THE EFFECTS OF ANIONS ON THE REACTIVITY OF \underline{d}^{6} TRANSITION METAL COMPLEXES

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STATEMENT

The experimental work described in this thesis has been carried out by the author in the Radiochemistry laboratories of the Leicester Polytechnic and also in the laboratories of the Department of Chemistry of the University of Leicester. No part of this work has been presented or is concurrently being presented for any other degree.

Signe

Fikry M. Mekhail

October 1972

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ABBREVIATIONS FOR LIGANDS

| L | unidentate ligand |
|-------------------|---|
| LL | bidentate ligand |
| en | ethylenediamine |
| phen | 1,10-phenanthroline |
| 5-nitro-phen | 5-nitro-1,10-phenanthroline |
| 4,7-diMe-phen | 4,7-dimethyl-1,10-phenanthroline |
| 3-sulphonato-phen | 3-sulphonato-1,10-phenanthroline |
| 5-sulphonato-phen | 5-sulphonato-1,10-phenanthroline |
| | |
| bipy | 2,2'-bipyridyl |
| terpy | 2,2',6',2"-terpyridyl |
| fz | ferrozine |
| hxSB | bis-(α -{2-pyridyl} benzylidene)- triethylenetetramine |

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SUMMARY

This thesis is concerned with the effects of anions on the reactivity of d⁶ transition metal complexes. These complexes include trans- $\operatorname{Iren}_2\operatorname{Cl}_2^+$, trans- $\operatorname{Rhen}_2\operatorname{Cl}_2^+$, cis- $\operatorname{Coen}_2\operatorname{Cl}_2^+$, tris-(1,10-phenanthroline)iron(II), tris-(ferrozine)iron(II) and a new low spin iron(II) complex, in which the ligand is the hexadentate Schiff base derived from phenyl 2-pyridyl ketone and triethylenetetramine.

Rates of substitution at trans- $\operatorname{Iren}_2\operatorname{Cl}_2^+$ and at trans-Rhen₂Cl₂⁺ show a marked dependence on the concentration, and a small dependence on the nature, of the incoming ligand. These results have been interpreted in terms of ion pair formation. Rates of aquation of cis-Coen₂Cl₂⁺, in 60%, 40%, and 20% dioxan-water, as in aqueous solution, show very little dependence on the nature and concentration of added anions. However rates of aquation of Fe(phen)₃²⁺, and its 5-nitro and 4,7-dimethyl derivatives, in 60%, 40%, and 20% dioxan-water are markedly sensitive both to the nature and concentration of a dided anions. Indicating an important role for ion pairs in these systems.

Low spin iron(II) complexes react directly with hydroxide, cyanide, and peroxodisulphate; kinetic parameters for these substitution and redox reactions are reported and discussed for the complexes of ferrozine and of the hexadentate Schiff base mentioned above. The dependence of reactivity on solvent composition has been investigated for bromide substitution at trans-Iren₂Cl₂⁺ (ethanol- and dioxan-water) and trans-Rhen₂Cl₂⁺ (dioxan-water), for aquation of cis-Coen₂Cl₂⁺ (dioxan-water), for aquation of Fe(phen)₃²⁺, Fe(5-NO₂-phen)₃²⁺, and Fe(4,7-diMe-phen)₃²⁺ (dioxan-water), and for the reaction of the iron(II) complexes of ferrozine and of the hexadentate Schiff base with cyanide (ethanol-water).

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CHAPTER 1

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INTRODUCTION

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CHAPTER 1

INTRODUCTION

1.1 Substitution Mechanisms

The term substitution in organic and inorganic reactions means the replacement of one group by another as shown below

$$MX_n + Y \rightleftharpoons MX_{n-1}Y + X \quad (1.1)$$

In the inorganic field most of the early work was devoted to non-labile transition metal complexes whose kinetics are easy to follow by conventional techniques¹. In recent years the development of a variety of stopped flow and relaxation techniques has permitted the intensive study of a large number of substitutions at labile centres².

Substitution mechanisms may be classified into homolysis i.e. free radical reactions :

 $M : X \longrightarrow M' + X \qquad (1.2)$

and heterolysis :

$$M : X \longrightarrow M^+ + :X^- \qquad (1.3)$$

The former is principally important in the gas phase and inert solvents; the latter is more usual in polar solvents - though radical reactions are not unknown in these³. Heterolytic substitution includes two main categories - electrophilic substitution, S_E , and nucleophilic substitution S_N . Electrophilic substitution is comparatively rare in reactions of transition metal complexes; one normally expects S_N attack at the positive metal centre. However electrophilic attack is important in metal-ion-catalysed aquation of d^6 metal complexes, such as $Co(NH_3)_5Cl^{2+}$, in the presence of Hg^{2+} . Nucleophilic substitution, S_N , can be subdivided further (as originally in organic chemistry) into S_N^{1} (substitution, nucleophilic, unimolecular) and S_N^2 (substitution, nucleophilic, bimolecular). The following reactions represent the two possibilities of S_N

$$MX \xrightarrow{slow} [M^+ + X^-] + Y^- \xrightarrow{fast} MY \quad (1.4)$$

$$MX \xrightarrow{+Y} [YMX] \xrightarrow{fast} MY + X \quad (1.5)$$

In ${\rm S}_{\rm N}{\rm 1}$ the rate determining step is the dissociation of the metal ligand bond M - X i.e. rate determining formation of a transition state of reduced coordination number followed by rapid reaction with the incoming nucleophile. On the other hand ${\rm S}^{}_{\rm N}2$ proceeds via the formation of a transition state of increased coordination number followed by loss of X - equation 1.5. The above reactions the leaving group correspond only to the limiting ${\rm S}^{}_N{\rm 1}$ and ${\rm S}^{}_N{\rm 2}$ mechanisms but often borderline mechanisms between ${\rm S}^{}_N{\rm 1}$ and ${\rm S}^{}_N{\rm 2}$ are The conceptual distinction between associative encountered. and dissociative mechanisms can be made by the timing of bond making and bond breaking. If they are synchronous it is then associative, but if bond breaking precedes bond making it is then dissociative.

As far as the mechanism of substitution of inorganic complexes is concerned the solvation of the ions in solution is also very important. All ions in solution are surrounded by solvent molecules or in other words by an outer-sphere solvation shell. The presence of any cations or anions in this solvation shell represents the formation of ion pairs. The latter may change the kinetics of substitution; often an ion pair has a higher reactivity than the free complex. This can be illustrated from the following schematic diagrams:



DIAGRAM 1.1

The solvation shell is represented by a circle. In the case of the free ion the first step in substitution involves

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dissociation of the ligand X to form a five-coordinate intermediate followed by one of the following three possibilities, a) reverse reaction and re-formation of the original ion, b) attack by one of the solvent molecules in the solvation shell, c) the intermediate will last long enough for a ligand Y to enter the solvation shell and take up the position in the coordination shell to give substitution. On the other hand if there is a ligand Y in the solvation shell the situation will be different. At least, from the statistical point of view, it will retard the reverse reaction of the dissociation and enhance the substitution of X by Y, so the apparent reactivities of the free ion and the ion pair will be different even though the mechanism is unimolecular. Relative reactions of free ions and ion pairs are discussed in more detail in section 1.5.2 below.

Similarly the bimolecular or associative mechanism can be illustrated by the following schematic diagrams :



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In the absence of any active potential nucleophile in the inner solvation shell the only choice for the free ion is the formation of a seven-coordinate aquo intermediate which is followed by the rapid dissociation of the leaving group X. On the other hand in the presence of a potential ligand Y there would be two possibilities, either the formation of an aquo intermediate or, by direct attack of the nucleophile Y moving from the outer solvation shell to the inner coordination sphere, formation of the product. It is therefore to be expected that for a bimolecular reaction the rate should be sensitive to the nature and concentration of the incoming nucleophile. This mechanism will be called S_N^2 IP to differentiate it from ordinary S_N^2 .

An alternative classification of the substitution mechanisms which in its emphasis on the role of solvation shell is particularly suitable for inorganic complexes in aqueous solution was suggested by Langford and Gray^4 . This provides a more informative definition of the limiting $\rm S_N1$, $\rm S_N2$ and borderline mechanisms. The terms $\rm S_N1$ and $\rm S_N2$ are replaced by dissociative path (D) and associative path (A) respectively. Now the five-and seven-coordinate species are real intermediates, albeit very transient. In addition the borderline mechanisms are called concerted or interchange mechanisms (I) where the leaving ligand is moving from the inner to the outer coordination sphere as the entering ligand is moving from the outer to the inner sphere with no formation of an intermediate :

 $MX_n \dots Y \longrightarrow MX_{n-1} Y \dots X$ (1.6)

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The difference between the limiting D and A, and the interchange, I, mechanisms can be illustrated diagrammatically:



DIAGRAM 1.3

In this diagram (1.3) path (a) corresponds to an I mechanism, path (b) to D or A.

The intimate interchange mechanism can be dissociative or associative or anything in between depending on whether or not the activation energy is affected by the requirement of the dissociation or the assistance of the entering group. The former case is called dissociative interchange (Id) whereas the latter is associative interchange (Ia). For complexes of the amminehalocobalt(III) type, nucleophilic substitution always goes via an aquo intermediate. The only possible exception is reaction with the conjugate base of the solvent, e.g. hydroxide ion in water, or acetate ion in acetic acid. Study of the base hydrolysis of the penta-amminechlorocobalt(III) complex shows that the rate dependence upon the concentration of the hydroxide ion is :

$$\frac{d [complex]}{dt} = k_{obs} [complex][0H]$$
(1.7)

which is consistent with an S_N^2 mechanism. This mechanism has been discussed by Tobe and Pearson⁵. Pearson argued that it involves a conjugate base, in other words is an S_N^1 CB mechanism (D CB according to Langford and Gray nomenclature) where a water molecule acts as the entering group subsequent to the rate-determining step :

$$Co(NH_3)_5 C1^{2+} + OH \xrightarrow{K} Co(NH_3)_4 (NH_2) C1^+ + H_2 O$$
 (1.8)

$$Co(NH_3)_4(NH_2)C1^+ + H_2O \longrightarrow Co(NH_3)_5OH^{2+} + C1^- (1.9)$$

Equilibrium (1.8) is a simple proton transfer from NH_3 to OH^- . This is followed by the slow dissociation (1.9) of the Co-Cl bond. The observed rate constant \mathbf{k}_{obs} in equation (1.7) is

$$k_{obs} = kK \qquad (1.10)$$

The operation of this mechanism has further been established by the hydroxide independence of base hydrolysis rates of complexes lacking an acidic proton⁶ such as $Co(0Ac)_2(bipy)_2^+$. The base hydrolysis of tris-(1,10phenanthroline)iron(II) and related complexes⁷ is another example where there is no acidic proton and the mechanism cannot be S_N^1 CB. Likewise there is evidence for associative cyanide attack at some low spin iron(II) complexes.

Some criteria including stoicheiometry, stereochemistry, rate laws, variation of rate constants and effect of solvent can be used as diagnostic tests of the mechanism⁸.

1.2 Bonding in Coordination Complexes

Because both associative and dissociative substitution mechanisms involve bond stretching in the transition state, the nature of the bonding between the central metal ion and the coordinated ligands contributes to a large extent towards the reactivity of the metal complexes. Of particular interest to bonding theory are the electrostatic and covalency contributions. The former is governed by the charge or dipole and size of the ligand; and the size and charge of the metal ion. The latter, covalency, depends on the extent of orbital overalp of the central metal ion and the ligand. Another aspect of particular importance to transition metal complexes is the crystal field effects. For symmetrical octahedral complexes there is a difference in energy between t_{2g} (d_{xy} , d_{xz} , d_{yz}) and e_g ($d_x^2-y^2$, d_z^2) levels :



DIAGRAM 1.4

Electrons in the t_{2g} levels thus have a stabilisation energy of $4D_q$ each. In five- or seven-coordinated transition states there will also be a splitting of the d levels by the ligand field. Rates of reaction will be affected by the crystal field stabilisation energies (CFSE) of the initial state and of the transition state; the crystal field activation energy (CFAE) is the difference between CFSE of the initial and transition states.

Table 1.1 shows the variation in the activation energy, E_a , and crystal field activation energy, CFAE, for tris-(1,10-phenanthroline) complexes of the first transition series. From the electrostatic point of view there should be a uniform pattern consistent with the systematic change in size from V²⁺ to Ni²⁺ complex ions.

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TABLE* 1.1

| System | Complex | E _a ,kcal | CFAE, Dq |
|----------------|-----------------------------|----------------------|----------|
| d ³ | $V(phen)_3^{2+}$ | 21.3 | 2 |
| d ⁵ | $Mn(phen)_3^{2+}$ | 10 ¹ | 0 |
| d ⁶ | $Fe(phen)_3^{2+}$ | 32.1 | 4 |
| d ⁷ | $Co(phen)_3^{2+}$ | 19.4 | 0 |
| d ⁸ | Ni(phen) $\frac{2}{3}^{2+}$ | 26.2 | 2 |

* reference 1, p.150.

Ŧ

P. Moore, personal communication.

The situation in Table 1.1 contradicts this view. This fluctuation in activation energy, E2, may be explained on the basis of the loss in crystal field stabilization energy. In any particular series the reactivity of the cation depends on the number of electrons in d orbital. Special attention must be drawn to the inertness of d^3 , d^6 , (and to a lesser extent $d^{8})$ electronic configurations where the losses in crystal field stabilization energy are large. It has been argued that if one of the t_{2g} orbitals is unoccupied (as in d^0 , d^1 , d^2) the substitution of the complex will then be fast via a dissociative or an associative intermediate with a minimum loss in crystal field activation energy. To conclude the above discussion one should say that if the CFSE of the activated complex is higher than that of the coordination compound there would be a gain in CFSE and consequently low activation energy and rapid substitution. On the other hand if the CFSE of the activated complex is less than the coordination compounds the opposite trend is expected.

There is an increase in inertness as one descends any transition metal group from 3d to 4d to 5d series. The splitting energy (Δ) increases by about 50% for the second transition series and by about 100% for the third series. As the radii of the third row transition metal cations are equal to the radii of their second row analogues, this latter increase in Δ must be attributed to the differing properties of the 4d and 5d orbitals.

So although the contribution of the crystal field is very small towards the bond strength it is moderately successful in explaining the relative reactivity in any particular electronic configuration for similar complexes where other factors are approximately equal.

The high stabilization caused by neutral ligands such as 1,10-phenanthroline in Fe(phen)₃²⁺, rather than charged ions cannot be explained only on the basis of the electrostatic theory. To ameliorate this situation some other aspects of bonding such as \mathcal{T} bonding, which is not considered in simple crystal field theory, can be taken into account. In the case of tris-(1,10-phenanthroline)iron(II) there is donation of electrons from the nitrogen atoms in phenanthroline to the empty orbitals in iron(II) (s,p,d_x²-_y²,d_z²) forming \mathcal{T} bonding. In addition there can be back donation of electrons from the filled t_{2g} orbitals on the iron(II) towards the unoccupied \mathcal{T}^* orbitals on the phenanthroline to form \mathcal{T} - bonding as shown in the diagram below :



DIAGRAM 1.5

An empirical approach to correlating relative stabilities of complexes is the hard and soft acids and bases (HSAB) picture developed by Pearson⁹ from Ahrland, Chatt and Davies's¹⁰ class "a" and class "b" classification of ligands.

TABLE* 1.2

(All figures are $\log K_1$)

Acceptors

Relative affinities

| Class (a) | F — | > | C1 - | > | Br | > | I_ |
|------------------|------|---|-------------|---|-----------------|---|------------|
| In ³⁺ | 3.78 | | 2.36 | | 2.01 | | 1.64 |
| Class (b) | F - | ۷ | c1 - | 2 | Br ⁻ | < | I - |
| Hg^{2+} | 1.03 | | 6.74 | | 8.94 | | 12.87 |

* reference 10, p.271.

Hard or class (a) acids prefer to bind to small, nonpolarizable ligands such as \overline{F} and H_2^0 i.e. to hard bases. Soft or class (b) acids prefer to bind to large polarizable ligands such as \overline{I} and R_2^S i.e. soft bases (see Table 1.2). In terms of the \mathcal{T} - bonding theory hard acids are considered as a potential \mathcal{T} bond acceptor while soft acids as a potential d or p-electron \mathcal{T} bond donors. Such effects which are fairly small in magnitude in comparison with \mathcal{T} bonding interaction increase the bond strength.

1.3 Low Spin Iron(II) Complexes

Although both Co(III) and Fe(II) have the same d⁶ electronic configuration one finds that almost all Co(III) complexes (with the exception of $Co(0H_2)_6^{3+}$ and CoF_6^{3-}) are low spin and inert while the latter Fe(II) forms only a few low spin complexes. The only ligands which can cause spin pairing in Fe²⁺ are cyanide ion and heteroaromatic amines containing the structure N < C = C > N such as phen, bipy, terpy and Schiff bases of the following formula :



Thus, for example, the magnetic moments for Fe(phen)²⁺, Fe(phen)₂²⁺, and Fe(phen)₃²⁺ are 5.2, 5.2, and 0 respectively.

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The logarithms of the respective stability constants are 5.85, 5.25 and 10.0^{12} . This very unusual high stabilization as the number of phenanthroline increases from two to three is related to the large increase in the splitting energy (Δ) which makes it energetically more favourable to pair electrons in the t_{2g} levels rather than to have unpaired electrons in the upper e_g levels. While in general one needs three bidentate heteroaromatic ligands of the phenanthroline type to cause spin pairing, there are a few examples of low spin complexes of formula $Fe(LL)_2(X)_2$. Thus for LL = 1,10-phenanthroline, $X = CN^-$, CNO^- , NO_2^- or RSO_2^- the complexes are high-spin¹³. Similarly the ligand field effect of cyanide is sufficiently great that $Fe(CN)_4$ (en)²⁻ is also, like $Fe(CN)_6^{4-}$, low-spin¹⁴.

It is difficult to make direct comparisons of kinetic parameters between say, penta-amminechlorocobalt(III) and tris-(1,10-phenanthroline)iron(II) because of the difference in the electrostatic charge and also in the bond strengths of Fe-N and Co-Cl.

1.4 Effects of Anions

These can be classified into two main categories either direct or indirect effects.

1.4.1 <u>Direct Effect</u> - This is sometimes called normal substitution. It is more common for square planar d^8 metal complexes e.g. Pt²⁺. It is also known although rare for some d⁶ complexes. This can be illustrated by the action of cyanide^{7a} and hydroxide^{7b} on Fe(LL) $_3^{2+}$ where LL phen, bipy, terpy or a Schiff base of the type



1.4.2 <u>Indirect Effect</u> - This effect is often observed in the substitution reactions especially for d⁶ metal complexes. This can be illustrated by the substitution reactions in transition metal complexes e.g. the acid hydrolysis of penta-amminehalocobalt(III) complexes. Even though at high concentration of the haloacid the net chemical reaction is the substitution by the anionic species in solution, the reaction itself proceeds via an aquo intermediate as shown below

$$Co(NH_3)_5 C1^{2+} + H_2^0 \implies Co(NH_3)_5 H_2^{0^{3+}} + C1^-$$
 (1.11)

$$Co(NH_3)_5H_2O^{3+} + x^- - Co(NH_3)_5X^{2+} + H_2O$$
 (1.12)

The effect of various anions on the acid hydrolysis of the above complex¹⁵ and other complexes of the type $Men_2Cl_2^+$, where M = RhIII, IrIII, has been discussed in the literature¹⁶ in terms of ion pair formation. The effect of ion pairing on the reactivity of the complex will be discussed separately in section 1.5.2.

1.5 Ion Association

1.5.1 <u>Theoretical Approach</u> - Ions in solution are sensitive to their environment and can interact with any other ionic species in solution. The general effect of added electrolytes on solutions (salt effect) can be divided into either primary effects where the activity coefficient of the complex ion changes or secondary effects which are called common ion effects.

The former is the more relevant as far as the present work is concerned and will be dealt with in more detail. The dependence of the activity coefficient χ_i on the ionic strength can be illustrated by the Debye-Huckel formula¹⁷

$$-\log \gamma_{i} = \frac{Az^{2} \sqrt{\ell^{2}}}{1 + B \sqrt{\ell^{2}}} \qquad (1.13)$$

where Z is the charge of the ion, \mathcal{U} is the ionic strength; A and B are constants.

Equation (1.13) can only be used for dilute solutions with ionic strength less than 0.1M. For strong solutions equation (1.13) can be modified either by inserting a term linear in $\ell^{\mathcal{U}}$, or one can keep the ionic strength constant by adding an inert electrolyte such as sodium perchlorate and to assume any change in the ionic strength due to replacing part of the sodium perchlorate by a reagent is negligible.

The more specific effect of adding ions of opposite sign is the formation of ion pairs :



where K_{TP} is the ion association constant.

There have been several attempts to calculate $K_{\rm IP}$ values and each method has its limitations. Bjerrum's approach¹⁸ was based on a purely electrostatic assumption and required the definition of an arbitrary distance "q" at which the ions are considered to be in the form of ion pairs. The relation is

$$K_{IP} = \frac{4 \pi N}{1000} \int_{a}^{q} \exp(\frac{z_A z_B e^2}{DrKT}) r^2 dr$$
 (1.14)

However the modified equation by Fuoss¹⁹ avoided the difficulty encountered by Bjerrum's "q" value and assumes that only ions in actual contact as forming ion pairs. The equation is

$$K_{IP} = \frac{4\pi r^{3}N}{300} \exp \left(\frac{-z_{A}z_{B}e^{2}}{DrKT}\right)$$
(1.15)

Equation (1.15) has a wide application in predicting the variation of $K_{\rm IP}$ with the solvent dielectric constant D. It has been proved experimentally that there is a linear relationship between log $K_{\rm IP}$ and the reciprocal of D. But still this electrostatic approach is not good enough. For instance it cannot explain the lack of evidence for ion pairs in the ions ${\rm Coen}_3^{3+}$ and ${\rm Fe}({\rm CN})_6^{3-}(20)$.

