
20%	1.44	2.5	3.6	4.7	0.34	0.044
30%	2.2	4.4	6.1	8.5	0.15	0.082

CYANIDE RESULTS:-

	$10^3 k_{\text{OBS}}/\text{s}^{-1}$	$k_2$ $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$
[KCN]/mol. $\text{dm}^{-3}$	0.100	
HPMA:		
10%	3.2	0.032
20%	5.1	0.051
30%	6.6	0.066
DMSO:		
10%	3.48	0.035
20%	4.0	0.04
30%	5.4	0.054

FIGURE 8

A plot of the derived second order rate constants ( $k_2$ ) for the attack of cyanide and hydroxide anions at the  $\text{Fe}(\text{bipy})_3^{2+}$  cation in some binary aqueous mixtures at 308.2 K.



poor in terms of solvation of anionic species. Our results would seem to infer that HMPA is a much poorer solvent in this respect in aqueous mixtures than DMSO in the same aqueous mixtures.

### Thermodynamic analysis:

Throughout the previous discussions on the bimolecular reaction between cyanide and  $\text{Fe}(\text{bipy})_3^{2+}$  we have stressed the importance of solvation changes occurring at the cyanide anion when considering factors influencing the reactivity trends for this reaction. Thus it would seem logical to make some attempt to estimate the size of these changes, as the solvent composition is varied. This can be done by estimating the Gibbs free energies of transfer for cyanide anion from say water to a particular mixed aqueous solvent. These transfer parameters for ions are estimated from the changes in the chemical potential of an ion ( $\mu_i$ ), which is defined as a measure of the ion-solvent interaction, e.g:-

$$\mu_i = \left\{ \frac{\partial G}{\partial n_i} \right\}_{P, T, (\text{other ions}) = \text{const.}} \quad [9]$$

where  $\partial G$  = changes in Gibbs free energy for the 'i' ions;  $\partial n_i$  = number of ions of species 'i', at constant pressure and temperature; and all other ions are kept constant.

Thus the free energy of transfer of an ion is defined in terms of equation 9 in the following way:- If there are two solvent media, (x) and (y), then the free energy of transfer of an ion (i) from medium (x) to medium (y) is expressed as shown in equation 10.

$$\delta_m \mu_i^\ominus = \mu_i^\ominus (y) - \mu_i^\ominus (x) \quad \dots\dots [10]$$

Hence  $\delta_m \mu_i^\ominus$  is a measure of the change in the ion-solvent interaction



caused by a change in either solvent composition or solvent.

Applying these ideas to our reaction scheme, the solvent dependence of  $\Delta G^\ddagger$  and  $\delta_m \Delta G^\ddagger$ , (the Gibbs free energy for the reaction and its associated transfer value) can be expressed in terms of the separate dependences of the chemical potentials of cyanide ion, iron-(II) compound and transition state thus:-

$$\delta_m \Delta G^\ddagger = \delta_m \mu^\ddagger (\text{T.st.}) - \delta_m \mu^\oplus (\text{iron-(II) cation}) - \delta_m \mu^\ominus (\text{cyanide})$$

..... [11]

Using our previous arguments about the relative importance of solvation changes at each of the three species, we will ignore the first two terms on the right hand side of equation 11. This simplified result can now be used to predict rate variations with solvent, since if cyanide ion is destabilised on adding a co-solvent to water, i.e.  $\delta_m \mu^\ominus (\text{CN}^-) > 0$ , then  $\delta_m \Delta G^\ddagger$  will decrease, hence the rate constant will increase. The relationship between the reaction rate and  $\delta_m \mu^\ominus (\text{CN}^-)$  is depicted in equation 12:-

$$k_2/k_0 = \exp. \left\{ \delta_m \mu^\ominus (\text{CN}^-) / RT \right\} \quad \text{..... [12]}$$

- where  $k_2$  = second order rate constant in a mixed solvent, and  $k_0$  is the same rate constant in pure water, arbitrarily chosen as medium (x) defined previously.

Thus if we can somehow estimate values of  $\delta_m \mu^\ominus (\text{CN}^-)$  in the series of mixed aqueous solvents used in the kinetic analysis, we can compare measured and predicted kinetic variations using equation 12, and hence see if our previous arguments concerning solvation changes were correct. The methods by which single ion values are estimated from the experimentally determined parent  $\delta_m \mu^\ominus (\text{Salt})$  values are both varied and complicated. Several extra-

thermodynamic assumptions must be made in any such method and because of these there is some disagreement between the values of the same parameters produced by different workers, each making their own assumptions and arbitrary reference values. Unfortunately, the extent of available information on these transfer functions is minimal for aqueous mixtures at the present time, however their importance in kinetic analysis is too obvious. Thus due to this sparsity of data for cyanide we are forced to make the initial assumption that,  $\delta_{m\mu}^{\ominus}(\text{CN}^-) = \delta_{m\mu}^{\ominus}(\text{Cl}^-)$  to enable us to proceed with our analysis. This assumption is based upon several facts concerning these anions, the first being that their thermochemical radii are very similar, (e.g.  $r(\text{CN}^-) = 1.84 \text{ \AA}$  cf.  $r(\text{Cl}^-) = 1.81 \text{ \AA}$ ). Secondly, the single ion enthalpies of hydration of these ions are close, (e.g.  $\text{CN}^- = -347 \text{ kJ. mol}^{-1}$  cf.  $\text{Cl}^- = -352 \text{ kJ. mol}^{-1}$ ),<sup>(128)</sup> and finally the single ion split used for both these ions is the same.

Using this previously mentioned assumption enabled us to obtain estimates for  $\delta_{m\mu}^{\ominus}(\text{CN}^-)$  for several different sets of solvent mixtures from data available in the literature. However it should be stated here that due to several literature sources being used by us for this work, several anomalies occurred. For instance, two different sources have calculated  $\delta_{m\mu}^{\ominus}(\text{Cl}^-)$  for the transfer from water to methanol. Parker et al.<sup>(129)</sup> give the ion transfer function as  $12.6 \text{ kJ. mol}^{-1}$  (on the molar scale), basing this value on the seemingly good assumption:-

$$\delta_{m\mu}^{\ominus}(\text{Ph}_4\text{B}^-) = \delta_{m\mu}^{\ominus}(\text{Ph}_4\text{As}^+),$$

whereas Abraham<sup>(130)</sup> gives the same parameter a value of  $20.3 \text{ kJ. mol}^{-1}$ , basing this value on the different assumption:-

$$\delta_{m\mu}^{\ominus}(\text{Me}_4\text{N}^+) = 0.$$

Thus whenever one is conducting an analysis which relies on literature sources of the above functions it is extremely important to state both the single ion split used and the assumptions necessary to perform that calculation. However provided one can make reasonable assumptions about the validity of single ion splits, and either ignore or estimate transition state solvation effects this type of thermodynamic analysis can be very useful to examine the controlling factors of a particular reaction.

The following section deals with the thermodynamic theory used in the analyses along with the individual methods employed to calculate the single ion values for each set of solvent mixtures. Finally a comparison between estimated and measured kinetic data is made to examine the validity of both the single ion assumptions and of our argument concerning solvation characteristics of  $\text{CN}^-$ ,  $\text{Fe}(\text{bipy})_3^{2+}$  and the transition state.

#### Results and methods:

All co-solvent measures used by us have been expressed in percentage by volume before mixing. In the following work it was necessary to convert these values to the weight-percent scale, since all of the literature sources of transfer functions used this second scale. The values for one of these scales are displayed in Table 5. Further plots of literature values for weight percent against  $\delta_{\text{m}\mu}^{\oplus}(\text{Cl}^-)$  allowed us to obtain single ion values for our weight percents by interpolation of these plots. A second problem encountered was due to each literature source of  $\delta_{\text{m}\mu}^{\oplus}(\text{Cl}^-)$  using different units, thus for our purposes it was necessary to convert these to a single arbitrarily chosen scale, (units of  $\text{kJ} \cdot \text{mol}^{-1}$ ) i.e. the molarity scale. This conversion employed the following relationships:-

The chemical

potential of a 1:1 salt,  $\mu_2$  (e.g. KCN, KCl) can be expressed by three

distinct equations, e.g:-

$$\begin{aligned}\mu_2 &= \mu_2^\ominus + R.T. \ln m_2 \gamma_2 && \text{(molality scale, } m_2 = \text{molality of co-solvent)} \\ \mu_2 &= \mu_2^\ominus + R.T. \ln x_2 f_2 && \text{(mole fraction scale, } x_2 = \text{mole fraction of co-solvent)} \\ \mu_2 &= \mu_2^\ominus + R.T. \ln c_2 y_2 && \text{(molarity scale, } c_2 = \text{molarity of co-solvent)}\end{aligned}$$

In each of these expressions,  $\mu_2^\ominus$  represents the chemical potential of the salt at its standard state, (at the same temperature and pressure as  $\mu_2$  and is the hypothetical value of  $\mu_2$  when the second term is zero). The second term in these expressions (on the right hand side) can be further split up into two parts, e.g:-

$$\mu_2 = \mu_2 (\text{ideal}) + R.T. \ln \gamma_2, \text{ or } +RT. \ln f_2 \text{ or } +RT. \ln y_2,$$

this latter term expressing the non-ideality of the solute. Also each of these expressions can be separated into its ionic components, e.g:-

$$\text{For a 1:1 salt, } \mu_+ = \mu_+^\ominus + R.T. \ln a_+ \text{ and } \mu_- = \mu_-^\ominus + R.T. \ln a_-.$$

Hence  $a_2 = (a_+) \cdot (a_-)$ , where  $a_2$  = activity  
and

$a_2 \equiv m_2 \cdot \gamma_2, c_2 \cdot y_2, x_2 \cdot f_2$  on each scale; thus if we define a mean ionic activity coefficient as follows:-

Since  $a_2 = (m_2)^2 \cdot (\gamma_+) \cdot (\gamma_-)$ , Let  $(\gamma_\pm)^2 = (\gamma_+) \cdot (\gamma_-)$ , as  
for the other scales.

$$\begin{aligned}\therefore \mu_2 &= \mu_2^\ominus + RT. \ln (m_2)^2 \cdot (\gamma_\pm)^2 \\ &= \mu_2^\ominus + 2RT. \begin{aligned} &\ln m_2 \cdot \gamma_\pm \\ &\ln c_2 \cdot y_\pm \\ &\ln x_2 \cdot f_\pm \end{aligned} \quad \dots\dots [13]\end{aligned}$$

Thus by use of the three combined expressions shown in equation 13 we can easily transfer from one scale to another. This relationship applies equally well for the case where  $\mu_2$  is replaced by a transfer parameter for a single ion, as is shown in the following scale conversions.

(1) METHANOL-WATER mixtures:-

Plots of  $\delta_{m\mu}^{\ominus} (\text{Cl}^-)$  against solvent weight percent values obtained from the literature<sup>(131)</sup> were made and our values obtained by interpolation. The literature values for both cations and anions were estimated from previously published solubility and e.m.f. data. The separation into single ion values was based ultimately on calculations for the transfer of a tetrahedrally solvated proton from water into aqueous methanol. Thence  $\delta_{m\mu}^{\ominus} (\text{Cl}^-)$  values were obtained from known  $\delta_{m\mu}^{\ominus} (\text{HCl})$  values. We obtained  $\delta_{m\mu}^{\ominus} (\text{CN}^-) = \delta_{m\mu}^{\ominus} (\text{Cl}^-)$  by interpretation of Wells's values as described above and converted them from the solution standard state, the hypothetical solution where the mole fraction is unity to the standard state where the concentration of solute is  $1.0 \text{ mol. dm}^{-3}$  i.e:

$$\delta_{m\mu}^{\ominus} (\text{Cl}^-)_X \rightarrow \delta_{m\mu}^{\ominus} (\text{Cl}^-)_C$$

$$\begin{array}{ccc} \text{mole fraction} & \rightarrow & \text{molarity} \\ \text{scale} & & \text{scale} \end{array}$$

Using two of the expressions in equation 13, (i.e. those relating to mole fraction and molarity scales) and equating these we can arrive at equation 14:-

$$\mu_2^{\ominus} (c) = \mu_2^{\ominus} (x) + 2RT \ln \left\{ \frac{x_2 \cdot f_{\pm}}{c_2 \cdot \gamma_{\pm}} \right\} \quad \dots\dots [14].$$

By further lengthy treatment of this equation and skilful rearrange-

ment, it is possible to obtain equation 15:-

$$\delta_{m\mu}^{\oplus} (c) = \delta_{m\mu}^{\oplus} (x) - 11.40 \cdot \log. \left\{ \frac{18.016 \cdot p_m}{M_x \cdot p_o} \right\} \dots\dots [15]$$

Where  $p_m$  and  $p_o$  are the densities of the mixture and of pure water at the reaction temperature and  $M_x$  is defined as in equation 16, W being the weight percent of co-solvent.

$$M_x = 100 \cdot \left\{ \frac{W}{32.043} + \frac{100 - W}{18.016} \right\}^{-1} \dots\dots [16]$$

All the values on the right hand side of equation 15 are known (or can be obtained or calculated) thus conversion to  $\delta_{m\mu}^{\oplus} (CN^-)$  on the molarity scale can be accomplished.

## (2) ACETONE-WATER mixtures:-

Values of  $\delta_{m\mu}^{\oplus} (Cl^-)$  in various acetone-water mixtures were obtained from the tables published by Bax et al.,<sup>(132)</sup> and plotted against weight percent of acetone. Interpolation of this plot gave us our  $\delta_{m\mu}^{\oplus} (CN^-)$  values at the appropriate weight percent values. Although this plot was overall non-linear, over the range which we were interested in a linear relationship seemed to exist. No scale-conversion was necessary for these values, since these workers had used the same scale as used by us, i.e. the molarity scale.

## (3) ETHANOL-WATER mixtures:-

Insufficient data are available for similar calculations to be made for these solvent mixtures.

(4) TERT-BUTYL ALCOHOL-WATER mixtures:-

The quantities  $\delta_{m\mu}^{\ominus}$  for alkali metal chlorides were taken from the compilation given by Pointud et al.,<sup>(133)</sup> for the above mixtures when  $0 < W < 40$ , ( $W$  = weight percent of co-solvent). Values of  $\delta_{m\mu}^{\ominus} (Cl^-)$  were calculated from a least squares fit of the numbers for each solvent mixture to the expression:-

$$\delta_{m\mu}^{\ominus} (MCl) = (B/r^+) + \delta_{m\mu}^{\ominus} (Cl^-),$$

where  $B$  is a constant and  $r^+$  is the Pauling radius of the cation, hence making  $\delta_{m\mu}^{\ominus} (Cl^-)$  take the value of  $\delta_{m\mu}^{\ominus} (MCl)$  in the limiting case where  $r \rightarrow \infty$ . This method was used by Feakins<sup>(134)</sup> to analyse the data for methanol-water mixtures.

As in the previous calculations our values were interpolated from the plot of  $\delta_{m\mu}^{\ominus} (Cl^-)$  against weight percent of co-solvent. These results thus obtained were on the molality scale and were converted to the molarity scale using equation 13. A lengthy calculation eventually gives equation 17, from which  $\delta_{m\mu}^{\ominus} (CN^-)$  on the molarity scale can be calculated, e.g:-

$$\delta_{m\mu}^{\ominus} (c) = \delta_{m\mu}^{\ominus} (m) + R.T. \ln \left\{ \frac{1}{p_m} \right\} \quad \dots [17]$$

where  $\delta_{m\mu}^{\ominus} (c)$  and  $\delta_{m\mu}^{\ominus} (m)$  are the transfer functions on the molarity and molality scales respectively;  $p_m$  is the density.

(5) DIOXAN-WATER mixtures:-

Although enough data are available for these mixtures, the present situation with respect to single ion values for Gibbs free energies of transfer from water to aqueous dioxan is unclear.<sup>(135)</sup> The main source of data, calculated using Feakins's method has been criticised by Feakins himself at a later stage after its publication. Thus we have

not attempted to estimate values of  $\delta_{m\mu}^{\ominus}(\text{CN}^-)$  in this series of mixtures.

(6) ETHYLENE GLYCOL-WATER mixtures:-

Plots of  $\delta_{m\mu}^{\ominus}(\text{CN}^-)$  against co-solvent weight percent were obtained from the literature<sup>(136)</sup> and our values obtained by interpolation after conversion to the molarity scale. The free energies of transfer of salts MX and acids HX were calculated from published data on electrode potentials and the autoprotolysis constant and separated into the single ion values by starting with a value for the proton transfer function calculated from a consideration of the spherical entity  $(\text{H}_3\text{O}^+)(\text{H}_2\text{O})_4$ .

(7) GLYCEROL-WATER mixtures:-

Plots analogous to those made in the previous study were used to extrapolate an appropriate value for  $\delta_{m\mu}^{\ominus}(\text{CN}^-)$  in our solvent mixture. Single ion values were obtained by Wells<sup>(137)</sup> via the same methods described for methanol-water mixtures.

No data are available for either DMSO or HMPA-water mixtures.

Discussion:

Predictions of reactivity trends for the reaction between  $\text{Fe}(\text{bipy})_3^{2+}$  and  $\text{CN}^-$  have been made solely based upon solvation changes at the smaller cyanide anion. The solvation effects at the larger iron-(II) cationic species and the transition state have been totally ignored, the arguments for this gross assumption being stated elsewhere in this Chapter. The values of the ratio  $(k_2/k_0)$  defined previously in terms of  $\delta_{m\mu}^{\ominus}(\text{CN}^-)$  in equation 12 are compared with the experimentally determined ratios, and



these are listed together in Table 5. The agreement between these two sets of values is on the whole extremely good especially when one considers the numerous approximations involved both in deriving the transfer functions and in ignoring other contributory solvation effects apart from cyanide. The correlation for aqueous acetone mixtures is however not so good. This may possibly be due to the initial basic assumption that solvation effects at cyanide and chloride ions are the same. This does not necessarily detract from the other good agreements since it is not unreasonable that the solvation of these two ions could be similar in solvent mixtures containing hydroxylic co-solvents such as alcohols, but significantly different when the co-solvent is non-hydroxylic, such as acetone. We should also bear in mind that cyanides eventually react with organic ketones, hence some specialised solvation may be occurring at cyanide in aqueous acetone mixtures.

Parker et al.<sup>(129)</sup> have pointed out that  $\delta_{\text{ml}}^{\ominus}$  for anions going from water to pure solvents show a complex pattern, in part accounted for by the differences in intensity of hydrogen-bonding interactions between ions and solvent.

Thus it would seem that solvation changes at the small cyanide ion are almost wholly responsible for the reactivity variation with solvent composition for this reaction. This result is similar to that obtained for the reaction between  $\text{Pt}(\text{bipy})\text{Cl}_2$  and thiourea (see Chapter 5), where solvation changes of the reactant species dominated the reactivity trends in aqueous solvent mixtures. Both of these reactions are mainly associative in character so it is of interest to see that in neither case are the solvation changes of the transition state of any large importance. A comparison with the results obtained from the reaction of iron-(III) with thiocyanate in water and dimethyl sulphoxide however does not yield a similar correlation.<sup>(138)</sup>

TABLE 5

Ratios ( $k_2/k_0$ ) of rate constants for cyanide attack at the  $\text{Fe}(\text{bipy})_3^{2+}$  ion in binary aqueous mixtures ( $k_2$ ), to that in water ( $k_0$ ); as calculated from estimated values for transfer of cyanide ion (from water to mixed solvent) and as determined experimentally. Solvent compositions are by volume (and mole fraction) before mixing.

CO-SOLVENT	COMPOSITION		$\delta_{\text{m}\mu}^{\ominus} (\text{CN}^-)$ J. mol <sup>-1</sup>	$k_2/k_0$	
	V/V	M.F.		calc.	exptl.
METHANOL:	10%	0.048	850	1.4	1.6
	20%	0.102	2100	2.3	2.1
	30%	0.163	3550	4.0	3.2
ACETONE:	10%	0.033	1880	2.1	1.5
	20%	0.072	4390	5.6	2.1
	30%	0.117	7110	16.0	3.0
t-BUTYL ALCOHOL:	9.7%	0.02	1790	2.0	1.4
	18.0%	0.04	3310	3.8	3.6
	28.4%	0.07	5260	8.3	7.0
	36.9%	0.10	6710	15.0	9.5
	43.0%	0.125	7780	23.0	16.0
	48.2%	0.15	9020	38.0	16.0
ETHYLENE GLYCOL:	10%	0.044	535	1.2	1.8
	20%	0.094	1155	1.6	2.25
	30%	0.151	1845	2.1	2.7
GLYCEROL:	50%	0.198	695	1.3	2.2

TABLE 6

Various data values, including logarithmic functions of second order rate constants and associated solvent parameters, all of which have been used in graphical correlations throughout this Chapter.

SOLVENT:	V/V	$1/D^b$	$x_2$	$E_T^c$	$\gamma^d$	$\log(k_{AQ}(LIM))$	$\log(k_2)$
WATER:	100%	0.0128	0			-2.78	-2.11 <sup>a</sup> -1.55
METHANOL:	10%	0.014	0.048	62.2	3.28	-2.57	-1.36
	20%	0.0148	0.010	61.0	3.03	-2.64	-1.24
	30%	0.0158	0.163	60.0	2.75	-2.70	-1.05
ETHANOL:	10%	0.0142	0.033	61.7	3.31	-2.64	-1.40
	20%	0.0152	0.071	60.0	3.05	-2.72	-1.22
	30%	0.0166	0.117	58.0	2.72	-2.82	-1.10
1,4 DIOXAN:	10%	0.0152	0.023	61.1	3.22	-2.55	-1.24
	20%	0.0174	0.050	58.6	2.88	-2.62	-1.05
	30%	0.0207	0.083	57.2	2.46	-2.68	-0.90
ACETONE:	10%	0.0142	0.033	61.4	3.23		-1.38
	20%	0.0152	0.071	59.8	2.91		-1.23
	30%	0.0165	0.117	58.1	2.48		-1.07
t-BUTYL ALCOHOL: <sup>a</sup>	9.74%		0.02				-1.96
	18.0%		0.04				-1.55
	28.4%		0.07				-1.27
	36.9%		0.10				-1.14
	43.0%		0.125				-0.93
	48.2%		0.15				-0.89
D.M.S.O:	10%		0.028				-1.42
	20%		0.060				-1.40
	30%		0.098				-1.27
HMPA:	10%		0.011				-1.49
	20%		0.025				-1.29
	30%		0.042				-1.18
ETHYLENE GLYCOL: <sup>a</sup>	10%	0.0139	0.044				-1.854
	20%	0.0145	0.094				-1.77
	30%	0.0151	0.151				-1.68
GLYCEROL:	50%		0.198				-1.21

[<sup>a</sup> These values correspond to T = 298.2 K]  
 [<sup>b</sup> Obtained from references 145-6]  
 [<sup>c</sup> Obtained from reference 104]  
 [<sup>d</sup> Obtained from reference 147]

In this reaction the large value calculated for  $\delta_{\text{ml}}^{\ominus} (\text{NCS}^-)$  is not matched by a large difference in rate constant in the two solvents. If the reaction is treated as being mainly dissociative then the solvation changes at the thiocyanate anion would be unimportant, and thus the rate variation relatively independent of  $\delta_{\text{ml}}^{\ominus} (\text{NCS}^-)$ . However, under some reaction conditions the formation rate constant is found to be greater than the rate of solvent exchange. This observation requires at least some associative character to transition state formation,<sup>(139)</sup> although the degree of this may be much less than that for the  $\text{Fe}(\text{bipy})_3^{2+} + \text{CN}^-$  reaction.

A comparison between the nucleophilic attack of cyanide and hydroxide on  $\text{Fe}(\text{bipy})_3^{2+}$  has been described previously (see Figure 8). In the light of this thermodynamic analysis we can see that correlation between the reactivity trends for cyanide attack at the iron-(II) cation and those for hydroxide attack must be due to the solvation changes at the smaller hydroxide anion being larger than those at cyanide.

Thus,

$$\delta_{\text{ml}}^{\ominus} (\text{OH}^-) > \delta_{\text{ml}}^{\ominus} (\text{CN}^-)$$

must also be true, assuming that solvation changes at both  $\text{Fe}(\text{bipy})_3^{2+}$  and the transition state (which will be different for each reaction, if they are both bimolecular; also the actual position of attack may be different for each of these nucleophiles, thus this may affect the solvation characteristics of the transition state) are equally small for both of these reactions.

#### Salt effects.

- on the reaction between  $\text{Fe}(\text{bipy})_3^{2+} + \text{CN}^-$ .

### Introduction:-

It is a well known fact that solvents play a very important part in reactions, both in terms of their effects on reaction rate and upon the reaction mechanism. Although extensive work has been done in this area of reaction kinetics, relatively little interest has been shown in the analogous effects of so-called 'inert salts' (i.e. salts such as KCl, NaBr,  $(\text{Me})_4\text{NCl}$ , etc., which take no direct part in a reaction but influence that reaction indirectly via their effects on the solvent-structure) upon reaction kinetics. In the majority of cases these two effects are synonymous, both operating via these solvent structure changes.

Some of the first work done involving the use of such salts to 'disturb' a solvent was on the reaction involving hydrolysis of tert-butyl chloride,<sup>(140)</sup> incorporating a limited range of salts. In more recent years some interesting salt effects have been observed both for a purely dissociative reaction and also for a reaction which is only partially dissociative. This latter reaction is the general base catalysed solvolysis of two (aryl-sulphonyl)-methyl perchlorates,  $(\text{RSO}_2\text{CH}_2\text{OCIO}_3)$ .<sup>(141)</sup> This particular study

set out to probe the effects of variation in water structure upon this type of proton transfer reaction. The conclusion reached by these workers was that the observed salt effects were caused by either a destabilisation of the substrate, a stabilisation of the transition state or both simultaneously. Their results made it impossible to distinguish between these three possibilities. The former investigation mentioned was carried out on the aquation of the  $\text{Fe}(\text{5NO}_2\text{-phen})_3^{2+}$  cation in water.<sup>(142)</sup> The actual mechanism for this reaction had not been established unequivocally, but there is now sufficient evidence<sup>†</sup> to suggest a primarily dissociative process

[<sup>†</sup> Although cyanide attack at  $\text{Fe}(\text{LL})_3^{2+}$  cations is mainly associative, the relative nucleophilicity of water for iron-(II) as compared with  $\text{CN}^-$  or  $\text{OH}^-$  anions is very small, hence associative attack of water at this cation would seem an unlikely process.]

with possibly a small degree of associative character.

Both of the previous investigations produced evidence for similar salt effects occurring in the solvent mixtures studied, both in terms of magnitude and direction of effect on the reaction rate. Indeed, comparison of plots of  $\log(k)$  against the added salt concentration for the aquation of the  $\text{Fe}(\text{5NO}_2\text{-phen})_3^{2+}$  ion and those for the aquation of  $\text{Me}_3\text{NSO}_3$  <sup>(143)</sup> produced exactly the same pattern. These effects should be contrasted with those found for the aquation (an associative process) of the  $\text{S}_2\text{O}_7^{2-}$  anion <sup>(144)</sup> where exactly opposite effects are evident,

The following investigation was prompted by the previously described work on the analogous  $\text{Fe}(\text{5NO}_2\text{-phen})_3^{2+}$  reaction. Although these two reactions differ in terms of their molecularity, they are similar structurally as far as the cationic species are concerned.

#### Experimental:-

A solution containing the  $\text{Fe}(\text{bipy})_3^{2+}$  cation was made up as described previously. The salts used in our investigation are listed here:-  $\text{KCl}$ ,  $\text{KBr}$ ,  $\text{LiCl}$ ,  $(\text{CH}_3)_4\text{NCl}$ ,  $(\text{n-Bu})_4\text{NBr}$ . In each case these reagents were used without further purification. By varying the salt concentration with the potassium cyanide concentration, the ionic strength in a set of runs was maintained at a constant value. All runs were conducted as described previously at 308.2 K in 100% water.

#### Results:-

Using the previously listed range of added salts, (similar to those used by other workers) several sets of kinetic data were accumulated. Sets of  $k_{\text{OBS}}$  obtained at various cyanide and added salt concentrations at a total

ionic strength of  $1.0 \text{ mol. dm}^{-3}$  are to be found in Table 7. The salts used in this set of reactions were KBr, KCl and  $(\text{CH}_3)_4\text{NCl}$ . The consequence of the presence of these salts upon the reaction is displayed graphically in Figure 9. From examination of past work done on a similar reaction<sup>(142)</sup> it would seem that the size of the cation of the added salts plays an important part in the salt effect. Thus two extremes of cation-size were selected. The first, tetra n-butyl ammonium bromide,  $(\text{n-Bu})_4\text{NBr}$  was compared with potassium bromide, however due to the large molecular weight of this molecule, physical restrictions dictated that the maximum practical concentration possible was  $0.5567 \text{ mol. dm}^{-3}$ .<sup>†</sup> The effects of this salt on our reaction are shown graphically in Figure 9, and the individual  $k_{\text{OBS}}$  values are listed with the relevant ion concentrations in Table 8, in which the total ionic strength was  $0.33 \text{ mol. dm}^{-3}$ . At the small-cation extreme, a comparison between lithium chloride and potassium chloride at a total ionic strength of  $1.0 \text{ mol. dm}^{-3}$  gave the following result:-

$$\left. \begin{array}{l} k_{\text{OBS}} (\text{KCl}) = 0.119 \times 10^{-2} \text{ s}^{-1} \\ k_{\text{OBS}} (\text{LiCl}) = 0.117 \times 10^{-2} \text{ s}^{-1} \end{array} \right\} T = 298.2 \text{ K}$$

Similar comparisons using large and small anions were not attempted because of solubility problems; i.e. large anions such as tetra-phenylboronate cause precipitation of large cations such as  $\text{Fe}(\text{bipy})_3^{2+}$ .

#### Discussion:-

As can be seen from the plots in Figure 9, no observable salt-effects were apparent in any of the kinetic runs, implying that this reaction seems

[<sup>†</sup> A single run was carried out at this concentration; the rate constant from this was not significantly different from the same run using the same concentration of KBr. Due to solubility problems above  $0.4 \text{ mol. dm}^{-3}$ , a full set of results was not obtained above this concentration.]

TABLE 7

First order rate constants ( $k_{\text{OBS}}$ ) for the reaction between  $\text{Fe}(\text{bipy})_3^{2+}$  and cyanide anion in aqueous media containing added inert-salts; at 308.2 K at a total ionic strength of  $1.0 \text{ mol. dm}^{-3}$  maintained with various salts listed below.

	$10^3 k_{\text{OBS}}/\text{s}^{-1}$			
$[\text{KCN}]/\text{mol. dm}^{-3}$	0.25	0.50	0.75	1.00
$[\text{SALT}]/\text{mol. dm}^{-3}$	0.75	0.50	0.25	-
SALT:				
KCl	3.70	6.60	11.00	13.80
KBr	3.40	7.10	10.40	13.80
$\text{Me}_4\text{NCl}$	3.70	7.10	10.70	13.80



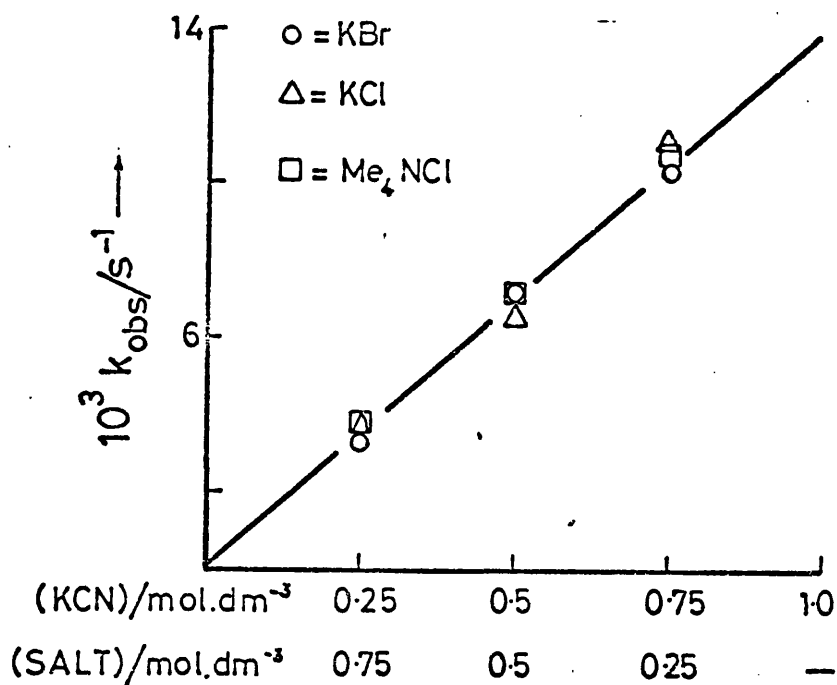
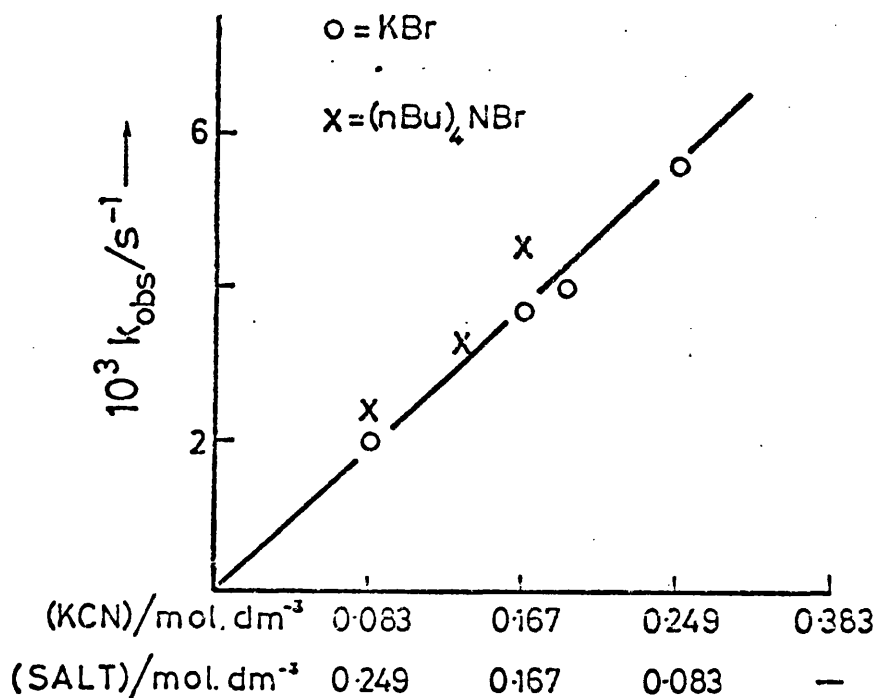
TABLE 8

First order rate constants ( $k_{\text{OBS}}$ ) for the reaction between  $\text{Fe}(\text{bipy})_3^{2+}$  and cyanide anion in aqueous media containing added inert salts; at 308.2 K and a total ionic strength of  $0.333 \text{ mol. dm}^{-3}$  maintained with the salts listed below.

SALT:		KBr	$(\text{nBu})_4\text{NBr}$
[SALT] $\text{mol. dm}^{-3}$	[KCN] $\text{mol. dm}^{-3}$	$10^3 k_{\text{OBS}}/\text{s}^{-1}$	
	0.333		7.20
0.083	0.250	5.60	-
0.133	0.200	4.00	-
0.167	0.167	3.70	4.50
0.200	0.133	-	3.30
0.250	0.083	2.00	2.40

**FIGURE 9**

Plots of the variation in the observed first order rate constant ( $k_{\text{OBS}}$ ) for the attack of cyanide anion at the  $\text{Fe}(\text{bipy})_3^{2+}$  cation against the concentration of potassium cyanide, where the identity of the added 'inert' salt is varied. All of these runs were carried out in 100% water at the total ionic strengths noted below, at 298.2 K.



to be relatively insensitive to solvent structure changes. The observation that large reactivity variations did occur for the aquation of the structurally similar  $\text{Fe}(\text{5NO}_2\text{-phen})_3^{2+}$  cation as compared with the absence of such effects here is perhaps strange. However if one follows logically from the arguments used in this previous study<sup>(142)</sup> one is forced into one of the following conclusions. Firstly, the  $\text{Fe}(\text{bipy})_3^{2+}$  cation must be much less hydrophobic than the  $\text{Fe}(\text{5NO}_2\text{-phen})_3^{2+}$  ion and that the solvation changes at the  $\text{Fe}(\text{bipy})_3^{2+}$  are comparable to those of the transition state. The other alternative is that the solvation changes at the cyanide anion are of much greater importance as has been outlined previously. The likelihood of the former of these two conclusions being correct is slight, although the bipy compound may be less hydrophobic than the substituted phen, (see Chapter 6 for a discussion of this with respect to the bipy and phen compounds,  $\text{Fe}(\text{LL})_2(\text{CN})_2$ ) the solvation effects on the  $\text{Fe}(\text{bipy})_3^{2+}$  and the associative transition state are unlikely to be comparable. This view is based on the observation that although these two species will probably be similar in size, one is a 2+ ion and the other a 1+ ion. Thus the second conclusion is most likely correct. The  $\text{5NO}_2\text{-phen}$  compound would be expected to interact more strongly with surrounding solvent molecules due to the hydrophilic nitro-group sticking out into the first solvation sphere. Also, in the case of the  $\text{Fe}(\text{bipy})_3^{2+} + \text{CN}^-$  reaction, we have already stressed the importance of solvation changes at the cyanide. Thus it may be that  $\mu^\ominus(\text{CN}^-)$  is only slightly affected by added salts, i.e.:-

$$\mu^\ominus(\text{CN}^-)_{\text{H}_2\text{O}} - \mu^\ominus(\text{CN}^-)_{\text{SALT}/\text{H}_2\text{O}} = \text{SMALL}$$

This observation may be explained by comparing the strong cyanide-water interaction with the weaker  $\text{R}_4\text{N}^+$ -water interaction, thus the re-structuring effects of the added salts may not be able to compete with the stronger

cyanide-water interactions. This would therefore allow both the  $\text{Fe}(\text{bipy})_3^{2+}$  and the transition state to 'feel' the solvation changes due to the added salts, as occurs for the  $\text{Fe}(\text{5NO}_2\text{-phen})_3^{2+}$ . But because of the weak solvent interaction of these large ions by comparison with  $\text{CN}^-$ , no observable rate variation would be expected.

Throughout this investigation the 'swamping' of other solvent-molecule effects by the large cyanide-solvent interaction has been evident. It is perhaps surprising that in a bimolecular reaction, all of the reactivity trends so far discussed can be interpreted solely in terms of the solvation changes at only one of the reactant species. However a similar but less forceful result is described in Chapter 5, where in some mixed aqueous solvents, the reaction between  $\text{Pt}(\text{bipy})\text{Cl}_2$  and thiourea is almost solely dependent on solvation changes at the platinum compound; similar changes at thiourea and the transition state being small by comparison. A fuller discussion of this is attempted in that Chapter.

## CHAPTER 2

Title: An investigation of solvent effects on visible and ultra-violet  
absorption spectra of transition metal compounds.

## Introduction

Most absorption spectra of inorganic compounds are fairly insensitive to solvent effects,<sup>(201)</sup> although in recent years several investigations have found the opposite to be true. To date, many transition-metals have been found to form compounds which display an absorption dependence on solvent, (often referred to as Solvatochromism).

This type of behaviour was first noted in the field of organic chemistry, initially by Schlenk,<sup>(202)</sup> and at a later date by Brooker,<sup>(203)</sup> and independently by Kiprianov.<sup>(204)</sup> Brooker suggested at that time, that these effects should be used as a measure of solvent polarity. Since then, several solvent-scales have been invented, usually based upon dyes used by the above mentioned workers. One of the best known (and best accepted) of these is the  $E_T/Z$  scale. This measure was first put forward by Kosower et al.,<sup>(205)</sup> using the negative solvatochromic (i.e. shifts to longer wavelengths in less polar solvents) effects of 1-alkyl pyridinium iodides (see Fig. A).

Thus ' $E_T$ ' is defined as the molar transition energy, calculated from the position of the absorption maximum, e.g:

$$E_T \text{ (k.cal.mol}^{-1}\text{)} = 2.859 \times 10^{-3} \cdot \bar{\nu}$$

where  $\bar{\nu}$  is the wavelength of the absorption measured in reciprocal centimetres.

A later more detailed analysis by Reichardt and co-workers,<sup>(206)</sup> using the same approach as Kosower, extended this work to cover around thirty

different organic dyes before choosing one particular dye on which to base their solvent-scale. The compound chosen, (because of its extremely large solvent sensitivity) was the pyridinium N-phenolbetaine shown in Fig. B, in its two resonance forms, where R = phenyl. This type of compound consists of an electron donating group and an electron accepting group joined together by a conjugated system. The explanation for the magnitude of the solvent shifts displayed by this type of compound is related to their zwitterionic nature. These molecules possess two extreme resonance forms, one a polar form, and the other a delocalised or quinoidal form (see Fig. B). Thus as the polarity of the solvent is increased, there will be a similar shift in the electron distribution of the ground state towards the polar resonance form, while, by the Frank-Condon principle, the structure of the excited state will be only slightly affected. Hence the change in the wavelength of maximum absorption will be directly related to the change in energy of the ground state produced by the variation in solvent polarity.

Although many other solvent parameters have been 'invented', (e.g.  $\Sigma$ -values<sup>(205)</sup>) the 'E<sub>T</sub>-values' are the only ones which relate directly to solvent effects on intramolecular charge-transfer bands.<sup>†</sup> Thus this particular 'solvation measure' has been extremely useful in correlations involving transition-metal compounds, (where intramolecular charge-transfer is quite a common occurrence) which display solvent dependent absorption shifts. Also, other simpler parameters, such as dielectric constant or dipole moment have proved to be unsatisfactory when used in correlations of this type, (hence the need for these empirical solvent parameters).

Various explanations of the solvent dependence of absorption maxima

[<sup>†</sup> The previously mentioned ' $\Sigma$ -values' are also concerned with charge transfer bands, but between different molecules (i.e. intermolecular) and this scale is less detailed, having fewer solvent assignments due to solubility problems.]

FIG. A: 1 ethyl-4-methoxycarbonyl-pyridinium iodide

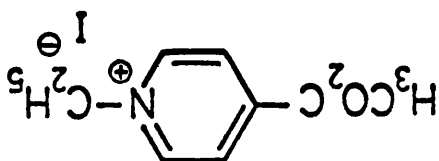


FIG. B:

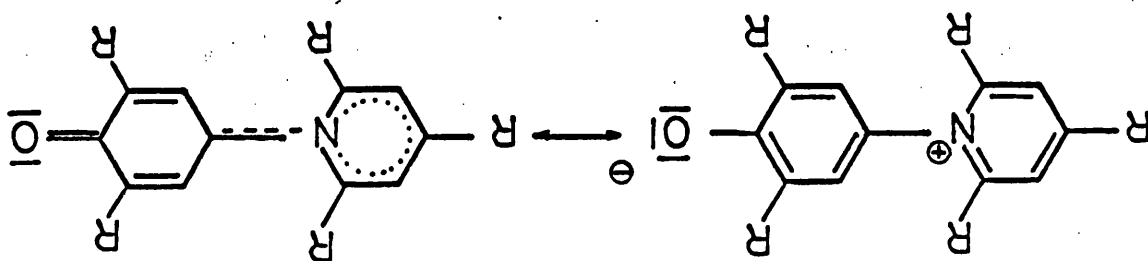
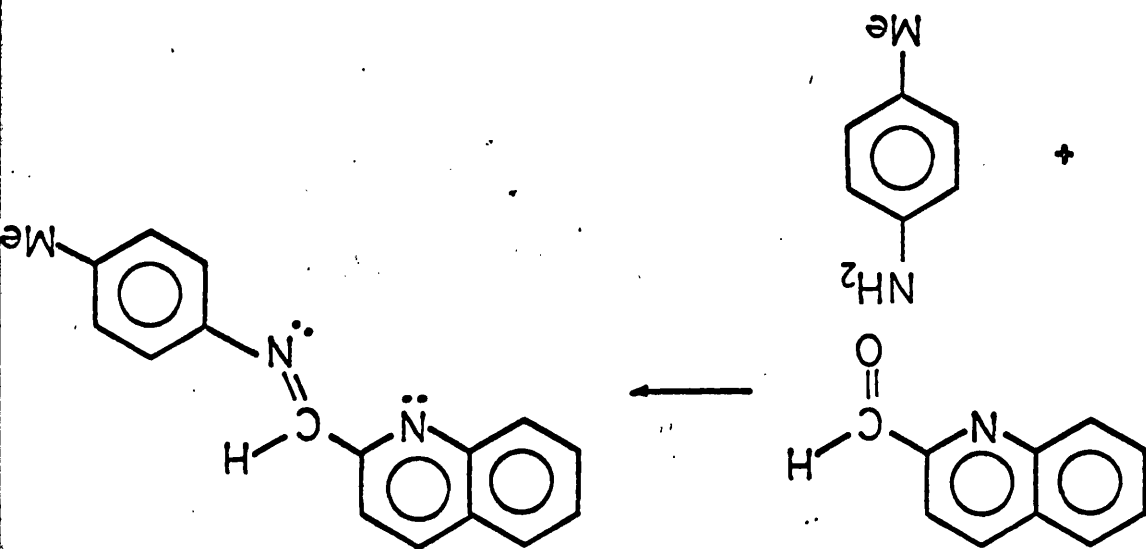


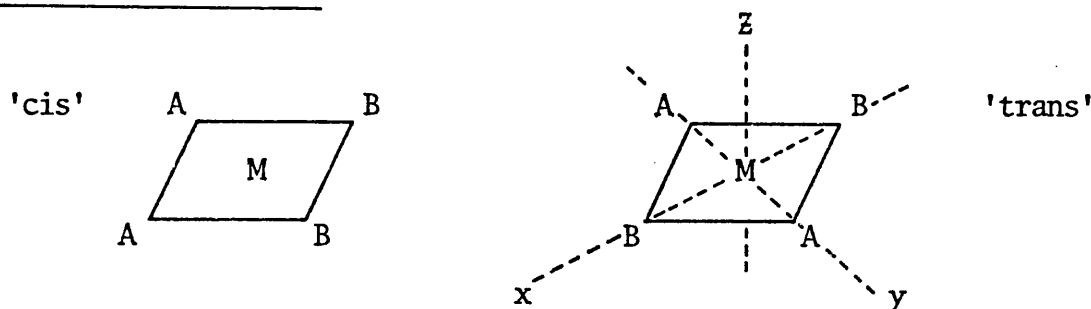
FIG. C:





for transition-metal compounds have been put forward, and a more detailed examination of these is to be found in a later section. However, in the light of some of the more recent studies in this field, it seems that one of the criteria necessary (for a compound to display solvatochromism) is that some (or all) of the ligands present can couple electronically both to the metal and to each other, (i.e. usually via the  $\Pi$ -electron system).<sup>(207,208,209)</sup> Using this as a premise, we can, using a very simplified bonding approach, examine some (common) structure types to see if we would expect them to display a solvent dependence in their absorption spectra. In the following survey we will consider the cis- and trans-isomers of square planar and octahedral compounds, (i.e.  $MA_2B_2$  and  $MA_4B_2$ ), and make the assumption that both the ligands, A and B are capable of a  $\Pi$ -bonding type interaction. All of the bonding considerations used will refer only to d-orbital interactions, since only these will be available (by geometric restrictions) for  $\Pi$ -interactions. Thus when a d- $\sigma$  bond is described, s and p contributions will also be assumed to be present, but for the sake of simplicity are not mentioned.<sup>†</sup>

#### Square planar compounds



The table shown below contains the possible M-A and M-B bonding inter-

[<sup>†</sup> N.B. It should be remembered however that  $\sigma$ -bonding is overwhelmingly important in terms of an actual compound's stability, but that in the above argument we are interested in the weaker  $\Pi$ -interactions.]

actions (both  $\sigma$  and  $\Pi$ ) along with the influence, via these orbitals of the ligands upon each other, (labelled A-M-B).

cis:-

Orbital type:-	M—A	M—B	A—M—B
Bond type (d-orbitals only)			
$\sigma$	xy	xy	Strong
$\Pi$	xz, yz	xz, yz	Strong

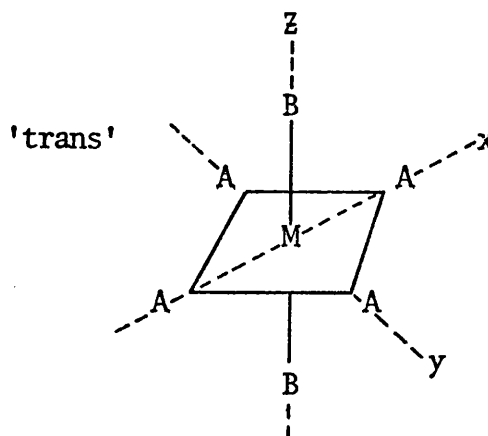
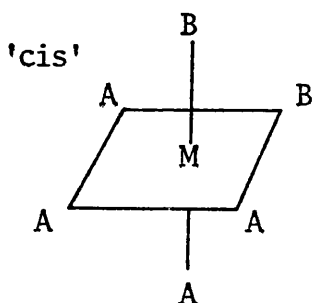
(i.e. the above combinations are those that exist for the five possible d-orbitals:- xy, xz, yz,  $x^2-y^2$  and  $z^2$ )

trans:-

$\sigma$	xy	xy	Strong
$\Pi$	xz	yz	Weak

From these results, we can see that a strong  $\sigma$  (trans) interaction between ligands is possible for both of the isomers, but only the cis-isomer has the possibility of a strong  $\Pi$ -interaction between the ligands.

