KINETICS AND MECHANISMS OF THE OXIDATION - REDUCTION AND THE SUBSTITUTION REACTIONS OF SOME METAL ION COMPLEXES IN ACID SOLUTION.

BY

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August, 198 2

D E C L A R A T I O N

I, hereby declare that this thesis has been written by me, and that it is a record of my own research work. It has not been presented in any previous application for a degree. All quotations are distinguished by quotation marks and the sources of information are specifically acknowledged by means of references.

JOHNSON FEMI IYUN

Date: 25/8/82

D E D I C A T I O N

This thesis is dedicated to my parents, Mr. J.I. Iyun and Mrs. C.A. Iyun and to my sisters Dupe, Funmilayo, Olawunmi, Omotola, Anike and Ibiyémi, for the support, understanding and goodwill they have continuously displayed both before and throughout the course of this investigation.

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

I wish to express my profound gratitude to my supervisor Professor J.A. Adegite who has put in everything possible to make the completion of this project possible. I will like to thank him most especially for all the efforts he put in and the risks he undertook travelling down from his new posting to ensure the proper veting of the write-up of this thesis. I will like to thank Dr. H.T. Bozimo and Professor U.D. Gomwalk, the present and immediate-past Head of Department for making both the facilities and enough time available for the completion of this work. I will also like to thank Mr. F. Smith for the able way he provided the much needed technical assistance. I am grateful to Dr. M.A. Olatunji, Mr. A. Ayoko and Miss B. Mailvaganam for the professional interaction I had with them throughout the duration of this investigation.

My thanks go to Dr. C.M.A.O. Martins and Dr. A.C. Ajibade for the encouragement and useful advice they generously provided.

I am indebted to Dr. A.O. Olayemi both for his encouragement and for virtually abandoning one of his research equipments - the S.P. 1750 spectrophotometer to enable me carry out part of this investigation and to Dr. F. Banks and Mr. L. Fugerson for carrying out the computer analysis. I thank Dr. A. Adeyemi for making the original of this Ph.D Thesis available for consultation. My thanks also go to Mr. A.G. Adeleke for typing this thesis.

Finally I will like to express my sincere thanks and appreciation to all the staff of Chemistry Department for the assistance and encouragement provided in one way or the other during the course of this investigation.

A B R E V I A T I O N S

SYMBOL	NAME
$edta^{4-}$	ethylenediamine tetraacetic acid tetraanion
hedta	N-(hydroxyethyl) ethylene diamine tetraacetic acid.
en	ethylene diaamine
pyr	pyrazine
py	pyridine
isn	isonicotamide
NTA^{3-}	nitrilotriacetate trianion
Cyt-c	Cytochrome c.
2,2'-bpy	2,2'-bipyridyl
1,10-phen	1,10-phenanthroline
terpy	2,2',2''-terpyridyl.
i.s.	inner sphere
o.s	outer-sphere
aq	aqueous
k	rate constant
K	Equilibrium constant
pK	$-\log_{10}K$
E	redox potential
$E_{\frac{1}{2}}$	polarographic half-wave potential

A_B_§_T_R_A_C_T

The kinetics and mechanism of the oxidation of $Ti(H_20)g^{3+}$ and Ti -edta by aqueous solutions of bromine and iodine has been investigated. At T = 25°C, I = 1.0M-($CFgS0_3$-Li^+ + CF_3S0_3H)[H^+] *m* 0.034 - 0.274M and X = 453nm, the rate equation for the oxidation of $Ti(H_20)_6^{3+}$ by bromine was found to be:

$$\frac{Z^{\wedge}_{dt}}{[Br_2]} = \frac{JS|}{[H^+]} \frac{[Br_9][Ti(lll)]}{+K} + \frac{\wedge}{[H]} \frac{[Ti(lll)][Br:]}{+K}$$

where k = 9.2 x $10^{-3}M^{-1}s^{-1}$ and K = 4.5 x $10^{\sim 3}$M.

At [H] = 1.0M, [Br^-]. ='0.05 - 0.4M, the apparent second-order rate constant decreases as [Br^-] increases. From the analysis of the data under these conditions, values of the second-order rate constants for the oxidation of $Ti(H_20)_{fi}^{2+}$ by Br_2 and $Br_„^-$ were computed to be (3.88 ± °-4> x iP²*f" s" and (29.4 ± l.DM'V¹ respectively. The rate equation for the oxidation of $Ti(H_20)_6^{\wedge +}$ by iodine was found to be,

$$\frac{j\,r\,\tau\ -i}{_____} = \frac{k_l K_a}{[H^+] + K_a}[Ti(lll)][I_0] + \frac{k_2 K_a}{[H^+] + K_a}[Ti(lll)][II].$$

For the conditions [H^+] = 0.0036 - 0.20M, 1= 1.OM (LiCl), T=25°C and X = 468m, $k_, = 5.3 \times 10^2 M^{-1}s^{-1}$ $k_n = 6.9M^{-1}s^{-1}$ and K • 3.2×10^{-3}M.'

The apparent second-order rate constant for the oxidation 111 of Ti -edta by bromine and iodine showed a biphasic dependence on pH in the range pH = 0.5 - 6.0 for bromine and pH = 0.15 - 7.45 for iodine. Below pH = 2.5, the second-order rate constant is independent of pH but for pH > 2.5 the rate constant increases with pH.

Tine observed biphasic dependence is interpreted as being a constsquence of the change in the identity of the Ti -edta species as the pH of the reaction medium changes. The second-order irate constant was fitted, using a non-linear least-mean-square computer programme with $(l/_{v}$ edta$)^2$ into an equation of the form:

$$_{k}\text{edta} \wedge \frac{k_2 + k_2K_1[H^+]\sim\wedge + kgKjK\wedge H^*"]"^2}{1 + K_1[H^+]"^1 + K_1K_2[H^+]"^2}$$

With K_ and K_0 fixed as earlier determined as 9.55 x 10^{-3}M and 2.29 x 10^{-O}M respectively for the oxidation by bromine k_2=(3.H6 +0.42)xl0^4jr^{1}s-^-aEdk_3 - (8.31 ± 0.2) x 10^7M~^{1}s"^{1} while for thte oxidation by iodine,

k_2 = (3.13 ± 0.32) x 10^3M^{-1}s^{-1} and k_g = (2.33 ± 0.45) x 10^6M^{-1}s~^{1}

A"£ pH = 1.0, the rate constant for the oxidation of Ti^{ill}-^edta by Br_2 and Br" were found to be (3.62 ± 0.15) x 10 M^{-1}s~ and (2_,33 ± 0.07) x 10 M^{-1}s respectively. In the region pH < 22„5 where rate is insensitive to pH changes, k, (I2) and k^^{vdta}(I~) were obtained as 8.5 x 10^3M^{-I}s~^{1} and 2.6 x 10^2M~^{1}s"^{1} respectively.

It is proposed that the electron transfer in these reactions proceed by a series of univalent changes with the production of *X~ (X = Br, I) as a transient intermediate. Available evidence from the obtained data support an outer-sphere electron transfer mechanism for these reactions. The oxidation rates of Ti -edta by Br,,, [Br„]~, I„ and [IJ~ show excellent correlation with Marcus equation for cross-reactions. From this the hoanonuclear exchange rate for Ti-edta + Ti-»edta~ is estimated at 32M~ s~ . It is suggested that the faster redox

reactions of Ti -edta compared to TiOH is due to its more facilbe self-exchange rate rather than a more favourable redox potenrtial.

In the oxidation of seven iron(ll) polypyridine (and ^substituted polypyrndine) complexes by bromine the correlation of the electron transfer rates with the redox potential of the rate-determining step gave a slope of 0.78 and intercept of 4. The non-conformity with Marcus equation has been rationalized in the light of the basic assumptions of the Marcus model. The dependence of the rates of some of these reactions on $[H^+]$ has been ascribed to tine bascity of sOme of the polypyridine ligands.

The chloride and thiocyanate assisted cleavage of $[(bpy)_0ClRuORuCl(bpy)^{2+}]$ is both acid and anion dependent. The obtained data suggests that the cleavage of the oxide bridge most probably occur by a dissociative mechanism. The order of the second-order rate constants obtained at I = 0.5M and T = (26 ± 1)°C and X= 648nm in the reduction of $[(bpy)_2ClRuORuCl(bpy_2^{2+})]$ by Eu^{2+}, Cr^{2+}, U^{3*}, $Ru(NHg)^{2+}$ V^{2+}, Ti^{*-} $^{2+}$ and Ti^{in}-edta did not correlate the order of the reducing potential of these reducing ions. The reactivity order observed did however highlight the relative importance of the symmetry of the orbitals of participating ions in electron transfer reactions. The importance of orbital symmetry in these reactions was further confirmed by the nature of chloride and thiocyanate ion catalysis of these reactions. The base catalysis observed in the reactions of li^{3+}_{aq} and Ti^{111}-edta is interpreted as implicating a higher redox reactivity by

the hydrolysed species $TIOH^{2+}$ and $Ti(OH)edta^{2-}$. The rate data obtained and on the basis of the reducing ions suggests that these reactions most probably proceed by the outer-splhere mechanism.

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C H A P T E R 1

GENERAL INTRODUCTION

Conceptual Development In Redox Reaction Mechanisms.

C H A P T E R 1

GENERAL INTRODUCTION

CONCEPTUAL DEVELOPMENTS IN OXIDATION - REDUCTION REACTIONS

Extensive investigations have been conducted into oxidation-reduction reactions of metal ions in solution. These reactions are very important in a wide area of Chemistry, Biochemistry and Chemical Technology. Much more challenging in the study of these electron transfer reactions is the realisation that proper understanding of these "electron transfer" processes constitute an inevitable prerequisite to the understanding, development, and eventual effective control of a wide area of science and technology. The kinetic and mechanistic studies of electron transfer reactions has thus witnessed a considerable upsurge in the past few decades, both in terms of *a priori* theoretical treatments and extensive experimental investigations as evidenced by the number of review articles that have appeared[1-14].

The pursuit of knowledge in this area of studies has been facilitated in recent times by the ready availability of radioisotopes and the development of a wide range of techniques for monitoring the rate of movement of these electrons between two metal ion centers or between a metal ion and a ligand. The range of techniques now vary from conventional spectrophotometric techniques for cases where an electron transfer reaction is slow to continuous and stopped - flow methods for fast reactions.

Other methods include perturbation techniques for reactions that are approaching diffusion controlled limits, electron spin resonance, electron paramagnetic resonance and nuclear magnetic resonance spectroscopy. Electrochemical techniques have also provided useful complementary data towards the proper understanding of these reactions. A lot of review articles on the various methods are available[15-18].

Recent developments in redox chemistry now show that the basic principles which are operative for simpler systems involving metal ions in solution extend with some modifications to biologically important processes like the reactions of metalloproteins, photo-induced electron transfer processes, intervalence transfer and the reactions of the hydrated electron.

FRANCK - CONDON RESTRICTION

The redox kineticist owes much of his ability to discuss electron transfer reactions in terms of constituent elementary steps, detailed reaction trajectories and potential surfaces despite the obvious complexities introduced by the study of the reaction in solution rather than in the gas phase to an effect called the 'Franck-condon Restriction.'[19,20] This restriction which must be satisfied by electron transfer process in solution stipulates that, "the act of electron transfer takes place within a time ($\sim 10^{-15}$s) that is very much shorter than the time ($> 10^{-13}$s) required for the nucleii to change their position." This implies that the nucleii are virtually frozen in position during the act of electron transfer. Two obvious consequences of this

restriction are:

(1) The reactant activated complex must be identical within limits of uncertainty with the products activated complex. Consequently, the energy of the activated complex as described by nuclear co-ordinates must be two-fold degenerate. The absence of such a degeneracy will imply that there is the possibility of finding a situation where the energy of the product activated complex was higher than that of the reactants' activated complex and one could devise, at least in principle, ways in which to capture this energy to defeat the first law of thermodynamics.

The possibility of the generation of vibrationally excited molecule is thus taken care of by the reorganization of reactants and products molecules in the activated complex. The total change in free-energy of activation could then be written according to Marcus[21] as:

$$\Delta G^{\ddagger} = \Delta G_t^{\ddagger} + \Delta G_i^{\ddagger} + \Delta G_o^{\ddagger} \qquad \text{.....(1)}$$

where $\Delta G_t^{\ddagger}$ = association free energy

$\Delta G_i^{\ddagger}$ = inner-sphere reorganization energy

$\Delta G_o^{\ddagger}$ = outer-sphere reorganization energy.

(2) The second consequence of the "Franck-Condon Restriction" is that no angular momentum can be transferred to or from the transition state during the act of electron transfer and a restriction is also imposed on the change in spin angular momentum. For example the exchange reaction[22];

$$Co(phen)_3^{2+} + *Co(phen)_3^{3+} = Co(phen)_3^{3+} + *Co(phen)_3^{2+} \quad ....(2)$$

involve simply the transfer of electron from the e_g . orbital of one cobalt ion to that of the other and has a rate of $1.1M^{-1}\ s^{-1}$ at 25^oC whereas the exchange reaction:

$$Co(NH_3)_6^{2+} + *Co(NH_3)_6^{3+} = Co(NH_3)_6^{3+} + *Co(NH_3)_6^{2+} \quad ....(3)$$

[23]

requires simultaneous electron transfer and change in spin multiplicity and it is thus slow with a rate of $10^{-9}\ M^{-1}\ s^{-1}$ at 25^oC.

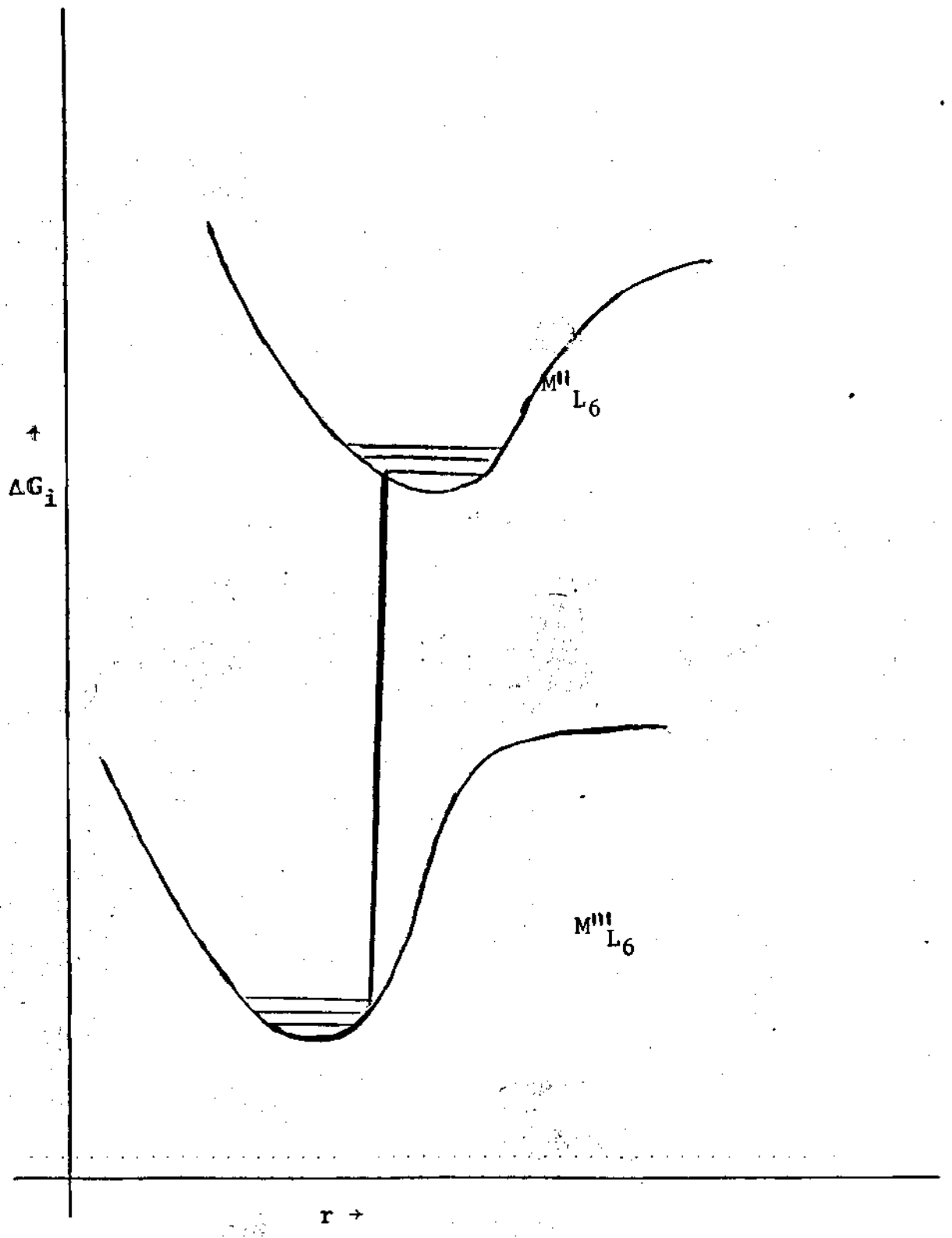
This restriction is however usually reduced by spin-orbit coupling. Hence in terms of potential surfaces the "Franck-Condon principle" requires that the electron transfer be described by vertical transitions between energy wells as shown in Figure (1.1).

ELECTRON TRANSFER REACTIONS

The transfer of electrons can occur between two identical metal ion centers existing in different oxidation states in what is usually referred to as homonuclear electron exchange reactions. For such reactions the reactant and product ion concentrations are the same and hence, the overall free energy of the reaction is approximately zero with the possibility of very small differences in the free energies of the reactants

Figure 1.1

ENERGY WELL FOR ELECTRON TRANSFER.



and products existing as a result of mixing. The obvious problem of such reactions is that of monitoring the rate of electron transfer. This problem has however been adequately taken care of by the use of isotopic labelling techniques for slow exchange reactions and the nuclear magnetic resonance spectroscopic technique for exchange reactions that are very fast. Examples of such reactions are given in equations (4 - 8).

$$V^{2+} + {}^{*}V^{3+} = V^{3+} + {}^{*}V^{2+} \quad \text{.....(4)}$$

$$FeEDTA^{2-} + {}^{*}FeEDTA^{-} = FeEDTA^{-} + {}^{*}FeEDTA^{2-} \quad \text{.....(5)}$$

$$Tl^{1} + {}^{*}Tl^{III} = Tl^{III} + {}^{*}Tl^{1} \quad \text{.....(6)}$$

$$*PtCl_6^{2-} + PtCl_4^{2-} = *PtCl_4^{2-} + PtCl_6^{2-} \quad \text{.....(7)}$$

$$*Fe(phen)_3^{3+} + Fe(phen)_3^{2+} = *Fe(phen)_3^{2+} + Fe(phen)_3^{2+} \quad \text{..(8)}$$

When different metal ion centers are involved in electron transfer reactions the difference in the product and reactants necessarily implies that a net change in the free energy of the reaction is inevitable, i.e. $\Delta G^{\Theta} \neq 0$. Actually, for most of these reactions $\Delta G^{\Theta} < 0$. For a few of them however, $\Delta G^{\Theta} > 0$ and the driving force for such reactions is provided by the necessity to maintain the equilibrium concentration of certain intermediate species in one or more of the reaction steps. Examples of such electron transfer reactions in which $\Delta G^{\Theta} < 0$ are given in equations (9 - 15):

$$Co(NH_3)_5X^{8+} + Cr^{2+} + 5H^+ = CrX^{2+} + Co^{2+} + 5NH_4^+ \quad .....(9)$$

$$Fe^{11}cyt\text{-}c + Ru(NH_3)_6^{3+} = Fe^{111}cyt\text{-}c + Ru(NH_3)_6^{2+} \quad .....(10)$$

$$Co(en)_3^{3+} + Ru(NH_3)_6^{2+} = Co(en)_3^{2+} + Ru(NH_3)_6^{3+} \quad .....(11)$$

$$Fe(LL)_3^{3+} + 2I^- = Fe(LL)_3^{2+} + I_2 \quad .....(12)$$

$$2V^{2+} + Br_2 = 2V^{3+} + 2Br^- \quad .....(13)$$

$$2Fe^{2+} + Tl^{3+} = 2Fe^{3+} + Tl^+ \quad .....(14)$$

$$2Eu^{2+} + Cl_2 = 2Eu^{3+} + 2Cl^- \quad .....(15)$$

For reactions in which the oxidant and reductant undergo equal changes in the oxidation state as in equations (9 - 11) above, the reactions are said to be complementary. When there are unequal changes in oxidation states by the oxidant and reductant as in equations (12 - 15), such reactions are termed non-complementary reactions. In reactions involving multiple oxidation state changes, the points of mechanistic interest center around whether more than one electron is transferred in a single step or in a series of univalent changes and on which intermediates are formed in the process. Investigations have revealed that the two mechanistic options are possible. In fact vanadium(11) has been found to react[24] with Hg(11) to produce V(1V) in a step that involves a direct two-electron transfer whereas the oxidation reactions involving iodine and triiodide occurs in a series of univalent changes with $\cdot I_2^-$ as a transient intermediate. Direct two electron transfer paths have also been identified in the chromium(11) reduction of platinum(1V),

$\{Pt(NH_3)_5Cl\}^{3+}$ and $\{Pt(NH_3)_5OH\}^{3+}$[30]. The reaction[31] of thallium(111) with iron(11) is inhibited by iron(111) ion thus implicating univalent redox reaction steps. Binuclear complexes have also been found[32] to act as two equivalent oxidizing and reducing agents if electron transfer within the complex is sufficiently rapid.

Generally from reports of previous investigations[33], non-complementary reactions have five options as to the way in which the electrons are transferred:

(1) One step termolecular process:

$$2A^{m+} + B^{n+} \rightarrow 2A^{(m+1)+} + B^{(n-2)+} \quad \ldots\ldots\ldots(16)$$

$$\text{Rate} = k\{A^{m+}\}^2\{B^{n+}\} \quad \ldots\ldots\ldots(17)$$

e.g. $2Fe(11) + O_2$; $2Pu^{111} + O_2$[34]

No known reaction between ions goes by this mechanism. This is however expected in the light of the unfavourable electrostatic forces that must be overcome in bringing together three ions of the same charge sign. In reactions in which the overall order of the reaction is third-order as in the oxidation[35] of I^- by $Fe(CN)_6^{3-}$ where the rate law has been reported as:

$$\text{Rate} = k\{Fe(CN)_6^{3-}\}\{I^-\}^2 \quad \ldots\ldots\ldots(18)$$

the second order dependence has been rationalized in terms of a rapid preequilibrium:

$$Fe(CN)_6^{3-} + I^- \rightleftharpoons Fe(CN)_6I^{4-} \text{ (fast)}$$

followed by the rate determining step:

$$Fe(CN)_6I^{4-} + I^- \rightarrow Fe(CN)_6^{4-} + I_2^- \text{ (slow)}$$

The implication of this reaction sequence is that the third-order rate expression is not a consequence of a single termolecular rate-determining step.

(2) One step bimolecular process involving a dimeric species of one of the reactants, e.g. the electron transfer reaction involving cobalt(11) and lead(11) in acetic acid[36] has the rate law:

$$\text{Rate} = k\,K\{Co(111)\}^2\{Pb(1V)\} \qquad \ldots\ldots\ldots(19)$$

The mechanism usually proposed to explain such rate laws is represented in equations (20 and 21)

$$A^{m+} + A^{m+} \rightleftharpoons (A^{m+})_2 \qquad \ldots\ldots\ldots(20)$$

$$(A^{m+})_2 + B^{n+} \rightarrow 2A^{(m+1)+} + B^{(n-2)+} \qquad \ldots\ldots\ldots(21)$$

$$\text{Rate} = k\,K\{A^{m+}\}^2\{B^{n+}\} \qquad \ldots\ldots\ldots(22)$$

(3) Bimolecular process with initial univalent change. Such reactions are often characterized by inhibition by one of the products. The Fe(11) +Tl(111)[31], Co(11) + Tl[37] and Fe(11) + Sn(11)[38] reactions that proceed by the general paths given by equations (23 and 24) provide good examples of this:

$$A^{m+} + B^{n+} \underset{k-1}{\overset{K_1}{\rightleftharpoons}} A^{(m+1)+} + B^{(n-1)+} \qquad \ldots\ldots\ldots(23)$$

$$A^{m+} + B^{(n-1)+} \xrightarrow{k_2} A^{(m+1)+} \qquad \ldots\ldots\ldots(24)$$

$$\text{Rate} = \frac{k_1 k_2\{A^{m+}\}^2\{B^{n+}\}}{k_{-1}\{A^{(m+1)+}\} + k_2 A^{m+}} \qquad \ldots\ldots\ldots(25)$$

Redox reactions in which $\cdot X_2^-$ is proposed as transient species are also examples of reactions that go by this mechanistic possibility. Such a mechanism has been proposed for the reactions[39,40]:

$$2V(111) + I_2 \rightarrow 2V(1V) + 2I^- \quad \text{.....(26}$$

$$2Fe^{11} + Cl_2 \rightarrow 2Fe(111) + 2Cl^- \quad \text{.....(27)}$$

(4) Bimolecular processes with initial two-equivalent change e.g.

$Cr(11) + O_2$; $Cr(11) + HClO$; $Cr(11) + Tl(111)$[41].

The mechanism (e.g. in the $Cr(11) + Tl(111)$ reaction is:

$$Cr(11) + Tl(111) \rightleftharpoons Cr(1V) + Tl(1) \quad \text{.....(28)}$$

$$Cr(1V) + Cr(11) \rightarrow \{Cr(111)\}_2 \quad \text{.....(29)}$$

The $\{Cr(111)\}_2$ dimer formed is stable enough to be isolated on an ion exchange column. The formation of such dimers provides unequivocal evidence for an initial two-electron transfer. The absence of such dimeric species in the oxidation[42] of Cr(11) by H_2O_2, Cl_2, Br_2, Fe(111) and Cu(11) led the authors to conclude that these latter oxidants are one electron oxidants.

(5) Bimolecular process with initial disproportionation:

$$2A^{m+} \underset{\text{slow}}{\rightleftharpoons} A^{(m-1)+} + A^{(m+1)+} \quad \text{.....(30)}$$

$$A^{(m+1)+} + B^{n+} \rightarrow A^{(m-1)+} + B^{(n-2)+} \quad \text{.....(31)}$$

$$\text{Rate} = K\,(A^{m+})^2 \quad \text{.....(32)}$$

The oxidation of water[43] by Ag(11) is believed to proceed by this mechanism with the rate law:

$$\text{Rate} = \frac{k\,\{Ag(11)\}^2}{\{Ag(1)\}} = \frac{d}{dt}\{Ag(11)\} \quad \text{.....(33)}$$

This is consistent with the mechanism:

$$2Ag(11) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ag(1) + Ag(111) \quad \text{.....(34)}$$

$$Ag(111) + H_2O \xrightarrow{k_2} \text{Products} \quad \text{.....-(35)}$$

The application of the steady-state approximation to the above scheme leads to the rate law given by equation (33). Some reactions involving Hg(1) and some metal ions have also been found to proceed by this mechanism. Some examples of these are the $(Hg^1)_2 + Tl^{111}$[44], $(Hg^1)_2 + 2Mn^{111}$[45] and the $(Hg^1)_2 + 2CO^{111}$[46] reactions.

On knowing that a particular electron transfer reaction is homonuclear or heteronuclear, complementary or non-complementary, the question of the mode or mechanism of electron transfer now rest on being able to answer certain pertinent questions, some of which are:

(1) How does the rate of electron-transfer compare with the rate of substitution into the inner co-ordination sphere of reactant ions?

(2) Is it possible to identify or infer the closeness of approach of reactant metal centers in the activated complex prior to electron transfer?

(3) If the reaction is not thermodynamically feasible, what then provides the driving force?

(4) If more than one electron is transferred, how many are transferred at a time?

(5) How can the acid and base catalysis usually observed in some of these reactions be interpreted? Is it rationalizable in terms of the structure of the reactants, transition state or products?

(6) Are the large variations in rates which usually accompany the variation of reactant ions diagnostic of the effect of the variation of electronic structure of reactant ions on the rate and mode of electron transfer?

Various attempts to provide answers to these and other questions have been made employing the couples: Cr(11)/Cr(111), Co(11)/Co(111), Fe(11)/Fe(111) and very recently Ru(11)/Ru(111).

However, as far back as 1954, Taube and co-workers[47] have identified two types of stoichiometric mechanisms that are operative when electrons are transferred between two metal ions in solution. These are (i) the inner-sphere mechanism and (ii) the outer-sphere mechanism.

THE INNER-SPHERE MECHANISM.

In the inner-sphere mechanism, substitution into the inner-coordination sphere of reactant ions preceed electron transfer. The transition state must thus consist of two metal ions joined by a common ligand. In terms of reaction steps the inner-sphere mechanism can be represented as follows:

(i) $Red^{\cdot}_{(1)} + X - Ox_{(2)} \rightarrow Red^{\cdot}_{(1)} - X - Ox_{(2)}$ (bridge formation) .....(36)

or $Red^{\cdot}_{(1)} - X + Ox_{(2)} \rightarrow Red^{\cdot}_{(1)} - X - Ox_{(2)}$ (Very uncommon) .....(37)

(ii) $Red^{\cdot}_{(1)} - X - Ox_{(2)} \rightarrow Ox_{(1)} - X - {}^{\cdot}Red_{(2)}$ (electron transfer) .....(38)

(iii) $Ox_{(1)} - X - {}^{\cdot}Red_{(2)} \rightarrow Ox_{(1)} - X^{+} \; {}^{\cdot}Red_{(2)}$
or $Ox_{(1)} + X - {}^{\cdot}Red_{(2)}$
or $Ox_{(1)} + {}^{\cdot}Red_{(2)} + X$
} bridge breaking .....(39)

(Ox = oxidant, Red = reductant)

Processes (i) and (iii) are nothing more complicated than ligand substitution reactions and only (ii) involves any change in oxidation state. Occasionally, it is possible to find a two-stage electron transfer process with ligand mediating:

(iv) $Red_{(1)}^{\cdot}\text{-}X\text{-}Ox_{(2)} \rightarrow Ox_{(1)}\text{-}\dot{X}\text{-}Ox_{(2)}$ .....(40)

(v) $Ox_{(1)}\text{-}X\text{-}Ox_{(2)}^{\cdot} \rightarrow Ox_{(1)}\text{-}X\text{-}Red_{(2)}$ .....(41)

The evidence for this type of process is discussed later.

The classical example of a reaction proceeding by the inner-sphere mechanism is the reaction[47]:

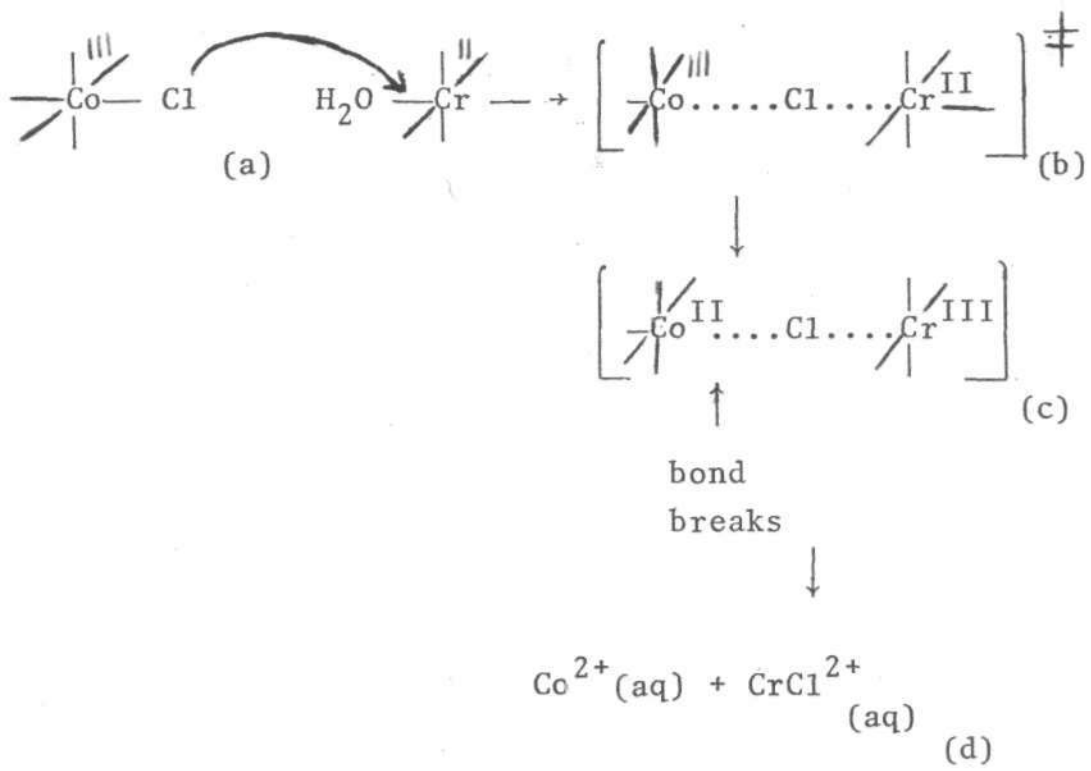
$$Co(NH_3)_5Cl^{2+} + Cr^{2+}_{(aq)} + 5H^+ \rightarrow Co^{2+}_{(aq)} + CrCl + 5NH_4^+ \quad ....(42)$$

When the inner-sphere reaction scheme is applied to the above reaction, it implies that at no time does the chloride ion break free of the influence of at least one of the metals. In support of this, it has been found that $^{36}Cl^-$ is not incorporated into the $CrCl^{2+}$ product when the reaction takes place in the presence of $^{36}Cl^-$. Taube, Myers and Rich thus found that the chloride ion was transferred from the substitution-inert Co(111) complex[48] to the substitution inert product Cr(111) complex ion[49].

Based on the substitution-inert character of the Co(111) and Cr(111) complexes and the substitution lability of the Cr^{2+}(aq) complex, the sharing of the transferred ligand

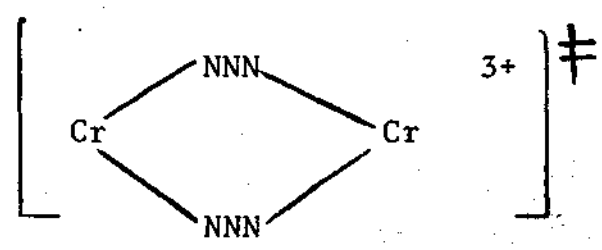
between the inner-coordination sphere of the two reactant ioms in the activated complex was postulated. Their conclusion was further confirmed by the fact that a comparison of the rate constant for this reaction, (> 10^3 M^{-1} S^{-1} at 25°C) with that for the aquation[50] of the $Co(NH_3)_5Cl^{2+}$ cation (1.7 x 10^{-6} S^{-1} at 25°C) shows that the chloride cannot become detached from the cobalt prior to the formation of the transition state. Similarly the rate constant for the formation[51] of $CrCl^{2+}$ from Cr^{3+}(aq) (3 x 10^{-8} M^{-1} S^{-1} at 25°C) is very much less than the redox rate constant, so the chloride must be bonded to the chromium before the transition state separates into the products.

The mechanism for the reaction is thus given as:



A lot of other reactions have since been found to occur by the inner-sphere mechanism. Some intermediates that have either been detected because of the substitution characteristics of the oxidant-reductant pair or otherwise inferred from kinetic data are presented in Table (1.1).

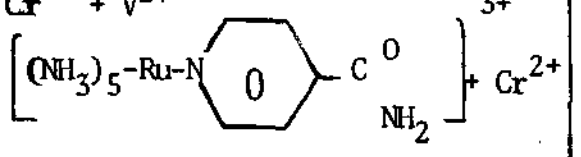
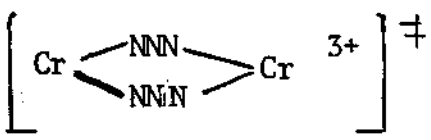
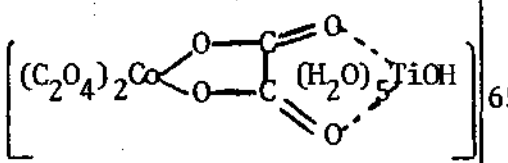
Interestingly it has been observed[41] that inner-sphere reactions could involve double bridging in the transition state[54,64,67]. For instance this has been observed by Haim[67a] in the reaction of Cis-$Cr(N_3)_2^+$, Cis-$Co(NH_3)_4(N_3)_2^+$ and Cis.$Co(en)_2(HCO_2)_2^+$ with $Cr^{2+}(aq)$. Two ligands were transferred from the oxidant to the reductant and thus the cis-$Cr(N_3)_2^+$ obtained as the partial product of the reaction led to the proposition of a transition state of the form:



In this mechanism, whether the bridging ligand is transferred depends on the relative stability of the bond formed compared to that broken. In the reaction of $Cr^{2+}(aq)$ with $IrCl_6^{2-}$ there is convincing evidence[47b] for an inner-sphere path involving the formation of

Table 1.1.

Bridged intermediates identified or inferred for some redox reactions.

Reactant	bridged intermediate	Ref
Cr^{II} + Ru^{III} chlorocomplexes	Cr^{III} - Cl - Ru^{II}	52
Cr^{II} + $IrCl_6^{2-}$	Cr^{III} - Cl - Ir^{III}	53
$Co(CN)_5^{3-}$ + $Fe(CN)_6^{3-}$	Co^{III} - NC - Fe^{II}	54
$Co(CN)_5^{3-}$ + $IrCl_6^{2-}$	Co^{III} - Cl - Ir^{III}	55
$CoEDTA^{2-}$ + $Fe(CN)_6^{3-}$	Co^{III} - NC - Fe^{II}	56
Fe^{II} + $Co(NH_3)_5NTA$	Fe^{II} - NTA - Co^{III}	57
Cr^{II} + V^{IV}	Cr^{III} - $(OH)_2$-V^{III}	58
		59
Cr^{II} + U^{IV}	$\{(H_2O)_5Cr^{III}\text{-}O\text{-}U^{IV}\text{-}O\}^{4+}$	60
Cr^{II} + Np^{IV}	$\{(H_2O)_5Cr^{III}\text{-}O\text{-}Np^{V}\text{-}O\}^{4+}$	61
V^{2+} + Hg^{2+}	$\{VHgOH^{3+}\}$	62
V(v) + Ti(III)	$\{Ti.....OH.....VO_2\}^{3+}$	63
Cis - $Cr(N_3)_2^+$ + Cr^{2+}		
$Ti(H_2O)_6^{3+}$ + $Co(C_2O_4)_3^{3-}$		65
Ti^{3+} + $Ru(NH_3)_5NCS^{2+}$	$\{Ru(NH_3)_5NCS\text{-}TiOH\}^{4+}$	66

{Cr - Cl - $IrCl_5$} as an intermediate but the products are $Cr(H_2O)_6^{3+}$ and $IrCl_6^{3-}$. This means that electron transfer occurs by the inner-sphere mechanism without the transfer of the bridging ligand from $IrCl_6^{2-}$ to $Cr^{2+}aq$.

The transfer of the bridging group is thus incidental to electron transfer. In the majority of the reactions so far identified as proceeding by the inner-sphere mechanism, the inert complex ion oxidant provides the bridging ligand. However a few cases have been reported where the reductant ion provides the bridge. The $Fe(CN)_6^{4-}/CrO_4^{2-}$ reaction[68] in which $\{(CN)_5FeCNCrO_4\}^{6-}$ is an intermediate provides a good example.

ENERGETICS OF THE INNER-SPHERE MECHANISM.

The detailed elementary steps for the inner-sphere mechanism has been independently proposed by Sutin[58], Bennet[10] and Linck[12].

Their propositions entail that the inner-sphere reaction mechanism could be represented by the following reaction scheme:

Step 1.

(a) Encounter Complex Formation

$$L_5M^{III}{}_X{}^{m+} + M^{II}(H_2O)_6^{n+} \underset{}{\overset{K_p}{\rightleftharpoons}} \{L_5M^{III}\ X\ M^{II}(H_2O)_6\}^{(m+n)+}$$

(b) Precursor complex formation

$$\{L_5M^{III}\ X\ M^{II}(H_2O)_6\}^{(m+n)+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \{L_5M^{III}\text{-}X\text{-}M^{II}(H_2O)_5\}^{(m+n)+} + H_2O$$

Step 2.

(a) Precursor activation

$$\{L_5M^{III}\text{-}X\text{-}M^{II}(H_2O)_5\}^{(m+n)+} \rightleftharpoons \{L_5M^{III}\text{-}X\text{-}M^{II}(H_2O)_5\}^{\ddagger}$$

(b) Electron transfer

$$\{L_5M^{III}\text{-}X\text{-}M^{II}(H_2O)_5^{(m+n)+}\}^{\ddagger} \rightleftharpoons \{L_5M^{II}\text{-}X\text{-}M^{III}(H_2O)_5^{(m+n)+}\}^{\ddagger}$$

Step 3.

(a) Successor complex deactivation

$$\{L_5M^{II}\text{-}X\text{-}M^{III}(H_2O)_5^{(m+n)+}\}^{\ddagger} \rightleftharpoons \{L_5M^{II}\text{-}X\text{-}M^{III}(H_2O)_5^{(m+n)+}\}$$

(b) Successor complex decomposition

$$\{L_5M^{II}\text{-}X\text{-}M^{III}(H_2O)^{(m+n)+}\} \rightleftharpoons L_5M^{IIm+} + M^{III}(H_2O)_5^{n+}$$

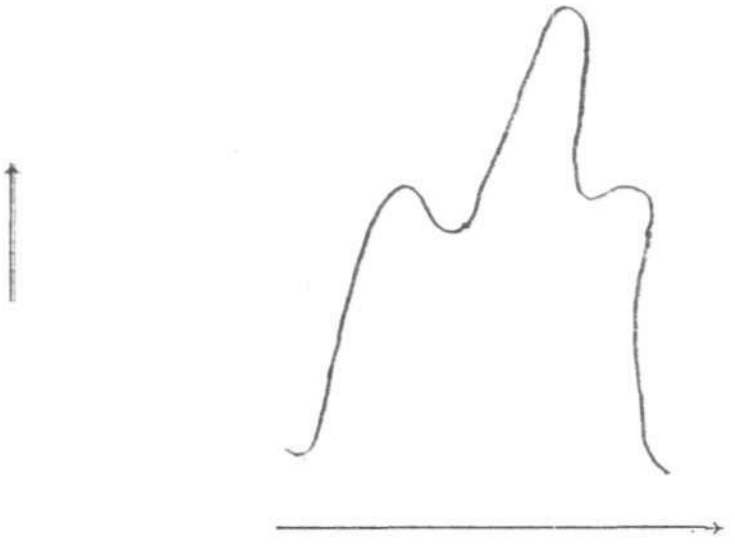
$$\downarrow \qquad\qquad \downarrow$$

Products Products.

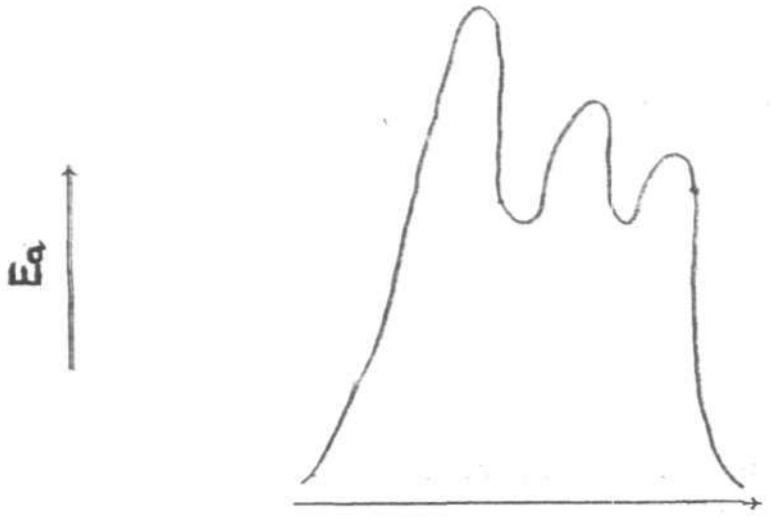
Extensive investigation has revealed that the precursor complex formation, electron transfer or the decomposition of the activated complex could be the rate limiting step. Diagramatically these possibilities can be illustrated with the potential energy profiles shown in Figure (1.2).

Figure 1.2

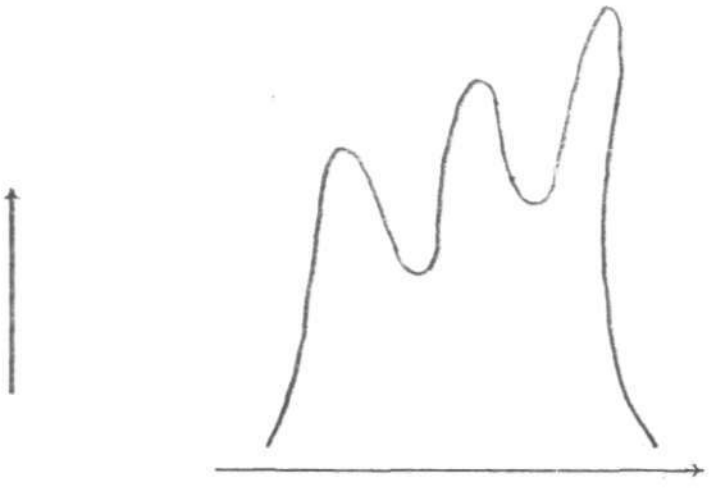
Potential energy diagram as a function of reaction coordinate.



Scheme 1



Scheme 2



Scheme 3

Reaction Coordinate.

Scheme 1.

Both the formation of the precursor complex and the decomposition of the postcursor complex are very fast compared to the electron transfer step and hence the latter is the rate determining step. Formation of the bridge is fast and reversible and the scheme can be considered as a rapidly attained preequilibrium followed by a relatively slow 'rearrangement'.

In situation where the thermodynamic stability of the bridged species is small, the kinetic form will be of the simple second-order form associated with redox reactions.

However when a significant fraction is in the form of the bridged species, a departure from the second-order kinetics will be observed although this latter situation is only a rare occurence. In redox reaction literature, it appears that this scheme is the dominant path adopted by the bulk of the reactions. However the Fe^{2+} + $Co(NH_3)_5NTA$ reaction[69] provides the classic illustration of this scheme:

$$Co(NH_3)_5NTA + Fe^{2+} \underset{}{\overset{K}{\rightleftharpoons}} \{Co(NH_3)_5NTAFe\}^{2+}$$

$$\{Co(NH_3)_5NTA\ Fe\} \xrightarrow{k} FeNTA + Co^{2+} + \quad \ldots\ldots\ldots\ldots (42)$$

with $K = 1.1 \times 10^6 M^{-1}$ and $k = 9.4 \times 10^{-2} s^{-1}$ at 25°C and 1.0M ionic strength.

The characteristic feature of this type of activation for an inner-sphere mechanism is that the rate is very sensitive to the nature of the reductant, the oxidant and the bridge. Ample examples highlighting this feature have

been given by Tobe[70]. In most of such reactions a combination of the criteria previously outlined have been employed to justify the assignment of an inner-sphere mechanism. Another major feature of the process when bridge formation is not rate-determining is the sensitivity of rate to the overall free-energy change in the reaction. Thus, Co(111) is a much better oxidizing agent than Cr(111) and this is reflected in the ratio of the rate constants for the reaction[71]:

$$Cr^{2+} + M(NH_3)_5X^{2+} \rightarrow M^{2+} + Cr(H_2O)_5X^{2+} + 5NH_3 \quad ....(43)$$

where $M = Cr^{3+}_{(aq)}$ or Co^{3+}_{aq} and

the ratio $k_2(Co)/k_2(Cr) = 10^9$.

Likewise Fe^{2+} is a poorer reducing agent than Cr^{2+}:

Scheme 2.

If the substitution lability of the substrates is less than the rate of electron transfer, and if for some reasons, the outer-sphere mechanism does not take over, then the rate of redox reaction may be controlled by the rate of substitution or anation of the more labile component of the reactant species. Hence, the process can be considered as anation followed by the usual simple second-order rate law that is found when pre-equilibrium association is small. The implication of this is that the kinetic form alone will not distinguish a rate-determining bridge formation from other possibilities, but the rate constant will. This will be virtually independent of

the nature of the less labile components and certainly independent of the overall free-energy change for the overall redox reaction. Thus, the substitution characteristics of moderately labile ions like V^{2+}[72] and Ti^{3+}[73] imposes restriction on the rates at which electron transfer could occur by the inner-sphere mechanism. For example, for the V^{2+} reduction of $Co(NH_3)_5X^{n+}$[74] ($X = C_2O_4^{2-}$, N_3^-) and trans - $Co(en)_2H_2ON_3^{2+}$[75], k varies from 4.5 → 18.1 M^{-1} S^{-1} at 25°C. Also, in the reduction of $Co(NH_3)_5X^{2+}$ (X =F, Br, I)[76] cis-$Co(en)_2H_2OCl^{2+}$ and trans - $Co(en)_2H_2OF^{2+}$[77] by Cr^{2+}, the rate constants fall in the range (1.4 → 6.0) x 10^5 M^{-1} s^{-1} at 25°C.

Hence, the internal similarities in rate when V^{2+} and Cr^{2+} are employed as reductants indicate that substitution into the inner-coordination sphere of these ions is rate-limiting. This conclusion is butressed by the fact that the electron transfer rates are similar to the rate of substitution into the inner-coordination sphere of these ions. Reactions occuring by scheme 2 are said to be substitution-controlled redox reactions.

Scheme 3.

The prerequisite for this scheme to be operative is that both the oxidized product of the reducing ion and the reduced form of the oxidizing species should be substitution-inert. Hence, the reactants and products complex should

be in equilibrium. A classic example of a reaction that utilizes this pathway is that of the oxidation of $\{CoEDTA\}^{2-}$ by $Fe(CN)_6^{3-}$[69,78]:

$$Co(EDTA)^{2-} + Fe(CN)_6^{3} \underset{86s^{-1}}{\overset{1.2 \times 10^5 M^{-1}S^{-1}}{\rightleftharpoons}} \{EDTACoCNFe(CN)_5\}^{5-} \quad \ldots(44)$$

This binuclear intermediate is sufficiently stable that its oxidation by $Fe(CN)_6^{3-}$ has been achieved. Other examples have been provided in the Cr^{2+} reduction of cis-$Ru(NH_3)_4Cl_2^{+}$[79], cis-$Ru(NH_3)_5Cl^{2+}$ and cis-$Ru(NH_3)_4H_2OCl^{2+}$[80]. In the latter example, the empirical rate law obtained is:

$$\text{Rate} = \frac{k_o K\{Cr^{2+}\}\{Ru^{III}\}}{1 + K\{Cr^{2+}\}} \quad \ldots\ldots(45)$$

In the extreme case of the operation of this scheme in redox reactions, the binuclear product can be sufficiently stable as not to decompose to the monomers. Thus the reactions between $Co(CN)_5^{3-}$ and $Fe(CN)_6^{3-}$ gives the complex anion $\{(CN)_5CoNCFe(CN)_5\}^{6-}$ which has been obtained as a crystalline salt. The properties are consistent with the presence of a t_{2g}^6 (Co(III) and a t_{2g}^6 Fe(II) and further oxidation gave the isolable $\{(CN)_5CoNCFe(CN)_5\}^{5-}$ ion.

If the overall free-energy change is not too great for a reaction utilizing this activation path in an inner-sphere mechanism, the act of electron transfer will be reversible. Provided the reverse redox path and the bridge breaking can occur at similar rates, the actual bridged product will not build up to any significant concentration, but the kinetics will depart from the simple second-order rate law. In the reaction[79]:

$$Cr^{2+}(aq) + \{Ru(NH_3)_5Cl\}^{2+} \rightarrow \{Cr(H_2O)_5Cl\}^{2+} + \{Ru(NH_3)_5OH_2\}^{2+} \quad .....(46)$$

the rate becomes independent of the $Cr^{2+}(aq)$ concentration when this is present in sufficient excess.

This limiting rate represents the aquation of the $\{(NH_3)_5Ru^{II}ClCr^{III}(H_2O)_5\}^{4+}$ complex.

THE OUTER-SPHERE MECHANISM.

In reactions that occur by the outer-sphere mechanism, the reactants enjoy the circumstantial privilege of retaining their coordination integrity in the activated complex prior to and during the act of electron transfer. However, in compliance with the Franck-Condon restriction, distortion of metal-ligand bonds could and does occur in the transition state. Examples of reactions that occur by the outer-sphere mechanism are:

(i) $^{*}Fe(bpy)_3^{3+} + Fe(bpy)_3^{2+} \rightarrow {}^{*}Fe(bpy)_3^{2+} + Fe(bpy)_3^{3+}$

(ii) $Cr(EDTA)^{2-} + Co(EDTA)^{-} \rightarrow Cr(EDTA)^{-} + Co(EDTA)^{2-}$

(iii) $Ru(NH_3)_6^{2+} + Co(NH_3)_5X^{2+} \rightarrow Ru(NH_3)_6^{3+} + Co(NH_3)_5X^{+}$

(iv) $Fe^{2+}(aq) + IrCl_6^{2-} \rightarrow Fe^{3+}(aq) + IrCl_6^{3-}$

(v) $Cr^{2+}(aq) + Ru(NH_3)_6^{3+} \rightarrow Cr^{3+}(aq) + Ru(NH_3)_6^{2+}$

ENERGETICS OF THE OUTER-SPHERE MECHANISM.

Since the outer-sphere reaction mechanism is characterized by the retention of the coordination integrity of reactant ions before and during the formation of the transition state, the energetics of the process can be formulated in terms

of the following reaction sequence[58]:

1. Precursor association:

$$A + B \rightleftharpoons A||B$$

2. Precursor activation:

$$A||B \rightleftharpoons \{A||B\}^{\ddagger}$$

3. Electron transfer:

$$\{A||B\}^{\ddagger} \rightleftharpoons A^{-}||B^{+}$$

4. Postcursor dissociation:

$$A^{-}||B^{+} \rightarrow A^{-} + B^{+}$$

(A and B are reactant ions. || denotes that no chemical bonds have been made or broken during the process of electron transfer).

Steps (1), (2) and (4) are very fast, while step (3), the electron transfer step constitute the rate determining step. Most outer-sphere oxidants and reductants are relatively inert on the time-scale of oxidation-reduction reactions. For example in the reaction[81] represented by equation (47),

$$Fe(CN)_6^{4-} + Mo(CN)_8^{3-} \rightarrow Fe(CN)_6^{3-} + Mo(CN)_8^{4-} \quad \text{.....(47)}$$

the substitution inertness of the reactants makes the obvious choice of mechanism the outer-sphere. It must be pointed out at this juncture that very many cases exist where reagents e.g. $Eu^{2+}(aq)$, $Fe^{2+}(aq)$ and $Fe^{X2+}(aq)$ which are substitution labile are involved and yet the redox reaction is outer-sphere[82]. Hence although the unequivocal demonstration of coordination shell retention requires a set of reagents which undergo substitution, it must not be assumed that this is a property of the outer-sphere mechanism.

The bulk of efforts in mechanistic studies of redox reactions had been directed at identifying which of these two mechanisms is adopted by the reaction of interest. Some of the criteria commonly employed in the diagnosis of mechanism are briefly summarized below:

(1) k redox versus k substitution

Since the inner-sphere mechanism demands that substitution into the inner coordination sphere of one of the reactant ions preceed the electron transfer, the comparison of the rate of electron transfer (k redox) and the rate of substitution (k substitution) into the inner coordination sphere of the more labile of the reactant ions affords direct insight into the mechanistic pathways of many electron transfer reactions. When k sub >> k redox and there is a suitable bridging ligand, the inner-sphere mechanism may operate whereas in cases where k redox >> k sub the outer-sphere mechanism is suggested . For example, reactions involving V^{2+} (d^3, in which the rate of water exchange is $100 s^{-1}$ at 25^oC[83,84]) with Fe^{3+}[86] and cis-$Ru(NH_3)_4 Cl_2^+$[85] with k redox values of 1.8×10^4 M^{-1} S^{-1} and 9.8×10^3 M^{-1} s^{-1} respectively were classified as occuring by the outer-sphere mechanism on the basis of this premise Some other reactions of $V^{2+}(aq)$[87] that have been diagonized as occuring probably by the outer-sphere mechanism because the measured rate of electron transfer rules out the possibility of substitution preceeding electron transfer are presented in Table (1.2).

TABLE 1.2[86]

Some outer-sphere redox reactions of V^{2+}.

Oxidant	$k(M^{-1} s^{-1})$
$RuCl^{2+}$	1.9×10^4
Fe^{3+}	1.8×10^4
FeX^{2+} (X = Cl, N_3^-, NCS^{-1})	$4.6 - 6.6 \times 10^5$
Br_2	$30. \times 10^4$
I_2	7.5×10^3

Other examples include the electron exchange reaction between ferrocene and ferrocinium ions and electron transfer reactions such as those of phenanthroline complex of iron(11), ruthenium(11) or osmium(11) with such oxidants as hexachloro-iridate(1V)[88]. For these reactions electron transfer is complete within a fraction of a second whereas the half-life of liberation of ligand from complex is in the order of minutes, hours or even days. The reaction[89]:
$\{Fe(Me_2bpy)_3\}^{2+} + \{Fe(phen)_3\}^{3+} \rightarrow \{FeMe_2(bpy)_3\}^{3+} + \{Fe(phen)_3\}^{2+}$
has k redox = 10^8 M^{-1} s^{-1} at 25°C whereas the half-life of substitution for the reactant ions is approximately 1.4×10^4s at 25°C and is thus classified as occuring by the outersphere mechanism.

(2) Product Identification.

The first unequivocal evidence of the use of this criterion was provided by Taube, Myers and Rich[47a] where, by the intellectual exploitation of the labile-inert characteristics of the oxidant-reductant pair, in conjuction

with the use of isotopic labelling techniques, they were able to associate the $CrCl^{2+}$ product with a binuclear intermediate of the form $\{(NH_3)_5Co - Cl - Cr^{4+}\}^{+}$. Some other cases where product identification has been used to implicate a bridged transition state include $Co(C_2O_4)_3^{3-}$ + Fe^{2+} reaction[90] where the fairly labile product, $FeC_2O_4^{+}$ was identified by stopped - flow method and the $Co(NH_3)_5CN^{2+}$ + Cr^{2+}[91] and $FeNCS^{2+}$ + Cr^{2+}[92] reactions. The identification of unstable isomers where the 'wrong-end' of the ligand is bonded, which subsequently undergoes isomerization to the more stable isomer provide interesting examples of the use of this criterion. For example, the full kinetic study of the chromium(11) reduction[91] of $Co(NH_3)_5(CN)^{2+}$ revealed the sequence:

$$Co(NH_3)_5(CN)^{2+} + Cr^{2+} \xrightarrow{5H^+} CrNC^{2+} + Co^{2+}(aq) + 5NH_4^+ \quad ....(49)$$

$$CrNC^{2+} \rightarrow CrCN^{2+} \quad ....(50)$$

$$CrCN^{2+} \overset{H^+}{\rightarrow} Cr^{3+}(aq) + HCN \quad ....(51)$$

The known rates of isomerization of $CrNC^{2+}$ to $CrCN^{2+}$, the more thermodynamically favoured product and the known rate of aquation of $CrCN^{2+}$ permit the last two stages of the redox reaction sequence to be assigned to equations (49 - 51). Similar mechanistic pathways operate for some other reactions. For example the reductions of $Co(NH_3)_5NO_2^{2+}$ by $Co(CN)_5^{3-}$ and partly for chromium(11) reduction of $Co(NH_3)_5(SCN)^{2+}$[94].

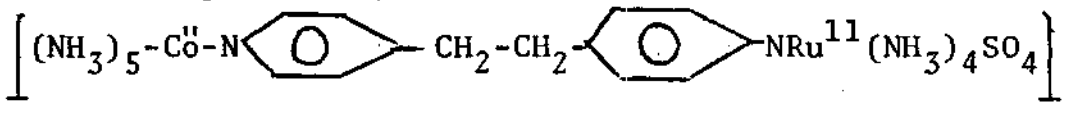
In particular, the criterion of product identification has been a very useful diagnostic tool for a lot of chromium(11) reductions[95] of Co(111), Cr(111), and Fe(111) oxidants. This has been made possible because most redox reactions involving Cr(11) are rapid and the rate of hydrolysis of most Cr(111) complexes slow. Other common reducing agents that can lead to products leisurely characterizable include $Co(CN)_5^{3-}$[96], $Ru(NH_3)_5H_2O^{2+}$[97]. With Fe^{2+}, V^{2+}, Eu^{2+} however, products hydrolyze rapidly making their detection difficult except in some cases, as in the $Co(NH_3)_5SCN^{2+}/V^{2+}$ reaction where the stopped flow technique has been used to advantage[98-100].

(3) Identification of binuclear intermediate.

For a binuclear intermediate to be identifiable in reactions of the inner-sphere mechanism both the reduced oxidant and the oxidized reductant must be relatively inert and the rate of decomposition of the intermediate must be slower than the rate of electron transfer. Systems that have met these prerequisites, and hence where this criterion has provided conclusive evidence of mechanism include the $UO_2^{2+} + Cr^{2+}$[101] and $NpO^{2+} + Cr(11)$[102] reactions where the intermediates $\{OUOCr\}^{4+}$ and $\{Cr^{11}\text{-}O\text{-}Np^{1V}O\}$ were identified respectively. $\{EDTACoNCFe(CN)_5\}^{5-}$[103] and VOV^{4+}[104] have also been identified in the reactions of $Co(EDTA)^{2-}$ with $Fe(CN)_6^{3-}$ and $VO^{2+} + V^{2+}$ respectively.

In some cases, the existence of binuclear intermediates have been inferred from kinetic data or from empirical rate law because of the ephemeral nature of the intermediate,

which makes direct identification with currently available physicochemical techniques difficult. Such indirectly identified binuclear intermediate include $CrOHV^{5+}$[105] and $[OHTi\ X\ Co(NH_3)_5^{5+}]$[106]. It is worth mentioning that the identification of binuclear intermediates is a necessary but not sufficient condition for the diagnosis of the inner-sphere mechanism. Such intermediates could actually exist and yet the products form directly from such reactants. The existence of such possibilities has been demonstrated by Taube et al[107] when they prepared the stable analog of an inner-sphere complex,



and demonstrated that electron transfer occured independent of the connecting chains.

(4) Use of ambidentate potential bridging ligand.

The difference in rate of electron transfer observed with symmetrical and unsymmetrical bridging ligands also form a basis for determining whether some reactions utilize the outer- or the inner-sphere mechanism[108-114]. The use of such a criterion highlights the importance of precursor stability on electron transfer reactions. In certain cases the efficiency of the bridge is rationalized on the basis of the intrisic barrier to electron transfer by correcting the observed rate constants for differences in the free-energy of the reaction. For the majority of electron

transfer reactions involving bridges, especially by ambidentate ligands, the barrier to electron transfer reactions can be broken into two parts: the thermodynamic and the intrisic barriers. The intrisic barrier represented by $\Delta G_1^{\ddagger}$ and $\Delta G_2^{\ddagger}$ (where 1 and 2 refers to the homonuclear exchange reactions involving the reactants 1 and 2) and the thermodynamic contribution, ΔG^{o}. Differences in reaction rates can thus be a consequence of either or both of these contributions. For instance the azido/thiocyanato rate comparison reflects changes which occur primarily in the thermodynamic contribution. Hence the difference in rate when these two ligands are attached to a 'parent' complex have been interpreted in terms of the stability of the precursor complex formed prior to electron transfer[108]. Other rate effects may reflect changes in both the thermodynamic and intrisic contributions to electron transfer. An example is the electron transfer reactions involving actinide elements[115] as well as some inner-sphere reactions which have been considered in terms of these two parameters[116]. When the oxidizing and reducing ions are hard metal centers, then the inner-sphere reaction is expected to proceed faster when the bridging group is azide rather than isothiocyanate because the metal-nitrogen bonds are expected to be more stable than the metal-sulphur bonds.

Similar free energy considerations predict a faster reaction for thiocyanato complex over the azido or isothiocyanato complexes. Hence, the general trend of a lot of work done in this area especially employing mostly cobalt(111)

oxidants is[115,117].

$M(SCN)^{2+} > M(N_3)^{2+} > M(NCS)^{2+}$

(M = Cr(III) or $Co(NH_3)_5$)

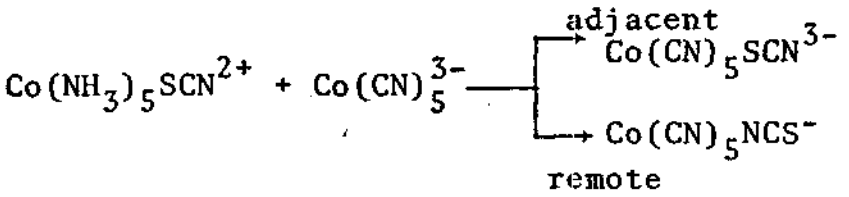
Usually k_{SCN}/k_{NCS} is of the order of 10^4 in most cases. However for V(II) reactions the smaller ratio of about 10^2 can be attributed to the substitution limitation into the inner-coordination sphere of $V^{2+}(aq)$[117]. Some results involving the use of this criterion is given below in Table (1.3)[118,119].

Table 1.3

M^{n+}	K_{SCN}	K_{N_3}	K_{NCS-}
Cr^{2+}	4,200	16,000	1
Cr^{3+}	10,000	16,000	1
Fe^{2+}	40,000	3,000	1
$Co(CN)_5^{3-}$	2,000	1.6	1
V^{2+}	100	1.4	1
Eu^{2+}	6,200	3.86	1
$Co(NH_3)_6^{2+}$	6.5×10^4	$3,9 \times 10^3$	1

Similarity in rate implicates the outer-sphere mechanism while the converse is true for reactions of the inner-sphere mechanism. It is worth mentioning that the validity of the use of this criterion has been confirmed by the more definitive product criterion used in the reduction of some cobalt(111) complexes by Fe^{2+}[117].

A further development in the use of ambidentate ligands is the introduction of the concept of adjacent and remote attack.[120] Thus for $Co(NH_3)_5SCN^{2+}$ and $Co(CN)_5^{3-}$ two modes of attack are possible[121] viz:



However the reaction proceeds exclusively by adjacent attack.

The reduction of $Co(NH_3)_5SCN^{2+}$ by Cr(11) occur by parallel adjacent and remote attack evidenced by the 'wrong bonded' product identified[122]. Recently, evidence has been provided for the remote attack of titanium(111) at an unprotonated carboxylate in the titanium(111) reductions of binuclear and tetranuclear μ-carboxylate cobalt(111)-ammine complexes[122b].

Another extention of the use of ambidentate ligands is the use of polyatomic bridging ligands in inner-sphere electron transfer reactions[123]. Extensive work has been done in this area notably by Gould et al[124] and Taube and co-workers[75,125], primarily to determine the effects of the various structural variations of organic bridging ligands on electron transfer reactions.

Some of the salient features highlighted by the use of these organic bridges include:

(1) that in the over 200 carboxylato pentaammine cobalt(111) complexes studied with Cr(11), the rate of electron transfer is slow unless the organic bridging ligand contains a conjugated bond system in addition to a group that is capable of binding to Cr(11).

(2) in certain cases, steric effects are very important, thus for Cr(11)-carboxylato pentaamine cobalt(111) complexes rate decreases in the order.

$$HCOO^- > CH_3COO^- > (CH_3)_2CCOO^-$$

(3) some of the work highlights the importance of chelation in the transition state of electron transfer reactions[65,116,127-129].

THE ROLE OF THE BRIDGING LIGAND IN INNER-SPHERE ELECTRON TRANSFER REACTIONS.

The possession of an unshared pair of electrons is a precondition for a coordinated ligand to act as a bridge in the electron transfer reactions that proceed by the inner-sphere mechanism. The mechanistic designation of the extreme role of the bridging ligand in such reactions has been given as the 'chemical', 'radical' or 'stepwise' mechanism. A brief description of each of the mechanism is given below:

Chemical mechanism.