It is possible to estimate ion association constants directly from kinetic results²¹. Thus, for example, ion association constants for chloride with $\operatorname{cis-Coen_2Cl_2}^+$ in methanol^{21a}, and for a variety of anions with divalent transition metal cations in water^{21b}, have been determined from the variation of reaction rate with added ion concentration. The former system is analogous with those discussed in Chapter 3; a method of deriving ion association constants from kinetic results is detailed here.

Assuming the following substitution reaction can occur by two routes either direct replacement or via ion pair formation



where M can stand for Co(III), Rh(III) or Ir(III)

k is the rate constant for reaction of the free ion k_{IP} that for reaction of the ion pair K_{IP} the equilibrium constant for ion pair formation

$$K_{IP} = \frac{\left[\text{ion pair} \right]}{\left[\text{free ion} \right] \left[X^{-} \right]};$$

[ion pair] = K_{IP} [free ion] [X⁻] (1.16)

Also

$$\begin{bmatrix} \text{trans-Men}_2 \text{Cl}_2 \end{bmatrix} = \begin{bmatrix} \text{free ion} \\ \text{free ion} \end{bmatrix} + \begin{bmatrix} \text{ion pair} \\ \text{free ion} \end{bmatrix} \begin{bmatrix} 1.17 \end{bmatrix}$$
Therefore

$$\begin{bmatrix} \text{free ion} \end{bmatrix} = \frac{\begin{bmatrix} \text{trans-Men}_2 \text{Cl}_2 \end{bmatrix}}{1 + K \begin{bmatrix} \text{x} \end{bmatrix}}$$
(1.18)

Hence

$$d \left[\text{trans-Men}_2 X C \right] / dt = k \left[\text{free ion} + k_{IP} \left[\text{ion pair} \right] (1.19) \right]$$

Substitute for the concentration of the free ion from equation (1.18) into equation (1.19).

$$d\left[\operatorname{trans-Men}_{2}XC1\right]/dt = k \frac{\left[\operatorname{trans-Men}_{2}C1_{2}\right]}{1 + K\left[X^{-}\right]} + k_{1P}K\left[X\right] \frac{\left[\operatorname{trans-Men}_{2}C1_{2}\right]}{1 + K\left[X^{-}\right]}$$
$$= \frac{k + k_{1P}K_{1P}\left[X^{-}\right]}{1 + K\left[X^{-}\right]} \left[\operatorname{trans-Men}_{2}C1_{2}\right]$$
$$= k_{obs} \left[\operatorname{trans-Men}_{2}C1_{2}\right] \qquad (1.20)$$

where
$$k_{obs} = \frac{k + k_{IP} K_{IP} [X]}{1 + K [X]}$$
 (1.21)

Equation (1.21) can be rearranged to give

$$\frac{1}{k_{obs} - k} = \frac{1}{(k_{IP} - k) K_{IP} [x]} + \frac{1}{k_{IP} - k}$$
(1.22)

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Thus a plot of $1/(k_{obs} - k) \underline{vs} 1/[X]$ should give a straight line whose slope is equal to $1/(k_{IP} - k) K_{IP}$ and intercept equal to $1/(k_{IP} - k)$ and hence K_{IP} can be obtained from dividing the intercept by the slope. This method is by far the most useful one for treatment of the kinetic data in Chapter 3.

1.5.2 <u>The Stoicheiometry and Reactivity of Ion Pairs</u> -The role of ion pairs in affecting the rate of reactions is well established. Methods of detection of ion pairs together with their stability constants have been reviewed by Beck^{22} . In 1953 kinetic evidence was presented for the presence of ion pairs during the anation of aquopenta-amminecobalt(III) with sulphate ion²³. It has been shown⁵ that for isotopic exchange of chloride with cis-Coen₂Cl₂⁺ in methanol the rate constant increases as the concentration of added nucleophile increases until finally the rate is constant (limiting rate) upon the addition of more reagents - as shown in the diagram below.



[Y⁻]

This is the typical behaviour for a mechanism in which ion-pairing plays a significant role. With increasing concentration of added anion, there is an increase in the concentration of ion pairs with a corresponding increase in k_{obs} up to a limit beyond which further addition of anions does not change the effective concentration of the ion-pairs. The stoicheiometry of the aggregates could be 1:1, 1:2 or even 1:3 as in for example trans-Coen $_2NO_2H_2O^{2+}$, which associates with three bromide ions³ in acetone at 25° C. The maximum number of anions in the aggregates represent a limiting stoicheiometry that is achieved when the repulsion between the anions are greater than the attractive force holding them together. However 1:1 ion pair formation is most common as will be discussed later in Chapter 3.

The enchanced reactivity of ion pairs in kinetic studies could be interpreted in terms of the effective charge on the central metal ion. The presence of a negative anion Y in the solvation shell of the complex reduces the effective charge on the central metal ion which in turn weakens the metal ligand bond and hence a higher rate of substitution would be expected.



DIAGRAM 1.7



DIAGRAM 1.8

It can also be seen from the above diagram 1.7 that the displaced group X in the transition state can return to its original position i.e. retention, whereas this is less likely in the presence of ligand Y in the solvation shell (diagram 1.8). This explains the difference in reactivity between the free ion and the ion pair in the interchange process of a unimolecular reaction. The presence of an anion in the solvation shell of the complex and formation of ion pairs does not necessarily lead to an associative mechanism. As mentioned previously the timing of bond breaking and/or bond making is the critical factor.

1.0 Solvent Effects

The influence of solvents on reaction rates was early studied for aliphatic substitution and elimination by Hughes and Ingold^{25} . The various aspects of solvent effects on reaction rates and mechanisms have been reviewed by Amis^{26} and with special reference to organic reactions by Leffler and Grunwald²⁷. Variation of rates may be ascribed to differences in the free energies of solvation of the initial states and of transition states.



If the transition state is more solvated than the initial state (diagram 1.9), the free energy of activation ΔG^{\neq} required to overcome the energy barrier will be reduced in magnitude and a faster reaction is expected. On the contrary if the initial state is more solvated than the transition state (diagram 1.10) e.g. in the Menschutkin reaction²⁸ of trimethylamine with methyl iodide the reaction rate will be slower. However, there are cases where the solvation of the initial and transition states is of

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comparable importance 29 (diagram 1.11) such as in the reaction between tetraethyltin and mercuric chloride.

Some other thermodynamic parameters which reflect the effect of solvent structure on the kinetic behaviour are enthalpy and entropy of activation. The variation of the activation parameters ΔG^{\neq} , ΔH^{\neq} and $-T \Delta S^{\neq}$ as a function of mol fraction of methanol is shown in Figure 1.1 below for the reaction of nickel(II) with bipyridyl³⁰.



FIGURE 1.1 Kinetic parameters for reaction of Ni^{‡+} with 2.2'bipyridyl in methanol-water mixtures. Values of ΔH^{\pm} and ΔS^{\pm} are relative to water. The curve labelled P is from Pearson and Ellgen. Inset: Rate profile at the boiling points of the solvent

The free energy of activation ΔG^{\neq} can be measured more accurately (from kinetic data) than ΔH^{\neq} and ΔS^{\neq} . Nevertheless it can easily be seen from Figure 1.1 that the activation parameters ΔH^{\neq} and ΔS^{\neq} are much more sensitive to the environment than is the free energy of activation ΔG^{\neq} . A similar conclusion was drawn for the dissocation of tris-(1,10-phenanthroline)iron(II) in aqueous t-butyl alcohol³¹.

However, solvation of the reacting species is governed
to a large extent by the polarity of the solvent which in turn determines the order of the intermolecular forces between the solvent and the solute. Some considerations have been given to the electrostatic interaction of the dielectric constant D. The relationship between the rates and the dielectric constant of the medium has been expressed as^{32}

$$\ln k = \ln k_0 - U - \frac{D - 1}{2D + 1}$$
(1.23)

where k and k_0 are the rate constants in media with dielectric constants D and 1 respectively. U is a constant which is independent of the solvent.

A linear relationship between ln k and D-1/2D + 1 or simply 1/D (where D \gg 1) was established³³. But in some other cases the correlation of rates with dielectric constant was found not fully satisfactory³⁴. This is because the dielectric constant is macroscopic and not microscopic. Also the solvating power is not controlled only by the dielectric constant macro or micro but also by the nucleophilicity and ionizing power of the solvent.

More comprehensive measures of the solvating power of solvents are provided by the empirical parameters³² Z, E_T (spectroscopic) and Y (kinetic). The most relevant kinetically based parameter to the present study is the Y value, which like Z and E_T incorporates both polarity and nucleophilicity of the solvent. The relationship between the logarithm of the rate constant and Y values was originally formulated by Grunwald and Winstein³⁵ in 1948.

$$\log_{10} k_{A/K_B} = m (Y_A - Y_B)$$
 (1.24)

where k_A and k_B are the rate constants of an S_N^1 solvolysis in solvents A and B; m is a constant at a given temperature and depends on the sensitivity of the compound being solvolysed towards a change in the ionizing power of the solvent.

Values of Y were derived by choosing the S_N^{1} solvolysis of a standard compound, t-butyl chloride, in a given solvent A and in 80% ethanol. The value of Y in 80% ethanol was fixed as zero and m is 1.00. Thus the general equation is

$$\log_{10} k/k_0 = mY$$
 (1.25)

where k and k_0 are the rate constants in the given solvent and 80% ethanol, under the same conditions, respectively. Equation 1.25 is a linear free energy relationship since log k is proportional to the free energy of activation. Recently the choice of t-butyl chloride as a reference compound was criticised³⁶ due to the possible elimination reaction which might occur in parallel with solvolysis. 1 - Adamantyl halides of the following chemical formula



were claimed as better reference substrates, for rearward nucleophilic attack and elimination are impossible.

Values of Y have been reported for several solvent mixtures and the superiority of these empirical mY correlations over others such as those with functions of the dielectric constant have been demonstrated 34 . For an S_N2 reaction the plot of log k \underline{vs} Y for one pair of solvents is a curved one with a mean slope (m) less than one. The ratio of the rates of solvolysis in two different solvents which have the same ionizing power Y but different nucleophilicity (e.g. 40% ethanol and 92% formic acid) has been used to test the molecularity of the rate determining step³⁷. For phosphoryl compounds $R_1 R_2 POC1$, (where R_1 or R_2 = Me, OEt, Me₂N) the ratio of solvolysis rates R was compared with those for the typical S_N^{-1} and S_N^{-2} solvolyses of t-BuCl (R=0.689) and MeBr (R=200) respectively. The conclusion was that solvolyses of all these phosphoryl compounds are bimolecular. However, it is noteworthy that the ratio for Me(OEt)POC1 is 11,000 which is remarkably larger than the ratio of 200 for MeBr.

The Grunwald-Winstein mY plot was originally used to correlate the solvolysis rates of organic compounds and then extended to include the above phosphorus-chlorine³⁸, and sulphur-chlorine³⁹, compounds. It has also been applied to the isomerization⁴⁰ of $Pt(PPh_3)_2(C_2Cl_4)$ where the rate determining step is the solvolysis of the chloride,



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followed by rapid attack of chloride on metal ion. It has been shown that my plots are of particular interest in the study of transition metal-halide complexes 4^{1} . There is a good correlation between log k and Y for several amminehalocobalt(III) complexes 4^2 in various mixed aqueous solvents. The slope (m) has a value ranging from 0.23 to 0.36 for a dissociative mechanism of Co-Cl bond breaking. The lower values of m compared with those of organic chlorides can be attributed to the lower solvation requirement of the inorganic moiety. The value of m is slightly lower for Co-Br than Co-Cl, as for C-Br compared with C-Cl. For reactions involving Cr-Cl bonds values of m are still less than for Co-Cl, being about 0.1 to 0.2, but the situation for Cr-NCS complexes is confused⁴³. Thus although a lot of study has been devoted to the use of mY plots in cobalt(III)-halide complexes extension to other systems with very different leaving groups e.g. Fe-phen should be made with some scepticism.

Many organic cosolvents, i.e. alcohols, acetonitrile, dioxan, carboxylic acids affect the structure of water⁴⁴. The effects of nature and concentration of alcohols on the structure of water have been reviewed by Franks and Ives⁴⁵. Spectroscopic and relaxation techniques⁴⁶ showed that t-butyl alcohol enhances the structure of water when present at mole fraction of ≤ 0.04 , whereas, above this limit disruptive action on water structure was noticed. The disruptive effect on water structure is reflected and well illustrated in the kinetic behaviour of some transition metal complexes. For example in the aquation of tris-(1,10-phenanthroline)iron(II) and some ligand substituted derivatives³¹ in aqueous t-butyl alcohol there is a break in the continuity of the rate constant trend at mole fraction of ≤ 0.04 . Recently the action of methanol on the structure of water has also been described in conjunction with the kinetic study of the formation of the mono-(2,2'-bipyridyl)nickel(II) complex³⁰.

An extra difficulty which arises in mixed solvents is selective solvation. An N.M.R. method for determining the preferential or selective solvation of Cr(III) complexes has been developed by Behrendt, Langford and Frankel⁴⁷. In aqueous acetonitrile $Cr(NCS)_{0}^{3^{-}}$ was found to have preference for acetonitrile.

Unfortunately this method cannot be extended to cobalt(III) and iron(II) complexes; there is no direct way of monitoring the composition of the secondary solvation shell of these species.

CHAPTER 2

EXPERIMENTAL

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| | | chloride | | |
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2.5.5 Activation parameters

1

CHAPTER 2

EXPERIMENTAL

2.1 Preparation of Complexes

2.1.1 <u>cis-Bisethylenediaminedichlorocobalt(III)</u> chloride - trans- $\left[\operatorname{Coen}_2\operatorname{Cl}_2\right]$ Cl was prepared by the published method⁴⁸. 60 cm³ of 10% ethylenediamine was added to 16.0 g of $\operatorname{CoCl}_2.6H_20$ in 50 cm³ water. A vigorous stream of air was drawn for 10 hours followed by the addition of 35 cm³ concentrated hydrochloric acid. The solution was evaporated until a crust formed and left to stand overnight. The bright green crystals were filtered, washed with alcohol, ether and dried at 110°C.

trans- $\left[\operatorname{Coen}_2\operatorname{Cl}_2\right]$ Cl was converted to the cis form by evaporation on a water bath to almost dryness. This process was repeated twice to ensure that all the solid was in the cis form.

2.1.2 <u>trans-Bisethylenediaminedichlororhodium(III) chloride</u> - trans- $\left[\operatorname{Rhen}_2\operatorname{Cl}_2\right]\operatorname{NO}_3$ was prepared by the method of Johnson and Basolo⁴⁹. 1.0 g of RhCl₃.3H₂O and 1.0 g of ethylenediamine dihydro-chloride were dissolved in 50 cm³ water containing 0.426 g of potassium hydroxide. The mixture was refluxed until the solution was clear then a solution of 0.426 g of potassium hydroxide in 50 cm³ water was added in 5 cm³ portions. The resulting golden yellow solution was evaporated to half its original volume on a water bath, then 20 cm³ concentrated nitric acid were added with stirring. After two hours the yellow precipitate was filtered off, dissolved in the minimum amount of water and filtered into ice-cold concentrated nitric acid. The product was collected and washed with cold dilute nitric acid, ethanol, and ether, and air-dried.

trans- $[\text{Rhen}_2\text{Cl}_2]$ NO₃ was converted into the chloride or bromide form by passing through an anion exchange column of De-Acidite FF X8(100-200) in the chloride or bromide form as required. The solution was then evaporated in vacuo and the product was kept in a desiccator.

2.1.3 trans-Bisethylenediaminedichloroiridium(III) chloride - trans- $\left[\operatorname{Iren}_2\operatorname{Cl}_2\right]\operatorname{ClO}_4$ was prepared by a similar method to that of Bauer and Basolo⁵⁰. 3.0 g of $IrCl_3 \cdot 3H_2^0$ was dissolved in 30 cm^3 water and heated until all the residue disappeared. 4.3 g of ethylenediaminedihydrochloride was added in small portions with continuous shaking. After boiling for a few minutes 0.2 cm^3 of hypophosphorous acid was added as a catalyst and the solution boiled for another 10 minutes. The colour of the solution turned brownish green. 4.0 cm^3 of concentrated hydrochloric acid was added to complete the precipitation and the solution boiled until the final volume was about 20 cm^3 . The solution was left overnight and the green precipitate filtered off. This intermediate, 3.6 g, was transferred into a 108 cm^3 round bottom flask. 3.6 cm^3 of ethylenediamine was added in two portions and the solution boiled under reflux for one hour, then evaporated to 10 cm^3 . After cooling, the solution was neutralized (litmus) with concentrated hydrochloric acid, boiled for 5 minutes, cooled and 2.0 cm^3 of 70% perchloric acid was added. The yellow

precipitate was filtered off, washed with cold water and recrystallised from hot water by adding 1.0 cm³ of 70% perchloric acid and leaving to stand overnight. The yellow crystals were collected on filter paper, washed with cold water, ethanol, and ether, and then air-dried. The yield was 0.76 g.

trans- $\left[\operatorname{Iren}_2\operatorname{Cl}_2\right]\operatorname{ClO}_4$ was converted into the chloride or bromide form by passing through De-Acidite FF anion exchange resin as described above for trans- $\left[\operatorname{Rhen}_2\operatorname{Cl}_2\right]\operatorname{Cl}$.

Low spin iron(II) complexes : 1,10-phenanthroline 2.1.4 and related ligands - Solutions of all the iron(II) phenanthroline or ferrozine complexes were prepared by mixing iron(II) ammonium sulphate (AnalaR) solution with slight excess of the reagents 51 (1,10-phenanthroline, 5 nitrophenanthroline, 4,7-dimethylphenanthroline, 1,10-phenanthroline-3-sulphonic acid, or ferrozine) to avoid the formation of mono and bis complexes. The mixture was shaken and allowed to stand for a while. The solution was then filtered to remove any undissolved impurities, and diluted to the required concentration before using it for any kinetic runs. All of the complexes mentioned above have charge transfer spectra Fe-LL of maximum absorption in the visible region between 500 and 600 nm. Values of the molar extinction coefficients (E) are shown below.

| Complex | ε | λ/nm | Ref |
|--------------------------------|-------|--------------|-----|
| $Fe(phen)_3^{2+}$ | 11100 | 510 | 52 |
| Fe(5-nitrophen) 3^{2+} | 11500 | 510 | 52 |
| Fe(4,7-dimethylphen) 3^{2+} | 14000 | 510 | 53 |
| Fe(3-sulphonato-phen) 3^{2+} | 10840 | 517 | 54 |
| $Fe(fz)_3^{4-}$ | 27900 | 562 | 55 |

2.1.5 Low spin iron(II) complexes : Hexadentate Schiff base ligand - The method used here is similar to the general preparation procedure for Schiff base complexes of the type $Fe(SB)_3^{2+}$ where



2 g of AnalaR iron(II) ammonium sulphate was dissolved in 10 cm^3 water followed by the addition of 7.3 cm^3 of triethylenetetramine. The reactants after being shaken gave a reddish brown colour. 9.3 g of 2-benzoylpyridine was dissolved in 10 cm^3 of methanol and added to the reaction mixture. The mixture was left overnight at room temperature, when the colour changed to dark blue. The intensely coloured solution was filtered to remove any unreacted reagents. The hexadentate Schiff base complex (Chapter 6) was precipitated from aqueous solution in the presence of high concentration of sodium perchlorate. The crystals were filtered off and washed with several portions of water and left to dry in vacuo.

| Analysis | | | С | Н | N |
|----------------|--|---|------|-----|------|
| Calculated for | $\left[Fe(C_{30}H_{32}N_6) \right] (C10_4)_2$ | : | 49.3 | 4.4 | 11.5 |
| Found | | : | 48.9 | 4.6 | 11.9 |

2.2 Labelling of Complexes with Chlorine-36

2.2.1 $\underline{\operatorname{trans}}_{\operatorname{Rhen}_2\operatorname{Cl}_2}\operatorname{Cl}_2$ - About 0.5 g of trans- $\overline{\operatorname{Rhen}_2\operatorname{Cl}_2}\operatorname{Cl}$ was transferred to a 10 cm³ flask, 1.0 cm³ of 0.2 M - H³⁰Cl(40 μ Ci) was added and the volume made up to the mark. The flask was securely stoppered and shaken until all the solid had dissolved and then left in a water bath at 80°C for three hours. The solution was passed through De-Acidite FF X8(100-200) in the chloride or bromide form as required to exchange all active chloride outside the complex with inactive chloride or bromide. The resin was washed with two column volumes of water to ensure that no complex remained absorbed on the resin. Electrophoresis of a sample of the product showed that there was no active anionic chloride. The solution was evaporated in vacuo and the solid was stored in a desiccator.

2.2.2 <u>trans-[ren₂Cl₂]Cl</u> - About 0.7 g of trans-[ren₂Cl₂]Cl was mixed with 50 μ Ci H ³⁶Cl and the solution was left in a water bath at 90°C for two weeks. A similar procedure to that mentioned above for trans-[Rhen₂Cl₂]Cl was followed.