Octahedral compounds



A table similar to that used for the square planar geometry is shown here for the octahedral compounds.

cis:-

Orbital type:-	M—B	M—A	A—M—B
Bond type (d-orbitals only)			
$\sigma$	$z^2, x^2-y^2$	$z^2, x^2-y^2$	Strong
$\Pi$	$xy, yz$	$xy, yz, xz$	Strong

trans:-

$\sigma$	$z^2$	$x^2-y^2$	Weak
$\Pi$	$xz, yz$	$xz, yz, xy$	Strong

The table shows that, for the cis-isomer, strong inter-ligand interactions are possible for both  $\sigma$  and  $\Pi$ , but that in the trans-isomer, only one of these is possible. Thus in both of these structural types, the cis-isomers alone seem to possess the desired electronic structures to satisfy the criteria mentioned earlier. Of the work done so far on transition metal compounds, very few trans-compounds<sup>(211,212)</sup> have been found to display solvatochromic behaviour and of those that have, these effects are very much less than those for similar cis-compounds. The compounds examined by us are, therefore, all cis-isomers. Another reason for this is that it can be very difficult to prepare trans-compounds because of unfavourable ligand-ligand steric interactions present in these compounds. Such compounds can usually be made only by a process which is best described as stereochemical engineering (i.e. by designing ligands which, when built into molecular models, would seem to give only minimal unfavourable interactions).

## Preparations

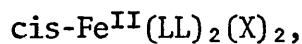
The preparations listed herein are ordered 'group-wise' across the Periodic table.

### cis-M(CO)<sub>4</sub>(LL) complexes,

where M = chromium, molybdenum or tungsten, and 'LL' is one of the following bidentate ligands:- 2,2'-bipyridyl; 1,10-phenanthroline; 4,7 dimethyl-1,10-phenanthroline; 5 chloro-1,10-phenanthroline; 5 nitro-1,10-phenanthroline. All of these compounds were made as described in the literature by Stiddard,<sup>(213)</sup> and characterised by their carbonyl infra-red and U.V./visible absorption spectra. The compound containing 5 nitro-1,10-phenanthroline did not materialise when treated by the above method and was discarded.

A similar compound where M = tungsten, and LL = Schiff-base was also made but, due to difficulties encountered during the preparation, only a very small yield was obtained, which contained some quantities of starting material. A later repeat experiment gave the same result. The method used is described here. 0.4g of tungsten hexacarbonyl was dissolved in a minimum volume of dimethyl sulphoxide ( 20ml) and to this was added with stirring, 0.2g of phenyl-2-pyridyl ketone and 0.12g of p-toluidine. The resulting mixture was warmed and stirred for several days. Unfortunately, due to the low stability (as compared with, say, 2,2'-bipyridyl) of the Schiff-base, it was not possible to reflux this mixture. Some dark green crystals were isolated in low yield. It was not possible to establish their identity, (by infra-red for example) due to relatively large amounts of impurity being present also.<sup>†</sup>

[ <sup>†</sup> A recent attempt to make a similar compound using a tetra-dentate Schiff-base, which is stable to refluxing, succeeded, and a good yield was obtained.]



where iron-(II) is in a low spin environment.

(a) This first set of preparations is concerned with, X = cyanide, and LL = Schiff-base. The Schiff-bases employed in the following preparations were all made in-situ by reacting either phenyl-2-pyridyl ketone or pyridyl-2-aldehyde with an aniline. The anilines used were as listed here:- 3,4 dimethyl-: 3,5 dimethyl-: 4 methyl-: 4 nitro-: and 4 bromo-aniline, along with unsubstituted aniline. In all of these preparations (about twelve altogether) the ratio of iron : organic ligand was 1:3 to 3.5.

Several methods were used in these preparations, however the only (and possibly the crucial) difference between them being either the timing or rate of addition of potassium cyanide. The initial method used was as follows. To an aqueous solution of iron-(II) ammonium sulphate was added the correct quantity (defined previously) of an aniline with continuous stirring. The (chosen) other component of the Schiff-base was then added with further stirring, producing an immediate colour change, signifying the formation of a tris-Schiff-base complex of iron-(II). After standing for ~30 mins. (to ensure complete reaction) this solution was filtered, thus removing any remaining organic material, (as a solid or an oil usually). A five-fold excess of potassium cyanide was then added with stirring and an immediate tarry precipitate was formed. Attempts to purify this failed, possibly due to the obviously large amounts of organic impurities present.

A total of four methods were employed in these preparations, and in each of these the product came down contaminated with either a plastic-like organic polymer, (found to be resistant to chromic acid, all the apparatus coated with this material was thrown away) or unreacted starting materials. The methods used were similar to those used in the literature preparations

for analogous compounds. <sup>(214,215)</sup>

(b) The following preparations are concerned with: X = cyanide, and LL = 2,2'-bipyridyl, 1,10-phenanthroline, 5 chloro-1,10-phenanthroline, 4,7-dimethyl-1,10-phenanthroline and, finally, di-2-pyridyl ketone.

These complexes were made by a modified version of that used by Schilt <sup>(214)</sup> and all of them possess a 'cis' geometry. <sup>(216)</sup> The method used by us was much simpler than the above mentioned version, and gave a good yield with minimum contamination by cyanide and unreacted organic ligand. The method used is described as follows. To a warm aqueous solution of iron-(II) ammonium sulphate was added the solid bidentate ligand, (ratio 3 to 3.5:1, LL:Fe). This mixture was then shaken for ~20 minutes, or until all the solid has dissolved, at a temperature of 313 K. A five-fold excess of potassium cyanide in a minimum volume of water was then made up, and added slowly over a period of ~30 minutes with continuous stirring at 313 K. The resulting solution is allowed to cool to room temperature, from which the solid product can be removed (in good yield) by suction filtration almost immediately. The product can then be washed copiously with water, (to remove any excess of potassium cyanide) ethanol, (to remove any unreacted organic ligand) and finally with diethyl ether and dried (initially) by suction and then over P<sub>2</sub>O<sub>5</sub> under vacuo. The product species were identified by their visible absorption spectra. <sup>(214)</sup>

The compound containing the ligand di-2-pyridyl ketone could not be isolated by the above procedure, although visual evidence seemed to suggest that this was in fact formed. After addition of the organic ligand to the iron-(II) ammonium sulphate solution, it should be noted that a brown solution was formed. This would seem to indicate that the tris-species has been produced, although previous evidence obtained from molecular models casts doubt on this idea due to unfavourable ligand-ligand interactions,

(N.B. this colour change may be due to the formation of a hemi-acetal containing complex). Addition of excess of potassium cyanide produced a colour change to purple, but only after refluxing for a short period of time. The visible absorption spectra showed a large peak, at 599 nm in water, which shifted to 650 nm in 90% methanol-water mixtures.

(c) Preparation of compounds of the form:  $\text{Fe}^{\text{II}}(\text{LL})_2(\text{NCS})_2$ ;

where LL =

di-2-pyridyl ketone.

This compound has been previously made by McWhinnie and co-worker<sup>(217)</sup> who concluded, from Mossbauer and magnetic moment measurements, that it possesses a trans-geometry. However, the same workers suggest that this ligand is very similar, electronically speaking, to 1,10-phenanthroline, which would seem to contradict the previous statement, (if one considers analogous 1,10-phenanthroline compounds). If this compound does have a 'trans' geometry, one would expect that the reasons for this would be related to steric hindrance. However, molecular model evidence suggests that the 'cis' geometry should be the more favourable of the two.

The preparation used by us was similar to that used for the previous cyanide-analogue. A solid product was isolated in this case, but was found to be insoluble in all of the available common organic solvents. A diffuse reflectance spectrum was obtained for this compound, the result of which can be found in Table 8.

- where LL =

2,2'-bipyridyl.

This compound was prepared by a similar method to that used by Madeja<sup>(218)</sup> who prepared the analogous 1,10-phenanthroline compound.<sup>†</sup> Unfortunately,

[ <sup>†</sup> Evidence for the 'phen' analogue having a temperature dependent ground state has also been put forward by Madeja,<sup>(219)</sup> hence this may also be so for our compound.]

the product isolated appeared to be  $[\text{Fe}^{\text{II}}(\text{bipy})_3^{2+}(\text{NCS})_2^{2-}]$ , thus the second stage of the reaction, (i.e. conversion of this species to the product) did not seem to have occurred. A second attempt to make the desired product which involved refluxing the ionic complex under nitrogen also failed, and so this preparation was abandoned.

Preparations of compounds of the form:  $\text{Fe}^{\text{II}}(\text{bipy})_2(\text{CN})_2\text{Hg}(\text{X})_2$ .

where X = cyanide and thiocyanate.

These compounds were prepared by simple addition of the two components, (i.e.  $\text{Fe}^{\text{II}}(\text{bipy})_2(\text{CN})_2 + \text{Hg}(\text{X})_2$ ) in the correct stoichiometric ratio in dichloro-methane. The yields of product were approximately quantitative, precipitation occurring immediately on addition of the iron(II) compound to a warm solution of the mercury compound. Both of the products were found to be extremely insoluble, impurities were removed by washing with hot (60°C) dichloro-methane/ethanol, (although due to the low solubility of the initial mercury compounds used, their complete removal via this procedure is unlikely). After drying under vacuo the products were sent away for analysis, the results of which are shown here:-

COMPOUND ELEMENTS PRESENT:	Fe	Hg	C	N	H	S
<u>Fe(bipy)<sub>2</sub>(CN)<sub>2</sub>Hg(CN)<sub>2</sub></u>						
*Analysed % by weight =	8.5	26.25	44.18	16.41	2.73	-
Theoretical % by weight =	8.32	29.86	42.79	16.64	2.38	-
(* Total = 98.07%)						
<u>Fe(bipy)<sub>2</sub>(CN)<sub>2</sub>Hg(NCS)<sub>2</sub></u>						
*Analysed % by weight =	6.97	27.39	37.49	14.45	1.99	8.84
Theoretical % by weight =	7.59	27.27	39.1	15.2	2.17	8.68
(* Total = 97.03%)						



As can be seen from these results, the two compounds are of reasonably high purity, (i.e. the discrepancies in the above results are random, and are not related in any way to any of the groups present in these molecules).

The compound containing only cyanide groups (i.e. instead of cyanide and thiocyanate), has been reported previously by Beck et al.,<sup>(220)</sup> who expressed doubt in the existence of a 1:2 adduct (i.e.  $\text{Fe}(\text{bipy})_2(\text{CN})_2[\text{Hg}(\text{CN})_2]_2$ ). However, by mixing the components of this compound in the appropriate stoichiometries, a product was isolated, and purified as for the previous compounds. The infra-red spectra of both the 1:1 and 1:2 adducts can be found in Table 10. Combining these results with a comparative X-ray powder study proved that the 1:2 adducts were in fact impure samples of the 1:1 adduct.

As was stated earlier, these compounds are insoluble in many of the common organic solvents and so the only data available on these was obtained by diffuse reflectance, (see Table 8).

#### Preparations of compounds of the form: $\text{K}_2[\text{Fe}(\text{bipy})(\text{CN})_2(\text{X})_2]$

This type of compound where X = cyanide has been reported previously by Schilt.<sup>(214)</sup> However, the analogous compounds where X = cyanate or thiocyanate were not attempted by that worker. The preparation of these compounds was attempted by us using a procedure analogous to that used by the previous worker for the tetra-cyano-species. Unfortunately, after heating for several days an impure green product was isolated for each of the previous ligands. These compounds seemed to be a mixture of unreacted 'KX' and probably some iron(III) species. These preparations were not carried any further.

#### Preparation of $\text{cis-Ru}^{\text{II}}(\text{bipy})_2(\text{CN})_2$

This compound has been prepared via several different methods;<sup>(221,222)</sup>

TABLE 10

Infra-red data for both the reactant species  $\text{Fe}(\text{bipy})_2(\text{CN})_2$  - [I],  $\text{Hg}(\text{SCN})_2$  - [II] and the proposed 1:1 product - [III] and the 1:2 adduct - [IV]. All values listed in this table are in wavenumbers, ( $\text{cm}^{-1}$ ).

I	II	III	IV
650 (s)		660 (m)	665 (m)
730 (s)	710 (m)	730 (s)	730 (w)
750 (m)		750 (w)	750 (w)
770 (s)		765 (s)	765 (s)
800 (m)		805 (w)	805 (w)
890 (m)	860 (m)	890 (w)	900 (b)
905 (w)	910 (m)		
950 (w)		970 (w)	970 (w)
970 (m)			
1000 (m)			
1040 (m)		1040 (m)	1045 (w)
1060 (m)		1060 (m)	1065 (m)
1070 (m)			
1100 (w)		1100 (w)	1100 (w)
1150 (s)	1150 (w)	1150 (m)	1150 (m)
1170 (s)		1160 (s)	1160 (b)
1210 (m)		1230 (m)	1230 (m)
1220 (s)		1240 (m)	1240 (m)
1310 (s)		1270 (m)	1270 (w)
1560 (m)		1310 (m)	1300 (s)
1600 (m)		1560 (m)	1570 (m)
1970 (w)		1600 (m)	1600 (b)
2080 (s)		2160 (s)	2150 (s)
	2350 (s)	2180 (s)	2180 (s)
		2240 (s)	2240 (s)

[KEY: s, strong; b, broad; w, weak; m, medium.]

the one used by Schilt relies firstly upon preparing a ruthenium-(III) ion, and then reducing this compound to give the desired product. By analogy with the corresponding iron-(II) compound, we thought that the more direct route should work equally well in this case also. Unfortunately, after refluxing the tris-bidentate ruthenium-(II) compound for several days with potassium cyanide, no change occurred in the visible/U.V. absorption spectra, (i.e. Absorption peaks:- 670, 452, 350 and 287 nm).

The preparation was then repeated using the method employed by Schilt,<sup>(221)</sup> but only a small impure product was isolated. An absorption spectrum of the product was found to change with time, indicating that the product contained some unreacted starting material. No attempt was made to make the 'phen' compound, since other workers isolated only tarry products.<sup>(222)</sup>

Preparations of compounds of the form:  $\text{Co}^{\text{II}}(\text{LL})_2(\text{CN})_2$

- where LL = 2,2'-bipyridyl, 1,10-phenanthroline, and 4,7-dimethyl-1,10-phenanthroline.

These compounds were prepared exactly as described in ref. (223), however they were found to be extremely air sensitive, some of which even decomposed while drying under vacuo. Hence these compounds would not be suitable for the particular study which we are undertaking, and so these compounds were discarded.

Preparation of compounds of the form:  $\text{Pt}^{\text{II}}(\text{LL})\text{Cl}_2$

- where LL = 2,2'-bipyridyl, 1,10-phenanthroline, and 4,7-dimethyl-1,10-phenanthroline.

These compounds were prepared by the literature method,<sup>(224)</sup> and characterised by their U.V. absorption spectra,<sup>(225)</sup> (i.e. the spectrum of the bipyridyl compound has been reported in the previous reference and, as the other adducts produced similar spectra, it would seem reasonable to

assign to them the same formulae.)

Preparations of compounds of the form:  $\text{Cu}^{\text{II}}(\text{LL})(\text{CN})_2$

(a) - where LL = 1,10-phenanthroline.

This compound has been reported quite recently,<sup>(226)</sup> and is said to be square planar. Its anomalous stability is due to the presence of the bidentate group, which behaves as a strong  $\sigma$ -donor ligand, thus preventing electron-transfer from the cyanide groups to the cupric ion thence reducing it to copper-(I). The method used in the previous study was adhered to, and a purple product isolated. This product was found to be insoluble in many of the common organic solvents; diffuse reflectance data obtained for this compound can be found in Table 8. (N.B. This compound was found to be slightly air-sensitive over a period of several weeks, giving a red product, the nature of which was not investigated.)

(b) - where LL = Schiff-base.

The base chosen was that formed from quinolyl-2-aldehyde and para-toluidine, (i.e. 4 methyl-aniline), and is drawn in Fig. C. This species co-ordinates to the metal through the nitrogen atoms as in the symmetrical bidentate groups, (e.g. 2,2'-bipyridyl).

The method used is as follows. A quantity of hydrated copper-(II) nitrate was dissolved in a minimum volume of water and a quantity (stoichiometric ratio, Ligand:Copper = 2:1) of quinolyl-2-aldehyde in a minimum volume of ethanol was added to this with continuous stirring. The appropriate amount (stoichiometry as above) of para-toluidine was then added with further stirring. The resulting dark coloured solution was filtered, (to remove any organic tar or oils formed) and to this was added a two-fold excess of potassium cyanide dissolved in a minimum quantity of water. The mixture was stirred for ~30 minutes and then filtered to isolate

the purple product. After intensive washing with a varied series of organic solvents and drying over  $P_2O_5$  under vacuo, the compound was sent away for analysis. The results obtained are listed here:-

	C	N	H	Cu*
Theoretical % by weight =	62.95	12.05	4.17	18.6 ‡
Actual % by weight =	62.0	15.4	3.87	18.06

(\* calculated by subtraction)

The unexpected result for nitrogen is strange in that neither the carbon nor hydrogen analyses are similarly in error. We therefore assume that this may be due to difficulty in breaking up the Schiff-base during the analysis.

As was found for the previous copper compound, this one is also extremely insoluble. A diffuse reflectance spectrum has thus been obtained for this compound and the result can be found in Table 8.

Preparations of compounds of the form:  $Hg^{II}(phen)X_2$

- where X = cyanide or thiocyanate.

These compounds were prepared as described previously,<sup>(227)</sup> and were characterised by their U.V. absorption spectra.

[ ‡ This theoretical calculation is based upon the assumption that the stoichiometric ratio in the product will be 1 x Cu : 1 x Schiff-base : 2 x cyanide group (i.e. that the copper is tetra-co-ordinate).]

## Experimental

Solutions were prepared using the purest solvents available, (usually AnalaR-grade) and all spectra run on either a Unicam SP800 or SP8000 recording spectrophotometer. The wavelength calibration of these instruments were checked periodically using standard holmium and didymium glass filters. Diffuse reflectance results were obtained using a Beckmann DK2A recording spectrophotometer.

## Results

Compounds of chromium, molybdenum and tungsten:- Visible absorption spectra of compounds with the general formula,  $M(CO)_4(bipy)$  were obtained in as many solvents as was permitted by solubility restrictions and the values of their absorption (visible) maxima along with relevant  $E_T$  parameters are listed in Table 1. The effect of this change in identity of the central ion is shown graphically in Figure 1, where the frequencies of maximum absorption of the chromium and tungsten compounds are plotted together. A plot for the tungsten compound (frequencies of maximum absorption) against the  $E_T$  values for the solvents used is shown in Figure 2.<sup>†</sup> The equivalent plots for the other two metal species would look entirely similar.

A ligand (bidentate) comparison for compounds with the general formula,  $W(CO)_4(LL)$  has also been performed. Lists of frequencies of maximum absorption for the various 'LL' species are to be found in Table 2. The largest effect of the ligand variations is shown graphically in Figure 3, where the absorption data for LL = 5 chloro-1, 10-phenanthroline have been

[<sup>†</sup> This plot shows two distinct regions, associated with hydroxylic and non-hydroxylic solvents, the exceptions present are all chlorine containing solvents. This phenomenon will be explained later in this section.]

TABLE 1

Solvent variation of absorption maxima ( $\text{kc.cm}^{-1}$ ) for compounds of the type  $\text{M}(\text{CO})_4(\text{bipy})$ , where  $\text{M} = \text{Cr}, \text{W}, \text{Mo}$ ; along with the relevant solvents and their  $E_T$  ( $\text{kcal. mol}^{-1}$ ) parameters.

SOLVENT	$E_T$		$\bar{\nu}$	
Methanol	55.5	-	21.79	21.14
Ethanol	51.9	-	21.41	20.83
Benzyl alcohol	50.8	-	21.69	21.32
n-Propanol	50.7	19.68	21.05	20.49
n-Butanol	50.2	19.65	20.92	20.33
i-Propanol	48.6		21.05	20.20
Methyl nitrite	46.3	21.14	22.68	22.12
D.M.S.O.	45.0	21.32	22.78	22.32
t-Butyl alcohol	43.9		20.88	20.08
D.M.F.	43.8	21.19	22.88	22.12
Acetone	42.2	20.58	22.08	21.60
Phenyl nitrite	42.0	20.37	21.74	21.32
1,2 diCl-ethane	41.9	20.00	21.46	20.92
Acetophenone	41.3	20.37	21.88	-
Methylethyl-ketone	41.3	20.41	22.12	21.37
Dichloromethane	41.1	19.80	21.32	20.62
Cyclohexanone	40.8	20.20	21.74	21.05
Chloroform	39.1	19.23	20.58	19.96
1,2 dimethoxyethane	38.2	20.12	21.65	21.05
Ethyl bromide	37.6	19.34	20.96	20.16
Chlorobenzene	37.5	19.38	20.66	20.00
Anisole	37.2	19.84	21.19	20.45
Phenetol	36.4	19.57	21.01	20.28
Diethyl-ether	34.6	18.94	20.20	19.61
Benzene	34.5	18.94	20.30	19.65
Carbon tetrachloride	32.5	-	19.84	19.23

FIGURE 1

Correlation between the frequencies of maximum absorption ( $\bar{\nu}$ ,  $\text{kc. cm}^{-1}$ ) for the compounds  $\text{Cr}(\text{CO})_4(\text{bipy})$  and  $\text{W}(\text{CO})_4(\text{bipy})$  in a range of organic solvents.

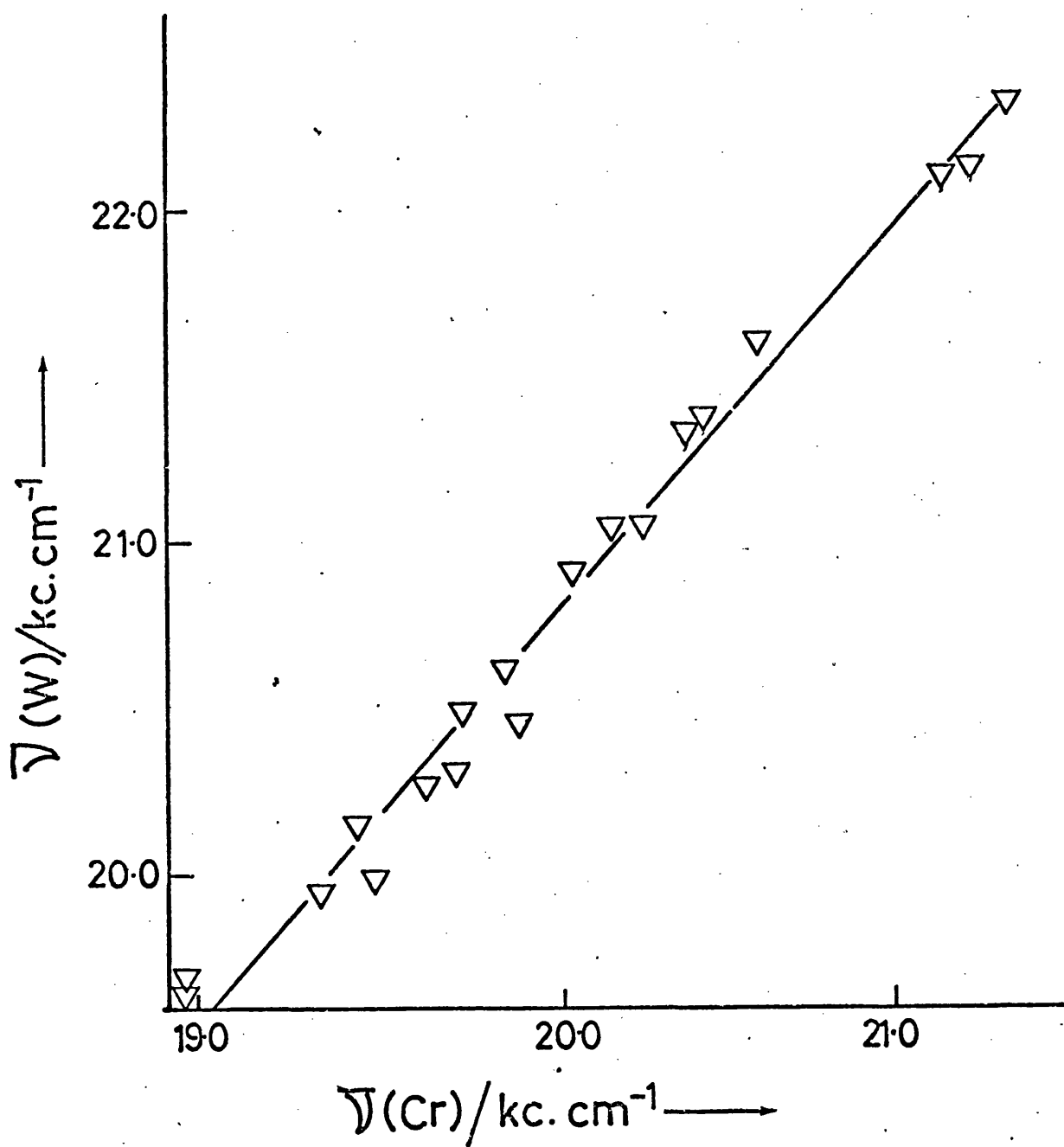




FIGURE 2

Correlation between frequencies of maximum absorption ( $\bar{\nu}$ ,  $\text{kc. cm}^{-1}$ ) for the compound  $\text{W(CO)}_4(\text{bipy})$  and solvent  $E_T$  values ( $\text{kcal. mol}^{-1}$ ).

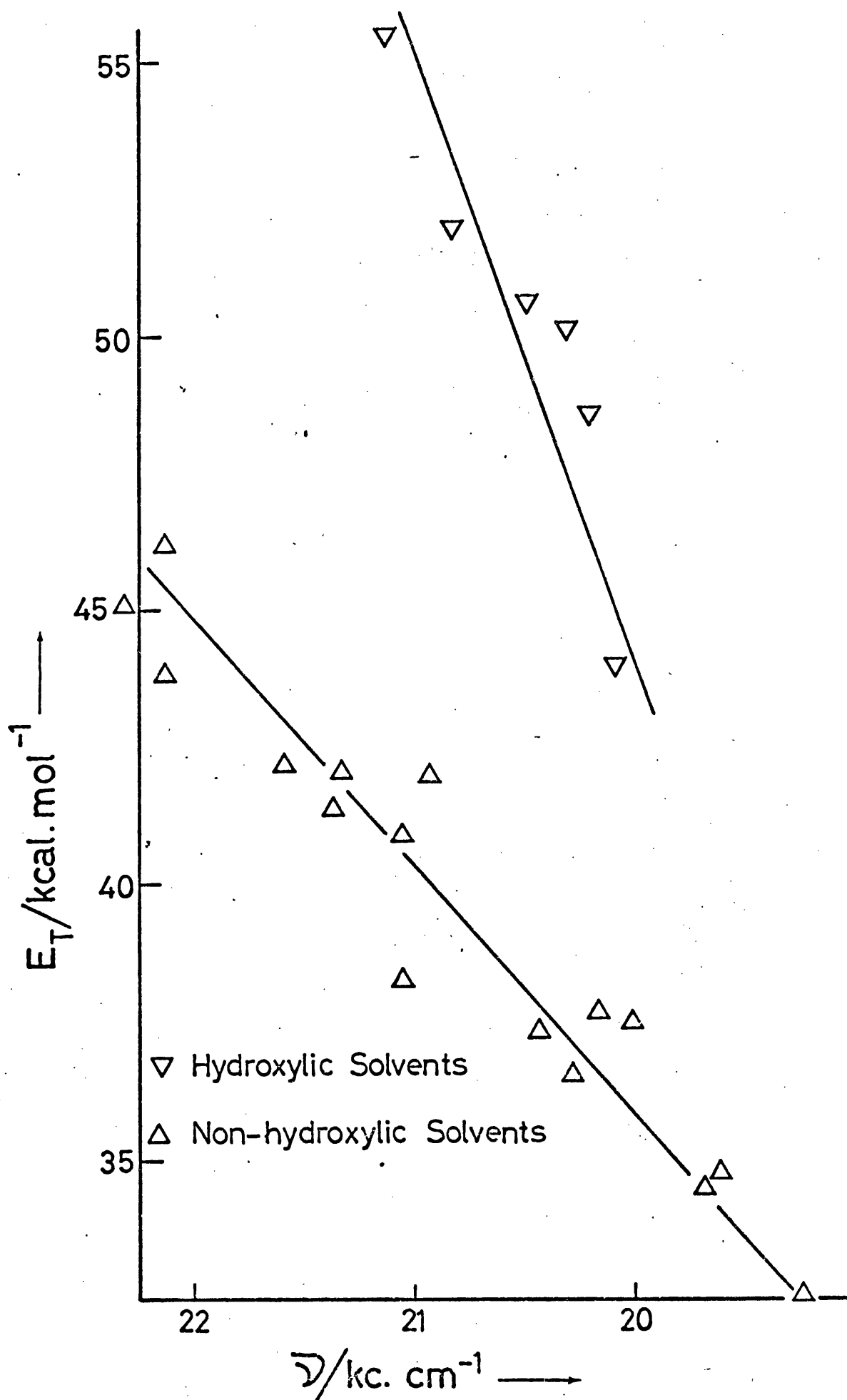


TABLE 2

Solvent variation of absorption maxima ( $\text{kc.cm}^{-1}$ ) for compounds of the type  $\text{W}(\text{CO})_4(\text{LL})$  where LL = phen; 4,7 dimethyl-phen; 5 Cl-phen, along with the relevant solvents.

SOLVENT	$\bar{\nu}$		
	phen	4,7 diMephen	5 Clphen
Methanol	20.79	22.17	21.19
Ethanol	20.20	21.83	20.75
Benzyl alcohol	20.70	22.22	21.32
Methyl nitrite	21.65	22.94	22.12
D.M.S.O.	21.83	22.88	22.22
Aniline	21.14	21.74	21.23
D.M.F.	21.46	22.62	21.93
Acetone	21.05	22.27	21.69
Phenyl nitrite	20.75	22.08	20.79
1,2 diCl-ethane	20.08	21.74	20.75
Acetophenone	20.70	22.32	21.28
Methylethyl-ketone	20.62	22.27	21.19
Dichloromethane	20.08	21.74	20.75
Cyclohexanone	20.45	21.83	21.50
Chloroform	19.49	21.28	19.69
1,2 dimethoxy-ethane	20.34	21.60	20.88
Ethyl bromide	19.65	21.05	20.20
Chlorobenzene	19.57	21.19	20.16
Anisole	20.00	21.41	20.66
Phenetol	19.80	21.14	20.28
Diethyl-ether	19.05	20.33	19.53
Benzene	19.23	20.45	19.80

plotted against the 4,7 dimethyl-1,10-phenanthroline analogue. A similar ligand variation has also been obtained for the molybdenum compound, (of the same general formula) where in this case, LL = 2,2'-bipyridyl and a diazabutadiene, (obtained from ref. [228]). The results from this study are listed in Table 3. [N.B. The diazabutadiene used was, N,N -di-tert-butyl-1,4 diazabutadiene.]

All of the above compounds were plotted against the  $E_T$  solvent parameter, and also in the relevant cases, against each other. The computed best slopes of these graphs, (calculated using a linear least mean squares analysis on a PDP11 computer) are tabulated together in Tables 6 and 7, along with their associated percentage errors, i.e. as obtained as defined in the Appendix, from the standard error of the mean.

#### Compounds of low-spin iron-(II):-

Variations in frequency of maximum absorption for compounds with the general formula,  $Fe^{II}(LL)_2(CN)_2$ , for several different 'LL' ligands are listed along with the appropriate  $E_T$  solvent parameters in Table 4. A plot for the 1,10-phenanthroline adduct, (arbitrarily chosen) against  $E_T$  values can be found in Figure 4. A graphical ligand comparison, using the two extremes (electronically speaking) in ligand, (i.e. 4,7 dimethyl-1,10-phenanthroline and 5 chloro-1,10-phenanthroline) is shown in Figure 5. Only a small number of points associated with non-hydroxylic solvents are present, partly due to solubility constraints and partly by choice. As has been observed for the previous compounds used, all of the chlorine containing solvents, (which possess at least one proton) fall neither on a line corresponding to hydroxylic nor non-hydroxylic solvents. In the usual case, these points fall between these

FIGURE 3

Correlation between frequencies of maximum absorption ( $\bar{\nu}$ ,  $\text{kc.cm}^{-1}$ ) for the two compounds,  $\text{W(CO)}_4(5\text{Cl-phen})$  = Y axis, and  $\text{W(CO)}_4(4,7 \text{ diMe-phen})$  = X axis, in a series of organic solvents.

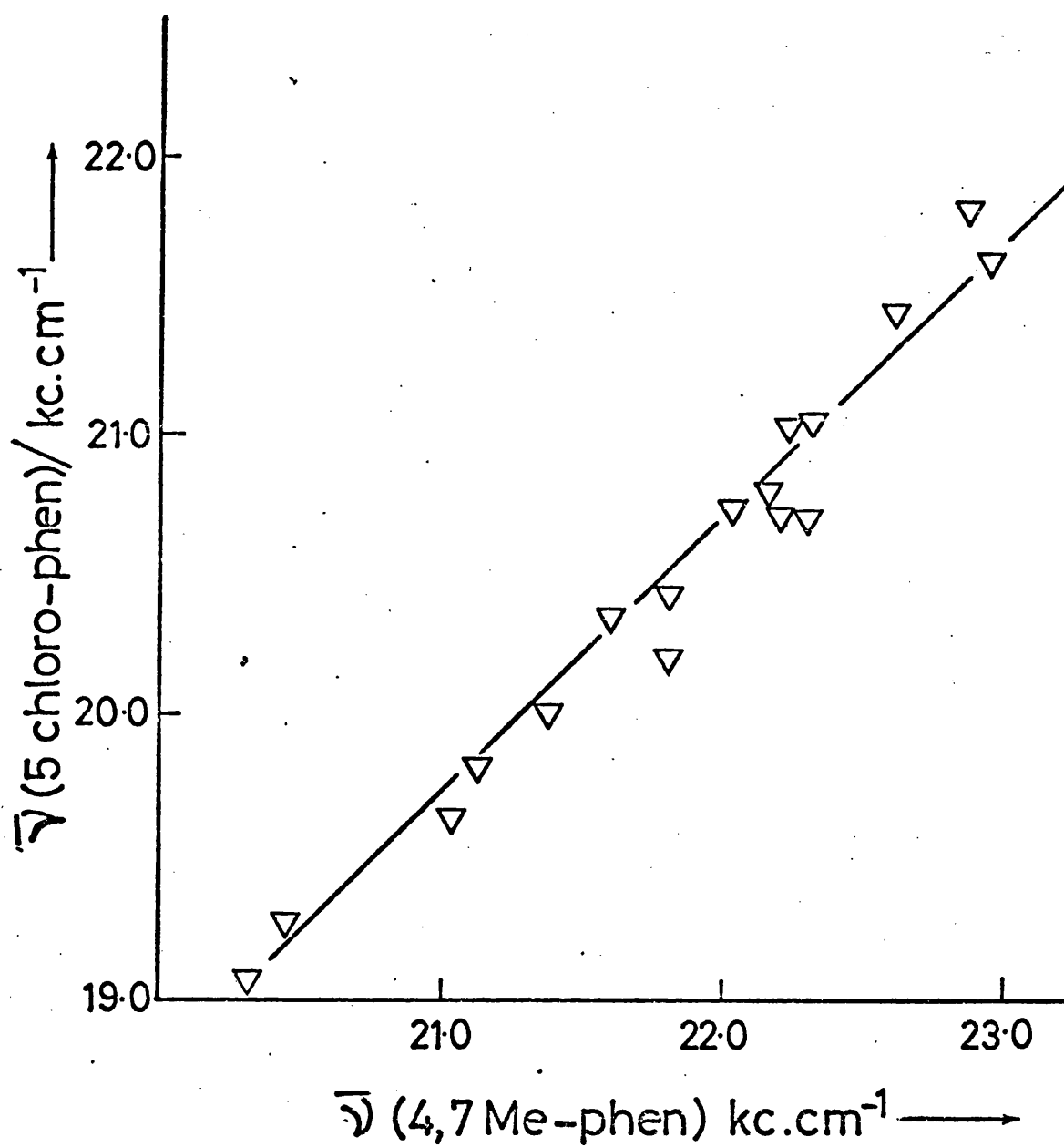


TABLE 3

Solvent variation of absorption maxima ( $\text{kc.cm}^{-1}$ ) for the compound  $\text{Mo(CO)}_4(\text{diaz})$ , along with the relevant solvents, obtained from reference 228.

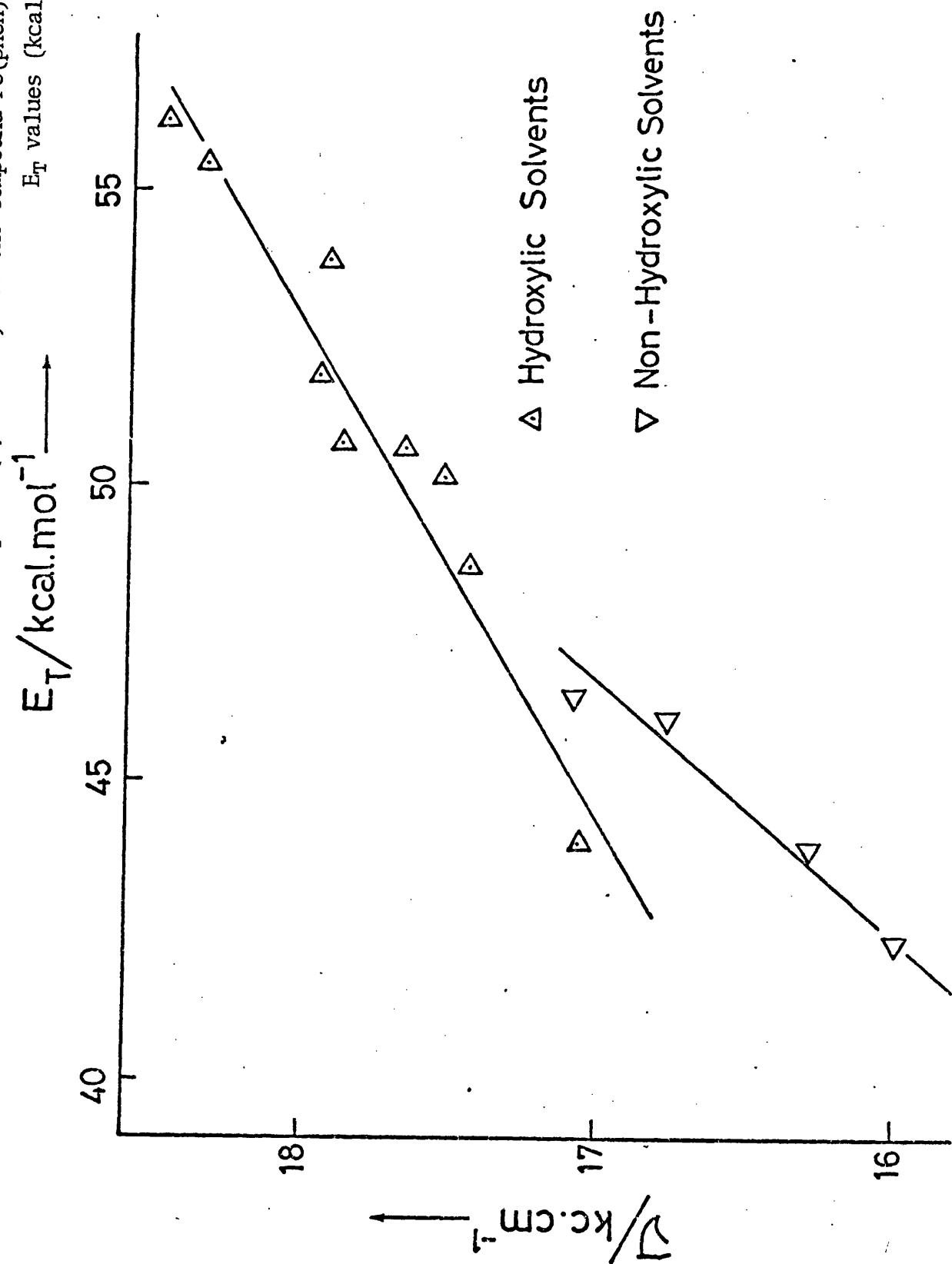
SOLVENT	$\bar{\nu}$
D.M.S.O.	21.12
D.M.F.	20.96
Acetonitrile	20.83
Acetone	20.40
Methanol	19.88
Dioxan	19.23
Chloroform	18.93
Carbon tetrachloride	18.02
Cyclohexane	17.75

TABLE 4

Solvent variation of absorption maxima ( $\text{kc.cm}^{-1}$ ) for compounds of the type  $\text{Fe(LL)}_2(\text{CN})_2$  where LL = phen; 4,7 dimethyl-phen; 5 Cl-phen, in hydroxylic and non-hydroxylic solvents with their  $E_T$  ( $\text{kcal. mol}^{-1}$ ) parameters.

	$E_T$	$\bar{\nu}$		
<u>HYDROXYLIC SOLVENTS</u>		phen	4,7 diMephen	5 Clphen
Water	63.1	19.38	19.80	19.19
Ethylene glycol	56.3	18.48	18.87	18.05
Methanol	55.5	18.35	18.73	17.95
Diethylene glycol	53.8	17.92	-	17.70
Triethylene glycol	53.5	17.61	-	17.42
Ethanol	51.9	17.95	18.25	17.57
Benzyl alcohol	50.8	17.89	18.18	17.57
n-Propanol	50.7	17.67	18.02	17.45
n-Butanol	50.2	17.54	17.95	17.42
i-Propanol	48.6	17.45	17.83	17.24
t-butyl alcohol	43.9	17.07	17.36	-
<u>NON-HYDROXYLIC SOLVENTS</u>				
Methyl nitrite	46.3	17.09	17.54	16.92
Acetonitrile	46.0	16.78	17.01	16.50
D.M.S.O.	45.0	16.60	16.75	16.37
D.M.F.	43.8	16.29	16.53	16.13
Acetone	42.2	16.00	16.47	15.87
1,2 diCl-ethane	41.9	16.45	-	16.23
Dichloromethane	41.1	16.78	17.06	-
Pyridine	40.2	-	-	15.95

Correlation between the frequencies of maximum absorption ( $\bar{\nu}$ ,  $\text{kc.cm}^{-1}$ ) for the compound  $\text{Fe}(\text{phen})_2(\text{CN})_2$  and solvent  $E_T$  values ( $\text{kcal. mol}^{-1}$ ).



two regions.<sup>†</sup> This seems to indicate to us that they should therefore be treated separately, or as is the case here, ignored for the sake of clarity.

Results for compounds with the general formula,  $\text{Fe}(\text{pyCOpy})_2\text{X}_2$  have also been obtained. For the compound where  $\text{X}$  = cyanide, the pertinent data can be found in Table 5, and a plot of these values against the solvent parameter,  $E_T$  is shown in Figure 6. Analogous results for the compound where  $\text{X}$  = thiocyanate, in pure non-aqueous solvents were not good, possibly due to solubility problems encountered therein, and so these values are not tabulated. By use of diffuse reflectance however, a value for the wavelength of maximum absorption was obtained. Similar results for other insoluble compounds were also obtained, and all of these results are listed in Table 8. Unfortunately, the large uncertainties associated with these measurements forbade the use of this technique to ascertain whether the previously mentioned 1:2 adducts of bis-(2,2'-bipyridyl)-dicyano-iron-(II) and mercuric cyanide (or thiocyanate) were identical to the 1:1 adducts of the same compounds.

Computed results for some of the slopes of the previously mentioned plots, along with their percentage errors can be found in Tables 6 and 7.

#### Compounds of copper-(II), platinum-(II) and mercury-(II):

Both of the copper-(II) compounds made were found to be insoluble, (see preparative section for the details) and so their absorption maxima were obtained by diffuse reflectance, and are listed in Table 8. The compounds containing platinum-

[<sup>†</sup> The evidence seems to suggest that these solvents are hydrogen-bonding to some extent, thus as would be expected, they have intermediate character in the above mentioned plots. Solvents behaving thus are as follows:- chloroform, dichloro-methane, 1,2 dichloro-ethane, chloro-benzene.]



FIGURE 5

Correlation between frequencies of maximum absorption ( $\bar{\nu}$ ,  $\text{kc.cm}^{-1}$ ) for the two compounds  $\text{Fe}(4,7 \text{ diMe-phen})_2(\text{CN})_2 = \text{X axis}$ , and  $\text{Fe}(5\text{Cl-phen})_2(\text{CN})_2 = \text{Y axis}$ , in a series of organic solvents.