In cases where a bridging ligand X, is potentially reducible and a redox reaction occurs by the inner-sphere mechanism, there is the possibility of a two-stage electron transfer process with the ligand mediating.

$$\text{(i)}\quad A^{n+} - X - B^{m+} \underset{}{\overset{K}{\rightleftharpoons}} A^{(n+1)+} - \dot{X} - B^{m+} \quad \ldots\ldots\ldots(52)$$

$$\text{(ii)}\quad A^{(n+1)+} - \dot{X} - B^{m+} \xrightarrow{k} A^{(n+1)+} - X - B^{(m-1)+} \quad \ldots\ldots(53)$$

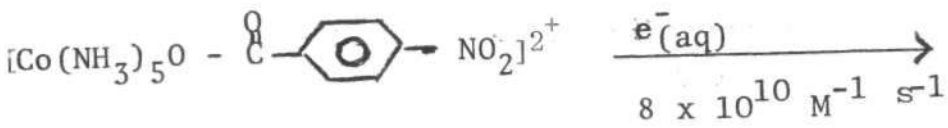
The condition to be met for this two-stage mechanism to operate is that $\Delta G^{o} < 0$ or $E^{o} > 0$ for each stage. A similar scheme also applies when X is an oxidizable ligand. In the latter case a filled ligand orbital of high energy could yield an electron to the oxidant and remain depleted for a time before accepting a replacement from the reductant.

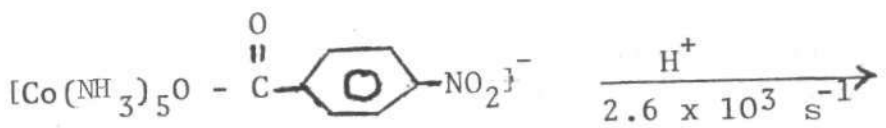
This alternative has however not been extensively studied. Since the chemical mechanism involves a transitory reduction or oxidation of the bridging ligand, then the bridging ligand role involves both thermodynamic and

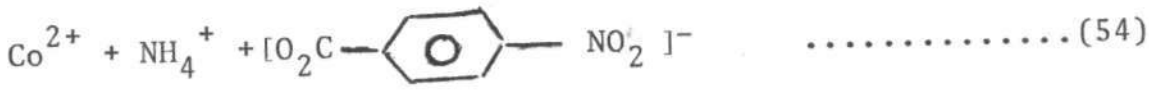
kinetic contributions and the measured rate in such a process will be a function of the equilibrium constant K , and the electron transfer rate constant k.

Direct evidence of the Chemical Mechanism.

Direct evidence for the operation of the chemical mechanism has been provided in the pulse radiolytic studies of p-nitrobenzoato pentaamine cobalt(111) ion[130]:







.....(54)

Hoffman and Simic attributed the first order decay observed for the metastable intermediate (A) to intramolecular electron transfer within the radical ion intermediate formed. This means that the hydrated electron is not transferred directly to the Co(111) center but resides for some time on the bound ligand before being transferred from ligand to the Co(111) center within the radical ion intermediate (A). This reasoning is in line with an earlier obtained spectroscopic evidence of a coordinated radical by - product in the chromium(11) reduction[131] of the $Co(NH_3)_5\ (p\text{-}NO_2C_6H_4CO_2)^{2+}$ cation and hence confirms the operation of a chemical mechanism.

Indirect evidence of the chemical mechanism.

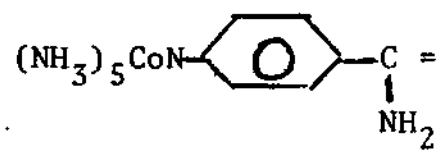
Since radical intermediate are very transient in nature, indirect methods for their identification have been devised. Two criteria that have been used for the indirect establishment of the chemical mechanism experimentally are, the ligand variation approach and the metal center variation approach.

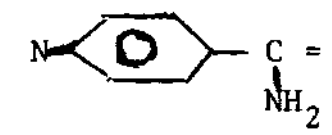
In the ligand variation approach, the rates are examined for the reduction of the same metal center using bridging ligands which are as similar as possible except for the presence of a low-lying orbital in one of them. For example[59], the parallel reduction of $(NH_3)_5Co(O_2CCHO)^{2+}$ by $Cr^{2+}(aq)$ at a rate ($> 7 \times 10^3\ M^{-1}S^{-1}$) much faster than for the reduction of $(NH_3)_5Co(O_2CCH_2OH)^{2+}$ ($3.1M^{-1}s^{-1}$) seems attributable to a chemical mechanism with a reducible ligand.

In the metal center variation approach, two metal centers, with the same charge and a similar propensity to perturb the energy of the ligand orbitals in questions, are chosen which differ substantially in their reactivities via presumably the resonance transfer mechanism. When a certain ligand is bound to either metal center and similar rates with particular reactants result, this is taken as evidence of the chemical mechanism.

An example of a case where the deduction of mechanism has been based on such a premise is when isonicotamide

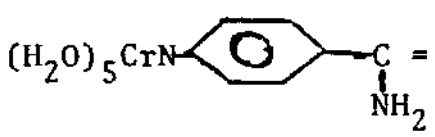
acts as a bridging ligand in the reactions shown below[132]:

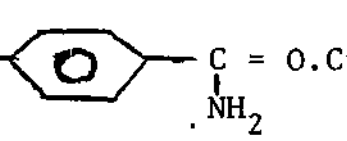


$$Co^{2+}(aq) + 5NH_3 + \text{} \quad \text{.....(55)}$$

$$k_{CoA_5L} = 17.6\ M^{-1}\ S^{-1} \text{ at } 25^oC$$

and



$$Cr^{2+}(aq) + \text{} \quad \text{.....(56)}$$

$$k_{CrA_5L} = 1.8\ M^{-1}\ S^{-1} \text{ at } 25^oC$$

The rate ratio $k_{CoA_5L}/k_{CrA_5L} = 0$ for the above reactions does not reflect the difference of 0.6volts in the redox potentials of these reactions.

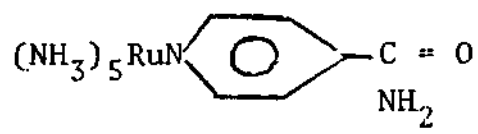
The chemical mechanism was suggested for these reactions. Also the similarity in rate when fumarate ($k_{CoA_5L}/kCrA_5L = 0.4$)[13] and maleate ($k_{CoA_5L}/k_{CrA_5L} = 50$)[134] are the bridging ligands has been interpreted in terms of direct participation of the ligand bridge in the electron transfer process.

On the other hand the chemical mechanism was ruled out for cases where k_{CoA_5L}/k_{CrA_5L} are in the range 10^5 to 10^7 ($L = OH^-, F^-, CH_3CO_2^-$) since these values are in conformity with the discrimination expected on the basis of the thermodynamic oxidizing powers of the Co(11) and Cr(111) complexes[131b]. It is worth pointing out however that this

criterion of metal center variation applies only in the likely case that the rate limiting barrier is the electron transfer to the ligand orbital which is of similar energy when bound to either of the metals.

Other systems where evidence have also been provided for the operation of the chemical mechanism are those involving the $Cr^{2+}(aq)$ reduction of the $(NH_3)_5Co\text{-}O\text{-}C$[124a] moeity and the Eu(11) reduction of pentaamine isonicotamide complexes[135].

From results of investigations, it seem that an essential feature of the chemical mechanism is that whether or not the transfer of electron to the bridge becomes a separate stage depends not only on the nature of the reductant and the bridging ligand, but also upon the oxidant. For example the complex,



has similar oxidizing properties to the Co(111) analogue and yet its rate of reaction with $Cr^{2+}(aq)$ is some 2×10^4 times faster[59]. It has been suggested[136] that the Co(111) and Cr(111) atoms allow the electron to reside on the bridging ligand because both accept the electron in an e_g orbital. This has σ symmetry and therefore does not interact directly with the Π system of the ligand, which, presumably accomodate the extra electron. The t_{2g}^5Ru(111) accepts the electron into a t_{2g} orbital which has Π symmetry

and can therefore interact with the Π system of the bridging ligand.

The matching of Cr(11) and Ru(111) is thus more likely to lead to what is usually termed a resonance transfer, without a stepwise feature.

The Resonance Mechanism.

The resonance mechanism has been used to describe the motion of the electron between metal centers through bridging ligands that operate on a 'give and take policy'. The reductant loses an electron to the bridge as the bridge loses a 'personal' electron to the oxidant. Naturally cases where a radical intermediate is not directly or indirectly detectable in a binuclear precursor complex are said to involve the resonance mechanism. Hence cases of bridging involving halide ions and ambidentate ligands utilize the resonance mechanistic pathway. In fact, in the inner-sphere reactions resonance transfer corresponds[137] to either 'direct exchange' between metal orbitals or "double exchange" wherein the bridging ligand simulaneously loses an electron to the oxidant and recieves one from the reductant. For outer-sphere reactions this corresponds to what is called "adiabatic transfer".[138].

When the resonance mechanism involves extensive orbital overlap between the metal centers through the bridging ligands then the 'super-exchange' mechanism can be said to be

operating[137]. Such effects have been suggested for some electron transfer reactions involving Ruthenium(111) and titanium(111) complexes[138b].

Non-bridging-ligand effect.

Extensive investigation has been carried out to determine the effect of non-bridging ligands on the rate of electron transfer reactions[133, 138-152], and a lot of false alarms have been raised in the rationalization of both the magnitude and order of these effects. However Earley's review[9] and the $CrEDTA^{-}$ + $Cr(NH_3)_5L^{2+}$ work[154] has shown that some of these effects are consequences of changes in the overall free energy of reaction ΔG^{θ}. In the absence of E^{o} values for Co(111) ammine complexes, people tend to invoke all sorts of complicated ligand field and electronic structure effects to rationalize the observed data. While the former effects may be important the extent of their influence has definitely been overblown in a lot of hitherto presented rationalizations. For example, for Co(111) complexes of the type $\{Coen_2ACl\}^{n+}$ in their reaction with Fe^{2+}, an inner-sphere mechanism can be demonstrated by the transient appearance of $FeCl^{2+}$[155]. When A is cis to the chlorine, the order of effectiveness is: NH_3 < -NCS < H_2O < Cl, the rates covering the range 1.8×10^{-5} to 1.6×10^{-3} M^{-1} s^{-1} at 25°C. When A is trans to the bridge the effect is much more marked, the sequence being NH_3 < NCS < N_3 < H_2O, with rates covering the range 6.6×10^{-5} to 2.4×10^{-1} M^{-1} s^{-1} at 25°C. A less systemati

variation has been observed for Cr(111) oxidants[156]. It has been suggested that the effectiveness of the non-bridging ligand is related to its ligand field strength, but in fact it is more likely that the σ-bonding ability of the ligand is more relevant[157]. Moreover the cis-$\{CoenACl\}^{n+}$ oxidants have the same ligand trans to the chloride bridge and variation in A has a smaller effect on the reactivity. Much more, these complexes are reduced by an outer-sphere mechanism, whereas the reactions of Ru(111) complexes with V^{2+}, which have an outer-sphere mechanism[158] do not conform to these patterns. From the above , it seems that arguments are tailored to rationalize rather than explain observed effect of the perturbation of these non-bridging ligands. Maybe when E^{o} values for most of these systems become available, the effects will be better understood in terms of the free-energy changes that accompany them.

Effect of Electronic Structure variation on rates of electron transfer reactions.

One of the most striking features of transition metal chemistry is the excellent correlation of physical properties with electronic structure[137,159-169]. Results of investigations confirm that the mediating ability of the bridging ligand in outer- and especially in inner-sphere reactions are not unrelated to the electronic

structure of the two metal centers involved. Both the symmetry of the donor-acceptor orbitals in terms of compliance with the Franck-Condon requirements for activation and the sysmmetry of the metal and ligand orbitals in facilitating electron transfer have been invoked in a lot of these rationalizations[12,75e,170,171]. For instance, in the electron transfer involving the metal centers A and B, the order obtained is $Cl^- > N_3^- > CH_3CO_2^-$ when electron moves from $e_g \rightarrow e_g$ orbitals,[172-177,75a,85], while the order $N_3^- > Cl^- > CH_3CO_2^-$ [178-180] is obtained when electron moves from e_g to $t_{2}g$ orbital and $t_{2}g$ to e_g orbital gives the order $N_3^- >> Cl^-$[181].

Taube and Linck[182] rationalized these results in terms of a lower activation energy pathway being provided when the following symmetry conditions are satisfied:

(i)	A	L	B
	e_g	σ	e_g
(ii)	A	L	B
	$t_{2}g$	Π	$t_{2}g$

where A and B are oxidants and reductants respectively.

Thus Cl^- is a better bridging ligand in inner-sphere reactions than N_3^- or CH_3COO^- when the donor-acceptor orbitals are of e_g symmetery and the favourable overlap of the $t_{2}g$ orbital with the Π-system of the azide or acetate makes them a better mediator than Cl^- in cases involving donor-acceptor orbitals of $t_{2}g$ symmetry.

The enhancement in rate observed[183] when isonicotamide is the bridging ligand for Ru(111) - Cr(11) reactions when compared with analogous reactions involving cobalt(111) reactions has also been rationalized on the basis of the symmetry of the oxidant, bridging ligand and reductant. It has earlier been mentioned[187] that where there is incongruent matching of orbitals and the bridging ligand is potentially reducible or oxidizable, then the chemical mechanism becomes preferred to the resonance mechanism. The change in electronic structure may also change the structure of the reactant ion. For instance, the oxidation of Cr^{2+} involves loss of an ϵ_g electron and hence change from tetragonal to octahedral structure occurs.

Therefore considering the reduction of $Ru(NH_3)_5py^{3+}$ and $Co(NH_3)_5py^{3+}$ by Cr^{2+} $k = 3.4 \times 10^3$ M^{-1} s^{-1} and 4.3×10^{-3} M^{-1} s^{-1} respectively as compared with the reduction of the pentaamine acetates of Ru^{11} and Co^{11} with $k = 5.6 \times 10^4$ $M^{-1}s^{-1}$ and 3.5×10^{-1} M^{-1} s^{-1} respectively, it is evident that the Co^{111} system gains a factor of ten or more in rate on going from an outer-sphere to an inner-sphere mechanism. This observed effect has been explained in terms of the complementary motion needed for the coordination sphere rearrangement when a reductant loses an e_g electron to an oxidant. That reduction by $V^{2+}(aq)$ reactions of the outer-sphere mechanism is faster than the corresponding ones of $Cr^{2+}(aq)$ is expected since Cr^{2+} requires more drastic bond length changes upon oxidation than $V^{2+}_{(aq)}$ requires.

The study of organic bridging ligands[124] also highlights the importance of orbital symmetry on the rate and mechanism of electron transfer reactions.

A very interesting extension of the effect of orbital symmetry on electron transfer rates is in its use in the rationalization[186] of anion catalysis usually observed for outer-sphere reactions.

The geometery of the transition state of outer-sphere electron transfer reactions makes such reactions susceptible to anion catalysis whereas they are expected to have little effect on inner-sphere reactions. Exceptions to this presurposition arises in reactions of aquoions with aquoions e.g. $Fe^{3+}(aq) + Cr^{2+}(aq)$ in which added chloride ion complexes with Fe^{3+} to form $FeCl^{2+}$ and Cl^- can then act as a bridge[187]. Nevertheless, anion catalysis has been an extensively used criterion for providing complementary data to the diagnosis of the mechanistic pathway by which electron transfer occurs. For instance it has provided useful complementary data in reactions involving $Ru(NH_3)_5X^{2+}$ and $U^{3+}(aq)$ (X = Cl, Br, I, OH, H_2O) and some $Fe(LL)_3^{3+}$ and $Co(LL)_3^{3+}$ reactions[187] with V^{2+}, Cr^{2+} and $Ru(NH_3)_6^{2+}$. In the latter reactions Sutin and Przystas[186] based their vigorous treatment of anion catalysis on thermodynamic and symmetry restrictions. Similar arguments earlier given by Stritar and Taube[125d] consists of the consideration of the orbital through with the electron is transferred. On the basis of

symmetry arguements the data in Table (1.4) can be rationalized. Hence for chromium(11) and vanadium(11) reactions k_{SCN}/k_{Cl} increases in the order:

$Co(NH_3)_6^{3+} < Co(en)_3^{3+} < Co(phen)_3^{3+}$

although coulombic considerations predict a constant ratio. Charge considerations predict a reverse order:

$Co(NH_3)_6^{3+} > Co(en)_3^{3+} > Co(phen)_3^{3+}$

Table (1.5) however sheds more light on the observed pattern with maximum rate enhancement occuring with V^{2+} - SCN - $Co(phen)_3^{3+}$ system which can be classified as a $\pi - \pi - \pi$ system. If we however consider the transfer from cobalt to phenanthroline, the system becomes $\pi - \pi - \pi - \sigma$. Such arguements are not tenable for the $VNCS^+$ - $Fe(phen)_3^{3+}$ reaction in which it has been proposed that the electron travels through a'π-electron superway'. Theweffects of chloride are generally not large with maximum rate enhancement observed for the $CrCl^+$ - $Co(NH_3)_6^{3+}$ reaction $a-\sigma-\sigma-\sigma$ system. The net effect of opposing symmetry trends is that thiocyanate favours the order: $(Co(phen)_3^{3+} > Co(en)_3^{3+} > Co(NH_3)$ and chloride favours the order: $(Co(NH_3)_6^{3+} > Co(en)_6^{3+} > Co(phen$ as evidenced in the Table (1.5). This comparison was also extended to rationalize the anion assisted iron(11) reaction. Interestingly, although not peculiar to NCS^- alone, the rationalization of the observed reactivity could be made, independently of sysmmetry arguements,but in terms of the stability of precursor complexes.

TABLE 1.4

RATE CONSTANTS FOR ANION-ASSISTED OUTER-SPHERE REACTIONS[186]

Reactants	k_o M^{-1} s^{-1}	k_{Cl} M^{-1} s^{-1}	k_{SCN}[c]	k_{SCN}[d] M^{-1} s^{-1}
$Co(phen)_3^{3+}$ - Fe^{3+}	5.3×10^{2}[b] 1.0×10^{3}[c]	2.0×10^{7}[c]		
Cr^{2+} - $Co(NH_3)_6^{3+}$	1.0×10^{-3} 8.8×10^{-5}[c] 7.2×10^{-3}	1.1×10^{-2} 1.2×10^{-1}[e] 6.0×10^{-1}	7.3×10^{-1}	1.4×10^{-1}
Cr^{2+} - $Co(en)_3^{3+}$	3.4×10^{-4} $\sim 2 \times 10^{5}$	1.5×10^{-3}	3.2×10^{-1}	1.5
Cr^{2+} - $Co(phen)_3^{3+}$	3.0×10^{1}	1.7×10^{2}	2.2×10^{5} 8.0×10^{4}; 3.8×10^{4}	
V^{2+} - $Co(NH_3)_6^{3+}$	1.0×10^{-2} 4.4×10^{-3} 3.7×10^{-3}	2.4×10^{-2} 3.5×10^{-2} 2.1×10^{-2}	2.4×10	8.1×10^{2}
V^{2+} - $Co(en)_3^{3+}$	7.2×10^{-4} 2.0×10^{-4}	1.9×10^{-3}	2.4	5.6×10^{-2}
V^{2+} - $Co(phen)_3^{3+}$	3.8×10^{3}	6.0×10^{3}	6.3×10^{7} 2.3×10^{7}	

[b] $[H^+] = 1.0M$ [c] $[H^+] = 0.01M$ [d] $[SCN^-]$ dependence in IM Cl^- unless noted

Table 1.5[186]

Ratio of Anion - Assisted Electron Transfer Rates:

Reactants	k_{SCN}/k_{Cl}	k_{NNN}/k_{SCN}
Fe^{2+} - FeX^{2+}	2.8×10	3.0×10^{4}
Cr^{2+} - CrX^{2+}	3.3×10^{-2}	2.4×10^{4}
Cr^{2+} - FeX^{2+}	9.1×10	5.2×10
Cr^{2+} - $Co(NH_3)_5X^{2+}$	1.3×10^{-2}	5×10^{4}
$Cr(bpy)_3^{2+}$ - $Co(NH_3)_5X^{2+}$	2.7×10	1.3
Fe^{2+} - $Fe(phen)_3^{3+}$	4.1×10^{3}	4.1×10^{-1}
Fe^{2+} - $Co(phen)_3^{3+}$	5.4×10^{2}	1.3
Cr^{2+} - $Co(phen)_3^{3+}$	1.3×10^{3}	
Cr^{2+} - $Co(NH_3)_6^{3+}$	6.1×10	
Cr^{2+} - $Co(en)_3^{3+}$	2.1×10^{2}	
V^{2+} - $Co(phen)_3^{3+}$	1.0×10^{4}	
V^{2+} - $Co(en)_3^{3+}$	1.3×10^{3}	
V^{2+} - $Co(NH_3)_6^{3+}$	1.0×10^{3}	

Dependence of the rate of oxidation - reduction reactions on hydrogen ion concentration.

Most reactions are affected by the pH of the reaction medium. It is therefore necessary to study as wide as possible a range of pH in order to determine the extent of $\{H^+\}$ involvement in a reaction and if possible delineate the reactive forms of the reactant species in solution. Hydrogen ion dependence of a reaction can arise under the following situations:

(1) in cases where one of the reactants is in an acid-base equilibrium in the pH range of interest. An evidence of this type of situation is the resemblance of the rate/pH profile to the profile of an acid-base titration curve. The reaction scheme generally associated with such a situation can be written in terms of acid AH, and its conjugate base A, which reacts with base B, a situation which usually leads to an inverse dependence of the rate of reaction on the hydrogen ion concentration. The scheme, (equations (57 - 59):

$$AH \underset{}{\overset{K_{AH}}{\rightleftharpoons}} A + H^+ \qquad \text{.....(57)}$$

$$A + B \xrightarrow{k_A} \text{Products} \qquad \text{.....(58)}$$

$$AH + B \xrightarrow{k_{AH}} \text{Products} \qquad \text{.....(59)}$$

can also be viewed as a structural requirement of one of the species prior to electron transfer in accordance with 'Franck - Condon's' principle. The rate expression can be formulated in terms of $\{A\} + \{A\}\{B\}$ as:

$$\frac{-d}{dt}\left[\{AH\} + \{A\}\right] = k\{AH\} + K_A\{A\}\{B\}^n \quad \ldots\ldots\ldots(60)$$

where k is the experimental rate constant, first-order if n = 0 and second order if n = 1 or

$$\frac{-d}{dt}\left[\{AH\} + \{A\}\right] = k\{AH\}\{B^n\} + K_A\{H\}\{B\}^n \quad \ldots\ldots\ldots(61)$$

If we combine equations (60) and (61) above and substitute,

$$K_{AH} = \frac{\{A\}\{H^+\}}{\{AH\}} \quad \text{we}$$

obtain equation (62):

$$k = \frac{K_{AH}\{H^+\} + K_A K_{AH}}{\{H^+\} + K_{AH}}$$

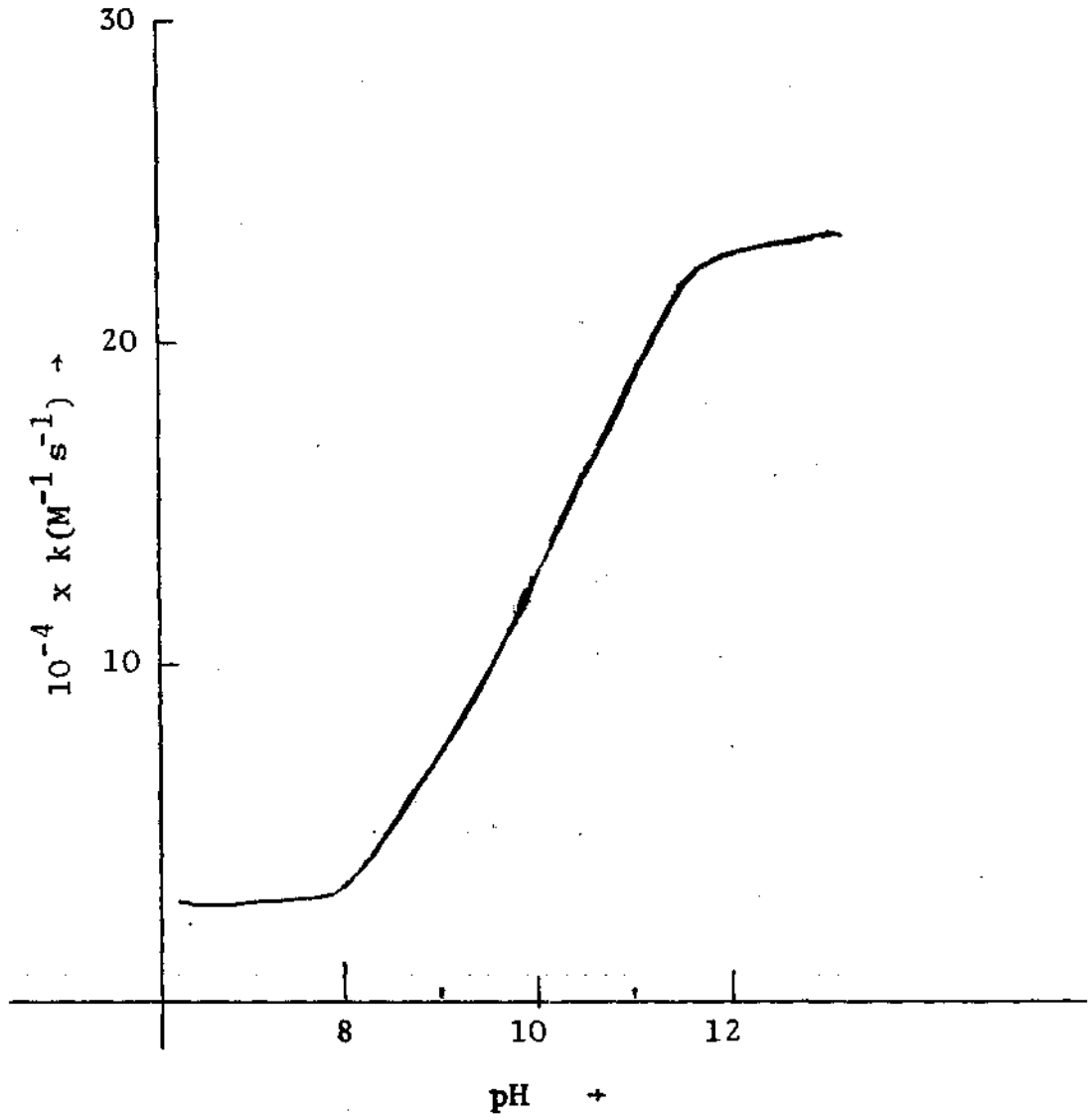
$$= \frac{K_{AH} + k K_{AH}\{H^+\}^{-1}}{1 + K_{AH}\{H^+\}} \quad \ldots\ldots\ldots\ldots\ldots(62)$$

A plot of k versus pH is a sigmoidal curve as shown in Figure (1.3). Such a profile has been observed in the oxidation of Co(11) - trien complex by molecular oxygen(O_2)[190] and the rate constant fits equation with $K_{AH} = 6 \times 10^{-12}\ M^{-1}$.

It is possible to obtain simplified forms of this type of acid dependence if:

Figure 1.3

Rate - pH profile.



acid-base equilibrium is unreactive, in which case we obtain:

$$k = k_{AH}\,(1 + K_{AH}\,(H^+)^{-1}) \qquad \text{.....(63)}$$

(2) One form predominates over the whole pH range of investigation, yet the other form is more reactive. i.e.

(a) $\{A\} >> \{AH\}$, $\{H^+\} << K_{AH}$ then

$$k = K_A + \frac{k_{AH}\{H^+\}}{K_{AH}} \qquad \text{.....(64)}$$

(b) $\{AH\} >> \{A\}$, $\{H^+\} >> K_{AH}$ then,

$$k = K_{AH} + \frac{k_A K_{AH}}{\{H^+\}} \qquad \text{.....(65)}$$

Ambiguity in interpretation of the rate law:

$$V = k\,\{A\}\,\{B\}\,\{H^+\}^n \qquad \text{.....(66)}$$

however arises when A and B are both acidic and n = -1 and A and B are both basic and n = 1 and therefore the role of AH with B or BH with A cannot be explicitly resolved. In such situations only plausible rationalizations can be tendered. Cases where acid-dependence of the type (1) has been encountered include a lot of Ti(111) reactions[191,192] e.g.

(i) $Ti^{III} + Hg^{II} \rightarrow Ti^{IV} + Hg^{I}$

with $k_{ob} = k_4\{H^+\} + k_5\{H^+\}^{-2}$

(ii) $Ti^{III} + Pu(IV) \rightarrow$ Products

with rate $= \frac{-d\{Ti^{III}\}}{dt}$

$$= k_6\,\{Ti^{III}\}\,\{Pu^{IV}\}\,\{H^+\}^{-1} \qquad \text{.....(67)}$$

and the reaction[193] of $Cr^{2+}(aq)$ with $Fe^{3+}(aq)$ with the deduced rate law of the form:

$$\frac{-d\{Fe^{3+}\}}{dt} = k\{Cr^{2+}\}\{Fe^{3+}\}\{H^+\}^{-1} \quad .....(68)$$

where the $\{H^+\}^{-1}$ term is probably due to the reaction:

$$Fe^{3+}(aq) \rightleftharpoons FeOH^{2+} + H^+$$

(2) The second type of acid dependence usually commonly encountered in redox reactions can be described as a compromise between reactants and products losing a proton in what may be called a concerted mechanism. Schematically this can be represented as follows:

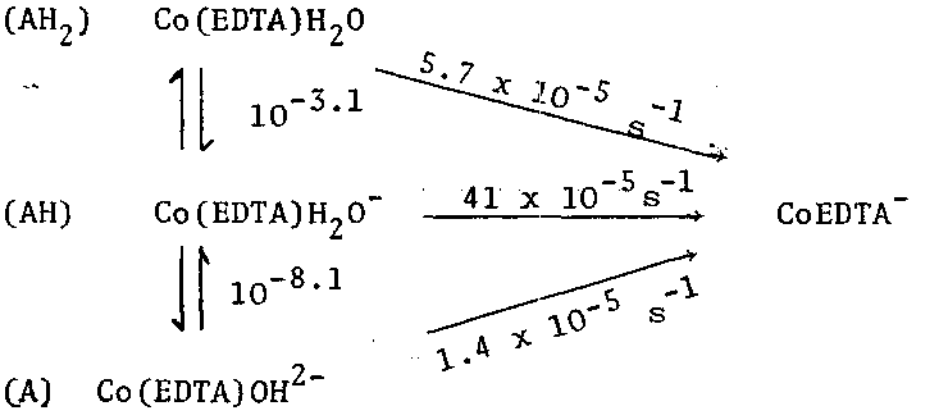
$$A^{III}OH_2 + B^{II} \underset{}{\overset{K}{\rightleftharpoons}} A^{III} - \overset{H}{O} - B^{II-} + H^+$$

$$A^{III} - \overset{H}{O} - B^{II-} \xrightarrow{k} A^{II} - \overset{H}{O} - B^{III} \longrightarrow \text{Products} \quad ...(69)$$

Many examples of this type of acid dependence exists in literature especially in the chemistry of the actinides, for the (+V) and (+Vl) oxidation states they exist as oxocations MO_2^+ and MO_2^{2+} respectively, and for high valence state transition metal complexes V(lV), VO^{2+}, V(V), VO_2^+, Ti(lV), TiO^{2+}, Cr(Vl), $HCrO_4^-$. In fact such cases where interpretation has been given in terms of the transition state losing a proton relative to the ground state in order to utilize a more efficient hydroxide bridge has been suggested in the reaction[194] of Ti^{IV} and V^{2+} where a transition state of the form $TiOHV^{4+}$ was proposed. The $\{H^+\}^{-1}$ term in the reaction of Cr^{2+} with V^{3+} is also interpretable in terms of the formation of $VOHCr^{4+}$ from V^{3+} and Cr^{2+} prior to the electron transfer step[58].

However these interpretations are not unique in that these intermediates could also be formed as a result of a pre-electron transfer hydrolysis of one of the reactant species.

It is worth mentioning that complex acid dependence of rates of reactions are observed when the reactions of at least three acid - base related species or two equilibria are involved. For this type of situation, the sigmodal shape of the rate constant/pH profile associated with the dependence of type 1 gives way to a bell-shaped or inverted bell-shaped plots. Such a situation arises when there is (i) diprotic reactants AH_2 e.g. the cobalt(111) complex of EDTA which exists in the form[195]:



and the first order rate constants at 15°C for ring closure versus pH conform to an equation of the form:

$$k = \frac{k_{AH_2}\{H^+\}^2 + k_{AH_2}K_{AH_2}\{H^+\} + k_A K_{AH}K_{AH_2}}{\{H^+\}^2 + K_{AH_2}\{H^+\} + K_{AH}K_{AH_2}} \qquad \ldots\ldots\ldots(70)$$

(ii) two protic reactants and in this case it is very difficult to separate the reaction couples. For example in the reaction of carbonic anhydrase with sulfonamides[196], the second-order association rate constant varies with pH. Since this can arise either through reaction of the acid form of the enzyme with the basic deprotonated sulfonamide or vice-versa. In principle therefore, separation of reactant couples is difficult.

METAL ION-LIGAND REDOX REACTION.

Of interest in the field of redox reactions are those involving metal ions and organic and inorganic substrates[33c,197-20]

The chromium(Vl) oxidation of oxalic acid[204], the oxidation of EDTA by Neptunium(Vl)[205] and the reaction of ascobic acid with Uranium(Vl)[206] provide examples of these type of redox reactions.

The review already published[194] highlights the mechanistic details of these reactions. Results of investigations show that we can conveniently classify these reactions into two groups, those for which there is evidence for an intermediate complex of significant life-time and those for which there is no such evidence. The former cases are said to occur via the inner-sphere mechanism with the possibility of inner-sphere complex in many cases more pronounced with neutral and negatively charged substrates when compared with their cationic counterparts. For the latter class however it is difficult to tell whether lack of evidence for an intermediate indicates the absence of such a species or merely that it is too short-lived

for the detection techniques employed. Cases where spectrophotometric evidence of intermediate formation have been obtained include the reaction of manganese(111) with hydrazoic acid, hydrogen peroxide and hydroquinone[207], iron(111) reaction with sulphite[208], thiosulphate, catechol, thiols[209], cysteine, thiomalic acid[210] and thiourea[211]; cobalt(111) reaction with cysteine, malic acid and thiomalic acid; thalium(111) reaction with hypophosphite, oxalic acid and alkenols and the reaction of cerium(1V) with hypophosphite, acetic acid, alcohols, hydroquinone and malic acid[212].

Kinetic evidence for intermediate complex formation have been obtained for the reactions of thalium(111) with hypophosphite[213], alkenes[214] and alkenols[215], cyclohexanes[216], O-dihydroxy aromatics[217] and oxalate; the reaction of iron(111) with hydrogen peroxide; iodide, sulphite[218], thiocyanate, acetylacetone and catechol[209] the reactions of cobalt(111) with hydrazoic acid, hydrogen peroxide; iodide, sulphite, thiocyanate, acetylacetone and catechol; the reactions of cobalt(111) with hydrazoic acid, hydrogen peroxide, alcohols, pyridine carboxaldehydes[219] and some organic acids.

Cases where no evidence of intermediate formation has been found include the reactions of silver(11) with dithionate[220]; silver(11) ascobate[221]; thallium(111) with cathecol[222], iron(111) with acetone[223], quinols, thiols and hydrazine; cobalt(111)[224] with bromide, chlorine dioxide and lactic acid, malic acid and phenylacetic acid.

In some cases where highly inert oxidants are involved, outersphere ion association may preceed electron transfer. In many of these cases especially those involving halogen and halide species, the generation of radical intermediates in the course of electron transfer has been suggested. A very recent example is the oxidation of iodide by poly (pyridine)-iron(111)[29] where the following reaction sequence involving radical intermediate was proposed:

$$Fe(LL)_3^{3+} + I^- \underset{}{\overset{K_{1P}}{\rightleftharpoons}} Fe(LL)_3/I^{2+} \quad \text{.....(71)}$$

$$Fe(LL)_3/I^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe(LL)_3^{2+} + I_2^{\cdot} \quad \text{.....(72)}$$

$$Fe(LL)_3/I^{2+} + I^- \xrightarrow{k_2} Fe(LL)_3^{2+} + I_2^{\cdot} \quad \text{.....(73)}$$

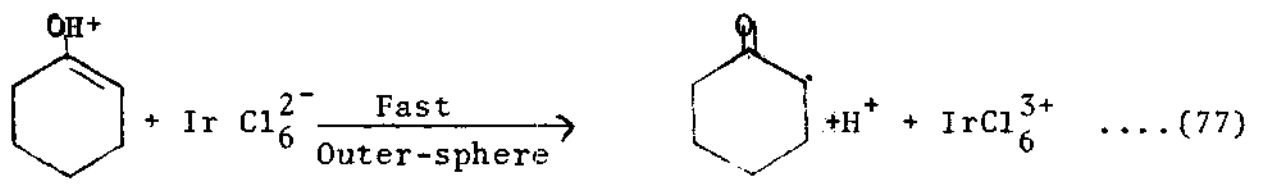
$$Fe(LL)_3/I^{2+} + I^{\cdot} \xrightarrow{k_3} Fe(LL)_3^{2+} + I_2 \quad \text{.....(74)}$$

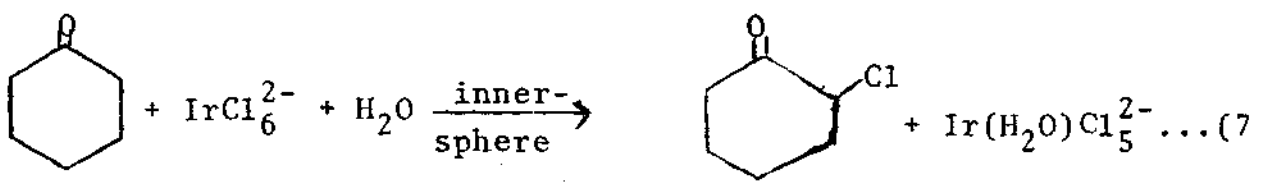
$$Fe(LL)_3/I^{2+} + I_2^{\cdot} \xrightarrow{k_4} Fe(LL)_3^{2+} + I_3^- \quad \text{.....(75)}$$

$$\text{rate} = -\tfrac{1}{2}\frac{d}{dt}\{Fe(LL)_3^{2+}\} = \frac{d}{dt}\{I^-\}$$

$$+ k_1K_{1P}\{Fe(LL)_3^{3+}\}\{I^-\} + k_2K_{1P}\{Fe(LL)_3^{3+}\}\{I^-\}^2 \quad \text{...(76}$$

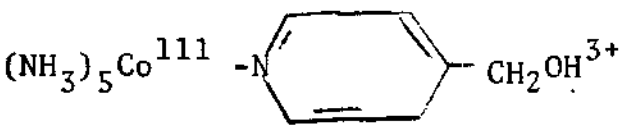
Another reaction also involving the formation of very reactive intermediate and which involves both inner- and outer-sphere processes in that of $IrCl_6^{2-}$ with cyclohexanol[207], viz:





Obviously ligand oxidation or reduction which involves complexation before electron-transfer will only proceed if there is a favourable free energy change and the stability of

the complex formed with respect to the intramolecular electron transfer will be dependent on the electron affinity of the bound ligand. For instance in the reaction of the one-electron oxidant Ce(1V) or Co(111) with



the observed kinetic data was rationalized by invoking internal redox reaction in one of the reaction steps[219].

Energetics.

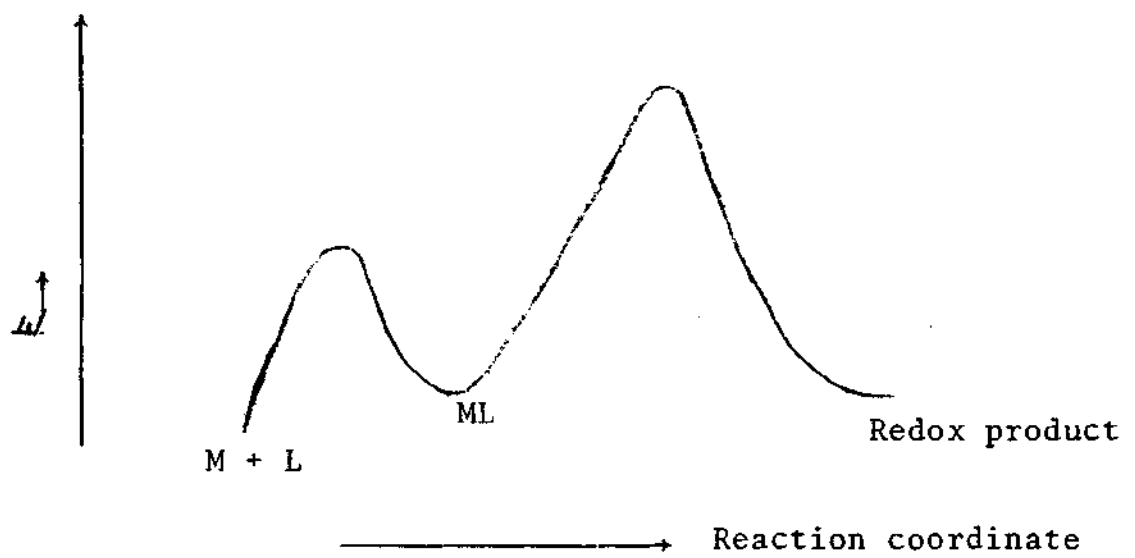
Schematically, metal ion-ligand redox reaction can be represented as

(1) $M + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML \xrightarrow{k_2}$ products .....(79)

Cases where there is evidence of transient inner-sphere complex which may lie along the reaction profile i.e. (Figure 1.4).

Figure 1.4

Reaction Profile for Metalion-Ligand redox reaction.



Examples are (a) the iron(III)[197,199] cyanocomplexes oxidation of reducing anions such as SO_3^{2-}, NO_2^-, I^- which probably involve rapid formation of intermediate i.e.

$$Fe(CN)_6^{3-} + SO_3^{2-} \rightleftharpoons Fe(CN)_5(CNSO_3)^{4-} + Fe(CN)_6^{4-} \quad .....(80)$$

$$Fe(CN)_5(CNSO_3)^{4-} + H_2O \rightarrow Fe(CN)_6^{4-} + SO_4^{2-} + H^+(Slow) \quad ...(81)$$

(b) Reaction of complexes with molecular oxygen e.g. In perchlorate medium $Fe(H_2O)_6^{2+}$ reacts with O_2 according to the reaction sequence[225]:

$$Fe^{2+} + O_2 \rightleftharpoons FeO_2^+ \text{ (rapid)} \quad .....(82)$$

$$FeO_2^{2+} + Fe(H_2O)_6^{2+} \rightarrow FeO_2H^{2+} + Fe(H_2O)_5OH^{2+} \text{ rds.} \quad .....(83)$$

$$FeO_2H^{2+} + H^+ \rightarrow Fe^{3+} + H_2O_2 \quad .....(84)$$

$$FeOH^{2+} + H^+ \rightarrow Fe^{3+} \quad .....(85)$$

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O$$

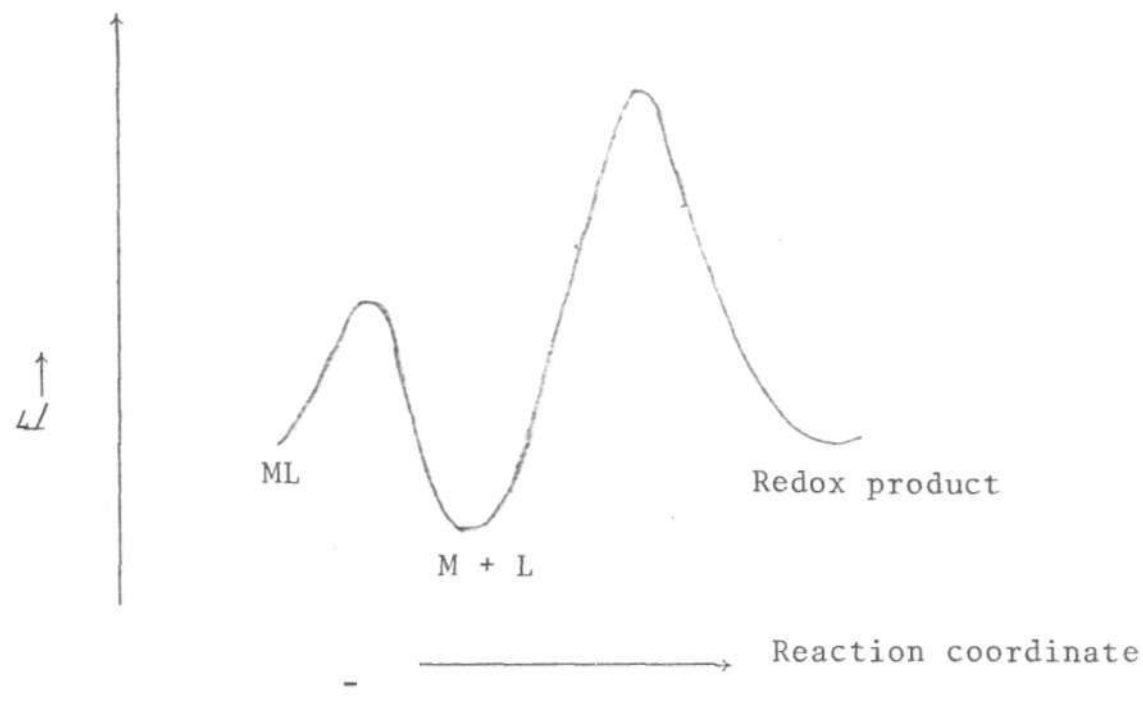
(c) The kinetic results of the vandium(v) oxidation indicate[226] a rapidly established preequilibrium to form a $[V(OH_2)I]^{2+}$ species whose simultaneous electron transfer and dissociation to VO^{2+}; an iodide atom and bromine occurs by initial one electron transfer.

(2) $M + L \rightleftharpoons ML$

$$M + L \rightarrow \text{products} \quad .....(86)$$

This involves the formation of complex which is extraneous and does not lead to products i.e. (Figure 1.5)

Figure 1.5



For example the reduction[225] of ClO_4^- by Ru^{2+} involves the complexation of these two species which proceed at comparable rate with their redox reaction.

In fact in cases where the redox process is so much slower than the complex formation step it is possible to isolate and characterize the intermediate complex. A good example is afforded by the thallium(111) oxidation of certain alkenes[174] In the extreme the 'intermediate' complex may be resistant to internal redox reaction that it appears indefinitely stable. For instance, iron(111) oxidizes thiomalic acid via a spectrophotometrically characterized blue intermediate[227] but iron(111) reacts with malic acid[228] to produce a malate complex which

undergoes no further oxidation.

Inherent in the two schemes given above are the following possibilities:

(a) if $k_{-1} > k_{-2}$ there is the possibility that we could observe both the formation and decomposition of any intermediate formed. For example organo-chromium intermediates have been proposed for the chromium(11) reductions of benzyl chloride, where the intermediacy of $PhCH_2Cr^{2+}$ cation was demonstrated[229],

(b) if ML is in a steady state, the observed rate constants and activation parameters must definitely be dependent on the magnitudes of k_1, k_2 and k_{-1} where the observed rate constants are usually of the form

$$k_{obs} = \frac{k_1 k_2}{k_{-1} + k_2} \qquad \text{.....(87)}$$

For example the reaction of $Nidien^{2+}$ with $EDTA^{4-}$ occurs[230] via the intermediate formation of Ni(dien) $EDTA^{2-}$ and obeys the rate law:

$$V = \frac{k_1 k_2 \{Nidien_2^{2+}\} \{EDTA\}}{k_{-1} \{dien\} + k_2 \{EDTA\}} \qquad \text{.....(88)}$$

(c) If $k_2 >> k_{-1}$ the redox reaction rate will be limited by the rate of formation of the complex and $k_{obs} = k_1$.

Such substitution limited rates have been proposed for some investigated cases. This situation is common in $Co^{3+}(aq)$ oxidations. Hence for the reactions of $Co^{3+}(aq)$ with oxidizable substrates there is such a small

range of observed rate constants that one is led to postulate S_N1 substitution at the cobalt as rate-determining.

In considering the reactions of aquometal ions and ligands, the possibility of $M^{n+}aq$ and $M(OH)^{(n-1)+}aq$ being involved with the substrate is often considered. Hence for both cobalt(111) and Manganese(111), $M(OH)^{2+}aq$ seem to be a more reactive oxidant than $M^{3+}(aq)$. This can be seen clearly in the cobalt(111) oxidation of benzene. For example[231], where the intermediacy of $benzeneH^{+}$ or cobalt(111) - benzene complex to complicate the interpretation of the observed kinetics, both seem highly implausible. For aquocations such as $Fe^{3+}(aq)$ the amount of this reagent in the forms of $Fe^{2+}(aq)$ and of $Fe(OH)^{2+}(aq)$ can be specified because the pK of $Fe^{3+}(aq)$ is known fairly accurately.

The major difficulties that has been encountered in the study of these reactions arise firstly as a consequences of instability with respect to the oxidizing center (water in most cases) which complicates kinetic monitoring especially for slow reactions. This complication arises as a result of the possibility of formation of mixed complexes. Such cases have been reported in some oxidations involving $Co^{3+}(aq)$ and Mn^{3+}[232].

MIXED VALENCE COMPOUNDS AND INTERVALENCE TRANSFER.

The study of these systems suggests a close correlation between colour, crystal structure, magnetism and electronic conductivity. Thus mixed-valence systems have been of special interest because their properties are not just merely the properties of the two metal ions taken separately but the interaction between the metal ions have been found to result in very dramatic changes in the physico-chemical properties of the system. For example, $W^{VI}O_3$ and $LiW^{V}O_3$ are insulators whereas the mixed-valence compound $Li_xW^{V}W_{1-x}O_3$ is a conductor. Also, the crystals $K_4Fe^{II}(CN)_6$ and $Fe_2^{III}(SO_4)_3$ are pale yellow whereas $KFe^{III}Fe^{II}(CN)_6$ is deep blue.

It has also been observed that paramagnetic substances may become ferromagnetic or diamagnetic all by changing the oxidation state of a part of the metal ion in the system by one or more units.

Actually, the most striking feature of many mixed valence compounds is the presence of intense absorption in the visible region of the spectrum, not present in compounds containing either valence state alone.

The pioneering work in the field of mixed valence chemistry was done by Robin and Day[233]. However, further extensive experimental investigations by Taube[234-236], Meyer[237-249] and associates and Mayor and Day[250], have put both the study of mixed-valence compounds and intervalence electron transfer on a sound experimental footing.

Robin and Day proposed a classification scheme for mixed-valence compounds based essentially on the strength and symmetry of the ligand fields about the metal ion and their relationship to the value of α, which measures the extent of delocalization of the excess electron. The general characteristics of the four classes of mixed valence compounds, proposed by Robin and Day are given below:

Classes of Mixed Valence Compounds and their General characteristics

Class 1.

1) Metal ions in ligand fields of very different symmetry and/or strength. i.e. tetrahedral vs octahedral.

2) $\alpha = 0$; localized valencies, valencies very firmly trapped.

3) Insulators; resistivity of 10^{10} Ohm cm^{-1} or greater.

4) No mixed valence transitions in the visible region.

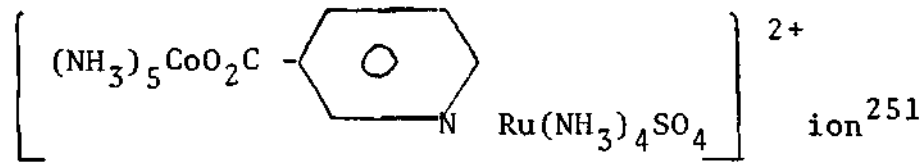
5) Clearly shows spectra of constituent ions (IR or U.V)

6) Magnetically dilute, paramagnetic or diamagnetic to very low temperatures.

Electrons which distinguish the valence of one ion from another are so firmly trapped that virtually no magnetic coupling between partly filled shells on adjacent metal ions is possible. For these class 1 mixed valence compounds, the visible spectra are merely the sum of the spectra of the constituent ions. In fact they are mostly colourless

compounds, with absorption bands usually greater than $27{,}000cm^{-1}$.

Examples of a class 1 mixed valence ion are the



ion[251]

and the μ-diphosphine-bridged dimer $\{(bpy)ClRu(Ph_2PCH_2PPh_2)RuCl(bpy)_2\}X_2$ ($X = ClO_4$ or PF_6)[252].

Class 11.

1) Metal ions in ligand fields of nearly identical symmetry, differing from one another by distortion of only a few tenths A^o.

2) $\alpha > 0$: valencies distinguishable, but with slight delocalization.

3) Semiconductors: resistivity in the range $10 - 10^7$ ohm cm^{-1}.

4) One or more mixed-valence transition in the visible region

5) Shows spectra of constituent ions at very nearly their normal frequencies.

6) Magnetically dilute, with both ferromagnetic and anti-ferromagnetic interactions at low temperatures.

The absorption of this class falls between 14,000 and $27{,}000cm^{-1}$ and these are absent from the spectra of constituent ions. The energy of transition is:

$$h\nu = E_A + E_B + E_{mad}$$

where A and B are the metal ion sites, E_A and E_B are the

changes in internal energy at sites A and B respectively and Emad is the Madelung energy expended in moving the optical electron from A to B in the electrostatic field. The two metal energy terms corresponds to the ionization potential and electron affinities of the sites A and B. Examples of compounds that fell into this class are

$$Cs_4Sb^{III}Sb^{V}Cl_2 \quad \text{and} \quad KFe^{II}Fe^{III}(CN)_6.$$

Another example is the mixed valence complex,

$$\{(NH_3)_5Ru\}_2pyr,^{250,255}$$

where the absorption and Mossbauer spectra suggests that the Ru^{II} and Ru^{III} centers retain their identity despite the similarity in ligand environment.

Class IIIA.

1) Metal ions indistinguishable but grouped into polynuclear clusters.

2) α maximal locally.

3) Probably insulating.

4) One or more mixed-valence transitions in the visible region.

5) Spectra of constituent ions not discernable.

6) Magnetically dilute.

Polynnuclear mixed-valence anions, cations, and neutral species in which the sites of all metal ions are equivalent. Since the distinction between the metal ion sites A and B is lost, $E_A = -E_B$ and Emad is zero.

No constituent ion spectra is therefore recognizable. For example the complex ion $\{(bpy)_2ClRu(py_3)Ru(bpy)_2Cl\}^{2+}$ falls into this class[236].

Class 111B.

1) All metal ions indistinguishable.

2) α maximal: Complete delocalization over cation subiattice.

3) Metallic conductivity: resistivity in the range 10^{-1} - 10^{-6} ohm cm^{-1}.

4) Absorption edge in the infrared, opaque with metallic reflectivity in the visible region.

5) Spectra of constituent ion not discernable.

6) Either ferromagnetic with high curie temperature or diamagnetic depending upon the presence or absence of local moments.

An example of a Robin and Day mixed valence class 111B metal ion are $\{(bpy)_2RuClORuCl(bpy)\}^{2+}$[237] and $Os_2\ O(bpy)_2(terpy)_2\}^{4+}$

In summary, possible variations of mixing of metal ion sites A and B from zero to complete mixing have been observed. For cases where the metal ion sites A and B do not mix, the precursor and successor states have two maxima of a mixed valence complex of Robin and Day class 1. Excitation from the precursor (p) state to the successor(s) state ($p \rightarrow s^*$) has zero probability. For weak interactions, where local valencies still exist (class 11) $p \rightarrow s^*$ transition produces

intervalence transfer band, the extent and thus the resonance energy of which can be estimated from the transition dipole. In cases of stronger interaction, the ground state can have appreciable mixing of the (A+ .....B) and (A....B+) configuration (systems (A^+....B) and (A....B^+) may be binuclear complexes of more-or-less fixed geometry or they may be reactive pairs in systems undergoing bimolecular reaction). These are equivalent to the precursor(s) and successor(s) states respectively.

If however the resonance energy exceeds the critical value, states p and s coalese with a class lll complex which can be preferably termed 'average valence' complex and it is characterized by an electronic transition and no longer has intervalence transfer.

It is worth mentioning at this juncture that a classification similar to that of Robin and Day has also been proposed by Endicott[254] and this classification is also based on the similar criteria of the mixing and non-mixing of reactants and products ground state and excited state wave functions.

Recently, considerable insight has been gained into the factors affecting electron transfer reactions by studying the rates of intramolecular transfer within binuclear complexes. It can now be asserted that both the radiative (optical) or radiationless (thermal) routes of electron transfer are rationalizable by similar formalism.

In the first case, the reaction is initiated by bombarding the sample with light of appriopriate wavelength.

The radiationless route is the 'dark route' since it does not require light. Thermal electron transfer results from the coupling of electronic and vibrational motion of reactant species. The activation energy of the thermal process and the transition energy of the optical process are each dependent on two factors:

(1) the electron affinity differential of the donor and acceptor sites,

(2) the ability of the reactant sites to satisfy the Franck Condon's restriction in terms of the non-equilibrium state of the electronically excited species with respect to atomic motion.

The theories of electron transfer have been aimed at the parameterization of the Franck Condon's barrier to electron transfer[255] and numerous attempts have been made to compare theoretical predictions with experimental results. However the little success recorded has been due generally to the difficulty of separating the electron transfer processes from the complex formation and rearrangement process that preceed it. Cannon has written an excellent review on optical electron transfer[256].

Before discussing further let us first distiguish between thermal elctron transfer and optically excited electron transfer processes.

Thermal Electron Transfer.

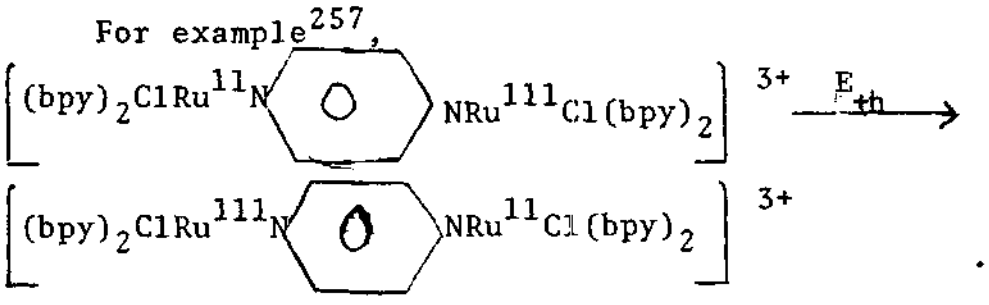
This can be represented by the following equation:

$$(M_1^+ \ldots M_2)(env) \xrightarrow{E_{th}} (M_1 \ldots M_2^+)(env)$$

precursor binuclear complex (p) — successor binuclear complex (s)

(env = the metal ion - solvent environment, $M_1 \ldots M_2$ can be rigid binuclear complexes or reactive pairs in systems undergoing a binuclear reaction where the metal centers differ by one electron).

For example[257],



.....(89)

Optically excited electron transfer process.

This can be represented by the following general equation:

$$(M_1^+ \ldots . M_2)(env) \xrightarrow[\Delta G_f]{Lhv = Eop} (M_1 \ldots\ldots M_2^+)(env^*) \quad \ldots\ldots(90)$$

(p) (s*)

(L = Avogadro number)

The electronic configuration of S* is different from that of p but it still retains the ligand environment of p. v measures the molar energy, enthalpy and free energy of the process above.

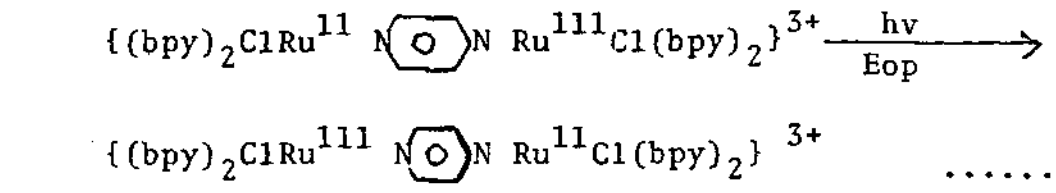
$Lhv \approx \Delta G$.

Theoretically, the reverse electron transfer process is also possible[248,258], viz:

$$(M_1 \ldots M_2^+)(env) \xrightarrow{\Delta Gr} (M^+ \ldots M_2)(env) \quad \ldots\ldots(91)$$

$$\Delta G_f = \Delta G_r$$

For example,

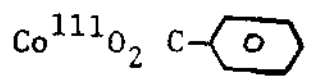
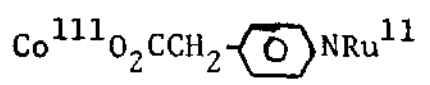
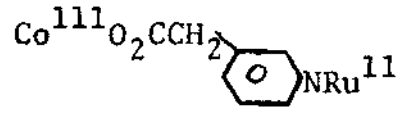


$$\{(bpy)_2ClRu^{II}\ N\bigcirc N\ Ru^{III}Cl(bpy)_2\}^{3+} \xrightarrow[Eop]{h\nu} \{(bpy)_2ClRu^{III}\ N\bigcirc N\ Ru^{II}Cl(bpy)_2\}^{3+} \quad \ldots\ldots\ldots(92)$$

Optical intervalence transfer has been defined as an optical transition which involves an electron from one nearly localized site to an adjacent one. The donor and acceptor sites being metal ions which possess more than one accessible oxidation state.

Most work on intervalence transfer have been based on Ru(11 and Co(111) homonuclear and heteronuclear complexes which are either generated in situ or synthesized with half-lives of several days in solution thus making such complexes ideal for experimental studies.

Thus, the measurement of the rate of interamolecular electron transfer has been successful for some Co(111)-Ru(111) binuclear complexes bridged by pyridinecarboxylate ligands. Some examples of these are[255]:

Complex	k_{sec}-1
	1×10^{2}
	1.6×10^{-2}
	1.6×10^{-3}
	5.5×10^{-3}

The point of interest in these types of studies has been the importance of configuration on the rate of electron transfer and the possibility of the actual electron transfer by-passing the bridging ligand and proceeding by the outer-sphere mechanism. Also of importance are the consequences of electronic and steric considerations on the rate of electron transfer. In certain cases, the rate of formation and dissociation of the precursor and successor complexes have been measured and also the rate of electron transfer. For example in the reaction[259]:

$$Co(NH_3)_5(4,4\text{-bpy})^{3+} + Fe(CN)_5OH_2^{3-} \underset{k_d}{\overset{k_t}{\rightleftharpoons}}$$

$$(NH_3)_5Co^{III}N\langle O-O\rangle NFe^{II}(CN)_5 \xrightarrow{k_{et}}$$

$$(NH_3)_5Co^{II} - N\langle O-O\rangle NFe^{II}(CN)_5 \qquad \text{.....(93)}$$

$k_f = 5.5 \times 10^3\ s^{-1}$, $k_d = 4.5 \times 10^{-3}\ s^{-1}$

$k_{et} = 2.6 \times 10^{-3}\ s^{-1}$

Electron transfer involving binuclear complexes of the form:

$(NH_3)_5Ru^{II}$-L-$Ru^{III}(NH_3)_5^{n+}$ where L is a bifunctional group have also been studied[260], for example

$$(NH_3)_5Ru^{II} - N\langle O-O\rangle NRu^{III}(NH_3)_5^{5+}.$$

Also studied[261] are symmetrical and unsymmetrical heteronuclear molecules e.g.

$$(NH_3)_5Ru^{II}- N\langle O-O\rangle N\text{-}Rh^{III}(NH_3)_5^{5+} \text{ and}$$

$$(NH_3)_5Ru^{II}- N\langle O-O\rangle NRu^{III}(NH_3)_4Cl^{4+}$$

The vertical transitions in these complexes have been found to obey the Franck Condon's restriction. The intervalence process being represented as:

$$(2,3) \xrightarrow{h\nu} (3,2)^*$$

which is true for all intervalence transfers. One obvious fact in this type of studies however is that the vibrationally excited products must relax to products vibrational ground state with the release of thermal energy which heats up the solution infinitesimally during this relaxation process.

Theory of Intervalence Transfer.

Hush[262] has developed an elegant theory of intervalence transfer. When sysmmetrical homonuclear binuclear complexes undergoing one electron transfer are involved in this classical barrier crossing treatment (based on Franck Condon's principle) he concluded that

$$\Delta Eop = 4\Delta E_{th}^{\ddagger} \qquad \ldots\ldots\ldots(49)$$

and

$$\Delta Eop = h\nu_{max} - (16 \ln 2 kT)^{-1} \Delta E_{\frac{1}{2}}^2$$

where k = Boltzmann's constant

T = Temperature in degrees absolute,

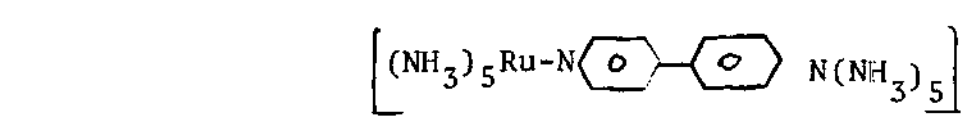
$\Delta E_{\frac{1}{2}}$ is the band width at half height.

At 300°C this can be simplified to

$$\bar{\nu} = \frac{\Delta E_{\frac{1}{2}}^2}{2310}, \qquad \text{where } \bar{\nu} \text{ is in } cm^{-1}.$$

Immense information is obtained about intervalence electron transfer for ruthenium binuclears. For example, by simply running the spectra of the dimers in each of the

{2,2}, {2,3} and {3,3 } oxidation states. A typical example of such spectra is given in Figure(1.6) for



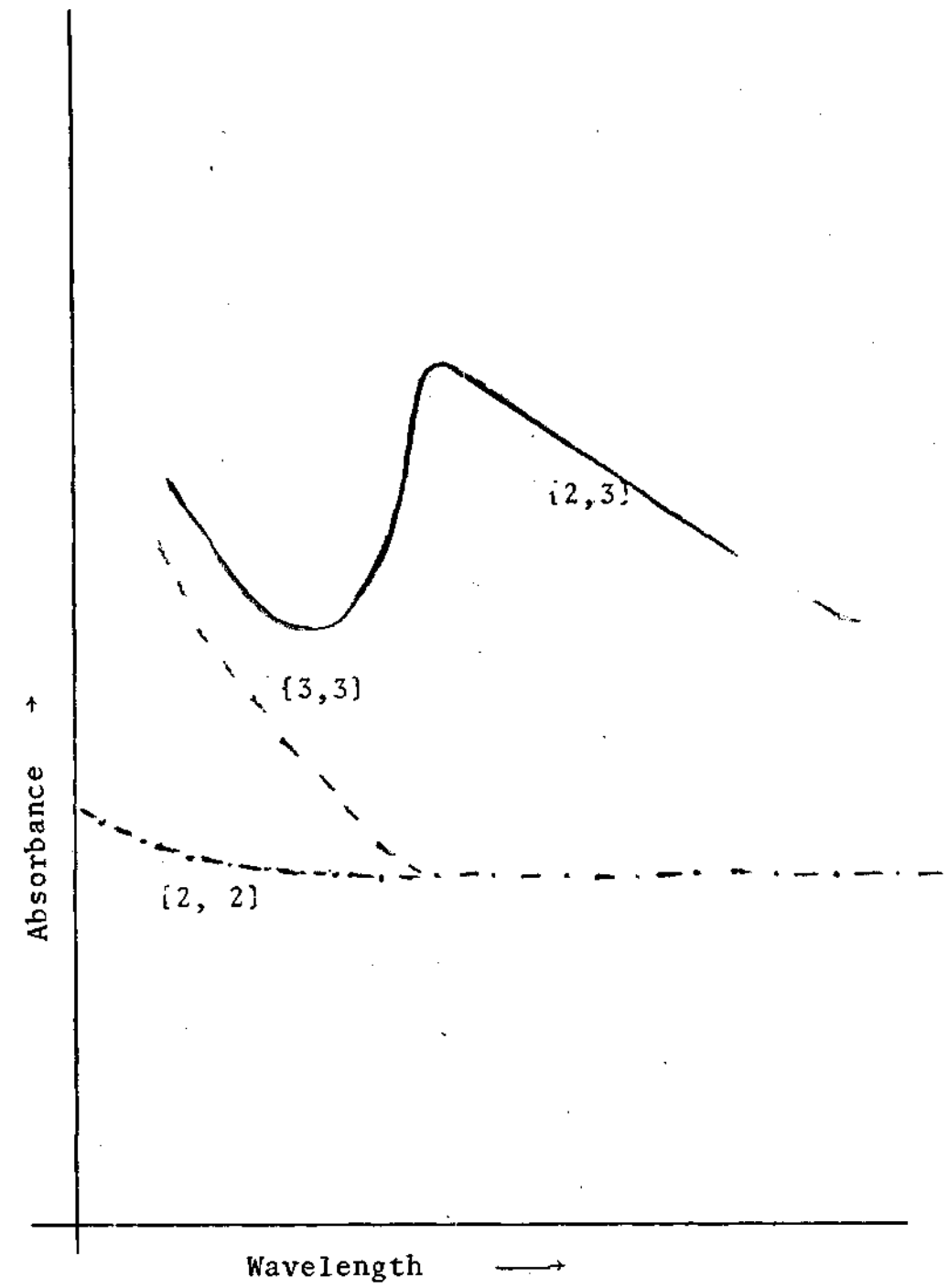
$^{4+,5+,6+}$[263]

Most intervalence bands are Gaussian in shape on an energy scale. The oscillator strength of these types of curves being given by the expression:

$f = 4.6 \times 10^{-9} E_{max} \Delta E_{\frac{1}{2}}$ where E_{max} is the extinction coefficient of the band maximum and $\Delta E_{\frac{1}{2}}$ is the half-width at half-height in wave number (cm^{-1})

As a consequence of the ruthenium vibrations, the intervalence band is usually found in the near infra-red spectrum (~700 - 800nm). The {2,2} and {3,3} oxidation states of the dimers characteristically give no absorption in the visible and near IR spectrum but the {2,3} dimer gives a broad intervalence band with properties which may be interpreted by Hush's theory. Like Marcus' theory for outer-sphere electron transfer reactions, the theory of Hush for intervalence electron transfer is only applicable to cases where there is minimal coupling between the electronic states of the 'twin' ions in a binuclear complex. Definitely the extent of electronic coupling is a function of the electronic delocalization over the dimer. The oscillator strength of the intervalence (IT) band is also directly related to the degree of delocalization.