2.3 <u>Radiochemical Determination of Rates of Isotopic</u> <u>Exchange and Substitution Reactions</u>

2.3.1 Kinetic experiments - The kinetic runs were carried out by taking an accurate weight of the labelled trans- $\left[\operatorname{Iren}_2 \operatorname{Cl}_2\right] X$ or trans- $\left[\operatorname{Rhen}_2 \operatorname{Cl}_2\right] X$, where $X = \operatorname{Cl}^-$, Br⁻ or NO₃⁻, to make a 5.0X10⁻³ M solution, which was transferred into a 10 cm³ standard flask, to which the correct amount of HCl, KBr or KNO2 was added. The volume was made up with water or water and organic cosolvent, dioxan (scintillation grade) or ethanol, according to the desired volume percentage of the mixed solvent. The flask was securely stoppered and left to stand in a constant temperature bath controlled by contact thermometer and relay box. The bath was filled with water covered with a layer of paraffin oil of about two cm thickness to minimise evaporation of water. It was necessary to standardise the techniques employed to reduce the number of variables. A 1 cm³ aliquot was withdrawn from the reaction mixture at suitable time intervals, depending on the rate of substitution at complex in question. The aliquots taken during each run were usually made up to 10 \mbox{cm}^3 in standard flasks. The activity of each aliquot was first measured and then the solution was transferred to a beaker and all ionizable chloride and/or bromide precipitated by adding a small excess of a standard silver nitrate solution. The precipitate was filtered off through Whatman 42 papers. The precipitate was washed with several portions of water and the filtrate collected and made up to 25 cm^3 in a standard flask. 10.0 cm^3 aliquots of this latter solution were transferred to a Geiger-Müller tube for counting the activity. Each kinetic run was repeated at least twice.

2.3.2 <u>Analysis</u> - The method used throughout this work for the measurement of chlorine-36 was direct beta-counting. A Geiger-Müller probe was used in conjunction with a Philips Scaler PW 4032. The voltage was kept at 570 volts as this was found to be near the centre of the plateau of the Geiger-Müller probe. Regular checks were made of the background and the efficiency of the counter. The total counts were usually of the order of 10,000 to minimise the statistical error due to the random nature of radioactivity and correction for dead time was always made. Each counting was repeated three times and the average was taken.

2.4 <u>Spectrophotometric Estimation of Aquation Rates of</u> <u>Cobalt(III) and Iron(II) Complexes</u>

The most convenient technique to study aquation of cobalt(III) and iron(II) complexes is spectrophotometry, provided that the complex has characteristic absorption peaks with sufficiently large molar extinction coefficients. It is advantageous to study the spectra in the visible region i.e. 750 - 350 nm rather than ultraviolet because of the problems associated with the very high absorption of some anions such as NO_3^- , Br⁻ or I⁻ if present in solution⁵⁷.

All the spectra were recorded using an SP 800 A recording spectrophotometer fitted with an SP 825 Series 2 Programme Controller. The cell compartment of the spectrophotometer was thermostatted by running water through it from a water bath whose temperature was maintained constant by a contact thermometer and relay controlled heater. The

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temperature inside the cell was checked periodically by the use of a thermocouple.

2.4.1 $\underline{\operatorname{cis}} \underbrace{\operatorname{Coen}_2 \operatorname{Cl}_2} \operatorname{Cl}$ - An accurate weight of $\operatorname{cis} \underbrace{\operatorname{Coen}_2 \operatorname{Cl}_2} \operatorname{Cl}$ to make 2×10^{-2} M solution was dissolved in water or dioxan-water mixture (20%, 40% and 60% v/v) containing the desired amount of acid or salt and previously thermostatted at 35°C. The solution was transferred quickly to a one cm spectrophotometer silica cell and the spectrum of each solution was recorded periodically in the visible region i.e. 750 -350 nm.

Iron(II) complexes - For kinetic runs involving 2.4.2 the iron(11) complexes the following method was used. A11 component solutions and solvents, viz., dioxan, iron(II) complexes, acids of different molarities and water, were thermostatted separately before mixing. The appropriate volume of each solution was transferred by a pipette into the one cm cell placed in the thermostatted cell compartment of the spectrophotometer so as the total volume in the cell is 3 cm^3 . The optical density of the solution was recorded periodically e.g. after 5 minutes intervals for tris-(1,10phenanthroline)iron(II), 10 minutes intervals for tris-(4,7dimethyl-1,10-phenanthroline)iron(II) and continuous recording for tris-(5-nitro-1,10-phenanthroline)iron(II) complexes at fixed wavelength, 510 nm. In all cases the coloured solutions became colourless at the end of each kinetic run indicating that the reaction proceeds to completion.

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2.5 Treatment of Results

2.5.1 <u>Ligand substitution</u> - The rate constants of ligand substitution were determined from the following equation

$$-kt = \ln \frac{a - x}{a}$$
 (2.1)

The initial activity, a,of the labelled complexes, $Men_2Cl_2^+$ where M = Rh(III) or Ir(III), was measured as well as the remaining activity after substitution, (a - x), at time t. The results obtained were found to give a good linear relationship between logarithms (a - x)/a and time t. The rate constant, k, was calculated from the gradient.

2.5.2 <u>lsotopic exchange</u> - Isotopic exchange data were treated in accordance with McKay's equation⁵⁸:

$$-Rt = \frac{nab}{na + b} \ln (1 - F)$$
 (2.2)

$$-k_1 t = \ln (1 - F)$$
 (2.3)

where
$$k_1 = \frac{R(na + b)}{nab}$$
 (2.4)

R is the rate of exchange; a = concentration of the complex $(mol \ dm^{-3})$; b = total concentration of chloride ions $(mol \ dm^{-3})$; n = number of chloride ions in the complex ion; F is the fraction exchanged at time t. F was calculated from the equilibrium concentration or in other words the activity of the complex at equilibrium as follows. The total activity of the solution was measured before precipitation of ionic chloride with silver nitrate (see section 2.3.1). The equilibrium activity i.e. maximum activity of the complex due to the exchange of inactive chloride from inside by active chloride from outside the complex is :

$$\begin{array}{l} \mbox{equilibrium} \\ \mbox{activity} \end{array} = \begin{array}{c} \mbox{total} \\ \mbox{activity} \end{array} x \end{array} \\ \begin{array}{c} \mbox{concentration of chloride ions} \\ \mbox{in the complex} \\ \mbox{total concentration of chloride} \\ \mbox{outside the complex} \end{array} \end{array}$$

Therefore, $F = \frac{activity of the complex at time t}{equilibrium activity}$

when values of log (1 - F) were plotted against time t, straight lines passing through the origin were obtained for over 60% of fraction exchanged. From the value of the gradient k_1 was obtained and hence k_2 for the exchange of one chloride ion of the complex was calculated from the equation

$$k_2 = \frac{b}{na + b} k_1 \tag{2.5}$$

All results for isotopic exchange and substitution reactions were processed on a Honeywell series 200 computer using a least-mean-squares programme, to give the rate constants with their standard deviations (see Appendix 1).

2.5.3 <u>Aquation of cis- $\boxed{\text{Coen}_2\text{Cl}_2}$ Cl</u> - The aquation reactions were followed spectrophotometrically up to at least 70% of complete reaction. The rate constants were calculated from the absorbance readings at 560 nm, a

wavelength of maximum absorption for $\operatorname{cis-Coen}_2 \operatorname{Cl}_2^+$, according to the first order kinetic equation

$$kt = \ln \frac{A_{\infty} - A_{0}}{A_{\infty} - A_{t}}$$
(2.6)

where A_0 , A_t and A_{ω} are the absorbance readings at time zero, t and infinity respectively. Values of log $(A_{\omega} - A_0)/(A_{\omega} - A_t)$ were plotted against time t and the rate constant was calculated from the gradient.

2.5.4 <u>Aquation of iron(II)-phenanthroline complexes</u> -The aquation of the iron(II)-1,10-phenanthroline complexes was also followed spectrophotometrically, at the respective wavelengths of maximum absorption in the visible region (see section 2.1.4). In all water-dioxan mixtures used in this investigation, these aquation reactions proceeded to completion; the optical density at the end of each run was zero. Rate constants were, therefore, calculated from the gradients of plots of logarithms of absorbance against time.

2.5.5 <u>Activation parameters</u> - Energies of activation, ΔE^{\neq} , with their standard deviations, were calculated by a standard least-mean-squares procedure, using the programme in Appendix 1. Enthalpies of activation, ΔH^{\neq} , were calculated from

$$\Delta H^{\neq} = \Delta E^{\neq} - RT$$

Entropies of activation, Δs^{\neq} , were then derived from these activation enthalpies and respective rate constants using

the usual transition-state expression 59 :

$$\underline{\mathbf{k}}_{\mathrm{r.}} = \frac{\mathrm{kT}}{\mathrm{h}} - \mathrm{e}^{\Delta \mathrm{S}^{\neq}/\mathrm{R}} \cdot \mathrm{e}^{-\Delta \mathrm{H}^{\neq}/\mathrm{RT}}$$
(2.7)

where $\boldsymbol{k}_{\rm P},$ k and h are the rate constant, Boltzmann constant and Plank's constant respectively.

CHAPTER 3

IRIDIUM(III), RHODIUM(III) AND COBALT(III) COMPLEXES

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CHAPTER 3

IRIDIUM(III), RHODIUM(III) AND COBALT(III) COMPLEXES

3.1 Introduction

The study of isotopic exchange and substitution reactions at chloroamine complexes of iridium(III), rhodium(III), and cobalt(III) in mixed solvents was carried out to throw more light on two aspects of kinetic importance. These are the solvation effects and also the effects of the nature and concentration of anions on reaction rates. Comparison of these kinetic results is interesting as far as the mechanism of the reaction is concerned in showing trends in the group cobalt(III), rhodium(III) and iridium(III). Since the solvation of the initial and transition states of such complexes contributes to a large extent towards determining the rates of these reactions, the influence of solvent composition on the rates and mechanism was also investigated. The original choice of dioxan as organic cosolvent was made for three reasons. Firstly, it is miscible with water, has reasonable solvent properties and can be used in radiochemical work, i.e. estimation of ³⁰Cl by scintillation counting. But unfortunately it was found that liquid scintillation assay was not a reliable method because of the presence of quenching agents in solution such as silver nitrate. Secondly, it is suitable for kinetic work since it cannot act as a reducing agent compared with methanol or ethanol. Thirdly, it is reluctant to coordinate to transition metal ions.

3.2 <u>Isotopic Exchange and Substitution Reactions of</u> $\frac{\text{trans-Iren}_2 C1_2^+}{2}$

There have been preparative⁶⁰ and kinetic⁶¹ studies of ligand substitution of cis- and trans- $\operatorname{Iren}_2\operatorname{Cl}_2^+$. Bauer and Basolo⁶¹ found the rate of ligand substitution to be independent of the nature and concentration of the incoming nucleophile. Although they were not able to distinguish between associative and dissociative mechanisms from their experimental results, they claimed the formation of an aquo intermediate (3.1) as the rate determining step followed by fast interchange (3.2).

$$\operatorname{trans-Iren}_{2}\operatorname{CloH}_{2}^{2+} + \operatorname{H}_{2}^{0} \rightleftharpoons \operatorname{trans-Iren}_{2}\operatorname{CloH}_{2}^{2+} \qquad (3.1)$$

$$\operatorname{trans-Iren}_{2}\operatorname{CloH}_{2}^{2+} + x^{-} \longrightarrow \operatorname{trans-Iren}_{2}\operatorname{Clx}^{+} \qquad (3.2)$$

In view of the reluctance of haloammineiridium(III) complexes to undergo any detectable aquation, except in the presence of a halogenophile such as mercury(II), the above mechanism seems unlikely.

Recent work on isotopic exchange¹⁶ of cis- and trans-Men₂Cl₂⁺, where M = Rh(III) or Ir(III), in aqueous solutions was interpreted in terms of formation of ion pairs. The goemetry of the complex, cis or trans, was also found to have a significant effect on the rates of exchange; exchange rates at the cis complexes were faster than at the trans analogues.

The variation of rate constants of chloride exchange, and bromide and nitrite substitution in trans- $Iren_2Cl_2^+$, in aqueous and aqueous-dioxan mixtures, as a function of concentration of the respective nucleophile is shown in Figures 3.1 and 3.2 and Tables 3.1, 3.2 and 3.3.

TABLE 3.1

Rate constants of isotopic exchange at trans-Iren $_2$ Cl $_2^+$ at 90°C

| % dioxan | [C1 ⁻] /M | $10^{7} k/s^{-1}$ |
|----------|-----------------------|-------------------------|
| 0 | 0.017 | $1.5 \pm .1$ |
| | 0.027 | 1.9 <u>+</u> .1 |
| | 0.053 | $2.5 \pm .2$ |
| | 0.100 | $3 \cdot 2 \pm \cdot 2$ |
| | 0.500 | $4.2 \pm .1$ |
| 20 | 0.012 | $0.55 \pm .12$ |
| | 0.016 | 0.65 + .14 |
| | 0.102 | 0.90 <u>+</u> .12 |
| | 0.370 | $1.00 \pm .13$ |
| | 0.925 | $0.98 \pm .13$ |
| | | |



 \mathbf{V} 60% v/v dioxan and at 80°C.

TABLE 3.2

Variation in rate constants of substitution at $trans-Iren_2Cl_2^+$ with bromide at different temperatures and solvent compositions

| % | nonaqueous component (v/v dioxan) | temp/°C | [Br]/M | $10^7 k/s^{-1}$ |
|---|--------------------------------------|---------|---------|------------------|
| | 0 | 90 | 0.0168 | 7.0 <u>+</u> 0.2 |
| | | | 0.0486 | 9.2 ± 0.2 |
| | | | 0.1084 | 10.6 ± 0.3 |
| | | | 0.202 | 11.9 ± 0.3 |
| | | | 0.493 | 12.9 ± 0.3 |
| | | | 0.856 | 12.8 ± 0.2 |
| | 20 | 90 | 0.01378 | 3.4 ± 0.2 |
| | | | 0.0478 | 5.5 ± 0.4 |
| | | | 0.0996 | 9.5 ± 0.2 |
| | | | 0.4639 | 9.8 ± 0.1 |
| | | | 0.971 | 9.1 ± 0.2 |
| | 40 | 90 | 0.112 | 3.9 ± 0.1 |
| | | | 0.523 | 4.9 ± 0.2 |
| | | | 1.007 | 4.9 ± 0.01 |
| | 60 | 90 | 0.0174 | 2.2 ± 0.2 |
| | | | 0.038 | 2.7 ± 0.1 |
| | | | 0.085 | 3.1 ± 0.1 |
| | | | 0.442 | 3.7 ± 0.2 |
| | | | 0.9007 | 3.9 ± 0.2 |
| | 60 | 80 | 0.0163 | 0.7 ± 0.1 |
| | | | 0.0210 | 0.8 + 0.1 |
| | | | 0.1059 | 1.2 ± 0.1 |
| | | | 0.204 | 1.3 ± 0.2 |
| | | | 0.399 | 1.6 ± 0.3 |
| | | | 0.762 | 1.6 ± 0.4 |
| | | | 1.004 | 1.8 ± 0.1 |



a function of incoming ligand concentration
90°C in aqueous solution: ● chloride;
O bromide; ■ iodide; ▲ nitrite;

Xchloride in 20% dioxan.

TABLE 3.3

Rate constants of substitution $at_1 \text{ trans-lren}_2 \text{Cl}_2^+$ with nitrite in water at 90°C

| [N0 ₂ ⁻]/M | $10^7 k/s^{-1}$ |
|-----------------------------------|-----------------|
| 0.006 | $5.9 \pm .2$ |
| 0.010 | $7.7 \pm .1$ |
| 0.024 | $9.6 \pm .3$ |
| 0.105 | $10.9 \pm .4$ |
| 0.445 | $11.3 \pm .2$ |
| 1.00 | $10.9 \pm .1$ |

In all cases studied the rate constant varies with the incoming ligand concentration, reaching a limiting rate at an incoming ligand concentration above approximately 0.2 M. This behaviour echoes the trends observed for chloride exchange at cis-Coen₂Cl₂⁺ in methanol⁵ and at trans-Iren₂Cl₂⁺ in water¹⁶.

There are two predominant mechanisms which need to be considered before attempting to explain these results :

a) Dissociative mechanism D (S_N^{-1}) in which the rate determining step is controlled by the dissociation of the metal-halogen bond. The rate law for this process is

$$\frac{d[complex]}{dt} = k_1[complex]$$

In this case one would expect the rate to be invariant as the concentration of the incoming nucleophile varies.

b) Associative mechanism A (S_N^2) or formation of an intermediate of a higher coordination number. The rate law is

$$\frac{d[complex]}{dt} = k[complex][nucleophile]$$

Here the rate will show a first-order dependence on the concentration of the nucleophile.

The results in Tables 3.1 to 3.3 and illustrated in Figures 3.1 and 3.2 conform to neither of the above mechanisms.

The kinetic pattern which best fits the present results is that of ion pair formation, in a similar manner to the behaviour previously reported for isotopic exchange in $\operatorname{cis-Coen_2Cl_2}^+$ in methanol⁵. As the concentration of the incoming nucleophile X increases, more ion pairs are formed by the rapidly established pre-equilibrium (3.3)

trans-Iren₂Cl₂⁺ +
$$X^{-}$$
 $\xleftarrow{K_{1P}}$ trans-Iren₂Cl₂⁺, X^{-} (3.3)

This will either be followed by rate-determining ligand interchange (3.4) within the ion pair,

$$\operatorname{trans-Iren_2Cl_2^+, X^-} \xrightarrow{k_{IP}} \operatorname{trans-Iren_2ClX^+, Cl^-}$$
(3.4)

or by dissociative interchange with the X-ligand, or conceivably from the primary solvation shell (see section 1.1).

The rate law is

where k_{obs} as described earlier in section 1.5.1 is given by the following equation

$$k_{obs} = \frac{k + k_{IP}K_{IP}[X^{-}]}{1 + K_{IP}[X^{-}]}$$

As will be shown later there is a good correlation between k_{obs} -1 versus $[X^{-}]^{-1}$. This gives support to the assumption of ion pair formation as a relevant aspect of the present mechanism.

However, it is difficult to distinguish between the associative ion pair or dissociative ion pair mechanism merely on the basis of the present kinetic results. One possible approach to this problem is to compare rates of anation or substitution with those of water exchange. This approach has suggested that there is some degree of associative character to substitution in some iridium(III) complexes⁶²; it is however not possible to apply here since there are no suitable reactions for such kinetic comparisons.

Although Bauer and Basolo⁶¹ have not reported a significant ion pair effect in kinetics of substitution at trans-Iren₂Cl₂⁺ in aqueous solution at 130[°]C the evidence now exists for ion pairing involving $Men_2Cl_2^+$ in non-aqueous⁴ solvents for cobalt(III) and aqueous solution¹⁶ for rhodium(III) and iridium(III). At higher temperature, 130[°]C

ion pair formation is less likely to occur, albeit the change in association constant is small with temperature variation, due to the thermal energy of the solvent.

TABLE 3.4

Variation of rate constants of substitution at trans-Iren₂Cl₂⁺ with the nature of incoming nucleophile at $90^{\circ}C$

| x ⁻ | $10^7 k_{IP} / s^{-1}$ |
|-----------------|------------------------|
| c1 ⁻ | 4.3 |
| Br | 12.6 |
| NO_2^- | 11.2 |
| 1 ⁻ | 14.5 |

The results in Table 3.4 show the dependence of the limiting rates of exchange and substitution on the nature of the incoming nucleophile. The rates increase in the following order

 $C1^{-} < N0_{2}^{-} < Br^{-} < 1^{-}$

The rate constant for iodide substitution, $14.5 \times 10^{-7} s^{-1}$, was derived by interpolation of the Bauer and Basolo⁶¹ results at 0.2 M iodide concentration. The difference in magnitude in rate constants (k_{IP}) for different incoming anions is relatively small; it is highly unlikely that the mechanism is fully associative. It is of interest in this connection to note the very large variation in rate constants with varying the nature of anions for purely associative compared with dissociative substitution reactions of the hexa-aquairon(III) cation (Table 3.5).

| TUDDD 0. |) |
|----------|---|
|----------|---|

| Kinetic da | ta for the substitution reac | tions* of |
|------------------------|---|----------------|
| $Fe(H_2^{0})_{6}^{3+}$ | $+ x^{-} \rightarrow Fe(H_2^{0})_5 x^2$ | $+ + H_2^0$ |
| x ⁻ | $k_2/1mol^{-1}s^{-1}$ | k_{1}/s^{-1} |
| cı ⁻ | 9.4 | 18 |
| Br | 20 | 31 |
| NCS | 127 | 20 |
| F | 5400 | - |
| s04 ²⁻ | 6400 | - |

* from reference 63: k_1 is the rate constant for dissociation; k_2 is that for nucleophilic attack.

The effect of the nature of anions on substitution in platinum(II) complexes⁶⁴ provides another example of behaviour typical of an associative mechanism. The increase in rate constants for substitution at trans- $\mathrm{Iren_2Cl_2}^+$ as the incoming nucleophile changes from Cl⁻ to I⁻ is the opposite trend to the one expected for an associative mechanism¹⁶. Since the smaller the size of the hydrated nucleophile and greater its charge the easier will be the nucleophilic

attack and also the formation of a seven-coordinated intermediate will be enhanced because of the smaller expansion required.

However, the unexpectedly low rate of nitrite ion substitution, based on the size of the hydrated nitrite ion, may be due to steric hinderance in the interchange process.

