"KINETIC STUDIES OF THE AQUATION OF SOME NITRO AMINE COBALT (III) COMPLEXES USING METAL IONS AS CATALYSTS"

A Thesis Presented To

AHMADU BELLO UNIVERSITY

For The Degree Of

MASTER OF SCIENCE

By

MOBOLANLE ADEGBOYEGA OLATUNJI B.Sc. (HONOURS)

Department of Chemistry
Ahmadu Bello University
ZARIA

September I97I

C O N T E N T

	Page
A C K N O W L E D G E M E N T	(i)
A B S T R A C T...	(ii)
INTRODUCTION	1
History of Inorganic reaction mechanism	1
CHAPTER 1	
MECHANISMS OF SUBSTITUTION REACTIONS	1
1.1 Electronic Configuration	3
1.2 Stereochemistry of Inorganic metal complexes ...	6
1.3 Size and charge of the metal ion and ligands ...	11
CHAPTER 2	
CATALYTIC EFFECT OF CATIONS ON THE SUBSTITUTION REACTIONS OF OCTAHEDRAL COMPLEXES	13
2.1 Acid catalysed aquation or acid hydrolysis	14
2.2 Cations as catalysts	18
CHAPTER 3	
AN ACCOUNT OF THE WORK DONE	21
3.1 Mercury (II)-catalysed aquation of trans-dinitro-tetrammine Cobalt (III) nitrate	22
3.2 Thallium (III)-catalysed aquation of trans-dinitrotetrammine Cobalt (III) nitrate	36
CHAPTER 4	
4.1 Mercury (II)-catalysed aquation of trans-dinitro bisethylenediamine Cobalt (III) nitrate	49
4.2 Thallium (III)-catalysed aquation of trans-dinitrobisethylenediamine Cobalt (III)	59
CHAPTER 5	
GENERAL DISCUSSION OF RESULTS AND MECHANISM	69
R E F E R E N C E S	75

A C K N O W L E D G E M E N T S

I wish to express my sincere thanks to my supervisor, Dr. U. D. Comwalk, for his helpful comment and advice during the course of the work and to Professor A. R. Mathieson, Head of the Department of Chemistry and Deputy Vice-Chancellor, for giving me the opportunity and necessary encouragement to embark on the work.

My thanks also go to the following: the Chief Technician, Laboratory Assistants and the Storekeepers who have helped in one way or the other in making the work a success and to Mr. Joshua K. Olaku for his efficient typing of the manuscript.

Finally, I would like to express my gratitude to Ahmadu Bello University for the scholarship award which made it possible for the work to be carried out.

ABSTRACT

The mercury (ii) and thallium (ill) catalysed aquation of trans-dinitrotetrammine Cobalt (ill) and trans-dinitrobisethylenediamine Cobalt (ill) nitrates have been studied over a wide temperature range of 30 "to 50 C at various constant hydrogen ion concentrations of between 0,1 to 1.8 M. The ionic strength of the different reactions were also kept constant between 0.2 to 2,0 M. In the cation concentration range used [0.01 to 0.30 M] the increase in rate in the different reactions with the exception of the one involving $[Co(NH_3)_4(NO_2)_2]NO_3$ and Tl^{3+} were interpreted in terms of two complex species - a protonated species $[co(AA)_2(NO_2)(NO_2H]^{2+}$ and a cation associated species $[CO(AA)_2(NO_2M)J]^{n+1}$.

Reaction rate constants have been ubteined and thermodynamic parameters derived for all the reactions. For the reaction of the trans-dinitrotetrammine Cobalt (ill) complex using mercury (II) as catalyst, the activation energies and entropies of activation are as follows:

Ea = 25.7 K Cals/mole, $\Delta\delta^*$ = 9.30 e.u. [at 25° for the protonated species]

Ea = 18.6 K cals/mole, $\Delta\delta^*$ = -9.00 e.u. [at 25° for the mercury (II) associated species]

Using thallium (ill) as catalyst for the same complex the calculated activation energy and entropy of activation for the thallium (ill) associated species at 25 are:

Ea = 16.6 k cals/mole; A 6 = -6.80 e.u.

Under the hydrogen ion concentration used, no reaction due to the protonated species was observed. However an initial fast reaction which was attributed to the hydroxide catalysed reaction was observed.

In the case of trans-dinitrobisethylenediamine Cobalt (ill) complex, two intermediate complex species were involved in all the reactions involving the two metal ions. For the mercury (il) catalysed aquation,

Ea = 23.4 k cals/mole, $\Delta\delta^*$ = -4.56 e.u. [at 25° for the protonated species]

Ea = 19.2 k cals/mole, $\Delta\delta^*$ = -13.6 e.u. [at 25° for the mercury (II) associated species]

For the thallium (III) catalysed aquation,

Ea = 22.6 k cal/mole; $\Delta\delta^*$ = -7.40 e.u. [at 25° for the protonated species]

Ea = 16.5 k cal/mole; $\Delta\delta^*$ = -21.64 e.u. [at 25° for the thallium (III) associated species]

The mechanism of the reactions was discussed in terms of solvent assisted dissociation process.

INTRODUCTION

History of Inorganic Reaction Mechanisms

The field of inorganic reaction mechanisms is not a new one, for as early as the turn of the century several chemists were studying the kinetics of oxidation-reduction and acid-base reactions. In the succeeding years, particularly around 1930, acid-base catalysis was investigated rather carefully. These early investigations were carried out mostly by physical chemists, who employed only kinetics on simple aqueous mixtures and were interested mainly in testing the theories current at that time.

In recent years, the inorganic chemists have become aware of the large array of systems available to them for study, both by the kinetic methods of the physical chemist and by the detailed stereochemical techniques of the Organic Chemist. The relatively late entry of the pure inorganic chemist into the area of mechanisms was not due to lack of interest. Infact, until the complex pattern of structures and bonding in inorganic molecules was partially resolved, there was little that the inorganic chemist could do in the area of mechanisms except for reaction kinetics. The nature of bonding in inorganic compounds is not yet fully resolved, and there are many structures to be worked out. There is no doubt, however, that the field of reaction mechanisms for inorganic compounds is receiving considerable attention at present and this thesis reports one of such.

CHAPTER 1

MECHANISMS OF SUBSTITUTION REACTIONS

Most of the kinetic work on substitution reactions in recent years has been done in an endeavour to attach SN1 and SN2 labels. However, mechanisms other than these extremes are possible.

Langford and Gray[1] proposed that ligand replacement reactions can proceed via (a) a dissociative path in which the leaving group is lost in the first (rate-determining) step, thus producing an intermediate of reduced coordination number which may be detectable on account of its varying reactivity to different reagents; or (b) an associative path in which the entering group adds on in the first (rate-determining) step, thus producing an intermediate of increased coordination number; a departure from second-order kinetics is sometimes observed in certain cases; or (c) a concerted path (or interchange) in which the leaving ligand is moving from the inner to the outer coordination sphere at the same time as the entering ligand is moving from the outer to the inner sphere. A characteristic of interchange mechanism is therefore the absence of any detectable intermediate of modified coordination number. Dissociative and associative mechanisms are represented by SN1 and SN2 respectively.

In considering the reactivity of complex compounds the rate at which

they react is often more important than their stability; i.e. the speed at which equilibrium is reached is considered rather than the position of the equilibrium. Although a thermodynamically stable compound often reacts slowly, and unstable complexes often react quickly, this is not always the case. An example of this can be found in the various reactions in which "labelled" cyanide ions exchange with the unlabelled cyanide ions in some complexes. It was discovered that the four-coordinate complexes exchange cyanide ions rapidly, whereas the six-coordinate complex exchange only slowly.

The reaction rates vary widely, and depend upon the nature of the reactants and the experimental conditions but complexes can be grouped under two fairly distinct 'reactivity classes':

1. Labile complexes, which react quickly (within the time of mixing).
2. Inert complexes which react only slowly.

The distinction is surprisingly clear cut, and there are relatively few borderline cases. It is found that reactivity is very closely linked with the electronic configuration of the metal ion and depends much less upon such factors as the nature of the substituting ion, its charge and its radius.

1.1 Electronic Configuration:

H. Taube[2] in one of his papers pointed out that for octahedral complexes there is a correlation between lability and electronic configuration in that metal ions having only three of the d-orbitals (the t_{2g} set) occupied by electrons are especially slow in substitution. Examples that can be cited are Cr^{3+} complexes (d^3 configuration) the

Fe^{2+} and Co^{3+} complexes (d^6 configuration).

In accounting for the correlation, Taube stressed the importance of the energy difference between the ground state of the complex and the activated intermediate in the substitution reaction. The non labile complexes are those in which the three non bonding d-orbitals are occupied by electrons. Two d-orbitals (dx^2-y^2 and dz^2) are hybridized along with an S and three P-orbitals to give an octahedral set (d^2SP^3 or SP^3d^2 depending on which type of d-orbitals are made use of in the bonding) for binding six ligands. Because all the d-orbitals are used up, none is available for accommodating an incoming substituent. Any other electronic configuration leaves available at least one d-orbital of energy comparable to one of the d's used in hybrid bond formation. This empty d-orbital can bind an added ligand, the reaction then being completed by expulsion of a different ligand.

The explanation just given for complex-ion lability is the valence bond approach and has been criticized as being too restrictive, requiring as a pre-condition, that all labile complex ion substitutions proceed via a coordination number seven type of intermediate. There is a ligand-field explanation which avoids this restriction. It ascribes activation energy differences between various central metal ions to differences in loss of ligand field stabilization energy on going from six coordination to either seven (pentagonal bipyramid) or five (square pyramid) coordination. It should be noted that the difference between the C.F.S.E. of a compound and that of the activated complex derived from the compound affects the rate of reaction because the change in activated complex is added to the

activation energy for the process. If the activated complex is less crystal field stabilized than the original compound, the rate of reaction will be less than when the opposite is true. The greatest less of stabilization energy occurs for atoms having the three d orbitals (t_2g set) occupied (either singly or doubly) and having no electrons in the upper set e_g. These are complexes which are slow to substitute.

Where the two theories agree, the agreement with experiment is perfect, but where the theories disagree the evidence is definitely on the side of the crystal field theory rather than the valence bond approach.

In the above discussion it is mentioned that ligand substitution can go through an intermediate state in which the coordination number is either decreased to five or increased to seven. In the former case, the octahedral complex must dissociate prior to taking on the new substituent. Since this can proceed by a unimolecular reaction, the mechanism is often designated SN1 (substitution, nucleophilic, first-order). In the latter case, the octahedral complex must add the new substituent as a seventh group prior to expulsion of one of the others. Since this addition can proceed by a bimolecular reaction, the mechanism is designate SN2.

Both of these mechanism are the limiting cases of a general substitution which can be represented as follows:

$$Y + MX_6 \longrightarrow Y\ldots\ldots MX_5\ldots\ldots X \longrightarrow YMX_5 + X$$

In the one limiting case (SN1), the M-X bond would have broken completely before the M-Y bond is formed; the rate of substitution would then be independent of the concentration of Y. In the other limiting case (SN2), the M-Y bond would have formed before the M-X bond started to break, the

rate of substitution would then depend directly on the concentration of Y. It is difficult to isolate the bond-making from the bond breaking steps both in principle and experimentally. One major source of difficulty in interpreting the experiments comes from the possible participation of the solvent. Thus a rate independent of Y could denote either SN1 mechanism or SN2 mechanism with the participation of the solvent molecule.

1.2 Stereochemistry of Inorganic Metal Complexes:

Because it is rather difficult to get significant information on substitution mechanisms from kinetic studies alone, considerable work has been done on the sterochemical analysis of the products formed in the substitution reactions. The purpose of such experiment is to decide whether the entering ligand occupies the same position formerly occupied by the leaving group ("direct attack") or whether the entering ligand takes up a position cis to the site of the leaving group ("edge displacement") or trans to the site of the leaving group ("trans elimination").

Experiments have been done with the pure isomers to find out whether the products retain the configuration of the original pure samples or not. Such experiments do not allow a decision between SN1 and SN2 mechanisms but they may give some information concerning proximity of entering and leaving groups.

If the substitution occurs by an SN1 mechanism, dissociation must occur first. For the case where MX_4AB reacts with Y to give MX_4AY and B this means:

$$MX_4AB \longrightarrow MX_4A + B$$

If the configuration of the MX_4A grouping remains the same in the inter-

mediate as it was in the initial complex MX_4AB, then incoming group Y can only take up position vacated by B (cis or trans to A). In other words, the original configuration is retained, a cis product results from a cis reactant, and a trans product, from a trans reactant.

On the other hand, if the intermediate MX_4A, rearranges to give a more symmetrical intermediate, then the addition of Y may occur at more than one position, thus leading to cis or trans products. A possible intermediate geometry on rearrangement is the trigonal bipyramid with A in the equatorial plane: Y can attack at two positions as shown in Figure 1.1 below

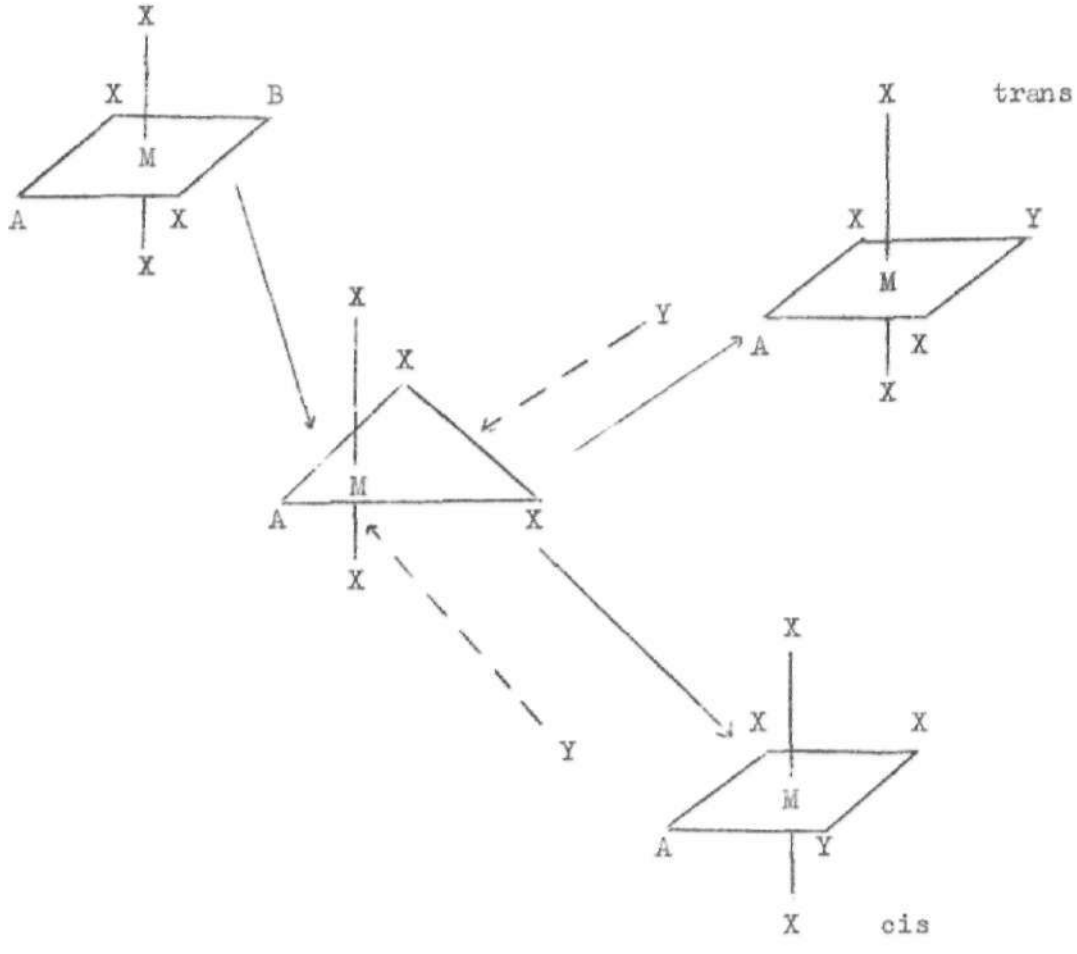


Figure 1.1 Possible path of SN1 substitution assuming trigonal bipyramid intermediate.

If the Y attack is limited to the edges of the equatorial plane and ignoring selective interactions between Y and the other ligands, in the case shown, cis-substituted product would be twice as probable as the trans product. However, due to the ligand-ligand repulsion, attack is more probable on the face than on the edge and extensive rearrangement is subsequently needed to form the octahedral product. The course of this rearrangement would determine the geometry of the product.

If the substitution occurs by an SN2 mechanism, the first step would be addition of Y to MX_4AB to give MX_4ABY. B then leaves and rearrangement to final product occurs. The geometry of the product is determined by the geometry of the seven-coordinate intermediate and the mode of the rearrangement. The incoming group may associate with the complex to form a seven-coordinate intermediate by "direct attack", "edge displacement", or "trans elimination".

"Direct attack" can be visualized as a process, illustrated in Figure 1.2 below, in which Y approaches the centre of a face adjacent to B, and, as B leaves, Y moves in to take its place.

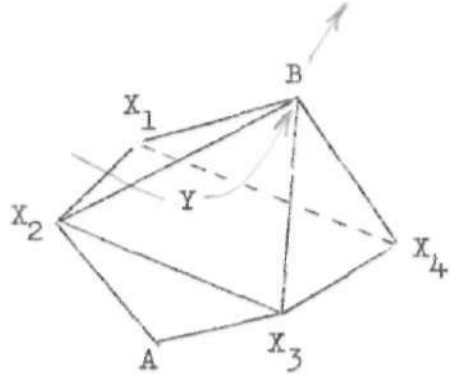


Figure 1.2 Substitution by direct attack

The original configuration is retained, so that cis-MX_4AB gives cis-MX_4AY and trans-MX_4AB gives trans-MX_4AY.

Edge displacement is more complicated. It involves, after the formation of the seven-coordinate intermediate, a simultaneous shift of three ligands - viz, the substituting Y, X_1 and B as represented diagramatically below.

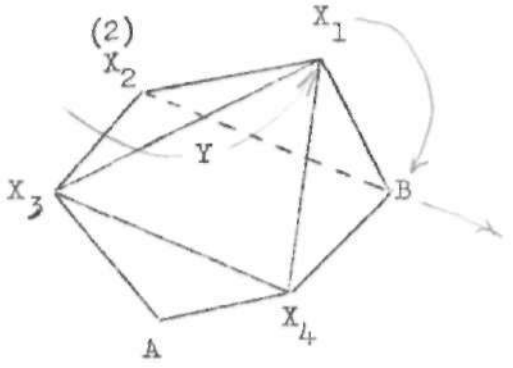


Figure 1.3 Substitution by edge displacement

The configuration of the final product depends on the relative placing of A in the original complex with respect to B and, more importantly, with respect to the X_1 ligand that moves. If A is cis to B and trans to the moving X_1, (as in the diagram), the final product will be trans; if A is cis to B and cis to the moving X_1 (positions X_2 and X_4 in the diagram) the final product will be cis. Thus cis MX_4AB can give either cis-MX_4AY or trans-MX_4AY. If A is trans to B, it must be cis to the moving X_1 (position X_3) and the product would be cis, so that on substitution by edge displacement, trans-MX_4AB gives cis-MX_4AY.

Trans elimination is another form of "edge displacement" only that here, a restriction is imposed i.e. Y always substitutes at a site trans

to the one vacated by B. It also involves a simultaneous shift of four ligands as indicated in Figure 1.4 below.

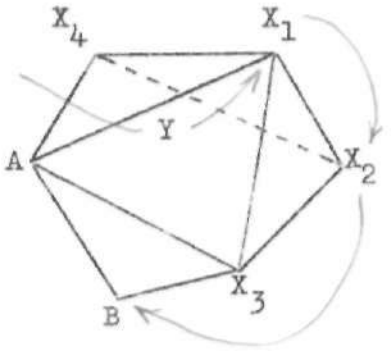


Figure 1.4 Substitution by trans elimination

Table 1.1 below summarizes the predicted products for each mechanism discussed.

TABLE 1.1

SN1			SN2	
Reactant	No rearrangement	With rearrangement	Direct attack	Edge displacement
trans	trans	cis and/or trans	trans	cis
cis	cis	cis and/or trans	cis	cis and/or trans

It can be seen that there is no way a product analysis can be used to decide between SN1 and SN2 mechanisms. However if configuration is not retained during reaction, it can be safely concluded that a direct attack by SN2 mechanism is not operating. If a trans isomer gives a trans

product, then "edge displacement" mechanism is not likely.

1.3 Size and Charge of the Metal Ion and Ligands:

Using simple electrostatic arguments it is possible to speculate what will be the influence of changes in sizes and charges of the central metal ion, the entering group, the displaced group and the passive non-replaced ligands on the rate of the three possible processes.

Assuming other factors remain constant, increasing the charge on the central metal atom will increase the strength of the metal-ligand bond and hinder a dissociative mechanism, but will favour an associative process by aiding new bond formation with an entering group. Increased size of the central metal atom is expected to weaken the metal-ligand bond and also facilitate the accommodation of an entering group, hence an increase of rate is predicted irrespective of mechanism. As the rate-determining step in a dissociative process does not involve the entering group, it is obvious that changes in charge or size of the entering nucleophile will have no effect on the rate. In an associative process, increased charge of the substituent will increase the rate by promoting new bond formation, but increased size will impede bond formation.

Regardless of mechanism, it is to be expected that increase in negative charge of the leaving group will reduce the rate of substitution: bond-breaking is rendered more difficult, as is also bond formation due to the smaller effective positive charge on the central metal ion. An increase in size of the leaving group will make rupture of the metal-ligand bond easier and assist a dissociative process; but the rate of

reaction via an associative mechanism will be reduced due to difficulty in expanding the coordination number (Steric effect).

The nature of the non-labile, unreplaced ligands can affect the rate A greater negative charge on the non-labile ligands will help a dissociative process by repelling the reactive group but, since bond formation is made more difficult, will decrease the rate of an associative process. Steric strain resulting from increasing the size of the non-reactive ligands will assist a dissociative process but, by hindering the expansion of the coordination shell, will decrease the rate via an associative mechanism.

This approach is over simplified and cannot be expected to be complete. For example no account of Π bonding has been given. It may be anticipated that in certain cases unsaturated ligands will be effective as displacing reagents because of the chance of increased bonding in the transition state. Such double bonded ligands will also be difficult to displace when already present in the coordination sphere. Also for a complexes where covalent bonding is an especially important factor, an electrostatic picture will not be very reliable.