Figure 1.6



spectra of the complex ions:

$$\{(NH_3)_5Ru - N\langle O \rangle - \langle O \rangle NRu(NH_3)_5\}^{4+,5+,6+}$$

Consequently, strong coupling between metal bands ($\Delta E_{\frac{1}{2}}$ will be too small) and with high extinction coefficient than predicted by Hush's theory. Also, the distance between the metal centers determine the energy of the IT bands (ΔEop). ΔEop is also sensitive both to the identity of the metal centers and the nature of the bridging ligands present in the first coordination spheres of the metal centers.

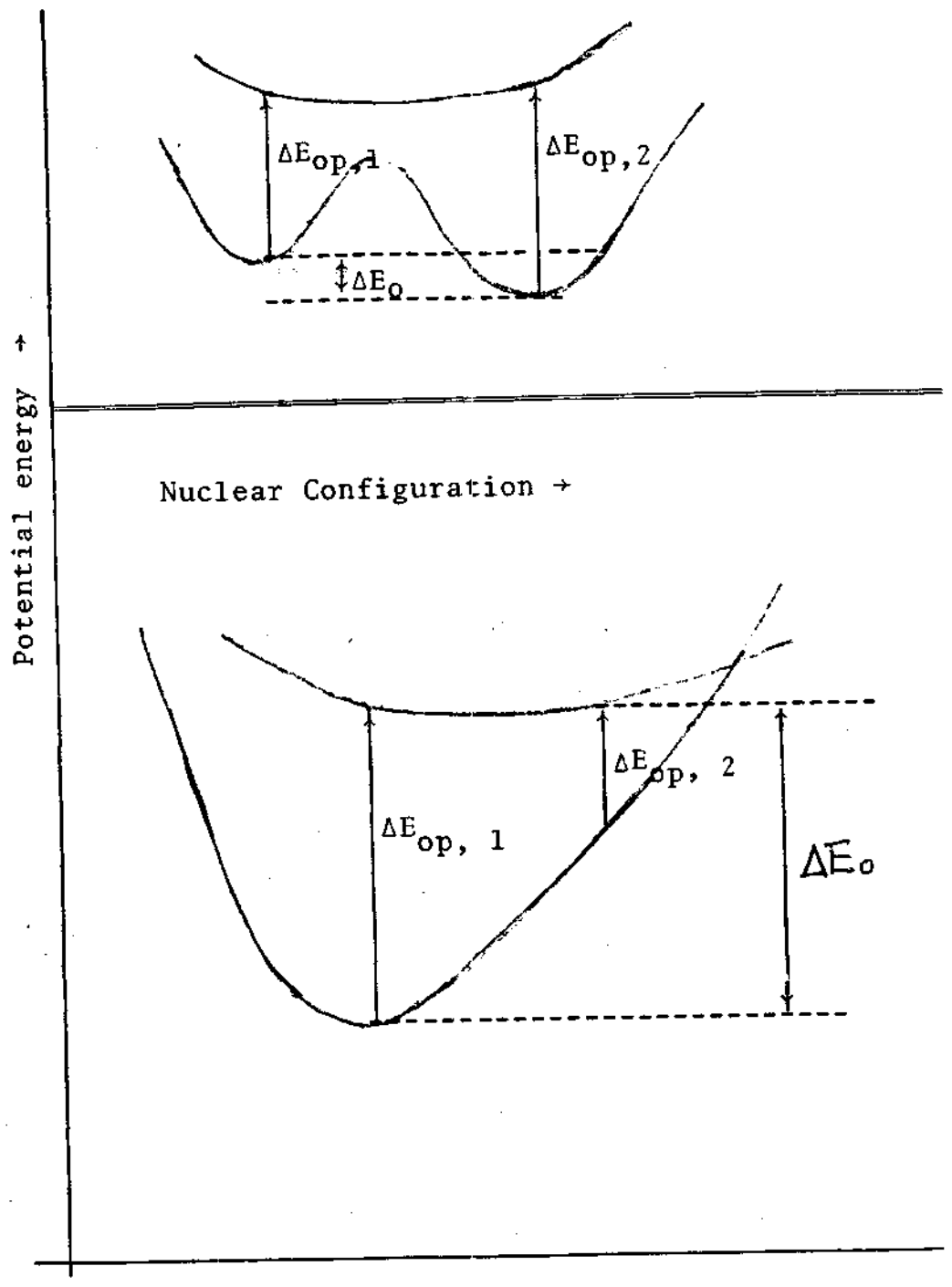
It is further related to the energy of the Franck condon's barrier ($\Delta E_{th}^{\ddagger}$) by the equation:

$$\Delta Eop = 4\ \Delta E_{th}^{\ddagger}$$

The consideration of heteronuclear or unsymmetrical homonuclear electron transfer reactions also highlights one of the predictions of Hush. For these types of complexes, two possible transitions are expected, one from each minimum of the potential energy surface (Figure 1.7). However, only one IT band is usually observed for these binuclears even in the heteronuclear case, in conformity with the predictions of Hush. The reason adduced by Hush for this usually observed phenomenon is that the ratio of the number of reactant molecules to the number of product molecules will be determined by ΔE_o. Therefore, since product molecules outnumber reactant molecules, there will be many more product potential transitions arising from products potential wells than from reactants potential wells and therefore transitions from the reactants potential

Figure 1.7

Potential energy diagram showing possible inter-valence transitions.



wells will not be seen because their fewness in number will result in very low intensity. The possibility is however that they may contribute to a slight broadening of the observed IT band from the products potential well, in excess of what would be predicted by Hush's theory.

Pin-pointing the actual potential well responsible for the origin of transition will however be difficult for homonuclear electron transfer because the reactants and products are identical.

If ΔE_{op} is exceptionally large, the possibility of the intersection of the potential energy surfaces of the reactants and products exists, if both potential minima are on the same side of the intersection point. Two optical transitions are hence expected, one from each well but this time, one of them ($\Delta E_{op,\ 2}$) corresponds to an emission spectrum rather than an absorption and fluorescence is expected to be observed. This phenomena which is very common in organic charge transfer spectra[264] has apparently not been observed in simple inorganic binuclear - complexes.

Mixed-valence Complexes of Ruthenium.

The reactivity of bound nitrosyl and nitro groups and the use of a series of stepwise reactions[244,245] has been exploited in the preparation of a series of ligand-bridged dimeric and oligomeric complexes of ruthenium. Meyer et al have prepared ruthenium[237,238] complexes of the form:

$\{(bpy)_2ClRu(L)RuCl(bpy)_2\}^{2+}$,

using a series of N-heterocyclic ligands and oxygen atom. They have employed L = pyrazine, 4,4'-bipyridine and trans-1,2-bis(4-py) ethylene. They have also prepared pyrazine-bridged oligomeric complexes with controlled chain lengths. For example,[234]

$\{(bpy)_2ClRu(py_3)\{Ru(bpy)_2(py_3)\}(py_3)\}\ Ru(bpy)_2\}^{(2n+2)+}$

with n = 0 to 4. From the study of the stoichiometry, the geometrical coordination at each ruthenium site in these complexes has been most likely cis[265-267]

Taube and associates[234-236] have also prepared a series of mixed-valence complexes of ruthenium. The motivation in this area of studies has been the urge to bridge the gap between our understanding of electron transfer in simple chemical reactions and electron transfer as is encountered in extended arrays of atoms such as semi-conductors and conductors.

The question of fundamental importance in ligand-bridged metal complexes are as stated earlier, the nature and the extent of metal-metal interactions across the bridging ligands and the consequences of the interactions on the chemical and physical properties of the systems.[245,268] Cases where significant trapping energies exist favour localized valencies[244,256,268] whereas orbital overlap leads to electronic delocalization and eventual reduction in the vibrational trapping energy thus making the two metal sites in a homonuclear binuclear equivalent on the vibrational time scale.[235,236] Extensive experimental investigation has been carried out of recent on the mixed valence complexes of ruthenium.

Complexes of ruthenium(111) have been found to be spin paired d^5 cases with one unpaired electron[268-272] which means that for dimeric ions like,

$$\{(bpy)_2ClRu(py_3)RuCl(bpy)_2\}^{4+},$$

magnetic techniques provide a sensitive probe for detecting Ru(111) - Ru(111) electronic interactions. Measurements of magnetic susceptibilities on ligand-bridged oligomeric complexes containing ruthenium in +3 oxidation state could reveal extended magnetic interactions involving more than two metal sites[258].

From the results of these studies, it can be concluded that the extent of delocalization between ruthenium sites in ligand bridged systems is critically dependent on:

(i) the oxidation state of the metal site,

(ii) the bridging ligand and

(iii) the non-bridging ligand effects.

Metal - Metal electronic interactions in mixed-valence Ru(11) - Ru(111) complexes occur by overlap between $d\pi$(Ru) orbitals at two metal sites.

In some cases the extent of metal-metal overlap can be prolonged as shown by mixed valence ions like

$[(NH_3)_5Ru(NCCN)Ru(NH_3)_5]^{5+}$ and

$[(bpy)_2RuClORuCl(bpy)_2]^{3+}$[237]

where the additional electron appears to be delocalized between both metal sites on an infrared time scale.

The electronic resonance energy arising from orbital overlap in these ions must be sufficient to overcome the difference in the inner and the outer coordination sphere vibrational trapping energies. This difference in vibrational energies is a consequence of the changes in oxidation states at the metal centers. They would trap the additional electron on the Ru(11) site in the absence of significant electronic overlap.

For cases where a group like pyrazine is the bridging ligand, the Ru - Ru distance is large (6.9A^o) and hence, the metal - metal overlap must occur by metal-ligand mixing, e.g. $d\pi$(Ru(11) - π^*(py3) which essentially carries Ru(11) character across the ligand bridge to Ru(111). Ligands like pyrazine enjoys the availability

of both filled π and empty π* levels for mixing with d orbitals. For the Ru(111) - Ru(111) dimers and higher oligomers, the absence of low energy metal ligand charge transfer bands implies that dπ - π* (py_3) mixing is unimportant and the absence of significant magnetic interactions means that dπ - π (py_3) - dπ mixing is also unimportant. Therefore for a dimer like

$$[(bpy)_2\ ClRu\text{-}o\text{-}RuCl(bpy)_2]^{2+},^{237}$$

minimal electronic interaction is expected and it is in fact observed. In contrast to the Ru(111) - Ru(111) systems, in the mixed valence $\{(bpy)_2ClRu(py_3)RuCl(bpy)_2\}^{3+}$ the appearance of a low energy intervalence transfer band gives a clear evidence of an observable metal-metal interaction, viz. Ru(11) - Ru(111) $\xrightarrow{h\nu}$ Ru(111) - Ru(111)*

The difference between Ru(11) - Ru(111) and Ru(111)-Ru(111) cases suggest that the orbital mechanism for interaction in the mixed valence ions is by dπ(Ru(11) - π*(py_3)) mixing, since oxidation leads to orbital contraction of dπ orbitals and to their stabilization relative to π* (py_3).

In the study of ruthenium dimers bridged by some heterocycles, results indicate that there is no metal-metal interaction across these heterocycles.

It is of interest that the properties of inter-valence bands and the theoretical treatments given by Hush[262] and recently by Hop field[273] have made it possible to deduce

the role of solvent polarization and of the distance between redox sites in determining the optical and thermal barriers to intramolecular electron transfer through the bridging ligand. Unsaturated ligands have been found to promote electronic interactions by $d\pi(Ru) - \pi^*$ (bridge) mixing, and the magnitude of the effect can be calculated by the oscillator strength of the IT band.

The results of the study of mixed-valence ions have been applied by inference to related outer-sphere electron transfer reactions. However, given the information available for IT bands, it would be desirable to observe the transition directly in outer-sphere systems. Since there are no requirements that the observation of the IT bands be confi ed to cases where electron transfer occurs through a ligand bridge, the approach for outer-sphere systems had been to take advantage of coulombic binding between donor and acceptor sites within an ion pair,[274] viz:

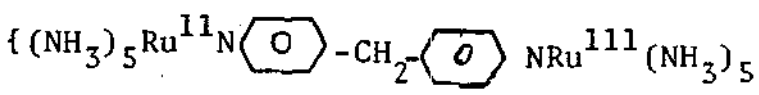
$$\{Ru^{III}(NH_3)_5py,Fe^{II}(CN)_6\}^- \xrightarrow[E_{op}]{h\nu} \{Ru(NH_3)_5py,Fe^{III}(CN)_6\}^{-*} \quad ..(95)$$

Another approach has also been used which devises chemical links between the redox sites which at the same time:

(a) has a region of saturation so as to minimize electronic coupling through the bridge,,

(b) constrains the redox sites to be in close contact.

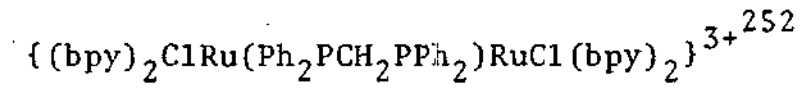
Taube and co-workers and Meyer and Sullivan repor
weak IT bands in the dimers (1), (2) and (3):



(1)



(2)



(3)

where a continuous region of unsaturation between the
sites do not exist.

More recent theoretical treatments have tended tc
emphasize the importance of phonon coupling between th
exchanging electron and the surrounding vibrational sy
and to point out that in thermal electron transfer, nu
tunnelling through the barrier may play an important r
For Ru-Ru binuclears, reasonable estimates for the
vibrational trapping energy in the absence of signific
delocalization had been made using the mononuclear
complexes which have the chemical and physical propert
of the redox sites in the mixed valence ions. Recentl
flash photolysis technique used to measure the self-ex

rate of $Ru(bpy)_3^{3+}/Ru(bpy)_3^{2+}$ at 25°C showed that the rate is near diffusion controlled limit.[275] It was then concluded that the slight activation barrier arises largely from the changes required in the outer coordination sphere. This view is consistent with the experimental structures of salts of the closely related ions $Fe(phen)_3^{2+}$ and $Fe(phen)_3^{3+}$ which shows nearly identical Fe - N bond distance in the two ions.

Hush[262] has given the expression for the variation of Eop with the dielctric properties of the surrounding medium as:

$$E_{op} = \lambda_i + \lambda_o = \lambda_i + (Me)^2(a_1/a_2 + a_2/2 - 1)\ (\frac{1}{n^2} - \frac{1}{Ds})$$

where λ_o is the outersphere contribution to E_{op}, M is the extent of charge transfer in the IT process, e is the unit of electrical charge, a_1 and a_2 are the molecular radii d is the internuclear separation of metal sites and n^2 and Ds are the optical and static dielectric constant of the medium and λ_i is the inner coordination sphere contribution to E_{op} and it include all other solvent-independent terms. E_{op} is the energy difference between the ground and the vertical mixed valence excited states. Optical excitation, which occurs instantaneously on the vibrational time scale produces Ru(11) and Ru(111) sites in equilibrium coordination environment of the other oxidation state.

An empirical test of Hush's theory has been carried out by Creutz and Taube[277] and independently by Meyer[278]. For the ion

$$\{(bpy)_2ClRu^{II}.4,4'bpy)(Ru^{III}Cl(bpy)_2\}^{3+},$$

Meyer obtained E_{op} in six different solvents and a plot of E_{op} vs $(1/D_{op} - 1/D_s)$ gave the expected linearity with a correlation coefficient of 0·99 and intercept

$\lambda_i = 6.3 \times 10^3 cm^{-1}$ which is the same within experimental errors as the value found for the ions $\{(bpy)_2ClRu^{II}(BPE)Ru^{III}Cl(bpy)_2\}^{3+}$ and $\{(bpy)_2ClRu^{II}(pyr)Ru^{III}Cl(bpy)_2\}^{3+}$. The observed ($7.91 \times 10^3 cm/A^o$) and calculated ($7.13 \times 10^3 cm/A^o$) slopes are in excellent agreement. A less satisfying situatior was however found for the ion $\{py(Ru4,4'-bpy)Ru(py)(bpy)_2\}^{3+}$ where a correlation coefficient of 0.79 was obtained.

Taube and Creutz have also made such an empirical test of Hush's theory on the ion $(NH_3)_5Ru^{II}pyrRu^{III}(NH_3)_5^{5+}$. However, in this case the calculated solvation sphere contribution;

$$E_{outer} = (1/a)\ (1/n^2 - 1/D)e^2 \qquad .....(96)$$

for all solvents studied are considerably greater than the total bands found. In addition, IT band position does not exhibit the solvent effect expected of the formula. Although the shift was in the right direction, their magnitude was only one-tenth as predicted.

In view of the approximate model on which Hush's theory is based, that solvent effects do not conform quantitatively with prediction cannot be construed as weakening the case for band assignment in this case.

REACTIONS OF 'EXOTIC' AND 'ESOTERIC' SYSTEM.

(1) Reactions of Biological Importance

The study of electron transfer reactions involving biologically important species, apart from their inorganic redox reactions or their modification has constituted a challenging field to the redox kineticist in recent times.

Extensive investigation into metalloprotein redox chemi stry, the chemistry of vitamin B_{12} and related inorganic model systems, alkali metal ion transport and biochemical activity and the use of lanthanide ions as nuclear magnetic resonance chemical probes in biological systems have been carried out and reviews have been written.[279] However of greater interest to the redox kineticist because of their efficiency, complexity and mechanistic intrigues are the reactions of metalloproteins.

Metalloproteins that have been investigated include[280] cytochrome-c, Plastocyanins, stellacyanins, Azurin and Ferredoxins and Rubredoxins. Studies have also been carried out on

(i) oxidases converting O_2 to $2H_2O$
i.e. laccase, ceruloplasmin, ascobate oxidase and cytochrome-c oxidase

(ii) oxidases converting O_2 to H_2O_2
i.e. Dihydroorotate dehydrogenase, Xanthine oxidase, aldehyde oxidase and copper enzymes:

D-Galactose, urate diamine and monoamine oxidase.

(iii) Oxygenase like cytochrome P-450, Dophamine-β-hydroxylase, protocatedinate-3,4-droxygenase.

(iv) Catalysis and Peroxidases like catalase, Horseradish Peroxidase, Cytochrome-c Peroxidase.

(v) Superoxide dismutase

(iv) Non-physiological reactions in aqueous media like those involving iron-sulphur, Heme-iron copper proteins and Protein-Protein reactions.

However because of the very wide scope of this field the reactions of ferricytochrome-^{c} will be discussed as a typical example of how mechanistic concepts of inorganic reactions are applied in the study of these systems.

Ferricytochrome-c, a relatively small metalloprotein (mol wt = 12384) functions as an electron carrier in the respiratory chain of all aerobic organisms.[281] Crystallographic study[280,282,283] has confirmed that the heme group is located in the crevise of the essentially globular protein, the iron lying in a plane of the porphyrin ring with its fifth coordination site occupied by a nitrogen atom of the imidazole ring of Histidine-18 and the remaining co-ordination site by sulphur atom of methionine-18. It has been established that the coordination environment of the heme iron is a function of pH, ionic strength and the ionic composition of the medium.

Attempts to understand the in vivo mechanism of electron transfer reactions involving cytochrome-c has led to the extensive investigation of the mechanism of its redox activities[284 - 290] Two mechanistic pathways have so far been identified for the reactions of metalloproteins.

The first is the adjacent-attack mechanism which occurs in its reaction with chromium(11) and dithionite ions[288,289] where electron transfer is governed by the rate limiting-event in the protein such as the opening of the crevise and/or substitution on the iron center (analogous to inner-sphere reactions). The limiting rate of the adjacent attack pathway ($k = 30\ s^{-1}$) obtained in the dithionite reaction is in good agreement with the rate of the heme-crevise opening of ferricytochrome-c as determined from ligand binding studies involving azide, imidazole pyridine[287]. In the latter study, the stability constant of the 1:1 complexes formed between ferricytochrome-c and ligands are azide $4.5M^{-1}$, imidazole 15.3 M^{-1} and pyridine $2.4M^{-1}$ and $25^{o}C$, pH = 7.0 and 1.0M ionic strength. The results were interpreted as being consistent with a model in which added ligands bind to the iron by displacing the coordinated methione-80. The kinetic rate constant of 60 s^{-1} was thus attributed to the rupture of the iron-sulphur bond.

The alternative mechanism which has been proposed for some homogeneous redox reaction of ferricytochrome-c and simple inorganic reagents[290] is that of remote-attack.

For this mechanism which is analogous to the outer-sphere mechanism, the electron transfer is proposed to occur through the exposed edge of the heme to the metal. Thus the exposed heme edge was proposed as a probable site of electron transfer from the metalloprotein in the oxidation to ferricytochrome-c by tris-(1,10 phenanthroline) cobalt(111). This reaction which followed second order kinetics has $k = 1.5 \times 10^3 M^{-1}s^{-1}$ (25^oC, μ = 0.1M(NaCl) pH = 7.0 (phosphate), $\Delta H^{\neq}$ = 11.3 Kcal mol^{-1} and ΔS = -6.2 cal. deg^{-1}).

The rate of oxidation was found to be pH independent in the pH range 6 to 9. The magnitude of the second-order rate constant when compared with the rate of substitution of azide, imidazole and pyridine at the iron center suggests that an alternative mechanism from substitution-limited electron transfer reaction is operating. In fact excellent agreement between experiment and Marcus theory implicated electron transfer as occuring by the same mechanism as those occuring in the protein self-exchange reaction.[291]

The complexity of the hydrogen ion dependence has been one interesting feature exemplified by the reactions[288,292,293] of ferricytochrome-c with Cr^{2+} or $Ru(NH_3)_6^{3+}$ and the oxidation of ferrocytochrome-c by $Co(phen)_3^{3+}$. The reactivity order of the identified electronic isomers of this protein has been given as low spin > high spin > mixed spin by a recent study involving chromous ion in acidic media.

The adjacent-attack mechanism was proposed for this reaction. In cases where remote attack occurs, the possibility of the relative rates of the mixed and high spin species being inverted has been suggested.

In a very recent study, Adegite and Okpanachi[293], working in a different medium suggested the reactivity order:

low spin > mixed spin > high spin

for the acid induced eletronic isomers of ferricytochrome-c and also proposed the electron transfer as occuring by the heme-edge mechanism with the transfer occuring from the reductant in this case, hexaammineruthenium(11) ion, to the ferric ion in the protein.

The complexity of the hydrogen ion dependence of this reaction is illustrated by the fact that at pH $\leq$ 2 in chloride medium, the rate constant at 25°C, μ = 0.10MC(NaCl) was $350/\{H^{+}\}\ M^{-1}\ s^{-1}$ while at pH >> 4.0 the rate constant was $3.9 \times 10^{4} + 1.0 \times 10^{8}\ \{H^{+}\}\ M^{-1}\ s^{-1}$.

The maximum redox reactivity occured at pH = 3 where non of the above expressions fits the dependence of rate constant on pH.

The rationalisation given by Adegite and Okpanachi for this complex pH-dependence is that <u>in vivo</u> electron transfer may be preceeded by a conformational change such that cytochrome-c adopts the most reactive form, which contains one or more redox-linked ionizable proton than the native conformer.

(2) The Hydrated Electron.

The hydrated electron[294] is a member of a large family of solvated electrons first discovered[295] in ammonia over a century ago and which is part of a larger group of trapped electrons in liquids and solids[296]. Of all the solvated electrons, the hydrated electron has been of particular interest to chemists. With a half-life of less than one milli-second it can be generated in sufficiently high concentration (10^{-7} - 10^{-5}M) by pulse radiolysis. The hydrated electron, as a versatile reagent because of its high redox potential[297] (E^{o} = -2.7v) has provided unprecedented opportunity to advance our knowledge in inorganic chemistry.

The $e^{-}aq$ is the most elementary nucleophile and the most characteristic reducing agent in aqueous systems. It undergoes one and the same process with any reactant. namely electron transfer. Usually considered as a losely bound electron donor, $e^{-}aq$ serves as a model for many thermal and photochemical redox processes. Its reactivity towards electron acceptors provides valuable information not only on the nature of the electron-transfer process but also on the nature of the acceptor center. Table (1.6)[298] shows some rate constants for the reactions of $e^{-}aq$ with metal ions at room temperature and pH ~7. The consideration of the above Table of the rate constants for the reaction of the hydrated electron requires certain generalisation both

Table 1.6

Rate constants for the reaction[298] of e^-_{aq} with some metal ions at room temperature and pH 7.

Reactant	k $dm^3.mole^{-1}$ S^{-1}
Cd^{2+}	5.2×10^{10}
Pb^{2+}	3.9×10^{10}
Co^{2+}	1.2×10^{10}
Ni^{2+}	2.2×10^{10}
Zn^{2+}	1.5×10^{9}
Fe^{2+}	1.6×10^{8}
Mn^{3+}	7.7×10^{7}
Ag^{+}	3.2×10^{10}
H^{+}	3.0×10^{10}
Cu^{2+}	2.9×10^{10}
Sn^{2+}	3.4×10^{9}
Cr^{2+}	4.2×10^{10}
Cr^{3+}	6.0×10^{10}
Al^{3+}	2.0×10^{9}
La^{3+}	3.4×10^{8}
Pr^{3+}	2.9×10^{8}
Nd^{3+}	5.9×10^{8}
Sm^{3+}	2.5×10^{10}
Eu^{3+}	6.1×10^{10}
Gd^{3+}	5.5×10^{8}
Ti^{3+}	3.0×10^{9}
Yb^{3+}	4.3×10^{10}
$Co(NH_3)_6^{3+}$	9×10^{10}
$Co(NO_2)_6^{3-}$	5.8×10^{10}
H^{+}	2.4×10^{10}
H_2O_2	1.2×10^{10}
O_2	1.8×10^{10}
NO	3.1×10^{10}
N_2O	8.7×10^{9}
CO_2	7.7×10^{9}
NO_3^-	1.1×10^{10}
SO_4^{2}	$< 10^{6}$
ClO_4	$\sim 10^{6}$
HAC	$< 10^{8}$
Ac	$< 10^{6}$

from the kinetic and thermodynamic stand-points:

(i) consequent on its high reactivity only rates greater than 10^4 M^{-1} s^{-1} are readily observed.

(ii) Generally it can be concluded that there is no general correlation between free-energy change and reactivity except for a linear correlation of reactivity that was reported with the M^{2+}/M^{3+} redox potentials for the reactions of Sm^{3+}, Yb^{3+} and Eu^{3+}. Thus its reactions with $Cr^{2+}(aq)$, $Co(NH_3)_5Cl^{2+}$, $Rh(NH_3)_6^{3+}$ and $Co(bpy)_3^{3+}$ k is about 5 x $10^{10}M^{-1}$ s^{-1} which is in line with the value expected for diffusion controlled reactions but does not reflect the free-energy changes for each of the reactions. Also the rate constants for the reactions of a number of ammine and aquo complexes have been shown to be similar inspite of quite pronounced variation in the oxidation-reduction potential. Explanation of reactivity rates in terms of electron affinity has been found to be unsatisfactory since the order of rate constants for 2+ transition metal ions is:

$Mn^{2+} < Fe^{2+} < Zn^{2+} < Co^{2+} < N_i^{2+} < Cu^{2+} < Cr^{2+}$

and the order of electron affinity is:

$Mn^{2+} < Fe^{2+} < Cr^{2+} < Co^{2+} < Zn^{2+} < N_i^{2+} < Cu^{2+}$

The suggestion has been made by Aubar[299] that the availability of vacant d orbitals on the central metal, and the gain in exchange energy on adding an electron are the major factors which determine the reactivity of transition metal ions. Thus the addition of an electron to Cr^{3+} ($t_{2g}^3 e_g^1$) ion is particularly favourable since

the electron spin is parallel to the four spins already present. With Mn^{2+} (t_{2g}^{3} e_g^{2}) on the other hand, a sixth electron must have its spin anti-parallel to the electrons already present and the reaction is less favourable. For Cu^{2+}, Cr^{2+} the gain in energy is similar while Zn^{2+} is expected to have a low reactivity since all the 3d orbitals are filled. Ligands such as cyanide may also affect reactivity because of its effect on ligand field and hence the electron density distribution. For example, ferrocyanide with a t_{2g}^{6} configuration is relatively unreactive ($k < 10^{5}$ M^{-1} s^{-1}) while low spin $Mn(CN)_6^{4-}$ on the other hand is more reactive than $Mn^{2+}(aq)$ ($k = 2.5 \times 10^{10}$ $M^{-1}s^{-1}$) because the added electron goes to the last vacancy in the t_{2g} level.

Ligands such as halide ions which do not strongly interact with d orbitals may affect reactivity by chanelling the $e^{-}aq$ from the solvent to the central atom. Anbar and Hart[300] have suggested that the efficiency of bridging is of the orde

$I^{-} > Cl^{-} > F^{-} > H_2O > NH_3 > RNH_2 > CN^{-} > OH^{-}$

The effectiveness of the halide ions is similar to that observed for outersphere reactions.

(3) Since well known oxidants react with $e^{-}aq$ at diffusion controlled rates, the contrary requires special explanation. For example Anbar and Hart reported the data for the reactions of $e^{-}aq$ with Sn^{11}, Cr^{11}, Cr^{111} and Al^{111}. The rate constants decreases as the pH changed from 7 to 14;

with Al^{111} the decrease is from 2.0×10^9 to 5.5×10^6 $M^{-1} s^{-1}$. This can be rationalized for instance on the basis of the fact that the hydrolysis of these metal ions becomes important as the pH increases.

The information now gathered for the reaction of e^-aq with representative compounds of about 66 elements enable us to classify the reactions of the hydrated electrons into the following categories:[301]

1a. Protonation:

$$H^+ + e^-aq \rightarrow H \quad \text{.....(97)}$$

$$H + H_2O \rightarrow H_2 + OH \quad \text{.....(98)}$$

$$CO_2 + e^-aq \rightarrow CO_2^- \quad \text{.....(99)}$$

$$CO_2^- + H_2O \rightarrow CO_2H + OH \quad \text{.....(100)}$$

1b. Protonation followed by dissociation

$$N_2O + e^-aq \rightarrow N_2O^- \quad \text{.....(101)}$$

$$N_2O^- + H_2O \rightarrow N_2OH + OH^- \quad \text{.....(102)}$$

$$N_2OH \rightarrow N_2 + OH \quad \text{.....(103)}$$

2. Disproportionation:

(i) $$I_2 + e^-aq \rightarrow I_2^- \quad \text{.....(104)}$$

$$I_2^- + I_2^- \rightarrow I_2 + 2I^- \quad \text{.....(105)}$$

(ii) $$Zn^{2+} + e^-aq \rightarrow Zn^+ \quad \text{.....(106)}$$

$$Zn^{2+} + Zn^+ \rightarrow Zn^o + Zn^{2+} \quad \text{.....(107)}$$

3. Association:

(i) $$Tl^+ + e^-aq \rightarrow Tl^o \quad \text{.....(108)}$$

$$Tl^o + Tl^+ \rightarrow Tl_2^+ \quad \text{.....(109)}$$

(ii) $$Ag^+ + e^-aq \rightarrow Ag^o \quad \text{.....(110)}$$

$$Ag^o + Ag^+ \rightarrow Ag_2^+ \quad \text{.....(111)}$$

4. Dissociation:

(i) $H_3O^+ + e^-aq \rightarrow H_3O \rightarrow H + H_2O$ .....(112)

(ii) $ClO^- + e^-aq \rightarrow ClO^{2-} \rightarrow Cl^- + O^-$ .....(113)

The above examples highlights one major benefit that has been derived from the study of the reactions of the hydrated electron which is its synthetic potentials. Thus the hydrated electron produces a large number of reactive reduced intermediates, many for the first time and many of which are excellent electron donors and being less efficient than e^-aq are used as selective reducing agents in homogeneous aqueous solutions. The life-time of these intermediate products may range from $< 10^{-10}$ seconds estimated for H^- and H_3O[302] through 10^{-9} seconds estimated for N_2OH up to "indefinite" life times for I_2^- or Zn^+[303] which are not limited by monomolecular decomposition or by reaction with the solvent. Table(1.7)shows some typical products of e^-aq reactions with some inorganic reactants.

The kinetic behavour of e^-aq in radiolyzed water:

$$H_2O \rightleftharpoons H_2O^+ + e^-_{se}$$

which is thermalized thus

$$e^-_{se} \rightarrow e^-_t \rightarrow e_{aq}$$

and

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH^-$$

giving the overall reaction

$$2H_2O \rightarrow H_3O^+ + OH^- + e^-aq$$

(complete within 10^{-11} seconds) has been very essential in the evaluation of radiolytic processes and in the use

Table 1.7

Typical Products of e^-_{aq} reactions with some inorganic reactants.

Reactant	Primary Product	Secondary Product
H	H^-	H_2
CO_2	CO_2^-	$(CO_2)_2^{2-}$
N_2O	NO_2^-	$N_2 + O^-$
HF	HF^-	$H + F^-$
I_2	I_2^-	I^-
Ag^+	Ag^o	Ag_2^+
Zn^{2+}	Zn^+	Zn^o
Cu^{2+}	Cu^+	Cu^+
NH_4^+	NH_4	$NH_3 + H$
NO_3^-	NO_3^{2-}	NO_2
MnO_4^-	MnO_4^{2-}	MnO_4^{2-}
ClO^-	ClO^{2-}	$Cl^- + O^-$
$Fe(CN)_6^{3-}$	$Fe(CN)_6^{4-}$	$Fe(CN)_5^{3-} + CN^-$

of e^-aq as a tool in the study of reaction mechanism by pulse radiolysis. Much more additional evidence is gained in correlating obtained rate constants with H/D isotope effect in radiolyzed water.

Competition kinetics has also proved that the photochemically produced e^-aq is of the same reactivity as the radiolytically or chemically produced e^-aq. This is evidenced by the fact that photochemically produced e^-aq i.e.

$$Fe(CN)_6^{4-} + h\nu \rightarrow Fe(CN)_6^{3-} + e^-aq \quad \text{.....(114)}$$

and that formed from ionizing radiation or the reaction:

$$H + OH^- \rightarrow e^-aq + H_2O$$

have identical spectrum. Radiation of a variety of alcohols[304] have also produced solvated electrons with similar spectrum to that of e^-aq. In all these cases the broad spectrum of the hydrated electron has been rationalized in terms of the "Cavity model"[305] This model assumes that cavities are freely available in liquid water for instance and as a result of their pulsating nature, e^-aq rapidly moves from one cavity to the other. The pulsating nature of the cavities thus gives a wide distribution of potential energy thereby leading to the broadening of the optical spectra.

It is worth mentioning that from kinetics alone it can be concluded that the solvated electron is not however an intermediate in electron transfer reactions.

THEORETICAL CONSIDERATIONS:

Marcus theory and applications.

Several excellent reviews and monographs[13,255,306-314] have been written on the theoretical aspects of electron transfer reactions. The basis of all these theoretical treatments has been the Franck Condon's Principle which states that "electron transfer event occurs without a change in the nuclear configuration parameters." Reactions occuring by the outer sphere mechanism have been particularly suitable for these calculations because of their lack of bond-breaking or making during electron transfer. This makes it possible for rate constants to be calculated since the coordination shell and the immediate environment for the reactants and for the products will differ only as a result of the redox reaction. Since however some "common state" must be attained by each reactant (in line with Franck Condon's Principle) prior to the electron transfer step, it is the free-energy, ΔG^*, that is required to change the atomic coordinates from their equilibrium value to the values in the activated complex which must be calculated in any theory.

Of all the theoretical developments so far, Marcus[308-312] has had the most successful and sustained effort. Marcus' theory which was initially an ab initio calculation of absolute rate constants for homonuclear exchange reactions was later extended to cross-reactions. Marcus assumed

small electronic interaction between the reacting species which are treated as rigid spheres of radii a_1 and a_2, inside of which no change of interatomic distance occurs during the reaction. He further made the following assumptions

i) the probability of electron transfer within the activated complex is unity.

ii) the work terms of the self-exchange and cross reactions are the same.

iii) the motion of the inner-coordination spheres are harmonic with breathing force constants having the reduced value:

$$2f_i f_i^p \; / \; (f_i + f_i^p)$$

where f_i and f_i^p are the force constants for the symmetrical breathing vibrations of a species when it is a reactant and product respectively.

The free-energy, ΔG^*, can then be represented by the following expression:

$$\Delta G^* = \frac{\lambda}{4} + \frac{(\Delta G^o - w^p - W^r)}{2} + \frac{(\Delta G^o - w^p - w^r)^2}{4\lambda} \quad ....(115)$$

where $\lambda = \lambda_o + \lambda_i$ ....(116)

$$\lambda_o = (ne)^2 \left(\frac{1}{2a_i} + \frac{1}{2a_2} - \frac{1}{r}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \quad ....(117)$$

$$\lambda_i = \frac{f_i \, f_i^p}{f_i + f_i^p} (\Delta a_i)^2 + \frac{f_2 \, f_2^p}{f_2 + f_2^p} (\Delta a_2^o)^2 \quad ....(118)$$

The terms in the above expression are defined as follows:

(i) w^r and w^p are the work required to bring the reactants to their mean separation distance $(a_1 + a_2)$ and then remove the products to infinity. This term incorporates electrostatic and non-polar contributions

(ii) λ_o and λ_i are the free energy required to reorganize the solvent molecules around the reactants (the outer coordination shell) and to reorganize the inner-coordination shell of the reactants.

(iii) ΔG^o is the standard free energy of the reaction at the separation distance.

(iv) n is the number of electrons transferred. It was also assumed that:

$(a_1 + a_2)/_2 = (a_1\ a_2)^{\frac{1}{2}}$ and $a_i^o = a_i - a_i^p$

is the difference in the radius of the species i, when it is a reactant and when it is a product.

(v) D_{op} and D_s are the square of the refractive index and dielectric constant for the medium respectively.

The free energy, ΔG^*, is related to the free energy of activation $\Delta G^{\neq}$ by:

$$\Delta G^* = \Delta G^{\neq} + RT\ln\left(\frac{hz}{kT}\right) \quad \text{or}$$

$$\Delta G^* = \Delta G^{\neq} - 2.444\ K\ \text{cal mol}^{-1} \qquad \ldots\ldots\ldots(119)$$

and therefore the rate constant k is:

$$k = Z \exp\left(\frac{-\Delta G^*}{RT}\right) \qquad \ldots\ldots\ldots(120)$$

where $Z = 10^{11}\ M^{-1}\ s^{-1}$.

From this empirical derivation of Marcus we can also predict the activation parameters for these type of reactions. Thus if we rewrite equation (115) as

$$\Delta G^*_{12} = (\Delta G^*_{11} + \Delta G^*_{22})/_2 + \Delta G_{12}\ (1 + \alpha)/_2 \quad \ldots\ldots\ldots(121)$$

where ΔG^*_{11} , ΔG^*_{22} and ΔG^*_{12} are the free energy for the exchange and cross reactions respectively. Differentiating this expression gives!

$$\Delta S^*_{12} = \frac{(\Delta S^*_{11} + \Delta S^*_{22})}{2}\ (1 - 4\alpha^2) + \frac{\Delta Sn^o}{2}\ (1 + \alpha) \quad \ldots(122)$$

and

$$\Delta H^* = \frac{\Delta H^*_{11} + \Delta H^*_{22}}{2}\ (1 + 4\alpha^2) + \frac{\Delta H^o_{12}}{2}\ (1 + 2\alpha) \quad \ldots(123)$$

It is therefore possible to compare observed and calculated thermodynamic parameters by using the expressions,

$$\Delta G^{\ddagger} = \Delta G^* + RT\ln\left(\frac{hz}{kT}\right) \quad \ldots\ldots(124)$$

$$\Delta S^{\ddagger} = \Delta S^* + R\ln\left(\frac{hz}{kT}\right) - \tfrac{1}{2}R \quad \ldots\ldots\ldots\ldots(125)$$

$$\Delta H^{\ddagger} = \Delta H^* - \tfrac{1}{2}RT \quad \ldots\ldots\ldots\ldots(126)$$

Table (1.8) shows some observed and calculated rate constants, using Marcus theory for some electron transfer reactions. Table (1.9) also shows some observed and calculated thermodynamic parameters. Evident from these Tables is the fact that some systems display quantitative agreement while most systems show considerable deviation.

TABLE 1.8[315]

Comparison of observed and calculated rate constants for some systems.

	Reactants	$\log K'_{12}$	$k_{12\ obs}$ $M^{-1}S^{-1}$	$k_{12\ calc}$ $M^{-1}S^{-1}$	k_{obs}/k_{calc}
1)	$Ru(NH_3)_6^{2+}$ -Fe(111)Cyt-c	3.4	3.8×10^4	1.2×10^5	0.32
2)	Fe(11)Cyt-c -$Co(phen)_3^{3+}$	1.86	1.5×10^3	2.0×10^3	0.75
3)	$Ru(NH_3)_6^{2+}$ - $Ru(NH_3)_5py^{3+}$	4.40	1.4×10^6	4.0×10^6	0.35
4)	$Ru(NH_3)_6^{2+}$ - $Co(phen)_3^{3+}$	5.42	1.5×10^4	1.3×10^5	0.12
5)	$Ru(NH_3)_5py^{2+}$-$Co(phen)_3^{3+}$	3.39	2.0×10^3	1.1×10^4	0.18
6)	$Ru(NH_3)_5py^{2+}$ -$Ru(NH_3)_4bpy^{3+}$	0.25	1.1×10^8	3.9×10^7	~2.5
7)	V^{2+}aq - $Co(en)_3^{3+}$	5.19	5.8×10^{-4}	7.2×10^{-4}	1.2
8)	V^{2+}aq - $Ru(NH_3)_6^{3+}$	9.58	1.3×10^3	9.9×10^2	1.3
9)	V^{2+}aq - $Ru(NH_3)_5py^{3+}$	9.58	3.0×10^5	9.5×10^5	0.31
10)	V^{2+}aq -$Co(phen)_3^{3+}$	10.59	4.0×10^3	3.2×10^4	0.13
11)	V^{2+}aq - Fe^{2+}aq	16.90	1.8×10^4	1.7×10^4	0.011
12)	$Ru(NH_3)_4bpy^{2+}$ - Fe^{2+}aq	3.90	7.2×10^3	1.7×10^5	0.042
13)	$Ru(NH_3)_5isn^{2+}$ - Fe^{2+}aq	5.93	2.6×10^4	6.3×10^5	0.042
14)	$Ru(NH_3)_6^{2+}$ - Fe^{2+}aq	11.7	3.4×10^5	8.8×10^6	0.038
15)	Fe^{2+}aq - $Os(bpy)_3^{3+}$	1.53	1.4×10^3	4.9×10^5	2.9×10^{-3}
16)	Fe^{2+}aq - $Fe(phen)_3^{3+}$	5.42	3.7×10^4	2.3×10^7	1.6×10^{-3}
17)	Fe^{2+}aq - $Fe(bpy)_3^{3+}$	3.90	2.7×10^4	5.6×10^6	4.9×10^{-3}
18)	Fe^{2+}_{aq} - $Ru(bpy)_3^{3+}$	8.81	7.2×10^5	3.6×10^8	2.0×10^{-3}
19)	$Co(phen)_3^{2+}$ - Fe^{3+}aq	6.27	5.3×10^2	4.2×10^3	0.125
20)	$Co(phen)_3^{2+}$ - $Ru(bpy)_3^{3+}$	15.08	$>3 \times 10^7$	2.4×10^9	$>10^{-3}$
21)	$Ru(NH_3)_6^{2+}$ - $Ru(bpy)_3^{3+}$	20.51	$(3.7 \pm 0.6) \times 10^9$	2.9×10^9	~1

TABLE 1.9[315]

Observed and calculated Thermodynamic Parameters for electron transfer reactions at 25°C.

	Reactants	obsd		calc.	
		$\Delta H^{\ddagger}$ Kcal mol^{-1}	$\Delta S^{\ddagger}$ cal deg^{-1} mol^{-1}	$\Delta H^{\ddagger}$ K_{cal} mol^{-1}	$\Delta S^{\ddagger}$ cal deg^{-1} mol^{-1}
1)	V^{2+}_{aq} - Fe^{3+}_{aq}	4.0	125.5	+2.1	-24.4
2)	V^{2+}_{aq} - $Ru(NH_3)^{3+}_6$	0.6	-42	+2.1	-36.9
3)	V^{2+}_{aq} - $Co(phen)^{3+}_3$	3.8	-29	-0.7	-39.5
4)	V^{2+}_{aq} - $Co(bpy)^{3+}_3$	3.6	-33	+1.1	-36.1
5)	$Ru(NH_3)^{2+}_6$ - Fe^{2+}aq	3.2	-22	-7.91	-2.1
6)	$Ru(NH_3)^{2+}_6$ - $Co(phen)^{3+}_3$	4.2	-25	2.7	-26
7)	Fe^{2+}_{aq} - $Ru(bpy)^{3+}_3$	-0.3	-33	-2.9	-29

The ideas developed by Marcus however have been more usefully applied to the calculation of rate constants for reactions in terms of free energy change and rate constants for related reactions. Equation (121) can be written as

$$\Delta G^* = w^r + \frac{\lambda_i + \lambda_o}{4}\left(1 + \frac{\Delta G^o + w^p - w^r}{\lambda_i + \lambda_o}\right)^2 \quad .....(127)$$

If $(\Delta G^o - w^p - w^r)(\lambda_i + \lambda_o) < 1$

then

$$\Delta G^* \sim \frac{w^r + w^p}{2} + \frac{\lambda_i + \lambda_o}{4} + \frac{\Delta G^o}{2} \quad ....(128)$$

Considering the redox reaction of a series of related reagents (so that the only variable is ΔG^o) a plot of ΔG^* versus ΔG^o would be expected to be linear with slope of 0.5. Consider for instance the cross reaction;

$Ox_1 + Red_2 \rightleftharpoons Red_1 + Ox_2$ k_{12}, K_{12} and the related isotopic exchange reaction

$Ox_1 + Red_1 \rightleftharpoons Red_1 + Ox_1$ k_{11}

$Ox_2 + Red_2 \rightleftharpoons Red_2 + Ox_2 \quad k_{22}$

Assuming the work terms are negligible and

$$(\lambda_i + \lambda_o)_{12} = \frac{(\lambda_i + \lambda_o)_{11} + (\lambda_i + \lambda_o)_{22}}{2}$$

Combination with equation(119) yields[308].

$$\Delta G^{\ddagger} = 0.5\Delta G_{11} + 0.5\Delta G^{\ddagger}_{22} + 0.5\Delta G^{o}_{12} - 1.15RT \log f$$

$$\text{or} \quad k_{12} = (k_{11}k_{22}K_{12}f)^{\frac{1}{2}} \qquad \text{.....(130)}$$

where

$$\log^{f} = \frac{(\log K_{12})^2}{4 \log (k_{11}k_{22}/Z^2)} \qquad \text{.....(131)}$$

A plot of $(\Delta G_{12}^{\ddagger} + 1.15RT \log f)$ versus ΔG^{o}_{12} should therefore be linear with a slope of 0.5 and intercept $0.5\ (\Delta G_{11}^{\ddagger} + \Delta G_{22}^{\ddagger})$. For a series of reactions between one common reactant 1 and a number of closely related species 2, $\Delta G^{\ddagger}_{11}$ is constant and $\Delta G^{\ddagger}_{22}$ would not be expected to vary greatly so that the intercept is approximately constant. When the oxidizing power of Ox_1 and Ox_2 are comparable, f is very close to unity and the terms containing this may be omitted, leading to be expression:

$$\Delta G^{\ddagger}_{12} = 0.5\Delta G^{\ddagger}_{11} + 0.5\ \Delta G^{\ddagger}_{22} + 0.5\Delta G^{o}_{12} \quad ...(132)$$

Such linear free-energy relations have been demonstrated for a lot of redox reactions.

An example of the application of this modified Marcus expression is provided in the comparison of the kinetic reactivity of U^{3+} with other reducing aquoions i.e. V^{2+}, Eu^{2+}, Sm^{2+}, Yb^{2+}[188] The values of the parameters employed are presented on Table(1.10). Using the Marcus

expression as:

$$\log k_{12} + 0.5(\log k_{11} + \log f) = 0.5 \log k_{22} + 0.5 \lg K_{12},$$

a linear plot with slope 0.5 and intercept 0.5 log k_{22} is expected. The plot is presented in Figure (1.8)

Actual values obtained from this plot are a slope of 0.6 ± 0.09 and an intercept of -0.31 ± 1.69. This is comparable to the values of 0.5 and 1.46 expected. The slight difference between this calculated and observed parameters was attributed to the difference in the ionic strengths of the medium in which K_{12} was obtained. Other examples include application of reactions involving iron(III) phenanthroline complexes.

A large number of the application of this equation to isolated reaction systems rather than a reaction series plot have been made. Some of the quantities which are difficult to estimate in the calculation of absolute rate constants for isotopic exchange reactions cancel in the cross reaction.

Agreement between experimental and calculated rate constants have been considered a strong evidence of an outer sphere redox process being involved. Thus in the application of this linear free energy relation (LFER) to U^{3+}[188] it was suggested that the reaction proceeds by the outersphere reaction mechanism, in the light of the correlation obtained.

It is of interest to note that recent investigations indicate that LFER[316,317] also applies to some inner-sphere[318-320] reactions. An example of such recent

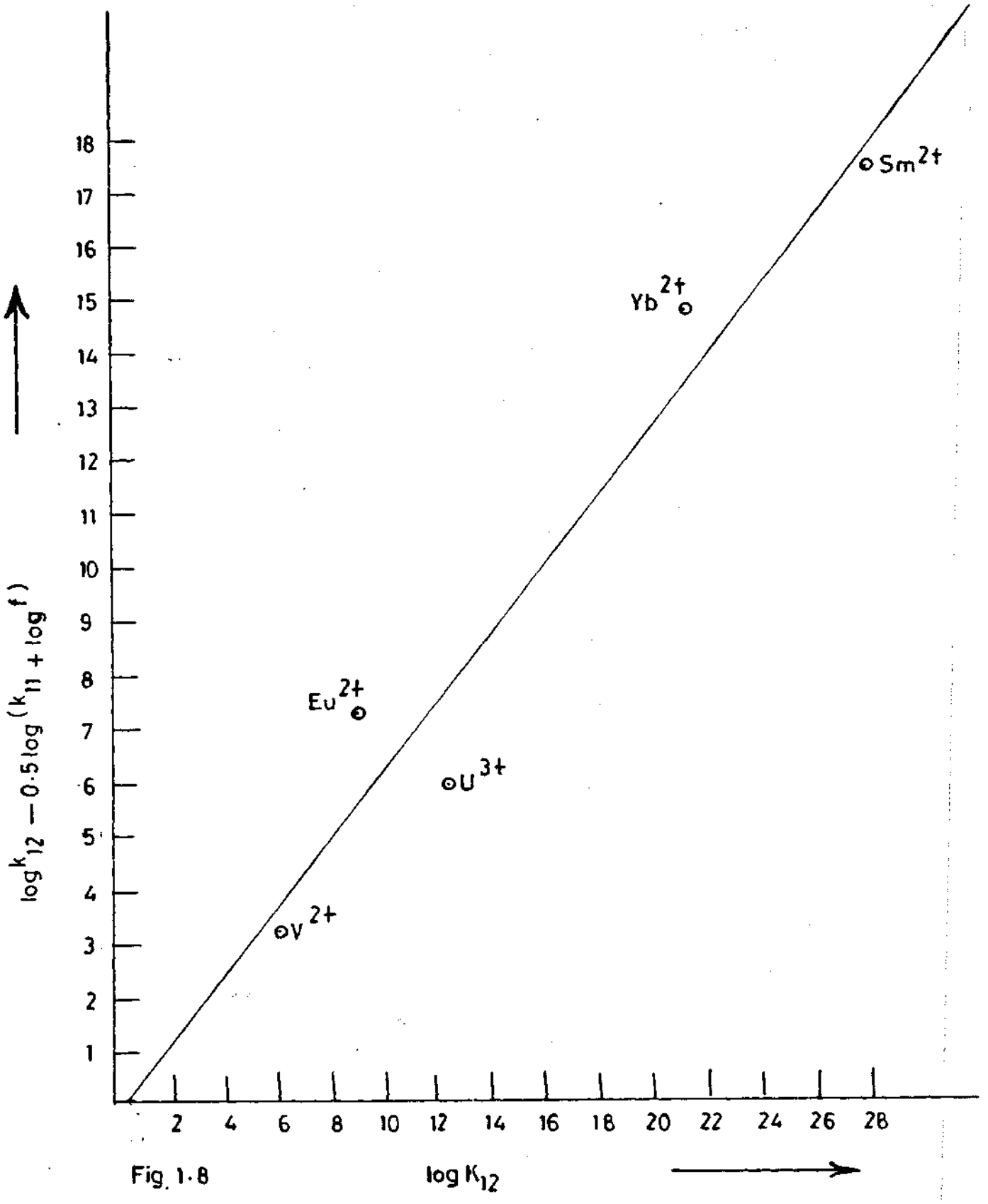


Fig. 1·8

Marcus correlation of rate constants with redox potentials for the reduction of $[Ru(NH_3)_6]^{3+}$ by some aqua-ions.

TABLE 1.10[188]

Values of constants employed in the test of Marcus Theory, Oxidant = $\{Ru(NH_3)_6\}^{3+}$, $k_{22} = 8.2 \times 10^2$ dm^3 mol^{-1} s^{-1}.

Reducing ion	k_{11}	k_{12}	K_{12}	log f
U^{3+}	1.66	9.5×10^2	3.46×10^{12}	-2.06
U^{2+}	1.0×10^{-2}	0.80×10^2	1.55×10^6	.0.41
Yb^{2+}	3.0×10^{-9}	4.5×10^7	1.55×10^6	-3.79
Sm^{2+}	5.0×10^{-12}	2.0×10^8	1.38×10^{26}	-6.12
Eu^{2+}	1.0×10^{-7}	2.3×10^2	1.41×10^9	-0.74

developments is provided by the rates of the inner-sphere reactions:[318]

$$Co(NH_3)_5Cl^{2+} + Cr^{2+} \rightarrow \text{products} \qquad k_{12}, K_{12}, f_{12}$$
$$Co(NH_3)_5Cl^{2+} + Fe^{2+} \rightarrow \text{products} \qquad k_{13}, K_{13}, f_{13}$$

which have been related to the equation:

$$\frac{k_{12}}{k_{13}} = \left(\frac{k_{11}k_{22}K_{12}f}{k_{11}k_{33}K_{13}f}\right)^{\frac{1}{2}} \simeq \left(\frac{k_{22}\ K_{12}}{k_{33}\ K_{13}}\right)^{\frac{1}{2}} \qquad .....(132)$$

where k_{22} and k_{33} are the rate constants for self-exchange in the $Cr^{2+}/CrCl^{2+}$ and $Fe^{2+}/FeCl^{2+}$ systems respectively. The validity of this expression is justified in Table (1.11) for this and a number of reduction pairs.[319] The same approach directed at the trio of reactions:

$$Cr\ SCN^{2+} + Cr^{2+} \rightarrow CrNCS^{2+} + Cr^{2+} \quad k_1(40M^{-1}s^{-1})$$
$$CrNNN^{2+} + Cr^{2+} \rightarrow CrNNN^{2+} + Cr^{2+} \quad k_2(6.1M^{-1}s^{-1})$$
$$CrNCS^{2+} + Cr^{2+} \rightarrow CrSCN^{2+} + Cr^{2+} \quad k_3(3.2M^{-1}s^{-1})$$

leads to the expression

$$k_2 = (k_1\ k_3)^{\frac{1}{2}}$$

Very recently, Davies and Earley[320] have provided evidence that for some $Cr(NH_3)_5Cl^{2+}$- $Cr(NH_3)_5L^{+}$ reactions, the changes in the free energy of activation directly parallel changes in the overall free energy of these reactions. For these reactions that utilize the innersphere mechanistic pathway they obtained the relationship:

$$\Delta \log k = 0.48E^{o}$$

TABLE 1.11

Calculated and observed Rate constants (k_{calc} and k_{obs}, $M^{-1} s^{-1}$) for Cr^{2+}aq Reduction of Co(111) complexes using (equation 132) and Data on Fe^{2+} Reductions[319]

Oxidant	log k_{obs}	log k_{calc}
$Co(NH_3)_5Cl^{2+}$	6.4	6.6
$Co(NH_3)_5F^{2+}$	6.9	5.5
$CisCoen_2(NCS)Cl^{2+}$	6.3	5.6
$trans\text{-}Coen_2(NCS)Cl^{2+}$	6.4	5.6

The test of Marcus theory has also been extended to systems involving intervalence transfer, notably by Taube[320] and Creutz and Meyer,[322] in attempts to compare observed and calculated barriers to electron transfer reactions in binuclear Ruthenium(11) - Ruthenium(111) complexes. This has been possible because in the limit where delocalization is negligible, both thermal and optical barriers to electron transfer are straight forward consequencies of the Franck Condon Principle.

The applicability of Marcus theory has also been examined using some bioinorganic, heterogeneous and photochemical electron transfer reactions in some efforts being made to delineate the electron transfer properties of metalloproteins[323,324] and excited states of inorganic complexes.[325]

Recently an interesting attempt has been made to see how Marcus theory applies in the so called "inverted" region.[326] This test is based on reactions involving the quenching of luminiscence of the charge transfer excited states of two dipyridine ruthenium(11) complexes (L = 2,2-bpy or 4,4-dimethyl 2,2-bpy).

The theory of the inverted region predicts that when

$$-\Delta G_{12}^{o} > 2(\Delta G_{11}^{*} + \Delta G_{22}^{*})$$

then the reaction rate constant should decrease as the free energy change becomes more favourable. The cross-over into the inverted region can be expressed as:

$$\log K_{12} = 2\log (Z^2 k_{11} k_{22}) \qquad \text{.....(133)}$$

The result of this work demonstrated a quantitative agreement with the prediction of Marcus.

An indirect application of Marcus theory in mechanistic categorization has been derived[14] in the method of rate-ratio comparison. If we consider an oxidant A, which is reduced by two reductants B and C, the ratio of the rate constants for the reduction can be expressed as

$$\frac{k_{AB}}{k_{AC}} = \frac{k_{AA}\ k_{BB}\ K_{AB}\ f_{AB}}{k_{AA}\ k_{CC}\ K_{AC}\ f_{AC}} \qquad \text{.....(134)}$$

Since the right hand side of the oxidant is independent of the oxidant A, to the effect that the f terms can be neglected or that they approximately cancel then

$$\frac{k_{AB}}{k_{AC}} = \frac{k_{BB}}{k_{CC}}\ K \qquad \text{.....(135)}$$

Therefore!

$$\log k_A = a \log k_B + b.$$

This modified Marcus expression has been very useful in providing additional evidence of the free-energy dependence of reactivity.[326] For exact correlation, a slope of unity is expected. Guenther and Linck,[324] Chen and Gould,[328] Hutchital et al[329] and recently Hand and coworkers have applied such semi-quantitative approach to the reduction of some μ-super-o x o - bis{pentammine Cobalt(111)} complexes by some aquoions and $Ru(NH_3)_6^{2+}$. Very recently Adegite and Dosumu and Ojo[330] obtained the relation:

$$\log k\ \{Cr(bpy)_3^{2+}\} = 0.83 \log k\ \{Ru(NH_3)_6^{2+}\} + 4.19$$

in some reactions involving some cobalt(111) ammine complexes. Thomson and Sykes[331] have also shown that a plot of log $k_{TiOH^{2+}}$ against log k_{V}^{2+} is linear for the outersphere reductions of some mononuclear cobalt(111) complexes, for which they obtained the relation:

$$\log k_{TiOH^{2+}} = 0.5 \log k_{v} - 0.55$$

For the reaction of Ti(111) with the binuclear and tetranuclear complexes of cobalt(111) with $Co(NH_3)_6^{3+}$ and $Co(bpy)_3^{3+}$, Hery and Wieghadt[332] obtained the expressions:

$$\log k_{TiOH} = (0.66 + 0.07) \log k_{V}^{2+} - (0.64 + 0.01)$$

and

$$\log k_{TiOH} = (0.57 \pm 0.1) \log k_{Cr} + (0.35 \pm 0.1).$$

respectively.

From investigations so far, it seems that a slope of 0.5. is characteristic of cobalt(111) and titanium(111) systems. A possible explanation of the observed deviation of the slopes of these systems from the expected value of unity might be the non-cancelation of the f-terms as expected from the basic assumption made in deriving equation (135). It is expected that the f-term will change as the driving potential of the reaction changes.

Gould[333] has warned us to excercise care in using these relative rates as criteria for mechanism. The warning was based on the result of the log-log plots for the reaction of two sets of $(NH_3)_5Co^{111}X$ complexes with Cr^{2+} and Eu^{2+} utilizing the outer- and the inner-sphere mechanisms

respectively. These plots gave points that fell close to the same regression line corresponding to the relationship:

$$\log k_{Eu} = 0.93 \log k_{Cr} + 0.93.$$

Therefore, these log-log plots do not discriminate between possible mechanisms. The warning does not however apply to cases where the coordination integrity of one of the reactants imposes the outer-sphere mechanism as its only mechanistic option.

The uncertainty in the use of this criterion as an indicator of mechanism can however be minimized. This involves the consideration of the rate ratio values in the light of their deviation from innersphere values in the appropriate reactivity range, rather than basing arguments on conformity with outersphere values. Even such arguments are indicative, rather than conclusive of mechanism because of the vagaries to which the inner-sphere reactions are subjected.

Haim and Sutin[334], Patel and Endicott[335] and Fay and Sutin[336] have suggested that an expression similar to equation(130) should hold for reactions occuring by the innersphere mechanism. One condition must be satisfied however. This is that the self-exchange rate for the reactants must be properly defined to take account of the bridging ligand. Such an empirical fit has been obtained for the V^{2+} and Fe^{2+} reaction[331] with Co(111) - Cl^- complexes, and given by the expression:

$$\log k_{V^{2+}} = 0.49 \log k_{Fe^{2+}} + b$$

Assessment of Marcus Theory.

Chou, Creutz and Sutin[315] have published an elegant review of the general applicability of Marcus theory in terms of the basic assumptions of the theory. Newton[5] has highlighted the fact that the force constant assumption cannot account for the deviation between observed and calculated rate constants and thermodynamic parameters. He pointed out that the introduction of anharmonicity will only lead to a deviation of about 1 - 2% between the expected and obseved parameters. Sondergaard, Ustring and Jortner[337] tried to rationalize these deviations by modifying the anharmonicity assumption. They were able to arrive at the conclusion that these effects cancel out to a large extent. By removing the Marcus assumption of the equivalence of precursor and successor stabilities, Sutin and Brunschig obtained a modified Marcus expression of the form

$$k_{12} = P_{12}\left(\frac{P_{21}\ k_{11}\ k_{22}\ K_{12}\ f}{P_{11}\ P_{22}}\right)^{\frac{1}{2}} \qquad .....(135)$$

with

$$\log f = \left(\frac{\log K_{12}\ P_{21}/P_{12}}{4\log K_{11}\ k_{22}\ h^2/P_{11}P_{22}k^{-2}T^{-2}}\right) \qquad ....(136)$$

where P_{11} P_{22} and P_{12} are the stabilities of the reactants and the precursor complex for exchange reaction. P_{21} is the stability of the successor complex. Their result for the system considered showed that if even $f_{12} \sim 1$ and

$P_{12}\ P_{21} > P_{11}\ P_{22}$, k_{12} calc > k_{12} obsd. The consideration of different kinds of ions show that non electrostatic terms may make $P_{11}P_{22} > P_{12}\ P_{21}$ and $k_{12} << k$ obsd.

Their results also show that when $P_{12}\ P_{21} = P_{11}\ P_{22}$ and $f_{12} << 1$, then the f term becomes important and (a) if $P_{11}P_{22} > 1$, then k_{12} calc > k_{12} obsd.

(b) if $P_{11}P_{22} < 1$, then k_{12} calc < K_{12} obsd

Therefore, differences are still expected between the k_{12} calc and k_{12} obsd, if even, the work functions of the precursor and successor complexes are the same, but the driving force becomes large.

An attempt to modify the adiabaticity assumption of Marcus was also made by Sutin and Bunschig.[338] They obtained a modified Marcus expression of the form:

$$k_{12} = P_{12}\left(\frac{k_{11}\ k_{22}\ K_{12}\ f_{12}}{P_{11}\ P_{22}}\right)^{\frac{1}{2}} \qquad \text{.....(137)}$$

with

$$\log f_{12} = \frac{(\log K_{12})^2}{4 \log k_{11}\ k_{22}/(P_{11}P_{22}Z^2)} \qquad \text{.....(138)}$$

This expression however reduces to equation(130) if $(P_{12})^2 = P_{11}P_{22}$. Hence even when the electron transfer process is adiabatic and provided the f correction is not substantial, equation(137) will correctly predict the rate constant k_{12} when $P_{12} = (P_{11}P_{22})^{\frac{1}{2}}$. An increase in the overall free-energy should lead to deviation between k obsd and k calc when the exchange and the cross reactions are

non-adiabatic.

From available literature, Marcus theory is generally successful in predicting the rate constants between +2 and +3 charged reactants to within a factor of 25. For the estimation of exchange rates, this represents a factor of $(25)^2$ (or nearly 10^3).

An exception to this generalization is the Fe^{2+} - ML_3^{2+} (M = Fe, Os, Ru) reactions[339-341] which are consistently ~ 500 times too slow. Some other exceptions include the reaction of the actinide ions[342-344] and certain cobalt(111) complexes[345]. Based on the calculations done for some V^{2+} reductions[346], it appears that the non-cancellation of the work terms and non-adiabatic terms cannot account for the observed descrepancies.

The limited available data for $\Delta H_{12}^{\ddagger}$ suggests that anharmonicity effects could be the origin of the slow observed rates. More thermodynamic data are therefore needed to butress this suggestion. For systems showing poor correlation between theory and experiment, a consideration of the calculated and observed $\Delta H_{12}^{\ddagger}$ and $\Delta S_{12}^{\ddagger}$ values could help locate the point of breakdown between theory and experiment.

