ELECTRON TRANSFER REACTIONS

A thesis presented in candidature for the degree of
Doctor of Philosophy

by

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SUMMARY

The electron transfer reaction between the cobalt (II) and cobalt (III) complexes of acetylacetone has been studied in both acetylacetone and toluene as solvent and it was found that the reaction proceeded much faster in the former. The reaction was found to obey second-order kinetics for the latter solvent and a more complicated kinetics in the former case. The activation energy was calculated and found to be 14.0 and 14.3 k cals/mole in acetylacetone and toluene respectively. The entropy of activation for the system using toluene as a solvent was found to be -40 e.u. while the value for the reaction in acetylacetone can be given an upper limit of - 31.5 e.u. The results from the study of the electron transfer reaction in mixed solvent, viz., acetylacetone with toluene, are interpreted as indicating that the electron transfer,in the presence of acetylacetone in the solvent,occurs by an "outer-sphere" reaction involving a proton bridge.

The study of the electron transfer reaction between the N-phenyl-salicylidene-imine type complexes of cobalt (II) and cobalt (III) was carried out in toluene as solvent. The reactions studied were found to obey first-order kinetics, the rate of reaction being dependent on the concentration of the cobalt (III) complexes and independent of the cobalt (II) species. The activation energy of these systems was found to be approximately 13.0 k cals/mole, and this is interpreted as being the energy of activation necessary to

allow the conversion of the diamagnetic cobalt (III) complex to a paramagnetic cobalt (III) complex. Furthermore the activation entropy values were found to be approximately -30 e.u. from which one can deduce that a major contribution to the entropy factor will be the difference in splitting of the energy values of the d orbitals of the reactants.

Pyridine was used as a solvent in the study of the electron transfer reactions between N,N′-ethylene-bis(salicylidene-imine) type complexes of cobalt (II) and cobalt (III). These systems gave fast electron transfer reactions which were complete during the time from mixing to separation of the complexes, thus no kinetic data could be calculated for these reactions.

The systems studied have allowed certain deductions to be made as to the effects of a change of ligand and a change of solvent on the rate of reaction and the reactant mechanism. It has been found that a change of the ligand has an effect on the rate of reaction which is most probably due to the change in the ligand field surrounding the complexed metal ion. Further, a change in the solvent for the acetylacetonato complexes has produced a reaction following a complicated kinetics, however this can be explained in terms of solvation of the complexes taking part in the electron transfer reaction, or by the dissociation of "dimer-molecules" formed by the reactants when dissolved in the solvent. It has also been found that the overall charge of the complex molecules does not appear to have any significant effect on the rate of reaction. Furthermore, in most of the systems investigated, support was given for the mechanism in which a bridged activated transition state complex is formed, due to the need to transfer a ligand molecule during the electron transfer reaction.

This thesis contains no material which has been accepted for the award of any other degree or diploma at any University and to the best of my knowledge contains no material previously published or written by any other person, except where due reference is made in the text.

ACKNOWLEDGEMENTS

I wish to acknowledge my superviser, Dr. B.O. West, for his interest and encouragement in the project and also to express my appreciation to Professor D.O. Jordan for his helpful discussions and advice in the presentation of the thesis. I also wish to thank Messrs. L. Kennelly and A. Bowers for both the work done and the advice given in the construction of apparatus used for the electron transfer experiments. I would also like to express my appreciation to all those who have entered into discussions on the interpretation of results obtained in the project.

INTRODUCTION.

Any oxidation-reduction reaction may be spoken of as an electron transfer reaction, although this term is strictly applied only to reactions for which the enthalpy change is zero, i.e., a reaction in which reactants and products are the same. A typical electron transfer reaction may be represented by the equation

$$M^{*a+} + M^{(a-n)+} \rightleftharpoons M^{*(a-n)+} + M^{a+}$$

Although several methods have been used for following electron transfer reactions, the one most commonly used, and the one employed for the work reported in this thesis, is that involving the use of radioactive tracers. The method consists of labelling an element M, in a valence state (a) in a compound, by using a radioactive isotope of M, M*. This is then reacted in a suitable solvent with a compound in which the valence state of M is (a - n) where n is the number of electrons transferred. The different valence states of the element are separated at various time intervals and the appearance of radioactivity in the valence state (a - n) is indicative of the existence of an electron transfer reaction. The rate of appearance of radioactivity in this valence state can be used as a measure of the rate of the electron transfer process. This method is satisfactory provided that there is no irreversible transfer of radioactivity by thermochemical reduction or oxidation, e.g.

$$M^{a+} \longrightarrow M^{(a-n)+} + ne$$

A number of reactions involving two ionic species have been studied using aqueous media. Some of the reactions are summarized in Table I. Only a few reactions, e.g., $(\mathrm{FeCP})\text{-}(\mathrm{FeCP})^+$ and $(\mathrm{Co\phi P})\text{-}(\mathrm{Co\phi P})^+$ have been studied in non-aqueous media in which one of the reactants is a neutral molecule. It was therefore considered that a study of reactions in which both reactants were neutral molecules could prove to be enlightening and advantageous in attempting to elucidate the effects of charge, solvent type and nature of the ligand on the rate and mechanism of electron transfer reactions.

The work reported in this thesis was originally designed therefore as a study of electron transfer reactions involving neutral molecules. However, the number of such systems available for study is limited and so it has also been necessary to study reactions in which only one of the species taking part is a neutral molecule.

The thesis is presented in essentially three parts, the first being a review of the work already carried out in the field of electron transfer reactions and presenting the various mechanisms that have been suggested. The second part deals with reactions involving reactants both of which are neutral complex molecules, while the third deals with reactants in which only one of the participating molecules is neutral.

TABLE I

Electron Transfer Reaction

System	Solvent	T°C	Rate Constant	Ref.
Fe^{2+}-Fe^{3+}	Aqueous $HClO_4$/HCl	0.0	0.87 l.mole^{-1}sec^{-1}	1
Fe^{2+}-$Fe(OH)^{2+}$	Aqueous $HClO_4$/HCl	0.0	1.0x10^{3} l.mole^{-1}sec^{-1}	1
Fe^{2+}-$FeCl^{2+}$	Aqueous HClO4/HCl	0.0	9.7 l.mole^{-1}sec^{-1}	1
Cr^{2+}-Cr^{3+}	Aqueous $HClO_4$	24.5	0.07 l.mole^{-1}hr^{-1}	2
Cr^{2+}-$Cr(OH)^{2+}$	Aqueous $HClO_4$	24.5	2.5x10^{3} l.mole^{-1}hr^{-1}	2
Co^{2+}-Co^{3+}	1M $HClO_4$	0.0	4.6 l.mole^{-1}min^{-1}	3
$Co(NH_3)_6{}^{2+}$ - $Co(NH_3)_6{}^{3+}$	Water	65	7.0x10^{3} l.mole^{-1}min^{-1}	4
$Coen_3{}^{2+}$ - $Coen_3{}^{3+}$	Water	25	0.188 l.mole^{-1}hr^{-1}	4
$FeEDTA^{2-}$ - $FeEDTA^{-}$	Water	20	very fast	5
CoØP - $CoØP^{+}$	Benzene	7	very fast	6
FeCP - $FeCP^{+}$	Alcohol	-65	very fast	7

ØP = tetraphenylporphine CP = cyclopentadiene

REFERENCES.

1. J. Silverman and R. W. Dodson, J.Phys.Chem. 56, 846 (1952).
2. A. Anderson and N. A. Bonner, J.Am.Chem.Soc. 76, 3826 (1954).
3. H. L. Friedman, H. Taube and J. P. Hunt, J.Chem.Phys. 18, 757 (1950).
4. W. B. Lewis, C. D. Corywll and J. W. Irvine, J.Chem.Soc.Suppl. Issue No. 2, 5386 (1949).
5. A. W. Adamson and K.S. Vorres, J.Inorg.Nucl.Shem. 3, 206 (1956).
6. G. D. Dorough and R. W. Dodson, Quarterly Prog.Reports B.N.L., July and Sept. BNL 132(S-11), 68 (1951).
7. F. S. Dainton et al., Internation,Conference on Radioisotopes in Scientific Research, abstract in Int.J.Appl.Rad. and Isotopes, 2, 259 (1957).

PART I

A Review of Electron Transfer Reactions.

Chapter 1.

CHAPTER I.

A Review of Electron Transfer Reactions

A. Introduction.

Electron transfer reactions between the rare gases and their ions can be explained simply in terms of the overlap of atomic orbitals (1). In solution, however, electron transfer reactions are much more complicated, since the extension in space of the electronic orbitals is somewhat limited by the presence of the solvent molecules. Thus the solvent molecules will play an important part in hindering the electron transfer reaction. As well as solvent molecules, the presence of ligands will act in a similar way by insulating the central metal ions against electron exchanges.

Several mechanisms have been suggested by which electron transfer can occur in solutions, among which are:

(1) An Electron Jump Theory proposed by Libby.

(2) An Electron Tunnelling Hypothesis introduced by Weiss and by Marcus, Zwolinsky and Eyring.

(3) A Bridged Activated Intermediate Mechanism suggested by Taube and his coworkers.

(4) An Electron Solvation Mechanism.

Although experimental evidence has been obtained which appears to support all of these mechanisms, most of the evidence supports the third mechanism.

Libby (2) has shown that unequal energies of reactants and products would result if a single electron transfer took place between two metal ions, differing by only one unit of charge, due to the different interaction of each of the metal ions with the environment. Furthermore the Frank-Condon Principle (3) forbids the rearrangement of coordinated groups during the actual electron transfer process, since the movement of an electron will be immeasurably fast by comparison with the movement of a nucleus. The combination of these two factors thus predicts the rearrangement of the normal environments of the two metal ions involved in the electron transfer reaction to an intermediate form (Fig. 1.2). This is clarified by considering an actual example:

$$Co(H_2O)_6^{2+} + Co(H_2O)_6^{3+} \longrightarrow Co^*(H_2O)_6^{3+} + Co^*(H_2O)_6^{2+}$$

$$\swarrow$$

$$Co(H_2O)_6^{3+} + Co(H_2O)_6^{2+} + \Delta H.$$

The cobalt ions will hold water molecules at distances such that a minimum potential energy within limits of vibrational changes is reached for the system (Fig. 1.1). The resulting ions after electron transfer will have an increased potential energy due to the water molecules now being too close or too far away to give the state of minimum energy.

The ions on reverting to their normal energy state will therefore liberate energy in the form of heat, thus violating the law for conservatio-n of energy. This violation will be avoided, if an intermediate structure is formed, since this will require energy from the surroundings, the same amount of energy being released after the electron transfer, when the ions revert to their state of minimum

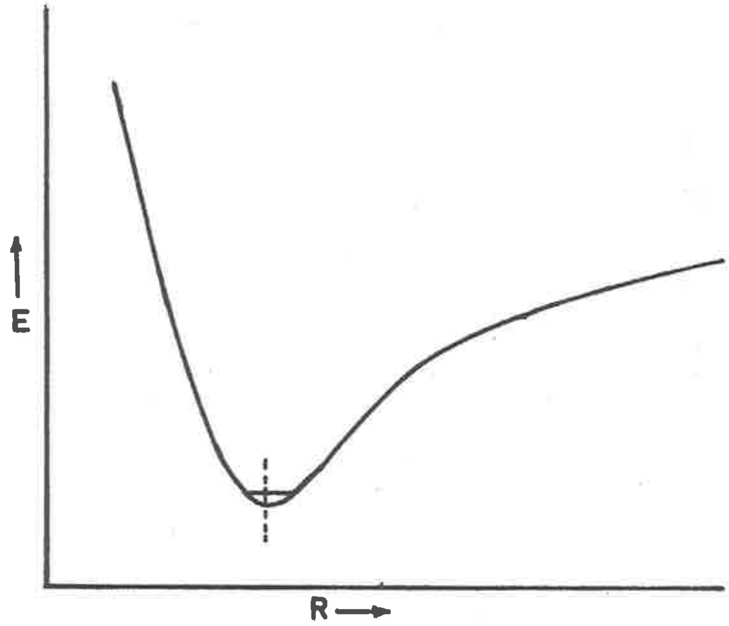

Fig.1.1 Change of potential energy with distance of ligand from metal ion.

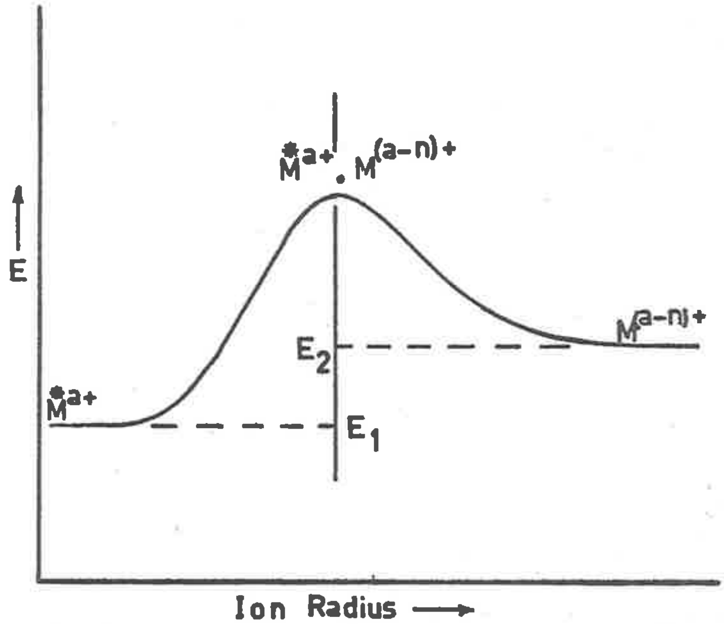

Fig.1.2 Change of potential energy in the formation of an activated transition state.

energy.

In all of the mechanisms to be discussed here it is necessary to have an intermediate structure, as predicted above, otherwise the law of conservation of energy will not be obeyed, the excess energy being liberated in the form of heat.

In recent years the crystal field theory has been applied in an effort to explain the electron transfer process. Even in this case the mechanism involving the use of intermediates, to aid in the electron transfer, is supported.

B. The Electron Jump Theory

Libby (2) has pointed out that a barrier to electron transfer will result from the Frank-Condon principle since the hydration atmospheres of the two ions undergoing exchange cannot change during the actual electron transfer. The energy of rearrangement of the hydration shells being the barrier to the electron transfer (Fig.1.2). Libby suggests that the electron transfers by jumping from one ion to the other, the electron having first acquired the energy needed to cross over the energy barrier. He suggests that the excess energy thus acquired by the reduced ion then leaks back slowly to the oxidized ion. The rearrangement of the two hydration shells would take place during the energy leaking process. When the two ions between which electron transfer is occurring are not the same, an exothermic reaction is generally favoured and rearrangement of structures could then take place after the electron transfer, as is proposed by Libby. The heat of reaction is the excess energy acquired during electron transfer. However, in reactions where both nuclei are of the same element in different valence states, it is, as pointed out on page 6, necessary to rearrange the structures to an intermediate form before the electron transfer.

Libby, by using the hydrogen molecule-ion as a model, i.e., for reactions in the gaseous state, has calculated the frequencies of electron transfer for 3 d wave functions. The frequency of transition is found to be large for distances of about 30 A^{o}. As the nuclear charge is increased the distance at which a particular frequency will occur is decreased approximately as the inverse of the nuclear charge. In applying the theory to the case of ions in aqueous solution, Libby has suggested that since there is no time for solvation of the electron, the mechanism should be similar to that in the gaseous state. The polarizability of the medium produces about a twofold reduction of the ionization potential and at the same time increases the height of the energy barrier to two or three times the predicted value, the overall effect being about the same as for the model case.

Libby has put the Frank-Condon principle in a different way when he states "The electron transfer is catalysed by complexing the exchanging ions in such a way that the complexes are symmetrical providing the geometries are the same within the vibrational amplitudes involved in zero point motion." For an electron transfer between two cations, the presence of anions in solution forming a linear complex will satisfy this principle of symmetry and at the same time will reduce the distance between the exchanging ions. The hydration shells will therefore be shared, the dissimilarities between the reacting species thus reduced and the exchange therefore facilitated.

It should also be pointed out that the electron wave functions will allow for the electron exchange or Redox reactions occurring through several layers of solvent molecules.

C. The Electron Tunnelling Hypothesis

The quantum mechanical phenomenon of potential energy barrier penetration by an electron is well known and is responsible for the transfer of electrons over distances normally greater than those corresponding to collision distances. This phenomenon forms the basis of calculations by Weiss (4) and Marcus, Zwolinsky and Eyring (5) who have developed an electron tunnelling theory. This theory explains the occurrence of electron transfer reactions at distances, between the reacting ions, too great to allow the previous mechanism to apply.

During the approach of the two reacting species, ionic repulsion is overcome and coordination and hydration shells are rearranged. This produces symmetrical electronic states for each of the reactants, which will allow the rapid transfer of an electron from one ion to the other. The transition state so formed should allow for a frequent exchange of electrons without having too high an energy of activation, thus the transmission coefficient of the electron exchange must be less than unity. The magnitude of the coefficient is approximately determined by the height and width of the potential energy barrier.

A one dimensional electrostatic model can be used to represent the electron tunnelling process (Fig. 1.3). Marcus et al. have assumed triangular potential energy barriers in order to simplify the algebraic calculations, however they stated that the true situation was intermediate between the two extreme forms of triangular

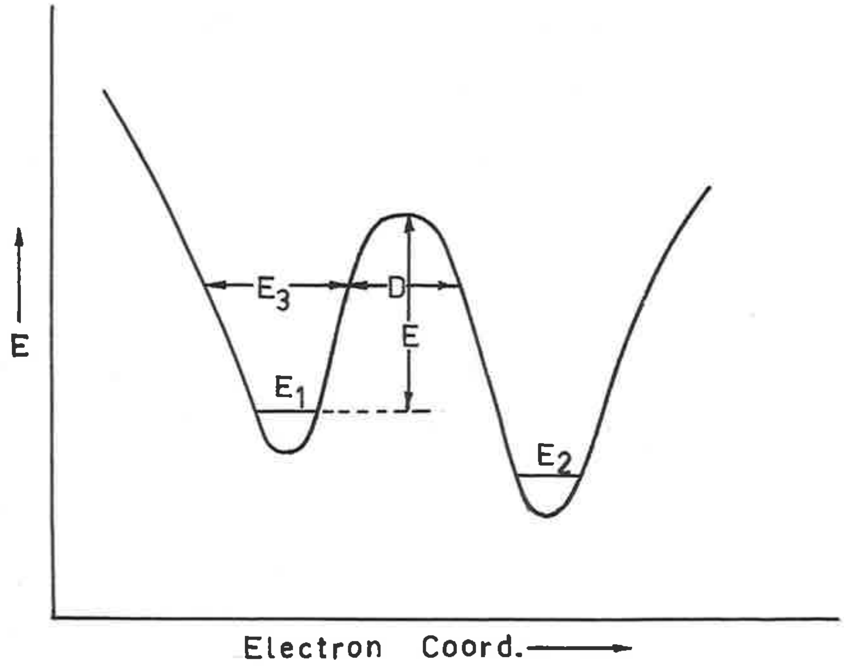

Fig. 1.3 Electron Transfer by Penetration of a Potential Energy Barrier.

E = height of energy barrier

D = width of barrier

E_1 and E_2 represent energies of ground states of electrons in cations 1 and 2

E_3 = potential energy of tunnelling electrons and rectangular barriers. The transmission coefficient was calculated as

$$K_e = \exp\left[-\frac{8\ d}{3h}\ (2m\ (E - E_3)\ )^{\frac{1}{2}}\right]$$

where d = width of barrier m = electron mass

E = height of barrier h = Plank's constant

E_3 = potential energy of the tunnelling electron.

The relationship between the triangular and rectangular boundaries is given by

$$\frac{K_{e_{rect}}}{K_{e_{tri}}} = 4\ \exp\left[-\frac{4}{3h}\ (mE)^{\frac{1}{2}}d\right]$$

Thus when $E = -2\ E_3$ the maximum potential energy of the system is zero and the distances through the two kinds of barriers are equal. The potential energies given here are those for the exchanging electron only and in no way include the energy of rearrangement of coordination or hydration shells. Such rearrangements can be assumed to have taken place prior to the construction of the potential energy barrier shown in Fig. 1.3, this being a necessity imposed by the Frank-Condon principle. The potential energy E is related to the ionization potential of the exchanging electron in its initial state, however, the evaluation of E is much more difficult. The shape of the curve is a function of the nature of the two ions concerned in the exchange, the distance between the ions and also of the dielectric constant of the media.

The rate constant for the electron transfer can be explained in terms of the transmission coefficient and the free energy of activation for the reaction and is given by:

$$k' = \frac{kT}{h} K_e . e^{-\Delta F^{\ddagger}/RT}$$

$\Delta F^{\ddagger}$ is the free energy of activation and is due to the rearrangement of the coordination or hydration shells, where necessary, and includes also a term dealing with the electrostatic repulsion energy. It should also at this stage be emphasised that the transmission coefficient is not temperature dependent and hence the barrier tunnelling phenomenon is different from the thermal barrier crossing.

The theory developed by Marcus et al. has the limitation that it was developed for similarly charged ions in aqueous solution. There would of course be no potential energy barrier, using the same arguments, if one or both of the species involved in the electron transfer reaction were neutral molecules; also the theory would not apply in the case where the ions were of opposite charge. However, the results obtained by considering actual experiments that had been carried out, e.g.

$$Ce^{3+} - Ce^{4+}; \quad Co(en)_3{}^{2+} - Co(en)_3{}^{3+} \text{ and } Fe^{2+} - Fe^{3+}$$

were sufficient to indicate that there was some justification for the theory.

Laidler (35) has considered that much of the theoretical treatment of the quantum mechanical tunnelling process has lacked really good agreement with experimental results. He has consequently extended previous theories by treating the reaction as a diffusion -

controlled process and thereby treating in a more detailed way the encounters between reacting ions. Using this approach Laidler has obtained good agreement between the theoretical and experimental values of the free energy of activation for the Fe^{2+}- Fe^{3+} reaction. Laidler has considered that the rate of reaction is so fast that there is insufficient time for the reorganisation of the solvent spheres before the actual electron transfer. He further considers that his treatment leaves no place for the rearrangement free energy and claims that this has been allowed for in the treatment of the repulsive energy and the potential energy barrier. However if before electron transfer there is no rearrangement of structures to an intermediate value it is difficult to see how there will not be an increase in the overall energy of the system (cf p6).

Zwickel and Taube (36) have investigated the electron transfer reactions between $Cr^{*}(bip)_3^{2+}$ and various cobalt (III) complexes and explained their results in terms of the quantum mechanical tunnelling process. They found that the rate of reaction was slower for the electron transfer with tris(ethylenediamine) cobalt (III) ion than with the hexaammine cobalt (III) ion and they explain this is being due to the longer tunnelling distance necessary for the ethylenediamine ligand. Furthermore the replacement of ammine groups in the $Co(NH_3)_6^{3+}$ ion with other ligands was found to increase the rate of reaction and this has been interpreted as a measure of the permeability of the substituted ligand to the tunnelling electron. Zwickel and Taube further interpret their results as indicating that the tunnelling

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* bip indicates bipyridine.

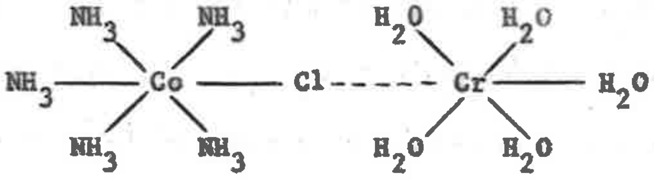
electron goes through an ammine group only when left with no other choice.

Platzman and Franck (6) have considered that electron transfer reactions cannot take place over the distances allowed by the tunnelling hypothesis. Also they state that the energy required to allow the two reacting ions to approach close enough to interfere with the first hydration shells is too great. The net result after considering their arguments is to be left without any satisfactory mechanism for electron transfer.

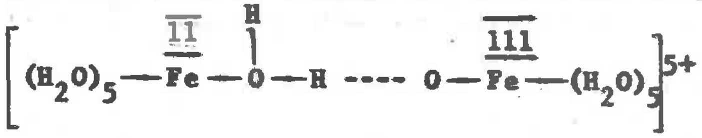
D. Bridged Activated Intermediates

Zener (7), in an attempt to explain the conductivity of electrons from one site to another in crystalline compounds, predicted that it occurs by means of bridging atoms or groups. Using as an example the electron transfer between a sodium atom and a sodium ion in crystalline sodium chloride he stated that the electron transfer takes place by means of a chloride ion bridge. Also in an explanation of the exchange between Mn^{2+} and Mn^{3+} he stated that the bridge between the two ions is most probably made by an oxygen ion. Taube et al. (8-11) developed this idea by applying it to electron transfer reactions in solution. They stated that the electron transfer between two ions in solution proceeds by means of a bridged activated complex as an intermediate.

Much of Taube's work has been devoted to a study of the electron transfer reactions between Cr^{2+} and various other cations. In the exchange reaction between Cr^{2+} ions and $Co(NH_3)_5Cl^{2+}$ in perchloric acid solution, Co^{2+} and $CrCl^{2+}$ ions were obtained. Since the cobaltic pentammine ion and the chromic ion are relatively inert to substitution of ligand, a radioactive isotope of chlorine was used to follow the reaction. Taube (9) has shown by this method that the chlorine from the cobaltic pentammine is quantitatively transferred to the chromic ion formed by the electron transfer reaction. He has also shown that the radioactive tracer used does not exchange with chloride ions in solution. He concluded that the mechanism of the electron transfer was therefore one in which a bridged activated complex was formed. The result of such a bridging mechanism is that an atom transfer takes place at the same time, but in the opposite direction, as electron exchange. The binuclear transition complex predicted is given as,

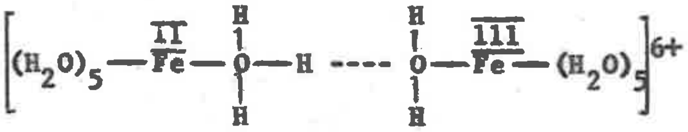


Hudis and Dodson (12) have made a study of the electron transfer reaction between iron (II) and iron (III) using an isotope labelling method. They have found that the use of heavy water slows the reaction by a factor of two, and they have therefore suggested that the possible path is through the transition complex:



$$\left[(H_2O)_5-\overset{\overline{II}}{Fe}-\overset{H}{\overset{|}{O}}-H\ \cdots\ O-\overset{\overline{III}}{Fe}-(H_2O)_5\right]^{5+}$$

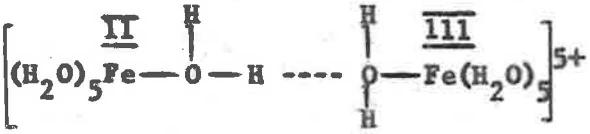
Reynolds and Lumry (13) have suggested an alternative mechanism for this reaction stating that it is possible for a ferrous hydroperoxy compound to be first formed and that this may undergo exchange with the ferric ion, viz.



$$\left[(H_2O)_5-\overset{II}{Fe}-\underset{H}{\overset{H}{O}}-H \text{ ---- } \underset{H}{\overset{H}{O}}-\overset{III}{Fe}-(H_2O)_5\right]^{6+}$$

In any case the latter authors have claimed that there are more wate molecules lying between the two hydration shells, and also that only inner shell water molecules are strong enough to undergo electron exchange at the bridge ends.

For microscopic reversibility a symmetrical structure is needed for the transition complex as is given in the latter example. The case where exchange occurs between two aquo ions is a more difficult one since the activated complex would be of the form:



$$\left[(H_2O)_5\overset{II}{Fe}-\overset{H}{O}-H \text{ ---- } \underset{H}{\overset{H}{O}}-\overset{III}{Fe}(H_2O)_5\right]^{5+}$$

which is not symmetrical. After exchange of the electron the above reaction would yield as products

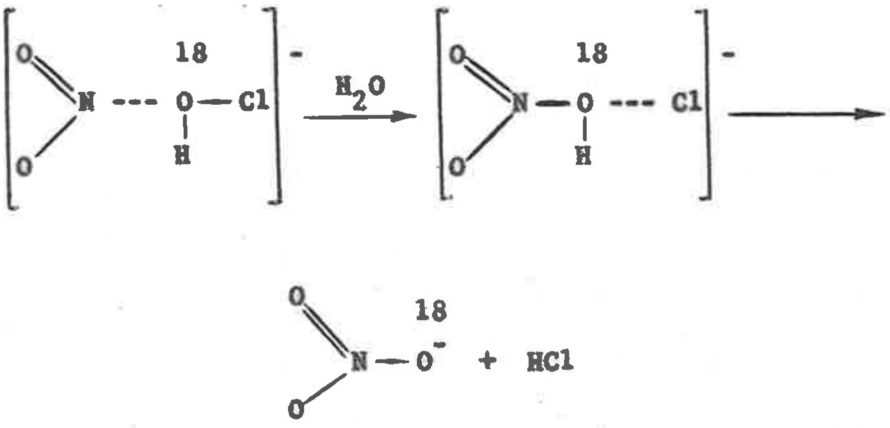
$$Fe(H_2O)_5(H_3O)^{3+} \quad \text{and} \quad Fe(H_2O)_5(OH)^{2+}$$

Since the principle of microscopic reversibility applies here, the reverse reaction to the one given must also occur. Calculations (1) based on the above reaction would indicate that nearly every collision between the products would result in an electron transfer, with the consequent reformation of the initial reactants, thus it would appear that the forward reaction is not favoured.

The specific isotope effect found with deuterium is indicative of an atom transfer process following the electron transfer reaction. Other possibilities may, however, occur since the effect may be due to a solvation phenomenon rather than an atom transfer. Another possibility is that a proton transfer in one direction and an atom transfer in the other may occur at the same time. This latter explanation probably is a little unreasonable on the grounds that the protons and hydrogen atoms would be much slower transferring than the electron, being of much greater mass. Thus by assuming this mechanism we could not account for the fast reaction observed.

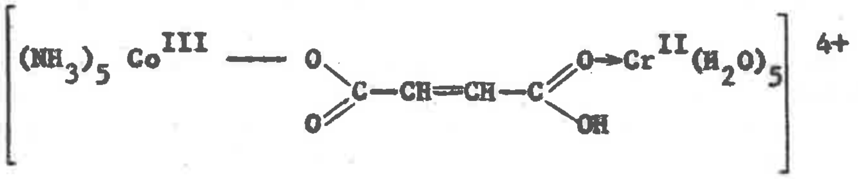
Evidence to support the possibility of hydrogen atom transfer is found in Dainton's (14) work on the illumination by U.V. light of aqueous solutions of bivalent cations of the first transition series. He found that photochemical reduction of the solvent took place with the evolution of hydrogen.

Further evidence for an atom transfer mechanism was found in the study of oxygen atom transfer made by Taube and Anbar (15,16). In a study of the reaction between ClO^- and NO_2^- ions, they found that an oxygen atom transferred from the ClO^- ion to the NO_2^- ion.
The suggested mechanism was given as:



The reaction was followed by use of oxygen 18 since neither ion undergoes oxygen exchange with solvent.

Taube et al (37) (10) have studied electron transfer reactions between Cr^{2+} and $[(NH_3)_5\ Co^{III}\ X]^{2+}$, where X represents fumaric, p-phthalic or maleic acids. They have interpreted the reaction as proceeding through a bridged transition state of the form

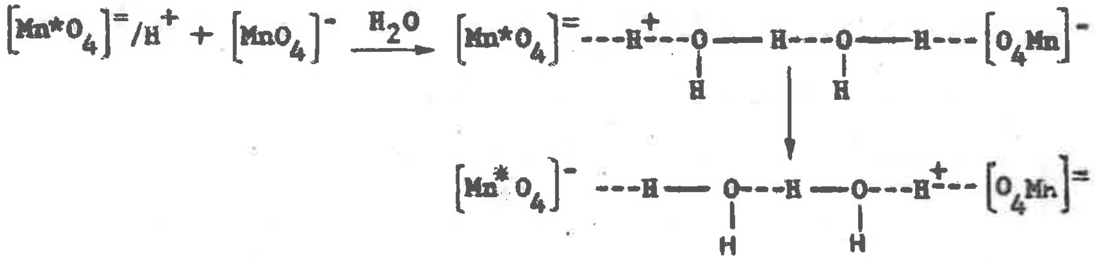


The electron transfer in this case is accompanied by the transfer of the acid bridging group from the oxidant to the reductant. Furthermore hydrolysis of the methyl ester of the fumarate bridge (38) during the electron transfer reaction and the subsequent incorporation of both the methyl alcohol and the fumaric acid groups in the first coordination sphere of the chromium (III) complex is used as evidence that the electron is transferred by a process of conduction through the conjugated π- electron system. Further evidence that π- electron systems can facilitate the electron transfer reaction is given by a comparison of the rates of reaction of the 5.nitro.1.10 phenanthroline complex (39) of Fe^{2+} and of the 1:10 phenanthroline complex of Fe^{2+} with Ce^{4+}. In the former case the reaction is much slower and this can be interpreted as due to the nitro group reacting with the π-electrons of the 1:10 phenanthroline and thus rendering the orbitals less available for the acceptance of electrons from the d orbitals of the metal ion.

Generally it has been accepted that the term "bridged" transition state should imply that the reactants undergo a rearrangement in structure so as to include, in the transition state, a bridging group common to each of the first spheres of coordination. Examples of this type of mechanism are to be found in the reactions so far discussed in this section. Further it will generally be found that electron transfers proceeding through the "inner sphere" (bridged) transition state will be followed by the transfer of the bridging group from the reductant to the oxidant. Thus the reactions may often be referred to as atom or group transfer reactions. However as Taube (9) has pointed out it is not necessary in all cases for atom or group transfer to follow the electron transfer and evidence supporting this is to be found in the reaction between Cr^{2+} and $[Fe(CN)_6]^{3-}$ ions. Since $[Fe(CN)_6]^{4-}$ does not readily undergo substitution of ligand, any of this product formed during reaction between the above ions will not release a $(CN)^-$ group to the oxidizer. The reaction yields an insoluble product in which the bridge persists.

Although the reactions so far discussed in this section have involved "inner sphere" (bridged) transition states it should be pointed out that the rate of many outer sphere reactions (i.e. reactions in which the first coordination spheres of the reactants remains unchanged) show a dependence on the concentration of cations (17) (18) or anions (41) (36) present in solution. This dependence may be interpreted as indicating that even the "outer sphere" reactions can proceed through a "bridged" transition state in which the bridge is more loosely bonded to the reactants than in the case of "inner sphere" reactions. Thus the term "bridged" should not be reserved specifically for defining the "inner sphere" type reactions as has been the generally accepted practice.

Examples of "outer sphere" reactions are the fast reactions $[Fe(CN)_6]^{3-}$-$[Fe(CN)_6]^{4-}$; $[Os(bip)_3]^{2+}$-$[Os(bip)_3]^{3+}$ and $[MnO_4]^{-}$-$[MnO_4]^{=}$. Zwolinski et al. (5) have attempted to explain these reactions in terms of the theory of energy barrier tunnelling by the electron. However it may be possible for ions in solution or even solvent molecules near the exchanging compounds, to form a bridge, by which means the electron exchange can take place, e.g.



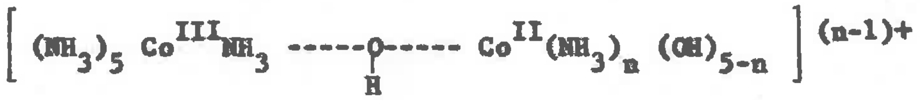
$$[Mn^*O_4]^{=}/H^{+} + [MnO_4]^{-} \xrightarrow{H_2O} [Mn^*O_4]^{=}\text{---}\overset{+}{H}\text{---}\underset{H}{O}\text{—}H\text{---}\underset{H}{O}\text{—}H\text{---}[O_4Mn]^{-}$$

$$\downarrow$$

$$[Mn^*O_4]^{-}\text{---}H\text{—}\underset{H}{O}\text{---}H\text{—}\underset{H}{O}\text{---}\overset{+}{H}\text{---}[O_4Mn]^{=}$$

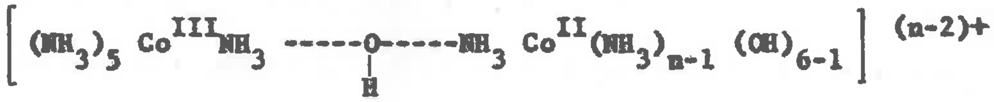
In the above example hydrogen atom transfer occurs across an outer solvation bridge.

Stranks (40) has studied the electron transfer reactions between $Co^{III}(NH_3)_6^{3+}$ and complexes of the general formula $[Co^{II}(NH_3)_n(OH)_{6-n}]^{(n-4)+}$ and has found that these reactions are catalysed by hydroxide ions. He concludes that these "outer sphere" reactions proceed via bridged transition states of the form



$$\left[(NH_3)_5\ Co^{III}NH_3 \text{-----}\underset{H}{O}\text{-----}\ Co^{II}(NH_3)_n\ (OH)_{5-n} \right]^{(n-1)+}$$

or



$$\left[(NH_3)_5\ Co^{III}NH_3 \text{-----}\underset{H}{O}\text{-----}NH_3\ Co^{II}(NH_3)_{n-1}\ (OH)_{6-1} \right]^{(n-2)+}$$

The former intermediate is the more favoured since it would allow a closer approach of the reactants and hence a greater extent of overlap of the electronic orbitals. The former intermediate is also supported by the observation that in at least 50% of the electron transfers the newly formed cobalt (III) complex had undergone hydroxide-ion substitution. Furthermore Stanks assumes that the chloride catalysed reactions also proceed through an analagous intermediate of the form,

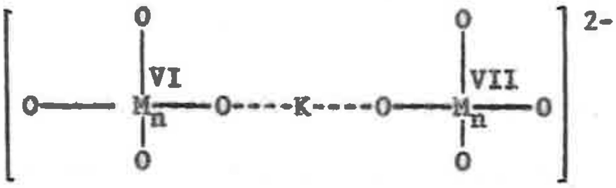
$$\left[(NH_3)_5\ Co^{III}NH_3\text{-----}Cl\text{-----}Co^{II}(NH_3)_n(OH)_{5-n} \right]^{(n-1)+}$$

however this cannot be demonstrated since the cobalt (III) chlorammine undergoes rapid hydrolysis, especially in basic solution, thus resulting in no net transfer of chloride ions. Stranks also concludes that electron transfers in cases such as the reaction between the tris(ethylenediamine) complexes of cobalt (II) and cobalt (III) may occur through an "outer sphere" bridged transition state.

Libby et al. (17,34) have studied the manganate-permanganate exchange using both solvent extraction and precipitation methods, and found that the half life of the reaction was too short to be measured. They attempted to explain the reaction mechanism in terms of the electron jump theory, stating (33) that it is necessary for a symmetrical complex to be formed in order that the electron jump can occur. Libby (33) also used the same theory to explain the electron transfer reaction between Ce^{3+} - Ce^{4+} in the presence of fluoride ions. The suggested formation of a symmetrical complex in these reactions supports the formation of a bridge between the two exchanging groups.

Sheppard and Wahl (18) in their study of the manganate-permanganate electron transfer reaction have shown a dependence of the rate of reaction on the concentration of cations, while there is no dependence on the concentration of other anions in solution.

A possible interpretation of their results is that a cation forms a bridge between the two anions concerned in the electron transfer such that an "outer-sphere" bridged complex of the type



$$\left[O-\overset{O}{\underset{O}{Mn^{VI}}}-O\cdots K\cdots O-\overset{O}{\underset{O}{Mn^{VII}}}-O \right]^{2-}$$

is formed.

E. Solvation of Electrons

Another means by which an electron could transfer from one compound to another is for the donor to release an electron to the solvent phase and for the solvent phase at some time later to hand the electron on to the acceptor. This can be represented by

$$M^{a+} + S \longrightarrow M^{(a+1)+} + S^-$$

$$\begin{tikzcd} S^- + M^{b+} \arrow[r, shift left] & S^- \text{----} M^{b+} \arrow[l, shift left] \arrow[d] \\ & S + M^{(b-1)+} \end{tikzcd}$$

Evidence supporting this hypothesis is to be found in work on alkali metal solutions in liquid ammonia. Kaplan and Kittel (19) interpreted their electron spin resonance data as evidence that electrons were removed from the alkali metals and held in cavities in the solvent, the cavities being between 2 and 4 times the size of the ammonia molecules. They suggest that the electrons can exist as free or paired electrons. These electrons in the cavities can be considered as if occupying a molecular orbital on the protons of adjacent ammonia molecules.

Libby (2) considers that electrons cannot exist in the free state in aqueous solution since there would be a tendency to reduce the water to yield hydrogen, viz.

$$e' + H_2O \longrightarrow \tfrac{1}{2}H_2 + OH^-$$

Examples of reduction of water are to be found in the evolution of hydrogen by the action of $[Co(CN)_6]^{4-}$ and Ce^{3+} from aqueous solutions of these ions.

Platzman and Franck have produced spectroscopic evidence, by studying the U.V. spectra of halogen ions in aqueous solutions, which were interpreted as indicating the removal of an electron from the halogen ion to a bound state partly on the halogen and partly on the surrounding solvent molecules. The removal of an electron from a reducing agent to the solvent in most cases is considered as difficult and requiring too great an activation energy. From these considerations this hypothesis would appear to be unacceptable in aqueous media, but in nonaqueous media it may provide an easier if not the only path by which electron transfer could proceed.

Grossman and Garner (20) have studied the electron transfer reaction between $[Co(NH_3)_6]^{2+}$ and $[Co(NH_3)_6]^{3+}$ in liquid ammonia solutions. Although they say their results are not reproducible due probably to catalytic quantities of oxygen being present, they consider that the reaction proceeds faster in liquid ammonia than in aqueous ammonia. These workers claim that if the enhanced rate is real it may be due to the unusual behaviour of the electron in the particular solvent used. The difference in dielectric constant has probably little influence on the rate in the light of evidence produced by Cohen, Sullivan, Amis and Hindeman (21). If in this case an electron is solvated it would most certainly provide an easier path for electron transfer than if it is necessary to form a bridged activated complex, however it is also quite probable that to some degree both mechanisms would apply in this particular case.

F. Application of the Ligand Field Theory to the Electron Transfer.

In considering electron transfer reactions we are interested in the effects brought about by the electron pairs on the ligand rather than by the electrostatic bonds in the complex compounds being investigated. Consequently it would be more advantageous to apply the Ligand Field Theory as proposed by Nyholm (22), rather than the Crystal Field Theory in order to explain the electron transfer reactions.

In the case of no applied field an electron in a "d" orbital can exist in any one of 5 degenerate d energy levels, viz., dxy, dyz, dxz, dz^2, dx^2-y^2, the former three being directed along the diagonals between the x, y and z axes, while the latter two are directed along the x, y and z (orthogonal axes). In a cubic field as is obtained with octahedral arrangement of ligands the orbitals are split into two discrete energy levels consisting of a doubly degenerate upper energy level and a lower triply degenerate level. Square planar arrangement of ligand molecules imposes an electron component on the cubic field and the energies are split into two lower doublets and an upper singlet.

As electrons are added to the orbitals under the influence of a cubic field with octahedral symmetry they will first occupy the lower d orbitals, viz., dxy, dyz, dxz, or d_ε orbitals when the fourth electron is introduced it will go into the upper energy levels, viz., the d_γ orbitals or will move into the lower d_ε orbitals giving spin pairing. As to which of the two cases will result depends on the energy separation of the doubly and triply degenerate states.

If the electron moves into the upper d_γ orbitals in preference to spin pairing with those in the d_ε orbitals the state corresponding to Pauling's "ionic" bonds will be formed, while if spin pairing of the electrons results by movement into the lower d_ε orbitals the so called "covalent" compounds of Pauling will be formed.

Orgel (23) suggests that a very important factor in field splitting of energy levels is to be found in the polarizability of the ligand which will of course depend on a high positive charge on the metal ion, a low electronegativity of the ligand atom and the extent of bonding between metal and ligand. The greater the polarizability the greater will be the ligand field and hence the smaller the ionic radius of the metal ion.

The energy required for direct electron transfer between di- and tri-valent ions is also given by Orgel (23) as

$$3\left[K_{II} + K_{III}\right]\left[r_{II} - r_{III}\right]^2$$

where "K" represents the force constants of the metal ligand bonds and "r" represents the radius of the metal ion. In applying the Frank-Condon Principle, which demands the electron transfer via an intermediate transition state, the energy for the electron-transfer reaction becomes about one-quarter of the amount needed for direct electron transfer since the distances r_{II} and r_{III} are now average distances.

The rate of the electron transfer process will depend on the difference in ionic radii, being greater as the term $(r_{II} - r_{III})$ becomes smaller. The value of this term will depend on the orbital from which the electron is transferring. The $(r_{II} - r_{III})$ term will be greater if the electron is in an antibonding orbital, e.g., in the d_γ orbitals.

Let us now consider the ferrous-ferric exchange. In this case the electron transfer will be rapid whether the ions are spin paired or spin free. For example, in the spin free state

$$Fe^{*2+}(d_\varepsilon)^4(d_\gamma)^2 + Fe^{3+}(d_\varepsilon)^3(d_\gamma)^2 \longrightarrow Fe^{*3+}(d_\varepsilon)^3(d_\gamma)^2 + Fe^{2+}(d_\varepsilon)^4(d_\gamma)^2$$

or in the spin paired state

$$\overset{*}{Fe}{}^{2+}(d_\varepsilon)^6 + Fe^{3+}(d_\varepsilon)^5 \longrightarrow \overset{*}{Fe}{}^{3+}(d_\varepsilon)^5 + Fe^{2+}(d_\varepsilon)^6$$

since the transferring electron is from one of the lower energy level (bonding) orbitals.

In the case of the chromous-chromic electron transfer reaction the rate will be much slower since the transferring electron is from one of the upper energy level (antibonding) orbitals, e.g.,

$$\overset{*}{Cr}{}^{2+}(d_\varepsilon)^3(d_\gamma)^1 + Cr^{3+}(d_\varepsilon)^3 \longrightarrow \overset{*}{Cr}{}^{3+}(d_\varepsilon)^3 + Cr^{2+}(d_\varepsilon)^3(d_\gamma)^1$$

The cobaltous-cobaltic exchange should proceed relatively slowly since this is also a transfer of an electron from one of the (d_γ) orbitals. However here there is also the problem of spin forbidden transitions, since not only is an electron transferred, but a rearrangement of the other electrons present is also necessary.

Taube et al. (24) in working with cobaltic ions in an aqueous perchlorate media found a rapid exchange of water ligand molecules, which is unexpected in view of the above discussion of the cobaltous-cobaltic exchange and since also the chromic ion undergoes a very slow exchange of water ligand molecules with solvent. They have suggested that this rapid exchange is probably due to the fact that water has a relatively low ligand field strength. This would result in the cobaltic ion having an energy value for the spin free state that was relatively close to the ground state or spin paired form. It is suggested that a difference of 4 kcals would result in approximately 99.9% of the cobaltic ion being in the dia-magnetic or ground state. The inference is that the rapid exchange may proceed if the diamagnetic cobaltic ion undergoes a rearrangement of electrons to give the spin free state which could then undergo a more rapid exchange with cobaltous ions since no violation of spin selection rules would result from the electron transfer. This can only be so provided the field strength of the ligand is not too strong.

The Ligand Field Theory does not in any way rule out Taube's suggested mechanism of a bridged activated complex being formed. Let us examine the chromous-chromic exchange in the presence of chloride ions. Since the electron transfer takes place from a (dz^2) orbital on the chromous ion to one on the chromic ion, we can neglect all other d electrons. The chloride ion is, before the electron transfer process begins, found in an equilibrium position with the chromic ion.

As a symmetrical complex is formed the (dz^2) orbitals become intermediate and the electron can be considered as being in a state of resonance between the two. The chloride ion can then proceed forward and so complete the electron transfer process or it can move backwards to its original position. The movement of the electron will always be opposite to that of the chloride ion. This explains why in many cases, where bridged activated complexes are formed, the apparent result is one of atom transfer.

It is interesting to examine the possibility of a difference in electron transfer rate resulting from the use of cis or trans isomers. The effect on which of the two isomers will exchange at the faster rate will of course depend on the particular ligands one is concerned with. Let us consider the case of $[Cr(NH_3)(H_2O)_4Cl]^{2+}$ ion in which the ligand ammonia has a greater field strength than the ligand water and hence destabilizes the (dz^2) orbital when in the trans position but has little effect on it when in the cis position. Therefore if electron transfer is assumed to go via a bridging mechanism, the reaction will be represented as follows:

$$[Cr(NH_3)Cl(H_2O)_4]^{2+} + [Cr(H_2O)_6]^{2+} \longrightarrow [Cr(NH_3)(H_2O)_5]^{2+}$$

$$+ [Cr(H_2O)_5Cl]^{2+}$$

and the trans isomer would be expected to exchange more slowly than the cis form.

Taube's mechanism for explaining the fast exchange between cobaltic and cobaltous ions has already been discussed and we shall now consider other mechanisms by which the reduction of cobaltic ion can take place, viz.,

(1) $Co(d_{\varepsilon})^6 + e^- \longrightarrow Co(d_{\varepsilon})^5(d_{\gamma})^2$

and (2) $Co(d_{\varepsilon})^6 + e^- \longrightarrow Co(d_{\varepsilon})^6(d_{\gamma})^1$

The first of these reactions should be a rather slow reaction due to the change in spin multiplicity and to the change in bond length due to the transfer of the two electrons to the (d_{γ}) orbitals. From a consideration of spin selection rules the second mechanism is the more favoured, however a great amount of energy is needed to promote the spin free cobaltous state to the excited spin paired state. If the cobaltic ion is in a spin paired state and the cobaltous ion is in a relatively spin free state the first mechanism would be preferred, however if both ions are in the spin paired states then the second mechanism should predominate. There will of course be many reactions which are intermediate to the above two.

The electron transfer reaction between cobaltous and cobaltic tetraphenyl-porphines in benzene as solvent has been found to occur rapidly by Dorough and Dodson (25). In order to explain the rate of the reaction they have suggested that pairing of electrons in the d orbitals of the cobaltous complex takes place, this is supported by magnetic data indicating that one unpaired electron is present in the complex. Thus at least one of the 3d orbitals could be used for cobalt-nitrogen bonding, e.g., dsp^2 hybridization giving square planar symmetry to the ligand about the central metal ion. They suggest that the odd electron in this case is also probably promoted to an outer orbital thus allowing d^2sp^3 hybridization, this being the favoured structure for energy reasons. They consider the cobaltic complex as octahedral since there are no unpaired electrons present. Both structures are thus similar and this facilitates the electron transfer process and a fast reaction results.

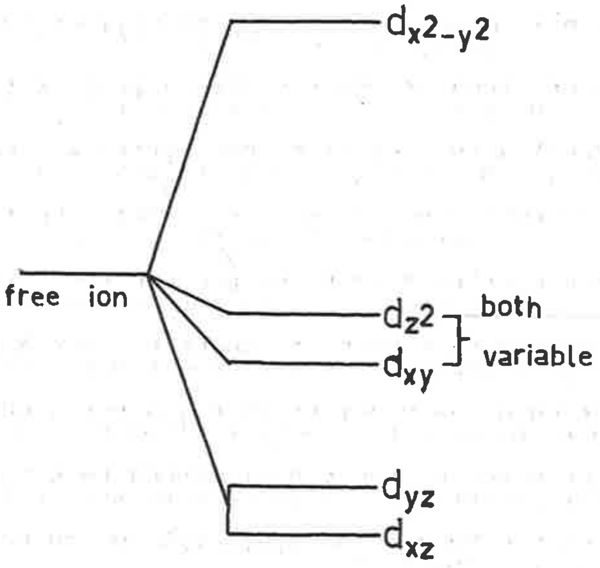


Fig. 1.4 Splitting of energy levels of 3d orbitals in cobalt-II-tetraphenylporphine

Let us now examine this reaction in terms of the Ligand Field Theory, since cobaltous-cobaltic exchanges are normally expected to be slow in terms of this theory. Since there is only one unpaired electron in the cobaltous complex it would indicate that there is a spin pairing which is the result of a square planar arrangement of the ligand molecule, which has a strong ligand field. If this is so, then the splitting of the energy levels and arrangement of electrons would be as in Fig. 1.4. Solvent molecules arranged along the dz^2 axis would tend to destabilize this orbital with the result that its energy value would increase and more separation between the dxy and dz^2 orbitals would result. In any case the bonds resulting here would be quite extended in space.

The cobaltic complex can probably be considered as having octahedral symmetry with solvent molecules bonded along the direction of the dz^2 orbital. Extension in space of these bonds would tend to stabilize the dz^2 orbitals thus lowering its energy value closer to that for the dz^2 of the cobaltous complex. Since the dz^2 orbitals then have energy values close to the same value a fast electron transfer might be expected, also in this case spin selection rules will not be violated.

If both complexes had octahedral symmetry it would necessitate promotion of the odd electron in the cobaltous complex to the 4s orbital in order that the electron transfer could proceed rapidly. If this electron were not promoted, and octahedral symmetry was obtained by hybridization of a 4p and a 4d orbital perpendicular to the $3d4s4p^2$ square plane, the electron transfer should be slow as it would be a d_γ electron exchange, which is a slow process (22).

G. Experimental Methods

So far only the mechanisms by which the electron transfer can take place have been discussed; it should therefore prove of interest to consider the methods by which one can study such reactions.

Tracer techniques have been the most commonly used method of study and this method has been outlined in the introduction of this thesis. The results obtained are generally analysed by applying the McKay (30) equation, i.e.,

$$\ln (1 - F) = - R \frac{(a + b)}{ab} t$$

where F= ratio of activity at time "t" of the originally inactive form to its activity at infinite time

"a" and "b" represent the analytical concentrations of the two oxidation states of the element being considered.

The above equation is true if there is neither irreversible oxidation or reduction occurring during the electron exchange process. If this is not the case then certain corrections have to be made. The corrections necessary are dealt with in Part II.

Two other methods have been applied to the study of electron transfer reactions. The first of these makes use of optical isomerism. The method is essentially to isolate an optical isomer of a non-labile complex of one of the valence states of an element, mix this with a labile complex of the element in a different oxidation state and measure the change in optical activity with time. During the electron transfer process there is a lowering of optical activity due to conversion to a racemic mixture. The rate of lowering of optical activity is proportional to the rate of the electron transfer process. It is a method which has a rather limited application, however it is a method which, provided optical isomers do exist and can be isolated, is quite useful. The method requires much less in the way of handling samples than does the previous technique.

The use of optical isomers as a means of studying electron transfer reactions has been applied by Dwyer (31) et al. in the study of the electron exchange between tris-(2.2′-dipyridyl)-osmium-(II) and tris-(2.2′-dipyridyl)-osmium-(III).

The third method makes use of nuclear magnetic resonance measurements. The electron transfer process has been found to have a line broadening effect on the N.M.R. spectra. This method has been applied to the study of Cu^{++}-Cu^{+} (32) exchange in the presence of hydrochloric acid solution. It is a method which is suitable for the study of very fast reactions which are not amenable to study by other techniques.

H. Conclusions

Although much evidence has been obtained in the field of electron transfer reactions, much more is still needed before any general mechanism can be suggested. Evidence that has been produced in favour of a particular mechanism has often in no way ruled out the possibility of other mechanisms applying. Indeed it is probably true to say that the mechanism which applies to any particular example will probably depend on the particular reaction being investigated, and this mechanism may be different from that for another reaction, or for the same pair of ions under different conditions.

REFERENCES

1. F. Basolo and R. G. Pearson, Mechanisms of Inorganic Reactions (Wiley), Chapter 7.
2. W. F. Libby, J.Phys.Chem. 56, 863 (1952).
3. E. U. Condon, Amer.J.Phys. 15, 365 (1947).
4. J. Weiss, Proc.Roy.Soc.London, A 222, 128 (1954).
5. R. J. Marcus, B. J. Zwolinski and H. Eyring, J.Phys.Chem., 58, 432 (1954).
6. R. Platzman and J. Franck, ZPhysik., 138, 411 (1954).
7. C. Zener, Phys.Rev. 82, 403 (1951).
8. H. Taube, H. Myers and R. L. Rich, J.Amer.Chem.Soc. 75, 4118 (1953).
9. H. Taube and H. Myers, Ibid. 76, 2103 (1954).
10. H. Taube, Ibid. 77, 4481 (1955).
11. H. Taube and E. L. King, Ibid. 76, 4053 (1954).
12. J. Hudis and R. W. Dodson, Ibid. 78, 911 (1956).
13. W. L. Reynolds and R. Lumry, J. Chem.Phys. 23, 2560 (1955).
14. F. S. Dainton, J.Chem.Soc. 1533 (1952).
15. M. Anbar and H. Taube, J.Amer.Chem.Soc. 76, 6243 (1954).
16. M. Anbar and H. Taube, Ibid. 77, 2993 (1955).
17. H. C. Hornig, G. L. Zimmerman and W. F. Libby, J.Amer.Chem.Soc. 72, 3800 (1950).
18. J. C. Sheppard and A. C. Wahl, J.Amer.Chem.Soc. 75, 5134 (1953); 79, 1020 (1957).

19. J. Kaplan and C. Kittel, J.Chem.Phys. 21, 1429 (1953).

20. J. J. Grossman and C. S. Garner, J.Chem.Phys. 28, 268 (1958).

21. D. Cohen et al., J.Amer.Chem.Soc. 78, 1543 (1956).

22. R. S. Nyholm, Report of 10th Solvay Council, Brussels (1956), p. 225.

23. L. E. Orgel, Ibid. p. 289.

24. H. L. Friedman, H. Taube and J. P. Hunt, J.Chem.Phys. 18, 757 (1950).

25. G. D. Dorough and R. W. Dodson, Quarterly Progress Reports, Brookhaven National Laboratory, July-Sept. BNL 132 (5-11) 68.

26. A. M. Armstrong and J. Halpen, Canad.J.Chem. 35, 1020 (1957).

27. F. Haber and J. Weiss, Proc.Roy.Soc.London, 332 (1934).

28. L. Michaelis, Trans.Electrochem.Soc. 71, 107 (1937).

29. W.C.E. Higginson and J. W. Marshall, J.Chem.Soc. 447 (1957).

30. H. A. C. McKay, Nature 142, 997 (1938).

31. F. P. Dwyer and E. C. Gyarfas, Nature 166, 481 (1950).

32. H. M. McConnell and H. E. Weaver, J.Chem.Phys. 25, 307 (1956).

33. H. C. Hornig and W. F. Libby, J.Phys.Chem. 56, 869 (1952).

34. W. F. Libby, J.Amer.Chem.Soc. 62, 1930 (1940).

35. K. J. Laidler, Canad.J.Chem. 37, 138 (1959).

36. A. M. Zwickel and H. Taube, Discuss. Faraday Soc. 29, 42 (1960).

37. H. Taube, Canad.J.Chem. 37, 129 (1959).

38. Fraser, Sebera and H. Taube, J.Amer.Chem.Soc. 81, 2906 (1959).

39. George and Irvine, J.Chem.Soc. (1954) 587.

40. D. R. Stranks, Discuss. Faraday Soc. 29, 73, (1960).

41. B. R. Baker, F. Basolo and H. M. Neumann, J.Phys.Chem. 63, 371 (1959).

PART II

Electron Transfer Reactions between Neutral Molecules

Chapter 2. The Electron Transfer Reaction between bis(acetylacetonato)cobalt(II) and tris(acetylacetonato) cobalt (III)

Chapter 3. The Electron Transfer Reaction between Cobalt(II) and Cobalt(II) N-phenylsalicylideneiminate Type Complexes.

CHAPTER 2.

The Electron Transfer Reaction between bis(acetylacetonato) Cobalt (II) and tris(acetylacetonato) Cobalt(III).

A. Introduction

Stranks (36) has prepared tables which provide an excellent summary of much of the information available on electron transfer reactions. It can be seen from these tables that most of the electron transfer reactions studied have been between ions, however in a few cases (37) (38) reactions between anion and a neutral molecule have been studied. Further the solvent most extensively used in the study of such reactions has been water or D_2O and only in relatively few cases (37) (38) have non-aqueous solvents been employed.