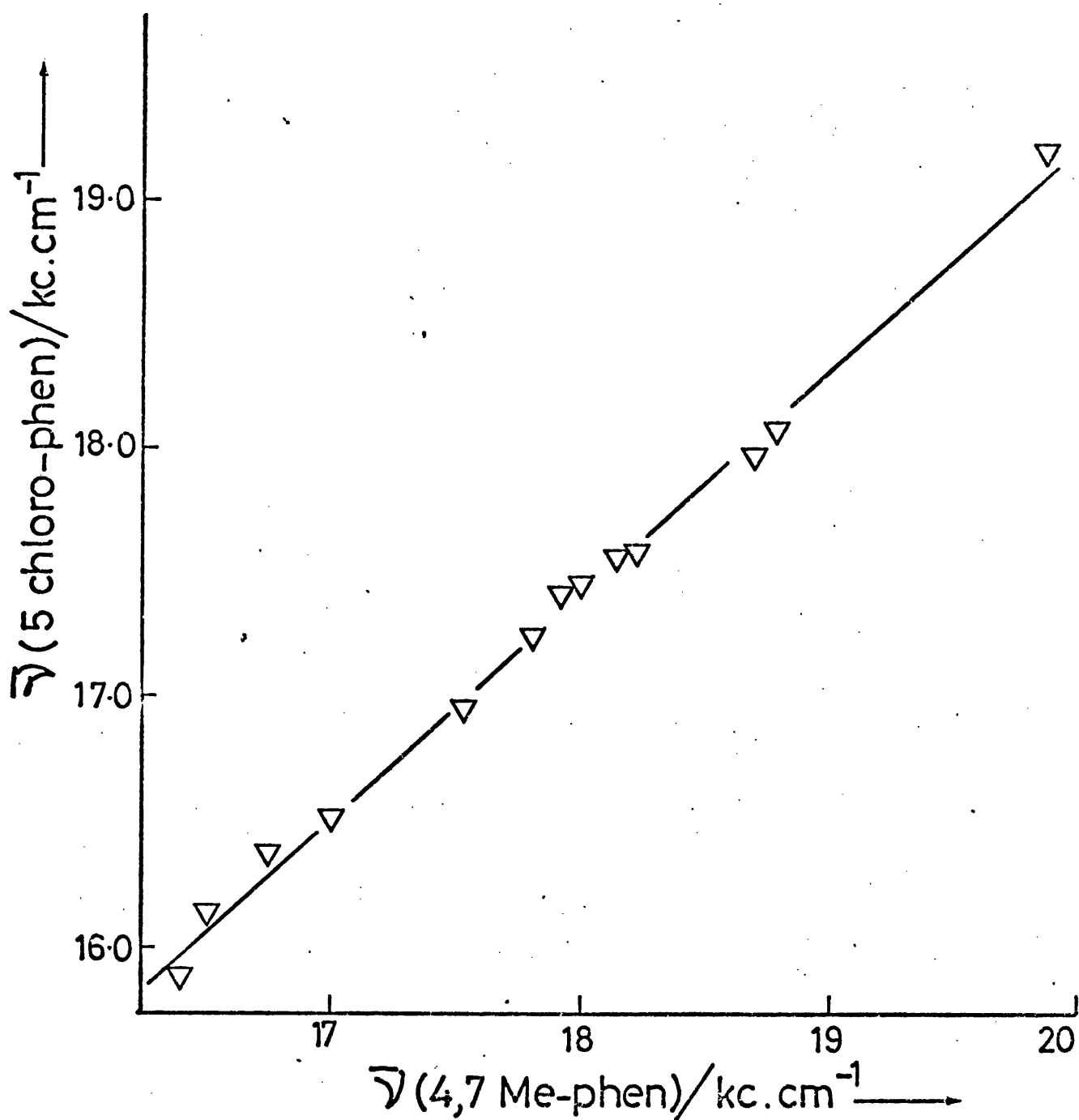


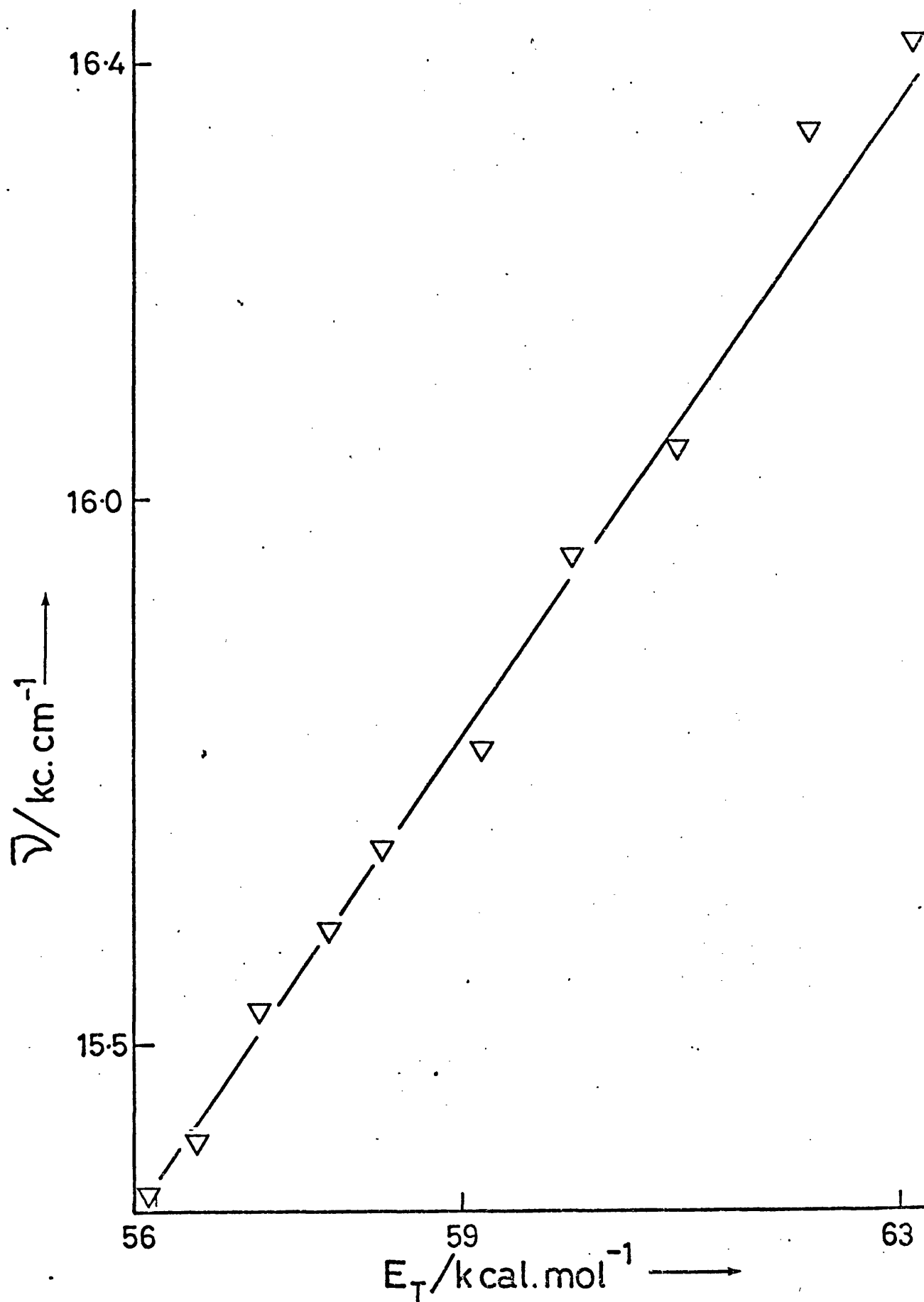
TABLE 5

Solvent variation of absorption maxima ( $\text{kc.cm}^{-1}$ ) for the compound  $\text{Fe}(\text{pyCOpy})_2(\text{CN})_2$  along with the relevant binary aqueous mixtures.

(CO-SOLVENT)	$\bar{\nu}$
METHANOL	
V/V%	
10	16.34
20	16.05
30	15.95
40	15.77
50	15.68
60	15.60
70	15.53
80	15.41
90	15.36

FIGURE 6

Correlation between frequencies of maximum absorption ( $\bar{\nu}$ ,  $\text{kc.cm}^{-1}$ ) for the compound  $\text{Fe}(\text{pyCOpy})_2(\text{CN})_2$  and solvent  $E_T$  values ( $\text{kcal. mol}^{-1}$ ).



(II) were found to be slightly solvatochromic. Four different absorption bands were used in the examination, as have been reported by Gillard,<sup>(225)</sup> (i.e. in Table 9, the results correspond to bands 1, 2 and 3 as designated by the previous worker) and the results of this study for the bipyridyl compound are displayed in Table 9. [N.B. Because of the small solvent dependence observed for this compound, further studies on the analogous phen compounds were not carried out.] No computed slope value was obtained for this compound, due to the mentioned 'small' solvent dependence.

The two mercury-(II) compounds prepared gave a similar solvent dependence pattern<sup>†</sup> to that described for the platinum compound. In both cases, due to the absorption bands being in the ultra-violet range of the spectrum, absorption by solvents often obscured the compound bands. A solvent blank was used in many such cases, but was not altogether satisfactory. Thus as was found for some of the iron-(II) compounds, a comparison between cyanide and thiocyanate ligands is again not possible.

## Discussion

As has already been stated, all of the compounds used in this study have a cis geometry, based upon infra-red, visible/U.V. and Mossbauer spectroscopic evidence.<sup>(217,222,229,230,231,232)</sup> In the following discussion, I will be dealing with the compounds used in two arbitrarily chosen groups. The first group contains those compounds which have six-co-ordinate metal centres, and in the second group, those that have only four-co-ordinate metal centres.

The first group contains the compounds of chromium-(0), molybdenum-(0),

[<sup>†</sup> The largest recorded absorption shifts for dicyano-(1,10-phenanthroline)-mercury-(II) was 3 nm.]

TABLE 6

Best slopes calculated for plots of  $E_T$  (kcal. mol<sup>-1</sup>) vs. frequencies of maximum absorption along with slopes from cross correlations between similar compounds. (In all cases, plots were observed to be linear.)

X-axis	Y-axis	No. pts.	SLOPE	± ERROR
$E_T$	$\text{Cr}(\text{CO})_4(\text{bipy})$	18	198.9	22.27
$E_T$	$\text{Mo}(\text{CO})_4(\text{bipy})$	19	219.5	22.00
$E_T$	$\text{W}(\text{CO})_4(\text{bipy})$	18	228.1	21.70
$\text{Cr}(\text{CO})_4(\text{bipy})$	$\text{Mo}(\text{CO})_4(\text{bipy})$	20	1.11	0.036
"	$\text{W}(\text{CO})_4(\text{bipy})$	20	1.14	0.040
$E_T^{(a)}$	$\text{Mo}(\text{CO})_4(\text{diaz})$	8	233.3	27.10
$\text{Mo}(\text{CO})_4(\text{diaz})^{(a)}$	$\text{Mo}(\text{CO})_4(\text{bipy})$	7	0.986	0.029
$\text{W}(\text{CO})_4(\text{bipy})$	$\text{W}(\text{CO})_4(\text{phen})$	20	0.943	0.060
"	$\text{W}(\text{CO})_4(4,7 \text{ diMe-phen})$	20	0.862	0.050
"	$\text{W}(\text{CO})_4(5 \text{ Cl-phen})$	20	0.958	0.030
$\text{W}(\text{CO})_4(\text{phen})$	"	20	0.972	0.060
"	$\text{W}(\text{CO})_4(4,7 \text{ diMe-phen})$	20	0.855	0.070

[ (a) from data in reference 228]

TABLE 7

Best slopes calculated for plots of  $E_T$  (kcal. mol<sup>-1</sup>) vs. frequencies of maximum absorption along with slopes from cross correlations between compounds with the general formula;  $Fe(LL)_2(CN)_2$ .

HYDROXYLIC SOLVENTS:

X-axis	Y-axis (LL)	No. pts.	SLOPE ±	ERROR
$E_T$	phen	11	121.4	12.7
$E_T$	4,7 diMe-phen	9	130.5	5.2
$E_T$	5 Cl-phen	10	129.3	13.2
(LL) phen	4,7 diMe-phen	9	1.039	0.024
"	5 Cl-phen	10	0.949	0.062
4,7 diMe-phen	"	8	0.937	0.059

NON-HYDROXYLIC SOLVENTS:

(LL) phen	(LL) 4,7 diMe-phen	6	0.966	0.16
"	5 Cl-phen	6	0.930	0.06
4,7 diMe-phen	"	5	0.881	0.13

(HYDROXYLIC SOLVENTS: <sup>a</sup>

bipy	phen	9	1.007	0.05
"	4,7 diMe-phen	9	0.959	0.02 )

[ <sup>a</sup>: from reference 233]

tungsten-(0), and iron-(II). In all of these compounds, a similar electronic transition is thought to be responsible for the visible absorption peaks,<sup>(208,233)</sup> and this will be described in more detail later. The frequencies reported for these compounds are in each case the lowest energy charge transfer bands in the visible region. The calculated slopes, (Tables 6 and 7) for the metal comparison of chromium, molybdenum and tungsten are all approximately equal to unity, (each of these gave a good linear relationship). As expected, the largest deviation from unity is to be found for the slope of the chromium vs. tungsten compound. This would seem to indicate that the extent of solvent interaction with each of the compounds remained fairly constant throughout the metal series. The correlations between frequency and the solvent parameter,  $E_T$ , were similar for all of these elements, including those for the iron-(II) compounds, (the values of the slopes can be found in Tables 6 and 7). All of these plots showed the usual two distinct regions,<sup>(208)</sup> associated with hydroxylic and non-hydroxylic solvents. The fact that such a difference is apparent is not particularly disturbing when one remembers that the  $E_T$  scale originated from a purely organic system. Also, this type of behaviour has been found to occur in some charge-transfer compounds of N,N -dimethylaniline and chloranil,<sup>(234)</sup> showing that this scale is not universally applicable, even in organic systems. For similar reasons, our partial mistrust of chlorine containing solvents, along with the exemption of organic acids, (e.g. acetic and formic acids which could protonate the compounds) from our analyses seem reasonable.<sup>(221,235)</sup> All of these observations can be taken to reflect the differences in the relative importances of hydrogen-bonding, lone-pair availability, and other such properties when one varies the system under study. Hence one would not expect to be able to define a single unique solvent parameter which would allow for the infinite number of variations

TABLE 8

Diffuse Reflectance data compiled for several insoluble compounds encountered while examining solvatochromic properties of a large range of inorganic compounds.

( $\lambda_{\max}$  = wavelength of maximum absorption)

COMPOUND	$\lambda_{\max}/\text{nm}$	$\pm$ Error/nm
Cu(phen) (CN) <sub>2</sub>	460	10
Cu(Q) (CN) <sub>2</sub> <sup>a</sup>	745	5
Fe(pyCOPy) <sub>2</sub> (NCS) <sub>2</sub>	460	10
Fe(bipy) <sub>2</sub> (CN) <sub>2</sub> Hg(CN) <sub>2</sub>	750	10
Fe(bipy) <sub>2</sub> (CN) <sub>2</sub> Hg(NCS) <sub>2</sub>	720	10
Fe(bipy) <sub>2</sub> (CN) <sub>2</sub> [Hg(CN) <sub>2</sub> ] <sub>2</sub>	740	10
Fe(bipy) <sub>2</sub> (CN) <sub>2</sub> [Hg(NCS) <sub>2</sub> ] <sub>2</sub>	715	10

[ <sup>a</sup> Q = quinoly1-2-methylene-p-toluidine]



TABLE 9

Solvent variation of absorption maxima ( $\text{kc.cm}^{-1}$ ) for the compound  $\text{Pt}(\text{bipy})\text{Cl}_2$ , followed at four different frequencies of maximum absorption along with the relevant solvents.

[KEY: abs- absorption by solvent prevented measurements being taken, (even using a solvent blank); b- solvent blank used; s- sparingly soluble; i- insoluble.]

SOLVENT:	$\bar{\nu} / \text{kc.cm}^{-1}$			
(Hydroxylic)	4	3	2	1
Water	47.62	s	31.17	s
Methanol	36.76	32.20	30.96	s
Ethane diol	-	31.75	30.81	26.18
Digol	36.23	32.00	30.86	26.18
Trigol	-	31.95	30.77	25.97
Ethanol	35.97	s	30.96	s
Benzyl alcohol	abs	abs	30.49	26.11
n-Propanol	36.63	s	s	s
i-Propanol	36.04	32.10	30.91	s
(Non-Hydroxylic)				
Methyl nitrite	abs	abs	abs	26.53 <sup>b</sup>
D.M.S.O.	-	31.65	30.58	26.08
D.M.F.	-	31.85	30.70	25.77
Acetone	abs	abs	30.67 <sup>b</sup>	25.45
1,2 diCl-ethane	35.34	31.95	30.77	25.32
Acetophenone	abs	abs	abs	25.18
Methylethyl ketone	abs	abs	30.72 <sup>b</sup>	25.19
Dichloromethane	-	32.00	30.86	25.38
Cyclohexanone	abs	abs	abs	25.03
Chloroform	35.15	32.00	30.82	25.06
1,2 diMethoxyethane	35.09	31.90	30.72	24.81
Chlorobenzene	i	i	i	i
Anisole	abs	abs	abs	24.69

which can occur from system to system.<sup>(236)</sup>

Several bidentate ligands were used for both the iron-(II) and the Group VIA compounds, similar results being obtained in both cases. The calculated slopes between analogous compounds where the bidentate group has been changed are listed in Tables 6 and 7. The largest solvent effects for both the iron and tungsten compounds, (i.e. where the bidentate ligand variations were identical) were between the 'extreme' substituted phenanthrolines, (i.e. 4,7 dimethyl- and 5 chloro-). One of these is strongly electron withdrawing, (the latter) and the other strongly electron donating, towards the phenanthroline group. In spite of these large electronic differences, the actual effect upon the charge-transfer absorption plot, (of the two compounds plotted against each other) is quite small. An analogous result has been found for the tris- (1,10-phenanthroline)-iron-(II) ions, when these substituents are present on the phen groups.<sup>(237)</sup>

Comparisons between the data obtained for the molybdenum compound, (i.e. (2,2'-bipyridyl)-tetracarbonyl-molybdenum-(0)) with results for the diazabutadiene compound, (with the same general formula, bipy having been replaced by this ligand) obtained from ref. (228), have been made. A plot of the two compounds against one-another gave a slope of  $0.986 \pm 0.029$ . This result along with those obtained in the previous ligand variation study, again illustrates the relatively small ligand dependence of the absorption maxima, (i.e. with respect to solvent effects).

Various attempts to explain the solvent dependence of absorption spectra of inorganic compounds<sup>(201)</sup> have been made over the years since their discovery. Williams,<sup>(238)</sup> seems to have been one of the first to put forward the basic electronic theory which is still accepted today. His argument was initially based upon observations of tris-bidentate species, (and later extended). He suggested that the visible absorption bands

observed for diamagnetic iron-(II)-aromatic di-imine compounds are due to the excitation of a 3d electron to a level which can couple or participate with the empty  $\pi$ -orbitals of the aromatic ligands. These absorption bands are not found for similar compounds of the same ligands, (where the metal ion is nickel, cobalt, or zinc), hence they must be due to the specific cations. This implies that iron-(II) is similar to copper-(I) in this type of cationic species. Combining this feature with the absence of similar absorption bands for more general iron-(II) and copper-(I) compounds, (e.g. with chloride anions) even if diamagnetic, leads to the following conclusion. The occurrence of such bands must be a consequence of a chelating conjugated di-imine, and, in the case of an iron-(II) compound, the metal must be in a low spin electron configuration with the 3d levels filled, (as in the copper-(I) ion) with either atomic or bonding electrons. Thus excitation of a 3d electron into a higher level (e.g. 5p) which can then be coupled with the empty  $\pi$ -levels of the ligand would explain the visible absorption spectra of the tris-compounds. This type of absorption is essentially a charge transfer from the metal ion to the ligand, and accounts for the shift to longer wavelength as the acceptor character of the ligand is increased.

Although this model can be used to explain the appearance of visible absorption bands for both the tris-bidentate and bis-bidentate iron(II) compounds, (i.e. tris-(2,2'-bipyridyl)-iron-(II) and bis-(2,2'-bipyridyl)-dicyano-iron-(II)), Williams did not attempt to extend it to account for solvent dependent absorption spectra.

The main question left unanswered at that time was the actual 'position of solvation' which caused the solvent dependence. Using infra-red evidence<sup>(239)</sup> for solvent effects upon carbonyl stretching frequencies on the compound, (2,2'-bipyridyl)-tetra-carbonyl-molybdenum-(0), along with observations which showed the solvent-bipy interaction to be small. Burgess<sup>(208)</sup> tentatively

assumed that the solvent effects were due to interaction with the carbonyl groups, (which back-bonded via the  $\Pi$ -orbitals to the metal) thus affecting the metal to bipy charge-transfer energy. This idea is equally suitable for the previously mentioned iron-(II) compounds, and has been employed by the same worker for these compounds also.<sup>(233)</sup> A similar theory has also been proposed by several other workers,<sup>(229,240)</sup> one of whom used semi-empirical computer models to determine the relative importance of  $\sigma$  and  $\Pi$ -bonding. Applying these ideas, we can see that we would only expect to observe a strong solvent dependence if certain criteria are met. One essential is the presence of a chelate species which can accept, (e.g. for an iron-(II) compound) or donate (e.g. for a mercury-(II) compound) electrons to (or from) the metal ion. Secondly, at least one of the non-chelating ligands must be able to not only  $\sigma$ -bond to the metal, but also participate in  $\Pi$ -bonding with the metal, thus interacting with the overall  $\Pi$ -system, which extends across the metal and onto the chelating group. [N.B. The ligands must also be in a suitable geometry to facilitate overlap between  $\Pi$ -orbitals, i.e. in the case of octahedral, and square planar geometries, this would be the 'cis' geometry.]

Several pieces of experimental evidence are available which give extremely good agreement with the previous model. For instance, protonation of the compound, bis-(2,2'-bipyridyl)-dicyano-iron-(II), which is believed to occur at the cyanide ligands,<sup>(235)</sup> causes a shift in absorption towards the blue end of the spectrum. This has been explained<sup>(229)</sup> by an increase in the  $\Pi$ -acceptor properties of the cyanide groups, (i.e. now  $C\equiv N-H^+$ ) thus lowering the ground state energy, (i.e. stabilising the iron-(II), relative to the iron-(III) which the excited state resembles). Thus the energy difference of the two levels will be increased, causing the observed blue shift,<sup>(214)</sup> (i.e. since the energy of the excited state will remain approxi-

mately unchanged, by the Frank-Condon principle). This type of behaviour has also been found for several different compounds formed by co-ordination of a Lewis acid to bis-(2,2'-bipyridyl)-dicyano-iron-(II), these adducts being formed by co-ordination of the acid to the cyanide groups. Thus for  $\text{BF}_3$ ,<sup>(240)</sup> and also for  $\text{MF}_4$  Lewis acids, (where M = silicon, germanium or tin),<sup>(241)</sup> blue shifts are observed in each case when these acids are co-ordinated to the iron(II) compound. These shifts were, (in many cases) larger than analogous solvent shifts for the unsubstituted compound as would be expected, since a solvent molecule interacting with a cyanide group will interact to a lesser extent than a bonding species.

An attempt to further support these ideas by examining the mercury-(II) cyanide and thiocyanate adducts with the same iron-(II) compound produced an unexpected result. Measurement of the visible absorption spectra of these adducts by diffuse reflectance in the solid phase, (see Table 8) indicated that the wavelength of maximum absorption had shifted to longer wavelength, (i.e. a red shift). As far as we know, these are the only adducts in which such behaviour has been found. If we assume that these adducts are similar structurally to those previously mentioned, (to the extent that co-ordination occurs through the cyanide group(s)) as is inferred by cyanide infra-red stretching frequencies, (cf. ref. [241]). Then the only explanation for the observed shifts would seem to be some form of interaction between the mercury and the  $\Pi^*$ -level of a cyanide group, as depicted in Figure D. In the absence of any mercury- $\Pi$  interaction, the cyanide-carbon to iron  $\sigma$ -bond would be weakened and the iron to cyanide  $\Pi$ -interaction relatively unaffected. Thus the iron(II) would be able to 'push' more electron density into the  $\Pi^*$  of the cyanide, thus lowering the ground state energy, (as is observed for the previous silicon, germanium and tin adducts). However, if the filled d- $\Pi$  orbitals on the mercury ion

can overlap with the empty  $\Pi^*$  of the cyanide group, it could then back-donate electron density into this orbital, thus competing with the iron-(II). This would obviously increase the ground state energy, (relative to the excited state) and hence result in a shift to longer wavelength. Such a scheme is shown in Figure D. [N.B. A  $\Pi$ -type interaction between mercury-(II) and presumably this orbital, ( $\Pi^*$ ) has already been postulated by Beck et al.,<sup>(220)</sup> although in that case it was to explain the absence of a 1:2 adduct being formed.]

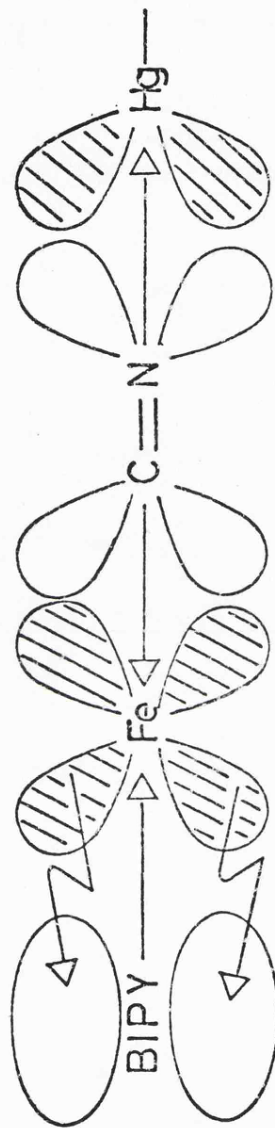
Although it would seem quite reasonable for mercury(II), (a  $d^{10}$  ion) to remove the extra electron density donated by the cyanide-nitrogen lone pair, (which otherwise would take it to  $d^{10}s^1$ ) via  $\Pi$ -back-bonding, the interesting point is that the tin(IV) adduct, (also a  $d^{10}$  ion) does not behave in a similar manner, but behaves like germanium and silicon, (where ~~filled~~ no  $d$ -orbitals are available) and also forms a 1:2 adduct. This behaviour may in part be a reflection upon the higher charge associated with this ion, (+4), possibly causing the  $d$ -orbitals to be contracted, thus preventing any overlap with the  $\Pi^*$  of the cyanide group. On the other hand, the two adducts, (mercury and tin) may be structurally dissimilar, (especially since one can form 1:2 adducts and the other cannot). Each mercury ion may be bonded to both cyanide groups, (as suggested by Beck,<sup>(220)</sup>) contrary to the structures proposed for the tin adducts.<sup>(241)</sup>

Similar evidence for solvatochromic behaviour being dependent upon solvent effects at carbonyl groups has also been found. The wavelength dependence of some carbonyl compounds has been found to be very sensitive to Lewis acid addition at the carbonyl groups.<sup>(209)</sup>

The remaining studies attempted in this Chapter were concerned with platinum-(II) and mercury-(II) compounds. Unfortunately, due to the combined problems of insolubility and high energy absorptions, (i.e. in the

FIGURE D

A molecular orbital picture for compounds of the type  $\text{Fe}(\text{bipy})_2(\text{CN})_2\text{Hg}(\text{CN})_2$ .



U.V. end of the spectrum, and so are often hidden under the solvent bands), the results were discouraging. Results for the compound, (2,2'-bipyridyl)-dichloro-platinum-(II) have been obtained previously by Gillard and co-workers,<sup>(225)</sup> and these indicated that the compound was slightly solvatochromic. Work by the same author using (2,2'-bipyridyl)-di-pyridyl-platinum-(II), which showed no evidence of solvent sensitivity, corroborates the previous ideas, (i.e. that solvent effects occur through non-aromatic ligands). The few results obtained for the mercury-(II) compounds, (i.e. general formula,  $\text{Hg}(\text{phen})\text{X}_2$ , where  $\text{X} = \text{CN}^-$ ,  $\text{NCS}^-$ ) have not been tabulated mainly due to their sparsity and inaccuracy, relative to the size of the solvent shifts observed.

As a result of our investigations we can say that, although both the mercury(II) and platinum(II) compounds are solvatochromic, they are much less sensitive, (in terms of size of wavelength shifts) than the compounds of chromium, molybdenum, tungsten and iron used in this survey.

The reasons for this can be explained by the operation of two independent factors. Firstly, for the mercury compounds used, the geometry of these is tetrahedral, and remembering the orbital-overlap argument, (set out in the introduction) we can see that  $\Pi$ -interactions for tetrahedral co-ordination would be only small. Secondly, in the platinum compounds examined, although one might have expected, (from the above mentioned argument) a solvent dependence of the same magnitude as, say, in the iron(II) compounds, this is not the case. This inconsistency is due to the different electronic properties of the non-aromatic groups, (i.e. cyanide and chloride). These two ligands are similar in that they both form strong  $\sigma$ -bonds to platinum-(II) or iron-(II). But they differ in their relative  $\Pi$ -bonding capabilities, (i.e.  $\text{Cl}^- < \text{CN}^-$ ). The perturbation of the orbital-energies on platinum or iron, (which are available for  $\Pi$ -bonding only) will



be greater for cyanide, thus solvation changes at a cyanide ligand will produce larger effects upon the absorption spectra of a compound, than similar solvation changes at a chloride ligand.

Hence the smaller solvent effects observed for the platinum and mercury compounds used in this study seem to fit in with the generally accepted ideas concerning solvatochromic behaviour.

Further investigations in this field using compounds with trans-geometries may provide some interesting anomalies to test the current ideas. However, it does not seem likely that the present theories can be that far removed from the whole truth of this matter.

### CHAPTER 3

Title: An investigation into the effects of micellar agents on a series of inorganic reactions in aqueous solution.

## Introduction

The unusual properties exhibited by aqueous solutions of detergent molecules were known as long ago as 1936, when the term, 'amphipathy' was introduced to explain these phenomena.<sup>(301)</sup> This term describes the simultaneous presence, in the same molecule, of separately satisfiable SYMpathy and ANTIpathy for the host water molecules.

In the intervening years much interest has been shown in these properties, and their effects on chemical and biological reactivity, producing what seems to be a reasonably well-understood area today.

In this chapter, we are concerned with reactions in detergent-water mixtures, and for this, the following explanation of the structure of the detergent within the bulk-water is applicable, (i.e. in non-aqueous solvents the following ideas will be of similar form, but modified somewhat depending upon the polarity and H-bonding properties of the solvent). The dispersal of a detergent in water varies with its concentration. There is a particular concentration band within which the detergent molecules exist as aggregates of various shapes and size, below this small range, they are found mainly in the form of monomers. Above this range, they tend to a homogeneous phase. This change over from monomeric to aggregates is known as the 'critical-micelle-concentration', (c.m.c.) and can be defined more accurately thus. The c.m.c. is the centre of a narrow concentration range where many physical and chemical properties<sup>†</sup> of the solution are found to

[<sup>†</sup> e.g. surface tension, viscosity, and the capacity to solubilise dyes.]

change abruptly, (but continuously), due to the formation of aggregate species. One of the commonest micelle-shapes found is the sphere, containing (usually) anything between twenty and a hundred molecules.<sup>(302)</sup> [See Figure A.] As depicted in the previous mentioned diagram, these aggregates are organised in such a way that the hydrophobic chains are 'hidden' within the structure, and are thus isolated from the bulk water. The hydrophilic head-groups radiate outwards into the water, producing a hydrophilic surface to the bulk-water. [N.B. If the solvent was non-polar, this arrangement would be reversed, the hydrophilic head-groups being located in the centre of the sphere.]

The micelle-monomer structure rearranging has been explained as an entropy directed process,<sup>(303,304)</sup> as one would expect from straightforward application of prevalent ideas on the nature of hydrophobic interactions. N.M.R. studies,<sup>(305)</sup> involving long chain sodium alkyl sulphates, (i.e. chain lengths greater than  $7\frac{1}{2}$  carbon atoms) have also been done, and these, along with other methods (such as T-jump<sup>(306)</sup>) have established upper and lower life-expectancy values for the micellar species. Although perhaps difficult to picture, the micelles in solution are continually forming and dissociating many times per second, (i.e. relaxation times obtained via T-jump measurements ranged between 1 and 300 msec,<sup>(307)</sup> depending upon the nature of the head group, the chain length and the concentration). However, to understand some of their properties, (particularly their catalytic effect) it may be easier to view them as though they are static.

The kinetic effects of micellar agents on chemical reactions can be

[ $\frac{1}{2}$  See ref. 335 for an explanation of this lower limit.]

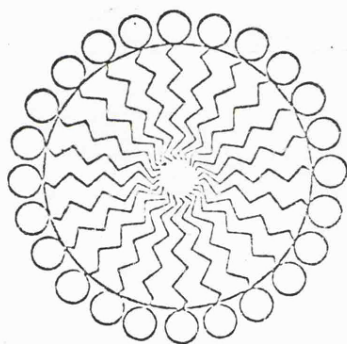
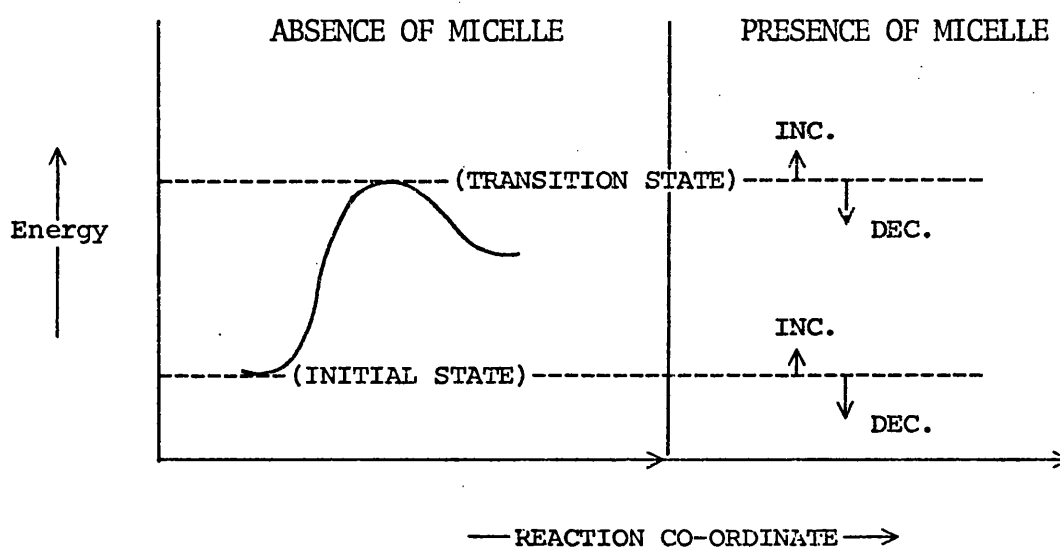


FIGURE A. (A MICELLE)

naively thought of in terms of the relative stabilising/destabilising influence of the micelles upon initial and transition state energies of a reaction. Thus in the following diagram, the micelles may affect either or both of these states, either favourably or unfavourably, (with respect to the free-energy of reaction): e.g.



Let us suppose that for a particular reaction, the initial state is stabilised by a quantity, 'B', and the transition state stabilised by a quantity, 'A', possessing the energy profile shown in the previous diagram. [N.B. Also, we assume that the difference between the energy of the transition state, ( $E_{T.S.}$ ) and the energy of the initial state, ( $E_{I.S.}$ ) is less than the sum of 'A' + 'B' i.e.  $(E_{T.S.} - E_{I.S.}) < (A + B)$ .] Even with this extreme simplification, there can be three possible results, depending upon the effect of the micelles on the free-energy of the reaction, e.g:

[1] For a rate enhancement; -  $A > B$  ,  $\therefore \frac{\Delta E_{T.S.}}{\Delta E_{I.S.}} > \text{UNITY}$

(i.e. where  $\Delta E$ 's are the free energy changes associated with each of these

reaction states.)

$$[2] \quad \text{For a rate retardation; - } A < B, \quad \therefore \quad \frac{\Delta E_{T.S.}}{\Delta E_{I.S.}} < \text{UNITY}$$

$$[3] \quad \text{For little effect; - } A \sim B, \quad \therefore \quad \frac{\Delta E_{T.S.}}{\Delta E_{I.S.}} \sim \text{UNITY}$$

Hence even where the individual micellar effects on the above states may be known, it will still be impossible to deduce the results of these effects upon the reaction rate.

However, if a molecule is incorporated into a micelle, this implies that it is stabilised relative to the molecule in bulk water, (otherwise one would not expect this to occur). Thus whenever micellar catalysis is seen to occur, this means that micellar stabilisation of the transition state more than offsets the aforementioned stabilisation of the initial state. The number of possible diagrams (of the previous type) are now decreased by this observation, since both states are decreased in energy. However we can see that the conditions, labelled (1), (2) and (3) still apply, only now they are applicable to the more general case (i.e. where A and B are of the same sign).

The actual interactions between a micelle and a molecule, (either solute, solvent or other), may be treated in terms of the attractive/repulsive forces between the molecule and the hydrophilic surface. Reactions in aqueous detergents where rate-effects are observed, are usually thought to be occurring either on this surface, (e.g. for ionic species), or in the hydrophobic micellar core, (e.g. for neutral non-polar species). The reasons for these assignments are as follows. In the case of ionic species, they would be expected to interact strongly with the hydrophilic-surface

and/or the bulk-water medium. The neutral, non-polar molecules, (e.g. benzene) will interact unfavourably with both the bulk-water medium and the hydrophilic surface, hence preferring the micellar core. Thus in cases of enhancement or retardation of reaction rate, the individual micelles can be thought of as microenvironments for the reacting species, as is observed in heterogeneous catalysis, catalysis by polyelectrolytes,<sup>(308)</sup> or liquid crystals,<sup>(309)</sup> or in enzymatic catalysis.<sup>(310)</sup>

Investigations into micellar catalysis have been going on for a large part of this century, however the first workers to point out the factors that were most likely responsible for the observed rate-effects were Duynstee & Grunwald in 1959.<sup>(311)</sup> Since that time much work has been directed towards this field, especially by organic reaction-kineticists. In virtually all of the organic reactions investigated which employed micellar agents, the rate-effects have been explained in terms of electrostatic effects on the initial and transition states. Examples of organic reactions where detergents have been incorporated into the systems are many, a short list of these is shown here:-

REACTION	REFERENCE
Hydrolysis of ortho-esters	312
Hydrolysis of phosphates and sulphates	313
Nucleophilic reactions of carboxylic esters	314,315
Aromatic substitution reactions	316,317.

Reactions involving inorganic systems to which detergents have been added are comparatively rare. The few reactions that have been studied show, in all but one case, rate effects which are much less significant than those found in organic systems. [e.g. Rate enhancements found for the dissociation of 1,4 cyanide adducts of a series of N-alkylpyridinium ions in aqueous detergent solutions produced a rate enhancement of the



order of  $10^3$  and equilibrium constants of  $\sim 2 \times 10^4$  greater than those in the absence of detergent species.<sup>(318)</sup> Similar magnitude rate enhancements are to be found in many other organic systems.] The only inorganic reaction to be studied which gave rate-enhancements of a similar size to those found in organic systems was the mercury-(II)-catalysed aquation of the  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$  cation in the presence of negatively charged surfactants. Other smaller effects have been noted, when polyelectrolytes have been included in the formation reactions of  $\text{Ni}_{\text{aq}}^{2+}$ ,<sup>(320)</sup> and also in the reduction of cobalt-(III) complexes by the  $\text{Ru}(\text{NH}_3)_6^{2+}$  cation,<sup>(321)</sup> as well as in the afore-mentioned mercury-(II)-catalysed aquation.<sup>(322)</sup>

As has been stated previously, the most important controlling factor, which has emerged from the much larger amount of work performed in organic systems is the importance of the electrostatic interactions in micellar catalysis. Hence one can immediately see that these interactions would be much stronger in the case of (charged) inorganic systems. Thus one would expect the corresponding rate-effects to be similarly large.

Our involvement in micellar catalysis stems from this last observation. The reaction between the tris-(2,2'-bipyridyl)-iron-(II) cation and cyanide only proceeds to the dicyano-product, no further reaction (with cyanide) occurring over several days.<sup>(323)</sup> We were interested at this time in the subsequent reaction between this dicyano-species and cyanide anion, to discover whether this mechanism was associative or dissociative in character. It was thus hoped that the addition of a detergent-species to this reaction mixture might produce a large rate-enhancement, (hopefully without affecting the mechanism) thus making the reaction more feasible to carry out.

Also since we have been interested in the past in various solvent-perturbing systems and their effects upon inorganic reactions, [e.g. the use of mixed aqueous solvents,<sup>(324)</sup> inert-salt effects,<sup>(325)</sup> and the use of

gels,<sup>(326)</sup>], it seemed of obvious interest to extend our work to include micellar catalysis.

Although the previously mentioned reaction stimulated our interest in this field of chemistry, it was not the first reaction which we examined, the reason for this being a publication at that time by M. J. Blandamer and D. J. Reid.<sup>(327)</sup> This paper put forward a mathematical argument which led to the conclusion that the largest catalytic activity (micellar) should be observed in systems where the reacting species (in a bimolecular reaction) are of like-charge. Thus the initial studies done by ourselves were concerned with such reactants.

#### Choice of detergent

In all of the reactions studied in this chapter, either one or both of the reactants are charged. Hence to obtain a favourable micelle-ion interaction two ionic detergents were chosen, one possessing a positively-charged and the other, a negatively-charged head group. These two detergents are well known and a relatively full investigation of their properties has been performed by various workers. The identity and formula of the detergents are as follows:-

- [1] An anionic detergent: sodium dodecyl sulphate,  $C_{12}H_{25}SO_4Na$ .
  - [2] A cationic detergent: hexadecyltrimethyl ammonium bromide,  $C_{16}H_{33}N(CH_3)_3Br$ .
- [N.B. The first of these will be hereafter abbreviated to NaLS, and the second of these to CTAB.]

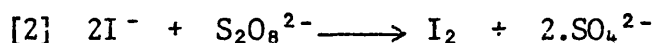
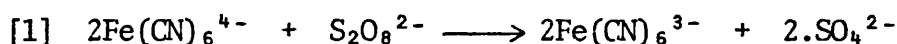
The c.m.c. values for these two detergents have been reported in the past, [i.e. CTAB =  $9 \times 10^{-4}$  mol.  $dm^{-3}$ ,<sup>(328)</sup>: NaLS =  $8 \times 10^{-3}$  mol.  $dm^{-3}$ ,<sup>(328)</sup>] although these values are particularly dependant upon the system under study, (e.g. ref. 319). As was pointed out in the introduction, it is not possible

to predict how a micelle will affect the reaction, however it is possible to at least ensure a favourable interaction, (if one should occur at all) between a micelle and anion, (i.e. CTAB would be expected to interact favourably with negative ions, and similarly NaLS with positive ions). A neutral ion should show no charge-type preference whatsoever. [N.B. It should be realised that a favourable interaction of the above type could equally produce a rate retardation rather than the desired acceleration, as will be seen in some of the following reactions.]

### Reactions 1 and 2

The oxidations of hexacyanoferrate-(II) and iodide by the peroxodisulphate ion.

e.g.



### Reaction 1

### Experimental

The cell contents were made up so as to contain peroxodisulphate and hexacyanoferrate-(II) ions in a ratio suitable for first-order conditions to occur. Since the latter of these species reacts with even traces of acid, the solution was made up in-situ with potassium hydroxide, thus preventing the reaction:-



All runs were followed at 420 nm, the absorption maximum of the reaction product, hexacyanoferrate-(III), and the temperature kept constant

at 298.15 K. Both cationic and anionic detergents were employed separately in the reactions, although it was expected that the cationic detergent should produce the larger rate effects.

## Results

The results consist of three distinct 'sets', the first two using the same (cationic) detergent, where the reactant concentrations were varied, the third set using the anionic detergent. These varied reactant conditions along with their rate constants can be found in Table 1. The results for the anionic detergent can be found in Table 2. In Set 1, the iron compound concentration was twenty-times that of the peroxodisulphate ion, implying (from the previous reaction equation) a ten-fold excess. An upper detergent concentration was found for these particular reaction concentrations, ( $2 \times 10^{-3}$  mol.  $\text{dm}^{-3}$  of CTAB) above which precipitation was seen to occur. The rate constants obtained have large errors associated with them, and so the rate variations may be meaningless.

As the micelle-ion interactions are obviously crucial, we thought that the large charge associated with the iron-compound may be producing an imbalance. Thus we reversed the ion ratios, such that the peroxodisulphate ion was now in excess, by doing this we also hoped to lessen the possibility of precipitation at higher CTAB concentrations. The results of these actions can be found in Table 1, labelled 'Set 2'. As can be seen from these results, a large rate enhancement occurs, maximising at a CTAB concentration of  $5 \times 10^{-5}$  mol.  $\text{dm}^{-3}$ . A logarithmic plot of the ratio of the reaction rate in the presence and absence of detergent against concentration of detergent is shown in Fig. 1, (labelled, Line I).

The last set of reactions, employing a negative detergent, NaLS,

TABLE 1

First order rate constants, ( $k_{\text{OBS}}$ ) for the reaction between hexacyanoferrate-(II) and peroxodisulphate anions in aqueous detergent solutions at 298.15 K.

Set 1:-  $[\text{Fe}(\text{CN})_6^{4-}] = 2 \times 10^{-3} \text{ mol. dm}^{-3}$ ,  $[\text{S}_2\text{O}_8^{2-}] = 10^{-4} \text{ mol. dm}^{-3}$   
 $[\text{KOH}] = 5 \times 10^{-4} \text{ mol. dm}^{-3}$

$10^5 [\text{CTAB}]/\text{mol. dm}^{-3}$	$10^4 k_{\text{OBS}}/\text{s}^{-1}$	% ERROR
-	4.6	2.0
2.0	3.5	1.5
4.0	4.3	2.9
6.0	3.7	3.0
8.0	3.5	8.0 <sup>a</sup>
9.0	4.2	6.0 <sup>a</sup>
10.0	5.6	4.0 <sup>a</sup>

( <sup>a</sup> Precipitation occurred after or during these kinetic runs.)

Set 2:-  $[\text{Fe}(\text{CN})_6^{4-}] = 1.33 \times 10^{-4} \text{ mol. dm}^{-3}$ ,  $[\text{S}_2\text{O}_8^{2-}] = 2 \times 10^{-3} \text{ mol. dm}^{-3}$   
 $[\text{KOH}] = 6 \times 10^{-4} \text{ mol. dm}^{-3}$

$10^5 [\text{CTAB}]/\text{mol. dm}^{-3}$	$10^4 k_{\text{OBS}}/\text{s}^{-1}$	$\log_{10} (k_{\text{OBS}}/k_0)$
-	0.5	0.0
1.0	4.0	0.90
3.0	7.0	1.15
5.0	16.0	1.50
7.0	12.0	1.38
8.0	9.30	1.27
10.0	6.6 <sup>a</sup>	1.12

( <sup>a</sup> Precipitation occurred above this concentration of CTAB.)

TABLE 2

First order rate constants, ( $k_{\text{OBS}}$ ) for the reaction between hexacyano-ferrate-(II) and peroxodisulphate anions in aqueous solutions containing NaLS, at 298.15 K.

$10^5 [\text{NaLS}]/\text{mol. dm}^{-3}$	$10^5 k_{\text{OBS}}/\text{s}^{-1}$	% ERROR
1.0	2.3	4.2
5.0	4.5	5.2
10.0	9.3	5.3
20.0	3.3	3.6

produced rate-constant values with large associated errors, mainly due to the total O.D. changes observed being extremely small, (even over a 12 hour period) perhaps indicating that the reactions were not going to completion. [N.B. The actual 'measured' errors were quite small, but the actual numbers should be treated with caution.] The results obtained can be found in Table 2, This measured rate variation with NaLS may thus be very small or even non-existent due to the above-mentioned problems.

[Note:- In the reactions using CTAB, the possibility of the reaction:-



cannot be ruled out. Hence a set of 'blank' runs were carried out, containing CTAB and peroxodisulphate alone in the cells. The O.D. range, 450-200 nm was then monitored for several hours. No measurable O.D. change was found over the entire wavelength range, thus a contribution from this reaction to our measured rate constants can be ignored. (This obviously applies to the following reaction also.)]

## Reaction 2

## Experimental

The cells used to monitor the reaction contained potassium iodide, potassium peroxodisulphate and a quantity of detergent. In all of the reactions the iodide was kept in excess over the peroxodisulphate ions, (i.e. the reasons for this are the same as in the previous reaction; an optimum ionic strength occurs in micellar systems, above which precipitation may occur, thus the ion with the smallest charge should be the one with the highest concentration, <sup>(329)</sup>). Individual reactions were monitored at 288 nm,

near to a product absorption, ( $I_2$ ) where a large O.D. change was observed. All reactions were carried out at 298.15 K.

## Results

Following along similar lines to those used in the previous reaction, the iodide anion concentration was kept at a twenty-fold excess over the peroxodisulphate ions according to reaction equation (2). The variation in first order rate constant, ( $k_{OBS}$ ) with detergent concentration is shown in Table 3. A plot of  $\log(k_{OBS}/k_0)$  against detergent concentration, (i.e. where  $k_0$  = reaction rate in absence of detergent) is also shown in Fig. 1, labelled line II. As in the previous reaction, precipitation occurred, preventing results from being obtained above a CTAB concentration of  $\sim 2 \times 10^{-4} \text{ mol. dm}^{-3}$ .