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C H A P T E R 2

Kinetics and Mechanism of the redox reaction of the Hexaaquo-titanium(lll) ion and Titanium(lll) Ethylenediamine tetraacetate complex by Aqueous Solutions of Bromine and Iodine.

I N T R O D U C T I O N

Aquotitanium(111) ion

Titanium metal is extensively used in construction engineering and its compounds have been of immense importance both in preparative and analytical chemistry.[1-16] The relative thermodynamic stability of the various titanium species in acid solution is summarized by the titanium potentials below:

$$Ti\ O^{2+} \xrightarrow{-0.1V} Ti^{3+} \xrightarrow{-0.37} Ti^{2+} \xrightarrow{-1.63V} Ti(s)$$

$$\text{---------- } -0.86V \text{ ----------}$$

Titanium(111) exists extensively in aqueous media. Titanium species in oxidation state I and II have no aqueous chemistry. All oxidation states of Titanium lower than the +1V are both thermodynamically and kinetically unstable with respect to Titanium 1V.

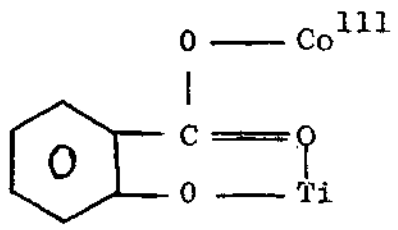
Very little attention has been given to the redox reactions of the milder titanium(111) ion in comparison to the extensive investigations already conducted into the redox reactions of more powerful reductants[17] like $Cr^{2+}(aq)$, $V^{2+}(aq)$ $Eu^{2+}(aq)$, $U^{3+}(aq)$ and $Ru(NH_3)_6^{2+}$ with $E^{\ominus}$ values-0.46, -0.26, -0.42, -0.61 and 0.1 volts respectively. Investigations into the redox reactions of titanium(111) have been hampered because like $Ru(NH_3)_6^{2+}$[18] Titanium(111) aquion reacts with perchlorate ion[19-21] which is the medium anion usually employed for dynamic studies involving metal ions in solution. Other commonly employed media like sulphate,[22] p-toluene sulphonate[23] and nitrate[24] have also led to very erratic and irreproducible data.

Recently, Orhanovic and Earley[25] found that trifluoromethane sulphonate medium proves innocent in cases involving titanium(111) aquoion in redox reactions. Sykes and Ellis,[26] Adegite and Ojo[27] also independently concluded that in reactions of titanium(111) with certain oxidants, the chloride medium provides a 'neutral' medium.

These findings have thus recently led to an upsurge in research interests about reactions involving this aquoion.

Titanium(111) aquoion can be described as a moderately labile ion. The study of the substitution reactions of $Ti^{3+}(aq)$ by Diebler[28,29] in which $C_2O_4^{2-}$ and NCS^- were the ligands, revealed that the substitution into the first coordination sphere of this ion is a function of the entering ligand as well as being acid-dependent. The rate constant for the exchange of the water ligand is now put at about $10^5 s^{-1}$[30] while the rate constant of ligation of NCS^- and $HClO_4$ have been reported by Diebler[28,29] as 8×10^{-3} and $8 \times 10^{-5} M^{-1} s^{-1}$ respectively. We can deduce from these results that the substitution reactions involving aquotitanium(111) ion proceeds by an associative mechanism, probably through an associative interchange (Ia)[31] mechanism. One can also infer from these results that the rate of the inner-sphere reactions of $Ti^{3+}(aq)$ should be less than $10^3 M^{-1} s^{-1}$ when the oxidants are acidopenta-ammine-Cobalt(111) complexes of the form $Co(NH_3)_5X^{2+}$. Substitution rates as high as $10^4 M^{-1} s^{-1}$ has however been obtained in cases involving oxalato-ruthenium(111) complexes[32] as the

oxidant. The enhancement in rate in the latter studies was attributed to chelation in the transition state. Chelated transition states have also been suggested in the inner-sphere reactions involving $Ti^{3+}(aq)$, where salicylato-Cobalt(111) ions are the reducible substrates.[33] The results of the latter studies were consistent with the intervention of chelated complex of the form:



Ojo et al[34] have also suggested the possibility of a chelated transition state occuring in the reaction of oxalato-Cobalt(11) complexes with aquotitanium(111) ion.

Table (2.1) presents the results and conclusions of some hitherto studied reactions of aquotitanium(111) ion. These reactions can be broadly categorized as follows:

(1) Reactions with aquometal ions[26,30,35] such as UO^{2+}, PuO^{2+}, Fe^{3+} and the reduction of TiO^{2+} by $Cr^{2+}(aq)$ and $V^{2+}(aq)$.

(2) Reactions with aqueous solutions of halogens I_2, I_3^-[36] and Cl_2.[37].

(3) Reactions with metal complexes; mostly investigated are Co^{111} and Ru^{111} complexes:

(a) $Co(NH_3)_5X^{n+}$[22,27,34,38 - 43a] ($X = F^-$, Cl^-, Br^- I^-, NCS^-, N_3^-, $RCOO^-$ (with R = H, CH_3 C_2H_5)) and many substituted carboxylate anions.[43b]

(b) Reactions with Ru(lll) complexes mostly $Ru(NH_3)_5X^{2+}$[32,44,45], where X = NH_3, Cl^-, Br^-, I^-, AcO, pyrazine, $C_2O_4^=$, isonicotamide, tetraammine like cis- and trans-$Ru(NH_3)_4C_2O_4^+$ and NCS^-.

An important feature in the redox reactions involving Ti(lll) aquoion is the dependence of the rate of such reactions on the hydrogen ion concentration of the reaction medium. The rate of electron transfer displays an inverse dependence on hydrogen ion concentration in all cases so far reported. The simplicity or complexity of this $[H^+]$ dependence has been a very useful diagnostic criterion for implicating the principal reactant titanium(lll) species in these reactions. It has also formed the basis for the formulation of the mechanistic pathway for a lot of these reactions involving this ion[22,26,27]. The comparison of the thermodynamically determined value of Ka,[45] the acid dissociation constant of the aquotitanium(lll) ion as described by the reaction:

$$Ti(H_2O)_6^{3+} \underset{}{\overset{K_a}{\rightleftharpoons}} Ti(H_2O)_5OH^{2+} + H^+ \qquad ....(2.1)$$

with the K_a value inferred from $[H^+]$ dependence data obtained in rate studies has been very useful in this respect. Agreement between these independently determined K_a values is suggestive of prior hydrolysis of $Ti(H_2O)_6^{3+}$ before the electron transfer step in these reactions that are of the outer-sphere mechanism.

Significant difference implicates the initial formation of a precursor binuclear intermediate which is then hydrolyzed prior to the electron transfer act.[32,44,45] Such a difference in these K_a values suggests an inner-sphere mechanistic pathway of electron transfer. The mechanistic rationalization of these modes of electron transfer are as follows:

Outer-sphere:

$$Ti(H_2O)_6^{3+} \underset{}{\overset{K_a}{\rightleftharpoons}} (H_2O)_5TiOH^{2+} + H^+ \quad ....(2.2)$$

$$(H_2O)_5TiOH^{2+} + MX^{n+} \xrightarrow{ket} \text{Product} \quad ....(2.3)$$

Inner-Sphere

$$Ti(H_2O)_6^{3+} + MX^{n+} \overset{K_1}{\rightleftharpoons} [M\text{-}X\text{-}Ti(H_2O)_5]^{(3+n)+} \quad ...(2.4)$$

$$[M\text{-}X\text{-}Ti(H_2O)_5]^{(3+n)+} \overset{K_2}{\rightleftharpoons} [M\text{-}X\text{-}TiOH(H_2O)_4]^{(2+n)+} + H^+ \quad ..(2.5)$$

$$[M\text{-}X\text{-}TiOH(H_2O)_5]^{(n+2)+} \xrightarrow{ket} \text{Products} \quad ...(2.6)$$

The same empirical rate law:

$$k_{obs} = \frac{k_{et}\, K}{[H^+] + K} \quad ....(2.7)$$

is obtained from the above schemes. However, K = Ka $[2\text{-}5 \times 10^{-3}M]$ for the outer-sphere reactions and $K = K_1K_2$ ($>> 2 \times 10^{-2}M$) for the electron transfer reactions of this ion that proceed by the inner-sphere mechanism. For reactions occuring by the inner-sphere mechanism K includes K_1 and $K_2 >> K_a$ since the highly charged binuclear intermediate will more easily lose a proton than $Ti(H_2O)_6^{3+}$ ion with a lower charge, hence the difference in K values for the outer and the inner-sphere electron transfer reactions involving aquotitanium(III) ion. In the oxidation of $Ti^{3+}(aq)$ by $Ru(NH_3)_4C_2O_4^+$, $Ru(NH_3)_5OOCH_3^{2+}$ and $Ru(NH_3)_5C_2O_4^+$ Adegite et al[32] obtained K_a = 0.2, 0.2 and 0.1 respectively. These values are too large to be consistent with values earlier obtained for some outer-sphere reactions and hence they did conclude that these reactions are of the inner-sphere mechanism.
For some of the reactions of $Ti^{3+}(aq)$ that occur by the inner-sphere mechanism, the formation of the precursor binuclear intermediate could be rate determining rather than the electron

transfer step, a phenomenon that has dominated most reactions involving $V^{2+}(aq)$[46,47] as reductants.

Other mechanistic criteria that have been employed to elucidate the mechanism of the reactions involving $Ti^{3+}(aq)$ include the Marcus correlation and the use of complexes containing ambidentate potential bridging ligands. An example of the use of the former criterion is the correlation of the kinetic rate constants obtained in the hexaaquo-titanium (111) reduction of a series of Co^{III}complexes with the rate constants obtained in the reduction by $Ru(NH_3)_6^{2+}$ and $V^{2+}(aq)$, when the same set of complexes are involved. The results obtained led to the conclusion that Ti^{III} reduction of μ-superoxo complex,

$$[(NH_3)_5Co O_2(NH_3)_5]^{5+}, \quad [Co(NH_3)_5X]^{(3-n)+}$$

where $X^{n-} = Cl^-$, Br^-, I^-, NH_3 and H_2O and $Co(bpy)_3^{3+}$ occur by the outer-sphere mechanism[40]. The authors did point out that Ti^{III} being a typical hard acid seems to prefer the inner-sphere path when reacting with hard base ligand complexes.

The comparison of the rate of reduction of the azido-pentaamine Cobalt(111) ion and the thiocyanato-pentaamine Cobalt(111) ion by aquotitanium(111) ion[26,39,48] provides an example of the use of the latter criterion. The inner-sphere mechanism is implicated by the large k_{NCS}/k_{N_3} ratio obtained in such investigations.

The study of the redox reactions involving aquotitanium(111) ion provides data for comparison with other d-metal ions. It also provides an opportunity for assessing how orbital interaction between oxidants and reductants affect electron transfer

rates. The transferred electron in titanium(111) is from a t_{2g} orbital. The comparison of the rates of electron transfer when oxidant orbitals are t_{2g} or eg will therefore be of significant contribution to the understanding of the factors affecting electron transfer processes.

Available data on titanium(111) reactions suggest that in the reactions of this ion that proceed by the inner-sphere mechanism, rates vary substantially among oxidants of the same charge type[27,39-41] Oxidants of less positive charge reacts faster than oxidants with more positive charge. The internal variations in rate constants observed separately for Ti(111) - Co(111) and Ru(111) - Ti(111) redox reactions can be rationalized on the basis of either the differences in the association constants or the influence of coulombic interaction on substitution rates into the inner-coordination sphere of aquotitanium(111) ion. The systematic variation within the two groups can however not be explained on such basis. The Ru(111) rate constants are consistently larger than the corresponding Co(111) rate constants.

The difference in rates can be attributed to greater cross-bridged electronic interaction of Ru(111) oxidants than for Co(111) oxidants. Efficient super-exchange interactions through π electron systems of the bridge between electron donor and electron acceptor facilitates the rate of electron transfer for Ru(111) oxidants. However, the disparity in the rates can be rationalized on the basis of the greater neuclophilicity of Ru(111) complexes towards titanium(111) than for the corresponding Cobalt(111) complexes.

Sufficient evidence exists that when a series of reactions occur by the outer-sphere mechanism and involve a common oxidant they follow Linear Free Energy Relationships[49] (L.F.E.R.). Earley and Davies[50] have also recently shown that some Cr(11)-Cr(111) reactions occuring by the inner-sphere mechanism also follow L.F.E.R. with a slope of 0.5. In the light of these findings, attempts have been made to establish a L.F.E.R. for some reactions of aquotitanium(111) ion. The reductions of $Ru(NH_3)_5H_2O^{3+}$, $Ru(NH_3)_5Py^{3+}$, $Ru(NH_3)_5pyr^{3+}$[51] and cis-$Ru(NH_3)_4(isn)_2^{3+}$[52] by $TiOH^{2+}$ have been shown to follow L.F.E.R with a slope of 0.5. However, the rate constants for the reduction of $Ru(NH_3)_5OAc^{2+}$, $Ru(NH_3)_5C_2O_4^{+}$ and $Ru(NH_3)_4C_2O_4^{+}$ do not fall on this line. It was therefore concluded that the latter reactions proceed by the inner-sphere mechanism while the former proceed by the outer-sphere mechanism.

TABLE 2.1

Some kinetic and thermodynamic parameters determined for some reactions involving aquotitanium(111) ion

SYSTEM	RATE LAW	$k_M^{-1}s^{-1}$	K_a	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	T	IM	Mechanism	Ref
(1) Ti^{III} + ClO_4^-	$k = 1.89 \times 10^{-4} + 1.25 \times 10^{-4}[H^+]$	$4 \times 10^{-4} < K$				25	1.0	i.s	20
(2) $TiOH^{2+}$ + $Co(NH_3)_5Cl^{2+}$ + $Co(en)_2Cl_2^+$ + trans $Co(en)_2Cl_2^+$	Rate= $k_2[Co(NH_3)_5Cl^{2+}][Ti(III)]$ $k_2 = \frac{k_{-1} K_h [H^+]^{-1}}{1 + K_h [H^+]}$		4.6×10^{-3}			25	1.0	Probably o.s	22
(3) Ti^{III} + V^{II} Ti^{III} + V^{IV}	$\frac{-d}{dt}[V^{II}] = k[V^{II}][Ti^{III}]$ $\frac{-d[V^{IV}]}{dt} = k[Ti^{III}][V^{IV}]$ $k = k_a' + k_b[H^+] + k_c[Cl^-]$	1.95 $k_b = 0.037 s^{-1}$ $K_c = 0.72 M^{-1}s^{-1}$					0.5	i.s (Substitution Controlled)	26
(4) Ti^{III} + $CoSCN^{2+}$	$\frac{-d}{dt}[Co(NH_3)_5SCN^{2+}]$ $= k_{obs}[Co(III)][Ti(III)]$ $k_{obs} = a + b[H^+]$	$a = 2.02 \pm 0.32 \times 10^{-3}$ $M^{-1}s^{-1}$ $b = 78.7 \pm 1.5 \times 10^{-3}$				25	1.0	Inner Sphere	27

TABLE 2.1 (CONT'D)

SYSTEM	RATE LAW	$k_M^{-1}s^{-1}$	K_a	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	T	IM	Mechanism	Ref
(5) Ti^{III} + $Ru(NH_3)_5OOCH_3^{2+}$	$k_b = Kk/(K + [H^+])$	7×10^2	0.2			25	1.0		
+ $Ru(NH_3)_5C_2O_4^+$		2.5×10^4	0.2			25	1.0	i.s	32
+ $Ru(NH_3)_4C_2O_4^+$		3.6×10^4	0.1			25	1.0		
(6) Ti^{III} + Salicylato cobalt(III) derivatives	rate = $[Ti^{III}]\,[Co^{III}]\,k_{lim}(1+[H^+]/K)^{-1}$	≥ 100				25	1.0	i.s	33
(7) Ti^{III} + $Co(phen)_3^{3+}$	Rate = $k_{obs}[Ti^{III}][M^{III}]$	$\underline{Co(C_2O_4)_3^{3-}}$							
+ $Co(C_2O_4)_3^{3-}$	$k_{obs} = k_o' + b[H^+]^{-1}$	$a = 5.30 \times 10^4$ mol $dm^{-3}s$							
+ $Fe(phen)_3^{3+}$		$b = 5.19 \times 10^{-3}s$				25	1.0		34
		$\underline{Fe(phen)_3^{3+}}$							
		$a = 0.14 \times 10^{-5}$ mol $dm^{-3}s$							
		$b = 3.17 \times 10^{-5}s$							

TABLE 2.1 (cont'd)

SYSTEM	RATE LAW	k_M-l_s-l	K_a	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	T	IM	Mechanism	Ref
(8) Ti^{III} + V^{V}	Stept 1 $k_1 = k_r + k_f[Ti^{III}]$ $k_f = a/(K_a' + [H^+])$ Step 2 $k_2 = b[Ti^{III}]/1 + K_a[Ti^{III}]$ $b = d/(e[H^+] + [H^+]^2)$ Step 3 $-\frac{d\ln}{dt}$ [Ti(1V)] = $f + g[H^+] + h[H^+]^2)$ [V(V)] $k_r = 9.09 \pm 0.76 s^{-1}$ $a = 2130 \pm 340 s^{-1}$ $b = c[H]^2$ $c = 100 \pm 23M\ s^{-1}$		0.04-0.03				5.0M	Probably i.s	35

TABLE 2.1 (cont'd)

SYSTEM	RATE LAW	$k_M^{-1}s^{-1}$	K_aM	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	T	IM	Mechanism	Ref
(9) Ti^{III} + I_2	$\frac{-d}{dt}[I_3^-] = \frac{k^{II}[Ti^{III}][I_3^-]}{[H^+][I^-]} + \frac{k^{II}[Ti^{III}][I_3^-]}{H^+} + K^1[Ti^{III}][H^+]$						1.025		36
(10) Ti^{III} + Cl_2 + HOCl		125 ± 8 (1.02±0.001) x 10^4		16±0.2	12.58	30	1.0	Probably i.s	37
(11) Ti(III) + $CoSCN^{2+}$ + CoN_3^{2+}	$k_{ox} = C[H^+]/(K_a + [H^+])(d + [H^+])$ $k_{ox} = a/(b + [H^+])$ $a = 2.21 \pm 0.07 s^{-1}$ $b = K_a$ $KN_3^-/k_{SCN^-} = 3.6 \times 10^4$		0.0745			25	1.0	i.s	38

TABLE 2.1 (cont'd)

SYSTEM	RATE LAW	k_M-1$_s$-1	K_a	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	T	I	Mechanism	Ref
(12) Ti^{III} + $Co(NH_3)_5DMN^{3+}$ + $Co(bpy)_3^{3+}$ + $Co(NH_3)_6^{3+}$	Rate = k_{obs}[Ti(III)][Co(III)] $k_{obs} = k_o + k_1[H^+]$	0.12 13 8.6×10^{-3}				25	1.0	o.s	40
(13) Ti^{III} + 17 pentaammine Cobalt(III) complexes		4×10^{-4} < K > 1.2×10^{2}				25	1.0	i.s	41
(14) Ti^{III} + Bis(2,2',2''-terpy)Co^{III} + Tris(1,10phen)Co(III)	$k = k_{Ti^{3+}} + \frac{k_{TiOH^{2+}} K_a [H^+]^{-1}}{1 + K_a [H^+]^{-1}}$	36 30	3.5×10^{-3}			25	1.0	o.s	42
(15) Ti^{III} + $Ru(NH_3)_6^{2+}$ + $Ru(NH_3)_5Cl^{2+}$	$k_2 = k_1$ [Ti(III)]	32 12	5×10^{-3}	41 35		25	1.0	o.s	44
(16) Ti^{3+} + $Ru(NH_3)_5NCS^{2+}$ + Ti^{III}(HEDTA)	$k_2 = kK/([H^+] + K)$	840 2.8×10^{4}		70		25 25	2.0 2.0	i.s i.s	48

TABLE 2.1 (cont'd)

SYSTEM	RATE LAW	$k_M^{-1}s^{-1}$	K_a	$\Delta H^{\neq}$, KJ mol^{+}	$\Delta S^{\neq}$ J mol^{-}k^{-1}	T	I	Mechanism	Ref
(17) Pu(Vl)$^{\prime}$ + Ti(lll)	$\frac{-d}{dt}$ [Pu(Vl)] = k_1[Pu(Vl)][Ti(lll)][H^+]$^{-1}$	108s^{-1}		10.3	-14.7	25	1.0		54
(18) Hydrolysis of Ti(lll)	log K = 12.9 at 15°C 12.71 at 25°C 12.26 at 35°C								55
(19) Ti^{lll} + Pu(lV)	$\frac{-d[Pu(lV)]}{dt}$ = $k_1[Pu^{4+}][Ti^{3+}][H^+]^{-1}$	59.5		16.7	15	25	1.02		56
(20) Ti^{lll} + $Ru(en)_3^{3+}$	Rate = k[Ru(lll)][Ti^{lll}][H^+] $^{-1}$	18.1				25	1.0	o.s	57
(21) Ti^{lll} + $Co(NH_3)_5Br^{2+}$ $Co(NH_3)_5F^{2+}$ +Cis and trans- $Co(en)_2H_2O(OH)^{2+}$		0.18 1 x 10^3 20 and 4 x 10^{-3}				25	1.0	i.s Substitution Limited	58

TABLE 2.1 (cont'd)

SYSTEM	RATE LAW	k	K_a	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	T°C	IM	Mechanism	Ref
(22)									
(a) Ti^{III} + Co(EDTA)$^-$	(a) $-d\ln[Co(EDTA^-)] = \frac{a[H^+]^{-1}[Ti^{III}] + e[H^+]^{-1}[Ti^{III}]^2}{1 + K_a[H^+]^{-1}}$		4.6×10^{-3}			25	1.0		
(b) + Co(HEDTA)OH_2			3.3×10^{-3}			25	1.0		
+ Co(HEDTA)Cl^-	$a = 0.29\ s^{-1}$		5.7×10^{-3}			25	1.0	59	
	(b) $\frac{-d\ln}{dt}$ (Co(HEDTA) = $\frac{a[H^+][Ti^{III}]}{1 + K_H[H^+]^{-1}}$								

Titanium(111) Ethylenediamine tetraacetate complex.

A review has recently been written[60] on the influence of EDTA-like ligands on the replacement rates for water molecules coordinated to various metal ions. Matsubara and Creutz did point out that metal ions with vacant t_{2g} orbitals (Class 1): Cr(111), Ti(111), Os(111), demonstrate very large increases in rate when EDTA or similar ligands replace water. They also concluded that metals with filled t_{2g} orbitals (Class 2): Co(111), Rh(111) and Ru(111) however demonstrate moderate increases.

Pecsok and Maveric,[61] Blumber and Koltoff[62] have independently carried out polarographic studies of the EDTA complexes of titanium(111). Their results suggested the existence of both the hydrolyzed and unhydrolyzed form of these complexes in solution. They did report that below pH = 2.5, the half-wave potential were reversible and independent of pH. Between pH = 3 and pH = 8 however, the half-wave potentials were irreversible and dependent on pH. They proposed the following electrode reactions:

$$TiY^{-} + e = TiY \quad pH < 2 \qquad ...(2.8)$$

$$TiOY^{2-} + 2H^{+} + e = TiY^{-} + H_2O \text{ pH } 2.5 - 8 \qquad ...(2.9)$$

The following equilibrium constants were also obtained:

$$TiY^{-} \underline{\underline{K}}_1 Ti^{3+} + Y^{-4} \quad K_1 = 5 \times 10^{23} M \qquad ...(2.10)$$

$$TiOY^{2-} \underline{\underline{K}}_2 TiO^{2+} + Y^{-4} \quad K_2 = 5 \times 10^{13} M \qquad ...(2.11)$$

$$Ti\ Y + H_2O \underline{\underline{K}}_3 TiO^{2+} + 2H^{+} + Y^{-4}, \quad K_3 = 3 \times 10^{-4} M \qquad ...(2.12)$$

Their results gave the standard redox potential of the reaction in equations (2.8) and (2.9) as -0.22V and 0.09V respectively. Podlahova and Podlaha,[63] using titration methods also characterized

the various forms of Ti(111)-EDTA complexes existing in solution as a function of pH. They proposed the following equilibria:

$$Ti(H_20)edtaH \overset{K_1}{\rightleftharpoons} Ti(H_20)(edta) + H^+ \quad pK_1=2.02\pm0.01 \quad ...(2.13)$$

$$Ti(H_20)(edta)^- + H_20 + H_20 \overset{K_2}{\rightleftharpoons} Ti(OH)(edta)^{2-} + H^+ \quad pK_2 = 8.64 \pm 0.01 \quad ...(2.14)$$

$$Ti(H_20)(edta)^{2-} + H_20 \overset{K_3}{\rightleftharpoons} Ti(OH)_2(edta)^{3-} + H^+ \quad pK_3 = 11.61 \pm 0.01 \quad ...(2.15)$$

Apart from confirming the results of earlier workers, they also proposed the existence of a third Ti^{111}-edta complex - $Ti(OH)(edta)^{3-}$ - between pH = 4 and pH = 11.

Kristine and Shepherd have recently reported their identification of the formation of $Ti(0_2)edta^{2-}$ when molecular oxygen is added to $Ti(edta)(H_20)^-$. They attributed the formation of the complex to the labilizing influence of the EDTA ligand. They also proposed the following reaction steps:

$$Ti(edta)(H_20)^- + 0_2 \overset{K_1}{\rightleftharpoons} Ti(0_2)(edta) + H_20 \quad ...(2.16)$$

$$K_1 = 1.2 \times 10^4 \text{ l mol}^{-1} S^{-1}$$

$$Ti(edta)(H_20)^- + Ti(0_2)edta + 2H_20 \xrightarrow{fast} 3H_20 + TiO(edta)^{2-} + Ti(0_2)(edta)^{2-} \quad ...(2.17)$$

Based on the water exchange rate of $10^7 S^{-1}$ earlier estimated by Sykes,[65] they were of the opinion that the oxidation of $Ti(edta)(H_20)^-$ by 0_2 may be substitution limited. This latter work is particularly important in that it constitutes an addition to the extensive studies that have been carried out on the formation of dioxygen, superoxo and peroxoadducts of

transition metal complexes in relation to oxygen transport and catalytic activation as in haem O_2 carriers, oxygenases and hydroxylases.

The kinetic investigation involving polycarboxylate complexes such as Cr^{II}-EDTA, Fe^{II}-CyDTA, M^{II}-CyDTA and M-EDTA (M=Mn, Co) have been reported.[66-85] The results of these investigations suggest a similarity in the gross features of the redox reactions of $M^{n+}(aq)$ and M^{n+}-EDTA. The identification of the inner-sphere or the outer-sphere path has however been demonstrated for a few of these systems. One such case is the reduction of Ethylene-diammine tetraacetato - cobaltate(III) complexes by Hexacyanoferrate(II).[82] The outer-sphere mechanism was indicated for the reduction of $CoEDTA^-$, $Co(EDTA)OH_2^-$ and $Co(EDTA)Cl^{2-}$ ions. Agreement with Marcus theory has also been invoked to suggest that the oxidation of M^{II}-CyDTA and M^{II}-EDTA (M=Fe,Co,Mn) proceed by the outershpere mechanism. However for the reaction between $Co\text{-}EDTA^{2-}$ and $Fe(CN)_6^{3-}$, an inner-sphere mechanism was proposed.[83-85] Recently, Earley and Lee[48] reported that for Ti^{III}, the rate of substitution for H_2O, HEDTA, and EDTA complexes are in the ratio $1:366:10^4$. Therefore, dispite the fact that Ti(III) has unfilled t_{2g} orbital and should be in Matsubara and Creutz[60] class 1, it is not as sensitive to labilization as other cations in this class. The substitution reactions of the ions in Class 1 are dissociative, but the substitution reaction of Ti(III) aquoion appears to have a large associative component. This was suggested as being probably responsible for the different behavior of Ti(III) as compared to other Class 1 trivalent ions.

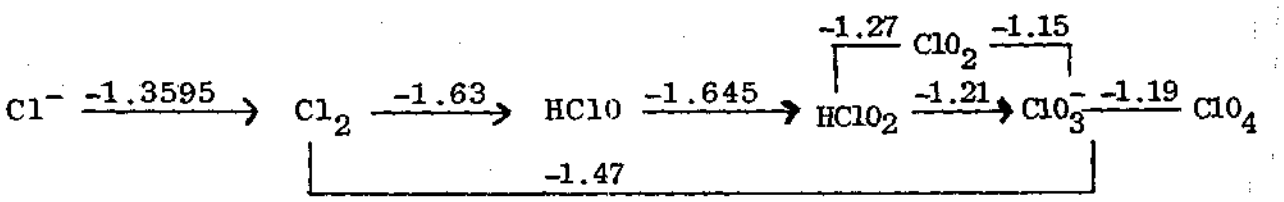
In the reactions of aquotitanium(111) ion, sufficient evidence exists for both the inner-sphere and the outer-sphere pathway.[86] The use of $Tiedta^-$ as reductants in electron transfer reactions is however a recent development. Rate studies involving the oxidation of Ti^{111}-edta by some cobalt(111) - ammine complexes have been reported by Sykes and Thomson.[66] They did conclude that this reductant utilizes both the outer-sphere and the inner-sphere mechanism in these reactions. As with the aquoion,[40] the latter mechanism is favoured when the appropriate lead-in atom (a hard base) is available on the oxidant.

Halogens.

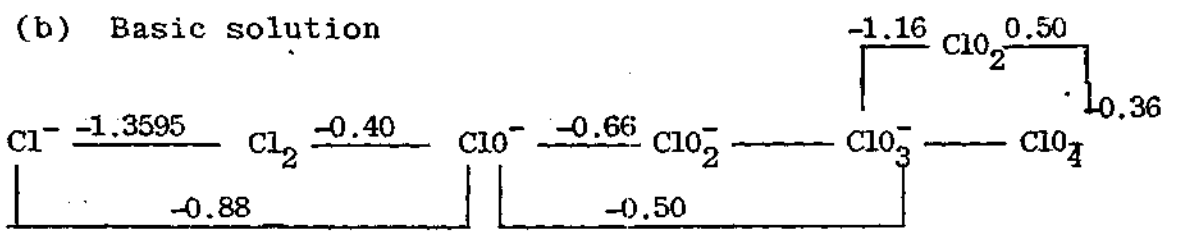
The potential diagrams of the halogens, X_2 (X = Cl, Br,I) in acidic and basic aqueous medium are given below:[88]

Chlorine.

(a) Acidic solution:

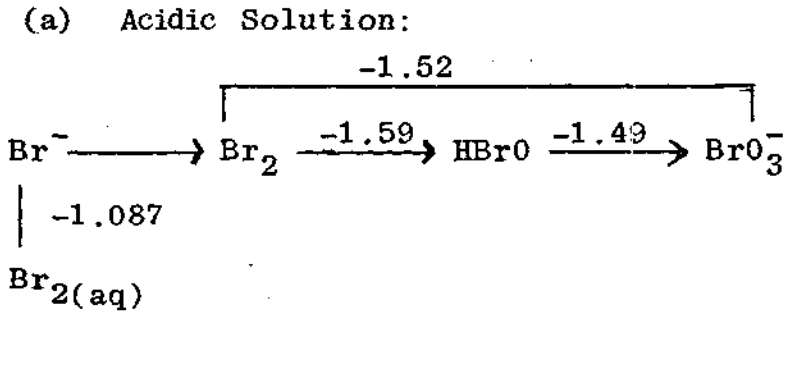


(b) Basic solution

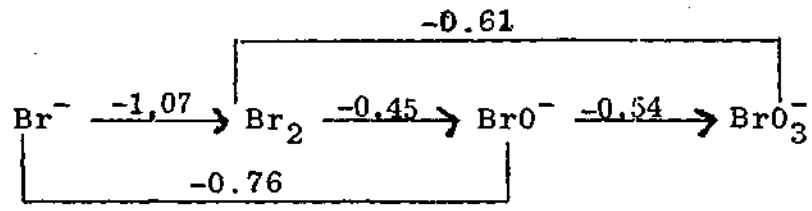


Bromine:

(a) Acidic Solution:

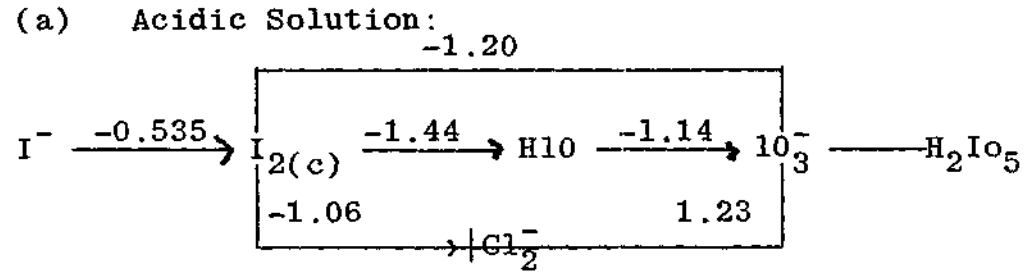


(b) Basic solution:

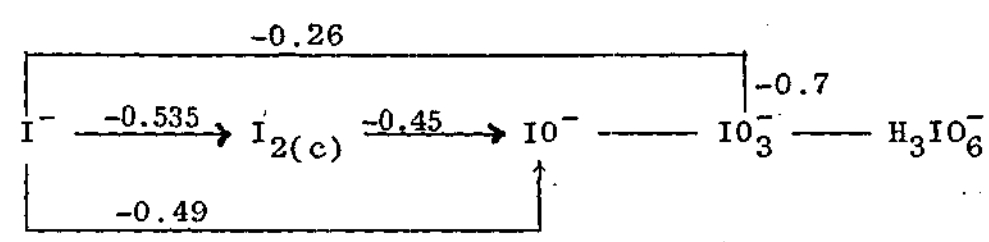


Iodine:

(a) Acidic Solution:



(b) Basic Solution:



Investigations into the kinetics and mechanism of the oxidation of halogens X_2(X = Cl, Br, I) are exciting in that they highlight the variations in group properties of these elements.[89] The kinetic data for some redox reactions involving halogens are presented in Table (2.2). Some points of interest from the reported reactions of halogens are briefly summarized below:

(1) For a common reductant the reactivity order:

$$k_{Cl_2} > k_{Br_2} > k_{I_2}$$

usually obtained, suggests that the overall free energy change ΔG^{o} is the most important rate-determing step in these

TABLE 2.2

Kinetic data for some halogen reactions

M^{n+}	E^o	k_{I_2}	$k_{I_3^-}$	$k_{Br_3^-}$		k_{Cl}	Ref I_2	Br_2	Cl_2
V^{2+}	-0.2	7.5×10^3	9.7×10^2	3.1×10^4		5×10^2	104	103	103
V^{3+}	0.36	1.2×10^{-2}	1.2×10^{-2}	4.6	<4.6	>103	96	97	
VO^{2+}	1.0	-				5.3			98
Ti^{3+}	0.1	1.6×10^{-2}		1.0×10^2	$<10^2$	1.3×10^2	99		100
Fe^{2+}	0.77	1.5×10^{-4}	2.4×10^{-4}	0.76	34	80	117	105	115
CoEDTA $^{2-}$		5.2×10^{-4}	3.1×10^{-5}	7.3×10^{-2}	5.42×10^{-2}		106	106	
CoCyDTA $^{2-}$	0.38	6.4×10^{-5}	2.2×10^{-5}	2.0×10^{-3}	1.1×10^{-3}		106	106	
FeCyDTA $^{2-}$	0.15	1.24×10^6	5.0×10^3	9.3×10^6	1.2×10^6		106	106	
FeEDTA $^{2-}$		1.6×10^6	4.4×10^3				106	106	
Eu^{2+}	-0.42	6.1×10^3	4.4×10^3	$\sim 5 \times 10^4$			119	119	
U^{3+}	-0.63	3.9×10^5	0.31×10^2	7.2×10^5	$<7.2 \times 10^5$	$>10^6$	113	112	
U^{4+}	0.334	9.9×10^{-4}	1.2×10^{-4}	1.1×10^{-3}	$<1.1 \times 10^{-3}$	7.4×10^{-2}	93	94	95

reactions.[90a] The reverse reactivity order is usually observed in reactions involving halides.[90b] Exceptions that have been reported to this reactivity order of the halogens include $MO_2^{IV} + X_2$ reaction[91] where disproportionation,

$$MO_2^{IV} \rightleftharpoons MO^{III} + MO^{V}$$

is the rate-determining step. The reverse order of reactivity was also reported for the $Bi^{V} + X^{-}$ reaction.[92] In the latter reaction, substitution onto Bi^{V} was the rate-determining step. For reactions where X_2 is constant, variation of the reducing agent results in a reactivity order dependent on the reducing ion. Known exceptions to this latter assertion include the comparison of the reactivity order of the halogens in their reaction with U^{4+}[93-95] and V^{3+}[96,97]. The reactivity order observed for these ions is inversely proportional to their reducing ability. The inverted order can be rationalized on the basis of the drastic structural rearrangement that accompanies the U^{4+} to UO_2^{2+} conversion, as will be explained in the next section.

(2) The redox reactions involving halogens are usually characterized by acid-dependent terms which may be as a consequence of two factors:

(i) Hydrolysis: In aqueous medium, the following equilibria are established by halogens:

$$X_2 + H_2O \underset{}{\overset{K_1}{\rightleftharpoons}} H^+ + X^- + HOX^- \qquad ....(2.18)$$

$$X_2 + X^- \overset{K_2}{\rightleftharpoons} X_3^- \qquad ....(2.19)$$

$$X_2 + Y^- \rightleftharpoons X_2Y^- \qquad ....(2.20)$$

Reported values of K_1 and K_2 are[101]

	K_1 M ^{2}	K_2M^{-1}
Cl_2	4.66×10^{-4}	
Br_2	5.8×10^{-9}	17
I_2	3×10^{-13}	748

The predominant species in aqueous solutions of X_2 is therefore determined by the concentrations of H^+, X^- and Y^- in solution. Varying the concentrations of these ions should therefore affect the rate of the reaction provided the halogen species react at different rates.

k_{HOX} and k_{X_2} are very important in chlorine reaction, i.e. $Ti^{111} + Cl_2$, HOCl[100] and $[VO]^{2+}$ + HOCl[98] reactions, but they are not very important in redox reactions involving bromine and iodine in acidic solutions. In cases involving X_2 and X_3^- and where there is a very small or no complexation between the aquoion and X^-, the influence of X^- on rate can be attributed to differing reactivity of X_2 and X_3^-.

$k_{X_3^-}$ are important in reactions involving bromine and iodine but not important for chlorine reactions. No consistent pattern has been established for the oxidizing reactivity of X_2 and X_3^- with a reducing agent. The comparison of kinetic parameters suggests that cases where $k_{I_3^-} < k_{I_2}$ might be rationalized by the consideration of the activation enthalpy of such reactions. Such examples are the $U^{4+} + I_2$, I_3^-[93] and $V^{3+} + I_2$, I_3^-[96] reactions where the activation entropies are more positive for I_3^- than for I_2 reactions in conformity with electrostatic considerations.

(ii) Redox reactions in which aquaions are oxidized to oxo-cations by acid solutions of halogens seems to show similar hydrogen ion dependencies. Some kinetic data for the oxidation of some metal aqua-ions to oxo-cations by aqueous acid solutions of halogens are presented below

Reaction	Order with respect to $[H^+]$	Ref
$2V^{3+} + [I_3^-] + 2H_2O \rightarrow 2[VO]^{2+} + 3I^- + 4H^+$	-1	96
$2V^{3+} + Br_2 + 2H_2O \rightarrow 2[VO]^{2+} + 2Br^- + 4H^+$	-1	97
$2VO^{3+} + Cl_2 + 2H_2O \rightarrow 2[VO]^{2+} + 2Cl^- + 4H^+$	-1	98
$U^{4+} + Cl_2 + 2H_2 + 2H_2O \rightarrow [UO_2]^{2+} + 2Cl^- + 4H^+$	-2	95
$U^{4+} + Br_2 + 2H_2O \rightarrow [UO_2]^{2+} + 2Br^- + 4H^+$	-2	94
$U^{3+} + I_2 + 2H_2O \quad [UO_2]^{2+} + 2I^- + 4H^+$	-2	93
$2Ti^{3+} + I_3^- + 2H_2O \rightarrow 2[TiO]^{2+} + 3I^- + 4H^+$	-1	99
$2Ti^{3+} + Cl_2 + 2H_2O \rightarrow 2[TiO]^{2+} + 2Cl^- + 4H^+$	-1	100

Three generalizations appear common to these reactions:

(a) Direct electron transfer does not occur between the aquoion and the halogen, i.e. activation paths of the form:

$M^{n+}(aq) + X_2 \rightarrow$ (activated complex)* are unimportant in these reactions.

(b) The precursor hydrolyzed species formed before the electron transfer steps contain the same number of oxygen atoms as the final products, viz for $m^{n+} \rightarrow [MO]^{(n-1)+}$ the hydrolyzed species are $[M(OH)]^{(n-1)+}$ and $M^{n+} \rightarrow [MO_2]^{(n-2)+}$ the hydrolyzed species are $[M(OH)_2]^{(n-2)+}$.

(c) One cannot say with certainty whether the hydrolyzed species are involved in the formation of the inner-sphere activated complexes or intermediates, and therefore, the generally observed inverse hydrogen ion dependence is not necessarily evidence of an inner-sphere mechanism. The suggestion has been made.[100] that the $[H^+]^{-1}$ and $[H^+]^{-2}$ dependence of the rate constants of these reactions are due to prior formation of hydroxo aquoions that are structurally very close to the products and hence react with much lower activation energies than the aquaions. These hydroxo-complexes could then react with the halogens by either an outer-sphere or an inner-sphere mechanism. For example in the $U^{IV} - Cl_2$[95] and $V^{IV} - Cl_2$[98] reactions HOCl reacts with less hydrolyzed metal ion species than Cl_2. This was interpreted as being suggestive of an inner-sphere mechanism in which an oxygen atom is transferred from HOCl to the metal ion.

(3) The halogens are capable of acting as one electron or two electron transfer reductants respectively. Available information however suggests that in most reactions of halogens so far reported, X_2 undergoes univalent changes to form X_2^- as an intermediate. Typical examples that have been reported are: $V^{2+} + X_2$(X = 1, Br, or Cl),[103,104] $V^{3+} + X_2$ (X = 1 or Br),[96,97] $Ti^{3+} + X_2$ (X = I or Cl),[37,99] $Fe^{2+} + Br_2$,[105] $[M^{II}L]^{2-} + X_2$ (L = ethylenediaamine tetraacetate; M = Fe, Co or Mn; X=1 or Br)[106] and the $[VO]^{2+} + Cl_2$ reaction.[98] The chlorine radical anion has also been proposed as an intermediate in the Mn^{III}

catalysis of the oxidation[107] of oxalate by $[MnO_4^-]$, the chloride-catalyzed oxidation[108] of Tl^1 by Mn^{111}, and the oxidation of Cl^- by Co^{111}[109] Such halogen-ion radicals have in fact been identified in the flash photolysis[110] and pulse radiolysis studies[111] of aqueous halide solutions. The rate of their disproportionation and oxidation reactions with aqua metal complex ions, e.g. Fe^{2+}, Co^{2+}, Mn^{2+} have been measured.[112] Estimates of the redox potential of the X_2- $[X_2^{-\cdot}]$ couple, based on the thermodynamic parameters of the X atom has also been made by various workers.[112-114]

Considering the hypothetical non-complemetary reaction involving halogens:

$$2M^{n+} + X_2 = 2M^{(n+1)+} + 2X^- \qquad ...(2.21)$$

the reaction steps usually proposed are:

$$M^{n+} + X_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M^{(n+1)+} + X_2^{-\cdot} \qquad ...(2.22)$$

$$M^{n+} + X_2^{-\cdot} \xrightarrow{k_2} M^{(n+1)+} + 2X^- \qquad ...(2.23)$$

The ΔG^o for equation (2.22) is suggested as being of immense importance in determining the rate of these reactions. In cases where $E^o_{M^{(n+1)+}/M^{n+}}$ is positive $k_2 << k_{-1}$, kinetic reversibility is expected since $M^{(n+1)+}$ should inhibit the reaction. Thus, the observed inhibition by vanadium(V) in the reduction[98] of Cl_2 by $[VO]^{2+}$ and the attendant complexity in the empirical rate law led the authors to conclude that the reaction proceeds by a series of one electron changes in which $[Cl_2]^{-\cdot}$ is a reactive intermediate. Such a situation has also been observed for the Fe^{2+}/Br_2[105] reaction.

In such cases: inhibition by product provides the empirical evidence for the above mechanism. When $k_2 >> k_{-1}$, conformity to strictly second order kinetics is expected. Examples of such reactions are Ti^{3+}/X_2[99,100] and V^{2+}/X_2[103,104] reactions. Indirect evidence is usually needed to justify the univalent change in such cases. In the $U^{4+} + X_2$[93-95] reaction, a direct two-electron transfer was invoked. The fact that U(V) was not detected made the investigators to suggest the possibility that these intermediates probably react so fast with $X_2^{-\cdot}$ that the net observable effect appears like direct two-electron transfer.

(4) The classification of the redox reactions involving halogens into the inner-or the outer-sphere mechanism requires some caution. Equations (2.22) and (2.23) show that these reactions usually involve two steps. The possibility is that the two steps may be of the same or different mechanism. For example in the reaction, $Cr^{2+} + Cl_2$, product identification confirmed that 75% of the reaction occured by the inner-sphere mechanism while 25% was by the outer-sphere mechanism.[115] Usually, the distinction between the two mechanisms is not unequivocally made because of the lability of the reactant and product species in most of these reactions. Most attempts to classify the reactions of halogens into the inner-sphere or the outer-sphere mechanisms are therefore based on less definitive indirect criteria.

E X P E R I M E N T A L

Preparation of 0.02M KIO_3

Potassium iodate sample was dried in an oven at about $110^{o}C$ and then cooled in a dessicator. 1.07g of this sample was weighed accurately and dissolved in water to make up to $250cm^3$ of 0.02M KIO_3 solution. This was the primary standard for the iodometric titrations.

Preparation and standardization of $Na_2S_2O_3$(0.1M)

26 - 27g of analar grade sodium thiosulphate crystals, $Na_2S_2O_3.5H_2O$ was weighed and dissolved in water. The $Na_2S_2O_3$ solution was standardized against potassium iodate as described below:

$10cm^3$ of 0.02M KIO_3 and $5cm^3$ of dilute sulphuric acid were added to a saturated solution of potassium iodide(KI). The iodine librated was titrated against sodium thiosulphate using starch solution as the indicator. The molarity of the $Na_2S_2O_3$ solution was calculated using the following equations:

$$IO_3 + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

$$I_2 + 2S_2O_3^{=} \rightarrow 2I^- + S_4O_6^{=}$$

Preparation and standardization of $Ce(SO_4)_2$ Solution.

About 40g of reagent grade ceric sulphate $Ce(SO_4)_2.4H_2O$ was weighed into a $250cm^3$ beaker and $25cm^3$ of 1:1 sulphuric acid was added and stirred with frequent addition of water.

The mixture was gently warmed until dissolution of a substantial portion of the ceric sulphate had occured. The solution was cooled and filtered into a one litre volumetric flask and then diluted up to the mark.

To $25cm^3$ of this Ce(1V) solution, an excess amount of saturated solution of potassium iodide was added. The librated iodine was then titrated against standard thiosulphate solution until the solution turned pale yellow. At this point, two drops of starch solution were added and the titration continued until the solution turned from blue - black to colourless. This marks the end-point. The molarity of the Ce(1V) solution was then determined from the following equations:

$$2Ce^{1V} + 2I^{-} \rightarrow I_2 + 2Ce^{111}$$

$$I_2 + 2S_2O_3^{=} \rightarrow 2I^{-} + S_4O_6^{=}$$

Preparation of $Ti(H_2O)_6^{3+}$ solution[32]

About 9g of pure titanium metal was put into $200cm^3$ of 3M CF_3SO_3H and the mixture stirred under an inert atmosphere of purified N_2 at about 60^oC for two days. After about 48 hours the purple $Ti^{3+}(aq)$ solution formed was quickly filtered, using vacuum filtration, to get rid of the undissolved titanium metal. The $Ti^{3+}(aq)$ solution was kept under N_2 for about 2 hours before it was finally kept in the deep freezer to minimize oxidation to titanium(1V).

Equation for the reaction:

$$Ti + 3H^{+} \rightarrow Ti^{3+} + 3/2H_2$$

Standardization of $Ti^{3+}(aq)$ solution.

(a) About $1.5cm^3$ of the $Ti^{3+}(aq)$ solution was pipetted and added to $50cm^3$ of standard cerium(1V) solution of about 0.10M. The excess cerium(1V) was determined by indirect iodometric titration using standardized thiosulphate solution and from the titration result, the concentration of $Ti^{3+}(aq)$ determined.

Determination of free acid in the prepared $Ti^{3+}(aq)$ solution.

The hydrogen ion concentration of titanium(111) stock solution was determined by two independent methods which gave the same results within ±1%. In the first method,[116] direct NaOH titration (carried out slowly with constant stirring) of diluted Ti(111) stock solution. A white deposit of $TiO_2(s)$ was observed. The $[H^+]$ present in the Ti(111) solution was obtained from the relation:

$[OH^-] = [H^+] + 3[Ti(111)]$, assuming quantitative conversion of TiO(s) by the equation:

$$4Ti^{3+} + O_2 + 12OH^- \rightarrow 4TiO_2(s) + 6H_2O.$$

More rapid addition of base to Ti(111) solution gave a blue, presumably polymeric, titanium containing material and non-reproducible titration results.

In the second method,[32] the free acid in the Ti(111) solution was determined by passing a known volume ($1cm^3$) of the solution through a cation exchange resin (Amberlite 120H) and the librated acid was titrated against a standard solution of sodium hydroxide.

The difference between the estimated $[H^+]$ and three times the $[Ti(III)]$ was taken as the concentration of the free acid in solution based on the following equation:

$$Ti^{3+} + Resin - H \rightarrow Ti^{3+}\text{-}Resin + 3H^+$$
$$+ \text{excess acid} \qquad + \text{excess acid} \qquad ...(2.28)$$

Preparation of Lithium perchlorate[117]

Lithium perchlorate was prepared by dissolving a known weight of B.D.H reagent grade lithium carbonate in a measured volume of 72% analar grade perchloric acid for three hours with stirring and the temperature kept constant at 80^oC. The resulting solution was filtered under pressure, cooled and left to crystallize overnight. The $LiClO_4$ was recrystallized in water. The concentration was determined by gravimetric analysis.

Preparation of standard sodium hydroxide and acids.

NaOH (B.D.H analar grade) in amples was diluted to $500cm^3$ in a volumetric flask. HCl and $HClO_4$ B.D.H grade were also diluted to the appriopriate concentrations based on the physical data, i.e. density of acid and percentage weight/volume. The exact concentrations of the acid were determined by titration against 0.3M NaOH using phenolphtalein as indicator.

Preparation of Zinc Amalgam.

B.D.H grade granulated zinc was thoroughly washed in a beaker with 6MHCl to scrub the surface. The acid was decanted and the zinc granules rinsed with doubly distilled water. Enough of 0.2M $HgCl_2$ in 1MHCl was added to cover the

zinc and the mixture was stirred for about 10 minutes. The Zinc analgam (Zn/Hg) formed was washed thoroughly with distilled water and kept under distilled water until used. Freshly prepared zinc amalgam was always used in all the kinetic runs.

Preparation of Bromine Solution.

Analar grade bromine liquid was diluted with doubly distilled water. The bromine concentration was determined by adding excess potassium iodide to a known volume of bromine solution and the librated iodine titrated against standard sodium thiosulphate. The bromine concentration was then determined as this concentration was then proportional to half the concentration of the thiosulphate.

Preparation of Iodine Solution.[118]

Because of the low solubility of iodine aqueous solutions of triiodide was prepared by dissolving resublimed iodine in potassium iodide (O.1M Analar grade). The concentration of triiodide was determined by titration against standard sodium thiosulphate.

Preparation of Ti^{111}-edta Solutions.[119]

Ti^{111}-edta solution was prepared by adding predetermined amount of titanium(111) solution to the reaction medium made up of $CF_3SOO^-Li^+$, sodium formate or sodium acetate (0.1M) CF_3COOH and Na_2H_2EDTA which is slightly in excess of the amount of titanium(111) to be added. Before addition of

titanium(111) however, all solutions were scrupulously de-aerated by bubbling nitrogen preveiously scrubbed in chromous solution towers to remove the last trace of oxygen.

Preparation of CF_3SO_3Li

CF_3SO_3Li was prepared from the reaction of Li_2CO_3 with trifluoromethanesulphonic acid and analyzed as previously described.[32]

KINETICS.

Preliminary studies of the kinetics of the $Ti(H_2O)_6^{3+}-X_2$ reactions (X = Br, I) showed that the measured rate constants were inconsistent in sulphate medium. Since earlier investigations have shown that $Ti(H_2O)_6^{3+}$ react with perchlorate ion,[20] the rate studies for these reactions were conducted in trifluoro-methane sulphonate or chloride media. These media had earlier been shown not to interfere with reactions[25-27] involving $Ti(H_2O)_6^{3+}$. A trifluoro-methane sulphonate medium was always used when investigating the effect of chloride on the rate of these reactions. It has also earlier been shown that the tendency of titanium(1V) to form polymeric species at millimolar acid concentrations is less in trifluoromethane medium.[32] The above reactions were however studied in the acid range.: $0.034 \leq [H^+] \leq 0.274M$ for X=Br and $0.0036 \leq [H^+] \leq 0.20M$ for X = I, where this effect is less evident and does not show any effect on the measured rate.

The Durrum-Gibson stopped-flow spectrophotometer was used to monitor the rate of these reactions where it was too fast for conventional techniques to be employed. The Pye-Unicam

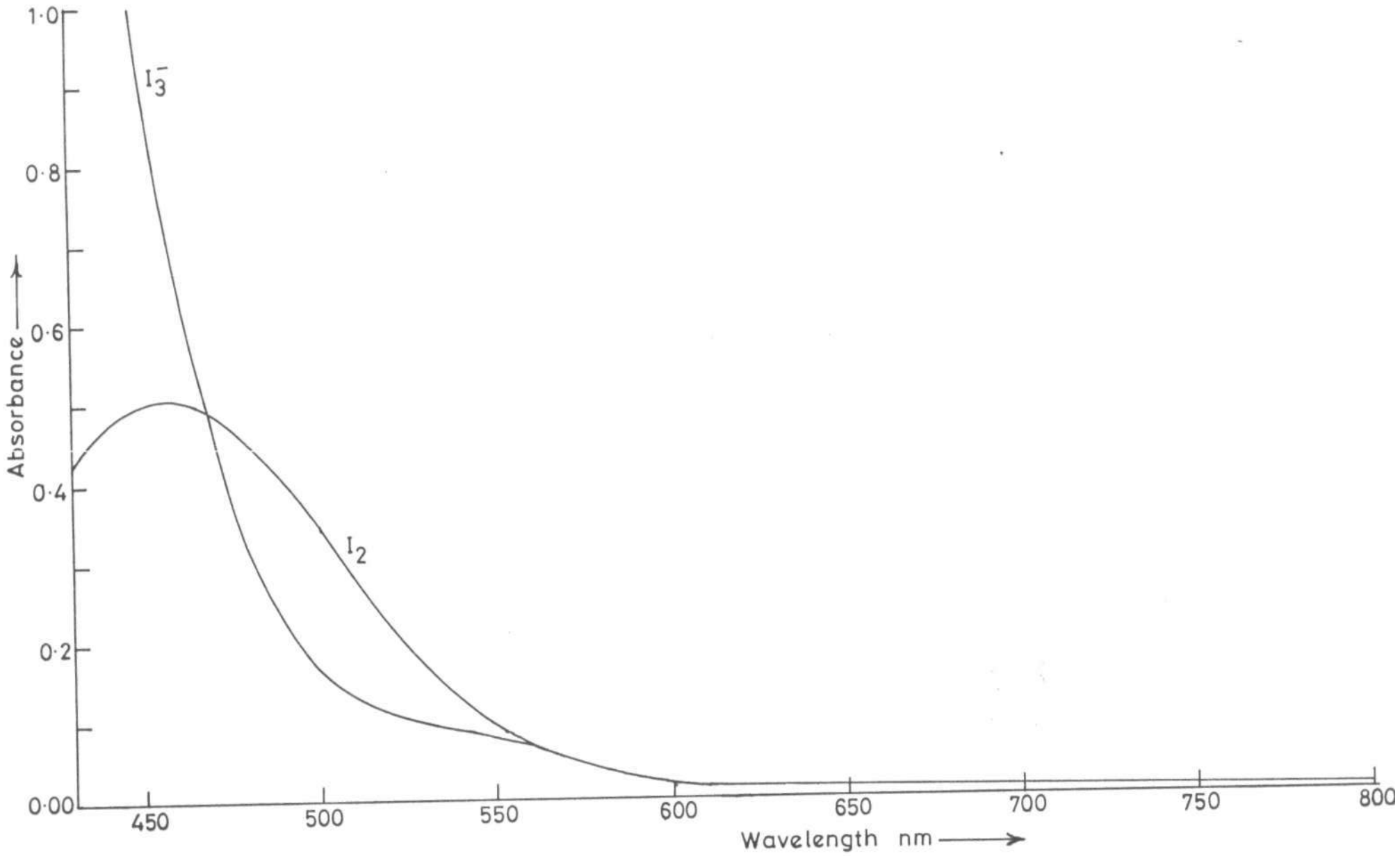


Fig. 2·1 Determination of the Isobiestic point for I_2/I_3^- solutions.
Spectra of I_2/I_3^- solutions.

S.P. 1750 spectrophotometer was however used to monitor the rates of the reactions when they were too slow for fast techniques to be employed.

The absorbance changes for these reactions were monitored at λ = 453nm and λ = 468nm, the isobiestic points for Br_2 and Br_3^- and I_2 and I_3^- respectively. (The isobiestic point for I_2/I_3^- is shown in Figure (2.1.) Except where indicated. Kinetic runs were conducted under pseudo-first-order conditions with $[Ti(III)] >> 20\ [X_2]_{Total}$.

Ionic strength was maintained constant at 0.5M with $CF_3SO_3^-Li^+$ or LiCl for all runs. The temperature was maintained at 25.0 ± 0.1^oC by circulating thermostated water from a bath through the cell compartments of the spectrophotometer.

The Ti^{III}-edta - X_2 reaction was also monitored at λ = 453nm (X = Br) and λ = 468nm (X=I) using a Durrum-Gibson stopped-flow spectrophotometer. Formate buffer was used to maintain a constant pH in the pH range 2.5 to 3.8. Acetate buffer was used in the pH range 3.7 to 6.0. To check the possibility of complexation of the Ti^{III}-edta species with CH_3COO^- and $HCOO^-$, the spectra of these solutions were investigated in the spectral region 300 - 600nm at constant pH of 1.0. There was no observable difference in the spectra of Ti^{III}-edta solution and Ti^{III}-edta solutions when they separately contained 0.1M CH_3COO^- and $HCOO^-$ respectively. For the same pH, the rate constants obtained by varying the buffer concentration from 0.05 to 0.2M agreed within 5% and therefore it was concluded that the rate of the reactions are

unaffected by formate or acetate ion. At pH = 3.7, the rate constant obtained was essentially the same irrespective of whether the buffer medium was formate or acetate.

The halogen solutions were made to contain calculated amounts of acid needed to attain the desired pH when the reactants were mixed in the reaction chamber. This arrangement was necessary to prevent an extensive hydrolysis of the X_2 solutions.

R E S U L T S

Determination of the stoichiometry of the reactions.

The stoichiometries of the Titanium(111)-X_2 and Ti^{111}-edta-X_2 reactions (X = Br, I) were determined by spectrophotometric titration at λ = 453nm (X = Br) and λ= 468nm (X = I) respectively. A known amount of the Titanium(111) or Ti^{111}-edta solution was pipetted into nine 25cm^3 volumetric flasks for each determination. Different volumes of the bromine or iodine solutions of known concentration were then pipetted into each of these flasks. The ionic strength was made up to 0.5M and the acid concentration kept at 0.1M for all the flasks. The reaction flasks were corked, properly shaken, thermostated at 25°C and left for about one hour to allow the reaction to go to completion. The absorbance of each of the flasks was then determined at the appropriate wavelength. The absorbance measurements were then plotted against the volumes of the halogen solution added as shown in Figures (2.2 - 2.5) From these plots, the equivalence point of the reactions were determined and hence the number of moles of each reactant consumed at the equivalence point was thus calculated. A typical run showing the method of calculation is presented below for the Ti^{111} - Br_2 reaction:

Equivalence point = 4.40cm^3 Br_2

No of moles of Ti^{111} = 1.75×10^{-2} moles

No of moles of Br_2 at the equivalence point

= 8.5×10^{-3}moles.

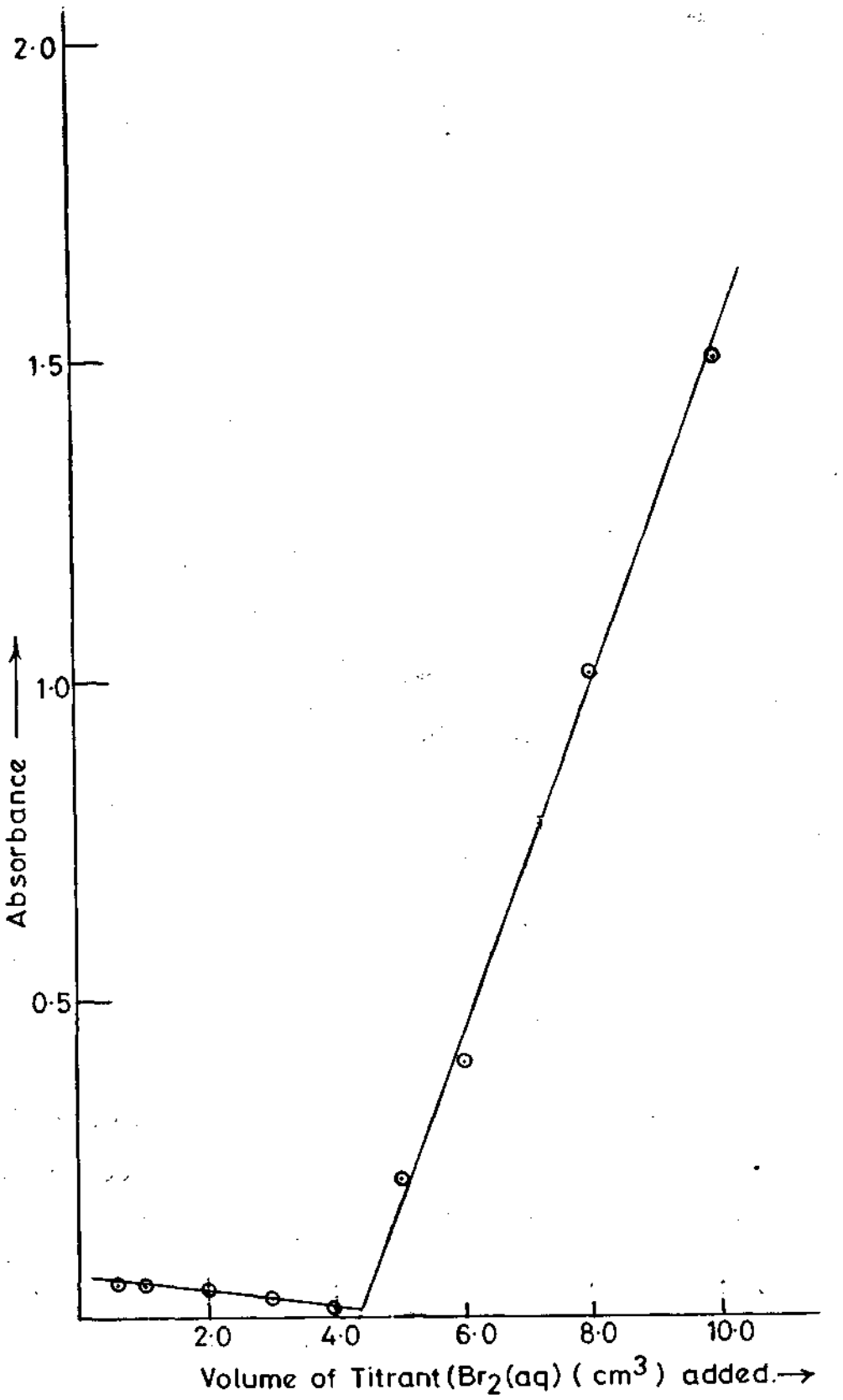


Fig. 2·2 Stoichiometry of Ti^{3+}(aq) – Br_2 reaction. Spectrophotometric Titration of Br_2(aq) vs Ti^{3+}(aq).

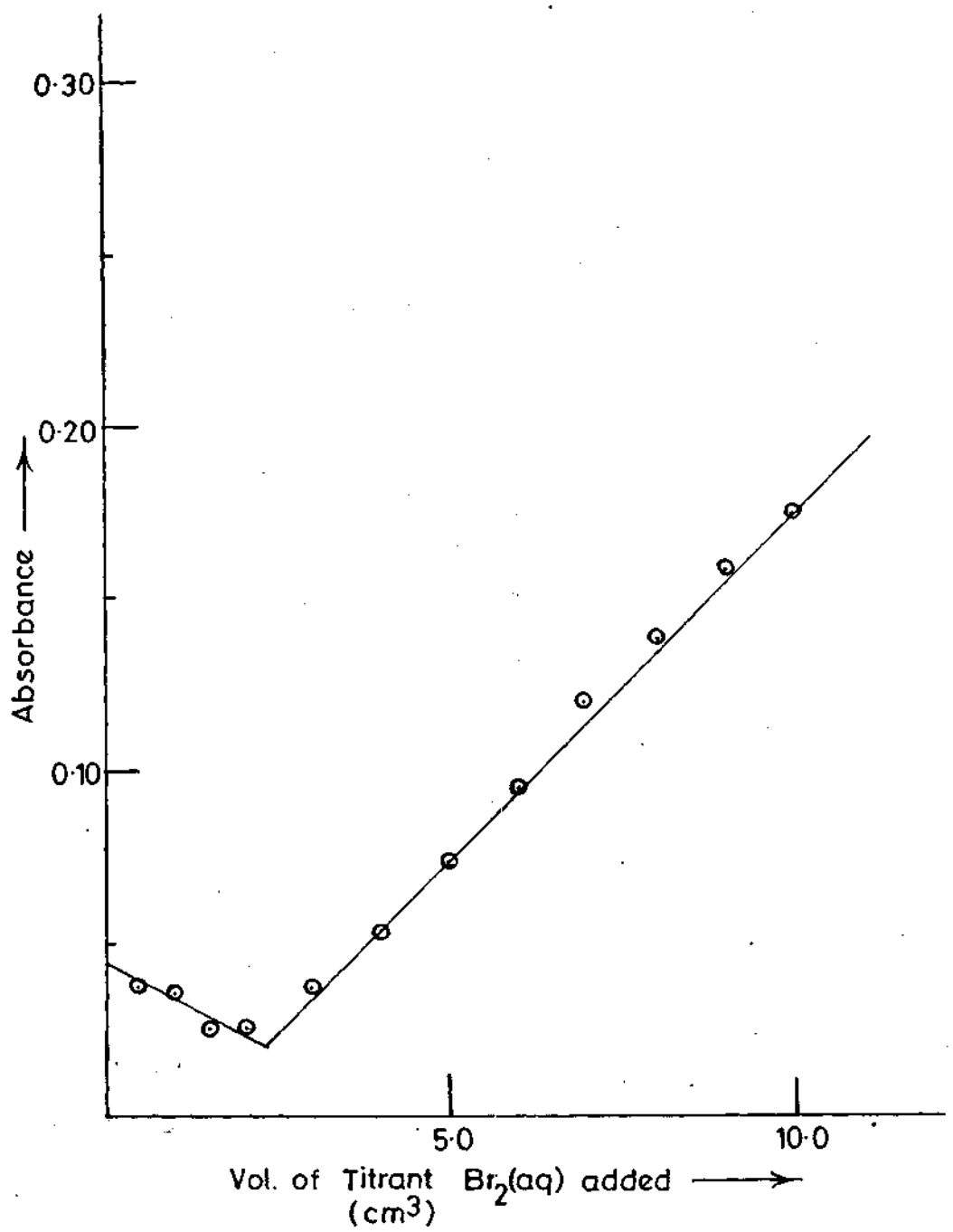


Fig. 2·3 Stoichiometry of Ti^{III}–edta–Br_2 reaction. Spectrophotometric Titration of Br_2(aq) versus Ti^{III}–edta.