Since the acetylacetonato complexes of cobalt (II) and cobalt (III) were easily prepared and since both were neutral complexes it was decided that it would be of considerable interest to study the electron transfer reaction between these two compounds. It was at the time felt that if the energy barrier to the electron transfer was as Marcus et al (5) predicted, due to the charge on the reacting species, then no such barrier should exist in this case and the reaction should proceed more rapidly than reactions involving charged cobalt species.

Since the cobalt (II) and cobalt (III) complexes with acetylacetone were neutral compounds their solubility in aqueous media was rather limited and it was therefore necessary to carry out the electron transfer reactions in organic solvents in which the complexes were soluble. Preliminary experiments using toluene as solvent showed that electron transfer was immeasurably slow at room temperature but proceeded at a measurable rate at 100°C. The need for such a high reaction temperature limited the choice of alternative solvents to those having appropriately high boiling points. Toluene, acetylacetone and pyridine were therefore used as reaction media. The use of three different solvents for the reaction also allowed a rather limited comparison of the effect of the solvent on the electron transfer reaction.

It should be pointed out that the accumulation of a large volume of data for the study of the electron transfer reaction between the acetylacetonato complexes of cobalt (II) and cobalt (III) was somewhat hindered when it was found that the cobalt (II) complex was not stable in the presence of oxygen. The instability required the development and use of more specialized experimental techniques and apparatus than those at first used. The final experimental techniques used are described in Chapter 6 and were designed to exclude oxygen completely from the reaction mixture. Furthermore, due to the instability of the cobalt (II) complex, there was a need to analyse all samples taken for cobalt content in both the cobalt (II) and cobalt (III) fractions. Thus the experimental work required to fully complete a kinetic run occupied a number of days and made the gathering of data a somewhat slow process.

B. The General Exchange Reaction.

Before proceeding to a discussion of the particular electron transfer reactions studied one should consider the general exchange reaction. McKay(2) in 1938 derived for the general reaction

$$CX + BX^{*} \rightleftharpoons CX^{*} + BX \qquad 2.1$$

an equation of the form

$$R = \frac{-a.b}{a+b} \cdot \frac{\ln(1-F)}{t} \qquad 2.2$$

where R is the rate of reaction; "a" and "b" are the molar concentrations of the species CX and BX respectively; * refers to a radioactively labelled atom X and F is the fraction of the exchange at time "t"

The value of F is given by

$$F = \frac{\left[{}^{A_t}/_{M_t} - {}^{A_o}/_{M_o}\right]}{\left[{}^{A_\infty}/_{M_\infty} - {}^{A_o}/_{M_o}\right]} \qquad 2.3$$

where A is the molar quantity of X^{*} transferred to CX and M is the molar concentrations of $CX + CX^{*}$. The subscript "t" shown in the equation indicates the time at which the observation is made.

The McKay equation (2.2) given above was derived for a system in which there were no irreversible chemical changes accompanying the reversable radioactive tracer exchange. However Leuhr et al (1) have derived an equation for the case when an irreversible change accompanies the exchange of radioactive tracer. They have shown that in non-stable systems it is important as to which species is used for the calculation of the exchange rate. Hence if the increasing fraction, say CX, is used for the calculation of the rate of reaction then an allowance has to be made for the quantity of BX converted to CX at the time the observation is made. The rate equation then becomes

$$-\ln (1-F) = Rt\frac{(a+b)}{ab} - \ln \frac{a(b - \rho t)}{b(a + \rho t)} \qquad 2.4$$

where ρ t is the total concentration of BX converted into CX at time "t". However their calculations also show that providing the decreasing fraction is the one used for the rate determination then equation 2.4 can be simplified, since there is no need to allow for the decrease in concentration of the species BX. The rate expression then becomes the same as for the McKay equation (2.2)

C. Toluene as Solvent

Toluene was chosen as a solvent for the electron transfer study since, apart from satisfying the requirements given in section A, it was not expected to participate in the electron transfer mechanism to any appreciable extent. The reaction between cobalt (II) and cobalt (III) acetylacetonato complexes in toluene would necessitate the exchange of ligand following the electron transfer reaction e.g.

$$\overset{*}{Co}^{III}(acac)_3 + Co(acac)_2 \rightleftharpoons \overset{*}{Co}^{II}(acac)_2 + Co^{III}(acac)_3$$

Although the exchange of ligand would occur during the overall mechanism of the reaction it is still preferable to classify the reaction as an electron transfer and not as a ligand exchange reaction. Electron transfer reactions can be placed into two broad classes (19) e.g. those in which there is no change in the coordination shells of the metal ions following the electron transfer and those in which there is a change in the coordination shell. The former are the so called "outer - sphere" reactions and the latter are the "inner - sphere" reactions. Thus in the case being considered, where the acetylacetone ligand is exchanged following the electron transfer, we may classify the exchange as an "inner - sphere" electron transfer reaction.

Experimental Method

The techniques employed for the study of the electron transfer reactions are given in detail in Chapter 6 however generally the method was to dissolve the cobalt complexes in the solvent and place samples of the solution in sealed glass tubes. The tubes were immersed in a thermostat for various time intervals, after which they were removed and the contents separated chromatographically on an alumina column. The separated cobalt (II) and cobalt (III) fractions were then analysed for cobalt concentration and for radio-activity and the values obtained were used for the determination of the reaction kinetics.

A check on the possibility of the electron transfer being catalytically induced by the separation proceedure was made. It was found, for samples taken at the start time of the reaction, that the quantity of exchange was zero and hence the reaction was not induced by separation.

Thermal Stability

Since the reactions were carried out at temperatures of approximately 100°C the thermal stability of the systems investigated should be considered. Charles and Pawlikowski (3) have produced evidence of the thermal decomposition of metal acetylacetonates at temperatures of 191°C. They found that both the cobalt (II) and cobalt (III) acetylacetonato complexes underwent decomposition, the

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* indicates a labelled atom and (acac) represents the acetylacetone ligand

latter being the more rapid. Since it was anticipated that the rate determinations should be based on measurements of the cobalt (II) complex and in view of equation 2.4 it was only necessary to determine if any of the cobalt (III) complex was irreversibly reduced to the cobalt (II) complex.

The study of the thermal reduction of the cobalt (III) acetylacetonato complex was carried out under reduced pressure and with complete removal of oxygen in order that the reduction reaction would be measured in the absence of any oxidation agency. The actual quantity of complex used for the determinations was not weighed accurately, however an approximately 0.01 molar solution of the complex in toluene was formed. The ratio of the counts in the cobalt (II) and cobalt (III) fractions after separation was used to obtain the value of the percentage reduction (R%) shown in graphical form in (Fig. 2.8).

The correction factor of equation 2.4 can be shown to be given by

$$\ln. \frac{x(100 - y)}{(100x + y)} \qquad 2.5$$

where $x = a/_b$ and y is the percentage reduction of BX at time "t". The correction factor approximates to zero provided y is small. In any case the slow reduction that was found to take place was such that any correction necessary was within the experimental error of ± 5% for the electron transfer measurements and hence could be neglected.

Oxidation of Cobalt (II) Complex

During the study of the electron transfer reaction it was found that there was in most cases an irreversible oxidation of the cobalt (II) acetylacetonato complex. (see Appendix A, Tables 17 to 25). The oxidation in toluene was in most cases only small, however it was necessary to know the quantity for the calculation of the value of F in equation 2.4 and thus required the determination of the cobalt present in the separated cobalt (II) and cobalt (III) fractions. Since the measurements were based on the decreasing species, e.g. the cobalt (II) complex the simplified form of equation 2.4 could be used in the calculation of the rate of reaction.

It is difficult to see what the oxidation product would be since no excess acetylacetone is present to be taken up into the structure of the cobalt complex on oxidation. It is also not readily apparent as to how the oxidation is affected since stringent precautions were taken to remove traces of oxygen from the reaction mixture. However either the precautions taken were not sufficient or the oxidation was caused by small quantities of water which may have been introduced with the solvent despite prior drying with sodium.

<u>The Rate Law</u>

The rate of the electron transfer may be expressed by the equation

$$R = k\left[Co^{II}\right]^{x}\left[Co^{III}\right]^{y} \qquad 2.6$$

where x and y are the orders of the reaction with respect to each of the species participating. If the reaction were to obey second order kinetics such that x = y = 1 then the rate of reaction would be given by

$$R = k\left[Co^{II}\right]\left[Co^{III}\right] \qquad 2.7$$

This equation is not without support since many electron transfer reactions have been found to obey second order kinetics (18).

Since the rate of the reaction will also be given by the McKay equation (2.2) as

$$R = \frac{[Co^{II}]\,[Co^{III}]}{[Co^{II}] + [Co^{III}]} \quad \frac{\ln 2}{t_{\frac{1}{2}}} \qquad 2.8$$

when the half life is substituted for the value of "t", we can equate the two values of equations 2.7 and 2.8 and obtain the equation

$$\frac{I}{[Co^{II}] + [Co^{III}]} = \frac{k\, t_{\frac{1}{2}}}{\ln 2} \qquad 2.9$$

Hence plotting the reciprocal of the total concentration of cobalt species against the half life of the reaction should give a linear relationship, the slope of the line having the value $\frac{k}{\ln 2}$. The relationship expressed by equation 2.9 will only be so provided

(1) That the solvent does not participate in the reaction mechanism

and (2) That the reaction obeys second order kinetics being first order with respect to each component.

since it is only under these conditions that the equation 2.7 can apply to the reaction.

The kinetics of the electron transfer reaction between cobalt (II) and cobalt (III) acetylacetonato complexes in toluene as solvent have been studied at a temperature of 98.7° ± 0.1°C. The results obtained are given in Appendix A (Tables 17 - 22) and are represented graphically in Figs. 2.1 - 2.6. The percentage of exchange (E%) shown on the graphs was found by expressing the value of F (equation 2.3) as a percentage.

The errors in the calculated percentage of exchange (E%) are ± 5% of the values obtained for E%. These errors result from three sources,

(1) An error in counting rate of ± 1% (see p.171).

(2) An error of ± 1% in the concentration measurements, due to the limitations of the instrument used.

and (3) An estimated error, obtained from a series of separations, of ± 1% due to the separation procedure.

The graph obtained by plotting the reciprocal of the total concentrations of cobalt against the half-life of the reactions, determined from Figs. 2.1 - 2.6, is shown in Fig. 2.9. The linear relationship found is in agreement with equation 2.9 thus indicating that the reaction in toluene is first order with respect to each of the reactants, e.g. Cobalt (II) and Cobalt (III) acetylacetonato complexes. The value of k obtained from the slope of the graph was found to be 2.36 ± (7%) litre.moles^{-1}.hrs.$^{-1}$

Energy and Entropy of Activation

The electron transfer reaction was studied at temperatures other than 98.7°C (Figs. 2.10-2.12) in order to determine the activation energy for the reaction. The results found are given in Table 2.1 and

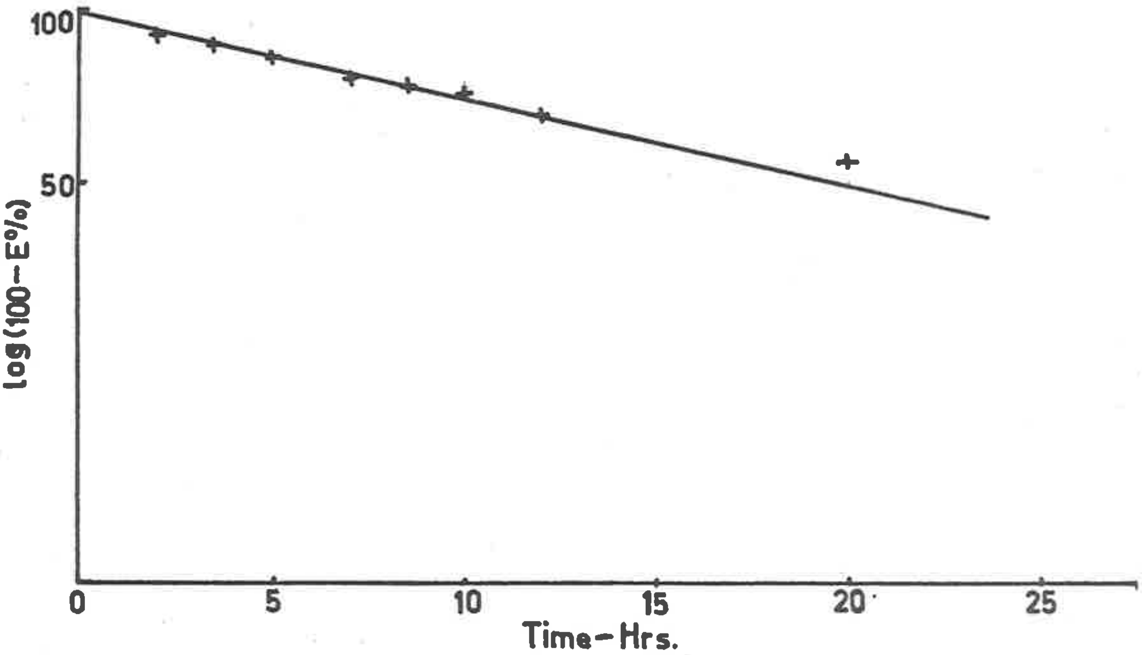

Fig.2. 1 $Co^{II}(acac)_2$- $Co^{III}(acac)_3$ electron transfer reaction in toluene at 98.7±0.1°C; Co^{II} 0.0193M & Co^{III} 0.0095M

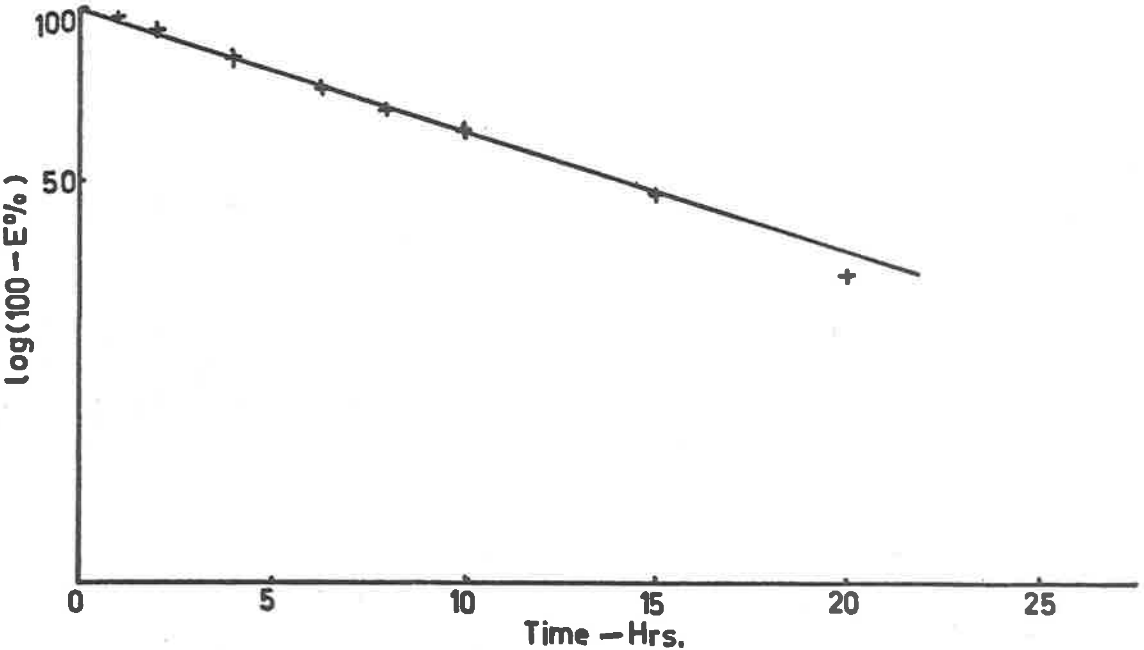

Fig.2. 2 $Co^{II}(acac)_2$- $Co^{III}(acac)_3$ electron transfer reaction in toluene at 98.7±0.1°C; Co^{II} 0.0200M & Co^{III} 0.0200M

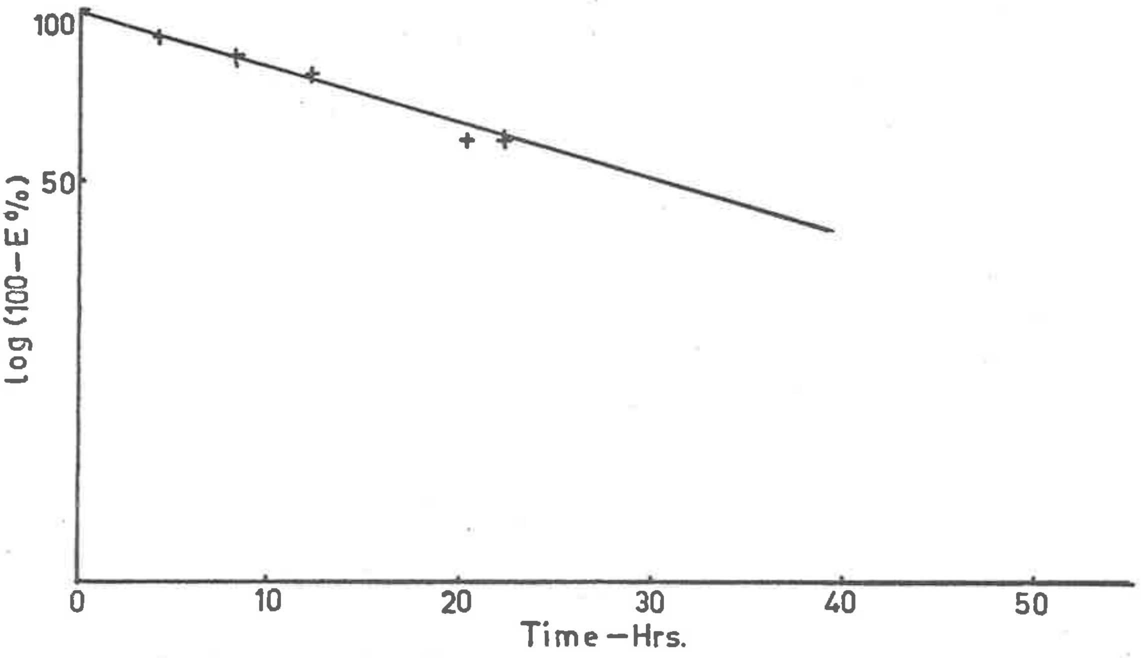

Fig.2. 3 $Co^{II}(acac)_2$- $Co^{III}(acac)_3$ electron transfer reaction in toluene at 98.7±0.1°C; Co^{II}0.0096M & Co^{III}0.0098M

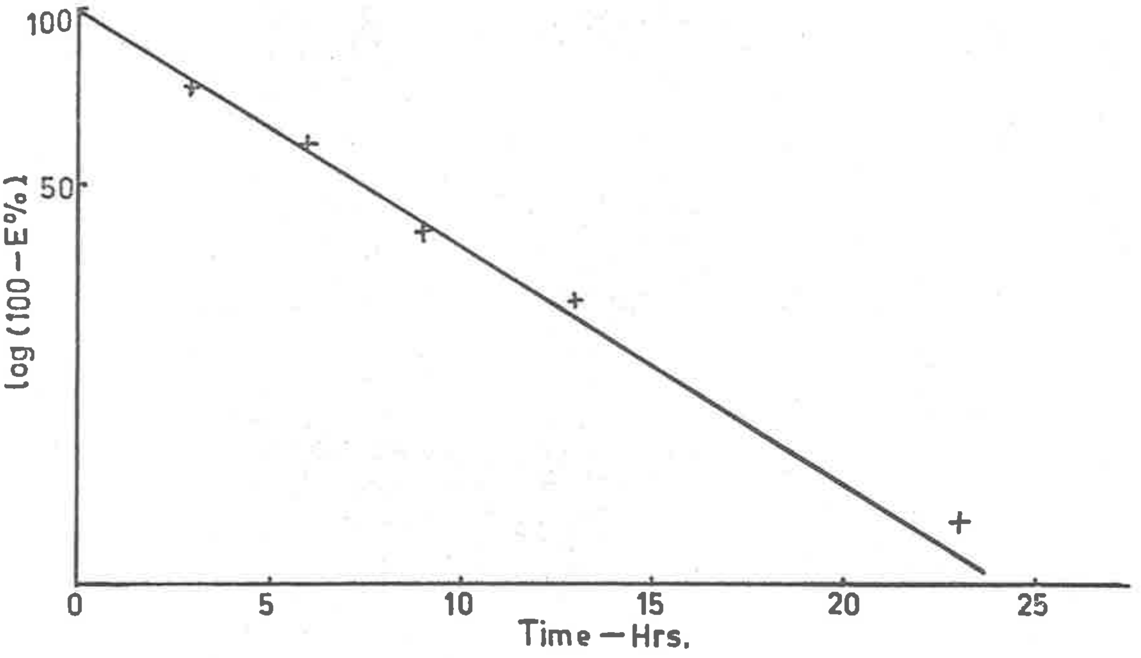

Fig.2. 4 $Co^{II}(acac)_2$- $Co^{III}(acac)_3$ electron transfer reaction in toluene at 98.7±0.1°C; Co^{II}0.0238M & Co^{III}0.0243M

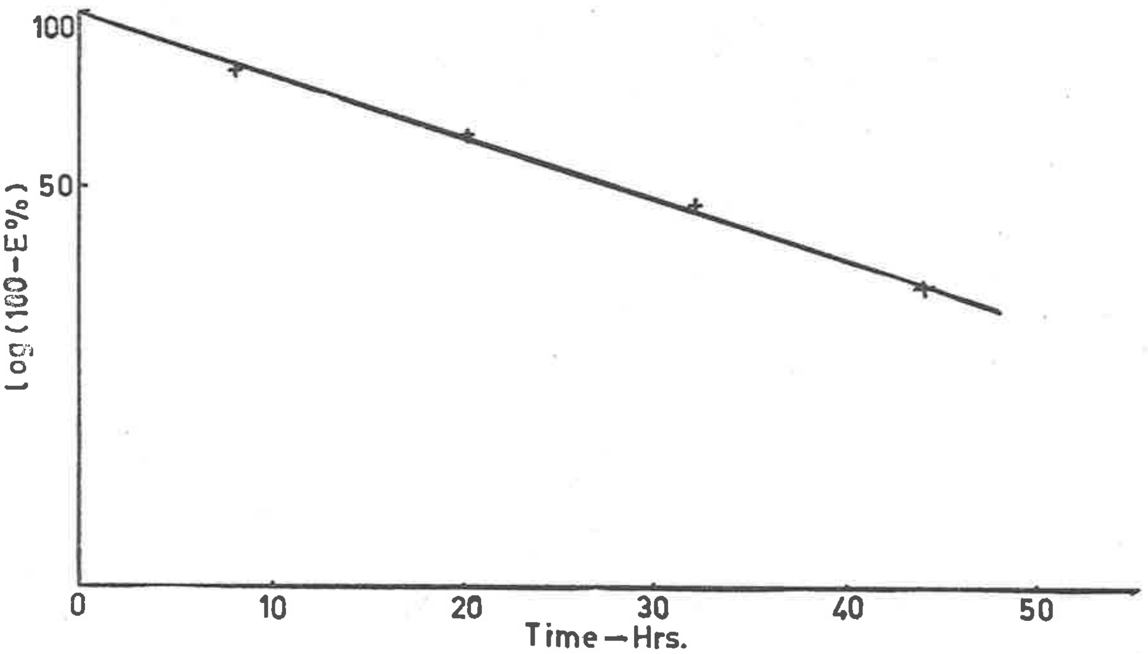

Fig.2.5 Co^{II}(acac)$_2$- Co^{III}(acac)$_3$ electron transfer reaction in toluene at 98.7±0.1°C; Co^{II}0.0092M & Co^{III}0.0103M

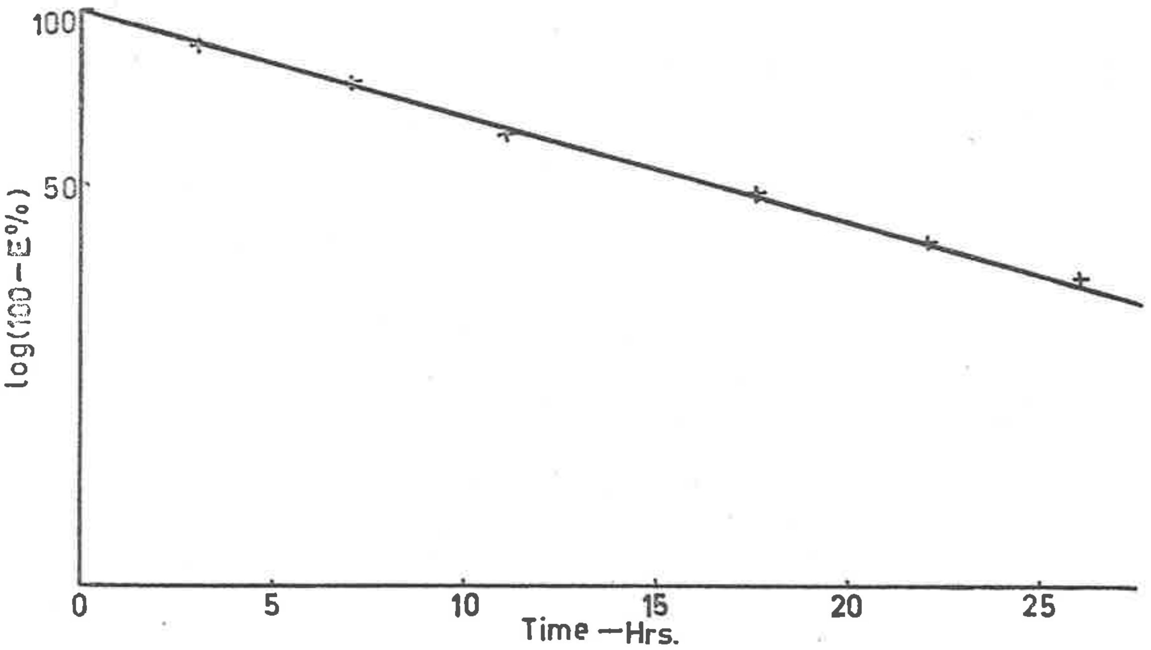

Fig.2.6 Co^{II}(acac)$_2$- Co^{III}(acac)$_3$ electron transfer reaction in toluene at 98.7±0.1°C; Co^{II}0.0190M & Co^{III}0.0195M

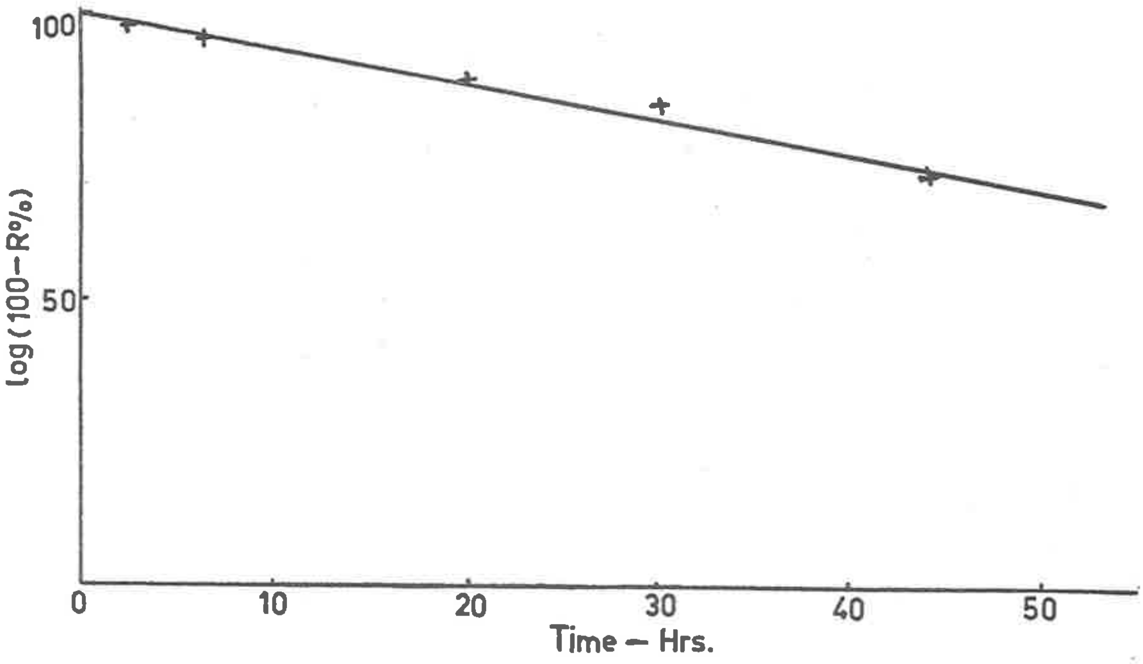

Fig.2. 7 Reduction of $Co^{III}(acac)_3$ in acetylacetone at 98.7±0.1°C

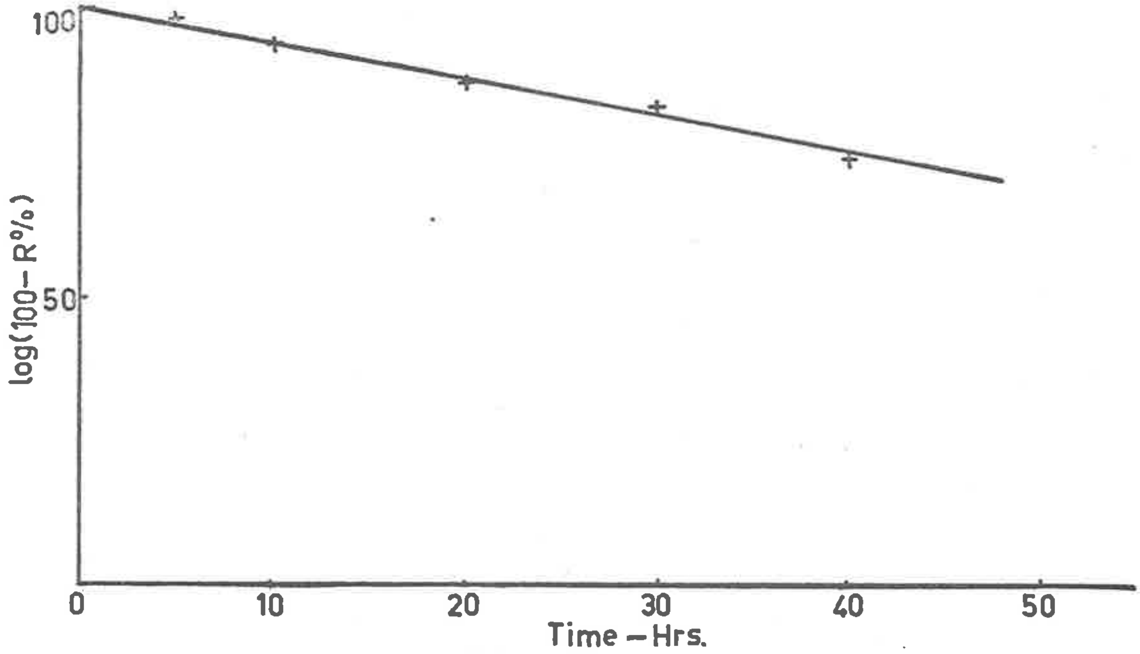

Fig.2. 8 Reduction of $Co^{III}(acac)_3$ in toluene at 98.7±0.1°C

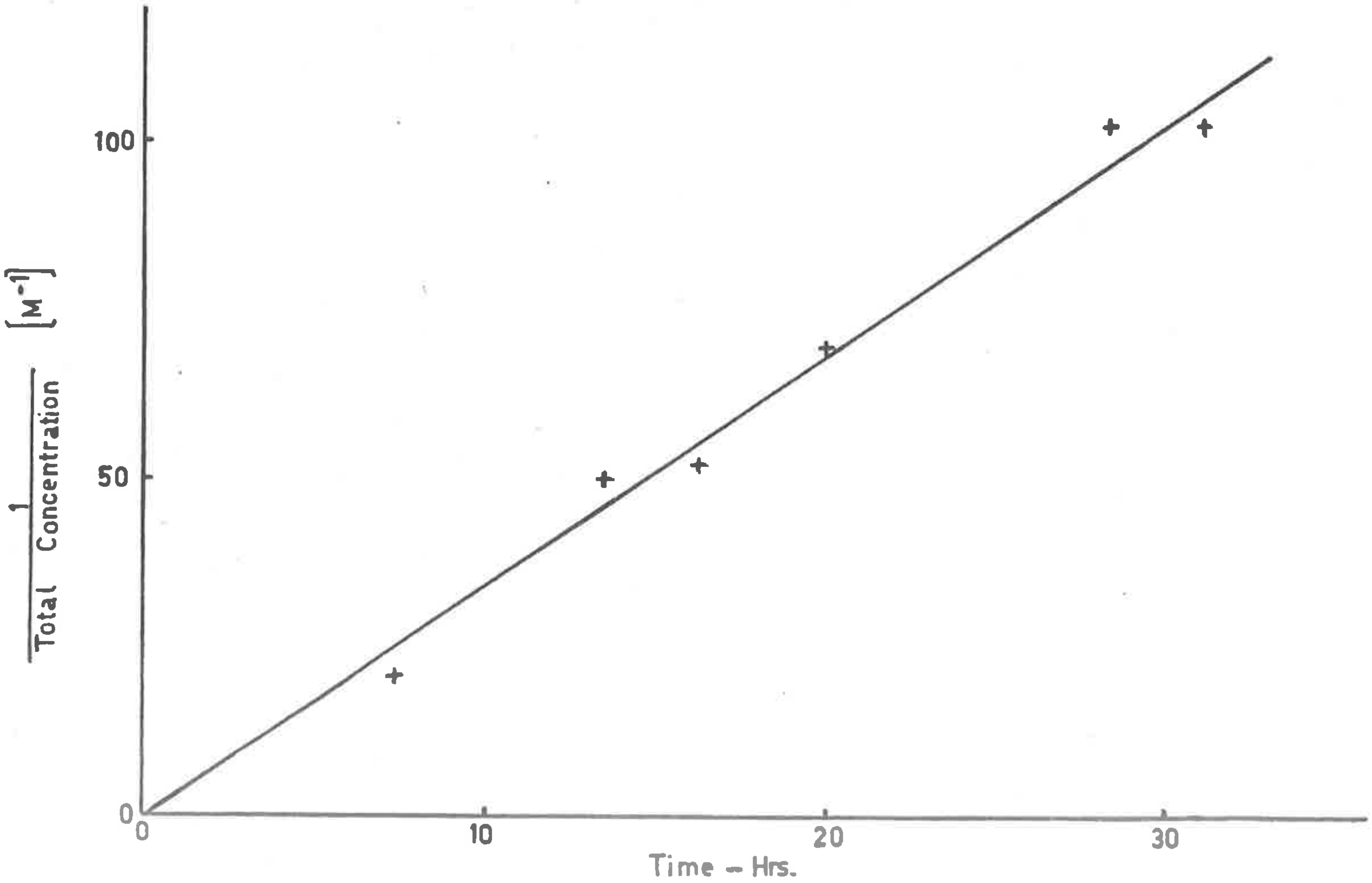

Fig.2. 9 $Co^{II}(acac)_2$- $Co^{III}(acac)_3$ electron transfer reaction in toluene at 98.7±0.1°C

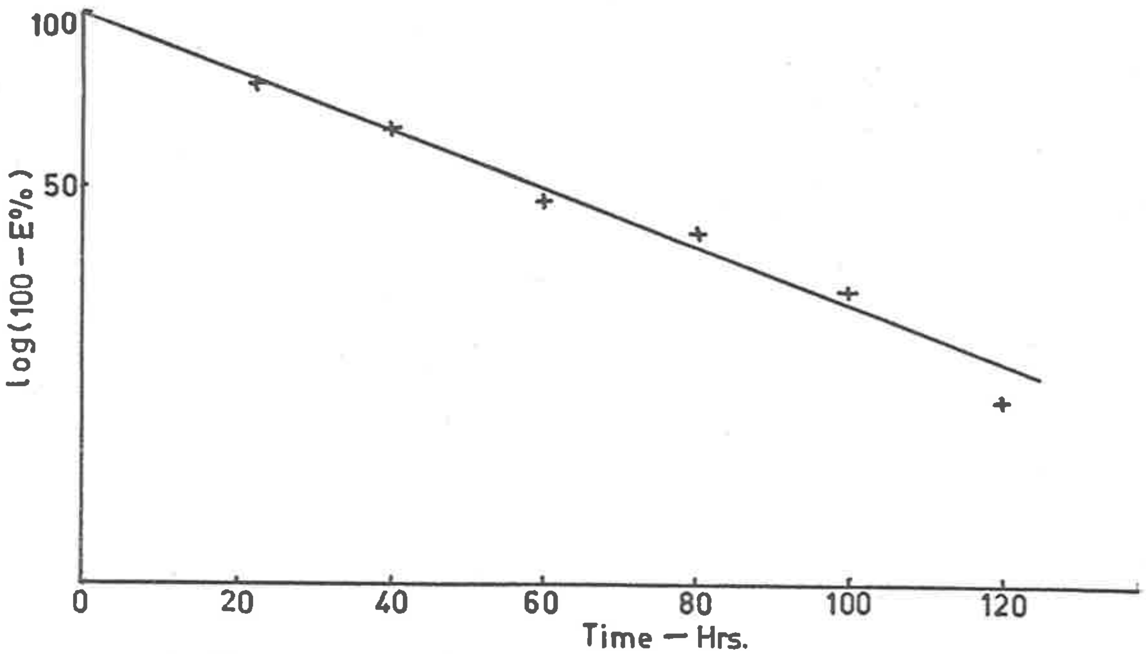

Fig.2.10 $Co^{II}(acac)_2$- $Co^{III}(acac)_3$ electron transfer reaction in toluene at 81.0±0.1°C; Co^{II} 0.5088M & Co^{III} 0.4948M

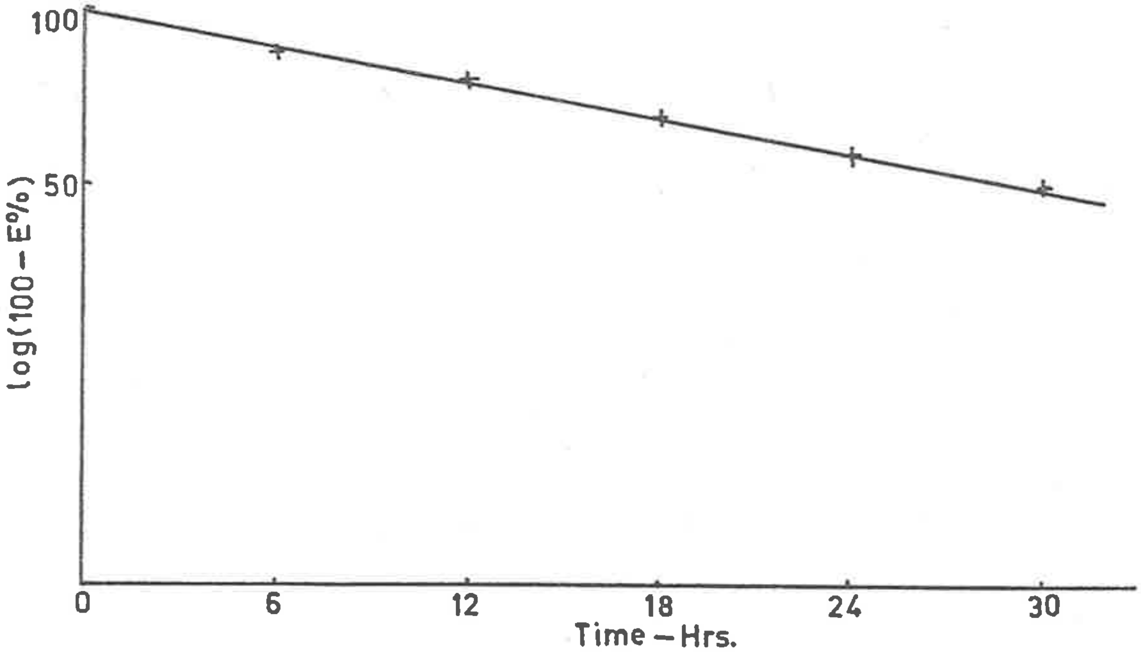

Fig.2.11 $Co^{II}(acac)_2$- $Co^{III}(acac)_3$ electron transfer reaction in toluene at 91.0±0.1°C; Co^{III} 0.0387M & Co^{II} 0.0357M

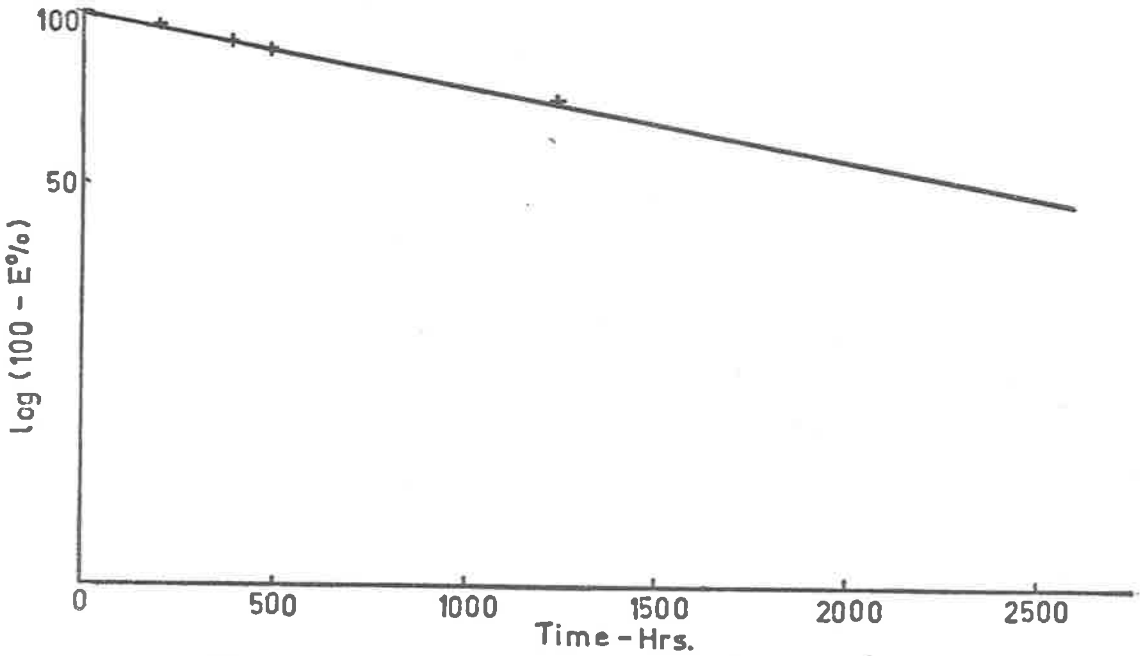

Fig.2.12 Co^{II}(acac)$_2$- Co^{III}(acac)$_3$ electron transfer reaction in toluene at 55.9±0.1°C; Co^{II}0.0357M & Co^{III}0.0387M

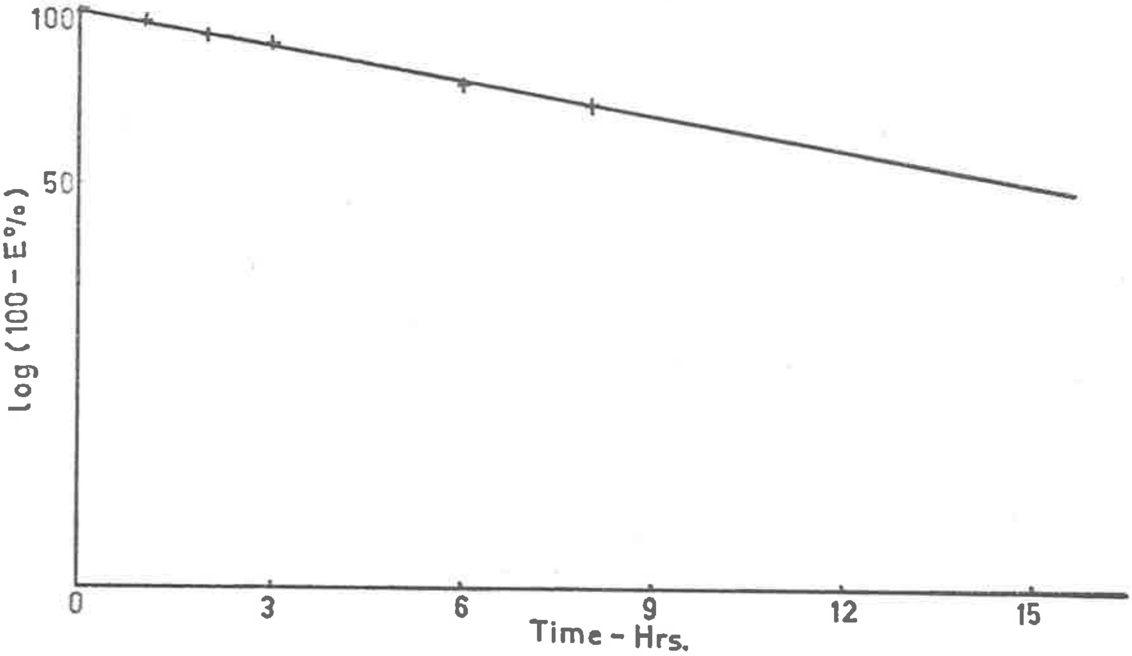

Fig.2.13 Co^{II}(acac)$_2$- Co^{III}(acac)$_3$ electron transfer reaction in pyridine at 98.7±0.1°C; Co^{II}0.0096M & Co^{III}0.0096M

the activation energy was calculated from the graph shown in Fig. 2.14. The value of the activation energy for the system was found to be 14.2 ± 2.5% k cals/mole.

TABLE 2.

Electron Transfer Reaction between bis-(Acac) Cobalt (II) and tris-(Acac) Cobalt (III) in Toluene. Variation of Half-life with Concentration and Temperature.

No	Concentrations (M)		Half-life (hrs)	k(litre moles^{-1} hrs^{-1})	Temp. °C
	Cobalt II	Cobalt III			
1	0.0193	0.0095	20.0		98.7 ± 0.1
2	0.0200	0.0200	14.5	(from Fig. 2.9)	98.7 ± 0.1
3	0.0096	0.0098	31.1	2.36 (± 7%)	98.7 ± 0.1
4	0.0238	0.0243	7.4		98.7 ± 0.1
5	0.0092	0.0103	28.3		98.7 ± 0.1
6	0.0190	0.0195	16.3		98.7 ± 0.1
7	0.0357	0.0387	2540	7.33×10^{-3}	55.9 ± 0.1
8	0.0509	0.0495	58.0	2.38×10^{-1}	81.0 ± 0.1
9	0.0357	0.0387	28.2	6.60×10^{-1}	91.0 ± 0.1

From an analysis of kinetic data of a reaction obeying second order kinetics the equation

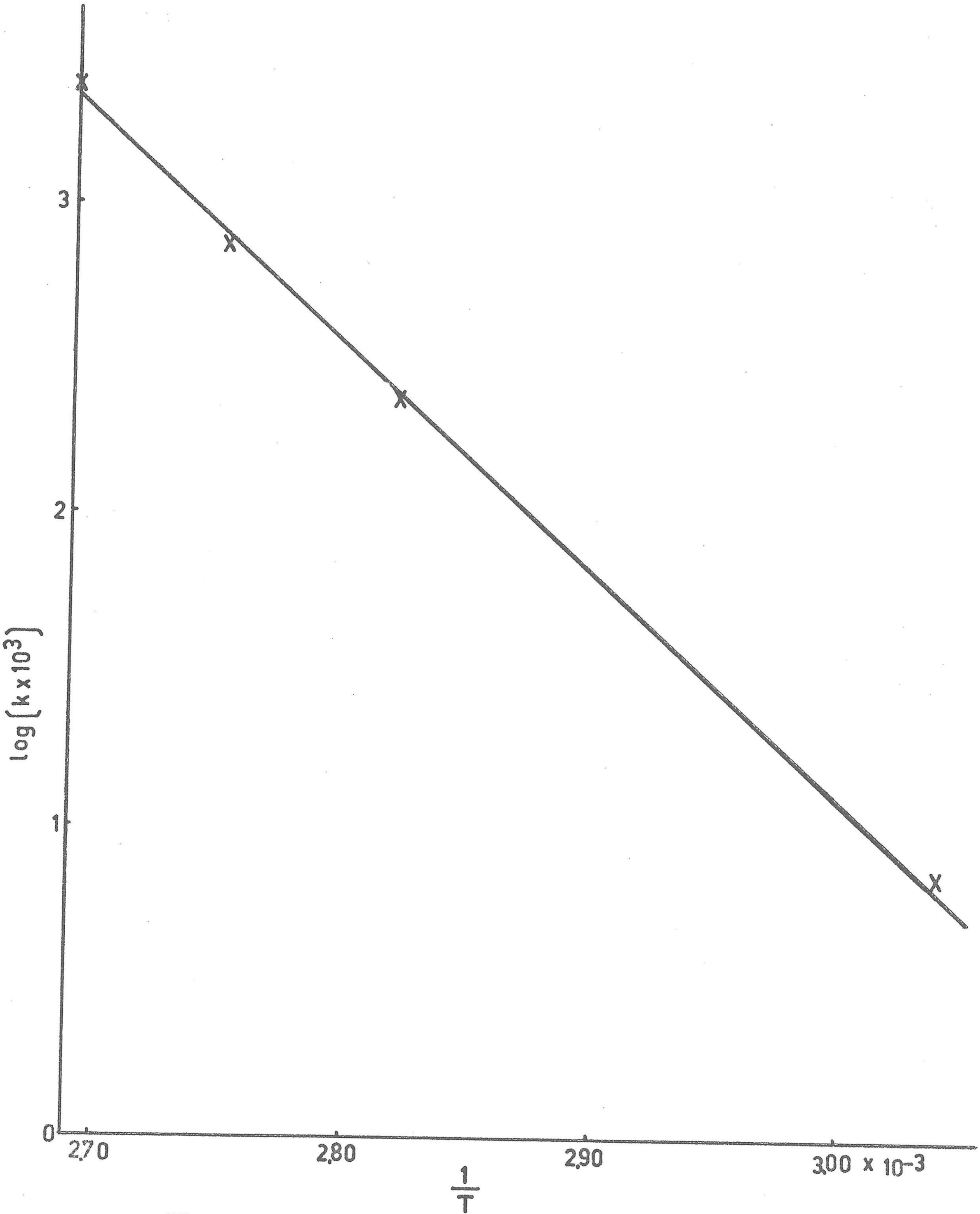

Fig.2.14 Co^{II}(acac)$_2$- Co^{III}(acac)$_3$ electron transfer reaction in toluene.

$$^{*}\qquad k_1 = \frac{kT}{h}\, e^{\Delta S^{\ddagger}/R} \,.\, e^{-\Delta H^{\ddagger}/RT}$$

has been derived. It has also been shown (20) that $\Delta H^{\ddagger} = Ea - 2RT$ for reactions obeying second order kinetics, thus substitution for $\Delta H^{\ddagger}$ in the above equation gives

$$k_1 = \frac{kT}{h}\, e^{\Delta S^{\ddagger}/R} \,.\, e^{-Ea/RT} \,.\, e^{2} \qquad 2.10$$

Hence substitution for Ea in equation 2.10 gives a value for $\Delta S^{\ddagger}$ of - 40 (± 5%) e.u. for the electron transfer reaction in toluene.

Table 2.2 compares the kinetic data for a series of electron transfer reactions between cobalt (II) and cobalt (III) complexes. In all cases except two the solvent used was water. Since most of the reactions shown are similar and might therefore be expected to have similar values of $\Delta S^{\ddagger}$ and Ea the comparable results observed for many of the reactions do not allow any worthwhile deductions to be made. However it is of interest to note the similarity in the values for the acetylacetonato complexes with those for the ammino type complexes and especially with the values for the ethylenediamine complexes. Unfortunately there is insufficient kinetic data available to allow a wider comparison than that shown in Table 2.2 to be made.

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* K_1 = Specific rate constant for the reaction
k = Boltzman constant, h = Planck's constant
$\Delta S^{\ddagger}$ = entropy of activation, $\Delta H^{\ddagger}$ = heat of activation
R is the gas constant and T is the absolute temperature

TABLE 2.2

Kinetic data for Cobalt II Cobalt III Electron Transfer Reactions

Reaction	Temp. °C	k Moles^{-1} Secs^{-1}	Ea	$\Delta S^{\ddagger}$	Ref.
(a) $Co\ (acac)_2$ - $Co\ (acac)_3$ (toluene)	98.7	6.55×10^{-4}	14.2	-40	This Thesis
$Co\ (NH_3)_6^{2+}$ - $Co(NH_3)_6^{3+}$	60	5.3×10^{-5}	13.5	-46	36
$Co\ (NH_3)_6^{2+}$ - $Co\ (NH_3)_6^{3}$ (liquid NH_3)	25	6×10^{-5}	23	-10	39
$Co\ (NH_3)_5\ H_2O^{2+}$ - $Co\ (NH_3)_5H_2O^{3+}$	60	7.5×10^{-4}	13.3	-43	36
$Co\ (NH_3)_n^{2+}$ - $Co\ (NH_3)_5\ OH^{2+}$	64.5	5.4×10^{-2}	13.4	-33	41
$Co\ (NH_3)_n^{2+}$ - $Co\ (NH_3)_4(OH)_2^{+}$ (trans)	64.5	2.5×10^{-1}	13.8	-29	41
$Co\ (NH_3)_n^{2+}$ - $Co\ (NH_3)_4\ (OH)_2^{+}$ cis	64.5	15×10^{-1}	-	-	41

TABLE 2.2 (Contd.)

Reaction	Temp. °C	k $\text{Moles}^{-1}\ \text{Secs}^{-1}$	Ea	$\Delta S^{\ddagger}$	Ref.
$^{(b)}$Co $(en)_3^{2+}$ - Co $(en)_3^{3+}$	25	5.0×10^{-5}	14.3	-33	42
$^{(c)}$Co $(phen)_3^{2+}$ - Co $(phen)_3^{3+}$	0	1.1	17	-4	26
$^{(d)}$Co $(EDTA)^{2-}$ - Co $(EDTA)^{-}$	85	2.1×10^{-4}	22	-17	40

(a) acac = acetylacetone (b) en = ethylenediamme (c) phen = 1:10 phenanthraline

(d) EDTA = ethylenediamme-tetracacetic acid

Mechanisms

The mechanisms that can be suggested for the electron transfer process in toluene are,

1) An acetyl-acetone radical may be dissociated from the cobalt (III) complex leaving behind a tetra-coordinated cobalt (III), which could then undergo an electron transfer with the tetra-coordinated cobalt (II) complex by means of an electron jump (4) or tunnelling (5) mechanism. This mechanism would be favoured in terms of the Franck-Condon Principle since the species involved in the exchange would have summetrical structures. However, the cobalt (III) acetylacetonato complex does not undergo appreciable exchange with cobalt ions in solution (11) (43), which would tend to indicate that the ligand molecules are bonded rather strongly to the central metal atom and would therefore be unlikely to be dissociated as an acetylacetone radical in toluene.

2) The second mechanism to be suggested makes use of the electron jump (4) or the tunnelling (5) hypothesis. In this case an electron could jump from the cobalt (II) complex to the cobalt (III) complex having first acquired the energy necessary to pass over the potential energy barrier. As shown in the equations given below this would produce a positively charged bis-(acetylacetonato) cobalt (III) ion and a negatively charged tris-(acetylacetonato) cobalt (II) ion. A negative acetylacetone ion would then dissociate from the latter and move slowly across to the positively charged cobalt (III) ion. i.e.

$$\begin{array}{rcl}
\mathrm{Co^{III}\ (acac)_3} & + & \mathrm{Co^{II}\ (acac)_2} \\
\text{electron} & \Big\downarrow & \text{transfer} \\
\mathrm{Co^{II}\ (acac)_3^-} & + & \mathrm{Co^{III}\ (acac)_2^+} \\
 & \Big\downarrow & \\
\mathrm{Co^{II}(acac)_2 + acac^-} & + & \mathrm{Co^{III}(acac)_2^+} \\
 & \Big\downarrow & \\
\mathrm{Co^{II}(acac)_2} & + & \mathrm{Co^{III}(acac)_3}
\end{array}$$

This mechanism is, however, unfavourable since the species involved in the electron transfer have unsymmetrical structures and the Franck-Condon Principle is not obeyed. Such an exchange mechanism would necessarily involve very large activation energies which is certainly not so in the case under consideration where $Ea = 14.2$ k cals/mole.

3) The mechanism may involve the formation of a bridged activated intermediate represented by Fig. 2.32a. Such an intermediate would necessitate the breaking of an oxygen-metal bond on the cobalt (III) species and the reformation of one on the cobalt (II) complex. The structure of the intermediate formed in this way would be symmetrical and would thus allow for an easier transition of the exchanging electron, since there would be no violation of the Franck - Condon Principle. Further the conjugation in the bridging ligand would allow the transfer of the electron to take place by movement through the π - electron system (19) (23) thus facilitating the electron transfer by lowering the resistance to it. These factors would be reflected in a relatively low activation energy for the electron transfer. Thus the relatively

low value of Ea = 14.2 k cals/mole found for the electron transfer would support this mechanism.

The rate of formation of an intermediate of the type suggested would be expected to follow second order kinetics, since it would depend on the collision of two molecules of the reacting species. Assuming that the rate of formation of such an intermediate as is suggested here is the rate determining step of the electron transfer reaction then support for this mechanism is given by the observed second order kinetics. Also from a consideration of the entropy of activation for the reaction further evidence to support the existence of a bridged activated intermediate complex in the mechanism of the electron transfer may be obtained.

In the normal interpretation of the entropy of activation (50) the negative value found would indicate that the formation of the transition state complex has a low probability and that the rate of reaction is slow. However when a reaction occurs between two complex molecules resulting in the formation of an activated intermediate complex and accompanied by a rearrangement of energies among the degrees of freedom, such that the activated intermediate has a more rigid structure, then there will be a decrease in the absolute entropy value. Certainly in the third suggested mechanism one would expect that the transition state would be more rigid than either of the individual reacting complexes. Thus the negative entropy of activation found, although indicating a low probability for the formation of an activated intermediate, does provide evidence to support this mechanism. Further the entropy of activation for the reaction between cobalt (III) and cobalt (III) acetylacetonato complexes compares with the values for the other reactions known to proceed via "inner sphere" bridge formation. (Table 2.3.)

TABLE 2.3

Electron Transfer Reactions with Bridged Transition States

Reactants	$\Delta S^{\ddagger}$	Ref.
$Cr(H_2O)_5F^{2+} + Cr^{2+}$	- 20 e.u.	30
$Co(NH_3)_5OH^{2+} + Cr^{2+}$	- 18 e.u.	31
$Co(NH_3)_5H_2O^{3+} + Cr^{2+}$	- 52 e.u.	31 & 32
$Cr(NH_3)_5F^{2+} + Cr^{2+}$	- 30 e.u.	33

Furthermore a positive entropy of activation would, although indicating a more probable transition state, not have produced such strong evidence of a bridged activated intermediate since other mechanisms not involving such transition states would also be expected to have positive values for $\Delta S^{\ddagger}$.

There have been some attempts to relate kinetic parameters, particularly $\Delta S^{\ddagger}$, to the mechanism of electron transfer reactions. This has however met with little success due to the lack of sufficient experimental data. Higginson (21) in an attempt to relate $\Delta S^{\ddagger}$ to the mechanism of the electron transfer has drawn attention to the fact that certain reactions e.g.