Several runs using NaLS were performed, but, due to the large percentage errors associated with these, they have not been listed.

## Discussion

In both of the previous reactions, there is approximately a twenty-five fold rate increase over the detergent-free reaction rate. Although this is still much smaller than the effects observed by Morawetz and co-worker,<sup>†</sup> it does seem to agree with the predictions made by M. J. Blandamer and D. J. Reid.<sup>(327)</sup> This difference in magnitude of rate enhancement may be due to the differences in the micelle forming properties of the respective detergents used, however a more likely explanation may be as follows.

Attempts to duplicate the above work, (Morawetz & Co.) by myself and others have resulted in failure, mainly due to vast solubility problems. This in itself may be the key to the problem. Morawetz & Co. were able to

[<sup>†</sup> i.e.  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+} + \text{Hg}^{2+}$ ]



TABLE 3

First order rate constants, ( $k_{\text{OBS}}$ ) for the reaction between iodide and peroxodisulphate anions in aqueous detergent solutions at 298.15 K.

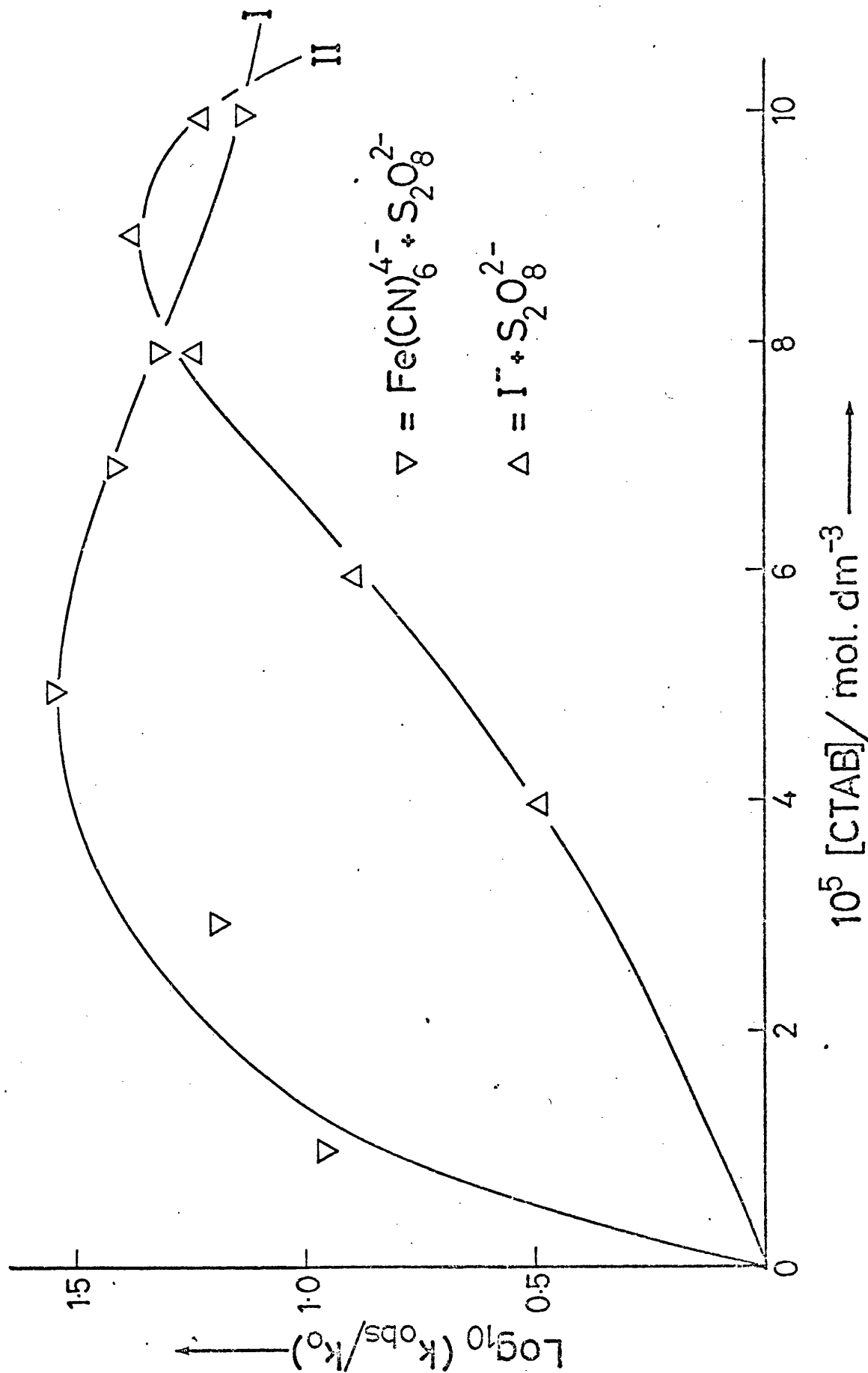
$$[\text{I}^-] = 4 \times 10^{-3} \text{ mol. dm}^{-3}, \quad [\text{S}_2\text{O}_8^{2-}] = 10^{-4} \text{ mol. dm}^{-3}$$

$10^5 [\text{CTAB}]/\text{mol. dm}^{-3}$	$10^4 k_{\text{OBS}}/\text{s}^{-1}$	$\log_{10} (k_{\text{OBS}}/k_0)$
-	2.2	0
4.0	5.0	0.36
6.0	17.0	0.89
8.0	37.0	1.23
9.0	55.0	1.4
10.0	36.0 <sup>a</sup>	1.21

( <sup>a</sup> Precipitation occurred in kinetic runs above this concentration of CTAB.)

FIGURE 1

Dependence of the logarithms of the ratios of rate constants for peroxodisulphate oxidation in the presence and absence of CTAB,  $\log_{10}(k_{\text{OBS}}/k_0)$ , on the concentration of CTAB; for iodide and hexacyanoferrate-(II) ions.



use very low concentrations of reactants in their studies, (by virtue of the use of a very sensitive spectrophotometer, i.e. a CARY-14.) hence precipitation, encountered at the higher concentrations necessary in our study, did not occur in their work. Thus a balance between a large reactant-detergent interaction, producing a rate-effect or precipitation, (or more often, colloid formation) must be found. This is obviously much easier at lower concentrations of reactants, (i.e. less than  $10^{-4}$  mol.  $\text{dm}^{-3}$ ). Hence similar magnitude rate enhancements to those found by Morawetz may occur for our two reactions at similar low reactant concentrations.

Unfortunately, the use of either a Unicam SP800 or SP8000 spectrophotometer does not allow us to employ such low reactant concentrations due to the limited sensitivity of these machines.

#### Reactions 3 and 4

The acid catalysed aquations of cis- and trans- bis-(ethylene diamine)-dichloro-cobalt-(III) species,  $(\text{Coen}_2\text{Cl}_2^+)$ .

#### Experimental

Two parallel investigations were carried out on each of these compounds, one involving a cationic and the other an anionic detergent additive. Both sets of reactions were carried out at 308.15 K. Because of the sensitivity of these compounds to the presence of alkali media, the deionised-water used was first screened to check its pH value, (found to be 6.5). In the presence of even small quantities of alkali, base hydrolysis occurs readily, causing precipitation of the product species.

Initially a set of results were obtained for the cis-isomer for the aquation in pure deionised water and in perchloric acid solutions, up to an acid concentration of  $6.67 \times 10^{-4}$  mol.  $\text{dm}^{-3}$ . Over this range the rate

seemed to be relatively independent of acid concentration as is shown by the results in Table 4, (part 1), and so all the other results pertaining to this reaction are at a pH = 6.5. [N.B. This may rule out any unfavourable acid-micelle interactions.] In reactions of the analogous trans-compound, the acid concentration was kept low, at  $0.01 \text{ mol. dm}^{-3}$ .

The initial concentrations of both cis- and trans-isomers were both approximately  $3 \times 10^{-3} \text{ mol. dm}^{-3}$ , the kinetic runs being followed at a suitable absorption maximum, (i.e. cis:- 270 nm, trans:- 310 nm). The rate constants for these reactions were calculated using a 'Guessed infinity routine' - program, (labelled Program 6 in the Appendix).

## Results

### - for cis-Coen<sub>2</sub>Cl<sub>2</sub><sup>+</sup>.

The effects of added detergent upon the aquation rates of this compound are shown in Table 4, (part 2). As can be seen from these values, the addition of NaLS produced a marked decrease in the observed first order rate constant, this effect being maximised at a detergent concentration,  $\sim 1.7 \times 10^{-4} \text{ mol. dm}^{-3}$ . Difficulties arising from opalescence (due to colloid formation) occurred at detergent concentrations above or at  $3 \times 10^{-4} \text{ mol. dm}^{-3}$ . A plot of  $k_{\text{OBS}}/k_0$ , (i.e. rate in detergent solution divided by the rate in the absence of detergent) against concentration of NaLS is to be found in Fig. 2, over as wide a concentration range as was possible.

Addition of CTAB to the reaction mixture produced only small rate-effects, which are summarised in Table 4, (part 3). Again opalescence prevented a larger range of CTAB concentrations being studied.

### - for trans-Coen<sub>2</sub>Cl<sub>2</sub><sup>+</sup>.

Following the observed trend shown by the action of NaLS with the cis-

TABLE 4

First order rate constants, ( $k_{\text{OBS}}$ ) for the aquation of  $\text{cis-Coen}_2\text{Cl}_2^+$  in pure aqueous and aqueous detergent solutions at 308.15 K.

Part 1:-  $[\text{cis-Coen}_2\text{Cl}_2^+] = 3 \times 10^{-3} \text{ mol. dm}^{-3}$

$10^3 [\text{H}^+]/\text{mol. dm}^{-3}$	$10^3 k_{\text{OBS}}/\text{s}^{-1}$	% ERROR
-	0.38	0.4
0.333	0.34	0.7
0.50	0.37	0.5
0.667	0.33	0.5

Part 2:- pH = 6.5,  $[\text{cis-Coen}_2\text{Cl}_2^+] = 3 \times 10^{-3} \text{ mol. dm}^{-3}$

$10^5 [\text{NaLS}]/\text{mol. dm}^{-3}$	$10^4 k_{\text{OBS}}/\text{s}^{-1}$	% ERROR
-	3.6	0.4
3.0	3.3	0.5
6.0	3.4	0.4
9.0	3.4	0.6
11.0	3.0	0.3
13.0	2.8	0.2
15.0	2.5	0.4
17.0	2.2	0.2
18.0	2.8	0.3
19.0	3.3	0.5
20.0	3.2	0.5

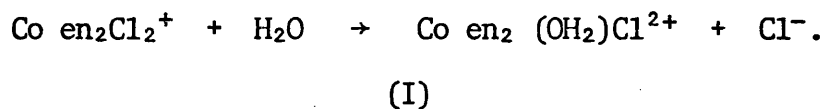
Part 3:- pH = 6.5,  $[\text{Coen}_2\text{Cl}_2^+] = 3 \times 10^{-3} \text{ mol. dm}^{-3}$

$10^4 [\text{CTAB}]/\text{mol. dm}^{-3}$	$10^4 k_{\text{OBS}}/\text{s}^{-1}$	% ERROR
5.0	3.4	0.6
8.0	3.6	0.6
10.0	3.3	0.6
12.0	3.3	0.4
16.0	3.3	0.7
25.0	3.4	0.5
30.0	3.3	0.3

isomer, a similar investigation with the trans-compound was carried out. Unfortunately opalescence was much more widespread, preventing results from being obtained over several NaLS concentration ranges, (i.e. between  $3 \times 10^{-4}$  and  $10^{-3}$  mol. dm $^{-3}$ , and above  $10^{-2}$  mol. dm $^{-3}$  of NaLS). The few results which were obtained are displayed in Table 5. From these results we can see that a rate enhancement, maximising at  $\sim 2.9 \times 10^{-4}$  mol. dm $^{-3}$ , and a corresponding rate retardation, maximising at  $7 \times 10^{-3}$  mol. dm $^{-3}$  are both evident. The difference in rate at these two 'peaks' is  $\sim 70\%$  of the rate in the absence of NaLS. A second set of results, using lower concentrations of the cobalt compound, (monitored at 248 nm) were carried out, enabling kinetic measurements up to a maximum NaLS concentration of  $1.1 \times 10^{-2}$  mol. dm $^{-3}$  to be made. A similar trend to that previously described for the higher concentration was found, the results of this are listed in Table 6.

### Discussion

The kinetics of aquation of cis- and trans-  $\text{Co en}_2\text{Cl}_2^+$  have been well studied in the past.<sup>(330,331)</sup> The rate determination step is the loss of the first chloride, e.g.



The subsequent further reaction of species (I) to give the di-aquo product, (i.e.  $\text{Co en}_2 (\text{OH}_2)_2^{3+}$ ) is much slower.<sup>(332)</sup> Thus the reaction monitored by us is the above first stage of this two-stage reaction, (i.e. the second stage is  $\sim 10^2$  times slower than the first stage and so its contribution towards the rate constants obtained for the first stage can be ignored). Various analyses, (e.g. Grunwald Winstein Y values analysis, ref.

TABLE 5

First order rate constants, ( $k_{\text{OBS}}$ ) for the aquation of  $\text{trans-Coen}_2\text{Cl}_2^+$  in aqueous detergent solutions at 308.15 K.

$$[\text{H}^+] = 10^{-2} \text{ mol. dm}^{-3}, \quad [\text{trans-Coen}_2\text{Cl}_2^+] = 3 \times 10^{-3} \text{ mol. dm}^{-3}$$

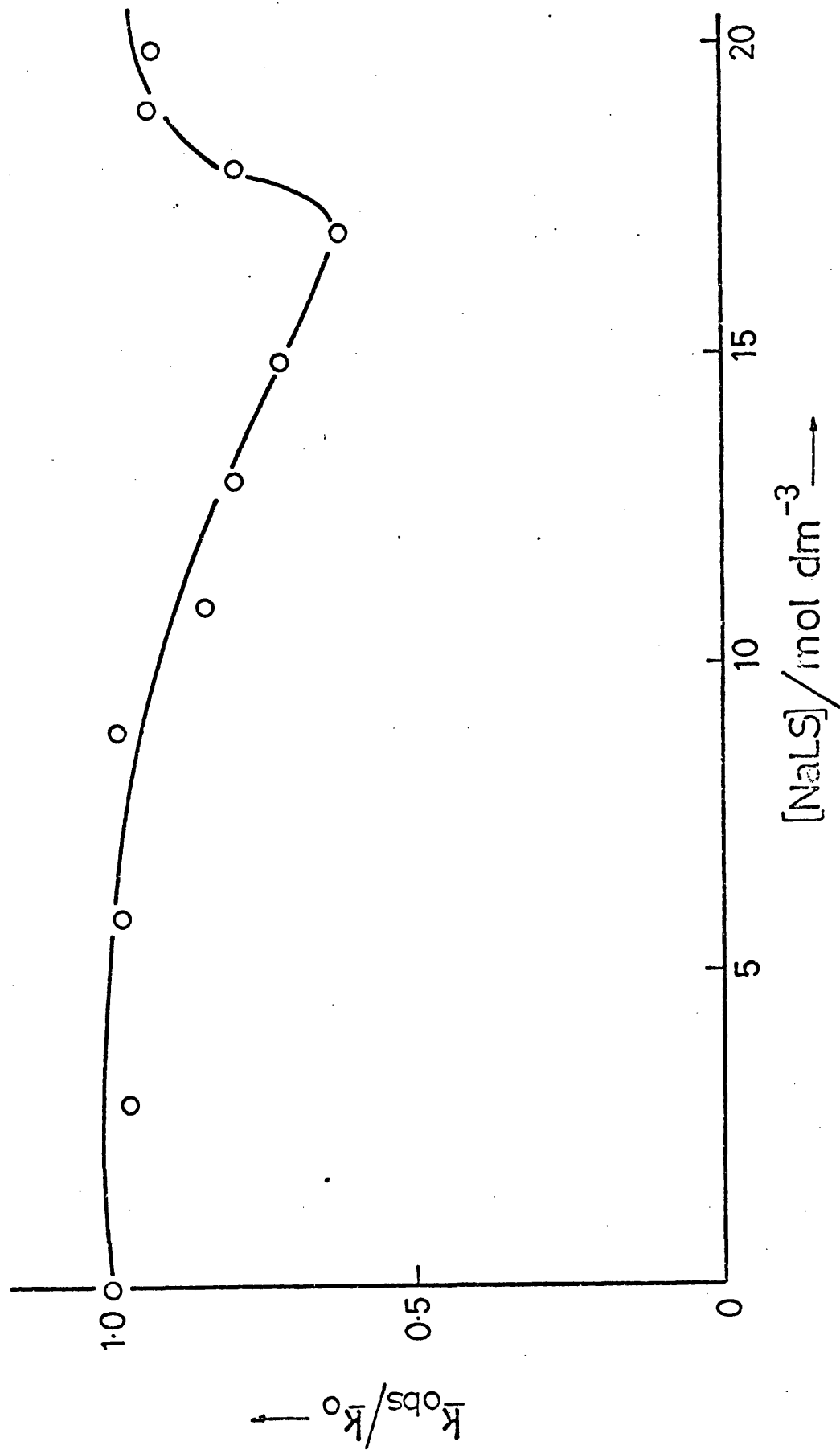
$10^4 [\text{NaLS}]/\text{mol. dm}^{-3}$	$10^4 k_{\text{OBS}}/\text{s}^{-1}$	% ERROR
-	1.55	0.4
0.1	1.44	0.3
0.4	1.45	0.3
0.7	1.45	0.3
1.0	1.65	0.4
2.3	1.47	0.4
2.6	1.59	0.6
2.9	1.76	0.6
(OPALESCENCE)		
10.0	1.50	0.6
40.0	1.36	0.6
70.0	1.05	0.4

TABLE 6

$$[\text{H}^+] = 10^{-2} \text{ mol. dm}^{-3}, \quad [\text{trans-Coen}_2\text{Cl}_2^+] = 10^{-3} \text{ mol. dm}^{-3}$$

$10^3 [\text{NaLS}]/\text{mol. dm}^{-3}$	$10^4 k_{\text{OBS}}/\text{s}^{-1}$	% ERROR
2.0	1.35	0.3
5.0	1.47	0.3
8.0	0.99	0.3
11.0	0.93	0.2

Dependence of the ratios of rate constants for aquation of the  $\text{cis-Coen}_2\text{Cl}_2^+$  cation in the presence and absence of NaLS,  $k_{\text{obs}}/k_0$ , on the concentration of NaLS.





330) applied to these reactions, (1st. stage only) have lead to the conclusion that the mechanism is primarily a dissociative one.

Thus in our investigations, for a decrease in rate to occur, this would seem to imply that the change in stabilisation of the initial state, (by the micelle), is greater than, or in the opposite direction to that for the transition state. [We assume that the stability of the initial state must be improved on interaction with a micelle for this interaction to take place.]

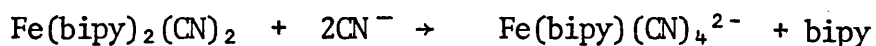
The precipitation described previously may be due to some ion-concentration effect, since in both sets of reactions it was seen to occur at an upper detergent concentration limit. However the trans-isomer also displayed an intermediate concentration range where precipitation occurred. No obvious explanation seems possible for this anomalous behaviour.

The rate profile obtained for the trans-isomer is particularly strange. Stabilisation effects on the initial and transition states seem to be reversed over the range examined, first producing rate enhancements and then rate retardations. A similar rate profile was not found for the cis-isomer. This would seem to highlight the large physical differences that exist between geometric isomers, (assuming that the controlling factors in these reactions are the electrostatic interactions).

Rate variations using CTAB as the added detergent produced only small effects, as expected. The interaction between the positively charged surface and either of the cationic species would seem to be a highly unfavourable one. Thus the observed variations may be solely due to total cell-ionic strength effects, as the concentration of detergent is varied.

Reaction 5

The reaction between cyanide anion and bis-(2,2'-bipyridyl)-dicyano-iron-(II).

Experimental

The iron compound used in this investigation was prepared as is described in the preparative section of Chapter 2 in this thesis. The detergent used in the investigation was a cationic species, (i.e. CTAB) chosen by considerations of ion-micelle interactions. The initial reactions were carried out at an ionic strength, (of potassium cyanide) of 0.01 mol.  $\text{dm}^{-3}$ . The concentration of detergent was varied over the range 0.65 to  $2.0 \times 10^{-2}$  mol.  $\text{dm}^{-3}$ , and the reaction monitored at ~520 nm. An initial (but small) O.D. change was observed in each case, and then no further change was observed. These runs were carried out both at 298.15 K and 308.15 K, both yielding similar O.D. changes.

At this point several different approaches were adopted, based upon one or more of the following assumptions:-

- ( i )  $[\text{CN}^-]$  : [MICELLE] is crucial for the reaction.
- ( ii ) The concentration of the iron compound is too high.
- (iii) The conditions are totally unsuitable for micellar catalysis.

The first of these assumptions stems from observations made by Kurz,<sup>(329)</sup> upon the effects of salts on micellar reagents, where inhibition of catalysis was seen to occur when the concentration of added salt is increased. Thus a set of runs were carried out at lower cyanide concentration, ( $\sim 2 \times 10^{-3}$  mol.  $\text{dm}^{-3}$ ). The results of this experiment were slightly better, (i.e. an O.D. change was noted to occur in a shorter time interval than in the previous reactions), however the total O.D. change was still very small.

The second of the above assumptions derives in part from work done by Morawetz,<sup>(319)</sup> who explained the low yields of product, (in the mercury-(II) catalysed aquation of  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ ) in terms of an inhibition of catalysis by the product. This only applies where one of the reactants has the same charge-type as the product, and they compete with each other for the micellar sites. Since the product of our reaction will be negatively charged, this argument can be seen to apply here. Thus by using a low concentration of the iron-(II) compound, and monitoring in the U.V. end of the spectrum, (i.e. concentration of iron-(II) compound  $10^{-5}$  mol.  $\text{dm}^{-3}$ , monitored at 287 nm), these effects, if they occurred may be avoided.

Unfortunately no improvement on the previous examinations occurred, the total O.D. changes were still very small. From these 'non-results' we conclude that the third assumption must therefore be correct. [N.B. It should be noted however that the check to see if (ii) is occurring was not 100% certain, so it may be that similar circumstances to those found by Morawetz are taking place here also.]

#### Reaction 6

The dissociation of the tris-(5 nitro-1,10 phenanthroline)-iron-(II) cation, in acid solution.<sup>(333)</sup>

As in the case of the previously mentioned cobalt compounds, the mechanism for this reaction is well established. This compound was chosen in the light of the known sensitivity of its aquation rate to solvent environment. The detergent used in this investigation is the negatively charged NaLS.

## Experimental and Results

All of the kinetic investigations were carried out at 298.15 K, and monitored at 510 nm, near an absorption maximum of this compound. The investigation was split up into four sections corresponding to variations in concentration of the different component species:-

Section 1: The concentration of the detergent was fixed at  $7 \times 10^{-3}$  mol. dm<sup>-3</sup>, (approximately the value of the c.m.c. reported for this detergent, <sup>(328)</sup>), and the concentration of added acid, (sulphuric acid was used in all runs) varied. These results, shown in Table 7, display only small changes in the reaction rate as the acid concentration is varied, (as is found in pure aqueous solution).

Section 2: The concentration of acid was kept constant and the detergent concentration varied in these runs. The results are also to be found in Table 7. Again only small variations in the reaction rates were observed, although the overall values were slightly larger than those obtained previously.

Section 3: In this section, the concentration of the iron-(II) complex ion was varied while the concentration of the other species were kept constant. These results can be found in Table 7.

Section 4: This, the final investigation employed CTAB as the micellar additive, the acid concentration being kept constant, at 1.37 mol. dm<sup>-3</sup>. These results are also listed in Table 7.

## Discussion

The dissociation of the tris-(5 nitro-1,10 phenanthroline)-iron-(II) cation in aqueous solutions has been intensively studied by other workers. <sup>(331,334)</sup> The rate determining step is the loss of one of the

TABLE 7

First order rate constants, ( $k_{\text{OBS}}$ ) for the aquation of  $\text{Fe}(\text{5NO}_2\text{-phen})_3^{2+}$  in acidic aqueous detergent solutions at 298.15 K.

Set 1:-  $[\text{Fe}(\text{5NO}_2\text{-phen})_3^{2+}] = 10^{-4} \text{ mol. dm}^{-3}$ ,  $[\text{NaLS}] = 7 \times 10^{-3} \text{ mol. dm}^{-3}$

$[\text{H}^+]/\text{mol. dm}^{-3}$	$10^3 k_{\text{OBS}}/\text{s}^{-1}$	'INFINITY' <sup>a</sup> (O.D.)
0.14	0.56	0.1
0.27	0.59	0.05
0.41	0.64	0.09
0.55	0.57	0.04
0.68	0.58	0.06
0.96	0.57	0.05
1.10	0.54	0.03

Set 2:-  $[\text{Fe}(\text{5NO}_2\text{-phen})_3^{2+}] = 10^{-4} \text{ mol. dm}^{-3}$   $[\text{H}^+] = 0.68 \text{ mol. dm}^{-3}$

$10^3 [\text{NaLS}]/\text{mol. dm}^{-3}$	$10^3 k_{\text{OBS}}/\text{s}^{-1}$	'INFINITY' <sup>a</sup> (O.D.)
0.47	0.67	0.09
0.70	0.70	0.105
0.93	0.66	0.089
1.40	0.66	0.087
1.87	0.62	0.068
2.33	0.62	0.055
3.50	0.59	0.055

[ <sup>a</sup> These infinity-values were measured; a guessed-infinity computer program was not used.]

Continued

TABLE 7 (Continued)

Set 3:-  $[\text{NaLS}] = 1.17 \times 10^{-3} \text{ mol. dm}^{-3}$ ,  $[\text{H}^+] = 0.68 \text{ mol. dm}^{-3}$

$10^5 [\text{Fe}(\text{5NO}_2\text{-phen})_3^{2+}]$ /mol. $\text{dm}^{-3}$	$10^3 k_{\text{OBS}}/\text{s}^{-1}$	'INFINITY' (O.D.)
2.67	0.52	0.039
3.33	0.52	0.040
5.0	0.64	0.114
6.67	0.70	0.224

Set 4:-  $[\text{Fe}(\text{5NO}_2\text{-phen})_3^{2+}] = 10^{-4} \text{ mol. dm}^{-3}$ ,  $[\text{H}^+] = 1.3 \text{ mol. dm}^{-3}$

$10^3 [\text{CTAB}]/\text{mol. dm}^{-3}$	$10^3 k_{\text{OBS}}/\text{s}^{-1}$	'INFINITY' (O.D.)
2.0	0.47	0.02
4.0	0.48	0.025
6.0	0.48	0.027
8.0	0.48	0.026
10.0	0.47	0.037
13.0	0.47	0.049
16.0	0.47	0.043

ligands, followed by protonation, (for details see Chapter 1). Although the reaction is independent of hydrogen ion concentration, a limiting concentration does occur below which the reaction does not go to completion, but instead equilibrates.<sup>(334)</sup>

The only interesting feature of our results is that the reaction seems to go to completion at much lower hydrogen ion concentrations than are found in the corresponding detergent free systems, (i.e. as low as  $0.2773 \text{ mol. dm}^{-3}$ ). In fact a trend in the infinity values with detergent concentration can be seen to occur in Table 7. However the initial rates, (primarily made up of  $k_f$ , the rate for the forward reaction) do not seem to vary, thus these effects in the equilibrium position would seem to reflect a similar change in the fourth order rate constant,<sup>(334)</sup> for the formation of the complex ion.

Note:-

As a result of the above set of investigations we decided that a larger effect might be produced if we replaced the 5 nitro-substituents by 3 sulphonato-groups ( $\text{SO}_3^-$ ). These were expected to interact to a greater extent with the hydrophilic surface of the micelles, (CTAB in this case) by virtue of the negative charges associated with these substituents. Preliminary investigations however showed only a small effect;\* presumably these groups are so hydrophilic that they are surrounded by water molecules and thus ignore the micelle surfaces.

[\* both CTAB and NaLS were used, the total difference in the rates between these two being 12%.]

## CHAPTER 4



Title: An investigation into organic peroxide attack on some transition metal compounds.

## Introduction

The following work is concerned with the decomposition of compounds with the general formula,  $M(CO)_4(LL)$ , .. (where  $M = Cr, Mo, W$ , and  $LL = bipy$  or  $phen$ ) when dissolved in some common organic solvents. These reactions were discovered accidentally while monitoring the solvatochromic properties of these compounds in various organic solvents, (this work is more fully described in Chapter 2 of this thesis). The visible absorption peak, ( 500 nm) of the compound,  $Cr(CO)_4(bipy)$  was found to decrease in height, (absorbance) when dissolved in several different organic solvents, (mainly ethers). This prompted us to perform the investigation outlined in this Chapter, where the solvents examined were all organic ethers.

The sensitivity of these organo-metallic compounds to the apparently common component of organic ethers is not only interesting in itself, but also if one considers that much work, (both kinetic and preparative chemistry) has and still is being done in these and other related solvents. <sup>(401,402,403)</sup>

The following study is in three parts, the first dealing with the identity of the attacking species, the second, a kinetic study of the reactions, and finally an analysis of the product species formed.

## Experimental:

All compounds were prepared and purified as described by Stiddard. <sup>(404)</sup>

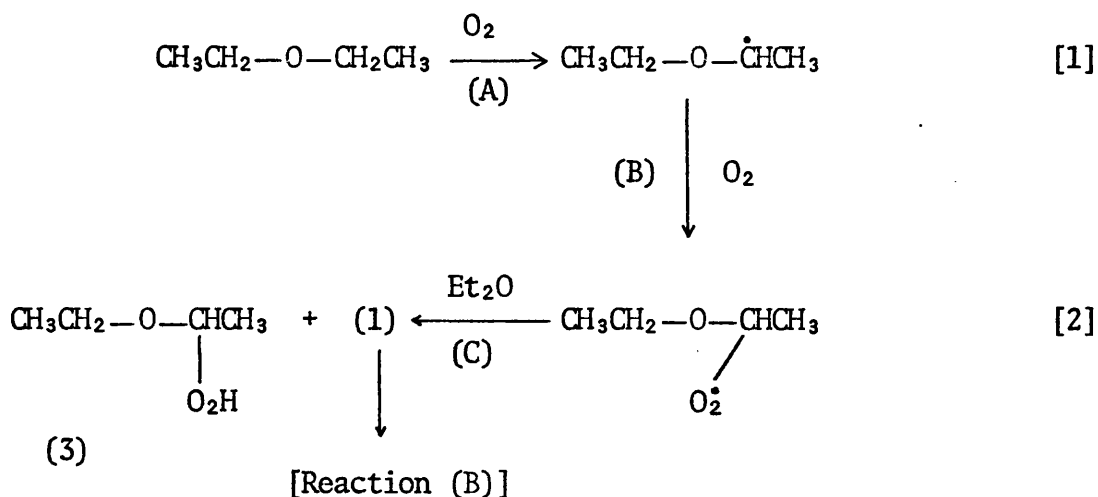
### Section 1: Identification of the attacking species.

In the light of the fact that many organic compounds undergo autoxida-

tion, (i.e. the slow oxidation of an organic compound by oxygen; the term slow meaning not accompanied by a flame) and that such a process occurs readily in ethers, it seemed most probable that our 'active-species' were autoxidation products. To be able to analyse for the presence of these compounds, we must first understand a little about the process of their formation. Fortunately, there are only two distinctly different mechanisms available for the autoxidation of organic ethers, and each of these is directly related to a particular structural type.

The ethers used initially in our investigation, (i.e. diethyl ether, 1,2 dimethoxy-ethane, and 1,4-dioxan) all possess one or more  $\alpha$ -hydrogen atoms, (adjacent to the oxygen). For this type of ether the following autoxidation route is generally applicable, (shown here for diethyl ether).

First of all, the labile  $\alpha$ -hydrogen atom is abstracted by molecular oxygen to give a radical species, (1). Further reaction with molecular oxygen then produces an oxy-radical via reaction (B) which then reacts with another ether molecule to produce a hydroperoxide, (3), e.g:-



As we can see, this is a chain reaction, species (1) once formed initially, propagates itself via reactions (B) and (C). Several other reactions can also occur, mainly producing termination of the radical chain,

e.g:

- (a) 2 x SPECIES (2)  $\longrightarrow$  NON-RADICAL PRODUCT.  
 (b) SPECIES (1) + SPECIES (2)  $\longrightarrow$  NON-RADICAL PRODUCT.  
 (c) 2 x SPECIES (1)  $\longrightarrow$  NON-RADICAL PRODUCT.

The relative importance of reactions (a), (b) and (c) depends upon the concentration of molecular oxygen in the system. However, the main product is the hydroperoxide, (i.e. species (3)). Although we cannot be certain that the hydroperoxide is the species responsible for our reaction, it would seem to be the most likely candidate, since it is the sole 'stable' product formed on a measurable scale. However, our main concern was not which of the species was responsible for our reaction, but how to remove them from the parent ether. This in fact was found to be a simple task, requiring us only to make up a slurry of activated alumina,<sup>(405)</sup> with the ether. This mixture is then made up into a column,<sup>†</sup> and the ether passed through this several times. When diethyl ether was treated thus, and a quantity of (2,2'-bipyridyl)-tetracarbonyl-tungsten-(0) added, no change in the visible absorption spectrum of this compound was observed over a lengthy period. [N.B. A sample of untreated ether produced an observable spectral change over several hours.] Similarly, if fresh sodium-dried diethyl ether, (in which no reaction was observed) is irradiated with a U.V. lamp while being aerated, and then a portion of the previous compound added to this, a spectral change is then observed over a relatively short period.

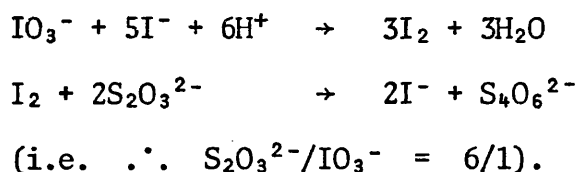
These experiments seem to establish unequivocally that the afore-

[<sup>†</sup> This method both removes peroxides and dries the ether simultaneously, however it should be noted that, where the concentration of peroxide is high, this may result in an explosion if the column is allowed to dry-out. To prevent this, the column, (after use) should be washed thoroughly with a 2% solution of iron-(II) sulphate.]

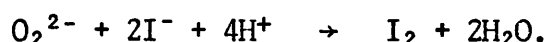
mentioned autoxidation products alone are responsible for the observed reactions. The next step would seem to be to find a method of measuring the concentration of these peroxide species in any particular sample of ether, (i.e. the concentration of peroxide species depends not only upon the chemical properties of the ether, but also upon other factors such as the length and conditions of storage). The following method was employed by us to calculate the concentration of 'oxidising-species' present in any ether. [N.B. It was assumed that no other naturally-occurring oxidising-species other than those produced by autoxidation would be present.]

Method<sup>(406)</sup>:-

Sodium thiosulphate was first standardised using a known weight of potassium iodate along with a quantity of acidified potassium iodide solution. The ratio of thiosulphate anion to iodate anion can be calculated from the combined equations:-



To the ether whose peroxide concentration was required, was added a portion of acidified potassium iodide, ( if the ether was immiscible with water, this mixture was mechanically shaken for 1 hour) and the resulting solution shaken until the dark brown colour of iodine had fully developed, e.g:-



This solution was then titrated against the standard thiosulphate solution using a starch indicator, (added close to the end point to produce

a sharp colour change). [N.B. If the above mentioned brown colour is not allowed to fully develop, inaccurate results will be obtained. Thus the solution under test was usually warmed slightly to speed up this reaction, and also, after titration, left to stand to see if any further colouring occurred.]

Results obtained via this method for several common organic ethers, taken directly from their bottles without further purification, are tabulated here:-

COMPOUND	CONCENTRATION OF OXIDISING SPECIES, (mol. dm <sup>-3</sup> ).
Diethyl ether	0.00173
Sodium dried diethyl ether	0.0
1,2 dimethoxy-ethane	0.01
1,4 dioxan	0.30

Although it is common practice to store diethyl ether over sodium, this is not the case for many other ethers, hence exceptionally high peroxide concentrations may be expected to occur in these cases. From the above results along with observations made during this work, the tendency for peroxide formation to occur decreases in the following order:-

1,4 dioxan > tetrahydrofuran > 1,2 dimethoxy-ethane > diethyl ether.

Thus large amounts of peroxide will be formed over a relatively short period, ( 1 day even when stored in a dark-glass bottle) in 1,4 dioxan whereas only small amounts will accumulate in diethyl ether over a similar time. This pattern is obviously a reflection upon the stability of both the parent ethers and their radical off-spring, (i.e. since the rate determining step is the  $\alpha$ -hydrogen abstraction, this will be facilitated by the presence of adjacent electron donating groups).

The following kinetic examination illuminates the dangers of using non-purified, (or even in the case of 1,4 dioxan, purified solvent after several hours aging) organic ethers (and other solvents) as solvents for organo-metallic compounds.

## Section 2: (Kinetics)

As predicted by the relative abundances of 'oxidising-species' listed in the previous table, the rate of reaction of the (2,2'-bipyridyl)-tetra-carbonyl-chromium-(0) increased with increase in peroxide content. The reaction rate in diethyl ether was found to be very slow even after this solvent had been exposed to U.V. radiation for a prolonged period of time. Thus a set of runs were carried out using the next ether in the series, (i.e. 1,2 dimethoxy-ethane) and the kinetic results along with the concentration of 'oxidising-species' are listed in Table 1, part (a). Precipitation was noted to occur after all of these runs, upon standing for an hour or two. Values obtained for this complex in 1,4 dioxan were of the same order, (i.e.  $\sim 10^{-3} \text{ s}^{-1}$ ), however the rate of dissolution was comparable to the rate of reaction, thus preventing accurate results from being obtained. To overcome this, several runs were attempted in mixtures of dimethyl sulphoxide/dioxan and also methyl cyanide/dioxan, (i.e. chosen because of the increased solubility of the compound in these pure solvents). Unfortunately, the former of these mixtures gave non-homogeneous solutions and in the latter, an induction period was observed; the results obtained are displayed in Table 1, part (b).

As a result of these problems, we decided to concentrate upon reactions involving the (kinetically speaking) well-behaved 1,2 dimethoxy-ethane. Several samples of this solvent, each containing a different quantity of 'oxidising-species' were available, so one of these was arbitrarily chosen

TABLE 1

First order rate constants ( $k_{\text{OBS}}$ ) for the reaction between the compound  $\text{Cr}(\text{CO})_4(\text{bipy})$  and 'oxidising species' in, (a) 1,2 dimethoxy-ethane, and (b) 1,4 dioxan-organic solvent mixtures, at 299.1 K and 298.8 K respectively.

$$[\text{Cr}(\text{CO})_4(\text{bipy})] = 2.8 \times 10^{-4} \text{ mol. dm}^{-3}$$

(a)

$10^2$ [oxidising species] /mol. $\text{dm}^{-3}$	$10^3 k_{\text{OBS}}/\text{s}^{-1}$
0.562	2.2
0.810	2.8
1.060	4.0

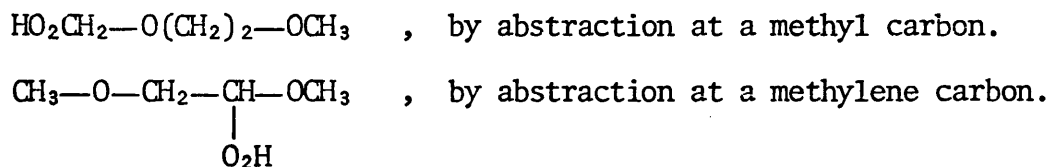
(b) The dioxan 'oxidising species' concentration was maintained at  $0.30 \text{ mol. dm}^{-3}$  in all runs.

Mixture ratio by volume	Induction period /s	$10^2 k_{\text{OBS}}/\text{s}^{-1}$	% error
$\text{CH}_3\text{CN}/\text{DIOXAN}$			
29:1	144	1.2	1.14
29:1	160	1.4	0.98
$\text{DMSO}/\text{DIOXAN}$			
12:1	-	1.5	0.92

to obtain some activation parameters for this reaction. [N.B. Explanation of Activation parameters can be found in the latter part of the Appendix.] Applying the Arrhenius equation to our results enabled us to calculate the energy of activation, and thence the enthalpy and entropy of activations for the reaction. All of these results are to be found in Table 2.

### Discussion

As has been previously pointed out, the hydroperoxide species is the sole stable autoxidation product in ethers possessing  $\alpha$ -hydrogen atoms. Thus it would seem reasonable to assume that it is either this species, or its breakdown products which are responsible for our reaction. Unfortunately, because this species is the product of an asymmetric ether, two different hydroperoxides may be formed, (i.e.  $\alpha$ -hydrogen abstraction may occur either at one of the methyls of the methoxy-group or at one of the methylene groups), e.g:-



The relative concentration of these two species will obviously depend upon the strengths of the original  $\alpha\text{C}-\text{H}$  bonds and also upon the stabilities of the initial carbon radicals formed, as outlined earlier. Although this will produce problems in product analysis it does not necessarily detract from the kinetic results. This statement is clarified when one considers that, it is only the 'oxidising' power of the peroxide species, (i.e.  $\text{R}-\text{O}_2\text{H}$ ) which is presumably responsible for the reaction. Thus small variations in the nature of the R-group would be expected to have little effect on the kinetic results.



TABLE 2

Variation in first order rate constants ( $k_{\text{OBS}}$ ) with temperature for the reaction between the compound  $\text{Cr}(\text{CO})_4(\text{bipy})$  and 'oxidising species' present in 1,2 dimethoxy-ethane, along with associated Activation parameters derived from these results.

$$[\text{Cr}(\text{CO})_4(\text{bipy})] = 2.8 \times 10^{-4} \text{ mol. dm}^{-3}$$

Temperature/K	$10^2 k_{\text{OBS}}/\text{s}^{-1}$
288.6	0.247
304.0	0.425
308.7	0.596
309.7	0.62
313.7	0.833
318.6	1.43

Activation parameters:-  $E_{\text{A}} = 16.05 \pm 0.62 \text{ kcal. mol}^{-1}$

$$\text{A-factor} = 10^{\dagger} (9.13 \pm 0.44) \text{ dm}^3 \cdot \text{mol. s}^{-1}$$

$$\Delta H^{\ddagger} = 15.45 \text{ kcal. mol}^{-1}$$

$$\Delta S^{\ddagger} = -18.82 \text{ cal. mol}^{-1} \text{ }^{\circ}\text{K}^{-1}.$$

The rate constants obtained in the solvent 1,2 dimethoxy-ethane have been compared with similar results obtained from the reaction between organo-phosphites and our compound along with the analogous phenanthroline adduct of chromium-(0).<sup>(407,408)</sup> The rate constants obtained by us<sup>†</sup> are ~ 100 times greater than the analogous values cited in these references. This fact, along with the observation that the half life of our reaction is much smaller than in any of these substitution reactions, (i.e. substitution by attack at the central metal ion) seems to indicate a different mechanism to be operating here, (e.g. attack at a co-ordinated ligand). A comparison of activation parameters with some literature values for organo-phosphite attack at similar compounds, (i.e. refs. 407-410 inclusive) showed our  $\Delta H^\ddagger$  to be smaller, (i.e. 15.45 kcal cf. 33 kcal. mol<sup>-1</sup>) than that for the corresponding associative reaction between a phosphite and one of the above compounds. The value of  $\Delta S^\ddagger$  for our reaction was negative in sign, and lay within the range found for the previously mentioned phosphite reactions.

A comparison for some common organic radical-compound reactions showed  $\Delta S^\ddagger$  for our reaction to be similar to values obtained for the reaction of an organic compound with either an alkyl, alkoxy or an alkyl-peroxy radical species.<sup>(411,412)</sup> This would again seem to give support to the theory that our reaction involves attack at a co-ordinated ligand, (i.e. in this case, an organic ligand).

In an attempt to overcome some of the difficulties encountered with 1,2 dimethoxy-ethane, (i.e. the possibility of two active species and the problems ensuing from this) a symmetrical stable peroxide was obtained, i.e.

[ <sup>†</sup> Our values were first converted to  $k_2$ 's by division by the concentration of oxidising species; also, our values were much larger than the  $k_1$  values listed.]

### Di-tert-butyl peroxide (DTBP)

Unlike the peroxide and hydroperoxide species so far encountered, this compound is quite stable, and is obtainable 'neat', making concentration and handling into straightforward procedures.

### Experimental and Results:-

The reaction using either the chromium or tungsten compounds, (i.e.  $M(CO)_4(bipy)$ ) in pure DTBP was very fast, preventing rate constants from being obtained by conventional techniques. To counteract this, DTBP was diluted with fresh xylene, (with which the peroxide was immediately miscible and in which the inorganic compounds were soluble) and kinetic data obtained for these mixtures. Several problems occurred during this investigation, the first being due to precipitation towards the end of each kinetic run, hence a 'guessed-infinity' routine was made necessary. [N.B. See Appendix for details of this and other computer programs.] The second, and most distressing problem was not discovered until a plot of the results was drawn, (i.e. Figure 1). This plot displayed a non-zero intercept at zero peroxide concentration. This was subsequently found to be a reaction with oxygenated xylene, since when this solvent was de-oxygenated, no reaction was evident. The value of the intercept extrapolated from the plot showed good agreement with the result obtained kinetically. The kinetic results along with the concentration of DTBP for both the chromium and tungsten adducts containing bipy and phen respectively are to be found in Tables 3 and 4, part (a). The results obtained for 'neat' xylene are displayed in Table 4, part (b). Plots of the rate constant, ( $k_{OBS}$ ) against peroxide concentration have also been drawn, labelled Figures 1 and 2, for the chromium and tungsten compounds, (i.e.  $Cr(CO)_4(bipy)$ ,  $W(CO)_4(phen)$ ).

FIGURE 1

A plot of the observed first order rate constants ( $k_{\text{OBS}}$ ) for the attack of oxidising species on the compound  $\text{Cr}(\text{CO})_4(\text{bipy})$  against concentration of DTBP in DTBP-xylene mixtures at 313.2 K and 298.2 K.