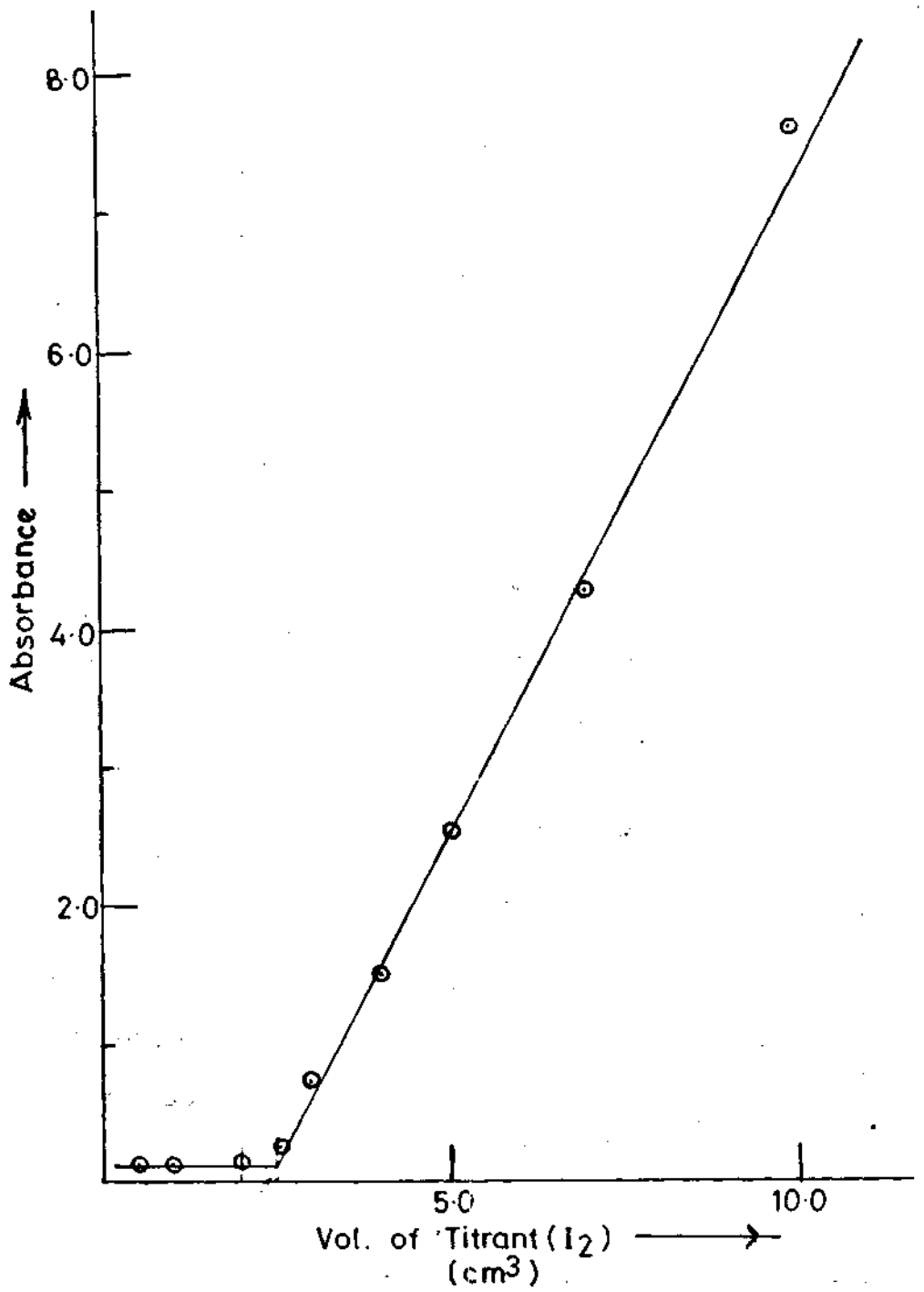


Fig. 2·4 Stoichiometry of the $Ti^{3+}(aq) - I_2$ reaction.
Spectrophotometric Titration of $I_2(aq)$ vs $T^{3+}(aq)$

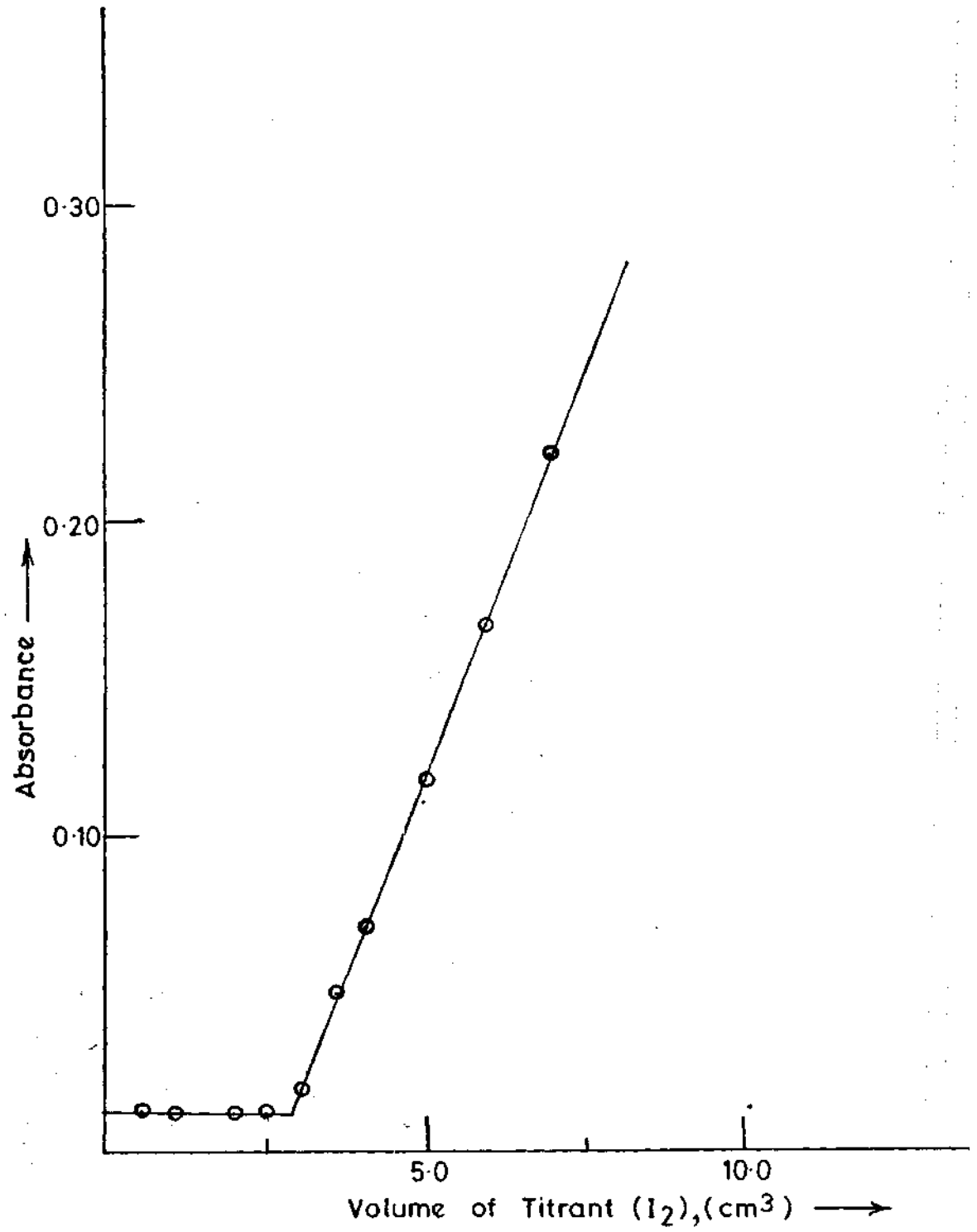


Fig. 2·5 Stoichiometry of Ti^{III}-edta-I_2 reaction
Spectrophotometric Titration of I_2(aq)
versus Ti^{III}-edta.

$$\frac{\text{No of moles of } Ti^{III} \text{ at eq. point} = 1.75 \times 10^{-2}}{\text{No of moles of } Br_2 \text{ at eq point} = 8.5 \times 10^{-3}}$$

$$= 2.04$$

Hence the stoichiometry of the Ti^{III}-Br_2 reaction is in the ratio 2:1. Similar calculations gave the stiochiometry of the

Ti^{III}-edta - Br_2, Ti^{III}-I_2 and Ti^{III}-edta -I_2 reactions as being in the ratio 2 : 1

Determination of the order of the Titanium(111) - Bromine reaction.

At constant acid concentration and constant ionic strength of 0.5M($CF_3SO_3^-Li^+$), the rate constants were measured under pseudo-first-order conditions with $[Ti^{3+}] > 20\ [Br_2]$. The pseudo-first-order plots were linear to more than 90% reaction confirming that the reaction is first-order in bromine concentration. A typical plot is shown in Figure (2.6). The pseudo-first-order rate constants were then measured for five different Titanium(111) concentrations in the range $1.9 \times 10^{-2}M \leqslant [Ti^{III}] \leqslant 5.5 \times 10^{-2}M$. An increase in the pseudo-first-order rate constants was observed as the $[Ti^{III}]$ increases as shown in Table (2.3).

A plot of log k_{obs} versus log $[Ti^{III}]$ was linear with a slope of 0.96 ± 0.02 (Figure 2.7). The linearity of this plot and the slope of approximately unity obtained confirms that the order of the reaction with respect of titanium(111) concentration is one. The second-order rate constants, k_o

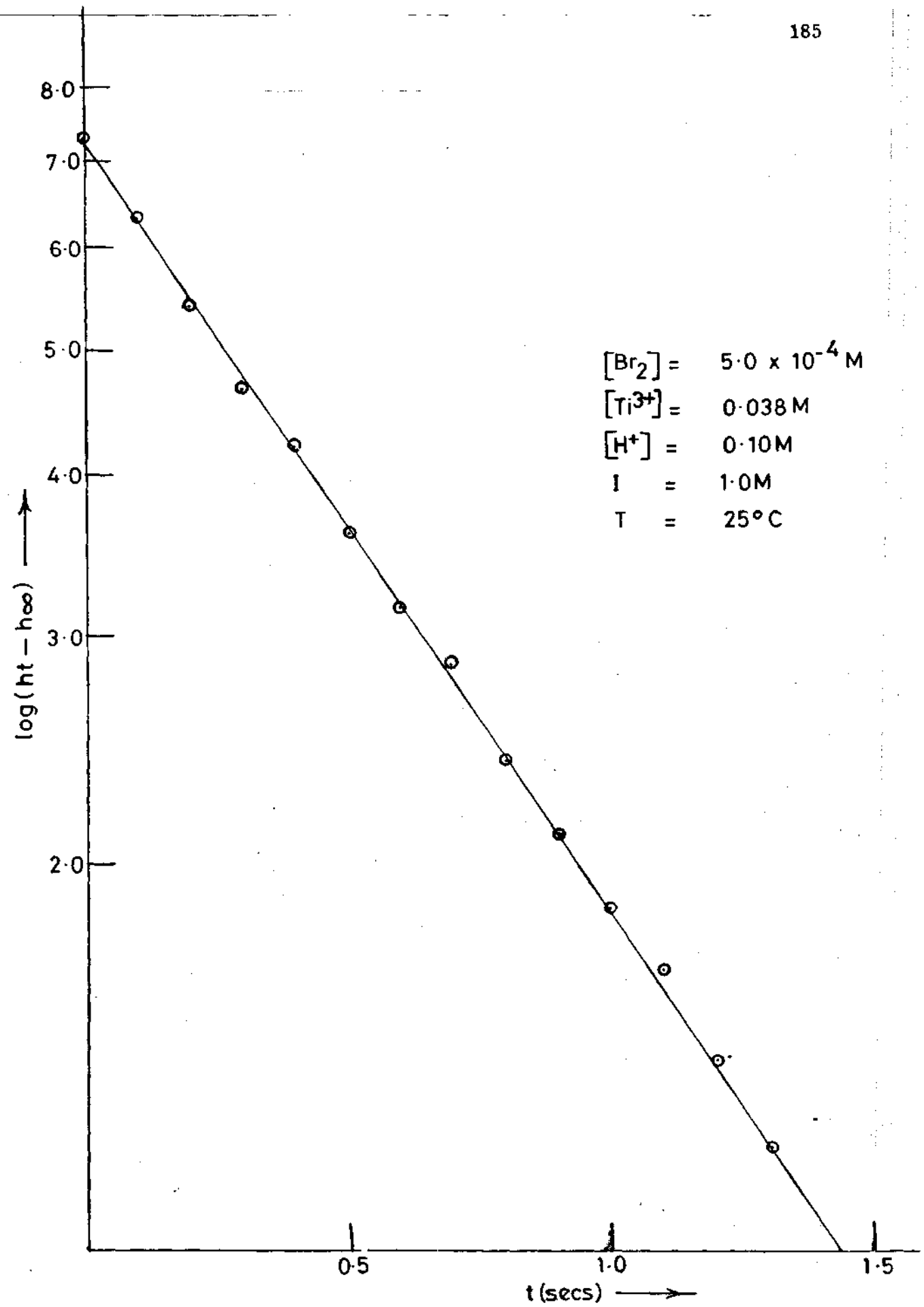


Fig. 2·6 Typical Pseudo-First-Order plot for $Ti^{3+}(aq) - Br_2$ reaction.

computed as k_{obs}/ [Ti(III)] was constant and independent of [Ti(III)] and are presented in Table (2.4).

TABLE 2.3

Second order rate constants for the $Ti(H_2O)_6^{3+}$ + Br_2 reaction

$[Br_2] = 5.0 \times 10^{-4}M$, I = 1.0M, $(CF_3SO_3Li^+)$ $[H^+] = 0.10M$,

T = 2.5 ± 0.1°C, λ = 453nm.

10^3M Ti^{3+}	k_{obs} s^{-1}	$10^{-2}k_oM^{-1}s^{-1}$
19.0	7.6	3.8
25.0	10.2	3.98
38.0	13.2	3.9
37.2	14.5	3.9
55	19.7	3.7

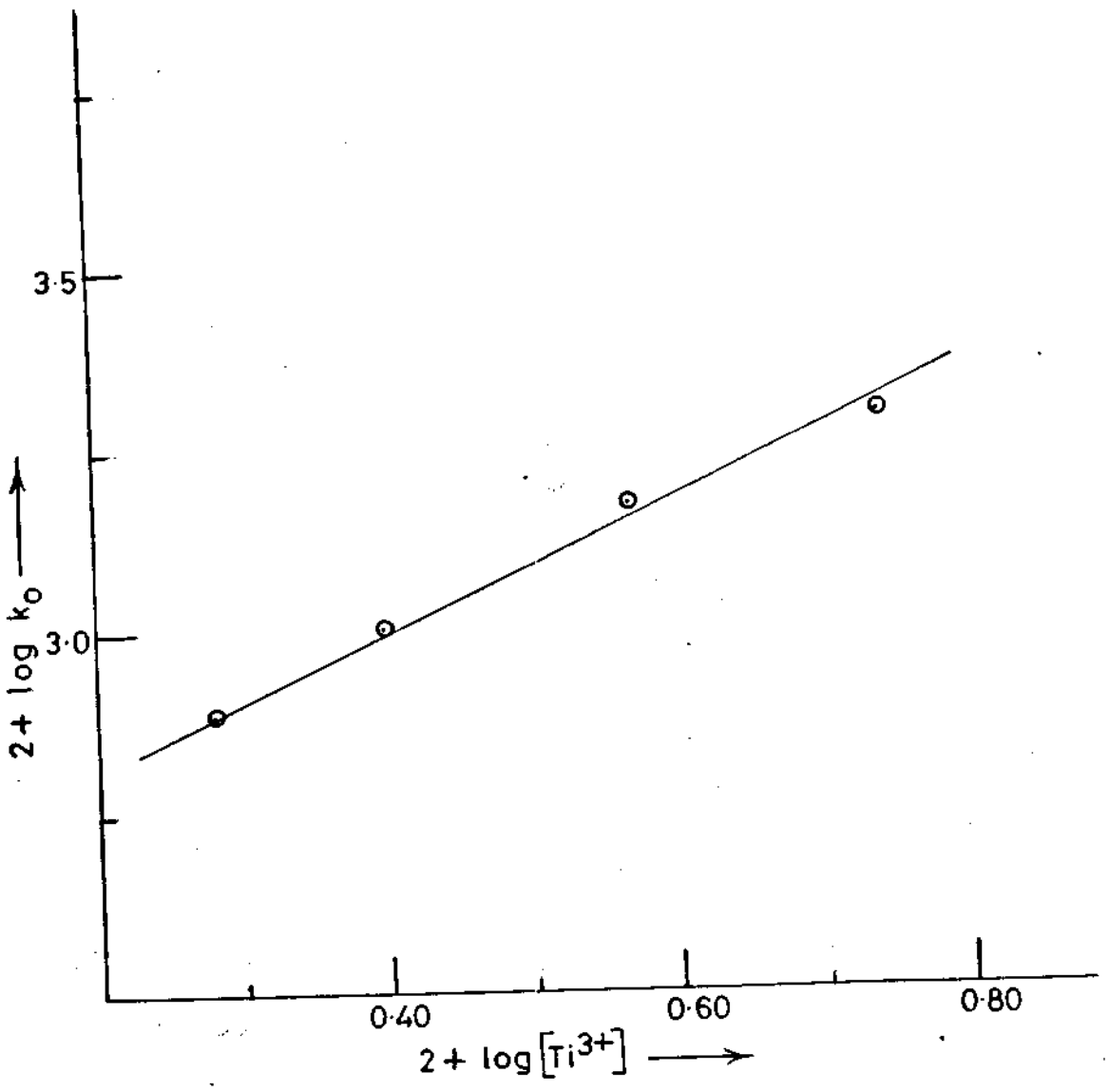


Fig. 2·7 Determination of order for the Ti^{3+} aq – Br_2 system. Plot of $2 + \log k_o$ versus $2 + \log [Ti^{3+}]$

Acid dependence of -the $Ti(H_2O)_6^{3+}$ - Br_2 reaction.

The effect of acid on the rate of the reaction was investigated at 0.1M bromide concentration. The concentrations of titanium(111) and bromine solutions were kept constant for all these runs while the ionic stength was maintained at 0.5M. The second-order rate constants k_o decreases as the acid concentration increases. The results are presented in Table (2.4)

TABLE 2.4

Second-order rate constants for the Ti^{3+}-Br_2 reaction.

$[Br_2] = (5.0 - 8.0) \times 10^{-4}$, $I = 0.5M(CF_3SO_3^-Li^+)$,

$T = 25.0 \pm 0.1M$ $\lambda = 453nm$

10^2M [Ti(111)]	$[H^+]$,mM	$10^{-2}k_o$ M^{-1} s^{-1}
1.1	26	10.8
1.1	36	7.4
1.1	46	6.85
1.1	66	4.8
1.1	86	4.4
1.1	100	3.9
1.1	126	3.4
1.1	134	3.0
1.1	174	2.3
1.1	254	1.9
1.1	274	1.5

When k_o is plotted against $[H^+]^{-1}$ the smooth curve shown in Figure (2.8) is obtained. However a plot of k_o^{-1} versus $[H^+]$ is linear with a finite intercept for the acid range $0.026M \leq [H^+] \leq 0.274M$ investigated. This plot is shown in Figure (2.9). The rate of the reaction can thus be written as:

$$\frac{-d}{dt}[Br_2] = k_o [Ti(III)] [Br_2]_T \qquad ...(2.24)$$

with $k_o^{-1} = e + f[H^+]$.

Least - mean - square analysis of the data for the k_{obs}^{-1} versus $[H^+]$ plot gave

$$e = (1.08 \pm 0.15) \times 10^{-4} MS^{-1}$$

$$f = (2.41 \pm 0.07) \times 10^{-2} S$$

Effect of Chloride on the rate of the reaction.

Keeping [Ti(III)] , $[Br_2]$ and $[H^+]$ constant, the rate of the reaction was measured at different chloride ion concentrations. The results, presented in Table (2.5) shows that the second-order rate constants k_o^{cl} measured, increases with increasing chloride ion concentration.

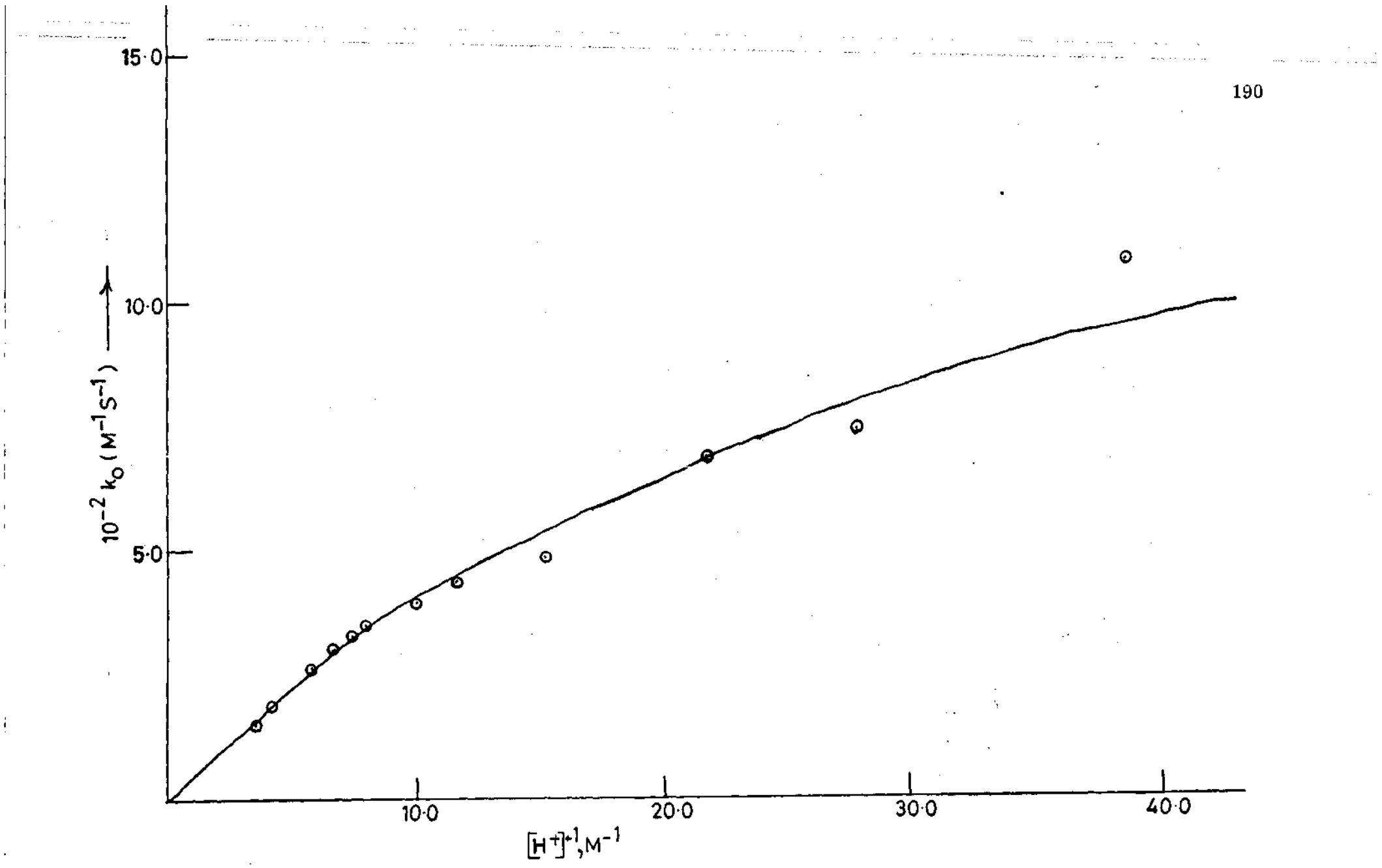


Fig. 2·8 Plot of k_0 versus $[H^+]^{-1}$ for the Ti^3 (aq) – Br_2 reaction.

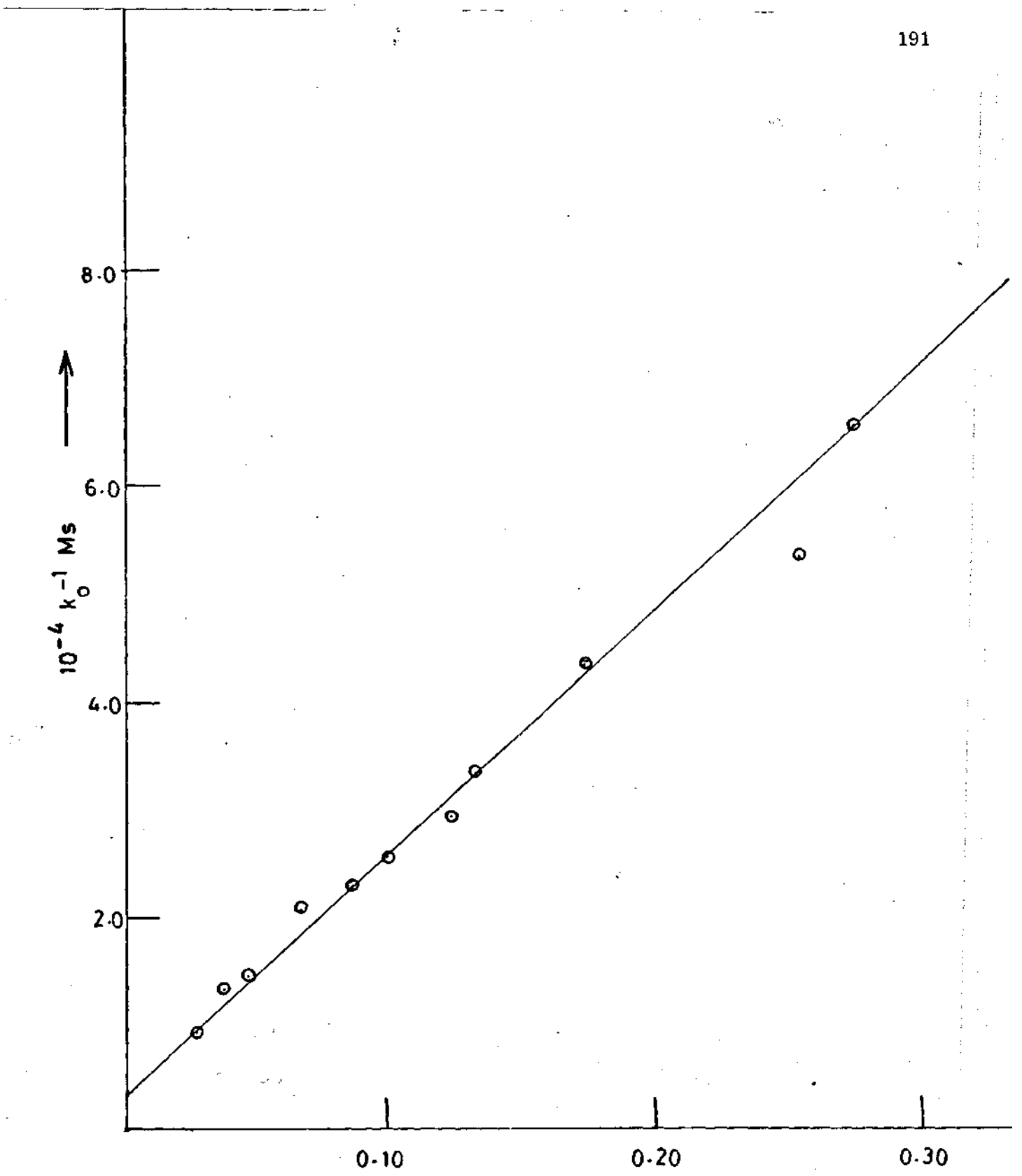


Fig. 2·9

Plot of k_o^{-1} versus $[H^+]$ for the $Ti^{3+}(aq) - Br_2$ system.

TABLE 2.5

Chloride ion dependence of the rate of the reaction of $Ti(H_2O)_6^{3+}$ with bromine.

$[Br_2] = 5.0 \times 10^{-4}M$, $I = 1.0M$ $(CF_3SO_3^-Li^+)$

$T = 2.50 \pm 0.1^oC$, $\lambda = 453nm$

10^2M [Ti(111)]	$[H^+]M$	$10[Cl^-]M$	$10^{-2}k_o^{Cl}M^{-1}S^{-1}$
1.3	0.10	0.1	6.4
1.3	0.10	0.5	7.4
1.3	0.10	1.0	15
1.3	0.10	2.0	25
1.3	0.10	4.0	54
1.3	0.10	5.0	63

A plot of k_o^{Cl} versus $[Cl^-]$, shown in Figure (2.10), is linear with a finite intercept. This implies that the rate equation with respect to chloride ion concentration can be represented by the equation:

$$k_o^{Cl} = c + d\,[Cl^-] \qquad \ldots(2.25)$$

Least-mean square analysis gives,

$c = (3.8 \pm 0.1) \times 10^2 M^{-1}S^{-1}$

$d = (1.00 \pm 0.01) \times 10^4 M^{-2}S^{-1}$.

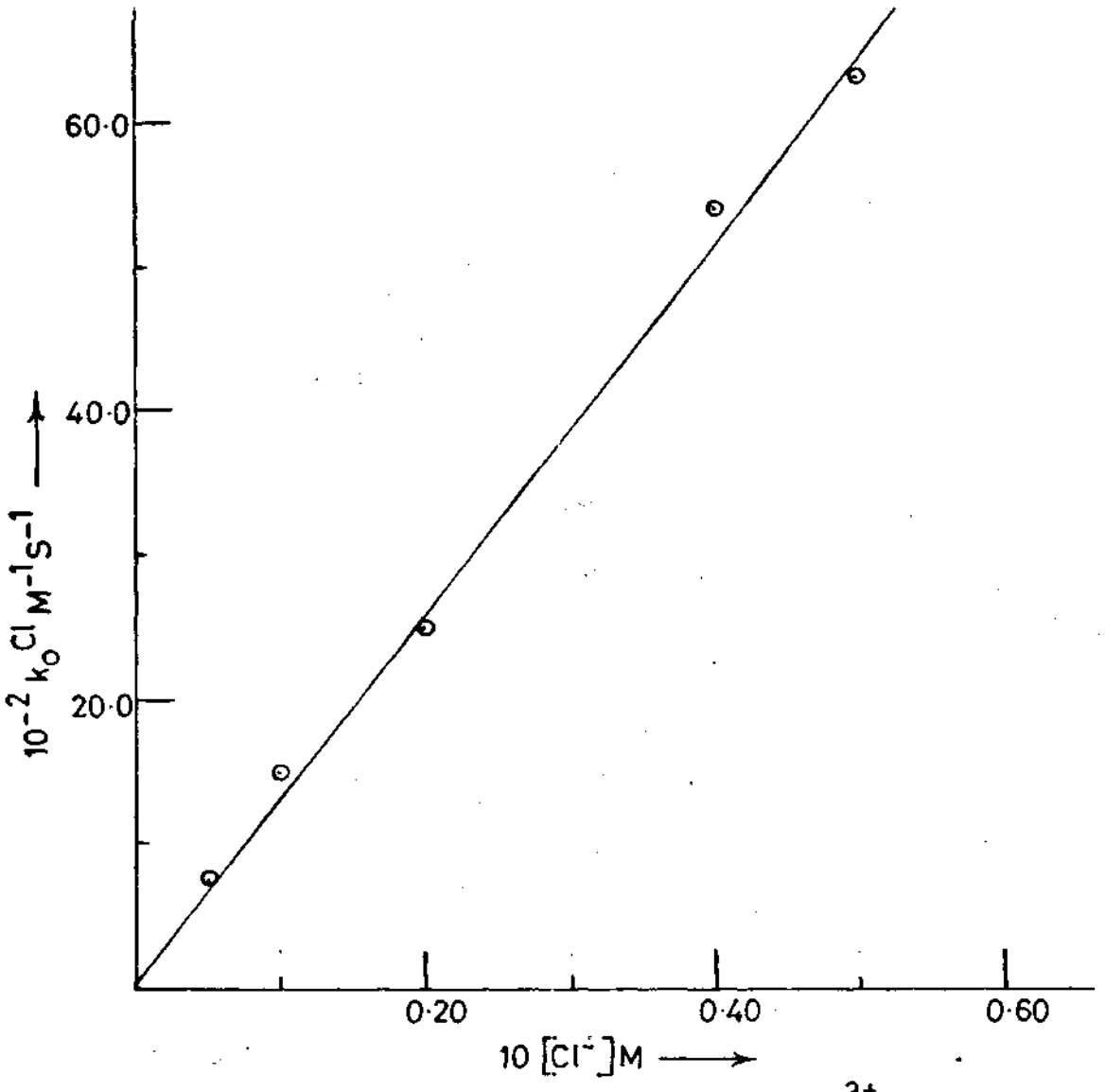


Fig. 2·10 Chloride dependence of the $Ti^{3+}(aq)-Br$ reaction. Plot of k_o^{Cl} versus $[Cl^-]$

Effect of bromide ion on the rate of the reaction of $Ti(H_2O)_6^{3+}$ and bromine.

The effect of bromide ion concentration on the rate of the title reaction was also investigated. The bromide-dependent second-order rate constants, k_o^{Br} are presented in Table (2.6).

TABLE 2.6

Bromide-dependent second-order rate constants for the $Ti(H_2O)_6^{3+}$-Br_2 reaction.

$[Br_2] = 5.0 \times 10^{-4}$ M, I = 0.5M ($CF_3SO_3^-Li^+$)

T = 25.0 ± 0.1°C, λ = 453nm

10^2M [Ti(III)]	$[H^+]$ M	10 $[Br^-]$M	$10^{-2}k_o^{Br}M^{-1}s^{-1}$
1.4	0.10	0.2	3.0
1.4	0.10	0.5	2.3
1.4	0.10	1.0	1.6
1.4	0.10	2.0	1.1
1.4	0.10	4.0	0.8

k_o^{Br} decreases with increasing bromide ion concentration. The equilibrium represented by the equation:

$$Br_2 + Br^- \underset{}{\overset{K_{Br_3^-}}{\rightleftharpoons}} Br_3^- \quad K_{Br_3} = 17M \qquad ...(2.26)$$

is very fast[120] compared with the redox reaction of interest in this work.

The decrease in rate observed with increasing bromide ion concentration therefore suggests that Br_2 and Br_3^- react at different rates. Such rationalization has been made for a lot of other reactions involving halogens.[90,93,103,106]

In the presence of bromide ion therefore, we can propose the following activation paths for the reaction of interest:

$$Ti(III) + Br_2 \xrightarrow{k_1} Ti(IV) + Br_2^- \quad \ldots(2.27)$$

$$Ti(III) + Br_3^- \xrightarrow{k_2} Ti(V) + Br_2^- + Br^- \quad \ldots(2.28)$$

From equation (2.26) it follows that

$$K_{Br_3^-} = \frac{[Br_3^-]}{[Br_2][Br^-]} \quad \ldots.(2.29)$$

$$\text{or } [Br_3^-] = K_{Br_3}[Br_2][Br^-]$$

From equations (2.27) and (2.28), the rate of the reaction can be expressed as:

$$\text{rate} = k_1 [Ti(III)][Br_2] + k_2 [Br_3^-][Ti(III)] \quad \ldots(2.30)$$

Substituting for Br_3^- gives

$$\text{rate} = k_1 [Ti(III)][Br_2] + K_{Br_3} k_2 [Ti(III)][Br_2][Br^-]$$

$$= [Ti(III)][Br_2][k_1 + K_{Br_3} k_2 [Br^-]] \quad \ldots(2.31)$$

But the rate is also given by

$$\text{rate} = k_o [Ti(III)][Br_2]_T$$

where $[Br_2]_T = [Br_2] + [Br_3^-]$

Therefore,

$$\text{rate} = k_o [Ti(III)][Br_2] + [Br_3^-]$$

Substituting for $[Br_3^-]$ gives rate $= k_o [Ti(III)]\{Br_2\} + K_{Br_3}\{Br_2\}\{Br^-\}$

$$\text{or } k_o\{Ti(III)\}\{Br_2\}[1 + K_{Br_3}\{Br^-\}] \quad \ldots(2.32)$$

Comparing equations (2.31) and (2.32) gives:

$$k_o \{1 + K_{Br_3^-} \{Br^-\}\} = \{k_1 + K_{Br_3^-} k_2 \{Br^-\}\} \quad ...(2.33)$$

A plot of the left-handside of equation (2.33) against $\{Br^-\}$should be linear with intercept k_1 and slope $K_{Br_3^-} k_2$. The plot is shown in Figure (2.11). It is linear and the least-mean-square computation of the slope and intercept gave:

$$\text{Intercept} = k_1 = (3.88 \pm 0.04) \times 10^2 M^{-1} S^{-1}$$

$$\text{Slope} = K_{Br_3^-} k_2 = 499.8 M^{-2} s^{-1}$$

and therefore,

$$k_2 = 29{\cdot}4 \pm 1.1 \ M^{-1} S^{-1}$$

<u>Ti^{III}-edta - Bromine reaction</u>.

With the $\{Ti^{III}$-edta$\}$ in excess, this reaction was too fast to be followed on the Durrum-Gibson stopped-flow spectrophotometer at the bromine concentration that would give measurable absorbance changes under pseudo-first-order conditions. It was therefore decided that the rate measurements should be carried out using equivalent concentrations of the oxidant and reductant species i.e.

$$\{Br_2\}_o = \tfrac{1}{2} \{Ti(III)\} \quad ...(2.34)$$

The plots of $\frac{1}{\{Br_2\}}$ versus time were linear to more than 80% of the reaction. A typical plot is shown in Figure (2.12). This confirms that the reaction is first-order in $\{Br_2\}$ and first-order in $\{Ti^{III}$-edta$\}$. This conclusion was further butressed by the constancy of k_o^{edta}, the second-order rate constants at constant pH obtained at different initial concentrations of Ti(III) and Br_2 as shown in Table (2.7).

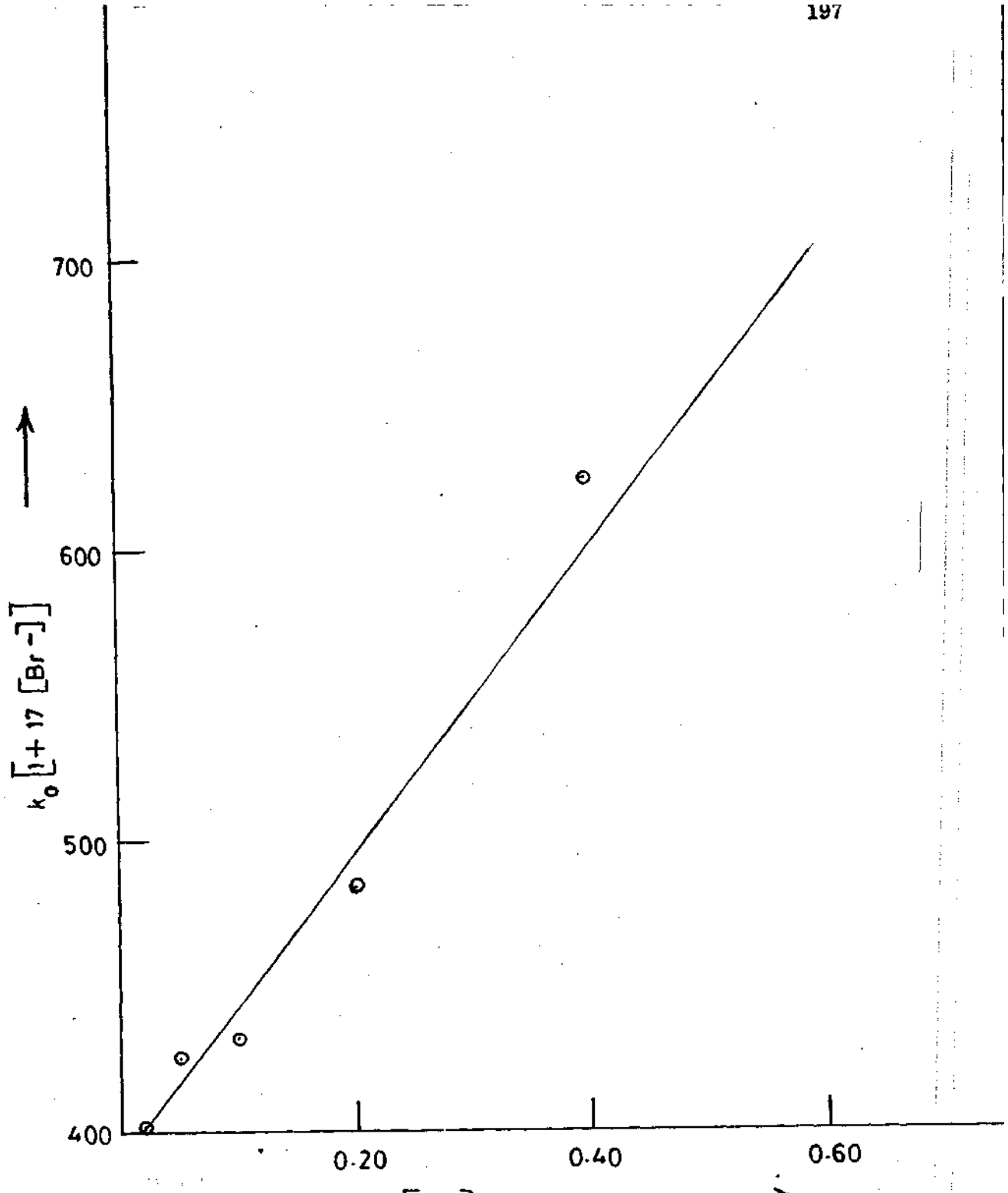


Fig. 2·11

Plot of $k_o\left[1+17\ [Br^-]\right]$ versus $[Br^-]$ for the $Ti^{3+}(aq)$ — Br_2 system

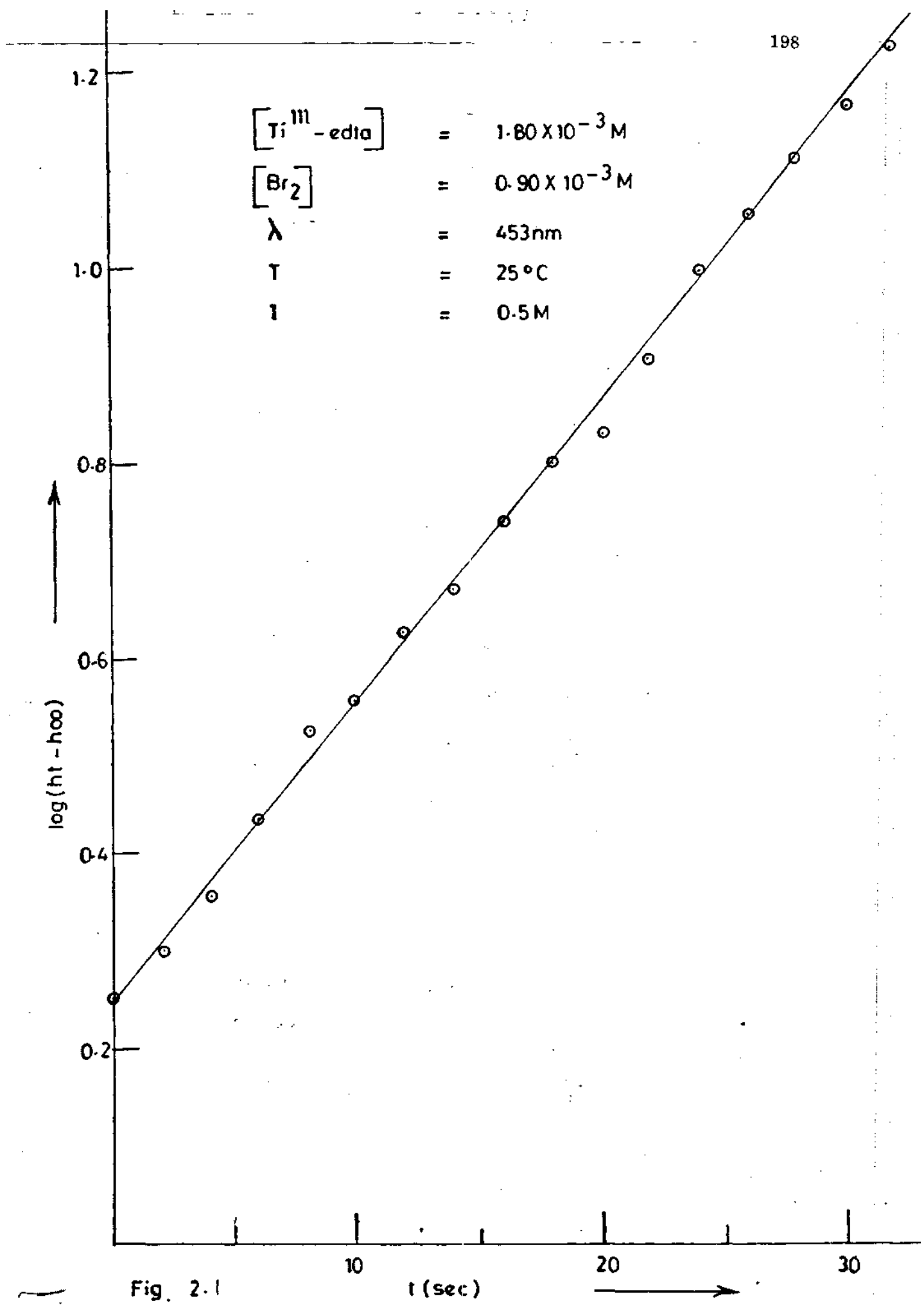


Fig. 2.1

Typical Pseudo-First-Order plot for the Ti^{III} — edta — Br_2 reaction.

TABLE 2.7

Second-order rate constants for the reaction of Ti^{III}-edta with bromine.

I = 1.0M ($CF_3SO_3^-Li^+$ + CH_3COONa)

T = 2.5 ± 0.1°C pH = 1.0

$10^3 M\{Ti^{III}\text{-edta}\}$	$10^3 M.\{Br_2\}$	$10^{-4}\ k_o^{edta}{}_M^{-1}\ ^{-1}$
2.30	1.15	3.5
1.80	0.90	3.5
1.52	0.76	3.6
1.32	0.66	3.5(a)

(a) Average of four rate constants in which the concentration of acetate was varied from 0.05 to 0.40M while ionic strength remained constant at 1.0M. Rate constants obtained were within 5% of each other.

Bromide dependence of the Ti^{III}-edta - Br_2 reaction.

The second-order rate constants were then determined as a function of bromide ion concentrations while keeping $[Ti^{III}\text{-edta}]$ and $[Br_2]$ constant and maintaining a constant pH of 1.0. The second-order rate constants, k_o^{edta}, obtained when $[Br^-]$ was varied from 0.05 to 0.30M are presented in Table (2.8)

k_o^{edta} decreases as $\{Br^-\}$increases.

The dependence of k_o^{edta} on $\{Br^-\}$was also interpreted to mean that Br_2 and Br_3^- react at different rates with the Ti^{III}-edta complex ion. From the intercept of the linear plot (shown in Figure (2.13)) of:

$$k_o^{edta}\left(1 + K_{Br_3}\{Br^-\}\right) \text{ versus } \{Br^-\},$$

k_3 and k_4 were computed as follows:

$k_3 = (3.62 \pm 0.50) \times 10^4\ M^{-1}s^{-1}$

$k_4 = (2.33 \pm 0.07) \times 10^4\ M^{-1}s^{-1}$

(pH = 1.0, I = 1.OM ($CH_3COONa + CF_3SO_3^-Li^+$)

T = 25°C respectively)

k_3 and k_4 are the rate constants for the following reations:

$$Ti^{III}\text{-edta} + Br_2 \xrightarrow{k_3} \text{Products} \qquad ...(2.35)$$

$$Ti^{III}\text{-edta} + Br_3^- \xrightarrow{k_4} \text{Products} \qquad ...(2.36)$$

TABLE 2.8

Bromide dependent second-order rate constants for the Ti^{III}-edta - Bromine reaction.

$\{Ti^{III}\text{-edta}\} = 1.80 \times 10^{-3}M$, $\{Br_2\} = 0.9 \times 10^{-3}M$

I = 1.0M, T = 25°C pH = 1.0M

pH	$\{Br^-\}M$	$10^{-4}\ k_7\ M^{-1}S^{-1}$
1.0	0.05	3.42
1.0	0.10	3.24
1.0	0.15	2.17
1.0	0.20	2.59
1.0	0.30	2.0

pH dependence of the Ti^{III}-edta - Bromine reaction

The pH dependence of the rate of the Ti^{III}-edta-bromine reaction was also investigated in the pH range 1.0 - 6.05.

A constant pH medium was maintained for each run by using formate or acetate buffer as appropriate. Acetate or formate concentration was also varied for each run. The results show that changes in acetate or formate concentrations have no effect on the rate of the reaction. Since changes in $\{Br^-\}$affects the rate of the reactions, the effect of pH variation on rate was investigated at 0.1M bromide concentration for all runs.

The results obtained are presented in Table (2.9).

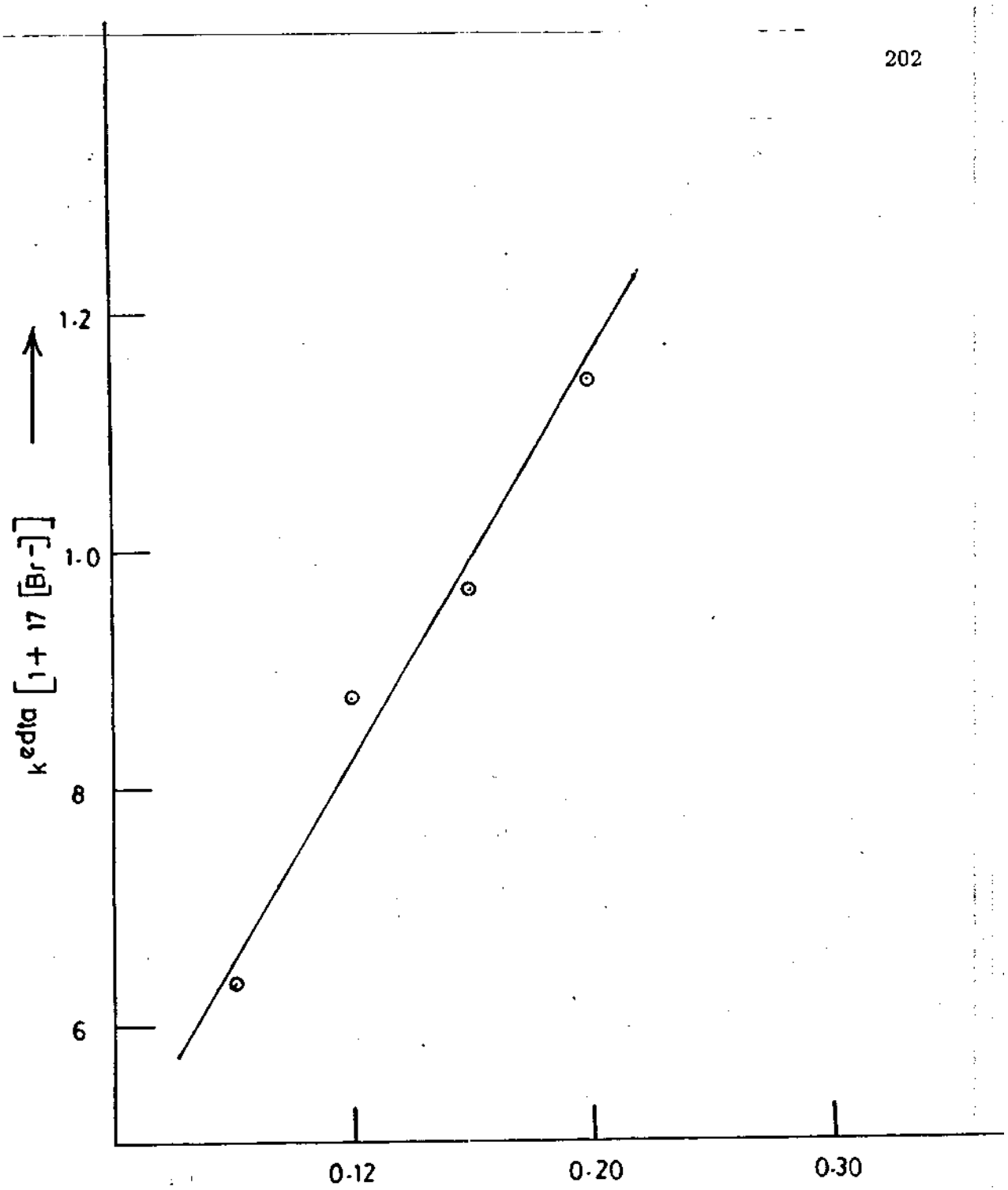


Fig. 2-13

Bro mide dependence of the Ti^{III}–edta – Br_2 reaction.

Plot of $k_o^{edta}\left[1+17\,[Br^-]\right]$ versus $[Br^-]$

TABLE 2.9

pH dependent second-order rate constants of the reaction of Ti^{III}-edta with Bromine.

I = 1.0M (CF_3SO_3-Li^+ + Buffer), T = 25·0 ± 0.1°C.

pH	10^3M {Ti^{III}-edta}	10^3M{Br_2}	{Br^-}M	$10^{-4}K_o^{edta}$	Buffer medium
1.0	2.0	1.0	0.10	2.9	
1.6	1.5	0.75	0.10	2.9	
2.35	1.5	0.75	0.10	3.0	Formate
2.95	1.5	0.75	0.10	2.8	"
3.45	1.5	0.75	0.10	3.5	"
3.65	1.5	0.75	0.10	3.2b	Acetate/ formate
3.85	1.5	0 75	0.10	3.7	"
4.55	1.5	0.75	0.10	4.5	"
5.10	1.5	0.75	0.10	7.8	"
5.43	1.5	0.75	0.10	8.0	"
5.50	1.5	0.80	0.10	13.7	"
5.85	1.5	0.80	0.10	18.0	"
6.05	1.5	0.80	0.10	19.3	"

(b) Average of results obtained from medium containing either acetate or formate. Rate constants obtained using either ion as the buffer medium were within 5% of each other. Hence the rate is insensitive either to whether acetate or formate is the buffer.

Bromine solution was always acidic, containing, bromide ion while the Ti^{111}-edta solution contained the acetate or formate. This arrangement surpresses the formation of HOBr before the reactants were mixed. The pH reported was therefore for a mixture of equal volumes of the reactant solutions. These steps are necessary to avoid complications that could arise from hydrolysis of Br_2 to produce HOBr according to the equation:

$$Br_2 + H_2O \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} HOBr + Br \qquad \ldots.(2.37)$$

k_5 has been reported[120] as $110M^{-1}s^{-1}$ which is two orders of magnitude less than the rate of the reaction of interest. The interference of HOBr with the reaction being investigated, if any, is thus not significant on the time-scale of the redox reaction. It is therefore safe to assume that the observed effect of pH on the rate of the reaction cannot be attributed to the changing concentration of HOBr as the pH of the reaction medium changes.

The obtained data for the Ti^{111}-edta + Br_2 reaction was fitted into an equation of the form:

$$k_o^{edta} = \frac{k_7 + k_7 K_1 \left[H^+\right]^{-1} + k_8 K_1 K_2 \left[H^+\right]^{-2}}{1 + K_1 \left[H^+\right] + K_1 K_2 \left[H^+\right]^{-2}} \qquad \ldots(2.38)$$

using non-linear least-mean-square computer analysis with $(1/k_o^{edta})^2$ weighting and the values of K_1 and K_2 fixed as reported by Podlahova and Podlaha[63] i.e.

$$pK_1 = 2.02 \pm 0.01$$

$$pK_2 = 8.64 \pm 0.02.$$

in their titration study of Ti^{111}-edta solutions.

The values of k_7 and k_8 so determined are as follows:

$$k_7 = (3.16 \pm 0.42) \times 10^4 M^{-1}s^{-1}$$

$$k_8 = (8.31 \pm 0.2) \times 10^7 M^{-1}s^{-1}$$

From the computed values of k_7 and k_8 and the values of K_1 and K_2 as reported by Podlahova and Podlaha the values of k_o^{edta} was estimated for the various pH values investigated and are compared with k_o^{edta}(expt) as presented in Table (2.10) The agreement between the calculated and observed k_o^{edta} is evidenced by the correlation coefficient of 0.995 obtained.

TABLE 2.10

Observed and estimated pH-dependent second-order rate constants for the oxidation of Ti^{111}-edta by aqueous solution of bromine.

pH	$10^{-4}k_o^{edta}$(expt) $M^{-1}s^{-1}$	$10^{-4}k_o^{edta}$(calc) $M^{-1}s^{-1}$
1	2.9	2.8
1.6	2.9	2.9
2.35	3.0	3.18
2.95	2.8	3.3
3.45	3.5	3.4
3.65	3.2	3.43
3.85	3.7	3.5
4.55	4.5	4.02
5.1	7.8	5.7
5.43	8.0	8.4
5.5	13.7	9.2
5.85	18	16.5
6.05	19.3	24.1

A plot of k_o^{edta}(expt) and k_o^{edta}(calc) versus pH respectively is also presented in Figure (2.14).

The pH dependent second-order rate constants for the reaction of Ti^{III}-edta with Br_2 was also fitted by rearranging equation (2.38) into the form:

$$k_o^{edta}\left[1 + K_1[H^+] + K_1K_2[H^+]^{-2} - k_7\right)[H^+] - k_7K_1$$

$$= k_8K_1K_2[H^+] \qquad \ldots(2.38b)$$

A plot of the left-hand-side of the above equation against $K_1K_2[H^+]$ was linear with slope $k_8 = (8.12\pm0.34) \times 10^7 M^{-1}s^{-1}$ as shown in Figure (2.15).

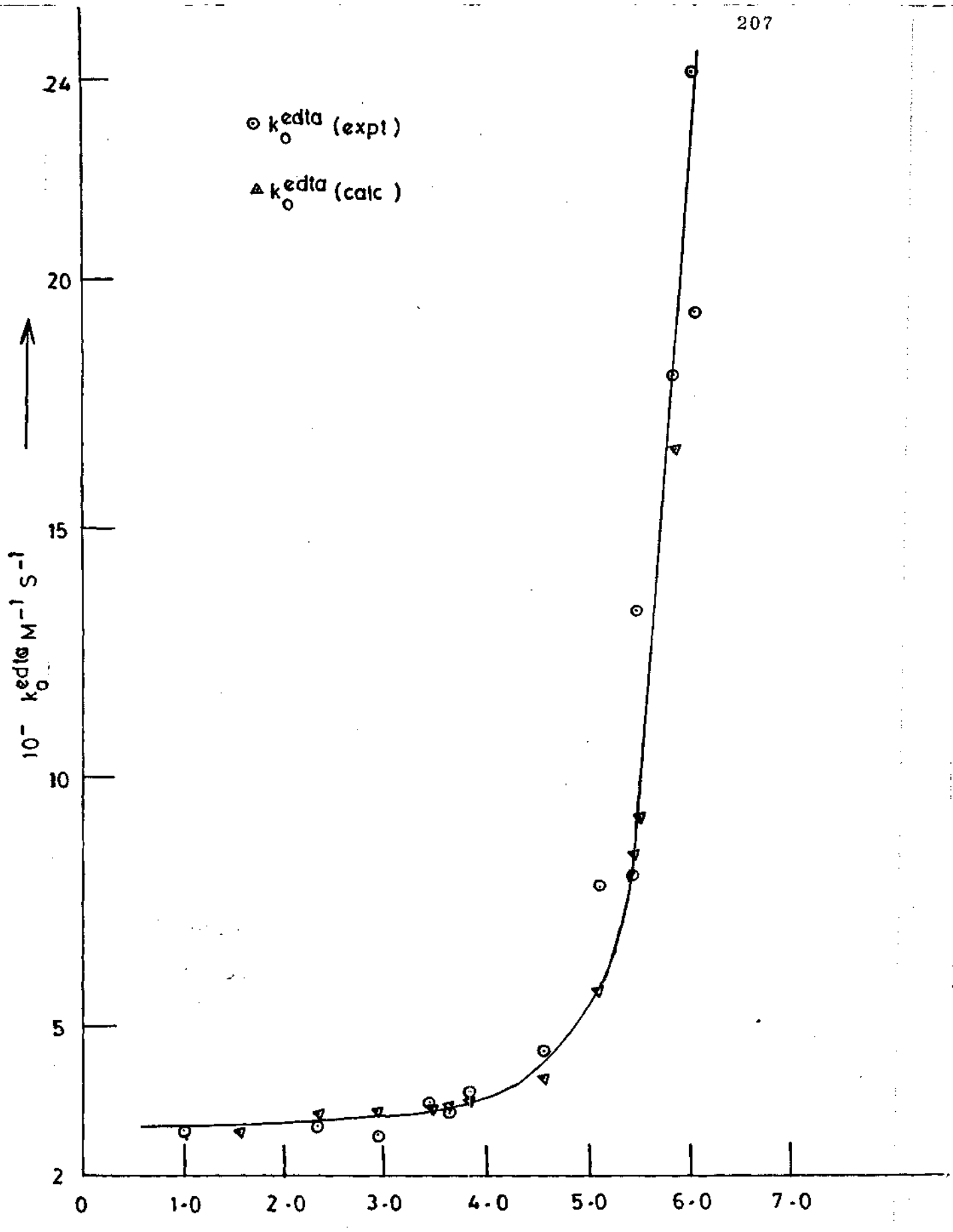


Fig. 2-14

Plot of k_o^{edta} (expt) and k_o^{edta} (calc) versus PH for the Ti^{III} – edta – Br_2 system.

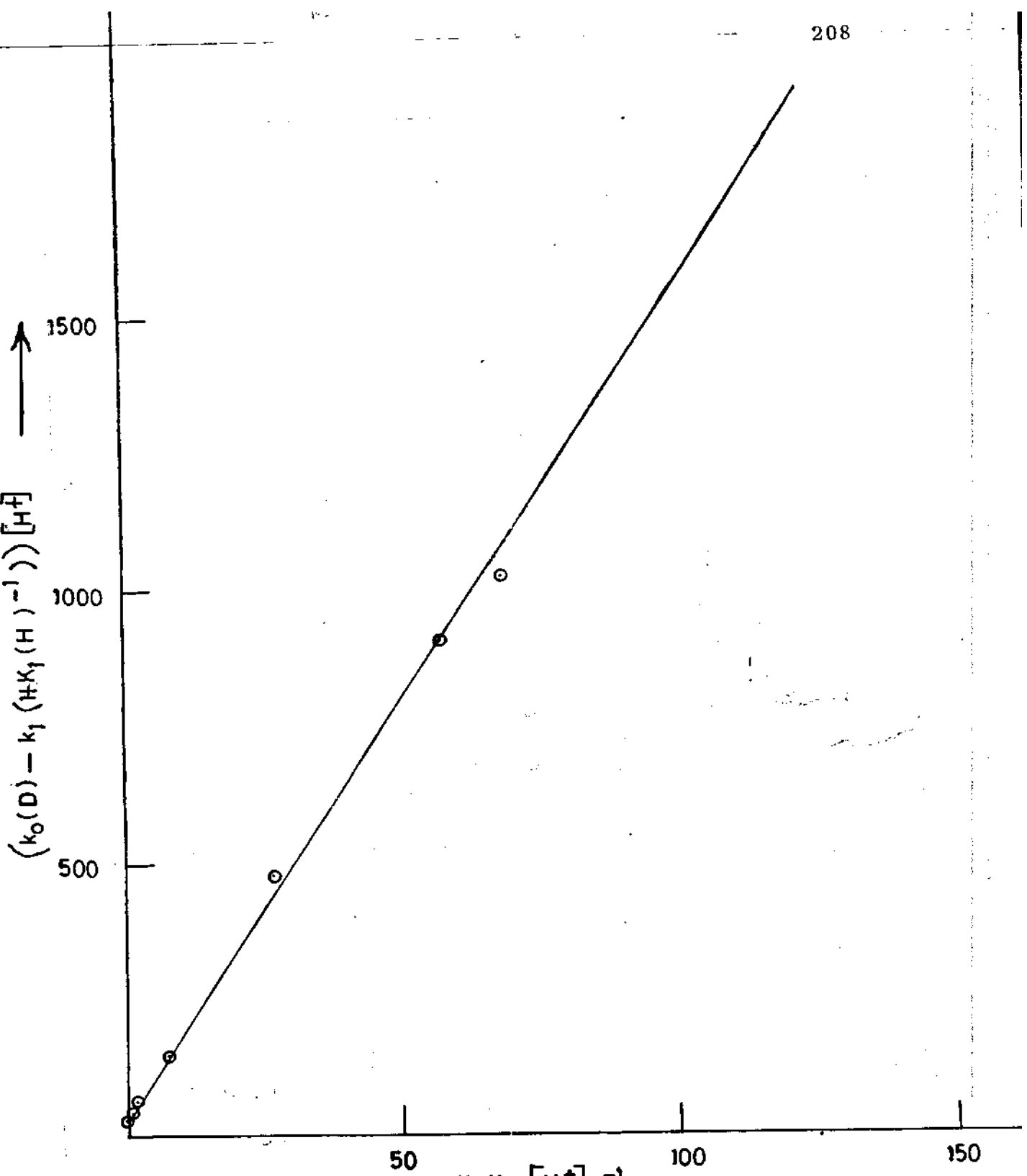


Fig. 2.15

Plot of $\left(k_o^{edta}\left[1+K_1[H^+]^{-1}+K_1K_2[H^+]^{-2}\right]-k_1(1+K_1[H^+]^{-1})\right)[H^+]$ versus $K_1K_2[H^+]^{-1}$ for the Ti^{III}-edta —Br_2 system.

OXIDATION OF AQUOTITANIUM(111) ION BY AQUEOUS SOLUTION OF IODINE.

Determination of the order of the reaction.

The plot of log (A_t - A_∞) versus time (A_t and A_∞ being absorbances of iodine at time t and the end of the reaction respectively) were linear for more than 90% of the reaction. A typical plot is presented in Figure (2.16).