TABLE 3.6

Variation of rate constants for bromide substitution at trans-Iren $_2\text{Cl}_2^+$ with temperature in 60% v/v dioxan

| Temp/ ^O C | $10^7 k/s^{-1}$ |
|----------------------|------------------|
| 76.5 | 0.6 <u>+</u> 0.1 |
| 80.0 | 0.7 ± 0.2 |
| 85.3 | 1.8 ± 0.1 |
| 90.2 | 2.4 ± 0.2 |
| 96.4 | 4.7 ± 0.3 |

The effect of solvent composition is shown in Figure 3.1 where there is a systematic decrease in the limiting rate constants k_{IP} as the percentage of dioxan increases from 0 to 60%. This is the expected trend since a decrease in the dielectric constant of the solvent mixture causes an increase in the free energy of activation for an ionic reaction as has previously been mentioned in section 1.6.

The effect of temperature was studied for bromide substitution in 60% dioxan. The enthalpy of activation ΔH^{\neq} and entropy of activation ΔS^{\neq} were calculated as has been described before in section 2.5.5. From the results in Table 3.6 the enthalpy of activation is $26.5 \pm 1.5 \text{ k cal mol}^{-1}$ and entropy of activation is -16 ± 5 cal deg $^{-1}$ mol $^{-1}$. These are quite similar to the corresponding values for isotopic exchange¹⁶ at trans-Iren₂Cl₂⁺ in water.

The ion association constants K_{IP} were calculated, from the reported rates of isotopic exchange and substitution, from plots of $k_{obs}^{-1} \underline{vs} [\bar{x}]^{-1}$ (equation 1.22, section 1.5.1), illustrated in Figure 3.3. There is always a good correlation The applicability of equation 1.21 in these systems is consistant with a mechanism in which ion pair formation is a dominant feature. Table 3.7 shows that the values of K_{IP} increase in the order $Cl^- < Br^- < NO_2^-$. This might be expected, as the softer anions could lead to higher ion pair formation

TABLE 3.7

Ion association constants, K_{IP} , for trans-Iren₂Cl₂⁺, X⁻ in water at 90[°]C

| x ⁻ | KIP | |
|-----------------|------|--|
| c1 ⁻ | ` 28 | |
| Br | 80 | |
| NO ₂ | 207 | |



FIGURE 3.3 Plot of k_{obs}^{-1} vs $[X^{-}]^{-1}$ in trans- $Iren_2Cl_2^{+}$: • chloride; • bromide; • nitrite.

3.3 <u>Isotopic Exchange and Substitution Reactions of</u> <u>trans-Rhen₂Cl₂⁺</u>

Several studies on hydrolysis⁶⁵ and substitution⁶⁶ reactions of trans-Rhen₂Cl₂⁺ have been attempted to establish the similarities as well as the differences between rhodium(III) and cobalt(III) complexes. Rhodium(III) like iridium(III) complexes are easier to study than the corresponding cobalt(III) complexes because of the lack of complications arising from stereochemical rearrangements. However studies of substitution at rhodium(III) can be complicated by the operation of both aquation and ligand Rates of substitution of halo-amine exchange reactions. rhodium(III) complexes were found to vary slightly with the nature and concentration of the incoming nucleophile⁶⁶. There is a controversy in the literature about whether associative or dissociative behaviour predominates for amminehalorhodium (III) complexes, and the matter is still open for further discussion. For instance some workers⁶ argued for the formation of an aquo intermediate as the rate determining step based on the evidence that the rates of substitution are almost equal to the rates of hydrolysis. The formation of an aquo intermediate, however, does not indicate whether an associative or a dissociative process is the major operating mechanism. However the formation of a five-coordinate intermediate was considered $\mathbf{b}^{\mathbf{b}_0}$ as another likely possibility. The reactions can be summarized in the scheme :

 \rightleftharpoons Rhen₂ x^{2+} + x^{-} $\operatorname{Rhen}_2 \operatorname{XOH}_2^{2+} + x^- \rightleftharpoons \operatorname{Rhen}_2 \operatorname{X}_2^+$ Rhen₂XY⁺

The present work on bromide substitution at trans-Rhen₂Cl₂⁺ shows that ion pairs play an important role in the mechanism of these reactions. There is a uniform pattern of rate dependence on bromide concentration in water, 20% and 40% dioxan as shown in Table 3.8 and illustrated in Figure 3.4 together with the isotopic exchange curve for comparison.

TABLE 3.8

Rate constants of substitution at trans- $Rhen_2Cl_2^+$ with bromide at 80.3°C

 $10^{5} k/s^{-1}$

| | % nonaqueous | s component | (v/v dioxan) | |
|-----------------------------|--------------------|-------------------|---------------|-----|
| $\left[Br^{-} \right] / M$ | 0 | 20 | 40 | |
| 0.006 | $1.02 \pm .06^{a}$ | $0.95 \pm .04$ | 0.74 <u>+</u> | .05 |
| 0.010 | $1.30 \pm .05$ | 1.15 <u>+</u> .05 | 0.81 <u>+</u> | .05 |
| 0.015 | $1.6 \pm .06$ | | | |
| 0.035 | 1.8 <u>+</u> .07 | | | |
| 0.050 | $2.0 \pm .09$ | | | |
| 0.055 | $2.1 \pm .05$ | $1.54 \pm .07$ | 0.89 <u>+</u> | .06 |
| 0.105 | $2.2 \pm .1$ | $1.50 \pm .10$ | 0.89 <u>+</u> | .07 |
| 0.205 | $2.4 \pm .1$ | 1.54 ± .10 | 0.95 <u>+</u> | .06 |
| 0.50 | $2.5 \pm .1$ | $1.66 \pm .04$ | 0.99 <u>+</u> | .10 |
| 1.00 | $2.5 \pm .1$ | | | |

^a the error limits quoted are the calculated standard deviations.



FIGURE 3.4 The dependence of first-order rate constant (\underline{k}) for substitution at <u>trans</u>- Rhen₂Cl₂ ⁺ on nature and concentration of the anion (Y), and on solvent composition, at 80.3°C. 1 : chloride exchange, in water; 2 : bromide substitution, in water; 3 : bromide substitution, in 20% dioxan; 4 : bromide substitution, in 40% dioxan.

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In all cases the rate of reaction increases, tending to a limiting value at high concentration, as the concentration of bromide increases. This kinetic pattern is the same as has been observed earlier for ligand substitution at trans-Iren₂Cl₂⁺ (section 3.2) and can be interpreted by the reaction scheme

trans-Rhen₂Cl₂⁺ + Br⁻ $\xleftarrow{K_{IP}}$ trans-Rhen₂Cl₂⁺, Br⁻ k_{TP} Rhen₂ClBr⁺

with $k \ll k_{IP}$.

There are two uncertain features of the mechanism of these substitution reactions. The first is whether, as for analogous reactions of cobalt(III) complexes, an aquo intermediate is involved. The second is whether the substitution process or processes proceed via dissociative (D), or associative (A) mechanisms or via some intermediate interchange ($I_d \rightarrow I_a$) character. Mention was made earlier in section 3.2 that since aminehaloiridium(III) complexes do not aquate easily, and also because of the slower rate of aquation than of chloride exchange at analogous rhodium(III) complexes, then the intermediacy of an aquo intermediate seems unlikely; its existence is not needed to explain the present kinetic results.

Ion association constants (K_{IP}) have been calculated from kinetic results as described before in section 1.5.1 from the slopes and intercepts of $k_{obs}^{-1} \quad \underline{vs} \quad \left[Br^{-1} \right]^{-1}$ plots,



FIGURE 3.5 Plots of k_{obs}^{-1} vs $[X^{-}]^{-1}$ for bromide substitution at trans- Rhen₂Cl₂ ⁺ in: • water; Δ 20% dioxan; • 40% dioxan.

as shown in Figure 3.5. Table 3.9 includes values of K_{IP} and the limiting rate constants k_{IP} in water, 20% and 40% dioxan derived from these plots.

TABLE 3.9

Ion association constants, K_{IP} , and limiting rates, k_{IP} ,

for substitution at trans-Rhen₂Cl₂⁺ at 80° C

| x ⁻ | Solvent | $10^{5} k_{IP} / s^{-1}$ | ĸ _{ip} |
|-----------------|------------|--------------------------|-----------------|
| Br | water | 2.4 | 117 <u>+</u> 2 |
| Br | 20% dioxan | 1.55 | 240 <u>+</u> 7 |
| Br | 40% dioxan | 1.0 | 600 <u>+</u> 44 |
| C1 ⁻ | water | 3.9 | 17 <u>+</u> 10 |

The increase in K_{IP} for the ion pair trans-Rhen₂Cl₂⁺, Br⁻ with increasing proportion of dioxan, and thus with decreasing dielectric constant of the solvent is the expected trend. K_{IP} for bromide association with the present rhodium(III) complex is much larger than K_{IP} for its association with chloride. Again here a similarity exists between rhodium(III) and iridium(III) complexes, which suggests that the greater polarisability of bromide is the determining factor in controlling K_{IP} values in these systems. Also the decrease in rate constants with an increase in dioxan concentration echoes the behaviour which has already been discussed for the iridium(III) complex (section 3.2).

3.4 <u>Aquation of cis-Coen₂Cl₂⁺</u>

Ammine- and amine-halocobalt(III) complexes are by far the most thoroughly studied complexes in aqueous^{4,67}, mixed^{33,42,68} and nonaqueous⁵ solvents. A great deal of work has been devoted to assigning the mechanism of substitution reactions in such complexes from detailed kinetic studies with a wide range of factors such as concentration, acidity, medium and nature of ligands. It is now generally accepted that substitution, including base hydrolysis, in amminehalocobalt(III) proceeds by a dissociative mechanism.

It has also been demonstrated that several hexaammine and amminehalocobalt(III) complexes undergo aquation or anation via ion pair formation; inter alia $Co(NH_3)_5(OH_2)^{3+}$ and $Co(NH_3)_5Cl^{2+}$ form ion pairs in aqueous solutions^{15,67}. Isotopic exchange in cis-Coen₂Cl₂⁺ in methanol⁵ is consistent with the intermediate formation of the ion pair $Coen_2Cl_2^+, Cl^-$, with an association constant of 250 at 25°C.

In view of the lack of any kinetic evidence for significant ion pairing between cis- or trans- $\text{Coen}_2\text{Cl}_2^+$ and anions in aqueous solution, the important role played by such ion pairs in each of the larger and equally charged rhodium(III) and iridium(III) analogues in section 3.2 and 3.3 is rather surprising. Therefore it was a matter of interest to investigate the effect of the nature and concentration of added anions on aquation rates of cis- $\text{Coen}_2\text{Cl}_2^+$ in water and in aqueous dioxan (up to 60% v/v dioxan). The results are shown in Table 3.10. The rate

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TABLE 3.10

Rate constants (k) for aquation of cis- $Coen_2Cl_2^+$ in water-dioxan mixtures, at $35.0^{\circ}C$

 $10^{3} k/s^{-1}$

| Acid | [acid]/M | water | , % d | lioxan (v | /v) |
|-------------------------------------|----------|------------|--------------|------------|------|
| | • • | | 20 | 40 | 60 |
| нсі | 0.0001 | 1.4 | 0.57 | 0.41 | 0.26 |
| | 0.001 | - | 0.57 | 0.41 | 0.26 |
| · · · · | 0.01 | 1.12 | - | - | - |
| | 0.1 | 1.10 | 0.58 | 0.44 | 0.27 |
| | 0.6 | – . | - | 0.43 | - |
| | 1.0 | - | 0.53 | 0.38 | 0.23 |
| H ₂ SO ₄ | 0.1 | 1.2 | _ | - ' | 0.33 |
| H ₃ PO ₄ | 0.1 | 1.2 | | 0.47 | 0.27 |
| HClo4 | 0.1 | 1.0 | - * | 0.50 | · _ |
| с1 ₃ с.со ₂ н | 0.1 | 1.1 | - | 0.45 | 0.26 |
| NaBr,0.1M + HCl | 0.0001 | 1.3 | - | 0.48 | |

constants, in a given solvent, are almost constant and independent of the nature and concentration of various anions; chloride, sulphate, perchlorate, and trichloroacetate, even in 60% dioxan. These results are unexpected in the light of the behaviour of analogous rhodium(III) and iridium(III) complexes, but are consistent with the normal behaviour of single-positive charged cobalt(III) complexes where there is no evidence yet for association with singly charged anions in aqueous solution. There are two possibilities; either cis-Coen₂Cl₂⁺ does not form ion pair in aqueous and aqueous dioxan solutions, or the ion association constant is too high and cannot be detected by this kinetic method. But from the ion association of $\operatorname{cis-Coen}_2\operatorname{Cl}_2^+,\operatorname{Cl}^-$ in methanol the corresponding value in water is expected to be low. This value of K_{IP} in water is about 10 and worked out from equation 1.15 by substitution for the different values of the dielectric constants in water and in methanol.

3.5 Solvent Effects

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The present section will deal with solvent effects only in terms of Grunwald-Winstein treatment, since more extensive review has already been given in section 1.6.

3.5.1 <u>trans-Iren₂Cl₂⁺</u> - The variation of the limiting rate constants k_{IP} for bromide substitution at 90°C in aqueous dioxan and in aqueous ethanol with the solvating power Y is shown in Table 3.11. The values of Y are at 25°C [‡] and taken from reference 34. There is a correlation between the logarithms of the rate constants and the Y values of the mixed solvents (0 - 60% v/v dioxan or ethanol) as shown in Figure 3.6. In water-rich solvents the plot approximates to a straight line with slope (m) 0.25. The curvature at high concentrations of

The values of m obviously depend on temperature but the variation, at least for organic substrates, is relatively small³⁵.



FIGURE 3.6 Correlation of the logarithms of the rate constant for the substitution of trans- $\operatorname{Iren}_2\operatorname{Cl}_2^+$ in mixed aqueous solvents with solvent Y values. Nonaqueous component: \bigcirc dioxan; \blacktriangle ethanol. non-aqueous component arises, possibly, because the Grunwald-Winstein approach was developed for organic It would be better if one could devise a new systems. scale for solvolysis of inorganic complexes by choosing a thoroughly studied inorganic complex as a standard instead of t-butyl chloride. Nevertheless the curvature observed for the reaction of trans-Iren₂Cl₂⁺ is similar to that observed for $\operatorname{cis-Coen}_2\operatorname{Cl}_2^+$. The m value of 0.25 for trans-Iren $_2Cl_2^+$ is the same as that for the aquation⁴¹ of trans-Coen₂Cl₂⁺ and similar to that of cis-Coen₂Cl₂⁺ (m = 0.35)⁶⁸. The results are consistent with a dissociative mechanism with (as solvation of the leaving chloride will be a constant factor) the solvation requirements of the Iren₂Cl moiety very similar to those of the Coen₂Cl moiety.

TABLE 3.11

Rate constants for bromide substitution at trans-Iren₂Cl₂⁺ as a function of Y values at $90^{\circ}C$

| % nonaqueous component (v/v) | Y | $10^7 k/s^{-1}$ |
|---------------------------------|-------|-----------------|
| 0 | 3.493 | 12.5 |
| 20) | 2.877 | 9.5 |
| 40) dioxan | 1.945 | 5.0 |
| 60) | 0.715 | 3.5 |
| 20) | 3.051 | 9.3 |
|) ethanol 60) | 1.124 | 5.6 |

3.5.2 <u>trans-Rhen₂Cl₂⁺</u> - The effect of solvent composition on the rate of bromide substitution at $80^{\circ}C$ is shown in Table 3.12. Like trans-Iren $_2$ Cl $_2^+$ there seems to be a correlation (though here we have only three points) between logarithms of rate constants and Y values as illustrated in Figure 3.7. The mY plot in aqueous dioxan mixtures (0 - 40% v/v dioxan) defines a slightly curved line of average slope +0.25. It is of interest to note that this value is in good agreement with the very similar values for the analogous cobalt(III) and the previously discussed iridium(III) reactions. It is surprising that aquation of $Rh(NH_2)_5 Cl^{2+}$ in aqueous ethanol⁴² was reported to give an mY plot with a negative slope (m = -0.25). It was suggested that the anomalous increase in rate with increasing ethanol content might be due to catalysis of aquation by rhodium(I) or rhodium(II) species generated by ethanol reduction of rhodium(III). This catalytic effect of ethanol has also been reported for substitution reactions at $Rh(OH_2)Cl_5^{2-}$ (ref. 69a) and $Rhpy_4Cl_2^+$ (ref. 69b), though no such catalysis has been detected for $Rhen_2Cl_2^+$ (ref. 69B) or Rhphen $_{2}X_{2}$ (ref. 69c).

The rates of chloride exchange at trans-Rhen₂Cl₂⁺ in 60% dioxan were also determined. These are 7.1 x 10^{-7} , 8.9 x 10^{-7} , and 17 x 10^{-7} s⁻¹ in 0.011, 0.10, and 0.92 Mhydrochloric acid respectively and at 70.5°C. The limiting rate of about 2 x 10^{-6} s⁻¹ here and that at the same temperature in water define an mY plot of slope about +0.3, similar to that for bromide substitution.





Correlation of the logarithms of the rate constant for: O bromide substitution; O chloride exchange at trans- Rhen₂Cl₂ ⁺ in aqueous dioxan with solvent Y values.

TABLE 3.12

Variation of rate constants for bromide substitution at trans-Rhen₂Cl₂⁺ with solvent composition at 80° C.

| % v/v dioxan | Y | $10^{5} k/s^{-1}$ |
|--------------|-------|-------------------|
| 0 | 3.493 | 2.4 |
| 20 | 2.877 | 1.6 |
| 40 | 1.945 | 1.0 |

Finally the present results of aquation of $\operatorname{cis-Coen}_2 \operatorname{Cl}_2^+$ in aqueous dioxan are consistent with the published mY plot for aquation in water-rich mixed aqueous solvents⁴².

CHAPTER 4

IRON(II)-PHENANTHROLINE COMPLEXES

| 4.1 | Introduction |
|-----|--------------------------------|
| 4.2 | Effects of Anions |
| 4.3 | Effects of Solvent Composition |
| | on Rates of Dissociation |

<u>CHAPTER 4</u>

IRON(II)-PHENANTHROLINE COMPLEXES

4.1 Introduction

The previous Chapter described the kinetic behaviour of cobalt(III), rhodium(III) and iridium(III) complexes in aqueous and aqueous dioxan solutions. In view of the isoelectronic structure of these metal ions with iron(II), it is of particular interest to study the reactivity of phenanthroline-iron(II) complexes in water and in aqueous dioxan and to compare substitution mechanisms with those for octahedral cobalt(III) haloammines complexes. It is known that tris-(1,10-phenanthroline)iron(II) complexes are stable in the pH range 2 - 9 but outside this range considerable dissociation is expected. The first kinetic study 70 of acid dissociation of these complexes showed that dissociation is of the first-order in the complex but independent of the acid concentration. The formation and dissociation of the complex can be represented by the following reactions :

$$Fe^{2+}$$
 + phen \Longrightarrow $Fe(phen)^{2+}$ (4.1)

$$Fe(phen)^{2+} + phen \iff Fe(phen)_2^{2+}$$
(4.2)

$$Fe(phen)_2^{2+} + phen \iff Fe(phen)_3^{2+}$$
(4.3)

Reaction (4.3) is the rate determining step in formation or dissociation. In acid solution the leaving ligand, 1,10phenanthroline, is protonated; it can accommodate only one hydrogen ion between the two nitrogen $atoms^{71}$. Thus it is expected that dissociation will proceed to the right hand side according to the following equation :

 $Fe(phen)_{3}^{2+} + 3H^{+} + aq \longrightarrow Fe^{2+}, aq + 3 phen. H^{+}$ (4.4)

The rate-determining loss of the first ligand from the tris-complex is accompanied by change in the spin of the complex from low spin to high spin^{11b}; the loss of the second and third ligands are fast. Dickens, Basolo, and Neumann⁷² have shown that rates of aquation of tris-(1,10-phenanthroline) iron(II) vary slightly with the concentration of anions. There are very few anions which can react directly with tris-(1,10-phenanthroline)iron(II) and cause substitution. Cyanide and hydroxide lead to direct substitution; reaction with peroxodisulphate involves dissociation and oxidation. It would be expected that added anions might have enhancing effects on rates via ion pair formation especially in aqueous organic mixtures, where the dielectric constant is low.

The present work is a systematic study of the effects of solvent composition and added anions on rates of aquation of tris-(1,10-phenanthroline)iron(II) and its ligand substituted derivatives in water and in aqueous dioxan (up to 60% v/v dioxan). From investigation of the variation of aquation rate constants with solvent composition it is possible to make suggestions about the mechanisms of these aquations and the importance of solvation in determining reactivity.

4.2 Effects of Anions

In all the solvent mixtures and acids studied the dissociation of the iron(II) complex followed first-order kinetics to at least 70% of complete reaction. **Observed** first-order rate constant for aquation of tris-(1,10phenanthroline)iron(II) and its 5-nitro-, 3-sulphonato-, and 4,7-dimethyl-derivatives in the presence of various acids, in a range of dioxan-water mixtures, are reported in Tables 4.1 to 4.4. The general pattern of dependence of reactivity on the nature and concentration of added anions is illustrated in Figure 4.1, for the tris-(1,10-phenanthroline)iron(II) complex in 60% v/v dioxan. In 20% and 40% v/v dioxan the pattern is similar, Figures 4.2 and 4.3, though with a smaller range of aquation rate constants over the range of acids. For the unsubstituted complex in all three solvent mixtures, and for the 5-nitro-, and 4,7-dimethyl derivatives in 60% dioxan, Figures 4.4 and 4.5, the order of decreasing rate constant is always, within the limits of experimental uncertainty,

 $H_3PO_4 > HC1 > C1_3CCO_2H > H_2SO_4 > HC1O_4$

In all cases phosphoric and hydrochloric acids tend to increase reactivity, sulphuric and perchloric acids to decrease reactivity. It is thus a straightforward manner to extrapolate the rate constant <u>vs</u> acid concentration plots back to a common point at zero acid concentration for each complex and solvent mixture. Aquation rate constants estimated at zero acid concentration are shown in Table 4.5.