CHAPTER 2

CATALYTIC EFFECT OF CATIONS ON THE SUBSTITUTION REACTIONS OF OCTAHEDRAL COMPLEXES

When Berzelius[3] first put forward the suggestion that some reactions should be classified together as "catalysed", the emphasis then was placed almost entirely upon the nature and amount of products rather than upon the rate of their formation. He thought there was a special force, a "catalytic force of bodies", which caused the increased yield. However it is now known that a catalyst does not increase the yield of a reaction but it increases the rate of approach to an equilibrium position which is thermodynamically possible, but difficult to reach in the absence of a catalyst. This it does by providing "an alternative and more speedy route" (to quote Hinshelwood's definition[4] of a catalysed reaction), which can usually be explained in terms of normal chemical reactions between catalyst and substrate to give intermediates, which eventually yield the products and regenerate the catalyst.

More often the intermediates are very reactive species present in low concentrations even relative to the catalyst. They may be saturated compounds, ions, free radicals or atoms and they may exist in the gas or liquid phase or be bound to a surface. Their behaviour can be explained by their unusual reactivity and this, in turn, by their structure rather

than by any special "power" peculiar to catalysed reactions.

Reactions in solution which are catalysed by acids, bases, cations and anions form one large subdivision of catalysed reactions which proceed by simple homogeneous steps involving molecules ions or free radicals as intermediates. The intermediates have been identified as ionic species usually formed by the extraction of a proton from, or, addition of a proton to, the reactant or substrate molecule; occassionally too, a larger charged group is added or removed.

Since this type of reaction forms the basis of the present work, perhaps it would not be out of place to briefly discuss some of the work carried out in this field.

To some extent hydrogen ion can be appropriately grouped under the main heading cations, and its catalytic behaviour treated along with others accordingly. But in view of the numerous studies that have been done using it as catalysts especially in the aquation of some inorganic metal complexes, it will be worthwhile to treat it separately before giving a general consideration to other cations.

2.1 Acid-Catalysed Aquation or Acid Hydrolysis:

Of all the replacement reations of octahedral coordination compounds the most widely studied are those in which aquo complexes are formed by acid hydrolysis, e.g.

$$\left[MA_5X\right]^{n+} + H_3O^+ \longrightarrow \left[MA_5H_2O\right]^{(n+1)+} + H^+X^-$$

Acid hydrolysis implies no more than hydrolysis under acid conditions; the rate of reaction may or may not be proportional to the concentration of

the acid used. The greater bulk of work performed has been concerned with the acid hydrolysis of Co(III) complexes. This is because substitution reactions in Co(III) complexes are slow enough to study using the conventional methods, and it has been found that these reactions proceed indirectly via reaction with the solvent molecules.

For these acid hydrolysis, the form of the rate laws is compatible with mechanism (a) or (b).

(a) $\left[MA_5X\right]^{n+} \xrightarrow[\text{slow}]{k_a} \left[MA_5\right]^{(n+1)+} + X^-$

$\left[MA_5\right]^{(n+1)+} + H_2O \xrightarrow{\text{fast}} \left[MA_5H_2O\right]^{(n+1)+}$

Rate $= k_a \left[MA_5X^{n+}\right]$

(b) $\left[MA_5X\right]^{n+} + H_2O \xrightarrow[\text{slow}]{K_b} \left[MA_5XH_2O\right]^{n+} \longrightarrow \left[MA_5H_2O\right]^{(n+1)+} + X^-$

Rate $= k_b \left[MA_5X^{n+}\right]\left[H_2O\right]^{n+} = k_b^1 \left[MA_5X^{n+}\right]$.

Reference to other experimental data has to be made to distinguish between dissociative mechanism (a) and associative mechanism (b). Some fruitful lines of approach have been to study the effects of the variation of non-replaceable groups present in the complex. This approach would cover the steric, inductive and Π bonding effects. The overall charge on the complex, effect of the leaving group and solvent effect are also taken into consideration (most of these have been discussed earlier on).

All systems whose rates of hydrolysis depend to some extent on the concentration of the acid used are said to be acid-catalysed and changes were thought to be due to the formation of protonated species in solution.

These systems fall into two catergories:

(a) Complexes containing ligands derived from weak acids, e.g. $\left[M(NH_3)_5X\right]^{n+}$ where X = F^-, N_3^-, $RCOO^-$, CO_3^{2-}, or NO_2^-, and $\left[Co(en)_2X_2\right]^+$ where X = NO_2^- or N_3^-.

(b) Complexes containing polydentate ligands e.g. $\left[M(EDTA)\right]^{n-}$ where M = Ni(II) and Fe(III), $\left[M(C_2O_4)_3\right]$ where M = Co(III), Cr(III) or Rh (III), $\left[M(bipy)_3\right]^{2+}$ where M = Fe(II) or Ni(II), and $\left[Ni(en)_3\right]^{2+}$.

For complexes in catergory (a), acid catalysis is due to the tendency of the strongly basic ligand to attach proton[5], for example

$$\left[M(NH_3)_5(RCOO)\right]^{2+} + H^+ \underset{}{\overset{K}{\rightleftharpoons}} \left[M(NH_3)_5(RCOOH)\right]^{3+} \quad \text{(fast)}$$

Aquation then results from the following species

$$\left[M(NH_3)_5(RCOO)\right]^{2+} + H_2O \xrightarrow{k_1} \left[M(NH_3)_5(H_2O)\right]^{3+} + RCOO^-$$

and $$\left[M(NH_3)_5(RCOOH)\right]^{3+} + H_2O \xrightarrow{k_2} \left[M(NH_3)_5(H_2O)\right]^{3+} + RCOOH.$$

The rate law is then given as

$$\text{Rate} = k_1\left[M(NH_3)_5(RCOO)^{2+}\right] + k_{H^+}\left[M(NH_3)_5(RCOO)^{2+}\right]\left[H^+\right]$$

where $k_H = k_2K$. The observed rate constant (k_{obs}) is then defined by $k_{obs} = k_1 + k_2K\left[H^+\right]$, and a plot of k_{obs} versus $\left[H^+\right]$ is linear with an intercept equal to k_1 and a gradient k_2K. This was illustrated by Mancelli, Basolo and Pearson[5] for a series of pentammine complexes of Co(III),

Rh(III) and Ir(III).

Another example of the above postulate is the acid-catalysed aquation of trans-dinitrotetrammine Cobalt (III) nitrate by U. D. Gomwalk and A. McAuley[6]. In their own work, two conjugate acids of the complex ion were said to be formed according to the equilibria:

$$\left[Co(NH_3)_4(NO_2)_2\right]^+ + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} \left[Co(NH_3)_4(NO_2)(NO_2H)\right]^{2+}$$

$$\left[Co(NH_3)_4(NO_2)(NO_2H)\right]^{2+} + H^+ \overset{K_2}{\rightleftharpoons} \left[Co(NH_3)_4(NO_2H)_2\right]^{3+}$$

If all the three species react, the acid catalysis was interpreted as being due to the reactions:

$$\left[Co(NH_3)_4(NO_2)_2\right]^+ + H_2O \xrightarrow{k_o} \left[Co(NH_3)_4(NO_2)(H_2O)\right]^{2+} + NO_2^-$$

$$\left[Co(NH_3)_4(NO_2)(NO_2H)\right]^{2+} + H_2O \xrightarrow{k_1} \left[Co(NH_3)_4(NO_2)(H_2O)\right]^{2+} + HNO_2$$

$$\left[Co(NH_3)_4(NO_2H)_2\right]^{3+} + H_2O \xrightarrow{k_2} \left[Co(NH_3)_4(NO_2H)(H_2O)\right]^{3+} + HNO_2$$

Inclusion of terms for the total concentration of Cobalt (III) complex present then yielded the rate law.

$$\text{Rate} = \frac{\left\{k_o + k_1^1\left[H^+\right] + k_2^1\left[H^+\right]^2\right\}\left[Co^{III}_{tot}\right]}{\left\{1 + K_1\left[H^+\right] + K_1K_2\left[H^+\right]^2\right\}}$$

where $k_1^1 = k_1K$, $k_2^1 = k_2K_1K_2$, and $\left[Co^{III}_{tot}\right]$ was the initial concentration of the trans-dinitrotetrammine Cobalt (III) complex. Since spontaneous aquation was very slow and since equilibria (2) and (3) involved the association of like charges, the stability constants K_1 and K_2 were also

said to be small, so that $1 \gg K_1[H^+] + K_1K_2[H^+]^2$. Hence the expression for the observed curvature reduced to

$$K_{obs} = k_1^1[H^+] + k_2^1[H^+]^2.$$

and a plot of $k_{obs}/[H^+]$ against $[H^+]$ gave good linearity at all temperatures.

3.2 Cations as Catalysts:

Cations other than hydrogen ions have also been used as catalysts for the aquation of inorganic complexes. The most common of these are the Hg^{++}, Ag^+ and Tl^{3+} ions. Various people have employed these to study the reactions of some metal complexes. No generalised theories have been put forward to explain their catalytic behaviour. The various workers that have used them put forward different suggestions to account for the rate data they obtained.

Posey and Taube[7] have studied oxygen-18 fractionation in the Hg^{2+} catalysed aquation of halogenopentammine Cobalt (III) complexes ($X = Cl^-$, Br^- and I^-) and found that the enrichment of oxygen-16 in the $Co(NH_3)_5H_2O^{3+}$ product over the oxygen-16 content of the water solvent (fractionation factor $[f]$) was the same in each case. According to them, this was an indication of the formation of a common intermediate independent of the leaving group. Thus they reached a conclusion that for the series $[Co(NH_3)_5X] + Hg^{2+}$ the mechanism was one of SN1 type. With both Ag^+ and Tl^{3+} the reactions were said to be leaving group dependent i.e. the bond with water was being formed while that with the halide was being broken [SN2 mechanism] and in the case of thallium (III) they suggested that the

entering water molecule may come from the thallium coordination sphere.

Higginson and his co-workers[8,9] have studied the catalytic effect of bivalent and tervalent cations on the elimination of chloride from the chloro (ethylenediamine-triacetatoacetate) Cobalt (III) complex [the final product was the sexadetate ethylene-diamine tetra-acetate Cobalt (III) complex]. They found mercury (II) and thallium (III) to be particularly effective catalysts. The strong catalytic effect of Tl^{3+} and Hg^{2+} ($k_{Tl} > k_{Hg}$) was explained in terms of the affinity of these species for chloride (and carboxylate) ions.

S. C. Chan and S. F. Chan[10] worked on the mercury (II) catalysed aquation of both chloro- and bromo (amine) bis (ethylenediamine) Cobalt (III) complexes and the observed second-order kinetics were explained by the formation of an activated complex Co-Cl-Hg or Co-Br-Hg, which yielded aquo (amine) bis ethylenediamine Cobalt (III) products by aquation process.

Espenson and Hubbard[11] studied the kinetics of the mercury (II) catalysed aquation of the chloro penta-amine chromium (III) cation and attempted to relate its transition state with that of an innersphere electron transfer reaction. While the formation of binuclear species M-Cl-Hg in these cases is a strong possibility, there has been no evidence, spectral or otherwise, for such an intermediate. A recent paper[12] reported that in one of a number of similar reactions studied, there was such evidence, which its authors have not seen fit to generalize.

Nevertheless whether a binuclear intermediate or an activated complex was involved, the outgoing group was approximated to $HgCl^{+}$. Taking other factors into consideration like the e l e c t r o n displacement

effects of the non-participating ligand, the nature of the outgoing ligand particularly its size and charge, a conclusion was reached by the authors that in the mercury (II) catalysed aquation of cis-$\left[Co(en)_2(RNH_2)Cl\right]^{2+}$ cations, the rate-determining step would be unimolecular.

Finally, the kinetics of thallium (III) and mercury (II) catalysed aquation of the chloro-pentammine Cobalt (III) and cis- and trans-dichloro-bis ethylenediamine Cobalt (III) complexes were also recently studied by Miss. S. W. Poong, B. Kipling and A. G. Sykes[13]. They also suggested the formation of a stable binuclear adduct of cis- $Co(en)_2 Cl_2$ with Hg^{2+} but not with Tl^{3+}. It is hoped that the present work would throw some light as to the nature of these activated complexes.

CHAPTER 3

AN ACCOUNT OF THE WORK DONE

It was originally intended to study the aquation of trans-dinitrotetrammine Cobalt (III) complex using various cations as catalysts and to observe the effect (if any) of the differences in the positive charges they carry on the rate of reaction. Preliminary investigations were carried out using Hg^{2+}, Tl^{3+}, Al^{3+}, Ga^{3+}, In^{3+}, Cd^{2+}, Zn^{2+}, Ag^{+}, Ca^{2+} and Pt^{2+}. Out of these only Hg^{2+} and Tl^{3+} ions were found suitable for a detailed investigation. This thesis is therefore a report of the catalytic effect of Hg^{2+} and Tl^{3+} ions on the trans-dinitro-tetrammine Cobalt (III) complex and the trans-dinitro-bis ethylenediamine Cobalt (III) complex.

Perhaps it is worth pointing out here that quantitative comparison of the reactivity of the two complexes as evident by the rate results obtained, would be difficult in that different ionic strengths had to be used in the different cases. This arose from the fact that the hydrolysis which normally takes place when these cations are present in aqueous solutions had to be suppressed using different concentrations of acid as the degree of hydrolysis are not the same for the two cations used. It has also been established (by U. D. Comwalk for the tetrammine and staples

for ethylenediamine Cobalt (III) that the trans-dinitrotetrammine Cobalt (III) complex is by far more reactive than the ethylenediamine analogue. Hence higher concentrations of both the acid and the catalysts (Hg^{2+} and Tl^{3+}) had to be used in the latter case inorder to obtain an appreciable change in the spectrophotometer readings. This is another reason why the ionic strength could not be made the same for all the systems studied.

The acid-catalysed hydrolysis of the two complexes studied has been carried out by two different workers: Gomwalk and Staples. Staples[4] investigated the replacement of one of the nitro-groups of cis- and trans-$\left[Co(en)_2(NO_2)_2\right]$-$NO_3$ in a perchloric acid medium and suggested an SN2 CA mechanism for the aquation. Gomwalk and McAuley[6] studied the acid-catalysed aquation of trans-$\left[Co(NH_3)_4$-$(NO_2)_2\right]NO_3$ over a temperature range from 25-40° at an ionic strength of 2.5 M and interpreted the rate results in terms of reactions involving two conjugate acid ions $\left[Co(NH_3)_4$-$(NO_2)(NO_2H)\right]^{2+}$ and $\left[Co(NH_3)_4(NO_2H)_2\right]^{3+}$. The present studies seek to extend their work by using metal ions instead of hydrogen ions.

3.1 MERCURY (II) CATALYSED AQUATION OF TRANS-DINITRO-TETRAMMINE COBALT (III) NITRATE:

The mercury (II) catalysed aquation of the dinitrotetrammine Cobaltate (III) ion was investigated over the temperature range 30-45° at an ionic strength of 0.2 M in nitric acid media. In the mercury (II) concentration range 0.01-0.04 M and constant acid concentration 0.1 M, the increase in rate may be interpreted in all cases in terms of the reaction of the complex ions $\left[Co(NH_3)_4(NO_2)_2\right]^{+}$, $\left[Co(NH_3)_4(NO_2)(NO_2H)\right]^{2+}$ and $\left[Co(NH_3)_4(NO_2)(NO_2Hg)\right]^{3+}$. Reaction rate constants and thermodynamic

parameters have been derived. Mechanisms of these reactions are also discussed.

Experimental:

The trans-Dinitrotetrammine Cobalt (III) nitrate used was prepared by methods described in the literature[15]. Analysis of the complex carried out show that the Cobalt content of the complex was 21.10% as against 20.95% for the calculated value. All reagents used were of A.R. grade, and grade "A" glassware was used where possible.

The stock solution of nitric acid used for the reaction was 4.730 M and so the required volume of the acid necessary to make the acid concentration 0.10 M was calculated. The presence of acid was necessary to suppress the hydrolysis of Hg^{2+}.

$$Hg^{2+} + 2OH^{-} \rightleftharpoons Hg(OH)_2$$

The concentration of the Hg^{2+} was varied in each case. This was done by weighing out the exact weight of red mercuric oxide necessary to make the desired concentration in 100 mls. This weight was first dissolved in the required volume of nitric acid and was rinsed into a round-bottomed flask with a known volume of water.

A stock solution of 1 M sodium nitrate was prepared and the volume of this solution required to make the overall ionic strength 0.20 M was calculated and measured into the same round-bottomed flask. This was then thermostated. The remaining volume to give the final 100 mls. of solution is the volume of water to be added. This latter volume was

measured out accurately and used to dissolve a weighed quantity of the complex necessary to make the concentration of the complex 3×10^{-3} M in 100 ml. solution in a dark bottle. The solution in the dark bottle was shaken thoroughly to make sure that all the crystals of the complex had gone into solution after which it was put in the thermostat set at the required temperature. The reaction had to be carried out in dark bottles since previous investigations have shown that the product [nitro aquo tetrammine Cobalt (III)] was light sensitive[6], there being photo reduction at the Cobalt centre to Co^{2+}.

K i n e t i c s:

When thermal equilibrium had been reached, the reaction was started by injecting the solution in the round bottomed flask containing Hg^{2+}, acid and water and which had already been thermostated into the Cobalt solution. The solutions were then mixed and immediately placed in stoppered spectrophotometer cell. Optical densities were then measured at certain intervals of time at 440 nm using a Unicam S.P. 500 spectrophometer. The thermostat used was of the conventional design, capable of holding temperatures constant to $\pm$ 0.1°, and the water from this thermostat was circulated through the cell compartment by a pump thereby maintaining it at the required temperature.

The above procedure was carried out at 30° and was repeated at 35, 40 and 45°.

Results and Discussion:

Large excess of the Hg^{2+} ions over the complex ions was used so as to establish pseudo-first order conditions. Accordingly the plot of log $(OD_t - OD_\infty)$ against time showed good linearity at all temperatures studied (OD_t is the optical density at time t and OD_∞ is the optical density at infinite time). About sixty to seventy percent of the reaction was found to obey first-order rate law in each case (see Figure 3.1 to 3.4).

The various rate constants obtained for each of the temperatures are shown in Table 3.1 and plots of these observed rate constants against mercury ion concentration gave good linearity at all temperatures (Figure 3.5).

Previously[16] the variation of k_{obs} with acid concentration was considered as a function of the ionic strength of the medium, an interpretation which was supported by changes in the electron-transfer band in the spectrum of the complex. In the present-work, however, the ionic strength was kept constant and spectral changes were thought to be due to the formation of intermediate species involving H^+ and Hg^{2+}.