$Co(NH_3)_6^{3+}$ --- Cr^{2+} and $Co(NH_3)_6^{3+}$ --- $Cr(dipyridyl)_3^{2+}$

have negative entropies of activation although the mechanism does not involve a bridged activated complex. However Higginson in his work has used an interpretation for bridged activated complexes similar to that used by Taube et al (22). The latter workers define a bridged activated complex as one in which the coordination sphere is involved in the formation of the bridge e.g. "inner-sphere" reactions. It should however be pointed out that even in cases where the electron transfer is an "outer-sphere" reaction a bridge may be formed in the transition state (18). Thus in the reaction between Cr^{2+} and $Co(NH_3)_6^{3+}$ it is highly probable that an anion is involved in bridge formation, especially since the reaction shows a dependence on the nature of the anion present in solution (22). A transition state complex not involving a bridging anion is certainly difficult to imagine in this case. However, whether or not bridging does occur in the transition state, many workers are in agreement that a negative entropy of activation does indicate the formation of a transition state complex.

Newton and Rabideau (24) have shown a correlation between the entropy of the activated transition state complex and the charge on the transition state complex. However Higginson et al (25) have attempted to relate the value of $\Delta S^{\ddagger}$ to the charge of the transition state complex. The examples they have used show good agreement with the assumption that the value of $\Delta S^{\ddagger}$ is due to the total charge on the reacting species. From their results one would predict a value of approximately 12 e.u.

for the reaction between neutral molecules. However the reaction between cobalt (II) and cobalt (III) acetylacetonato complexes in toluene has as we have seen, a value of -40 e.u., which does not agree with the assumptions of Higginson et al. A significant difference between the reactions considered by Higginson and the reaction between the cobalt (II) and cobalt (III) acetylacetonato complexes is that in the former cases there is little, if any, difference in the structures of the reactants while in the latter case there is a very significant difference due to the cobalt (II) complex having a weak ligand field while the cobalt (III) has a strong ligand field. Further since the values of $\Delta S^{\ddagger}$ for many reactions do not fit the relationship predicted by Higginson it suggests that the entropy of activation does not have a simple relationship to any one factor. However by a consideration of the two types of reactions e.g. those of Higginson and those studied in this work, one can suggest that the value of $\Delta S^{\ddagger}$ is due to at least two factors. These being,

(1) The total charge on the reactants.

and (2) The difference in electronic structures resulting from a difference in the ligand fields in each reactant.

Two further factors which may have an effect on the entropy of activation are,

(1) The solvent - due either to the different degrees of solvation of the reactants or to the direct participation of the solvent in the electron transfer mechanism.

(2) The nature of the bridging group in the reactions proceeding via bridged activated intermediates.

The evaluation of the effects of each of these factors on the value of $\Delta S^{\ddagger}$ will only be possible on the accumulation of much more experimental data.

The predicted influence of several factors on the value of $\Delta S^{\ddagger}$ leads one to predict that the activation energy of the electron transfer reaction is similarly dependent on several factors and not only on the charge of the reactants as is predicted by Marcus et al (5). The nature of any bridging groups and the effect of solvation would probably be reflected in changes of width of the potential energy barrier. However the main factors influencing the height of the energy barrier would be the total charge on the reactants and the difference in the electronic structures of metal atoms in the reacting complexes. Assuming that for the reaction between neutral molecules there is no effect of charge on the height of the energy barrier then the activation energy can be explained in terms of the differences in electronic structures of the central metal atoms in the reactants. For the cobalt (II) and cobalt (III) acetylacetonato complexes the difference in electronic structure of the central metal atom is due to the splitting of the 5-degenerate energy state of the 3 d orbitals into various upper and lower energy states by the ligand field of the complexes. In the case of the cobalt (II) complex the degree of splitting is less due to a lower ligand field than in the cobalt (III) complex. Thus the activation energy can be explained as the energy necessary to rearrange the energy states of the 3 d orbitals of the cobalt complexes to intermediate values. During the rearrangement of the energy states of the 3 d orbitals a rearrangement of electronic structures would also take place. The rearrangement of the electronic structures would also facilitate the formation of a symmetrical intermediate as required by the Franck - Condon Principle for the fast movement of the electron during the actual exchange.

The explanation of the activation energy given above has been on the assumption that there is no effect of charge for the reaction between neutral molecules. This assumption may however be incorrect since, due to the difference in electronegativity of the central metal atom and the ligand molecules, a separation of charges within the complex molecules will almost certainly take place. Thus the approach of two charged coordination spheres may have an influence on the activation energy value. The same may be true for the value of the entropy of activation.

D. Acetylacetone as Solvent

Acetylacetone was used as a solvent for the electron transfer reaction between cobalt (II) and cobalt (III) acetylacetonato complexes since it satisfied the requirements given in section A of this Chapter and further since it was desired to gain information into the effect of the solvent on the electron transfer reaction. Furthermore the choice of this solvent provided a rather unique system for study since the acetylacetone was not only acting as solvent but was also present as the ligand molecules of the cobalt complexes. The electron transfer reaction was carried out at $98.7^{\circ} \pm 0.1^{\circ}C$ for the same reason that this temperature was chosen when toluene was used as the solvent.

Also the experimental technique employed for the study of the electron transfer reaction was similar to that outlined in Section C.

Thermal Stability

It was necessary to study the reduction of cobalt (III) acetylacetonato complex in acetylacetone since if reduction occurred to any appreciable extent the calculation of the rate of reaction would need modification so as to include a correction factor (1). The rate of reaction in the case of substantial reduction occurring would be given by equation 2.4. The procedure for the study of the reduction of the cobalt (III) complex was similar to that used when toluene was solvent for the system. The results are shown in Fig. 2.7.

It will be seen from a comparison with the toluene case that the extent of reduction was again negligible. The simplified form of equation 2.4 could therefore be used for the calculation of the rate of reaction provided such calculations were based on the measurements of the cobalt (II) complex.

Oxidation of the Cobalt (II) Complex

In early experiments it was found that a plot of log $\left[100-\% \text{ Exchange}\right]$ against time gave, instead of the expected straight line, a graph with a tendency to curve upwards at the longer time intervals Fig. 2.15. In early calculations it was assumed that the molarities of the reactants taking part in the electron transfer reaction did not change with time. This however was not the case, as subsequent experiments showed, since the bis-(acetylacetonato) cobalt (II) was irreversibly

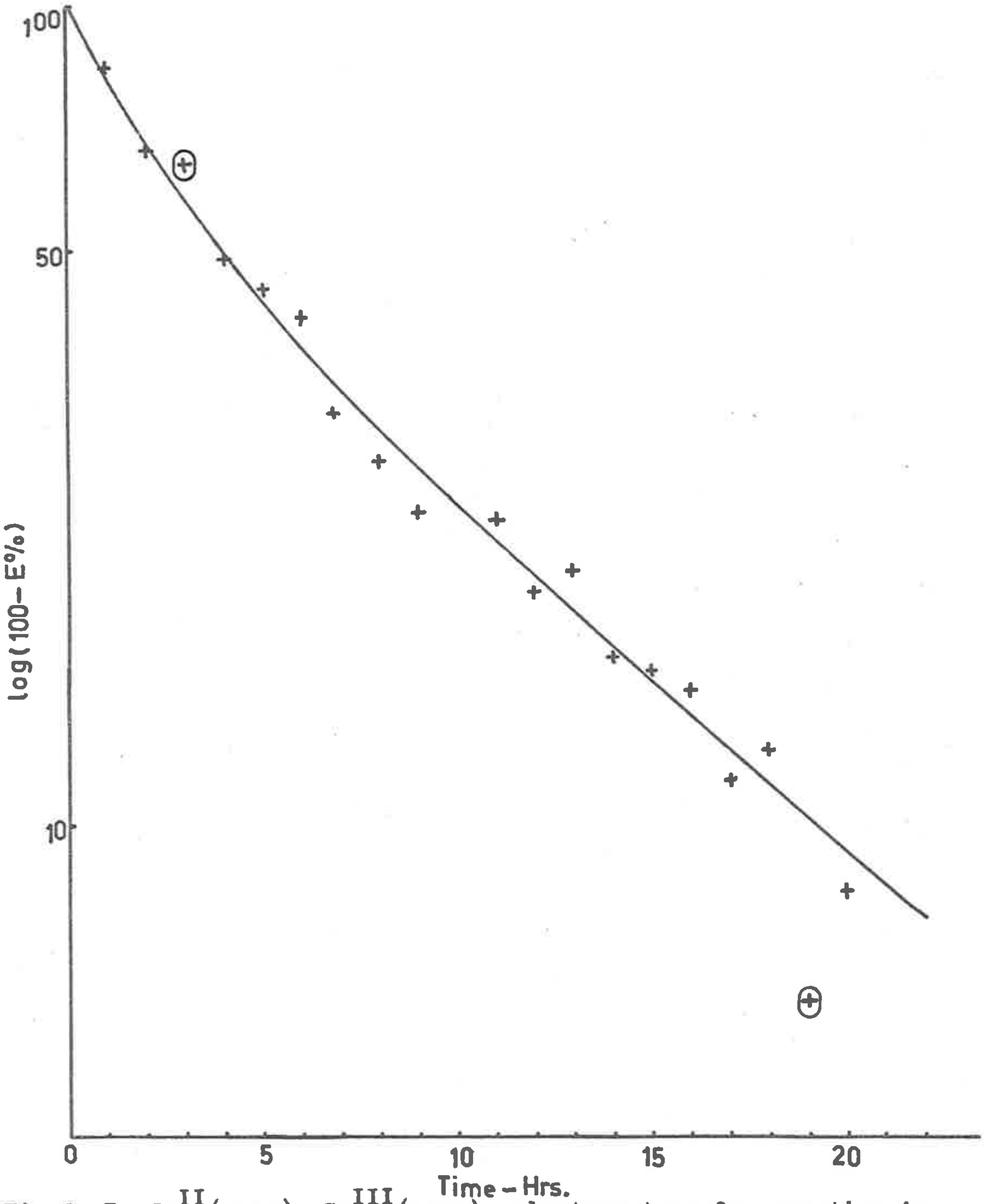


Fig.2.15 $Co^{II}(acac)_2$–$Co^{III}(acac)_3$ electron transfer reaction in acetylacetone at 98.7±0.1°C; Co^{II}0.0112M & Co^{III}0.0112M

oxidized during the course of the experiment.

An examination of the method of calculation of the percentage of electron transfer occurring will show how an upward curvature of the graph was caused. The percentage of electron transfer (E%) was found by multiplying the value of F from the equation 2.3 by 100. If the cobalt (II) complex was initially inactive, as was chosen in the experiments carried out, this would simplify the value of E% such that

$$E\% = \frac{A_t \quad M_{\infty}}{M_t \quad A_{\infty}} \times 100 \qquad 2.11$$

where A_{∞}/M_{∞} is the molar specific activity of the cobalt (II) complex at infinite time. A_{∞}/M_{∞} will be equal to the ratio of total activity to the total molarity, which is a constant for any particular experiment. Thus, if, as was assumed, no oxidation took place then Mt would also be constant. Consequently the value calculated for E% would be less than the true value since the quantity A_t found experimentally would be less than that for the case when no oxidation occurred. Thus there was an upward curvature of the graph at longer time intervals, where the amount of oxidation was greater and the values of A_t and E% consequently lower. It will be seen from this explanation that it became necessary to analyse for the quantity of cobalt (II) complex, in any sample taken, in order to calculate the true value of E%. In all experiments conducted it was found that an irreversible oxidation did take place during the reaction (see Tables 2-13 Appendix A.).

Assuming no irreversible oxidation the errors in the points shown in Fig. 2.15 would be ± 3% of E%, arising from a counting error of ± 1% (see p.171) and from an estimated error of ± 1% in separation procedure. Thus the two points indicated by ⊕ need explaining since unlike the other points on the graph they lie outside the error of ± 3%. The explanation that may be put forward for the deviation is that the separation of the samples into cobalt (II) and cobalt (III) fractions was probably not complete due to insufficient washing during the separation procedure. Thus the error of separation would be underestimated at ± 1% for at least these two points. However it was felt that the curvature of the graph was indeed a real indication that oxidation was in fact taking place and this is certainly borne out by the oxidation shown in Tables 2 - 13 (Appendix A).

The Rate Law

If acetylacetone is added to the solvent there is the possibility of an effect on the rate of the electron transfer reaction due to the direct participation of this in the reaction mechanism. Thus the rate of reaction may be expressed by

$$R = k\left[Co^{II}\right]^{x}\left[Co^{III}\right]^{y}\left[H.acac\right]^{z} \qquad 2.12$$

where $\left[H.acac\right]$ is the concentration of acetylacetone in the solvent.

It has been found that the rate of certain electron transfer reactions in aqueous media has a dependence on the pH of solution (44) (45). The influence of the pH on the electron transfer may occur in two ways (44).

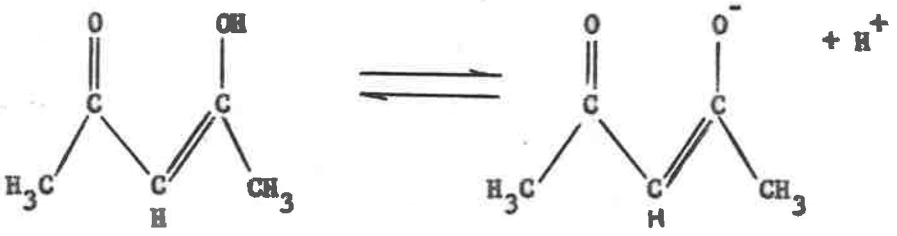
(1) Due to an effect on the equilibrium reaction for the formation of a complex necessary for the electron transfer mechanism e.g.

$$M\,A_x^{(n-x)+} + x\,H^+ \rightleftharpoons M^{n+} + x\,H\,A$$

or (2) Due to the participation of a weak acid or anion of a weak acid in the electron transfer mechanism. This will be especially true if the hydrogen ion is necessary for the formation of a bridged activated transition state. Thus when acetylacetone is added to the solvent the reaction mechanism any depend on the equilibrium.

$$Co^{II}\,(acac)_3\,H \rightleftharpoons Co^{II}\,(acac)_3^- + H^+ \qquad 2.13$$

Hence since the enol form of the acetylacetone can undergo ionization producing hydrogen ions i.e.



2.14

the rate of the electron transfer may be expressed by

$$R = k_1 \left[Co^{II}\right]^x \left[Co^{III}\right]^y \left[H^+\right]^W \qquad 2.15$$

If K_D is the dissociation constant of acetylacetone then the relationship between $\left[H^+\right]$ and $\left[H.acac\right]$ is given by

$$\left[H+\right] = \sqrt{K_{D.}\left[Hacac\right]} \qquad 2.16$$

Substitution of $\left[H^+\right]$ from equation 2.14 in 2.13 gives

$$R = k_2 \left[Co^{II}\right]^x \left[Co^{III}\right]^y \left[Hacac\right]^{W/2} \qquad 2.17$$

where $k_2 = K_D^{W/2} \,.\, k_1$

It will be seen that equations 2.17 and 2.12 are similar. Further by keeping the acetylacetone concentrations constant both equations reduce to the form

$$R = k_3 \left[Co^{II}\right]^x \left[Co^{III}\right]^y \qquad 2.18$$

<u>The effect of Acetylacetone on the Rate of Reaction</u>

It has already been suggested above that the concentration of acetylacetone in the solvent may have an effect on the rate of the electron transfer. Any effect could be due to

(1) The change in the dielectric constant for the solvent. However in view of the evidence produced by Cohen (10) and Baker (26) it is not to be expected that this effect, if present at all, will be very great.

(2) The displacement of the equilibrium for the formation of the tris-(acetylacetonato) cobaltate-(II) complex e.g.

$$Co^{II}(acac)_2 + H\ acac \rightleftharpoons Co^{II}(acac)_3^- + H^+ \qquad 2.19$$

or (3) The change in the hydrogen ion concentration, produced by the ionization of the enol form of the acetylacetone (equation 2.14)

In all of these cases the rate of reaction may be expressed by either equation 2.12 or 2.17. If the concentrations of cobalt (II) and cobalt (III) complexes are kept constant then the rate of reaction may be expressed by an equation of the general form.

$$R = K \left[\mathrm{H\ acac}\right]^{Z} \qquad 2.20$$

Further a combination of this with equation 2.8 gives the relationship

$$\frac{\ln 2}{t_{\frac{1}{2}}} = K \left[\mathrm{H\ acac}\right]^{Z} \qquad 2.21$$

Hence if the cobalt (II) and cobalt (III) concentrations are kept constant then a plot of log $t_{\frac{1}{2}}$ against log % concentration of acetylacetone should give a straight line graph of slope - Z, where Z is the order of the electron transfer reaction in acetylacetone, or half the order of the reaction in hydrogen ion concentration (equations 2.12 and 2.17).

Of the three possible causes given above for the effect, on the rate of reaction, of the addition of acetylacetone to the system only the second and third need be considered. Dwyer and Sargeson (46) determined that the dissociation of tris-(acetylacetonato)cobaltate-(II)ion in 80% dioxan was such that $pK \simeq 6$ and they also estimated that in pure water $pK \simeq 0.4$. Calculations based on the latter value and an acetylacetone concentration of *2 M give a value of 98% for the degree of formation of the tris(acetylacetonato) complex of cobalt (II). In mixtures of acetylacetone and toluene it can be expected that the value of pK will be greater than o.4. Hence it can be expected that the degree of formation of the complex $Co^{II}(acac)_3^-$ ion, for a minimum concentration of acetylacetone of 20% $\left[{}^{V}/_{V}\right]$ in toluene, will be greater than 98%. Thus if the displacement of the equilibrium for the reaction represented by equation 2.19 was a factor determining the rate of the electron transfer reaction no significant difference in effect would be expected for concentrations of acetylacetone greater than 20% $\left[{}^{V}/_{V}\right]$.

The tris-(acetylacetonato)cobaltate-(II) ion is the anion of a weak acid and will therefore be expected to take part in an equilibrium reaction (equation 2.13) with hydrogen ions. Since acetylacetone may undergo ionization to produce hydrogen ions (equation 2.14) it can be expected that an increase in concentration of acetylacetone in the solvent will cause the greater formation of the weak acid form of the tris-(acetylacetonato)cobaltate-(II) by the common ion effect. Thus if the mechanism of the electron transfer involves the weak acid $Co^{II}(acac)_3H$ in the presence of acetylacetone then an increase in the concentration of acetylacetone in the solvent, provided the concentration is kept greater than 20% $\left[{}^{V}/_{V}\right]$, would be expected to cause an increase in the rate of reaction.

The electron transfer was studied at a temperature of 98.7° ± 0.1°C and at concentrations of cobalt(II) and cobalt(III) complexes of 0.0100 molar in mixtures of acetylacetone and toluene as solvent. The results

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* For a 20% $\left[{}^{V}/_{V}\right]$ mixture of acetylacetone and toluene the concentration of acetylacetone is approximately 2.M

obtained are shown graphically in Figs. 2.16 and 2.17. A plot of log $t_{\frac{1}{2}}$, calculated from Figs. 2.16 and 2.17, against log % $\left[\text{Hacac}\right]$ is shown in Fig. 2.18 and the slope of the graph is - 0.57 (± 10%). Hence the order of the reaction is 0.57 (± 10%) in acetylacetone or 1.14 (± 10%) in hydrogen ion concentration. Since the minimum concentration of acetylacetone used in the solvent was 20% $\left[{}^{V}/_{V}\right]$ the results obtained may be interpreted as an indication that the weak acid $\left[\text{Co}^{II}(\text{acac})_3\ \text{H}\right]$ is involved in the mechanism when acetylacetone is present.

An assumption that is made in obtaining equation 2.20 is that the order of the reaction in each of the cobalt complexes is constant at all concentrations of acetylacetone. Since this may not be true the order of the reaction obtained from the graph in Fig. 2.18 may not have any real meaning. However it is felt that the variation of half life of the electron transfer with a change in acetylacetone concentration in the solvent does indicate the participation of $\left[\text{Co}^{II}(\text{acac})_3\text{H}\right]$ in the reaction mechanism.

Kinetics of the Electron Transfer in Acetylacetone

The electron transfer reaction at 98.7° ± 0.1°C in acetylacetone was found to proceed more rapidly using the same reactant concentrations than it was in toluene as solvent, e.g. at initial reactant concentrations of 0.0100 M the half-life was ≃ 4 hours in acetylacetone as opposed to ≃ 30 hours in toluene. The electron Transfer was studied at 98.7° ± 0.1°C and at various reactant concentrations in order to obtain the kinetics of the reaction. The results of the study are given in Tables 2-9 of

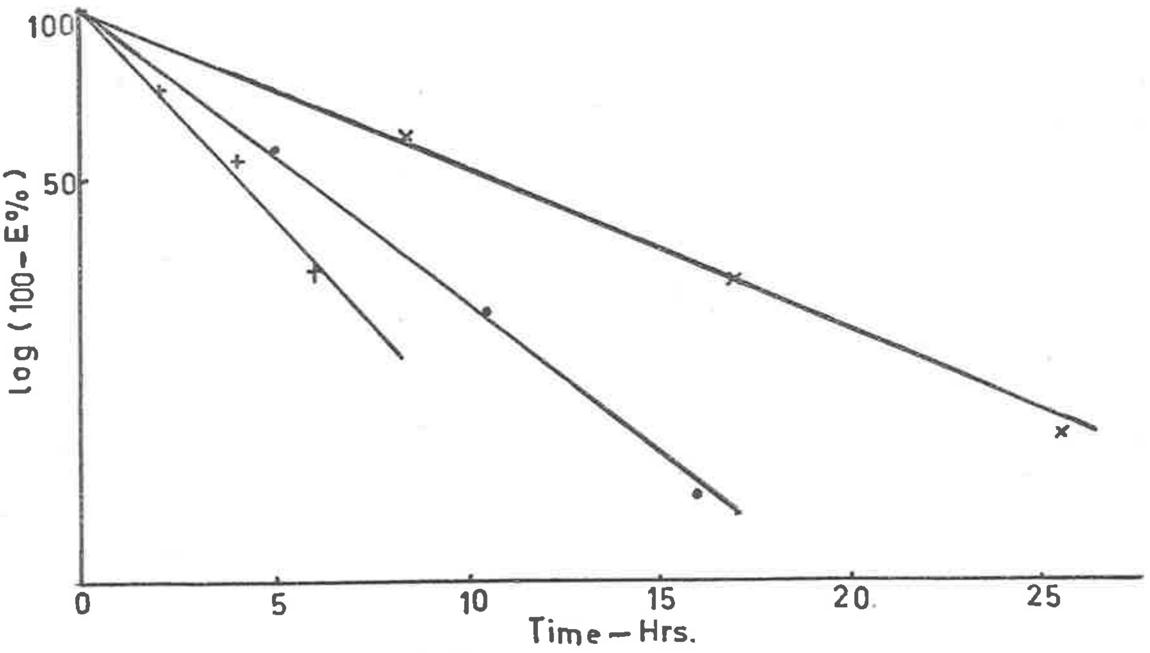


Fig.2.16 $Co^{II}(acac)_2$- $Co^{III}(acac)_3$ electron transfer reaction in mixed solvent; + =100%acac ; • =60%acac ; X =20%acac.

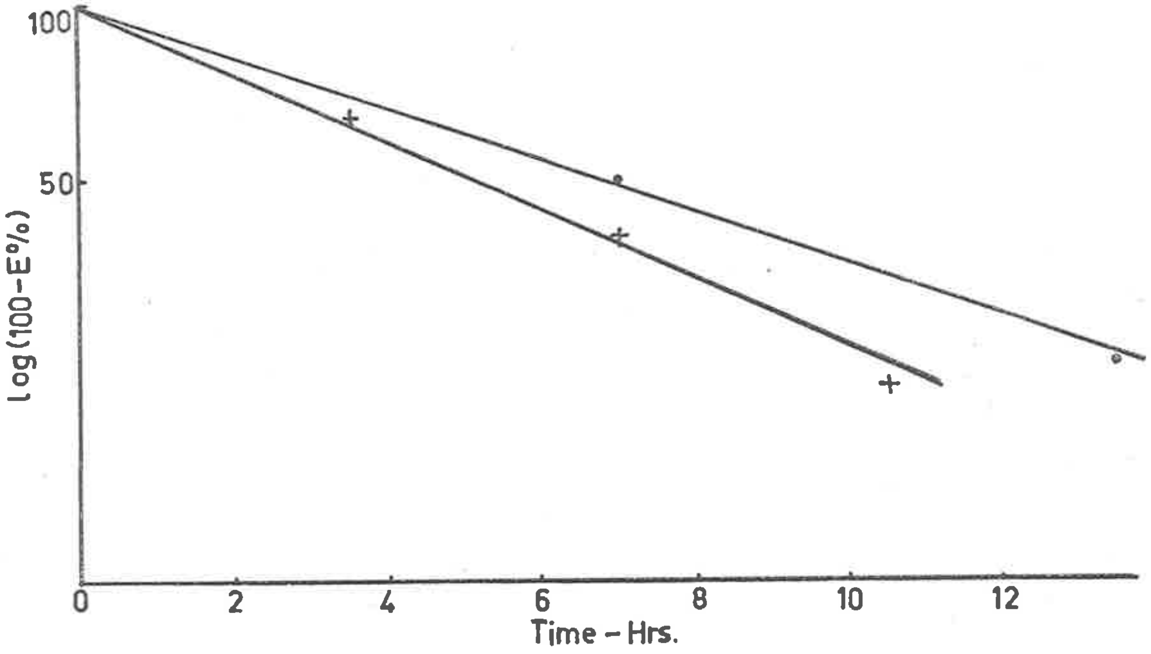


Fig.2.17 $Co^{II}(acac)_2$- $Co^{III}(acac)_3$ electron transfer reaction in mixed solvent; + =80%acac ; • =40%acac.

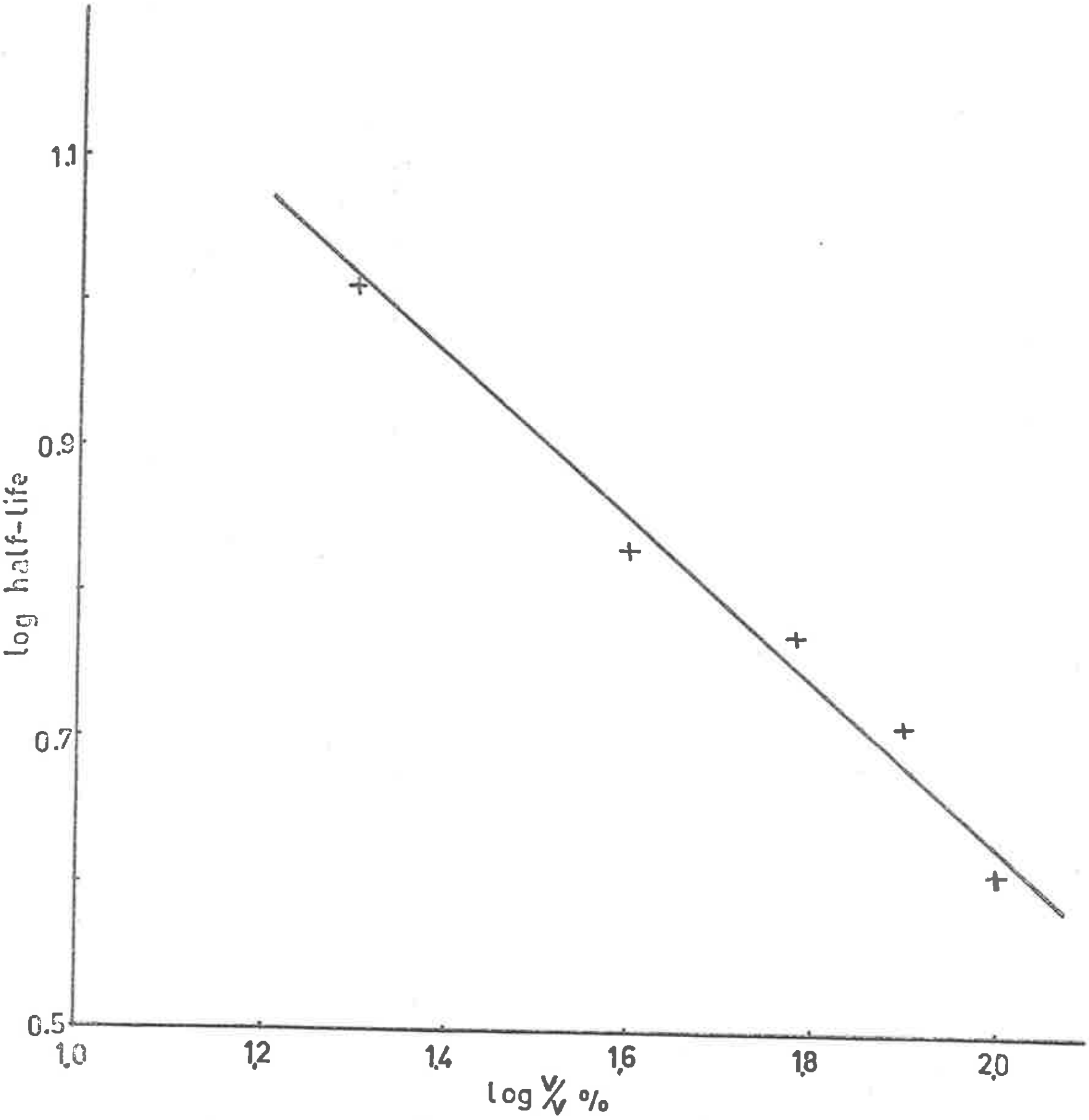


Fig.2.18 $Co^{II}(acac)_2$- $Co^{III}(acac)_3$ electron transfer reaction in mixed solvent.

Appendix A and are shown graphically in Figs. 2.19 to 2.26. Equating the rates of reaction given by equations 2.7 and 2.18 for each of the reactions studied yields eight equations and by taking logarithms of these the following equations were obtained

$$\log k_1 - 2.0177\,x - 2.0177\,y = -3.1164 \qquad 2.22$$

$$\log k_1 - 1.7167\,x - 1.7167\,y = -2.7680 \qquad 2.23$$

$$\log k_1 - 1.7144\,x - 2.0655\,y = -3.0181 \qquad 2.24$$

$$\log k_1 - 1.7670\,x - 1.9788\,y = -2.9367 \qquad 2.25$$

$$\log k_1 - 1.7645\,x - 1.9788\,y = -2.9278 \qquad 2.26$$

$$\log k_1 - 2.0177\,x - 1.7144\,y = -2.9650 \qquad 2.27$$

$$\log k_1 - 1.9508\,x - 1.9508\,y = -3.0239 \qquad 2.29$$

$$\log k_1 - 1.3188\,x - 1.3169\,y = -2.4106 \qquad 2.29$$

By taking combinations of these three at a time, solutions for the values of x and y were obtained and these are shown in Table 2.4. It should be pointed out that some of the possible combinations will not yield results due to the coefficients of the x and y terms being the same. The root means square values $\left[\text{i.e. } \sqrt{\frac{\sum nx^2}{n}}\,\right]$ of x and y are 0.57 and 0.70 respectively. The standard deviations in the values of x and y are ± 0.14 and ± 0.30 respectively. The standard deviations are somewhat larger than would be expected considering the errors in the calculated value of E%(± 5%) and also considering the very good linear agreement of the plots of log (100-E%) against time (Figs. 2.19-2.26). The possible causes of these rather large errors are as yet unknown but are believed to be a reflection of the complex nature of the exchange in acetylacetone as evidenced by the

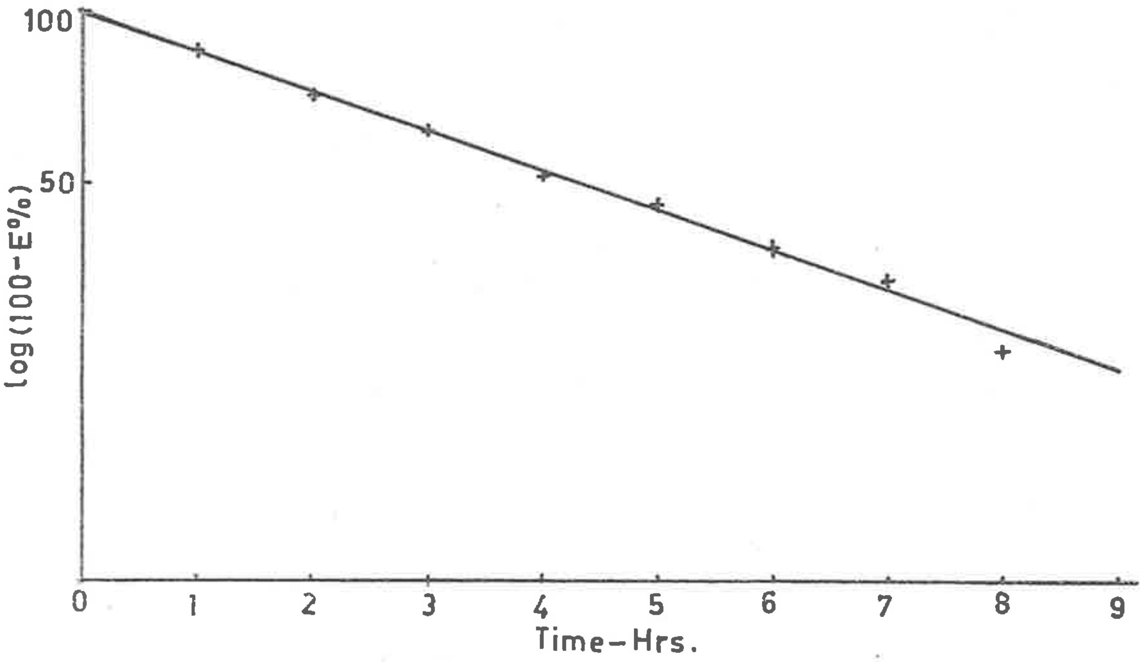


Fig.2.19 $Co^{II}(acac)_2$- $Co^{III}(acac)_3$ electron transfer reaction in acetylacetone at 98.7±0.1°C; Co^{II} 0.0096M & Co^{III} 0.0096M

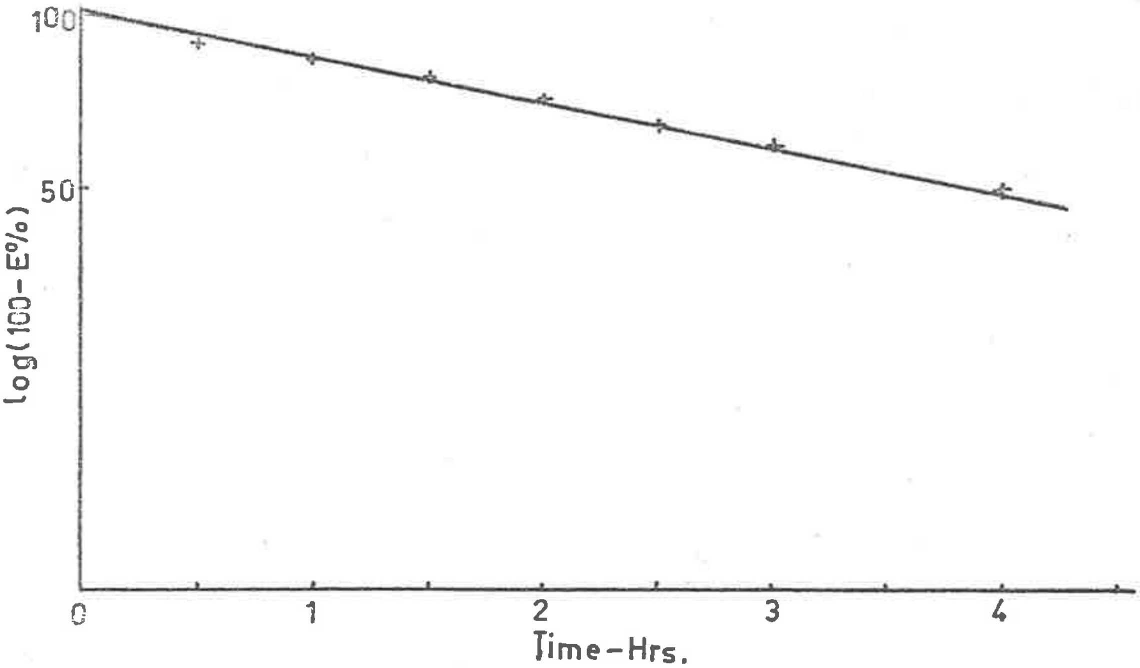


Fig.2.20 $Co^{II}(acac)_2$- $Co^{III}(acac)_3$ electron transfer reaction in acetylacetone at 98.7±0.1°C; Co^{II} 0.0192M & Co^{III} 0.0192M

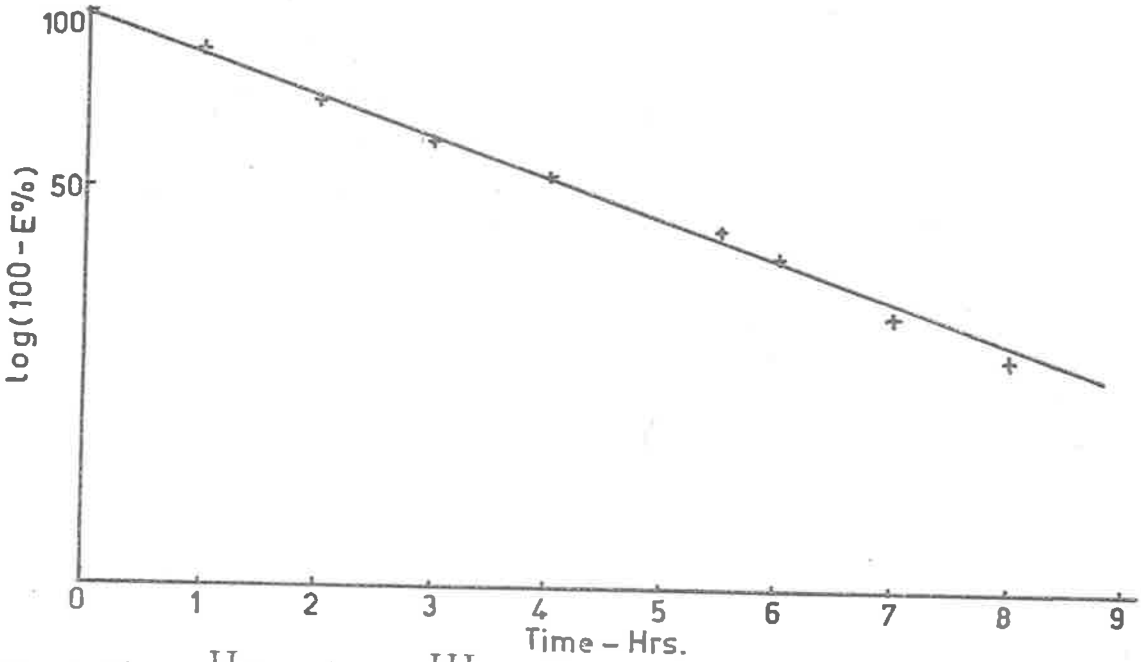


Fig.2.21 $Co^{II}(acac)_2$- $Co^{III}(acac)_3$ electron transfer reaction in acetylacetone at 98.7±0.1°C; Co^{II} 0.0193M & Co^{III} 0.0086M

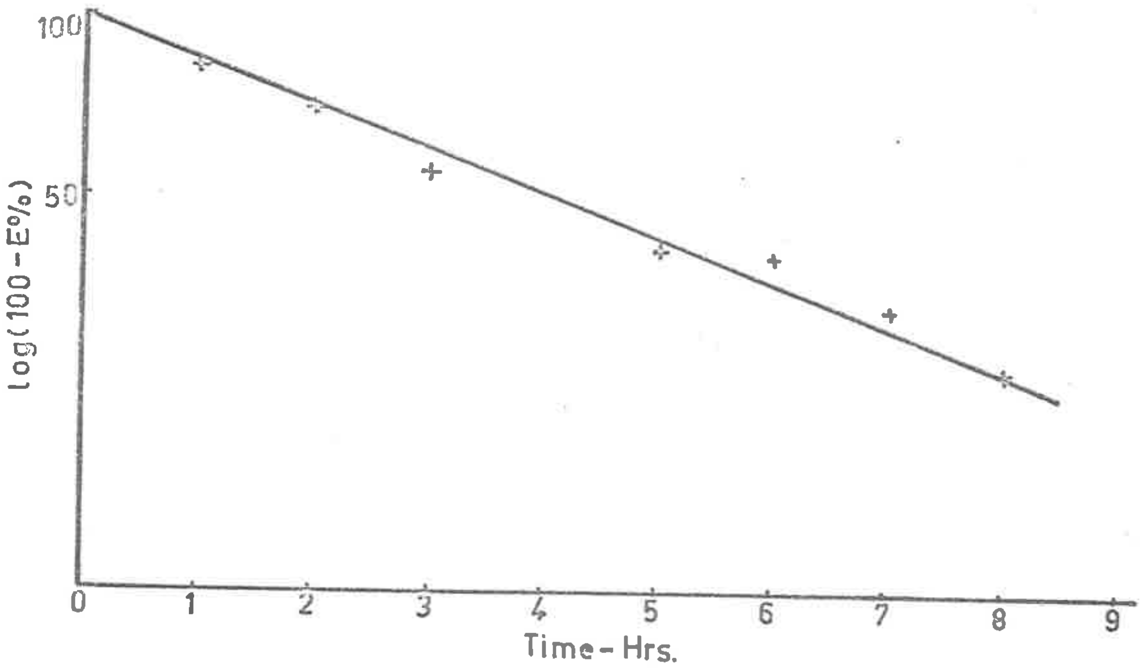


Fig.2.22 $Co^{II}(acac)_2$- $Co^{III}(acac)_3$ electron transfer reaction in acetylacetone at 98.7±0.1°C; Co^{II} 0.0171M & Co^{III} 0.0105M

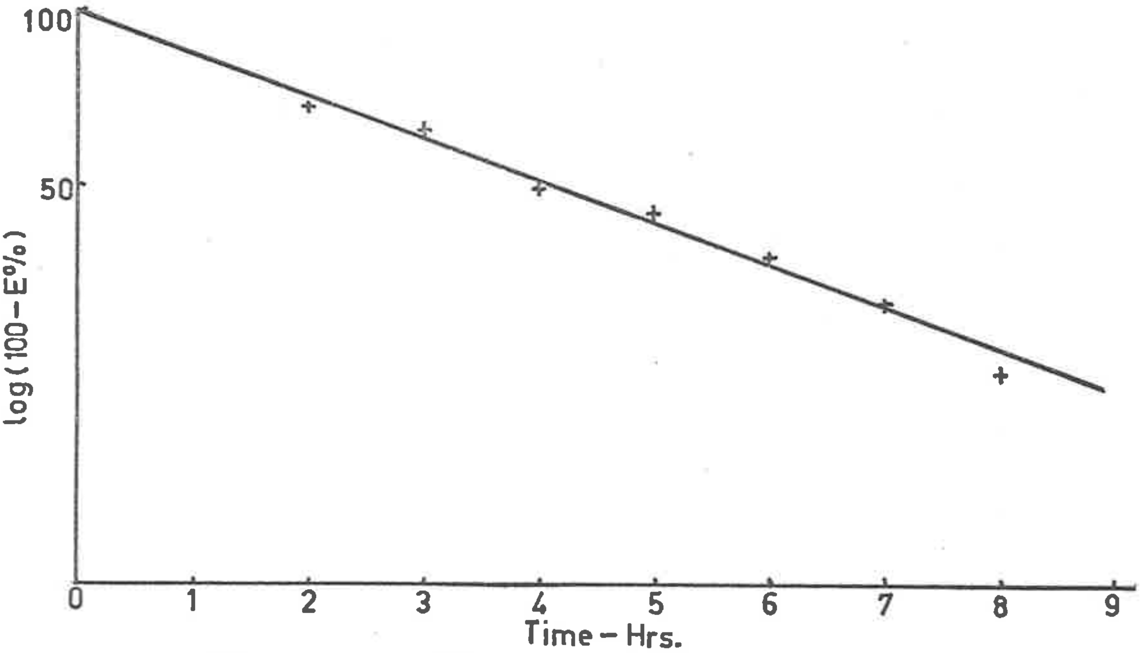


Fig.2.23 Co^{II}(acac)$_2$- Co^{III}(acac)$_3$ electron transfer reaction in acetylacetone at 98.7±0.1°C; Co^{II}0.0112M & Co^{III}0.0112M

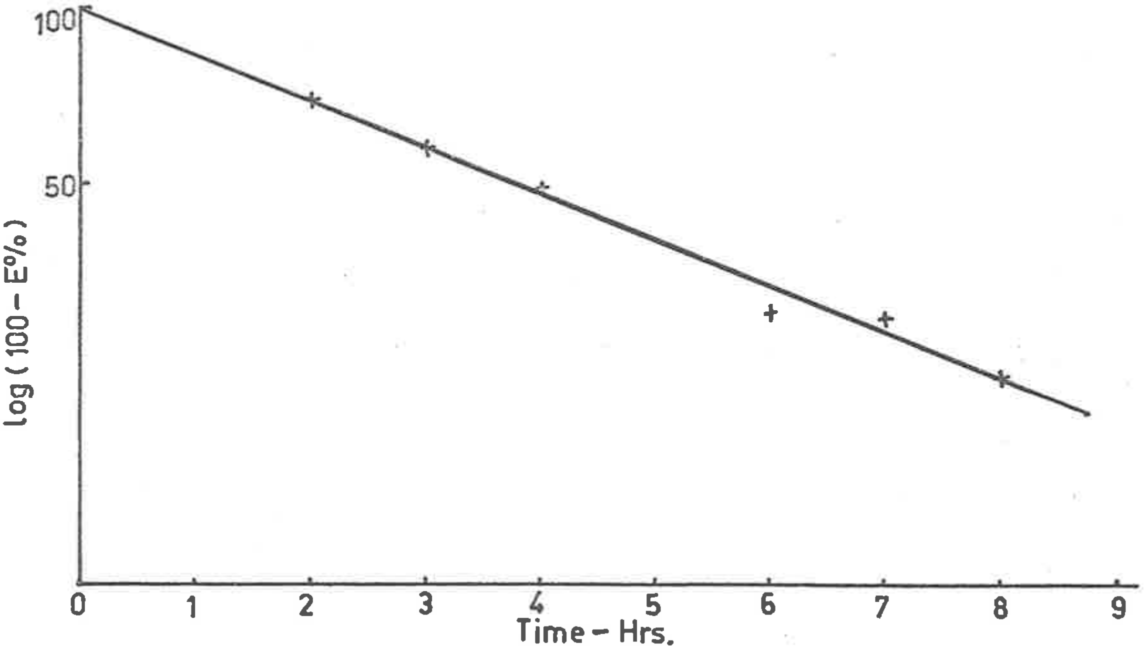


Fig.2.24 Co^{II}(acac)$_2$-Co^{III}(acac)$_3$ electron transfer reaction in acetylacetone at 98.7±0.1°C; Co^{II}0.0172M & Co^{III}0.0105M

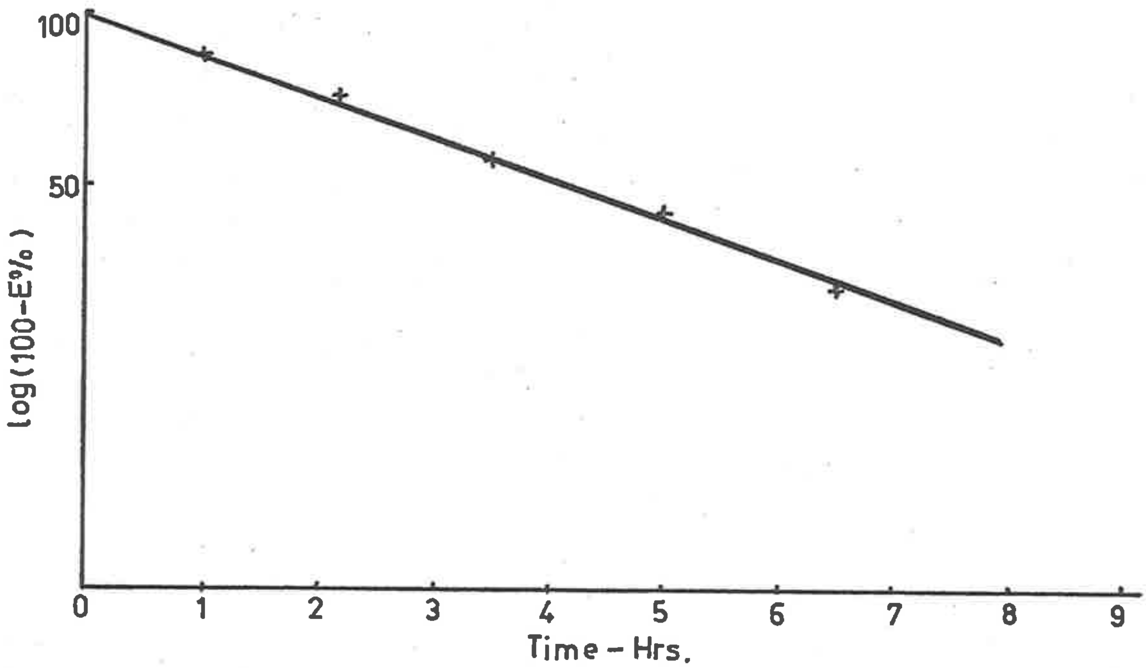


Fig.2. 25 $Co^{II}(acac)_2$- $Co^{III}(acac)_3$ electron transfer reaction in acetylacetone at 98.7±0.1°C; Co^{II}0.0480M & Co^{III}0.0482M

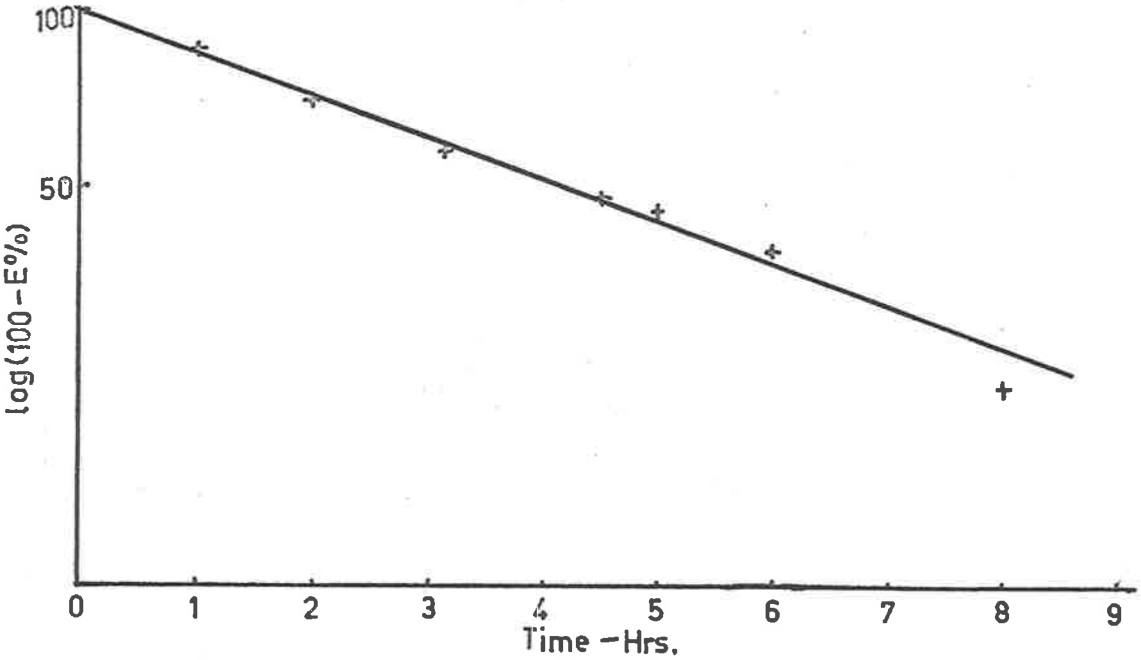


Fig.2.26 $Co^{II}(acac)_2$- $Co^{III}(acac)_3$ electron transfer reaction in acetylacetone at 98.7±0.1°C; Co^{II}0.0096M & Co^{III}0.0193M

TABLE 2.4

The order for the Electron Transfer Reaction Rate with Acetylacetone as solvent.

Combination	x*	y**	Combination	x	y
9.10.11	.438	.720	10.12.14	.658	.517
9.10.12	.636	.522	10.12.15	.583	.714
9.10.13	.672	.486	10.12.16	.314	.583
9.10.14	.658	.499	10.13.14	.659	.488
9.11.12	.522	1.256	10.13.15	.592	.500
9.11.13	.538	1.357	10.13.16	.351	.544
9.11.14	.403	.499	10.14.15	.658	.187
9.11.15	.522	1.251	10.14.16	.656	.241
9.11.16	.452	.811	11.12.15	.680	1.351
9.12.14	.639	.500	11.13.15	.739	1.473
9.12.15	.593	.789	11.14.15	.169	.297
9.12.16	.663	.348	11.14.16	.474	.561
9.13.14	.670	.500	11.15.16	.333	.636
9.13.15	.630	.752	12.14.15	.535	.401
9.13.16	.698	.313	12.14.16	.555	.419
9.14.15	.883	.500	12.15.16	.540	.429
9.14.16	.512	.500	13.14.15	.580	.413
10.11.14	.661	.765	13.15.16	.577	.392
10.11.15	.384	.741	14.15.16	.561	.408
10.11.16	.181	.716	13.14.16	.506	.400

The combinations 11.12.14 and 11.13.14 yield abnormally high results for the values of x and y and are consequently neglected. Other combinations not listed have no solution for x or y due to the coefficient of the x and y terms being equal.

The mean square averages for x and y are 0.578 and 0.696 respectively.

*x is order for cobalt II; **is order for cobalt III.

fractional orders found for cobalt(II) and cobalt(III) species.

It can be seen from Table 2.4 that there is a considerable scattering of the values of x and y. However data showing such a scattering, although not desirable for obtaining a good interpretation of the kinetics, may still be used. The use of results showing considerable scatter is not unique and other workers (26) have fitted such data to certain rate equations. Because of the large standard deviations for the values of x and y one may consider two extreme cases for the rate equation i.e.

$$R = k_1 \left[Co^{II}\right]^{\frac{1}{2}} \left[Co^{III}\right]^{\frac{1}{2}} \qquad 2.30$$

or

$$R = k_1 \left[Co^{II}\right]^{\frac{1}{2}} \left[Co^{III}\right] \qquad 2.31$$

Due to the large standard deviations, no consideration has been given to the expression for the rate of reaction being given by

$$R = k_1 \left[Co^{II}\right]^{.57} \left[Co^{III}\right]^{.70}$$

Reaction Mechanisms

The interpretation of the mechanism of the reaction in terms of the dependence of the rate on the order of each component would seem easy using the approach of Baker et al (26). These workers in studying the electron transfer reactions between cobalt (II) and cobalt (III) 1:10-phenanthroline complexes found that the rate of reaction was dependent on the first order of the cobalt (III) concentration and the half order of the cobalt (II) concentration in the presence of chloride ions. They interpreted their results as indicating the formation of ion pairs between the tris(1:10 phenanthroline)-cobalt-(III) ion and the chloride ions and the reaction as following the path.

$$Co\ (phen)_3^{3+} — Cl^- \rightleftharpoons Co\ (phen)_3^{3+} + Cl^-$$

$$Co\ (phen)_3^{3+} + Co\ (phen)_3^{2+} \longrightarrow \text{electron transfer}$$

An examination of the suggested path however shows that this would produce a rate dependence of a half order on the concentration of the cobalt (III) complex rather than the cobalt (II). They say that in view of the nature of the complex ions it would be difficult to explain the fractional order in any other way, hence one is left without an explanation of their results.

One can give an interpretation of the mechanism of the reaction between the cobalt (II) and cobalt (III) acetylacetonato complexes in acetylacetone using a similar approach to that of Baker et al (26) e.g.

(1) If the rate of reaction is expressed by equation 2.31.

The kinetic results would be explained if the mechanism was via the sequence of reactions,

$$2H.acac + 2\ Co^{II}(acac)_2 \xrightarrow{\text{fast}} [Co^{II}(acac)_3H]_2$$

$$[Co^{II}(acac)_3\ H]_2 \rightleftharpoons 2\ \ Co^{II}(acac)_3\ H$$

$$Co^{II}(acac)_3H + Co^{III}(acac)_3 \longrightarrow \text{electron transfer.}$$

This mechanism assumes that the cobalt (II) acetylacetonato complex reacts rapidly with the solvent to form the six co-ordinate cobalt (II) complex as a dimeric species. That a reaction between the bis(acetylacetonato) cobalt (II) and the solvent does take place is almost certain in view of the evidence supporting the formation of a six co-ordinate cobalt (II) acetylacetonato complex. This evidence may be summarized as

(a) Preparation of the bis(acetylacetonato) cobalt (II) in aqueous media yields a dihydrate complex (Chapter 6).

(b) Salts of the tris(acetylacetonato)cobaltate-(II) ion are easily prepared (8) particularly by using the alkali salts of acetylacetone (47).

(c) Anhydrous bis(acetylacetonato)cobalt(II) takes up solvent into its structure when dissolved in such solvents as acetone or alcohol.

(d) The dissociation constant of the tris(acetylacetonato) cobaltate-(II) ion was determined by Dwyer and Sargeson (46) as $\simeq 6$ in an 80% dioxan-water mixture and $\simeq 0.4$ in pure water.

Furthermore a comparison with the tris(acetylacetonato)nickel (II) (52) might suggest that the cobalt (II) acetylacetonato complex could exist in a polymerized form in the solution. However Cotton (48) has shown that the cobalt complex is monomeric in methylenedichloride. Attempts were made by boiling point elevation experiments on acetylacetone solutions of the complex, to determine whether or not a dimeric species of the cobalt (II) complex was formed in acetylacetone at approximately 100°C. These attempts were however without success due to the very low molecule boiling point elevation values and also due to the rather limited solubility of the cobalt (II) complex in acetylacetone.

(2) If the rate of reaction is expressed by equation 2.30

In this case the kinetics may be explained by three possible mechanisms for the reaction,

(a) The reaction may proceed via the sequence,

$$\text{H acac} + \text{Co}^{\text{II}}(\text{acac})_2 \xrightarrow{\text{fast}} \text{Co}^{\text{II}}(\text{acac})_3\text{H} \rightleftharpoons \text{Co}^{\text{II}}(\text{acac})_3^- + \text{H}^+$$

$$\text{Co}^{\text{II}}(\text{acac})_3^- \rightleftharpoons \text{Co}^{\text{II}}(\text{acac})_2 + (\text{acac})^-$$

$$\text{Co}^{\text{III}}(\text{acac})_3 \rightleftharpoons \text{Co}(\text{acac})_2^+ + (\text{acac})^-$$

$$\text{Co}^{\text{II}}(\text{acac})_2 + \text{Co}^{\text{III}}(\text{acac})_2^+ \longrightarrow \text{electron transfer}$$

This mechanism assumes that the bis(acetylacetonato) complex reacts rapidly with the solvent to form the tris(acetylacetonato) complex ion which as has already been discussed is a valid assumption. Further the production of $\text{Co}^{\text{II}}(\text{acac})_2$ could then be a rate determining step for the electron transfer.

In terms of the Franck - Condon Principle the mechanism suggested above would be favoured due to the symmetrical structures of the species undergoing the actual electron transfer reaction. However this explanation of the fractional order of the reaction would seem incorrect on the grounds that the cobalt (III) complex does not readily undergo cation exchange (11) (43) and hence is very stable and would not therefore be expected to dissociate to the $\text{Co}^{\text{III}}(\text{acac})_2^+$ ion. Furthermore the presence of acetylacetone as the solvent could be expected to lower any tendency for either the cobalt (II) or cobalt (III) complexes to dissociate in the way shown.