Dependence of rate constants for aquation of $Fe(phen)_3^{2+}$ on nature and concentration of acid, in 60% dioxan, at $35.0^{\circ}C.$ 1 : H_3PO_4 ; 2 : HCl; 3 : $CCl_3 \cdot CO_2H$; 4 : H_2SO_4 ; 5 : HClO₄.

TABLE 4.1

First-order rate constants (\underline{k}) for the aquation of tris-(1,10-phenanthroline)iron(II)⁻ in aqueous dioxan (composition by volume quoted) at 35.0^oC

| 20% | dioxan |
|-----|--------|
|-----|--------|

| | | | $10^4 k/s$ | -1 | |
|---------|-----|--------------------------------|--------------------------------|-------|------------------------------------|
| Acid /M | HC1 | H ₃ PO ₄ | H ₂ SO ₄ | HC104 | сс1 ₃ со ₂ н |
| 0.01 | 4.2 | 4.3 | 4.2 | 3.5 | 4.2 |
| 0.05 | 4.3 | | | | |
| 0.10 | 4.5 | 4.7 | 4.3 | 3.1 | 4.2 |
| 0.20 | 4.6 | | | | |
| 0.45 | | | | | 3 • 3 |
| 0.49 | | 4.7 | | 2.5 | |
| 0.56 | 4.6 | | 3.9 | | |
| 0.90 | | | | | 2.2 |
| 0.98 | 4.3 | 4.3 | | 1.85 | |
| 1.11 | | | 3.3 | | |

| | 10^{4}k/s^{-1} | | | | |
|--------|--------------------------|--------------------------------|--------------------------------|-------|------------------------------------|
| Acid/M | HC1 | ^H 3 ^{PO} 4 | ^H 2 ^{S0} 4 | HC104 | сс1 ₃ со ₂ н |
| 0.01 | 6.4 | 6.2 | 5.8 | 5.3 | 6.5 |
| 0.02 | 6.5 | 6.9 | | | |
| 0.03 | | 7.0 | | | |
| 0.04 | | 7.3 | | | |
| 0.06 | | 7.6 | | | |
| 0.10 | 7.0 | 8.1 | 5.7 | 4.2 | 7.2 |
| 0.20 | 7 • 3 | 8.3 | | | |
| 0.45 | | | | 3.2 | 7.6 |
| 0.50 | | 8.2 | | | |
| 0.56 | 7.6 | | 5.0 | | |
| 0.90 | | | | | 7.2 |
| 0.95 | . 7.7 | | | | · . |
| 0.98 | | 7.9 | | 2.4 | |
| 1.11 | 7.6 | | 3.8 | | |

40% dioxan

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| | $10^4 k/s^{-1}$ | | | | |
|---------|-----------------|--------------------------------|--------------------------------|-------|----------|
| Acid /M | нс1 | H ₃ PO ₄ | H ₂ SO ₄ | HC104 | ссізсозн |
| 0.01 | 15.0 | 17.0 | 9.0 | 7.4 | 14.3 |
| 0.05 | 17.6 | 20.6 | 9.0 | 5.9 | · . |
| 0.10 | 19.4 | 23.6 | 8.7 | 5.5 | 21.2 |
| 0.20 | 20.7 | 26.4 | 8.3 | 4.4 | 22.3 |
| 0.50 | | 26.7 | | 3.6 | |
| 0.56 | 21.8 | | 6.7 | | |
| 0.90 | | | | | 20.2 |
| 0.95 | 22.4 | | | | |
| 0.98 | | 21.9 | | 3.3 | |
| 1.11 | | | 5.3 | | |

60% dioxan



Fe(phen)₃²⁺ on nature and concentration of acid, in 20% dioxan, at 35° C. 1 : H₃PO₄; 2 : HCl; 3 : H₂SO₄; 4 : CCl₃CO₂H; 5 : HClO₄.



FIGURE 4.3

Dependence of rate constants for aquation of $Fe(phen)_3^{2+}$ on nature and concentration of acid, in 40% dioxan, at $35^{\circ}C$. 1 : H_3PO_4 ; 2 : HCl; 3 : $CC1_3CO_2H$; 4 : H_2SO_4 ; 5 : HClO₄.

TABLE 4.2

First-order rate constants (k) for the aquation of tris-(5-nitro-1,10-phenanthroline)iron(II) in 60% dioxan at 35.0°C

| | | 10 ³ k | /s ⁻¹ | |
|---------|------|-------------------|--------------------------------|--------------------------------|
| Acid /M | нс1 | HC104 | H ₂ SO ₄ | H ₃ PO ₄ |
| 0.001 | 14.6 | 5.7 | 17.3 | 49.0 |
| 0.01 | 26.0 | 4.3 | 12.7 | |
| 0.10 | 34.0 | 2.4 | 11.8 | |
| 0.20 | 39.0 | 1.6 | 9.9 | |
| 0.33 | 43.0 | | | |
| 0.40 | 45.0 | | | • . |
| 0.49 | | 1.2 | | |
| 0.55 | | | 8.1 | |
| 0.57 | 48.0 | | | |
| 0.80 | | 0.8 | | |
| 0.89 | | | 6.8 | |
| 0.98 | | 0.6 | | |
| 1.12 | 55.0 | | 6.7 | |

TABLE 4.3

First-order rate constants (k) for the aquation of tris-(4,7-dimethyl-1,10-phenanthroline)iron(II) in 60% dioxan at 35.0 °C

| Acid /M | нс1 | H ₂ SO ₄ | H ₃ PO ₄ |
|---------|-------|--------------------------------|--------------------------------|
| 0.001 | 5.8 | 5.5 | 6.3 |
| 0.010 | 7 • 3 | 5.6 | 7.7 |
| 0.066 | 8.5 | 5.2 | 8.6 |
| 0.10 | 8.5 | 5.1 | 8.6 |
| 0.20 | 8.5 | 4.6 | 8.8 |
| 0.40 | 8.4 | | 8.6 |
| 0.49 | | | 8.7 |
| 0.55 | | 3.8 | |
| 0.57 | 8.6 | | |
| 0.65 | | | 7.7 |
| 0.77 | 8.5 | 3.4 | |
| 0.97 | | | 6.1 |
| 1.14 | | 2. 8 | |

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First-order rate constants (k) for the aquation of tris-(3-sulphonato-1,10-phenanthroline)iron(II) in molar acids, 60% dioxan at 35.0°C

| Acid | $10^{3} k/s^{-1}$ |
|--------------------------------|-------------------|
| ^H 3 ^{PO} 4 | 3.3 |
| HC1 | 2.9 |
| ^H 2 ^{SO} 4 | 1.7 |
| HC10 | 0.99 |

| TUDDD +•) | TA | BL | E | 4 | • 5 |
|------------|----|----|---|---|-----|
|------------|----|----|---|---|-----|

First-order rate constants (k) for the aquation of tris-(1,10-phenanthroline)iron(II) complexes in aqueous dioxan, extrapolated to zero concentration at 35.0 °C

| | | % dioxa | (v/v) | | | |
|-------------|-------------------|---------|-------|-------|--|--|
| Substituent | 0 | 20 | 40 | 60 | | |
| | $10^4 k/s^{-1}$ | | | | | |
| | a | | | | | |
| none | 3.7 | 4.0 | 5.5 | 11.0 | | |
| 5-nitro | 23.0 ^b | | | 150.0 | | |
| 4,7-diMe | 1.1 ^b | | | 0.55 | | |

reference 84 а

reference 80 b



FIGURE 4.4

Dependence of rate constants for equation of $Fe(5-NO_2-phen)_3^{2+}$ on nature and concentration of acid, in 60% dioxan, at $35^{\circ}C$. 1 : HCl; $2 : H_2SO_4$; 3 : HClO₄; \bigoplus H₃PO₄.





FIGURE 4.5

Dependence of rate constants for aquation of $Fe(4,7-diMe-phen)_3^{2+}$ on nature and concentration of acid, in 60% dioxan, at 35° C. 1 : HCl; $2 : H_3 PO_4; 3 : H_2 SO_4.$

Dickens, Basolo and Neumann⁷² have shown that in aqueous solution HSO_4^- retards the dissociation of tris-(1,10-phenanthroline)iron(II) more effectively than Cl⁻. Their results also show a slight decrease in rate constants as the concentration of chloride ions increases. Further investigation of the dissociation of Fe(bipy)₃²⁺ and Fe(phen)₃²⁺ in aqueous methanol⁷³ shows a larger acceleration effect on rates than that of Dickens, Basolo and Neumann. The effectiveness of acceleration is in the following order

 $c1^{-} \gg HSO_{4}^{-} > C1O_{4}^{-}$

The large difference in rates in the presence of C1 to that in HSO_4^- or ClO_4^- was explained as a result of the formation of ion pairs. Although ion pairs are not unknown even for Clo_{4}^{-} in aqueous solution^{74,75}, it seems that they are less reactive than the free ion in the case of tris-(1,10phenanthroline) iron(II). In view of the acceleration effect of H_2PO_4 , Cl^- and $Cl_3CCO_2^-$ on rates of dissociation in aqueous dioxan one cannot exclude the possible formation of These could be easily formed by the presence of ion pairs. added anions in the three pockets created by the three planar ligand of the complex cation⁷⁶. This can occur either with or without replacement of solvent molecules from these pockets 7^3 . The order of increase in rates of dissociation in the presence of various anions, as shown in Figures 4.1 to 4.5, are

 $H_2PO_4^- > C1^- > C1_3CCO_2^- > HSO_4^- > C1O_4^-$

This is the expected order of ion pair kinetic effectiveness.

An attempt to calculate the ion pair association constants, K_{1P} , is hindered for two reasons. Firstly it is difficult to define a base line corresponding to no ion pairing, since even with perchlorate as the added ion, the possibility of significant ion-pairing cannot be excluded^{74,75}. Secondly the lack of any published data on pK values of acids in aqueous-dioxan, except for HCl in 70% and 82% v/v dioxan⁷⁷, prevents estimation of anion concentration.

To account for the retarding action caused by HSO_{4}^{-} and some other competing factors must be operating. C107 Assuming that the acid strength of perchloric or sulphuric acid is relatively much higher than that of phosphoric or hydrochloric acid in aqueous dioxan, it follows that more hydrogen ions are present when perchloric or sulphuric acid is added to the reacting mixtures. The presence of such a large concentration of hydrogen ions as well as the anions will reduce the activity of water and hence lower rates of aquation may be observed. It is interesting that the effect of anions on aquation rates varies with the complex - for instance the ratio of the rate constant for aquation in molar hydrochloric acid to that in molar sulphuric acid is 2.7 for $Fe(4,7-diMephen)_{3}^{2+}$, 4.3 for $Fe(phen)_{3}^{2+}$, and 9 for $Fe(5-NO_2-phen)_3^{2+}$ in 60% dioxan. The complex whose rate varies most with the nature of the anion is the one with the strongly electron-withdrawing nitro-substituent and thus the most positive iron atom.

The variation of the rate constant for aquation of Fe(phen) $_3^{2+}$ in acid mixtures e.g. phosphoric-perchloric

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FIGURE 4.6 Dependence of rate constants for aquation of $Fe(phen)_3^{2+}$ on composition of acid mixture, 1 : HClO₄-HCl; 2 : HClO₄-H₃PO₄, of constant overall molarity, in 60% dioxan, at 35^oC. acids or hydrochloric-perchloric acids of constant molarity, in 60% dioxan, is illustrated in Figure 4.6. The rates in phosphoric-perchloric acid mixture are more or less the same as that in pure perchloric acid whereas in hydrochloricperchloric acid mixture the rates are slightly higher than that in perchloric acid only. This behaviour suggests that the strengths of these acids are such that ionization of phosphoric acid or hydrochloric acid is suppressed by the perchloric.

$$HC10_4 \longrightarrow H^+ + C10_4^- \qquad (4.5)$$

HC1
$$\rightleftharpoons$$
 H⁺ + C1⁻ (4.6)

$$H_3^{PO}_4 \iff H^+ + H_2^{PO}_4$$
 (4.7)

Thus in the presence of perchloric acid the equilibrium (4.6) and/or (4.7) will be shifted to the left hand side and consequently the effective concentration of the more reactive $C1^-$ or $H_2P0_4^-$ ion pairs will be reduced. There is sharp increase in rates only in H_3P0_4 or HCl : HCl0₄ molar ratios of greater than about 5.

4.3 Effects of Solvent Composition on Rates of Dissociation

Several investigations of aquation of tris-(1,10phenanthroline)iron(II) and its substituted ligand derivatives have been carried out in mixed aqueous organic solvents. In acidic methanol-water mixtures⁷³ the rate of aquation of

tris-(1,10-phenanthroline)iron(II) increases at first and reaches a maximum at a mole fraction of 0.7 of methanol, and then decreases to a very small value, as the proportion of methanol increases from mole fraction zero to unity. The activation energy for aquation of tris-(1,10-phenanthroline)iron(II) in 60% methanol was found to be 28.3 ± 0.5 kcal mol^{-1} and that in water 29.9 \pm 0.2 kcal mol⁻¹.78 A similar initial increase in rate with increasing proportion of organic component has been observed for aquation of this cation in aqueous acetonitrile⁷⁹, and in aqueous acetone⁷⁸. Rates of aquation of tris-(5-nitro-1, 10-phenanthroline) iron(II) are also faster in most water-rich solvent mixtures, for example aqueous mixtures with methanol⁷⁸, ethanol⁸⁰, n- and $iso-propanol^{78}$, t-butyl alcohol³¹, acetonitrile⁷⁹, and acetone⁷⁸. The only exception is formic acid⁸⁰, for in aqueous formic acid aquation rates decrease steadily as the mole fraction of formic acid increases. On the other hand aquation rates of tris-(4,7-diMe-1,10-phenanthroline)iron(II) are in all known cases lower in mixed aqueous solvents, for example ethanol⁸⁰, t-butyl alcohol³¹, acetonitrile⁷⁹, and formic acid 80 mixtures, than in water.

There are several studies on the effects of organic solvent on the structure of water e.g. acetonitrile⁸¹, dioxan⁸², by ultrasonic techniques; propylene oxide, acetone, tetrahydrofuran, dioxan, and t-butyl alcohol whose effects were monitored by proton magnetic resonance⁸³. Dioxan like other organic solvents e.g. alcohols whose properties have been reviewed by Franks and Ives⁴⁵, breaks the structure of water.

Aquation of tris-(1,10-phenanthroline)iron(II) and its



FIGURE 4.7

First-order rate constants, extrapolated to zero acid concentration, for aquation of $\text{Fe(phen)}_3^{2+}(0)$, of $\text{Fe(5-NO}_2\text{-phen)}_3^{2+}(+)$, and of $\text{Fe(4,7-diMe-phen)}_3^{2+}(\Delta)$, at 35°C in various water-dioxan solvent mixtures.

ligand substituted derivatives was conducted in acid solution and it is known that the ions thus introduced have an effect on aquation rates both in aqueous and aqueous organic solution. However effects of added ions do not obscure reactivity trends arising from solvent variation. From the kinetic results in the various acids in each solvent mixture it is possible to extrapolate to zero acid concentration as shown in Table 4.5 and Figure 4.7. It is thus possible to determine the effect of solvent composition on reactivity in the absence of added ion effects. Figure 4.7 shows that both the unsubstituted and the 5-nitro-complexes aquate more rapidly as the proportion of dioxan increases, but the rate of aquation of the 4,7-dimethyl complex is less in 60% dioxan than in water. It is of interest to note that in aqueous dioxan the rate of aquation of the 4,7-dimethyl-complex decreases as the mol fraction of organic cosolvent increases. The rates of aquation in water or mixed solvents depend on the substituent and decrease in the following order

5-nitro-phen > phen > 4,7-dimethyl-phen

This marked contrast in behaviour may be due to differences in mechanism between these complexes, or may arise from differences in solvation of the ligands in the complexes or as leaving groups.

The difference in mechanism between 4,7-dimethyl- and 5-nitro-complex may be explained in terms of the substituent effects on the metal ligand bond as has previously been

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pointed out^{84,85}. The donation of a lone pair of electrons from nitrogen to iron atom provides \mathcal{J} -bonding while the reverse donation of t_{2g} electrons from iron to phenanthroline provides \mathcal{T} -bonding. Since 4,7-dimethyl groups are in para positions to the nitrogen atoms and act as electron donors, their effect will increase \mathcal{J} -bonding but reduce \mathcal{T} -bonding. On the other hand 5-nitro is an electron withdrawing group and will have the opposite effect on the iron-nitrogen bond. The overall strength of the metal-ligand bond is reflected in the stability constants of these complexes which are shown in Table 4.6.

TABLE 4.6

Stability constants of $Fe(LL)_3^{2+}$ complexes

| LL | $\log \beta_3$ | Reference |
|--------------------|----------------|-----------|
| 5-nitro-1,10-phen | 17.8 | 86 |
| 1,10-phen | 21.1 | 87 |
| 4,7-diMe-1,10-phen | 23.1 | 88 |

The electron donation or withdrawing property of the substituent groups will also affect the electron density in the vicinity of the iron atom. So in the case of the 5-nitro group the iron atom should have more positive charge which will in turn facilitate nucleophilic attack and hence an associative character is possible. On the contrary 4,7dimethyl groups should increase the electron density at the iron atom and facilitate the breaking of the iron-nitrogen bond so that a dissociative mechanism is most likely. This is only a qualitative description of the relative contribution



FIGURE 4.8 Variation of rate constants for aquation of $Fe(5NO_2-phen)_3^{2+}$ with solvent composition, at $35^{\circ}C$, in aqueous organic mixed solvents. $0 : EtOH; + : t-BuOH; \Delta : MeCN; \bullet : H.CO_2H;$ $\Box : dioxan; mol fraction <u>x</u> of organic component.$



FLGURE 4.9

Variation of rate constants for aquation of $Fe(4,7-diMe-phen)_3^{2+}$ with solvent composition, at $35^{\circ}C$, in aqueous organic mixed solvents; key as Fig. 4.8.
of dissociative and associative mechanisms towards the aquation reactions.

However there may be another reason for the difference in behaviour between 5-nitro- and 4,7-dimethyl-complexes based on solvation of the initial state. In aqueous t-butyl alcohol, where the structure of water is disrupted⁴⁶ when the mole fraction of t-butanol is above 0.04, it has been shown that tris-(4,7-dimethyl-1,10-phenanthroline)iron(II) perchlorate is much more soluble than the corresponding 5-nitro-complex⁸⁹. It is expected, therefore, that the free energy of activation, ΔG^{\neq} , will increase and hence slow rates of aquation for the 4,7-dimethyl-complex would be observed in a similar water structure breaking solvent such as dioxan.

Finally the nature of organic cosolvent, whether it produces structure breaking or making, is also important. There are more kinetic data available for the aquation of the 5-nitro- and 4,7-dimethyl-complexes in several mixed aqueous-organic solvents at 35° C. These data are summarized in Figures 4.8 and 4.9 together with the results in aqueous Particularly for the 5-nitro-complex, the kinetic dioxan. consequences of water structure breaking of cosolvents such as ethanol, t-butyl alcohol, acetonitrile, or dioxan; and of water structure making e.g. of formic acid, are vividly shown in these Figures. Comparison of aquation rates at constant mol fraction of organic cosolvent, Figure 4.8, shows that for the 5-nitro-complex there is always an increase in rates of aquation in structure breaking solvents while the rates decrease in structure making solvents. As

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a matter of fact this is the expected behaviour. As previously adumbrated, aquation of the 5-nitro-complex is most likely to proceed via an associative path and thus the availability of water will influence the rates. For instance in aqueous-dioxan or -ethanol more water molecules are available to attack the positive metal ion which enhances the aquation. On the other hand in aqueous formic acid where water is firmly bonded into the solvent structure less water molecules are available and aquation decreases. For the 4,7-dimethyl-complex rates of aquation always decrease in all mixed solvents as shown in Figure 4.9. This is consistant once more with a marked difference in mechanism between the 4,7-dimethyl- and the 5-nitro-complexes.

The Grunwald-Winstein treatment of the variation of reactivity in solvolysis with solvent composition has been used in Chapter 3 as a diagnostic test of the mechanism. Likewise it might prove useful here in an attempt to determine the dissociative and/or associative nature of aquation of these complexes. A plot of logarithms of rate constants for aquation of tris-(1,10-phenanthroline)iron(II), and its 5-nitro and 4,7-dimethyl substituted derivatives, against Y values is shown in Figure 4.10. Some other results for aquation of these complexes in aqueous-organic mixtures, where the organic component is methanol, ethanol, or formic acid, are also available. Unfortunately in most of these other cases aquation rate constants have either been done at a different temperature e.g. in methanol⁷³ at 25.5° C or in the presence of relatively high concentration of acid, e.g. in ethanol and formic acid⁸⁰. Nonetheless the scatter of the

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FIGURE 4.10

Correlation of the logarithms of the rate constant for aquation of, 1 : $Fe(5-NO_2-phen)_3^{2+}$; 2 : $Fe(phen)_3^{2+}$; 3 : $Fe(4,7-diMe-phen)_3^{2+}$, in mixed aqueous solvents with Y values. Nonaqueous component : \bigcirc dioxan; \blacktriangle ethanol. points in mY plots for aquation of these complexes in dioxan-, ethanol- and formic acid-water mixtures is very much larger than could possibly be attributed to the variation of acid molarity between the various systems. The lack of correlation could be due to several factors the mechanism is far from pure dissociative, contribution of ion pairs and also the leaving group are so different from chloride, as in the aquation of cis- and trans-Coen $_2$ Cl $_2^+$ and leaving groups differ from each other (depending on substituent). This makes the extrapolation from the original type of Grunwald-Winstein substitution beyond the permissible limits. It is, therefore, impossible to probe the mechanisms using the Grunwald-Winstein treatment. 0ne can only therefore consider qualitatively the variations of rate constants for aquation of these complexes in aqueousorganic solvents, as has already been done earlier in this section.