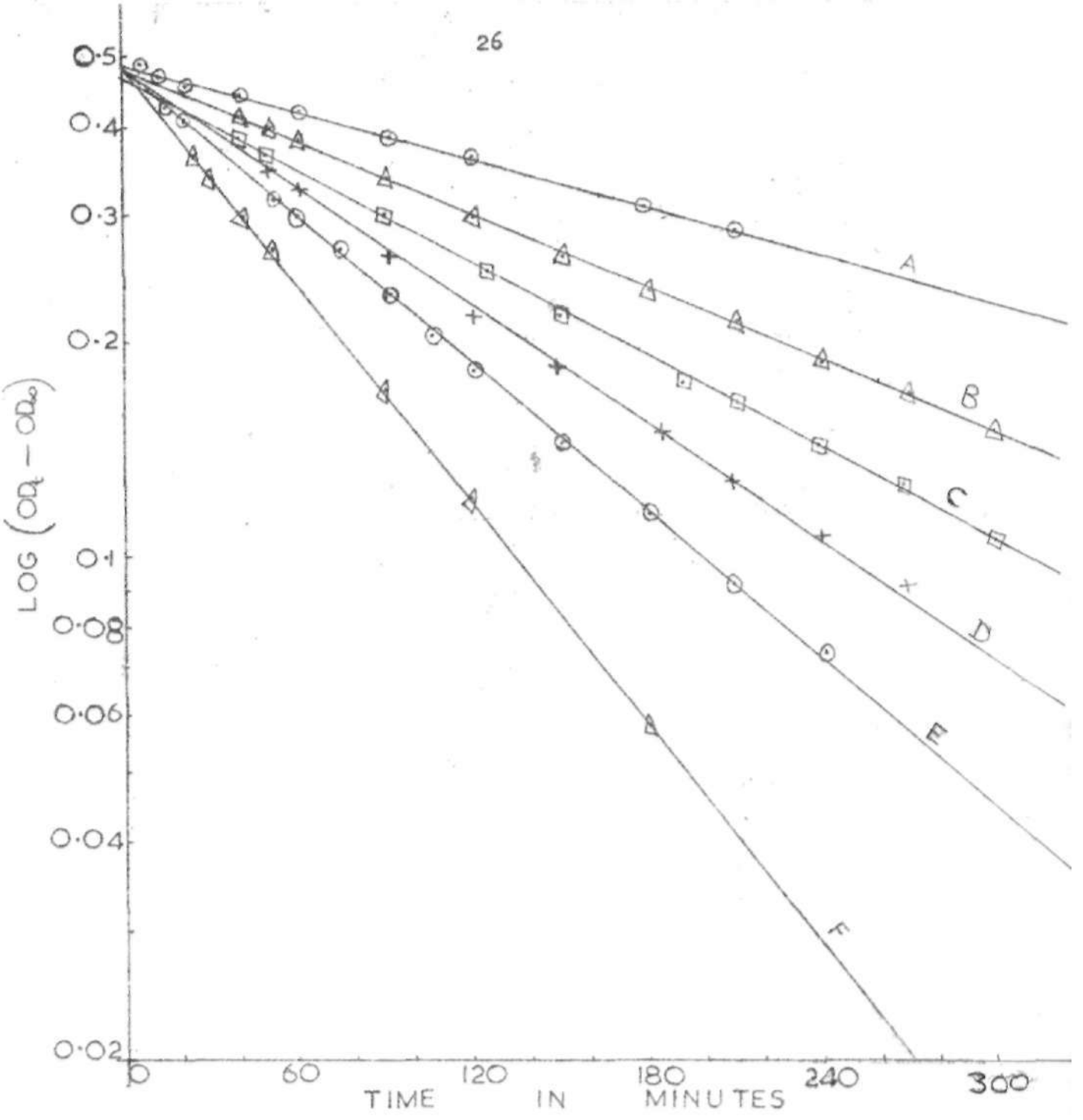


FIG 3·1

PLOTS OF LOG $(OD_t - OD_\infty)$ AGAINST TIME FOR DIFFERENT MERCURY [II] ION CONCENTRATIONS AT 30.0°

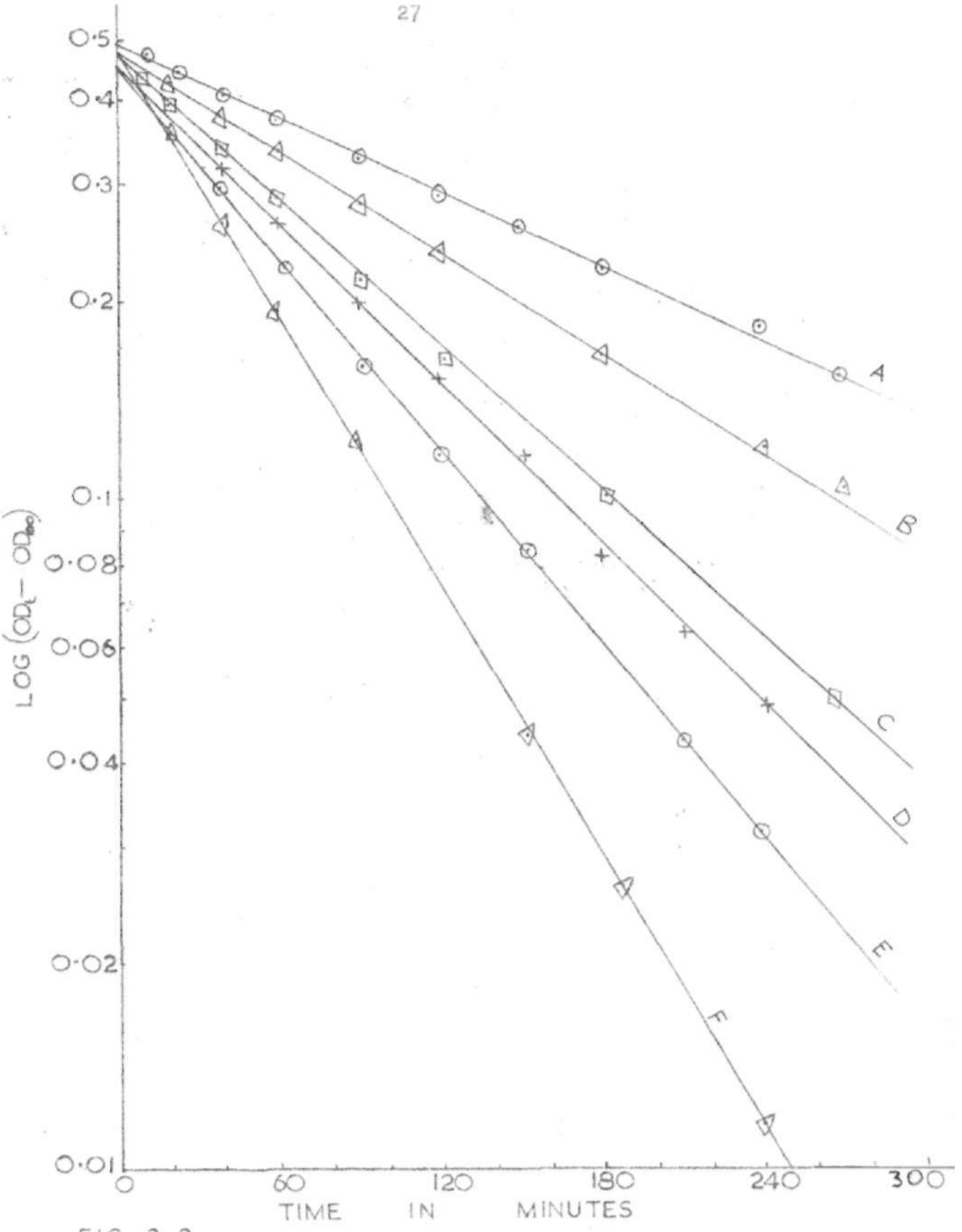


FIG 3·2

PLOTS OF LOG ($OD_t - OD_\infty$) AGAINST TIME FOR DIFFERENT MERCURY (II) ION CONCENTRATIONS AT 35.0°

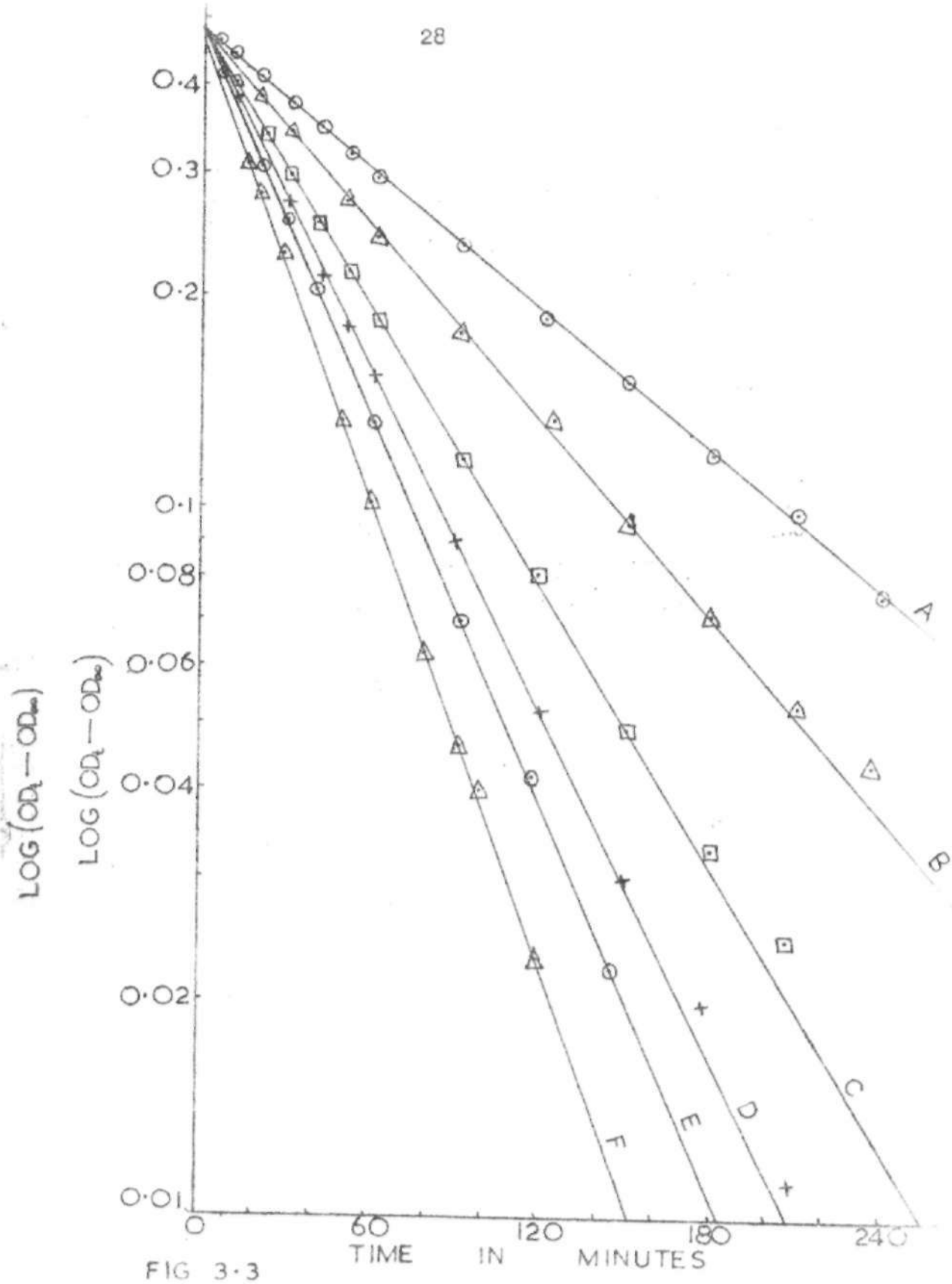


FIG 3·3

PLOTS OF LOG ($OD_t - OD_\infty$) AGAINST TIME FOR DIFFERENT MERCURY (II) ION CONCENTRATIONS AT 39.5°

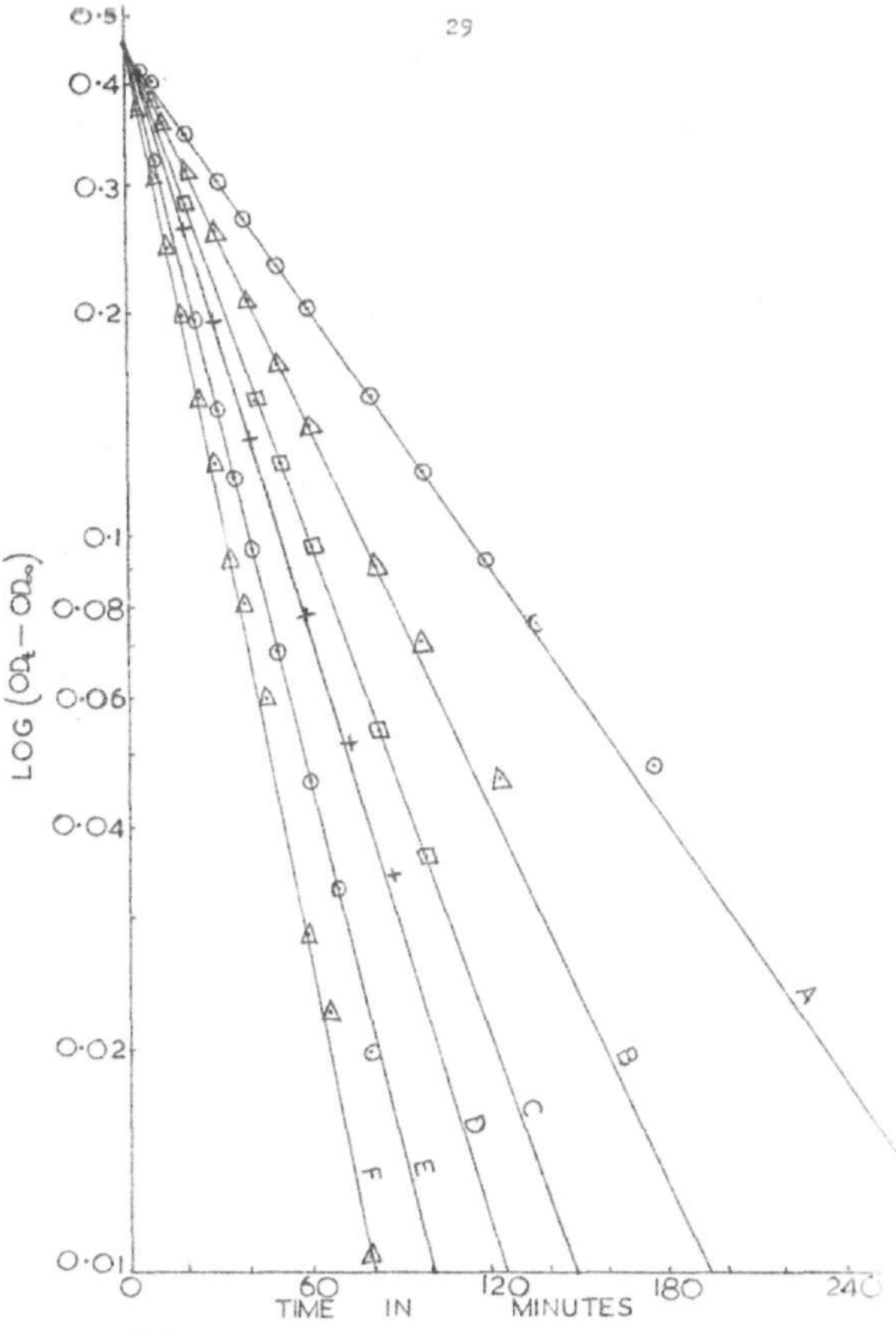


FIG 3·4

PLOTS OF LOG ($OD_t - OD_\infty$) AGAINST TIME FOR DIFFERENT MERCURY (II) ION CONCENTRATIONS AT 44.7°

TABLE 3.1

Concentration of the acid was kept constant at 0.1 M
The total ionic strength was also kept constant at 0.2 M

$10^3[Co^{III}\ Complex]$ x 10^{-3} M	$10^3[Hg^{2+}]$ M	$10^5\ k_{obs}$ (Sec^{-1})	$10^3[Co^{III}]$ M	$10^3[Hg^{2+}]$ M	$10^5\ k_{obs}$
	30°C			35°C	
3.01	A = 10.01	4.18	2.99	A = 9.98	7.36
3.00	B = 14.97	6.55	3.00	B = 15.04	9.90
2.98	C = 20.03	8.80	3.04	C = 20.00	14.76
3.00	D = 25.02	10.80	3.02	D = 25.01	16.25
3.00	E = 30.00	13.58	3.02	E = 30.03	18.70
2.96	F = 45.00	19.30	3.00	F = 40.00	26.20
	39.5°C			44.7°C	
2.99	A = 9.99	12.72	3.04	A = 9.99	22.20
3.03	B = 15.04	17.30	3.00	B = 14.95	31.94
2.98	C = 20.03	24.72	3.01	C = 19.98	42.70
3.00	D = 24.99	30.34	3.01	D = 24.99	47.60
3.00	E = 30.05	33.40	2.99	E = 30.04	64.25
3.02	F = 35.00	38.90	2.99	F = 35.06	71.00
3.03	G = 40.01	42.50	3.04	G = 40.00	76.00

In purely acid medium Gomwalk and McAuley[6] explained the rate data obtained in terms of two cunjugate acid species, $\left[Co(NH_3)_4(NO_2)(NO_2H)\right]^{2+}$ and $\left[Co(NH_3)_4(NO_2H)_2\right]^{3+}$. But in the present acidity conditions and in the precence of mercury ion, two intermediate complex ion species may be formed.

$$\left[Co(NH_3)_4(NO_2)_2\right]^+ + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} \left[Co(NH_3)_4(NO_2)(NO_2H)\right]^{2+} \quad \ldots\ldots\ldots\ldots (3.1)$$

$$\left[Co(NH_3)_4(NO_2)_2\right]^+ + Hg^{++} \underset{}{\overset{K_2}{\rightleftharpoons}} \left[Co(NH_3)_4(NO_2)(NO_2Hg)\right]^{3+} \quad \ldots\ldots\ldots (3.2)$$

If all the three species react, the acid/Hg^{2+} catalysis may be interpreted as being due to the reactions:

$$\left[Co(NH_3)_4(NO_2)_2\right]^+ + H_2O \xrightarrow{k_o} \left[Co(NH_3)_4(NO_2)(H_2O)\right]^{2+} + NO_2^- \quad \ldots\ldots (3.3)$$

$$\left[Co(NH_3)_4(NO_2)(NO_2H)\right]^{2+} + H_2O \xrightarrow{k_1} \left[Co(NH_3)_4(NO_2)(H_2O)\right]^{2+} + HNO_2 \quad \ldots (3.4)$$

$$\left[Co(NH_3)_4(NO_2)(NO_2Hg)\right]^{3+} + H_2O \xrightarrow{k_2} \left[Co(NH_3)_4(NO_2)(H_2O)\right]^{2+} + Hg^{++}NO_2^- \quad (3.5)$$

$$\text{Rate} = k_o\left[Co(NH_3)_4(NO_2)_2\right]^+ + k_1\left[Co(NH_3)_4(NO_2)(NO_2H)\right]^{2+} + k_2^-\left[Co(NH_3)_4(NO_2)(NO_2Hg)\right]^{3+}$$

$$= k_o\left[Co(NH_3)_4(NO_2)_2\right]^+ + \underbrace{\frac{k_1K_1}{K_1^1}}\left[Co(NH_3)_4(NO_2)_2\right]^+\left[H^+\right] + \underbrace{\frac{k_2K_2}{K_2^1}}\left[Co(NH_3)_4(NO_2)_2\right]^+\left[Hg^{2+}\right] \quad \ldots\ldots (3.6)$$

$$Co^{III}_{tot} = \left[Co(NH_3)_4(NO_2)_2\right]^+ + \left[Co(NH_3)_4(NO_2)(NO_2H)\right]^{2+} + \left[Co(NH_3)_4(NO_2)(NO_2Hg)\right]^{3+}$$

$$= \left[Co(NH_3)_4(NO_2)_2\right]^+ + K_1\left[Co(NH_3)_4(NO_2)_2\right]\left[H^+\right] + K_2\left[Co(NH_3)_4(NO_2)_2\right]\left[Hg^{2+}\right]$$

$$= \left[Co(NH_3)_4(NO_2)_2\right]^+ \left\{1 + K_1\left[H^+\right] + K_2\left[Hg^{2+}\right]\right\} \quad .. \quad .. \quad .. \quad .. \quad ..(3.7)$$

$$\therefore \quad \left[Co(NH_3)_4(NO_2)_2\right] = \frac{Co^{III}_{tot}}{1 + K_1\left[H^+\right] + K_2\left[Hg^{2+}\right]} \quad .. \quad .. \quad .. \quad .. \quad .. \quad ..(3.8)$$

Substituting equation (3.8) in equation (3.6)

$$\text{Rate} = \frac{\left\{k_o + K_1^1\left[H^+\right] + k_2^1\left[Hg^{++}\right]\right\}C^{III}_{tot}}{1 + K_1\left[H^+\right] + K_2\left[Hg^{++}\right]} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad ..(3.9)$$

Since spontaneous aquation is very slow[6] and since equilibria (3.1) and (3.2) involve the association of the like charges, the stability constants K_1 and K_2 will also be very small, so that $1 \gg K_1\left[H^+\right] + K_2\left[Hg^{++}\right]$.

Therefore equation (3.9) reduces to

$$\text{Rate} = \left\{k_1^1\left[H^+\right] + k_2^1\left[Hg^{++}\right]\right\} Co^{III}_{tot} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad ..(3.10)$$

But because the reaction is pseudo first-order

$$\text{Rate} = k_{obs}\left[Co^{III}_{tot}\right] \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad ..(3.11)$$

Comparing equation (3.10) with (3.11)

$$\therefore \quad k_{obs} = k_1^1\left[H^+\right] + k_2^1\left[Hg^{++}\right] \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad ..(3.12)$$

If this proposed mechanism is correct then a plot of k_{obs} against $\left[Hg^{++}\right]$ for each of the temperature should be a straight line graph the slope

of which should give k_2^1 and the intercept $k_1^1[H^+]$. Figure (3.5) shows good linearity at all the four temperatures in agreement with the proposed mechanism. The values of k_1^1 and k_2^1 at each temperature derived from the intercepts and slopes are shown in Table 3.2. Arrhenius plots of the equations involving the two intermediate species are also shown in Figure 3.6.

TABLE 3.2

Variation of rate parameters with temperature

Temperature	$10^4 k_1^1$ (sec^{-1})	$10^3 k_2^1$ (sec^{-1})
30.0°	0.50	4.13
35.0°	1.00	5.96
39.5°	1.80	10.58
44.5°	3.50	19.35

The calculated activation energies (Ea) and entropies of activation ΔS^* for the reactions are:

Ea = 25.7 K cals/mole; $\Delta S^* = 9.30$ eu (reaction 3.4)

Ea = 18.6 K cals/mole; $\Delta S^* = -9.00$ eu (reaction 3.5)

The Ea values for the singly protonated species may be compared with that of 26.2 K cal/mole obtained for the same complex in purely acid (perchloric acid) medium[6].