From the slope of each of these linear plots, the pseudo-first-order rate constants, k_{obs} was determined for different initial concentrations of Titanium(111). The results are presented in Table (2.11)

TABLE 2.11

$\Sigma [I_2] = (1.0 - 2.5) \times 10^{-4}$M, $[I^-] = 4.0 \times 10^{-3}$M

$[H^+] = 1.0$M, $I = 1.0$M

$10^3 [Ti^{3+}]_o$, M	$10^2 k_{obs}$ s^{-1}	k_o M^{-1} s^{-1}
3.15	0.33	1.04
15.8	1.72	1.09
31.5	3.52	1.12
47.3	4.93	1.04
63.1	6.81	1.08

A plot of log k_{obs} versus log [Ti(111)] was linear (Figure 2.17) and least-mean-square analysis gave the slope as 1.01 ±0.04. The linearity of the pseudo-first-order plot and the slope of unity obtained in the latter plot confirm that this reaction, under the specified conditions is strictly first order in $[Ti^{3+}]$ and first-order in $[I_2]$. This thus implies that with the iodide ion and hydrogen ion concentrations kept constant, the rate of the reaction

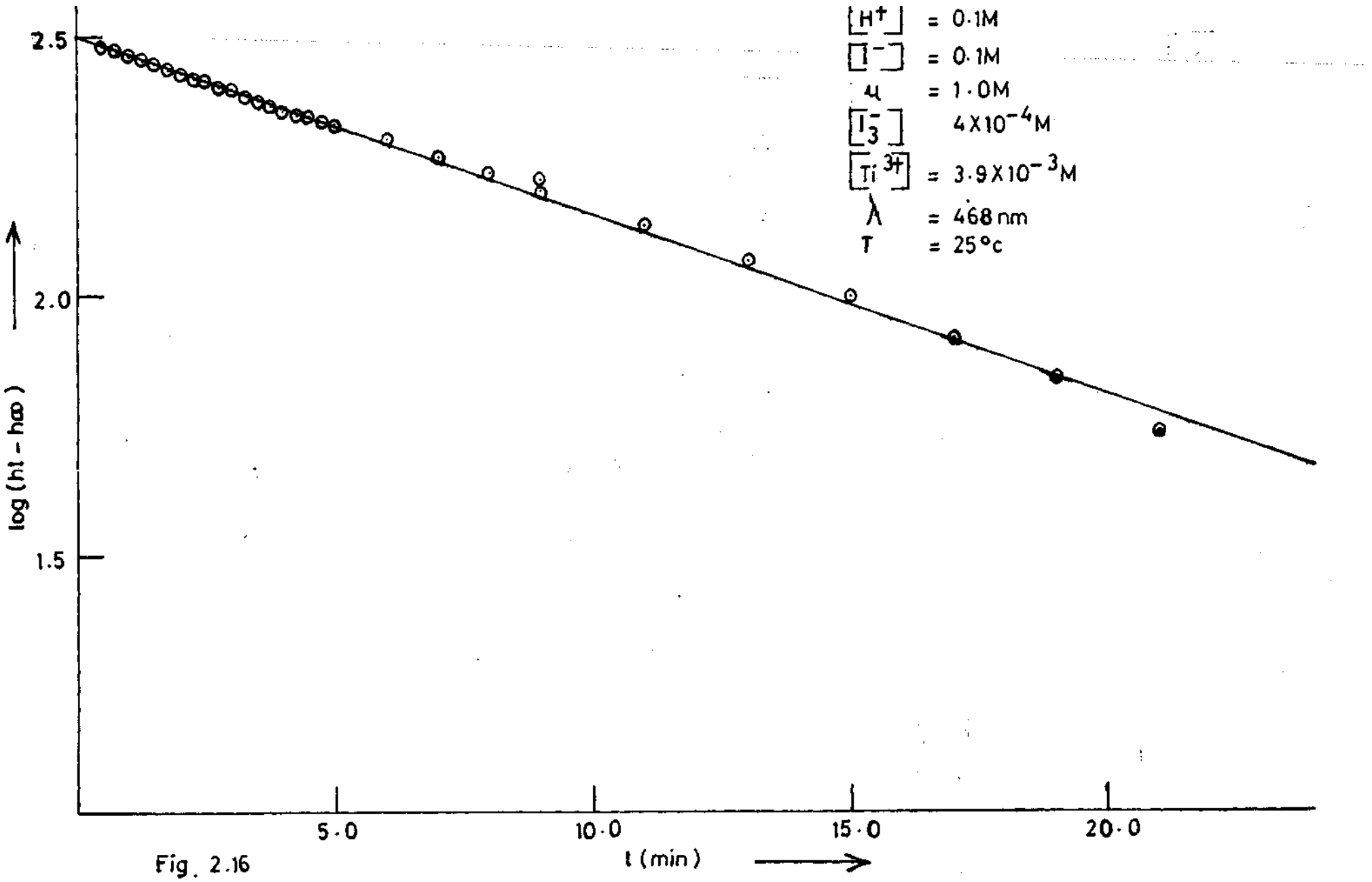


Fig. 2.16

Typical Pseudo-First-Order Plot for the $Ti^{3+}aq - I_2$ system

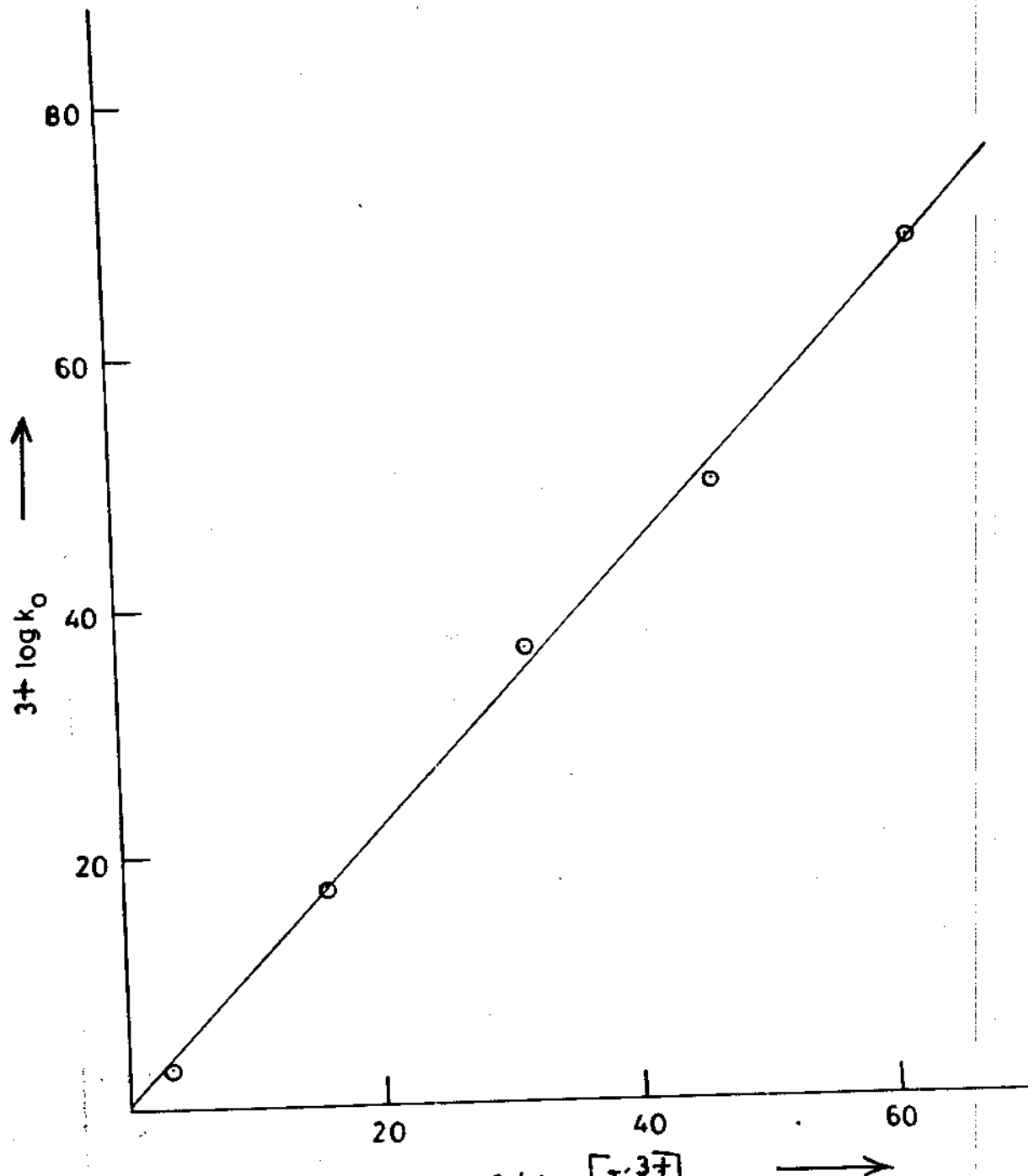


Fig. 2.17

Determination of the Order of the $Ti^{3+}(aq) + I_2$ reaction.

Plot of log k_o versus log $[Ti^{3+}]$

can be written as:

$$-\tfrac{1}{2}\frac{d}{dt}[Ti(III)] = \frac{d[I_2]}{dt} = k_o[Ti(III)][I_2]_T \quad ...(2.39)$$

where $k_o = k_{obs}/[Ti(III)]$ and k_o is the second-order rate constant.

Effect of Iodide at different acid concentrations on the $Ti^{3+}(aq) + I_2$ reaction.

In a solution containing I_2 and I^-, the following very fast equilibrium is set up[121]

$$I_2 + I^- \underset{}{\overset{K_{I_3^-}}{\rightleftharpoons}} I_3^- \quad K_{I_3^-} = 748M^{-1} \quad ....(2.40)$$

The results of previous investigations show that the rates of reduction of I_2 and I_3^- by the same reductant are not the same. Therefore, in order to resolve k into its component rate constants (i.e. k_{I_2} and $k_{I_3^-}$, rate constants (i.e. k_{I_2} and k_{I_3}, rate constants for the iodine and triiodide respectively) the following activation paths were assumed:

$$Ti(III) + I_2 \xrightarrow{k_{I_2}} \text{(activated complex)} \quad ...(2.41)$$

$$Ti(III) + I_3^- \xrightarrow{k_{I_3^-}} \text{(activated complex)} \quad ...(2.42)$$

As in the $Ti^{3+}(aq)$ - Br system, from equation (2.40), (2.41) and (2.42) equation (2.43) can be deduced:

$$k_o(1 + K_{I_3^-}[I^-]) = k_{I_2} + k_{I_3^-} K_{I_3^-}[I^-] \quad ...(2.43)$$

A plot of the left handside of equation (2.43) versus $[I^-]$ should be linear with an intercept k_{I_2} and Slope $k_{I_3} K_{I_3^-}$. Thus k_o was determined at different iodide concentrations, varying from 0.004 to 0.10M at constant acid concentration. This was repeated for 15 other acid concentrations in the acid range $0.0036 \leq [H^+] \leq 0.20M$

The results obtained are presented in Table (2.12).

TABLE 2.12

Effect of iodide at different acid concentrations on $Ti^{3+}aq + I_2$ reaction.

$[Ti(III)] = (2.0 - 200.0) \times 10^{-3}M$, $[I_2]_T = (1.0\text{-}4.0) \times 10^{-4}M$

$I = 1.0M(LiCl)$ $T = (25.0 \pm 0.1)^{o}C.$

(a) $[H^+] = 3.6 \times 10^{-3}M$

$[I^-]$, M	k_o	$k_o (1 + 748 [I^-])$
0.01	27.5	236
0.04	12.3	380.3
0.07	10.1	536
0.10	9.1	688

(b) $[H^+] = 5.4 \times 10^{-3}M$

$[I^-]$, M	k_o	$k_o (1 + 748 [I^-])$
0.01	23.7	201
0.04	11.5	356
0.07	9.4	502
0.10	8.6	651

(c) $[H^+] = 7.2 \times 10^{-3}M$

$[I^-]$, M	k_o	$k_o (1 + 748 [I^-])$
0.01	23.3	197.6
0.04	7.8	241.2
0.07	6.8	363.3
0.10	5	379

(d) $[H^+] = 9.0 \times 10^{-3}M$

$[I^-]$,M	$k_o M^{-1} s^{-1}$	$k_o (1 + 748 [I^-])$
0.01	17.9	152
0.04	6.8	210
0.07	4.63	247
0.10	3.97	300

(e) $[H^+] = 10.8 \times 10^{-3}M$

$[I^-]$,M	$k_o M^{-1} s^{-1}$	$k_o (1 + 748 [I^-])$
0.01	15.5	131
0.04	5.7	176
0.07	4.54	242
0.10	3.8	283

(f) $[H^+] = 14.4 \times 10^{-3}M$

$[I^-]$,M	$k_o M^{-1} s^{-1}$	$k_o (1 + 748 [I^-])$
0.01	11.5	97.5
0.04	4.2	130
0.07	2.87	155
0.10	2.43	184

(g) $[H^+] = 15 \times 10^{-3}M$

$[I^-]$,M	$k_o M^{-1} s^{-1}$	$k_o (1 + 748 [I^-])$
0.01	10.55	89.5
0.04	3.91	120.9
0.07	2.98	159
0.10	2.18	165.5

(h) $[H^+] = 15.8 \times 10^{-3}M$

$[I^-]M$	$k_o M^{-1}s^{-1}$	$k_o (1 + 748 [I^-])$
0.008	8.82	61.6
0.02	4.57	72.9
0.04	3.13	96.8
0.08	2.06	125.3
0.10	1.94	156.6
0.15	1.73	195.8

(i) $[H^+] = 26.4 \times 10^{-3}M$

$[I^-]$,M	$k_o M^{-1}s^{-1}$	$k_o (1 + 748 [I^-])$
0.008	7.85	54.52
0.02	4.0	63.8
0.04	2.32	71.7
0.08	1.46	87.4
0.10	1.35	102.3
0.15	1.19	134.7

(j) $[H^+] = 30.0 \times 10^{-3}M$

$[I^-]$,M	$k_o M^{-1}s^{-1}$	$k_o (1 + 748 \cdot [I^-])$
0.01	4.42	37.5
0.03	2.29	53.7
0.05	1.98	76.4
0.08	1.30	79.1
0.10	1.26	95.5

(k) $[H^+]$ = 50.0×10^{-3}M.

$[I^-]$,M	$k_o M^{-I} s^{-1}$	$k_o(1 + 748\,[I^-])$
0.01	2.28	19.3
0.03	1.42	33.3
0.05	0.98	59.9
0.08	0.74	45.02
0.10	0.71	53.8

(l) $[H^+]$ = 60.0×10^{-3}M

$[I^-]$M	$k_o M^{-1} s^{-1}$	$k_o(1 + 748\,[I^+])$
0.01	3.59	30.4
0.04	1.34	41.6
0.07	0.98	52.3
0.10	0.76	57.6

(m) $[H^+]$ = 80×10^{-3}M

$[I^-]$,M	$k_o M^{-1} s^{-1}$	$k_o(1 + 748\,[I^-])$
0.01	3.05	25.9
0.04	1.06	32.9
0.07	0.63	36.3
0.10	0.53	40.3

(n) $[H^+]$ = 100×10^{-3}M

$[I^-]$ M	$k_o M^{-1} s^{-1}$	$k_o(1 + 748\,[I^-])$
0.01	2.05	17.4
0.04	0.69	21.3
0.07	0.5	26.7
0.10	0.36	27.3

$[H^+] = 150 \times 10^{-3}M$

$[I^-]$, M	$k\ M^{-1}s^{-1}$	$k(1 + 748[I^-])$
0.01	1.14	9.7
0.04	0.48	14.8
0.07	0.35	18.9
0.10	0.3	22.7

$[H^+] = 200.0 \times 10^{-3}M$

$[I^-]$, M	$k\ M^{-1}s^{-1}$	$k(1 + 748[I^-])$
0.01	1.05	8.9
0.04	0.43	13.3
0.07	0.3	16
0.10	0.26	19.7

For each acid concentration investigated k_o decreases as $[I^-]$ increases, implying that I_2 reacts faster than I_3^-. The plot of k_o $1 + 748[I^-]$ versus $[I^-]$ in linear for all the acid concentrations investigated. Three such plots for $[H^+] = 0.009M$, 0.0144M and 0.08M respectively are presented in Figure (2.18) From the least-mean-square computation of such plots, k_{I_2} and $k_{I_3^-}$ were determined from the slopes and intercepts of such plots for the 16 different acid concentrations. The results are presented in Table (2.13)

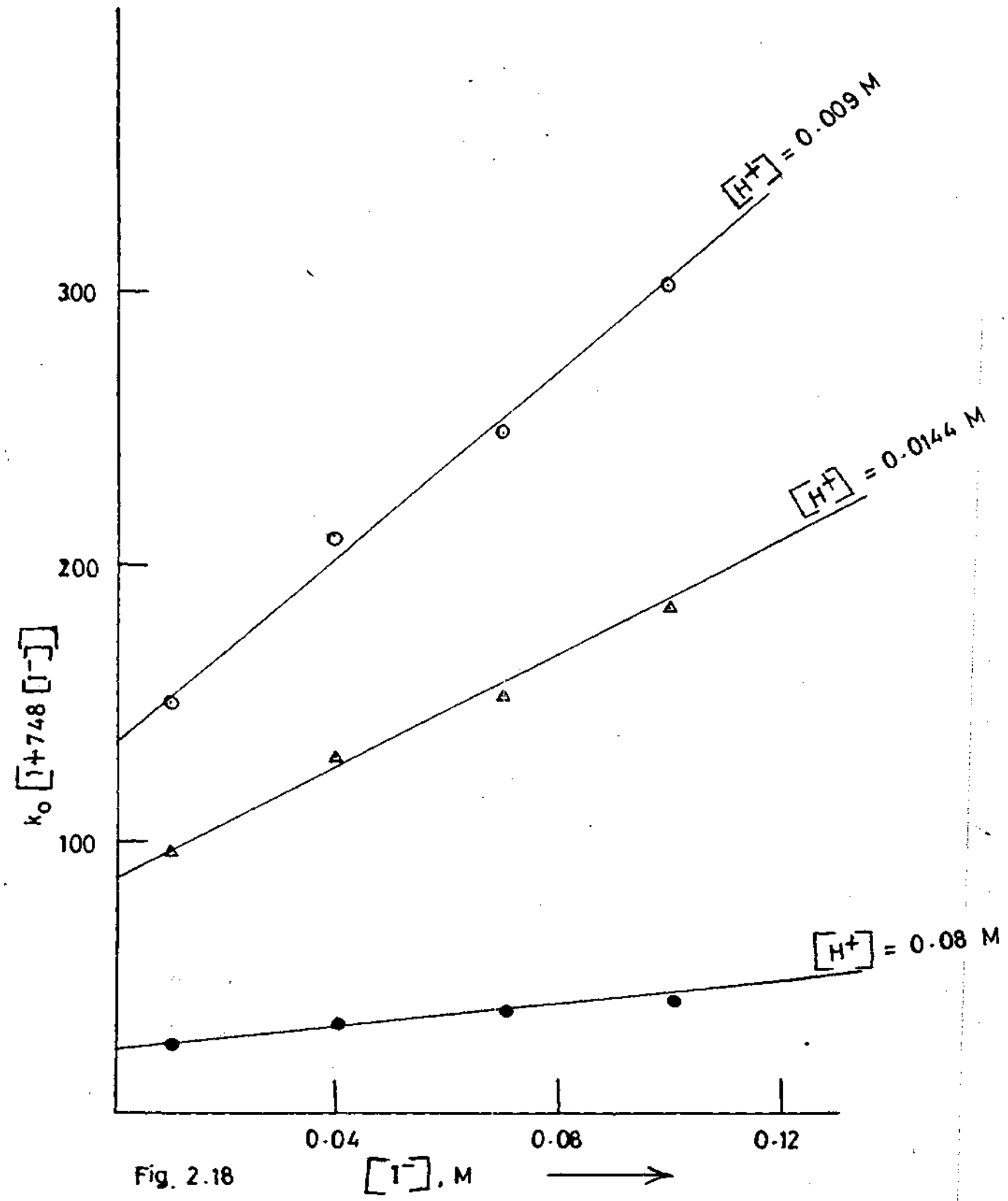


Fig. 2.18

Effect of Iodide at different acid concentrations on the Ti^{3+} aq + I_2 reaction shown by a plot of $k_o(1 + k_{I_3^-}[I^-])$ vs $[I^-]$

Table 2.13

Rate constants for Ti(III) + I_2, I_3^- reactions.

$[H^+]$, mM	$10^{-2}k_{I_2}$ $M^{-1}s^{-1}$	k_{I_3} $M^{-1}s^{-1}$
3.6	1.81	6.8
5.4	1.53	6.7
7.2	1.42	5.0
9.0	1.39	2.2
10.8	1.12	2.4
14.4	0.89	1.3
15.0	0.85	1.2
15.8	0.57	1.4
26.4	0.52	0.7
30.0	0.34	0.67
50.0	0.32	0.46
60.0	0.29	0.39
80.0	0.21	0.23
100.0	0.81	0.21
150.0	0.01	0.14
200.0	0.084	0.12

The data presented in Table (2.13) show that both k_{I_2} increases as $[H^+]$ decreases. k_{I_2} and $k_{I_3^-}$ were plotted against $[H^+]^{-1}$ as shown in Figure (2.19).

These plots are non-linear. However, the plot of $k_{I_2}^{-1}$ and $k_{I_3^-}^{-1}$ against $[H^+]$ was linear with a finite intercept as shown in Figure (2.20) Hence the rate constants vary with $[H^+]$ according to equations (2.44) and (2.45) respectively.

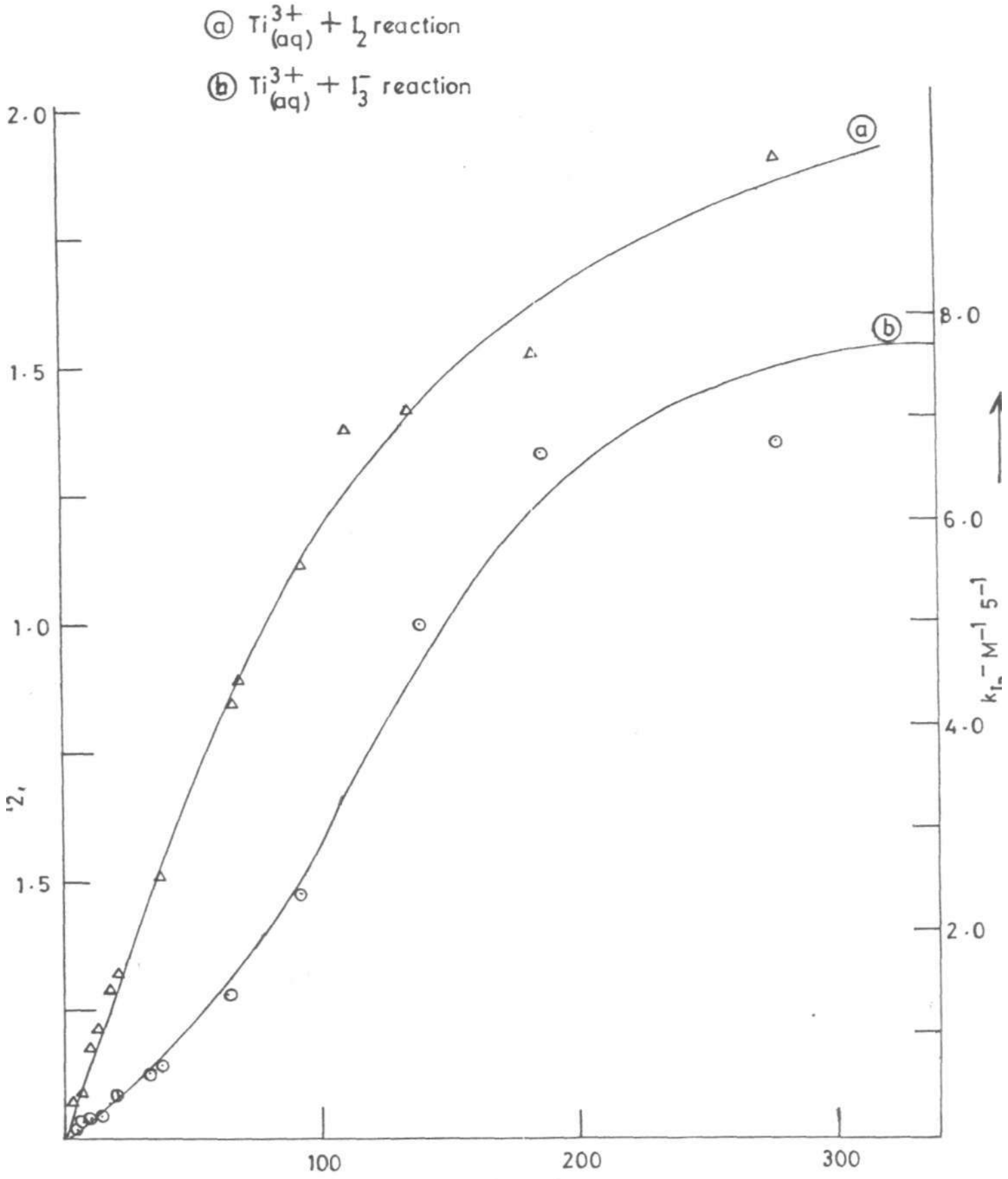


Fig. 2.19

Acid Dependence of the $Ti^{3+} + I_2$, I_3^- reactions

Plot of k versus $[H^+]^{-1}$

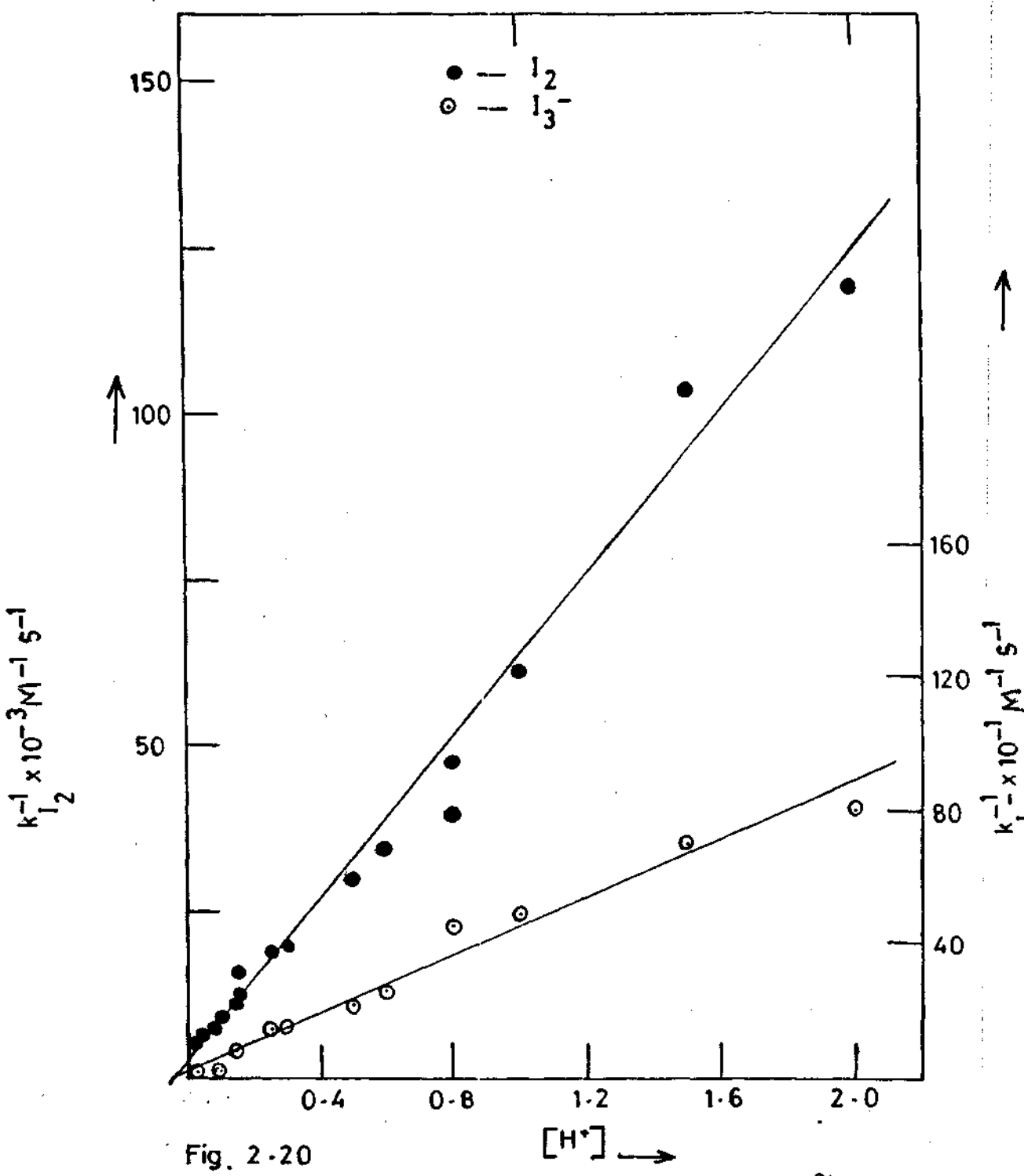


Fig. 2·20

Effect of acid on the rate constants for the $Ti^{3+}(aq) + I_2\ I_3^-$ reactions shown by the plot of $k^{-1}_{I_2}$ or $k^{-1}_{I_3^-}$ vs $[H^+]$

$$k_{I_2} = \frac{1}{a_1 + b_1 [H^+]} \qquad \ldots(2.44)$$

$$k_{I_3^-} = \frac{1}{a_2 + b_2 [H^+]} \qquad \ldots(2.45)$$

Least mean square analysis of the values for the plots gave values of a and b as

$a_1 = (1.90 \pm 0.09) \times 10^{-3}$ Ms

$b_1 = (6.24 \pm 0.01) \times 10^{-}$ s

$a_2 = (1.46 \pm 0.02)$ Ms

$b_2 = (4.38 \pm 4.8)$ s

The rate equation for the title reaction under our experimental conditions can now be written as;

$$\frac{-d}{dt}[I_2]_T = -\tfrac{1}{2}\frac{d}{dt}[Ti(III)] = \frac{[Ti(III)][I_2]}{a_1 + b_1[H^+]} + \frac{[Ti(III)][I_3^-]}{a_2 + b_2[H^+]} \qquad \ldots(2.46)$$

Chloride dependence of $Ti^{3+}(aq) + I_2$ reaction.

In order to determine the effect of added chloride ion on the rate of the title reaction, the second-order rate constant at different $[Cl^-]$'s were measured while maintaining a constant acid concentration and ionic strength. The results are presented in Table (2.14).

TABLE 2.14

$[H^+]$ = 0.10M, I = 1.0M($CF_3SO_3^-Li^+$)

$[I_2]$= 1.0 x 10^{-4}M, $[I^-]$ = 0.1M

10^3 $[Ti^{3+}]$ M	$[Cl^-]$, M	k_o^{Cl} $M^{-1}s^{-1}$
6.3	0.2	1.18
6.3	0.4	1.04
6.3	0.6	1.11
6.3	1.0	1.09

The values of k_o^{Cl} obtained are within 5% of each other and show no systematic variation with increasing chloride ion concentration. The conclusion can therefore be reached as in many other Ti(111) reactions[25-27] that chloride has no effect on the rate of the Ti^{3+}(aq) + I_2 reaction and that the mixed trihalide ion I_2Cl^- if formed reacts at the same rate with Ti^{3+}aq as molecular iodine.

Ti^{111}-edta - Iodine reaction.

The order of this reaction was also shown to be first-order in [Ti(111)] and also first order in $[I_2]_T$. The second-order rate constant was then determined as a function of pH. As in the reaction of Ti^{111}-edta with bromine, the dependence of the rate on pH is biphasic. k_o^{edta} increases as pH increases above pH = 3. but it is independent of pH for pH $\lesssim$ 3. The result of the k_o^{edta} variation with pH are presented in Table (2.15)

The data obtained was analysed as reported under the Ti^{111}-edta -Br_2 reaction and the values of k_{10} and k_{11} obtained are as follows:

$$k_{10} = (3.13 \pm 0.32) \times 10^3 \ M^{-1}s^{-1}$$

$$k_{11} = (2.33 \pm 0.45) \times 10^6 \ M^{-1}s^{-1}$$

TABLE 2.15

Observed and estimated pH-dependent Second-order rate constans for the oxidation of Ti^{III}-edta by aqueous iodine solutions. $[Ti^{III}\text{-edta}] = (2.0 - 8.0) \times 10^{-3}M$, $[I_2]_T = (1.0 - 2.0) \times 10^{-4}M$.

$I = 1.0M(LiCl + CH_3COONa)$, $T = 25^oC$

pH	$10^{-3}k_o^{edta}(expt)M^{-1}s^{-1}$ [a]	$10^{-3}k_o^{edta}(calc)M^{-1}s^{-1}$
0.15	2.3	2.2
0.75	2.3	2.24
1.7	2.9	2.7
2.25	2.5	3.2
2.8	3.0	3.6
3.43	3.2	3.76
3.95	3.6	3.84
4.3	3.9	3.9
4.4	4.1	3.93
4.58	4.13	4.0
4.85	4.5	4.2
4.95	4.9	4.3
5.13	5.3	4.5
5.46	6.9	5.3
5.58	7.3	5.75
5.83	12	7.25
6.8	51	35.5
7.4	96	124.8
7.45	130	138.7

a at pH = 0.75 and I = 1.0M, k_o^{edta} value was determined for acetate concsntrations 0.05, 0.10, 0.15 and 0.2M and it was found that k_o^{edta} values of $2.3 \times 10^3 M^{-1}s^{-1}$ obtained confirms that k_o^{edta} values of $2.3 \times 10^3\ M^{-1}s^{-1}$ obtained confirms that k_o^{edta} is independent of acetate concentration.

The values of k_o^{edta} estimated are also presented in Table (2.15).

Figure (2.21) shows the plot of k_o^{edta}(expt) and k_o^{edta}(calc) respectively against pH. These plots which are biphasic, show a good correlation between the estimated and experimental second-order rate constans k_o^{edta}.

It is worth mentioning that at pH = 0.75 and I = 1.0M, k_o^{edta} values was determined for acetate concentrations 0.05, 0.10, 0.15 and 0.2M respectively and it was found out that the k_o^{edta} value of 2.3×10^3 $M^{-1}s^{-1}$ obtained confirms that k_o^{edta} is independent of acetate concentration.

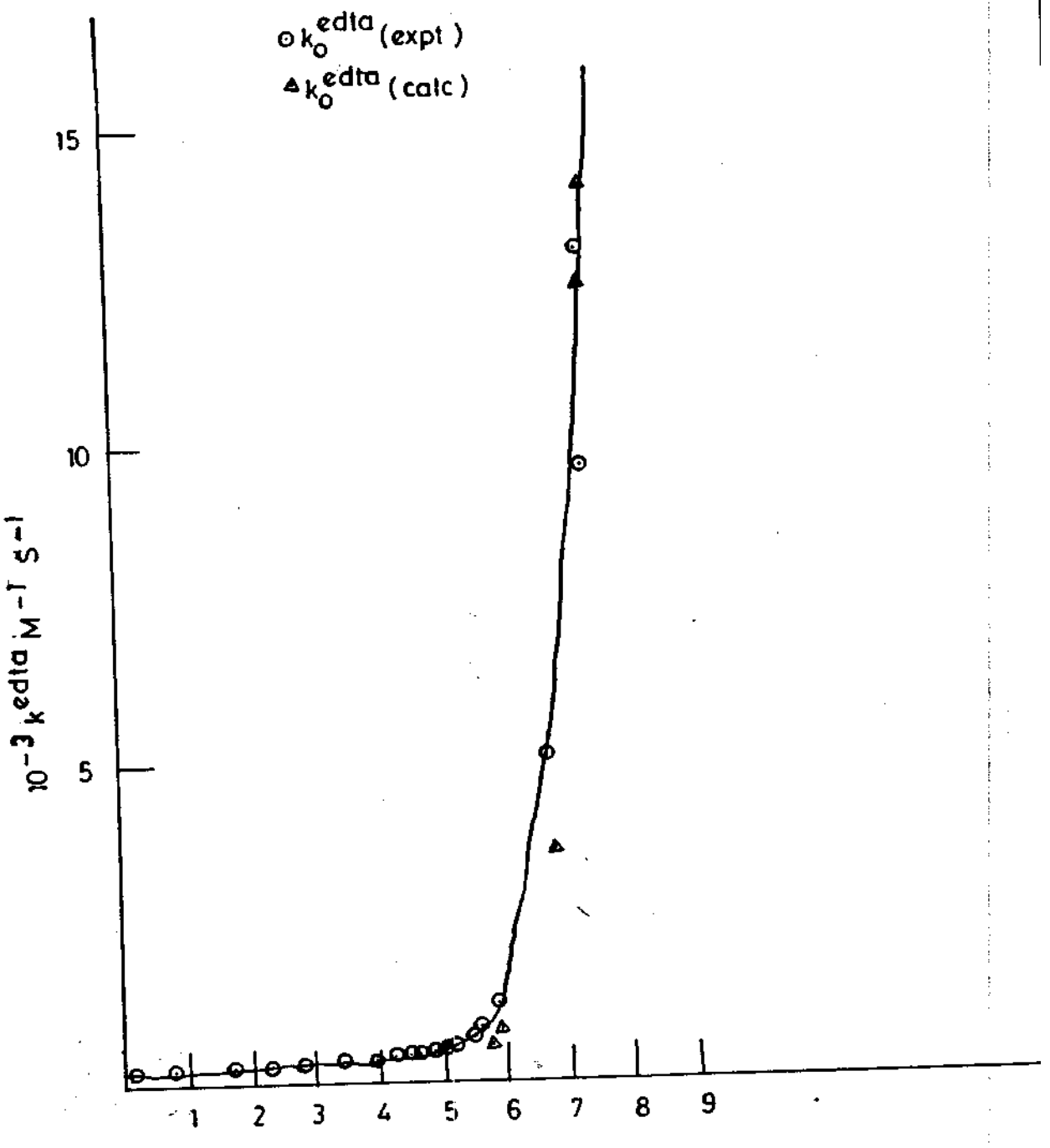


Fig. 2-21

Plot of k_o^{edta} (calc) and k_o^{edta} (expt) versus pH for the I_2 — Ti^{III}-edta reaction.

Effect of Iodide ion Concentration.

The effect of iodide on the Ti^{111}-edta - I_2 reaction was determined by keeping all variable parameters constant and varying iodide concentration from 0.004 to 0.03M. The rate constant of the reaction decreases as iodide concentration increases. The second-order rate constants obtained are shown in Table (2.16).

TABLE 2.16

$[Ti^{111}\text{-edta}] = 7.3 \times 10^{-3}$ M, $[I_2]$ =

I = 1.0M(LiCl), t = 25°C, pH = 1.0

10^2 $[I^-]$M	$10^{-3} k_o^{edta}$ $M^{-1}s^{-1}$
0.4	2.29
1.0	1.1
1.52	0.94
2.02	0.78
3.0	0.63

As in the $Ti^{3+}aq + I_2$ reaction $k_o^{edta}(1 + K_{I_3^-}[I^-])$ was plotted against $[I^-]$ at pH = 1.0 (Figure 2.22). From the least mean square analysis of the slope and intercept of this plot, the following values of $k_{I_2}^{edta}$ and $k_{I_3^-}^{edta}$ were obtained respectively:

$$k_{I_2}^{edta} = (8.52 \pm 0.28) \times 10^3 \ M^{-1}s^{-1}$$

$$k_{I_3}^{edta} = (2.63 \pm 0.21) \times 10^2 \ M^{-1}s^{-1}.$$

This results confirm earlier results that the rate of reaction of Ti^{111}-edta with I_3^- is slower than that with I_2.

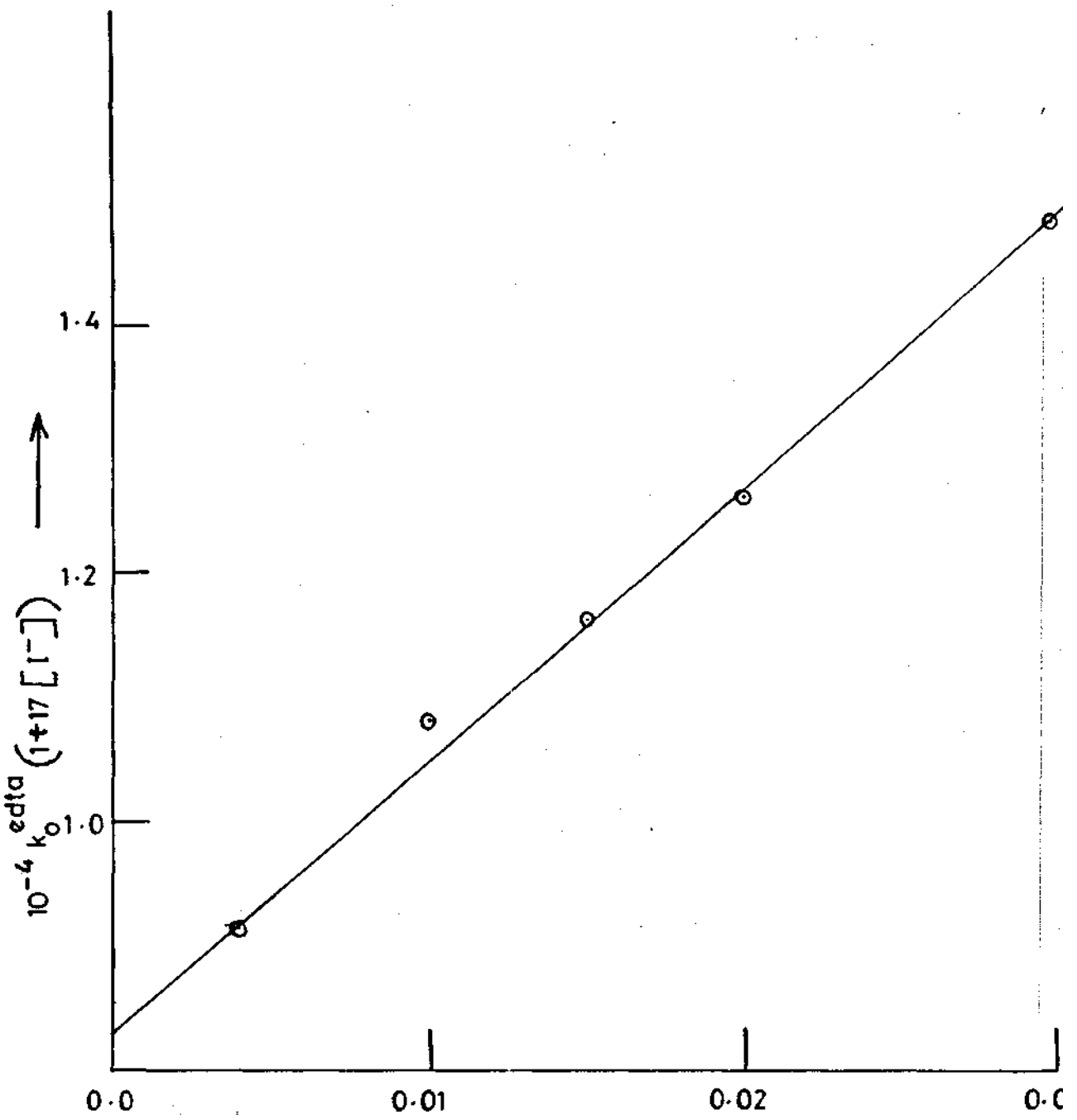


Fig. 2.22

Effect of Iodide on the rate of the Ti^{III}-edta $-I_2$ reaction shown by the plot of $k_o^{edta}\left(1+k_{I_3^-}[I^-]\right)$ Versus $[I^-]$

D I S C U S S I O N

The result of the stoichiometric determination, the strict adherence to second-order kinetics without any attendant complications of inhibitions by the products unequivocally show that the reaction proceeds by a simple bimolecular interaction leading to a series of univalent changes as it is commonly encountered in previously investigated halogen reactions.[37,96-98,106,122,123] Therefore, these reactions are non-complementary in redox reaction termonology. The following reaction sequence is suggested to account for the observed kinetic data:

$$Ti(III) + X_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ti(IV) + X_2^{\cdot -} \quad \text{(rds)} \qquad \ldots(2.47)$$

$$Ti(III) + X_2^{\cdot -} \xrightarrow{k_2} Ti(IV) + 2X^- \quad \text{(fast)} \qquad \ldots(2.48)$$

In the above scheme, and for all halogens of interest in this work, $k_2 >> k_{-1}$ and a simple second-order rate equation;

$$\text{Rate} = k_{obs}[Ti(III)][X_2] \qquad \ldots(2.49)$$

ensues. This is consistent with the observed empirical rate equation obtained from the kinetic data.

The nature of the acid dependence observed for the rate of the $Ti^{III} + Br_2$ reaction is similar to that observed for the $Ti^{III} + I_2$ reaction. Similar inverse acid dependence has been reported for a lot of oxidation reactions involving the aquotitanium(III) ion.[34-40] As in earlier studies of related systems, a general interpretation of such a dependence is that a fast protolytic equilibrium is established by

Ti^{3+}(aq) prior to the electron transfer step. The implication of this is that Ti^{3+}(aq) is partitioned between the kinetically native form, with an acidity constant K_a and an active basic form. The latter accounts for the dependence of such reactions on the acidity of the reaction medium.

The reaction of Ti^{3+}(aq) with these halogens also consists of two kinetic components. The first involves $Ti^{3+}(aq) + X_2$ and the second, $Ti^{3+}(aq) + X_3^-$. In the oxidation of Ti^{3+}(aq) by aqueous solutions of iodine the following reaction sequence can be proposed:

$$Ti^{3+}(aq) \underset{}{\overset{K_a}{\rightleftharpoons}} TiOH^{2+} + H^+ \qquad ...(2.50)$$

$$TiOH^{2+} + I_2 \xrightarrow{k_1'} \text{(activated complex)}^* \qquad ...(2.51)$$

$$TiOH^{2+} + I_3^- \xrightarrow{k_2} \text{(activated complex)}^* \qquad ...(2.52)$$

The above scheme gives a rate law of the form:

$$\text{Rate} = \frac{-d}{dt}[Ti(III)] = \frac{k_1 K_a [Ti(III)][I_2]}{[H^+] + K_a} +$$

$$\frac{k_2 K_a [Ti(III)][I_3^-]}{[H^+] + K_a} \qquad ...(2.53)$$

Since equation (2.46) is identical with equation (2.53), then

$$a_1 = 1/k_1$$

$$b_1 = 1/k_1 K_a$$

and

$$a_2 = 1/k_2$$

$$b_2 = 1/k_2 K_a$$

The values of k and K_a computed are,

$$k_1 = 5 \times 10^2 M^{-1}s^{-1}$$

$$K_a \text{ (from } a_1 \text{ and } b_1) = 3 \times 10^{-3} M.$$

and $$k_2 = 6.9 M^{-1}s^{-1}$$

$$K_a \text{(from } a_2 \text{ and } b_2) = 3.2 \times 10^{-3} M$$

For the reaction of $Ti^{3+}(aq)$ with bromine the following reaction sequence can be proposed:

$$[Ti(H_2O)_6]^{3+} \underset{}{\overset{K_a}{\rightleftharpoons}} [(H_2O)_5TiOH]^{2+} + H^+ \qquad ...(2.54)$$

$$[Ti(H_2O)_5OH]^{2+} + Br_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(H_2O)_5TiO]^{2+} + H^+ + Br_2^{\cdot -} \qquad ...(2.55)$$

$$[(H_2O)_5TiOH]^{2+} + Br_2^{\cdot -} \xrightarrow{k_2} [(H_2O)_5TiO]^{2+} + 2Br^- \qquad ...(2.56)$$

If the steady-state approximation is applied to the above scheme and the following assumptions are made,

(1) that $k_2 K_a [Ti^{3+}][H^+] >> k_{-1}[TiO^{2+}][H^+]$

and

(ii) $[Ti(III)] = [Ti(H_2O)_6^{3+}] + [TiOH^{2+}]$

then the following equation is derived:

$$k_o = \frac{k_1 K_a [H^+]^{-1}}{1 + K_a [H^+]^{-1}} \qquad ...(2.57)$$

From equations (2.24a) and (2.57), it follows that $1/k_1 = e$ and $1/k_1 K_a = f$ and therefore,

$k_1 = 9.2 \times 10^3 M^{-1}s^{-1}$ and

$K_a = 4.5 \times 10^{-3} M$

The dependence of the $Ti^{3+}(aq) + I_2$ reaction on $[I^-]$ is as a result of the equilibrium,[121]

$$I_2 + I^- \underset{}{\overset{K}{\rightleftharpoons}} I_3^- \quad K = 748M^{-1}$$

$[I_3^-]$ increases with increasing $[I^-]$ whereas k_{obs} decreases as $[I^-]$ increases. This means that I_3^- reacts more slowly than I_2 as confirmed by the result of the analysis of the observed data. This also confirms earlier results that I_3^- reacts at a slower rate than I_2[124]. On the examination of the effect of $[Cl^-]$ on this reaction it was found that the observed rate constants were within 5% of each other and showed no systematic variation with Cl^-. This is consistent with the results of many other $Ti^{3+}(aq)$ reactions where a chloride medium is innocent of the rate studies.[27] The dependence of the rate of the $Ti^{3+}(aq) + Br_2$ reaction on Br^- is also as a result of the equilibrium.[120]

$$Br_2 + Br^- \underset{}{\overset{K}{\rightleftharpoons}} Br_3^- \quad K = 17M^{-1}$$

Analysis of the observed data also shows that $k_{Br_2} > k_{Br_3^-}$.

It was however found that the rate of the $Ti^{3+}(aq) + Br_2$ reaction increased with $[Cl^-]$ and follows an equation of the form:

$$k_o^{Cl} = c + d\ [Cl^-]$$

The values of c and d were determined as

$$c = (3.8 \pm 0.1) \times 10^2 M^{-1}s^{-1}$$

$$d = (1.00 \pm 0.01) \times 10^4 M^{-2}s^{-1}$$

The results of previous investigations[27] involving aquotatanium(111) ion and the result of the $Ti^{3+}(aq) + I_2$ reaction shows that $Ti^{3+}(aq)$ reactions are innocent of $[Cl^-]$.

The dependence of the $Ti^{3+}(aq) + Br_2$ reaction on $[Cl^-]$ can therefore be rationalized on the basis of either of two reasons. The first is that there is the possibility of the equilibrium,

$$Br_2 + Cl^- \underset{\longleftarrow}{\xrightarrow{K'}} Br_2Cl$$

being established and that Br_2Cl^- reacts faster than Br_2 with aquotitanium(111)(111) ion. Although the possibility of the existence of the interhalogen anion Br_2Cl^- is not in doubt[89], no value of K has been reported in literature. The second possibility is that the $Ti^{3+}(aq) + Br_2$ reaction occurs by the outer-sphere mechanism with the chloride ion acting as a catalyst for this reaction. The first possibility however fits the observed dependence as follows. The reaction sequence is.

$$Br_2 + Cl^- \underset{k_1}{\overset{K}{\rightleftharpoons}} Br_2Cl^- \qquad ...(2.58)$$

$$Ti^{3+}(aq) + Br_2 \xrightarrow{k_1} \text{(activated complex)} \qquad ...(2.59)$$

$$Ti^{3+}(aq) + Br_2Cl^- \xrightarrow{k_2} \text{(activated complex)} \qquad ..(2.60)$$

$$\text{Rate} = k_1 [Ti(111)] [Br_2] + k_2 [Ti(111)] [Br_2Cl^-]$$

$$= [Ti(111)] [Br_2] (k_1 + k_2K^1 [Cl^-])$$

$$\therefore \quad k_o^{cl} = k_1 + k_2K^1 [Cl^-] \qquad ...(2.61)$$

Since equation (2.61) is identical with equation (2.25) then,

$$c = k_1 = (3.8 \pm 0.1) \times 10^2 M^{-1}s^{-1}$$

$$d = k_2K' = (1.00 \pm 0.01) \times 10^4 M^{-2}s^{-1}$$

It is worth highlighting at this juncture that some two and a half decades ago, Winstein and Johnson[99b] did publish their findings on the rate of oxidation of $Ti(H_2O)_6^{3+}$

by aqueous iodine. Their conclusion was that the reaction obeys a rate law of the form:

$$\frac{-d}{dt}[I_2] = -\tfrac{1}{2}\frac{d}{dt}[Ti(III)] = \frac{k_1[Ti(III)][I_2]}{[H^+]} + \frac{k_2[Ti(III)][I_3^-]}{[H^+]} + \frac{k_3[Ti(III)]}{[H^+]} \quad ....(2.62)$$

They varied their $[Ti(III)]$ and $[I_2]$ only four-fold and their investigation was limited to high acid concentration. They were also unable to offer plausible explanation for the acid-independent term in their rate law. Recent investigations show that a complex acid dependence is a common feature of Ti(III) reactions.

In the work of Winstein and Johnson,[99b] it was not possible to delinate the salient features involving the reaction of aquotatanium(III) ion. We tried to analyze their results to afford a direct comparison with the results of this investigation. This was done by plotting $k_o(1 + K_{I_3^-}[I^-])$ against $[I^-]$. From the slopes and intercepts of such plots, k_{I_2} and $k_{I_3^-}$ were obtained respectively. This was possible for only three acid concentrations and the results are as follows:

$[H^+] = 0.1M$, $k_{I_2} = 7.4M^{-1}s^{-1}$, $k_{I_3^-} = 0.009M^{-1}s^{-1}$

$[H^+] = 0.177$, $k_{I_2} = 3.69M^{-1}s^{-1}$ $k_{I_3^-} = 0.008M^{-1}s^{-1}$

$[H^+] = 0.329$, $k_{I_2} = 1.82M^{-1}s^{-1}$ $k_{I_3^-} = 0.005M^{-1}s^{-1}$

It was only possible to employ three iodide concentrations for these acid concentrations and these are:

$[I^-]$ = 0.098, 0.179 and 0.342M.

For values of $[I^-] > 0.342M$, $k_{obs}(1 + k_{I_3}[I^-])$ was independent of $[I^-]$. The major disparities between the result of this investigation and those of Johnson and Winstein are:

(1) That the rate equation obtained in this study has no iodine independent term,

(2) That although the acid dependence equation obtained in this work approximates to theirs at high acid concentrations, It is however more complex than what they reported.

The values of the rate constants k_{I_2} and $k_{I_3^-}$ obtained in this work are higher than those that could be obtained from their data. To ascertain that the above disparity are not a consequence of the presence of impurities in the Titanium(lll) solutions, the rate constant for the $Ti^{3+}(aq)$ + $Ru(NH_3)_6^{3+}$ reaction was measured for comparison. The following result was obtained.

$[Ru(NH)_6^{3+}] = 1.34 \times 10^{-3}M$, $[Ti^{3+}] = 1.25 \times 10^{-5}M$

$[H^+] = 0.2M$, $t = 25^oC$, $I = 1.0M$ and $k = 0.90M^{-1}s^{-1}$

This measured rate constant is in excellent agreement with the values of $k = 0.858M^{-1}s^{-1}$ at $[H^+] = 0.206M$ obtained by Davies and Earley[44] under similar conditions. Comparing the results of this work and those earlier reported by Johnson and Winstein, we prefer to accept our results for the following reasons:

(1) This investigation covers a wider range of reactants and acid concentrations than the earlier studies. A wide range of reactant and acid concentration is deemed necessary for the correct interpretation of reactions involving aquotitanium(lll) ion. This is because of the complexity of the acid dependence of the rate constant often found in $Ti^{3+}aq$ redox reactions. [Ti(lll)] was varied 22-fold while the acid range employed in this work was from 0.0055 to 0.2M. Winstein and Johnson varied their acid concentration only four times within the acid range 0.1 - 0.5M.

(i) For the three acid concentrations for which k_{I_2} and $k_{I_3^-}$ could be determined in Winstein and Johnson's work, the iodide concentration was too high so that the iodide exist predominantly as I_3^-. This means that the $k_{I_3^-}$ determined from their data is likely to have a greater error than $k_{I_3^-}$ obtained from this work. A similar disagreement between earlier rate constants has been reported for the $Ti^{3+}(aq) + Co(NH_3)_5Cl^{2+}$ reaction[22] and the result of more recent investigations.[25] The study of the Ti(lll) + X_2 (X = Br, I) reactions completes the full kinetic study of the reaction.[37]

$$2Ti^{3+} + 2H_2O + X_2 \rightarrow 2\ TiO^{2+} + 2X^- + 5H^+$$

and highlights some of the salient mechanistic features characteristic of the reactivities of the halogens in solutions. For these reactions, the reactivity order is:

$$k_{Cl_2} > k_{Br_2} > k_{I_2} \quad \text{and}$$

$$k_{X_2} > k_{X_3^-} \qquad (X = Cl, Br, I)$$

Similar reactivity order has been reported for a lot of reactions involving halogens.[73,90,103,106] The only few exceptions are cases where electron transfer is not rate-determining.[91,92] The observed reactivity order parallels the order of the redox potentials.[88]

$$X_2 + 2e^- \rightarrow 2X^- \qquad \ldots(2.63)$$

E^o = 1.3595 (X = Cl)

= 1.087 (X = Br)

= 0.5355 (X = I)

However that $k_{X_3^-} < k_{X_2}$ cannot be rationalized on such terms. For each of the systems E^o for the $X_3^-/3X^-$ and $X_2/2X^-$ couples (for $X_3^-/3X$, E^o = 0.536 and 1.05 for X = I, Br respectively) are similar. The lower $k_{X_3^-}$ for each system probably shows that the effect of intrisic factors on rate is greater for X_3^- than for cases where X_2 is being reduced.

Greater insight may be gained into these reactions if we consider that the reactions are non-complementary in redox reaction terminology. They occur by a series of univalent steps with the transient intermediate $X_2^{\cdot -}$ being kinetically suggested. The basic activation paths are therefore:

$$Ti^{III} + X_2 \underset{}{\overset{k_1}{\rightleftharpoons}} Ti^{IV} + [X_2]^{\cdot -} \qquad \ldots(2.64)$$

$$Ti^{III} + [X_2]^{\cdot -} \xrightarrow{k_2} Ti^{IV} + 2X^- \qquad \ldots(2.65)$$

Generally, when halogens react by the above activation paths, reversibility in the first step and the expected product inhibition by Ti^{IV} seems to depend on the free energy ΔG^o for the first step.[37]

If E^{o} for the $M^{n+} \rightarrow M^{(n-1)+}$ couple is much less than for $X_2 \rightarrow [X_2]^{\cdot -}$ (X = Cl, Br I) then ΔG^{o} for the first step will be less than zero and the first step will not be reversible in a strictly kinetic sense. No inhibition by $M^{(n-1)+}$, the product of the reaction is thus expected to be observed. If the reverse is true however, then the first step will be reversible and M^{n+} is expected to inhibit the reaction. That no product inhibition was observed in this investigation suggests that the $Ti^{111} + X_2$ (X = Br, I) reactions fall into the former class. Other examples in this class are the $V^{111} + I_2$[96] and $V^{111} + Br_2$[97] reactions The $V^{1V} - X_2$ (X = Cl, Br) reactions. (E^{o} = 1.0V for $V^{1V} - V^{V}$ couple, 0.4 - 0.6V estimated for $Cl_2 \rightarrow [Cl_2]^{\cdot -}$ and $Br_2 \rightarrow [Br_2]^{\cdot -}$ couples).[88,98,112,114,125,126] which are strongly inhibited by V^{V} and $Fe^{11} - Br_2$[105] (E^{o} = 0.77V for $Fe^{2+} \rightarrow Fe^{3+}$ couple) inhibited by Fe^{111} provide a good example of the latter class.

In general, the overall activation paths proposed to explain each of these reactions depend on the pH of the medium which determines the integrity of both the Ti(111) species and the halogen species with respect to hydrolysis. Three activation paths $Ti(OH)^{2+} + Cl_2$, $TiCl^{2+}$ + HOCl and Ti^{3+} + HOCl were proposed as the important activation paths for the Ti^{111}-Cl_2 reaction.[37]

The uncertainty as to whether Ti^{IV} exists as $[TiO]^{2+}$ or $[Ti(OH)_2]^{2+}$ notwithstanding that Ti^{III} exists predominantly in acid solution is well documented.[127] It thus implies that the oxidation of Ti^{III} to Ti^{IV} is accompanied by the conversion of an aquoion to an oxo or hydroxo cation. Reactions in which aquoions are oxidized to oxocations by acid solutions of halogens show similar hydrogen ion dependencies. The result of this investigation and the ealier study of the Ti(III) + Cl_2 reaction by Adegite and Edeogu[37] show that this is also true for aquotitanium(III) ion. The participation of such hydrolyzed species in the formation of inner-sphere precursor binuclear intermediate is not necessarily automatic but depends on some other factors. This is evidenced by the study of these Ti(III) + X_2 reactions, where the inner-sphere mechanism was suggested for the $TiOH^{2+}$ + HOCl reaction[37] while our investigation of the Ti(III) + Br_2 and Ti(III) + I_2 reactions prefer the outer-sphere mechanism. The inner-sphere mechanism proposed for the former reaction has been rationalized on the basis of the hard and soft acids and bases principle. Since Ti^{3+}(aq) hardly uses Cl^- as a bridging ligand, the attachment in the Ti^{3+}(aq) + HOCl reaction is probably through the oxygen atom.

One very strong evidence to back up the deduction that the Ti^{III} + X_2 (X = Br, I) reactions occur by the outer-sphere mechanism is the magnitude of the kinetically determined value

of K_a, the acid dissociation constant of Ti(lll) aquoion.

The mean value of K_a = 3.1 x 10^{-3}M for the Ti^{lll} - I_2 system and K_a value for Ti^{lll}-Br_2 reaction is 4.5 x 10^{-3}M. These values are in good agreement with earlier obtained value of 3.5 x $10^{-3}M^{-1}$ by Orhavonic for some outer-sphere reactions of aquotatanium(lll) ion with Cobalt(lll) complex.[42] Some other data on some outer-sphere reactions involving aquotitanium(lll) ion as reductant have been fitted with K_a values of 1.6 x 10^{-3}M and 4.6 x 10^{-3}M respectively.[25,41] These values are at least an order of magnitude less than similar equilibrium constants derived for more complex hydrolytic pathways in the reactions of Ti^{3+}(aq) ion that proceed by the inner-sphere mechanism. For inner-sphere reactions involving Ti^{3+}aq, K_a values as high as 0.01 → 0.16 have been reported. The experimental value of K_a as determined by independent[128] workers although not under identical conditions puts its value in the range (1.6 ~ 6.9) x 10^{-3}M. The arguement that the Ti^{lll} + X_2 reactions (X = 1, Br) occur by the outer-sphere mechanism is supported by the comparison of the rate of electron-transfer reactions involving Ti^{3+}(aq) with the rate of substitution into the inner-coordination sphere of Ti^{3+}aq. Categorical statements can only be made on the Ti(lll) + Br_2 reaction though. The rate of electron transfer for the latter reaction is 9.2 x $10^3M^{-1}s^{-1}$. For this reaction to occur by the inner-sphere mechanism, substitution into the inner-coordination

sphere must proceed the electron-transfer process. The rate constant of substitution of NCS^- and $HC_2O_4^-$ onto $Ti^{3+}aq$ ion have been reported to be $8 \times 10^3 M^{-1}s^{-1}$ and $4 \times 10^5 M^{-1}s^{-1}$ respectively by Diebler.[28] The substitution mechanism is also reported to be associative. Both NCS^- and $HC_2O_4^-$ are definitely more nucleophilic than Br_2 and I_2. It thus means that for substitution of bromine into the inner-coordination sphere of $Ti^{3+}(aq)$ to preceed the electron transfer the rate constants for the electron transfer must be less than the value of $9.2 \times 10^3\ M^{-1}s^{-1}$ obtained for the $TiOH^{2+} + Br_2$ reactions. The obtained data thus seem to rule out the inner-sphere mechanism.

The dependence of the rate of the reaction of Ti^{111}-edta with aqueous bromine and iodine solutions on pH is biphasic as shown in Figure (2.14). Such a biphasic dependence has been observed in the reaction of Ti^{111}-edta with $Co(NH_3)_6^{3+}$ and $Co(NH_3)NCS^{2+}$[119].

These reactions are: pH independent below, pH = 3 but shows an increase in rate as pH increases above pH = 3

As in earlier investigations such a dependence on pH can be attributed to differing reactivities of the Ti^{111} species present in solution. These are $[Ti(H_2O)(H\ edta)]$, $[Ti(H_2O)\ edta]^-$ and $[Ti(OH)(edta)]^{2-}$[63]

The principal activation paths for these reactions can be proposed as follows:

$$TiY \underset{}{\overset{K_1}{\rightleftharpoons}} TiY^- + H^+ \qquad \ldots(2.66)$$

$$TiY^- \overset{K_2}{\rightleftharpoons} TiY^{2-} + H^+ \qquad \ldots(2.67)$$

$$TiY^- \overset{k_1}{\rightleftharpoons} \text{(activated complex)} \qquad \ldots(2.68)$$

$$TiY^- + X_2 \xrightarrow{k_2} \text{(activated complex)} \qquad \ldots(2.69)$$

$$TiY^{2-} + X_2 \xrightarrow{k_3} \text{(activated complex)} \qquad \ldots(2.70)$$

(where Y = edta, X = Br, I)

From the above scheme we obtain,

$$k_o^{edta} = \frac{k_1 + k_2K_1[H^+]^{-1} + k_3K_1K_2[H^+]^{-2}}{1 + K_1[H^+]^{-1} + K_1K_2[H^+]^{-2}} \qquad \ldots(2.71)$$

From the titration studies of Ti^{111}-edta solutions at varying pH by Podlahova and Podlaha the first two species above exist pH < 3.

Our results did show that these two species react at the same rate i.e. $k_1 = k_2$. This is also supported by the result of previous investigations. Therefore equation (2.71) becomes

$$k_o^{edta} = \frac{k_2 + k_2K_1[H^+]^{-1} + k_3K_1K_2[H^+]^{-2}}{1 + K_1[H^+]^{-1} + K_1K_2[H^+]^{-2}} \qquad \ldots(2\ 72)$$

Using non-linear-mean-square computer programme to fit the experimentally observed data into equation (2.72) with values of K_1 and K_2 fixed respectively as reported by Podlahova and Podlaha,[63] for the different pH values investigated

gave for the Ti^{III} edta + Br_2 system

$$k_2 = k_7 = (3.15 \pm 0.42) \times 10^4 M^{-1}s^{-1}$$

$$k_3 = k_8 = (8.31 \pm 0.2) \times 10^7 M^{-1}s^{-1}$$

respectively and for the Ti^{III}-edta + I_2 system.

$$k_2 = k_{10} = (3.13 \pm 0.32) \times 10^3 M^{-1}s^{-1}$$

$$k_3 = k_{11} = (2.33 \pm 0.45) \times 10^6 M^{-1}s^{-1}$$

respectively.

The data presented in Table (2.10) and (1.15) show that there is a reasonable agreement between the calculated rate constants and the experimental values. This implies that the model proposed is reasonably adequate to account for the complex ion dependence obtained in the Ti(111)–edta systems.

However, a detailed examination reveals that:

(i) the average value of the computed rate constant in the pH - independent region is about 12.4% higher than the experimental value.

(ii) In the range $3 \leqslant pH \leqslant 5$ the calculated values of the rate constants are lower than the experimental values of the rate constants while at the highest pH value the computed value is higher than the experimental. However it is comforting that generally the difference between the calculated and observed rate constant does not show a systematic trend throughout the pH region. Many factors particularly uncertainty in the nature of the Titanium-edta species present in solution and limitations in the accuracy of the computer programme employed could have made significant contributions to these differences. The first factor is

supported by results of previous workers who have made studies in the nature of Ti^{III}-edta species in solution. Their results[63] show that although the three species employed in our model $Ti(H_2O)H$ edta , $Ti(H_2O)edta^-$ and $Ti(OH)edta^{2-}$ are the dominant species in solution other less identifiable polymerized hydrolysed species are also present. In our calculations, the kinetic significance of such species has not been quantified.

The linearity of the $(k_o^{edta}[1 + K_1[H^+]^{-1} + K_1K_2[H^+]^{-2} - k_2)[H^+] - k_2K_1$ versus $K_1K_2[H^+]$ plot also goes to confirm the proposed model for this reactions.