(b) The kinetics of the reaction would be explained if the mechanism of the reaction was

$$[Co^{II}(acac)_3\ H]_2 \rightleftharpoons 2\ Co^{II}(acac)_3\ H$$

$$[Co^{III}(acac)_3]_2 \rightleftharpoons 2\ Co^{III}(acac)_3\ H$$

$$Co^{III}(acac)_3 + Co^{II}(acac)_3\ H \longrightarrow \text{electron transfer}$$

This mechanism assumes that the cobalt complexes form dimeric species when dissolved in acetylacetone. This possibility has already been discussed for the cobalt (II) complex however the possible formation of a cobalt (III) dimer should be considered. Since the dimerization of the tris(acetylacetonato) cobalt (III) would necessitate the breaking and reforming of metal-ligand bonds it would not be expected to occur to any great extent in solution due to the reasonably high stability of the cobalt (III) complex (11), (43). Dimerization of the cobalt (III) complex could however take place during the initial preparation of the compound. If however this was the case then, unless acetylacetone was playing a very unexpected part in the reaction, one would also expect to find the electron transfer with a half order rate dependence on the cobalt (III) concentration in toluene. As in the case of the cobalt (II) complex the existence or nonexistence of a dimeric tris(acetylacetonato) cobalt(III) could not be proved by boiling point elevation methods, although it has been shown to be monomeric (49) in benzene by freezing point depression methods.

(c) The fractional order observed for the reaction may also be explained in terms of reactant molecules being prevented from collision and hence reaction due to solvent shielding. The solvent molecules could be bound to the reactant molecules by hydrogen bonding (27) and Van der Waals type forces, although one would expect that the effect of these forces at 100°C would not be very great due to the increased thermal energies of the reactant molecules.

Molecules of the cobalt (II) and cobalt (III) complexes, with sufficient energy of activation to allow the electron transfer to proceed if collision between two unshielded molecules takes place, may be placed into either one of two classifications.

(1) Those molecules which are prevented from reacting due to solvent shielding and which may be termed "non-active" molecules

and (2) Those molecules which are without solvent shielding and may be termed "active" molecules.

The relative extent to which shielding can occur will be a function of the concentration of the cobalt complexes. In the experiments carried out the extent of solvent shielding would be similar since the concentrations of the cobalt complexes are not varied to any great extent. However the small variations that are made to the concentrations of the complexes could explain the large scatter of the values of x and y shown in Table 2.4.

If this explanation of solvent shielding is correct then the mechanism may be represented as

$$\left[\mathrm{Co}^{II}(\mathrm{acac})_3\mathrm{H}\right] n\,\mathrm{S} \rightleftharpoons \mathrm{Co}^{II}(\mathrm{acac})_3\,\mathrm{H} + n\,\mathrm{S}$$

$$\left[\mathrm{Co}^{III}(\mathrm{acac})_3\right] m\,\mathrm{S} \rightleftharpoons \mathrm{Co}^{III}(\mathrm{acac})_3 + m\,\mathrm{S}$$

$$Co^{II}(acac)_3\ H \quad + \quad Co^{III}(acac)_3 \longrightarrow \text{electron transfer.}$$

Where S represents Solvent molecules. In this case as in previous mechanisms it is assumed that the bis(acetylacetonato)cobalt (II) reacts with acetylacetone when dissolved in it to form the tris(acetylacetonato) cobaltate-(II) ion.

In considering the foregoing discussions it would appear that the most likely overall reaction mechanism is represented by either the first mechanism discussed (i.e. where the rate of reaction is expressed by equation 2.31) or by the last (i.e. where the rate of reaction is expressed by equation 2.30).

Activation Energy and Entropy of Activation

The electron transfer reaction was studied in acetylacetone at various temperatures (Figs. 2.27 - 2.30) in order to determine the activation energy. A summary of the results of the electron transfer reaction is given in Table 2.5. The activation energy was calculated from the slope of the graph shown in Fig. 2.31 and was found to be 14.0 (± 10%) k cals/mole.

The magnetic moment of the tris(acetylacetonato)cobaltate (II) ion was determined by Dwyer and Sargeson (47) and was found to be similar to the value found by Cotton (48) for the bis(acetylacetonato)cobalt(II). Hence the central metal atom will be in an electron spin free state in either toluene, where it will occur as the bis(acetylacetonato) complex, or in acetylacetone where it will occur as the tris(acetylacetonato)cobalt (II) complex ion. Further, since the cobalt (III) complex will be in an electron spin paired state in either of the solvents used, one could expect

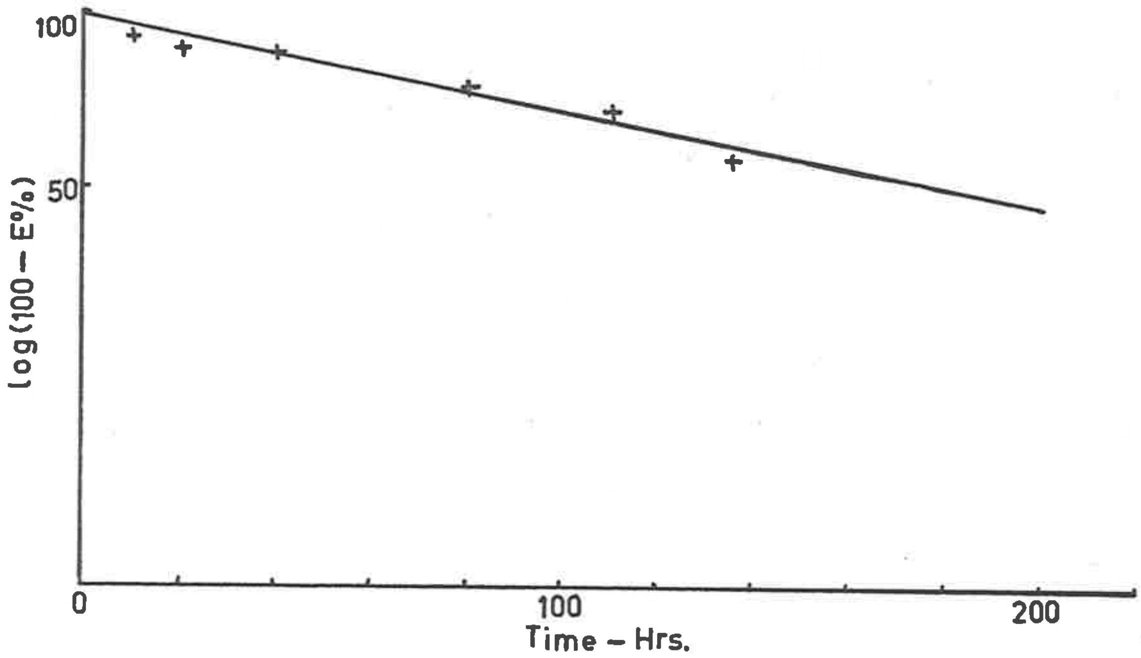


Fig.2.27 $Co^{II}(acac)_2$– $Co^{III}(acac)_3$ electron transfer reaction in acetylacetone at 69.6±0.1°C; Co^{II} 0.0145M & Co^{III} 0.0099M

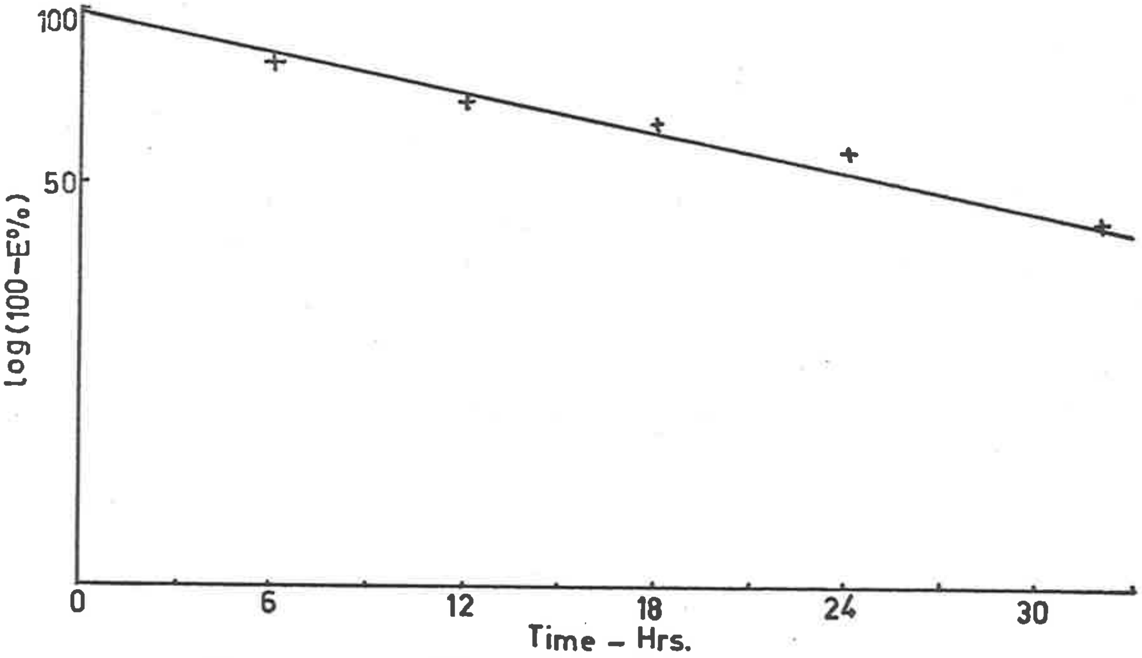
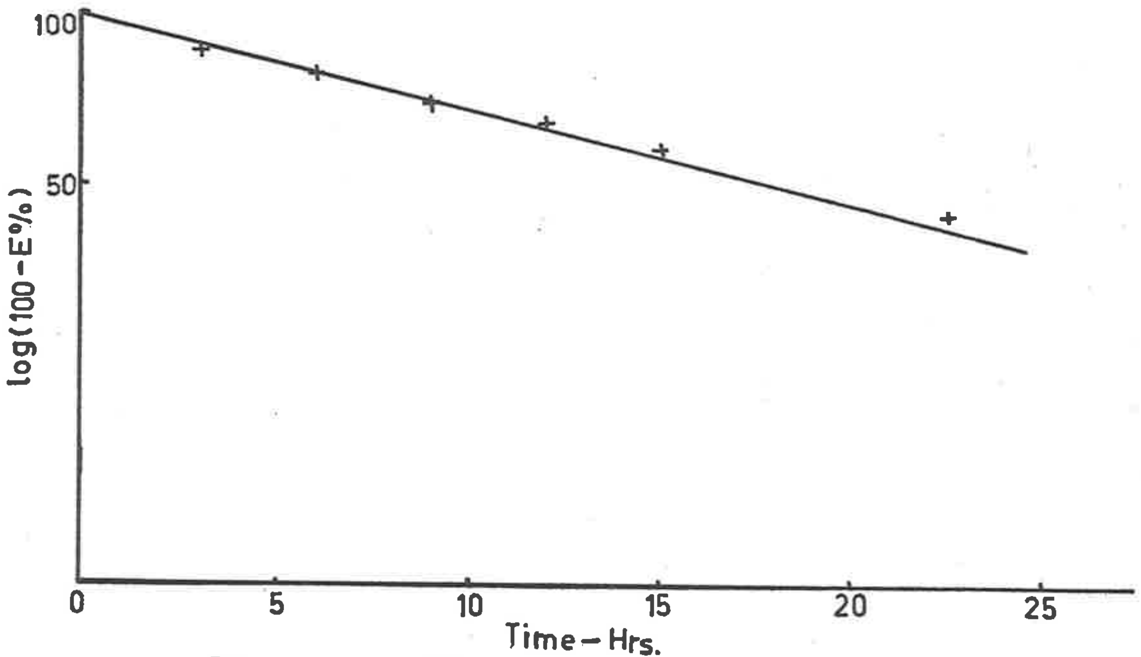
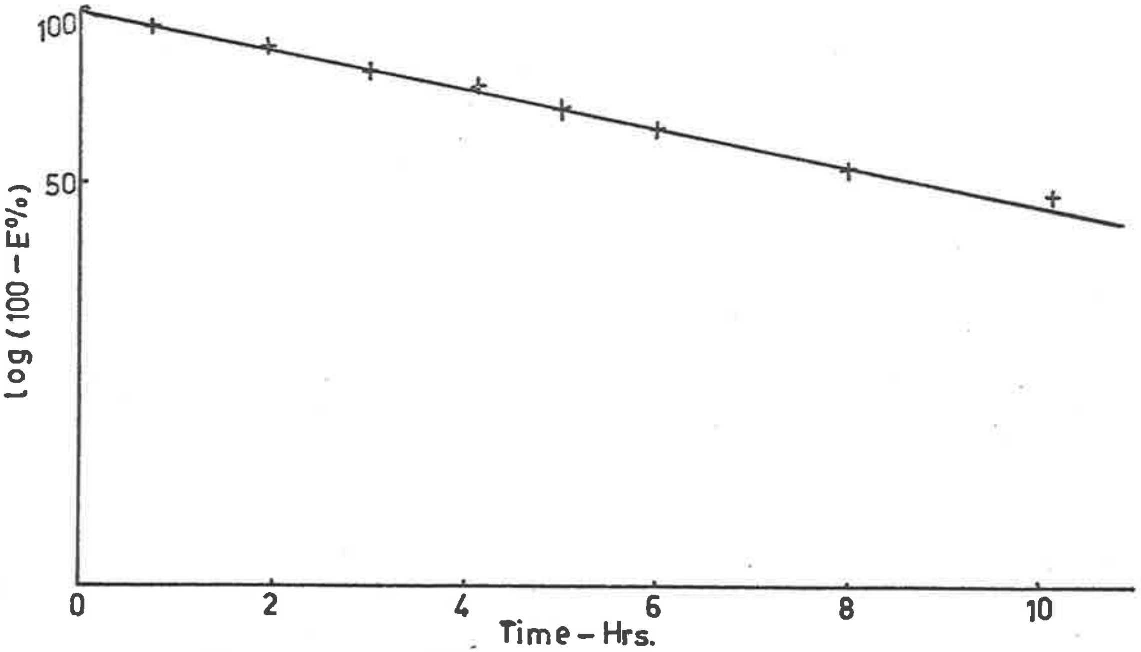


Fig.2.28 $Co^{II}(acac)_2$– $Co^{III}(acac)_3$ electron transfer reaction in acetylacetone at 83.6±0.1°C; Co^{II} 0.0137M & Co^{III} 0.0155M



<u>Fig.2.29</u> $Co^{II}(acac)_2$- $Co^{III}(acac)_3$ electron transfer reaction in acetylacetone at 89.9±0.1°C: Co^{II}0.0152M & Co^{III}0.0174M



<u>Fig.2. 30</u> $Co^{II}(acac)_2$- $Co^{III}(acac)_3$ electron transfer reaction in acetylacetone at 96.0±0.1°C; Co^{II}0.0112M & Co^{III}0.0112M

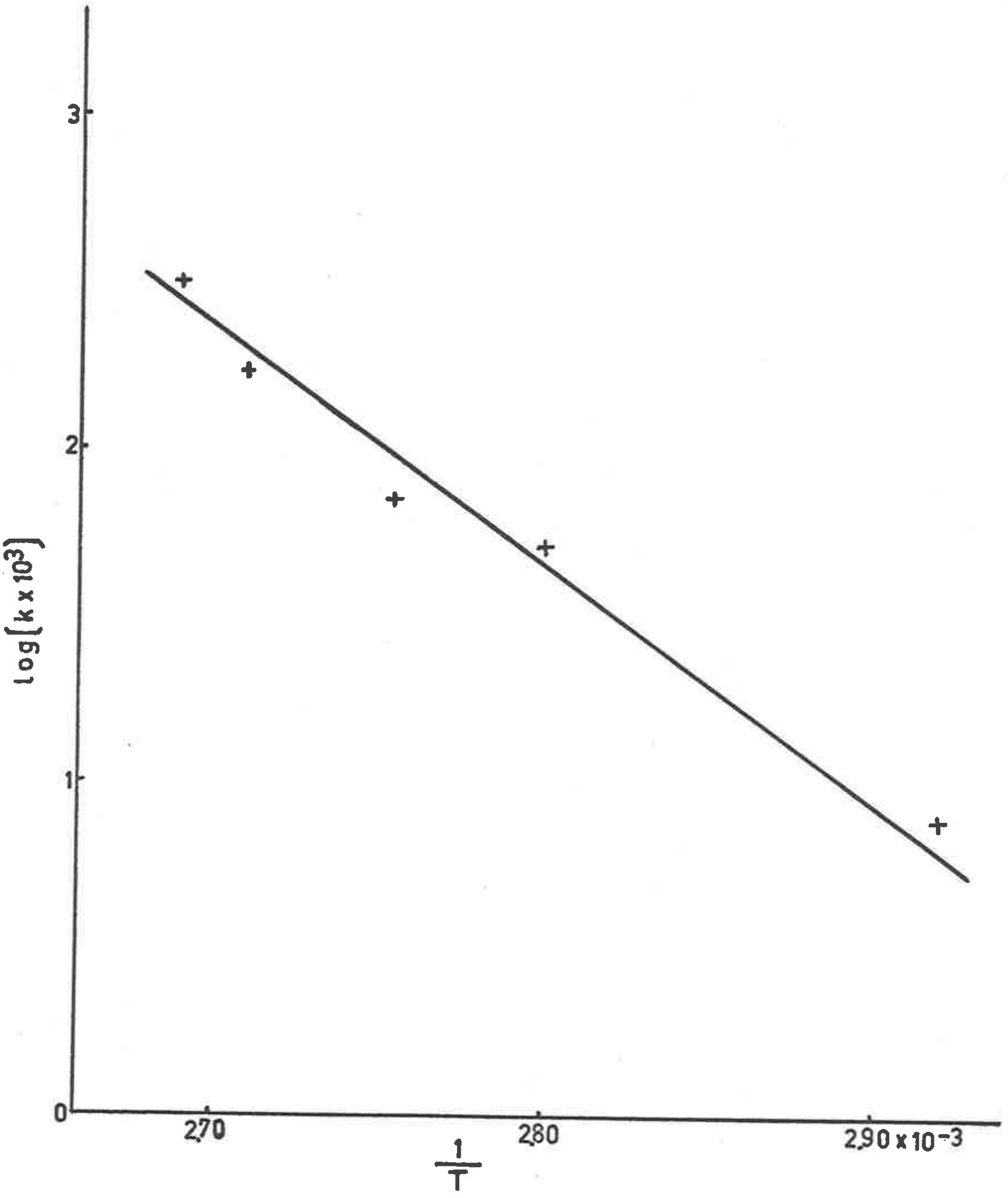


Fig.2.31 Co^{II}(acac)$_2$- Co^{III}(acac)$_3$ electron transfer reaction in acetylacetone.

TABLE 2.5

Electron Transfer Reaction between bis-(Acac) Cobalt (II) and tris-(Acac) Cobalt (III) in Acetylacetone. Variation of Reaction Rate Constant with Temperature.

No.	Concentrations (M)		Half-life	$^*k_3$	Temp. °C
	Cobalt II	Cobalt III	(hrs.)		
1	.0096	.0096	4.4	3.44×10^{-1}	98.7 ± 0.1
2	.0192	.0192	3.9	3.17×10^{-1}	98.7 ± 0.1
3	.0193	.0086	4.3	2.79×10^{-1}	98.7 ± 0.1
4	.0171	.0105	3.9	3.50×10^{-1}	98.7 ± 0.1
5	.0112	.0112	4.1	3.50×10^{-1}	98.7 ± 0.1
6	.0172	.0105	3.8	3.59×10^{-1}	98.7 ± 0.1
7	.0480	.0482	4.3	2.24×10^{-1}	98.7 ± 0.1
8	.0096	.0193	4.1	2.99×10^{-1}	98.7 ± 0.1
9	.0145	.0099	180	7.86×10^{-3}	69.6 ± 0.1
10	.0137	.0155	26.5	4.99×10^{-2}	83.6 ± 0.1
11	.0152	.0174	18.3	7.00×10^{-2}	89.9 ± 0.1
12	.0112	.0112	8.7	1.64×10^{-1}	96.0 ± 0.1

*Units of k_3 are obtained from $R = k_3\ (Co^{II})^x\ (Co^{III})^y$

the electron transfer reaction to have similar values for the activation energy, the probable significance of which is discussed in section C, for both toluene and acetylacetone solvent systems. This is found to be the case since the activation energy for the toluene as solvent was found to be 14.2(± 2.5%)k cals/mole.

Substitution of the activation energy for the acetylacetone solvent system in equation 2.10 gave calculated value of - 46 (± 15%) e.u. for the entropy of activation. Comparison of this value with that for the toluene system - 40(± 5%)e.u. would indicate that the reaction proceeded more slowly in the former solvent. However this is not the case and the decrease in the calculated entropy of activation, compared with the value for the reaction in toluene, can be accounted for as being due to the use of the average value of k_1 (Table 2.5,) which includes a term for the participation of the solvent in the rate of reaction (equations 2.17, 2.18).

A probable upper limit to the entropy of activation for the reaction in acetylacetone can be obtained by assuming the reaction to obey a second order kinetics. The maximum second order rate constant, at 98.7 ± 0.1°C, that can be calculated from data in Table 2.5 is 16.4 (± 20%) $\text{moles}^{-1}\text{hours}^{-1}$ (reaction No.1). When this is substituted in equation 2.10 the calculated entropy of activation is -37 (± 15%) e.u. Hence the probable upper limit to the entropy of activation for the reaction in acetylacetone is -31.5 e.u. This value is still a significantly large negative value and use will be made of this fact in the interpretation of possible electron transfer mechanisms.

The Electron Transfer

It will be seen from the two most probable overall reaction mechanisms for the reaction between the cobalt (II) and cobalt (III) acetylacetonato complexes that the actual electron transfer step is the same viz.

$$Co^{II}(acac)_3H + Co^{III}(acac)_3 \longrightarrow \text{electron transfer}$$

The mechanism by which the actual electron transfer takes place will have several possibilities

(1) The mechanism of electron jump (4)

In this mechanism the molecules would need to approach close enough for the electron to jump from one molecule to the other and this may be actual contact of the neutral complexes. Libby (4) suggests that the electron jump between two cations may take place through several layers of solvent. However in this case the chance of such a happening would be somewhat lessened due to the shielding effect of the ligand molecules bound to the central metal atoms.

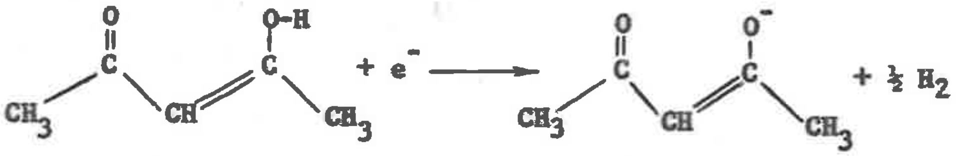
(2) Penetration of the potential energy barrier (5)

Due to the charge on molecules between which an electron transfer reaction is taking place a repulsion and hence a potential energy barrier will result. In the case being considered here at least one of the molecules is a netural molecule and as such may be considered as having zero charge. Thus no Marcus type potential energy barrier (5) should be formed. However polarization within the molecules is to be expected and this would result in an electrostatic repulsion and hence a potential energy barrier to the electron transfer reaction.

The mechanism of potential energy barrier penetration is essentially the same as the electron jump mechanism, however the energy requirements are less. Also the distance at which electron transfer could take place would be somewhat greater than allowed by the electron jump mechanism. The consequence is that solvent shielding as suggested in one of the overall reaction mechanisms would probably be nonexistent. Furthermore, if electron transfer was to occur through several layers of solvent, as allowed by the barrier penetration mechanism, then a contribution to the potential energy barrier could be expected from the dieletric constant of the solvent. Cohen et al (10) have produced evidence that a change of the dielectric constant of the solvent does not change the rate of reaction. This is further supported by the reaction between the 1.10 phenanthroline complexes of cobalt (II) and cobalt (III) in water-acetone mixtures (26) and in which it was found that the result did not fit the Marcus (5) model over the entire range of values of the dielectric constant. The conclusion that can be drawn from this evidence is that the electron transfer occurs through a compact transition state and not through an extended one. This is further supported by a consideration of the probable maximum entropy of activation for the electron transfer reaction, which in acetylacetone as solvent was found to be - 31.5 e.u. If the electron transfer were to proceed through an extended transition state the entropy of activation would be expected to be more positive (28) and not to have a value comparable with other electron transfers known to proceed via a compact bridged transition state (Table 2.3) . Furthermore the value of the probable maximum entropy of activation may be compared with the case when toluene was used as solvent i.e. $\Delta S^{\ddagger} = -40$ (± 5%)e.u. In the latter case the reaction almost certainly goes by way of a compact bridged transition state.

(3) Solvation of the Electron

The electron undergoing transfer may be released by the donor molecule and may then exist as a free or solvated electron for some finite time before reacting with the exceptor molecule. The essential difference between this mechanism and the electron jump mechanism is the time for which the electron may exist in the free or solvated state in solution. Although electrons may exist in solution (6) when such solvents as liquid ammonia are used, it is highly unlikely that this would be the case in acetylacetone. The existence of electrons in liquid ammonia solutions is attributed to the low value of the autionization constant $\left[K_{NH_3} = 1.9\times10^{-23}\right]$ (34), however the value for acetylacetone would probably be comparable to that for water.* Thus acetylacetone could be expected to act in a similar way to water (4), in the presence of electrons, in that it would undergo reduction with the evolution of hydrogen and the formation of an acetylacetonate ion i.e.



However in reactions carried out under sealed conditions no liberation of hydrogen could be detected.

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* see footnote p.100

(4) A bridged activated transition state complex.

The large negative value of the probable maximum entropy of activation may be used in a qualitative way as evidence that a bridged activated transition state complex is formed (cf. section C). There are several bridged intermediates that can be postulated for the system investigated, these being represented diagrammatically in Fig. 2.32.

If bis(acetylacetonato)cobalt (II) does not react with acetylacetone to form the tris(acetylacetonato)cobalt-(II) ion then the structure shown in Fig. 2.32(a) would apply. This structure will be seen as the same as that suggested for the bridged transition state when toluene was used as the solvent. Thus the entropy of activation for the electron transfer proceeding via this intermediate would be expected to be the same as found when toluene was solvent, viz. -40(± 5%)e.u., and the reaction would be expected to proceed at the same rate and to obey the same kinetics.

The intermediate structures shown in Figs. 2.32 b and c could be expected if acetylacetone reacts with the cobalt (II) complex to form the tris(acetylacetonato) complex ion. The electron transfer proceedint via the intermediate shown in Fig. 2.32 b would seem unlikely on the grounds of the energy requirement for the breaking of not only one metal-ligand bond, as the previous mechanism requires, but two.

The most likely path for the electron transfer via a bridged activated complex is shown by Fig. 2.32 c. In this case it would be unnecessary to break and reform any of the existing metal-ligand bonds, thus lowering the activation energy needed for the electron transfer

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* The pK of acetylacetone in water is given (9) as 8.95 at 30°C and at infinite dilution.

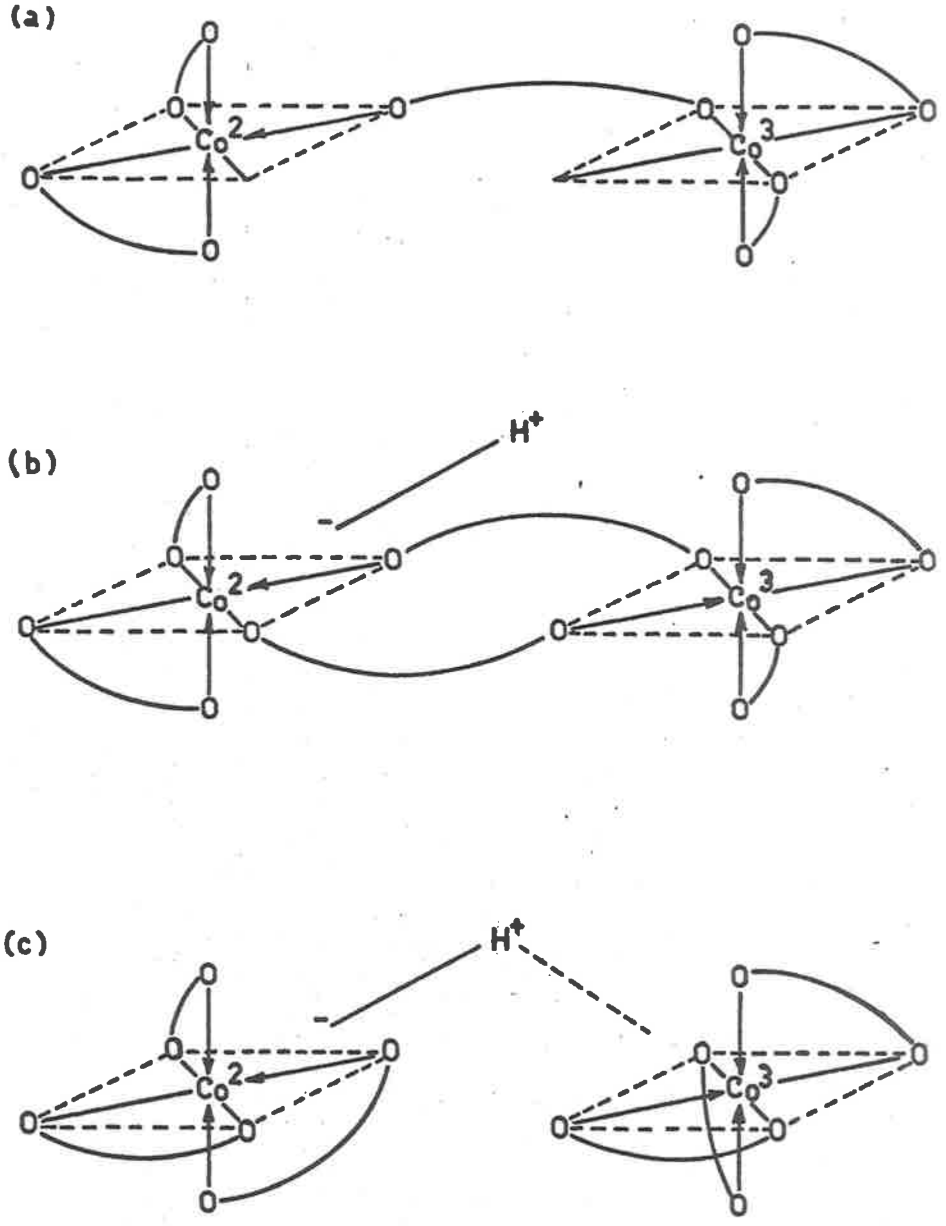

Fig.2.32 Activated transition state complexes.

reaction. The proton forming the bridge would as an extreme case be hydrogen bonded (18) to two oxygen atoms as shown in Fig. 2.33. A better idea of the structure of the intermediate would be gained if it were considered as a resonance hybrid of several possible extreme cases similar to that shown in Fig. 2.33. This type of intermediate is also supported by the results obtained using mixtures of acetylacetone and toluene as the solvent for the reaction. However the three activated bridged transition states will all have symmetrical structures and would therefore, in terms of the Franck-Condon Principle (35), provide favoured paths for the electron transfer provided the energy states of the electrons in the reacting cobalt species are equivalent.

A further possible way in which the electron transfer could take place via a bridging mechanism is shown in Fig. 2.34. In this case a conjugated bridge system is formed by the hydrogen bonding of several solvent molecules and the two complex molecules undergoing electron transfer. The activated intermediate in this case would, on transfer of the electron, exchange a hydrogen atom at each end of the solvent bridge and the movement of the electron would be facilitated by the conjugated system (29). However if this mechanism were the one for the actual electron transfer step then the overall mechanism involving solvation of the complexes would not present a barrier to the electron transfer and the solvent shielding proposed would be nonexistent. Further this mechanism can be considered as an electron penetration of a potential energy barrier which results from the dielectric constant for the solvent.

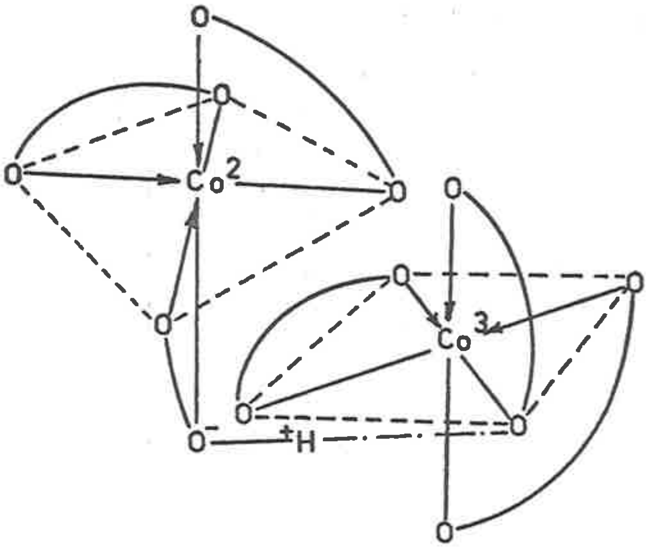

Fig.2.33 II atom bridging in the transition state complex

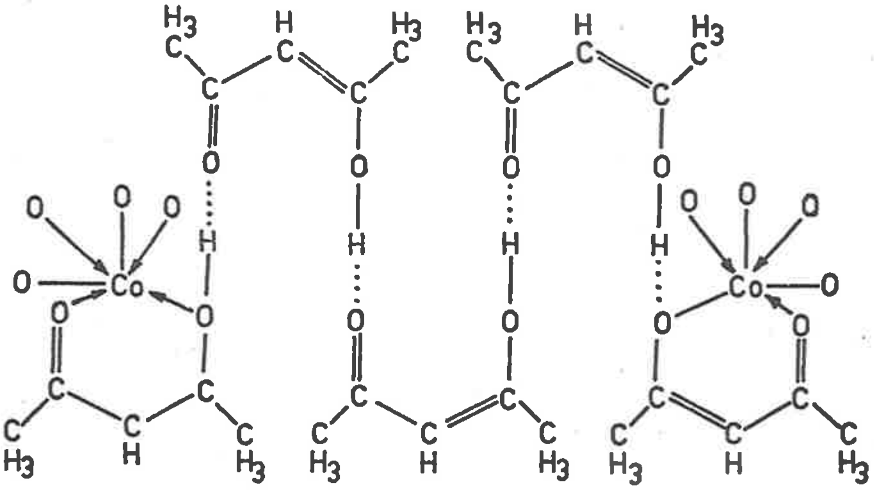

Fig.2.34 Solvent bridging in the transition state complex

Also it has already been pointed out that the electron penetration of the potential energy barrier for an extended transition state is not supported by the large negative entropy of activation.

In view of the evidence available the most likely explanation of the electron transfer step of the reaction is that the exchange occurs through a compact transition state. The compact transition state is best explained in terms of a bridged activated complex which is supported by the probable maximum entropy of activation. Furthermore the most favourable of the bridged transition states is that represented by Fig. 2.32 c which is supported by the mixed solvent experiments. However further work, which might assist in the establishment of whether or not a hydrogen ion is involved in the bridge formation in the presence of acetylacetone, would be to carry out the experiments using deuterated acetylacetone. One would expect that when deuterated acetylacetone was used as solvent, provided the same conditions of temperature and reactant concentrations were applied, there would be a twofold decrease in the rate of reaction if the hydrogen ion was the bridging group. However if, in the transition state complex, the much larger acetylacetone group was used for forming the bridge between the reactants, a maximum decrease in the rate of reaction of only 15% would be expected. The 15% decrease in the rate of reaction should occur if two fully deuterated acetylacetone groups formed a double bridge as in Fig. 2.32 b. If only one acetylacetone was used the decrease in rate of reaction should be about 7%.

E. Pyridine as Solvent

An attempt was made to study the electron transfer reaction between the acetylacetonato complexes of cobalt in pyridine as solvent at a temperature of 98.7 ± 0.1°C. In a preliminary experiment Fig. 2.13, it was found that the half life was of the order of 15 hours. However, doubt was cast on the results obtained when it was found on repeating the experiment, that reduction had occurred to a great extent. In order to test the reduction of the cobalt (III) complex in pyridine a sample was reacted in the presence of air with pyridine and it was found that after five to six hours at the boiling point of pyridine a substantial quantity of the originally cobalt (III) complex was found to have changed colour from green to red.

It was felt that due to the reduction taking place in pyridine and also due to the unknown and probably varied species that would be in solution after only a short time, due to the complexing properties of the solvent, that further study of the electron transfer reaction would not prove advantageous.

F. Electron Transfer Spectra

Some workers (14, 15) have reported the existence of electron transfer bands in spectral studies of species undergoing electron transfer reactions. An attempt was made to study the existence of such bands in the case of the electron exchange reaction between the cobalt (II)-cobalt (III) acetylacetonato complexes. The results obtained are shown in Fig. 2.35 and it can be seen from this diagram that the spectrum for the mixture of the cobalt compounds in the sum of the spectra for the cobalt (II) and cobalt (III) complexes. There are, in fact, no

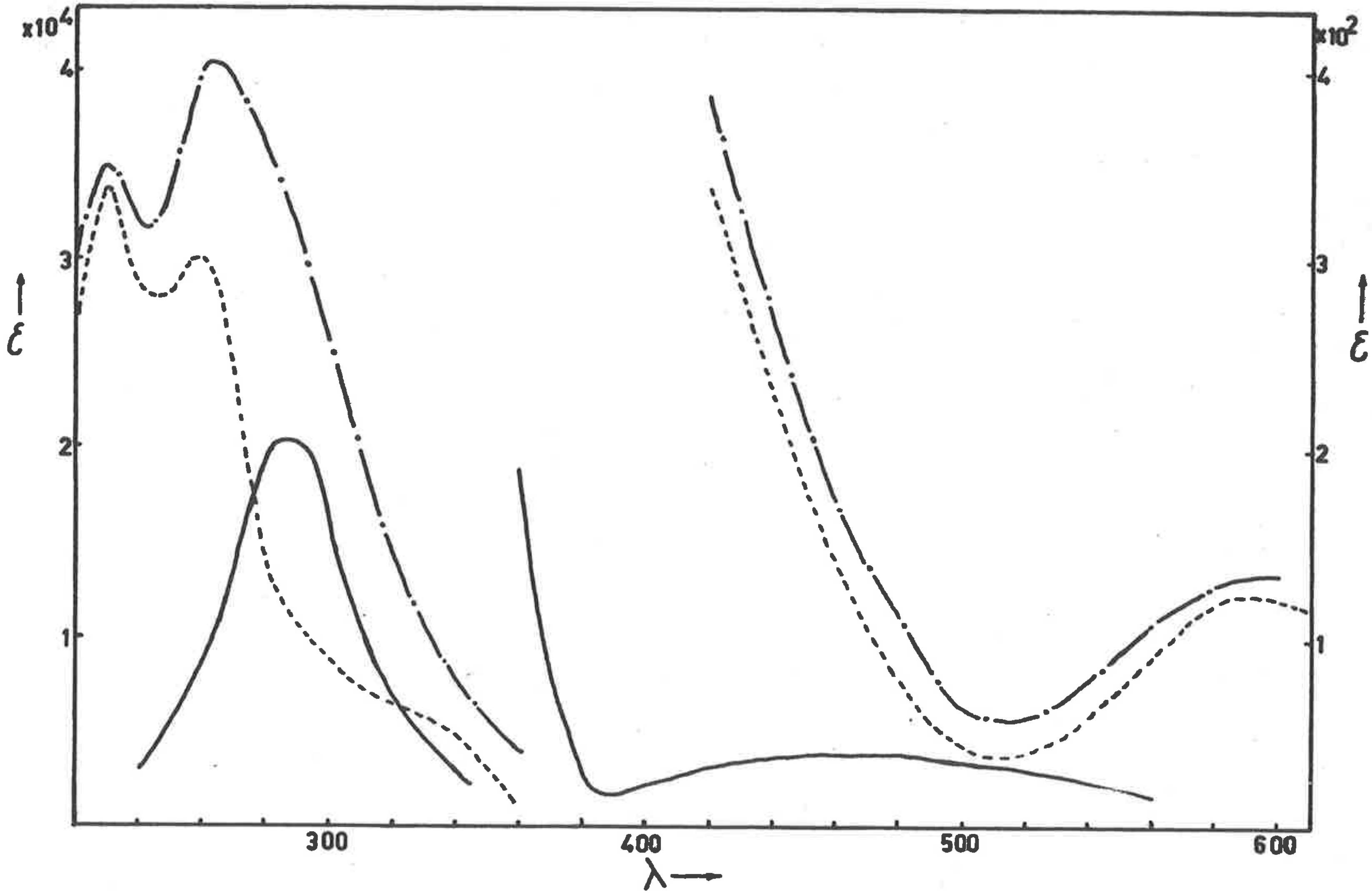

Fig.2.35 Spectra of Co^{II}(acac)$_2$ and Co^{III}(acac)$_3$; —— Co^{II}; ----Co^{III}; —.—mixture: in S.V.R. at 25°C

abnormal peak shifts or bands which can be attributed to an electron transfer reaction. The reaction at 98.7°C has a half-life of approximately 4 hours, while the study of the spectra was carried out at room temperature in ethanol solution. The half-life at this temperature would be of the order of many thousands of hours. The requirements for the measurement of electron transfer spectra bands will be that a large number of electron transitions should take place in a relatively short time. This not being the case at room temperature it was not surprising that no spectral evidence for the electron transfer reaction was obtained in this work. The determination of the spectra at the temperature of the kinetic study would require considerable modifications to the spectroscopic apparatus and could be the subject of further work.

G. The Electron Transfer Reaction between the Acetylacetonato Complexes of Iron (III) and Iron (II)

An attempt was made to study the electron transfer reaction between iron (II) and iron (III) acetylacetonato complexes. The compounds were prepared as on p.176 . The iron (II) compound was stable, for reasonable periods of time, if in the dry state; however, if a solution of this were exposed to air a rapid oxidation took place.

Attempts to separate the two complexes met with difficulty. Attempts were made using chromatography, precipitation of the alkali metal salts of the trisacetylacetonato complex of iron (II) and solvent extraction of the 2.2'-dipyridyl complex of iron (II). As these methods of separation all proved unsatisfactory the project was not proceeded with.

An attempt was made, however, to study the reaction by means of spectra measurements. The reaction should be fast, since the electron exchange would be a t_{2g} exchange (16). The attempts met with failure due to the rapid oxidation of the iron (II) species in solution. The solutions in ethanol were prepared under a nitrogen atmosphere, however by the time the measurement was commenced oxidation of the very dilute solutions of the iron (II) complex was found to have taken place. This was probably due to very small traces of oxygen that could not be removed from the system. That oxidation took place was evident from the spectra obtained since it was the same for the originally iron (II) complex as it was for the iron (III) species. The spectra of the iron (III) acetylacetonato complex is given in Fig. 2.36.

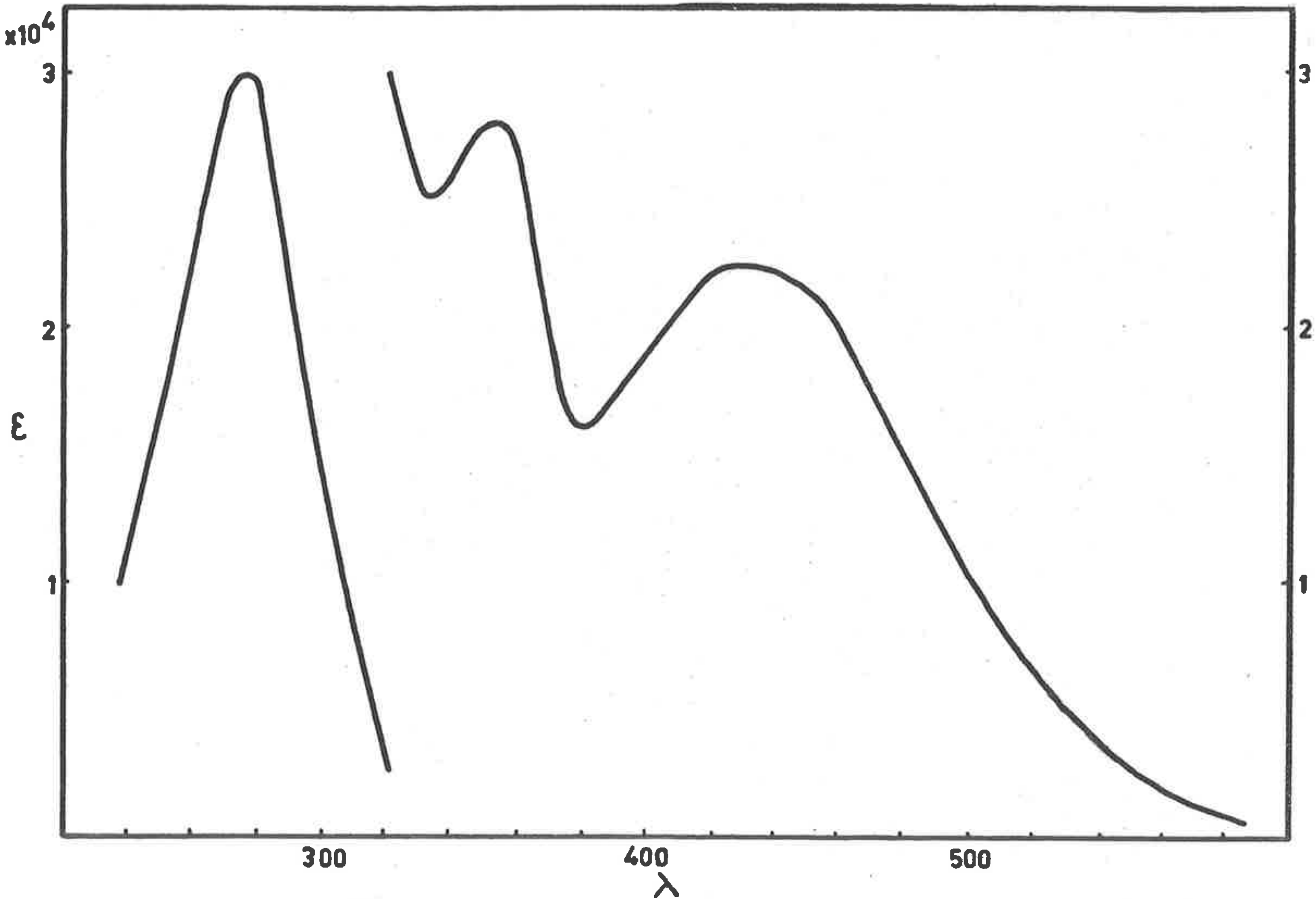

Fig.2.36 Spectrum of $Fe^{III}(acac)_3$ in S.V.R.

CHAPTER 3

The Electron Transfer Reaction between Cobalt (II) and Cobalt (III) N-phenylsalicylideneiminato Type Complexes.

A. The Electron Transfer Reaction between bis(N-p-tolylsalicylideneiminato Cobalt (II) and tris(N-p-tolylsalicylideneiminato) Cobalt (III).

It was found that the rate of the electron transfer was faster for the p-tolsal * complexes than for the acetylacetonato complexes in toluene and that lower temperatures could be used at which the reactions proceeded at a measurable rate. The temperature chosen for the kinetic study of the electron transfer reaction was 55°C. Both compounds were soluble in toluene, the solvent used for the acetylacetone experiments and this was therefore chosen as the solvent in this particular case. Further it was not considered likely that toluene could take part in the electron transfer reaction. Unlike bis(acetylacetonato) cobalt (II) the cobalt (II) complex in this system was not found to undergo oxidation during the course of the kinetic experiments. Reduction did, however, occur (Table 3.1) but this was so small as to make corrections to the percentage of exchange unnecessary and the rate of reaction was thus calculated using the simplified form of equation 2.4.

The experiments were carried out in a similar manner to that used for the study of the electron transfer reaction between the cobalt

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* p-tolsal indicates the n-p-tolylsalicylideneimine

acetylacetonato complexes, viz. the cobalt(III) complex was labelled with Co^{60} and the reactants separated by chromatographic procedures with alumina, however it was unnecessary to seal the samples under nitrogen, as was done in the acetylacetone reactions, since oxidation of the cobalt (II) p-tolsal complex did not occur readily under the experimental conditions used. The results for each experiment carried out are shown in Figs. 3.1-3.16. The errors in the percentage of exchange plotted on the graphs are ± 3% of E%. These arise from an error of + 1% in the counting rate (see p.171) and an estimated error of ± 1% in the separation procedure. The error in separation procedure was obtained from a series of experimental separations.

TABLE 3.1

Reduction of Tris-(p-tolsal)-cobalt(III) in Toluene at 55° ± 0.1°C.

Concentration Co^{III} 0.0100 M.

No.	Time (hrs)	Counts / 100 secs		%R
		Cobalt III	Cobalt II	
1	1.0	2858	30	1.0
2	2.0	2882	39	1.3
3	3.0	2919	49	1.6
4	6.5	3074	98	3.0

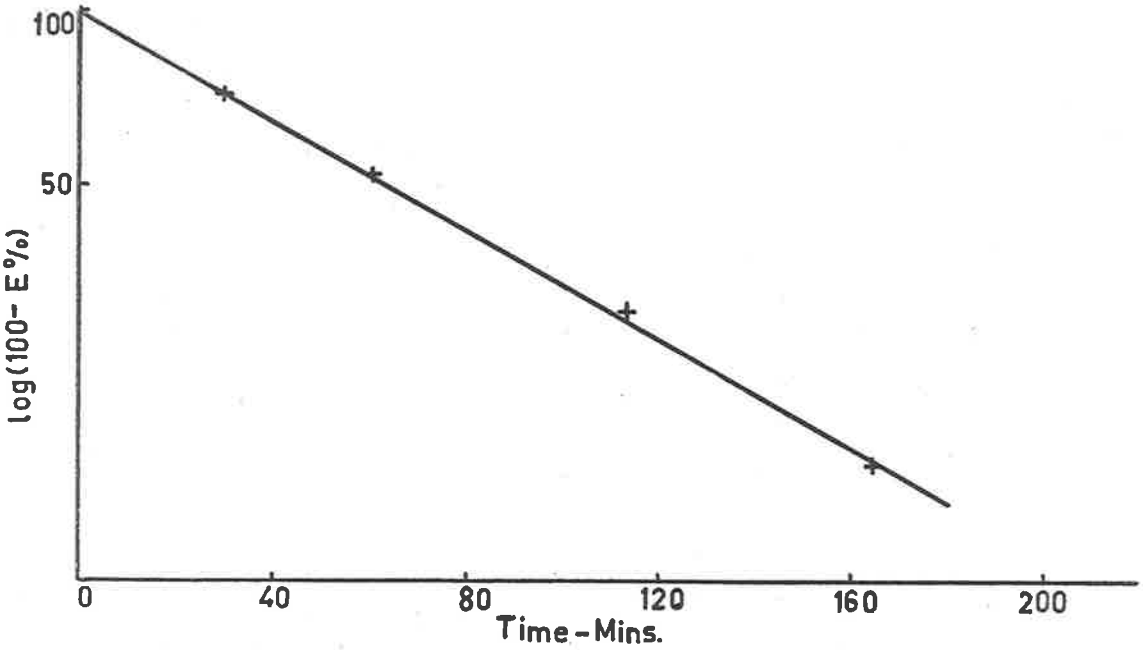


Fig.3.1 Co^{II}(p-tolsal)$_2$ - Co^{III}(p-tolsal)$_3$ electron transfer reaction in toluene at 55.0°C;Co^{II} 0.0100M & Co^{III} 0.0098M

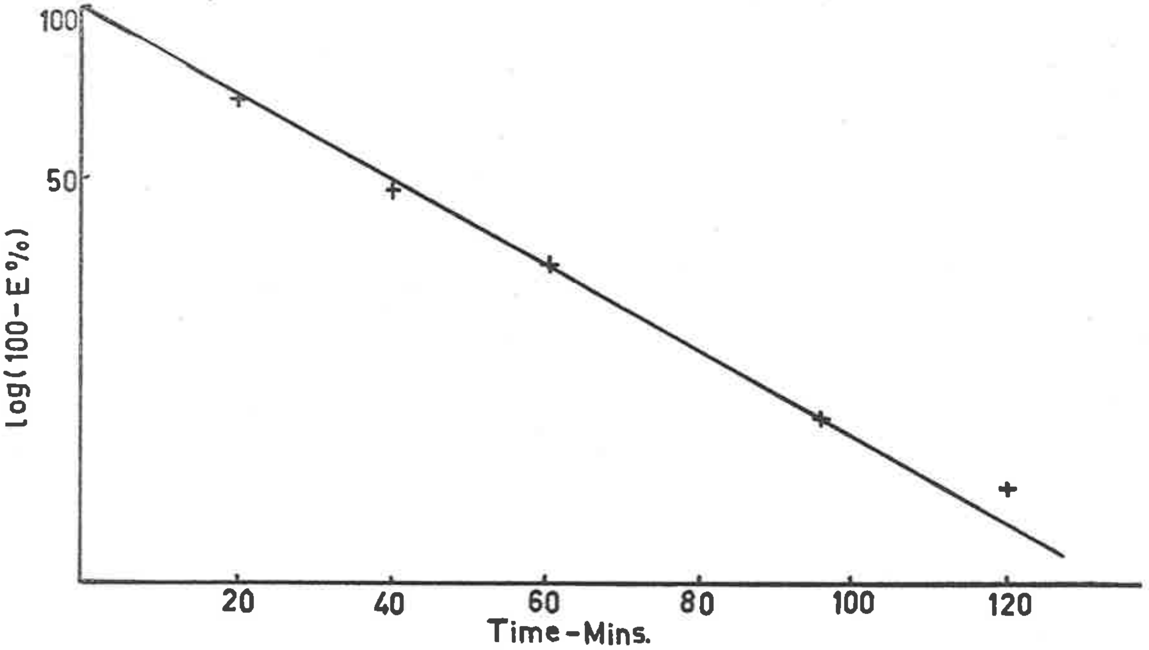


Fig.3.2 Co^{II}(p-tolsal)$_2$ - Co^{III}(p-tolsal)$_3$ electron transfer reaction in toluene at 55.0°C;Co^{II} 0.0051M & Co^{III} 0.0097M

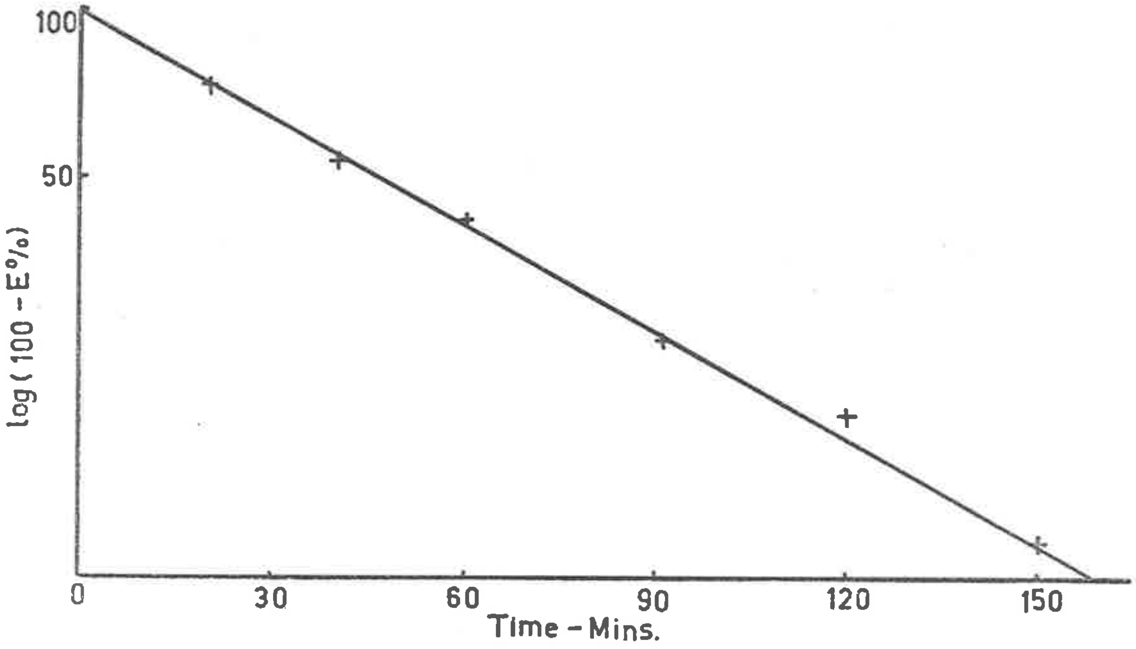


Fig.3.3 Co^{II}(p-tolsal)$_2$ - Co^{III}(p-tolsal)$_3$ electron transfer reaction in toluene at 55.0°C;Co^{II} 0.0076M & Co^{III} 0.0098M

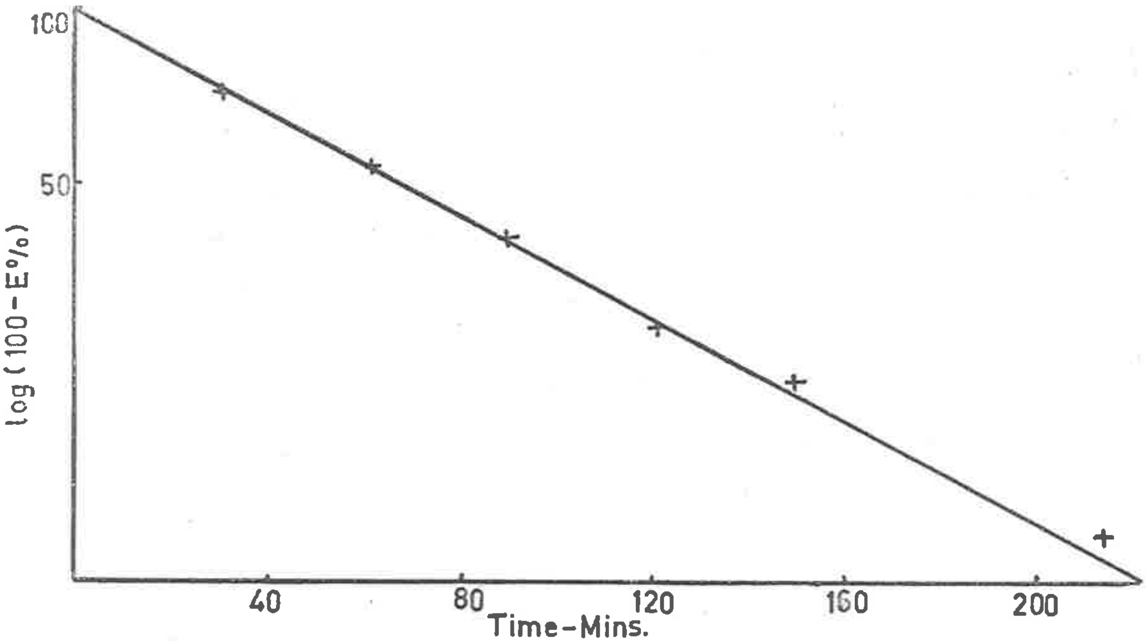


Fig.3.4 Co^{II}(p-tolsal)$_2$ - Co^{III}(p-tolsal)$_3$ electron transfer reaction in toluene at 55.0°C;Co^{II} 0.0152M & Co^{III} 0.0097M

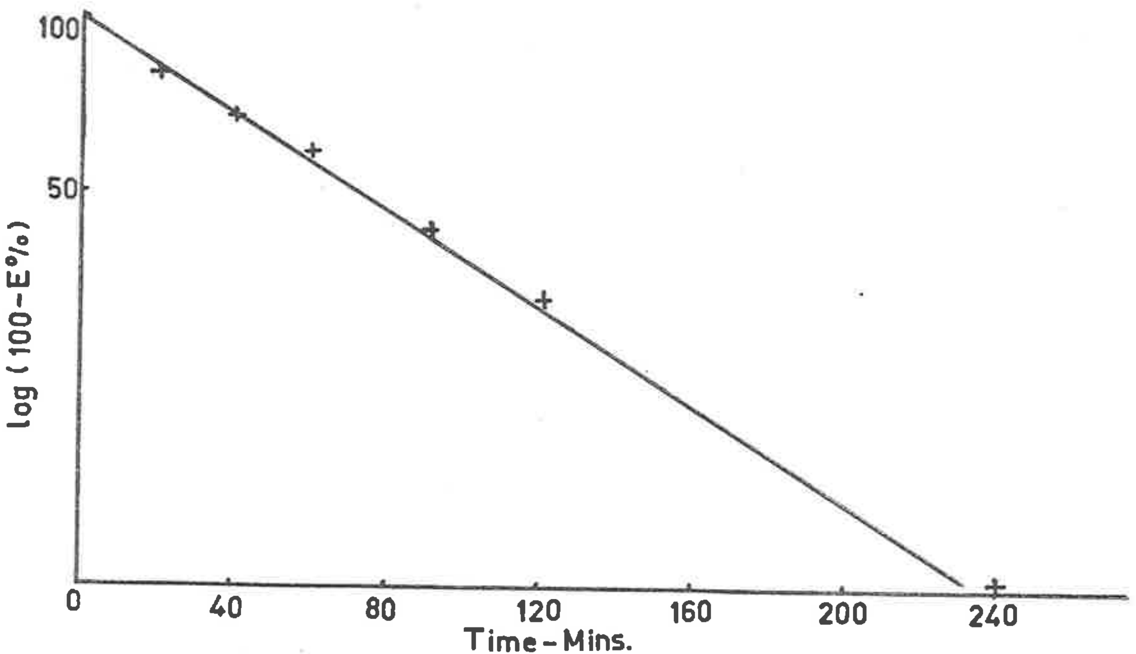


Fig.3.5 Co^{II}(p-tolsal)$_2$ - Co^{III}(p-tolsal)$_3$ electron transfer reaction in toluene at 55.0°C;Co^{III}0.0097M & Co^{II}0.0200M