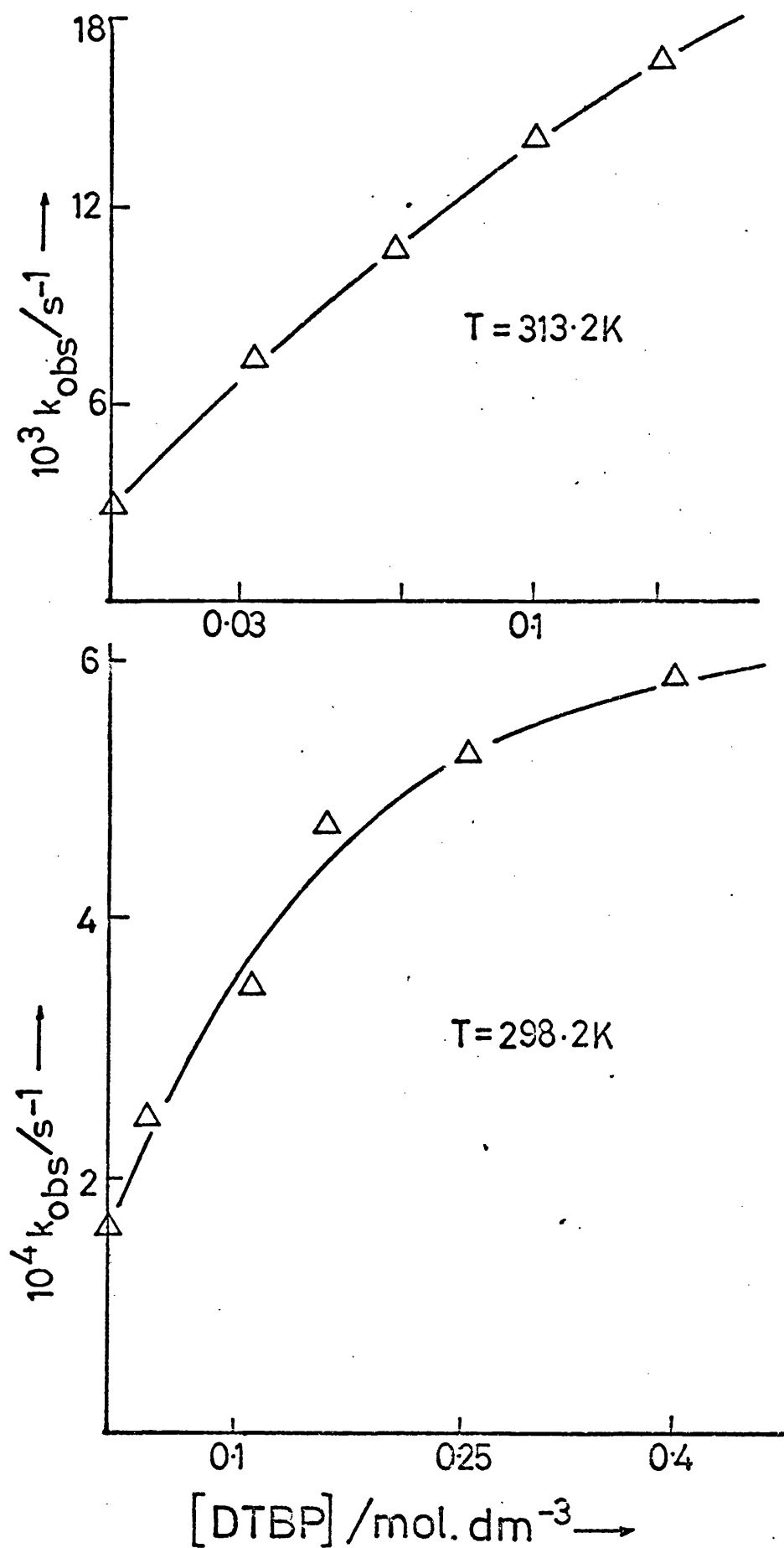


TABLE 3

Variation in first order rate constants ( $k_{\text{OBS}}$ ) with concentration of DTBP for the reaction of  $\text{Cr}(\text{CO})_4(\text{bipy})$  with DTBP in DTBP-xylene mixtures; at 298.2 K and 313.2 K.

$$[\text{Cr}(\text{CO})_4(\text{bipy})] = 2.8 \times 10^{-4} \text{ mol. dm}^{-3}$$

(T = 298.2 K)

[DTBP] mol. dm <sup>-3</sup>	10 <sup>4</sup> $k_{\text{OBS}}/\text{s}^{-1}$
-	1.65 <sup>a</sup>
0.181	2.45
0.543	3.50
0.907	4.80
1.360	5.30
1.813	5.66

(T = 313.2 K)

[DTBP] mol. dm <sup>-3</sup>	10 <sup>4</sup> $k_{\text{OBS}}/\text{s}^{-1}$
-	2.4 <sup>a</sup>
0.181	7.5
0.360	10.8
0.543	14.4
0.720	17.0

[ <sup>a</sup> Reaction in pure xylene]

TABLE 4

Variation in first order rate constants ( $k_{\text{OBS}}$ ) with concentration of DTBP for the reaction of the compound  $\text{W}(\text{CO})_4(\text{phen})$  in DTBP-xylene mixtures, (a); along with rate constants for the reaction between compounds of the type  $\text{M}(\text{CO})_4(\text{LL})$  with fresh (oxygenated) xylene, (b).

(a)  $T = 308.2 \text{ K}$ ,  $[\text{W}(\text{CO})_4(\text{phen})] = 2.8 \times 10^{-4} \text{ mol. dm}^{-3}$

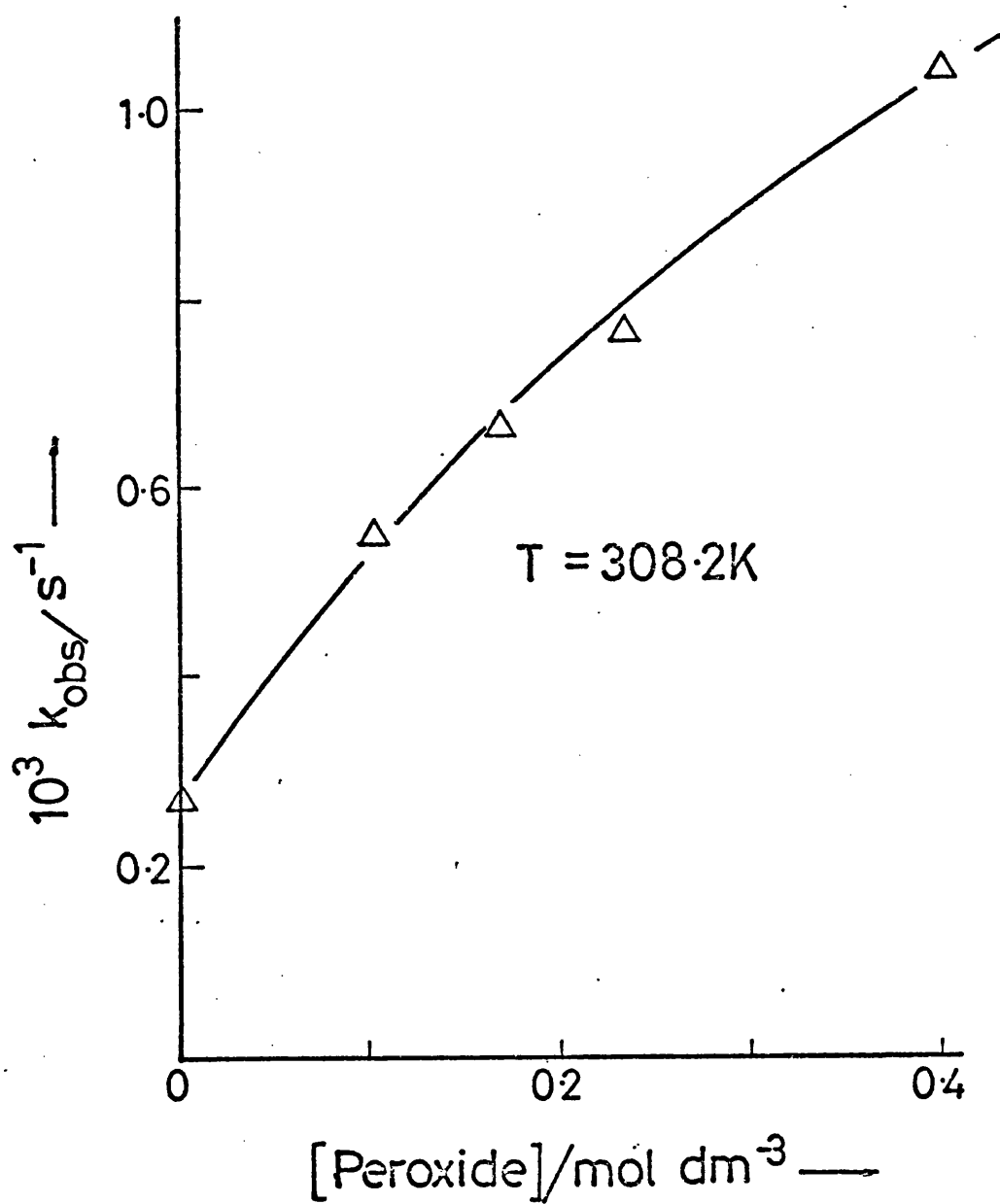
[DTBP] $\text{mol. dm}^{-3}$	$10^4 k_{\text{OBS}}/\text{s}^{-1}$
-	3.00
0.10	5.50
0.167	6.75
0.233	7.70
0.4	10.40

(b)  $T = 313.2 \text{ K}$ ,  $[\text{M}(\text{CO})_4(\text{LL})] = 2.8 \times 10^{-4} \text{ mol. dm}^{-3}$

COMPOUND	$10^4 k_{\text{OBS}}/\text{s}^{-1}$
$\text{Cr}(\text{CO})_4(\text{bipy})$	2.4
$\text{W}(\text{CO})_4(\text{bipy})$	3.0
$\text{W}(\text{CO})_4(\text{phen})$	2.8

FIGURE 2

A plot of the observed first order rate constants ( $k_{\text{OBS}}$ ) for the attack of oxidising species on the compound  $\text{W}(\text{CO})_4(\text{phen})$  against the concentration of DTBP in DTBP-xylene mixtures.



Discussion:-

Both the chromium and tungsten compounds were observed to react at similar rates with DTBP. Comparison between the results obtained for the chromium adduct with 1,2 dimethoxy-ethane and with DTBP is difficult, (since in the former case we are concerned with a small concentration of hydroperoxide whereas for DTBP, the active reagent is a radical breakdown product whose concentration is incalculable), however we can say that the rates are of similar magnitude. [N.B. This reagent was selected primarily to aid product analysis, thus a detailed kinetic analysis was not carried out.] The following section of this Chapter is concerned with the product-analysis, both for the 1,2 dimethoxy-ethane and the DTBP reaction.

Section 3: Analysis of reaction products.

The initial reaction studied was between (2,2'-bipyridyl)-tetracarbonyl-chromium-(0) and oxidising species present in 1,2 dimethoxy-ethane. As has previously been pointed out, there are probably two 'active-species' present in this solvent, hence one might expect two products to be formed. However, since these two 'active-species' are chemically similar we assume that the products formed will also be similar. Using this premise, several analytical approaches were followed to try to establish the nature of these products and thence disentangle the reaction mechanism, e.g:-

- (i) Product isolation:- A solution of the chromium compound in 1,2 dimethoxy-ethane was stirred for 24 hours and the resulting precipitate removed by filtration. The remaining solvent displayed a different U.V. spectrum to that of the pure solvent, (i.e. pure solvent gave an absorption at 217 nm, the previous solvent showed a broad band, 290-230 nm). This product-solvent was then tested for free (i.e. unco-ordinated<sup>†</sup>) and oxidised, (i.e. unco-ordinated) bipyridyl by the

[<sup>†</sup> i.e. meaning not co-ordinated to a metal centre.]



following method. Solid iron-(II) ammonium sulphate was added to the solvent and shaken for several minutes. No colour change was noted to occur.<sup>†</sup> However on addition of an aqueous solution of sodium dithionite, an immediate red colour was formed, (i.e.  $\text{Fe}(\text{bipy})_3^{2+}$ ). Thus the product solvent was found to contain un-co-ordinated-bipyridyl, (i.e. in some form or other).

- (ii) Precipitate analysis:- The previous test was carried out on the solid product and in this case gave a negative response, indicating that no contamination by free bipyridyl had occurred. After repeated washing with several organic solvents, (and also water) the insoluble product was dried under vacuo. A melting point performed on this dry sample showed no discernible change, (under a microscope) up to 593 K.

Infra-red spectra of the initial and product species are displayed in Table 5. Comparison of these spectra produced some anomalous results. For instance, the product showed no evidence of any carbonyl bands, (using several mulls) yet in the region associated with Cr—CO bending vibrations,<sup>(413)</sup> several bands are present. Some of these bands may be due, therefore, to bipyridyl, thus introducing the possibility of a dimeric (or even trimeric) product, which would in turn explain the very high melting point, (i.e. greater than 593 K).

Due to the extremely low solubility of this product it was not possible to use N.M.R. techniques in this analysis.

A quantity of material was sent away for analysis, and gave the following results:- Chromium, 18.25%: Hydrogen, 5.3%: Carbon, 35.15%: Nitrogen, 5.7%: Total = 64.4%. Since the only other element present in our reaction

[ <sup>†</sup> This may mean either that the iron-(II) has been oxidised to iron-(III), and/or any bipyridyl present may have been oxidised.]

TABLE 5

Infra-red data expressed in wavenumbers ( $\text{cm}^{-1}$ ) for both reactant and product species used in the analyses.

[KEY: A =  $\text{Cr}(\text{CO})_4(\text{bipy})$ : B = A + 1,2 dimethoxy-ethane: C = A + DTBP:

E =  $\text{W}(\text{CO})_4(\text{bipy})$ : F = E + DTBP.]

[( ) meaning:- s, strong; b, broad; m, medium; w, weak.]

$\bar{\nu}/\text{cm}^{-1}$				
A	B	C	E	F
	3500 (b)	3500 (b)		3400 (b)
1910 (m)			1900 (m)	
1875 (s)			1850 (s)	
1855 (s)			1800 (s,b)	
1800 (m)	1705 (w)	1650 (w)		1650 (w)
1603 (w)	1605 (s)	1600 (s)	1590 (w)	1595 (s)
1460 (b)	1496 (w)			
1440 (m)	1460 (s)			
1430 (w)	1375 (s)			
1310 (w)	1368 (m)			
1280 (m)	1320 (w)	1320 (w)	1315 (w)	
1240 (m)	1248 (w)			
1170 (w)	1196 (w)			
1160 (w)				
1120 (m)	1120 (w)	1110 (w)		1100 (w)
1070 (w)	1060 (m)			
1010 (w)	1036 (m)	1030 (m)	1030 (m)	1030 (w)
970 (m)	1016 (m)			
896 (m)	950-904 (m,b)	920 (b)	935 (s)	950 (s)
760 (m)	805 (w)	810-770 (b,s)	895 (s)	900 (s)
675 (s)	776 (m)		760 (s)	775 (s)
664 (s)	688 (w)			
654 (s)	666 (w)			
580 (s)	536 (w)			
516 (w)				

is oxygen, then our product must contain 35.6% of this element.

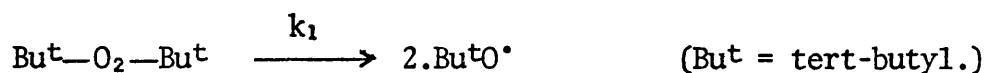
A detailed mathematical analysis of these numbers did not yield any viable molecular formulae. The presence of nitrogen seems to suggest that bipyridyl is present in the molecule, combining this information with the solvent analysis, supports the view that the species is not monomeric. The chromium to nitrogen ratio calculated from the above results is 1:1.16, possibly indicating a dimeric product. However rationalising the above results from this premise is not possible. Thus this analysis was not taken any further.

The second reaction studied was between the compounds,  $M(CO)_4(bipy)$ , (where M = chromium and tungsten) and the radical species present in DTBP.

Before entering into a detailed account of the various analytical methods used on the products of these reactions, a brief departure into the dissociation pathways available for DTBP may prove to be advantageous towards our understanding of the reaction under study. DTBP undergoes slow autoxidation, (i.e. it is a stable species relative to many other organic peroxides) however the initial steps differ from those described previously, (for diethyl ether, etc.) by virtue of the absence of any  $\alpha$ -hydrogen atoms, (i.e. adjacent to the peroxide group). This is also probably responsible for the increased stability of this compound.

The dissociation pathway for the pure liquid is shown here:-<sup>(414,415)</sup>

Initiation, via unimolecular homolytic fission, ( $k_1 = 3 \times 10^{-9} \text{ s}^{-1}$  in benzene; ref. 412):

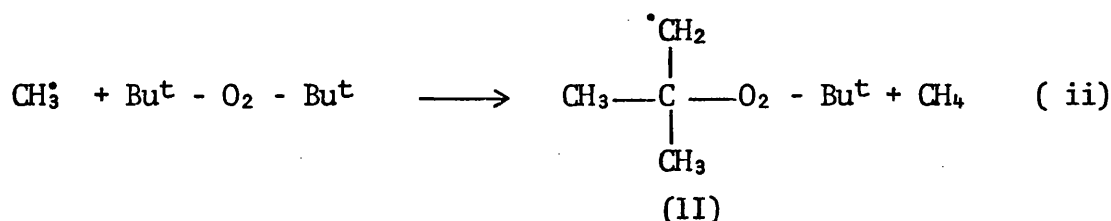
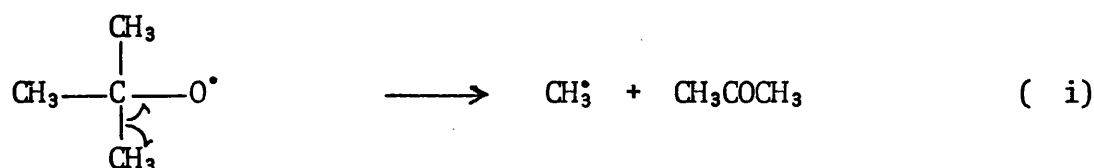


- followed via either of three propagation steps thus,

( i)  $\beta$ -scission producing acetone,

- (ii) hydrogen abstraction with the parent molecule, producing methane,
- (iii) and finally H abstraction as above, via a different radical species.

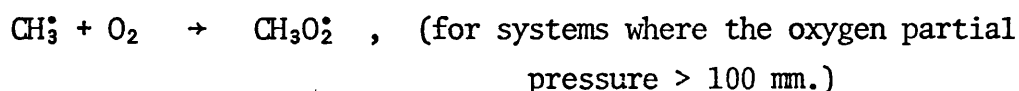
These reactions are shown here:-



The termination steps available are mainly radical recombination, after in one case, (i.e. (II)) an internal radical rearrangement.

From the above treatment, we can see that several radical species are produced, however the most important of these is the methyl radical, (i.e. since all the other radical species are able to undergo rearrangement, in each case giving a methyl radical as the product, and also in terms of reactivity). Thus we appear to be dealing with a methyl radical generator, (DTBP) and so we would expect this species to be the one responsible for the observed reaction (with our compound). Unfortunately, the system is not as straightforward as this. A recent review by Ingold,<sup>(416)</sup> has pointed out that while the previous mechanism is in essence correct, the actual

identity of the active radical species is not so clear-cut. Although methyl radicals are produced as described, unless the solvent has previously been 'purged' of oxygen, rapid addition between the methyl radicals and molecular oxygen will occur, (i.e. the rate of this reaction is diffusion controlled, a reported value for  $k_2 \sim 10^9 \text{ l. mol}^{-1} \cdot \text{s}^{-1}$ .), to give an alkyl-peroxy radical, e.g:-



Hence in our reaction, the rate controlling step probably involves attack of the above peroxy radical upon the substrate. [N.B. It may be that our reaction mixtures contain a mixture of these two types of radicals, but since the solvents were not degassed, this seems unlikely.]

The principal reactions of alkyl peroxy radicals are as follows, (obtained from studies in organic and inorganic systems,<sup>(414)</sup>):- addition to unsaturated systems, hydrogen abstraction, radical displacement, oxygen atom transfer and one electron transfer. From the following section dealing with the product analysis, we may be able to decide which of these reactions is occurring.

Product isolation:- Solutions of the chromium and tungsten compounds,  $\text{M}(\text{CO})_4(\text{bipy})$  were made up in xylene initially, but after examining the analogous kinetic results, the products obtained were discarded, and a second solvent chosen, i.e. 1,2 dichloro-ethane. A two-fold excess of DTBP was added to each of these solutions and after stirring for several hours at 313 K a precipitate was isolated from each mixture. These products were washed with the usual selection of solvents and dried under vacuo. Analysis of the product solvent, (as described previously) for free bipyridyl gave a negative result.

Precipitate analysis:- Neither of these was soluble in any of the wide range of solvents available to us, thus preventing the use of either N.M.R. or U.V. spectroscopy. Melting points of both compounds were found to be greater than 593 K. Infra-red spectra for the reactants and products were obtained for comparative purposes and are to be found in Table 5. The only conclusions to be drawn from these are that there are no carbonyl bands present in the product, and a large broad band ( $3500\text{ cm}^{-1}$ ) is present indicative of either N—H or O—H groups. [N.B. After drying under vacuo at 353 K for 24 hours this band was still present, hence it is not due to water.]

Attempts to use E.S.R. techniques to establish the number of free (unpaired) electrons failed, due to large broad signals being produced, (typical of paramagnetic solids). Also, due to the small amount of product material available, it was not possible to use a Gouy balance for similar investigations.

Finally mass spectra were obtained for both products, and by combining these with analysis results, (supplied by the Butterworth micro-analytical company) it was hoped that the identities of the products might be unveiled. These results are to be found in Table 6. A molecular-ion peak was not found for the tungsten compound, only 'noise' occurring above  $\sim 280$  units, indicating that the two compounds were dissimilar. On examining the analyses, one must sadly come to the same conclusion, the metal:nitrogen ratios being quite dissimilar. The mass peak obtained for the chromium compound indicates a very large molecule to be formed. The absence of a similar peak for the tungsten compound suggests that such a peak, (expected at  $\sim 600$  units by analogy with the chromium compound) may occur possibly at a higher value still. The reason that this was not observed may be due to difficulties in volatilising enough of this material to obtain a good spectrum.

TABLE 6

Analytical data obtained from the Butterworth microanalytical company for the products of the reactions between  $\text{Cr}(\text{CO})_4(\text{bipy})$  and  $\text{W}(\text{CO})_4(\text{bipy})$  with DTBP.

METAL	M	C	N	O	H	TOTAL
Cr	23.8%	34.0%	6.94%	(31.76%) <sup>‡</sup>	3.5 %	100%
Atom Ratio:-	1.0	6.19	1.05	4.4	7.65	
W	46.2%	26.5%	5.4 %	18.75%	1.98%	98.86%
Atom Ratio:-	1.0	8.75	1.54	4.67	7.88	

(<sup>‡</sup> assigned by division from 100%)

MASS SPECTROMETER RESULTS:- <sup>a</sup>

	Cr-compound	W-compound
Molecular ion peak:-	480 ± 20	- (non observed)

[ <sup>a</sup> Further analysis of spectra obtained was carried out, but as this did not yield any positive contributions, the details of this analysis and the two spectra are not described here.]

The only conclusion which can be drawn from the large assemblage of facts is one which can be said to be the 'curse' of radical chemistry, i.e: In any radical reaction the number of individual products obtained is proportional to the amount of effort expended in their investigation, (and is never less than two!).



## CHAPTER 5

Title: An investigation of solvent effects on the Initial and Transition states for the reaction of (2,2'-bipyridyl)-dichloro-platinum-(II) in Aqueous Dioxan and Aqueous Tetrahydrofuran with Thiourea.

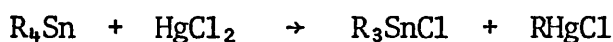
### Introduction

For particular reaction series where a rate variation with solvent is observed, it is not always possible to predict the behaviour solely by considering either solvent effects upon the initial or transition states. It is therefore necessary to take into consideration the relative solvent effects on each of these, and from these make suitable deductions as to the overall effect upon the reaction rate. This type of analysis is made possible by combining knowledge of both kinetic results and reactant solvation, (e.g. via solubility data), and has been attempted by several workers.

Thus examination of the solvolysis of t-butyl chloride in water-rich mixtures,<sup>(501-3)</sup> where values for the transfer parameters,  $\delta_m\Delta H^\ddagger$  and  $\delta_m\Delta S^\ddagger$ , (i.e. transfer from an arbitrarily chosen solvent mixture, usually 100% water to the other water mixtures: See Chapter 1) gave a non-linear dependence when plotted together, at first does not seem to be very helpful. However by use of Henry's law constants for t-butyl chloride it was made possible for the above transfer parameters to be dissected into their component initial and transition state effects, (i.e. this was done for  $\delta_m\Delta G^\ddagger$ ,  $\delta_m\Delta S^\ddagger$  as well as  $\delta_m\Delta H^\ddagger$ ). By doing these calculations, the complexity of the previously mentioned plot is found to be mainly due to solvent effects on the t-butyl chloride initial state, the transition state following a much simpler behaviour similar to that exhibited by uni-valent electrolytes. In other words, for water-rich mixtures, (i.e. water-methanol,

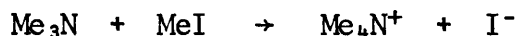
water-ethanol mixtures were used in these investigations) the initial state solvation is extremely important, the transition state solvation effects being much less so.

Similarly, a detailed analysis of reactions of tetra-alkyl tin compounds with mercury-(II) chloride in methanol-water solvent mixtures, <sup>(504)</sup> i.e:



(these reactions proceeding via bimolecular substitution), produced the result that while the entropy of activation term is equally concerned with both the initial and transition states, the enthalpy of activation term is mainly concerned with solvent stabilisation effects in the initial state.

An analogous result has also been found for the Menshutkin reaction of trimethylamine with methyl iodide, <sup>(505)</sup> i.e:



The accelerating effect, (upon the reaction rate) on addition of solvent water to this reaction is entirely due to a large increase in the free energy of the reactants. A similar reaction involving trimethylamine with p-nitro-benzyl chloride could only be understood in terms of the opposite or intermediate control. The variation in free energy of the transition state is generally larger than the corresponding free energies of the reactants. <sup>(505)</sup>

Examples of a reaction where the transition state solvation effects are of major importance is typified by the demetallation of tetra-alkyl lead compounds with iodine, <sup>(506)</sup> where again both initial and transition state effects are of comparable importance to reactivity trends. The previous reference contained extensive studies of these effects pertaining to both  $S_N$  and  $S_E$  reactions at saturated carbon atoms in a vast range of solvents. By use of a suitable model ion-pair this worker was also able to

estimate the charge separation in the transition state for some of these reactions, (i.e. provided the transition state is electrically neutral).

In this Chapter we will be aiming at extending this type of analysis of solvent effects to cover a transition metal compound reaction. Unfortunately, increased difficulties are often encountered when trying to apply such an analysis to inorganic systems by virtue of the presence of charged species. Thus one often has to face the problem of estimating the individual solvation characteristics of single ion species. There are several ways to avoid this necessary evil. One of these, used in the past by other workers, is to examine the differences between the reactivity trends for two or more similar complexes of identical charge. This has been done for the aquation of the substituted tris-1,10 phenanthroline complexes,  $\text{Fe}(\text{5NO}_2\text{-phen})_3^{2+}$  and  $\text{Fe}(\text{4,7 diMe-phen})_3^{2+}$  in water-t-butyl alcohol mixtures.<sup>(507)</sup> Although this type of analysis is more qualitative, (i.e. single ion values of activation parameters are avoided) it was still possible to make some tacit assumptions about the relative solvation effects of the two states, particularly by reference to work concerning the actual solvent structure.<sup>(508)</sup>

If one must study a single reaction it would obviously be beneficial to be able to obtain estimates of the previously mentioned single ion parameters. In some cases it is possible, by skilful use of available thermodynamic data, pertaining to solvation to obtain these values. However, the accuracy of these numbers depends to a large extent upon the circumstances from which they are extracted. This approach has been used previously by ourselves,<sup>(509)</sup> for the reaction between the  $\text{Fe}(\text{bipy})_3^{2+}$  cation and cyanide anion in several series of mixed aqueous solvents, (i.e. see Chapter 1 of this thesis), with moderate success. As is explained in the relevant Chapter, solvation effects at the larger iron-(II) cation were expected to

be very small in comparison with similar effects at the smaller cyanide anion, (i.e. relative changes in solvation). This expectation has been borne out by the small rate variations in the dissociative aquation of iron-(II) complexes with solvent composition, (509, and also in Chapter 1, 510).

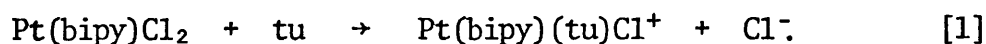
As can be seen from the 'thermodynamics' section in Chapter 1, several assumptions were necessary before breakdown of the initial state into its component ion-solvent parameters was possible. This is obviously the weak link in this type of approach, since if data are sparse this leads to bigger and bigger assumptions, and hence the likelihood of good agreement is decreased.

An analogous attempt to break down the individual solvent effects of the reactant species has been done for the reaction of  $\text{Re}(\text{CO})_5\text{I}$  with cyanide ion.<sup>(512)</sup> In principal this approach should be easier to apply here, since one of the reactants is a neutral species. However, separation into initial and transition state contributions for this reaction foundered on the large uncertainties in the chemical potentials of the cyanide ion in the organic-rich solvent mixtures in which the kinetics could be monitored, (i.e. dictated by solubility).

From the previous two paragraphs we can see that an ideal transition-metal complex system will be one which contains no ionic species. Thus a reaction of this type, featuring an uncharged compound with an uncharged ligand in which both of these species are soluble in a suitable range of solvents or solvent mixtures would allow us to avoid the type of assumption necessary to the previous studies. By obtaining both kinetics and solubilities, (or other sources of information concerning the dependence of chemical potential on solvent composition) measured over a suitable range of solvent mixtures, it becomes a relatively easy task to separate

out the previously described initial and transition state contributions.

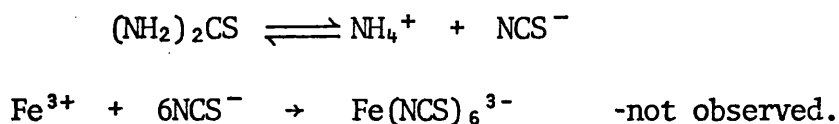
Sources of such reactions as described above are obviously rare. It would seem however that the area of chemistry concerning platinum in a +2 oxidation state contains several neutral compounds. One of these,  $\text{Pt}(\text{bipy})\text{Cl}_2$  was chosen by us for the study presented here. Initial attempts to use the analogous compound,  $\text{Pt}(\text{pty})_2\text{Cl}_2$  were hindered due to kinetic and solubility difficulties.<sup>†</sup> The neutral ligand used by us was thiourea,  $(\text{NH}_2)_2\text{CS}$ , and the initial replacement of a chloride ion by this ligand is the reaction which we have obtained results for, i.e:



(i.e.  $\text{tu} = \text{thiourea}$ )

### Experimental

The compounds dichloro-dipyridyl-platinum-(II) and (2,2'-bipyridyl)-dichloro-platinum-(II) were prepared as described in the relevant literature.<sup>(513,514)</sup> Because the possibility of an equilibrium between thiourea and ammonium thiocyanate occurring cannot be completely ignored, the following test was used. A solution (aqueous) of thiourea and iron-(III) sulphate was made up and thermostatted at 298 K for several days. Over this period, no colour change was observed, thus equilibration followed by subsequent formation of  $\text{Fe}(\text{SCN})_6^{3-}$  did not occur, i.e:



[<sup>†</sup> The extinction coefficient for this compound is much less than that for the corresponding bipy adduct, thus to obtain a reasonable change in optical density in a reaction, a relatively large concentration of this compound is needed. Thus solubility difficulties occurred in some solvent mixtures.]

The thiourea absorption bands were in the range 280-220 nm, thus it was necessary to monitor the reaction at wavelengths outside this range. As the  $\text{Pt}(\text{bipy})\text{Cl}_2$  compound possesses several absorption bands,<sup>(515)</sup> this did not represent any grave difficulties. Solubilities of this compound were determined by equilibrating an excess of this compound with solvent mixtures of appropriate composition. After filtration of these, the concentrations were estimated spectrophotometrically by monitoring optical densities at 310 and 380 nm.

Kinetic runs were carried out in 10mm silica cells in the thermostatted cell compartment of a Unicam SP800A recording spectrophotometer. [N.B. Both co-solvents were screened for peroxides, which were removed as described in Chapter 4, and care taken to prevent their re-formation.]

## Results

Kinetics:- All runs were conducted with thiourea in large excess, under which conditions first-order kinetics were obeyed over at least three half-lives. Subsequent reaction between the product of reaction [1] and thiourea was not observed, indicating that it is very slow. In all solvent mixtures, an isosbestic point was seen to occur at  $\sim 360$  nm, which persisted throughout each reaction, (hence the previously mentioned second stage does not occur to any significant extent over several half-lives of the first stage). The rate constants obtained were computed (using Program 8 in the Appendix) from absorbance changes at 310 and 380 nm, corresponding to the appearance of the product and disappearance of the starting compound respectively. For a given run, identical rate constants were obtained from absorbance changes at the two wavelengths.

The computed first order rate constants,  $k_{\text{OBS}}$ , for the reaction in

water + tetrahydrofuran mixtures at 298.2 K are displayed in Table 1. These values are consistent with the usual two-term rate law for substitution at square planar compounds, equation [2]:-

$$-d[\text{Pt}(\text{bipy})\text{Cl}_2]/dt = \{k_1 + k_2[\text{tu}]\} [\text{Pt}(\text{bipy})\text{Cl}_2] \quad [2]$$

The individual values of  $k_1$  and  $k_2$  for each solvent mixture obtained by a least squares analysis are also listed in Table 1. These  $k_1$  values are subject to considerable uncertainties as this reaction pathway makes only a minor contribution to the overall rate constant,  $k_{\text{OBS}}$  at the range of concentrations of thiourea employed by us. The analogous  $k_1$  terms for the reaction in 1,4 dioxan-water mixtures are similarly low under the conditions used in our investigation. Thus the  $k_2$  values were obtained directly from the corresponding  $k_{\text{OBS}}$  values by division by the concentration of thiourea, (0.01 mol. dm<sup>-3</sup>).

The resulting  $k_2$  values for both reactions are displayed in the relevant sections of Table 2.

Solubilities:- The measured solubilities of  $\text{Pt}(\text{bipy})\text{Cl}_2$  in the various solvent mixtures used in this study can be found in Table 2. These results were measured at the appropriate temperature corresponding to that used in the kinetic runs, (i.e. 293.2 K for dioxan-water and 298.2 K for tetrahydrofuran-water mixtures).<sup>†</sup> The solvent-mixture ranges for each of these two co-solvents were up to a lower co-solvent concentration limit, (i.e. for dioxan,  $x_2 = 0.050$ ; for tetrahydrofuran,  $x_2 = 0.097$ ) established by the decrease in solubility of the  $\text{Pt}(\text{bipy})\text{Cl}_2$  as the amount of water solvent is increased. [N.B. Although solubility could still be measured

[<sup>†</sup> Solubility data for thiourea made it necessary for us to follow the reaction at two different temperatures.]



TABLE 2

Solubilities (S) of  $\text{Pt}(\text{bipy})\text{Cl}_2$ , second-order rate constants ( $k_2$ ) for the reaction of  $\text{Pt}(\text{bipy})\text{Cl}_2$  with thiourea, and transfer functions  $\delta_{\text{m}\mu}^\ominus$  and  $\delta_{\text{m}}\Delta G^\ddagger$  for reactants and reaction, in mixed aqueous solvents containing mole fraction  $x_2$  of organic component. For each of the two series of solvent mixtures the transfer parameters refer to transfer from the mixture of lowest  $x_2$ .

Dioxan (293.2 K)

$x_2$	0.050	0.083	0.124	0.175	0.241
$\delta_{\text{m}\mu}^\ominus (\text{tu})/\text{kJ.mol}^{-1}$	0	-0.052	-0.097	-0.181	-0.199
$10^5 \text{S}(\text{Pt}(\text{bipy})\text{Cl}_2)/\text{mol. dm}^{-3}$	7.0	9.3	16.7	29.3	40.2
$\delta_{\text{m}\mu}^\ominus (\text{Pt}(\text{bipy})\text{Cl}_2)/\text{kJ.mol}^{-1}$	0	-0.71	-2.16	-3.55	-4.33
$\Sigma \delta_{\text{m}\mu}^\ominus (\text{reactants})/\text{kJ.mol}^{-1}$	0	-0.76	-2.26	-3.73	-4.53
$k_2/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	2.5	2.0	1.35	0.90	0.50
$\delta_{\text{m}}\Delta G^\ddagger/\text{kJ.mol}^{-1}$	0	+0.54	+1.50	+2.49	+3.93

Tetrahydrofuran (298.2 K)

$x_2$	0.097	0.143	0.200	0.510
$\delta_{\text{m}\mu}^\ominus (\text{tu})/\text{kJ.mol}^{-1}$	0	-0.66	-1.20	-2.06
$10^5 \text{S}(\text{Pt}(\text{bipy})\text{Cl}_2)/\text{mol. dm}^{-3}$	21	33	61	90
$\delta_{\text{m}\mu}^\ominus (\text{Pt}(\text{bipy})\text{Cl}_2)/\text{kJ. mol}^{-1}$	0	-0.16	-1.70	-2.67
$\Sigma \delta_{\text{m}\mu}^\ominus (\text{reactants})/\text{kJ.mol}^{-1}$	0	-0.82	-2.90	-4.73
$k_2/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	1.27	0.70	0.27	0.20
$\delta_{\text{m}}\Delta G^\ddagger/\text{kJ.mol}^{-1}$	0	+1.48	+3.83	+4.61

TABLE 1

Average first-order rate constants,  $k_{\text{OBS}}$ , and derived first- and second-order rate constants  $k_1$  and  $k_2$  for the reaction of  $\text{Pt}(\text{bipy})\text{Cl}_2$  with thiourea in water + tetrahydrofuran solvent mixtures (mole fraction  $x_2$  tetrahydrofuran) at 298.2 K.

$10^3 k_1/\text{s}^{-1}$      $k_2/\text{M}^{-1} \text{s}^{-1}$

<u><math>x_2 = 0.510</math></u>						
[thiourea]/mol. $\text{dm}^{-3}$	0.025	0.050	0.075	0.100	} ca. 1	0.20±0.01
$10^3 k_{\text{OBS}}/\text{s}^{-1}$	4.6	9.1	13.4	19.6		
<u><math>x_2 = 0.200</math></u>						
[thiourea]/mol. $\text{dm}^{-3}$	0.025	0.035	0.050	0.070	} ca. 2	0.32±0.02
$10^3 k_{\text{OBS}}/\text{s}^{-1}$	12	15	19	25		
<u><math>x_2 = 0.143</math></u>						
[thiourea]/mol. $\text{dm}^{-3}$	0.010	0.020	0.030	0.040	} ca. 1	0.71±0.04
$10^3 k_{\text{OBS}}/\text{s}^{-1}$	6.8	15	21	29		
<u><math>x_2 = 0.098</math></u>						
[thiourea]/mol. $\text{dm}^{-3}$	0.0033	0.0100	0.0133	0.0167	} ca. 2	1.27±0.13
$10^3 k_{\text{OBS}}/\text{s}^{-1}$	6.3	16	18	24		

below this, corresponding kinetics were not possible due to the small absorbance changes involved.]

Transfer functions:- Of utmost importance in this investigation was the calculation of transfer parameters corresponding to the change in the chemical potential of the Pt(bipy)Cl<sub>2</sub> and thiourea in their solution standard states,  $\delta_m \mu^\ominus$ , with the variation in mole fraction of the co-solvent. Applying this with reference to thiourea, we have equation [3], e.g:-

$$\delta_m \mu^\ominus (\text{tu}) = \mu^\ominus (\text{tu}:x_1) - \mu^\ominus (\text{tu}:x^*_1) \quad \dots\dots [3]$$

(where  $x_1$  = mole fraction of water.) Thus this equation describes the change in the chemical potential in the solution standard state, (denoted by  $^\ominus$ ) on going from a mixture of water mole fraction of  $x^*_1$  to a second mixture, of mole fraction  $x_1$ .

Hence this type of expression can be applied equally well to our neutral platinum compound, and also to the transition state for the reaction.

Similarly the change in the activation Gibbs function,  $\delta_m \Delta G^\ddagger$  is shown in equation [4]:-

$$\delta_m \Delta G^\ddagger = \Delta G^\ddagger (x_1) - \Delta G^\ddagger (x^*_1) \quad \dots\dots [4]$$

and is given by equation [5]:-

$$\delta_m \Delta G^\ddagger = \delta_m \mu^\ddagger - \delta_m \mu^\ominus (\text{compound}) - \delta_m \mu^\ominus (\text{tu}) \quad \dots\dots [5]$$

These values,  $\delta_m \Delta G^\ddagger$  can be calculated from the rate constants for the reaction in the corresponding two mixtures,  $x_1$  and  $x^*_1$ , using the following relationship:-

$$\delta_m \Delta G^\ddagger = -RT \cdot \ln k_2(x_1)/k_2(x^*_1) \quad \dots\dots [6]$$

In many such studies, the chosen reference system normally corresponds

to the situation where  $x_1 = 1$ , i.e. pure water, (see Chapter 1 for instance). Thus solubilities and rate constants for the various mixtures are compared with those obtained in pure water. [N.B. or in a pure solvent, not necessarily water, usually depending upon constraints met due to solubility problems.] Unfortunately, due to difficulties with the solubility of the platinum compound (described previously) it was not possible to use pure water as a reference point. Also, the pure organic solvents could not be used due to similar solubility problems, (i.e. in organic rich mixtures the product formed would be insoluble, thus interfering with the kinetics, as well as the fact that the solubility plot of thiourea with organic co-solvent minimises at high co-solvent concentration). Thus we were forced to choose an arbitrary solvent mixture upon which to base our transfer functions.

In each of the two sets of solvent mixtures we have chosen the most water-rich mixture as our standard. The transfer functions with reference to these two values are to be found in Table 2. Hence for the case where tetrahydrofuran is the co-solvent, then, using our previous nomenclature in equations [3] and [4],  $x_1^* = 0.913$ , similarly for dioxan,  $x_1^* = 0.950$ , as in Table 2. Thus the  $\delta_m$ -functions indicate the effect of changing  $x_1$  relative to the standard (arbitrary) mole fraction,  $x_1^*$ .

The transfer functions  $\delta_{\mu}^{\ominus}$  (compound) for the platinum compound were calculated from the measured solubilities in the solvent mixtures. The equivalent functions for thiourea in the two distinct sets were obtained from the following literature sources. Where the co-solvent was 1,4 dioxan, solubilities were obtained directly from work done by Angelescu & Cornea.<sup>(516)</sup> The corresponding results for tetrahydrofuran mixtures were calculated from values of  $d\mu^{\ominus}(\text{tu})/dx_1$  for eight tetrahydrofuran-water mixtures over the range  $0.4902 < x_1 < 0.9866$ , (at 298 K) reported by Treiner & Tziac.<sup>(517)</sup>

The value of the previous differential at  $x_1 = 1$  was calculated by fitting this differential on  $x_1$  over the afore-mentioned mole fraction range, to the equation shown below, [7]:-

$$d\mu^{\ominus}(\text{tu}) = a + bx_1 + cx_1^2 \quad \dots [7]$$

A least squares technique was used to perform this fit via use of a computer. In the same computer program, (Fortran for Cyber 72) the calculated value of the differential at  $x_1 = 1$  was combined with similar values obtained at other mole fractions whence the required transfer functions  $\delta_{\text{m}\mu}^{\ominus}(\text{tu})$  were evaluated using a numerical integration technique. [N.B. Dr. M. J. Blandamer was responsible for these methods and computer programs.]

### Discussion

As can be seen in Table 2, the solubilities of both the platinum-(II) compound and of thiourea increase as the proportion of the organic co-solvents are increased. By similar observation we see that the reaction rate decreases as the proportion of organic co-solvent increases in both series of solvent mixtures. These two separate observations and how they are related by the various activation (transfer) parameters is shown graphically in Figure 1, (plotted from the values listed in Table 2). In both of the diagrams displayed, one for each set of data for each co-solvent, it is obvious as to which are the major controlling influences in this reaction. The full line represents the predicted variation of  $\delta_{\text{m}}\Delta G^{\ddagger}$  (the broken line) from considerations of initial state solvation parameters only, (i.e.  $\Sigma\delta_{\text{m}\mu}^{\ominus}(\text{reactants})$ ). This close agreement between observed and predicted variations in these functions suggests that the solvent effects operating on the transition state, (i.e. in other words its chemical-potential dependence

on solvent) are of much less importance, by virtue of their relatively small size.

Further analysis of these diagrams enables us to separate these effects into their individual reactant components. Thus for the 1,4 dioxan-water system, the relative sizes of change in the chemical potentials for the two species,  $\text{Pt}(\text{bipy})\text{Cl}_2$  and thiourea indicate that (as these changes are greatest for the platinum-(II) compound) it is this change for the platinum-(II) compound that is the major controlling factor. Thus solvation changes at this species is mainly responsible for the reaction rate variations observed over the solvent-mixture range studied by us.

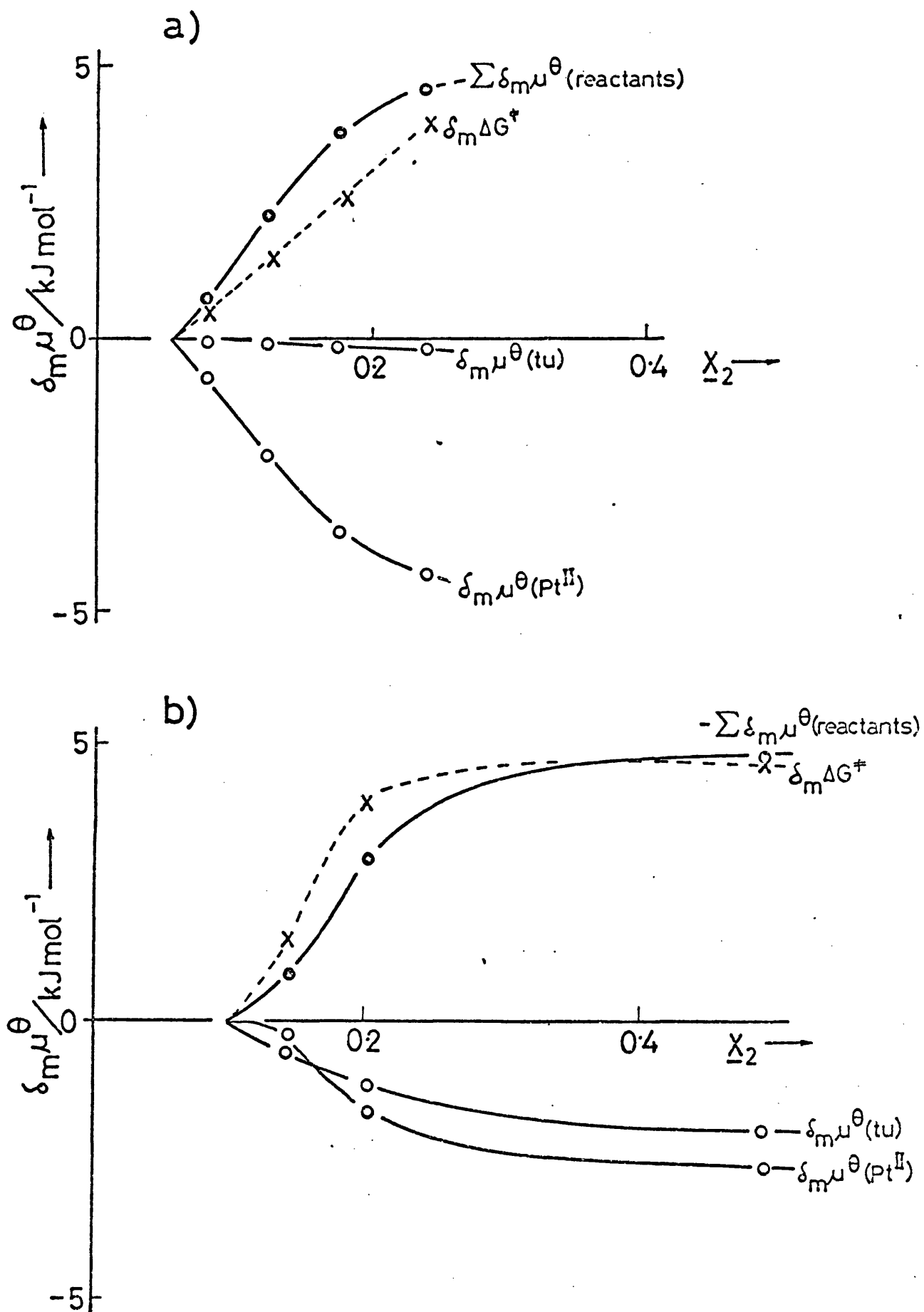
Similar considerations for the tetrahydrofuran-water mixtures, (which cover a wider range of solvent compositions) lead us to the conclusion that, since similar plots are drawn for the two reactants, solvation effects on the chemical potentials of both reactants are mutually responsible for the observed reaction rate variations. The transition state effects are again very small.

This type of behaviour has been noted previously for the reactions of tetra-alkyl tin compounds with mercury-(II) chloride and in the Menshutkin reaction of trimethylaniline with methyl iodide, both of which are discussed in detail in the introduction of this Chapter.