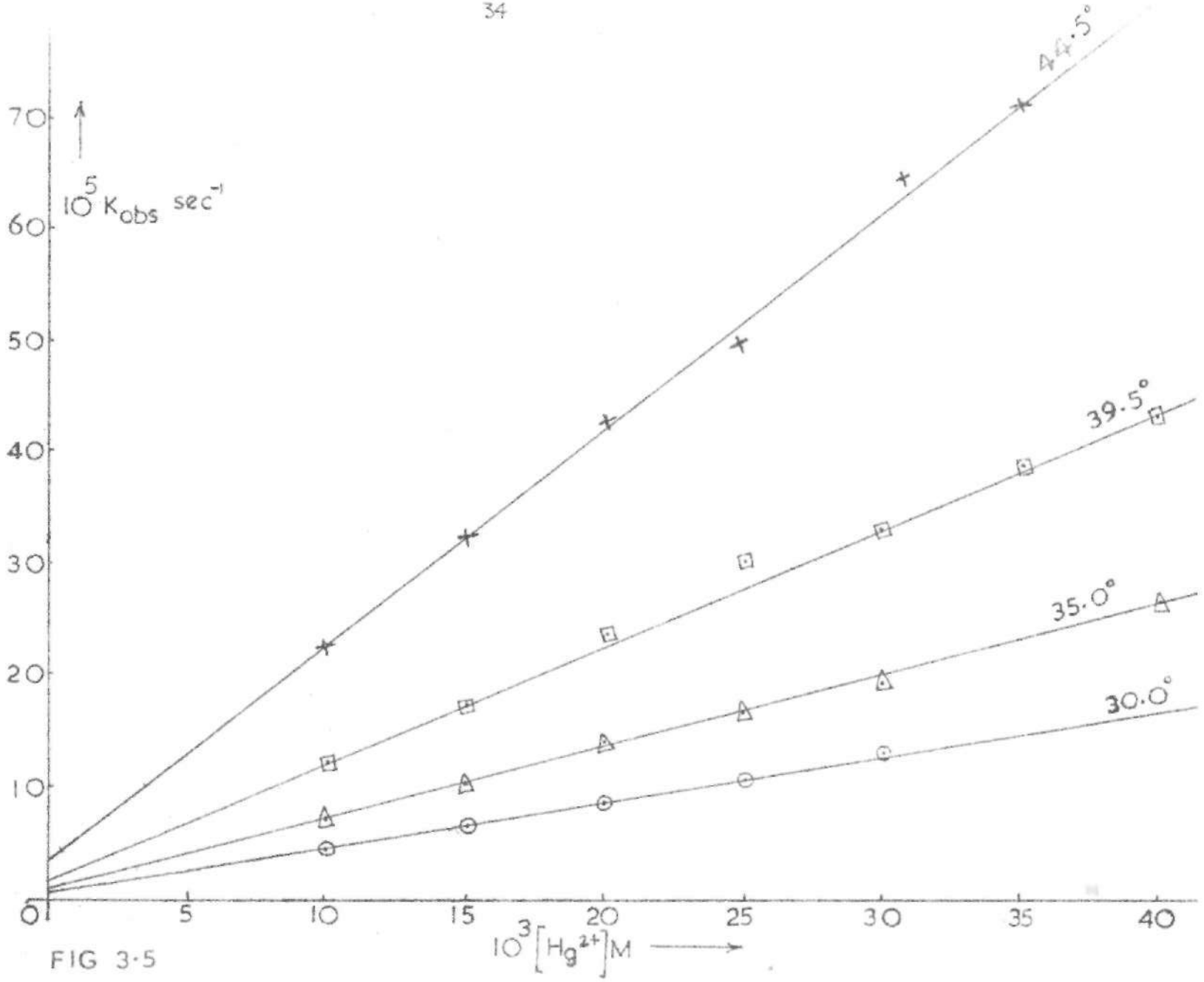


FIG 3·5

GRAPH OF k_{obs} AGAINST $[Hg^{2+}]$ FOR $[Co(NH_3)_4(NO_2)_2]NO_3$ AT 30.0, 35.0, 39.5 AND 44.5°

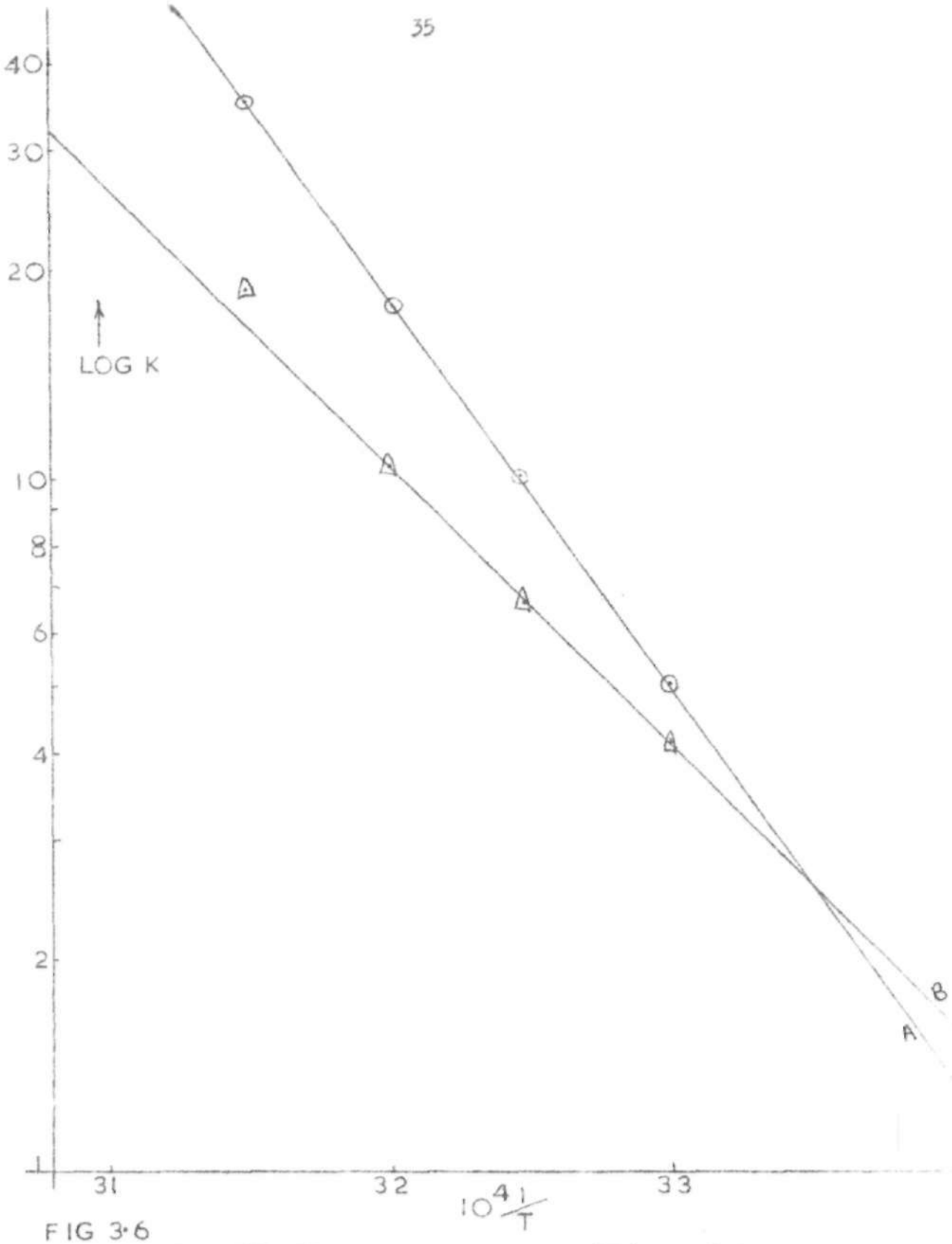


FIG 3·6

ARRHENIUS PLOT FOR THE MERCURY (II) CATALYSED AQUATION OF $[Co(NH_3)_4(NO_2)_2]NO_3$ AT 30.0, 35.0, 39.5 AND 44.5°
A = REACTION (3.4) B = REACTION (3.5)

3.2 THALLIUM (III) - CATALYSED AQUATION OF TRANS-DINITRO-TETRAMMINE COBALT (III) NITRATE:

Thallium (III) catalysed aquation of the trans-dinitro Cobaltate (III) ion was also investigated over the temperature range 30-45^{o} at an ionic strength of 0.5 M in nitric acid medium. Within the various concentrations of the thallium (III) metal ions used, 0.01-0.04 M and constant acid concentration 0.4 M, the increase in rate may be interpreted in terms of the reaction of the complex ions $\left[Co(NH_3)_4(NO_2)_2\right]^{+}$, and $\left[Co(NH_3)_4(NO_2)(NO_2Tl)\right]^{4+}$. Rate constant for each reaction have been obtained and thermodynamic parameters have also been derived. Mechanism of the reactions are discussed.

Experimental:

The trans-Dinitrotetrammine Cobalt (III) nitrate used was the same as that used in the case of the mercury (II) catalysed aquation of the same complex already described.

Stock solution of thallic nitrate was prepared by a modified method employed by K. B. Gupta and Y. K. Gupta[17] as follows: Analar thallous nitrate was oxidized with bromine and thallic oxide was precipitated by treating the resulting solution with sodium hydroxide solution. The oxide was thoroughly washed until no more bromine was detected, and then dissolved in nitric acid. The oxide was reprecipitated and redissolved in nitric acid to ensure removal of foreign ions. The Stock solution was standardized as follows:- A known volume of Tl^{3+} in nitric acid solution was diluted to yield less than 0.5 M solution in nitric acid and added to a 2% solution of potassium iodide. The liberated iodine was

titrated against standard sodium thiosulphate solution. The end point was marked by the change from dirty blue to the clear yellow of the precipitate of thallous iodide. The dilution of the reaction mixture was necessary as concentrated solution of nitric acid liberate iodine from a solution KI. The final solution thus standardized was 0.519 M in 4.73 M nitric acid.

The tendency for Tl^{3+} ions to hydrolyse is greater than in the case of Hg^{2+}, therefore a higher concentration of the acid had to be used in order to suppress the hydrolysis as much as possible as mentioned earlier. Even then slight hydrolysis still took place as was observed in the rate data. This will be discussed later in the Chapter.

The concentration of the Tl^{3+} was varied at each temperature. This was done by calculating the various volumes necessary to give the desired concentrations in a 100 ml. solution. The concentrations of H^{+} ions in the various volumes were also calculated and the volume of acid to be taken in each case from a Stock solution of pure nitric acid to make total H^{+} ion concentration 0.4 M was also known. The ionic strength was maintained constant, this time, at 0.5 M using a Stock solution of 1 M sodium nitrate. These calculated volumes were pipetted out from the various Stock solutions into a round-bottomed flask with a known volume of water. This was then thermostated. The remaining volume to give the final 100 mls. of solution is the volume of water to be added. This latter volume was measured out accurately and used to dissolve a weighed quantity of the complex necessary to make the concentration of the complex 0.003 M in 100 ml. solution in a dark bottle. The solution in the dark bottle was shaken thoroughly to make

sure that all the crystals of the complex had gone into solution after which it was put in the thermostat set at the required temperature.

The kinetic part of the experiment followed exactly the same pattern as that described for the mercury (II) catalysed aquation.

Results and Discussion:

From the conditions of the experiments the various reactions were expected to be pseudo first-order and the plot of log $(OD_t - OD_\infty)$ against time for each of the Tl^{3+} concentrations at constant temperature showed good linearity except for an initial fast reaction. See Figures 3.7 to 3.10. The reaction was about sixty to seventy percent complete.

The various rate constant obtained for each of the temperatures are shown in Table 3.3. Plots of these observed rate constants against thallium (III) ion concentrations gave good linearity at all temperatures but with negative intercept which was contrary to what was expected (Figure 3.11). This graph however was plotted without given due consideration to the presence of $Tl(OH)^{2+}$. The various concentrations of $Tl(OH)^{2+}$ present in each of the Tl^{3+} concentration were calculated (from the hydrolysis constant vis 7.2×10^{-2} at 25^{o}) and the amount of Tl^{3+} existing in the hydrolysed form was substracted from the initial concentrations of Tl^{3+}. This latter concentrations of Tl^{3+} were then plotted against