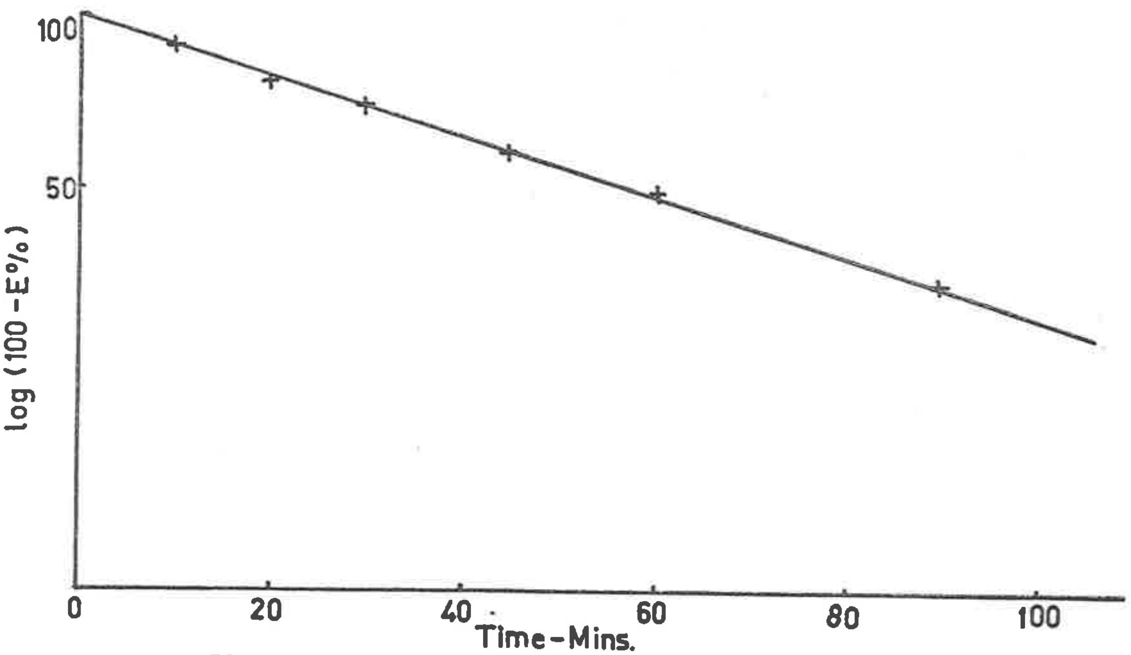


Fig.3.6 Co^{II}(p-tolsal)$_2$ - Co^{III}(p-tolsal)$_3$ electron transfer reaction in toluene at 55.0°C;Co^{II}0.0179M & Co^{III}0.0198M

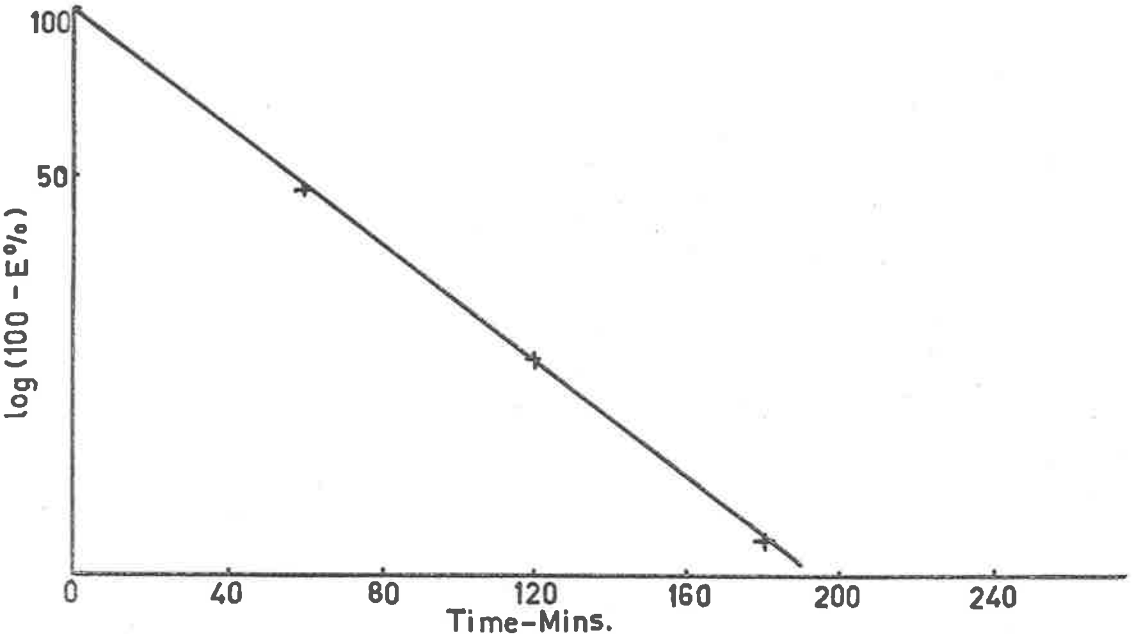


Fig.3.7 Co^{II}(p-tolsal)$_2$ - Co^{III}(p-tolsal)$_3$ electron transfer reaction in toluene at 55.0°C; Co^{II} 0.0050M & Co^{III} 0.0048M

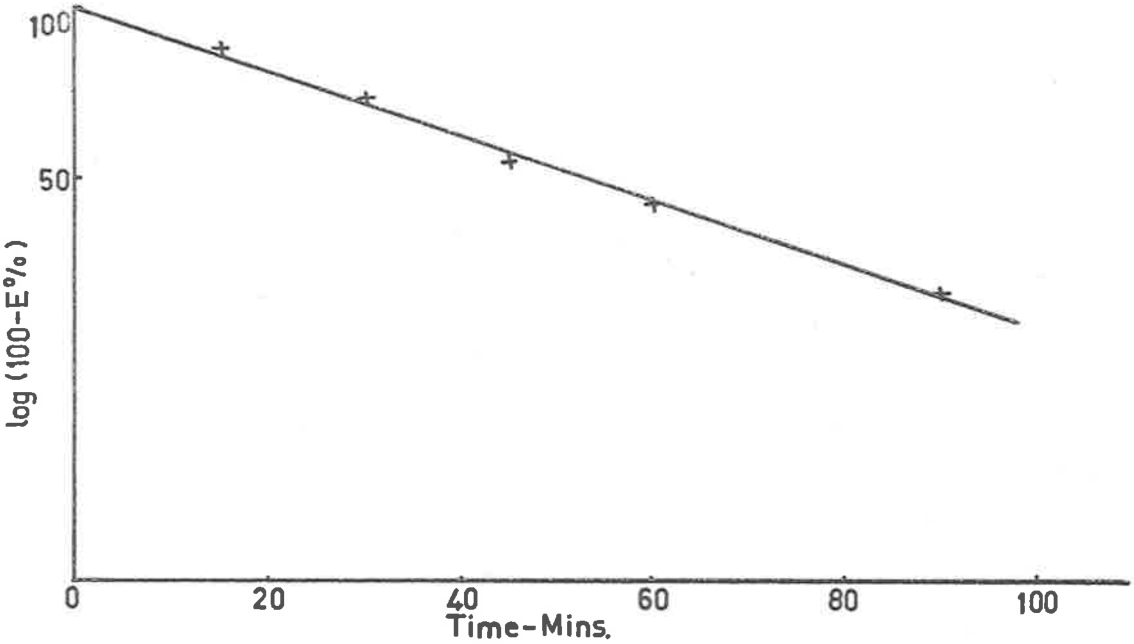


Fig.3.8 Co^{II}(p-tolsal)$_2$ - Co^{III}(p-tolsal)$_3$ electron transfer reaction in toluene at 55.0°C; Co^{II} 0.0100M & Co^{III} 0.0146M

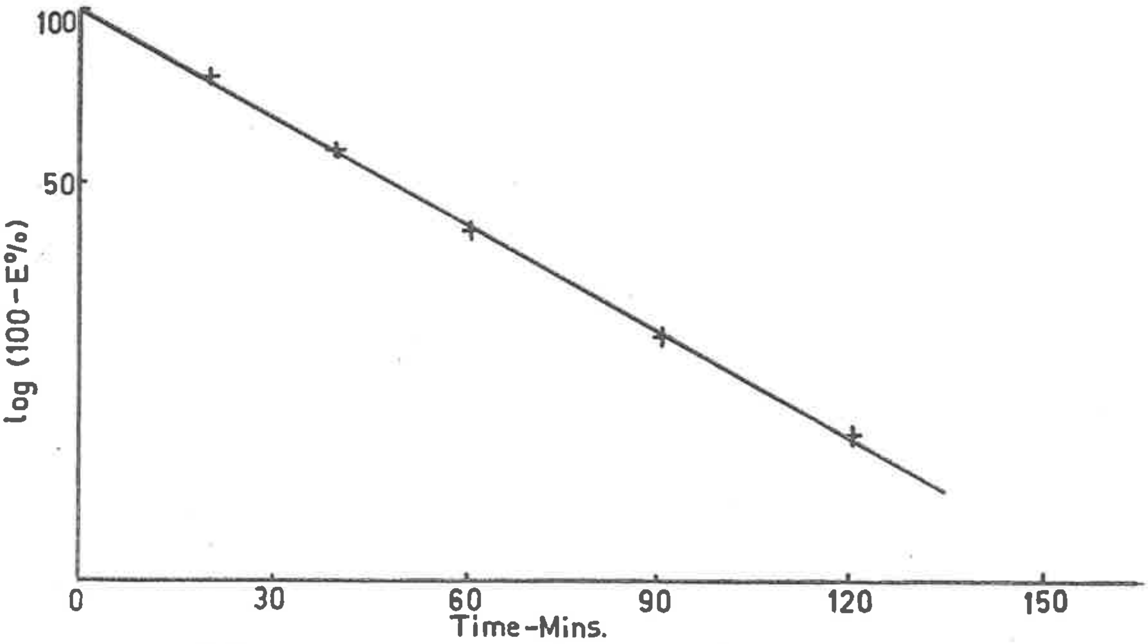


Fig.3.9 Co^{III}(p-tolsal)$_3$ - Co^{II}(p-tolsal)$_2$ electron transfer reaction in toluene at 55°C;Co^{III}0.0148M & Co^{II}0.0100M

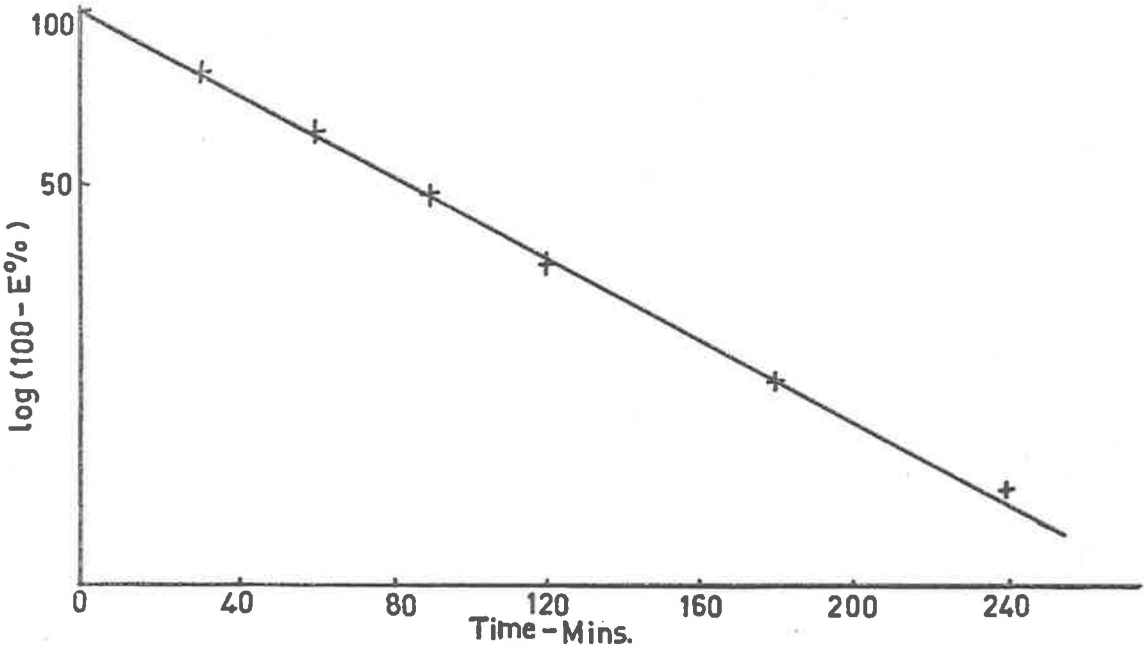


Fig.3.10 Co^{III}(p-tolsal)$_3$ - Co^{II}(p-tolsal)$_2$ electron transfer reaction in toluene at 55°C;Co^{III}0.0047M & Co^{II}0.0100M

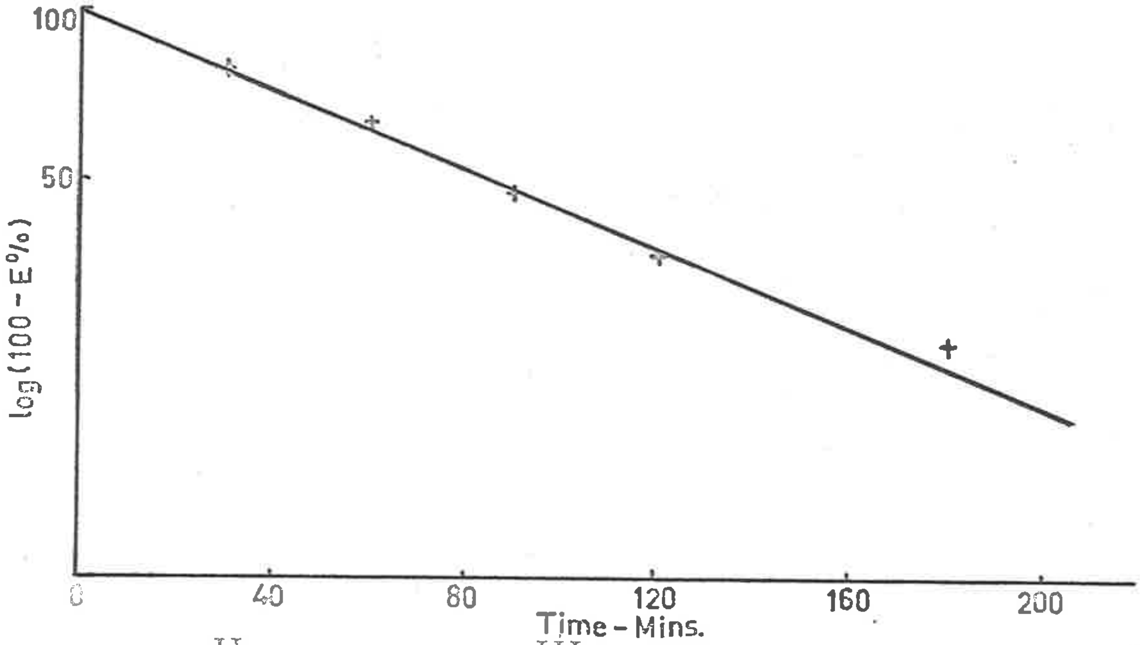


Fig.3.11 Co^{II}(p-tolsal)$_2$ – Co^{III}(p-tolsal)$_3$ electron transfer reaction in toluene at 55.0°C;Co^{II} 0.0100M & Co^{III} 0.0023M

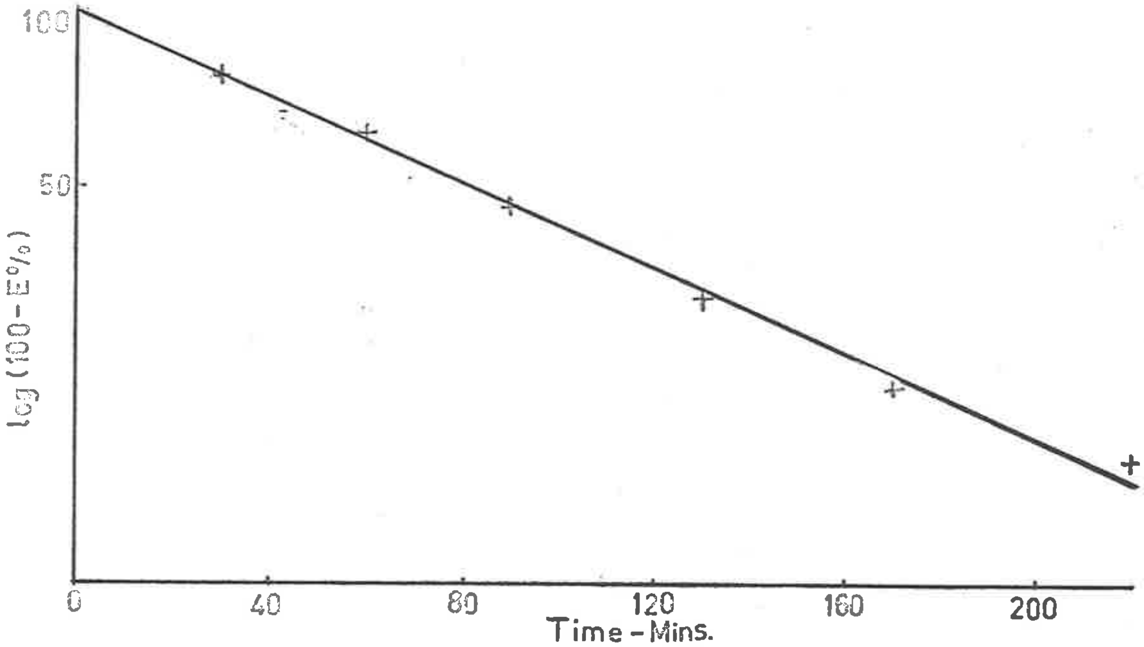


Fig.3.12 Co^{II}(p-tolsal)$_2$ – Co^{III}(p-tolsal)$_3$ electron transfer reaction in toluene at 55.0°C;Co^{II} 0.0100M & Co^{III} 0.0058M

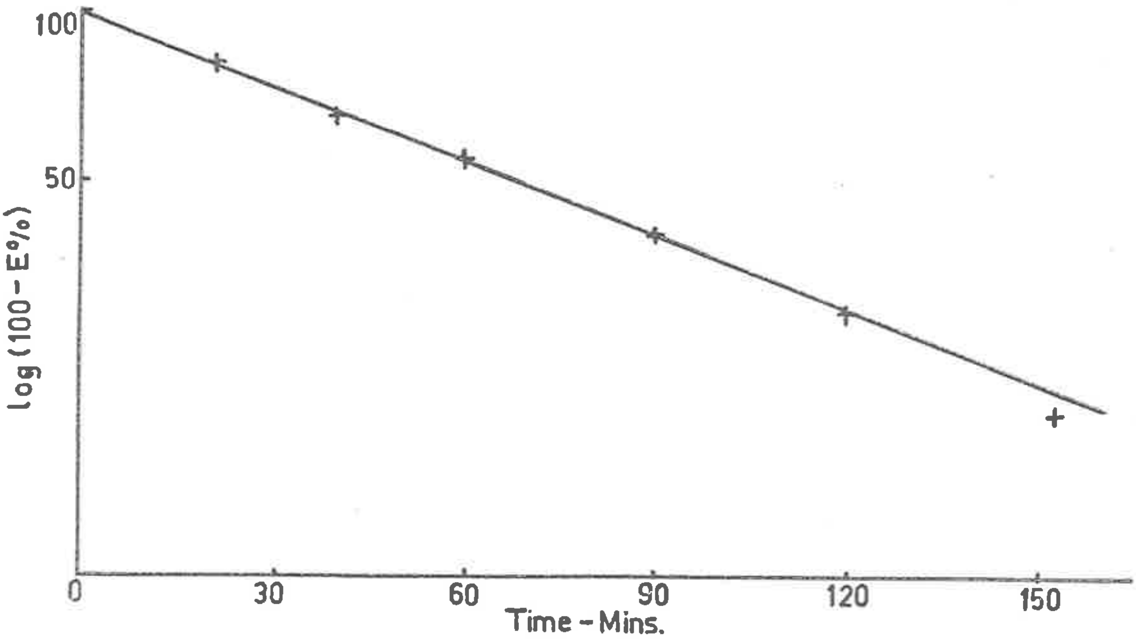


Fig.3.13 Co^{II}(p-tolsal)$_2$ - Co^{III}(p-tolsal)$_3$ electron transfer reaction in toluene at 55.0°C;Co^{II} 0.0100M & Co^{III} 0.0077M

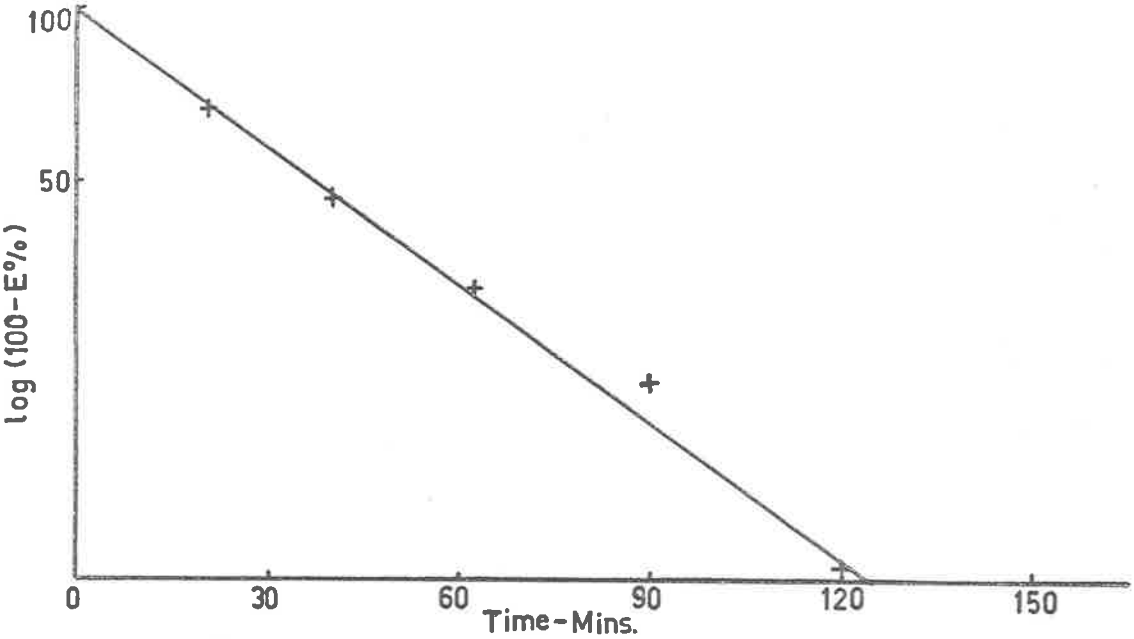


Fig.3.14 Co^{II}(p-tolsal)$_2$ - Co^{III}(p-tolsal)$_3$ electron transfer reaction in toluene at 55.0°C;Co^{II} 0.0100M & Co^{III} 0.0194M

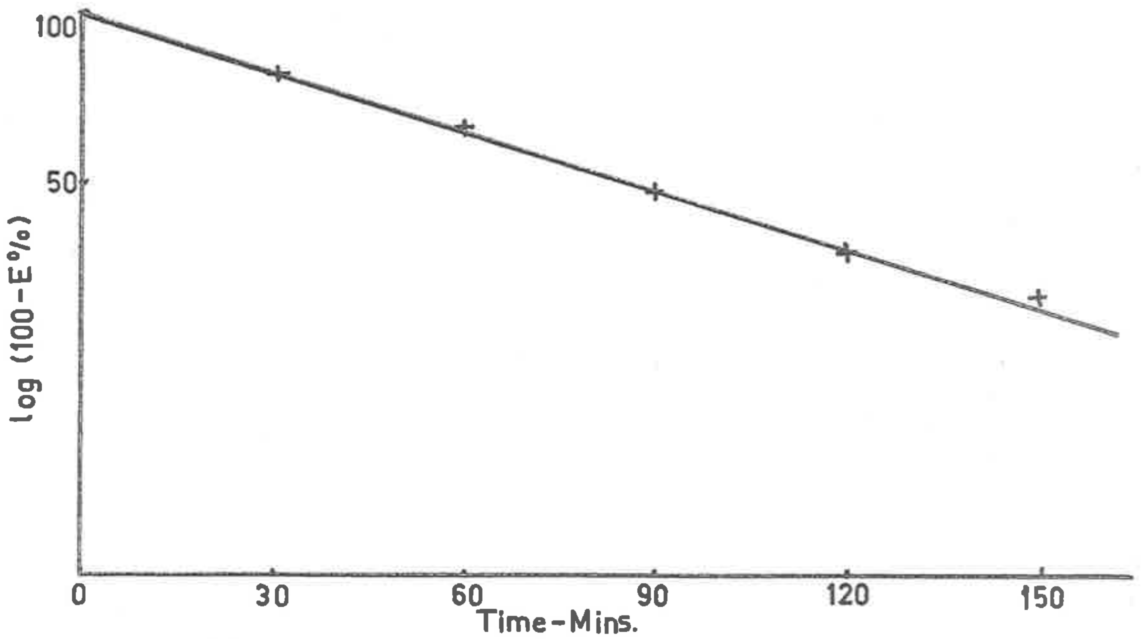


Fig.3.15 Co^{III}(p-tolsal)$_3$ - Co^{II}(p-tolsal)$_2$ electron transfer reaction in toluene at 55.0°C;Co^{III}0.0024M & Co^{II}0.0100M

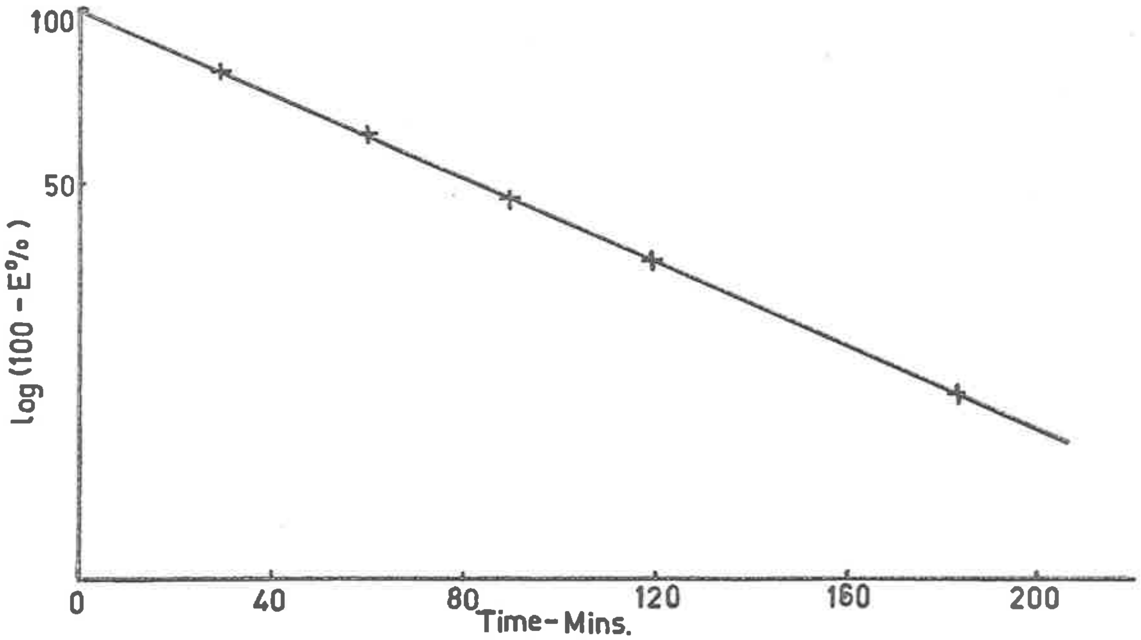


Fig.3.16 Co^{III}(p-tolsal)$_3$ - Co^{II}(p-tolsal)$_2$ electron transfer reaction in toluene at 55.0°C;Co^{III}0.0047M & Co^{II}0.0100M

The Rate Equation

Table 3.2 shows the variation of the rate of electron transfer reaction with concentration of cobalt complexes at 55°C ± 0.1°C. Provided the solvent takes no part in the reaction, the rate of the electron transfer may be expressed by

$$R = k\left[Co^{II}\right]^{x}\left[Co^{III}\right]^{y}$$

Hence, keeping the concentration of one of the reactants constant, a plot of log R against the log of the concentration of the other reactant should give a straight line graph. The slope of the graph would then be equal to the order of the reaction in that complex for which the concentration was varied. Treatment of the results in this way (Fig. 3.17) gave the values of $x = 0$ and $y = 1$ for the orders of the reaction in cobalt (II) and cobalt (III) respectively. The rate of reaction is therefore expressed by

$$R = k\left[Co^{III}\right] \qquad 3.1$$

at 55°C ± 0.1°C.

The kinetics for the reaction were also studied at a temperature of 60° ± 0.1°C. and the results found (Figs. 3.21 - 3.23) show that the rate of reaction is also expressed by equation 3.1 at this temperature.

The Effect of p-tolsal on the Rate of Reaction

From a comparison of this system with the acetylacetone system one might expect that the addition of ligand would cause the formation of the tris(p-tolsal) cobalt (II) species i.e.

TABLE 3.2

Electron Transfer Reaction between Cobalt (II)-p-tolsal and Cobalt (III)-p-tolsal

Variation of Rate of Reaction with Concentration

Run No.	Concentration (M) Cobalt II	Concentration (M) Cobalt III	Half-life (mins.)	Rate of Reaction moles litre^{-1}mins^{-1}	k (mins.$^{-1}$)	Temperature °C
1	.0100	.0098	61.0	2.80×10^{-5}	2.85×10^{-3}	55.0 ± 0.1
2	.0051	.0097	40.0	2.90×10^{-5}	2.98×10^{-3}	55.0 ± 0.1
3	.0076	.0098	47.0	3.15×10^{-5}	3.22×10^{-3}	55.0 ± 0.1
4	.0152	.0097	67.0	3.06×10^{-5}	3.14×10^{-3}	55.0 ± 0.1
5	.0200	.0097	72.0	3.17×10^{-5}	3.25×10^{-3}	55.0 ± 0.1
6	.0179	.0198	58.0	5.62×10^{-5}	2.84×10^{-3}	55.0 ± 0.1
7	.0050	.0048	58.0	1.46×10^{-5}	3.05×10^{-3}	55.0 ± 0.1
8	.0100	.0146	54.0	3.80×10^{-5}	2.60×10^{-3}	55.0 ± 0.1
9	.0100	.0148	49.5	4.14×10^{-5}	2.80×10^{-3}	55.0 ± 0.1
10	.0100	.0047	85.0	1.30×10^{-5}	2.80×10^{-3}	55.0 ± 0.1
11	.0100	.0023	86.0	7.62×10^{-6}	3.28×10^{-3}	55.0 ± 0.1
12	.0100	.0058	81.0	1.58×10^{-5}	2.72×10^{-3}	55.0 ± 0.1
13	.0100	.0077	69.0	2.19×10^{-5}	2.84×10^{-3}	55.0 ± 0.1
14	.0100	.0194	37.0	6.19×10^{-5}	3.19×10^{-3}	55.0 ± 0.1
15	.0100	.0024	88.0	7.68×10^{-6}	3.16×10^{-3}	55.0 ± 0.1
16	.0100	.0047	84.0	1.31×10^{-5}	2.81×10^{-3}	55.0 ± 0.1

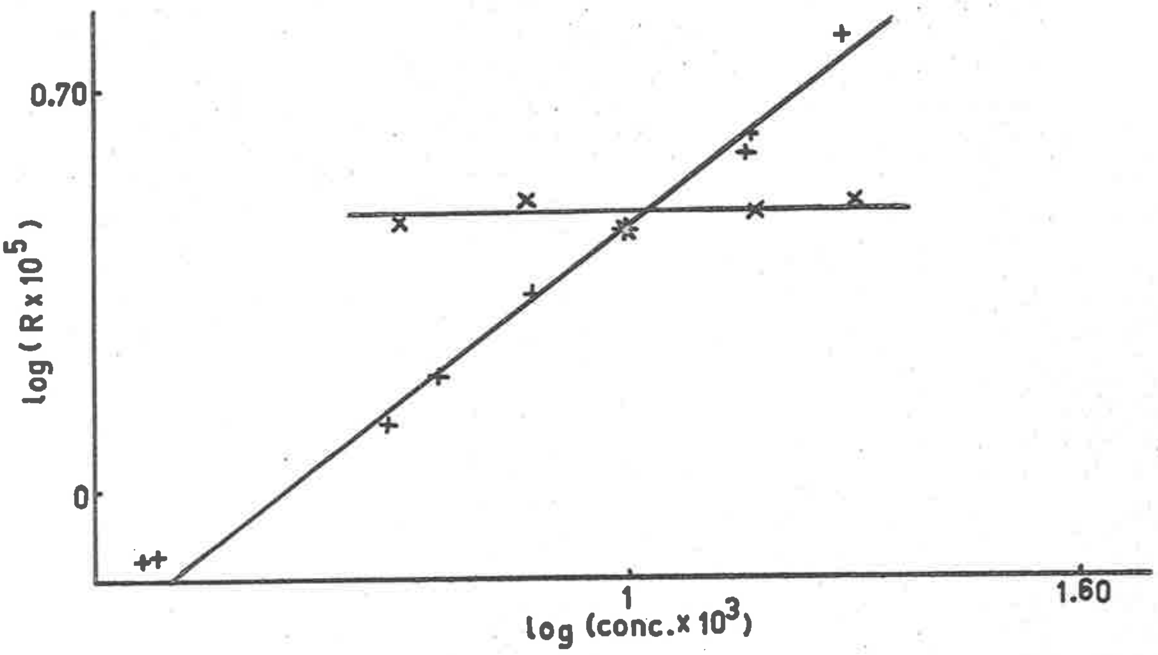


Fig.3.17 Co^{II}(p-tolsal)$_2$ - Co^{III}(p-tolsal)$_3$ electron transfer reaction in toluene at 55.0°C

+ = Co^{III} variable, Co^{II} constant

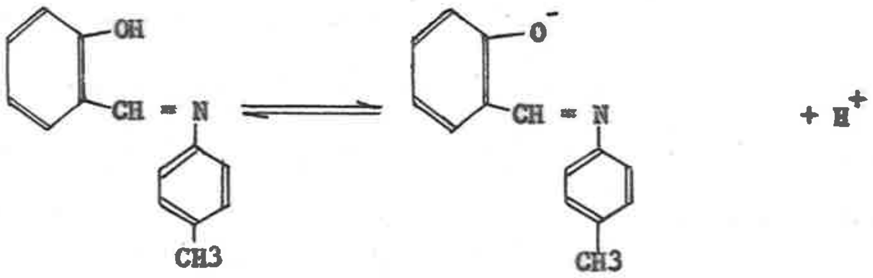
x = Co^{III} constant, Co^{II} variable

$$Co^{II}(p\text{-tolsal})_2 \quad + \quad H\ p\text{-tolsal} \rightleftharpoons H\ Co^{II}(p\text{-tolsal})_3$$

The existence of this complex species could make the formation of a symmetrical intermediate easier as it would not then necessitate the breaking of any metal-ligand bonds on the cobalt(III) complex (see the electron transfer mechanisms for the acetylacetonato complexes - Chapter 2) and thus it would be expected that the effect of the added ligand may be to increase the rate of reaction. This effect would be expected to cease operating when sufficient excess ligand was present to cause all of the cobalt (II) to exist in the form of the tris(p-tolsal) cobaltate (II) complex. If the cobalt (II)-tris species were to dissociate thus

$$H\ Co^{II}(p\text{-tolsal})_3 \rightleftharpoons Co^{II}(p\text{-tolsal})_3^- \quad + H^+$$

then further addition of N-p-tolylsalicylideneimine may influence the rate of reaction by the ionization.



, thus decreasing the proportion of the $Co^{II}(p\text{-tolsal})_3^-$ ions by a common ion effect. The electron transfer could then occur by an "outer sphere" mechanism in which a hydrogen ion bridge was formed between the reactants (Chapter 2 - mechanisms for the electron transfer in acetylacetone).

Two reactions were carried out adding small quantities of N-p-tolylsalicylideneimine (Figs. 3.18-3.19). It can be seen from Table 3.4 that there is an apparent increase in the rate of reaction by about 10% on making the solution 0.0200 Molar in ligand. However a doubling of this concentration did not produce any further increase in the rate of reaction. Further a comparison of the results of Table 3.4 with those in Table 3.2 will show that the apparent increase in the rate of reaction is just within the errors of the rate of reaction without ligand added. Hence for the small quantities of ligand added to the system no significant change in the rate of reaction occurred. It was not possible however to ascertain the effect of substantially higher concentration of added ligand due to the increased difficulty of separation of the reactants. The cobalt (II) complex in the presence of an excess of ligand tends to move rapidly through the alumina column used for the separation, thus not giving complete separation of the reactants.

The Activation Energy and Entropy of Activation

The electron transfer reaction was also studied at temperatures of 50° ± 0.1°C. and 60° ± 0.1°C. (Figs. 3.20-3.23) in order to obtain the activation energy. This was calculated from the slope of the graph in (Fig. 3.34) as 13.0 (± 9%) k cals/mole.

It has been shown (20) that for reactions obeying first order kinetics the specific rate constant is given by

$$k' = \frac{kt}{h} \quad e^{\Delta S^{\ddagger}/R} . \quad e^{-Ea/RT} .e \qquad 3.2$$

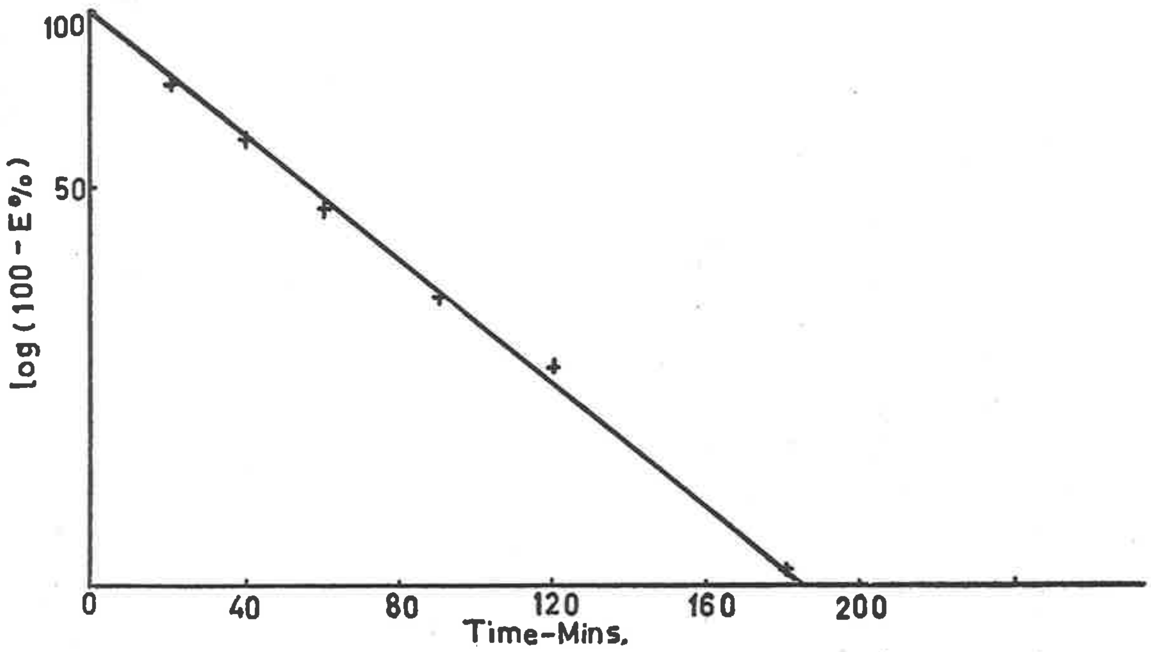


Fig.3.18 $Co^{II}(\underline{p}\text{-tolsal})_2 - Co^{III}(\underline{p}\text{-tolsal})_3$ electron transfer reaction in toluene at 55.0°C; Co^{II} 0.0100M & Co^{III} 0.0098M and sal-p-tol 0.0200M

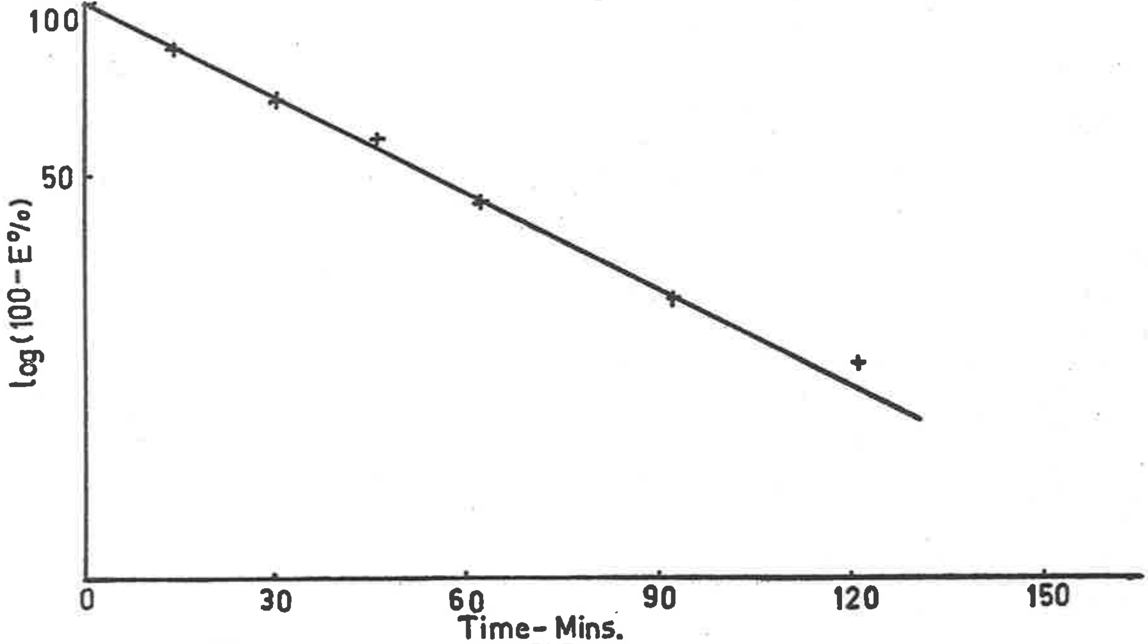


Fig.3.19 $Co^{II}(\underline{p}\text{-tolsal})_2 - Co^{III}(\underline{p}\text{-tolsal})_3$ electron transfer reaction in toluene at 55.0°C; Co^{II} 0.0100M & Co^{III} 0.0098M and sal-p-tol 0.0400M

TABLE 3.3

Electron Transfer Reaction between Cobalt(II-p-tolsal and Cobalt(III)-p-tolsal

Variation of Rate of Reaction with Concentration and Temperature

Run No.	Concentration (M)		Half-life (mins)	Rate of Reaction moles $litre^{-1}$ min^{-1}	k ($mins^{-1}$)	Temperature °C
	Cobalt II	Cobalt III				
1	.0100	.0097	114.0	1.50×10^{-5}	1.54×10^{-3}	50.0 ± 0.1
2	.0100	.0098	26.0	6.58×10^{-5}	6.75×10^{-3}	60.0 ± 0.1
3	.0100	.0049	35.0	3.23×10^{-5}	6.65×10^{-3}	60.0 ± 0.1
4	.0200	.0098	34.5	6.58×10^{-5}	6.74×10^{-3}	60.0 ± 0.1

TABLE 3.4

Electron Transfer Reaction between Cobalt(II)-*p*-tolsal and Cobalt(III)-*p*-tolsal
in Toluene
Variation of Rate of Reaction with Added *p*-tolylsalicylideneimine at 55.0 ± 0.1°C.

Run No.	Concentration (M)		Half-life (mins)	Rate of Reaction moles $litre^{-1}$ min^{-1}	k ($mins^{-1}$)	Concentration (M) *p*-tolsal
	Cobalt II	Cobalt III				
1	.0100	.0098	61.0	2.80×10^{-5}	2.85×10^{-3}	0.000
2	.0100	.0098	55.0	3.11×10^{-5}	3.19×10^{-3}	0.0200
3	.0100	.0098	55.0	3.11×10^{-5}	3.19×10^{-3}	0.0400

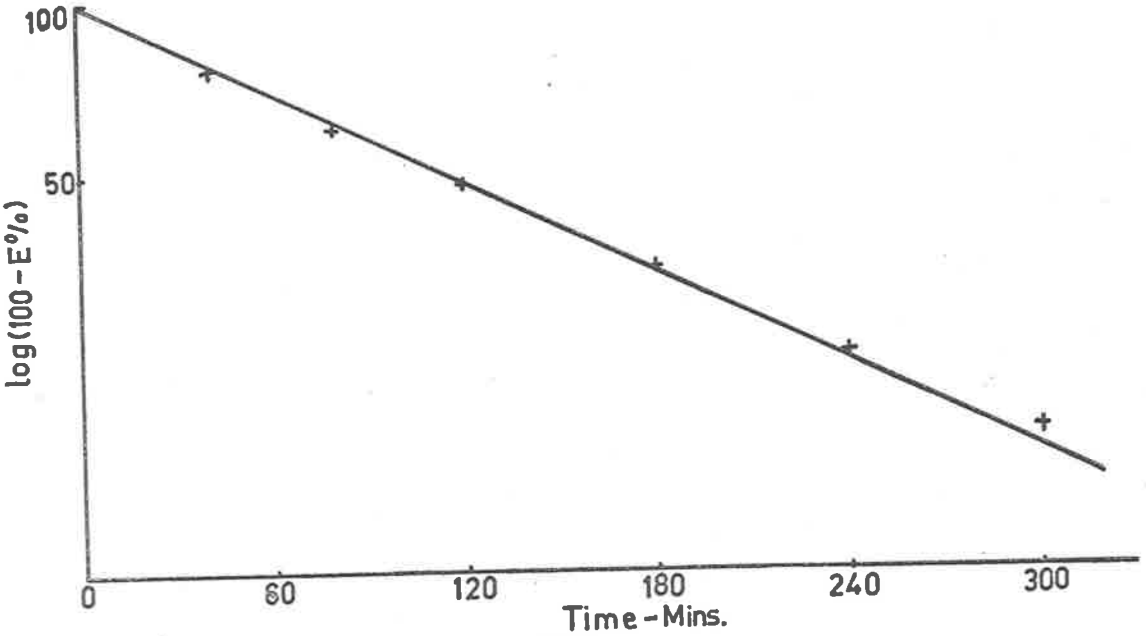


Fig.3.20 Co^{II}(p-tolsal $)_2$ - Co^{III}(p-tolsal $)_3$ electron transfer reaction in toluene at 50.0°C;Co^{II} 0.0100M & Co^{III} 0.0097M

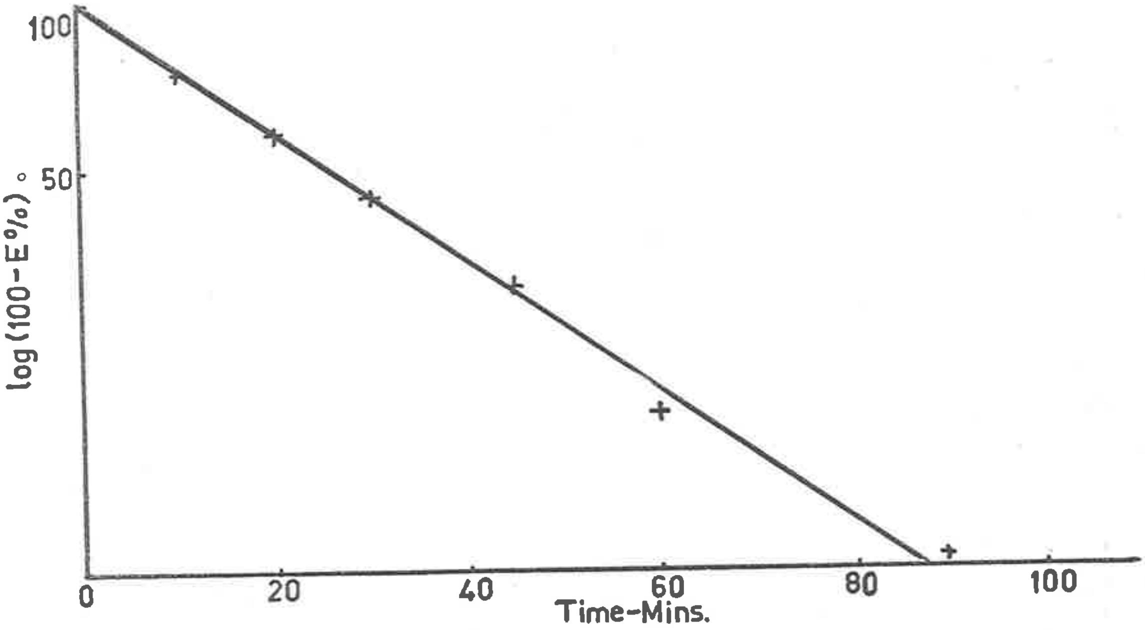


Fig.3.21 Co^{II}(p-tolsal $)_2$ - Co^{III}(p-tolsal $)_3$ electron transfer reaction in toluene at 60.0°C;Co^{II} 0.0100M & Co^{III} 0.0098M

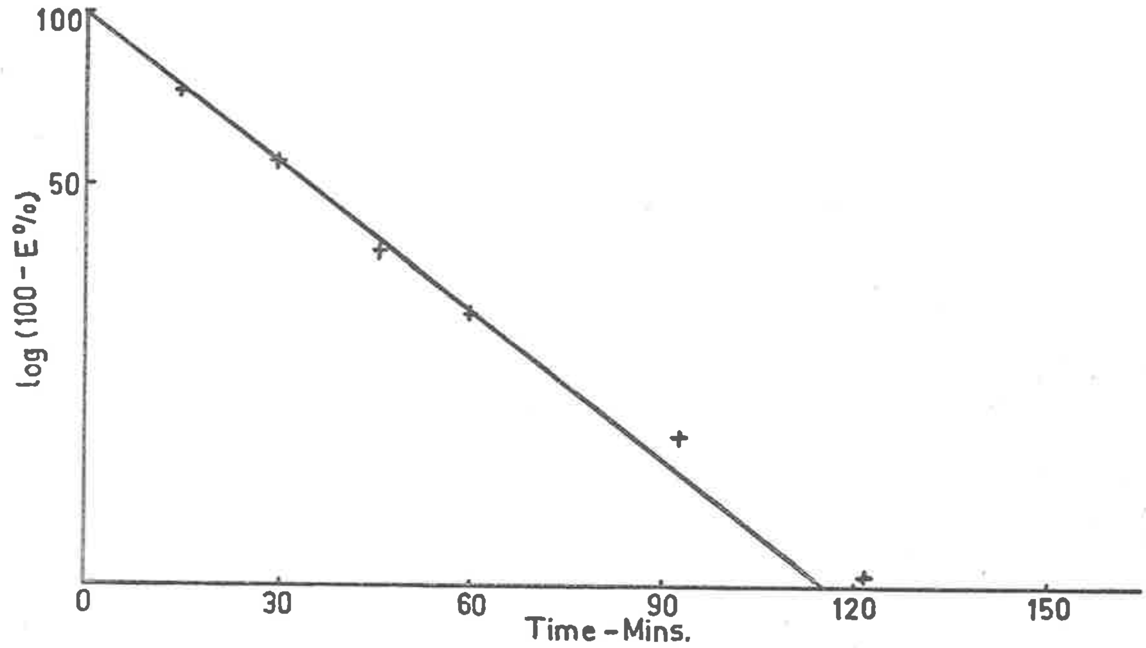


Fig.3.22 Co^{II}(p-tolsal)$_2$ – Co^{III}(p-tolsal)$_3$ electron transfer reaction in toluene at 60.0°C;Co^{II} 0.0100M & Co^{III} 0.0049M

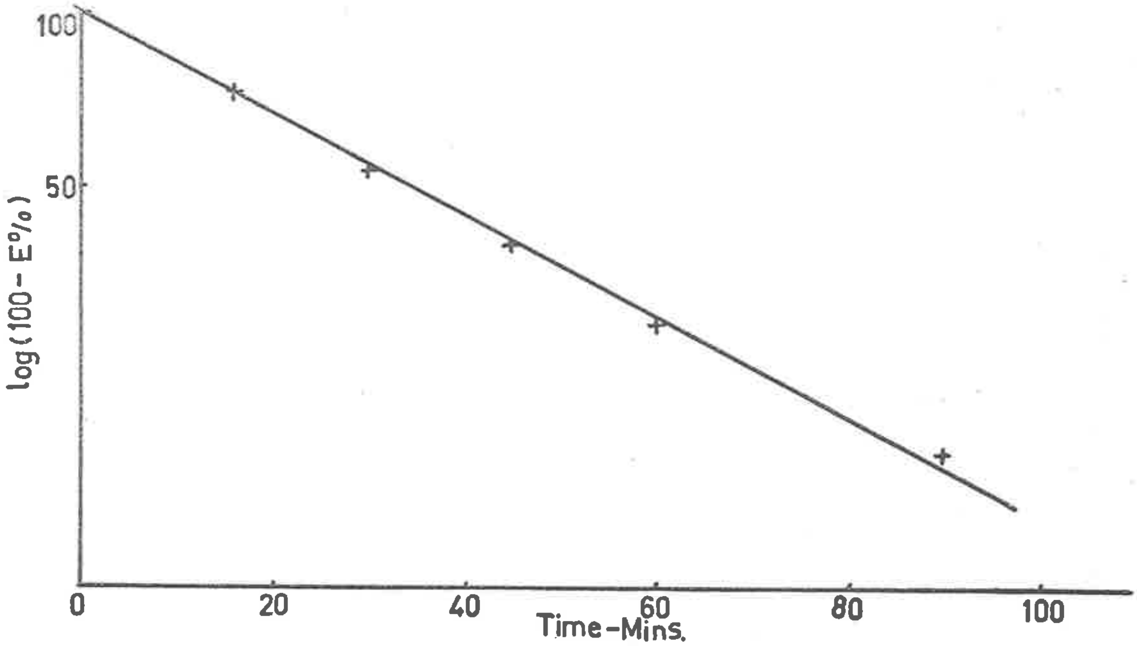


Fig.3.23 Co^{II}(p-tolsal)$_2$ – Co^{III}(p-tolsal)$_3$ electron transfer reaction in toluene at 60.0°C;Co^{II} 0.0200M & Co^{III} 0.0098M

where k'= the specific rate constant, k = Boltzman constant, h = Planck's constant, $\Delta S^{\ddagger}$= entropy of activation, Ea = Activation Energy, R = gas constant and T = absolute temperature. Substituting the calculated value of the activation energy and the appropriate value of the k' in equation 3.2 gave an entropy of activation of - 29.2 (± 6%) e.u.

B. The Electron Transfer Reaction between bis(N-phenylsalicylideneiminato)cobalt(II) and tris(N-phenylsalicylideneiminato) cobalt (III).

The electron transfer reaction between bis(phensal)* cobalt (II) and tris(phensal)cobalt(III) was also studied in toluene at a temperature of 55° ± 0.1°C. (Figs. 3.24 - 3.30). The order of the reaction with respect to each of the complexes was determined (Fig. 3.33) as in the previous case and as before it was found that the rate of reaction was expressed by the equation 3.1.

The electron transfer was also studied at temperatures of 50° ± 0.1°C and 60° ± 0.1°C (Figs. 3.31 & 3.32) in order to obtain the activation energy of the reaction. The activation energy calculated from the slope of the graph in (Fig. 3.35) was found to be 13.4 (± 3%)k cals/mole. Substitution of this value in equation 3.2 gave an entropy of activation of -28.6(± 2%) e.u.

C. General Discussion.

The electron transfer reactions between the phensal type complexes of cobalt(II) and cobalt(III), as in the case for the reactions between

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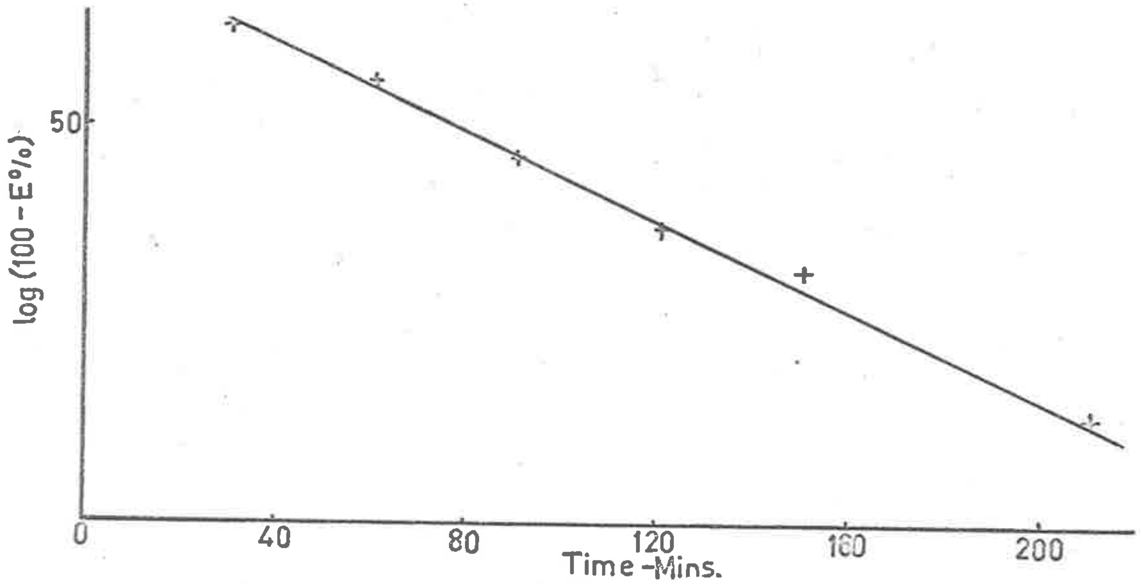
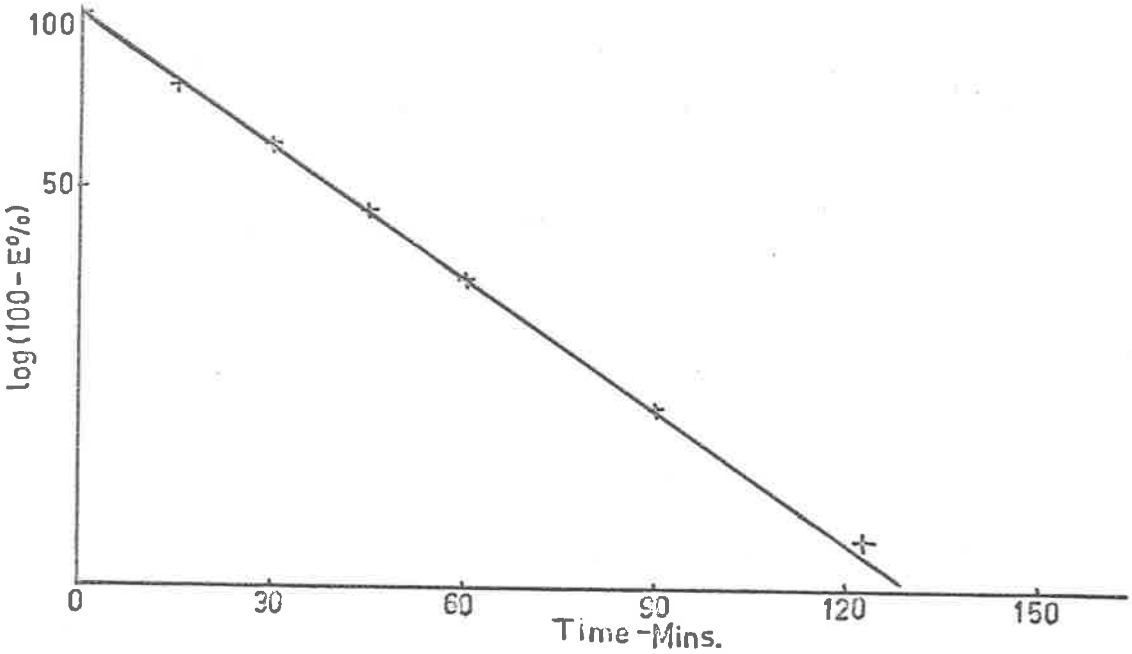
* phensal indicates the N,phenylsalicylideneimine ion.