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CHAPTER 5

IRON(II)-FERROZINE COMPLEX

- 5.1 Introduction
- 5.2 Aquation
- 5.3 Reaction with Hydroxide
- 5.4 Reaction with Cyanide
 - 5.4.1 General
 - 5.4.2 Dissociation
 - 5.4.3 Cyanide Attack
 - 5.4.4 Solvent Effects
- 5.5 Reaction with Peroxodisulphate

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5.6 Conclusion

CHAPTER 5.

IRON(II)-FERROZINE COMPLEX

5.1 Introduction

In the previous Chapter the indirect effects of anions on the dissociation of tris-(1,10-phenanthroline)iron(II) and its ligand substituted derivatives were discussed. Since the ferrozine ligand, shown below, contains the same chelating structure $N \neq \frac{C-C}{N}$ as in 1,10-phenanthroline



ferrozine

it is then expected that the tris-(ferrozine)iron(II) complex will have similar properties and show similar kinetic behaviour to analogous 1,10-phenanthroline and 2,2'bipyridyl iron(II) complexes. In this Chapter the extension of the kinetic study described in Chapter 4 to direct and indirect effects of anions on the reactivity of tris-(ferrozine)iron(II) in aqueous solution is reported, and the behaviour of this complex compared with that of the wellstudied tris-(1,10-phenanthroline)iron(II) complexes. The present work is concerned specifically with investigation of aquation of the tris-(ferrozine)iron(II) complex and its reactions with hydroxide and peroxodisulphate in aqueous solution and reaction with cyanide in water and aqueous ethanol.

Aquation of the analogous 1,10-phenanthroline-iron(II) complexes has been described in Chapter 4. The alkali fission of tris-(1,10-phenanthroline)iron(II) has been reported by Margerum^{7b} and later substituent effects have been studied by Burgess and Prince⁸⁵. The rate law is

$$-d[Fe(phen)_{3}^{2+}]/dt = k_{obs}[Fe(phen)_{3}^{2+}]$$
 (5.1)

The observed rate constant, k_{obs} , over the hydroxide range 0 to 5 M is a function of the first, second and third order in hydroxide ion concentration as shown below

$$k_{obs} = k_1 + k_2[OH^-] + k_3[OH^-]^2 + k_4[OH^-]^3$$
 (5.2)

In the presence of hydroxide ions and dissolved oxygen⁹⁰ dissociation of tris-(1,10-phenanthroline)iron(II) proceeds to completion, with the eventual formation of ferric oxide.

The reaction of tris-(1,10-phenanthroline)iron(II) complexes with cyanide^{7a} has a similar kinetic pattern to that of alkali fission. The rate law is

$$-d[complex]/dt = k_{obs}[complex]$$
(5.3)

where $k_{obs} = k_1 + k_2 [CN]$ (5.4)

It was suggested that the mechanism involves two parallel reactions. One is rate-determining dissociation of the phenanthroline ligand from the complex (5.5) followed by further rapid reaction with cyanide ion. The other pathway is rate-determining cyanide attack at the iron.

$$Fe(phen)_{3}^{2+} \underbrace{slow}_{fast} Fe(phen)_{2}^{2+} + phen \qquad (5.5)$$

$$fast \downarrow CN^{-}$$

$$products$$

Margerum and Morgenthaler^{7a} suggested the possible intermediacy of ion pairs to explain the acceleration of the dissociation reactions in the presence of hydroxide or cyanide ions :

e.g.

They also found the rate of dissociation of tris-(1,10phenanthroline)iron(II) in the presence of cyanide and in methanol to be 400 times faster than the corresponding one in water. This observation was explained as a result of more ion pair formation in a solvent of much lower dielectric constant than water. This is not necessarily true, since the leaving group is possibly more solvated by methanol than by water and hence higher rates of dissociation may be expected. There are further studies on substitution reactions at $Fe(LL)_3^{2+}$ where LL = phen or Schiff base (SB) of the formula



with cyanide in mixed solvents 91,92 .

The reaction of peroxodisulphate with $Fe(phen)_3^{2+}$ and related cations in aqueous solutions⁹³, aqueous acetonitrile⁹² and aqueous t-butyl alcohol⁹³ follows the same kinetic pattern mentioned above. In the presence of an excess of peroxodisulphate the rate law is

$$-d[complex]/dt = k_{obs}[complex]$$
(5.6)

$$k_{obs} = k_1 + k_2 [S_2 0_8^{2-}]$$
 (5.7)

The k_1 term is thought to arise from rate-determining dissociation of a ligand molecule, with rapid subsequent oxidation; the k_2 term corresponds to direct oxidation of the iron(II) complex to its iron(III) analogue. It is interesting that Fe(phen)₃²⁺ and analogous complexes react with peroxodiphosphate entirely by rate-determining dissociation followed by rapid (inner-sphere) oxidation⁹⁴.

5.2 Aquation

The aquation of tris-(ferrozine)iron(II) was investigated as a function of acid concentration in each of hydrochloric and sulphuric acids at 35^oC. Aquation follows first-order kinetics up to at least 80% of complete reaction. The ionic strength was maintained constant, 0.333 M, by the addition of sodium chloride or potassium sulphate in the case of hydrochloric and sulphuric acids respectively. The results are shown in Table 5.1 and illustrated in Figure 5.1, where values of observed rate constants are plotted against the hydrogen ion concentration. There is an increase in the rate

TABLE 5.1

First-order rate constants (k) for aquation of tris-(ferrozine)iron(II) in aqueous solution at $35.0^{\circ}C$

| HCl /M ^a | 0.017 | 0.033 | 0.066 | 0.099 | 0.132 | 0.165 | 0.231 | 0.333 |
|--|-------|-------|-------|-------|-------|-------|-------|-------|
| $10^4 k/s^{-1}$ | 1.16 | 1.27 | 1.49 | 1.66 | 1.69 | 1.74 | 1.92 | 2.02 |
| н ₂ s0 ₄ /м ^b | 0.011 | 0.044 | 0.077 | 0.110 | | | | |
| $10^4 k/s^{-1}$ | 0.98 | 1.53 | 1.78 | 1.96 | | | | |

a ionic strength 0.333M, maintained with sodium chloride;
 b ionic strength 0.333M, maintained with potassium sulphate.

of the dissociation of tris-(ferrozine)iron(II) as the acid concentration increases. But the rate reaches a limiting value at hydrogen ion concentrations above about 0.22 M.





This acid dependence of aquation rates suggests a very similar behaviour to that of $Fe(bipy)_3^{2+}$ or $Fe(5-NH_2-phen)_3^{2+}$. The acid catalysis of the aquation of $Fe(bipy)_3^{2+}$ (ref.95), as of $Co(bipy)_3^{2+}$ (ref.96), has been ascribed to the protonation of the nitrogen atom on the flexible 2,2'bipyridyl ligand by the following reaction scheme :



 $M = Fe^{2+}$ or Co^{2+}

On the contrary the above argument cannot be applied to a rigid bidentate ligand such as 1,10-phenanthroline hence the step represented by k_4 in the above scheme will not occur. This is consistent with the acid independence of aquation of Fe(phen)₃²⁺. Thus the acid dependence of aquation of Fe(5-NH₂-phen)₃²⁺ has been explained differently



o : HC1; ● : H₂SO₄.

as due to the pH-dependent of protonation of the amino substituent 97 . The situation for the ferrozine complex, whose rates of aquation are acid dependent, could arise either from protonation of the triazine ring in a similar way to the $Fe(bipy)_{2}^{2+}$ complex, for the ferrozine ligand is flexible like 2,2'-bipyridyl, or to protonation of a sulphonato group, although the latter is less likely (cf. sulphonato-derivatives of the tris-(1,10-phenanthroline)iron(II) cation⁹⁷). It is difficult to tell from the kinetic results which situation occurs. The ultravioletvisible spectra of solutions of the ferrozine complex in water (pH 7) and in molar hydrochloric acid are identical, this suggests that equilibrium ligand protonation, as for 5-amino-1,10-phenanthroline, is the less likely explanation for the pH dependence of aquation rates for the ferrozine complex.

The rate of dissociation of the ferrozine complex in neutral solution can be estimated from a plot of observed rate constants, at 35° C, against logarithms of hydrogen ion concentrations (because this plot is linear) as shown in Figure 5.2. Extrapolation of this plot to zero acid concentration gives an intercept of 0.8 x 10^{-4} s⁻¹ for the aquation in neutral solution.

5.3 Reaction with Hydroxide

The reaction of the ferrozine complex with hydroxide was carried out at constant ionic strength, 0.333 M, in the presence of various salts such as sodium perchlorate, potassium nitrate, sodium chloride or potassium sulphate. The results are shown in Table 5.2.

TABLE 5.2

Average first-order rate constants (k) for reaction of tris-(ferrozine)iron(II) with hydroxide in aqueous solution at 35.0°C. Ionic strength maintained, at 0.333 M, by potassium nitrate, sodium chloride, potassium sulphate, or sodium perchlorate.

| [NaOH]/M | | 104 | k/s^{-1} | |
|----------|------------------|------|--------------------------------|--------|
| | кno ₃ | NaC1 | K ₂ SO ₄ | NaCl04 |
| 0.017 | 4.2 | | | |
| 0.033 | 7.9 | 9.5 | 11 | 2.5 |
| 0.050 | 12.2 | | | |
| 0.067 | 15.2 | | | |
| 0.083 | 18.3 | | | |
| 0.100 | 22 | | | |
| 0.133 | 29 | 29 | 30 | 13 |
| 0.167 | 31 | | | |
| 0.200 | 36 | | | |
| 0.233 | 42 | 41 | 42 | 26 |
| 0 267 | 46 | | | |
| 0.300 | 48 | | | |
| 0.333 | | 50 |) | |

It is expected that the base hydrolysis of this complex would be similar to that of iron(II) complexes $Fe(LL)_3^{2+}$

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FIGURE 5.3 Dependence of rate of dissociation of $Fe(fz)_3^{2+}$ on alkaline concentration at constant ionic strength maintained by added salts. $\bigcirc: KNO_3; \Delta: NaCl;$ $x: K_2SO_4; \bigcirc: NaClO_4.$ -109-

containing the chelating unit N = C = C > N. The rate law is

$$-d[Fe(LL)_{3}^{2+}]/dt = k_{obs}[Fe(LL)_{3}^{2+}] \\ = \left\{ k_{1} + k_{2}[OH^{-}] \right\} [Fe(LL)_{3}^{2+}]$$
(5.8)

where $k_1 + k_2[OH]$ correspond to k_{obs} in Table 5.2. Thus there should be a linear correlation between values of observed rate constants, k_{obs} , and the hydroxide ion concentration. However the plot for the ferrozine complex (Figure 5.3) is curved, with opposite curvature for perchlorate as added anions compared with chloride, nitrate Therefore the dependence of rate constant on and sulphate. hydroxide ion concentration cannot be represented simply by the rate law mentioned above but it should be similar to equation (5.2) where terms in $[OH^-]^2$ and probably $[OH^-]^3$ are needed to explain the present results. It is difficult to tell whether $k_{\underline{A}}$ in the above equation is of any significance. Nonetheless the curvature of the plot in Figure 5.3 indicates that k_2 must be positive when the added salt is perchlorate, negative when the added salts are chloride, nitrate or sulphate. The rate constant k₁ corresponding to rate-determining ligand dissociation can be determined by extrapolation from the intercept of the plot in Figure 5.3 to zero hydroxide ion concentration. The value of $k_1^{}$ at 35° C is less than 2 x 10^{-4} s⁻¹ which is more or less consistent with the previous value deduced from the acid dissociation in section 5.2. A second-order rate constant for hydroxide attack, k_2 , at $35^{\circ}C$ can be determined from the observed rate constant in 0.333 M-hydroxide and is equal to 0.015 $M^{-1} s^{-1}$.

5.4 Reaction with Cyanide

5.4.1 <u>General</u> - The reaction of the tris-(ferrozine)iron(II) complex with cyanide has been studied as a function of concentration of potassium cyanide^{*} (at constant ionic strength), temperature, and solvent composition. In the presence of an excess of cyanide the reaction is first-order with respect to the concentration of the ferrozine complex. The rate law is

$$-d[Fe(fz)^{4-}]/dt = k_{obs}[Fe(fz)^{4-}]$$
 (5.9)

Variation of the observed rate constant, k_{obs} , with cyanide concentration is reported in Table 5.3. In all cases studied there is a linear correlation between observed rate constants and cyanide concentrations as shown in Figure 5.4 :

$$-d[Fe(fz)^{4^{-}}]/dt = \left\{ k_{1} + k_{2}[CN^{-}] \right\} [Fe(fz)^{4^{-}}] \quad (5.10)$$

From the plots of k_{obs} against cyanide concentration values of k_1 and k_2 were determined from the intercept and slope respectively (Figure 5.4). These correspond to rates of dissociation of the complex, k_1 , and cyanide attack at the complex cation, k_2 , as shown in Table 5.3.

[^] The concentrations of free cyanide ion were calculated from the known amount of potassium cyanide added and the known values of the pK_a of HCN (ref.98) over the temperature range of these experiments.

| | | 000 | rrespoi | ıd with | those | define | d by e | quation | (2.10) | of the | text. | | 4 | |
|-----------------|-------|-------|---------|---------|-------|--------|-----------------------|---------|--------|--------|-------|-------|--------------------------------|------------------------|
| | | | | | | | $10^{4} \mathrm{k/s}$ | | | | | | | |
| Solvent | Temp. | | | | | | [KCN]/ | М | | | | 10 | $\frac{4_{\rm k_{1}/s}-1}{-1}$ | $10^4 \underline{k}_2$ |
| | | 0.017 | 0.033 | 0.066 | 0.099 | 0:133 | 0.165 | 0.198 | 0.231 | 0.267 | 0.297 | 0.333 | | 1mol. ⁻¹⁻¹ |
| Water | 25.3 | | 0.7 | 1.1 | | 1.6 | 2.0 | | 2.6 | 3.1 | 3.3 | 3.5 | 0.5 | 9.4 |
| | 28.4 | 0.9 | 1.2 | 1.8 | 2.4 | 2.8 | 3.3 | 3.6 | 4.4 | 4.5 | 4.9 | 5.4 | 0.8 | 14.2 |
| | 29.9 | 1.4 | 1.6 | 2.0 | 2.7 | 3.3 | 4.1 | 4.5 | 5.2 | 0.0 | 6.7 | 7.1 | 0.9 | 18.9 |
| | 34.5 | 1.9 | 2.8 | 3.9 | 5.4 | | | 8.4 | | 10.5 | 12.0 | 12.5 | 1.9 | 34 |
| | 38.8 | 3.6 | 5.3 | 7.9 | 9.8 | 11.2 | 15.2 | 16.3 | | 19.6 | 23.3 | 24.6 | 3.1 | 66 |
| | 44.1 | 7.8 | 9.8 | 14.6 | 18.5 | | 25.4 | 30.1 | 35.8 | | 42.1 | 44.1 | 6.4 | 119 |
| 10% ethanol | 35.0 | | 2.2 | | | 6.0 | | | 9.2 | | | 13.0 | 1.0 | 36 |
| 20% ethanol | 35.0 | | 2.1 | | | 6.0 | | | 10.2 | | | 14.8 | 0.7 | 41 |
| .30% ethanol | 35.0 | | 2.3 | | • | 7.7 | | | 12.9 | | | 19.3 | 0.4 | 53 |
| | | | | | | | | | | | | | | |

(\underline{k}) for reaction of tris-(ferrozine)iron(II) with cyanide at an ionic -, -. • 7 Ę (7 11. • + + • • • , • First order rate constants . ¢ q -

TABLE 5.3

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FIGURE 5.4





FIGURE 5.5 Plots of logarithms of rate constants for : 1, cyanide attack; 2, dissociation of $Fe(fz)_3^{2+}$ complex <u>vs</u> the reciprocal of absolute temperature.

2

The activation energies, E_a , for dissociation and for cyanide attack at ferrozine complex have been calculated from the variation of the corresponding rate constants k_1 and k_2 with temperatures. Plots of logarithms of rate constants <u>vs</u> the reciprocal of absolute temperature are shown in Figure 5.5 - whence E_a can be worked out from the gradient

of each graph. Values of ΔH^{\neq} and ΔS^{\neq} for dissociation and cyanide attack were calculated from the corresponding values of E_a (see section 2.5.5) and are given in Tables 5.4 and 5.5 together with some other published data for analogous 1,10-phenanthroline and 2,2'-bipyridyl iron(II) complexes for comparison.

TABLE 5.4

Activation parameters for dissociation of tris-(LL)iron(II) complexes in aqueous solution

| LL | $\Delta H^{\neq}/kcalmol^{-1}$ | $\Delta s^{\neq}/cal deg^{-1}mol^{-1}$ | Ref. |
|------------------------------|--------------------------------|--|------------|
| ferrozine | 25 <u>+</u> 1.5* | +6 <u>+</u> 4* | This work |
| bipy | 26.8 25.4 | +17 +21.5 | 95b 95a |
| phen | 31.4 29.3 | +28 +31 | 95b |
| 5-N0 ₂ -phen | 28 | +30 | |
| 4,7-diMe-phen | 27.8 | +23.8 | |
| 5-Cl-phen | 29.1 | +37 | |
| 5-Me-phen | 29.8 | +31 | |
| 5-Ph-phen | 29 | +30 | 84 |
| 5-Me-6-N0 ₂ -phen | 26 | +25 | |
| 5,6-diMe-phen | 29 | +27 | |
| 3,5,6,8-tetraMe-phe | en 29 | +31 | |
| 4,7-dihydroxo-phen | 17.7 | 4 | |
| $3-S0_3$ -phen | 21 | - 1 | 97 |
| $5-S0_{3}^{-}$ -phen | 26 | +9 | 97 |

* 90% confidence limits for this mean.

<u>Dissociation</u> - The activation enthalpy, ΔH^{\neq} , 5.4.2 for dissociation of tris-(ferrozine)iron(II) is of the same order of magnitude as those for 1,10-phenanthroline and 2,2'-bipyridyl iron(II) complexes. This is the expected trend for, as previously discussed in section 1.2, all low spin d^{6} complexes have high crystal field stabilization and activation energies. However the smaller enthalpy of activation for this ferrozine complex compared with 1,10phenanthroline iron(II) complex can be explained on the basis of the structural differences between ferrozine and 1,10-phenanthroline. Ferrozine has two main features; incorporation of a triazine ring and the presence of sulphonatophenyl substituents. The effect of the sulphonato substituents on the iron-ligand bond strength is reflected in the enthalpy of activation in Table 5.4 where values of ΔH^{\neq} for tris-(1,10-phenanthroline)iron(II) and its sulphonato derivatives are given. It is difficult to assess the effect of the triazine ring, if any, from the present kinetic results.

The entropy of activation, ΔS^{\neq} , for aquation of the ferrozine complex is much smaller than those of 2,2'bipyridyl and 1,10-phenanthroline iron(II) analogues, but it is very similar to those of the sulphonato derivatives of 1,10-phenanthroline-iron(II) complexes reported in Table 5.4. Indeed there is a good correlation (Figure 5.6) between enthalpies of activation and entropies of activation for a variety of iron(II) complexes including those of 2,2bipyridyl and 1,10-phenanthroline and its substituted derivatives, with the exception of the 4,7-dihydroxo-phen

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FIGURE 5.6

Correlation of activation enthalpies (ΔH^{\neq}) with activation entropies (ΔS^{\neq}) for aquation of lowspin iron(II) complexes Fe(LL)₃ⁿ⁺ in aqueous solution. 1 : fz; 2 : bipy; 3 : phen; 4 : 5-NO₂-phen; 5 : 4,7-diMe-phen; 6 : 5-Cl-phen; 7 : 5-Me-phen; 8 : 5-Ph-phen; 9 : 5-Me-6-NO₂-phen; 10 : 5,6-diMe-phen; 11 : 3,5,6,8-tetraMe-phen; 12 : 3-SO₃⁻-phen; 13 : 5-SO₃⁻-phen; 14 : 4,7dihydroxo-phen. complex, whose chemistry shows several unexpected features. It is of interest to note that the points for all iron(II) complexes which have hydrophilic ligands, e.g. ligands with sulphonato- or hydroxo- substituents lie on the left hand side of the graph in Figure 5.6. This indicates that it is solvation, rather than the electron- withdrawing or releasing character of the substituents, which is important in determining reactivities. Nonetheless the linear correlation shown in Figure 5.6 implies that there is a similarity of mechanism for all the iron(II) complexes listed in Table 5.4. The slope of the graph in Figure 5, which defines the so-called iso-kinetic temperature, is 250 K.²⁷

5.4.3 Cyanide Attack - The enthalpy of activation for cyanide attack at the ferrozine complex is comparable with that for cyanide attack at the analogous 1,10phenanthroline or 2,2'-bipyridyl complex (Table 5.5). Itseems that the presence of the triazine ring and the sulphonato substituents have together little effect on the ease of nucleophilic attack by cyanide. An entropy of activation of +12 caldeg⁻¹mol⁻¹ for cyanide attack at the ferrozine complex is unexpected. The tris-(ferrozine)iron(II) complex has a negative charge of -4 and a radius of approximately 7 A° (assuming a similar size to Fe(phen)₂²⁺, ref.72), so according to Laidler's electrostatic approach one expects a very small, negative entropy, about -9 calde g^{-1} mol⁻¹, from the electrostriction in the transition state. Laidler's prediction works satisfactorily for bipyridyl and Schiff base complexes. However the deviation

TABLE 5.5

Activation parameters for cyanide attack at tris-(LL)iron(II) complexes in aqueous solution

| LL | $\Delta H^{\neq}/kcal mol^{-1}$ | $\Delta s^{\neq}/cal deg^{-1}mol^{-1}$ | Ref. |
|-----------|---------------------------------|--|-----------|
| ferrozine | $25.2 \pm 1.2^*$ | +12 | This work |
| bipy | $23.0 \pm 0.6^*$ | +9 | 99 |
| phen | 20 ± 3 | - 3 | 7a |

* 90% confidence limits for the means.

from this rule represented by this positive entropy of activation is controlled by two variables, change of the charge on the complex and the incorporation of hydrophilic sulphonato substituents. This is in contrast to hydrophobic ligands, for example 1,10-phenanthroline and 2,2'-bipyridyl. It is difficult to assess the contribution of each variable separately. The only feasible approach to this problem is to determine ΔS^{\neq} for complexes such as 1,10-phenanthroline and 2,2'-bipyridyl iron(II) containing uncharged hydrophilic substituents. But since kinetic data on reactions of such complexes are not available in the literature, at present, it is difficult to come to any conclusion.