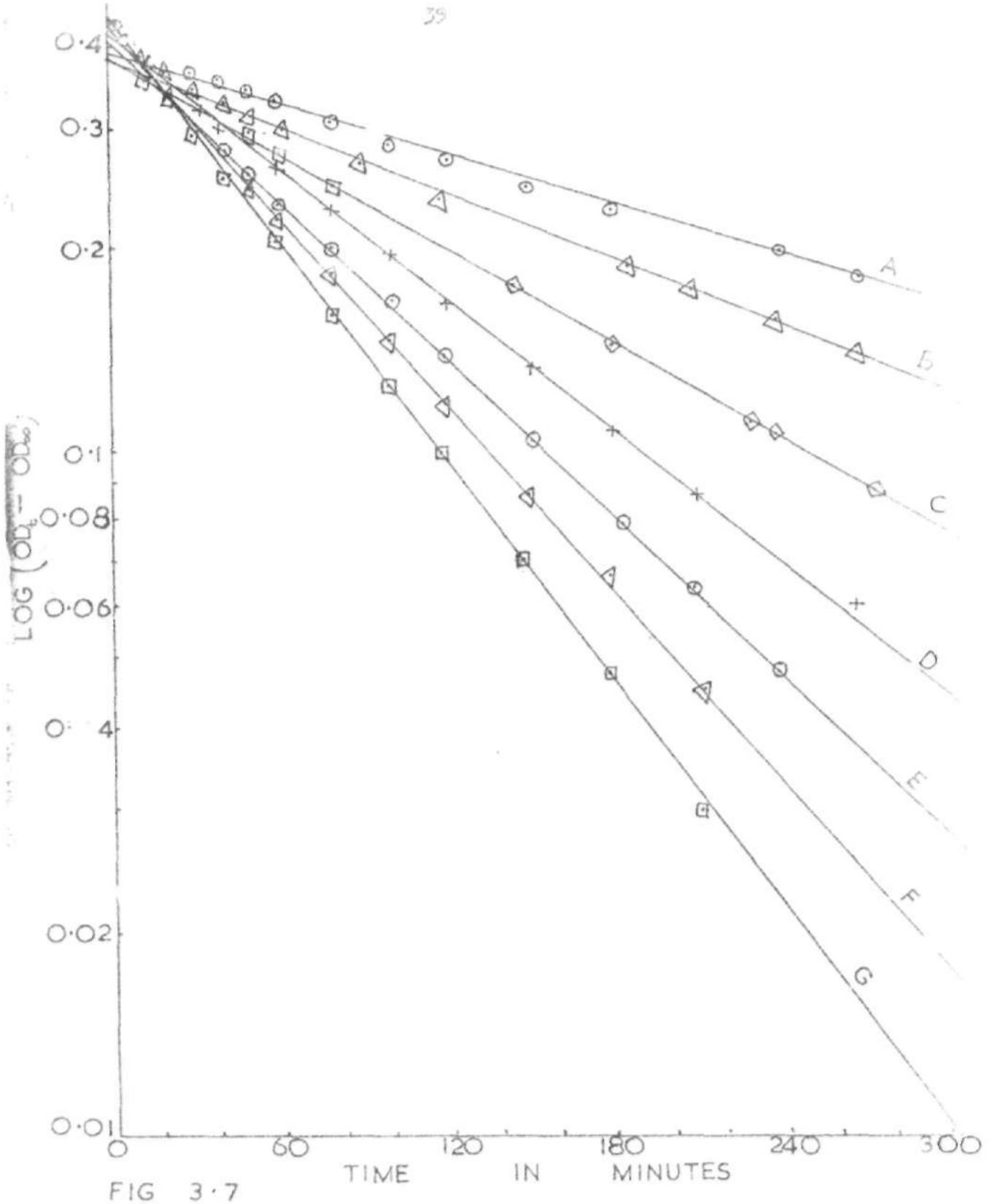


FIG 3·7

PLOTS OF LOG $(OD_t - OD_\infty)$ AGAINST TIME FOR DIFFERENT THALLIUM (III) ION CONCENTRATIONS AT 30.4°

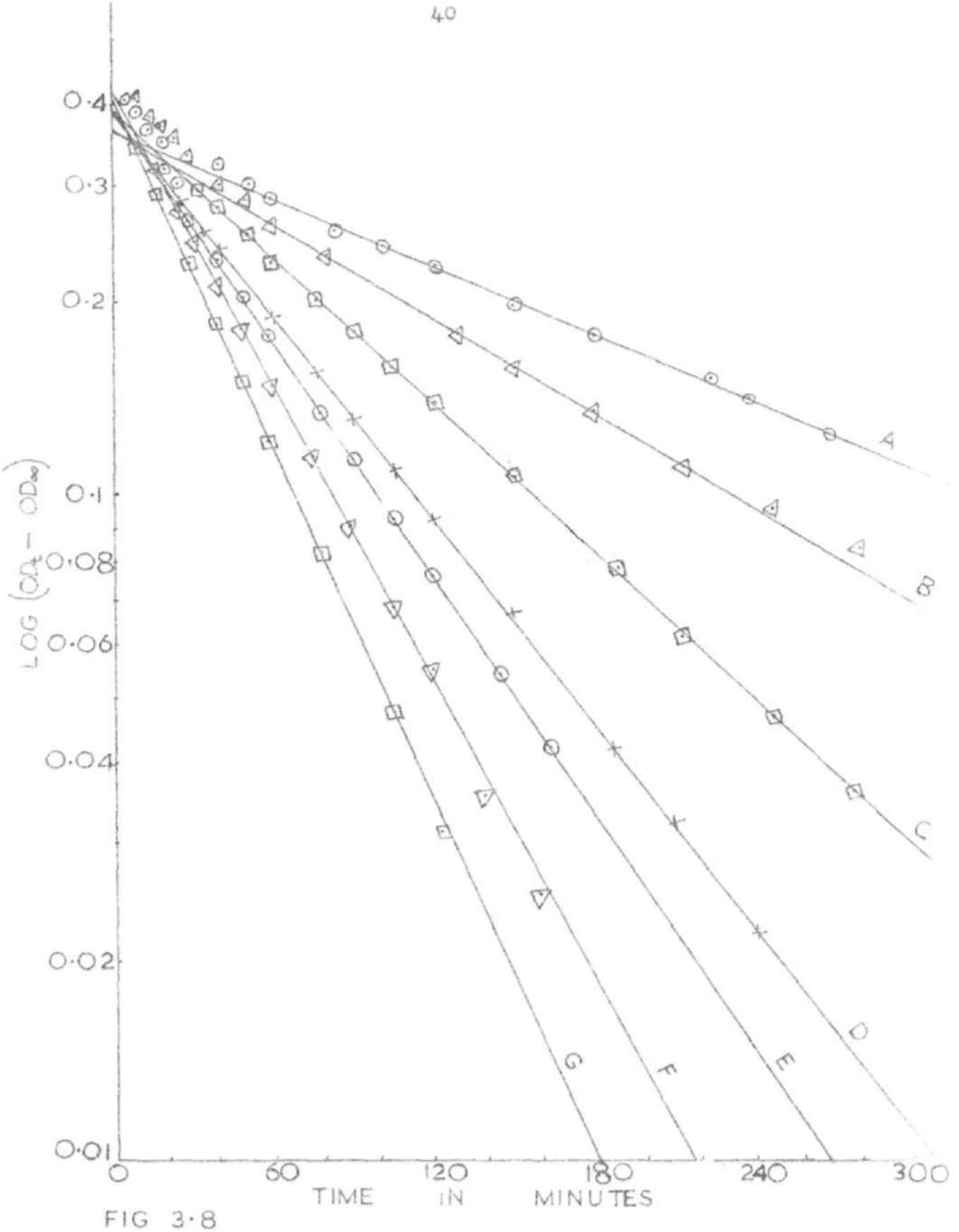


FIG 3·8

PLOTS OF LOG ($OD_t - OD_\infty$) AGAINST TIME FOR DIFFERENT THALLIUM (III) ION CONCENTRATIONS AT 34.7°

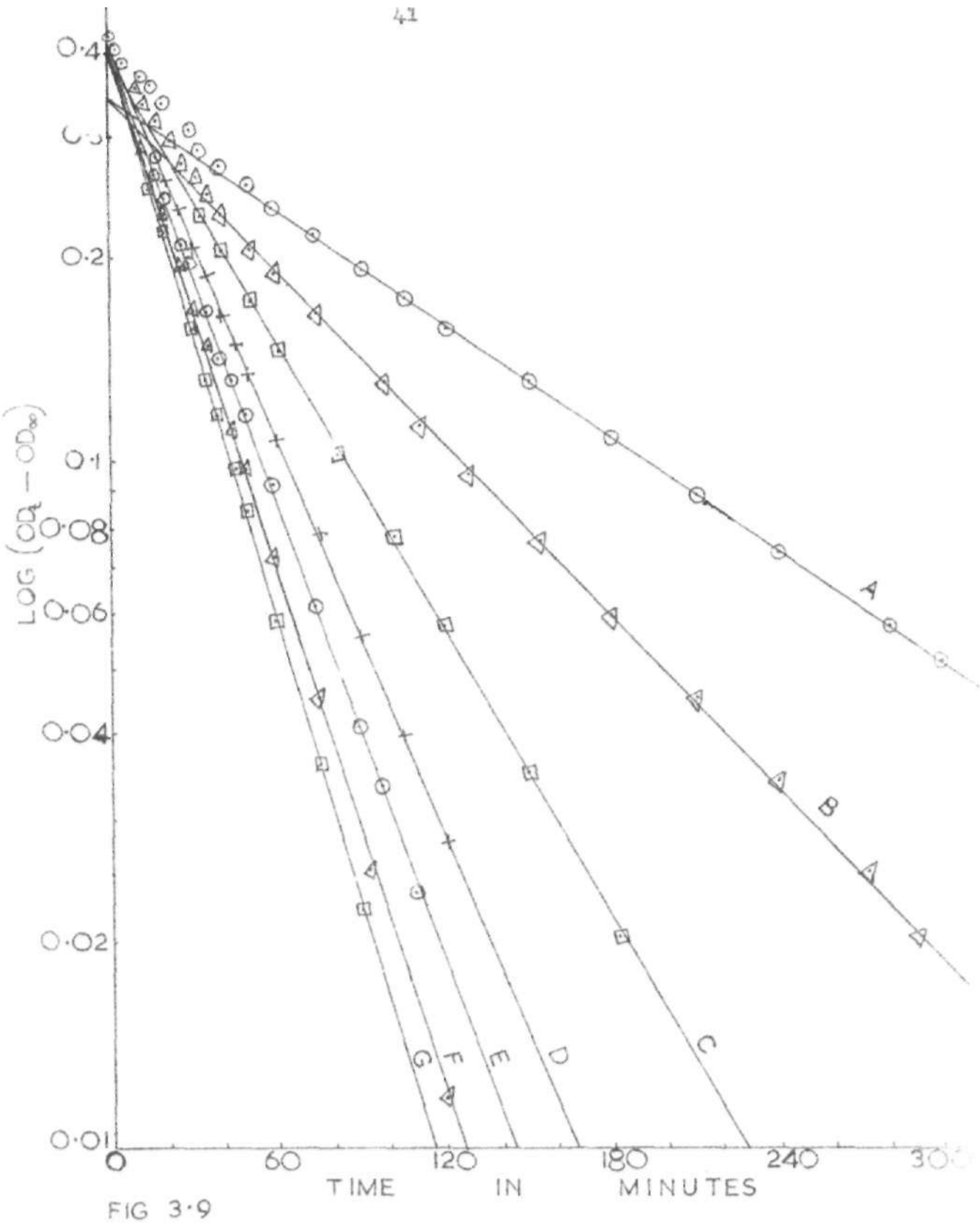


FIG 3·9

PLOTS OF LOG (OD_t OD_∞) AGAINST TIME FOR DIFFERENT THALLIUM (III) ION CONCENTRATION AT 40.0°

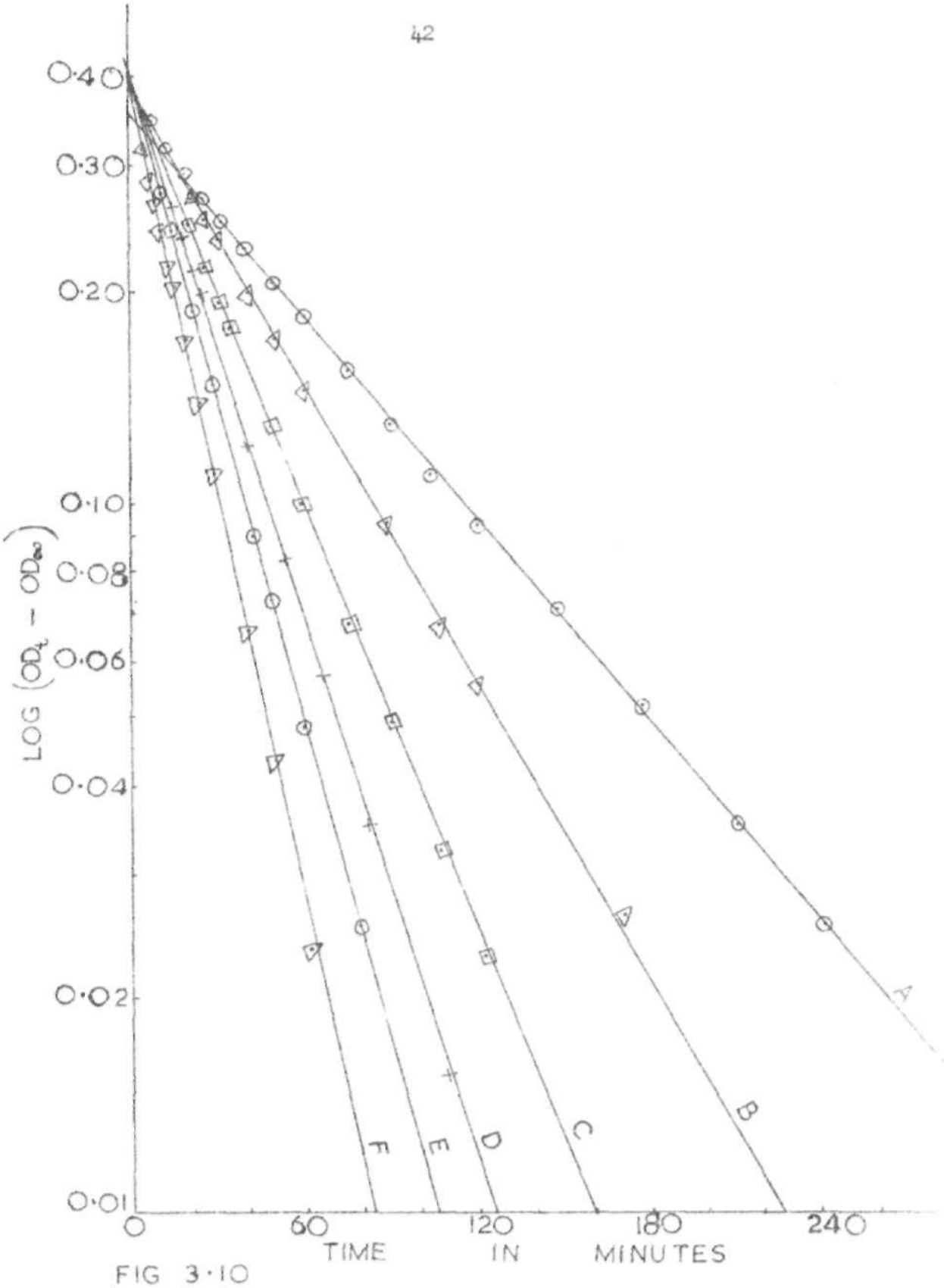


FIG 3·10

PLOTS OF LOG ($OD_t - OD_\infty$) AGAINST TIME FOR DIFFERENT THALLIUM (III) ION CONCENTRATIONS AT 44.2°

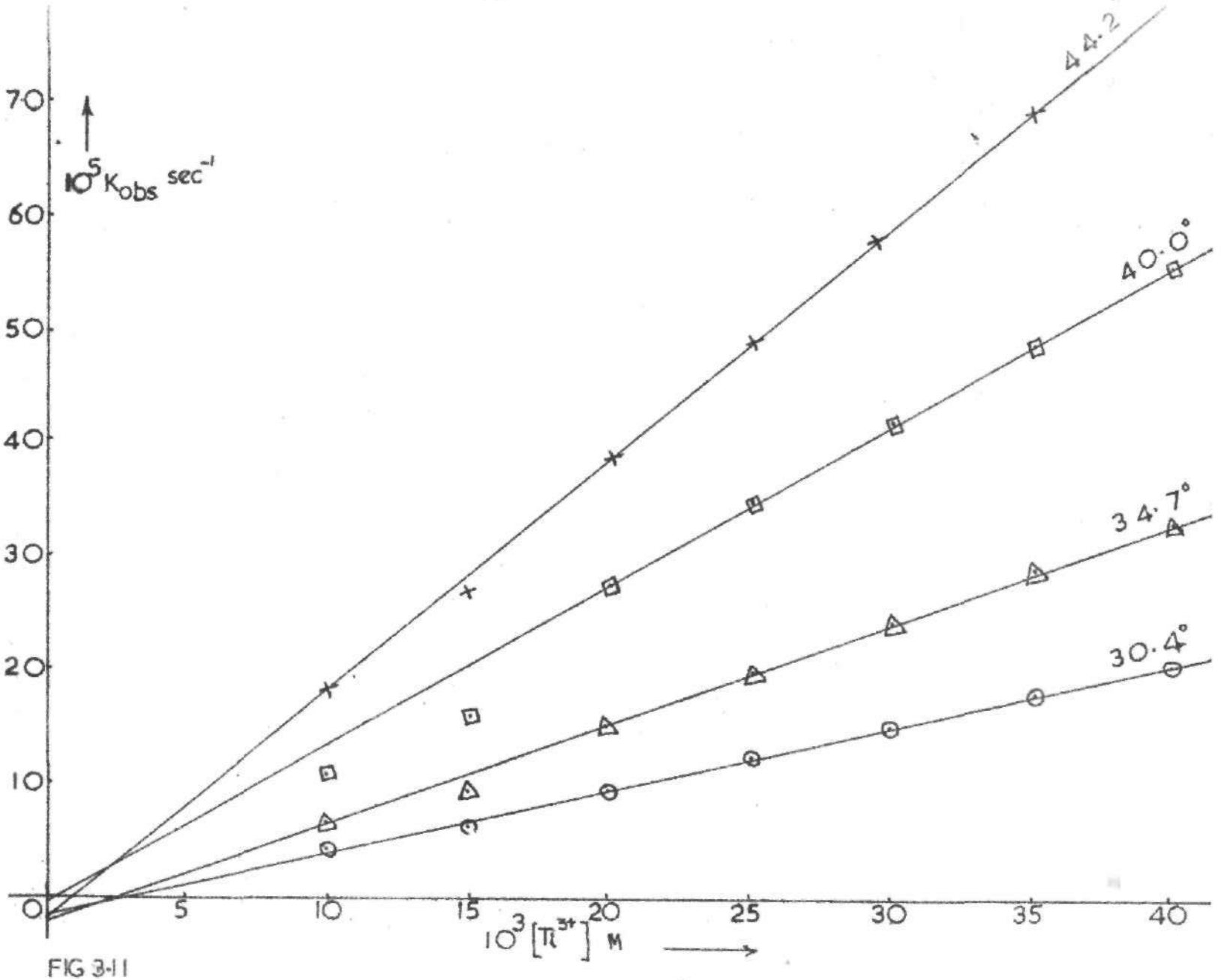


FIG 3-11

PLOTS OF OBSERVED RATE CONSTANT (k_{obs}) AGAINST THALLIUM (III) ION CONCENTRATION FOR $[Co(NO_3)_4(NO_2)_2]NO_3$

TABLE 3.3

Concentration of the acid was kept constant at 0.4 M
The total ionic strength was also kept constant at 0.5 M

$10^3[\text{Complex}]$ M	$10^3[Tl^{3+}]$ Initial	$10^3[Tl^{3+}]$M After Correction	$10^5 k_{obs}$ (Sec^{-1})	$10^3[\text{Complex}]$ M	$10^3[Tl^{3+}]$ Initial	$10^3[Tl^{3+}]$ After Correction	$10^5 k_{obs}$ (Sec^{-1})
	30.4°				34.7		
3.00	A = 10	9.28	4.77	2.98	A = 10.00	9.28	6.76
3.00	B = 15	13.92	6.32	3.01	B = 15.00	13.92	8.87
3.00	C = 20	18.56	9.32	3.00	C = 20.00	18.56	14.48
3.01	D = 25	23.20	12.49	3.00	D = 25.00	23.20	19.98
3.00	E = 30	27.84	15.21	3.00	E = 30.00	27.84	24.13
3.00	F = 35	32.48	18.06	3.01	F = 35.00	32.48	29.44
3.00	G = 40	37.12	20.25	3.00	G = 40.00	37.12	34.55
	40°				44.2°		
3.01	A = 10	9.28	10.98	3.01	A = 10	9.28	18.65
3.01	A = 15	13.92	16.03	3.00	B = 15	13.92	26.56
3.01	C = 20	18.56	27.62	2.99	C = 20	18.56	39.08
3.01	D = 25	23.20	36.55	2.99	D = 25	23.20	49.14
3.01	E = 30	27.84	42.42	3.00	E = 30	27.84	59.05
3.01	F = 35	32.48	48.85	2.99	F = 35	32.48	75.46
3.02	G = 40	37.12	55.02				

the observed rate constants and straight line graphs passing through the origin were obtained for all temperatures. See Figure 3.12. The zero intercept is an indication that in this system, unlike the Hg^{2+} catalysed system, H^+ ions catalysed aquation was negligible.

The mechanism of this reaction can be said to follow the same pattern as that described for the mercury (II) catalysed aquation of the same complex under consideration. The rate expression can therefore be written as

$$\text{Rate} = \frac{\left\{K_o + k_1^1\left[H^+\right] + k_2^1\left[Tl^{3+}\right]\right\}Co^{III}_{tot}}{1 + K_1\left[H^+\right] + K_2\left[Tl^{3+}\right]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.13)$$

Since spontaneous aquation is very slow just as with the previous case, and since equilibria similar to (3.1) and (3.2) involve the association of like charges, the stability constants K_1 and K_2 will also be very small, so that $1 \gg K_1\left[H^+\right] + K_2\left[Tl^{3+}\right]$. Therefore equation 3.13 reduces to

$$\text{Rate} = \left\{k_1^1\left[H^+\right] + k_2^1\left[Tl^{3+}\right]\right\} Co^{II}_{tot} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.14)$$

$$\therefore \quad k_{obs} = k_1^1\left[H^+\right] + k_2^1\left[Tl^{3+}\right]$$

But in the acidity condition used the hydrogen ion was found not to take part in the reaction

$$\therefore \quad k_{obs} = k_2^1\left[Tl^{3+}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.15)$$

If this proposed mechanism is correct then a plot of k_{obs} against $\left[Tl^{3+}\right]$ should be a straight line graph with a zero intercept, and the slope of

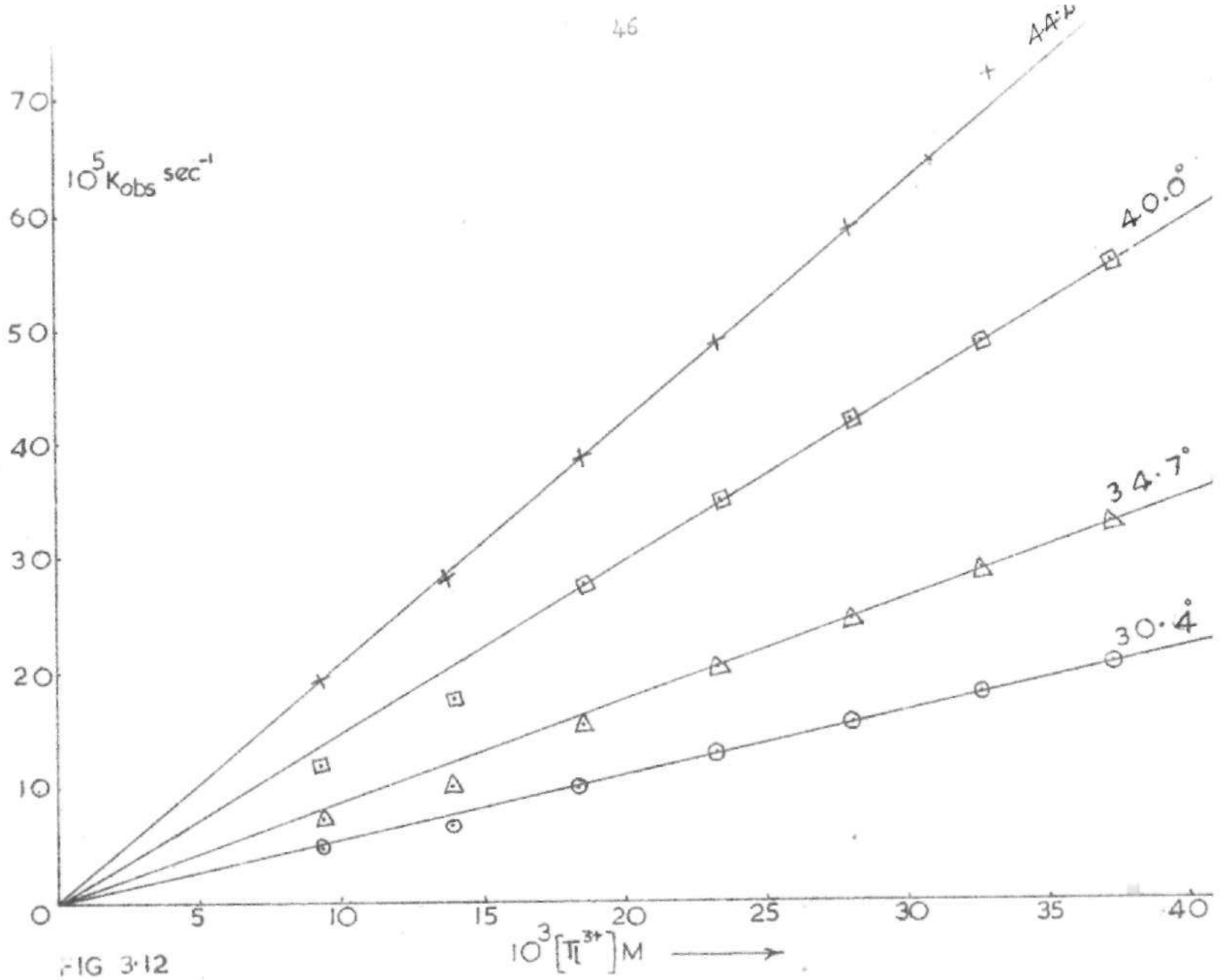


FIG 3·12

PLOTS OF OBSERVED RATE CONSTANT AGAINST CORRECTED THALLIUM (III) ION CONCENTRATION FOR $[Co(NH_3)_4(NO_2)_2]NO_3$

which should give k_2^1. This is in agreement with the experimental results after the appropriate correction for the base catalysed reaction due to hydrolysis had been made.

The values of k_2^1 at each temperature derived from the slopes are given in Table 3.4. Arrhenius plot for the aquation reaction is shown in Figure 3.13.

TABLE 3.4

Variation of rate parameter with temperaure

Temperature	$10^3 k_2^1$ (Sec^{-1})
30.4°	6.04
34.7°	8.75
40.0°	13.55
44.2°	21.40

The calculated activation energy Ea and entropy of activation ($\Delta\delta^*$) for the reaction are Ea = 16.6 k cals/mole; $\Delta\delta^*$ = -6.80 e.u.

Looking at the data obtained it is obvious that thallium (III) ion is a better catalyst than mercury (II) ion in the aquation of trans-dinitrotetrammine Cobalt (III) nitrate. This fact is supported by the slightly lower activation energy obtained in the case of thallium (III) [16.6 cal/mole] as compared to 18.6 k cal/mole for mercury (II). This will be discussed in some details in the last Chapter.

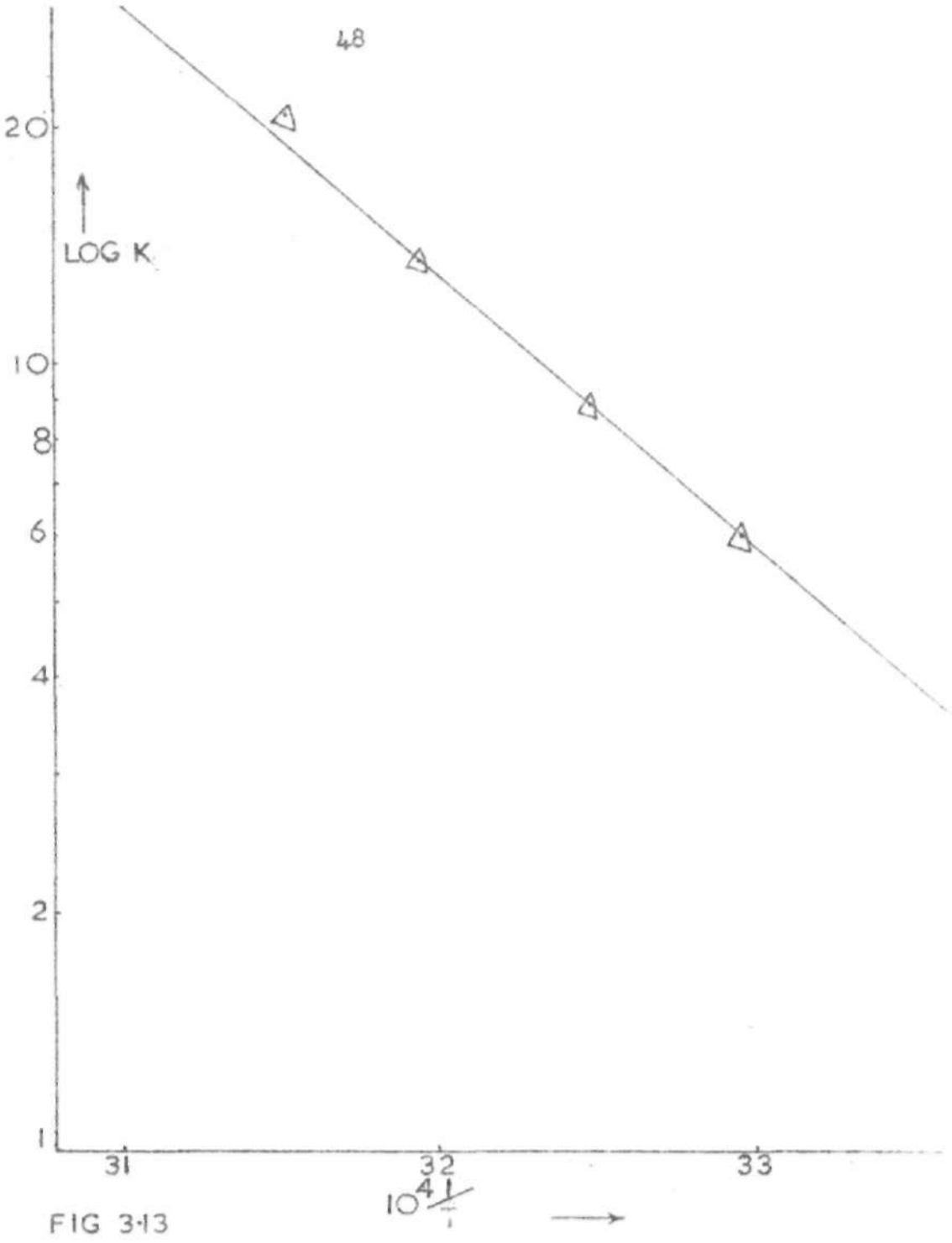


FIG 3·13

ARRHENIUS PLOT FOR THE THALLIUM (III) CATALYSED AQUATION OF $[Co(NH_3)_4(NO_2)_2]NO_3$

CHAPTER 4

This Chapter deals with the aquation of trans-dinitro bisethylenediamine Cobalt (III) nitrate using mercury (II) and thallium (III) cations as catalysts. The acid-catalysed aquation of this same complex had been studied by Staples[14] at 25; 35 and 35° and at ionic strength of 3.5 M. In his investigation, Staples discovered that aquation rate could only be studied in strongly acid solutions whereas in neutral or faintly acidic solutions the rate of aquation was immeasurably slow. With this in view higher concentrations of both the acid and cations were used to study the aquation of this complex than were used for the tetrammine analogue.

4.1 MERCURY (II) - CATALYSED AQUATION OF TRANS-DINITRO-BIS ENTHYLENEDIAMINE COBALT (III) NITRATE:

The mercury (II) catalysed aquation of trans-dinitro bis-ethylenediamine Cobalt (III) nitrate was studied at 35, 40, 45 and 50° over a wide range of mercury ion concentration (0.02-0.30 M) at ionic strength of 1.5 M. The concentration of the acid was maintained constant at 1 M. Within this concentration range used the increase in rate may be interpreted in terms of the reactions of the complex ions $\left[Co(en)_2(NO_2)(NO_2H)\right]^{2+}$ and $\left[Co(en)_2(NO_2)(NO_2Hg)\right]^{3+}$. Reaction rate constants and thermodynamic parameters have been derived and the mechanisms of the

reactions are discussed.

Experimental:

The trans-dinitro bis ethylenediamine Cobalt (III) nitrate used was prepared by methods described in the literature[18]. The analysis of the complex was carried out by determining its Cobalt content. The percentage of the Cobalt was found to be 17.9 as against the theoretical value of 17.7. All reagents used were of A.R. grade.

Preparation of other solutions were carried out in exactly the same way as those described for the mercury (II) catalysed aquation of trans-dinitrotetrammine Cobalt (III) nitrate, except that higher concentrations of both the acid and Hg^{2+} were used. The acid was maintained constant at 1.0 M and the concentrations of Hg^{2+} was varied between 0.02 and 0.30 M. The initial concentration of the complex used was about 0.003 M and the ionic strength of the medium was kept constant at 1.5 M.

Kinetics:

The kinetic measurements followed the same pattern as those described for the tetrammine complex. The wavelength of 440 nm was chosen for these measurements although Staples chose 400 nm for his measurements. The significance of these two wavelength is that 440 nm is the wavelength of maximum absorption for the complex, and 400 nm is the wavelength of common extinction coefficient for the trans and cis complexes respectively. Staples used the latter because he was interested in the comparison of the rates of reaction of the cis- and trans-complexes. In the present work, since the concentration of the complex must not be greater than 3.0×10^{-3} M

if pseudo first order conditions were to be established, the emphasis was on the wavelength of greatest absorption. Preliminary investigations showed that the wavelength of 440 nm was the most suitable.

Results and Discussions:

The conditions of the experiment were such as to make the reaction pseudo first-order. The reaction was about fifty to sixty percent complete. The plot of log $(OD_t - OD_\infty)$ against time for each of the Hg^{2+} concentrations used for a particular temperature gave good linearity within this limit. These are shown in Figure 4.1-4.4. The various rate constants obtained for each of the temperatures are shown in Table 4.1 and plots of these observed rate constants against mercury ion concentration gave good linearity at all temperatures. See Figure 4.5.