<u>Fig.3.24</u> $Co^{II}(phensal)_2 - Co^{III}(phensal)_3$ electron transfer reaction in toluene at 55.0°C; Co^{II} 0.0199M & Co^{III} 0.0100M



<u>Fig.3.25</u> $Co^{II}(phensal)_2 - Co^{III}(phensal)_3$ electron transfer reaction in toluene at 55.0°C; Co^{II} 0.0050M & Co^{III} 0.0100M

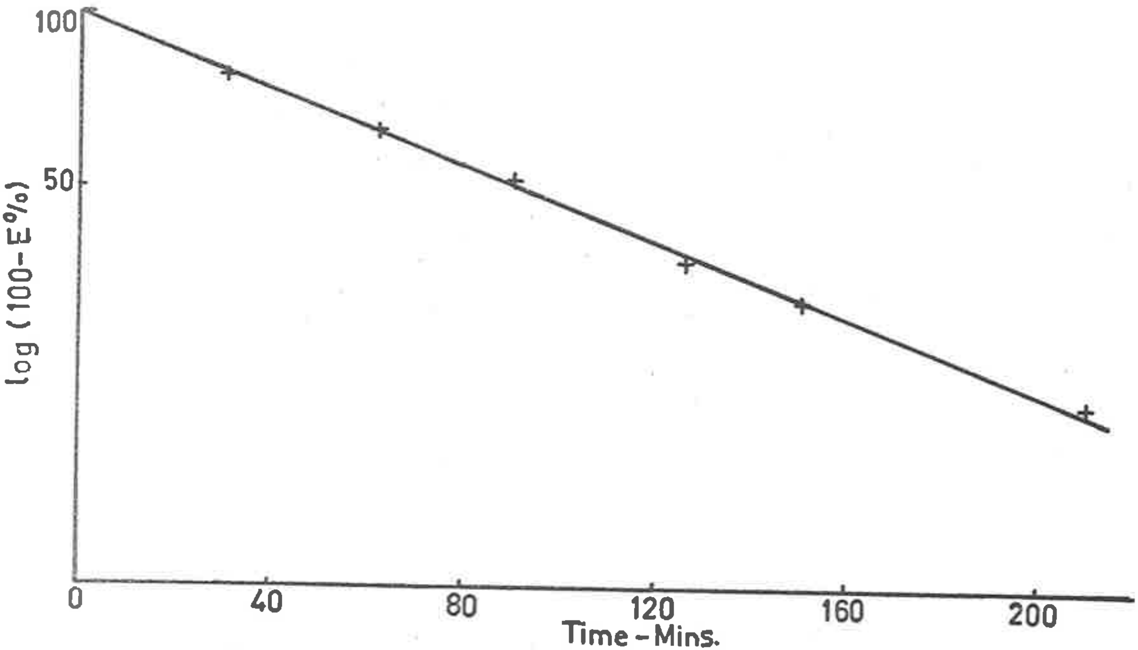


Fig.3.26 $Co^{II}(phensal)_2 - Co^{III}(phensal)_3$ electron transfer reaction in toluene at 55.0°C;Co^{II} 0.0398M & Co^{III} 0.0100M

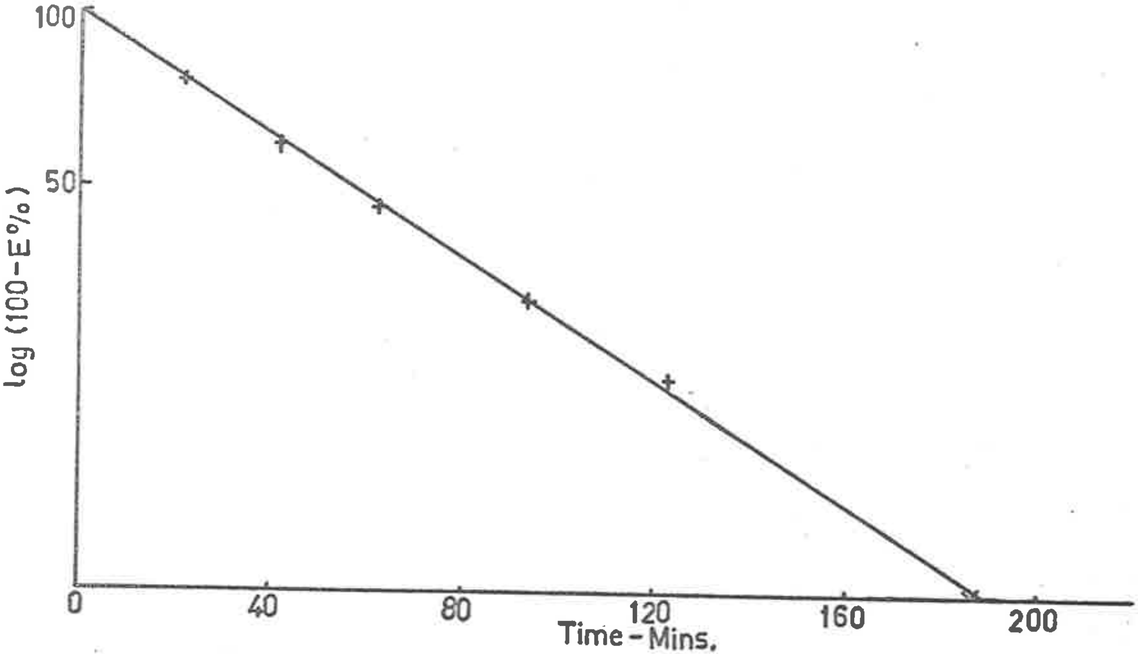


Fig.3.27 $Co^{II}(phensal)_2 - Co^{III}(phensal)_3$ electron transfer reaction in toluene at 55.0°C;Co^{II} 0.0100M & Co^{III} 0.0100M

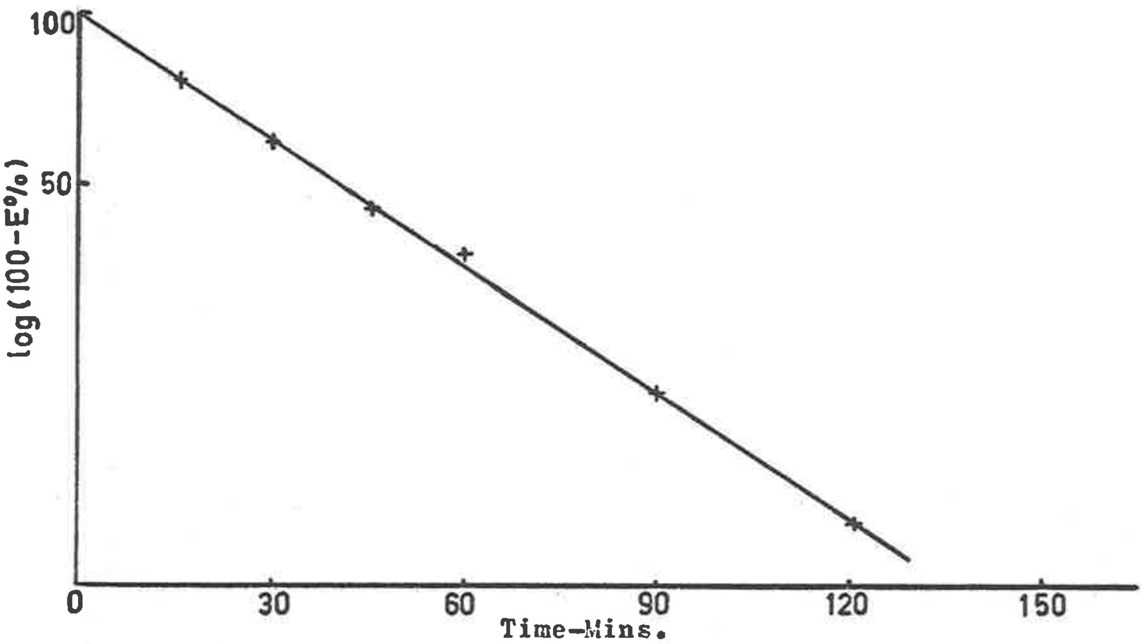


Fig.3.28 Co^{II}(phensal)$_2$ - Co^{III}(phensal)$_3$ electron transfer reaction in toluene at 55.0°C;Co^{II}0.0100M & Co^{III}0.0200M

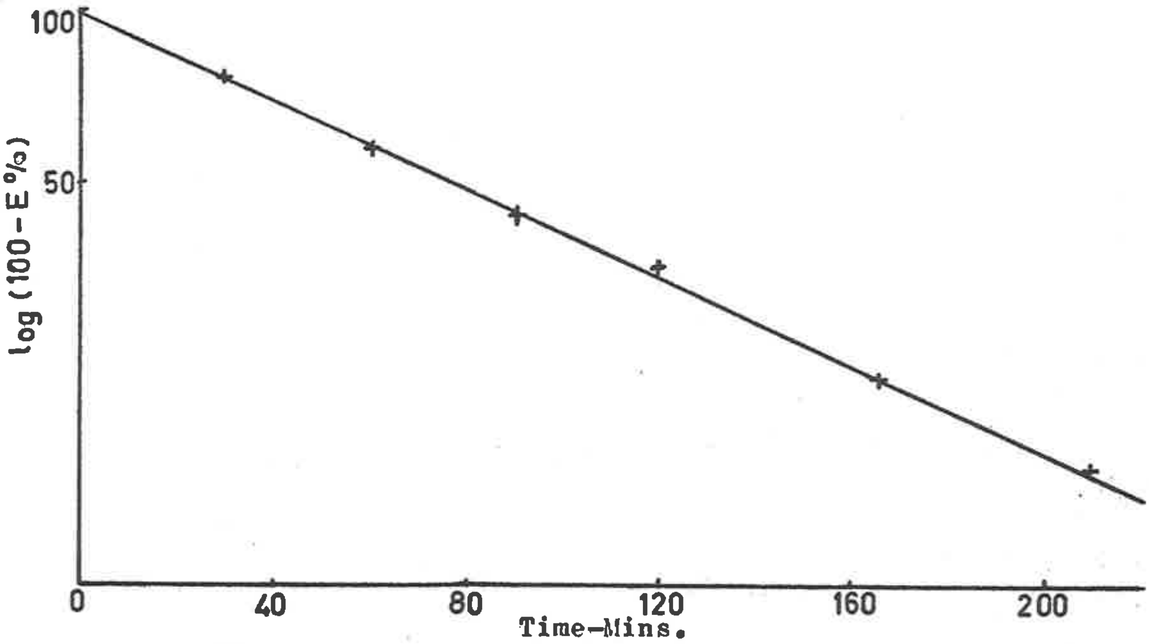


Fig.3.29 Co^{II}(phensal)$_2$ - Co^{III}(phensal)$_3$ electron transfer reaction in toluene at 55.0°C;Co^{II}0.0100M & Co^{III}0.0050M

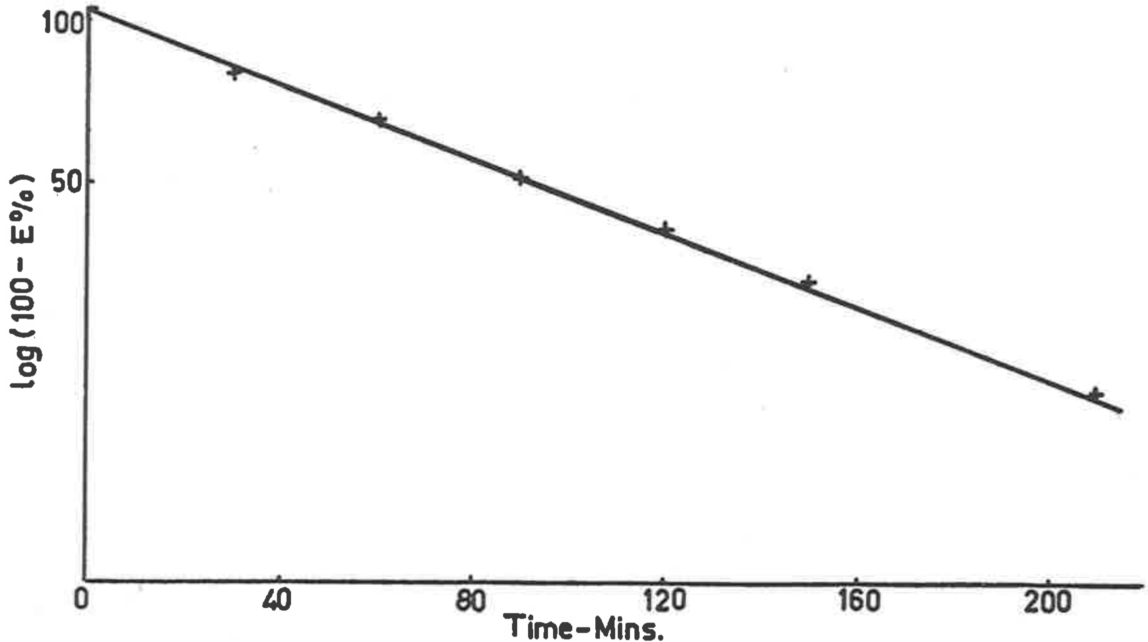


Fig.3.30 Co^{II}(phensal)$_2$ - Co^{III}(phensal)$_3$ electron transfer reaction in toluene at 55.0°C;Co^{II}0.0100M & Co^{III}0.0025M

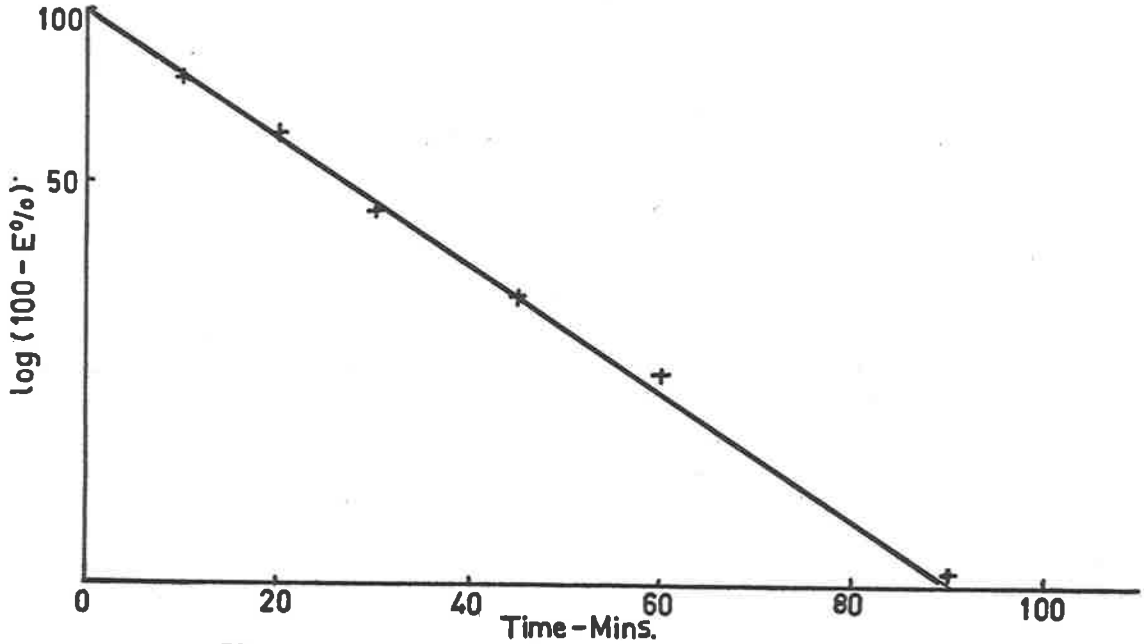


Fig.3.31 Co^{II}(phensal)$_2$ - Co^{III}(phensal)$_3$ electron transfer reaction in toluene at 60.0°C;Co^{II}0.0100M & Co^{III}0.0100M

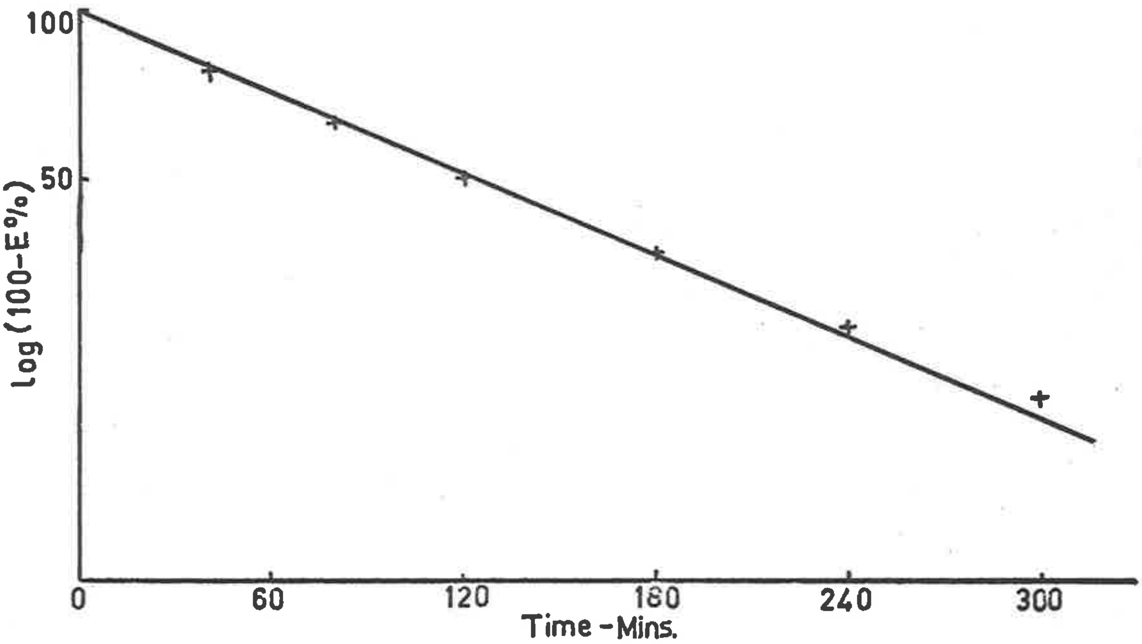


Fig.3.32 Co^{II}(phensal)$_2$ - Co^{III}(phensal)$_3$ electron transfer reaction in toluene at 50.0°C;Co^{II} 0.0100M & Co^{III} 0.0100M

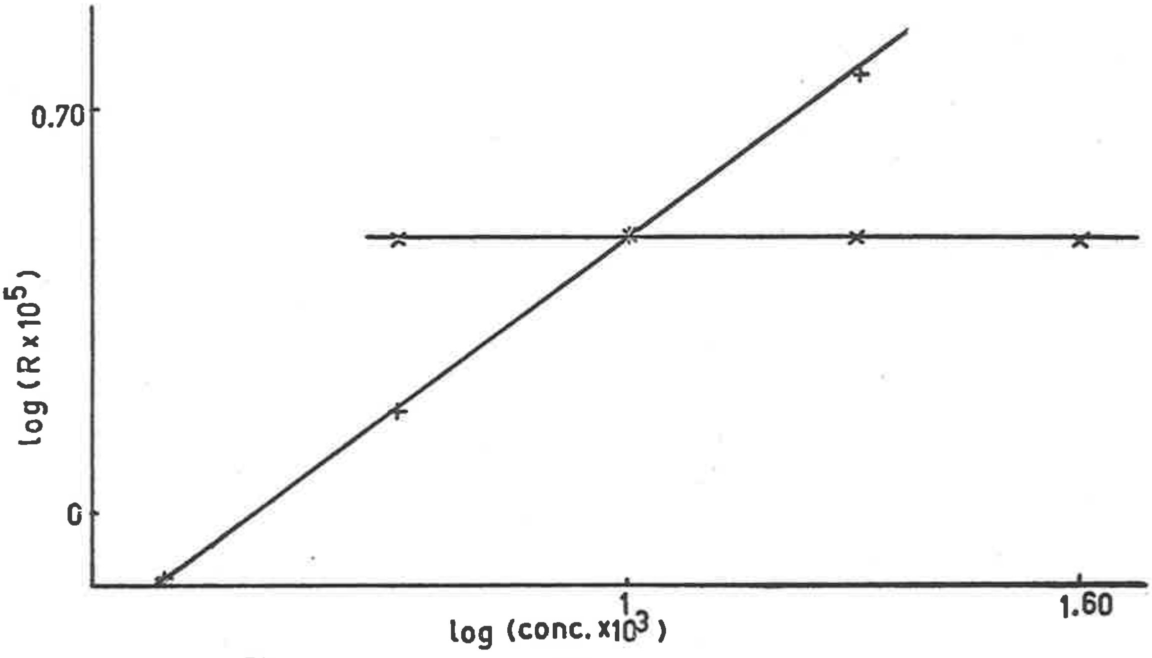


Fig.3.33 Co^{II}(phensal)$_2$ - Co^{III}(phensal)$_3$ electron transfer reaction in toluene at 55.0°C; + = Co^{III} variable,Co^{II} constant
x = Co^{III} constant,Co^{II} variable

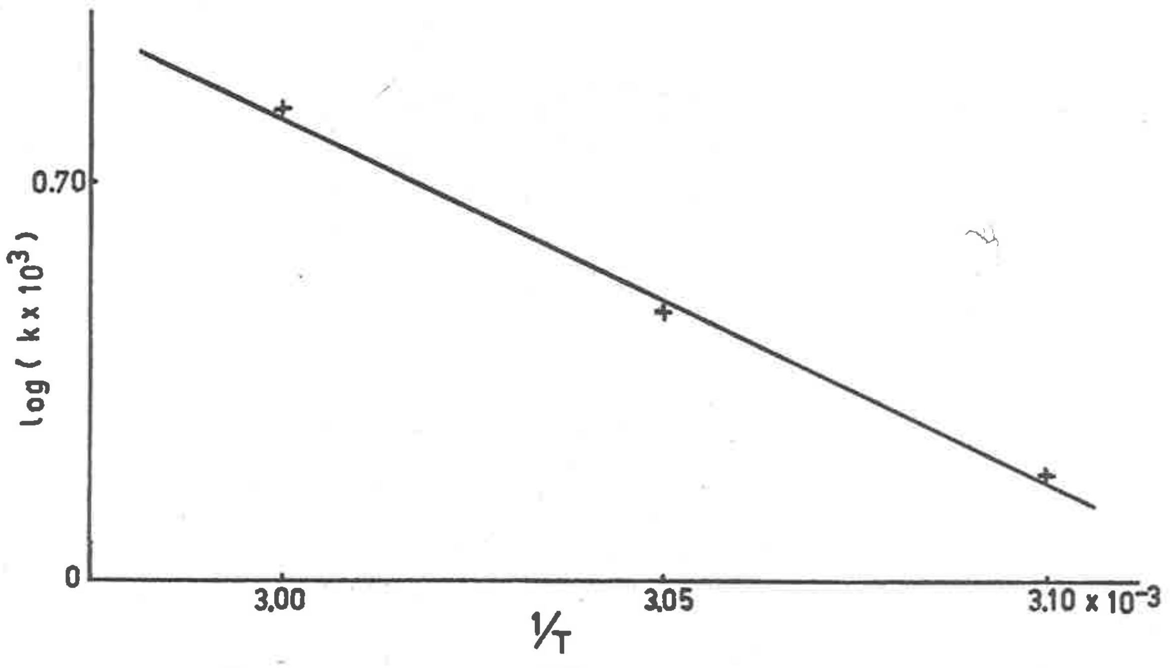


Fig.3.34 Co^{II}(p-tolsal)$_2$ - Co^{III}(p-tolsal)$_3$ electron transfer reaction in toluene

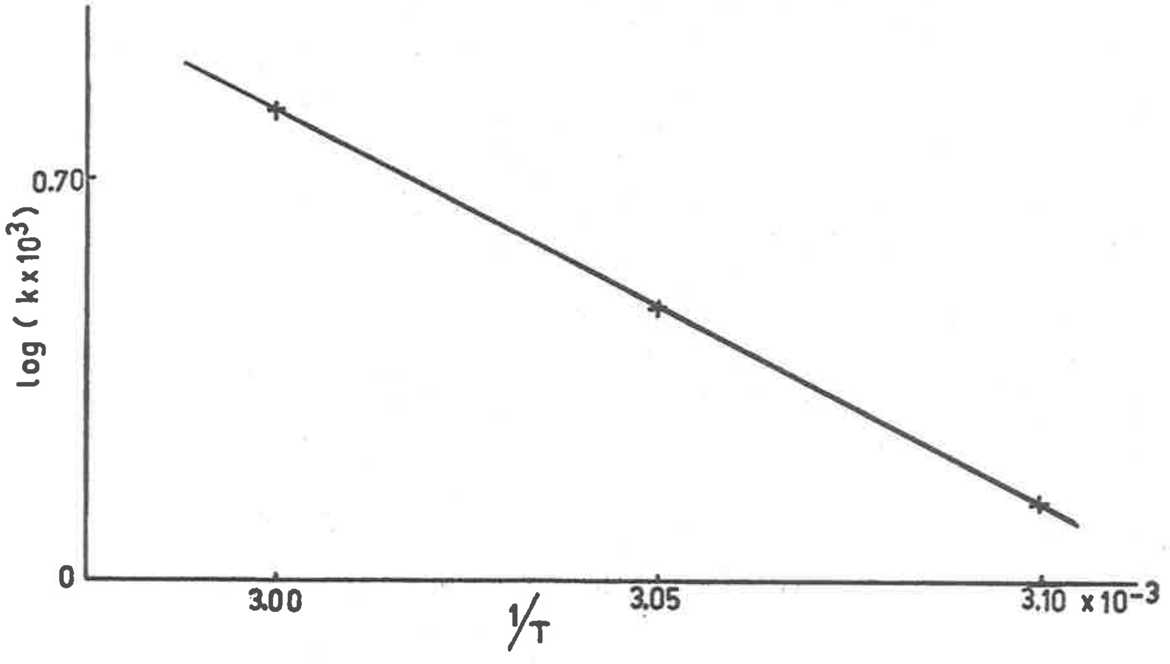


Fig.3.35 Co^{II}(phensal)$_2$ - Co^{III}(phensal)$_3$ electron transfer reaction in toluene

TABLE 3.5

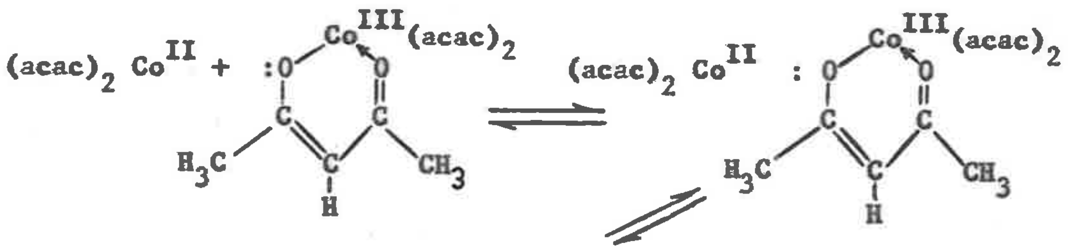
Electron Transfer Reaction between Cobalt (II)-phensal and Cobalt (III)-phensal

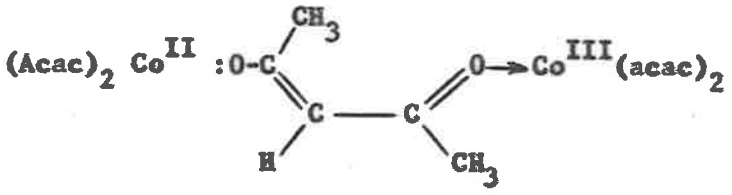
Variation of Rate of Reaction with Concentration and Temperature.

Run. No.	Concentration (M)		Half-life (mins)	Rate of Reaction (moles litres^{-1} mins^{-1})	k (mins^{-1})	Temperature (°C)
	Cobalt II	Cobalt III				
1	.0199	.0100	77.0	3.00×10^{-5}	3.00×10^{-3}	55.0 ± 0.1
2	.0050	.0100	38.5	2.99×10^{-5}	2.99×10^{-3}	55.0 ± 0.1
3	.0398	.0100	92.5	2.99×10^{-5}	2.99×10^{-3}	55.0 ± 0.1
4	.0100	.0100	57.5	3.01×10^{-5}	3.01×10^{-3}	55.0 ± 0.1
5	.0100	.0200	40.0	5.78×10^{-5}	2.89×10^{-3}	55.0 ± 0.1
6	.0100	.0050	77.0	1.49×10^{-5}	2.98×10^{-3}	55.0 ± 0.1
7	.0100	.0025	92.0	7.53×10^{-6}	3.01×10^{-3}	55.0 ± 0.1
8	.0100	.0100	26.5	6.53×10^{-5}	6.53×10^{-3}	60.0 ± 0.1
9	.0100	.0100	125.0	1.38×10^{-5}	1.38×10^{-3}	50.0 ± 0.1

the acetylacetonato complexes in toluene, must be accompanied by the exchange of ligand from the oxidant to the reductant. Hence despite the observed first order kinetics with respect to the concentration of the cobalt (III) species, a similar mechanism as that given for the reaction between the acetylacetonato complexes in toluene can be postulated, i.e. that the electron transfer proceeds via a bridged transition state complex.

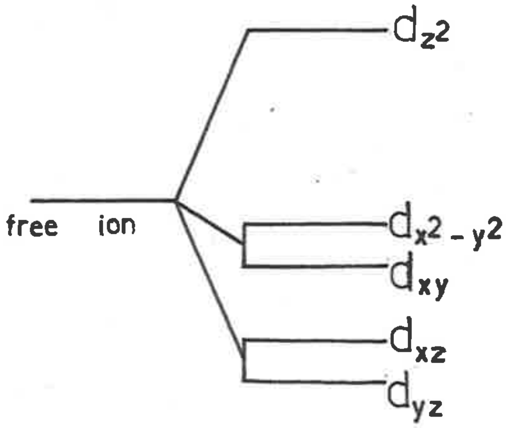
The difference in the observed kinetics for each of the two cases i.e. the reaction between the acetylacetonato complexes and that for the phensal type complexes, can be explained by the manner in which the transition state complex is formed. Firstly for the acetylacetonato complexes it has been established that the bis(acetylacetonato) cobalt (II) species is coordinately unsaturated (8) (46) and therefore has a tendency to readily coordinate with any available ligand. Hence in order to extend the bridging hypothesis already given and to obtain a more detailed picture of the formation of the transition state it is suggested that the cobalt (II) species may undergo an electrophilic attack on one of the oxygen molecules of the cobalt (III) complex. The cobalt (III) oxygen bond then breaking to give two five coordinate species, between which there is an acetylacetone bridge i.e.





During the final approach of the two complexes and the electrophilic attack by the cobalt (II) species on the oxygen atom the interference of the ligand fields of the two reactants would result in the extension of the cobalt (III)-ligand bonds and the contraction of the cobalt (II)-ligand bonds to the intermediate values. The forming of a bond between the cobalt (II) and an acetylacetone molecule of the cobalt (III) complex and the breaking of the oxygen-cobalt (III) bond would therefore be gradual processes and not occur in distinct stages.

It would seem that the most logical configuration of both the cobalt (III) and cobalt (II) complexes in the transition state would be that of a trigonal bipyramid arrangement, and that the changes in the ligand fields of the reactants during the formation of the transition state complex would allow a rearrangement of the energy values of the d orbitals of both complexes to those for such a configuration. The sequence of energy values of the d orbitals for a trigonal bipyramid arrangement being given by Basolo and Pearson as (54)



During the rearrangement of the d orbitals, electron spin unpairing of the cobalt (III) would also take place.

West (51) has found that the phensal type complexes of cobalt (II) add on ligands such as pyridine only weakly and that the products, on standing, readily revert to the four coordinate chelate. There is therefore little tendency for the phensal type cobalt (II) complexes to increase their coordination numbers beyond a value of four. It is therefore suggested that the primary process in the formation of the bridged transition state complex in the reactions between the phensal type complexes of cobalt (II) and cobalt (III) is the thermal breaking of one of the metal-ligand bonds of the cobalt (III) complex. This is then followed by the attachment of the "free end" (either-O^- or = N-) to a cobalt (II) molecule, the greater available electron density on the "free end" being considered to counteract the weak acceptor behaviour of the cobalt (II) in the phensal type complex. The observed first order kinetics then indicating that the rate controlling step of the reaction is the first bond breaking step.

The cobalt (III) complex has been shown to undergo decomposition to the cobalt (II) complex on continued heating, the thermal reduction occurring more readily than for the corresponding acetylacetonato complex. However the rate of the electron transfer reaction does not follow the observed rate of thermal decomposition (Table 3.1) as might be expected if the thermal breaking of the metal-ligand bond is the rate determining step. This can be explained by the cobalt (II) complex being a more ready acceptor of the "free end" of the ligand attached to the cobalt (III) than the medium in which the thermal reduction was carried out. Furthermore for the completion of thermal reduction it is necessary to break not only one metal-ligand bond but two, and the breaking of the second bond will occur less readily than the formation of a bridge by the linking of the "free end" of the ligand and a cobalt (II) and the subsequent electron transfer.

During the cobalt (III)-ligand bond breaking process, due to the changes occurring in bond distances and configuration and hence the ligand field, the electronic configuration of the cobalt would undergo rearrangement resulting in electron spin unpairing. The easy formation of a transition state complex with the electron spin free state of the cobalt (II) species would then be possible since the ligand molecules of the cobalt (II) are labile and hence would easily rearrange into the configuration needed for the transition state. This latter process would be faster than the former provided there was no significant change occurring in the bond distances and hence electron spin pairing of the cobalt (II) species during rearrangement. However the movement of the ligand molecules would affect the degree of splitting of the energy values of the d orbitals. It is considered that, as for the reaction between the acetylacetonato complexes, the most logical configuration of the cobalt species in the transition state is that of a trigonal bipyramid.

Application of the Franck-Condon Principle to electron transfer reactions places a restriction on the reaction such that no rearrangement of the structures of the reactants i.e. configuration and bond distances, may take place during the actual electron transfer. Furthermore the electron spin multiplicity, which is related to the electronic configuration of the reactants, should also undergo a minimum change during the actual electron exchange. The effect of a spin multiplicity restriction on the electron transfer has been proposed by Adamson and Vorres (40) for the reaction between the ethylenediaminetetraacetato complexes of cobalt. The reaction between the electron spin free cobalt (II) complex and the electron spin paired cobalt (III) complex results in an electron spin multiplicity change (ΔI) of two units, i.e.

$$\mathrm{Co^{II}(t_{2g})^4(e_g)^3 + Co^{III}(t_{2g})^6(e_g)^0 \rightleftharpoons Co^{III}(t_{2g})^4(e_g)^2 + Co^{II}(t_{2g})^6(e_g)^1}$$

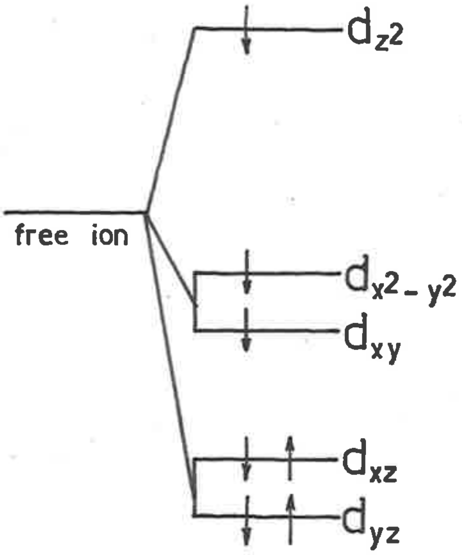
and is therefore restricted. Similarly the reaction between electron spin paired cobalt (II) and electron spin free cobalt (III) also results in a spin multiplicity change of two units. However when the electronic configurations undergo rearrangement to intermediate values then the spin multiplicity change becomes minimal i.e.

$$\mathrm{Co^{II}(t_{2g})^5(e_g)^2 + Co^{III}(t_{2g})^5(e_g)^1 \rightleftharpoons Co^{III}(t_{2g})^5(e_g)^1 + Co^{II}(t_{2g})^5(e_g)^2} \qquad (\Delta I = 0)$$

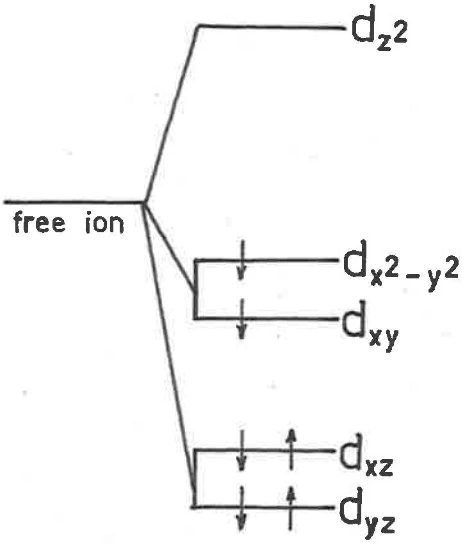
and the electron transfer becomes allowed.

The suggestion of a trigonal bipyramidal configuration for the cobalt species in the transition state, in both the acetylacetone case and the phensal type reactions, is made since the electron transfer is expected to occur through the ligand bridge and the orbital most available for conjugation with the bridging molecules will be that directed towards the bridging ligands viz. the dz^2 orbital. Further, the distribution of electrons in the various d orbitals of the cobalt in reactants with a trigonal bipyramidal configuration is

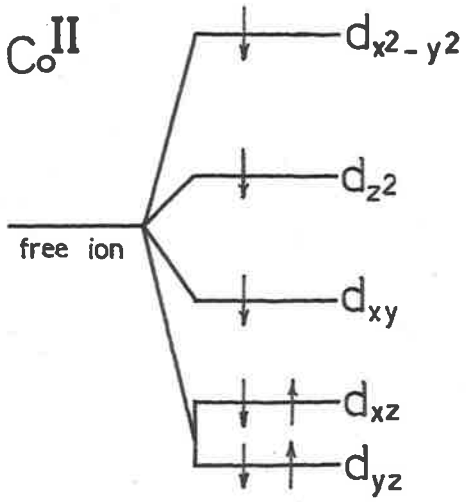
Cobalt (II)

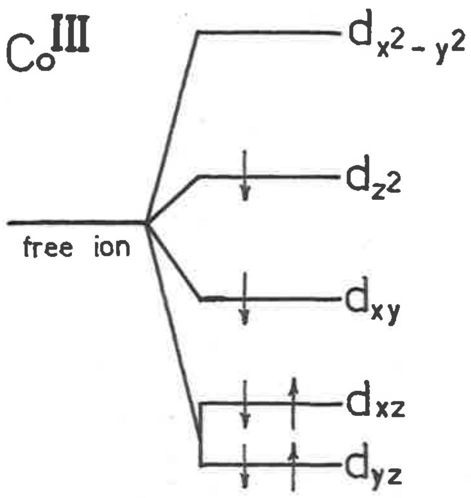


Cobalt (III)



and there will therefore be no spin multiplicity restriction for the exchange of an electron between the high energy dz^2 orbitals of the reactants. Such an electron transfer is analagous to those for reactions between octahedral complexes, e.g. $Co(NH_3)_5\ Cl^{++}$ and $Cr(H_2O)_6^{++}$, in which upper energy d orbitals are involved in the exchange and which Orgel (16) considers will be consequently slow. However if the other possible five coordinate species viz. square pyramidal, were to occur in the transition state then the electron transfer would need to occur between the $d_{x^2-y^2}$ orbitals of the cobalt atoms i.e.





in order to maintain a minimum change in the spin multiplicity. Thus the electron transfer in this latter case would not occur through the bridging molecule.

The rate of the bond breaking process and conversion of the resulting cobalt (III) species to the trigonal bipyramid structure necessary to form the transition state, since electron spin unpairing occurs at the same time, may be considered as a process of converting diamagnetic cobalt (III) to paramagnetic cobalt (III). Taube et al (17) made the suggestion that the exchange of ligand water of the cobalt (III) hexahydrate with solvent water was a fast reaction because the ligand field of the water was sufficiently weak to permit the cobalt (III) to exist partly in the paramagnetic state. Further Busch (53) considers that certain ligands will occur which allow partial electron spin unpairing or electron spin pairing of the metal atom. However in the case under study the reaction proceeding via the paramagnetic form will be mainly due to the inability of the cobalt (II) to undertake electrophilic attack on the cobalt (III) complex as suggested above. The dependence of the rate of reaction on the reactant concentrations may be calculated from theoretical considerations of the stepwise reactions.

$$Co_d^{III} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Co_p^{III}$$

$$Co_p^{III} + Co^{II} \xrightarrow{k_3} Co_p^{III} \quad Co^{II} \longrightarrow \text{electron transfer}$$

where the subscripts "p" and "d" represent paramagnetic(trigonal bipyramidal)and diamagnetic (octahedral) states of the cobalt (III).

The theoretical rate of reaction may be determined from a consideration of these equations. Since the rate of formation of paramagnetic cobalt (III) may be expressed by

$$\frac{d\left[Co_p^{III}\right]}{dt} = k_1 \left[Co_d^{III}\right]$$

and the rate of loss of $\left[Co_p^{III}\right]$ may be expressed by

$$-\frac{d\left[Co_p^{III}\right]}{dt} = k_2 \left[Co_p^{III}\right] + k_3 \left[Co_p^{III}\right]\left[Co^{II}\right]$$

if a steady state exists then

$$\left[Co_p^{III}\right] = \frac{k_1 \left[Co_d^{III}\right]}{k_2+k_3 \left[Co^{II}\right]} \qquad 3.3$$

Since within the transition state complex the electron transfer is expected to be extremely fast from one nucleus to the other (4) then the rate of electron transfer will be dependent on the rate of formation of the activated transition state. Hence the rate of electron transfer may be expressed by

$$R = k_3 \left[Co_p^{III}\right] \left[Co^{II}\right]$$

Substituting the value of $\left[Co_p^{III}\right]$ from equation 3.3 gives

$$R = \frac{k_3\left[Co^{II}\right] \ . \ k_1 \left[Co_d^{III}\right]}{k_2 + k_3 \left[Co^{II}\right]}$$

If the rate of formation of the activated transition state complex is very much faster than the rate of conversion of the electron spin free to electron spin paired cobalt (III), then $k_3 \left[Co^{II}\right] \gg k_2$ and hence the rate of electron transfer would approximate to

$$R = k_1 \left[Co_d^{III}\right]$$

Further if as is expected the equilibrium between the electron spin free and the electron spin paired cobalt (III) greatly favours the existence of the latter form then the rate of electron transfer would further approximate to

$$R = k_1 \left[Co^{III}\right] \qquad 3.4$$

The equation 3.4 is the same as the equation 3.1 which was determined experimentally for both the p-tolsal and the phensal systems.

When discussing the electron transfer reaction between the acetylacetonato complexes of cobalt, the large negative entropy of activation was used as evidence to support the formation of a compact transition state complex. However for the phensal type complexes the entropy of activation is expected to be the value for the rearrangement of the electronic structure of the cobalt (III) species and the large negative value found cannot in this case be used as evidence for the formation of a compact intermediate. The fact that a large negative entropy of activation has been found in this case, and which can be related to the rearrangement of the electronic structure of one of the species, may also serve to indicate that the interpretation of entropy as indicating a compact transition state complex being formed in other cases is not correct, but that a large contribution of the entropy factor may be due to the rearrangement of the electronic structures to an intermediate state.

The activation energies of the phensal type reactions are going to be related to the bond breaking process and the rearrangement of the resulting cobalt (III) species to the trigonal bipyramidal structure necessary to form the transition state and hence the energy difference between the electron spin paired and the electron spin free states of the cobalt (III) species. These values are found to be the same within experimental error and this is to be expected since there should be little if any difference in the bond breaking process or the ligand fields present in the cobalt (III) species for either of the complexing agents used.

Although it is thought that a paramagnetic form of the cobalt (III) species is present during the electron transfer it is also felt that the proportion of cobalt (III) species in this form will be relatively small. Magnetic measurements on solutions of these complexes at high temperatures would be of assistance to test the hypothesis.

References

1. C. P. Leuhr, G. E. Challinger and B. J. Masters, J.Am.Chem.Soc., 78, 1314 (1956).
2. H. A. C. McKay, Nature, 142, 997 (1938).
3. R. G. Charles and M. A. Pawlikowski, J.Phys.Chem., 62, 440 (1958).
4. W. F. Libby, J.Phys.Chem., 56, 863 (1952).
5. R. J. Marcus, B. J. Zwolinski and H. Eyring, J.Phys. Chem., 58, 432 (1954).
6. J. Kaplan and C. Kittel, J.Chem.Phys., 21, 1429 (1953).
7. H. Taube et al., J.Am.Chem.Soc., 75, 4118 (1953); 76, 2103 (1954); 76, 4053 (1954).
8. N. V. Sidgwick, "The Chemical Elements and Their Compounds", Oxford, 1952, p. 1406.
9. Stability Constants, London Chem. Soc., Part I, Table 120.
10. D. Cohen, J. C. Sullivan, E. S. Amis and J. C. Hindman, J.Am.Chem. Soc., 78, 1543 (1956)
11. B. O. West, J.Chem.Soc., 3115 (1952).
12. S. Glasstone, "Text-book of Physical Chemistry", MacMillan, 1953, pp. 1095-1104.
13. D. R. Stranks, A.N.Z.A.A.S. Conference, Brisbane, May, 1961.
14. J. Whitney and N. Davidson, J.Am.Chem.Soc., 69, 2076 (1947); 71, 3809 (1949).
15. L. E. Orgel, Quarterly Reviews, 8, 422 (1954).
16. L. E. Orgel, Reports of the 10th Solvay Conference, May 22-26 (1956), p. 289.
17. H. L. Friedman, J. P. Hunt, R. A. Plane and H. Taube, J.Am.Chem. Soc., 73, 4028 (1951).

18. J. Halpern, Quarterly Reviews, 15, 207 (1961).

19. J. Halpern and L. E. Orgel, Discuss. Faraday Soc. 29, 7 (1960).

20. K. J. Laidler, S. Glasstone and H. Eyring, "The Theory of Rate Processes", McGraw and Hill, (1941).

21. W. C. E. Higginson, Discuss. Faraday Soc. 29, 123 (1960).

22. A. M. Zwickel and H. Taube, ibid. 29, 42 (1960).

23. P. George and D. H. Irvine, J.Chem.Soc. (1954), 587.

24. T. W. Newton and S. W. Rabideau, J.Phys.Chem., 63, 365 (1959).

25. W. C. E. Higginson et al., Discuss. Faraday Soc. 29, 49 (1960).

26. B. R. Baker, F. Basolo and H. M. Neumann, J.Phys.Chem., 63, 371 (1959).

27. C. A. Coulson, "Valence", Oxford (1953).

28. J. B. Stead and W. C. E. Higginson, Discuss. Faraday Soc., 29, 126 (1960).

29. J. Halpern and L. E. Orgel, ibid., 29, 32, (1960).

30. D. L. Ball and E. L. King, J.Am.Chem.Soc., 80, 1091 (1958).

31. A. M. Zwickel and H. Taube, ibid., 81, 1288, (1959).

32. W. Kruse and H. Taube, ibid., 82, 526 (1960).

33. A. F. Ogard and H. Taube, ibid., 80, 1084 (1958).

34. L. F. Audrieth and J. Kleinberg, "Non-aqueous Solvents", Wiley, (1956) p. 95.

35. E. U. Condon, Amer.J.Phys. 15, 365 (1947).

36. J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry", Interscience, (1960) p. 148.

37. F. S. Dainton et al, International Conference on Radioistopes in Scientific Research, abstract in Int. J. Appl. Rad. and Isotopes 2, 259 (1957).

38. G. D. Dorough and R. W. Dodson, Quarterly Progress Report, Brookhaven National Laboratory, July-Sept. BNL132 (S-11) 68.

39. J. J. Grossman and C. S. Garner, J.Chem.Phys., 28, 268 (1958).

40. A. W. Adamson and K. S. Vorres, J. Inorg. Nucl. Chem. 3, 206 (1956).

41. D. R. Stranks, Discuss. Faraday Soc. 29, 73, (1960).

42. W. B. Lewis, C. D. Coryell and J. W. Irvine, J.Chem.Soc. (1949), 5386.

43. R. W. Kluiber, J.Am.Chem.Soc. 82, 4839, (1960).

44. E. Penna-Franca and R. W. Dodson, ibid., 77, 2651 (1955).

45. E. L. Goodenow and C. S. Garner., ibid. 77, 5272, (1955).

46. F. P. Dwyer and A. M. Sargeson, Proc. Roy. Soc. N.S.W., (1956), 141.

47. F. P. Dwyer and A. M. Sargeson, Proc. Roy. Soc. N.S.W., (1956), 29.

48. F. A. Cotton and R. H. Holm, J.Am.Chem.Soc. 82, 2979, (1960).

49. G. Urbain and A. Debierne, Compte Rendu, 129, 304, (1899).

50. A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms of Reactions", Wiley, (1961).

51. B. O. West, J.Chem.Soc. (1962), 1374.

52. O. J. Bullen, R. Mason and P. Pauling, Nature, 189, 291, (1961).

53. D. Busch, R. C. Stoufer and W. B. Hadley, J.Am.Chem.Soc., 83, 3732 (1961).

54. F. Basolo and R.G. Pearson, "Mechanisms of Inorganic Reactions", Wiley, (1958) p. 55.

PART III.

Electron Transfer Reactions between a Neutral Complex Molecule and a Complex Ion.

Chapter 4.

CHAPTER 4

Electron Transfer Reaction between a Neutral Complex Molecule and a Complex Ion

A. The Electron Transfer Reaction between the N,N'-ethylene-bis-(Salicylidene-iminato) Complexes of Cobalt (II) and (III)

The electron transfer reaction between salen*-cobalt (II) and diammino-salen-cobalt (III) chloride was attempted, however, due to the lack of mutual solubility of the complexes in any of the solvents chosen for the investigation this work could not be carried out. The camphor-10-sulphonate of the complex cobalt (III) ion was prepared and found to be soluble in pyridine, and since the cobalt (II) complex was also soluble the exchange was studied in this solvent at temperatures of 25°C and 0°C (Tables 4.1 and 4.2). These temperatures were chosen for the investigation, since the reaction was expected to occur rapidly at room temperature.

Solvent extraction was employed to separate the two cobalt complexes from the reaction mixture. For the reactions at 0°C, the separated fractions were analysed both radiometrically and chemically (Table 4.2). At 25°C, however, only radiometric analysis was employed as preliminary experiments had shown that at this temperature 100% separation was obtained.

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* Salen = N,N'-ethylene-bis-(salicylidene-iminato) ligand.

TABLE 4.1

Electron Transfer Reaction between Salen Complexes of Cobalt (II) and Cobalt (III)

Concentration of Cobalt (II) 0.0136 M; Concentration of Cobalt (III) 0.0147 M in Pyridine as Solvent at a Temperature of 25.0 ± 0.1°C.

No.	Time(mins)	counts / mins		E%
		Cobalt (II)	Cobalt(III)	
1	1.5	3542	3174	91.0
2	3.5	3360	3513	98.4
3	6.0	3340	3427	97.5
4	8.25	3499	3182	91.7

TABLE 4.2

Electron Transfer Reaction between Salen Complexes of Cobalt (II) and Cobalt (III)

Concentration of Cobalt (II) 0.0100 M; Concentration of Cobalt (III) 0.0115 M in Pyridine as Solvent at a Temperature of 0°C.

No.	Time (secs)	Counts / 100 secs		Concentration $Mx10^{-4}$		E %
		Cobalt(II)	Cobalt(III)	Cobalt(II)	Cobalt(III)	
1	47.5	3357	3403	4.80	4.95	99.1
2	146.0	3363	3600	4.94	5.10	101.8
3	346.0	3841	4001	5.46	5.84	98.7

B. Electron Transfer Reactions between the Sal-o-phen* and the Sal-propen Complexes of Cobalt (II) and (III)

The electron transfer reaction between sal-o-phen-cobalt (II) and diammino-(sal-o-phen)-cobalt (III) camphor-10-sulphonate was studied at 0^{o}c. in pyridine as solvent (Table 4.3). A study was also made of the similar system in which the quadridentate ligand was the sal-propen* molecule (Table 4.3).

TABLE 4.3

No.	Time (secs)	Counts / 100 secs		Concentration $Mx10^{-4}$		E %
		Cobalt(II)	Cobalt(III)	Cobalt(II)	Cobalt(III)	
1	53.5	1051	231	7.10	1.66	95.1
2	151.0	1280	273	8.70	1.90	98.5
3	42.5	246	580	3.15	7.13	101.3
4	140.0	147	571	1.81	7.13	99.6

Sample numbers 1 and 2 are the results for the electron transfer reaction between the sal-o-phen complexes, the concentrations being, cobalt (II) 0.0050 M and cobalt (III) 0.0095 M. Sample numbers 3 and 4 are the results for the electron transfer reaction between the sal-propen complexes, the concentrations at the commencement of the experiment being cobalt (II) 0.0100 M and cobalt (III) 0.0094 M.

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* Sal-o-phen = N,N'-o-phenylene-bis-(salicylidene-iminato)
Sal-propen = N,N'-propylene-bis-(Salicylidene-iminato)

C. The Exchange of Cobalt (II) Ions with the N,N'-ethylene-bis-(Salicylidene-iminato) Type Complexes of Cobalt (III)

From the results of the electron transfer experiments (Tables 4.1-4.3), it appeared that the reactions were fast. The same result would have been obtained if both the cobalt (II) and cobalt (III) complexes underwent a rapid exchange of complexed cobalt with cobalt ions in solution. Since West (1) found a rapid exchange of cobalt ions between cobalt acetate and N,N'-ethylene-bis-(salicylideneiminato)-cobalt (II) in pyridine, it was necessary to determine whether the cobalt (III) complexes also gave a rapid exchange with cobalt ions.

The exchange reactions of the cobalt ions between cobaltous perchlorate and the perchlorates of the complex cobalt (III) ions were studied in an 80% acetone-water mixture at 25°C. The cobalt (III) complex, after exchange, was precipitated as the p-toluene-sulphonate and the specific activity of the cobalt in the complex ion was determined. The results for the experiments are shown in Table 4.4. Sample numbers 1, 2 and 3 are the results for the exchange of cobaltous ions with the cobalt (III) (salen) complex ion, while 4 and 5 are the results for the exchange with the sal-o-phen and sal-propen complex ions respectively.

The results of the exchange experiments indicate that the reaction is slow, but faster than might have been expected for cobalt (III) complexes of the type investigated. Wilkins et al. (2) investigated the exchange between cobaltous salts and 1.10-phenanthroline complexes of cobalt (III) and found that there was a measurable rate of exchange. They explained this as being due to the existence of a small amount of cobaltous impurity in the cobalt (III) complex. In the preparation of cobalt (III) complexes, it seems that it is almost impossible to obtain them without some cobalt (II) impurity (see p. 175). Hence the existence of some cobalt (II) impurity in the experiments carried out would explain the more rapid exchange observed. However, the rate of exchange is still slow enough to indicate that the results obtained in the electron transfer experiments are due to an electron exchange and not to an exchange of the cobalt ions.

TABLE 4.4

No.	Time(hrs)	Counts/100 secs / Cobalt Complex	E %	Wt. of Complex	S
1	16.5	804	10.8	.0100	7.45×10^5
2	40.0	2344	26.0	.0121	7.45×10^5
3	64.0	4969	39.0	.0171	7.45×10^5
4	10.0	770	4.9	.0211	7.45×10^5
5	8.0	308	4.6	.0090	7.45×10^5

S = Specific activity at 100% exchange.
The original solutions of cobaltous perchlorate and complex used for the exchange study were made 0.0200 M and 0.0250 M respectively.

D. General Discussion

Calvin and Barkelew (3) carried out magnetic measurements on salen-cobalt (II) and found a value of 2170 for $10^6 \chi M$, from which they concluded that the cobalt ion has only one unpaired electron. Hence in terms of the Pauling theory there is, in the complex, dsp^2 hybridization of the orbitals of the cobalt ion to give a square planar configuration of the ligand around the central metal ion (Fig. 4.1). They also found that the values of $10^6 \chi M$ for the sal-o-phen-cobalt-II and the sal-propen-cobalt-II were 3360 and 2380 respectively. Although these values seem a little higher than what might have been expected, they were interpreted as indicating that these complexes are similar to the salen-cobalt (II) complex. Magnetic measurements on the cobalt (III) complexes with all three ligands indicates the existence of two unpaired electrons. (P203) The two ammonia molecules found to be present (P198) by analysis would be bonded by means of two pd hybrid orbitals along the direction of the antibonding d_{z^2} orbital. Consequently these bonds would be expected to be weaker than the four metal-quadridentate ligand bonds and also to be more extended in space. Evidence that the two metal-ammonia bonds are different to the other four metal-ligand bonds is found in the reaction of the complexes with approximately 5 Molar caustic soda solution, since ammonia is given off without destruction of the remainder of the complex. The cobalt (II) complexes could also be expected to form tetragonal structures in solvents which are able to coordinate in the remaining two octahedral positions, e.g. pyridine. As in the case of the

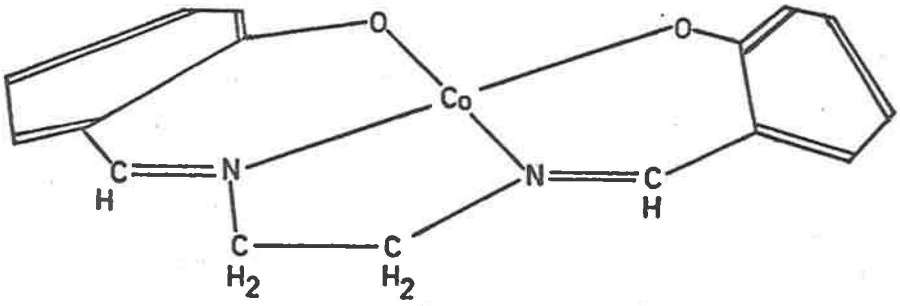

Fig.4.1 Ethylene-bis-(salicylidene-iminato)-cobalt^{II}

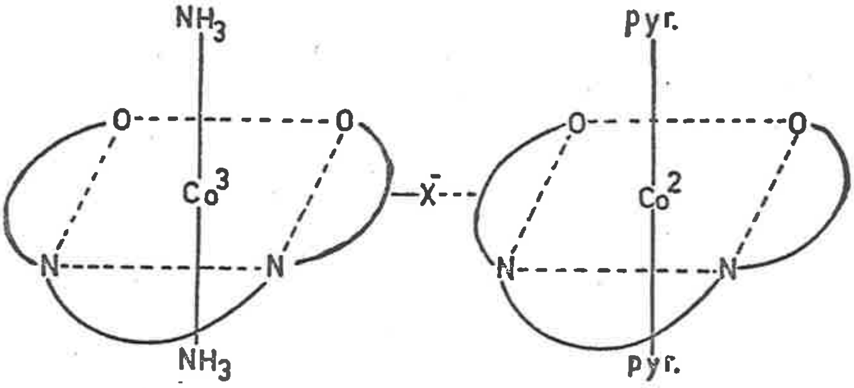

Fig.4.2 Anion bridged activated intermediate.