As to the mechanism by which the Ti^{III}-edta + X_2 (X = Br,I) reactions occur, the only convincing kinetic evidence for the outer-sphere mechanism is in the magnitude of

the rate constant for the oxidation of Ti^{III}-edta by X_2 (X = Br I) above pH=3. The rate constant obtained for these reactions is much higher than the substitution- controlled electron-transfer rates in the inner-sphere reaction of Ti edta$^-$ with $(NH_3)_5RuOAc^{2+}$, $Co(NH_3)_5SCN^{2+}$ and $Co(NH_3)_5N_3^{2+}$[32,19],

On comparative analysis with available results on the choice of mechanism by aquotitanium(III), two less convincing evidences seem to support an outer-sphere mechanism for reactions reported in this work. These are:

(i) The fact that inner-sphere reactions of $Ti^{3+}(aq)$ with metal complexes are accompanied by more complex acid dependence behavior than can be explained by merely invoking hydrolysis of aquotitanium(III) and

(ii) that inner-sphere reactions of Ti^{3+}(aq) have only been established for complexes where the "lead-in" ligands are typically Pearson's hard bases, whereas complexes with relatively soft bases like iodide react by the outer-sphere mechanism.[40]

Also to further confirm that the Ti^{III}-edta + X_2 (X = Br, I) reactions occur by the outer-sphere mechanism the Marcus correlation was employed. Marcus equation for cross reaction[129] is

$$\log k_{12} = \tfrac{1}{2} \log k_{11} + \tfrac{1}{2} \log k_{22} + \tfrac{1}{2} \log K_{12} + \tfrac{1}{2} \log f \quad ...(2.73)$$

where,

$$\log f = (\log K_{12})^2 / 4 \log k_{11} k_{22} Z^{-2} \quad ...(2.74)$$

k_{11} k_{22} are the homonuclear electron exchange rate constants for the reducing and oxidizing complexes respectively. k_{12} and K_{12} are respectively the rate and equilbrium constants for the cross-reaction, and $Z=10^{11} M^{-1} s^{-1}$ is the collision frequency for the uncharged reactant molecules. In making this correlation for all these reactions that are of the outer-sphere mechanism it is assumed that k_{22} for $I_2 + I_2^-$ is 8.5×10^4 $M^{-1}s^{-1}$ the value reported by Woodruff and Magerum and also the same as k_{22} for $I_3^- + I_3^{2-}$ $(I_2^- + I^-)$[126]. A similar assumption holds for $Br_2 + Br_2^-$ and

$$Br_3^- + Br_3^{3-} \quad (Br_2^- + Br)$$

with $k_{22} = 29 M^{-1}s^{-1}$.

K_{12} was calculated from the redox potentials for X_2 = I, 0.11V)[88] for

$$X_3 + e \rightarrow X_2 + X^- \quad (X = Br, 0.4V \quad X = I, -0.06V) \text{ and for}$$

$$Ti\ edta + e \rightarrow [Ti\ edta]^-, \quad ...(2.75)$$

E^{o} = 0.30V the value obtained from the polarograhic studies of Maverick and Pecsok.[61] k_{11}, the exchange rate constant for Ti edta + Ti edta $^{-}$ is unknown. However, we made the initial estimate from the data of the Ti edta + I_2 reaction on the assumption that 'f' in equation (2.73) is unity.[130] The initial value of k_{11} so obtained was $38M^{-1}s^{-1}$. This was then plugged into equation (2.74)to calculated f for each reaction. From equation (2.73) a plot of log k_{12} -½log k_{22} -½log f versus log K_{12} should be linear with a slope of 0.5 and an intercept of ½log k_{11}. With this impoved value of log k_{11}, the process was repreated until the initial value of k_{11} and that estimated from the intercept agree within 5%. The final result is a good linear plot (correlation coefficient 99.52% shown in Figure (2.23). The slope of 0.45 and from the intercept, the rate constant is $k_{11} = 32.0M^{-1}s^{-1}$. A slope of near half (0.48) has also been reported for such a correlation in the reactions of $TiOH^{2+}$ with some Ru(111) ammine complexes.[44,45] The excellent correlation obtained when the measured rate constants for the oxidation of Ti^{111}-edta by Br_2, Br_3^{-}, I_2 and I_3^{-} at pH < 3 are subjected to Marcus equation for cross-reactions suggests that the four reactions occur by the same mechanism and this we believe to be the outer-sphere mechanism.

The kinetically derived value[44] of k_{11} for $TiOH^{2+}$ is $0.01M^{-1}s^{-1}$ and the redox potential for the couple $TiOH^{3+}$ + e → $TiOH^{2+}$ is reported[45] as 0.08V. The corresponding

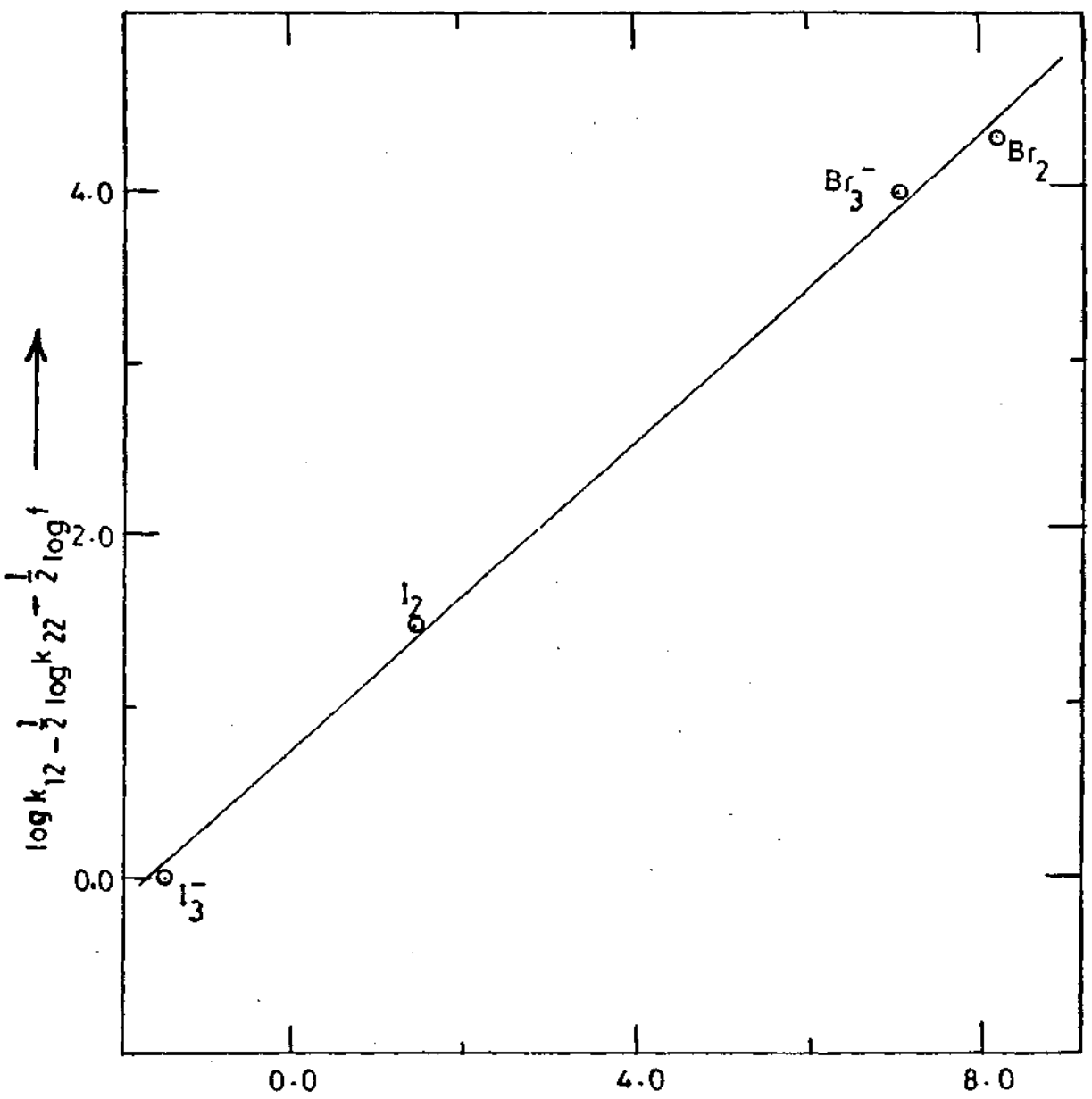


Fig. 2·23

Marcus plot for the $Ti^{3+}(aq) - X_2, X_3^-$ (X = Br, I) reactions.

values for the Ti edta + Ti edta $^{-}$ couples are 32 $M^{-1}s^{-1}$ and 0.03V respectively. Thus the more facile reducing ability of Ti^{III}-edta compared to $TiOH^{2+}$ is not so much due to a significantly different redox potential (ΔE^{o} between the ions is only 0.05V) but the large difference in their intrisic reducing ability as measured by the ratio of their homonuclear electron exchange rate constants.

$$k_{11}^{(Ti\ edta)} \Big| k_{11}^{(TiOH)} \quad \text{is}$$

about 3200.

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130. This assunption appears justifiable since K_{12} for this reaction is close to Unity.

C H A P T E R 3

Linear Free Energy in Redox Reactions: Oxidation of Poly(pyridine-Iron(11) Complexes and Substituted Poly(pyridine) - Iron(11) complexes by Aqueous solutions of Bromine.

CHAPTER 3

I N T R O D U C T I O N

A large number of redox reaction of substitution-inert polypyridine complexes of iron(11) and iron(111) have most commonly been investigated[1-12] with the aim of demonstrating Linear Free Energy Relations[14-19] between these reactants. Electron transfer processes involving these substitution-inert complexes must occur by the outer-sphere mechanism with the probability of the aromatic ligands participating in the electron transfer process being very high.

For these outer-sphere reductants, the measured rate of electron transfer might reasonably, as has been found for some cases,[3,4], compare with the predictions of Marcus[14] for adiabatic electron transfer processes.

When the outer-sphere electron transfer process is involved, Marcus has highlighted four main factors that are of importance in determining the speed of electron transfer. These are:

(1) the standard free energy of the redox step,

(2) the coulombic interactions of the charged reactants,

(3) the solvation of the charged reactants,

(4) the rearrangement of the inner- coordination spheres of the reactant species in order to meet the demands of the Franck condon principle.[20]

For (1) there are some isolated examples which suggest that the overall free energy change is of major importance in determining the rate of redox reactions. George and Irvine[21] suggest that the overall free energy will probably

account for the difference between the rate of oxidation of tris-bipyridyl Iron(11) ions by ceric ion in aqueous perchloric acid on the one hand and that in aqueous sulphuric acid on the other hand. A similar suggestion has been made concerning the rates of oxidation of tris-bipyridyl iron(11) ion by Thallic ion in aqueous perchloric acid[22]. The earlier work of Smith and coworkers[23] on the oxidation of $Fe(H_2O)_6^{2+}$ had shown that Fe(11) - Fe(111) polypyridine self-exchange rates estimated using Marcus cross-reaction equation are low. However, apart from the work of Irvine the study of the oxidation of ascorbic acid by these iron(111) complexes and $IrCl_6^{2-}$[13], the reaction schemes that have been suggested to these free energy correlation involving these polypyridine iron(11) complexes are characterized by,

(a) the possession of favourable rate-controlling electron transfer step, and,

(b) the transfer of an equal number of electrons (in most cases one electron) between reactants to form the final product.

As a continuation of the interest in the redox reactions involving the halogens, and as a means of assessing free energy correlations, the redox reactions of $Fe(LL)_3^{2+}$ (LL = 1,10-phen, 2,2-bpy, 5,6-$(CH_3)_2$ 1,10-phen, 4,7-$(CH_3)_2$ 1,10-phen, 2,2',2''-terpy, 4,4-$(CH_3)_2$ 2,2-bpy, 3,4,7,8-$(CH_3)_4$ 1,10-phen) with bromine have been investigated. It will be of interest to see how the rate of electron-transfer for these non-complementary reactions relate to either the standard free-energy of the rate-determining step or the overall free

energy of the reactions. Since these iron(11) polypyridine complexes are reacting with a common oxidant, bromine, with zero charge, charge effects will be unimportant in determining the rate of electron transfer. All the reactants employed in these work have approximately the same size so that to a large extent, solvation effects will cancel out. Hence direct correlation of redox rate constant with ΔE^{o} can be investigated.

E X P E R I M E N T A L

Preparation of $Fe(LL)_3^{2+}$ solutions:

(LL = 1,10-phen, 2,2-bpy, 2,2,2-terpy, 4,4-$(CH_3)_2$, 2,2bpy, 4,7-$(CH_3)_2$ 1,10 phen, 5,6-$(CH_3)_2$, 1,10 phen, 3,4,7,8$(CH_3)_4$ 1,10 phen)

Solutions of $Fe(LL)_3^{2+}$ were prepared by adding a known weight of ferrous ammonium sulphate to a solution containing a slight excess (5-10%) of a stoichiometric amount of analar grades of the respective ligand or by the dissolution of a known weight of commercially available (G.F. Smith) sample of the respective iron(11) complex in a known concentration of sulphuric acid solution. After proper filteration of the resulting solution, the concentration of the $Fe(LL)_3^{2+}$ solution so formed, which were all characterized by a red-orange colouration was determined spectrophotometrically by using the literature values of λ_{max} and extintion coefficients as given below in Table (3.1).

These concentration determinations were always done after scanning the prepared solution of the iron(11) complex and ascertaining that the observed λ_{max} correlates that reported in literature.

The values of the E^o for the $Fe(LL)_3^{3+}/Fe(LL)_3^{2+}$ couples obtained from literature sources are also included in Table (3.1)[3].

Table (3.1)

Absorption peaks, extintion coefficients and E^o of the $Fe(LL)_3^{2+}$ complexes.

Complex	$\lambda_{max(nm)}$[3]	ε cm^2mol^{-1}	E^oV
$Fe(1,10\text{-phen})_3^{2+}$	510	1.12×10^4	1.06[a]
$Fe(2,2\text{-bpy})_3^{2+}$	522	8650	1.035[b]
$Fe(5,6\text{-}(CH_3)_2\text{-}1,10\ phen)_3^{2+}$	512	1×10^4	0.97[a]
$Fe(2,2,2\text{-terpy})_3^{2+}$	553	$1,25 \times 10^4$	1.08[a]
$Fe(4,7\text{-}(CH_3)_2 1,10\ phen)_3^{2+}$	533	2.24×10^4	0.87[a]
$Fe(3,4,7,8\text{-}(CH_3)_4 1,10\ phen)_3^{2+}$	500	1.38×10^4	0.81[a]
$Fe(4,4\text{-}(CH_3)_2\ 2,2\ bpy)_3^{2+}$	529	8470	0.88[c]

a Ref 3

b Mean values of 1.05V reported in Ref. 24 and 1.02V in Ref. 13.

c M values of 0.84V quoted in ref 13 and 0.92V in ref. 24.

Preparation of bromine solution.

Bromine solution was prepared and standaridized as reported in Chapter 2.

KINETICS:

Preliminary investigations into the reactions involving these iron(11) polypyridine complexes showed that the reactions involving Fe(1,10 phen)$_3^{2+}$, Fe(2,2',2''-terpy)$_3^{2+}$ Fe(5,6-$(CH_3)_2$ 1,10-phen)$_3^{2+}$ and Fe(2,2-bpy)$_3^{2+}$ complexes and aqueous bromine were slow enough to be followed using the conventional techniques hence the S.P. 1750 spectrophotometer was used to monitor the progress of the reactions. However, since trial runs revealed that the reactions of bromine with Fe(3,4,7,8-$(CH_3)_4$-1,1o phen)$_3^{2+}$ Fe(4,4-$(CH_3)_2$ 2,2 bpy)$_3^{2+}$ and Fe(4,7-$(CH_3)_2$ 1,10-phen)$_3^{2+}$ were too fast for conventional techniques to be employed. The Durrum-Gibbson stopped-flow spectrophotometer was used to follow the progress of these latter reactions.

The progress of each of the reactions were always followed by monitoring the decrease in absorbance of the iron(11) polypyridine complexes at the λ_{max} [3] for these complexes as reported in the experimental section. The reactions were carried out under pseudo-first-order conditions with bromine concentration always in more than 100-fold excess over [Fe(LL)$_3^{2+}$] . The ionic strength was maintained at 0.5M (H_2SO_4/Li_2SO_4). The sulphate medium is not expected to have any effect on the rate of these reaction.[11] This is as a consequence of the inertness of the iron(11) polypyridine complexes and the fact that no complex formation between Br_2 and $SO_4^=$ has been reported in literature. Temperature was kept constant at 25 ± 1°C for each run by circulating thermostated water round the reaction compartment. The concentrations of the Fe(LL)$_3^{2+}$ complexes was always determined spectrophotometrically at their respective λ_{max} while that for

bromine was iodometrically determined. All concentrations were always determined immediately before the kinetic runs.

Determination of the Stoichiometry of the $Fe(LL)_3^{2+}$ - Br_2 reaction.

The stoichiometry of the $Fe(LL)_3^{2+}$ - Br_2 reactions (LL = 3,4,7,8-$(CH_3)_4$-1,10 phen, 2,2-bpy) was determined by spectrophotometric titration as described for the $Ti(H_20)_6^{3+}$-Br_2 reaction.

The absorbance of the solutions in each of the flasks was determined at the λ_{max} for the $Fe(LL)_3^{2+}$ complexes[3]. The plot of absorbance against the volume of bromine solution added are presented in Figure (3.1) and (3.2). From these plots the equivalence point of the reactions were determined and the stoichiometry of the reactions examined determined as follows:

(i) $Fe(3,4,7,8\text{-}(CH_3)_4$ 1,10 phen$)_3^{2+}$ - Br_2 reaction

1.97 : 1

(ii) $Fe(2,2\text{-bpy})_3^{2+}$ - Br_2 reaction

1.9 : 1

Hence the stoichiometry of two reaction examined is approximately 2:1. Since the stoichiometry of 2:1 was obtained for the reactions of these iron(11) polypyridine complexes with bromine, the 2:1 stiochiometry was assumed for the remaining five reactions. This implies that the overall reaction can be represented by the equation.

$$2Fe(LL)_3^{2+} + Br_2 = 2Fe(LL)_3^{3+} + 2Br^- \quad \text{.....(3.1)}$$

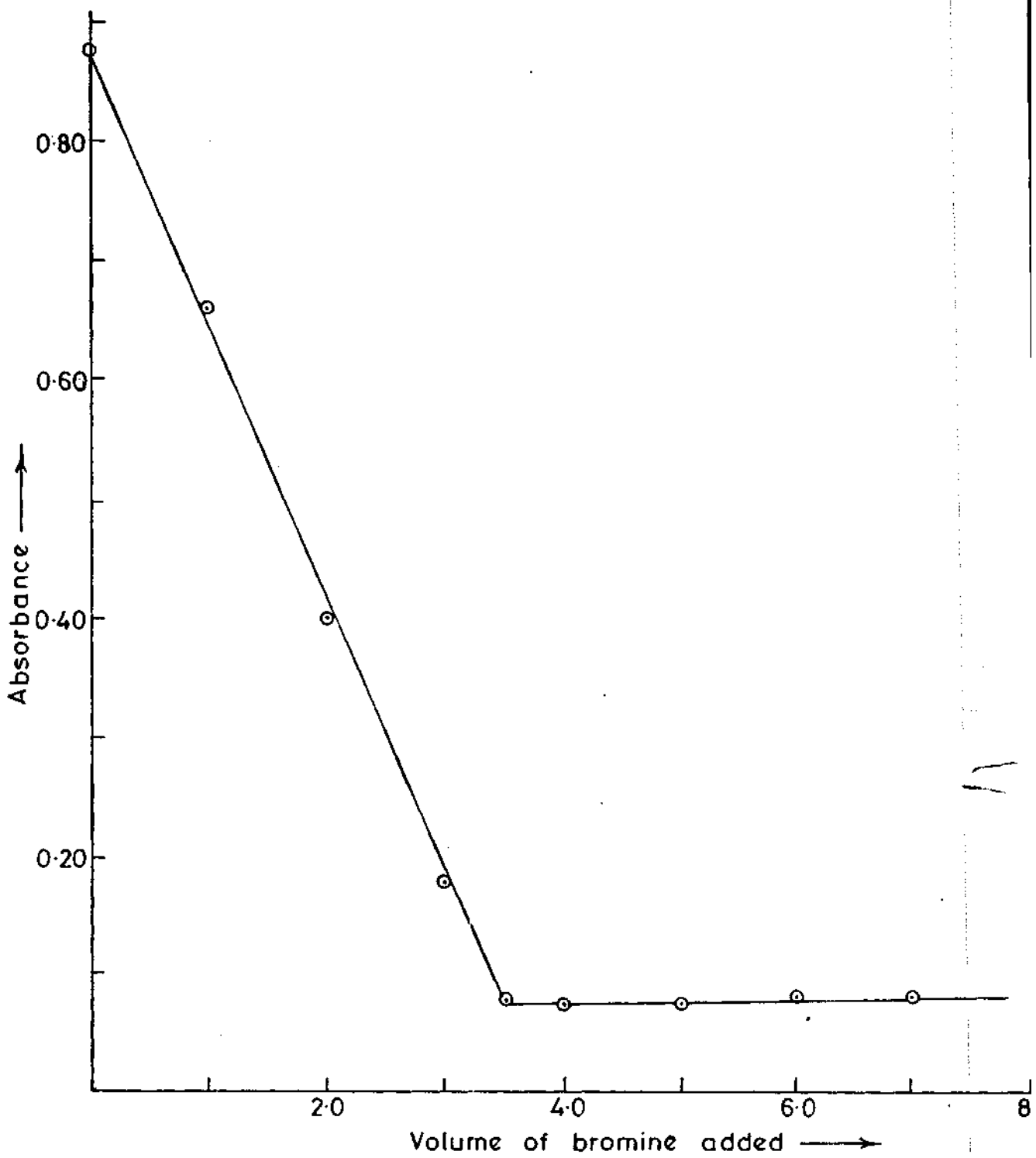


Fig. 3·1 Determination of the stoichiometry of the $Fe(3,4,7,8-(CH_3)_4-1,10-phen)_3^{2+}-Br_2$ reaction. Plot of absorbance versus volume of bromine added.

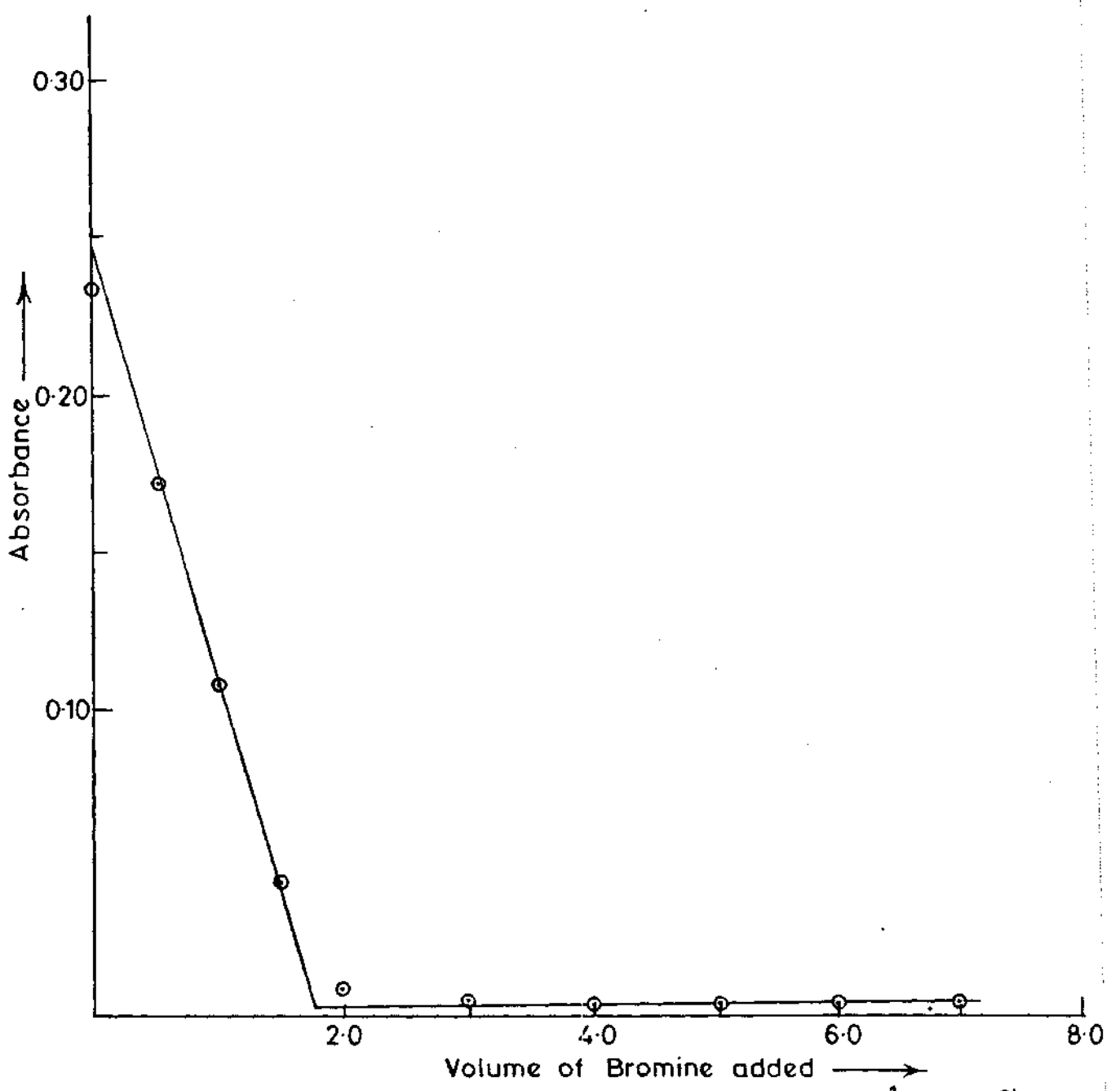
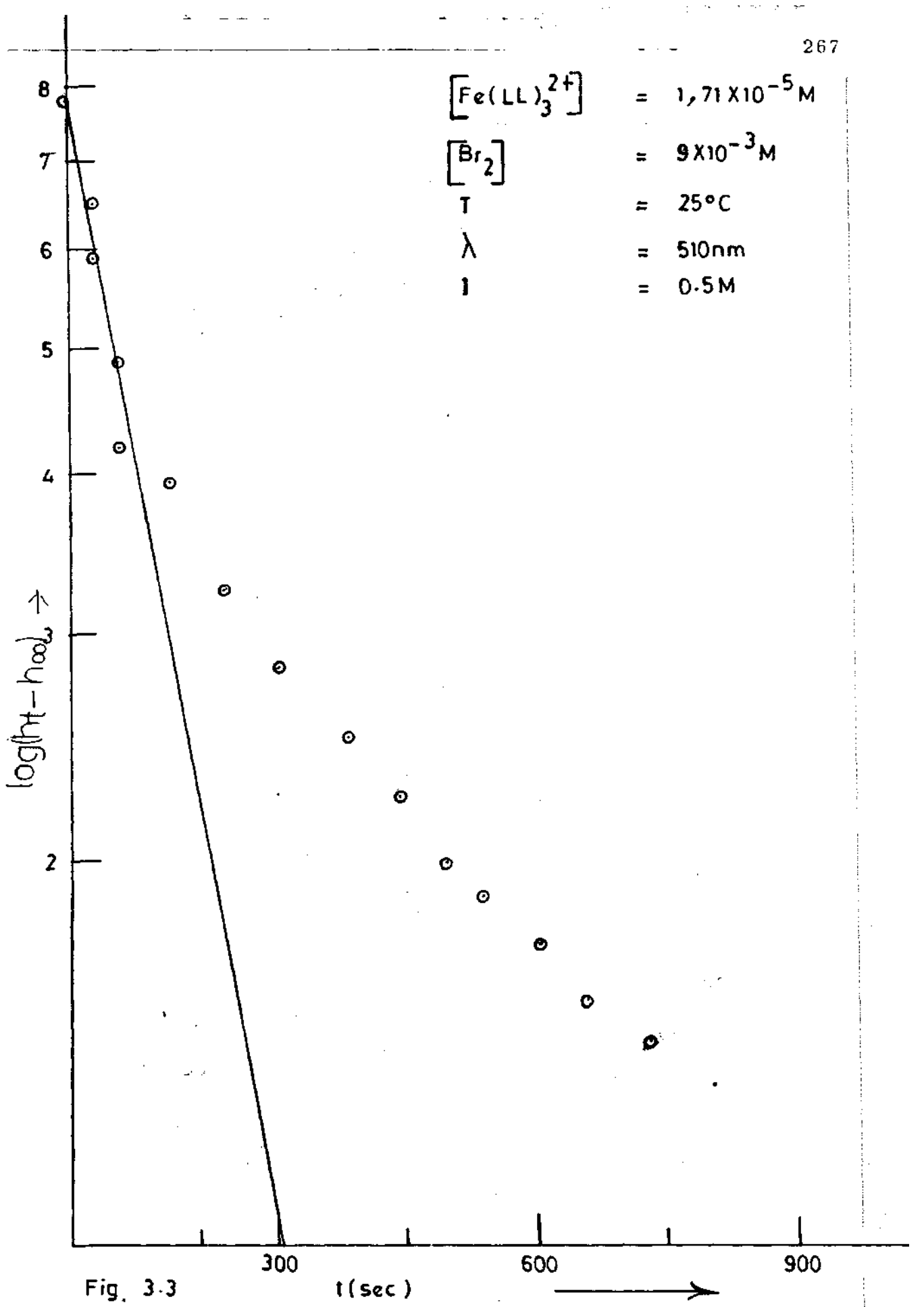


Fig. 3·2 Determination of the stoichiometry of $Fe(2,2^1\text{-bpy})_3^{2+}$-$Br_2$ reation. Plot of absorbance versus volume of bromine added.

R E S U L T S

The pseudo-first-order plots of log $(A_t - A_\infty)$ versus time were only linear to about 30 - 40% of the reactions as shown by the typical plots in Figures (3.3) to (3.8). Since these pseudo-first-order plots are non-linear, suggestive of strong inhibition, initial rates of the reactions were always taken as the rate of these reactions and the rate constants reported are at least an average of duplicate runs. Despite the non-linearity of the pseudo-first-order plots, the reactions were assumed to be second order, i.e. first-order in $Fe(LL)_3^{2+}$ and first-order in Br_2 . The second-order rate constants were thus calculated from the pseudo-first-order rate constants as obtained from the initial portion of the pseudo-first-order plots for each reaction and are preported in Tables (3.2 - 3.7).



$[Fe(LL)_3^{2+}]$ = $1,71 \times 10^{-5}$ M

$[Br_2]$ = 9×10^{-3} M

T = 25°C

λ = 510nm

I = 0.5 M

Fig. 3.3

Typical Pseudo-First-Order plot for the $Fe(1,10\text{-phen})_3^{2+}$ — Br_2 reaction.

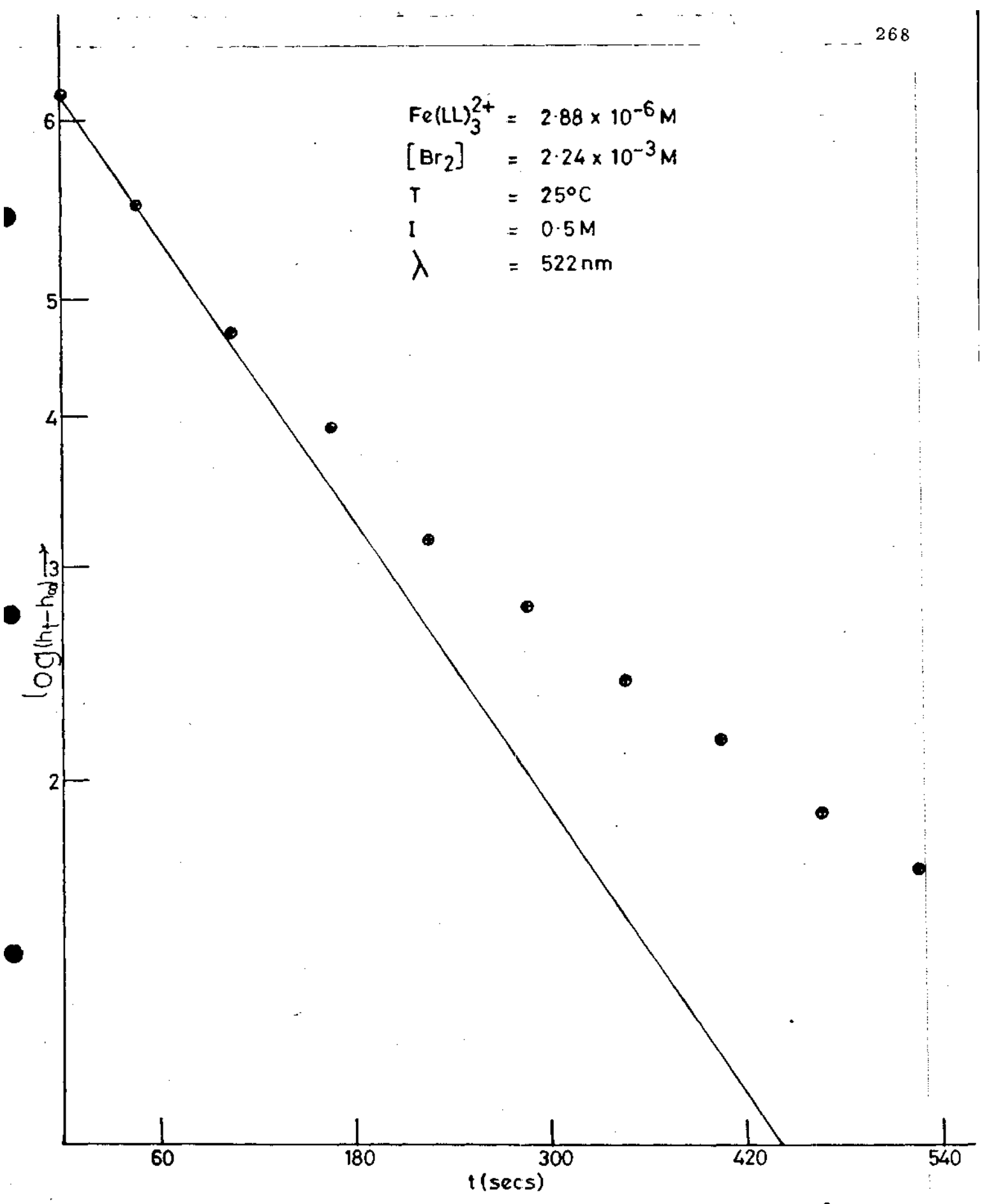
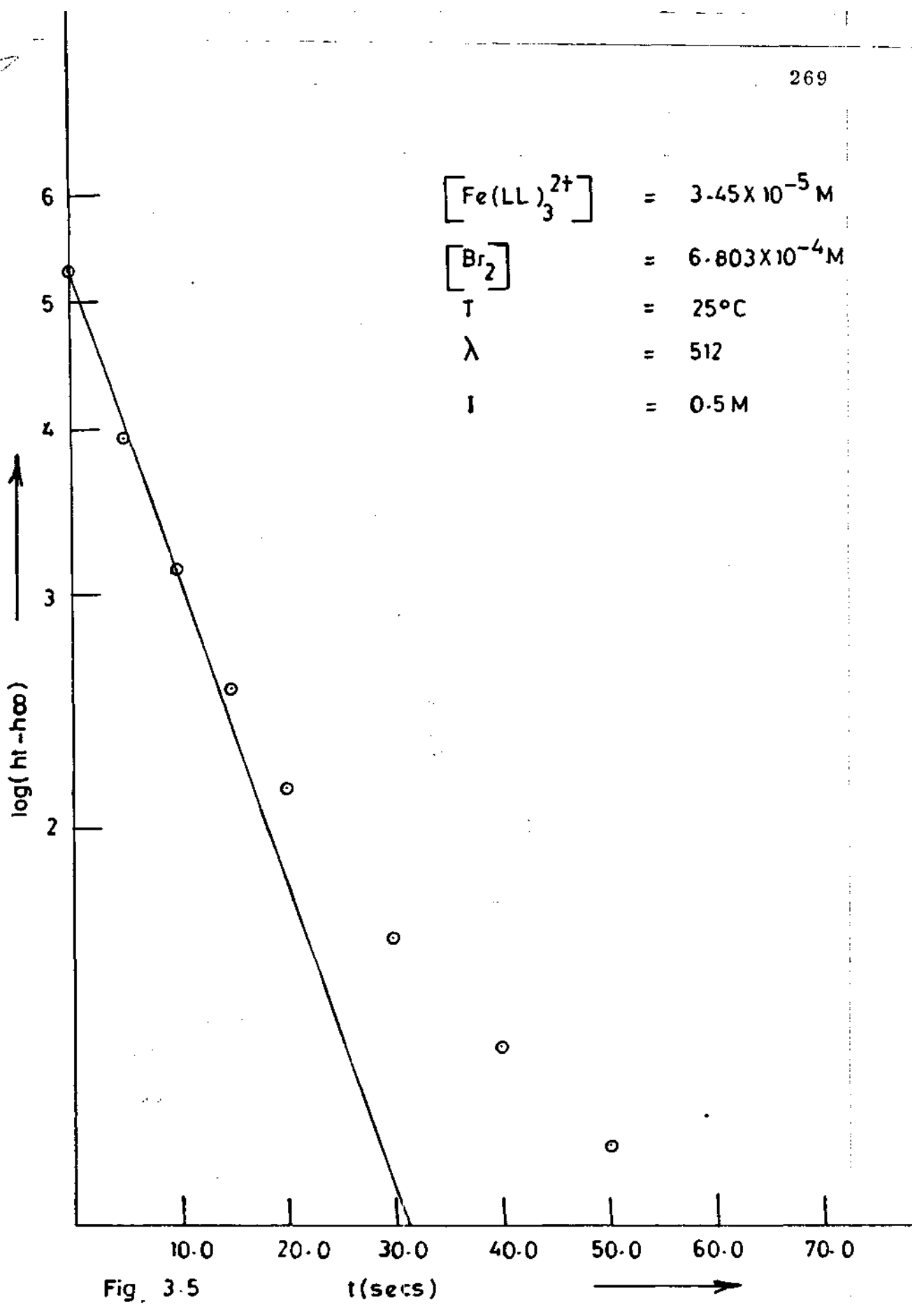


Fig. 3·4 Typical Pseudo-First-Order plot for the $Fe(2,2^1\text{-bpy})_3^{2+}$–$Br_2$ reaction



$\left[Fe(LL)_3^{2+}\right]$ = 3.45×10^{-5} M

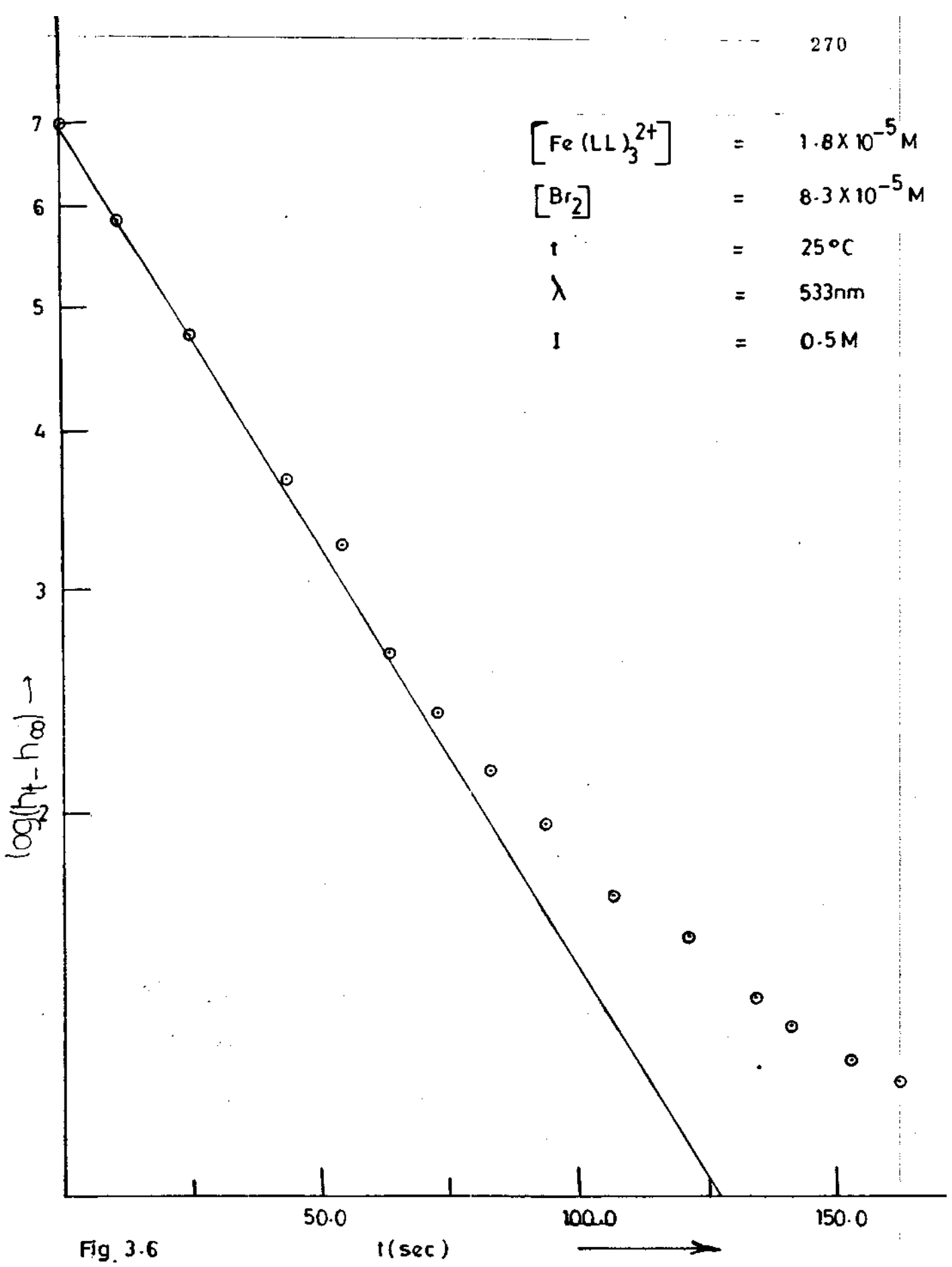
$\left[Br_2\right]$ = 6.803×10^{-4} M

T = 25°C

λ = 512

I = 0.5 M

Fig. 3.5 Typical Pseudo-First-Order for the $Fe(5,6,-(CH_3)_2,1,10\text{-phen})_3^{2+}$ —Br_2 reaction.



$[Fe(LL)_3^{2+}]$ = 1.8×10^{-5} M

$[Br_2]$ = 8.3×10^{-5} M

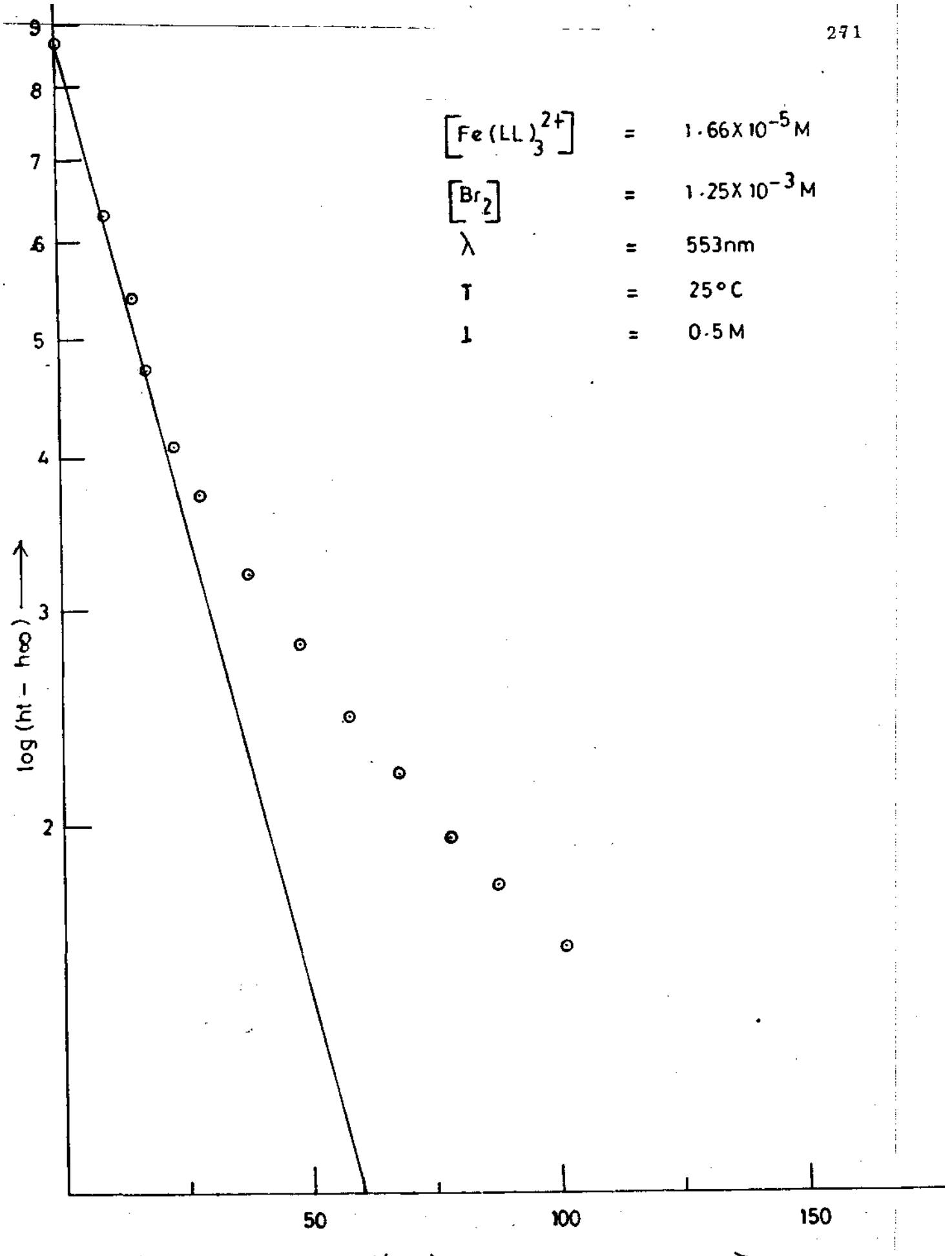
t = 25°C

λ = 533nm

I = 0·5 M

Fig. 3·6

Typical Pseudo-First-Order plot for the $Fe(4,7(CH_3)_2,1,10\ phen)_3^{2+}-Br_2$ reaction.



$[Fe(LL)_3^{2+}]$ = 1.66×10^{-5} M

$[Br_2]$ = 1.25×10^{-3} M

λ = 553nm

T = 25°C

μ = 0.5 M

Fig. 3.7

Typical Pseudo-First-Order plot for the $Fe(2,2',2''\text{-terpy})_3^{2+}$ — Br_2 reactio

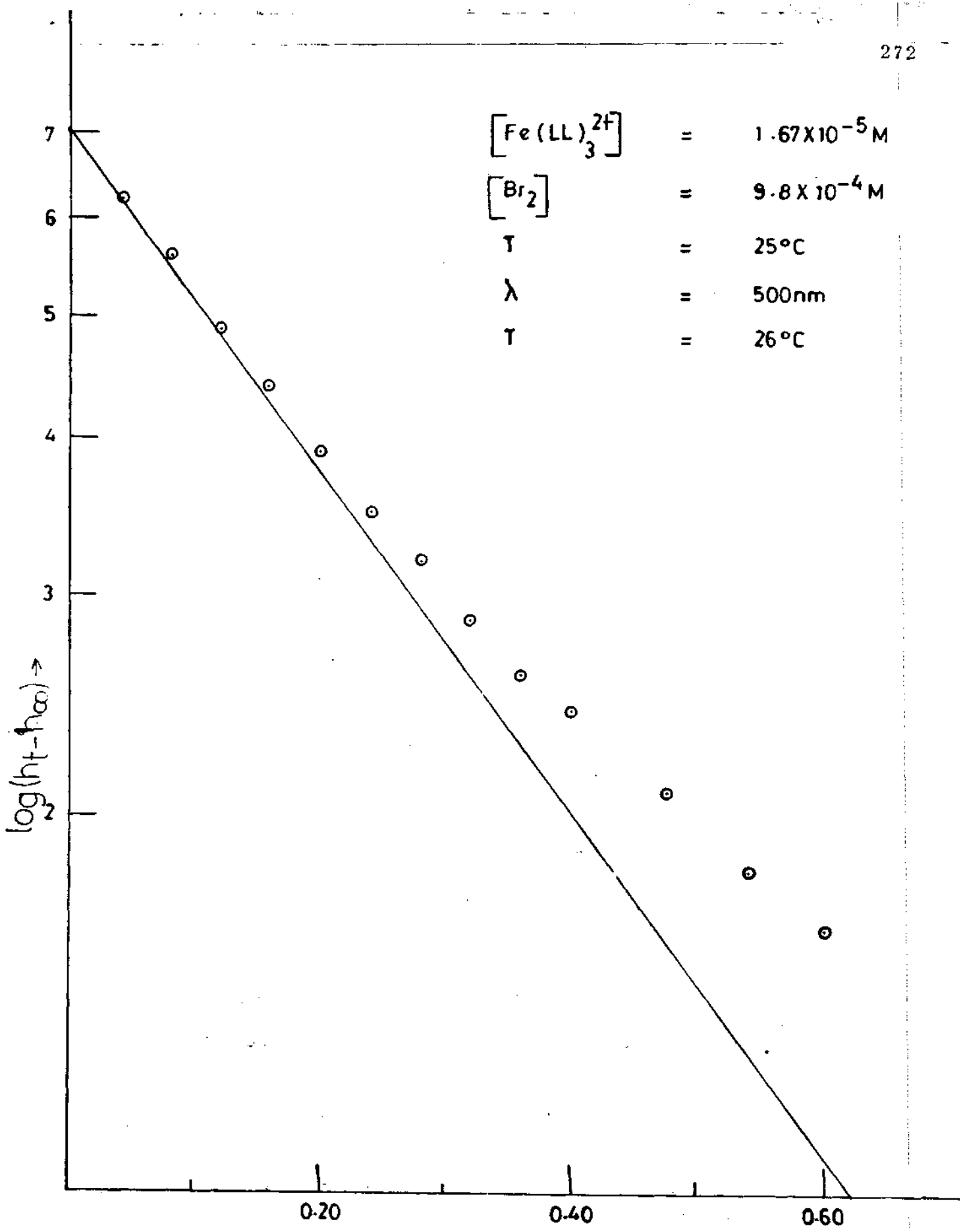


Fig. 3·8

Typical Pseudo - First - Order plot for the $Fe(3,4,7,8\text{-}(CH_3)_4\text{-}1,10\text{-phen})_3^{2+}$ — Br_2 reaction.

TABLE 3.2

Second-order rate constants for the $Fe(2,2\text{-bpy})_3^{2+}$ - Br_2 reaction

λ = 522nm, I = 0.5M(H_2SO_4/Li_2SO_4)

T = 25°C

10^4M $Fe(LL)_3^{2+}$	10^3M Br_2	$[H^+]$,M	k_{obs} $M^{-1}s^{-1}$
8.4	3.98	0.05	1.56
8.4	3.98	0.10	1.89
8.4	3.98	0.20	1.96
8.4	3.98	0.305	2.08
8.4	3.98	0.40	2.25
4.26	4.16	0.50	2.16
4.26	4.99	0.50	1.93
4.26	5.94	0.50	1.9
4.26	2.77	0.50	2.0
4.26	1.39	0.50	2.54
3.8	3.65	0.50	1.93
3.8	7.3	0.50	2.12
4.8	1.15	0.50	2.34
4.8	4.37	0.50	2.32
4.8	4.72	0.50	2.37
21.3	1.18	0.50	1.7
21.3	1.24	0.50	1.82
21.3	5.9	0.50	2.06

TABLE 3.3

Second order rate constants for the

$Fe(1,10\text{-phen})_3^{2+}$ - Br_2 reaction.

I = 0.50M ($H_2SO_4/Li_2S)_4$) T = 25°C

λ = 510nm

10^5M $Fe(LL)_3^{2+}$	10^3M Br_2	$[H^+]$M	$k_{obs}M^{-1}s^{-1}$
3.82	4.10	0.05	1.64
3.82	4.10	0.10	1.83
3.82	4.10	0.20	2.3
3.82	4.10	0.305	2.6
3.82	4.10	0.40	3.14
6.17	0.59	0.50	3.58
6.17	1.18	0.50	3.45
6.17	2.24	0.50	3.03
6.17	2.95	0.50	3.11

TABLE 3.4

Second-order rate constants for the

$Fe(5,6\text{-}(CH_3)_2\ 1,10\text{-phen})_3^{2+}$ - Br_2 reaction.

λ = 520nm, I = 0.5M(H_2SO + /Li_2SO_4)

T = 25°C

10^5M $Fe(LL)_3^{2+}$	10^3M Br_2	$[H^+]$,M	$k_{obs}M^{-1}s^{-1}$
3.45	6.8	0.05	41.8
3.45	6.8	0.10	43
3.45	6.8	0.20	42.9
3.45	6.8	0.30	41.8
3.45	6.8	0.40	41.3
3.45	6.8	0.50	41.5
3.4	0.61	0.50	43.5
3.4	0.97	0.50	40
3.4	1.22	0.50	41.4
3.4	1.46	0.50	41.3

TABLE 3.5

Second-order rate constants for the

$Fe(2,2,2\text{-terpy})_3^{2+}$ - Br_2 reaction

λ = 553nm, I = 0.5M(H_2SO_4/Li_2SO_4)

T = 25°C

10^5M $Fe(LL)_3^{2+}$	10^3M Br_2	H^+ M	k_{obs} $M^{-1}s^{-1}$
0.9	6.1	0.05	80.73
0.9	6.1	0.10	80.75
0.9	6.1	0.20	79.14
0.9	6.1	0.30	80.76
0.9	6.1	0.40	80.79
0.9	6.1	0.50	79

TABLE 3.6

Second-order rate constants for the

$Fe(4,4\text{-}(CH_3)_2 2,2\text{ - bpy})_3^{2+}$ - Br_2 reaction

λ = 532nm I = 0.5M(H_2SO_4/Li_2SO_4)

T 0 25°C

10^5M $Fe(LL)_3^{2+}$	10^3M Br_2	H^+ M	$k_{obs}M^{-1}s^{-1}$
1.68	0.89	0.50	295
1.68	1.77	0.50	295.4
1.68	2.66	0.50	294
1.68	3.55	0.50	298.6
1.68	4.10	0.30	295
1.68	4.30	0.10	195.6

TABLE 3.7

Second-order rate constants for the

$Fe(4,7\text{-}(CH_3)_2 1,10\ phen)_3^{2+}$ - Br_2 reaction

λ = 554nm, I = 0.5M(H_2SO_4/Li_2SO_4)

T = 25°C

10^5M $Fe(LL)_3^{2+}$	10^3M Br_2	H^+ M	$k_{obs}M^{-1}s^{-1}$
9.75	4.15	0.50	372
9.75	6.92	0.50	394.6
9.75	9.69	0.50	393.6
9.75	11.07	0.50	471.8
9.75	11.07	0.30	387
9.75	11.07	0.10	388

TABLE 3.8

Second - order rate constants for the

$Fe(3,\ 4,\ 7,\ 8\text{-}(CH_3)_4\ 1,10\text{-}phen)_3^{2+}$ - Br_2

λ = 500, I = 0.5M(H_2SO_4/Li_2SO_4)

T = 25°C.

10^5M $Fe(LL)_3^{2+}$	10^3M Br_2	H^+ M	$k_{obs}M^{-1}s^{-1}$
1.67	0.93	0.5	6344
1.67	1.19	0.3	6301
1.67	1.19	0.1	6299

Acid Dependence

The acid dependence of the reaction of the seven iron(11)-polypyridine complexes were investigated by determining the second-order rate constants while keeping the concentration of reactant ions constant. The acid concentration was varied from 0.05 - 0.5M. The results of such investigations are included in Tables (3.2 - 3.8).

Apart from the reaction of $Fe(2,2\text{-bpy})_3^{2+}$ and $Fe(1,10\text{-phen})_3^{2+}$ with bromine all the reactions of interest in investigation were acid-independent. The plots of k_o versus $[H^+]$ for the two acid dependent reactions are presented in Figures (3.9) and (3.10). These reactions display a linear dependence on $[H^+]$ with finite positive intercepts.

From the acid-dependence of these iron(11) polypyridine complexes, the observed rate constant k_{obs} can be written in the form:

$$k_{obs} = k_o' + k_H^+ [H^+]$$

where

$k_o = 1.7M^{-1}$ and $k_H^+ = 1.36M^{-1}s^{-1}$ for $Fe(2,2\text{-bpy})_3^{2+} - Br_2$ reactions and,

$k_o = 1.44\ M^{-1}s^{-1}$ and $k_H^+ = 4.15M^{-1}s^{-1}$ for the $Fe(1,10\text{-phen})_3^{2+} - Br_2$ reaction.

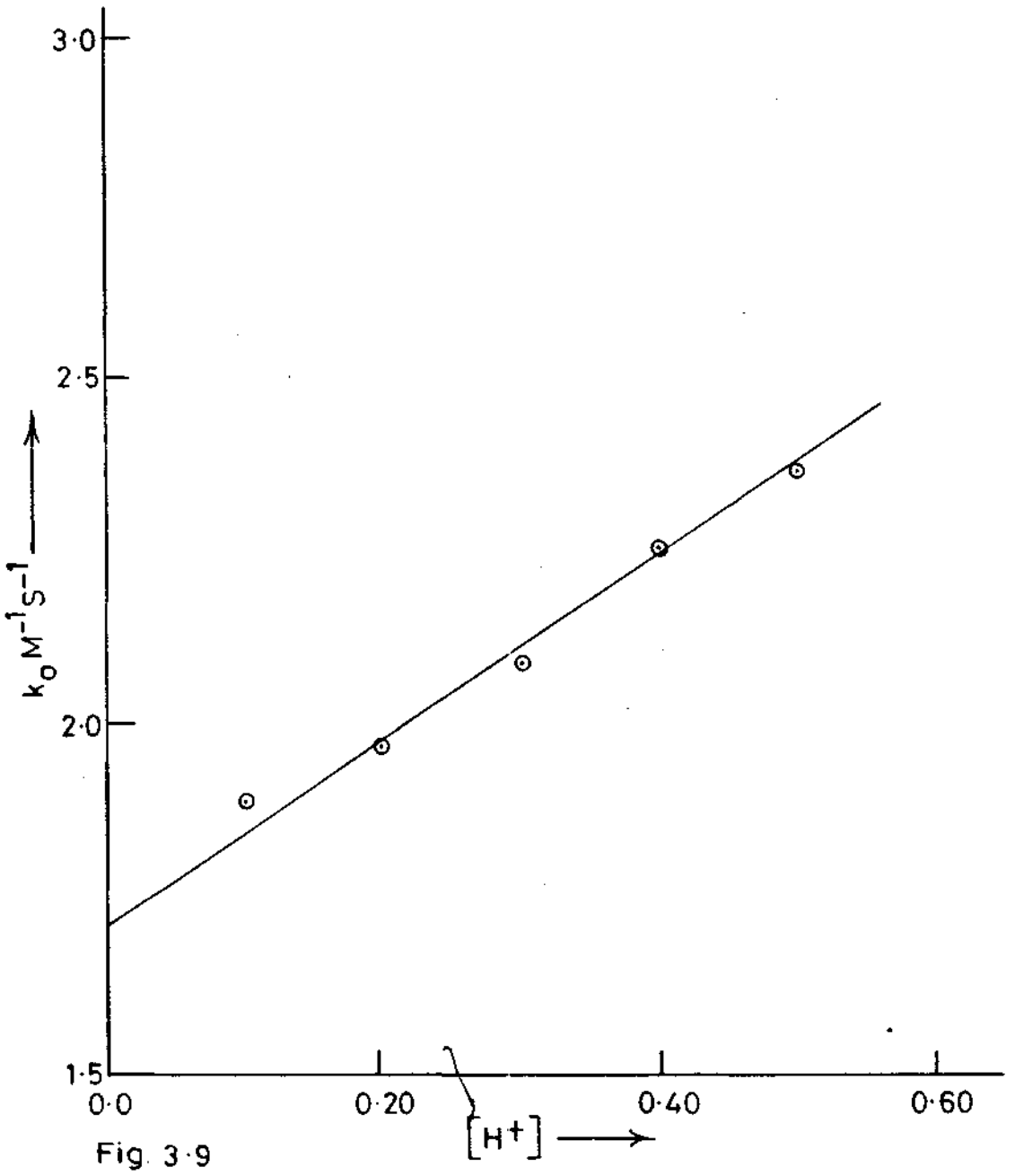


Fig. 3·9

Plot of the acid-dependent second-order rate constants for the $Fe(2,2^1\text{-bpy})_3^{2+}$ Br_2 reaction versus $[H^+]$

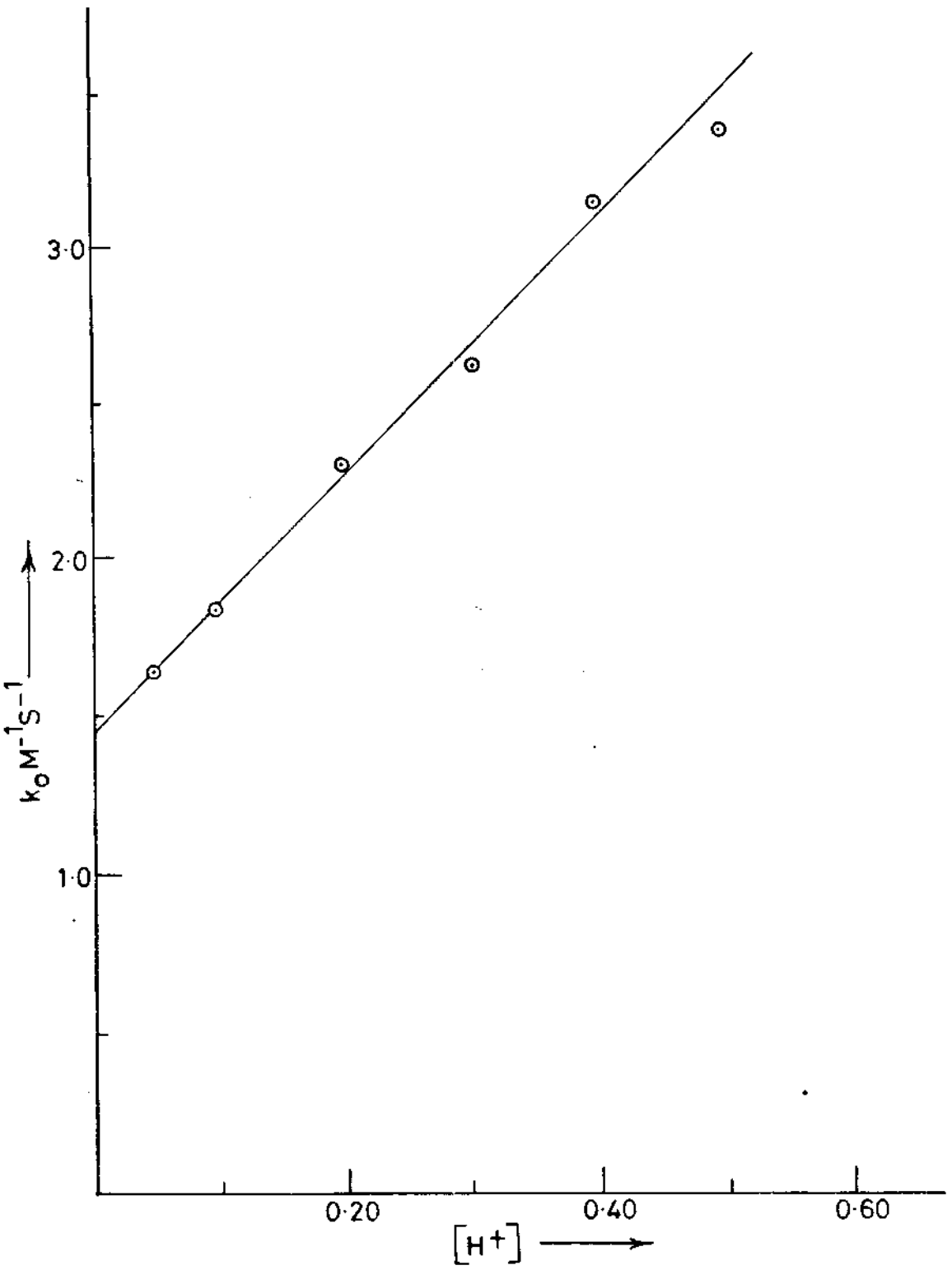


Fig. 3·10 Plot of the acid-dependent second-order rate constants for the $Fe(1,10\text{-phen})_3^{2+}$–$Br_2$ reaction versus $[H^+]$

Analysis of results:

The pseudo-first-order plots were linear to about 40-50% of each of the reactions. The nature of the curvature suggests that as the reaction proceeds, a back reaction becomes more effective and hence the following scheme can be proposed:

$$Fe(LL)_3^{2+} + Br_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe(LL)_3^{3+} + {}^{\cdot}Br_2^- \qquad \ldots(3.2)$$

$$Fe(LL)_3^{2+} + {}^{\cdot}Br_2^- \xrightarrow{k_2} Fe(LL)_3^{3+} + 2Br^- \qquad \ldots(3.3)$$

If we now apply the steady-state approximation to the concentration of ${}^{\cdot}Br_2^-$ we obtain,

$$[{}^{\cdot}Br_2^-] = \frac{k_1[Fe(LL)_3^{2+}][Br_2]}{k_{-1}[Fe(LL)_3^{3+}] + k_2[Fe(LL)_3^{2+}]} \qquad \ldots(3.4)$$

and hence the rate equation for the overall reaction becomes,

$$\text{Rate} = \frac{-d[Br_2]}{dt} = \frac{k_1k_2[Fe(LL)_3^{2+}]^2\,[Br_2]}{k_{-1}[Fe(LL)_3^{3}] + k_2[Fe(LL)_3^{2+}]} \qquad \ldots(3.5)$$

If $[Br_2] >> [Fe(LL)_3^{2+}]$ then

$$\text{Rate} = \frac{k_ok_2[Fe(LL)_3^{2+}]^2}{k_1[Fe(LL)_3^{3+}] + k_2\,[Fe(LL)_3^{2+}]} \qquad \ldots(3.6)$$

which is of the form

$$\frac{dx}{dt} = \frac{k_ok_2(a - x)^2}{k_{-1}x + k_2(a - x)} \qquad \ldots(3.7)$$

where a is the initial concentration of $Fe(LL)_3^{2+}$ and x is the amount of Br_2 consumed or half $Fe(LL)_3^{3+}$ formed. Assuming the $\frac{k_2}{k_{-1}} = R$ and integrating the above expression gives

$$(R - 1)\ln(a-x) - \frac{aR}{a - x} = (R - 1)\ln(a-R)' + k_o t \qquad ...(3.8)$$

Knowing the value of a and the value of x at different times, different values of R can be substituted into the above expression to recalculate the different values for the rate of change of each of the reactions with time. Using these newly calculated values of the rate of change, the left hand- side of equation(3.8) can be plotted against t to obtain k_o. This procedure was carried out for each run in all the reactions. The value of R that gave k_o very close to k_{obsd} derived from the initial portion of the pseudo-first-order plot, where the amount of product is very small and hence its effect on rate is negligible, for each run (with good correlation coefficient) was taken as the correct value of R for these runs. The average value of R for all runs in a reaction was taken as the true value of R for that particular reaction.

Some values of R determined for the reaction of $Fe(4,4\text{-}(CH_3)_2\ 2,2\ bpy)_3^{2+}$ and bromine are presented in Table (3.9). Figure (3.11) also show some of the plots from which these R values were obtained.