TABLE 4.1

Concentration of the acid kept constant at 1.0 M
Total ionic strength was also kept constant at 1.5 M

$[Hg^{++}]$M	$10^5 k_{obs}$ (Sec^{-1})	$[Hg^{++}]$ M	$10^5 k_{obs}$ (Sec^{-1})
	34.6°		40.6°
A = 0.02	3.80	A = 0.02	8.08
B = 0.5	5.60	B = 0.05	11.00
C = 0.10	7.61	C = 0.10	14.25
D = 0.20	11.15	D = 0.20	19.26
E = 0.30	14.61	E = 0.30	27.65
	44.7°		49.7°
A = 0.02	13.90	A = 0.02	22.20
B = 0.05	17.50	B = 0.05	32.50
C = 0.10	25.30	C = 0.10	49.10
D = 0.20	33.50	D = 0.20	64.40
E = 0.30	44.45	E = 0.30	86.50

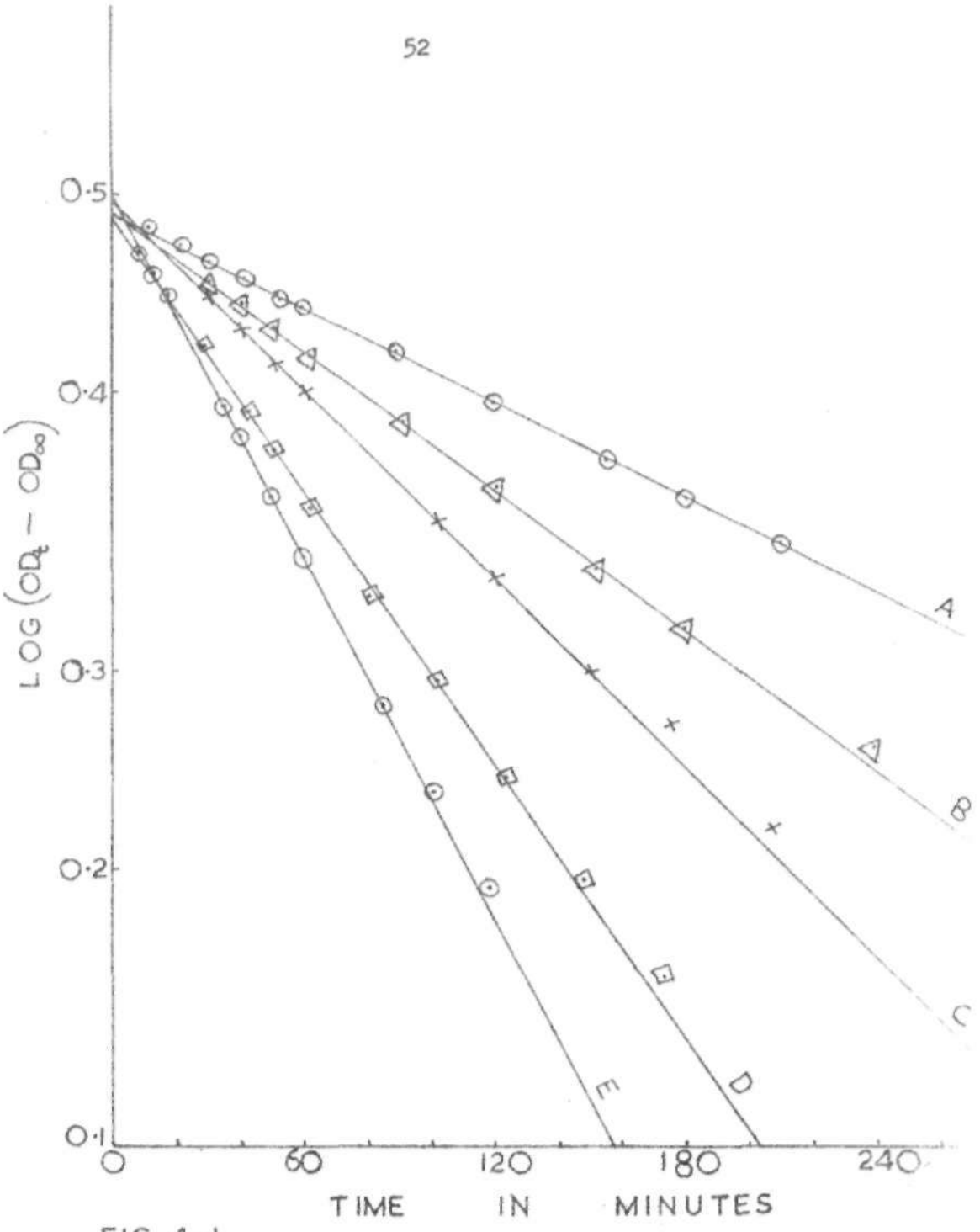


FIG 4·1

PLOTS OF LOG ($OD_t - OD_\infty$) AGAINST TIME FOR DIFFERENT MERCURY (II) ION CONCENTRATIONS AT 34.6°

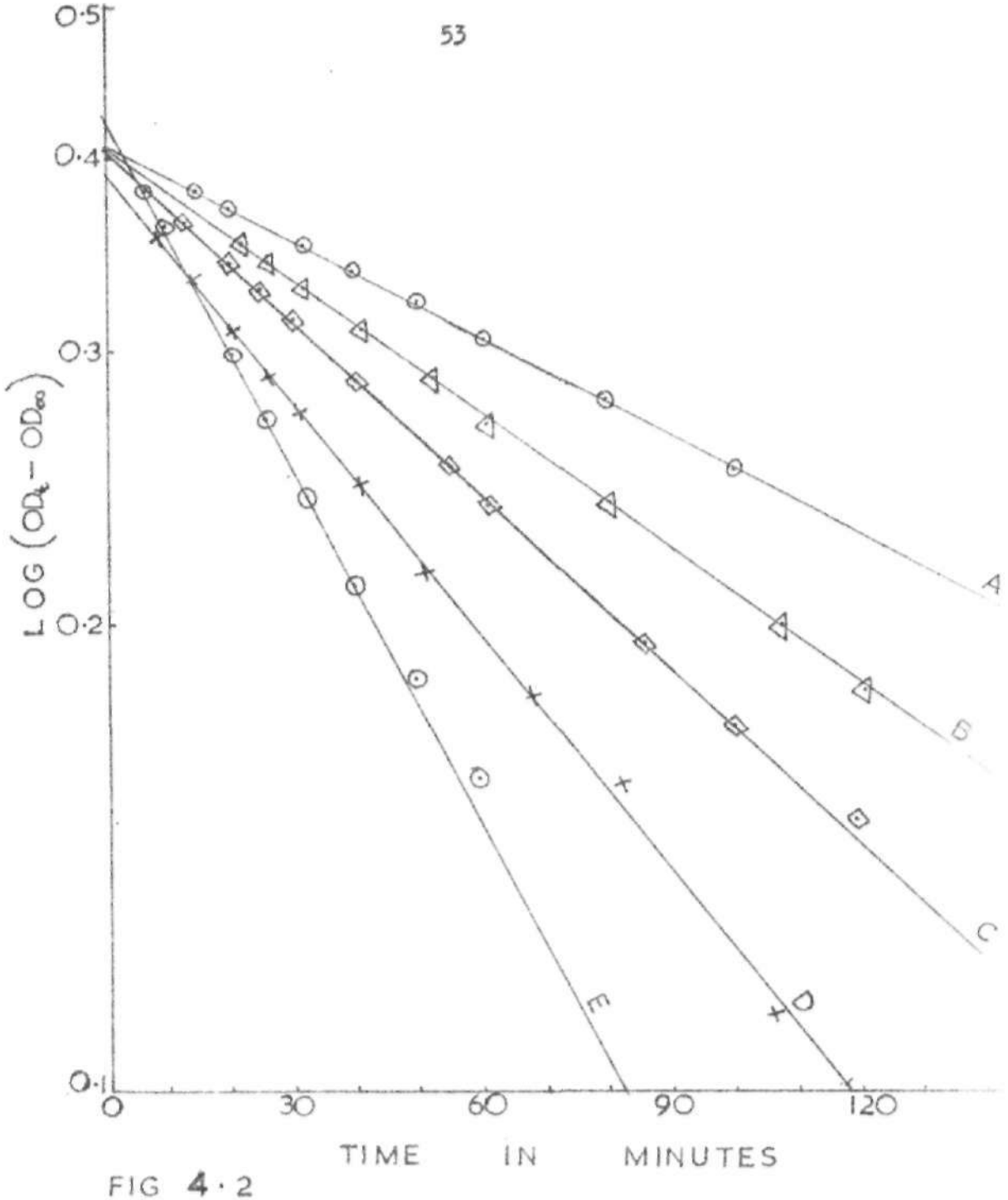


FIG 4·2

PLOTS OF LOG (OD_t-OD_∞) AGAINST TIME FOR DIFFERENT MERCURY (II) ION CONCENTRATIONS AT 40.6°

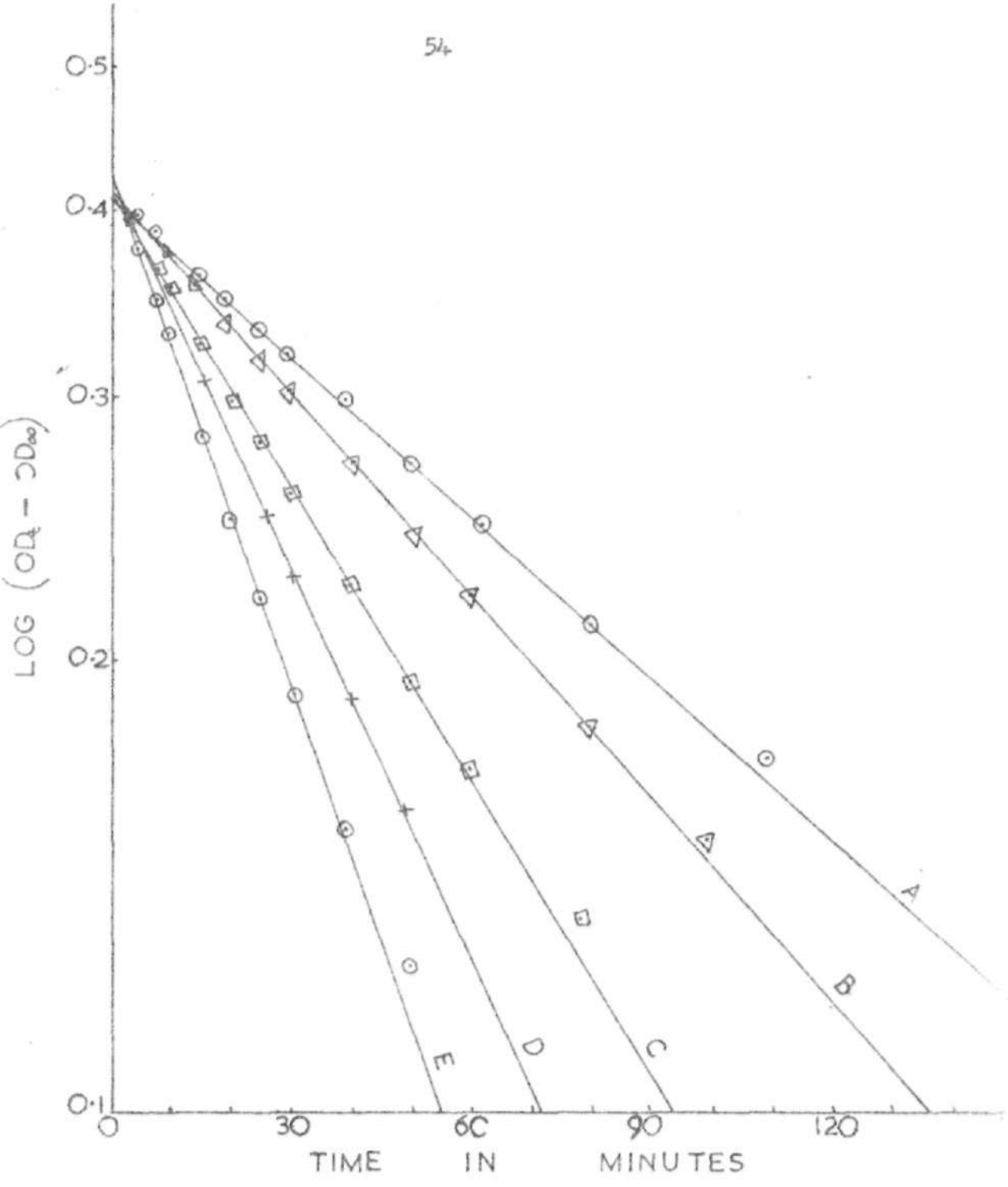


FIG 4·3

PLOTS OF LOG ($OD_t - OD_\infty$) AGAINST TIME FOR DIFFERENT MERCURY (II) ION CONCENTRATIONS AT 44.7°

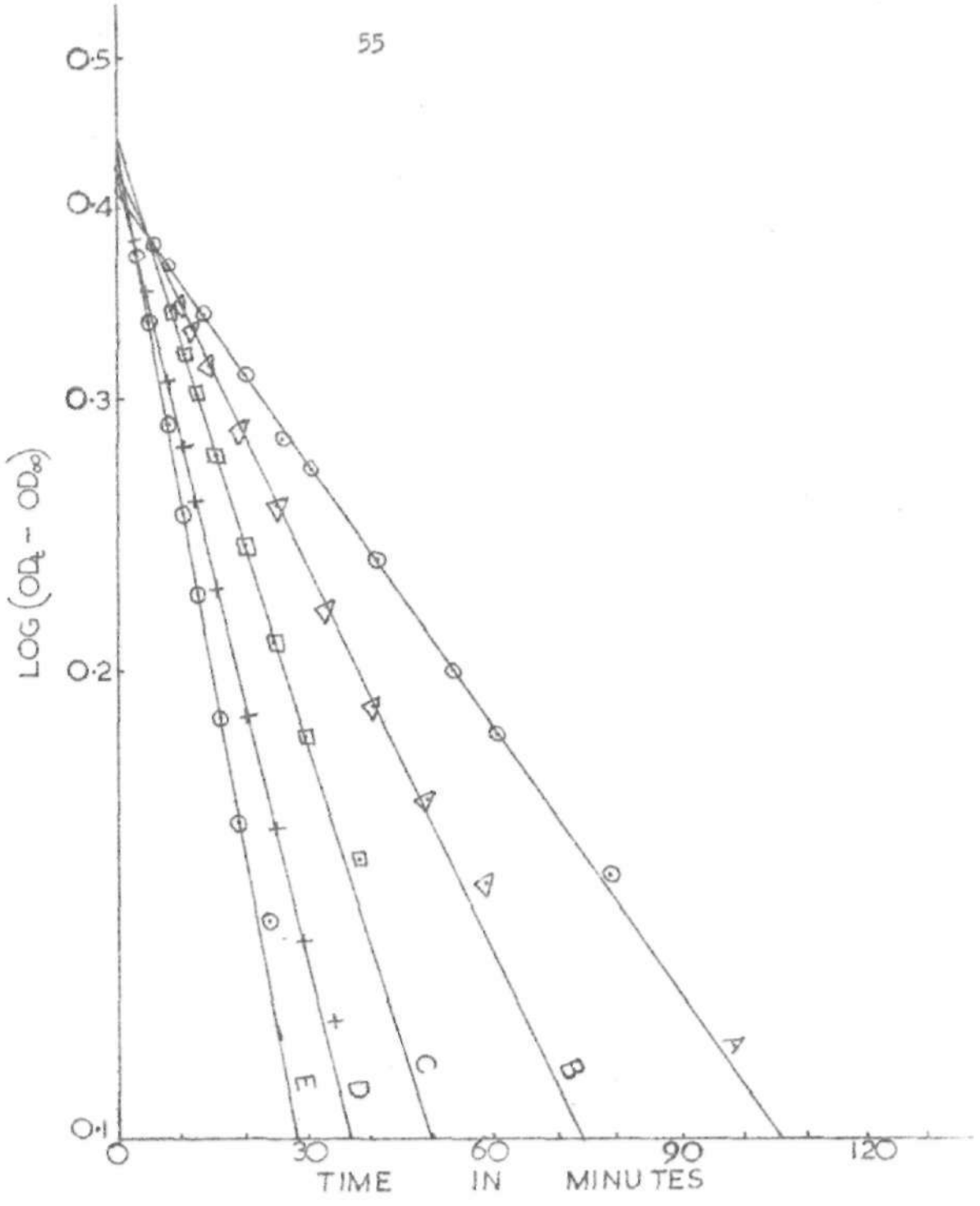


FIG 4·4

PLOTS OF LOG ($OD_t - OD_\infty$) AGAINST TIME FOR DIFFERENT MERCURY (II) ION CONCENTRATIONS AT 49.7°

Just as in the case of the trans-dinitro-tetrammine Cobalt (III) nitrate, the acid also played the dual role of a catalyst as well as a suppressor of hydrolysis. The rate equation similar to that stated for the reaction of the tetrammine complex is also proposed, i.e.

$$\text{Rate} = \frac{\left\{k_o + k_1^1\left[H^+\right] + k_2^1\left[Hg^{++}\right]\right\}Co^{II}_{tot}}{1 + K_1\left[H^+\right] + K_2\left[Hg^{++}\right]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.9)$$

and

$$k_{obs} = k_1^1\left[H^+\right] + k_2^1\left[Hg^{++}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.12$$

A straight line graph is therefore expected from a plot of k_{obs} against $\left[Hg^{++}\right]$ for each of the temperatures with a slope equal to k_2^1 and intercept equal to $k_1^1\left[H^+\right]$. Figure 4.5 shows good linearity at all temperatures in agreement with the postulate. The values of k_1^1 and k_2^1 at each temperature derived from the intercepts and slopes are given in Table 4.2. Arrhenius plots of the equations involving the two intermediate species are shown in Figure 4.6.

TABLE 4.2

Variation of rate parameters with temperature

Temperature	$10^5\ k_1^1\ (Sec^{-1})$	$10^5\ k_2^1\ (Sec^{-1})$
34.6	3.50	3.84
40.6	7.00	7.28
44.7	12.50	10.52
49.7	21.50	21.54