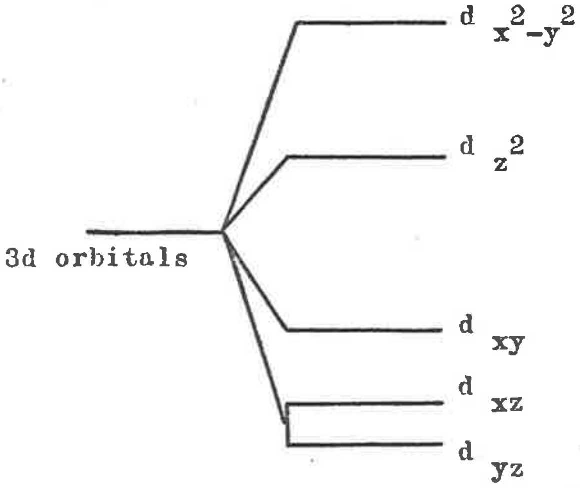

Fig.4.3 Splitting of the energy states of the 3d orbitals by the field from a square planar quadridentate ligand.

cobalt (III) complexes, two linear pd hybrid orbitals would be used for the bonding as before being extended in space.

The mechanism of the electron transfer most probably would occur by anion bridging,(i.e."outer sphere"reaction)between the two cobalt complexes (Fig. 4.2). The study of the effect of different bridging groups on the rate of electron exchange was not possible due to solubility factors. However, in view of the evidence found by Dorough and Dodson (4) it is not expected that different anions would produce any difference in the rate of the electron transfer reaction.

In a comparison of this type of complex with the tetraphenylporphine complex of cobalt (III), it is to be expected that, as in the latter case, spin pairing of the 3d electrons will take place. The quadridentate ligand may be considered as producing the main influence on the ligand field, since it has a rigid structure and must have a square planar arrangement about the central metal ion. Such a ligand would therefore cause a splitting of the energy states of the 3d orbitals as shown in Fig. 4.3. The influence of the tetraphenyl-porphine molecule on the ligand field would be greater than in the case of the N,N'-ethylene-bis-(salicylidene-iminato) type ligand since it will have a greater π orbital contribution and also it is much more rigid than the latter type ligands. In the second type of ligands two nitrogen atoms have been replaced by oxygen atoms and this would also be expected to decrease the ligand field. Therefore the effect would be that the energy states of the d_{z^2} and d_{yz} orbitals would have a much wider separation in the case where tetra-phenyl-porphine is complexed to the cobalt (III) than when the N,N'-ethylene-bis-salicylidene-iminato) type ligands are complexed.

The magnetic results can be explained as electron spin pairing of the 3d electrons in complexes with the former ligand and only partial electron spin pairing with cobalt complexes of the latter type ligands. The electronic structures of the cobalt (II) and cobalt (III) ions in the salen type complexes would therefore be similar, viz.

d^2_{yz}, d^2_{xz}, d^1_{xy} and $d^1_{z^2}$ $d^0_{x^2-y^2}$ for Cobalt (III)

and d^2_{yz} d^2_{xz} d^2_{xy} and $d^1_{z^2}$ $d^0_{x^2-y^2}$ for Cobalt (II)

and a rapid electron transfer would take place without the need for a large energy of rearrangement of electronic configurations of the reactants. Further, there will be no need to rearrange the first sphere of coordination for the formation of a symmetrical transition state since the reaction most probably is an "outer sphere" reaction. It should also be pointed out that the electronic structures proposed for the complexes would allow an electron exchange to take place between d orbitals in a low energy state which Orgel (5) considers will be fast reactions.

References

1. B. O. West, J.Chem.Soc., 395 (1954).
2. P. Ellis, R. G. Wilkins and M. Williams, J.Chem.Soc., 4456 (1957).
3. M. Calvin and C. H. Barkelew, J.Am.Chem.Soc., 68, 2267 (1946).
4. G. D. Dorough and R. W. Dodson, Quarterly Progress Reports, Brookhaven National Laboratory, July-Sept. (1951), BNL 132 (S-11) p. 68.
5. L. E. Orgel, Reports of the 10th Solvay Conference, May 22-26 (1956), p. 289.

PART IV

Conclusion and Experimental.

CHAPTER 5

Conclusion

Factors which might be expected to influence the rate at which electron transfer reactions proceed are,

1) The distance of separation of the reactants at electron transfer since this will affect the probability of electron tunnelling or jump process. The separation of the reactants will further depend on
    (a) The charge on the reactants
    (b) The dielectric constant of the solvent
    (c) The presence of ions of opposite charge to that of the reactants.
2) The permeability of the solvent to the electron passage
3) The permeability of the ligand molecules to the electron passage.

The experimental work reported in this thesis was carried out in an attempt to elucidate, more closely, the effect of some of these factors viz. charge, ligand and solvent type, on the rate of electron transfer reactions. The effect of charge has been investigated by the study of reactions between neutral complexes while that of the ligand has involved the study of a series of chelate type ligands. Due to solubility factors the reactions have been carried out in organic solvents, however, only a few of these have been used. Though only a few reactions have been studied it has been possible to make some deductions as to the effect of the various factors not only on the rate of reaction but also as to their effect on the reaction mechanism.

Firstly, when considering the acetylacetonato complexes of cobalt, it could be seen, even from the few solvents used, that the nature of the solvent is a very important factor in determining the rate of the electron transfer i.e. the rate was found to be faster in acetylacetone than in toluene as solvent. In view of the evidence of other workers (11) (12) the effect of the change of solvent cannot be explained as due to a change in the dielectric constant of the medium. Rather it can be explained in terms of a change in the reaction mechanism, i.e. in toluene the reaction is best explained as proceeding through an "inner sphere" bridged transition state, while the reaction in acetylacetone can be explained as involving an "outer sphere" bridged transition state. The latter reaction would occur with the greater probability due to there being no need, as in the former case, for the making and breaking of ligand-metal bonds. An attempt to also compare pyridine as solvent met without success due to the rapidity with which the cobalt (III) complex was reduced in this solvent.

It is observed that the rate at which electron transfer reactions proceed is rapid if the reactants both have similar electronic configurations e.g. Fe^{2+}-- $Fe\ (OH)^{2+}$ and $Co^{II}(\phi P)$-* $Co^{III}(\phi P)^{+}$ and slow if the electronic configurations are different, e.g. Cr^{2+}-- Cr^{3+} (see Table 1). Hence the change of electronic structure must be a major

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* ϕP represents the tetraphenylporphine ligand.

feature in determining the rate of electron transfer and consequently both the activation energy and activation entropy.

The activation energies obtained for the cobalt (II) - cobalt (III) reactions studied, except for the salen type reactions where the electron transfer was too rapid to allow the determination of kinetic data, are all comparable with those given for other such reactions in aqueous media (Table 2.2) and for which the reactants are electron spin free and electron spin paired respectively. This is as one would expect if a large portion of the activation energy were due to the rearrangement of the energy values of the d orbitals of the reactants. The rearrangement of the energy values of the d orbitals of the reactants would take place during the formation of the transition state or as is proposed for the phensal type reactions during the bond breaking process and the subsequent more rapid formation of the transition state. The energy of activation determined for the phensal type reactions being associated with the electronic rearrangement during the bond breaking process and subsequent rearrangement of Cobalt (III) species to a trigonal bipyramidal structure.

Although the entropy of activation was initially interpreted as an indication that a compact transition state is formed, this being the usual practice (13), doubt is cast on the interpretation in view of the large negative value found for the phensal type reactions. In the latter case the kinetics of the reaction were found to be first order in Cobalt (III) concentration and a major contribution to the entropy of activation must be interpreted as due to the rearrangement of the electronic structure of the cobalt (III) species. In view of the fact that the entropies of activation for many cobalt (II) - cobalt (III) reactions are of the same magnitude (Table 2.2) as that for the phensal type reactions, one is led to conclude that a large part of the entropy term in all these reactions is due to the rearrangement of the electronic structures of the reactants to some intermediate form.

Although there is doubt cast on the use of large negative entropies of activation as an indication of the formation of compact transition states, other considerations still lead one to the conclusion that such compact transition states do occur in the cases studied e.g. the need for a transfer of ligand in the cases studied, i.e. "inner sphere" reactions, and the considerations of Platzman and Franck (14) that the electron transfer cannot occur over large distances.

In the systems using the N-aryl-salicylideneiminato complexes of cobalt it was found that there was a change in the reaction kinetics compared with that of the acetylacetonato complexes in toluene. It has been suggested that this is due to the lack of any tendency for the cobalt (II) species in the former case, to undergo an electrophilic attack on the comparable cobalt (III) complex. The electron transfer reaction between the salen type complexes cannot be compared with the other cases due to the rapidity with which they proceed and hence the inability to the studied by the methods used.

In all of the cases studied here the ligand molecules have contained π electron systems and would therefore have facilitated the electron transfer, especially if used directly as the bridging group.

The influence of changing the ligand from an acetylacetone to a phensal type or salen type group would affect the rate of the electron transfer to some small degree due to the greater degree of conjugation, and hence electron permeability, in the first named ligand. However, the change in the degree of conjugation can not be used to explain the change in the observed rate of reaction. On the other hand the increased rate of reaction for the phensal type reactions compared with the reaction between the acetylacetonato complexes in toluene can be explained in terms of the difference in ligand fields of the reactants. i.e. the change of the ligand will produce a change in the ligand field around the ions between which electron transfer is to occur and this in turn will produce a change in the degree of splitting of the energy values of the 3 d orbitals of the cobalt species. The bigger the difference between the splitting of the energy values of the 3 d orbitals of the cobalt (II) and cobalt (III) then the greater will be the energy required for rearrangement of these orbitals and hence the greater the potential energy barrier to the electron transfer. However that this is not the only factor determining the rate of reaction has already been pointed out in the comparison of the reaction between the acetylacetonato complexes in toluene and acetylacetone as solvent.

The effect of the change of ligand on the rate of reaction is further illustrated by the comparison of the slow reactions between the acetylacetonato and the phensal type complex with the fast reactions between the salen type cobalt complexes. In the latter case the ligand molecule is quadridentate and therefore will produce a strong planar field around the cobalt ions, thus causing electron spin pairing in the cobalt (II). The existence of cobalt (II) and cobalt (III) species with similar electronic configurations and the absence of any need to involve the first sphere of co-ordination in any bridge forming process thus allows a rapid electron transfer. The anion present may then influence the "outer sphere" reaction by

(1) providing a bridge and thus an easier path for the electron transfer.

or (2) producing an ionic field in solution which would influence the potential difference between, and hence the approach of, the reacting species.

Since there was difficulty in selecting anions which allowed the cobalt (III) complex to be soluble in the solvents chosen, furthermore since the reaction was found to proceed very rapidly, the effect of the anion could not be determined. However a study of any electron transfer spectra resulting from the reaction may allow the determination of whether or not the anion is participating in bridge formation.

The reactions listed in Table 2.2 and those described in this work have certain features in common despite a wide variety of experimental conditions. Thus the rates of reaction are all slow and the entropies of activation where measured are relatively large and negative and the energies of activation are all similar. Thus the absence of charge on the reacting species does not appear to significantly alter the rate of exchange between electron spin free cobalt (II) and electron spin paired cobalt (III) complexes. The rate of exchange is slow whether the complexes are positively or negatively charged or as in the present case neutral. This observation together with the fact that the activation energies and entropies are of similar orders of magnitude is believed to indicate that the overriding feature of all these electron transfer reactions is the need to change the electronic configurations of cobalt (II) and cobalt (III), before electron transfer can actually take place, to similar energy configurations intermediate between the normal electron spin paired cobalt (III) and electron spin free cobalt (II).

In addition to the work carried out in this thesis, it would prove advantageous to make a study of the spectra of the various systems at the temperatures of the kinetic runs. Such a study might be expected to give electron transfer bands in the spectra, thus allowing a better interpretation of the electron transfer mechanism to be obtained. Further work on the acetylacetone system is also required in order to determine whether or not the hydrogen ion is acting as a bridging ion in the transition state complex and this may be achieved from the use of deuterated acetylacetone as solvent.

CHAPTER 6

EXPERIMENTAL

A. General

1. Solvents

(a) Acetylacetone

B.D.H. Acetylacetone was dried for several days over anhydrous sodium sulphate and the dried solvent was then purified by distillation at 139°C. The distillation was carried out in the presence of a small quantity of cobaltous acetate in order to remove any oxidants. During and after distillation dry "oxygen free" nitrogen gas was bubbled through the distillate to prevent the solution of oxygen from the atmosphere before use.

(b) Toluene

Sulphur free B.D.H. toluene was dried for several days over freshly prepared sodium wire. After refluxing for an hour over sodium the solvent was purified by distillation at 110°C, in an atmosphere of dry "oxygen free" nitrogen. Toluene required as a solvent was purified and used immediately, since when kept for only a few hours it was found that small quantities of water were absorbed and the bis(acetylacetonato) diaquo cobalt (II) precipitated from a solution of the anhydrous complex.

(c) Pyridine

B.D.H. Pyridine was kept for several days over potassium hydroxide pellets. The purification of the solvent was then carried out by distillation at 115°C in the presence of dry "oxygen free" nitrogen gas.

(d) Ethanol and S.V.R.

The same method of purification was used for both the ethanol used as a solvent and for the S.V.R. obtained from Tolley, Scott and Tolley and used for spectra studies. The purification was carried out by refluxing the required solvent over potassium hydroxide for about four hours. The solvent was then distilled at 78°C, and stored in a stoppered flask. The purified S.V.R. used for spectra studies was not kept for more than a week in order to reduce the possibility of any oxidation of the solvent occurring.

(e) Acetone

Analytical grade reagent from Standard Laboratories Pty. Ltd. was dried over anhydrous calcium sulphate and distilled at 56°C. The solvent was freshly prepared just prior to the experiments being carried out.

(f) Chloroform

B.P. Standard chloroform was extracted several times with water to remove water-soluble components and after separation from the final aqueous fraction was stored over anhydrous calcium chloride for several days. It was then distilled at 61°C just prior to being used.

2. Preparation of Dry, "oxygen free" Nitrogen Gas

Cylinders of commercial nitrogen supplied by C.I.G. were used as a source of nitrogen gas. The gas was purified by bubbling through two dreschler bottles which contained mixtures of chromous chloride solution and hydrochloric acid over zinc amalgam. The bottles were shaken continuously throughout each experiment in order to regenerate any chromous chloride oxidized by the removal of oxygen present in the commercial nitrogen gas. The nitrogen gas after deoxygenation was dried by passing through concentrated sulphuric acid, a column of soda-lime and finally a column of silica gel.

The chromous chloride solution was prepared by dissolving chromic chloride in water, adding concentrated hydrochloric acid and shaking with zinc amalgam. The zinc amalgam was prepared by heating a mixture of 3 grams of zinc and 100 grams of mercury in the presence of dilute sulphuric acid. When the zinc was dissolved the mixture was allowed to cool, separated from the aqueous layer, and filtered through a small hole in a filter paper.

3. Radiometric Analysis

Two methods of measurement were applied to radio-active solutions, these are described below.

(a) Geiger Counting

For the measurement of radio-activity by this method, glass skirted geiger tubes, type M12, produced by 20th Century Electronics, were used. The capacity of the tubes was approximately 20 mls., however it was found that the volume of a standard radio-active solution placed in the outer tube did not affect the number of counts obtained provided the inner geiger tube was completely covered.

The operating potential of each tube was given by the manufacturers, however it was necessary to check this value due to the possibility of a change occurring when kept for some time without use. The characteristics were determined, after an initial "running in" period, using saturated solutions of potassium salts. The effect of extraneous radiations producing a background count was reduced by fitting the tubes into lead towers fitted with removable lead covers. The thickness of the lead towers and covers was approximately 1½ inches.

(b) Scintillation Counting

Measurements by this method were made using an EKCO scintillation counter, type N550 A. The counter was fitted with a thallium iodide activated sodium iodide crystal, type N553 A. The operating conditions of the photomultiplier tube in the scintillation counter were given by the manufacturers and were accepted without checking.

4. Recording of Counts

The recording of the counts given by either the geiger tube or scintillation methods of measurement was made using either a Philips predetermined scaler, type PW4035, or an EKCO automatic scaler, type N530D. The only corrections applied to the counting rates obtained were those for background counts. The corrections were found by counting for approximately one hour, after having allowed the electronic circuits to warm up for a period of half an hour. The counting rates found for the background were 30 ± 5 counts per minute with the geiger tubes and approximately 140 counts per hundred seconds for the scintillation method.

Since cobalt 60 has a half-life of approximately 5.3 years no correction was necessary for the rate of decay. No resolving time corrections were applied since the counting rates used were sufficiently low. Also no corrections for density of the solvent were necessary since ethanol solutions were used for both cobalt (II) and cobalt (III) fractions being compared by the radiometric analysis.

The scaler circuits were checked periodically by applying a set of regularly spaced pulses to them. Also the counting circuits were checked from time to time, which in the case of measurements made with geiger tubes was done by determination of the tube characteristics with concentrated solutions of potassium salts. However, the scintillation counter was checked only by comparison of the background count rate observed from time to time; no alteration in this rate was taken to mean that the characteristics of the counting circuits were unchanged.

The counting of radio-active solutions was carried out for sufficient time for the rate to be known to within ± 1%. This time (1) was determined using the equation

$$t = \frac{10^4 k^2}{R(E_R\%)^2}$$

For a standard error k = 1 R = the rate in counts/unit time and $E_R\%$ is the percentage error of the rate.

5. Preparation of Samples for Counting

Solution counting was the only method employed and ethanol solutions of either a complex or of salts of the metal ion were prepared and made up to a volume of 50 ccs. in standard flasks. When geiger countint techniques were employed for the radiometric analysis, samples of the prepared radio-active solutions were placed in the skirted counting tubes, in order to completely cover the inner geiger tube. However, when scintillation techniques were employed 8 ml samples of the solution were measured by means of a medical type syringe, and placed in small polythene vessels situated over the thallium iodide activated sodium iodide crystal.

6. Decontamination of Apparatus

After each radio-active sample was counted the geiger counters were emptied and decontaminated before counting of the next sample. The tubes were emptied by withdrawing the solution through a fine glass capillary connected to a buchner flask, an Edwards vacuum pump and compressor, type RBFO, being used to place the buchner flask under a negative pressure. When emptied the geiger tubes were decontaminated by filling with 2 normal hydrochloric acid in ethanol; the solution was then withdrawn as before and the process repeated. A final washing was made with ethanol and the geiger tube was then dried by insertion of a sleeve of filter paper cut to the correct size. This method thus allowed the geiger tubes to be cleaned without removal from the counting circuit.

The polythene containers used for scintillation counting were removed from the counter, emptied and rinsed twice with two normal hydrochloric acid in ethanol. After a final washing with ethanol the vessels were set aside to dry in air.

All glass apparatus was decontaminated by washing thoroughly with two normal hydrochloric acid and then treating with hot chromic acid.

7. Chromatographic Alumina

In all electron transfer reactions studied except those reported in Chapter 4 chromatographic alumina, prepared by B.D.H., was used for the separation of the cobalt (II) and cobalt (III) complexes from samples of the reaction mixture. The alumina was, however, treated before use. The method of treatment was to wash thoroughly with an ethanol, hydrochloric acid mixture, followed by washing with ethanol and finally with distilled water. After drying at 110°C in an oven the alumina was heated at 300°C in an electric furnace for about 3 hours. On cooling, it was stored in an airtight jar until used.

B. Electron Transfer Reactions between Cobalt (II) and Cobalt (III) Acetylacetonato Complexes

1. Preparation of Reactants

(a) Bis(acetylacetonato)diaquo cobalt (II)

9.96 grams of cobalt acetate were dissolved in hot water to which had been added a small quantity of sodium acetate in order to prevent precipitation of cobaltous hydroxide. To the hot filtered solution was added an aqueous solution of sodium acetylacetonate, which was prepared by adding sufficient 0.1N sodium hydroxide solution to just dissolve 8.00 grams of acetylacetone. After cooling the mixture,the orange pink crystals of the bis(acetylacetonato)diaquo cobalt(II) were filtered off, washed with a small amount of acetone and air dried.

(b) Anhydrous bis(acetylacetonato)cobalt(II)

This compound was prepared by taking a small amount of the diaquo complex prepared by the method described above, and heating gently under reduced pressure in an apparatus shown in Fig. 6.1. Water was first given off by the diaquo complex, and the anhydrous complex then sublimed. The deep ruby red crystals of the anhydrous complex collected on the side of the vessel, from where they were removed and stored under

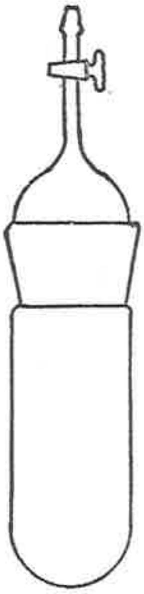

Fig.6.1 Sublimation Apparatus

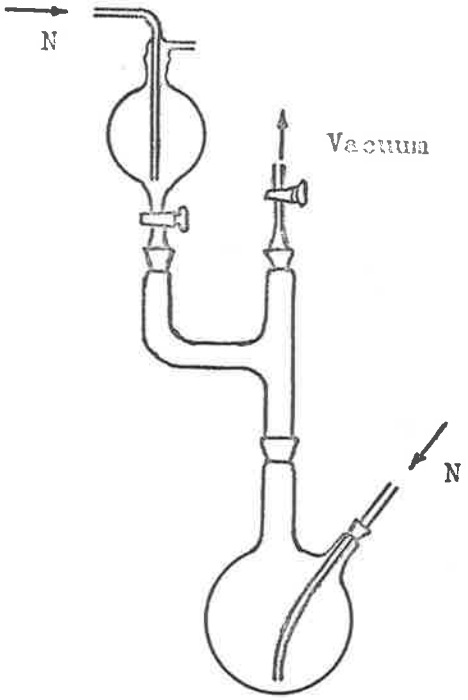

Fig.6.2

reduced pressure over phosphorus pentoxide. The anhydrous material was quite stable in air for short periods, however on long exposure it absorbed water vapour to reform the diaquo complex.

(Analysis: found 22.8 ± 0.2% Co.; theoretical 23.0%)

(c) Tris(acetylacetonato)cobalt(III) [Labelled]

4.98 grams of cobalt acetate were dissolved in a 60% alcohol-water mixture to which was added a small quantity of sodium acetate to act as a buffer. To the resulting solution was added 1 ml. of radioactive cobalt 60. The latter solution was obtained from the A.E.C. Laboratories at Amersham in the form of a cobalt sulphate solution containing 1 mc. per ml. 6.00 grams of acetylacetone were added to the cobalt acetate solution and to the resultant mixture was added sufficient 50 volume hydrogen peroxide, in small quantities, to effect oxidation of the cobalt II complex formed. The mixture was warmed in order to assist the rate of oxidation, care being taken that the heating rate was maintained so as to prevent excess frothing of the solution which changed from a red to a dark green colour. On cooling the solution dark green crystals of tris(acetylacetonato)cobalt(III) were formed. The crystals were filtered off and recrystallized from ethanol.

(d) Purification of tris(acetylacetonato)cobalt(III)

The complex prepared as above, even after several recrystallizations still contained a small quantity of bis(acetylacetonato)cobalt(II). Purification of the cobalt(III) complex was carried out by dissolving it in A.R. benzene and passing the solution through an alumina column; the latter was prepared by making a slurry of alumina in benzene and pouring this into a glass column at the bottom of which was sealed a sintered glass disc. The solution of the cobalt (III) complex after purification was evaporated to dryness under reduced pressure and the green compound obtained was stored in a stoppered glass bottle with no special precautions taken to prevent exposure to air or light.

(Analysis: found 16.4 ± 0.2% cobalt; theoretical 16.6%)

(e) Tris(acetylacetonato)iron(III) Labelled

2.00 grams of radio-active iron rods, obtained from the A.E.C. Laboratories at Amersham, were dissolved in nitric acid and the solution formed evaporated to small bulk. Water was added followed by ammonium hydroxide solution until a precipitate of ferric hydroxide was formed. The mixture was boiled, allowed to cool, and the supernatant liquid poured off. An ethanol solution containing 10.80 grams of acetylacetone was added to the precipitate and the mixture heated. A deep red solution was formed which on cooling gave deep red plate-like crystals of the tris(acetylacetonato)iron(III). The crystals were filtered off, recrystallized from ethanol, and after final collection of the product it was dried in a vacuum desiccator and stored in a stoppered glass vessel.

(Analysis: found 16.3 ± 0.2% iron; theoretical 16.7%)

(f) Bis(Acetylacetonato)iron(II)

The ferrous complex was prepared by adding 9.34 grams of ferrous sulphate to a mixture of pyridine and water (50% v/v). The mixture was heated under reduced pressure in an apparatus shown in Fig. 6.2.

An alcoholic solution containing 6.00 grams of acetylacetone was added slowly from the funnel B, after having been thoroughly scrubbed with "oxygen free" nitrogen gas. The brown solid formed was filtered in the absence of air, washed with a small quantity of ethanol and finally with a small quantity of ether. After drying in a vacuum desiccator, the complex was placed in an apparatus illustrated in Fig. 6.1, and dehydrated and sublimed at reduced pressure. The brown crystalline product was collected from the walls of the vessel and stored over phosphorus pentoxide in a vacuum desiccator.

2. Determination of the Chemical Concentration of Cobalt

(a) Analysis of the Cobalt(II) Fraction

An early attempt was made to determine the concentration of cobalt (II) complex by use of the colour of the complex formed by the reaction of cobalt (II) ions with dimethylglyoxime (2). This method, however, did not prove satisfactory because the colour of the solution of standard samples was found to vary too much. The method finally chosen for the analysis was the colorimetric determination (2) of the blue colour developed from the action of ammonium thiocyanate on cobaltous salts in ethanol. The method essentially consisted of taking 25 mls. of the ethanol solution of the cobalt (II) complex after it had been separated from the electron transfer reaction mixture and evaporating to dryness. The residue formed was dissolved in a 0.5 normal ammonium thiocyanate solution in ethanol. The blue solution formed was then made up to a standard volume and the absorption determined with a Unicam S.P. 350 spectrophotometer using 1 cm. square glass cells.

The calculation of the cobalt (II) complex concentration was made from the standard graph shown in Fig. 6.3.

(b) Analysis of the Cobalt (III) Fraction

The analysis for the determination of the concentration of the cobalt (III) complex was made by two methods. The first of these was employed when the concentration of the tris(acetylacetonato) cobalt (III) in the electron transfer reaction mixture was greater than 0.02 Molar. The method made use of the green colour of solutions of the complex, the adsorption of which were measured using a Unicam SP350 and 1 cm square glass cells. The concentration of the cobalt (III) complex was determined from the standard graph shown in Fig. 6.3

The second method was employed when the concentration of the cobalt (III) complex was less than 0.02 Molar. The solution of the cobalt (III) complex was evaporated to dryness under an infra-red lamp and the residue was digested in a mixture of concentrated sulphuric acid and nitric acid. On evaporation of this solution to dryness the residue formed was dissolved in a 0.5 normal ammonium thiocyanate solution in ethanol. The optical density of the blue colour developed was then measured as for the analysis of the cobalt (II) complex and the concentration of the cobalt (III) complex determined from the graph shown in Fig. 6.3

3. The Electron Transfer

(a) Acetylacetone and Toluene as Solvents

The technique employed in the study of the electron transfer reaction was to prepare solutions of the complexes in the appropriate solvent,

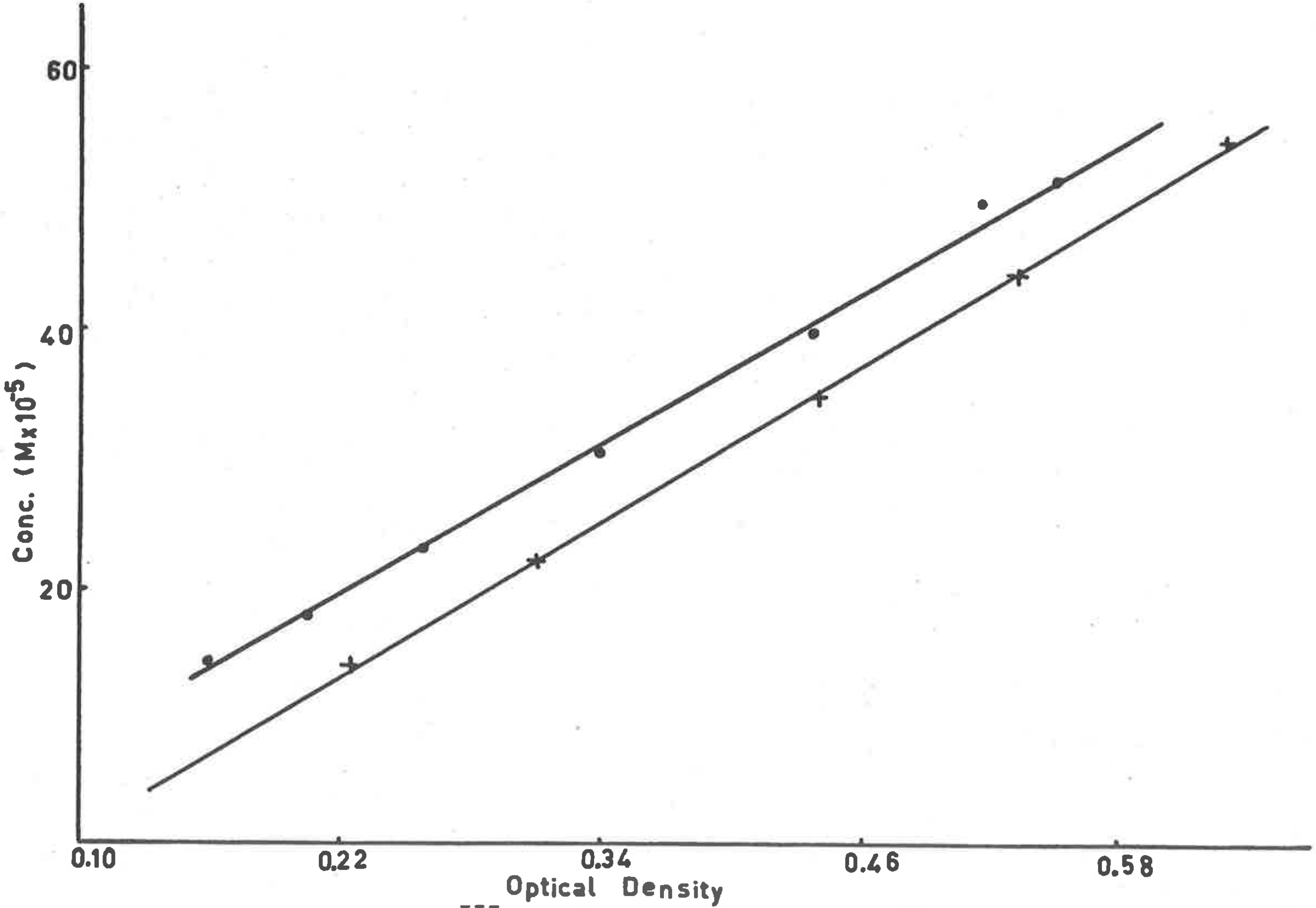

Fig.6.3 Analysis ; • = $Co^{III}(acac)_3$ in ethanol ; + = $Co^{II}(CNS)_4 \cdot (NH_4)_2$ in ethanol.
λ Max. 6160Å λ Max. 5900Å

and pipette 25 ml. aliquots of these into the reaction vessel A (Fig. 6.4). Dry "oxygen free" nitrogen was then bubbled through the reaction mixture for about an hour. By manipulation of the taps C, D and E of the apparatus and with a nitrogen gas pressure, a sample was blown from the flask A into the burette B. The sample was then run into the reaction tube R, which had first been treated to remove any traces of oxygen. The treatment consisted of consecutively reducing the pressure inside the tube R and refilling with dry "oxygen free" nitrogen gas; this procedure was carried out several times. When the solution for the electron transfer study was in the tube R, it was cooled in a bath of alcohol and dry-ice. The pressure in the tube was reduced slightly and the tube sealed off. The sealed tube was set aside and allowed to warm to room temperature. When a series of tubes had been prepared in this way a brass weight, to prevent floating, was hung on each and the tubes were then placed in a thermostat set at the temperature at which the electron transfer reaction was to be studied. At various intervals of time sample tubes were removed from the thermostat and cooled in an alcohol dry-ice mixture in order to stop the reaction. On allowing the reaction mixture to warm to room temperature a sample was taken and separated by means of an alumina column.

The alumina column was prepared by adding an alumina slurry in alcohol to a sintered glass chimney funnel about five inches long and three quarters of an inch in diameter. The alumina was found to give a very effective separation with the cobaltous ion remaining as a narrow pink band at the top of the column, while the cobaltic complex moved down

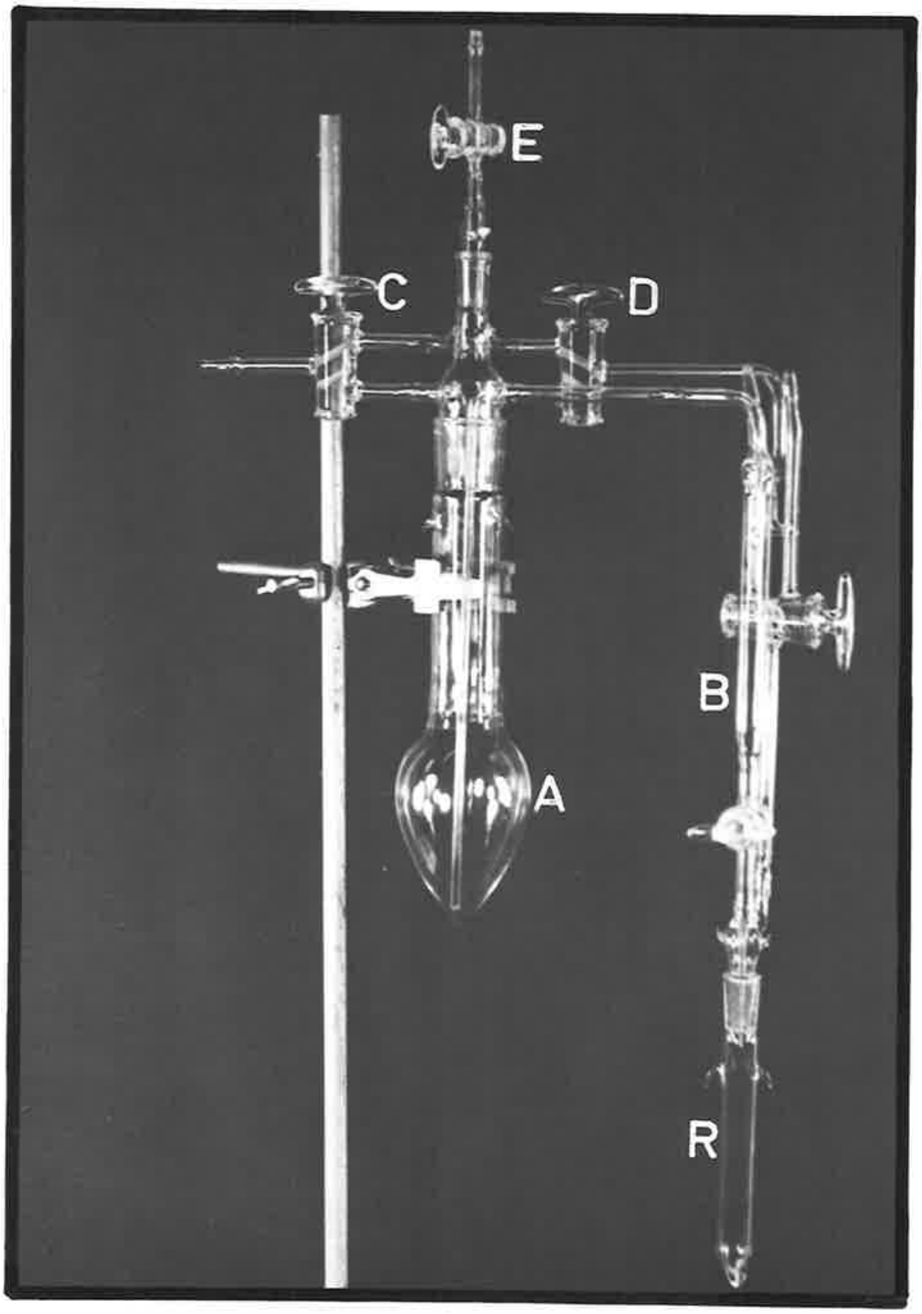

Fig.6.4

the column and was eluted with ethanol. This latter fraction was collected and made up to 50 mls. in a standard flask. Further treatment of the alumina column, however, was necessary to remove the strongly bound cobaltous ion. Two methods were employed for collecting the cobaltous ions, the first of which was to elute the column with 0.3 N hydrochloric acid in ethanol. The solution obtained was then collected and made up to 50 mls. in a standard flask ready for counting. For analysis of the cobalt (II) fraction, collected by this method, further treatment, as already described on page 177 , was necessary. However, no further treatment was necessary if the second method of eluting was employed. This consisted of eluting with an 0.5 N ammonium thiocyanate in ethanol solution. Although the latter method aided the analysis for the chemical concentration of cobalt (II) it was a much slower method since it required much more time and care in the elution of the blue tetra-thiocyanato cobalt complex from the alumina column.

(b) Exchange Studies in Mixed Solvent

The electron transfer studies in mixed solvents were carried out using a constant concentration of the two cobalt complexes, in order that a comparison of the results could be easily made. This was achieved by preparation of an acetylacetone solution of the complexes in the vessel A of an apparatus shown in Fig. 6.5a. Dry "oxygen free" nitrogen was bubbled through this solution for about an hour before samples were taken. Aliquots of 1 ml were measured from the burette B into glass reaction tubes. The samples were then diluted to a total volume of 5 ccs. by adding varying quantities of acetylacetone and toluene from two other vessels similar to that shown in Fig. 6.5a. The tubes

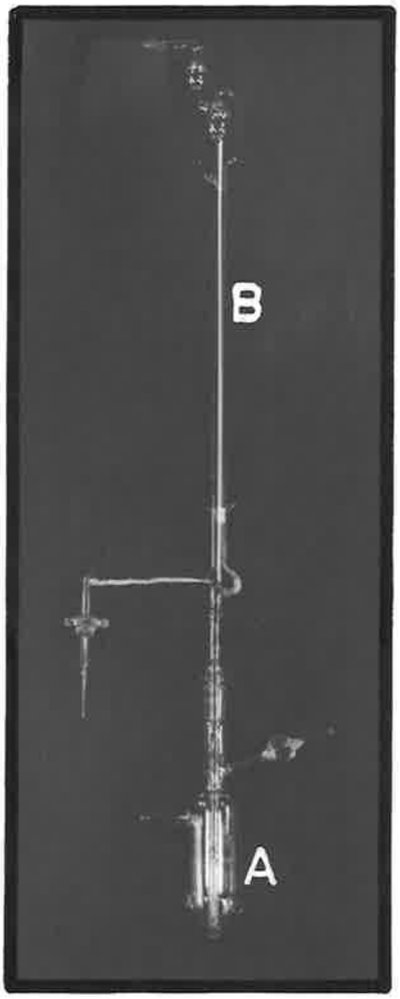

Fig.6.5a

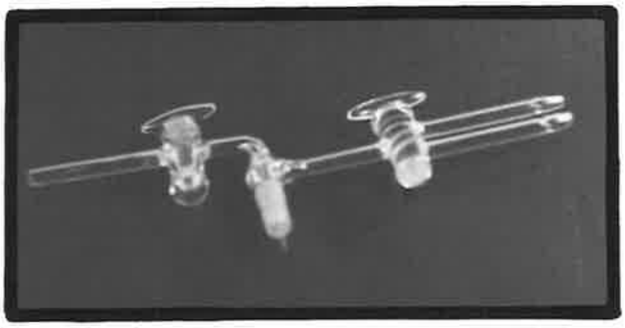

Fig.6.5b

containing the reaction mixture were then placed on an apparatus shown in Fig. 6.5b, and after freezing of the sample in a dry-ice ethanol mixture the tube was several times evacuated and filled with dry "oxygen free" nitrogen gas. The reaction tubes were sealed under slightly reduced pressure, allowed to warm to room temperature, a brass weight hung on them and finally they were placed in a thermostat set at the temperature at which the reaction was to be studied. The tubes were removed from the thermostat at varying intervals of time and the contents separated as described on page 180 .

4. The Thermal Decomposition of tris(acetylacetonato)cobalt(III)

A solution of tris(acetylacetonato)cobalt(III) was prepared in the reaction vessel A shown in Fig. 6.4 and after an initial treatment with dry "oxygen free" nitrogen gas, samples were forced by nitrogen pressure into the burette B and run from this into glass tubes ready for sealing. The tubes were removed from the apparatus, connected to a vacuum line, cooled in liquid air and evacuated. The solid formed on cooling was allowed to warm to room temperature with the tube closed. The tube was again cooled in liquid air, evacuated and finally sealed. A brass weight was hung on the sealed tubes and they were then placed in a thermostat at 98.7°C, from which they were removed at various time intervals. The samples were separated as described on page 180 and the fractions counted, the results being plotted on a graph of log $\left[100 - \% \text{ reduction}\right]$ against time (Figs. 2.14 and 2.15).

5. Electron Transfer Spectra

The measurement of spectra, in an attempt to determine the existence of electron transfer spectra bands, was carried out on solutions in S.V.R. using an Optica double beam recording spectrophotometer. No special precautions were taken for the experiments with the cobalt complexes except that freshly prepared solvent was used. However, for the experiments with the iron complexes an inert atmosphere of dry "oxygen free" nitrogen was used for the preparation of the solutions to be used. The solutions after preparation were placed in the spectrophotometer cells which were sealed in an atmosphere of nitrogen. The quartz cells used for the measurements were 1 cm. square and fitted with ground glass stoppers to enable sealing.

6. The Separation of Ferrous and Ferric Acetylacetonato Complexes.

Attempts were made to separate from solution a mixture of ferrous and ferric acetylacetone complexes, in order to study the electron transfer reaction between these compounds. The first method attempted was that using an alumina column which was prepared as described on page 180 However, this method was unsatisfactory since both the ferrous and ferric complexes distributed themselves throughout the column. Also this method might have been expected to have allowed a great deal of oxidation of the ferrous complex, since solutions of this compound are readily oxidised on exposure to air. Since the first method was unsatisfactory, the second method attempted was that of precipitation of salts of the tris(acetylacetonato) iron (II) ion. Although solutions of various salts of acetylacetone, e.g., potassium, sodium and ammonium, were added to the acetylacetone solution of the reaction mixture, no precipitation of a tris(acetylacetonato)iron(II) salt was obtained.

The third method made use of a solvent extraction procedure. In an qualitative attempt, 2,2'-dipyridyl in dilute sulphuric acid was added to a mixture of the ferrous and ferric acetylacetonato complexes in acetylacetone. The resultant mixture was shaken with chloroform and water and gave partition into two layers, the chloroform layer containing ferric acetylacetonato complex, while the aqueous layer was a deep blood red solution of a ferrous dipyridyl complex. However, when attempted on a quantitative basis the separation could not be made effective, even though many different conditions were tried. Since no effective method of separation was found for the two complexes the study of the electron transfer reaction was further attempted by measurement of the spectra of the complexes.

C. Electron Transfer Reaction between Cobalt (II) and Cobalt (III) N-phenyl-salicylidene-iminato Type Complexes

1. Preparation of Reactants

(a) Bis(p-tolsal)cobalt(II)

2.49 grams of cobalt acetate were dissolved in a small quantity of hot water to which was added a small quantity of sodium acetate in order to prevent the precipitation of cobaltous hydroxide. The hot filtered solution was added to a hot alcoholic solution containing 4.22 grams of p-tolyl-salicylideneimine which, on cooling of the deep red solution formed, gave deep red crystals of the required complex. It was not found necessary to carry out the preparation in the absence of air, as had been done by West (3), since only a small amount of oxidation of solutions of the complex was found to have taken place after several days of exposure to air.

The product obtained was purified by dissolving in hot alcohol and allowing to crystallize. After filtration, the recrystallized material was dried in a vacuum desiccator and stored in a glass jar. The dried product was found to be quite stable and did not undergo oxidation on exposure to air.

(Analysis: found 12.3 ± 0.2% cobalt; Theoretical 12.3%)

(b) Bis(phensal)cobalt(II)

This product was prepared in the same way as the previous complex from 2.49 grams of cobalt acetate and 3.94 grams of phenylsalicylideneimine and was found to be similar in appearance and stability against oxidation by the air.

(Analysis: 13.0 ± 0.2% cobalt; Theoretical 13.1%)

(c) Tris(p-tolsal)cobalt(III) Labelled

This complex was prepared by a method similar to that used by West (10). 2.49 grams of cobalt acetate were dissolved in a small quantity of hot water to which was added a small quantity of sodium acetate, and to the resulting solution was added 1 ml. of cobalt 60 solution. The hot cobalt solution, after filtering, was added to a hot alcoholic solution containing 6.33 grams of p-tolylsalicylideneimine and a small quantity of hydrogen peroxide (50 vols.) was added carefully to the solution in order to prevent frothing. The resultant solution after boiling for a few minutes was cooled and the khaki coloured crystals formed were collected by filtration and dried in air. The product obtained was purified by the same method as that used for the tris(acetylacetonato)cobalt(III) and given on page 175 i.e. by passing a benzene solution through an alumina column.

The only difference between this preparation and the one carried out by West (10) is the addition of the sodium acetate in the preparation outlined above. West found that in certain cases he obtained oils which did not readily crystallize; this, however, was never found to be the case using the above method of preparation.

(Analysis: found 8.4 ± 0.1% cobalt; theoretical 8.5%)

(d) Tris(phensal)cobalt(III) Labelled

This complex was prepared, by a similar method to that given above for the tris(p-tolsal)cobalt-III complex, from 2.49 grams of cobalt acetate and 5.90 grams of phenylsalicylideneimine. The product obtained was similar in appearance to the previous complex and was purified by the method described on page 175

(Analysis: found 9.0 ± 0.1% cobalt; theoretical 9.1%)

2. The Electron Transfer Reaction

The electron transfer reaction was carried out in a vessel similar to the one shown in Fig. 6.4. The flask A of the reaction vessel was immersed directly into a thermostat and dry "oxygen free" nitrogen gas passed through the vessel in order to remove air. Solutions of the two complexes, between which the electron transfer was to be studied, were prepared and placed in the thermostat for about half an hour. 25 ml. Aliquots of the solution for the reaction to be studied were then pipeted into the flask A of the reaction vessel. The time of starting the reaction was taken as the time when half of the second solution had been added to the first solution in the flask A. During the course of the reaction a continuous stream of dry "oxygen free" nitrogen gas, prepared as on p.168 , was bubbled through the reaction mixture.

At various time intervals samples were removed from flask A, by nitrogen gas pressure, into the burette B, from which they were run directly on to the top of an alumina column. Separation of the two complexes from the reaction mixture was then made using a chromatographic technique (p.180). The separated fractions were made up to 50 mls. in standard flasks and a scintillation technique of counting was used to estimate the amount of radio-activity in each. There was no need to analyse for the chemical concentration of cobalt in either of the separated fractions since no oxidation was detected in preliminary experiments, nor was the amount of reduction found to be significant.

3. The Thermal Reduction of tris(p-tolsal)cobalt(III)

The reduction of tris(p-tolsal)cobalt(III) was carried out by a method similar to that used for the exchange experiments. However, the radioactive tris(p-tolsal)cobalt(III) was placed directly into the flask A of the reaction vessel and 50 ccs. of toluene added.

D. Electron Transfer Reactions between the Cobalt(II) and Cobalt(III) Salen Type Complexes

1. Preparation of Reactants

(a) Preparation of N.N'-ethylene-bis(salicylidene-iminato)-Cobalt(II)

Tsumaki (4) prepared the salen-cobalt(II) complex and found that it gave a ready uptake of oxygen, the product formed being dark brown in colour. West (5) evolved a new method of preparation for the complex and found that the product he obtained did not react with oxygen. This latter method was the one by which labelled samples of the cobalt (II) complex were prepared ready for use in the electron transfer experiments.

The ligand was prepared by dissolving 12.2 grams of salicylaldehyde in a small quantity of ethyl alcohol and adding 4.2 grams of ethylenediamine as the monohydrate. The mixture was heated for several minutes and then cooled. Bright yellow plate-like crystals were obtained, which were recrystallized from ethyl alcohol and dried in air.

The cobalt (II) complex was prepared by a method similar to that developed by Bailes and Calvin (7). The N,N'-ethylene-bis-(salicylidene-imine) (2.68 grams) was dissolved in ethyl alcohol and placed in a round bottom flask, Fig. 5.2. Nitrogen was then bubbled through the solution which was heated to near its boiling point. 2.49 grams of cobalt acetate was added to a small quantity of alcohol and the mixture heated until all of the crystalline solid was converted to a pink amorphous powder. To the cobalt acetate was added 3/4 ml. of cobalt 60 solution, and the mixture was then run slowly into the ethanol solution of the ligand. The solution changed from a bright yellow colour to a deep red colour and a crystalline precipitate was formed. The hot solution was cooled, filtered under an atmosphere of nitrogen, washed several times with ethyl alcohol and finally washed once with ethyl ether. The product was dried in a vacuum desiccator and placed in an airtight jar.

The product obtained was stable to oxidation provided it was kept dry, however in certain organic solvents, e.g. ethanol and methanol, it was found that deep brown solutions were readily formed. However, pyridine was not such a solvent and bubbling oxygen through a pyridine solution of the complex for more than an hour did not appear to alter its colour.

(b) Preparation of N,N'(o-phenylene)bis(salicylidene-iminato)-cobalt(II)

Both the ligand and the complex were prepared by the same method as that used above. The complex formed was a red coloured crystalline product which in the dry state did not react with oxygen when exposed to the air.

(c) Preparation of N,N'-propylene-bis(salicylidene-iminato)-cobalt(II)

The complexing agent was prepared by a similar method to that used for the preparation of N,N'-ethylene-bis(salicylidene-imine), however, it did not crystallize but instead gave a yellow oil.

The cobalt(II) complex with this ligand could not be prepared as in the previous cases, since it was found to turn a dark brown colour on exposure to air, even in the dry state. The complex was therefore formed in situ before commencement of the electron transfer reaction. The method used was to prepare 0.0200 molar solutions of the ligand and of cobalt acetate (labelled) in pyridine. After bubbling dry "oxygen free" nitrogen gas through the solutions for approximately half an hour, aliquots of these solutions were pipetted directly into the reaction vessel. A deep red solution was formed and this did not darken in colour on standing for some time.

(d) Preparation of Diammino-N,N'-ethylene-bis(salicylidene-iminato) cobalt(III) chloride

Tsumaki (4) had prepared a compound that he claimed was N,N'-ethylene-bis(salicylidene-iminato)cobalt(III) chloride, however attempts to follow his method of preparation did not give good yields. A method for the preparation of the compound was found using as starting materials chloro-pentammino cobalt (III) dichloride and the N,N'-ethylene-bis-(salicylidene-imine).

The chloro-pentammino cobalt (III) dichloride was prepared by a method similar to that used by Willard and Hall (6). 5.0 grams of this complex was then dissolved in water at 75°C, and 5.4 grams of N,N'-ethylene-bis-(salicylidene-imine) was added. The mixture was kept at 75°C and stirred continuously for about four hours, during which time a light brown crystalline solid was formed. After cooling, the solution was filtered and the product obtained was added to a beaker of ethyl alcohol and heated to boiling. The hot solution was filtered, and the product obtained again treated in the same way in order to remove any unreacted ligand. The complex was then further purified by recrystallization several times from aqueous solution, to which had been added a small amount of ammonium hydroxide. The final product obtained was a yellow brown crystalline substance which on heating lost two molecules of water, becoming somewhat more golden brown in colour.

The perchlorate and the camphor-10-sulphonate were prepared by adding concentrated sodium perchlorate solution and camphor-10-sulphonic acid solution respectively to concentrated solutions of the complex chloride.

(e) Preparation of Diammino-N,N'-(o-phenylene)-bis(salicylidene-iminato)cobalt(III)Chloride

The method of preparation of this complex was similar to that for the previous compound, however the N,N'-(o-phenylene)-bis-(salicylidene-imine) was not as readily soluble in water as the previous ligand. In order to overcome the solubility problem the ligand in this case was dissolved in ethyl alcohol and the solution formed was added drop-wise to the hot aqueous solution of the chloropentammino cobalt (III) dichloride. The slow addition of the ligand solution gave an aqueous emulsion which reacted at a reasonable rate with the cobalt(III) pentammino complex. After keeping at 75°C for four hours, during which time continuous stirring was employed, the solution, together with the solid formed, was cooled and filtered. The red product obtained was purified as for the previous preparation. It was found that this product could also be prepared by adding N,N'-(o-phenylene)-bis(salicylidene-iminato) cobalt (II) to a solution of concentrated ammonium hydroxide and ammonium chloride and the mixture allowed to stand in air for several days.

(f) Preparation of Diammino-N,N'-propylene-bis(salicylidene-iminato) cobalt(III) Chloride

As was pointed out in the preparation of the cobalt (II) complex with this ligand, the complexing agent cannot be obtained in the crystalline form. A solution of the ligand in ethyl alcohol was prepared and this was added drop-wise to an aqueous solution of chloro-pentammino cobalt(III) dichloride. Care had to be taken in adding the ligand solution in order that a large quantity of the ligand was not formed as an oil on the bottom of the beaker in which the reaction was being carried out. The reaction was carried out as in the previous two experiments, and the light yellow-brown coloured product obtained was also purified by a method similar to that used for the two previously described complexes.

2. The Electron Transfer Reaction

The electron transfer reaction was carried out, under an atmosphere of dry "oxygen free" nitrogen gas, in the reaction vessel shown in Fig. 6.6. Solutions of the complexes, between which the electron transfer reaction was to be studied, were prepared in standard flasks and placed either in a thermostat at 25°C, or in an ice-water bath at 0°C. Dry "oxygen free" nitrogen gas was passed through the prepared solutions for ten minutes before the commencement of the electron transfer reaction and aliquots were then pipetted into the flask A of the reaction vessel. Half an hour before starting the electron transfer reaction, and throughout the reaction, the flask A was kept in a thermostat at 25°C or an ice-water bath. Samples of the reaction mixture were blown over, by means of gas pressure, from the flask A to the burette B, from which they were run into the funnel F. The funnel contained a mixture of 20 ccs. of chloroform and 20 ccs. of water, through which had been bubbling dry "oxygen free" nitrogen gas for fifteen minutes. The reaction mixture was shaken with the two solvents for five seconds, the cobalt(II) complex being extracted into the chloroform layer while the cobalt (III) complex was extracted into the aqueous layer.

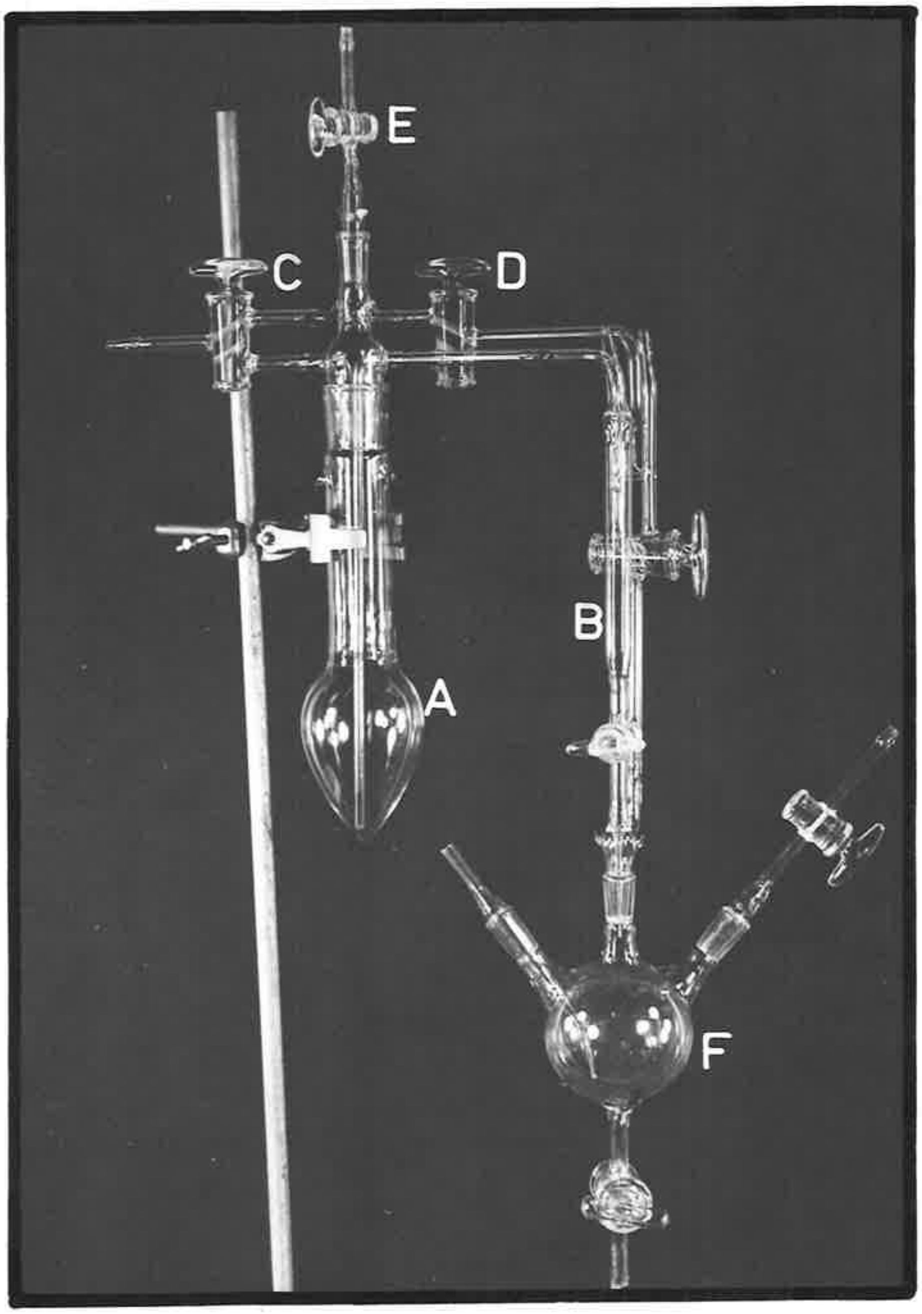

Fig.6.6

The starting time for the reaction was taken as the time when half of the second reactant had been added to the first reactant in flask A, while the time of completion was taken as the time when all of the solution from the burette B had been run into the funnel F. The results obtained indicate that although this time interval was short the reaction was 100% complete. Also since separation induced electron transfer reactions are not generally observed, it was felt that it was not necessary to check for such a possibility in this case.

The chemical analysis of the fractions from the solvent extraction separation was made in the following way. The fractions were evaporated to dryness and the precipitated complexes were destroyed with dilute sulphuric acid followed by treatment with concentrated nitric acid. The cobaltous salts obtained after evaporation of the acid solutions were reacted with an 0.20M solution of ammonium thiocyanate in alcohol. The blue solutions formed were made up to a standard volume and measured spectrophotometrically by means of a Unicam SP350 spectrophotometer. Radiometric analysis was also carried out on 8 ml aliquots of these prepared samples.