One may also compare this result with that obtained in Chapter 1 for the reaction between  $\text{Fe}(\text{bipy})_3^{2+}$  and cyanide anion in various aqueous mixtures, where the variation in reactivity was explained in terms of solvation changes at the cyanide anion. The changes in the initial state of the iron complex cation and the transition state seemingly contribute only a small amount to the reactivity trends. Essentially, this reaction is similar to the one studied here in that both reactivity trends are predominantly governed by changes in the initial state molecules, the transition state effects being comparatively small.

FIGURE 1

The variation of chemical potentials of the reactants and the transition state for the reaction of  $\text{Pt}(\text{bipy})\text{Cl}_2$  with thiourea, in (a) water + dioxan at 293.2 K and (b) water + tetrahydrofuran at 298.2 K.



## CHAPTER 6



Title:    Solubilities of  $\text{Fe}(\text{bipy})_2(\text{CN})_2$  and  $\text{Fe}(\text{phen})_2(\text{CN})_2$  in binary aqueous mixtures.

Introduction:

The following work was entered into to see if correlations similar to those found in solvatochromic studies of these compounds, (see Chapter 2 and ref. 601) occurred in solubility trends in several binary aqueous mixtures. The importance of solubility and solubility variations with solvent has been demonstrated in the past for kinetic dependence on reaction solvent. For instance in the aquation of the  $\text{Fe}(\text{5NO}_2\text{-phen})_3^{2+}$  (602) cation in a series of mixed aqueous solvents, good agreement was found between the variation in rate constant and the excess Gibbs functions for the corresponding mixed solvents. This excess Gibbs function,  $G^E$  is defined as the molar excess Gibbs function and expresses the extent to which the molar Gibbs function of mixing at a given temperature, pressure and mole fraction differs from that of the corresponding ideal mixture. Thus in the previously mentioned reference, this parameter was used as a measure of the solvation changes, (i.e. solvent water-co-solvent interactions) in the pure binary mixtures.

Similar correlations between solubility and kinetic trends have also been found to be of interest, particularly where the solvation characteristics of the ground state (reactant) molecules is important in determining the reactivity. Examples of this type of behaviour are to be found in Chapter 5 of this thesis, both in the introduction and more specifically the reaction system studied in that Chapter. In these latter cases, the solubility data are first converted to thermodynamic transfer functions which are then in an appropriate form for comparison with kinetic parameters

which have been treated in an analogous fashion.

The solubility trends for the compounds to be studied in this Chapter should be extremely interesting when one considers that the larger part of their 'molecular surface' is very hydrophobic. Thus small changes in the solvent composition would be expected to produce dramatic changes in the solubilities. Both compounds should become increasingly solubilised as the fraction of non-aqueous component is increased.

#### Experimental:

The two compounds were prepared by the method described in Chapter 2. Solvent mixtures were made up by volume before mixing from deionised water and the organic co-solvents, the latter being used without further purification, (except for 1,4 dioxan which was passed through a column of activated alumina, as described in Chapter 4). Quantities of each of the two compounds were added to the solvent mixtures, which were then mechanically shaken for ~1 hour, followed by thermostating in a water-bath maintained at 298 K for several hours. After this time, the samples were removed from the bath, re-shaken and a small volume of solution withdrawn from each and filtered, to remove undissolved compound. The clear solutions thus obtained were then introduced to the Atomic Absorption spectrometer and an iron concentration reading taken. This machine had previously been standardised and linearly calibrated over a suitable concentration range, and was always re-standardised, (using a freshly prepared acidic solution containing 10 µg/ml of iron-(II) ammonium sulphate) prior to its re-use.

The above process was repeated for each sample until several concurrent concentration readings, all giving the same result were obtained, (i.e. this procedure often stretched over several days).

### Results:

The results obtained for both compounds are listed together with several other parameters in Table 1. The excess Gibbs functions also listed in the same Table were all obtained from reference (602) and references included therein. Logarithmic plots of solubility (S) against mole fraction of organic co-solvent are displayed in Figures 1 and 2, for the bipy and phen adducts respectively. A cross-correlation (i.e. bipy against phen) is also shown in Figure 3. A logarithmic plot of solubility for the phen compound against the excess Gibbs functions for the relevant solvent mixtures is shown in Figure 4. The analogous plot for the bipy compound did not show quite such good agreement between these functions.

### Discussion:

The notable differences between the solubility trends for the bipy and phen compounds are perhaps surprising, since one would expect these two ligands to 'appear' similar as far as the surrounding solvent molecules are concerned.

However, on examining the overall solubility variations it would seem that although the total variation is approximately the same in each case, (approximately a 30-fold difference over the entire solvent range used) the individual solvent trends are dissimilar, (i.e. the plots displayed in Figures 1 and 2 are different shapes and the solvents are in a different order). As well as this is the good agreement between the phen compound solubilities and  $G^E$ , as compared with the corresponding plot for the bipy compound being poor. This former correlation is obviously a reflection on the importance of interference by solute-solvent interactions with the solute-solute interactions existing in the mixtures. Similar kinetic correla-

TABLE 1

Solubility data for the compounds  $\text{Fe}(\text{bipy})_2(\text{CN})_2$  and  $\text{Fe}(\text{phen})_2(\text{CN})_2$  in a series of binary aqueous mixtures at 298 K; along with the relevant mole fractions of organic co-solvents ( $x_2$ ) and excess Gibbs functions.

V/V%			Fe(bipy) <sub>2</sub> (CN) <sub>2</sub>			Fe(phen) <sub>2</sub> (CN) <sub>2</sub>	
	x <sub>2</sub>	G <sup>E</sup>	S	Log <sub>10</sub> (S)	S	Log <sub>10</sub> (S)	
		kJ.mol <sup>-1</sup>	μg.ml <sup>-1</sup> ‡		μg.ml <sup>-1</sup> ‡		
WATER:	-		11.0	1.041	2.0	0.301	
ETHANOL:	10%	0.033	107	19.0	1.279	5.0	0.699
	20%	0.072	224	39.0	1.591	10.0	1.0
	30%	0.117	349	61.0	1.785	22.5	1.352
METHANOL:	10%	0.048	116	28.0	1.447	4.0	0.602
	20%	0.102	211	80.0	1.903	7.0	0.845
	30%	0.163	284	162.0	2.210	14.0	1.146
DIOXAN:	10%	0.023		38.0	1.580	21.0	1.322
	20%	0.050		85.0	1.929	36.0	1.556
	30%	0.083		144.0	2.158	64.0	1.806
ACETONE:	10%	0.033	87	34.0	1.532	8.0	0.903
	20%	0.072	184	74.0	1.869	21.0	1.322
	30%	0.117	294	146.0	2.164	44.0	1.644
D.M.S.O:	10%	0.077	-201	15.0	1.176	6.0	0.778
	20%	0.100	-411	24.0	1.380	10.0	1.0
	30%	0.117	-620	36.0	1.556	15.0	1.176
ACETONITRILE:	10%	0.039	191	45.0	1.653	6.0	0.778
	20%	0.079	386	177.0	2.248	12.5	1.097
	30%	0.129	586	300.0	2.477	33.5	1.525
GLYCOL:	10%	0.044	-101	14.0	1.146	5.0	0.699
	20%	0.094	-197	14.0	1.146	9.0	0.954
	30%	0.151	-288	13.0	1.114	9.0	0.954
GLYCEROL:	10%	0.031	- 83	9.0	0.954	2.5	0.398
	20%	0.067	-173	9.0	0.954	4.0	0.602
	30%	0.110	-271	9.0	0.954	4.0	0.602

[  $\ddagger$  measured as  $\mu\text{g.ml}^{-1}$  of iron]

tions have been found for the aquation of the  $\text{Fe}(\text{5NO}_2\text{-phen})_3^{2+}$  cation<sup>(602)</sup> and the solvolysis of tert-butyl chloride, both of which are dissociative processes. These (dissociative) reactivity trends are obviously closely linked with solvation effects, and hence by analogy to solubility trends.

The overall magnitudes of the solubility values obtained for our two compounds can be seen to be much larger for the bipy compound, thus suggesting that these differences must be solely attributable to the identity of the bidentate ligands (i.e. and hence their interaction with the surrounding solvent molecules). This would seem to infer that these two ligands, (bipy and phen) must behave very differently in terms of solvent interaction, thus not appearing to the surrounding solvent molecules as two similar large hydrophobic groups, and possibly controlling the solubility trends of these compounds. This view is supported by the observation that each of these molecules, (i.e.  $\text{Fe}(\text{bipy})_2(\text{CN})_2$  and  $\text{Fe}(\text{phen})_2(\text{CN})_2$ ) has as a greater part of its molecular surface, which is the part of the molecule that interacts most strongly with solvent molecules, one of these bidentate groups. Thus if they both behaved as indistinguishable hydrophobic surfaces, then the compounds would be expected to display comparable solubility characteristics. The fact that this does not occur lends further support to the previously outlined views.

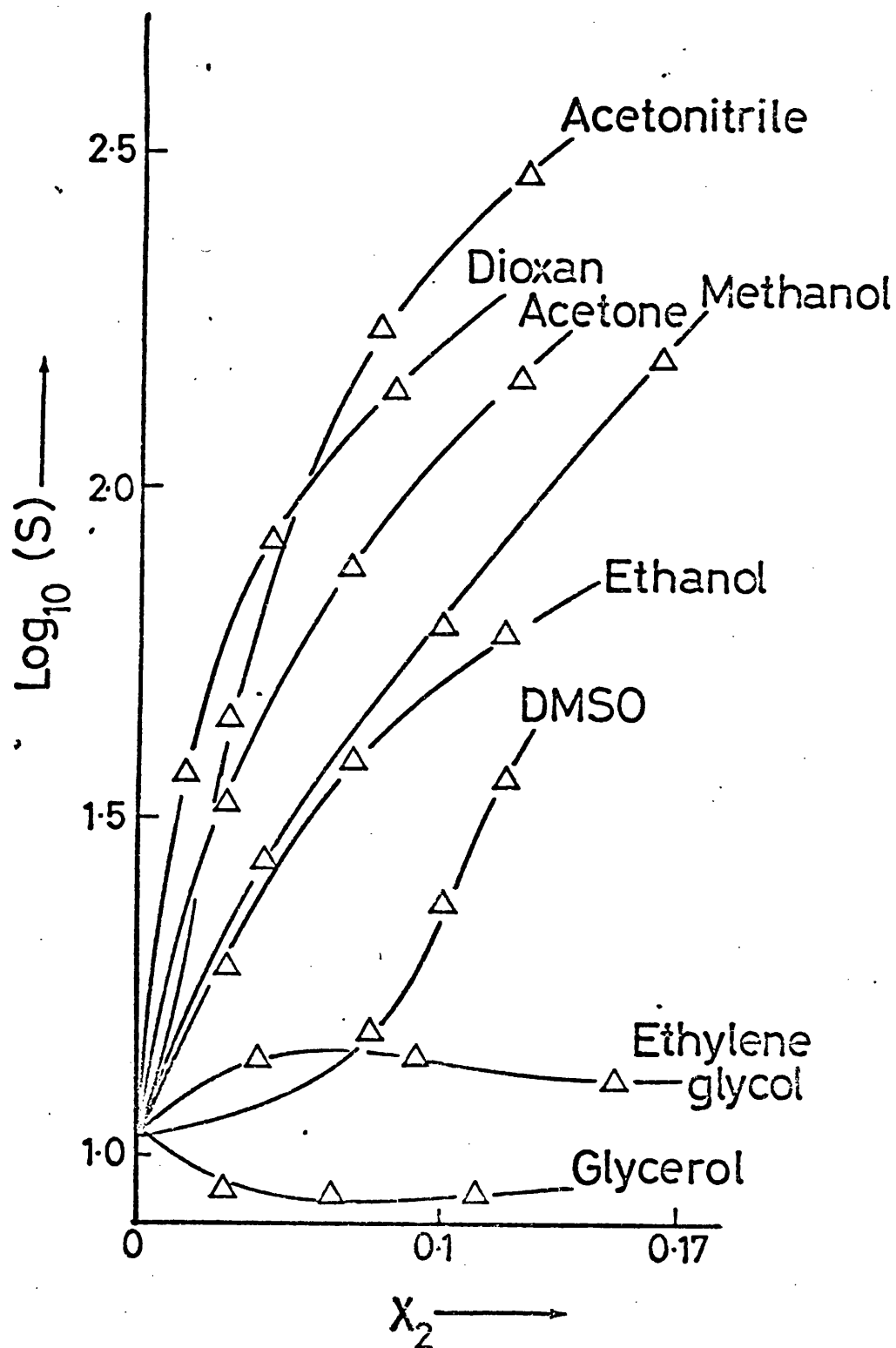
Thus the accompanying cyanide groups seem to play only a small part in the overall solubility picture for these compounds, in contrast to their solvation-dependent importance in dictating the solvatochromic properties of these same compounds.

The use of these solubility trends may also be of importance in future kinetic studies on these compounds, (e.g.  $\text{Fe}(\text{bipy})_2(\text{CN})_2 + \text{CN}^-$  or  $\text{OH}^-$ ; the former of these is at present being studied by a colleague to examine the dependence of the rate constant upon cyanide concentration) where one would

predict that, where reactant state solvation is important in deciding kinetic trends, then the solvation changes at both the larger  $\text{Fe(LL)}_2(\text{CN})_2$  and the smaller nucleophiles (i.e.  $\text{OH}^-$ ,  $\text{CN}^-$ ) may be of comparable importance. This follows from the large dependence of solubility of these iron compounds upon the solvent, which may be of the same order as the solvation changes at the small nucleophiles, (see Chapter 1). This is in contrast to the case of the species  $\text{Fe(bipy)}_3^{2+}$ , examined in Chapter 1, which was found to be relatively insignificant in terms of solvation effects when compared with the solvation changes for cyanide in a series of binary aqueous mixtures. This difference must be related to the presumably increased interaction between the organic co-solvent and the hydrophobic bipy groups in the absence of the di-positive charge; or conversely due to the decreased interaction of the solvent-water with the molecule in the absence of the di-positive charge.

FIGURE 1

A logarithmic plot of the solubility ( $S$ ) of the compound  $\text{Fe}(\text{bipy})_2(\text{CN})_2$  in a series of binary aqueous mixtures, against  $x_2$ , the mole fraction of the organic cosolvent at 298.2 K. Solubilities were measured in  $\mu\text{g}.\text{ml}^{-1}$ .



**FIGURE 2**

A logarithmic plot of the solubility ( $S$ ) of the compound  $\text{Fe}(\text{phen})_2(\text{CN})_2$ , in a series of binary aqueous mixtures, against  $x_2$ , the mole fraction of organic cosolvent at 298.2 K. Solubilities were measured in  $\mu\text{g}.\text{ml}^{-1}$ .

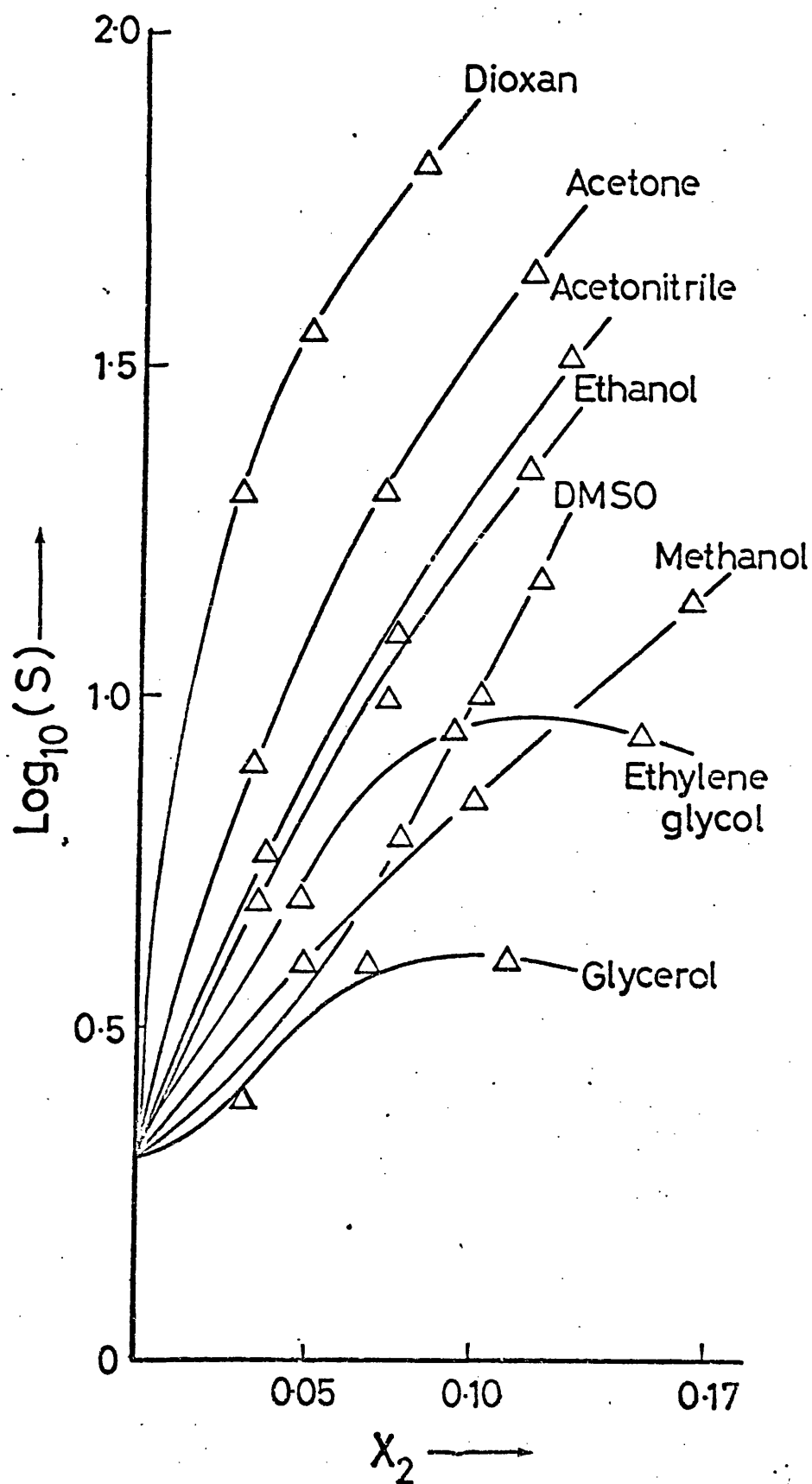




FIGURE 3

Correlation between the logarithmic plots of the solubilities ( $S$ ) of the compounds  $\text{Fe}(\text{bipy})_2(\text{CN})_2$  and  $\text{Fe}(\text{phen})_2(\text{CN})_2$  in the same set of binary aqueous mixtures at 298.2 K. Solubilities were measured in  $\mu\text{g}.\text{ml}^{-1}$ .

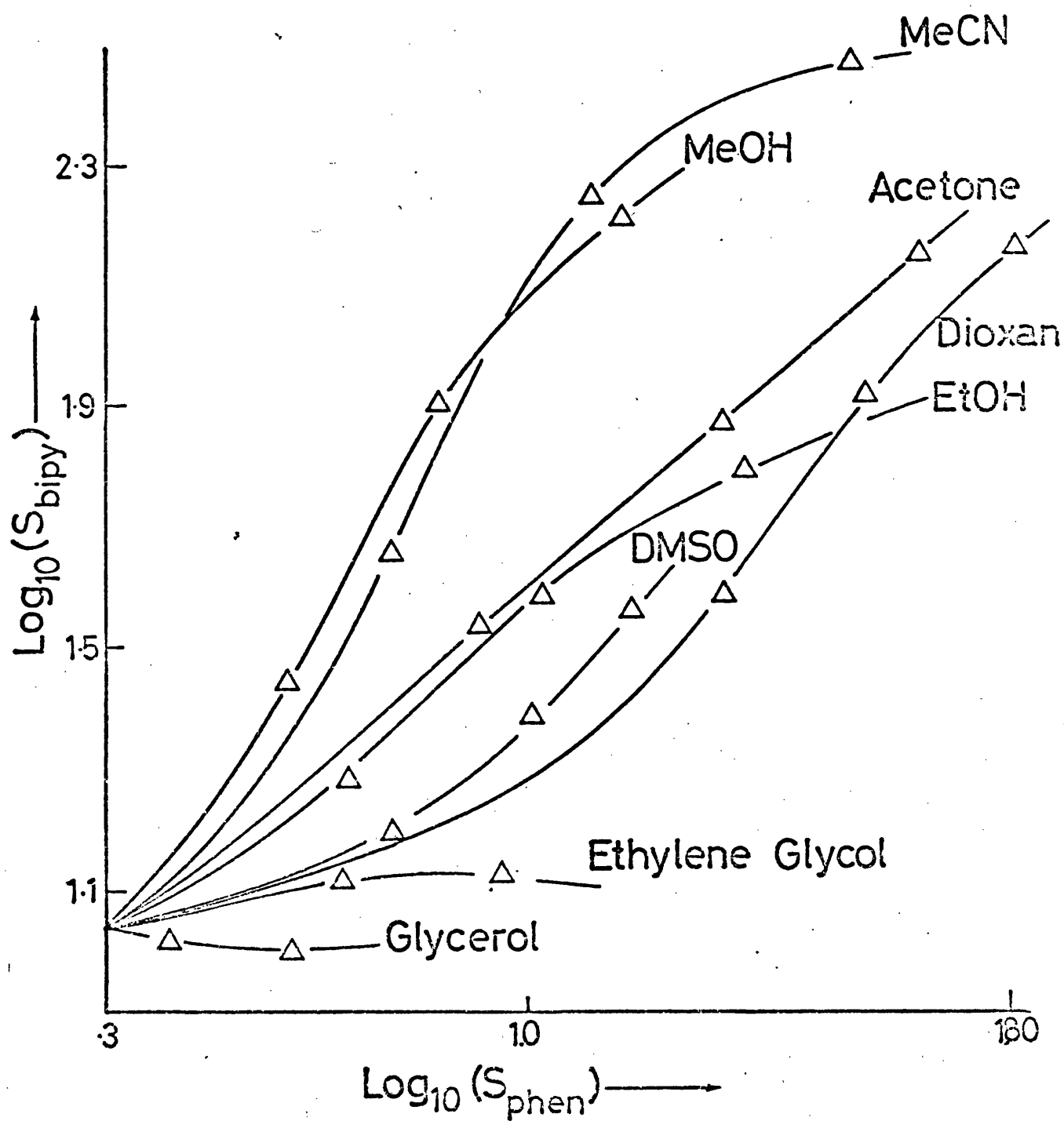
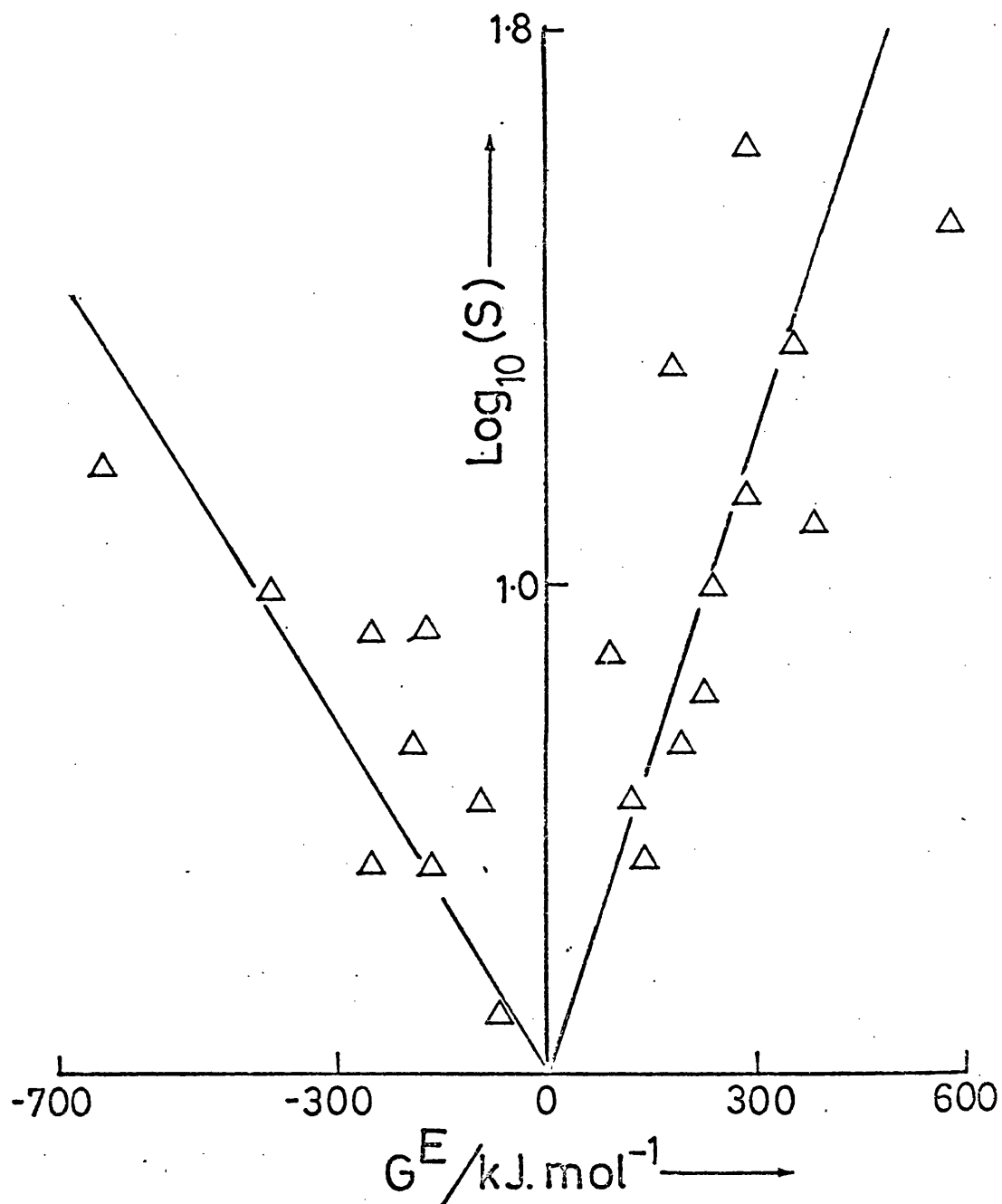


FIGURE 4

A logarithmic plot of the solubility ( $S$ ) of the compound  $\text{Fe}(\text{phen})_2(\text{CN})_2$ , against the excess Gibbs function for a series of binary aqueous mixtures at 298.2 K. Solubilities were measured in  $\mu\text{g}.\text{ml}^{-1}$ .

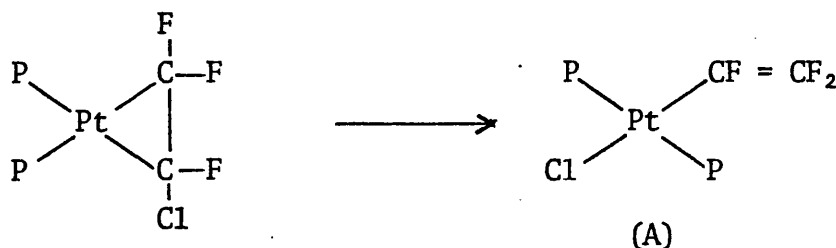


## CHAPTER 7

Title:    A kinetic investigation of the isomerisation reactions of  
platinum olefin and  $\Pi$ -bonded ketone compounds.

### Introduction

The isomerisation of a platinum-olefin compound to the corresponding vinyl compound was first observed for the compound  $(\text{PPh}_3)_2\text{Pt}(\text{CF}_2\text{CFCl})$ , which on heating to just below its melting point gave the trans-vinyl isomer, <sup>(701,702)</sup> e.g:-

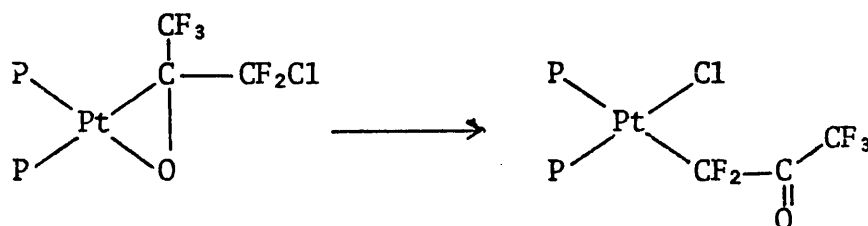


(Where P represents triphenyl phosphine,  $\text{PPh}_3$ .)

Similar reactions have been found for several other platinum-olefin compounds, containing other olefinic groups, (e.g.  $\text{C}_2\text{Cl}_4$ , <sup>(703)</sup>) or where the groups trans to the olefin are different, (e.g.  $\text{AsPh}_3$ , <sup>(704)</sup>). The reactivity trends which have emerged from such studies are many and varied. For instance, bromine containing olefinic compounds (e.g.  $[\text{PPh}_3]_2\text{Pt}[\text{CF}_2\text{CFBr}]$ ) appear to undergo vinyl isomerisations more readily than the analogous chloro-olefinic compounds, <sup>(702)</sup> both of which yield the trans-isomeric product. Similarly the compound  $(\text{MePPh}_2)_2\text{Pt}(\text{CF}_2\text{CFBr})$  isomerises at room temperature in ethanol again giving the trans-(vinyl)-product, <sup>(705)</sup> in contrast to the analogous chloro-olefinic compound, which isomerises only in refluxing n-butanol. <sup>(711)</sup> The fluoro-olefinic compound,  $(\text{PPh}_3)_2\text{Pt}(\text{CF}_2\text{CF}_2)$  does not undergo isomerisation under any circumstances. <sup>(706)</sup>

These observations suggest that the rate determination step in these vinylisation reactions involves heterolytic cleavage of carbon-halogen bonds.<sup>(707)</sup> Thus the observation that the previously mentioned tetrafluoro-compound does not react in this manner may be explained in terms of the high bond strength of C—F (relative to C—Cl or C—Br) and the low affinity of this halogen for platinum-(0), (again relative to chloride and bromide). Hence both the nature of the ligands trans to the olefin and the identity of the halogens on the olefin seem to affect the reactivity of this type of compound.

A similar isomerisation reaction is observed for  $\pi$ -bonded ketone compounds of platinum-(0), a halogeno-platinum compound analogous to species (A) in the previous diagram being formed, e.g:-



The following work in this Chapter both extends the halogeno-olefin isomerisation work carried out by other workers and starts a new investigation on the latter chloro-fluoro-ketone isomerisation, where similar controlling factors may be operating.

#### [1] Isomerisation of halogeno-olefin compounds.

##### Experimental:-

The compounds  $(\text{PPh}_3)_2\text{Pt}(\text{CF}_2\text{CFCl})$  and  $(\text{AsPh}_3)_2\text{Pt}(\text{CF}_2\text{CFCl})$  were obtained from Mr. D. A. Clarke. Kinetic investigations were carried out in a series of alcoholic solvents, namely methanol, ethanol and n-propanol at 318 K.

Individual cells were made up by the following method. To a pre-thermostatted cell containing one of the above solvents was added a small quantity of one of the above compounds. After successive shaking (to dissolve sufficient compound) and re-thermostating the solution was filtered and then replaced in the cell compartment and a kinetic run started.

#### Results:-

All of the kinetic runs performed on these compounds required at least twelve hours before enough data could be collected to obtain a reasonably accurate rate constant. Although temperature fluctuations in the cell-compartment were small, (as far as we were able to ascertain by periodic examinations of the reservoir bath temperature) several runs were usually necessary to give averaged results with small uncertainties. This type of behaviour has been noted before by a previous worker (M. M. Hunt, see ref. 711) when examining the isomerisation of  $(\text{AsPh}_3)_2\text{Pt}(\text{CF}_2\text{CFBr})$ .

The few results obtained by us are listed in Table 1, along with similar results for some analogous compounds for comparative purposes. A logarithmic plot of these rate constants against ' $1/D$ ' is shown in Figure 1.

#### Discussion:-

Several mechanisms have been proposed for this type of reaction, as listed below:-

- (a) intramolecular rearrangement,
- (b) loss of one phosphine (or arsine) ligand, rearrangement of the intermediate by one of the other three mechanisms, and recombination with the phosphine (or arsine) ligand,

TABLE 1

Average first order rate constants ( $k_{\text{OBS}}$ ) for the isomerisation of olefinic-platinum-(0) compounds at 318 K in several organic solvents.

(T = 318 K)

COMPOUND:- SOLVENT	(PPh <sub>3</sub> ) <sub>2</sub> Pt(CFCl.CF <sub>2</sub> ) 10 <sup>5</sup> k <sub>OBS</sub> /s <sup>-1</sup>	(AsPh <sub>3</sub> ) <sub>2</sub> Pt(CFCl.CF <sub>2</sub> )
METHANOL	9.1	14
ETHANOL	3.8	9.8
n-PROPANOL	(NO REACTION) <sup>a</sup>	8.8

(T = 313 K) <sup>b</sup>

	(1/D) <sup>d</sup>	(AsPh <sub>3</sub> ) <sub>2</sub> Pt(CFBrCF <sub>2</sub> )	(PPh <sub>3</sub> ) <sub>2</sub> Pt(C <sub>2</sub> Cl <sub>4</sub> )
METHANOL	0.036	13	35
ETHANOL	0.041	16.3	5.5
n-PROPANOL	0.0498	10.1	3.0
i-PROPANOL	0.055	5.3	0.82
n-BUTANOL	0.056	6.6	-
t-BUTYL ALCOHOL	0.0565	2.8	<0.1

(T = 293 K) <sup>c</sup>

	(PPh <sub>3</sub> ) <sub>2</sub> Pt(C <sub>2</sub> HCl <sub>3</sub> )
METHANOL	1400
ETHANOL	440
n-PROPANOL	330
i-PROPANOL	160
t-BUTYL ALCOHOL	15

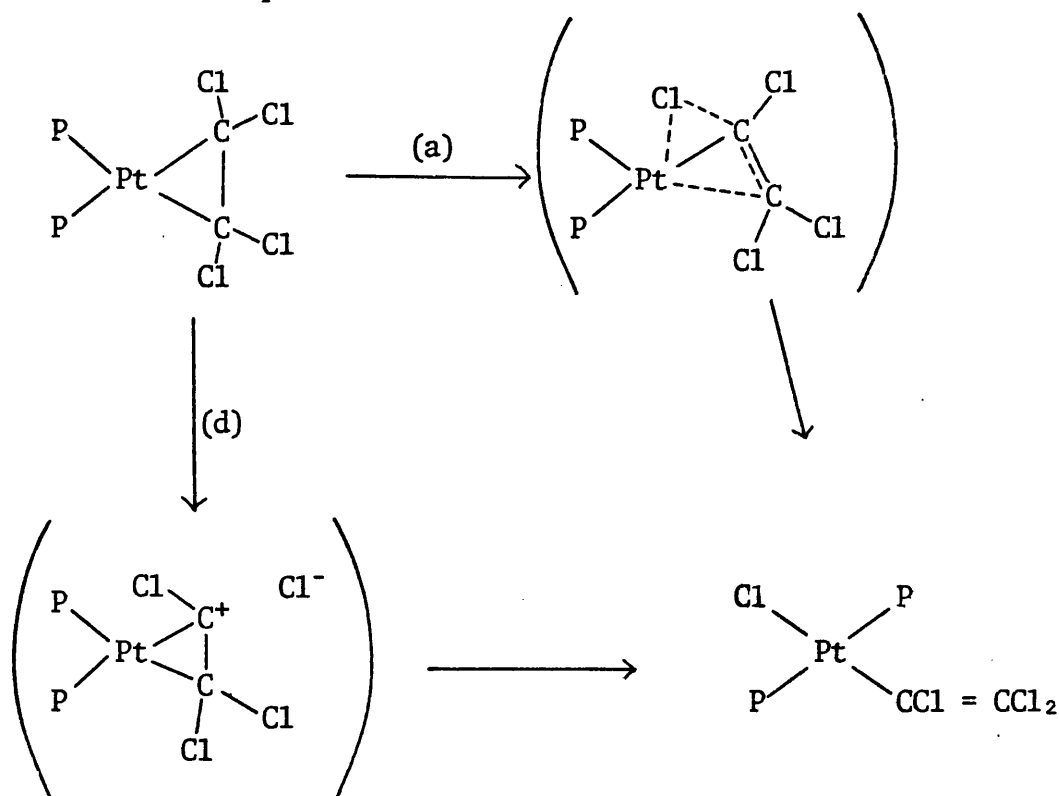
( <sup>a</sup> Very slow reaction, no change over 15 hours.)

[ <sup>b</sup> From ref. 711; <sup>c</sup> From ref. 708; <sup>d</sup> From ref. 712.]

- (c) loss of the olefin ligand followed by recombination and fission of this ligand so that one carbon and one halogen become attached to the platinum,
- (d) loss of a halogen from the olefin ligand, followed by rearrangement of the carbonium ion, and nucleophilic attack of the halide ion on platinum.

Previous workers, <sup>(710,711)</sup> have conducted many experiments, both kinetic and analytical in an investigation of the implications of these listed mechanisms. Although none of these experiments were able to positively disprove any of the four mechanisms, evidence against the mechanisms labelled (b) and (c) has led to their being discounted in more recent work. <sup>(708,709)</sup>

The remaining two mechanisms are shown here in more detail, for the tetrachloro-olefin compound:-



Evidence for either one of these mechanisms occurring in the absence of the other through a series of solvents was not obtained. The reason for



this may be partly explained if one considers that the solvents may to some extent have some influence over which of the two mechanisms occurs. This view is supported by observations that tetrachloroethylene and triphenylphosphine interfere with olefin isomerisations where the solvent is benzene. (710)

On examining our results and comparing the reactivity trends (Figure 1) with results obtained by other workers a surprising correlation emerges. The logarithmic plot shown in Figure 1 indicates that the two compounds,  $(\text{AsPh}_3)_2\text{Pt}(\text{CF}_2\text{CFC1})$  and  $(\text{AsPh}_3)_2\text{Pt}(\text{CF}_2\text{CFBr})$  give similar slopes; this is also evident for the compounds  $(\text{PPh}_3)_2\text{Pt}(\text{CF}_2\text{CFC1})$  and  $(\text{PPh}_3)_2\text{Pt}(\text{CCl}_2\text{CCl}_2)$ . These results would seem to be in conflict with those trends described earlier in the introduction, based on relative carbon-halogen bond strengths and the nature of the groups trans to the olefin.

Further investigation on this series of compounds is obviously required, for instance a systematic kinetic analysis replacing either one halogen or the trans-olefinic groups would be extremely helpful in understanding the overall reactivity patterns of these compounds. Unfortunately, due to preparative difficulties, this was not found to be possible for us to undertake at the present time.

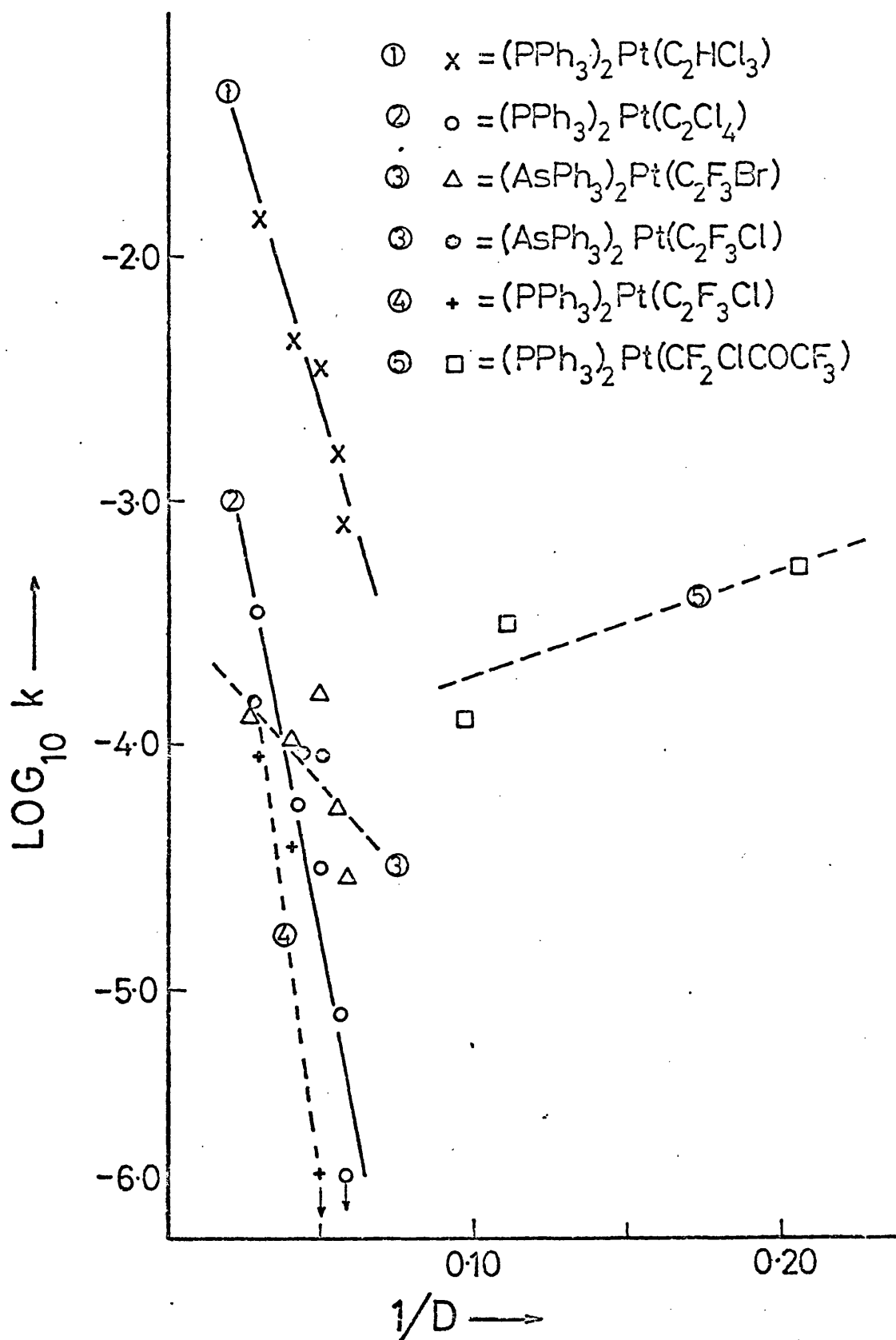
## [2] Isomerisation of a chlorofluoro-ketone compound.

### Experimental:-

The compound  $(\text{PPh}_3)_2\text{Pt}(\text{CF}_3\text{COCF}_2\text{Cl})$  was obtained from Mr. D. A. Clarke. Owing to the low solubility of this compound we were only able to find four solvents in which it was both soluble and did not have its absorption bands, ( $<280$  nm) hidden by solvent bands. The solvents used were as follows:- dichloromethane; chloroform; 1,2 dichloro-ethane; dimethylsulphoxide.

FIGURE 1

A logarithmic plot of the isomerisation rate constants for several platinum-(0) compounds in different solvents as a function of the dielectric constant of the organic solvents.



All kinetic runs were monitored at 276 nm, corresponding to an absorption shoulder over the largest temperature ranges allowed by the solvents used. The individual cells were made up by a similar method to that used for the previous platinum-olefin compounds.

### Results:-

Calculated rate constants, ( $k_{\text{OBS}}$ ) at various temperatures in three of the above (chlorine containing) solvents are displayed in Table 2. Activation parameters calculated from this data (see Appendix) are also listed in Table 3. In each of these three solvents used, an isosbestic point was observed, (i.e. at 315 nm). The reaction in dimethyl sulphoxide did not show any evidence of such a point, however further investigation seemed to indicate the presence of a transient isosbestic point, suggesting that a two stage reaction was occurring. This view was supported when product material, isolated from one of the other solvents was found to react with dimethyl sulphoxide to give the same final U.V. spectrum as was found for the complete reaction in this solvent.

### Discussion:-

The sensitivity of this compound to solvent is shown in Figure 1, along with several platinum-olefin isomerisation reactions. As can be seen in this plot, the platinum-ketone compound has a similar lack of solvent sensitivity to the platinum-olefin compounds,  $(\text{AsPh}_3)_2\text{Pt}(\text{CF}_2\text{CFCl})$  and  $(\text{AsPh}_3)_2\text{Pt}(\text{CF}_2\text{CFBr})$ . However, due to the small number of solvents used, this may not be a completely accurate picture of the situation.

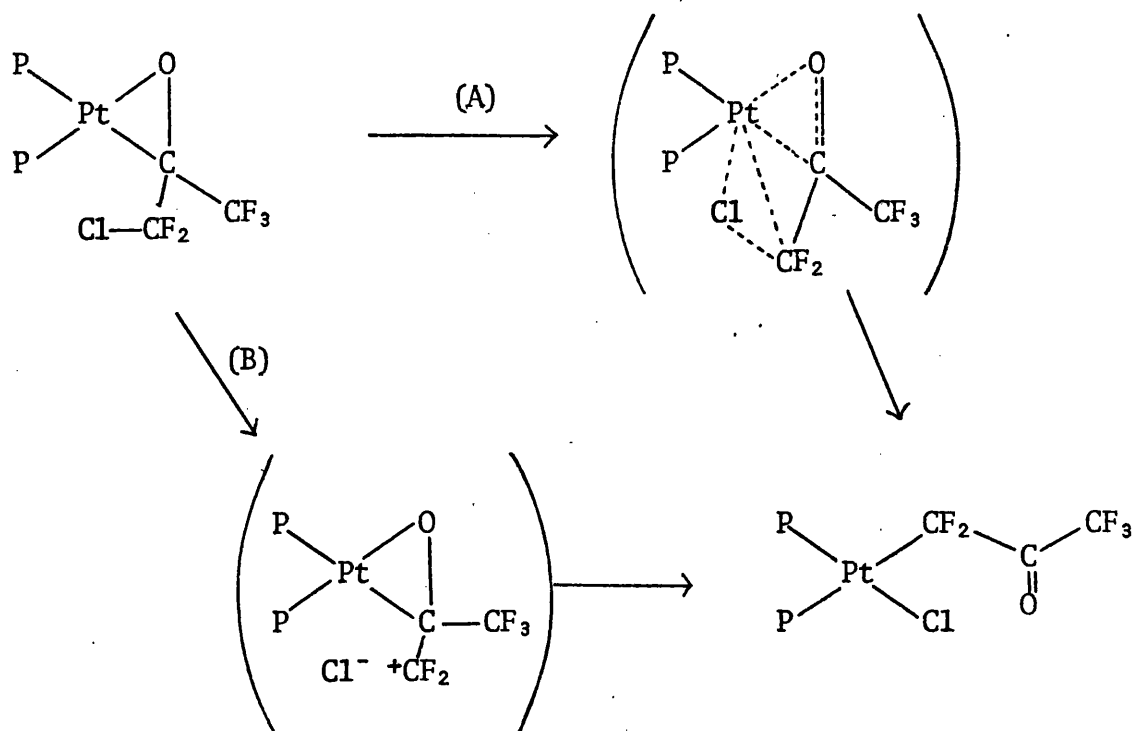
By comparison with the previously described platinum-halogeno-olefin isomerisations it would seem reasonable to propose similar mechanisms for the platinum-halogeno-ketone isomerisation, e.g:-

TABLE 2

First order rate constants, ( $k_{\text{OBS}}$ ) for the oxidative addition reaction of the compound  $(\text{PPh}_3)_2\text{Pt}(\text{CF}_3\text{COCF}_2\text{Cl})$  in several organic solvents at several different temperatures.

SOLVENT:-	CHLOROFORM	DICHLOROMETHANE	1,2-DICHLOROETHANE
$(1/D)^a$ :-	0.21	0.111	0.094
	$10^4 k_{\text{OBS}}/\text{s}^{-1}$		
T/K			
290.7		1.25	
292.2	1.15		
293.5		2.14	
294.2			9.46
297.4		2.74	
298.6			1.53
300.0		3.80	
300.2	5.30		
302.5	5.73		
302.9			2.05
303.5		4.92	
306.6			2.80
307.2	7.92		
310.5			3.52
313.1	12.30		
313.2	15.30		

[ a from references 713, 714]



As we can see, both of these mechanisms involve an increase in order on forming either of the above two transition states, and so this should be evident on examining the activation entropies in the three solvent mixtures. Due to the extra carbon atom, (i.e.  $\text{CF}_2\text{Cl}$ ) the ease of approach of chlorine to the platinum centre will be increased relative to the analogous olefin compounds. This may be responsible for the marked increase in reactivity displayed by the platinum chloro-fluoro-ketone compound.