5.4.4 <u>Solvent Effect</u> - The effect of solvent composition on the rates of the reaction of the ferrozine complex with cyanide is shown in Table 5.3 and Figure 5.7. These results show that there is an increase in the second-

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FIGURE 5.7 The dependence of observed first-order rate constant (k_{obs}) on total cyanide concentration for Fe(fz)₃²⁺ at 35°C. **O** : water; • : 10% ethanol; **D** : 20% ethanol; Δ : 30% ethanol.

order rate constant, k2, for cyanide attack while the firstorder rate constant, k_1 , for the dissociation of the ferrozine complex decreases as the percentage of ethanol increases from 0 to 30%. The increase or decrease in rates of dissociation depend both on the nature of the organic cosolvent and on the substituents. For instance, the results discussed in Chapter 4 show that the rate of dissociation of tris-(1,10-phenanthroline)iron(II) increases as the percentage of dioxan increases. But for 3- and 5sulphonato-derivatives of tris-(1,10-phenanthroline)iron(II) the rate of dissociation decreases as the concentration of acetonitrile increases 79 . The variation in k_1 with solvent composition is, possibly, due to modification of solvent structure. Acetonitrile and t-butyl alcohol affect the structure of water either by intercomponent hydrogen bonding with the former 101 or by water-water interaction in the latter case. Ethanol has a similar, though smaller, effect on the structure of water to t-butyl alcohol⁴⁵. But nevertheless in aqueous ethanol water molecules will become less easily available for incorporation into a transition state for aquation of increased coordination number. The kinetic consequences of that are smaller rates of dissociation in aqueous ethanol than in water. On the other hand the increase in rates for cyanide attack, k2, at the ferrozine complex is directly related to solvation effects of the ferrozine ligand. Hence the complex is more solvated in water than in aqueous ethanol, cyanide ion must first penetrate the solvation shell of the complex to come in close proximity to iron(II) which in turn will cause a decrease in k2,. On the contrary in aqueous ethanol the

complex is less solvated and it is easy for cyanide ion to approach iron(II) giving rise to high values of k_2 . This increase in k_2 is reminiscent of that reported for cyanide attack at tris-(1,10-phenanthroline)iron(II)⁹² and at analogous Schiff base complexes of iron(II)⁹¹.

The product of the reaction between tris-(ferrozine)iron(II) and cyanide under the present kinetic conditions has not been isolated. It is expected to be bis-(ferrozine)biscyanoiron(II) by analogy with the similar reaction of complexes of iron(II) with 2,2'-bipyridyl and 1,10phenanthroline. In the iron(II)-1,10-phenanthroline-cyanide series, the molar extinction coefficients for the charge transfer bands in the visible region (which correspond to Fe^{2+} phen charge transfer) for the complexes $Fe(phen)_3^{2+}$, $Fe(phen)_{2}(CN)_{2}$, $Fe(phen)(CN)_{4}^{2-}$ are 10⁴ (ref.52), 6 x 10³ (ref.102) and 4.4 x 10^3 (ref.102) respectively, i.e. in the ratios 3 : 2 : 1. The product from the reaction of tris-(ferrozine)iron(II) with cyanide has a molar extinction coefficient of about 0.7 times that of the starting material. This supports the suggestion that bis-(ferrozine)biscyanoiron(II) is a persistent intermediate en route to the ultimate products. It has been reported 103 that the charge transfer spectra of cis-Fe(LL)₂(CN)₂ complexes, where LL = bipy, phen or Schiff base, are markedly sensitive to solvent The sensitivity of these charge transfer bands variation. has been established from the correlation of the frequencies of maximum absorption $\mathcal{V}_{ extsf{max}}$ against Reichardt's solvent parameter 104 E_T. The variation of \mathcal{D}_{\max} , for the product of tris-(ferrozine)iron(II) complex plus cyanide, with the

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solvent parameter E_{T} is illustrated in Figure 5.8; results are given in Table 5.6.

TABLE 5.6

Wavelengths (λ) and frequencies (ν) of maximum absorption for the lowest energy charge-transfer band of

bis-ferrozine-bis-cyanoiron(II), $Fe(fz)_2(CN)_2$. Solvent E_T values from Ref.104. Temperature 25°C.

| Solvent | $E_{T} / k \text{ cal mol}^{-1}$ | λ/nm | $\mathcal{V}/\mathrm{cm}^{-1}$ |
|-------------|----------------------------------|--------------|--------------------------------|
| water | 63.1 | 574 | 17420 |
| 10% ethanol | 61.7 | 584 | 17120 |
| 20% ethanol | 60.0 | 594 | 16840 |
| 30% ethanol | 58.0 | 602 | 16610 |

The slope of the graph in Figure 5.8 is about $6 \ge 10^{-3} \ker = 10^{-1} \operatorname{cm}^{-1}$. This is similar to the solvent sensitivity of iron(II) \longrightarrow bipy¹⁰³, iron(II) \longrightarrow phen¹⁰³ and iron(II) \longrightarrow 3-S0₃⁻-phen¹⁰⁵ charge transfer bands in Fe(LL)₂(CN)₂ complexes, which corresponds to a slope of about 8 $\ge 10^{-3} \ker = 10^{-1} \operatorname{cm}^{-1}$ for the $\mathcal{V}_{\max} \cong \operatorname{E}_{\mathrm{T}}$ plot. It is also belie ed that the above complexes adopt a cisgeometry rather than a trans-configuration due to steric interference of the hydrogen atoms on the carbon atoms ortho to the ligating nitrogen atoms in the two rings. Thus it seems highly likely from the above discussion that the product of the reaction between tris-(ferrozine)iron(II) plus cyanide is Fe(fz)₂(CN)₂ and of cis-geometry.



FIGURE 5.8

Correlation between frequencies of maximum absorption (\mathcal{P}) for Fe(fz)₃²⁺ and solvent E_T values (k cal mol⁻¹).

5.5 Reaction with Peroxodisulphate

The reaction of tris-(ferrozine)iron(II) with peroxodisulphate was followed up to 50% of complete reaction; observed first-order rate constants (excess of peroxodisulphate) are given in Table 5.7. A plot of observed rate constants, k_{obs} , against peroxodisulphate concentration, Figure 5.9, gives a straight line with an intercept equal to 1.0 x 10⁻⁴s⁻¹.

TABLE 5.7

Average first order rate constants (k) for reaction of tris-(ferrozine)iron(II) with potassium peroxodisulphate in aqueous solution at 35.0°C., ionic strength maintained at 0.099M with sodium sulphate.

 $\begin{bmatrix} K_2 S_2 O_8 \end{bmatrix} / M \qquad 0.002 \ 0.003 \ 0.007 \ 0.010 \ 0.013 \ 0.020 \ 0.027 \ 0.033 \\ 10^4 k / s^{-1} \qquad 1.03 \ 1.09 \ 1.21 \ 1.34 \ 1.32 \ 1.58 \ 1.74 \ 1.97$

These results indicate a rate law of the following form

$$-d[Fe(fz)_{3}^{4-}]/dt = \left\{k_{1} + k_{2}[S_{2}O_{8}^{-}]\right\} [Fe(fz)_{3}^{4-}] \qquad (5.11)$$

This kinetic equation (5.11) is similar to that for tris-(1,10-phenanthroline)iron(II) (cf. equation 5.7) where there is a rate-determining ligand dissociation k_1 followed by the fast oxidation of iron(II) intermediates to its iron(III) analogues. The second-order rate constant for



FIGURE 5.9 The dependence of observed first-order rate constant (k_{obs}) on peroxodisulphate concentration for Fe(fz) $_3^{2+}$ in aqueous solution.

oxidation of this ferrozine-iron(II) complex, k_2 , can be worked out from the slope of the graph in Figure 5.9. It is 0.0029 $M^{-1}s^{-1}$ at 35°C. The rate constant estimated from Figure 5.8 for the dissociation of Fe(fz) $_3^{4-}$, 1.0 x 10⁻⁴s⁻¹, is in good agreement with that estimated for acid aquation in section 5.2. This indicates that the above assignment of mechanism is valid. The mechanism of the reaction of the ferrozine complex and other related iron(II) complexes with peroxodisulphate will be discussed later in section 6.5.

5.6 <u>Conclusion</u>

The general pattern of reactivity of the $Fe(fz)_3^{4-}$ complex in acid solution, and with hydroxide, cyanide and peroxodisulphate is very similar to that reported for the $Fe(bipy)_3^{2+}$ and $Fe(phen)_3^{2+}$ complexes. All results are simmarized in Tables 5.1 to 5.7 and illustrated in Figures 5.1 to 5.9. There are differences of details, and differences between the relative reactivities of the various complexes towards dissociation, nucleophilic attack, and oxidation, but the outline is the same for all low spin $Fe(LL)_3^{2+}$ complexes studied to date.

CHAPTER 6

IRON(II)-HEXADENTATE SCHIFF BASE COMPLEX

- 6.1 Introduction
- 6.2 Aquation
- 6.3 Reaction with Hydroxide
- 6.4 Reaction with Cyanide
- 6.5 Reaction with Peroxodisulphate
- 6.6 Conclusion

CHAPTER 6

1RON(11)-HEXADENTATE SCHIFF BASE COMPLEX

6.1 Introduction

Schiff bases of the following formula

(where R' can be alkyl or aryl) act as bidentate ligands and form very intensely coloured complexes with iron(II). The preparation of several N-alkyl Schiff base-iron(II) complexes has been reported by Murmann and Healy⁵⁶. This is in addition to the numerous iron(II) complexes of analogous Schiff bases derived from pyridine-2-aldehyde and pyridine-2-ketone with aromatic amines¹⁰⁶. Ever since the successful preparation of these complexes there has been considerable interest in the study of the kinetics and mechanisms of aquation¹⁰⁶, of reactions with nucleophilic reagents such as hydroxide^{107,108}, and cyanide⁹¹, and also of reactions with hydrogen peroxide¹⁰⁷

The present work describes the kinetic pattern of aquation and of reactions with hydroxide and cyanide for a new hexadentate Schiff base-iron(II) complex which is of
particular interest as far as the nature of its ligand is concerned. There are only few ligands beyond the aromatic bidentate diimines which can cause spin pairing in iron(II). This has previously been reviewed in section 1.3. Ligands can be arranged in descending order of their ligand field as follows

 $CN^{-} > phen > bipy > bidentate Schiff base > NO_{2}^{-} >$ en > NH₃ > NCS⁻ > H₂O > F⁻ > Cl⁻ > Br⁻

The new Schiff base ligand is hexadentate and incorporates two secondary aliphatic nitrogen atoms beside another two chelating units $N \approx \frac{C - C}{N} \cdot N$. The chemical formula of the hexadentate Schiff base is :

The preparation of the iron(II) complex of the above Schiff base has already been described in section 2.1.5. Elemental analysis of this complex shows that the molar ratio of the ligand to iron(II) is 1 : 1. It is stable, soluble in water, in alcohols, and in acetone, giving very intensely blue solutions. The visible absorption spectrum in Figure 6.1 shows that it has two absorption bands at 608 nm and 500 nm whose molar extinction coefficients (\boldsymbol{E}) are 7560 and 1920 respectively. These high values of \boldsymbol{E} can be



 λ/nm

FIGURE 6.1 Visible spectrum for $Fe(hxSB)^{2+}$ complex, 8.3×10^{-5} M, in aqueous solution measured in one cm silica cell.

attributed to charge transfer from $iron(II) \longrightarrow Schiff base$ ligand; the magnitudes are less than those for tris-(1,10-phenanthroline)iron(II) complexes. This is consistent with the presence of only two conjugated structures $N \xrightarrow{C \longrightarrow C} N$ in the hexadentate Schiff base complex. The geometry of the hexadentate Schiff base ligand around iron(II) can be represented by either a cis or a trans configuration :



cis

trans

In the above diagram only the coordinating nitrogen atoms are shown; N^{**} refers to aliphatic nitrogen atom. Since aquation of the above hexadentate Schiff base complex follows simple first-order kinetics (section 6.2), this indicates the presence of predominantly one isomer. The systematic name of the hexadentate Schiff base is [bis-(α -{2-pyridyl}benzylidene)triethylenetetramine]iron(II); it will be referred to as the hexadentate Schiff base (hxSB) complex throughout this Chapter.

0.2 Aquation

Aquation of the hexadentate Schiff base complex, Fe(hxSB)²⁺, was carried out in hydrochloric acid at an ionic strength of 0.333 M, maintained by addition of sodium chloride. The reaction follows first-order kinetics up to at least 60% of complete reaction. The disappearance of the blue colour of the complex at the end of each kinetic run indicated the complete dissociation of the complex. In acid solution the complex dissociates, presumably by the following reaction :

$$\operatorname{Fe}(\operatorname{hxSB})^{2+} + \operatorname{nH}^{+} \longrightarrow \operatorname{Fe}, \frac{2+}{\operatorname{aq}} + (\operatorname{hxSBH})^{n+} \quad (6.1)$$

Observed first-order rate constants for aquation (in the presence of a large excess of acid) are given in Table 0.1.

TABLE 6.1

First-order rate constants (k) for the aquation of the hexadentate Schiff base iron(II) complex in aqueous solution at 35°C. Ionic strength maintained at 0.333 M by sodium chloride

| [HC1]/M | $10^{5} k/s^{-1}$ |
|---------|-------------------|
| 0.066 | 0.35 |
| 0.099 | 0.59 |
| 0.132 | 0.93 |
| 0.198 | 1.78 |
| 0.231 | 2.13 |
| 0.264 | 2.50 |
| 0.297 | 2.89 |
| 0.333 | 3.30 |

The acid dependence for the aquation reaction is shown in Figure 6.2 where values of first-order rate constants are plotted \underline{vs} acid concentrations. At low acid concentration, below 0.13 M, the plot curves towards the origin while above that concentration there is an almost linear dependence on acid concentration.

There are two general patterns of behaviour for aquation of low spin iron(II) complexes in acid solution. Thus for complexes with a flexible leaving ligand, e.g. ferrozine (Chapter 5), 2,2'-bipyridy1⁹⁵, or 2,2',6',2"terpyridyl 109 , an acid-dependence for aquation has been established, whereas for complexes with a rigid leaving ligand, e.g. 1,10-phenanthroline, such an acid-dependence is not known⁷⁰. The aquation profile for the hexadentate Schiff base complex conforms to the general pattern of these complexes with flexible leaving ligands. However graphical comparison of the pH-rate profile of the hexadentate Schiff base complex with that of $Fe(fz)_2^{4-}$, $Fe(bipy)_3^{2+}$, and $Fe(terpy)_2^{2+}$ at low acid concentrations reveals the similarity of $Fe(hxSB)^{2+}$ to $Fe(terpy)_2^{2+}$ rather than to $Fe(bipy)_{3}^{2+}$ or $Fe(fz)_{3}^{4-}$. At high acid concentration the pH-rate profile for $Fe(hxSB)^{2+}$ may tend to a limiting rate; the aquation of $Fe(terpy)_2^{2+}$ reaches a limiting rate at about 10 M acid¹¹⁰. While the acid catalysis for $Fe(bipy)_3^{2+}$ can be explained by the intermediacy of monodentate and protonated species, the situation here for $Fe(terpy)_2^{2+}$ and $Fe(hxsb)^{2+}$ is more complicated. This must arise from the possible intermediacy of monodentate, bidentate and possibly higher species, and of respective protonated derivatives, in the



FIGURE 6.2 Graphs showing the ligand dissociation rate for $Fe(hxSB)^{2+}$ complex, Δ : in acid solution (HCl); **O**: in alkaline solution (NaOH).

case of Fe(hxSB)²⁺. It is difficult to propose a rate law for the aquation of the hexadentate Schiff base complex because of the consequent large number of possible intermediates of kinetic significance. Extrapolation of the graph in Figure 6.2 for acid dissociation to zero acid concentration (pH 7) indicates an extremely slow rate of dissociation in neutral solution which behaviour is similar to that of Fe(terpy)₂²⁺. This is the expected trend since as the chelation of the ligand increases e.g. from Fe(bipy)₃²⁺ to Fe(terpy)₂²⁺ the overall stability constant increases from 17.4 (ref.111) to 18.0 (ref.112) respectively.

6.3 Reaction with Hydroxide

The reaction of Fe(hxSB)²⁺ with hydroxide follows firstorder kinetics (in the presence of an excess of hydroxide). Observed first-order rate constants are given in Table 6.2 and illustrated in Figure 6.2 where values of rate constants are plotted against hydroxide ion concentration.

TABLE 6.2

First-order rate constants (k) for reaction of the hexadentate Schiff base iron(II) complex with hydroxide in aqueous solution at 35^oC. Ionic strength maintained at 0.333 M by sodium chloride

~

| [NaOH]/M | $10^{3} k/s^{-1}$ |
|----------|-------------------|
| 0.132 | 0.79 |
| 0.198 | 1.26 |
| 0.264 | 1.62 |
| 0.333 | 2.19 |

In general the rate law for alkali fission of analogous low spin iron(II) complexes (see Section 5.1) is :

$$-d[complex]/dt = \{k_1 + k_2[0H]\}[complex]$$
(6.2)

But extrapolation of the best fitting straight line in Figure 6.2 gives a negative intercept. It is more likely that the graph of rate constants against alkali concentrations is curved at low concentration; the simple rate law of equation (6.2) does not, therefore, operate for alkaline hydrolysis of Fe(hxSB)²⁺. It is interesting that the kinetic pattern for alkali fission of this hexadentate Schiff base complex is similar to that of 2,2',6',2"-terpyridyl iron(II) complex¹⁰⁹, but the latter is more reactive than the former.

6.4 <u>Reaction with Cyanide</u>

The hexadentate Schiff base complex reacts with cyanide in aqueous solution. The reaction was followed to at least 60% of completion; it was first-order in complex concentration in the presence of a large excess of cyanide. Table 6.3 summarizes all the results, where the effects of temperature, solvent composition and cyanide concentration on reaction rates are given. In all cases studied plots of observed first-order rate constants <u>vs</u> cyanide concentration gave straight lines passing, within experimental uncertainty, through the origin (Figure 6.3).

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First-order rate constants (k) for reaction of the hexadentate Schiff base iron(II) complex with cyanide at an ionic strength of 0.333 M maintained with potassium chloride.

| | $5_{k_2/M}^{-1} s^{-1}$ | | 0.94 | 2.1 | 3.9 | 4.3 | 6.3 | 8. 5 | 15.1 | 9.6 |
|-------------------|-------------------------|-------|-------|------|------|------|------|------|------|-------------|
| | 1 1 1 | 0.333 | 0.43 | 0.69 | 1.3 | 1.5 | 2.3 | 2.97 | 4.65 | I |
| | | 0.297 | | | | | | | | 2.9 |
| | | 0.264 | 0.37 | 0.59 | 1.1 | 1.3 | 1.86 | 2.40 | 3.33 | 2.5 |
| /s ⁻¹ |]/M | 0.231 | | | | | | | | 2.4 |
| 10 ⁵ k | [KCN | 0.198 | 0.31 | 0.45 | 0.77 | 0.97 | 1.43 | 1.85 | 2.57 | I |
| | | 0.165 | | | | | | | | 1.5 |
| | | 0.132 | 0.24 | 0.27 | 0.54 | 0.61 | 1.02 | 1.26 | 1.55 | 1.41 |
| | | 0.066 | | | | | | | | 0.65 |
| | Temp./ ⁰ C | | 25.3 | 30.6 | 35.1 | 37.6 | 39.7 | 42.1 | 45.5 | 25.3 |
| | Solvent | | Water | | | | | | | 50% ethanol |



FIGURE 0.3

The dependence of observed first-order rate constant (k_{obs}) on total cyanide concentration for Fe(hxSB)²⁺ in, **O**: water; **O**: 50% ethanol. 1: 45.5°C; 2: 25.3°C; 3: 42.1°C; 4: 39.7°C; 5: 37.6°C; 6: 35.1°C; 7: 30.6°C; 8: 25.3°C.



FIGURE 6.4 Plot of logarithms of rate constants for cyanide attack at $Fe(hxSB)^{2+}$ <u>vs</u> the reciprocal of absolute temperature.

The reaction of the hexadentate Schiff base complex with cyanide is thus first-order with respect to each of the reactants. The rate law is

$$-d[Fe(hxSB)^{2+}]/dt = k_2[Fe(hxSB)^{2+}][CN^{-}]$$
 (6.3)

This means that the rate of dissociation $(k_1 \text{ term})$ is negligible (cf. Fe(LL) $_3^{2+}$ complex, section 5.1, where k_1 is significant) as has previously been observed for acid and alkali fission of this hexadentate Schiff base complex in sections 6.2 and 6.3.