3. The Exchange Reaction between Cobaltous Perchlorate and the N,N'-ethylene-bis(salicylidene-iminato) Type Cobalt III Complexes

Labelled cobaltous perchlorate was first prepared by dissolving cobaltous carbonate in dilute perchloric acid, adding a small quantity of cobalt 60 solution, and evaporating the solution under reduced pressure until crystallization was effected. A 0.0400 molar solution of this was prepared in an 80% acetone-water mixture, and an aliquot added to a prepared 0.0500 molar solution of the perchlorate of the cobalt (III) complex also in an 80% acetone-water mixture. Samples of the reaction mixture were sealed in glass tubes and placed in a thermostat at 25°C. After various time intervals the tubes were removed from the thermostat, opened, and the cobalt (III) complex precipitated by adding a concentrated solution of sodium p-toluene-sulphonate. The precipitate formed was centrifuged, washed with a small quantity of distilled water, dried in an oven at 100°C and weighed as the p-toluene-sulphonate of diammino-N,N'-ethylene-bis(salicylideneiminato)cobalt(III). It should be pointed out that in preliminary experiments it was found that only the cobalt (III) complex and not the cobaltous salt was precipitated on the addition of the sodium p-toluene-sulphonate. The weighed sample of the salt of the cobalt (III) complex was dissolved in dilute hydrochloric acid solution, made up to 10 ccs. in a standard flask and counted by means of an EKCO scintillation counter.

The specific activity of the cobaltous perchlorate was obtained by weighing a sample, dissolving in 10 mls. of water and counting. From the value obtained the theoretical value for 100% exchange between cobaltous perchlorate and the cobalt (III) complex was obtained.

4. Analysis of the N,N'-ethylene-bis(salicylideneiminato) Type Complexes of Cobalt (III)

A gravimetric analysis for cobalt and chloride ions was made on the three N,N'-ethylene-bis(salicylideneiminato) type cobalt complexes. Also a determination was made for the amount of ammonia and water present in one of the complexes. The results of the analyses (Table 6.1) are in agreement with the theoretical chemical formula of $Co^{III}(NH_3)_2LCl.2H_2O$,

TABLE 6.1

Analysis of the Co^{III} Salen Type Complexes

	Co^{III}salen	Co^{III}sal-o-phen	Co^{III}sal-propen
Co found	13.5% ± 0.2%	12.7% ± 0.2%	13.2% ± 0.2%
Co theoret.	13.7%	12.7%	13.3%
Cl found	8.22% ± 0.08%	7.94% ± 0.08%	7.61% ± 0.08%
Cl theoret.	8.23%	7.98%	7.63%
Ammonia found	7.7 ± 0.2%		
Ammonia theoret.	7.9%		
Water found	8.1 ± 0.2%		
Water theoret.	8.4%		

where L refers to the quadridentate ligand. Furthermore, infra-red spectra (Figs. 6.7-6.9), which were determined on an Infracord 137 spectrophotometer, confirm the presence of the quadridentate ligand in the appropriate complexes.

The analysis for cobalt was made by digesting a weighed sample of the complex in a mixture of concentrated sulphuric and nitric acids. The solution formed was evaporated to small bulk and the acid remaining was neutralized with dilute sodium hydroxide. The solution was then treated with pyridine and ammonium thiocyanate (8) and the dithiocyanato tetra-pyridine cobalt (II) formed was filtered off, washed, dried and finally weighed.

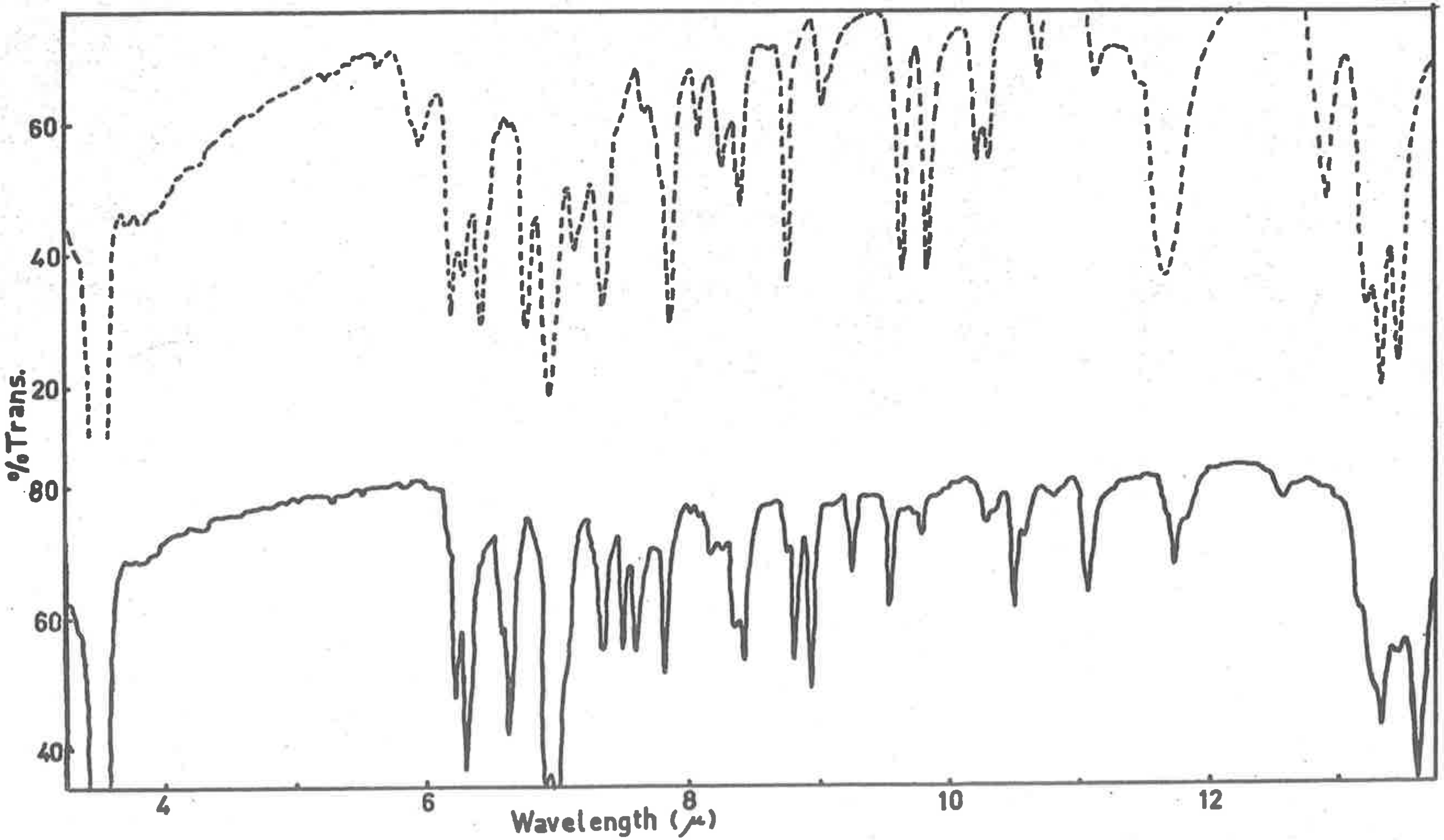

Fig.6.7 Infra-red Spectra ; ----- = Salen ; ——— = Co^{II}Salen.

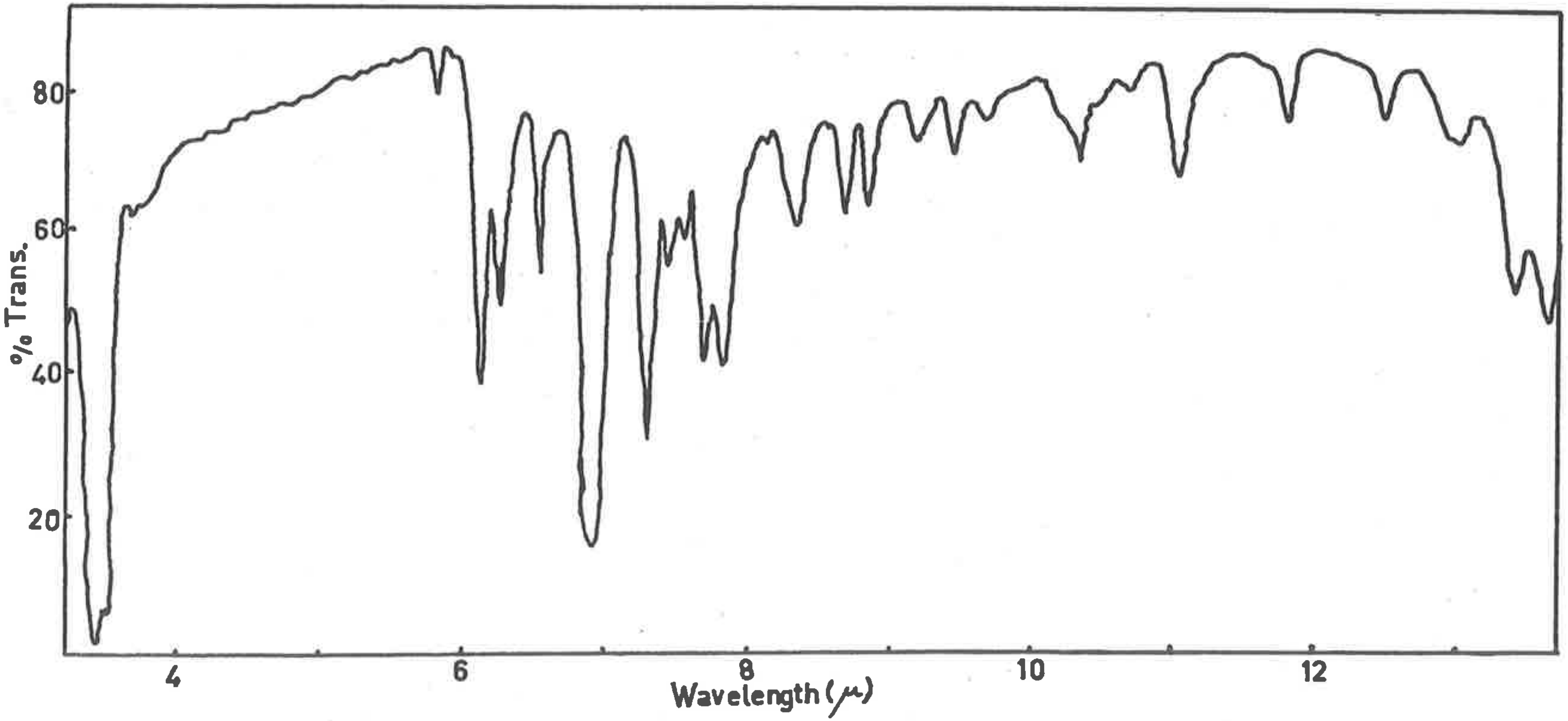

Fig.6.8 Infra-red Spectra ; $Co^{III}(NH_3)_2$Salen.Cl

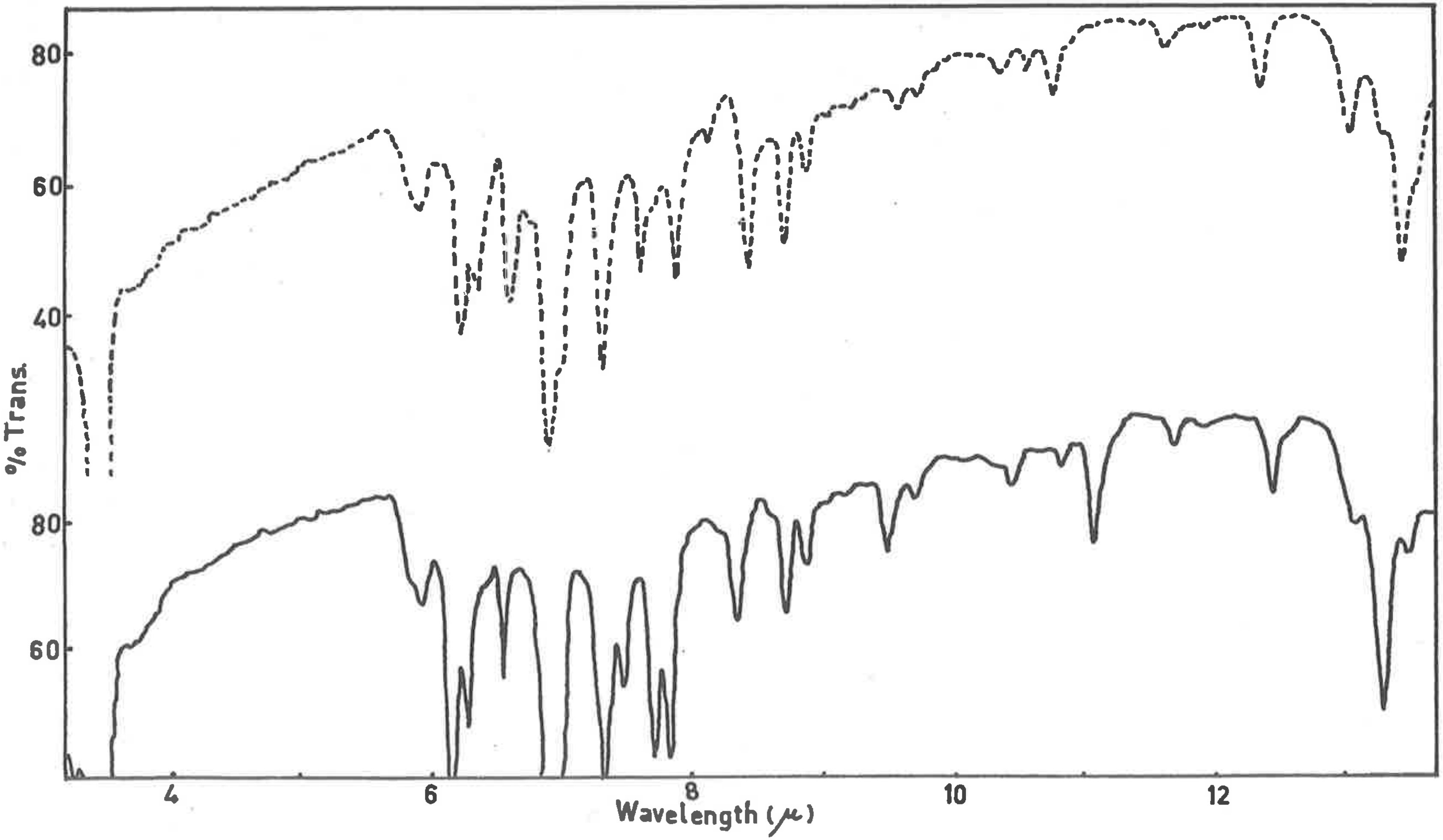

Fig. 6.9 Infra-red Spectra ; ---- = $Co^{III}(NH_3)_2$Sal-o-phen.Cl ; —— = $Co^{III}(NH_3)_2$Sal-propen.Cl

To analyse for chloride ions, a solution of the appropriate complex was acidified with dilute nitric acid and a silver nitrate solution was added until precipitation was complete. The silver chloride formed was filtered off and washed several times with dilute nitric acid and finally with distilled water. After drying, the precipitate was weighed and the percent of chloride calculated.

The amount of water present in the salen cobalt (III) complex was determined by the loss of weight of the compound after heating for several hours in an oven at 70°C. While the amount of ammonia present were determined by heating a weighed sample of the complex with a 5N sodium hydroxide solution and distilling the ammonia formed into a dilute hydrochloric acid solution. The excess acid was determined by back titration with standard caustic soda and the ammonia present in the complex molecule was calculated.

5. Measurement of the Magnetic Susceptibilities of the Co^{III} Salen Type Complexes

The magnetic susceptibilities of the complexes were measured using a Gouy balance for which the magnetic field was obtained with a permanent magnet. Samples of the complexes were ground to a fine powder in an agate mortar and packed uniformly into a calibrated glass tube. The values of the magnetic susceptibilities were determined from the measurements using the formula

$$10^6 \chi = \frac{a + BF}{W}$$

where F mgms. is the increase in weight of the complex when placed in the magnetic field and W gms. is the weight of the complex placed in the Gouy tube. 'a' and B are constants having the values of 0.008 and 0.850 respectively and which were calculated using $CuSO_4.5H_2O$ as a standard. The values obtained for the measurements are shown in Table 6.2.

Confirmation of the magnetic measurements by temperature and field variations would prove to be advantageous in deciding whether or not the cobalt in the complexes in actual fact has two unpaired electrons. However, although the complexes have not been studied in this way, the results obtained have been used to explain the fast electron transfer reactions observed between the cobalt (II) and cobalt (III) complexes with the salen type ligands. Furthermore, there is at least one other example (9) in which cobalt is partially spin free, i.e. $CoCl_3.(PEt_3)_2$; thus some support is given to the results obtained.

TABLE 6.2

Magnetic Measurements of the Co^{III}salen Type Complexes

	Co^{III}salen	Co^{III}sal-o-phen	Co^{III}sal-propen
Wt. of complex (gs.)	0.16527	0.12251	0.11919
Incr. of wt. in mag. field (mgms.)	1.68	1.61	1.66
$10^6{}_4$	8.69	11.24	11.90
$10^6{}_4$ Co	3644	5065	5091
u eff	2.95	3.49	3.49
Unpaired electrons	2	2	2
Temperature	24°C	24°C	24°C

REFERENCES

1. M. Calvin, C. Heidelberger, J.C. Reid, B.M. Tolbert and P.F. Yankwich, Isotopic Carbon, Wiley (1949), p. 285.
2. F.D. Snell and C.T. Snell, Colorimetric Methods of Analysis, Chapman and Hall (1936), p.327.
3. B.O. West, J. Chem. Soc., 3115 (1952).
4. T. Tsumaki, Bull.Chem.Soc.Japan, <u>13</u>, 252 (1938).
5. B.O. West, J. Chem. Soc., 395 (1954).
6. H.H. Willard and D. Hall, J.Amer.Chem.Soc., <u>49</u>, 2220 (1922).
7. R.H. Bailes and M. Calvin, J.Amer.Chem.Soc., <u>69</u>, 1886 (1947).
8. A.I. Vogel, Textbook of Quantitative Inorganic Analysis, Longmans (1955), p. 461.
9. E. Cartmell and G.W.A. Fowles, Valency and Molecular Structure, Butterworths (1956), p. 203.
10. B.O. West, J. Chem. Soc., 4944 (1960.)
11. D. Cohen et al., J.Amer.Chem.Soc. <u>78</u>, 1543 (1956).
12. B.R. Baker, F. Basolo and H.M. Neumann, J. Phys. Chem., <u>63</u> 371 (1959).
13. W.C.E. Higginson, Discuss. Faraday Soc. <u>29</u>, 123 (1960)
14. R. Platzman and J. Franck, Z. Physik, <u>138</u>, 411, (1954).

APPENDIX A

Tables of Results from Electron Transfer Reactions

Electron Transfer Reaction between:

		Tables
A.	Cobalt (II) and Cobalt (III) Acetylacetonato Complexes	1 - 26
B.	Cobalt (II) and Cobalt (III) p-tolsal Complexes	27 - 48
C.	Cobalt (II) and Cobalt (III) phensal Complexes	49 - 57

NOTE: All concentrations shown for the reactants are the concentrations of the solutions before mixing, therefore the concentration of reactants in the reaction mixture is half of the value shown. However, in the case of the concentrations of p-tolsal, Tables 47 and 48, the values shown are for the concentration in the reaction mixture.

TABLE 1

Electron Transfer Reaction between bis-(acac)cobalt (II) and tris-(Acac)cobalt(III) in Acetylacetone at a Temperature of 98.7 ± 0.1°C. Concentration of cobalt (II) 0.0112 M; Concentration of Cobalt (III) 0.0112 M.

No.	Time (hrs)	Counts / mins		E%	100 - E %
		Cobalt II	Cobalt III		
1	1	70	793	16.2	83.8
2	2	138	715	32.3	67.7
3	3	159	729	35.8	64.2
4	4	218	639	50.8	49.2
5	5	234	616	55.0	45.0
6	6	258	624	58.5	41.5
7	7	305	586	68.3	31.7
8	8	313	550	72.6	27.4
9	9	329	539	75.8	24.2
10	11	339	548	76.3	23.7
11	12	350	516	80.8	19.2
12	13	338	510	79.7	20.3
13	14	369	510	84.0	16.0
14	15	365	497	84.7	15.3
15	16	367	493	85.3	14.7
16	17	341	427	88.8	11.2
17	18	380	487	87.7	12.3
18	19	386	436	93.9	6.1
19	20	390	460	91.7	8.3

Acac indicates the acetylacetone ligand.

E % means the % of electron transfer having occurred at time "t".

TABLE 2

Electron Transfer Reaction between bis-(Acac) cobalt (II) and tris-(Acac) cobalt (III) in Acetylacetone at a Temperature of 98.7°C ± 0.1°C. Concentration of Cobalt (II) 0.0096 M; Concentration of Cobalt (III) 0.0096 M.

No.	Time (hrs)	Counts / 100 secs.		Concentrations ($M \times 10^{-6}$)		% E
		Cobalt II	Cobalt III	Cobalt II	Cobalt III	
1	0	14	7120	490	490	1
2	1	656	8509	484	484	14.3
3	2	1008	6360	408	456	29.0
4	3	1408	6138	420	446	38.5
5	4	1649	5564	408	464	48.9
6	5	2245	6449	446	500	54.8
7	6	2923	7118	524	584	61.6
8	7	3615	7899	576	652	66.9
9	8	2931	6610	428	624	75.5

TABLE 3

Electron Transfer Reaction between bis-(Acac)cobalt (II) and tris-(Acac)cobalt (III) in Acetylacetone at a Temperature of 98.7 ± 0.1°C. Concentration of Cobalt (II) 0.0192 M; Concentration of Cobalt (III) 0.0192 M.

No.	Time (hrs)	Counts / 100 secs.		Concentrations ($M \times 10^{-6}$)		% E
		Cobalt II	Cobalt III	Cobalt II	Cobalt III	
1	0.5	444	10235	310	310	10.3
2	1.0	1120	12460	394	400	16.6
3	1.5	1684	13083	424	440	23.6
4	2.0	2203	13088	440	470	29.7
5	2.5	2595	12329	430	470	36.3
6	3.0	2890	11471	420	460	42.3
7	4.0	3948	12409	470	530	51.2

TABLE 4

Electron Transfer Reaction between bis-(Acac)cobalt (II) and tris-(Acac)cobalt (III) in Acetylacetone at a temperature of 98.7 ± 0.1°C. Concentration of Cobalt (II) 0.0193 M; Concentration of Cobalt (III) 0.0086 M.

No.	Time (hrs)	Counts / 100 secs.		Concentrations ($Mx10^{-6}$)		E %
		Cobalt II	Cobalt III	Cobalt II	Cobalt III	
1	1.0	604	5633	1006	448	14.0
2	2.0	1446	5544	1126	502	29.9
3	3.0	1628	4284	948	430	40.0
4	4.0	2219	4542	1074	502	48.2
5	5.5	2312	3499	944	434	58.1
6	6.0	2938	3987	1100	514	62.3
7	7.0	2780	3051	930	430	69.8
8	8.0	3020	2863	939	456	75.0

TABLE 5

Electron Transfer Reaction between bis-(Acac)cobalt(II) and tris-(Acac)cobalt(III) in Acetylacetone at a Temperature of 98.7 ± 0.1°C. Concentration of Cobalt (II) 0.0171 M; Concentration of Cobalt (III) 0.0105 M.

No.	Time (hrs)	Counts / 100 secs.		Concentrations($Mx10^{-6}$)		E %
		Cobalt II	Cobalt III	Cobalt II	Cobalt III	
1	1	626	6019	520	530	19.0
2	2	1181	5261	603	437	31.6
3	3	1712	4894	550	449	47.0
4	5	2362	4352	544	406	61.4
5	6	2662	4347	564	360	62.2
6	7	2792	4007	602	408	68.9
7	8	1684	4303	305	522	76.2

TABLE 6

Electron Transfer Reaction between bis-(Acac)cobalt(II) and tris-(Acac)cobalt(III) in Acetylacetone at a Temperature of 98.7 ± 0.1°C. Concentration of Cobalt(II) 0.0112 M; Concentration of Cobalt(III) 0.0112 M.

No.	Time (hrs)	Counts / 100 secs		Concentrations (Mx10^{-6})		E %
		Cobalt II	Cobalt III	Cobalt II	Cobalt III	
1	2	138	715	540	540	32.3
2	3	159	729	526	592	38.1
3	4	214	643	530	550	50.9
4	5	234	616	530	546	55.8
5	6	258	624	518	599	63.0
6	7	295	596	544	585	68.7
7	8	313	550	514	579	77.0

TABLE 7

Electron Transfer Reaction between bis-(Acac)cobalt(II) and tris-(Acac)cobalt(III) in Acetylacetone at a Temperature of 98.7 ± 0.1°C. Concentration of Cobalt (II) 0.0172 M; Concentration of Cobalt (III) 0.0105 M.

No.	Time (hrs)	Counts / 100 secs		Concentrations (Mx10^{-6})		E %
		Cobalt II	Cobalt III	Cobalt II	Cobalt III	
1	2	1639	6681	840	512	31.7
2	3	2249	6184	840	530	43.5
3	4	2544	5593	798	524	51.8
4	6	2989	4115	694	461	70.0
5	7	3396	4324	776	480	71.2
6	8	2273	2514	478	300	77.3

TABLE 8

Electron Transfer Reaction between bis-(Acac)cobalt (II) and tris-(Acac)cobalt (III) in Acetylacetone at a Temperature of 98.7 ± 0.1°C. Concentration of Cobalt (II) 0.0137 M; Concentration of Cobalt (III) 0.0155 M.

No.	Time (hrs)	Counts / 100 secs		Concentrations ($M\times10^{-6}$)		E %
		Cobalt II	Cobalt III	Cobalt II	Cobalt III	
1	1	596	7725	243	238	14.2
2	2	957	7334	200	281	27.8
3	3½	1496	6757	197	284	44.2
4	5	1830	6356	196	285	55.0
5	6½	1992	6306	173	308	66.9

TABLE 9

Electron Transfer Reaction between bis-(Acac)cobalt (II) and tris-(Acac)cobalt(III) in Acetylacetone at a Temperature of 98.7 ± 0.1°C. Concentration of Cobalt (II) 0.0096 M; Concentration of Cobalt (III) 0.0193 M.

No.	Time (hrs.)	Counts / 100 secs		Concentrations ($M\times10^{-6}$)		E %
		Cobalt II	Cobalt III	Cobalt II	Cobalt III	
1	1	286	5854	480	965	14.0
2	2	612	5436	475	970	30.8
3	3	846	5208	480	965	42.1
4	4½	1068	5128	470	975	53.0
5	5	1098	5033	463	982	55.9
6	6	1177	4907	451	994	62.0
7	8	1530	4525	468	977	78.0

TABLE 10

Electron Transfer Reaction between bis-(Acac)cobalt (II) and tris-(Acac)cobalt (III) in Acetylacetone at a Temperature of 69.6 ± 0.1°C. Concentration of Cobalt (II) 0.0145 M; Concentration of Cobalt (III) 0.0099 M.

No.	Time (hrs)	Counts / 100 secs		Concentrations (Mx10^{-6})		E %
		Cobalt II	Cobalt III	Cobalt II	Cobalt III	
1	10	126	2534	571	371	7.8
2	20	150	2058	460	328	11.7
3	40	181	2053	462	336	13.9
4	80	343	2064	485	365	25.0
5	110	433	2026	482	391	31.9
6	135½	614	1686	476	309	44.0

TABLE 11

Electron Transfer Reaction between bis-(Acac)cobalt (II) and tris-(Acac)cobalt (III) in Acetylacetone at a Temperature of 83.6 ± 0.1°C. Concentration of Cobalt (II) 0.0137 M; Concentration of Cobalt (III) 0.0155 M.

No.	Time (hrs)	Counts / 100 secs		Concentrations (Mx10^{-6})		E %
		Cobalt II	Cobalt III	Cobalt II	Cobalt III	
1	6	1373	14303	660	800	19.4
2	12	2118	13238	660	800	30.5
3	18	2585	13021	680	780	35.5
4	24	3010	12573	660	800	42.7
5	32	3836	11858	626	834	57.0

TABLE 12

Electron Transfer Reaction between bis-(Acac)cobalt (II) and tris-(Acac)cobalt (III) in Acetylacetone at a Temperature of 89.9 ± 0.1°C. Concentration of Cobalt (II) 0.01522 M; Concentration of Cobalt (III) 0.01737 M.

No.	Time (hrs)	Counts / 100 secs		Concentrations ($Mx10^{-6}$)		E %
		Cobalt II	Cobalt III	Cobalt II	Cobalt III	
1	3	557	8403	761	868	13.3
2	6	855	7914	760	869	20.9
3	9	1267	7595	754	875	30.9
4	12	1411	7244	738	891	36.0
5	15	1701	6971	761	868	42.0
6	22.5	2190	6384	743	886	56.0

TABLE 13

Electron Transfer Reaction between bis-(Acac)cobalt (II) and tris-(Acac)cobalt (III) in Acetylacetone at a Temperature of 96.0 ± 0.1°C. Concentration of Cobalt (II) 0.0112 M; Concentration of Cobalt (III) 0.0112 M.

No.	Time (hrs)	Counts / 100 secs		Concentrations ($Mx10^{-6}$)		E %
		Cobalt II	Cobalt III	Cobalt II	Cobalt III	
1	0.75	76	2382	530	530	6.2
2	1.90	165	2432	558	562	12.8
3	3.0	226	1965	465	480	21.0
4	4.1	310	2101	500	540	26.7
5	5.0	370	1884	480	492	33.2
6	6.0	452	1948	510	525	38.2
7	8.0	565	1851	502	540	48.5
8	10.1	605	1733	495	513	52.7

TABLE 14

Reduction of tris-(Acac)cobalt (III) in Acetylacetone at a Temperature of 98.7 ± 0.1°C. Concentration Cobalt (III) 0.0100 Molar

No.	Time (hrs)	Counts / 100 secs		R %*	100 - R %
		Cobalt II	Cobalt III		
1	2.5	71	2024	3.3	96.7
2	6.5	163	2768	5.5	94.5
3	20	448	2490	15.2	84.8
4	30.5	583	2316	20.1	79.9
5	44	962	1958	32.9	67.1

TABLE 15

Reduction of tris-(Acac)cobalt (III) in Toluene at a Temperature of 98.7 ± 0.1°C. Concentration cobalt (III) 0.0100 Molar

No.	Time (hrs)	Counts / 100 secs		R %	100 - R%
		Cobalt II	Cobalt III		
1	5	66	2819	2.3	97.7
2	10	201	2319	8.0	92.0
3	20	319	1665	16.1	83.9
4	30	413	1591	20.6	79.4
5	40	941	2206	29.9	70.1

* R % indicates % reduction at time "t"

TABLE 16

Electron Exchange Reaction in Toluene; Acetylacetone Mixtures at a Temperature of 98.7 ± 0.1°C. Concentration of Cobalt (II) and Cobalt (III) at Commencement of Experiment is 0.0100.

Sample No.	Time (hrs)	Counts / 100 secs		Concentration ($Mx10^{-6}$)		V/V % Acac	E %
		Cobalt II	Cobalt III	Cobalt II	Cobalt III		
1	2	724	4346	204	196	100	28.0
2	4	1141	4074	189	211	100	46.4
3	6	1114	3994	132	268	100	66.1
4	3½	1068	4566	210	230	80	36.1
5	7	1178	3990	152	248	80	60.0
6	10½	1746	3445	172	228	80	78.2
7	5	722	4521	124	276	60	44.4
8	10½	1760	3552	188	212	60	70.5
9	16	2147	3080	191	209	60	86.0
10	7	1249	3929	191	209	40	50.5
11	13½	1869	3163	195	205	40	76.2
12	8½	1041	3976	208	192	20	39.9
13	17	1516	3714	173	227	20	67.0
14	25½	2178	2920	209	191	20	81.8

TABLE 17

Electron Transfer Reaction between bis-(Acac)cobalt (II) and tris-(Acac)cobalt (III) at 98.7 ± 0.1°C in Toluene; Concentration of Cobalt (II) 0.0193 M; Concentration of Cobalt (III) 0.0193 M.

No.	Time (hrs)	Counts / 100 secs		Concentration(Mx10^{-6})		E %
		Cobalt II	Cobalt III	Cobalt II	Cobalt III	
1	2	136	2052	1000	490	9.3
2	3.5	160	1838	866	494	12.6
3	5	376	2908	1542	694	16.5
4	7	355	1831	998	490	24.1
5	8.5	342	1631	872	471	26.6
6	10	442	2030	1038	645	29.0
7	12	339	1384	670	503	34.5
8	20	604	1521	904	543	45.4

TABLE 18

Electron Transfer Reaction between bis-(Acac)cobalt (II) and tris-(Acac)cobalt (III) at 98.7 ± 0.1°C in Toluene. Concentration of Cobalt (II) 0.0200 M; Concentration of Cobalt (III) 0.0095 M.

No.	Time (hrs)	Counts / 100 secs		Concentration(Mx10^{-6})		E %
		Cobalt II	Cobalt III	Cobalt II	Cobalt III	
1	1	62	2874	508	508	4.2
2	2	116	2820	512	508	7.9
3	4	254	2616	493	500	17.8
4	6.25	370	2320	461	470	27.8
5	8	493	2468	502	522	34.0
6	10	540	2244	485	480	38.6
7	15	746	2137	490	508	52.7
8	20	885	1846	464	481	66.0

TABLE 19

Electron Transfer Reaction between bis-(acac)cobalt (II) and tris-(Acac)cobalt (III) in Toluene. Concentration of Cobalt (II) 0.0096 M; Concentration of Cobalt (III) 0.0098 M; Temperature 98.7 ± 0.1°C.

No.	Time (hrs.)	Counts / 100 secs		Concentration(M$\times 10^{-6}$)		E %
		Cobalt II	Cobalt III	Cobalt II	Cobalt III	
1	4	119	2425	420	420	9.4
2	8	195	2273	405	410	15.9
3	12	293	2362	432	445	22.4
4	20	510	2080	420	435	40.1
5	22	613	2506	506	524	40.0

TABLE 20

Electron Transfer Reaction between bis-(Acac)cobalt (II) and tris-(Acac)cobalt (III) in Toluene. Concentration of Cobalt (II) 0.0238 M; Concentration of Cobalt (III) 0.0243 M; Temperature 98.7 ± 0.1°C.

No.	Time (hrs)	Counts / 100 secs		Concentration(M$\times 10^{-6}$)		E %
		Cobalt II	Cobalt III	Cobalt II	Cobalt III	
1	3	456	3027	230	250	27.4
2	6	728	2769	235	245	42.4
3	9	910	2685	205	275	59.2
4	13	1016	2432	205	275	69.0
5	23	1363	2132	215	265	87.1

TABLE 21

Electron Transfer Reaction between bis-(Acac)cobalt (II) and tris-(Acac)cobalt (III) in Toluene. Concentration of Cobalt (II) 0.0092 M; Concentration of Cobalt (III) 0.0103 M; Temperature 98.7 ± 0.1°C.

No.	Time (hrs)	Counts / 100 secs		Concentration($Mx10^{-6}$)		E %
		Cobalt II	Cobalt III	Cobalt II	Cobalt III	
1	8	115	1308	390	584	20.2
2	20	265	1206	452	522	38.7
3	32	358	1049	460	514	54.1
4	44	450	964	462	512	67.0

TABLE 22

Electron Transfer Reaction between bis-(Acac)cobalt (II) and tris-(Acac)cobalt (III) in Toluene. Concentration of Cobalt (II) 0.0190 M; Concentration of Cobalt (III) 0.0195 M; Temperature 98.7 ± 0.1°C.

No.	Time (hrs)	Counts / 100 secs		Concentration($Mx10^{-6}$)		E %
		Cobalt II	Cobalt III	Cobalt II	Cobalt III	
1	3.0	459	7747	908	1020	11.9
2	7.0	920	7411	848	1080	25.1
3	11.0	1515	6883	876	1052	39.7
4	17.5	1968	6436	868	1060	52.0
5	22.0	2476	5776	964	964	60.0
6	26.0	2427	5791	868	1060	65.6

TABLE 23

Electron Transfer Reaction between bis-(Acac)cobalt (II) and tris-(Acac)cobalt (III) in Toluene. Concentration of Cobalt (II) 0.0357 M; Concentration of Cobalt (III) 0.0387 M; Temperature 55.9 ± 0.1°C.

No.	Time (hrs)	Counts / 100 secs		Concentration(Mx10^{-6})		E %
		Cobalt II	Cobalt III	Cobalt II	Cobalt III	
1	192	37	2051	127	245	5.2
2	384	69	2033	132	240	9.2
3	480	93	1974	136	236	12.3
4	1240	217	1863	130	242	29.8

TABLE 24

Electron Transfer Reaction between bis-(Acac)cobalt (II) and tris-(Acac)cobalt (III) in Toluene. Concentration of Cobalt (II) 0.0509M; Concentration of Cobalt (III) 0.0495M; Temperature 81.0 ± 0.1°C.

No.	Time (hrs)	Counts / 100 secs		Concentration (Mx10^{-6})		E %
		Cobalt II	Cobalt III	Cobalt II	Cobalt III	
1	20	403	3172	217	285	26.1
2	40	677	2784	257	245	38.2
3	60	927	2611	245	257	53.7
4	80	771	2620	192	310	59.5
5	100	1178	2263	252	250	68.1
6	120	1364	2151	245	257	79.5

TABLE 25

Electron Transfer Reaction between bis-(Acac) Cobalt (II) and tris-(Acac) Cobalt (III) in Toluene. Concentration of Cobalt (II) 0.0357; Concentration of Cobalt (III) 0.0387 M; Temperature 91.0 ± 0.1°C.

No.	Time (hrs)	Counts / 100 secs		Concentration($M \times 10^{-6}$)		E %
		Cobalt II	Cobalt III	Cobalt II	Cobalt III	
1	6	155	1963	170	202	16.1
2	12	190	1872	135	237	25.4
3	18	143	1966	70	302	36.0
4	24	373	1677	158	214	42.8
5	30	375	1654	135	237	51.1

TABLE 26

Electron Transfer Reaction between bis-(Acac) Cobalt (II) and bis-(Acac) Cobalt (III) and Pyridine. Concentration of Cobalt (II) 0.0096 M; Concentration of Cobalt (III) 0.0096 M; Temperature 98.7 ± 0.1°C.

No.	Hrs.	Counts/min		E %	100 - E %
		Cobalt II	Cobalt III		
1	1	991	6511	3.0	97.0
2	2	2231	5341	8.0	92.0
3	3	385	6735	10.8	89.2
4	6	791	5773	24.1	75.9
5	8	930	5008	31.3	68.7

TABLE 27

Electron Transfer Reaction between Cobalt (II)-*p*-tolsal and Cobalt (III)-*p*-tolsal. Concentration of Cobalt (II) 0.0100 M; Concentration of Cobalt (III) 0.0098 M; Temperature 55.0 ± 0.1°C; Solvent Toluene.

No.	Time(mins	Counts / 100 secs		E %**	100 - E %
		Cobalt II	Cobalt III		
1	29.5	4985	27525	29.7	70.3
2	60	9144	28048	48.2	51.8
3	113	13370	24173	70.1	29.9
4	164	14912	20592	84.0	16.0
5	227	16272	19299	90.3	9.7

TABLE 28

Electron Transfer Reaction between Cobalt (II)-*p*-tolsal and Cobalt (III)-*p*-tolsal. Concentration of Cobalt (II) 0.0051 M; Concentration of Cobalt (III) 0.0097 M; Temperature 55.0 ± 0.1°C; Solvent Toluene.

No.	Time(mins)	Counts / 100 secs		E %	100 - E %
		Cobalt II	Cobalt III		
1	20.0	3482	28246	32.0	68.0
2	40.0	6514	29849	52.3	47.7
3	60.5	7325	25583	65.1	34.9
4	96.0	9506	24924	80.6	19.4
5	120.0	12263	29259	86.1	13.9

** *p*-tolsal refers to *p*-tolylsalicylideneimine ligand.

* E % means the % of electron transfer having occurred at time "t".

TABLE 29

Electron Transfer Reaction between Cobalt (II)-p-tolsal and Cobalt (III)-p-tolsal. Concentration of Cobalt (II) 0.0076 M; Concentration of Cobalt (III) 0.0098 M; Temperature 55.0 ± 0.1°C; Solvent Toluene.

No.	Time(mins)	Counts / 100 secs Cobalt II	Counts / 100 secs Cobalt III	E %	100 - E %
1	20.0	1527	11126	27.6	72.4
2	40.0	2849	11128	46.5	53.5
3	60.0	3643	10720	57.9	42.1
4	91.0	4732	9781	74.3	25.7
5	120.0	4662	8478	80.9	19.1
6	150.0	5709	9058	88.2	11.8

TABLE 30

Electron Transfer Reaction between Cobalt (II)-p-tolsal and Cobalt (III)-p-tolsal. Concentration of Cobalt (II) 0.0152 M; Concentration of Cobalt (III) 0.0097 M; Temperature 55.0 ± 0.1°C. Solvent Toluene.

No.	Time(mins)	Counts / 100 secs Cobalt II	Counts / 100 secs Cobalt III	E %	100 - E %
1	30.0	2417	11508	28.5	71.5
2	61.5	4157	10161	47.6	52.4
3	90.0	5990	10388	60.0	40.0
4	121.0	5050	6423	72.2	27.8
5	150.0	6015	6650	77.9	22.1
6	215.0	8665	7493	87.9	12.1

TABLE 31

Electron Transfer Reaction between Cobalt (II)-p-tolsal and Cobalt (III)-p-tolsal. Concentration of Cobalt (II) 0.200 M; Concentration of Cobalt (III) 0.0097 M; Temperature 55.0 ± 0.1°C. Solvent Toluene.

No.	Time(mins)	Counts / 100 secs Cobalt II	Counts / 100 secs Cobalt III	E %	100 - E %
1	20.5	4645	30827	19.5	80.5
2	40.5	7954	38566	32.5	67.5
3	60.0	9989	25449	42.0	58.0
4	92.5	14322	22266	58.3	41.7
5	121.0	15887	18953	67.9	32.1
6	240.0	20679	13709	89.6	10.4

TABLE 32

Electron Transfer Reaction between Cobalt (II)-p-tolsal and Cobalt (III)-p-tolsal. Concentration of Cobalt (II) 0.0679 M; Concentration of Cobalt (III) 0.0198 M; Temperature 55.0 ± 0.1°C. Solvent Toluene.

No.	Time(mins)	Counts / 100 secs Cobalt II	Counts / 100 secs Cobalt III	E %	100 - E %
1	10.0	3614	62899	10.7	89.3
2	20.0	6250	47285	23.0	77.0
3	30.0	9761	54532	29.9	70.1
4	45.5	13325	49191	42.0	58.0
5	60.5	15245	44648	50.1	49.9
6	90.0	21205	42089	66.0	34.0

TABLE 33

Electron Transfer Reaction between Cobalt (II)-p-tolsal and Cobalt (III)-p-tolsal. Concentration of Cobalt (II) 0.0050 M; Concentration of Cobalt (III) 0.0048 M; Temperature 55.0 ± 0.1°C. Solvent Toluene.

No.	Time(mins)	Counts / 100 secs Cobalt II	 Cobalt III	E %	100 - E %
1	60.0	4625	12454	53.0	47.0
2	120.0	8230	9932	76.6	23.4
3	180.0	7289	11326	88.6	11.4
4	240.0	9403	10203	94.0	6.0

TABLE 34

Electron Transfer Reaction between Cobalt (II)-p-tolsal and Cobalt (III)-p-tolsal. Concentration of Cobalt (II) 0.0100 M; Concentration of Cobalt (III) 0.0146 M; Temperature 55.0 ± 0.1°C; Solvent Toluene.

No.	Time(mins)	Counts / 100 secs Cobalt II	 Cobalt III	E %	100 - E %
1	15.5	2231	34603	14.9	85.1
2	30.0	5994	41571	31.0	69.0
3	45.0	9205	39914	46.1	53.9
4	60.0	9548	33157	55.0	45.0
5	90.5	14037	36535	68.4	31.6

TABLE 35

Electron Transfer Reaction between Cobalt (II)-p-tolsal and Cobalt (III)-p-tolsal. Concentration of Cobalt (II) 0.0100 M; Concentration of Cobalt (III) 0.0148 M; Temperature 55.0 ± 0.1°C. Solvent Toluene.

No.	Time(mins)	Counts / 100 secs		E %	100 - E %
		Cobalt II	Cobalt III		
1	20.5	3986	38820	23.0	77.0
2	40.0	9237	44147	42.7	57.3
3	61.0	12501	39965	58.8	41.2
4	91.0	15491	36638	73.4	26.6
5	120.5	16404	33082	81.8	18.2
6	151.0	22932	37105	94.4	5.6

TABLE 36

Electron Transfer Reaction between Cobalt (II)-p-tolsal and Cobalt (III)-p-tolsal. Concentration of Cobalt (II) 0.0100 M; Concentration of Cobalt (III) 0.0047 M; Temperature 55.0 ± 0.1°C; Solvent Toluene.

No.	Time(mins)	Counts / 100 secs		E %	100 - E %
		Cobalt II	Cobalt III		
1	30.5	3103	19477	20.1	79.9
2	60.0	3667	10363	38.2	61.8
3	90.0	5795	10397	52.2	47.8
4	120.0	7039	9037	63.9	36.1
5	180.0	8086	7193	77.3	22.7
6	240.0	9083	6474	85.2	14.8

TABLE 37

Electron Transfer Reaction between Cobalt (II)-p-tolsal and Cobalt (III)-p-tolsal. Concentration of Cobalt (II) 0.0100 M; Concentration of Cobalt (III) 0.0023 M; Temperature 55.0 ± 0.1°C; Solvent Toluene.

No.	Time(mins)	Counts / 100 secs		E %	100 - E %
		Cobalt II	Cobalt III		
1	30.0	1274	6181	21.0	79.9
2	60.0	2612	5916	37.7	62.3
3	90.5	3420	4603	52.4	47.6
4	120.0	4221	3929	63.7	36.3
5	180.0	5230	3443	74.2	25.8

TABLE 38

Electron Transfer Reaction between Cobalt (II)-p-tolsal and Cobalt (III)-p-tolsal. Concentration of Cobalt (II) 0.0100 M; Concentration of Cobalt (III) 0.0058 M; Temperature 55.0 ± 0.1°C; Solvent Toluene.

No.	Time(mins)	Counts / 100 secs		E %	100 - E %
		Cobalt II	Cobalt III		
1	30.0	1969	11984	22.3	77.7
2	60.0	4636	14432	38.4	61.6
3	90.0	6218	11950	54.1	45.9
4	130.0	7549	9974	68.1	31.9
5	170.0	9615	9862	78.0	22.0
6	220.0	10813	9726	83.2	16.8

TABLE 39

Electron Transfer Reaction between Cobalt (II)-*p*-tolsal and Cobalt (III)-*p*-tolsal. Concentration of Cobalt (II) 0.0100 M; Concentration of Cobalt (III) 0.0077 M; Temperature 55.0 ± 0.1°C; Solvent Toluene.

No.	Time(mins)	Counts / 100 secs		E %	100 - E %
		Cobalt II	Cobalt III		
1	21.0	1887	16669	18.0	82.0
2	40.0	4518	18140	35.2	64.8
3	60.0	8288	24243	45.1	54.9
4	90.0	8556	16995	59.3	40.7
5	120.0	11982	18113	70.4	29.6
6	153.0	11817	14257	80.2	19.8

TABLE 40

Electron Transfer Reaction between Cobalt (II)-*p*-tolsal and Cobalt (III)-*p*-tolsal. Concentration of Cobalt (II) 0.0100 M; Concentration of Cobalt (III) 0.0194 M; Temperature 55.0 ± 0.1°C; Solvent Toluene.

No.	Time(mins)	Counts / 100 secs		E %	100 - E %
		Cobalt II	Cobalt III		
1	20.5	7893	61565	33.3	66.7
2	40.0	13688	61483	53.3	46.7
3	62.0	17413	57670	67.9	32.1
4	90.0	18569	51268	77.9	22.1
5	120.0	21432	48887	89.3	10.7

TABLE 41

Electron Transfer Reaction between Cobalt (II)-*p*-tolsal and Cobalt (III)-*p*-tolsal. Concentration of Cobalt (II) 0.0100 M; Concentration of Cobalt (III) 0.0024 M; Temperature 55.0 ± 0.1°C; Solvent Toluene.

No.	Time(mins)	Counts / 100 secs		E %	100 - E %
		Cobalt II	Cobalt III		
1	31.0	436	2072	21.6	78.4
2	60.0	838	1918	37.7	62.3
3	90.0	1155	1611	51.8	48.2
4	120.0	1423	1415	62.1	37.9
5	150.0	1521	1228	68.6	31.4

TABLE 42

Electron Transfer Reaction between Cobalt (II)-*p*-tolsal and Cobalt (III)-*p*-tolsal. Concentration of Cobalt (II) 0.0100 M; Concentration of Cobalt (III) 0.0047 M; Temperature 55.0 ± 0.1°C; Solvent Toluene.

No.	Time(mins)	Counts / 100 secs		E %	100 - E %
		Cobalt II	Cobalt III		
1	30.0	2011	11932	21.2	78.8
2	60.5	4233	11523	39.5	60.5
3	90.5	6012	10582	53.2	46.8
4	120.0	6364	8380	63.4	36.6
5	184.0	7397	6490	78.3	21.7

TABLE 43

Electron Transfer Reaction between Cobalt (II)-*p*-tolsal and Cobalt (III)-*p*-tolsal. Concentration of Cobalt (II) 0.0100 M; Concentration of Cobalt (III) 0.0097 M; Temperature 50.0 ± 0.1°C; Solvent Toluene.

No.	Time(mins)	Counts / 100 secs Cobalt II	 Cobalt III	E %	100 - E %
1	41.0	1572	11534	23.6	76.4
2	80.0	3025	11873	40.0	60.0
3	120.0	3181	8790	52.4	47.6
4	180.0	4956	9763	66.4	33.6
5	240.0	4593	7297	76.1	23.9
6	300.0	5930	8270	82.3	17.7

TABLE 44

Electron Transfer Reaction between Cobalt (II)-p-tolsal and Cobalt (III)-*p*-tolsal. Concentration of Cobalt (II) 0.0100 M; Concentration of Cobalt (III) 0.0098 M; Temperature 60.0 ± 0.1°C; Solvent Toluene.

No.	Time(mins)	Counts / 100 secs Cobalt II	 Cobalt III	E %	100 - E %
1	10.0	1326	8836	25.6	74.4
2	20.0	2007	7451	41.8	58.2
3	30.0	3016	7791	55.0	45.0
4	45.0	4431	8295	68.6	31.4
5	60.0	4429	6360	81.0	19.0
6	90.0	5560	6704	89.2	10.8

TABLE 45

Electron Transfer Reaction between Cobalt (II)-*p*-tolsal and Cobalt (III)-*p*-tolsal. Concentration of Cobalt (II) 0.0100 M; Concentration of Cobalt (III) 0.0049 M; Temperature 60.0 ± 0.1°C; Solvent Toluene.

No.	Time(mins)	Counts / 100 secs		E %	100 - E %
		Cobalt II	Cobalt III		
1	15.0	910	4194	26.5	73.5
2	30.0	1678	3870	45.0	55.0
3	46.0	2651	3766	61.5	38.5
4	60.5	2886	3238	70.2	29.8
5	93.0	3015	2463	82.0	18.0
6	122.0	3623	2382	89.8	10.2

TABLE 46

Electron Transfer Reaction between Cobalt (II)-*p*-tolsal and Cobalt (III)-*p*-tolsal. Concentration of Cobalt (II) 0.0200 M; Concentration of Cobalt (III) 0.0098 M; Temperature 60.0 ± 0.1°C. Solvent Toluene.

No.	Time(mins)	Counts / 100 secs		E %	100 - E %
		Cobalt II	Cobalt III		
1	16.0	1771	7977	27.1	72.9
2	30.0	3029	6554	47.1	52.0
3	45.0	3936	5826	60.1	39.9
4	60.0	5416	5939	71.1	28.9
5	90.0	5657	4538	82.7	17.3
6	120.0	6783	4166	92.3	7.7

TABLE 47

Electron Transfer Reaction between Cobalt (II)-*p*-tolsal and Cobalt (III)-*p*-tolsal. Concentration of Cobalt (II) 0.0100 M; Concentration of Cobalt (III) 0.0098 M; Concentration sal-p-tol 0.0200 M; Temperature 55.0 ± 0.1°C; Solvent Toluene.

No.	Time(mins)	Counts / 100 secs		E %	100 - E %
		Cobalt II	Cobalt III		
1	20.5	1525	10573	24.8	75.2
2	40.5	2690	10565	40.0	60.0
3	60.5	3713	9639	54.8	45.2
4	90.5	4556	8630	68.2	31.8
5	120.0	5089	8074	76.2	23.8
6	181.0	6276	7565	89.2	10.8

TABLE 48

Electron Transfer Reaction between Cobalt (II)-*p*-tolsal and Cobalt (III)-*p*-tolsal. Concentration of Cobalt (II) 0.0100 M; Concentration of Cobalt (III) 0.0098 M; Concentration of sal-p-tol 0.0400 M; Temperature 55.0 ± 0.1°C; Solvent Toluene.

No.	Time(mins)	Counts / 100 secs		E %	100 - E %
		Cobalt II	Cobalt III		
1	14.0	1051	11007	17.2	82.8
2	30.0	2145	10626	33.1	66.9
3	46.0	2858	10236	43.0	57.0
4	62.0	3405	8654	55.6	44.4
5	94.0	4433	8198	69.1	30.9
6	121.0	5092	7971	76.8	23.2

TABLE 49

Electron Transfer Reaction between Cobalt (II)-phensal* and Cobalt (III)-phensal. Concentration of Cobalt (II) 0.0199 M; Concentration of Cobalt (III) 0.0100 M; in Toluene as Solvent at a Temperature of 55.0 ± 0.1°C.

No.	Time(mins)	Counts / 100 secs		E %	100 - E %
		Cobalt II	Cobalt III		
1	30.0	1453	7244	25.1	74.9
2	60.0	2535	6986	39.9	60.1
3	90.5	3724	6299	55.8	44.2
4	120.0	4531	5620	66.9	33.1
5	150.0	4523	4900	72.0	28.0
6	210.0	6445	5037	84.2	15.8

TABLE 50

Electron Transfer Reaction between Cobalt (II)-phensal and Cobalt (III)-phensal. Concentration of Cobalt (II) 0.0050 M; Concentration of Cobalt (III) 0.0100 M; in Toluene as Solvent at a Temperature of 55.0 ± 0.1°C.

No.	Time(mins)	Counts / 100 secs		E %	100 - E %
		Cobalt II	Cobalt III		
1	15.0	786	8536	25.3	74.7
2	30.0	1408	8828	41.4	58.6
3	45.0	1749	7806	54.9	45.1
4	60.0	2291	8135	66.0	34.0
5	90.5	2913	8140	79.2	20.8
6	123.0	2858	6893	87.9	12.1

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* phensal indicates the phenylsalicylideneimine ligand.

TABLE 51

Electron Transfer Reaction between Cobalt (II)-phensal and Cobalt (III)-phensal. Concentration of Cobalt (II) 0.0398 M; Concentration of Cobalt (III) 0.0100 M; in Toluene as Solvent at a Temperature of 55.0 ± 0.1°C.

No.	Time(mins)	Counts / 100 secs Cobalt II	 Cobalt III	E %	100 - E %
1	30.0	1544	7816	20.6	79.4
2	62.0	2693	6233	37.8	62.2
3	90.0	3198	5130	48.0	52.0
4	126.5	5043	5011	62.8	37.2
5	151.0	5216	4348	68.1	31.9
6	210.0	5791	3372	79.0	21.0

TABLE 52

Electron Transfer Reaction between Cobalt (II)-phensal and Cobalt (III)-phensal. Concentration of Cobalt (II) 0.0100 M; Concentration of Cobalt (III) 0.0100 M; in Toluene as Solvent at a Temperature of 55.0 ± 0.1°C.

No.	Time(mins)	Counts / 100 secs Cobalt II	 Cobalt III	E %	100 - E %
1	21.0	145	1061	24.0	76.0
2	41.0	228	879	41.2	58.8
3	62.0	284	761	54.2	45.8
4	93.0	364	700	68.4	31.6
5	123.0	423	677	77.0	23.0
6	187.0	507	620	90.0	10.0

TABLE 53

Electron Transfer Reaction between Cobalt (II)-phensal and Cobalt (III)-phensal. Concentration of Cobalt (II) 0.0100 M; Concentration of Cobalt (III) 0.0200 M; in Toluene as Solvent at a Temperature of 55.0 ± 0.1°C.

No.	Time(mins)	Counts / 100 secs		E %	100 - E%
		Cobalt II	Cobalt III		
1	15.5	156	1795	24.0	76.0
2	30.0	273	1747	40.5	59.5
3	45.5	355	1589	54.6	45.4
4	60.0	416	1597	62.1	37.9
5	90.0	515	1461	78.3	21.7
6	121.0	743	1816	87.0	13.0

TABLE 54

Electron Transfer Reaction between Cobalt (II)-phensal and Cobalt (III)-phensal. Concentration of Cobalt (II) 0.0100 M; Concentration of Cobalt (III) 0.0050 M; in Toluene as Solvent at a Temperature of 55.0 ± 0.1°C.

No.	Time(mins)	Counts / 100 secs		E %	100 - E %
		Cobalt II	Cobalt III		
1	30.0	796	4164	24.0	76.0
2	61.0	1683	4231	42.8	57.2
3	91.0	2085	3473	56.3	43.7
4	120.0	2577	3425	64.4	35.6
5	166.0	2893	2735	77.1	22.9
6	210.0	2909	2286	84.0	16.0

TABLE 55

Electron Transfer Reaction between Cobalt (II)-phensal and Cobalt (III)-phensal. Concentration of Cobalt (II) 0.0100 M; Concentration of Cobalt (III) 0.0025 M; in Toluene as Solvent at a Temperature of 55.0 ± 0.1°C.

No.	Time(mins)	Counts / 100 secs		E %	100 - E %
		Cobalt II	Cobalt III		
1	30.0	411	1947	21.8	78.2
2	60.0	765	1920	35.6	64.4
3	89.5	1066	1693	48.3	51.7
4	120.0	1680	1909	58.5	41.5
5	150.0	1471	1281	66.9	33.1
6	210.0	1738	1031	78.5	21.5

TABLE 56

Electron Transfer Reaction between Cobalt (II)-phensal and Cobalt (III)-phensal. Concentration of Cobalt (II) 0.0100 M; Concentration of Cobalt (III) 0.0100 M; in Toluene as Solvent at a Temperature of 60.0 ± 0.1°C.

No.	Time(mins)	Counts / 100 secs		E %	100 - E %
		Cobalt II	Cobalt III		
1	10.0	140	1024	24.0	76.0
2	20.0	221	894	39.8	60.2
3	30.0	307	789	56.0	44.0
4	45.0	411	790	68.6	31.4
5	60.0	445	710	77.0	23.0
6	90.0	357	442	89.4	10.6

TABLE 57

Electron Transfer Reaction between Cobalt (II)-phensal and Cobalt (III)-phensal. Concentration of Cobalt (II) 0.0100 M; Concentration of Cobalt (III) 0.0100 M; in Toluene as Solvent at a Temperature of 50.0 ± 0.1°C.

No.	Time(mins)	Counts / 100 secs		E %	100 - E %
		Cobalt II	Cobalt III		
1	41.0	112	922	21.8	78.2
2	80.0	179	778	37.4	62.6
3	120.0	268	820	49.2	50.8
4	180.0	323	703	63.0	37.0
5	240.0	334	587	72.4	27.6
6	300.0	405	621	79.0	21.0

APPENDIX B

Electron Transfer Reactions

A paper presented at the
Australian Atomic Energy Symposium, Sydney, 1958.

Cattrall, R. W., McKellar, J. R. & West, B. O. (1958, June). Electron transfer reactions. In. *Australian atomic energy symposium, proceedings of a Symposium on the Peaceful Uses of Atomic Energy in Australia.* (p. 628). Sydney, New South Wales.