The activation parameters obtained for the three chlorine-containing solvents are listed in Table 3. Only a small variation in  $\Delta H^\ddagger$  occurs with solvent, as is observed for the rate of reaction. However the odd result reported for the reaction in dimethyl sulphoxide seems to suggest that solvent interference may be more acute in highly polar solvents. It is also of interest to compare our  $\Delta S^\ddagger$  in chloroform with the same parameter for the ring opening of substituted 3-phenylcyclobutene-1,2-dione on platinum-(0). The  $\Delta S^\ddagger$  value for this compound in chloroform  $\sim 0$ , as compared

with  $-75 \text{ J K}^{-1} \text{ mol}^{-1}$  for our compound. This result must reflect the geometric differences between these compounds, the cyclobutene-dione being strained in both its initial and transition states whereas our compound becomes more strained in the transition state than the initial state, hence giving a more negative  $\Delta S^\ddagger$  value.

Again due to chemical difficulties (e.g. preparative and solubility) it was not possible to extend this investigation either by varying substituent groups or by using a larger range of solvents. If such an investigation is carried out in the future (i.e. using a wider range of solvents) it should be possible to get a firmer idea of whether this type of compound resembles the tetrachloro-olefin or the bromo-trifluoro-olefin compound described earlier. Also more evidence favouring either mechanism (A) or (B) might emerge from such work.

TABLE 3

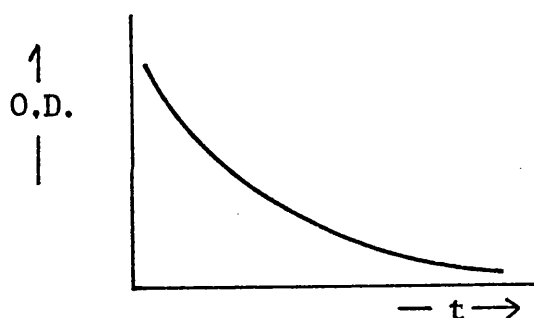
Activation parameters, calculated as described in the Appendix for the oxidative addition reaction of the platinum-(0) compound in several organic solvents.

SOLVENT:-	CHLOROFORM	DICHLOROMETHANE	1,2 DICHLORO-ETHANE
$E_A/\text{kcal. mol}^{-1}$	17.45 (2.0)	17.10 (1.3)	14.60 (0.8)
$\Delta H^\ddagger/\text{kcal. mol}^{-1}$	16.85 (2.0)	16.50 (1.3)	14.00 (0.8)
$\Delta S^\ddagger/\text{cal. K}^{-1} \text{ mol}^{-1}$	-17.8 (6.6)	-19.42 (3.9)	-29.3 (2.4)

[Numbers in parentheses represent the standard deviation of the parameter, i.e.  $\sigma$ .]

APPENDIXData Analysis

In all of the kinetics dealt with in this thesis, the data to be fed into the computer consists of optical density values with corresponding time values. These plots resemble smooth curves, some of which (although by no means all) tend to zero optical density (O.D.), e.g:



If we put the optical density values on the y-axis and the time (t) on the x-axis, (as above) we can see that the curve defining these points is exponential in type, (i.e. governed by an equation of the form  $y = e^{mx+c}$ ). This may not seem a particularly startling result, however upon taking natural logarithms of both sides of this equation we arrive at:-

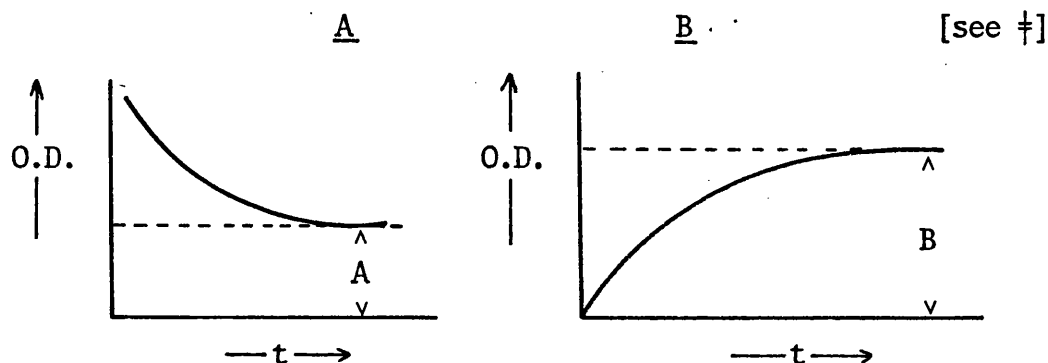
$$\log_e (y) = mx+c, \quad [1]$$

which is the equation of a straight line, the slope, (m) of which is the 'so-called' pseudo-first-order rate constant (in actual fact, the negative value of m is the rate constant, since in this example, the slope would be negative). This relationship can thus provide us with kinetic results, in the form of the above mentioned rate constant, from which contributory first and second order rate constants can be calculated.

Unfortunately, not all reactions produce plots of optical density vs time which give a final O.D. reading of zero, e.g. Fig. A & B. In these



cases it would seem that our previous equation, [1] is invalidated. However, all that is required is a shift of axis, such that the final O.D. (after the reaction has gone to completion) is set to the zero value on the y-axis, e.g:



This final O.D. value is normally called an 'infinity value', since it is the value that the O.D. would have after an infinite time has elapsed, (i.e. after the reaction has gone to completion).

Thus our equation now becomes,

$$(O.D._t - O.D._\infty) = e^{mt+c} \quad \text{for the curve in Fig. A.}$$

$$\text{and } (O.D._\infty - O.D._t) = e^{mt+c} \quad \text{for the curve in Fig. B.}$$

Substituting x and y for t and O.D. as in the previous case, we arrive at equations [2] and [3], e.g.

$$\log_e (y_i - k) = m.x_i + c \quad [2] \quad (\text{Fig. A.})$$

$$\log_e (k - y_i) = m.x_i + c \quad [3] \quad (\text{Fig. B.})$$

where k is a constant, and holds the value of the axis shift, (i.e. the 'infinity'). Since these two equations are linear, a least mean squares analysis (linear regression) will enable us to solve them. This type of analysis allows us to calculate the best (mathematically speaking) line-fit

[ ‡ 'A' represents an O.D. plot of the decrease in concentration of a species with time, and 'B' is the same for the increase in concentration of a species with time.]

for our data, (i.e. it is a method to find the best estimate of  $y$  corresponding to any particular value of  $x$ ; the collective result is termed the regression line of  $y$  on  $x$ ) and assumes that one of the sets of values, (in this case the  $x$ -values) is 'exact'.

The method is as follows:- Let the equation of the regression line be  $y = m.x + c$ , (where  $y$  has the value of the left hand side of either equation [2] or [3]), thus  $m$  and  $c$  are constants.

$$\text{Let } \bar{x} = \frac{1}{n} \sum_{i=1}^n x_i \quad \text{and} \quad \bar{y} = \frac{1}{n} \sum_{i=1}^n y_i ,$$

where  $n$  = the total number of experimental points, and  $(x_1, y_1) \dots (x_n, y_n)$  are the observed pairs of points. The predicted value of  $y$ , corresponding to  $x_1$  given by the previous equation is,  $(m.x_1 + c)$ .

Hence, (measured value - predicted value) =  $y_i - m.x_i - c$ .

Now, set  $U = \sum_{i=1}^n (y_i - m.x_i - c)^2$ , and choose the values of 'm' and

'c' such that  $U$  becomes stationary. Common sense tells us that this stationary value will be a minimum for the best fit of our results.

Differentiating with respect to  $m$  and  $c$  gives us:-

$$\frac{\delta U}{\delta c} = \sum_{i=1}^n [-2 (y_i - m.x_i - c)] \quad [3]$$

$$\frac{\delta U}{\delta m} = \sum_{i=1}^n [-2x_i. (y_i - m.x_i - c)] \quad [4]$$

For the best fit of our data, we said that  $U$  will be at a minimum value, hence  $\frac{\delta U}{\delta c} = \frac{\delta U}{\delta m} = 0$ , thus [3] and [4] become [5] and [6]

e.g.

$$\text{from [3], } \sum_{i=1}^n y_i - m. \sum_{i=1}^n x_i - c = 0 \quad [5]$$

$$\text{from [4], } \sum_{i=1}^n (x_i \cdot y_i) - m \cdot \sum_{i=1}^n (x_i^2) - c \cdot \sum_{i=1}^n x_i = 0 \quad [6]$$

Now, using our definitions of  $x$  and  $y$ , multiplying [5] by  $n$ , we arrive at,

$$n \cdot \bar{y} - n \cdot m \cdot \bar{x} - n \cdot c = 0$$

$$\text{i.e. } \bar{y} = m \cdot \bar{x} + c, \quad c = (\bar{y} - m \cdot \bar{x}).$$

Substituting this value of  $c$  in [6] gives us the following:

$$\sum_{i=1}^n (x_i \cdot y_i) - n \cdot \bar{x} \cdot (\bar{y} - m \cdot \bar{x}) - m \cdot \sum_{i=1}^n (x_i^2) = 0$$

$$\text{i.e. } m = \frac{\sum_{i=1}^n (x_i \cdot y_i) - n \cdot \bar{x} \cdot \bar{y}}{\sum_{i=1}^n (x_i^2) - n \cdot \bar{x}^2}$$

Or, in a more usable form for our data,

$$m = \frac{n \cdot \sum_{i=1}^n (x_i \cdot y_i) - \sum_{i=1}^n (x_i) \cdot \sum_{i=1}^n (y_i)}{n \cdot \sum_{i=1}^n (x_i^2) - \left( \sum_{i=1}^n (x_i) \right)^2} \quad [7]$$

This value ( $m$ ) is called the regression coefficient, and when applied to our data, gives the value of the pseudo first-order rate constant,  $k_{\text{OBS}}$ .

### Error Analysis

Any chemical or physical measurement necessarily involves a certain amount of error. There are two main types of error which occur usually, and they can be classified as either 'determinate' or 'indeterminate'. The first of these are errors whose magnitude can be detected, and thus corrected for, (e.g. due to poor calibration of equipment). The second type, however, are randomly produced, (e.g. by random fluctuations in, say, electronic equipment) and can only be accounted for by statistical analysis.

There are various methods available for the treatment of such errors, the one which has been used by us, is one of the better known, and is based upon the 'Standard deviation<sup>†</sup> measurement'. Applying this analysis to our regression line, we can calculate the Standard Error of the mean (S.E.). This is the measure of spread (or scatter) of our data about this line, the numerical quantity being related to the so-called residuals, (i.e.  $y(\text{expt}) - y(\text{calc.})$ , and the same for  $x$ ), thus in the following equation  $D_y$  is the residual of  $y$  values, and  $D_x$  the same for  $x$ :-

$$\text{S.E.} = \sqrt{\left( \frac{\sum_{i=1}^n (Dy_i)^2}{\sum_{i=1}^n (Dx_i)^2} \right) / (n-2)} \quad [8]$$

The actual meaning of the calculated S.E. is similar to that for a pure standard deviation measurement. Thus  $\pm 1.(\text{S.E.})$  indicates that 68% of the 'n' data points will be found between the limits of  $\pm(\text{S.E.})$ , similarly  $\pm 2.(\text{S.E.})$  represents 98.5% of the data within these limits. The value used in all of our programs to indicate the accuracy of the data is expressed as a percentage error in the regression coefficient, e.g:

$$\% \text{ error} = \frac{\text{S.E.}}{m} \times 100\% \quad [9]$$

Thus we can directly relate the relative magnitudes of the S.E. and the regression coefficient by the above formulation.

N.B. It should be noted that, from the above definition of S.E., it is incorrect to say that S.E. is the exact measure of the error in 'm', (i.e. we cannot write  $m \pm \text{S.E.}$ ) However, the value of the S.E. does relate directly to the 'real' error in 'm', and for this reason we feel that equation [9],

[<sup>†</sup> The strict definition of standard deviation, is the square root of the second moment around a mean. This type of analysis assumes a Gaussian or normal distribution of points about a given mean.]

while not an exact measure, does represent an indication of the size of the above 'real' error.

### Program descriptions

All of the programs described in this section are for the curve 'A' (see Fig. A) type analysis. However, to convert these to the curve 'B' (see Fig. B) type analysis requires only small amendments, (which are explained after the listing of the first program). The relevant flow diagrams and program listings are to be found under the appropriate section headings.

#### Program 1

This program solves the aforementioned equation [7]. Optical density and recorded time values are first fed into the computer followed by a value for the 'infinity', (i.e.  $O.D._t$  when  $t = \infty$ ) and from these the regression coefficient and its percentage error are calculated. There are two main problems encountered using this program. The first is that, for a particular reaction it may be either difficult,<sup>†</sup> (for a slow reaction) or impossible,<sup>†</sup> (for a two-stage process) to obtain an accurate 'infinity' value. Secondly, because it is necessary to input both O.D. and time values, this means that, although the actual computing time is short, the total time spent at the computer terminal is quite long. The following program was

[<sup>†</sup> In the case of a slow reaction, it may be necessary to wait for several hours before the O.D. remains constant, i.e. indicating that the reaction has gone to completion. Hence this limits the number of reactions which can be monitored each day. Also, if the solvent used is volatile, this may give an incorrect infinity value due to evaporation.

In a two-stage reaction, (where the second stage is slow enough to allow reasonably accurate values for the first stage to be collected), an infinity value will not be obtainable (for the first stage) unless it is possible to monitor on an isosbestic point for the second stage.]

written in such a way as to attempt to correct these two problems.

## Program 2

Correction of the latter of the previous problems, which is essentially a problem of the rate of data transfer to the computer can be accomplished quite easily. The time wasting part of the data transfer is the actual feeding in of the individual time and O.D. values. This is unavoidable for the O.D. values, but not for the time values. In all kinetic runs, the O.D. values are taken at regular time intervals. Hence if we program the computer to give the 'x-values' (i.e. on the time axis) unit separation, (i.e.  $x_1=1$ ,  $x_2=2$ , etc.) and at the final state of the computation divide the regression coefficient by the value of the time interval (in seconds). This will give us the desired result and reduce the data input by one half.

A solution to the first problem outlined in Program 1 is not so simple. At the time of writing this program, the only immediate (partial) solution was as follows. By placing a looping routine around the 'infinity' input line, several approximate values could be used, each giving a slightly different result. The result with the corresponding lowest percentage error is thus taken as the best result. The results obtained using this program gave low percentage errors, (usually less than 2%) 'infinity' values were usually found to an accuracy of  $\pm 0.02$  O.D. units.

The problem with this system was that tracing 'infinity' values to the accuracy mentioned was often a lengthy process, and if a result was not found within the loop-total, (i.e. set by the operator on input) all of the O.D. values had to be input again and the above procedure repeated. Thus, although this program allows us to be more systematic in our selection of an 'infinity', it still has its limitations.

Program 3

This program is essentially the same as the previous one, except for one refinement. This alteration was required to correct experimental faults which produced non-random errors in the measured O.D. values (hence not accountable for by statistical analysis). A sub-routine was added to the program, its function being to remove data points (from the computer analysis) from the beginning or end of a data set. The reasons for the removal of these points are as follows. For a fast reaction, (i.e. one where the total O.D. change is over within several minutes) if the thermostating or cell-mixing is not good, the initial O.D. readings may have large (non-random) errors associated with them. Similarly, if a reaction is not completely 'clean', (i.e. deviates from first order kinetics towards the end of a run) the O.D. readings towards the end of a run may be inaccurate. These errors can have very serious effects on the result obtained from the computer, and are not always detectable by the naked eye. Thus using this sub-routine, several results can be obtained using different ranges of data points and, if one of the previous experimental errors is occurring, we will be able to detect it and remove its influence.

Program 4

The biggest disadvantage in using either of the previous two programs is that the 'infinity'-looping routine is finite, thus it is necessary to decide upon the size of this loop-total prior to data input. This can be both difficult and, if the loop-total is too small, extremely tedious.

In the programs used so far, the value of the 'infinity' has always been a mathematically corrected value of the recorded value. In this program we shall introduce the concept of a 'guessed-infinity'. The calculation of such a value requires only that the range of data fed in

covers at least 80% of the total O.D. change (i.e. a better data-fit will be made possible by including this larger range of values). Also, by using a closed loop system we can effectively remove the problem of the finite-sized looping routine, and examine the results at our leisure.

The 'guessed-infinity' idea was based upon the following observation. For any particular reaction, a plot of the S.E.'s against the 'infinity' values for a series of results produced the bell-shaped curve shown in Figure 1. Although the 'steepness' of the sides of the curves varies from reaction to reaction, the overall shape is the same.

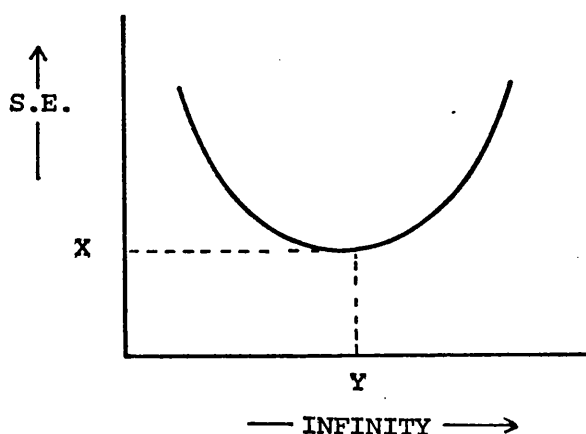


FIGURE 1

Hence for a particular 'infinity' value (Y) there is an associated minimum S.E. (X). Thus this value of the 'infinity' corresponds to the best mathematical fit of the data to the equation,  $y = m.x + c$ , (i.e. this value should be equivalent to the actual measured value, and was found to be so to an accuracy of  $\pm 1.0\%$  in the reactions used to test this program). Using this relationship a search routine was set up as outlined here.

After the usual data input, (i.e. O.D. values, time interval, and the data range to be used in the computations, governed by the variables Z and V) a further set of three variables, (P, R, O) are required. 'P' would be given a value (O.D.) below which we would not expect the best-infinity value to fall; 'R' would be given a value (O.D.) above which we would not expect the previously mentioned 'infinity' to reach (i.e. usually 'R' is given a



value just below the last optical density reading,  $y_n^{\dagger}$ ). The variable 'O' is known as the 'step'. Thus if  $O = 0.1$ , the program will calculate results of 'm' and percentage error for the corresponding 'infinity' values, P,  $P+0.1$ , up to R. Once these values are printed at the terminal, the best-fit (i.e. corresponding to the 'infinity' with the lowest percentage error) can be selected. Because the program operates in a closed-loop, we can choose to increase the accuracy of the result. By assigning new values to 'P' and 'R' about the previous best-'infinity' and a smaller 'step', say 0.01, a second set of results can thus be calculated. Using this method best-'infinity' values to an accuracy of  $\pm 0.001$  O.D. units can be calculated. (N.B. the value of  $\pm 0.001$  O.D. was selected because below this accuracy the change in the result (m) was found not to be significant.)

#### Program 5

This program is similar to the one previous except for the addition of an extra sub-routine and the fact that it does not operate in a closed-loop. Once the full set of results for all of the 'infinity' values have been calculated, they are stored under pre-defined labels, (c.f. program 4, where the results were printed out at this stage) and the new sub-routine is then called into play. This routine is in two parts, and is essentially a minimum (percentage error) search, comparing each error with its neighbours until it detects a minimum value, (e.g. if  $E$  = percentage error, then  $E(L)$  is compared with  $E(L-1)$ , and if it is less than this second value, it is carried through to the second part of the routine. Once here,  $E(L)$  is compared with  $E(L+1)$ , if it is less than this value, it is the desired result and the subscript value  $L$  is carried out of the sub-routine to the

[  $\dagger$  If  $R \geq y_n$  this produces a fatal computational error, i.e.  $\log_e$  (negative number) and so should be avoided.]

main program. The value of  $L$  corresponds to the storage indicators of the percentage error,  $E(L)$  and also the regression coefficient,  $A(L)$  and the 'infinity',  $W(L)$ . Thus these values alone are printed out at the computer terminal. If the value of  $E(L)$  is greater than the value of  $E(L+1)$ , then the first part of the routine is re-entered and the value of  $L$  is changed to begin the above sequence again. (This is done for all the 'L' values until a result is found.)

After finding a result and printing it at the terminal, the program halts, and waits for a command to re-start. One of three commands can be input at this stage, e.g:

- (1) a command to terminate the program,
- (2) a command to set up a new range of data points (via  $Z$  and  $V$ ) for re-computation, and then to (3),
- (3) or, finally, to set up a new range for the search (via  $P$  and  $R$ ), using a smaller value of '0' for increased accuracy.<sup>†</sup>

The data values input initially are stored until step (1) is used, this clears the data from the memory of the computer. Thus as many individual ranges of the O.D. values can be computed as is necessary to give the desired results, these values being stored indefinitely. Using this combination of a computer aided search linked with a variation in the number of data points used lead us to a high degree of accuracy. Percentage errors calculated by this method were usually less than 1.0%.

[<sup>†</sup> The actual size of the 'infinity' range and its step should be selected carefully, since to store the results, sufficient area in the computer must be reserved for these. The size of the computer thus limits the size of this range and, in this case, the integer part of  $(R-P)/O$  should not be allowed to exceed 30.

N.B. This value is also dependent upon the program length and so will vary between different programs.]

Program 6

This program was developed not for the general purpose run, but for calculating results from bad O.D. data. As mentioned earlier, the time consuming part of computing is the data transfer from graph to computer. The use of the unit time interval cut this by half, unfortunately certain circumstances can prevent this from being employed. For instance, if a single or several values (not necessarily in sequence) are obviously bad, (i.e. having a large associated error<sup>‡</sup>) to avoid these data points means that we must input both time and O.D. values - a tedious process.

Program 6 is an adapted version of the previous program written specially to solve the above problem as follows. Two new variables 'F' and 'S' were introduced such that 'S' was given 'positional-sense'. Thus if we wish to remove the 'i'-th data points from the computation, we would set  $S = i$ , for as many points as was necessary. Having done this, the subscripted variables  $F(S)$  would be given the value of zero. Then, just prior to the least squares computation, the x (time) and y (O.D.) values would be re-evaluated according to the following equations:-

$$\left. \begin{array}{l} x = x(I) \cdot F(I) \\ y = y(I) \cdot F(I) \end{array} \right\} I = \text{range of data values.}$$

where  $F(I)$  values would be equal to unity unless they were re-set by the S values. Hence all of the good data values would remain unaltered, (since  $F(I) = 1$ ) but the bad data would be removed (since  $F(S) = 0$ ). Using this adapted version, it is possible to obtain reasonably good results (in terms of the magnitude of the percentage error) from extremely bad data sets.

After the introduction of this program, modifications based upon

[ ‡ These can be caused by electronic or chemical faults such as gas bubbles suddenly forming or drifting up to the top of a solution.]

chemical kinetic difficulties would seem to be complete. The only other possible field for alterations being associated with a reduction in computer (operator) time. Such modifications would involve the transfer of the operator-based decisions to the computer. In this way, once the initial data has been fed into the program, no further 'human' interference would be needed.

#### Program 7

This program approximates very closely to that outlined in the previous paragraph. Program operation is as follows. Optical density values, the time interval and the initial range of 'infinities' are fed in along with two other variables whose use is outlined below. Once this has been done, the program runs completely independent of the operator. The other input devices mentioned are 'O', (the 'step') and a variable named 'M1'. If  $M1=4$ , then results will be computed for the data ranges,  $2 \rightarrow N$ ,  $2 \rightarrow (N-1)$  ...  $2 \rightarrow (N-M1)$ . The initial 'infinity' range should be as large as possible, (to ensure that it contains the 'best-infinity' value) the step being set at 0.1 O.D. units.

At this point we will make a slight digression and try to explain how this program actually works, and why a simpler approach was rejected. The simple method used a fixed small (but optimum - set by the low storage area available on the computer) range with a correspondingly small step-value. This range would then detect the direction in which the 'best-infinity' value lay (i.e. by comparing stored percentage errors for the small range) and slowly 'track' along towards the result, shifting the range (infinity) values as it proceeded. Unfortunately, this method seemed to require an extremely large computing time, (on a time-sharing terminal) relative to the following complicated approach. This second method may be better understood if the

relevant flow diagram is referred to while reading the explanation given here.

Once the initial data input is completed, the program increases the value of each O.D. point by  $10^{-6}$ .<sup>†</sup> The large range of 'infinity' values with the step of 0.1 units is then computed giving one of the following results:-

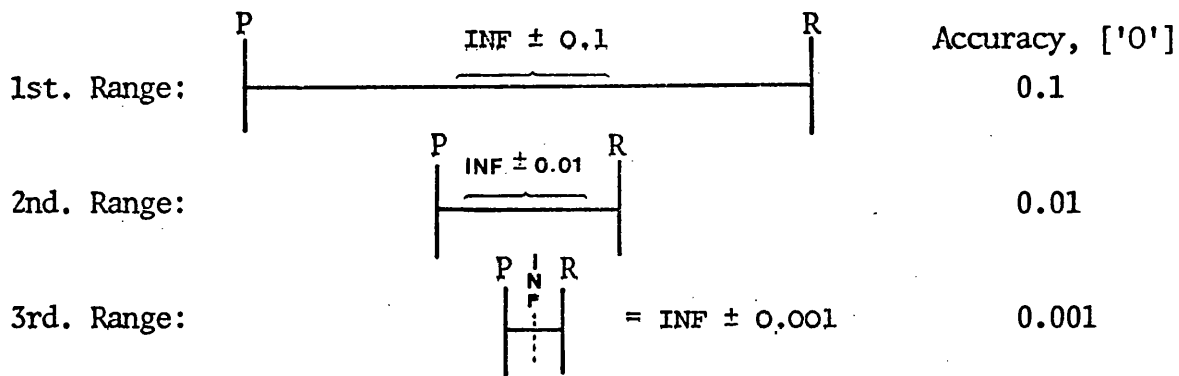
- (1) No minimum found in the range.
- (2) A result is found in the range.

Depending upon which of these occurs, the program executes accordingly. Thus if (1) results, then this causes a variable 'W6' to be set equal to  $(y_n - 10^{-6})$  and a new range is set up using this as a reference point. [N.B. the initial values of 'P' and 'R' are set such that if (1) occurs, then the 'best-infinity' is greater than 'R'.] Thus 'R' is given the value of 'W6', P set to  $(R - 0.09)$ , and finally 'O' to 0.01, and the computation routine is re-entered.

In the second case, [i.e. (2)], a new 'infinity-range' is set up using the previous 'best-infinity' as the central reference point, and the value of 'O' is decreased by a factor of ten. The computation routine is then re-entered. When either of the above two re-computations have been executed the control is again passed to (1) or (2). This is continued until a result arrives at (2), where the step value is 0.001 units. This is the final result and is printed out at the terminal.

The diagram shown here illustrates how the 'best-infinity' value is carried through successive ranges, increasing in accuracy as it does so:-

[<sup>†</sup> The variable 'W6' is later set equal to  $y_n - 10^{-6}$ , if  $y_n$  is not first increased by this value, the 'step' will not operate up to the maximum value possible (i.e. it will only proceed to  $(y_n - 0)$  instead of  $y_n$ ).]



As the range becomes smaller, the 'step' value is decreased, thus no problems with limited storage area occur.

N.B. So as not to duplicate many small loops in the program, (i.e. taking up extra storage) whether path (1) or (2) is used, the same routines assign the new ranges and steps in each case, this is possible because in both cases the ranges use the previous 'best-infinity' (i.e. for path (1) W6 is assigned to the variable corresponding to this value) as a reference point. This is best seen in the relevant flow diagram.

The variable 'M1' controls the number of complete computations performed as described previously. However, each of these computations is not performed completely oblivious of the others. Once a result has been found, this 'best-infinity' value is then used to select the new range ('P' to 'R'), since the loss of one or more data points towards the end of the data range should not cause the 'best-infinity' value to change very much.

In this way several results can be calculated for a single set of O.D. data with a minimum amount of operation time. For the PDP.11, this program represents the most efficient method for extracting polished results from raw data. No further programs or modifications to this program have been made.

Program 8

The availability of a new computer (Cyber 72) with much larger storage facilities than the PDP.11 made it possible for us to write a short program (relative to the previous programs) with all the capabilities of those used previously. Also, this program is able to handle many sets of data at one time. The fundamental change incorporated in this program is the use of a single large (i.e. currently set at a maximum of 900 'infinity' values) 'infinity-range'. This is made possible by the use of large arrays, (i.e. it is within the capability of this machine to store several very large arrays simultaneously) thus simplifying the 'best-infinity' routines. The data input is similar to that used before, except that the input devices used are in the form of READ-DATA statements. Another new feature is the use of the ABS function, which when used in conjunction with the LOG function, allows this single program to solve both type 'A' and type 'B' plots.

The program listing and a section of output are shown in the relevant section. The program is essentially in three sections, the middle section, (lines 900 to 7700) is reserved for data statements only. The first and last sections constitute the computational and error-detection routines respectively. The output, (shown on the page following the program listing) consists of the experimentally determined data values, their theoretical counterparts, (calculated from the regression coefficient) and the difference between these values.<sup>†</sup> A statement defining the curve type is also printed, along with the required results (i.e. slope, 'infinity', percentage error and data range used).

[<sup>†</sup> N.B. The signs of these values are as important as their magnitude, since for a well behaved reaction we would expect the experimental data to be scattered about the calculated line (O.D. vs t). Thus this can be used to detect data anomalies, such as bad thermostating or a two stage process.]

Miscellaneous ProgramsProgram 9

## 'The weighted guessed-infinity program'

This program is an adaptation of program 6 where a weighting factor has been added to the data input routine. The weighting device was set up in the following way, using two initial assumptions. The first of these is that no error occurs in the x-values (i.e. the time interval), which seems like a reasonable assumption, since an electronic clock is responsible for these values. The second is that all data points can be read to the same accuracy, governed by naked-eye observation. Now, where the error in the individual readings, (due to human limitations) is small by comparison with the difference between two consecutive O.D. readings, (which we shall call  $D_1 = O.D._t - O.D._{t+1}$ ) then the error can be ignored. Thus the data points at the beginning of a run will have only small uncertainties when measured by the previous criteria. However, as we approach the end of a run, the value of 'D' will approach the uncertainty value, (usually  $\sim 0.005$  O.D. units), hence becoming a problem. [N.B. These values are necessary for the computer to calculate a 'best-infinity' value.] To account for this error, a weighting factor,  $[J(I)]$  was introduced, whose magnitude depended upon the relative magnitudes of 'D' and the uncertainty value in the following way:-

$$J(I) = \frac{Y(I) \cdot [Y(I) - Y(I+1)]}{U} \quad (Y \equiv \text{O.D. values})$$

where the value contained in the square bracket is equal to 'D', and the denominator (U) is the uncertainty value. The program then uses a plot of  $\log_e (J(I) - \text{INF})$  vs time in the least mean squares analysis.



Unfortunately, the combination of this weighting process with the guessed-infinity routine proved to be antagonistic. The weighting device is obviously biased towards the initial data values, hence giving them more influence than the later values in the 'infinity' routines. Thus the 'best-infinity' value selection is based upon these initial values, (usually less than 60% of the data seemed to have any marked effect upon the 'infinity') and so this produces a meaningless result in the majority of cases, (i.e. as explained earlier, the use of a 'guessed-infinity' routine precludes the use of less than 80% of the total O.D. change).

Although both of these individual analyses (i.e. Guessed-infinity and Weighting parameters) are viable if used in each other's absence, we can see from the previous paragraph that they should not be used simultaneously. It may be possible to write a set of programs which employ these methods consecutively, although mathematically speaking the results obtained thus would be shrouded in doubt.

#### Program 10

##### 'The Guggenheim program'

The program listing and flow diagram are displayed in the relevant sections. At the time of writing this program, it was expected that suitable data (for its use) would be forthcoming, however this was not to be so. Thus the program has only been tested on imaginary data, and in this case seemed to perform correctly. A special feature, previously used in program 6, allowing any number of 'bad' data values to be discarded is present in this program also.

#### Program 11

##### 'A second-order kinetics program'

This program was written to solve equations produced by second-order kinetic traces. However, as in the previous case, its use was not required, nor was it tested (i.e. imaginary data for a second-order process are not 'easy' to fabricate, due to the extra complications introduced by this type of process). For this reason neither the flow diagram nor the program listing have been included in this thesis. The method used involved the calculation of the 'best-infinity' along with an estimation (done by the program, based upon an approximate value input by the operator) of the initial reaction time (i.e.  $t_0$  = time at which the reaction commences). The 'best-infinity' calculated should have a corresponding 'best  $t_0$ ' value (i.e. a plot of  $t_0$  values against percentage error would be of the same form as the previous plots of 'infinities' against percentage error), and using these two values the final result would then be calculated.

PROGRAM 1

-----

```

5 CLOSE3
10 OPEN "KB:"AS FILE 3
15 DIMX(30),Y(30)
20 LETS1=0:LETS2=0:LETS3=0:LETS4=0:LETD=0
25 PRINT"NO. POINTS=";
30 INPUT#3,N
35 FORI=1TON
40 PRINT"X(";I;")=";
45 INPUT#3,X(I)
50 PRINT"Y(";I;")=";
55 INPUT#3,Y(I)
60 NEXTI
65 PRINT"INFINITY=";
70 INPUT#3,W
75 FORI=1TON
80 LETX=X(I)
85 LETY=Y(I)
90 LETY=LOG(Y-W)
95 LETS1=S1+X
100 LETS2=S2+Y
105 LETS3=S3+X*Y
110 LETS4=S4+X*X
115 NEXTI
120 LETC=1/(N*S4-S1*S1)
125 LETA=(N*S3-S1*S2)*C
130 LETB=(S4*S2-S1*S3)*C
135 FORI=1TON
140 LETD2=A*X(I)+B-LOG(Y(I)-W)
145 LETD=D+D2*D2
150 NEXTI
155 LETD=D*C/(N-2)
160 PRINT"RATE CONSTANT="; -A
165 PRINT"STANDARD ERROR="; SQR(N*D)
170 PRINT" % ERROR=";(SQR(N*D))/(-1*A)*100
175 STOP
READY

```

FOR POSITIVE EXPONENTIALS, LINES 90 AND 140 SHOULD READ,

90 LETY=LOG(W-Y)

140 LETD2=A\*X(I)+B-LOG(W-Y(I))

# PROGRAM 2

-----

```

5 CLOSE3
10 OPEN "KB:" AS FILE 3
15 DIMX(30),Y(30)
20 LETS1=0:LETS2=0:LETS3=0:LETS4=0:LETD=0
25 PRINT"UNIT TIME INTERVAL=";
30 INPUT#3,Q
35 PRINT"NO. POINTS=";
40 INPUT#3,N
45 FORI=1TON
50 LETX(I)=I
55 PRINT"Y(";I;")=";
60 INPUT#3,Y(I)
65 NEXTI
70 PRINT"NO. INFINITIES=";
75 INPUT#3,N2
80 FORJ=1TON2
85 PRINT"INFINITY=";
90 INPUT#3,W
95 FORI=1TON
100 LETX=X(I)
105 LETY=Y(I)
110 LETY=LOG(Y-W)
115 LETS1=S1+X
120 LETS2=S2+Y
125 LETS3=S3+X*Y
130 LETS4=S4+X*X
135 NEXTI
140 LETC=1/(N*S4-S1*S1)
145 LETA=(N*S3-S1*S2)*C
150 LETB=(S4*S2-S1*S3)*C
155 FORI=1TON
160 LETD2=A*X(I)+B-LOG(Y-W)
165 LETD=D+D2*D2
170 NEXTI
175 LETD=D*C/(N-2)
180 PRINT"RATE CONSTANT=";-A/Q
185 PRINT"STANDARD ERROR=";SQR(N*D)
190 PRINT" % ERROR=";(SQR(N*D))/(-1*A)*100
195 LETS1=0:LETS2=0:LETS3=0:LETS4=0:LETD=0
200 NEXTJ
205 STOP
READY

```

# PROGRAM 3

-----

```

5 CLOSE3
10 OPEN "KB:" AS FILE 3
15 DIMX(30),Y(30)
20 LETS1=0:LETS2=0:LETS3=0:LETS4=0:LETD=0
25 PRINT"UNIT TIME INTERVAL=";
30 INPUT#3,Q
35 PRINT"NO. POINTS=";
40 INPUT#3,N
45 FORI=1TON
50 LETX(I)=I
55 PRINT"Y(";I;")=";
60 INPUT#3,Y(I)
65 NEXTI
70 PRINT"NO. INFINITIES=";:INPUT#3,N2
75 FORJ=1TON2
80 GOSUB210
85 PRINT"INFINITY=";
90 INPUT#3,W
95 FORI=Z TO V
100 LETX=X(I):LETY=Y(I)
105 LETY=LOG(Y-W)
110 LETS1=S1+X
115 LETS2=S2+Y
120 LETS3=S3+X*Y
125 LETS4=S4+X*X
130 NEXTI
135 LETG=(V-(Z-1))
140 LETC=1/(G*S4-S1*S1)
145 LETA=(G*S3-S1*S2)*C
150 LETB=(S4*S2-S1*S3)*C
155 FORI=Z TO V
160 LETD2=A*X(I)+B-LOG(Y-W)
165 LETD=D+D2*D2
170 NEXTI
175 LETD=D*C/(G-2)
180 PRINT"RATE CONSTANT=";-A/Q
185 PRINT"STANDARD ERROR=";SQR(G*D)
190 PRINT" % ERROR=";(SQR(G*D))/(-1*A)*100
195 LETS1=0:LETS2=0:LETS3=0:LETS4=0:LETD=0
200 NEXTJ
205 GOTO235
210 PRINT"1ST I VALUE=";
215 INPUT#3,Z
220 PRINT"LAST I VALUE=";
225 INPUT#3,V
230 RETURN
235 STOP
READY

```

PROGRAM 4

-----

```

5 CLOSE3
10 OPEN "KB:" AS FILE 3
15 DIMX(30),Y(30)
20 LETS1=0:LETS2=0:LETS3=0:LETS4=0:LETD=0
25 PRINT"UNIT TIME INTERVAL=";
30 INPUT#3,Q
35 PRINT"NO. POINTS=";
40 INPUT#3,N
45 FORI=1TON
50 LETX(I)=I
55 PRINT"Y(";I;")=";
60 INPUT#3,Y(I)
65 NEXTI
70 GOSUB200
75 PRINT"RANGE OF INF. + STEP=";
80 INPUT#3,P,R,0
85 PRINT"INFINITY=";W
90 FORI=Z TO V
95 LETX=X(I):LETY=Y(I)
100 LETY=LOG(Y-W)
105 LETS1=S1+X:LETS2=S2+Y
110 LETS3=S3+X*Y:LETS4=S4+X*X
115 NEXTI
120 LETC=(V-(Z=1))
125 LETC=1/(G*S4-S1*S1)
130 LETA=(G*S3-S1*S2)*C
135 LETB=(S4*S2-S1*S3)*C
140 FORI=Z TO V
145 LETD2=A*X(I)+B-LOG(Y(I)-W)
150 LETD=D+D2*D2
155 NEXTI
160 LETD=D*C/(G-2)
165 PRINT"RATE CONSTANT=";-A/Q
170 PRINT" % ERROR=";(SQR(G*D))/(-1*A)*100
175 LETS1=0:LETS2=0:LETS3=0:LETS4=0:LETD=0
180 NEXTW
185 GOTO75
190 REM...FINITE RANGE
200 PRINT"1ST I VALUE=";
205 INPUT#3,Z
210 PRINT"LAST I VALUE=";
215 INPUT#3,V
220 RETURN
READY

```

PROGRAM 5

-----

```

5 CLOSE 3
10 OPEN "KB:" AS FILE 3
15 DIMX(30),Y(30),A(30),E(30),W(30)
20 LETS1=0:LETS2=0:LETS3=0:LETS4=0:LETD=0:LETL=0
25 PRINT"UNIT TIME INTERVAL="";:INPUT#3,Q
35 PRINT"NO. POINTS="";:INPUT#3,N
45 FORI=1TON:LETX(I)=I
50 PRINT"Y(";I;")="";:INPUT#3,Y(I):NEXTI
55 GOSUB205
60 GOTO35
65 PRINT"FOR SAME DATA ,PRINT:GOTO85:"
70 PRINT"FOR DIFF. DATA , PRINT:GOTO55:"
75 PRINT" TO STOP ,PRINT:GOTO290:"
80 STOP
85 LETL=0
90 PRINT"RANGE OF INFINITY +STEP="";
95 INPUT#3,P,R,Q
100 FOR W=P TO R STEP Q
105 FORI=Z TO V
110 LETX=X(I):LETY=Y(I):LETY=LOG(Y-W)
120 LETS1=S1+X:LETS2=S2+Y
125 LETS3=S3+X*Y:LETS4=S4+X*X:NEXTI
130 LETG=(V-(Z-1))
135 LETC=1/(G*S4-S1*S1)
140 LETA=(G*S3-S1*S2)*C
145 LETB=(S4*S2-S1*S3)*C
150 FORI=Z TO V
155 LETD2=A*X(I)+B-LOG(Y(I)-W)
160 LETD=D+D2*D2:NEXTI
165 LETD=D*C/(G-2)
170 LETE=(SQR(G*D))/(-1*A)*100
175 LETL=L+1:LETE(L)=E:LETW(L)=W:LETA(L)=A
180 LETS1=0:LETS2=0:LETS3=0:LETS4=0:LETD=0
185 NEXTW
190 LETH=L
195 GOSUB220
200 GOTO65
205 PRINT"1ST I VALUE="";:INPUT#3,Z
210 PRINT"LAST I VALUE="";:INPUT#3,V
215 RETURN
220 LETH1=H-1
225 FORL=2 TOH1
235 IFE(L)<E(L-1) THEN255
240 PRINTE(L),E(L-1)
245 NEXT L
250 PRINT"NO MINIMUM IN THIS RANGE.":GOTO85
255 IFE(L)<E(L+1) THEN270
260 PRINTE(L),E(L+1)
265 GOTO245
270 PRINT" K-OBS="";-A(L)/Q," % ERROR="";E(L)
275 PRINT:PRINT" 5 ERROR="";E(L)
280 PRINT"INFINITY="";W(L)
285 RETURN
290 STOP

```

READY



# PROGRAM 6

-----

```

5 CLOSE 3
10 OPEN "KB:" AS FILE 3
15 DIMX(30),Y(30),A(30),E(30),W(30)
20 LETS1=0:LETS2=0:LETS3=0:LETS4=0:LETD=0:LETL=0:LETR=0
25 PRINT"UNIT TIME INTERVAL="";:INPUT#3,Q
35 PRINT"NO. POINTS="";:INPUT#3,N
45 FORI=1TO N:LETX(I)=1:LETF(I)=1
50 PRINT"Y(";I;")="";:INPUT#3,Y(I):NEXTI
55 GOSUB 170
60 GOTO 35
65 PRINT"FOR SAME DATA, PRINT:GOTO35:"
70 PRINT"FOR DIFF. DATA, PRINT:GOTO55:"
75 PRINT"TO STOP, PRINT:GOTO260"
80 STOP
85 LETL=0
90 PRINT"RANGE OF INFINITY+STEP="";:INPUT#3,P,R,O
95 FOR W=P TO R STEP O
100 FORI=2 TO V
105 LETX=X(I)*F(I):LETY=Y(I)*F(I)
110 IF F(I)=0 THEN 125
115 LETY=LOG(Y-W):LETS1=S1+X:LETS2=S2+Y:LETS3=S3+X*Y
120 LETS4=S4+X*X:NEXTI
125 LETG=(V-(Z-1)):LETC=1/(G*S4-S1*S1):LETA=(G*S3-S1*S2)*C
130 LETB=(S4*S2-S1*S3)*C
135 FORI=Z TO V:LETD2=A*X(I)+B-LOG(Y(I)-W):LETD=D+D2*D2
140 NEXTI:LETD=D*C/(G-2):LETE=(SQR(G*D))/(-1*A)*100
145 LETL=L+1:LETW(L)=W:LETE(L)=E:LETA(L)=A:LETS1=0:LETS2=0
150 LETS3=0:LETS4=0:LETD=0:NEXT W
155 LETH=L
160 GOSUB500
165 GOTO65
170 PRINT"1ST I VALUE="";:INPUT#3,Z
175 PRINT"LAST I VALUE="";:INPUT#3,V:LETRI=R1+1
180 IF R1>1 THEN RETURN
185 REM..DROP POINTS
190 PRINT"NO. POINTS TO BE DROPPED="";:INPUT#3,R1
195 IF R1=0 THEN35
200 PRINT"INPUT I VALUES OF POINTS NOW..."
205 FOR I=1 TO R1:INPUT#3,S:LETF(S)=0:NEXTI
210 GOTO35
215 LET H1=H-1:FORL=2 TO H1
220 IF E(L)<E(L-1) THEN235
225 PRINTE(L),E(L-1)
230 NEXTL
235 PRINT" NO MINIMUMU IN THIS RANGE.":GOTO 35
240 IF E(L)<E(L+1) THEN250
245 GOTO230
250 PRINT"K-OBS="";-A(L)/Q," % ERROR="";E(L)
255 PRINT:PRINT"INFINITY="";W(L):RETURN
260 STOP
READY

```



# PROGRAM 7

-----

```

5 REM ..K-OBS CALCULATION
10 DIMX(30),Y(30),E(20),W(20),A(20)
15 LETS1=0:LETS2=0:LETS3=0:LETS4=0:LETD=0:LETC6=0:LETN1=0
20 PRINT"M1="";:INPUTM1
25 PRINT"NO. POINTS & TIME INTERVAL="";:INPUTN,Q
30 FORI=1TON:LETX(I)=I:PRINT"Y(";I;")="";:INPUTY(I)
35 LETY(I)=Y(I)+1E+6:NEXT I
40 GOSUB 220
45 IF N1>1 THEN60
50 PRINT"RANGE OF INFINITY + STEP="";:INPUTP,R,O
55 LETL=0
58 PRINT"Z="";Z,"V="";V
60 FORW=P TO R STEP O
65 FORI=Z TO V:LETX=X(I):LETY=Y(I)
68 LETY=LOG(Y-W):LETS1=S1+X
70 LETS2=S2+Y:LETS3=S3+X*Y
73 LETS4=S4+X*X:NEXT I:LETG=(V-(Z-1))
75 LETC=1/(G*S4-S1*S1):LETA=(G*S3-S1*S2)*C
80 LETB=(S4*S2-S1*S3)*C:FORI=ZTOV:LETD2=A*X(I)+B-LOG(Y(I)-W)
85 LETD=D+D2*D2:NEXT I:LETD=D*C/(G-2)
88 LETE=(SQR(G*D))/(-1*A)*100
90 LETL=L+1:LETS1=0:LETS2=0:LETS3=0:LETS4=0:LETD=0
93 NEXT W
95 LETH=L:LETH1=H-1
98 PRINT"H="";H
100 FORL=2TOH1
105 IFE(L)<E(L-1) THEN125
110 PRINTE(L),W(L),E(L-1),W(L-1)
115 NEXT L
120 PRINT"NO SOLUTION FOUND.":GOTO270
125 IFE(L)<E(L+1) THEN135
130 PRINTE(L),W(L),E(L+1),W(L+1):GOTO115
135 IF O=0.1 THEN170
140 LETW6=0
145 IF O=0.01 THEN 195
150 PRINT"K-OBS="";-A(L)/Q,"% ERROR="";E(L),"INF="";W(L)
155 LETW6=W(L)
160 GOSUB 220
165 GOTO 55
170 LETP=W(L)-0.09:LETR=W(L)+0.09:LETO=0.01
175 IF R>Y(N)THEN185
180 GOTO55
185 LETR=Y(N)-0.01
190 GOTO55
READY