Values of the second-order rate constants, k_2 , for cyanide attack at iron(II), at different temperatures in water and in 50% ethanol, have been estimated from the gradients of the plots in Figure 6.3 and are given in Table 6.3.

The activation energy, Ea, for cyanide attack at the hexadentate Schiff base complex was estimated from a plot of logarithms of $k_2 \underline{vs}$ the reciprocal of the absolute temperature as shown in Figure 6.4. Thence values of the enthalpy and entropy of activation, ΔH^{\neq} and ΔS^{\neq} respectively, were worked out (see section 2.5.5) and are given in Table 6.4. The enthalpy of activation for the present hexadentate Schiff base complex and that for bis-(terpyridyl)iron(II) are of similar magnitude, as , expected for such similar low spin iron(II) complexes. But the entropy of activation for the hexadentate Schiff base complex is lower than that for Fe(bipy) $_3^{2+}$, Fe(terpy) $_2^{2+}$ and Fe(fz) $_3^{4-}$; comparison with the 1,10-phenanthroline

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analogue is difficult since the error in ΔH^{\neq} , and consequently in ΔS^{\neq} , is large. This relatively low entropy of activation for Fe(hxSB)²⁺ can be ascribed to the nature of the ligand itself and its geometry around the central atom (see Section 6.1).

TABLE 6.4

| Activat | ion parameters for | cyanide attack at tris- | (LL)iron(II) |
|---------|-----------------------------------|---------------------------|--------------|
| | complexes | in aqueous solution | |
| | . <i>≠ u</i> 1 | . ≠ (– 1 . – 1 | |
| LL | $\Delta H' / k \text{ cal mol}^-$ | $\Delta S' / cal deg mol$ | Ref. |
| 1 | | | |
| hxSB | 24.3 ± 1.1 | 0 | This work |
| fz | 25.2 ± 1.2 | +12 | This work |
| phen | 20 ± 3 | -3 | 7a |
| bipy | 23.0 ± 0.6 | +9 | 99 |
| terpy | 22.4 | +6 | 110 |

* SB = α -(2-pyridyl)benzylideneaniline; value of ΔH^{\neq} was estimated in 95% methanol.

-7

20.4

SB*

91

From the statistical point of view the reaction of the hexadentate Schiff base complex with cyanide is unfavourable since it proceeds with a decrease in the number of molecular species. Another important factor is the geometrical difference between $Fe(hxSB)^{2+}$ and all the other analogous complexes listed in Table 6.4. The geometrical arrangement of 2,2'-bipyridyl, 2,2',6',2"-terpyridyl or ferrozine ligands



FIGURE 6.5 Correlation of activation enthalpies (ΔH^{\neq}) with activation entropies (ΔS^{\neq}) for cyanide attack at low spin iron(II) complexes Fe(LL)₃²⁺ in aqueous solution. 1 : hxSB; 2 : fz; 3 : bipy; 4 : terpy; 5 : phen; 6 : SB (see Table 6.4). around iron(II) allows several paths by which cyanide ion can come into close proximity to the iron(II). But in the case of the hexadentate Schiff base complex the approach of the cyanide to the iron(II) is rendered more difficult by the bulky nature and arrangement of the hexadentate ligand. An attempted correlation of ΔH^{\neq} with ΔS^{\neq} values, for cyanide attack at a range of low spin iron(II) complexes, (Figure 6.5) shows a rough trend, but is of limited value in view of the short overall range of activation parameter values.

The rate of the reaction of the hexadentate Schiff base complex with cyanide in 50% ethanol at 25° C is ten times faster than that in water at the same temperature, see Table 6.3. This is the expected trend, since the less polar solvent, 50% ethanol, enhances the approach of the two oppositely charged species leading to an increased rate for cyanide attack at the complex.

The reaction of complexes of the type $Fe(LL)_{3}^{2+}$, where LL = phen, bipy or a bidentate Schiff base, with cyanide usually produces mixed ligand complexes of the type $Fe(LL)_{2}(CN)_{2}$. Further reactions of the latter with cyanide produce $Fe(LL)(CN)_{4}^{2-}$ and eventually $Fe(CN)_{6}^{4-}$ but these reactions are extremely slow. It is of interest to see whether the reaction of the hexadentate Schiff base complex with cyanide will produce the same type of complex mentioned above or proceed with complete displacement of the hexadentate ligand. It is most likely that cyanide ions will displace one unit of $N \stackrel{C-C}{\longrightarrow} N$ to produce (I).



Further reaction with cyanide to displace the two secondary aliphatic ligating nitrogen atoms, to give (II), should be an easy process.



In view of the geometry of the ligand around the complex it is difficult to imagine that the two secondary aliphatic nitrogen atoms can be displaced by cyanide before the complete separation of one of the terminal $N = \frac{C - C}{N}$ units. Fe(CN)₆⁴⁻ is not formed under the kinetic conditions; the kinetic product has a strong absorption band in the visible region, 540 nm; the product therefore either (I) or (II).

An attempt to isolate the reaction product of the

hexadentate Schiff base complex with cyanide for the purpose of analysis and identification was unsuccessful. The solid product obtained under similar conditions to the kinetic runs always contained a large amount of potassium cyanide. Purification of the product was impossible because the solubility characteristics of the kinetic product closely resemble those of potassium cyanide, i.e. very soluble in water, soluble in methanol, sparingly soluble in ethanol and insoluble in acetone. In addition the barium and hexaamminocobalt(III) salts of the kinetic product were also very soluble in water. Although the solubility characteristics of the product prevent its characterisation by analysis, nevertheless they suggest that the product may be a salt of an anionic species such as $Fe(hxSB)(CN)_4^{2-}$ rather than uncharged $Fe(hxSB)(CN)_2$.

Another criterion which can be used to support the above assumption that the reaction product is $Fe(hxSB)(CN)_4^{2-}$ rather than $Fe(hxSB)(CN)_2$ is the ratio of the molar extinction coefficients of the hexadentate complex to that of the product (see section 5.4). The value of the molar extinction coefficient of the low energy charge transfer band of the hexadentate Schiff base complex is 7560 and that for the reaction product is 3000 i.e. in the ratio 3 : 1.1. This suggests that one third of the original ligand is still attached to the iron(II) giving rise to the charge transfer band. In other words the more likely nature of the product is $Fe(hxSB)(CN)_4^{2-}$.

The charge transfer spectra of the compounds $\operatorname{cis-M(LL)}_2(L')_2$ and $\operatorname{cis-M(LL)}(L')_4$ are sensitive to solvent

variation^{103,113}. This has been established from a correlation of the frequency of maximum absorption \mathcal{V} max against E_T. The slope of such a correlation is used as an indicator of the sensitivity of the charge transfer band e.g. the slope of Fe(bipy)₂(CN)₂ or Fe(phen)₂(CN)₂ varies between 7.7 and 8.6 x 10⁻³ k cal mol⁻¹ but for Fe(bipy)(CN)₄²⁻, the slope is only 3.8 x 10⁻³ k cal mol⁻¹ (ref.103). The variation of \mathcal{V} max of the reaction product in a range of mixed solvents (up to 80% v/v ethanol or acetone) with their respective E_T values are given in Table 6.5 and illustrated in Figure 6.6.

TABLE 6.5

Frequencies $(\hat{\mathcal{V}})$ of maximum absorption for the lowest energy charge-transfer band of Fe(hxSB)²⁺. Solvent E_T values from Ref.104.

| % | nonaqueous | ethanol | | acetone | |
|---|------------|-----------------------------|------|-----------------------------|----------------|
| | | $\mathcal{V}_{max/cm}^{-1}$ | E T | $\mathcal{V}_{max/cm}^{-1}$ | Е _Т |
| | 0 | 18900 | 63.1 | | |
| | 20 | 18760 | 60.0 | | |
| | 40 | 18450 | 56.6 | | |
| | 60 | 18180 | 55.0 | 18020 | 54.5 |
| | 80 | 18020 | 53.7 | 17760 | 52 .2 |

The slope of the correlation line is $8 \times 10^{-3} \text{ kcal mol}^{-1}$ which is much less than the values of 13.4 and



FIGURE 6.6 Correlation between frequencies of maximum absorption (\mathcal{D}) for Fe(hxSB)²⁺ and solvent E_{T} values (k cal mol⁻¹).

15.3 x 10^{-3} k cal mol⁻¹ for the complexes Fe(LL)₂(CN)₂ where



in hydroxylic and non-hydroxylic solvents¹⁰³. Again this adds further support to the hypothesis that the product of the reaction of the hexadentate Schiff base complex with cyanide is $Fe(hxSB)(CN)_{4}^{2-}$.

6.5 <u>Reaction with Peroxodisulphate</u>

Reaction of the hexadentate Schiff base complex with peroxodisulphate is relatively fast. The half life of the reaction $(10^{-4}$ M-hexadentate Schiff base complex with 10^{-3} M-peroxodisulphate) is about 140 seconds. It has been shown in sections 6.2 to 6.4 that the rate constant for dissociation of the hexadentate Schiff base complex in neutral solution is very close to zero. This strongly suggests a second-order rate law for the reaction of the hexadentate Schiff base iron(II) complex with peroxodisulphate:

$$-d[Fe(hxSB)^{2+}]/dt = k_2[S_2 0_8^{2-}][Fe(hxSB)^{2+}]$$
 (6.4)

The rate constant k_2 in equation (6.4) is about 12 $M^{-1}s^{-1}$ at $25^{\circ}C$.

In general there are two major mechanisms by which electron transfer can occur in redox reactions. These are called inner-sphere and outer-sphere reactions. In an inner-sphere reaction the two metal ions are linked by a common bridging ligand at the time of electron transfer. A typical example of the inner-sphere mechanism is the reaction of $Cr(H_20)_6^{2+}$ with $Co(NH_3)_5Cl^{2+}$, the product is $Cr(H_20)_5 Cl^{2+}$ (ref.114). On the other hand in an outersphere reaction both metal ions retain their inner coordination spheres during the electron transfer. The lability of the reactants is an important factor in determining the mechanism of redox reaction. For example the reactions of $Fe(CN)_6^{4-}$ with $IrCl_6^{2-}$ or $Fe(phen)_3^{2+}$ with MnO_{A}^{-} are outer-sphere¹¹⁵, with electron transfer very much faster than bond breaking in both the initial compounds. The distinction between the inner-sphere and the outersphere mechanism can be represented diagramatically as shown below :



INNER-SPHERE

electron transfer

product



transition state

OUTER-SPHERE

↓ product

In view of the substitution inertness of the hexadentate Schiff base iron(II) complex, reaction with peroxodisulphate is highly unlikely to be inner-sphere. The reaction of $Fe(hxSB)^{2+}$ with peroxodisulphate is, by analogy with other iron(II) complex e.g. $Fe(bipy)_3^{2+}$ and $Fe(phen)_3^{2+}$, an outersphere one. This can be accomplished by electron transfer either from the periphery of the aquated complex or directly from the iron atom to peroxodisulphate.

If the mechanism of the reactions of the hexadentate Schiff base and ferrozine iron(II) complexes (see Chapter 5 for reactions of $Fe(fz)_3^{4-}$) with peroxodisulphate is outersphere, where orbital overlap is minimal, one expects a linear correlation between the logarithms of the second-order rate constants of oxidation (k₂) and the redox potentials (E⁰) of the respective iron(II) complexes¹¹⁶.

To investigate such a correlation, the redox potentials of the hexadentate Schiff base and of the ferrozine complexes were measured. This was carried out by titration of the respective iron(II) complexes against Ce(IV), in molar perchloric acid at 4° C, using a platinum electrode and a Calomel reference electrode. The values of E^o for the iron(II) complexes were determined by taking the redox value of Fe²⁺/Fe³⁺ measured under exactly the same potentiometric titration conditions as standard. It was necessary to carry out the titrations at 4° C to minimise acid aquation of the complex during the course of the redox potential determination. Assuming that dE^o/dt for Fe(hxSB)^{2+/3+} or Fe(fz)^{2+/3+} is approximately equal to that for Fe(phen)₃²⁺ (ref.117) then the estimated values of E^o for Fe(hxSB)²⁺ and Fe(fz)²⁺ at 25^oC are 1.03 V and 0.89 V respectively.

A plot of logarithms of the second-order rate constants for oxidation of hexadentate Schiff base, ferrozine and other related iron(II) complexes, Table 6.6, against their respective redox potentials is shown in Figure 6.7. In fact there is no good linear correlation but at least the expected trend for 2,2'-bipyridyl, 1,10-phenanthroline and their ligand substituted derivatives exists i.e. a decrease in the rates of oxidation as the redox potential increases. It is surprising that the rate of oxidation of the ferrozine complex by peroxodisulphate is slow despite its low value of E^{O} , whence one expects rapid reaction. However the scattering of points in Figure 6.7 may not be genuine, for two major Firstly the great diversity of thoughts among reasons. various workers who treat the kinetics of peroxodisulphate oxidation on the basis of a simple second-order model, or recognise the existence of parallel dissociation and oxidation or believe that ion pair formation, between the

TABLE 6.6

Second-order rate constants (k_2) of oxidation of low spin tris-(LL)iron(II) complexes by peroxodisulphate, at 35° C, and their respective redox potentials (E°) .

| LL | $k_2/M^{-1}s^{-1}$ | Ref. | E^{O}/v | Ref. |
|------------------------------|--------------------|-----------|-----------|-----------|
| phen | 0.433 | 118 | 1.06 | 120 |
| | 0.245 | 119 | 1.07 | 121 |
| | | | 1.14 | 122 |
| 5-NO ₂ -phen | 2.07 | 118 | 1.25 | 120 |
| _ | 0.45 | 119 | | |
| 5-Me-phen | 0.162 | 118 | 1.02 | 120 |
| | 0.157 | 119 | 1.15 | 122 |
| 5-C1-phen | 0.742 | 118 | 1.12 | 120 |
| | 0.143 | 119 | | |
| 5-Me-6-N0 ₂ -phen | 0.63 | 119 | 1.23 | 123 |
| 5,6-diMe-phen | 0.049 | 119 | 0.97 | 124 |
| 4,7-diMe-phen | 2.50 | 119 | 0.88 | 125 |
| 3,5,6,8-tetraMe-phen | 0.34 | 119 | 0.92 | 120 |
| 5-S0 ₃ -phen | 0.148 | 97 | 1.20 | 126 |
| $3-S0_3$ - phen | 1.04 | 97 | 1.23 | 126 |
| bipy | 0.73 | 119 | 1.12 | 122 |
| | 0.648 | 118 | 1.05 | 121 |
| 4,4'-diMe-bipy | 8.8 | 119 | 0.94 | 122 |
| | 9.86 | 118 | | |
| terpy | 0.85 | 119 | 0.93,12 | 5 124 |
| fz | 0.0029 | This work | 0.89 | This work |
| hxSB | 20 | This work | 1.03 | This work |



FIGURE 6.7

Correlation between logarithms of second-order rate constant (k_2) for oxidation of $Fe(LL)_3^{2+}$ by peroxodisulphate and their respective redox potentials (E°) . 1 : 5-NO₂-phen; 2 : 3-SO₃-phen; 3 : 5-Me-6-NO₂-phen; 4 : 5-SO₃-phen; 5 : 5-Me-phen; 6 : phen; 7 : 5-Cl-phen; 8 : bipy; 9 : terpy; 10 : 3,5,6,8-tetra-Me-phen; 11 : 5,6-diMe-phen; 12 : fz; 13 : 4,7-diMe-phen; 14 : 5,5'-diMe-bipy; 15 : 4,4'-diMe-bipy; 16 : hxSB. respective iron(II) complex and peroxodisulphate anion, plays an important role. Secondly values of the redox potentials in Table 6.6 were collected from a variety of sources and under different conditions such as medium, ionic strength and temperature.

6.6 Conclusion

The preparation of a new hexadentate Schiff base iron(II) complex has successfully been established. The interesting feature of this hexadentate ligand is the incorporation of the secondary aliphatic nitrogen atoms without causing a change in magnetic properties from Iow spin to high-spin. A high stability for this complex is suggested by its extremely low rate of dissociation in neutral solution. The kinetic pattern for aquation and for reactions with hydroxide, cyanide and peroxodisulphate is similar to that for other low spin iron(II) complexes, particularly to that of its closest analogue, the bis-terpyridyl-iron(II) complex.

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APPENDIX

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| P | ROGRAN : STLNRG |
|---------|---|
| FORTRAN | 200 SOURCE LISTING AND DIAGNOSTICS |
| 100 | SJERJUTINE STENRG (KONYVALOXYOANS) |
| 002 | DIMENSION NYVAL(1),XY(1),ANS(16) |
| 003 | SUMX=0.0 |
| 004 | SJMX2=0.0 |
| 005 | SUMY=0.0 |
| 005 | ANS(6)=0.0 |
| 007 | 5JMXY=0.0 |
| 010 | N=O |
| 011 | $N \lambda = 1$ |
| 012 | $N_1 = 2$ DD 2D 1=1.4K |
| 014 | M = NYVAL(1) |
| 015 | N=N+M |
| 016 | DO 10 1=1.0M |
| 017 | SUMX=SUMX+XY(NX) |
| 020 | SJMXZ=SUMXZ+XY(MX)*XY(MX) |
| 021 | SJMY=SUMY+XY(NY) |
| 022 | ANS(b) = ANS(b) + XY(NY) + XY(NY) |
| 023 | SUMXY=SUMXY÷XY(NX)*XY(NY) |
| 024 | 10 NY=NY+1 . |
| 025 | NX = NX + MYVAL(J) + I |
| 025 | |
| 030 | $\Delta N S(T) = 1 N$ |
| 031 | S1 = ANS(1) + SUMX2 - SUMX + SUMX |
| 032 | S2=ANS(1)*SUMXY-SUMX*SUMY |
| 033 | EN1 = EN - 1.0 |
| 034 | EN2 = EN1 - 1.0 |
| 035 | ANS(2) = S2751 |
| 036 | ANS(B) = SUMY/EN |
| 037 | ANS(4) = SUNX/EN |
| 040 | ANS(5) = ANS(3) - ANS(2)*ANS(4) $ANS(7) = ANS(7)*SURV$ |
| 041 | AXS(A) = ABS(2)*S2/BA |
| 043 | ANS(9) = ANS(6) - ANS(7) - ANS(8) |
| 044 | S4 = ANS(9)/(EN-2.0) |
| 045 | ENDSI = EN/51 |
| 046 | ANS(10) = SURT(1.0/(EN1*ENDS1)) |
| 047 | ANS(11) = SORT((ANS(6) - ANS(7))/EN1) |
| . 050 | ANS(12) = SORT(S4) |
| 051 | A13 = S4/LN |
| 052 | ANS(13) = SURT(A13) |
| 053 | ALA - SAMEMUSI ANS()A) \doteq SORT(ALA) |
| 055 | $ANS(15) = SORT(A13 + A14 \times ANS(4) \times ANS(4))$ |
| 056 | ANS(16) = ANS(8)/S4 |
| 057 | END |
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| | 요즘 그는 방법에 걸려서 가지 않는 것이 아파 가지 않는 것 같아요. 정말 밖에 있는 것 같아? |

| FORTRAN | | 200 SOURCE LISTING AND DIAGNOSTICS PROGR |
|---------|----|--|
| 001 | | DIMENSION NYVAL(12),XY(24),ANS(16),IALPH(26) |
| 002 | 88 | REAU(2.1)K |
| 003 | 1 | FURMAL(12) |
| 004 | | IF(K.EU.99) CALL EXIT |
| 005 | | READ(2,11)(IALPH(I),I=1,26) |
| 006 | 11 | FORHAT(26A3) |
| 007 | | DO LO IFISK |
| 010 | 10 | NYVAL(I)=1 |
| 011 | | KZ=ZAK |
| 012 | | DD 20 J=1.9K2.92 |
| 013 | | |
| 014 | 20 | KEAU(292)XY(J) 9XY(JI) |
| 015 | 2 | FURMAT(ZFIU,4) |
| 013 | | AUTTERS STENROLN INTERED AND AND A |
| 020 | 2 | EDRMAT(1H1,20x,2643/1H4,20x,13HN0, OF POINTS,2x,12/1H4,20x, |
| 020 | 5 | 2REX VALUES LAX BEY VALUES) |
| 021 | | $D_{1} \rightarrow U_{1} = 1 + k + 2 + 2$ |
| 022 | | J = J + 1 |
| 023 | 30 | WR1(E(3,4)XY(J),XY(J1) |
| 024 | 4 | FORMAT(1H2,20X,F12.7,4X,F12.7) |
| 025 | | WRITE(3,5)ANS(2),ANS(14),ANS(5),ANS(15) |
| 026 | 5 | FORMAT(1H4,20X,8H5LOPE = ,F12,7,2X,12HST. DEVN. = ,F12.7/ |
| | | 21+3,20X,12HINTERCEPT = ,F12.7,2X,12HST. DEVN. = ,F12.7) |
| 027 | | 60 IU 88 |
| 030 | | END |
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TEST DATA.

NO. OF POINTS 9

| X VALUES | Y VALUES |
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| 1.0000000 | •0565000 |
| 4.0000000 | •071110C |
| 5.0000000 | •0814000 |
| 6.000000 | •1152000 |
| 7.0000000 | •1169000 |
| 11.0000000 | •160500Ċ |
| 18.000000 | •2428000 |
| 26.0000000 | •3143000 |
| 38.0000000 | • 387200C |

SLOPE = .0094860 ST. DEVN. = .0004878

INTERCEPT = .0495040 ST. DEVN. = .0084362