The calculated activation energies (Ea) and entropies of activation

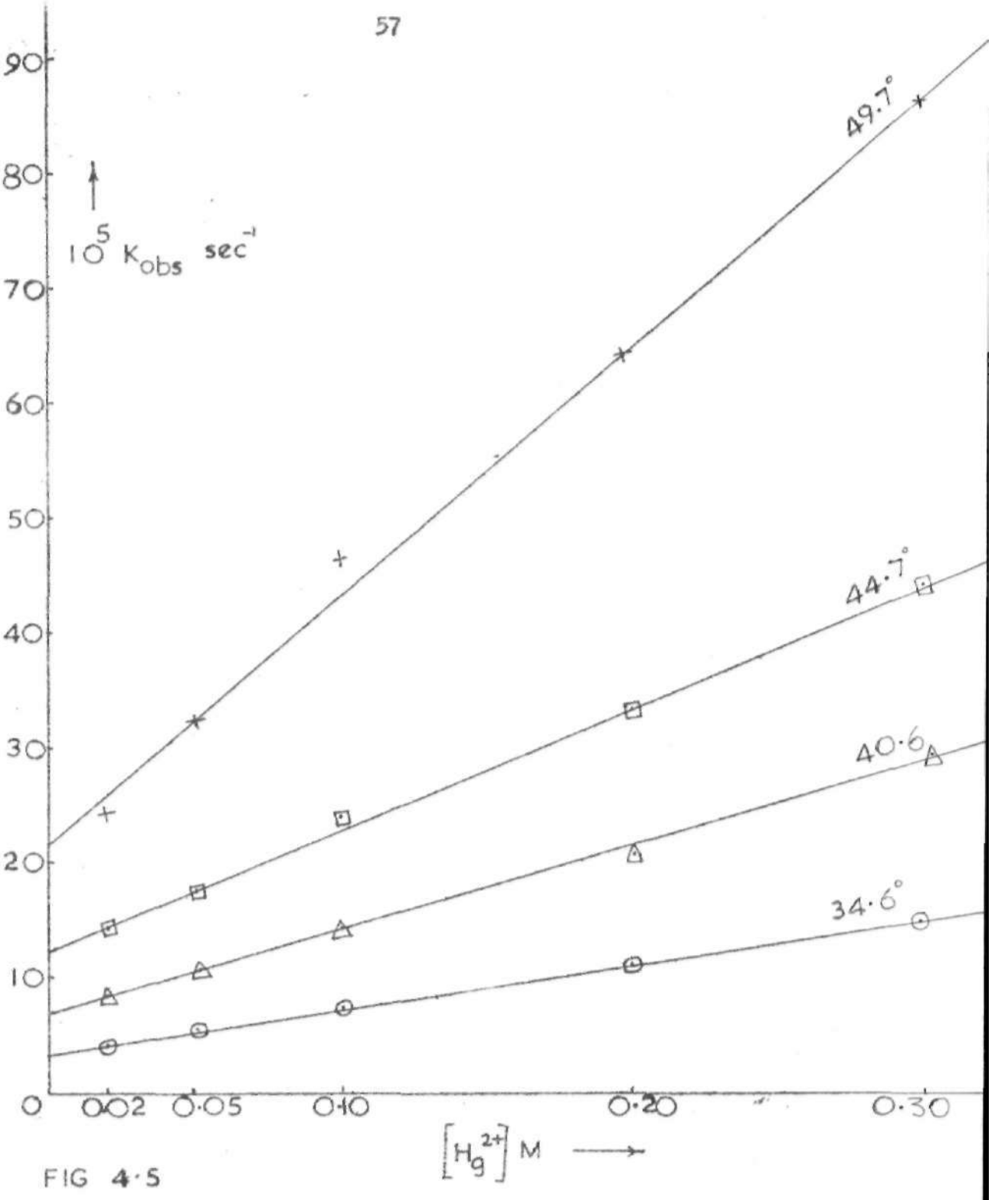


FIG 4·5

GRAPH OF OBSERVED RATE CONSTANT AGAINST MERCURY (II) ION CONCENTRATION FOR $[Co(en)_2(NO_2)_2]NO_3$

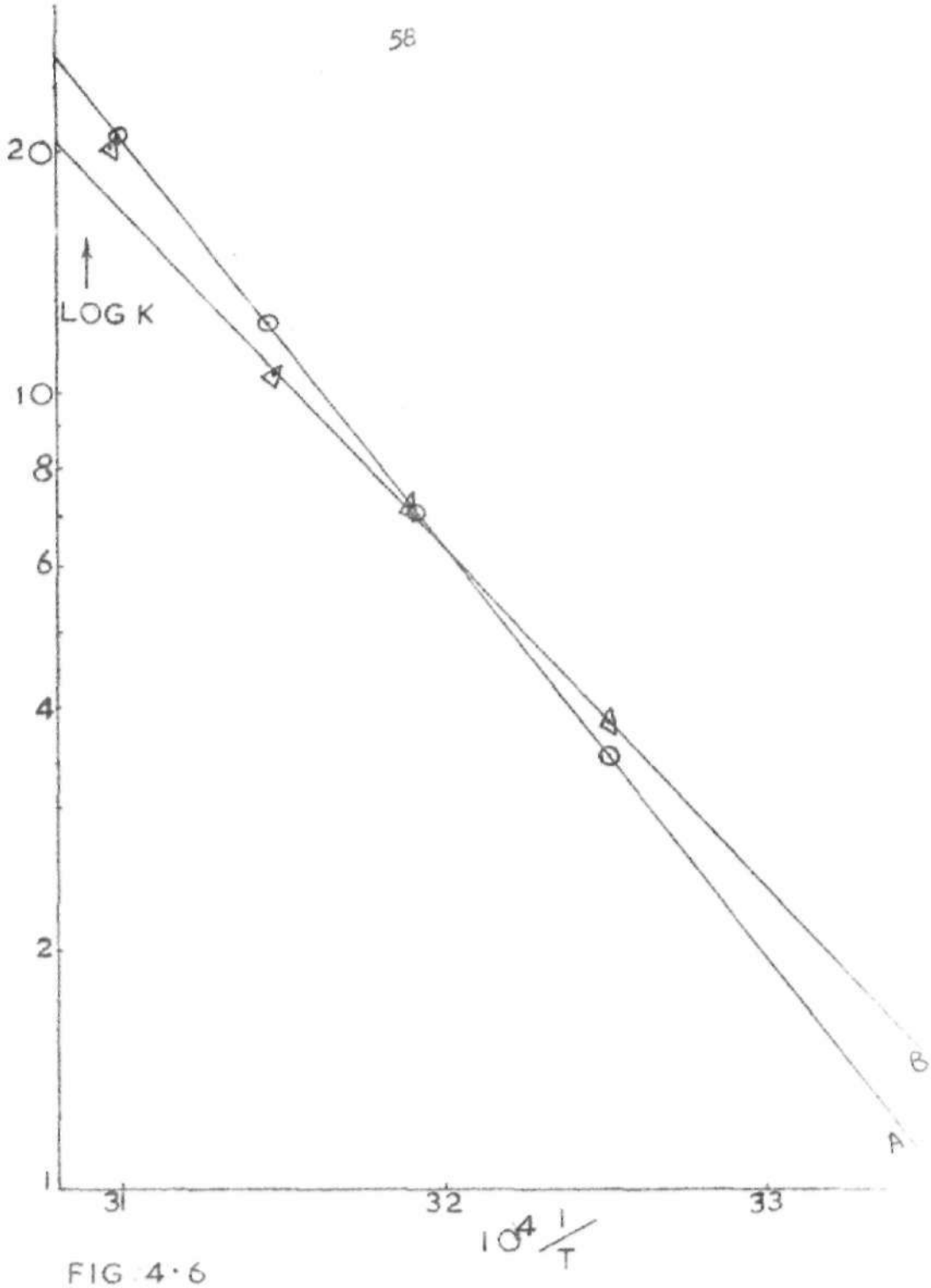


FIG 4·6

ARRHENIUS PLOTS: FOR THE MERCURY (II) CATALYSED AQUATION OF $[Co(en)_2(NO_2)_2]NO_3$

A = REACTION INVOLVING THE PROTONATED SPECIES

B = REACTION INVOLVING MERCURY (II) ASSOCIATED SPECIES

(ΔS^*) for the reactions are:

Ea = 23.4 K cals/mole; $\Delta S^* = -4.56$ eu (for the protonated species at 25°C)

and

Ea = 19.2 K cals/mole; $\Delta S^* = -13.6$ eu (for the mercury (II) associated species at 25°C)

The Ea value for the singly protonated species compared favourably with that obtained by Staples[14] in purely acid medium [25.6 K cal/mole].

4.2 THALLIUM (III) CATALYSED AQUATION OF TRANS-DINITRO-BIS-ETHYLENEDIAMINE COBALT (III) NITRATE:

The aquation of the same complex just discussed was also investigated at 30, 35, 40 and 45°C using thallium (III) metal ion as catalyst. At the range of thallium (III) ion concentrations used (0.02-0.20 M) and constant ionic strength of 2.0 M, the increase in rate may be interpreted in terms of two intermediate ion species $\left[Co(en)_2(NO_2)(NO_2H)\right]^{2+}$ and $\left[Co(en)_2(NO_2)(NO_2Tl)\right]^{4+}$. Reaction rate constants and thermodynamic parameters have been calculated. The mechanisms of the reactions are also discussed.

Experimental and Kinetics:

The experimental and kinetics part of this study is the same as that described for complex I except that higher concentrations of both the acid and thallium (III) were used; 1.8 M acid, 0.02-0.20 M Tl^{3+}, 0.003 M complex and the ionic strength of the medium was maintained constant at 2.0 M.

Results and Discussions:

The conditions of the experiment, like in the previous ones, were such as to make the reaction pseudo first order and plots of log $(OD_t - OD_\infty)$ against time gave good straight lines for all the temperatures. See Figures 4.7-4.10. The initial fast reaction observed in the case of the tetrammine was not observed here probably due to the higher concentration of acid used. The reaction was about fifty to sixty percent complete at all temperatures.

Table 4.3 show the various rate constants obtained for each of the temperature and plots of these observed rate constants against thallium (III) ion concentrations gave good linearity at all temperatures in agreement with the postulate. See Figure 6.11.

TABLE 5.3

Concentration of the acid was kept constant at 1.8 M
The total ionic strength was also kept constant at 2.0 M

$10^3[Tl^{3+}]$	$10^5 k_{obs}$ (Sec^{-1})	$10^3[Tl^{3+}]$ M	$10^5 k_{obs}$ (Sec^{-1})
	30.0°C		35.0°C
A = 0.02	4.80	A = 0.02	9.21
B = 0.05	5.92	B = 0.05	10.50
C = 0.10	7.20	C = 0.10	13.10
D = 0.20	9.35	D = 0.20	16.60
	39.5°		44.2°
A = 0.02	14.07	A = 0.02	23.50
B = 0.05	17.08	B = 0.05	28.10
C = 0.10	19.88	C = 0.10	33.00
D = 0.20	29.40	D = 0.20	43.20

In the case of the trans-dinitrotetrammine Cobalt (III) complex

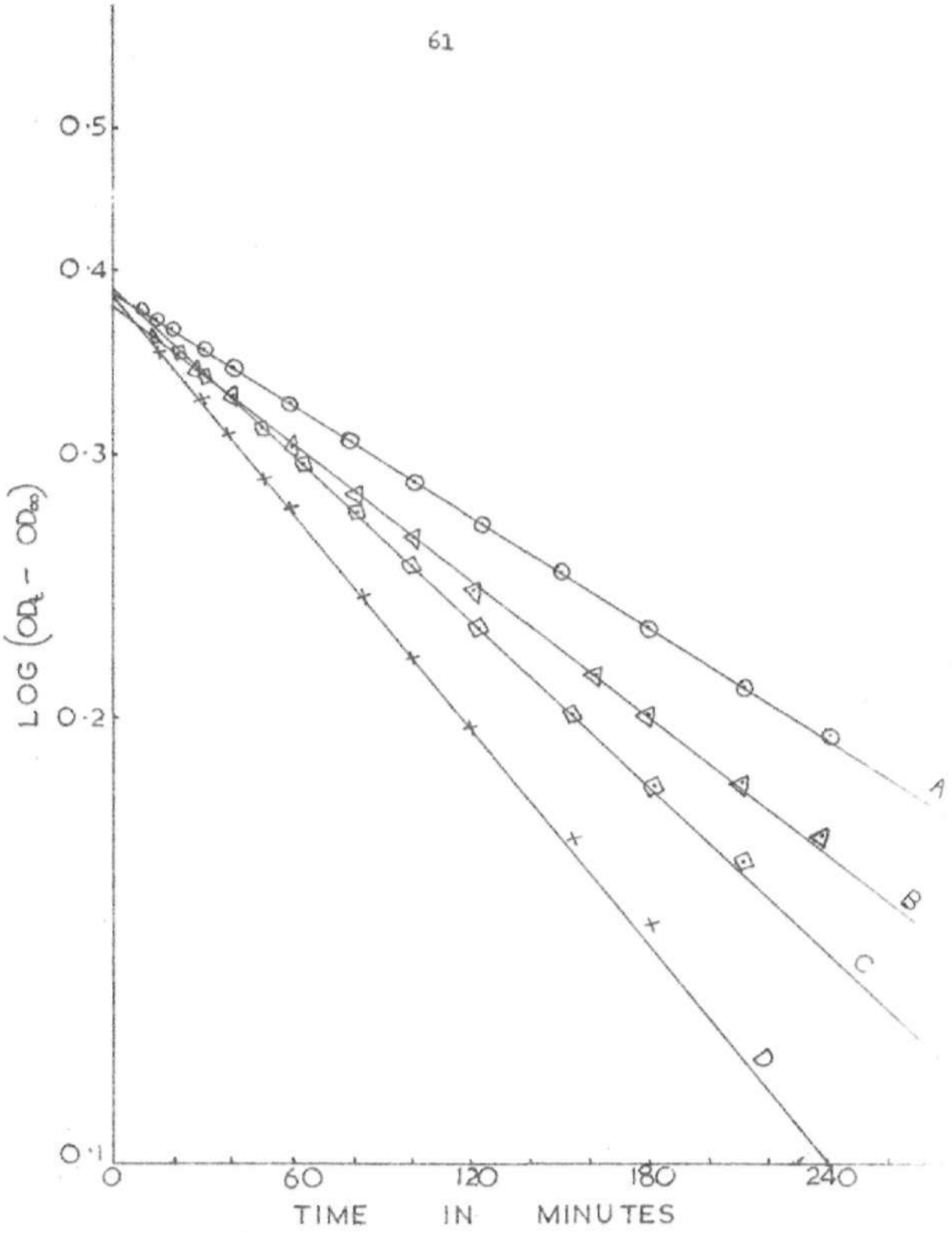


FIG 4·7

PLOTS OF LOG ($OD_t - OD_\infty$) AGAINST TIME FOR DIFFERENT THALLIUM (III) ION CONCENTRATIONS AT 30.0°

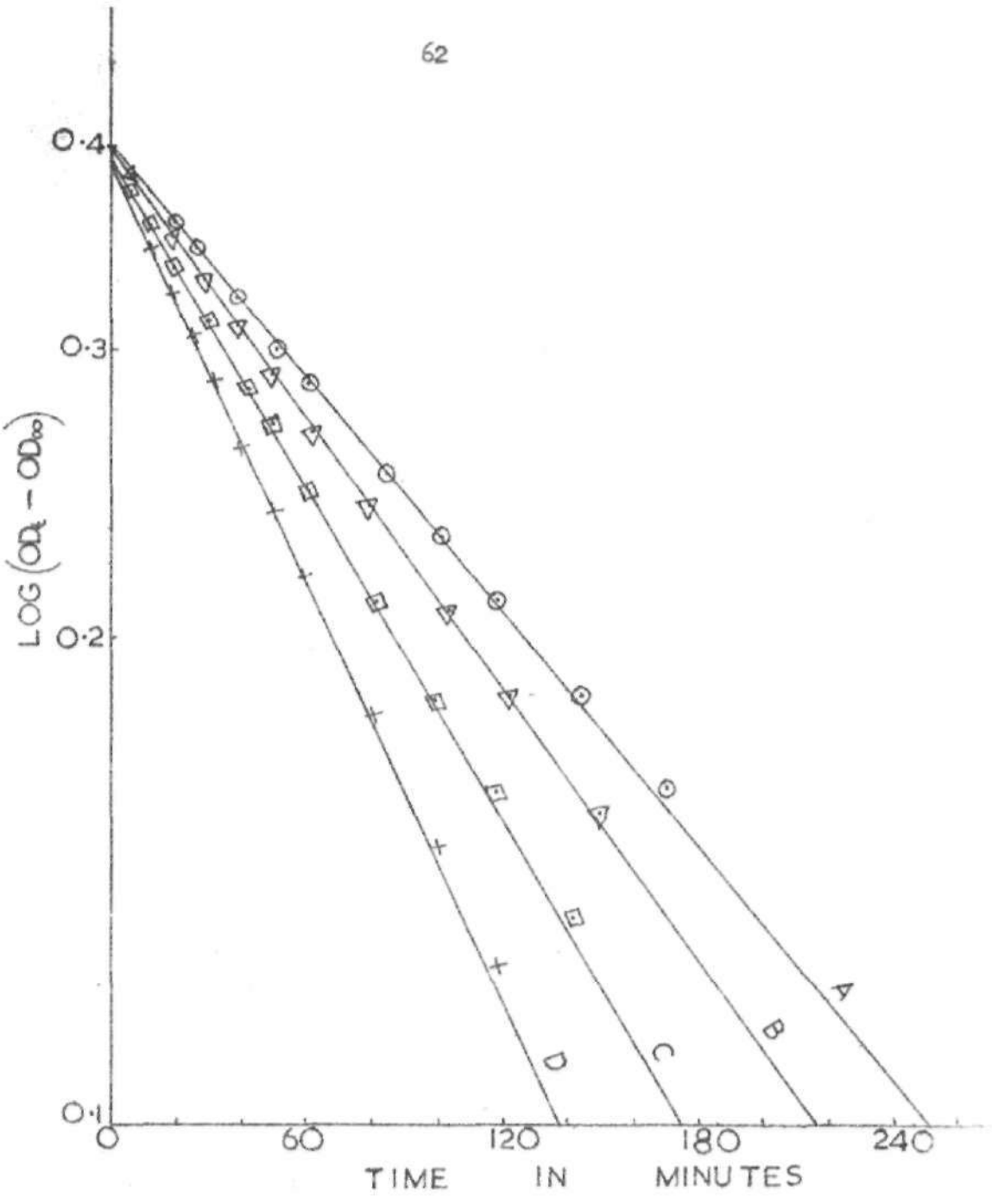


FIG 4·8

PLOTS OF LOG ($OD_t - OD_\infty$) AGAINST TIME FOR DIFFERENT THALLIUM (III) ION CONCENTRATIONS AT 35.0°

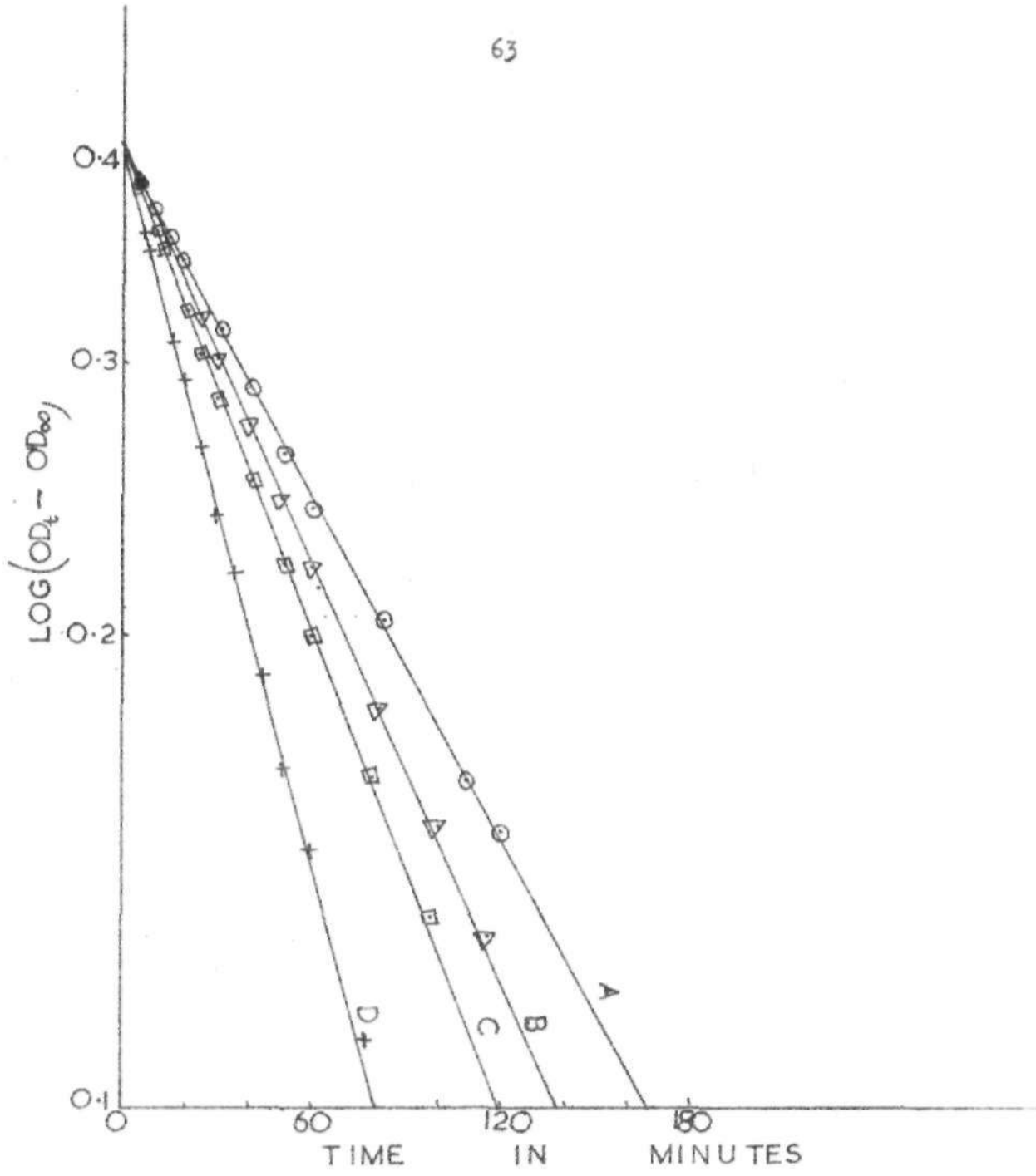


FIG 4·9

PLOTS OF LOG ($OD_t - OD_\infty$) AGAINST TIME FOR DIFFERENT THALLIUM (III) ION CONCENTRATIONS AT 39.5°

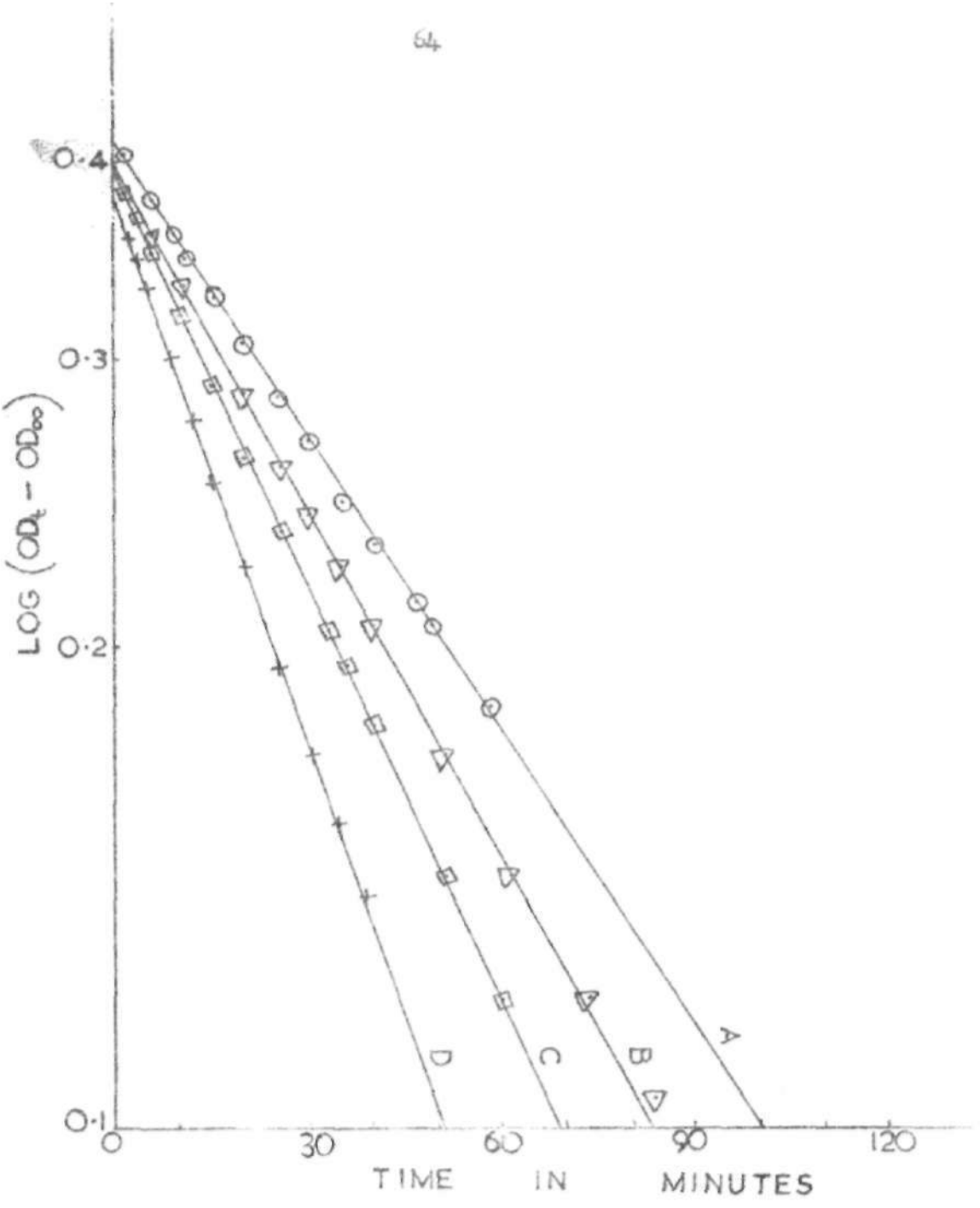


FIG 4·10

PLOTS OF LOG (OD$_t$-OD$_\infty$) AGAINST TIME FOR DIFFERENT THALLIUM (III) ION CONCENTRATIONS At 44.6°

where thallium (III) ion was also employed as a catalyst to study its aquation process, the increase in rate was interpreted in terms of $\left[Co(NH_3)_4(NO_2)(NO_2Tl)\right]^{4+}$ ion species alone. This is because the reaction was studied under limited acid concentration. Here, however, the concentration of the acid has been increased almost five fold; it is therefore expected that the excess acid after suppressing hydrolysis, would also perform its catalytic functions. The increase in rate may therefore be interpreted in terms of two complex ion species: $\left[Co(en)_2(NO_2)(NO_2H)\right]^{2+}$ and $\left[Co(en)_2(NO_2)(NO_2Tl)\right]^{4+}$.

$$\left[Co(en)_2(NO_2)_2\right]^{+} + H^{+} \underset{}{\overset{K_1}{\rightleftharpoons}} \left[Co(en)_2(NO_2)(NO_2H)\right]^{2+} \quad .. \; .. \; .. \; .. \; ..(4.1)$$

$$\left[Co(en)_2(NO_2)_2\right]^{+} + Tl^{3+} \underset{}{\overset{K_2}{\rightleftharpoons}} \left[Co(en)_2(NO_2)(NO_2Tl)\right]^{4+} \quad .. \; .. \; .. \; ..(4.2)$$

If all the three species react the acid/Tl^{3+} catalysis may be interpreted as being due to the reactions:

$$\left[Co(en)_2(NO_2)_2\right]^{+} + H_2O \xrightarrow{k_o} \left[Co(en)_2(NO_2)(H_2O)\right]^{2+} + NO_2 \quad .. \; .. \; ..(4.3)$$

$$\left[Co(en)_2(NO_2)(NO_2H)\right]^{2+} + H_2O \xrightarrow{K_1} \left[Co(en)_2(NO_2)(H_2O)\right]^{2+} + HNO_2 \quad ..(4.4)$$

$$\left[Co(en)_2(NO_2)(NO_2Tl)\right]^{4+} + H_2O \xrightarrow{k_2} \left[Co(en)_2(NO_2)(H_2O)\right]^{2+} + Tl^{+++}NO_2^{-} ...(4.5)$$

$$\therefore \quad \text{Rate} = \frac{\left\{k_o + k_1^1\left[H^+\right] + k_2^1\left[Tl^{3+}\right]\right\} Co^{III}_{tot}}{1 + K_1\left[H^+\right] + K_2\left[Tl^{3+}\right]} \quad .. \; .. \; .. \; .. \; .. \; ..(4.6)$$

Spontaneous aquation have been shown to be very slow[14] and since equilibria 4.1 and 4.2 involve the association of like charges the stability constants K_1 and K_2 will also be very small, so that

$1 \gg K_1 [H^+] + K_2 [Tl^{3+}]$. Therefore equation 4.6 reduces to

$$\text{Rate} = \left\{k_1^1 [H^+] + k_2^1 [Tl^{3+}]\right\} Co^{III}_{tot} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad ..(4.7)$$

$$\therefore \quad k_{obs} = k_1^1 [H^+] + k_2^1 [Tl^{3+}] \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad ..(4.8)$$

Equation 4.8 conforms to that of a straightline, hence a plot of k_{obs} against thallium ion concentration should be a straightline graph of slope k_2^1 and intercept $k_1^1 [H^+]$. Figure 4.11 show good linearity at all temperatures in agreement with the postulate. The values of k_1^1 and k_2^1 at each temperature derived from the intercept and slopes respectively are shown in Table 4.4. Arrhenius plots of the aquations involving the two intermediate complex ion species are shown in Figure 4.12.