```

\*\*\*\*\*CONTINUED ON NEXT PAGE.\*\*\*\*\*

( PROGRAM 7 CONTINUED )

```
190 GOTO55
195 LETP=W(L)-0.009:LETR=W(L)+0.009:LETO=0.001
200 IFR>Y(N) THEN210
205 GOTO55
210 LETR=Y(N)-0.001
215 GOTO55
220 LETZ=2:LETN1=N1+1
225 IF N1>M1 THEN350
230 LETV=N-N1
235 IF N1>1 THEN 245
240 RETURN
245 LETP=W(L)-0.4:LETR=W(L)+0.2
250 IFR>Y(N) THEN265
255 LETO=0.1
260 RETURN
265 LETT2=Y(N)-1E+6:LETR=T2:GOTO255
270 REM NO ANSWER,W....Y(N)
275 LETC6=C6+1
280 LETT=Y(N)-1E+6
285 IF C6<2 THENLET W6=T
290 IF O=0.1 THEN 300
295 IF O=0.01 THEN 325
300 LETP=W6-0.09
305 LETR=W6+0.08
310 IFR>Y(N) THEN LETR=T
315 LETO=0.01
320 GOTO 55
325 LETR=T
330 LETP=R-0.009
335 LETO=0.001
340 GOTO 55
350 END
READY
```

# PROGRAM 3 -----

```

0 PRINT"THIS IS JGCBAR WORKING"
0 DIMX(40),Y(40),W(900),E(900),A(900),P1(20)
5 DIM B(900)
0 FORI=1TO20
0 LET P1(I)=0
0 NEXTI
0 LETP1(1)=P1(1)+1
0 PRINT"DATA SET=";P1(1)
0 LETP1(10)=0
0 READ N,Q,P2,R,O,N1
25 PRINT
26 PRINT"N,Q,P2,R,O,N1";N,Q,P2,R,O,N1
28 GOSUB5000
35 IFQ>1E+6THEN3000
40 FORI=1TON
50 READY(I)
50 LETX(I)=I
70 PRINTY(I);
50 NEXTI
90 GOSUB5030
00 LETZ=2
10 LETP1(10)=P1(10)+1
20 LETV=N-P1(10)
25 PRINT
26 PRINT"Z,V";Z,V
30 IFP1(10)=N1+1 THEN190
40 LETL=0
50 FORI=2TO6
60 LETP1(I)=0
70 NEXTI
80 FORW=P2TORSTEPSO
85 IFL=1THEN6000
90 FORI=ZTOV
00 LETX=X(I)
10 LETY2=ABS(Y(I)-W)
20 LETY=LOG(Y2)
30 LETP1(2)=P1(2)+X
40 LETP1(3)=P1(3)+Y
50 LETP1(4)=P1(4)+X*Y
60 LETP1(5)=P1(5)+X*X
70 NEXTI
80 LETG=(V-(Z-1))
90 LETC=1/(G*P1(5)-P1(2)*P1(2))
000 LETA=(G*P1(4)-P1(2)*P1(3))*C
10 LETB=(P1(5)*P1(3)-P1(2)*P1(4))*C
20 FORI=ZTOV
25 LETY2=ABS(Y(I)-W)
30 LETD2=A*X(I)+B-LOG(Y2)
40 LETP1(6)=P1(6)+D2*D2
50 NEXTI

```

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( CONTINUED )

```
560 LETP1(6)=P1(6)*C/(G-2)
570 LETE=(SQR(G*P1(6)))/(-1*A)*100
580 LETL=L+1
590 LETE(L)=E
600 LETW(L)=W
610 LETA(L)=A
615 LETB(L)=B
620 FORI=2TO6
630 LETP1(I)=0
640 NEXTI
650 NEXTW
660 LETH=L
670 LETH1=H-1
680 FORL=2TOH1
690 IFE(L)<E(L-1) THEN730
700 NEXTL
710 GOSUB7350
720 GOTO750
730 IFE(L)<E(L+1) THEN750
740 GOTO700
750 PRINT
760 PRINT"K=";-A(L)/Q,"%=";E(L),"INFINITY=";W(L)
770 PRINT
775 GOSUB6530
780 GOTO310
790 REM.....DATA FORMAT EXPLAINED HERE*****
800 REM.DATA LINES,1000 TO 4990
820 REM..N=MAX. NO. PTS.,Q=TIME INT.,P=MIN. INFINITY
830 REM..R=MAXIMUM LIKELY INFINITY VALUE,0=STEP(0.001 USUALLY)
835 REM..N1=NO. PTS TO BE DROPPED,(IF N1=4,CALCS. FOR
840 REM..FOUR SETS OF Y VALUES WILL BE MADE..1TON,N-1...N-4
850 REM DATA ORDER..N,Q,P,R,0,N1,THEN Y VALUES FOR EACH DATA SET
1000 REM DATA START..
1010 DATA 21.96,0,0.399,0.001,1
1020 DATA 1.416,1.343,1.231,1.22,1.162,1.106,1.06,1.009
1030 DATA 0.967,0.925,0.882,0.843,0.803,0.77,0.74,0.703
1040 DATA 0.631,0.659,0.639,0.613,0.593
1050 DATA21.96,0,0.399,0.001,1
1060 DATA 1.411,1.333,1.264,1.2,1.133,1.077,1.021,0.972
1070 DATA 0.92,0.871,0.821,0.777,0.733,0.701,0.666,0.635
1080 DATA 0.603,0.581,0.545,0.52,0.497
4980 DATA 0,2E+9,0,0,0,0
4990 REM ..END OF DATA BLOCK..
5000 REM START CHECK SUB..
5010 IFN>40 THEN 6500
5015 IFN<4 THEN 6505
5020 IFQ<2THEN5100
5025 RETURN
5030 FORI=1TON
5040 IFY(I)>2THEN5105
5050 NEXTI
5060 RETURN
5100 PRINT"ABORT**,"Q<2"
```

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( CONTINUED )

```
5105 PRINT" Y DATA ERROR PROBABLY RESPONSIBLE"
5110 GOTO3000
6000 IFY(1)>Y(2)THEN6100
6020 PRINT"POSITIVE EXPONENTIAL"
6025 LETP1(15)=1
6030 GOTO390
6100 PRINT
6110 PRINT"NEGATIVE EXPONENTIAL"
6115 LETP1(15)=2
6120 GOTO390
6500 IFN>1E+6 THEN8000
6505 PRINT"N VALUE ERROR#####"
6507 GOTO3000
6510 GOTO7910
6530 REM***IMAGINARY POINTS***
6540 PRINT"REAL", "GUESS"
6550 FORI=1TON
6560 LETY3=A(L)*X(I)+B(L)
6570 LETZ1=EXP(Y3)
6575 IFP1(15)=1THEN6595
6580 LETZ2=W(L)+Z1
6585 GOTO6597
6595 LETZ2=W(L)-Z1
6597 LETD3=Y(I)-Z2
6600 PRINTY(I),Z2,D3
6610 NEXTI
6620 RETURN
7850 IFE(2)<E(H1)THEN7880
7860 PRINT"INFINITY>R SET"
7865 LETL=H
7870 RETURN
7880 PRINT"INFINITY<P SET"
7885 LETL=1
7887 RETURN
7900 PRINT"N<2 SO STOPPED"
7910 PRINT"N>40 SO **ABORT**"
8000 PRINT"IM FINISHED"
8010 END
READY.
```

THIS IS JGCEAR WORKING  
DATA SET= 1

( OUTPUT FROM PROGRAM 3 )

N,Q,P2,R,0,N1	21	96	0	.399
.001	1			
1.416	1.343	1.231	1.22	1.162 1.106 1.06 1.009 .967 .925 .832
.843	.803	.77	.74	.703 .631 .659 .613 .593
Z,V	2	20		

NEGATIVE EXPONENTIAL

K= 6.42606E-4 % = .339376 INFINITY= .25

REAL

GUESS

1.416	1.4176	-1.60457E-3
1.343	1.34775	-4.75162E-3
1.231	1.23203	-1.07767E-3
1.22	1.22033	-3.32732E-4
1.162	1.16223	-2.81734E-4
1.106	1.1077	-1.70369E-3
1.06	1.05639	3.60913E-3
1.009	1.00315	3.52211E-4
.967	.962791	4.20906E-3
.925	.920143	4.85240E-3
.832	.830055	1.94456E-3
.843	.842362	6.33172E-4
.803	.806923	1.07673E-3
.77	.773605	-3.60435E-3
.74	.74228	-2.27973E-3
.703	.712329	-4.82367E-3
.631	.63514	-4.13955E-3
.659	.659107	-1.06945E-4
.639	.634632	4.36323E-3
.613	.611621	1.37916E-3
.593	.589937	3.01344E-3

# PROGRAM 9

-----

```

5 CLOSE 3
10 OPEN "KB:" AS FILE 3
15 DIMX(30),Y(30),E(25),A(25),W(25),T(30),J1(30)
20 LETS1=0:LETS2=0:LETS3=0:LETS4=0:LETD=0:LETP1=0
25 PRINT"UNIT TIME INTERVAL="";:INPUT#3,Q
30 PRINT"NO. POINTS="";:INPUT#3,N
35 FORI=1TO N:LETX(I)=1:PRINT"Y(";I;")="";:INPUT#3,Y(I):NEXTI
40 GOSUB 225
45 GOSUB 155
50 GOTO 70
55 PRINT"FOR SAME DATA :GOTO70:,FOR DIFF. DATA:GOTO40:"
60 PRINT"TO STOP ,PRINT:GOTO600:"
65 STOP
70 LETL=0
75 PRINT"RANGE OF INF. +STEP="";:INPUT#3,P,R,O
80 FORW=P TO R STEP O
85 FORI=Z TO V
90 LETX=X(I):LETY=Y(I):LETY=LOG(Y-W)
95 LETS1=S1+X:LETS2=S2+Y:LETS3=S3+X*Y:LETS4=S4+X*X:NEXTI
100 LETG=(V-(Z-1)):LETC=1/(G*S4-S1*S1)
105 LETA=(G*S3-S1*S2)*C:LETB=(S4*S2-S1*S3)*C
110 FORI=1TON:LETD2=A*X(I)+B-LOG(Y(I)-W):LETD=D+D2*D2:NEXTI
115 LETD=D*C/(G-2):LETE=(SQR(G*D))/(-1*A)*100
125 LETL=L+1:LETE(L)=E:LETW(L)=W:LETA(L)=A
130 LETS1=0:LETS2=0:LETS3=0:LETS4=0:LETD=0
135 NEXTW:LETH=L
145 GOSUB350
150 GOTO55
155 PRINT"1ST I VALUE="";:INPUT#3,Z
160 PRINT"LAST I VALUE="";:INPUT#3,V
165 RETURN
170 LETH1=H-1
175 FORL=2 TO H1
180 IFE(L)<E(L-1) THEN200
185 PRINTE(L),E(L-1)
190 NEXT L
195 PRINT"NO MINIMUM IN THIS RANGE.":GOTO70
200 IFE(L)<E(L+1) THEN 210
205 PRINTE(L),E(L+1):GOTO190
210 PRINT"K-OBS="";-A(L)/Q,"% ERROR="";E(L)
215 PRINT"INFINITY="";W(L)
220 RETURN
225 LETN1=0
230 FORI=1TO N:LETT(I)=Y(I)-Y(I+1):LETN1=N1+1
235 IF N1=N-1 THEN245
240 NEXTI:GOTO250
245 LETI=N:LETT(I)=T(I-1)
250 PRINT"HUMAN ERROR="";:INPUT#3,M1
255 FORI=1TON:LETJ1(I)=Y(I)*T(I)/M1:NEXTI
260 FORI=1TON:LETY(I)=J1(I):NEXTI
265 RETURN
270 STOP
READY

```



PROGRAM 10

-----

```

5 CLOSE 2
7 OPEN "KB:" AS FILE 2
9 REM.....GUGGENHEIM,,,L SQ PROG
15 DIMX(50),Y(50),F(50),A1(50),B1(50)
18 LETS1=0:LETS2=0:LETS3=0:LETS4=0:LETD=0:LETR=0
25 PRINT"UNIT TIME INTERVAL="";:INPUTQ
30 PRINT:PRINT"NO. POINTS="";:INPUT#2,N
32 FORI=1TON:LETF(I)=1:NEXTI
33 FOR I=1TON:LETX(I)=F(I)*I/Q:NEXT I
43 PRINT:PRINT"1ST SET VALUES="
44 FORI=1TON:INPUT#2,A1(I):NEXT I
50 PRINT:PRINT"2ND SET VALUES="
55 FORI=1TON:INPUT#2,B1(I):NEXTI
58 FORI=1TO N
60 LETX=X(I)*F(I)
63 LETY(I)=F(I)*LOG(A1(I)-B1(I))
65 LETY=Y(I)
70 LETS1=S1+X:LETS2=S2+Y
75 LETS3=S3+X*Y:LETS4=S4+X*X:NEXT I
80 LETC=1/(N*S4-S1*S1):LETA=(N*S3-S1*S29*C
85 LETB=(S4*S2-S1*S3)*C
90 FORI=1TON:LETD2=A*X(I)+B-Y(I)
95 LETD=D+D2*D2:NEXT I
100 LETD=D*C/(N-2)
110 PRINT:PRINT"*****GRADIENT.....";-A,"*****"
115 PRINT"      % ERROR...";(SQR((N-R)*D))/(-1*A)*100
120 PRINT" DROP POINTS LOOP"
130 PRINT"NO. POINTS TO BE DROPPED="";
135 INPUT R
138 PRINT"INPUT I VALUES OF POINTS"
140 FORI=1 TO R
142 INPUT S:LETF(S)=0:NEXT I
145 FORI=1 TO R
147 IF S>20 THEN 200
150 LETN=N-R
160 GOTO 60
200 STOP
READY

```



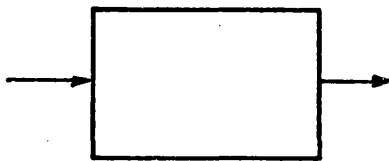
## Flowcharts

### Definition

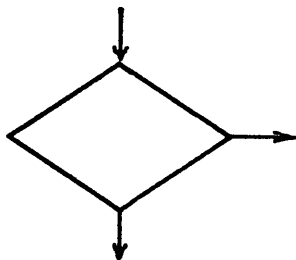
A flowchart shows the sequence of instructions to be obeyed by the computer under various conditions of data or intermediate calculated values.

### Conventions

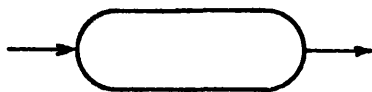
- (1) To make individual groups of instructions more legible, variously shaped boxes are used, each shape being indicative of the type of instruction used within, e.g.



A rectangular box is used to include a group of instructions which do not include any transfer instructions.



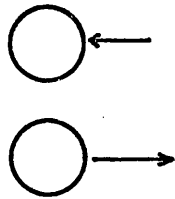
A rhomboid box contains test and transfer instructions. (See note 2)



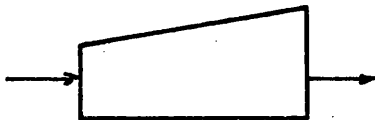
A box used for indicating the start and end of a program, and also for unconditional transfers (e.g. GOTO a line number).



A parallelogram box involves the reading or writing of data or results.



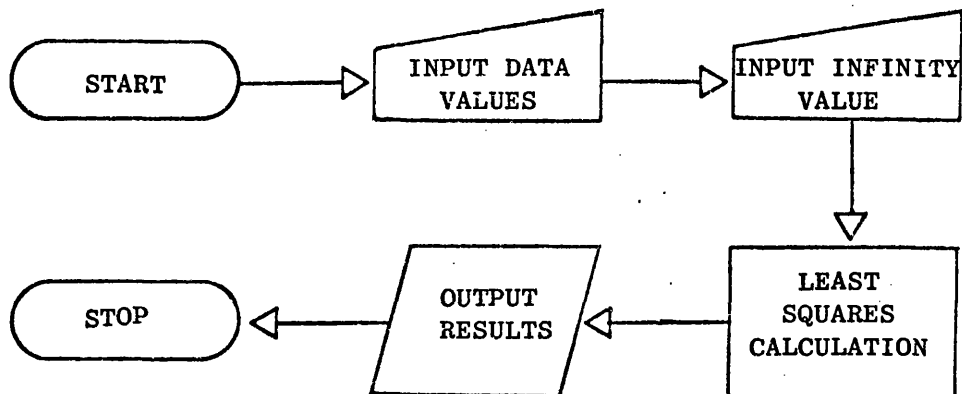
A circle denotes transfer to another part of the program, where a continuous line would be difficult to use. A number is usually included in the circle to show the transfer destination.



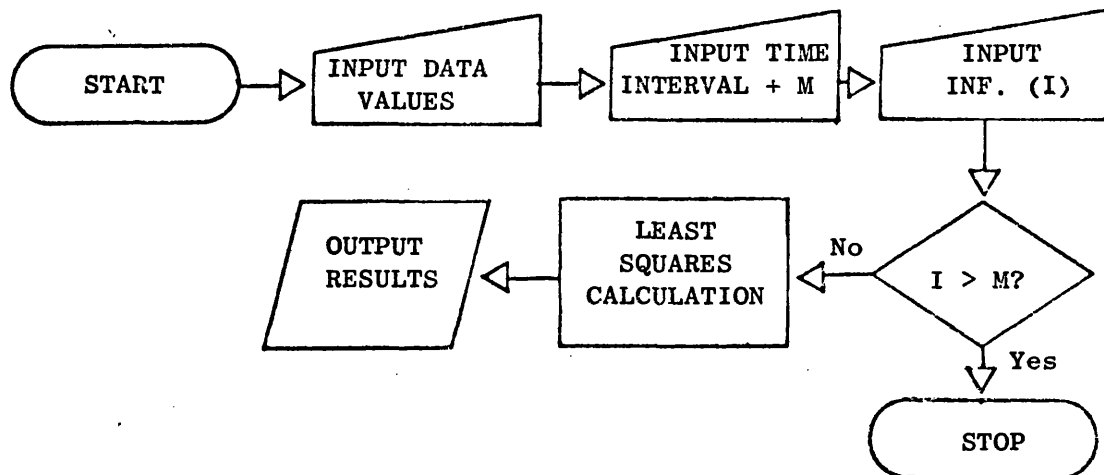
This box signifies the use of an on-line process at 'human speed', such as a data input from a keyboard.

- (2) The use of the rhomboid box is normally accompanied by labels, either 'YES' or 'NO' on the exit routes, to signify the alternative paths which can be followed, depending upon the result of the test.

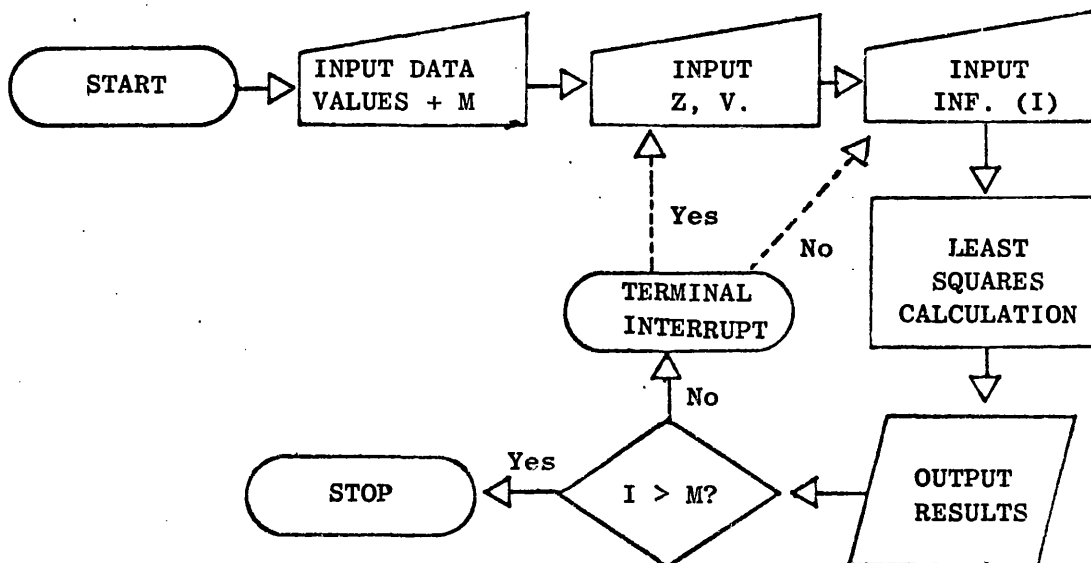
PROGRAM 1



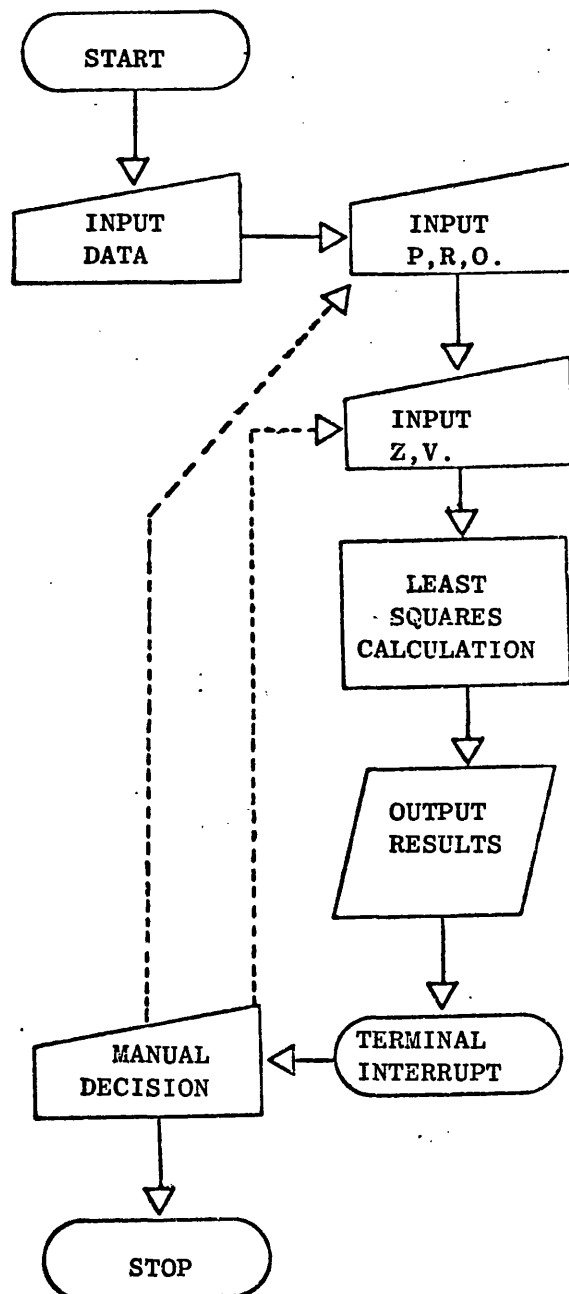
PROGRAM 2



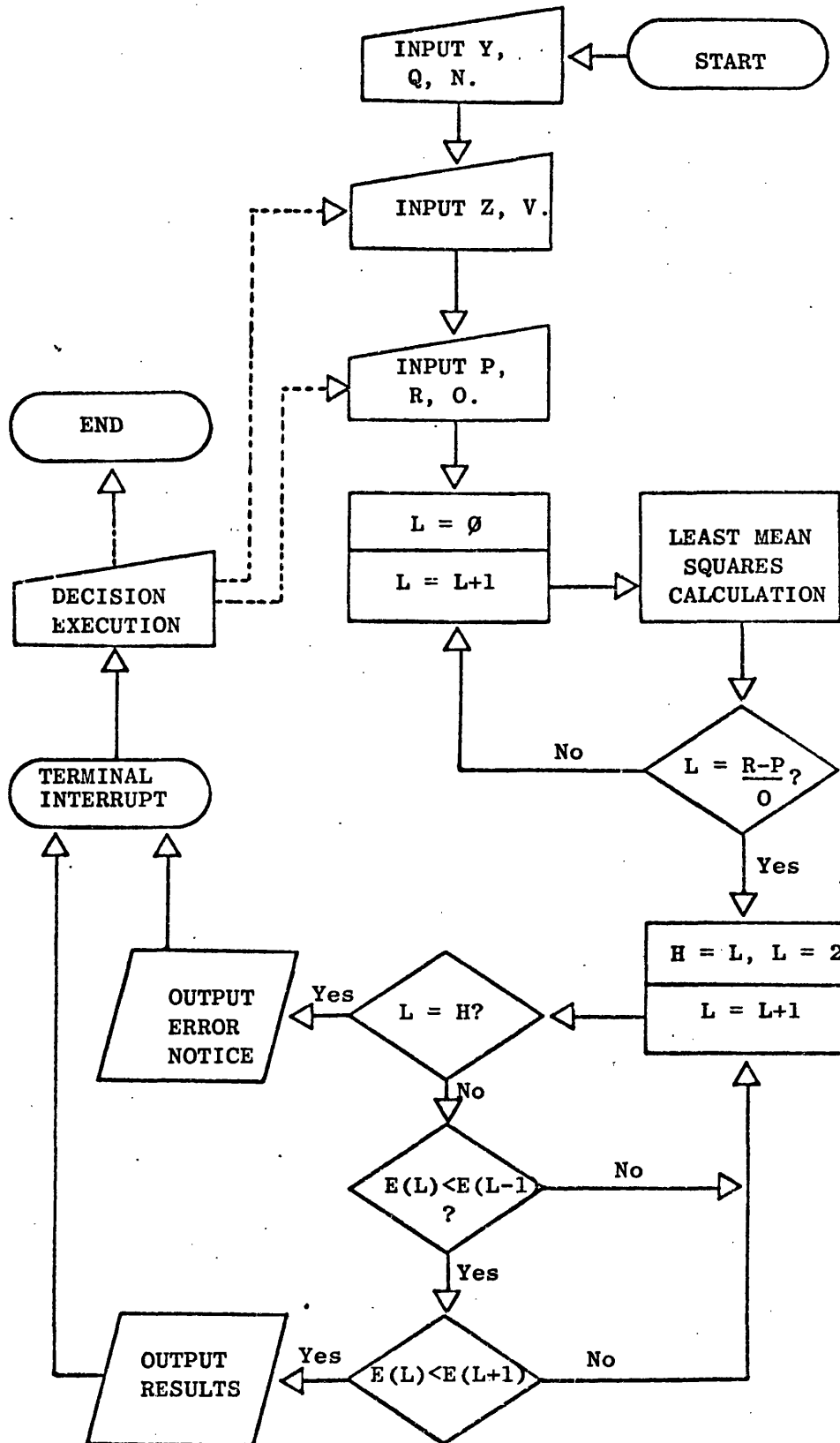
PROGRAM 3



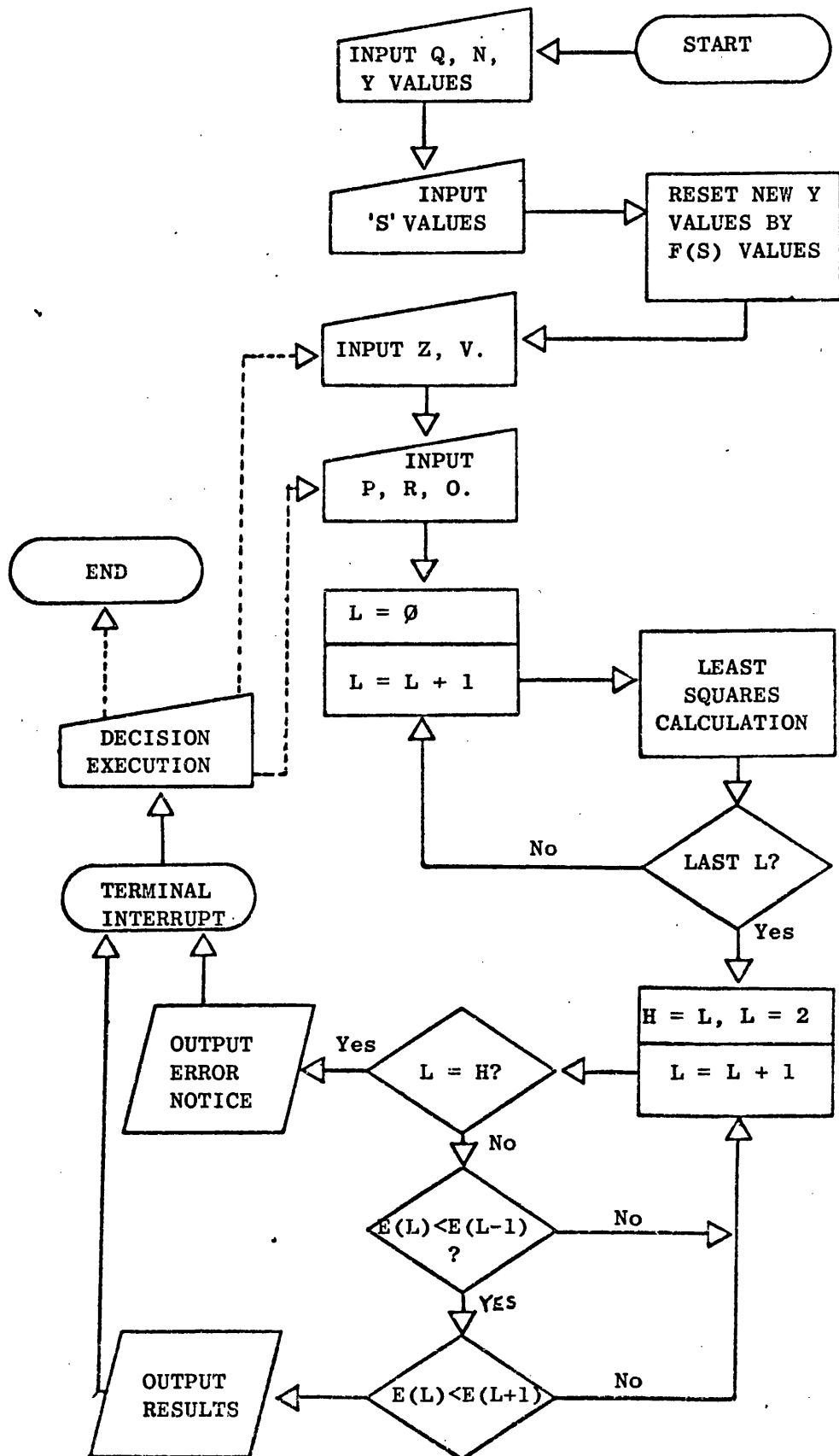
PROGRAM 4



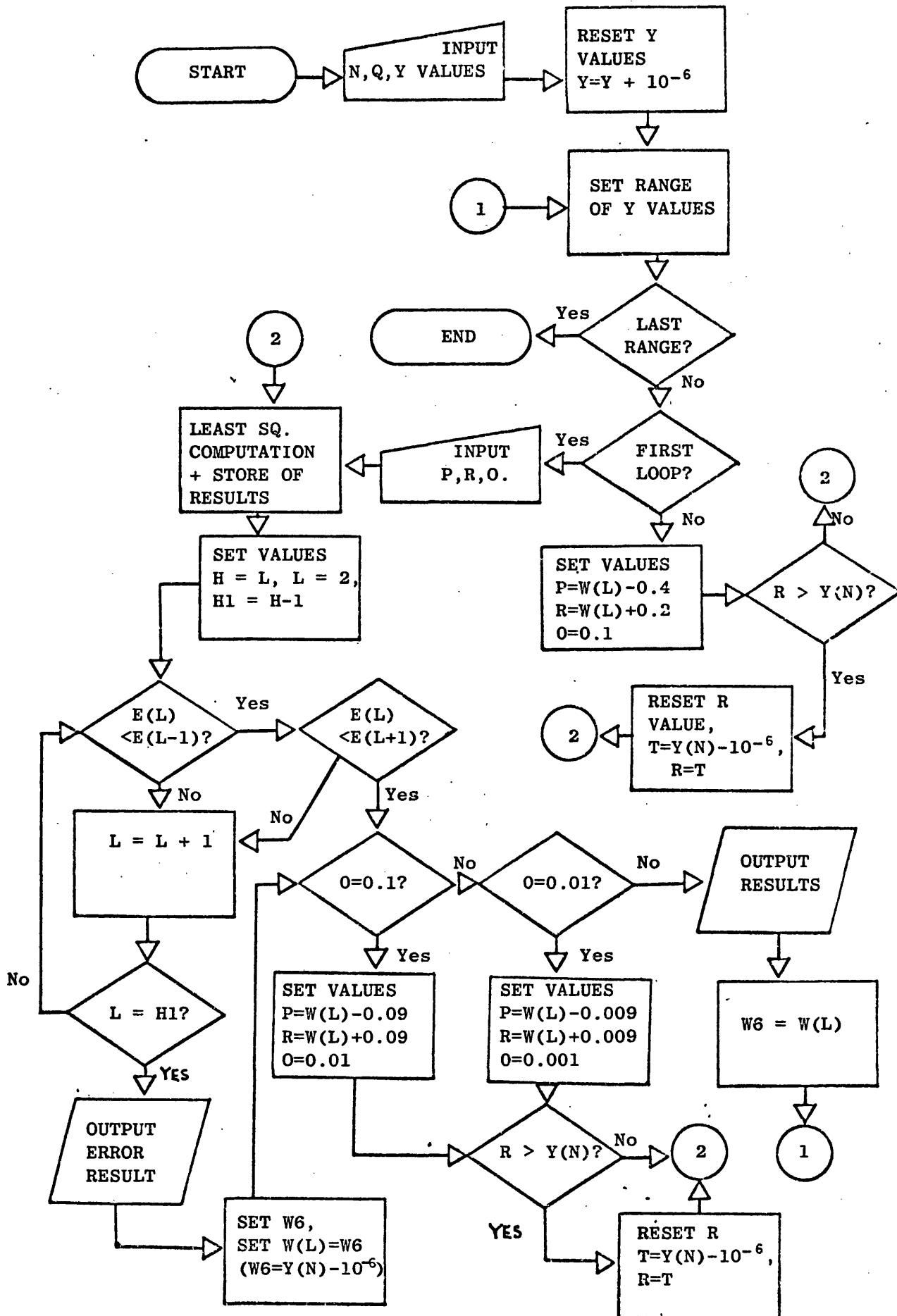
PROGRAM 5



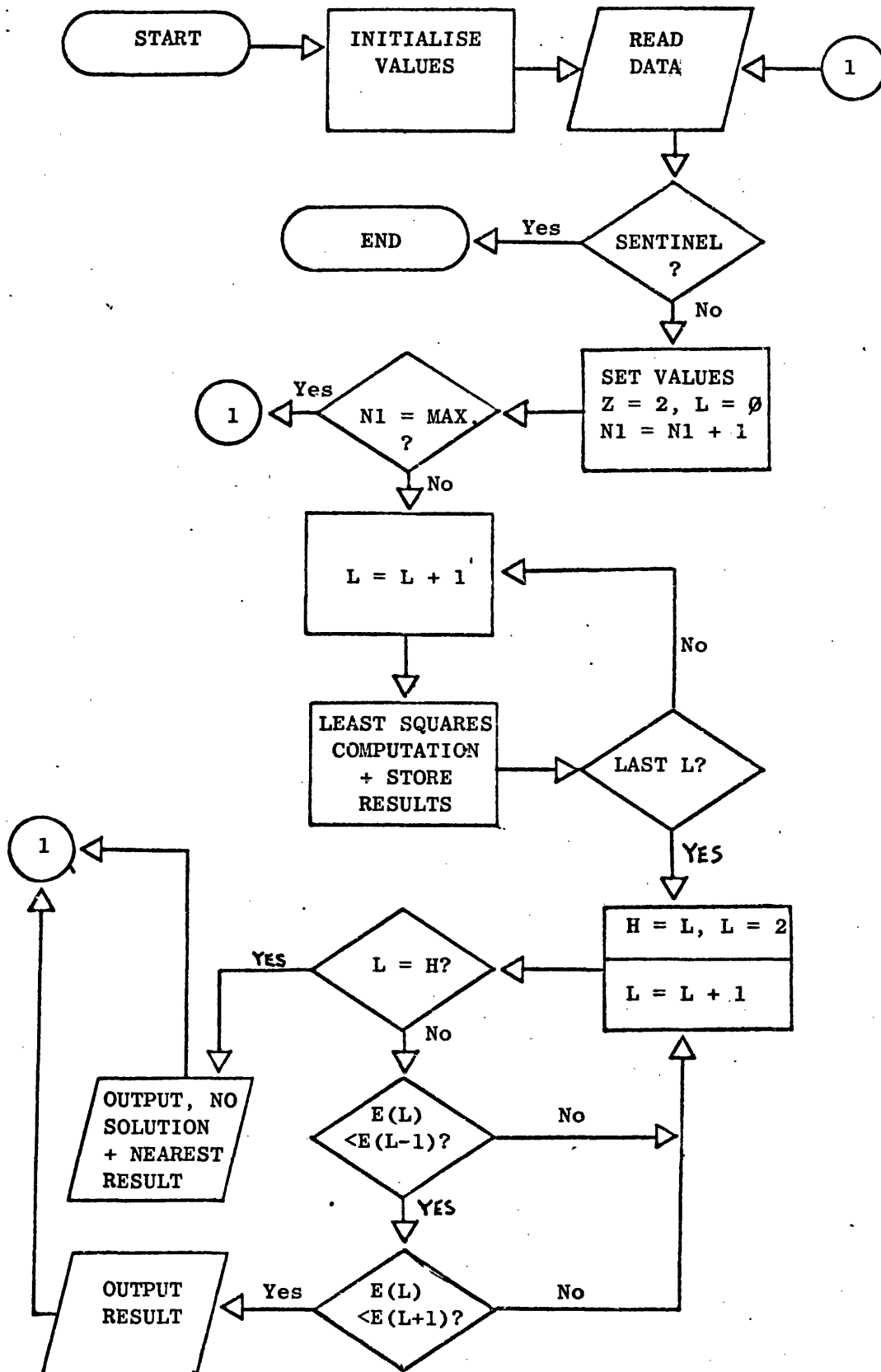
PROGRAM 6



PROGRAM 7

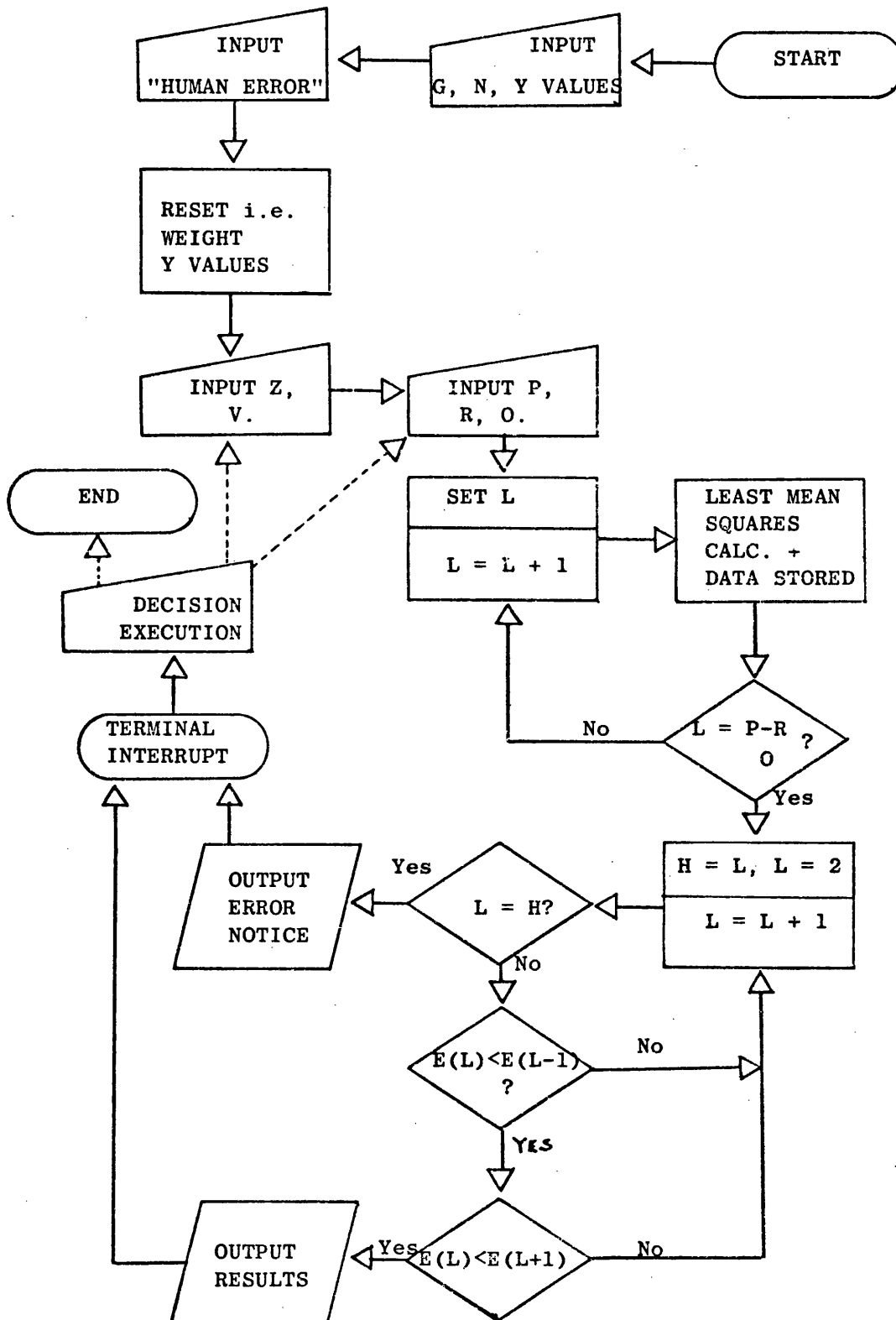


# PROGRAM 8





PROGRAM 9



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Notes:-

The statistical analysis described at the beginning of this Appendix was obtained in part from a course of mathematics lectures attended by myself as an undergraduate.

All of the (flowchart) symbols used in this thesis conform to the American National Standard Flowchart Symbols (A.N.S.I.) and their usage in Information Processing, X3.5, 1970.

ACTIVATION PARAMETERS

In 1932 Pelzer & Wigner<sup>(1)</sup> proposed a new theory of reaction rates to replace the older collision theory which has been extensively developed by Eyring and co-workers<sup>(2)</sup> to account for rates of reactions in condensed phases. This new theory differed from its predecessor in that it did not attempt to consider dynamical details of collision processes. Instead it concentrated on following the changes in the potential energy of the reactants as they approach each other from infinite separation and then part as different (product) molecules. This theory became predominantly known as the 'Transition state theory'. The basic ideas of this theory and how relevant activation parameters can be derived from its use are explained in the following paragraphs.

The main assumption of this theory is that all chemical reactions proceed via a transition state which is in thermodynamic equilibrium with the reactants even though the overall chemical reaction is irreversible, e.g:



- where  $C^*$  refers to the concentration of the activated molecules. Thus the rate of reaction is assumed to be proportional to the concentration of the activated molecules, which is governed by the laws of chemical equilibria. If we now define the equilibrium constant for the formation of the transition state,  $K^*$  thus:-

$$K^* = \frac{C^*}{C_A \cdot C_B} \quad \dots \quad [2]$$

Although the value of  $K^*$  cannot be measured experimentally, if we assume that the transition state is in true thermodynamic equilibrium with

the reactants,<sup>†</sup> then the result:-

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger = -RT \log_e K^* \quad \dots [3],[4]$$

- may be applied, where,

$\Delta G^\ddagger$  = standard free energy of formation of the transition state.

$\Delta H^\ddagger$  = standard enthalpy of formation of the transition state, (enthalpy of activation).

$\Delta S^\ddagger$  = standard entropy of formation of the transition state, (entropy of activation).

The values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  although not directly experimentally measureable can be obtained via a small amount of mathematical manipulation, e.g:

$\Delta H^\ddagger$ :- Enthalpy of Activation.

The dependence of reaction rate upon temperature was initially explained by Arrhenius, using arguments similar to those on which transition state theory was later based.<sup>†</sup> He arrived at equation [5] which when combined with Maxwell-Boltzmann theory of the distribution of energy among molecules gave equation [6] which is now known as the Arrhenius equation, e.g:

$$k_R = A \times (\text{fraction of the number of molecules with the necessary activation energy}) \quad [5]$$

(- where  $k_R$  = rate constant; and A is a proportionality constant.)

$$\text{giving, } k_R = A \cdot e^{-E/RT} \quad \dots [6]$$

[(-E/RT) is known as the Boltzmann factor, E being the activation energy, or the minimum amount of energy necessary for a reactant molecule to reach the transition state energy.]

[<sup>†</sup> i.e. that  $K^*$  is time independant.]

[<sup>†</sup> The original derivation was based upon the van't Hoff isochore.]

The quantity 'E' can thus be determined from several values of  $k_R$  at several temperatures; a plot of  $\log_e k_R$  vs  $1/T$  giving a slope of  $(-E/R)$ . Conversion of this result to a value of the enthalpy of activation requires further development of equation [3], (i.e. combining this with the fundamental equation for the rate constant for an ideal system) eventually yielding the result shown in equation [7]:-

$$E = \Delta H^\ddagger + RT \quad \dots [7]$$

$$(i.e. \Delta H^\ddagger = E - RT)$$

$\Delta S^\ddagger$ :- Entropy of Activation.

This species is contained in the above Arrhenius equation [6] as part of the previously named 'proportionality constant' which has been more recently described as a 'frequency factor'. A modified version of [6] can be obtained from equation [3] after taking anti-logarithms and replacing the variable  $K^*$  according to equation [8]:-

$$k_R = \left\{ \frac{R \cdot T \cdot K^*}{N \cdot h} \right\} \quad \dots [8]$$

- where  $N$  = Avogadro number;  $h$  = Planck's constant.

Thus we arrive at [9]:-

$$k_R = \left\{ \frac{RT}{Nh} \right\} \cdot \exp \left\{ \frac{\Delta S^\ddagger}{R} \right\} \cdot \exp \left\{ \frac{-\Delta H^\ddagger}{RT} \right\} \quad \dots [9]$$

- from which  $\Delta S^\ddagger$  can be calculated by rearrangement, provided  $k_R$  and  $\Delta H^\ddagger$  are known.

The exponential term in equation [6] is the same as the latter term in [9], since  $\Delta H^\ddagger$  represents the increase in heat content on forming the

transition state from the reactants, which is the energy of activation  $E$ . The 'A factor' is now revealed as being comprised of a numerical factor,  $(R.T/N.h)$ , dependent on temperature and an entropy term concerning changes in order-disorder in forming the transition state.

Thus using the relationships outlined in equations [6], [7] and [9] we can translate from the raw kinetic results to the individual activation parameters for a particular reaction.

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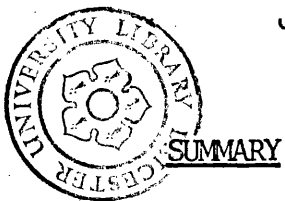
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The work in this thesis is concerned with three different aspects of the solution chemistry of several inorganic compounds. These aspects are kinetics, solvatochromism and solubility, each being directly linked to the solvent sensitivity of the compounds used.

The kinetic studies mainly involve investigations of kinetic trends for systems where the reaction mechanism is known, while constraints have been applied to the structure of the solvent medium. Comparisons between predicted and observed reactivity trends are thus discussed in terms of the solvation changes at the various reactant and transition state species. A correlation between these observed trends and those predicted semi-quantitatively by thermodynamic calculations which are based on various data pertaining to the systems, (e.g. solubility studies) have also been made where possible.

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The solvatochromic study extends previous research in this field and attempts to assimilate this available data into a single explanation of this phenomenon.

The solubility studies were undertaken both to augment some of the kinetic work and also to try and establish whether a common link existed between kinetic and solvatochromic properties of similar compounds.

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