TABLE 4.4

Variation of rate parameters with temperature

Temperature	$10^5 k_1^1$ (Sec^{-1})	$10^4 k_2^1$ (Sec^{-1})
30°	2.22	3.70
35°	4.33	5.50
39.5°	6.92	8.50
44.6°	11.67	12.00

Activation energies Ea and entropies of activation (ΔS^*) for the reactions involving $\left[Co(en)_2(NO_2)(NO_2H)\right]^{2+}$ and $\left[Co(en)_2(NO_2)(NO_2Tl)\right]^{4+}$ species are:

Ea = 22.6 K cals/mole; ΔS^* = -7.40 eu [For the protonated species at 25°C]

Ea = 16.5 K cals/mole; ΔS^* = -21.64 eu [For the thallium (III) associated species at 25°C]

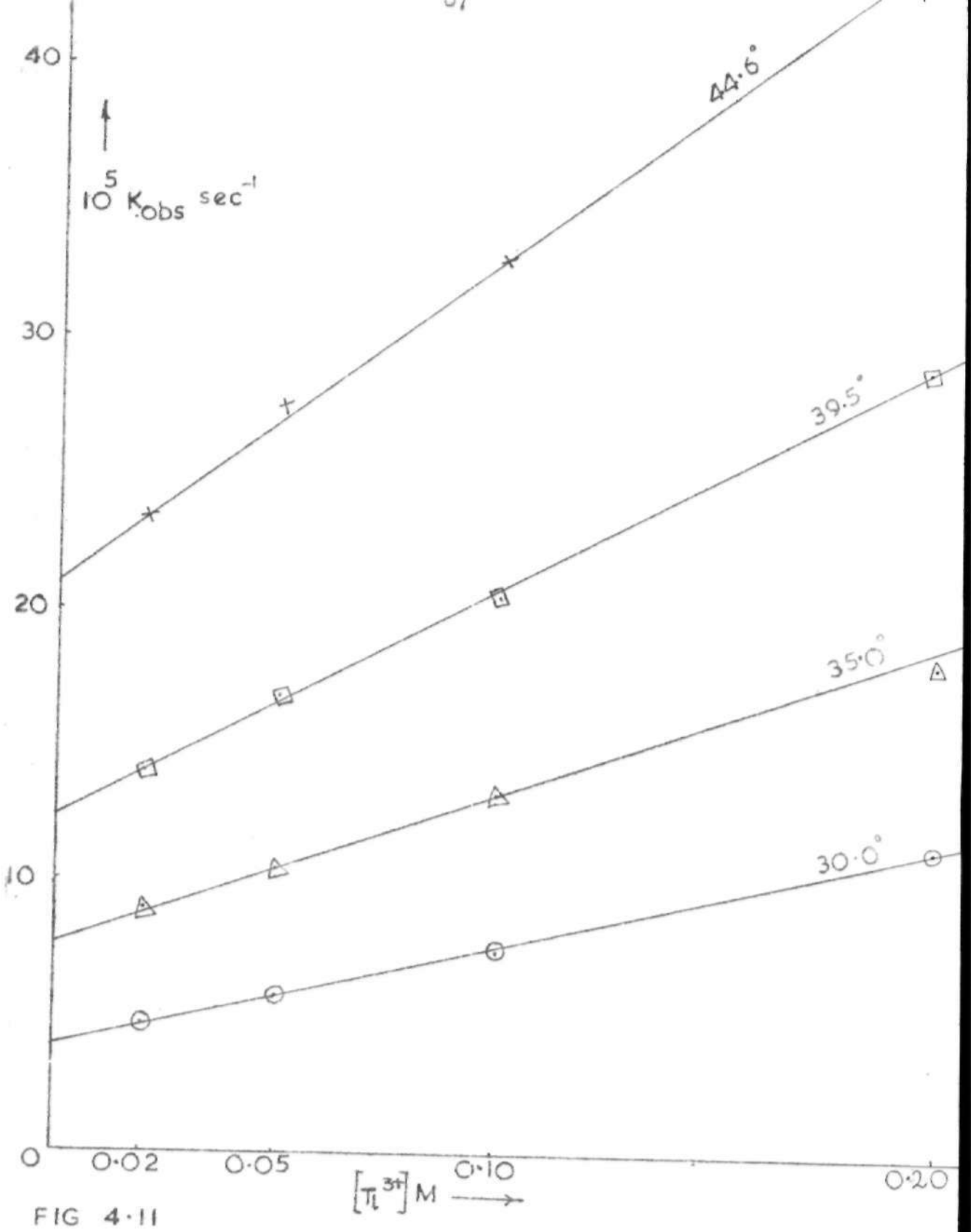


FIG 4·11

PLOTS OF OBSERVED RATE CONSTANTS (k_{obs}) AGAINST THALLIUM (III) ION CONCENTRATION FOR $[Co(en)_2(NO_2)_2]NO_3$

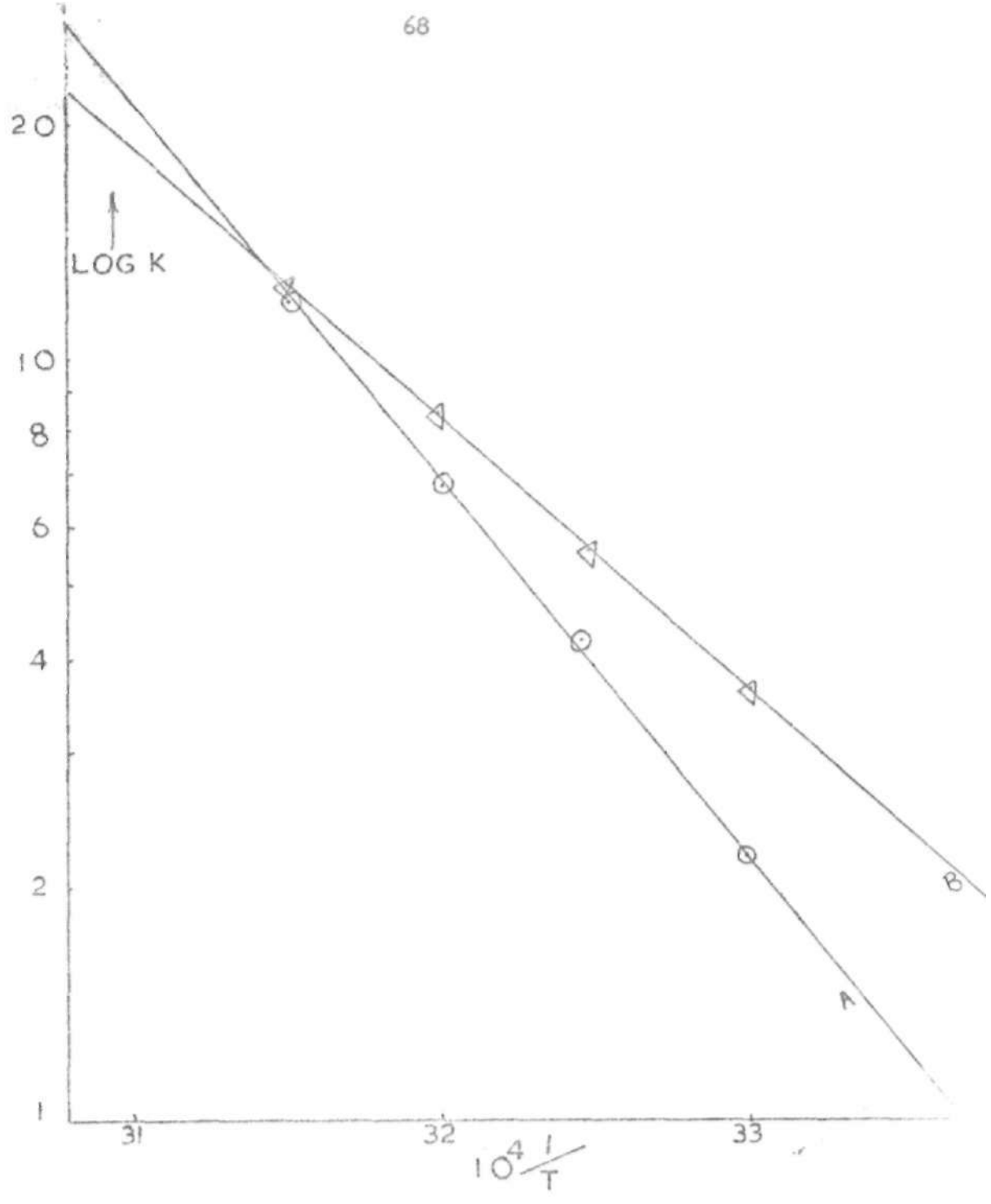


FIG 4·12

ARRHENIUS PLOTS FOR THE THALLIUM (III) CATALYSED AQUATION OF $[Co(en)_2(NO_2)_2]NO_3$

A = REACTION INVOLVING THE PROTONATED SPECIES

B = REACTION INVOLVING THE THALLIUM (III) ASSOCIATED SPECIES

CHAPTER 5

GENERAL DISCUSSION OF RESULTS AND MECHANISM

The studies of cation catalysed aquation of Cobalt (III) complexes have been undertaken by various workers in the past not only to show the catalytic effect of these metal ions but also to provide some information as to the nature of the activated complex which has been a subject of interest for a long time. Most of the work carried out in this field had been concerned with chloride ion as the leaving group and the general postulate is that a rapid pre-equilibrium between Cobalt (III) complexes and the cations used takes place to form complex-cation adducts which eventually yielded the aquo-products.

In order to fully understand the nature of the activated complex, considerable studies have been done on Cobalt (III) complexes of the type $\left[Co(en)_2XCl \right]^{n+}$ $^{18-22}$, (where X is the variable ligand). In all the cases studied, the evidence was towards complex formation between metal ions and Cobalt (III) complex. It is expected that the work carried out would further explain the nature of these activated complexes and thus throw some light into the mechanism of the reaction.

A summary of the rate constants and activation parameters obtained in the present work for the mercury (II) and thallium (III) catalysed aquation of trans-dinitro tetrammine Cobalt (III) and trans-dinitro bis-

ethylenediamine Cobalt (III) complexes have been given in Chapters 3 and 4 respectively. From these data, the Ea values obtained for the singly protonated species in all the reactions 25.7, 23.4 and 22.6 K cals/mole can be compared with those of 26.2, 24.9, and 25.6 K cals/mole for the trans-$\left[Co(NH_3)_4(NO_2)(NO_2H)\right]^{2+}$, trans- and cis $\left[Co(en)_2(NO_2)(NO_2H)\right]^{2+}$, species respectively[6,14]. The Ea and ΔS^* values for the metal ions induced reactions are relatively lower than those for the singly protonated species. The higer rates of reaction observed for these metal ion catalysed reactions when compared with the hydrogen ion catalysed reaction may in part be attributed to these factors.

Although the activation energies for the metal ion associated species are lower than those for the singly protonated species for the two complexes studied, they are not widely different, which may be an indication that similar mechanism operates for the two classes of reactions. The activation energy is lower when the entropy of activation is more negative. The lower the energy of activation the higher the rate of reaction, therefore entropy of activation is an important factor which affects the rates of reaction of these cobalt (III) ammine complexes. For the two complexes studied, the entropies of activation for all the reactions of metal ion associated species are relatively lower than those for the singly protonated species. This may be another reason why these cations are observed to be better catalysts than the hydrogen ions. Another factor which may be considered is the pre-equilibrium constant (K). The higher the value of K, the greater the overall rate of reaction is likely to be. The determining factor here is the affinity[12] of these ions for the outgoing ligand. The

greater the affinity the higher the value of K. In the present work it can be said that the affinity is expected to be greater in the case of the cations (because they carry greater number of positive charges) than the hydrogen ion and accordingly, higher values of K for the reactions involving these metal ions would be expected and these are likely to have contributed to the overall rate constants.

The mechanism of these type of reactions is not different from those already postulated for the acid-catalysed aquation of the two complexes i.e. the solvent assisted dissociation mechanism[6,14]. In this type of mechanism[23-25], there is a prior extension of the Co-X bond (X being the leaving group) to a certain critical distance with the subsequent involvement of the incoming nucleophile. Both groups are then partially bonded in the intermediate or transition state. The energy for such a process would then be seen as the activation energy. Where lengthening of the metal ligand bond is involved, it is expected that the group trans to the leaving group would have some influence on the bond extension. Thus the importance of a full knowledge of the nature and properties of the groups trans to the outgoing ligand cannot be over emphasized. In cases where the ligand trans to the outgoing one is the electron releasing type, electron displacement occurs from the ligand to the metal making it easier to break the Co-X bond (where X is the leaving group). The mechanism operating here is one of SN1. Where the electron withdrawing group such as a nitro group is in the trans position, as in the present work, there is thought to be back-donation of electrons in the non-bonding d-orbital of the Cobalt to the vacant anti bonding orbital of the nitro-group[26]. This renders the Cobalt

centre slightly positive thereby encouraging nucleophilic attack of solvent by an associative mechanism. The mechanism can be safely described as one of partial SN2.

The catalytic behaviour of the metal ions is a subject of recent interest and precise explanation has not yet been given. However, in the present work, the two cations $\left[Hg^{2+} \text{ and } Tl^{3+}\right]$ have proved to be better catalysts than the acid as indicated by the rate parameters obtained. Substantial decrease in both the energies and extropies of activation have been mentioned earlier as factors likely to enhance the rate of reaction. One of the probable reasons for the relative lowering of the activation energy in these type of reactions is polarisation. As a result of the higher positive charges carried by these cations Hg^{2+} and Tl^{3+} as compared to H^{+}, there is likely to be a greater polarisation of the NO-M bond, resulting in a weakening of the $Co-NO_2$ bond, which consequently results in a lower activation energy for the solvent assisted dissociative mechanism. This may also explain the lower values of entropy of activation $\Delta\delta^{*}$ obtained in all the reactions involving the cations. All that has been said so far are some of the possible factors that may be responsible for the increased rates of reactions observed in cases where cations are involved as catalysts as compared to hydrogen ions. The data obtained support these expressed views.

Discussion so far had been limited to comparative studies of cations and hydrogen ions as catalysts. A comparison of the relative effectiveness of Hg^{2+} and Tl^{3+} is particularly interesting since these are isoelectronic. F. A. Posey and H. Taube[7], Miss. S. W. Fong, B. Kipling and A. G. Sykes[13] studied the catalytic effectiveness of mercury (II) and

thallium (III) in the aquation of some Co(III) complexes and arrived at a conclusion that Hg^{2+} is a better catalyst than Tl^{3+}. Their explanation was based on an inner sphere type of mechanisms in which the size as well as the charge of Hg^{2+} seem to be more favourable. However there are also those whose experimental results show that Tl^{3+} is a better catalysts than Hg^{2+}. Prominent among this group in Tanner and Higginson[8]. These two workers have examined in detail the catalytic effect of a large number of metal ions on the reaction in which chloride is eliminated from the chloro ethylenediamine triacetato acetate Cobalt (III) and the strong catalytic effect of Tl^{3+} and Hg^{2+} ($k_{Tl} > k_{Hg}$) was explained in terms of the affinity of these species for chloride (and carboxylate) ions.

In the aquation of the two complexes studied i.e. trans-dinitro-tetrammine Cobalt (III) and trans-dinitro bis ethylenediamine Cobalt (III) nitrates using thallium (III) and mercury (II) as catalysts, the former is found to be a more effective catalyst than the latter. From the data obtained in the present work, the order of effectiveness may be given as $Tl^{3+} > Hg^{2+} > H^{+}$. The greater affinity of these cations for the nitro group and also the polarisation of NO-M bond (resulting in the weakening of the Co-NO_2 bond) by the cations which are expected to increase in increasing order of positive charges carried by the ions, are believed to be largely responsible.

A detailed discussion of the rate of reactions obtained in the case of trans-dinitro tetrammine Cobalt (III) and trans-dinitro bis ethylene-diamine Cobalt (III) nitrates seems inappropriate because different ionic strengths were used. However there is every indication that the

former reacts faster than the later in agreement with the established fact from acid catalysed hydrolysis of the two complexes[6,14]. This has been explained in terms of stabilising effect of chelation in complexes. Increasing chelation brought about by replacing two NH_3 ligands by one ethylene-diamine slows down the rate of catalysed aquation of metal complexes in a progressive manner[27].

As a concluding note it is worth pointing out that no attempt was made to isolate the product but the absorption spectra obtained in the tetrammine case corresponds to that obtained by Gomwalk[6] in purely acid medium.

REFERENCES

1. LANGFORD, C. H., and GRAY, H. B; Ligand Substitution Processes, P.14, Benjamin, 1965.

2. TAUBE, H.; Chem. Revs., 50, 69 (1962).

3. BERZELIUS, J. J., J. ber. Chem. Utersuch. Amt. Hannover 1836, 15, 237.

4. HINSHELWOOD, C. N., The Structure of Physical Chemistry: Oxford University Press, London, 1951, P.398.

5. BASOLO, MONACELLI AND PEARSON; J. Inorg. Nucl. Chem. 1962, 24, 1241.

6. GOMWALK, U. D., and McAULEY, A.: J. Chem. Soc. 1966, 1992.

7. POSEY, F. A., and TAUBE, H., J. Am. Chem. Soc. 79, 255, 1957.

8. TANNER, S. P. and HIGGINSON, W. C. E., J. Chem. Soc. (A). 1969, 1164.

9. DYKE, R., and HIGGINSON, W. C. E., J. Chem. Soc. 1963, 2788.

10. CHAN, S. C., and CHAN, S. F.; J. Chem. Soc. 1969, 202.

11. ESPENSION, J. H. and HUBBARD, S. R., Inorg. Chem. 1966, 5, 686.

12. BIFANO, C. and LINCK, R. G.; Inorg. Chem. 1968, 7, 908.

13. FOONG, S. W., KIPLING, B. and SYKES, A. G.; J. Chem. Soc(A) 118, 1971.

14. STAPLES, P. J.; J. Chem. Soc. 1964, 2534.

15. PALMER, W. G.; Experimental Inorganic Chemistry, Cambridge Univ. Press, 1954.

16. LALOR, G. C.; J. Chem. Soc.(A), 1966, 1.

17. GUPTA, K. S. and GUPTA, Y. K.; J. Chem. Soc. (A) 2, 1970, 256.

18. HORTZCLAW, SHEETY and McCARTY; Inorg. Synth., 4, 176.

19. LEOLIGER, D. A. and TAUBE, A.; Inorg. Chem. 5, 1375, 1966.

20. BUCKINGHAM, I., OLSEN, I. and SARGESON, A. M.; Australian J. Chem., 20, 597, 1967.

21. SARGESON, A. M.; Aust. J. Chem. 17, 385, 1964.

22. HUGHES, M. N. and TOBE, M. L.; J. Chem. Soc., 1204, 1965.

23. LANGFORD, C. H.; Inorg. Chem., 1965, 4, 265.

24. PEARSON, R. G., "Mechanisms of Inorganic Reactions", Advances in Chemistry series, American Chem. Soc., No. 49, 1965, P.22.

25. JONES, T. P., HARRIS, W. E., and WALLACE, W. J.; Canord. J. Chem., 1961, 39, 2371.

26. BASOLO, F.; "Survey of progress in Chemistry", ed. A. F. Scott, Vol. 2, Academic Press, New York, 1965, P.20.

27. BASOLO, F., and PEARSON, R. G.; Mechanism of Inorganic Reactions, John Wiley and Sons, Inc. New York, 1958, P.115-118.

SSSSSSSSSSSSSSS