TABLE 3.9

Some thermodynamic and kinetic parameters determined for the $Fe(LL)_3^{2+}$ - Br_2 reactions

SYSTEM	ΔE^o	K x 10^9	R	k_{obs}	k_{-1}	k_{-1} x 10^9	k_2 x 10^{-9}	E^o Fe^{II}/Fe^{III}
$Fe(2,2,-bpy)_3^{2+}$ - Br_2	-0.525	1.26	0.54	2.1	3.89	3.08	1.66	0.56
$Fe(1,10\ phen)_3^{2+}$ - Br_2	-0.55	0.48	3.0	3.3	1.1	2.31	6.93	1.06
$Fe(5,6-(CH_3)_2$i, 10 phen$)_3^{2+}$	-0.46	16	0.59	41.5	70.3	4.4	2.59	0.97
$Fe(2,2,2$ - terpy$)_3^{2+}$ - Br_2	-0.42	76.1	0.54	80.2	148.5	1.95	1.05	0.93
$Fe(4,4-(CH_3)_2 2,2-bpy)_3^{2+}$ - Br_2	-0.37	53.5	0.16	296	1849	3.42	0.55	0.88
$Fe(4,7-(CH_3)_2\ 1,10\ phen)_3^{2+}$ - Br_2	-0.36	791	0.45	387	859	1.09	0.49	0.87
$Fe(3,4,7,8-(CH)_3 1,10phen)_3^{2+}$ - Br_2.	-0.30	823	0.27	6300	2.3×10^4	2.84	0.76	0.81

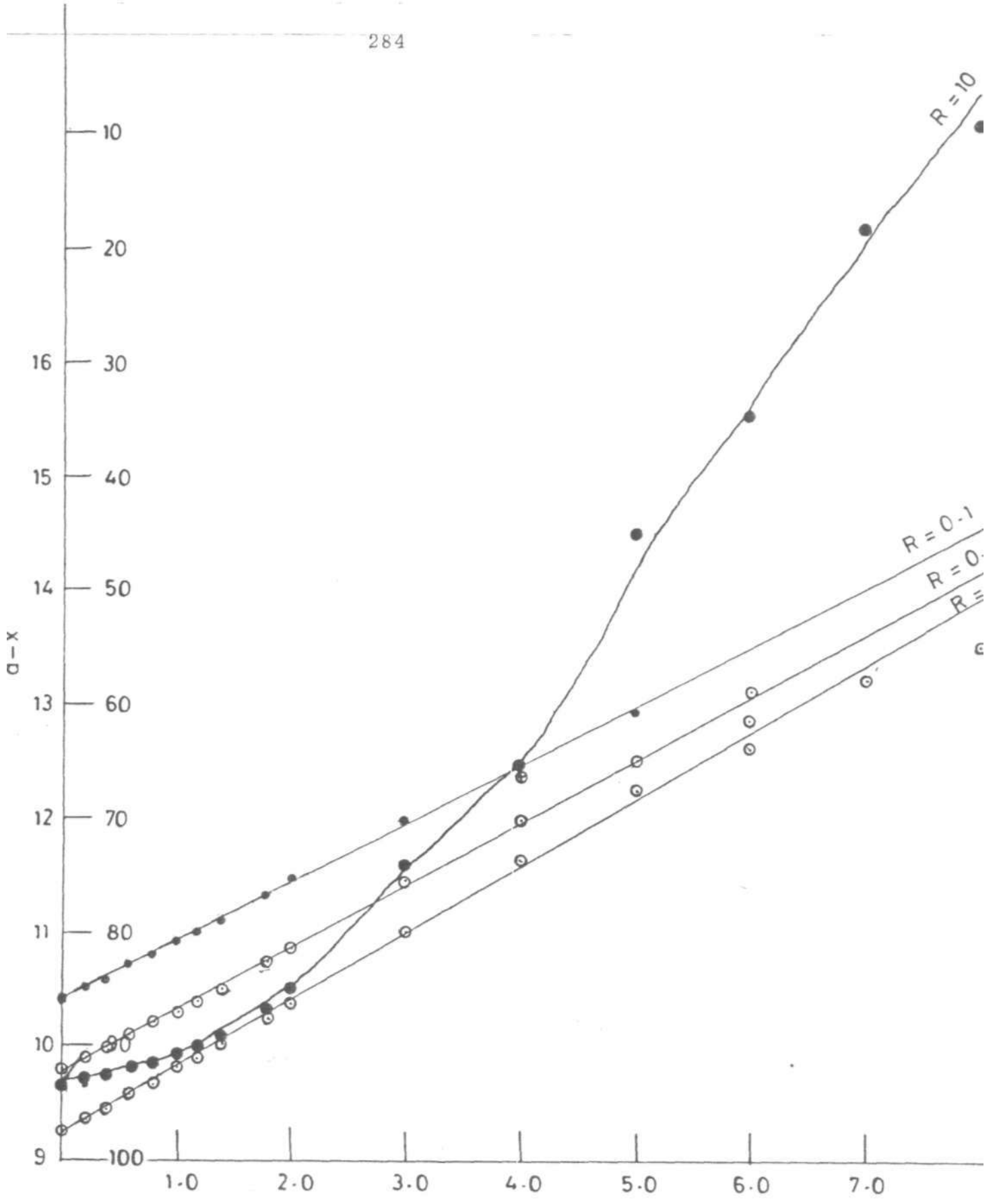


Fig. 3.9

Typical plots for the determination of $R = k_2\big|_{k_{-1}}$ for the oxidation of

$Fe(4,4'-(CH_3)_2-2,2'-bpy)_3^{2+}$ by Bromine.

TABLE (3.9)

R values calculated for the

$Fe\ (4,4\text{-}(CH_3)_2\ 2,2\text{-bpy})_3^{2+}$ - Br_2 reaction.

$\{Fe(LL)_3^{2+}\} = 1.08 \times 10^{-5}M$,

$\{Br_2\} = 2.81 \times 10^{-3}M$.

$k_o = 193.72M^{-1}$

R	0.08	0.10	0.14	0.16
$k_{(calc)}(M^{-1}s^{-1})$	145.6	153.2	168.4	191.2
R	0.18	0.20	0.21	10
$k_{(calc)}M^{-1}s^{-1}$	198.1	205.2	208.5	3.6×10^3

The preferred R for this system was taken as 0.16. This is because apart from being from a very linear plot it has the best correlation coefficient of 98.7% when compared with other linear plots obtained as shown in Figure (3.11). The value of $k_{calc} = 191.2M^{-1}s^{-1}$ is also in good agreement with the experimentally determined $k_o = 193.72M^{-1}s^{-1}$ obtained from the initial portion of the pseudo-first-order plots.

The average value of $R = k_2/k_{-1}$ so obtained for each of the systems investigated in this work are presented below:

System	R
$Fe(1,10\text{-phen})_3^{2+} - Br_2$	3.0
$Fe(5,6\text{-}(CH_3)\text{-}1,10\ phen)_3^{2+} - Br_2$	0.59
$Fe(2,2\text{-bpy})_3^{2+} - Br_2$	0.54
$Fe(2,2,2\text{-terpy})_3^{2+} - Br_2$	0.54
$Fe(4,4\text{-}(CH_3)_2\ 2,2\ bpy)_3^{2+} - Br_2$	0.16
$Fe(4,7\text{-}(CH_3)_2\ 1,10\ phen)_3^{2+} - Br_2$	0.45
$Fe(3,4,7,8\text{-}(CH_3)_4\ 1,10\ phen)^{2+} - Br_2$	0.27

Using the E^o values reported for the Fe^{II}/Fe^{III} couple involving these phenanthroline complexes and the E^o value for the reaction:[25]

$$Br_2 + e \rightleftharpoons {}^{\cdot}Br_2^- \qquad \ldots(3.9) \qquad E^o = 0.51V$$

the equilibrium constant $K = \frac{k_1}{k_{-1}}$ was calculated for equation (3.2). Based on the assumption that $k_o = \frac{k_2 k_1}{k_{-1}}$

with the value of R determined for each system, the respective rate constants k_2, k_1 and k_{-1} for each of the reactions was calculated and are presented in Table (3.9).

Linear Free Energy Correlation

The Marcus relation[14] for outer-sphere reactions is given by the expression

$$k_{12} = (k_{11}k_{22}K_{12}f)^{\frac{1}{2}} \qquad ...(3.10)$$

where $\log f = (\log K_{12})^2/(4\log k_{11}k_{22}/Z^2)$

and Z is the collision frequency for the uncharged reactant molecules in solution, usually taken as $10^{11}M^{-1}s^{-1}$. Equation (3.10) can be re-written as,

$$\log k_{12} - 0.5\,(\log k_{11} + \log f) = 0.5\log k_{22} + 0.5\log K_{12} \qquad ...(3.11)$$

For a series of reactions occuring by the outer-sphere mechanism and involving a common oxidant, a plot of the left-hand-side of the above equation against $\log K_{12}$ should be linear with slope 0.5 and intercept $0.5\log k_{22}$. Based on this linear free energy relationship, the rate of reactions of the seven iron(11) polypyridine complexes with bromine investigated in this work has been correlated with the free energy change of the rate-determining step. This correlation of free energy change with rate was however done for $k_1 = k_{12}$ as determined in the analysis of the results, using obtained R values. k_1 is defined as the rate of the reaction

$$Fe(LL)_3^{2+} + Br_2 \xrightarrow{k_1} Fe(LL)_3^{3+} + {}^{\cdot}Br_2^- \qquad ...(3.12)$$

which is the rate constant for the forward step of the rate determining step as postulated for the reactions of interest.

K_{12} are those reported in Table (3.10) calculated from the ΔE^{o} for the reaction in equation (3.12) ($E^{o}(\cdot Br_2/Br_2)$ = 0.51V). $k_{22}(Fe(LL)_3^{3+}/Fe(LL)_3^{2+})$ = $3.3 \times 10^{8} M^{-1}s^{-1}$ was employed for these calculations as earlier reported in literature.[26] The result of the calculated parameters used for the Marcus plot is presented below in Table (3.10)

TABLE 3.10

Some calculated parameters employed in the Marcus plot for the $Fe(LL)_3^{2+}$ - Br_2 reactions

Complex	$\log k_{12} - 0.5(\log k_{22} + \log f)$	$\log K_{12}$
1. $Fe(3,4,7,8\text{-}(CH_3)_4\text{-}1,10\ phen)_3^{2+}$	0.494	6.08
2. $Fe(4,4\text{-}(CH_3)_2 2,2\text{-}bpy)_3^{2+}$	-0.583	-6.27
3. $Fe(4,7\text{-}(CH_3)_2 1,10\ phen)_3^{2+}$	-0.938	-6.10
4. $Fe(2,2,2'terpy)_3^{2+}$	-1.56	-7.12
5. $Fe(5,6\text{-}(CH_3)_2 1,10\ phen)_3^{2+}$	-1.78	-7.8
6. $Fe(2,2\text{-}bpy)_3^{2+}$	-2.85	-8.9
7. $Fe(1,10\ phen)_3^{2+}$	-3.32	-9.32

The plot of the left-hand-side of equations (3.11) against log K_{12} gave a linear plot as shown in Figure (3.10) Least-mean-square analysis of the data employed for this plot gave a slope and intercept 0.78± and 4.0± respectively. From the intercept it follows that $0.5 \log k_{11}(Br_2/Br_2^-) = 4$ or $k_{11} = 10^8 M^{-1}s^{-1}$

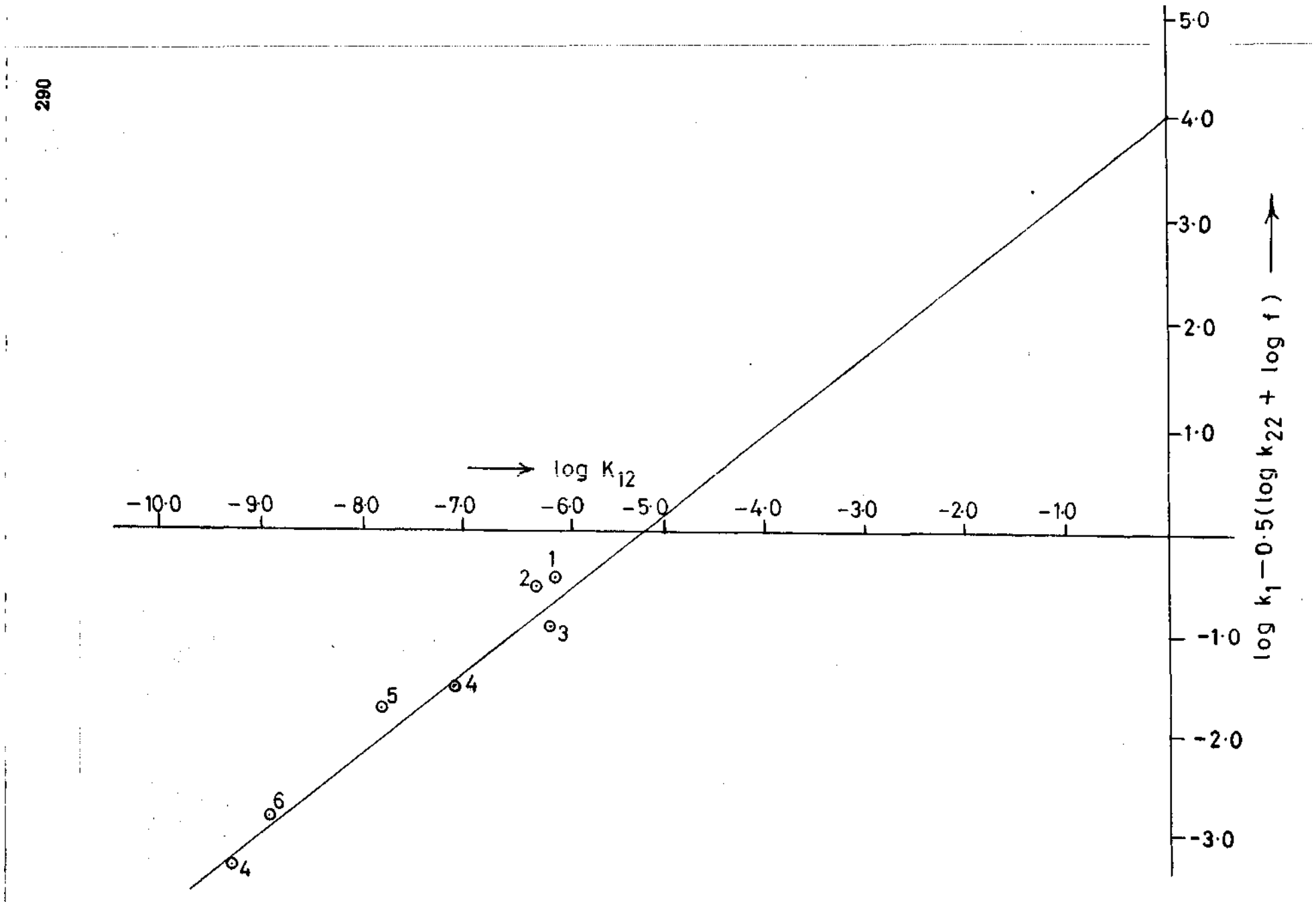


Fig. 3·11 Marcus plot for the $Fe(LL)_3^{2+}$ − Br reactions.

D I S C U S S I O N

The stoichiometry determined for two of the reactions involving these iron(11)-polypyridine complexes and aqueous bromine showed that two moles of the $Fe(LL)_3^{2+}$ complex is consumed by one mole of bromine. The overall reaction of these non-complementary reactions can hence be represented as:

$$2Fe(LL)_3^{2+} + Br_2 = 2Fe(LL)_3^{3+} + 2Br^-$$

The pseudo-first-order plots of the reactions were linear only to between 30 - 40% of the reaction and thereafter the curvature obtained suggests an increasingly important back reaction or inhibition by one of the products. The non-linearity of the pseudo-first-order plots made the determination of the order of the reaction difficult. However most reactions that have been investigated involving halogens have been rationalized by a series of univalent steps with $\cdot X_2^-$ as a transient intermediate.[27-36] The following mechanistic steps consistent with earlier investigated reactions of halogens is therefore proposed for all the reactions of interest in this investigation:

$$Fe(LL)_3^{2+} + Br_2 \underset{}{\overset{k_1}{\rightleftharpoons}} Fe(LL)_3^{3+} + \cdot Br_2^- \qquad ...(3.2)$$

$$Fe(LL)_2^{2+} + \cdot Br_2^- \xrightarrow{k_2} Fe(LL)_3^{3+} + 2Br^- \qquad ...(3.3)$$

Since equation (3.2) is usually the rate determining step for such a mechanism because the second step of the postulated mechanism involving the reaction of the halogen radical,

$^{\cdot}Br_2^-$, is expected to be very fast, an order of two was assumed for the reaction of interest in this investigation. The application of the steady state hypothesis to $^{\cdot}Br_2^-$ gave a rate law of the form:

$$\text{Rate} = \frac{-d}{dt}[Br_2] = \frac{k_1 k_2 [Fe(LL)_3^{2+}]^2 [Br_2]}{k_{-1}[Fe(LL)_3^{3+}] + k_2[Fe(LL)_3^{2+}]}$$

The "extent of reversibility" for each of the reactions investigated, given by $R = k_2/k_{-1}$, was determined by iterative procedure as stated under the results section. The R values ranged from 0.16 to 0.59 except for the reaction involving the $Fe(1,10\text{-phen})_3^{2+}$ complex where R was 3.0. The exceptionally high value of R for the latter complex may be as a result of the dissociation of the $Fe(1,10\text{-phen})_2^{3+}$ product of the reaction in the acid medium employed. The R values obtained for these reactions highlight the relative importance of the back reaction on the overall reaction for each of the system investigated. From the values of R for each of the reactions of interest and K, the equilibrium constant calculated from ΔE^o for these reactions, the value of k_1, k_{-1} and k_2 were calculated. For all the reactions, apart from that involving the $Fe(1,10\text{-phen})_3^{2+}$ complex, k_{-1} was about twice the value of k_2.

Since Marcus published his theory in 1959,[14] predicting a simple relationship between the rate constant k_{12} for electron transfer and K_{12}, the equilibrium constant for the reaction, several systems displaying the correct free energy dependence have been reported. For example the $Fe^{2+}(aq)$

reductions of polypyridine iron(111) complexes the cerium(1V) oxidation of polypyridine iron(11) complexes[4] and the oxidation of iodide by poly(pyridine)-iron(111) complexes and hexachloroiridate(1V) ion. In the latter work when the pertinent work terms were included in the Marcus equation for cross-reactions excellent agreement between calculated and observed rate constants was obtained for all the oxidants. The Marcus cross-reaction relation has also been tested for the reactions of interest in this work. A plot of $\log k_1 - 0.5(\log k_{22} + \log f)$ versus $\log K_{12}$ for all the systems investigated gave a slope of 0.78 and an intercept of 4. Since from the relation the intercept should be $0.5 \log k_{11}$ ($k_{11} = 29M^{-1}s^{-1}$ - exchange rate for $Br_2/\cdot Br_2^-$ couple)[25] then $k_{11} = 100M^{-1}s^{-1}$. Inherent in the assumption of Marcus in deriving the relation is an expected slope of 0.5. Hence the slope obtained is much higher than the theoretically predicted value. Also the value of $k_{11} = 100M^{-1}s^{-1}$ calculated from the intercept of the Marcus plot is much higher than the value of $29M^{-1}s^{-1}$ earlier reported[25] for the exchange reaction involving $\cdot Br_2^-$ and Br_2.

Such a poor agreement between theory and experiment had earlier been noted[3,4,37] for some Fe^{2+} - $M(LL)_3^{3+}$ reactions (LL = 2,2′-bpy or 1,10-phen derivative and M = Fe, Ru and Os) For the $Fe^{2+}aq$ - $Ru(LL)_3^{3+}$ plot the descrapancy was only in the intercept of the plot.

Marcus theory of adiabatic electron transfer proceeds from the assumptions that within the activated complex for electron transfer, the probability of electron transfer

is unity. Other additional assumptions made are that the work terms for the self-exchange and cross-reactions are the same, that the electron-transfer reagents may be treated as spherical, structureless reactants and that the motion of the inner coordination shells are harmonic. Various attempts have been made to assess these assumptions with the aim of modifying the Marcus relation to allow a better fit between theory and experiment.

However in the reactions of interest in this investigation, apart from $Fe(2,2'\text{-bpy})_2^{2+}$, all the $Fe(LL)_3^{2+}$ complexes are approximately of the same size hence solvation effects is unimportant. Moreover, Br_2 has no change hence coulombic effects are negligible. To be able to rationalize the poor fit between theory and experiment in the application of the Marcus theory to the reactions of interest in this work one needs to take a closer look at the systems in general. It has earlier been suggested that the large descrepances usually observed for the iron, osmium and ruthenium polypyridine complexes do not merely result from the presence of polypyridine ligands but depends on the complex as a whole.[24] Iron, ruthenium and Osmium polypyridine complexes manifest several properties as a class. In the divalent state, relatively strong mixing of the metal d and ligand π^* orbitals occur so that significant metal electron density exists on the ligands. This mixing of the orbitals may probably account for the high self-exchange rates ($\sim 1.2 \times 10^9 M^{-1}s^{-1}$) that has been reported for

the iron(II)polypyridine complexes[38]. The assessment of the slowness of the $Fe^{2+}aq$ - $M(LL)_3^{3+}$(M = Fe, Os, Ru) cross reactions led to the conclusion that it is as a result of the fact that the cross-reaction cannot proceed via a detailed pathway which is common to the exchange process for both reactants,($\pi^* \rightarrow \pi^*$) pathway is highly favoured for the $Fe(LL)_3^{3+,2+}$ exchange reaction[24]. Such a mismatch of orbitals w characterized all the reaction investigated in this work could result in the breakdown of the Marcus model for two reasons:

(1) the first possibility is that of non-adiabaticity of electron-transfer and furthermore

i.e. $P_{12} \neq (P_{11}P_{22})^{\frac{1}{2}}$

(where p is the probability of electron transfer).

This implies that the overlap of orbital between Br_2 and the $Fe(LL)_3^{2+}$complexes may be much proper than the geometric mean of overlap of orbitals involving the exchange reactions, of these reactants

(2) the second possibility is that, inherent in the Marcus treatment is the assumption that the interaction between reactant and product surfaces is large enough for the probability of crossing to be unity but not so large that the height of the barrier is appreciably lowered. It is concievable that the $\pi^* \rightarrow \pi^*$ interaction most probably for the $Fe(LL)_3^{2+}$- $Fe(LL)_3^{3+}$exchange reactions may result in a splitting energy too large for the assumptions of the original Marcus treatment to apply. If this is the case the exchange reaction would be effectively too rapid:that is its rate will not be determined by the zero interaction

barrier but by a barrier lowered by the interaction energy. In cross-reactions where the special $\pi^* - \pi^*$ interaction operative in exchange reactions is not possible, the zero interaction approximation determines the appriopriate intrisic barrier to electron transfer.

The acid-dependence study of the reactions of interest in this investigation showed that only the reactions involving $Fe(1,10\text{-phen})_3^{2+}$ and $Fe(2,2\text{-bpy})_3^{2+}$ with bromine showed any dependence of rate on the acid concentration of the reaction medium. The rates of these reactions increased with $[H^+]$ in the acid range. The linear dependence on $[H^+]$ observed follow a rate law of the form.

$$k_{obs} = k_o + k_{H^+}[H^+]$$

with k_o and k_{H^+} the acid independent and acid-dependent rate constants respectively.

This observation is contrary to the dependence observed in the study of the kinetics of the oxidation of iron(11) ion by Tris (1,10-phen) - iron(111) ion where the rate of the reaction increased with decreasing acid concentration.[39] The acid dependence of the latter reaction was rationalized on the basis of reversible association of $Fe(phen)_3^{3+}$ with H^+ to yield $H\,Fe(phen)_3^{4+}$[21,40] which reacts at a slower rate than the native complex. A number of oxidation-reduction reactions of iron(11) polypyridine complexes that have also been studied showed that the effect of acid on individual reaction rate is small.[41]

That the change in $[H^+]$ affected only two out of the seven reactions investigated indicates that it is the $Fe(1,10phen)_3^{2+}$ and $Fe(2,2\ bpy)_3^{2+}$ that are responsible for the increases in rate with $[H^+]$ not the bromine. Bipyridine and phenanthroline behave as weak bases usually forming monoprotonated species,[42]. Although the basicity of these ligands is expected to decrease considerably on complexation it is still expected that $Fe(LL)_3^{2+}$ will be more basic than $Fe(LL)_3^{3+}$. Hence the observed increase in rate with $[H^+]$ for the reaction of the $Fe(1,10\ phen)_3^{2+}$ and $Fe(2,2'bpy)_3^{2+}$ ions with Br_2 may be attributed to the formation of $HFe(LL)_3^{3+}$ species which reacts at a faster rate with Br_2 due to increased polarization and hence enhanced coulombic interaction. Lack of dependence of the reactions involving the other substituted polypyridine iron(11)-complexes on $[H^+]$ might by due to the steric hinderance leading to the inassessibility of the nitorgen atoms in these complexes to protonation.

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C H A P T E R 4

Substitution Reaction: Thiocyanate and Chloride ion assisted dissociation of the oxo-bridged dimer $[(bpy)_2ClRuORuCl(bpy)_2^{2+}]$ in acidic medium.

C H A P T E R 4

A brief Outline of Mechanistic Concepts and Terminologies in Substitution Processes:

Substitution reactions are reactions which could either involve the replacement of a coordinated ligand by a free ligand in solution or the replacement of a coordinated metal ion by a free ligand in solution. A change in oxidation state of the metal ion center might be a consequence of substitution but no change in oxidation state occurs during substitution. Intense kinetic studies have been conducted into substitution reactions especially into those involving octahedral and square-planar complexes.[1-10] Investigations have revealed that the rate constants for substitution vary from extremely slow exchange of NH_3 with $Co(NH_3)_6^{3+}$ ion in aqueous ammonia solution,[11] where no exchange takes place in 162 days to the diffusion controlled exchange of H_2O between $Cu(H_2O)_6^{2+}$ and water with half-life approximately 10^{-8} seconds.[12] For this upper limit of substitution the whole armour of techniques available must be utilized in the measurement of rates of such fast processes.

The metal ions that undergo substitution into their inner coordination spheres in a matter of seconds are designated "labile", whereas those in which substitution occur in a minute or more are usually considered

as 'inert' complexes[13].

The importance of substitution reactions in coordination chemistry cannot be over-estimated. They are very frequently the first step in a redox process or in a dimerization or polymerization reaction[14-17]. The proper understanding of the kinetics of substitution reactions thus constitutes an inevitable prerequisite for defining the best conditions for a preparative or analytical procedure in coordination chemistry. Of importance are substitution reactions in the reactions of metalloenzymes and the transport of metal ions through cell membrances.[19]

The molecularity with respect to substitution reactions can be defined in terms of the timing of the bond-making or bond-breaking aspects of substitution. This bond-making or bond-breaking processes have been found to be either synchronous or non-synchronous.

The synchronous process takes place in one step and has one transition state with no intermediates and can be represented by the following equation:

$$L + M'X \rightleftharpoons L....M'....X \rightarrow LM' + X \quad .....(4.1)$$

This is described by the energy profile shown in Figure (4.1).

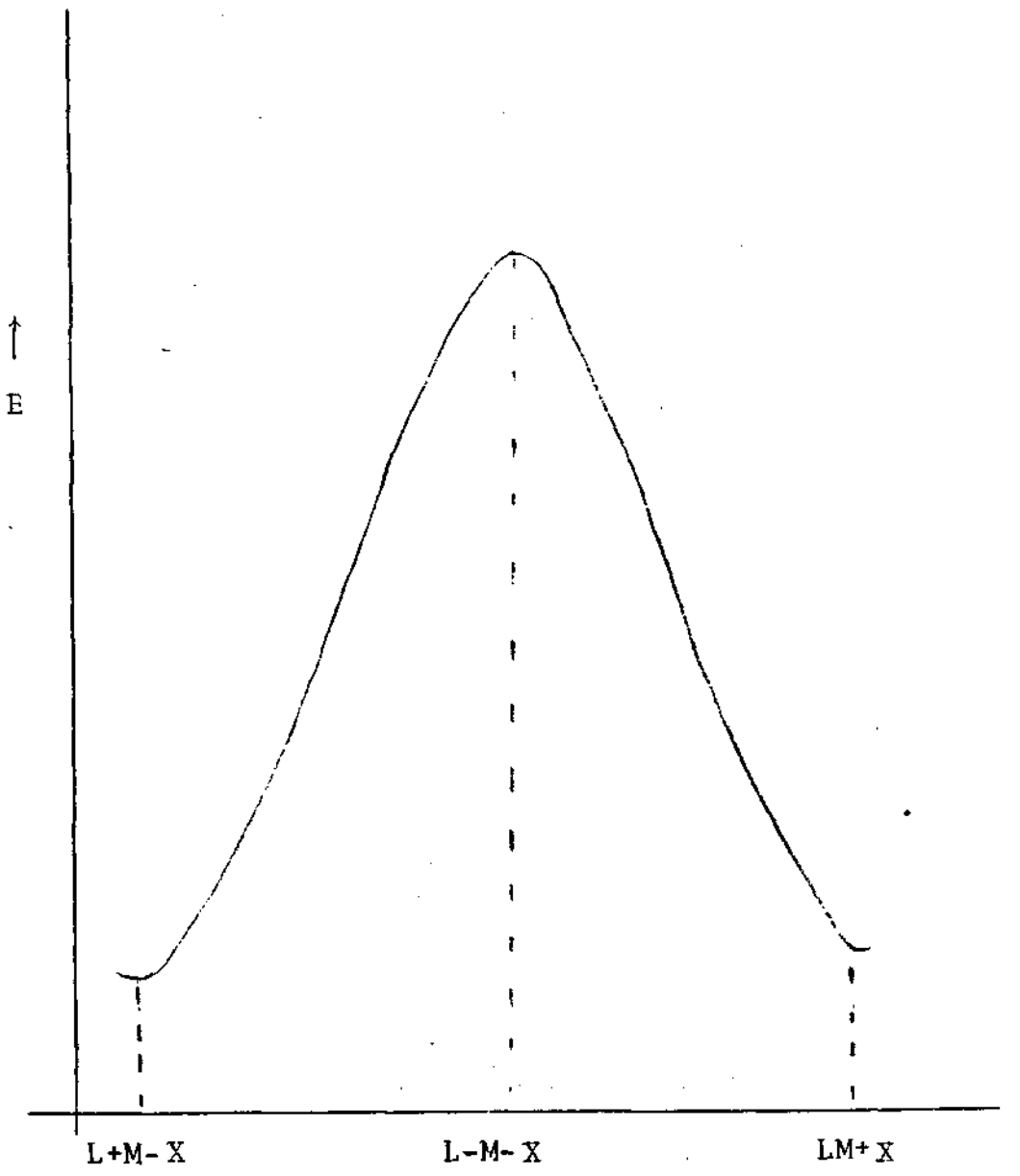


Figure 4.1: Energy profile for synchronous substitution process.

For this synchronous substitution process, the transition state determines both the energetics (rate) and the stereochemistry of the reaction.

There are two options for the non-synchronous process: (i) bond-breaking preceeding bond-making (dissociative) or (ii) bond-making preceeding bond-making (associative). In both cases there will be an intermediate as represented by the energy profiles shown in Figures (4.2).

Some highlights of the above schemes are:

(i) the intermediate is different from the transition state

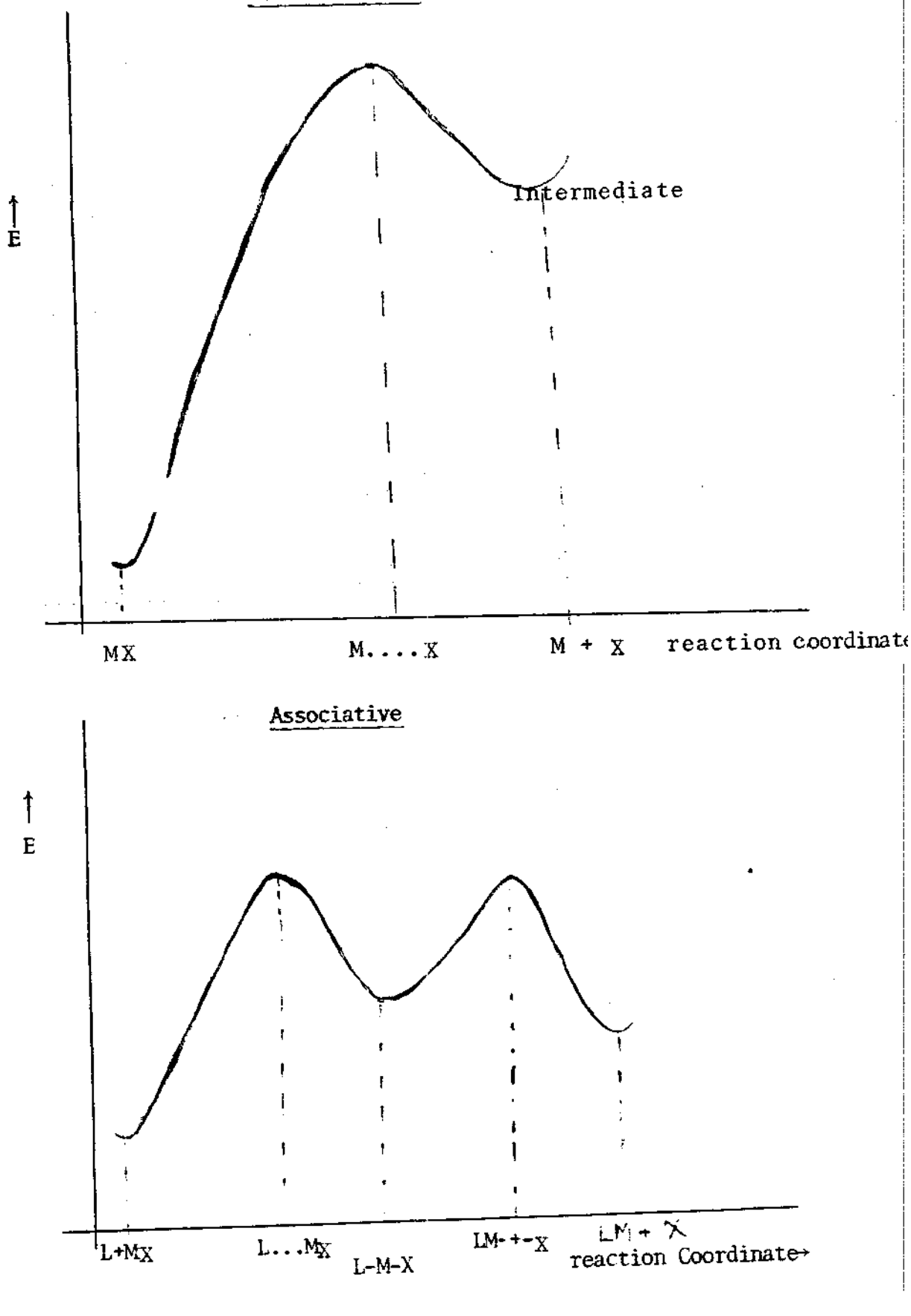
(ii) when there is an intermediate, there are two transition states, one for each stage of substitution,

(iii) there is no restriction upon the lifetime of the intermediate. (although generally it may be extremely short-lived and highly reactive, this may not necessarily be the case).

The original S_N nomenclature proposed by Ingold[20] has now been modified to take account of lower coordination number. Cases where definite evidence of an intermediate of lower coordination number exist is referred to as S_N 1 lim (lim = limiting) and the extreme case of associative mechanism when the intermediate has virtually no bond weakening is termed S_N 2 lim and the rest is placed in between. An attempt to provide an operational definition of substitution reactions has been made by Langfold and Gray in their excellent monograph on substitution reactions.[21]

Figure (4.2)

Energy profile for the non-syncronous substitution process.



They introduced the concept of stiochiometric mechanism and proposed three simple pathways:

1) the dissociative (D)[20] process with an intermediate of lower coordination number (equivalent to S_N1)[21] For this process the entering ligand does not interact with the reaction center in the transition state. Using the substitution of aquometal ions as an example, the following reaction steps can be proposed,[22]

$$M - OH_2 \rightleftharpoons M + OH_2 \qquad k_1, k_{-1} \qquad \ldots.(4.2)$$

$$M + L \rightarrow M - L \qquad k_2 \qquad \ldots.(4.3)$$

Applying the steady state approximation we obtain the rate:

$$\frac{-d}{dt}[M\text{-}OH_2] = \frac{k_1 k_2 \{M\text{-}OH_2\}\{L\}}{K_{-1}\{H_2O\} + k_{-2}\{L\}}$$

and if k/L is the second-order rate constant, equation can be written as:

$$\frac{-d}{dt}\{M - OH_2\} = k\{M\text{-}OH_2\} = a\frac{\{M\text{-}OH_2\}\{L\}}{1 + b\{L\}} \qquad (4.5)$$

where

$$a = \frac{k_1 k_2}{k_{-1}\{H_2O\}} \qquad \text{and} \qquad b = \frac{k_2}{k_{-1}\{H_2O\}}$$

The values of k are proportional to L when L is low, so that k/L will be second-order rate constant. In a few systems however, as the concentration of L becomes high, deviation from constancy for the function k/L are

observed and eventually a point may be reached in which k is a constant and it is no longer dependent on L as observed[23] in the replacement of H_2O in Co(111) hematoporphyrine $1X(H_2O)_2$ by CN^- and NCS^- as shown in Figure (4.3).

The limiting rate with NCS^- is clearly shown but the deviation from linearity is barely discernable with CN^-. In the limit of an S_N1 reaction, second order kinetics are obtained when $k_2[L] \ll k_{-1}[H_2O]$, that is, when the intermediate is much more effectively scavenged by H_2O than by the ligand L. This leads to second order rates equivalent to $k_1k_2/k_{-1}[H_2O]$. At high ligand concentrations, L may effectively compete with H_2O for the intermediate and loss of $M\text{-}OH_2$ will be governed by first order step, k_1.

Strong labilizing groups such as CH_3, CN^-, or SO_3^{2-} when present in a complex, promote the dissociative mechanism. In certain instances, there is a reduction in the reaction times from say hours normal with Co(111)[24,25] and Pt(1V)[26,27] to seconds.

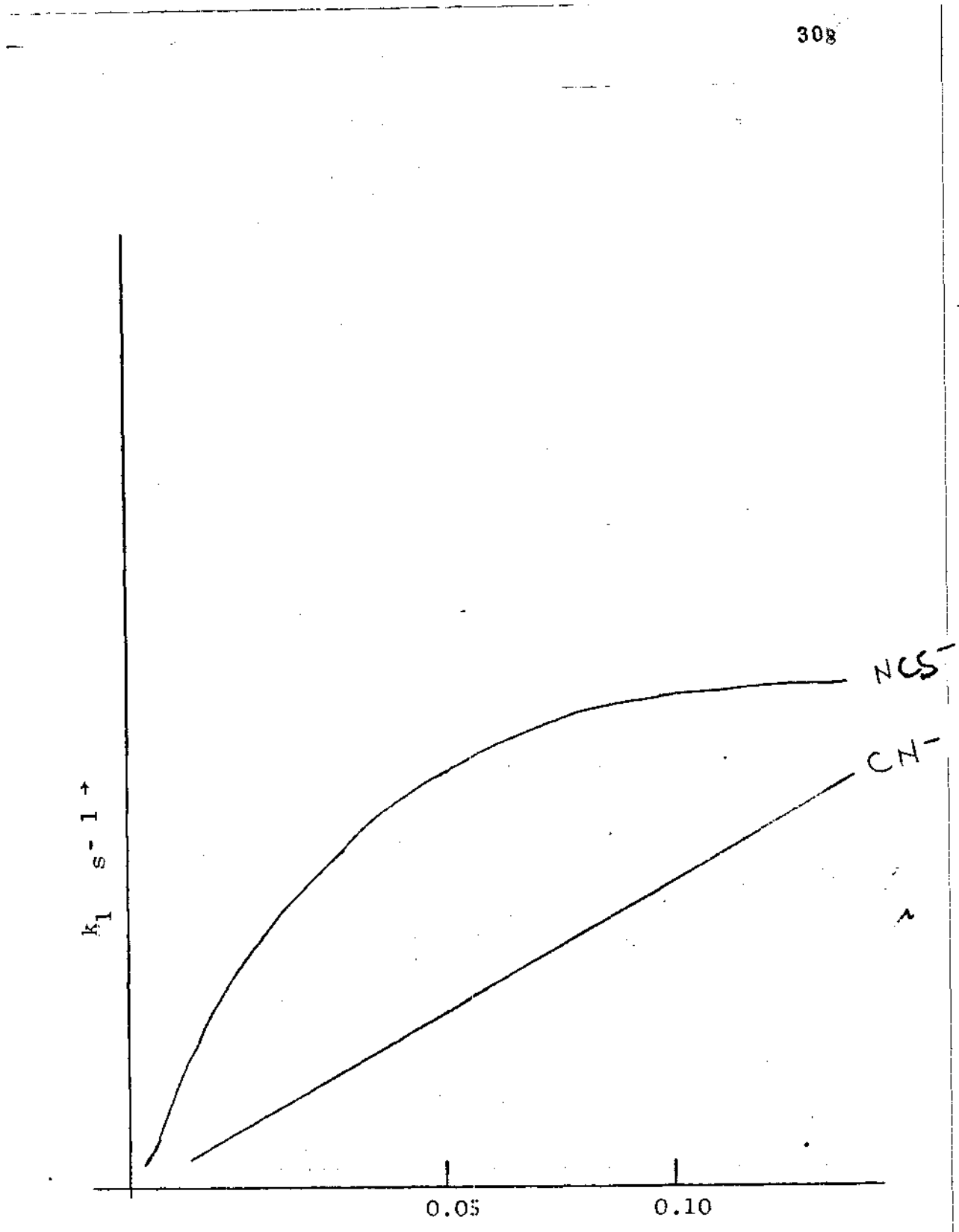


Figure 4.3: Pseudo-first-order rate constant ($k_1 sec^{-1}$) versus [anion] for replacement of H_2O in Co(111) hematoporphyrin $1X(H_2O)_2$ by CN^- and NCS^-. The limiting rate with NCS^- is clearly shown but the deviation from linearity is barely discernable with CN^-

The rate constants for the reactions of $Fe(H_2O)_6^{3+}$ and $Cr(H_2O)_6^{2+}$ with a variety of ligands are wider spread than the rate constants for $FeOH^{2+}$ and $CrOH^{2+}$. The possibility is that this may result from the coordinated hydroxyl group promoting dissociation through Π-bonding.[28] The ligand dependence would be more pronounced, were it not for compensating $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values.[29] Although a dissociative mechanism is favoured in a number of the reactions of octahedral complexes, evidence is growing for a contribution by the attacking ligand in selected systems.

(2) The Interchange(I)[20] or S_N1 IP (ion pair) mechanism in which the act of substitution is synchronous although no intermediate is involved. For an aquo complex, this involves the dissociative interchange of H_2O and within an outersphere complex or ion pair which is rapidly formed from reactants, viz:

$$M\text{-}OH_2 + L \rightleftharpoons M\text{-}OH_2.L \qquad K_o \qquad \text{.....(4.6)}$$

$$M\text{-}OH_2.L \rightarrow M\text{-}L + OH_2 \qquad k_o \qquad \text{.....(4.7)}$$

The application of the steady state approximation leads to a similar kinetic expression as for the dissociative case, i.e.

$$\frac{-d}{dt}\{M\text{-}OH_2\} = \frac{k_o K_o \{M\text{-}OH_2\}\{L\}_o}{1 + K_o\{L\}_o} \qquad \text{.....(4.8)}$$

where $\{L\}_o$ indicates the total starting concentration of the species. Comparison with equation (4.5) shows that $a = k_o K_o$ and $b = K_o$.

For the interchange mechanism, second order kinetics hold when k_o {L} < 1. Here, there is a very small build-up of the outer-sphere complex and the second-order rate constant is equivalent to $k_c K_o$. At high {L} when the ion pair formation is complete, $k_o\{L_o\} > 1$ and the reaction being studied is the interchange within the outersphere complex, rate constant is equal to k_o.

(3) When substitution involves an intermediate of higher coordination number, then the associative (A)[20] mechanism is said to be taking place i.e.

$$H_2O—M^+ L \rightleftharpoons H_2O....M....L$$

$$H_2O.....M.....L \rightarrow M-L + H_2O \qquad (4.9)$$

In this case the entering ligand bonds with the metal ion in the transition state.

These categories of substitution reactions are modified by what is called the intimate mechanism which relates to the activation process and can be dissociative(d) or associative (a).

Various experimental means of distinguishing between the possible mechanisms have become available.[30,31]

In a 'd' (dissociatively activated) intimate mechanism, the rate of reaction should be insensitive to the nature of the entering group (except for small effects arising from solvation interactions), while the rate of an 'a'

(associatively activated) intimate mechanism should be very sensitive to the nature of the entering groups. Kinetic and stereochemical techniques that can be used to detect the presence of the reactive intermediates can only provide means of assigning an 'A' or 'D' label which can only be done when evidence for the appropriate intermediate is forthcoming. Since the 'A' mechanism must be associatively activated and the 'D' mechanism dissociatively activated, then the subscript Aa and Dd becomes redundant. For the interchange mechanism, the evidence can be produced for a reactive intermediate. The interchange mechanism can be Ia or Id. There is no difficulty in identifying Ia with synchronous bimolecular process, but the Id mechanism is best distinguished in terms of the life-time of the intermediate. If it lives long enough to equilibrate its solvation environment it will obey the tests characteristic of a 'D' mechanism. If it has to interact with the environment it has inherited, then the mechanism is Id. The various ways of determining molecularity are very much interconnected and the relationship between them and the criteria of rate are shown in Table[32](4.4)

Provided discussion is restricted to nucleophilic substitution reactions, the characteristic features of the mechanisms of different coordination geometries are shown on Table (4.5).

TABLE 4.4

	Evidence for an Intermediate of lower coordination number	No evidence for an intermediate		Evidence for an Intermediate of higher coordination number
Stiochiometric Mechanism	D	I		A
Intimate Mechanism	D	Id	Ia	A
Ingold Definition	S_N 1 lim	S_N 1	S_N 2	S_N 2
Sensitivity of rate to the nature of entering groups	Rate Independent of entering group			Rate dependent on the nature of entering group.

TABLE 4.5

Coordination number	Geometry	Characteristic Mechanisms
4	Tetrahedral	Depends on electron configuration e.g D, Id, for C; A, Ia for Si, Ge, D, Ia, A for P, D, Id for transition elements in low oxidation states, Ia, A for intermediate and high oxidation state.
4	Planar	A
5		Insignificant data for systematic discussion.
6	Octahedral	D, Id (Ia)
7 and higher		hardly studied

Octahedral Substitution

This involves the studies of (i) labile and (ii) inert complexes. For labile complexes, the system is taken at equilibrium, perturbation is applied and the relaxation examined. Methods employed include the stopped-flow, temperature jump, n.m.r. and ultrasonic absorption. Although the approach enables a wide variety of reactions to be studied, the investigator is usually at the mercy of the equilibrium requirements of the system and is not in a position to control the nature of the substrates adequately.

With respect to aquometal ions, apart from $Cr(H_2O)_6^{3+}$[28] and $Rh(H_2O)_6^{3+}$[33-35] the aquometal cations exchange their ligands in solvent water with great rapidity.

The rate of octahedral substitution is rarely strongly dependent on the entering group, and when the effects due to pre-equilibrium association, proton transfer and other phenomena are taken into account, it is not greatly dependent upon its concentration either. Hence, a 'd' intimate mechanism is more plausible than an 'a' mechanism. Unequivocal evidence is usually provided by the characterization of a reactive five-coordinate intermediate in terms of competition, discrimination and stereochemistry.[36-42] With respect to the role of the solvent, if the substrate is unable to discriminate between reagents, then the mob rule wins. The diagnosis

of mechanism could be made from rate comparison or from activation parameters. A dissociative process will have a positive activation entropy while an associative mechanism should have a negative entropy of activation.[43] Activation enthalpies are not very diagnostic for single reactions. Activation volumes can also be a useful diagnostic tool.[44] A positive activation volume suggests a dissociative process while the converse is true for the associative process. Other diagnotic criteria include the variation of rate with ionic strength,[45] the variation of rate with ligand substituents[46] and the variation of rate with solvent composition.[47]

Substitution Reactions of Ruthenium(11)-Ruthenium(111) Complexes.

When compared with other bivalent metal ions, the substitution characteristics of hexaaquo-ruthenium(11) ion lies in the inert-labile border area as shown in Table(4.6).

Table (4.7) also shows that a dissociative mechanism is favoured with water exchange rate constant estimated as ~ 10^{-1} s^{-1}.[48] Infact the oxidation of Ru^{2+} by ClO_4^-[49] and $CrCl^{2+}$[50] ion appears also to be controlled by substitution at Ru^{2+}. The similarity of activation parameters ($\Delta H^{\ddagger}$ = 17 ± 1.5 K cal mol^{-1} $\Delta S^{\ddagger}$ = -5 ± 2 eu) for the reaction of the $Ru(NH_3)_5H_2O^{2+}$ ion with some

TABLE 4.6

Rate constants (log k $M^{-1}s^{-1}$) for Reactions of Aquated Bivalent Metal ions with ligands at 25°C

	V^{2+} d^3	Cr^{2+} hsd^4	Mn^{2+} hsd^5	Fe^{2+} hsd^6	Ru^{2+} hsd^6	Co^{2+} hsd^7	Ni^{2+} d^8	Cu^{2+} d^9	Zn^{2+} d^{10}	Cd^{2+} d^{10}
NH_3	-	-	-	-	-	5.1	3.7	8.3	6.6	-
Phen	0.5	8.0	~5.4	-	-	5.3	3.4	7.9	6.8	77.0
X^-	1.5	-	6.5	5.9	-2.0	5.3	3.9	8.7	-	-
$EDTAH^{3+}$	_	_	8.7	6.0	-	7.1	5.3	9.3	~9	9.6
H_2O	2.0	8.5	7.5	6.5	-	6.3	4.3	9.3	7.5	8.2

TABLE 4.7[a]

Rate constants ($k_1 M^{-1} s^{-1}$) for some reaction of Ru^{2+} ion at 25°C.

Reactant	10^{-3} x k $M^{-1}s^{-1}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
ClO_4^-	3.2	19.4	-5
Cl^-	8.5	19.8	-1
Br^-	10.9	19.5	-2
I^-	10.5	19.4	-5

a = T.W. Kallen and J.E. Earley
Inorg. Chem. 10, 1152 (1971)

TABLE 4.8[b]

Rate constants (log $k_1 M^{-1} s^{-1}$) for Reactions of Aquated tervalent Metal ions with ligands at 25°C

Ligand	Ti^{3+} d^1	V^{3+} d^2	Cr^{3+} d^3	Mn^{3+} hsd^4	Fe^{3+} hsd^5	Ru^{3+} hsd^5	Co^{3+} hsd^6	Rh^{3+} hsd^6
H_2O	5.0	-	-5.7	-	4.3	-	-	-7.5
HN_3	-	-0.4	-	-	0.4	-	-	-
X^-	3.6	2.1	-5.7	~4	2.1	-6	1.9	-

(b) R.G. Wilkins

"The study of the kinetics and Mech. of Transition Metal complexes" (Allyn & Bacon) Chpt 4 p. 221

unidentate ligands including N_2, N_2O, CO, NH_3, Py, CH_3CN and imidazole,[51] as well as with $Ru(NH_3)_5N_2^{2+}$[52] (to form a bridged dimer) show that the replacement of water may likely take place by a dissociative mechanism.

Direct replacement of one ligand by another, without solvent participation, has been observed in the reaction.[53]

$Ru(NH_3)_6^{3+} + NO + H^+ \rightarrow Ru(NH_3)_5NO^{3+} + NH_4^+$ which takes

which takes place much more rapidly than could be explained by aquation of the hexammine as a first step. A bimolecular mechanism with a seven coordinate intermediate or transition state might appear more likely with such a d^5 system, in which there are available orbitals for attack by the entering group.

The limited data available indicate that substitution occurs without stereochange.

The relative inertness of $Ru(NH_3)_6^{3+}$[54] and $Ru(phen)_3^{2+}$[55] towards substitution makes these ruthenium complexes definite although weak, outer-sphere reductants.

$Ru(H_2O)_6^{3+}$ is an inert ion when compared with other trivalent ions as shown in Table (4.8) with a t_{2g}^5 configuration, ruthenium(111) has an unpaired electron that can be used in bonding with an entering ligand making the formation of a heptacoordinate intermediate a distinct possibility. Hence with ligands like NO, having a single electron, $Ru(NH_3)_6^{3+}$ and other Ru(111) complexes react

by a bimolecular mechanism.[56] This same mechanism also operates for the hydrolysis of $RuCl_6^{3-}$ in a strong acid.[55a] The few Ru(111) complexes whose substitution reactions have been studied have been found to undergo rapid base hydrolysis, spontaneous and Hg(11)-induced aquation with complete retention of configuration. It has been suggested that a square-pyramidal intermediate may probably be involved.[55b] Ru(111) has been observed to catalyze the anation of Ru^{2+} and a number of Ru(111) complexes. For example[55c] $Ru(NH_3)_5py^{3+}$ appears to undergo reversible disproportionation in alkaline solution. This has been shown by chemical tests and the observation of second-order kinetics for the loss of Ru(111).

Oxo-bridged Ruthenium(111) dimer.

Transition metal ions or atoms linked by a bridging ligand differ significantly from their mononuclear analogues in the that there are various possibilities in terms of the interaction between the bridged metal ions. There could be strong direct metal-metal bonding, strong intermetal interaction through a bridging ligand, weak metal - metal interaction through space or through a bridging ligand or there could be no evidence at all of metal-metal bonding electronic interaction.

Robin and Day[56] have classified these into three categories - classes 1 - 3. Well characterized examples of compounds in which there are strong metal-metal interactions across a bridging ligand are however uncommon. Nevertheless with recently developed elegant synthetic routes by Meyer and coworkers,[57] a number of exotic ruthenium complexes, particularly oxo-bridged dimers and oxobridged ruthenium clusters have been prepared and some of their properties reported.[58-62]

The oxobridged dimer, $[(LL)_2XRu\text{-}o\text{-}RuX(LL)_2]^{n+}$[58] (LL = αα-bpy, or 1,10 phenanthroline, x = Cl, NO_2 or H_2O) fall into the Robin and Day Class III, in that they have physiocochemical properties which are unusual when compared to related monomeric complexes. These properties can however be explained by invoking chemically significant interactions between the

ruthenium ions across the oxide bridge. Some of its properties are:

(1) The generation of the mixed valence ion $\{(bpy)_2ClRuORuCl(bpy)_2\}^{3+}$ at a reasonable potential of E^o = 0.68V in acetonitrile and the +4 ion in which ruthenium has a formal charge of +4.

(2) Although some other cases involving ligand bridged dimer eg. $\{(bpy)_2ClRu(py_3)RuCl(bpy)_2\}^{2+}$[63] and $\{(bpy)_2Ru(NO_2)Ru(bpy)_2\}^{4+}$[64] are reasonably stable in acetonitrile, the reduction of Ru(111) - Ru(111) in acetonitrile results in decomposition of the dimeric unit to give monomeric products; $Ru(bpy)_2(CH_3CN)Cl^+$ and $Ru(bpy)_2(CH_3CN)_2^{2+}$.

(3) The comparison of $E_{\frac{1}{2}}$ values show that the +2 dimeric ions are remarkably poor oxidants with respect to related (2,2'-bipyridine) ruthenium (111) ions e.g.

$\{(bpy)_2ClRuORuCl(bpy)_2\}^{2+} + e \rightarrow$

$\{(bpy)_2ClRuORuCl(bpy)_2\}^{+}$ $\quad E_{\frac{1}{2}} = -0.32V$.....(4.10)

$Ru(bpy)_2Cl^+ + e \rightarrow Ru(bpy)_2Cl_2$ $\quad E_{\frac{1}{2}} = 0.30V$ .....(4.11)

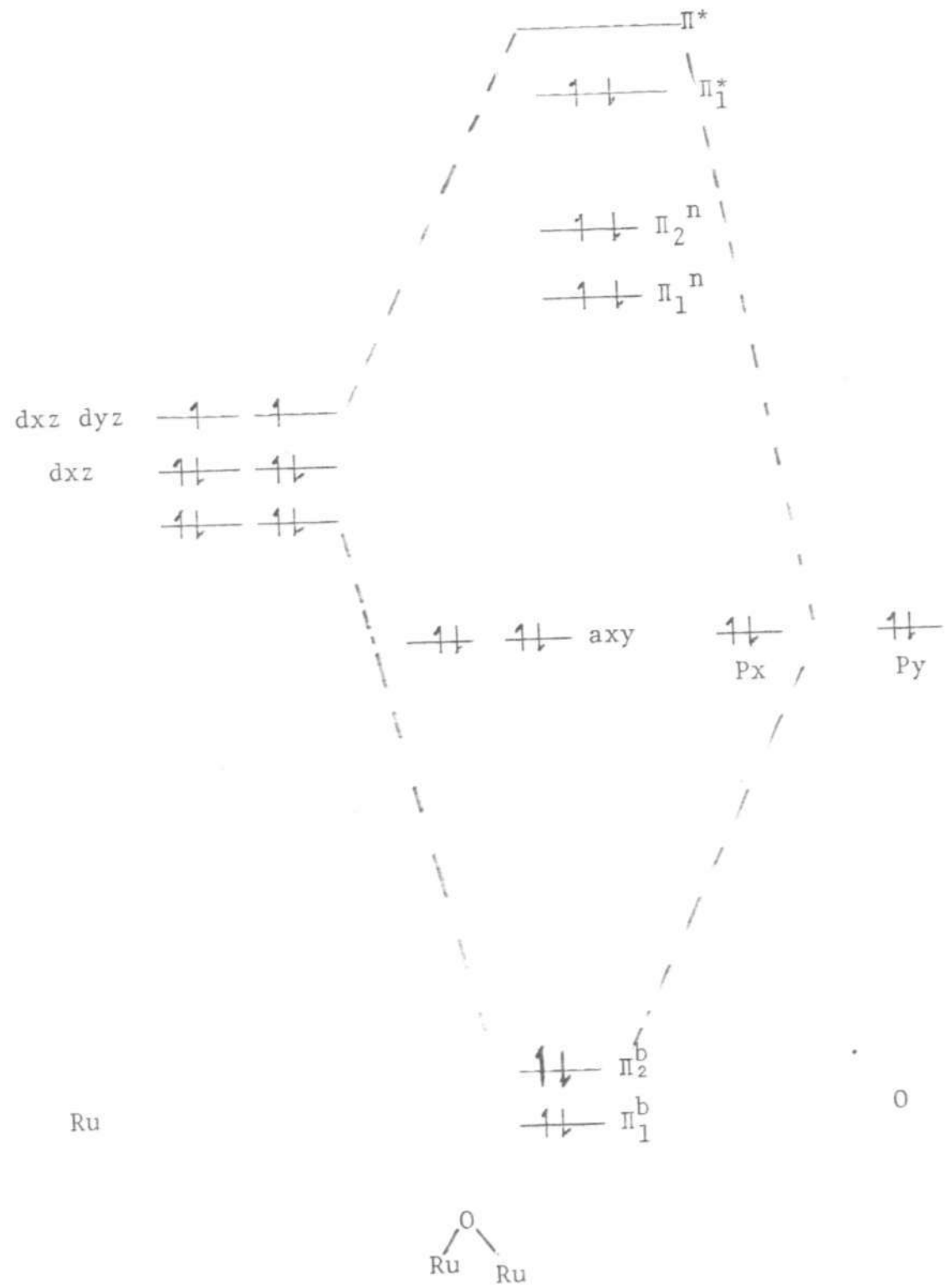
(4) The presence of high intensity, low energy bands which are unusual. For the mixed valence ion, $\{(bpy)_2ClRuORuCl(bpy)_2\}^{3+}$ the band is considerably blue shifted from λ_{max} 668nm for the +2 ion to 470nm for the +3 ion and the intensity

remains high. Such high intense and low energy bands are not observed for other bis(2,2'-bpy) complexes of either ruthenium(11) or ruthenium(111) but are reminscent of ruthenium red.[59]

(5) The photoelectron data indicate that in the mixed valence ion $[(bpy)_2ClRuORuCl(bpy)_2](Pf_6)_2$ the ruthenium centers are equivalent excluding the presence of Ru(111) and Ru(1V) ion and therefore, the dimer falls into the Class 111 of Robin and Day's classification.[56]

(6) Magnetic data indicate that the μ-oxo systems give a singlet state.[58] No evidence of interdimer coupling. Xm is not field dependent. The interpretation of the magnetic data is that coupling between the ruthenium ion is strong and the electron system is delocalized. Molecular models indicate that a too pronounced bending of the Ru-o-Ru moeity is not possible because of the bulkiness of the polypyridine ligands and hence direct interaction through space is unlikely. This prediction has been confirmed by X-ray studies of $[(phen)_2NORuORuNO(phen)_2^{2+}]$ in which the Ru-o-Ru angle is found to be 178°. Hence strong Ru-Ru interactions, if they occur, must occur via the bridging ligand.

(7) Molecular orbital scheme for the μ-oxobridged dimer based on the model given by Orgel for the linear ion $[Cl_5RuORuCl_5]$ is given below:[59]



Molecular orbital scheme for $[(bpy)_2ClRuORuCl(bpy)_2^{2+}]$

In this scheme which is slightly modified from Orgel's, the direction for labelling the d orbitals of each of the ruthenium ions is taken along the Ru-O-Ru linkage. The degeneracy of the t_2g orbitals is lifted further than in $\{Cl_5RuORuCl_5\}^{4-}$ because of the lower symmetry of the bis(2,2'-bpy)ruthenium ions. A bent Ru-O-Ru linkage would also cause loss in degeneracy. This molecular orbital scheme accounts adequately for the unusual physical and chemical properties of this oxo-bridged ruthenium dimer. Using this scheme, the valence levels of the system, are molecular orbitals delocalized over both ruthenium ions.

The valence orbitals thus have both ruthenium and bridging oxide character. The Ru- -Ru interactions are strong and hence the valence levels (Π_1^* and Π_2^* in the above scheme) are significantly destabilized compared to the non-bonding d levels. (Π_1^n and Π_2^n and dxy). From the difference in $E_{\frac{1}{2}}$ values for the closely related couples: $\{(bpy)_2ClRuORu(bpy)_2\}^2$ ($E_{\frac{1}{2}}$ = -0.32V) and $Ru(bpy)_2Cl^{+,o}$ ($E_{\frac{1}{2}}$ = 0.3V), it can be estimated that the extent of destabilization may be several kilcolories per mole. The identity of the ruthenium ions is thus lost in determining the physicochemical properties of the system, and such properties will be controlled largely by the valence orbitals which are delocalized and include the properties of the two ruthenium ion and the bridging ligand. Similar strong interaction has been

reported from the spectra and reported properties of the ion $\{Os_2O(bpy)_2(terpy)_2\}^{4+}$.[65] Also the oxo-bridged complexes of iron have properties that are usually consistent with magnetically coupled systems in which the unpaired electron is locally on the iron(111) ions.[66-70] In contrast to the ruthenium and Osmium systems, the extent of metal-metal interaction between iron(111) ions is however apparently insufficient to change appreciably the chemical and electronic properties of the dimeric ions possibly because of the lesser d orbital extension of Fe(111) when compared to Ru(111) and Osmium(111).

Very recently the oxobridged dimer $\{(NH_3)_5RuORu(NH_3)_5\}^{4+}$ and the analogous 5+ mixed-valence ion were prepared and characterized by Bauman and Meyer.[71] The properties of the ions were consistent with strong electronic coupling between the ruthenium ions through the oxo-ligand, and there appeared to be orbital delocalization in the mixed-valence ion, which is formally a Ru(111) - Ru(1V) ion.

There has been no reported kinetic data on the oxobridged dimer, $\{(bpy)_2ClRu\text{-}O\text{-}RuCl(bpy)_2\}^{2+}$ although Meyer et al[58] found qualitatively that the dissociation of the dimer is affected independently by acid and anions and greatly enhanced when both acid and anion are present together. Thus in HCl the following reaction occurs:

$$\{(bpy)_2ClRuORuCl(bpy)_2\}^{2+} + 2HCl \rightarrow 2\{Ru(bpy)_2Cl_2\}^{2+} + H_2O \qquad .....(4.12)$$

Meyer et al[58] also reported the reduction potentials and the relevant $E_{\frac{1}{2}}$ data for the oxobridged dimer as:

$$RuORu^{4+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} RuORu^{3+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} RuORu^{2+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} RuORu^{+}$$

1.91V 0.68V -0.32V

$$\underset{-1.0V}{\overset{+e^-}{\rightleftharpoons}} RuORu \rightarrow \text{decomposition products.}$$

With respect to redox reactions, spectrophotometric titration of the dimer with Cr^{2+} gave a 2:1 Cr^{2+}- dimer stoichiometry according to the following equation

$$\{(bpy)_2ClRuORuCl(bpy)_2\}^{2+} + H_2O + 2H^+ + 2Cr^{2+}$$
$$\rightarrow \quad 2\{Ru(bpy)_2(H_2O)Cl\}^{+} + 2Cr(III) \qquad \text{.....(4.13)}$$

This observation ruled out a peroxide bridged dimer of the form:

$\{(bpy)_2ClRuO_2RuCl(bpy)_2\}^{2+}$ since

if this was the case then 4 moles of chromium should be consumed per mole of dimer. Meyer et al[58] also followed the oxidation of the dimer in acetonitrile spectrophotometrically and observed that the complex was smoothly and clearly oxidized (isobiestic points 364, 423, 523nm). by Ce(IV) to a mixed-valence μ-oxoruthenium(III) ruthenium(II) ion.

In this project, both the kinetics of the dissociation of the oxobridge, and the reduction of the dimer by various metal ions were investigated.

Substitution Reactions of Bridged Complexes.

Studies have been carried out on the acid and base - assisted cleavage of dimeric Cobalt(111) bridged complexes. The sole product of the cleavage of di μ-dihydroxo-tetrakis (ethylenediamine) dicobalt(111) ion by $HClO_4$ and HNO_3 is cis - $\{Co(en)_2(H_2O)_2\}^{3+}$[72,73] The mechanism that has been proposed involves the H^+ - assisted opening of the OH bridges and the intermediate formed anates at a rate which is inverse in $\{H^+\}$. The cleavage of the Co-O bond of the intermediate is enhanced by labilizing groups such as Cl^- and SO_4^{2-}. The rates of the aquation and the chloride anation of ring-opened chloro-aquo amido bridged complex of Cobalt(111) has also been reported.[74] The hydroxo-amido complex loses one NH_3 from each Cobalt atom in perchlorate medium and the product forms a triply-bridged complex.[75] However the acid hydrolysis of μ-dihydroxo-bis(dioxalato)Cobaltate(111) gives Co^{11} as the final product.

The reactivities of Cl^- and SCN^- ion in their attack on hydroxo bridges of Cobalt(111) binuclear complexes are similar[76,77] and the rate of decomposition of the superoxido complex, $[(NH_3)_5\ CoO_2Co(NH_3)_5^{5+}]$ is similar to that of the decomposition of $[(NH_3)_5CoNH_2Co(NH_3)_5^{5+}]$. Early studies by Grant and Hamm[78] and of Connick and Thomson[71] on the acid cleavage of Cr^{111} complexes with two hydroxo bridges provides evidence of the intermediate formation of a single OH-bridged species. Wolcolt and Hunt[79] have reported studies in the acid cleavage of di-μ-hydroxo-

tetrakis(O-phen) chromium(111). The experimental rate law fits two mechanisms in which the respective opening of the first bridge and the second bridge has been considered as rate-determining. The acid cleavage of single hydroxy-bridged Cr^{111} complexes has also been reported.[80] One interesting observation is that the rates of these reactions are apparently increased by the presence of chloride ion.

No kinetic data on the substitution of the oxo-bridged complex $[(Ru(bpy)_2Cl)_2O^{2+}]$ has been reported. Meyer et al[58] however reported that the dissociation of this dimer occurs slowly, independently in the presence of acid and chloride ions and that the presence of both ions enhance the rate of dissociation. As a prelude to the study of the redox reactions of the oxobridged dimer with some aquometal ions, its substitution reaction in media containing both acid and anions like Cl^- and NCS^- were investigated and the results obtained are reported in this chapter.

E X P E R I M E N T A L :

Preparation of the oxobridged complex $\{(bpy)_2\text{-}\underset{Cl}{Ru} - O - \underset{Cl}{Ru}(bpy)_2\}(PF_6)_2$

The oxobridged complex $[(bpy)_2\underset{Cl}{Ru} - O - \underset{Cl}{Ru}(bpy)_2](PF_6)_2$ was prepared according to the method outlined by Meyer et al.[58] This is a two-stage process involving the substitution of a chloride ion in a $(bpy)_2Ru\begin{smallmatrix}Cl\\Cl\end{smallmatrix}$ complex by the more labile nitrosyl (NO) group and the replacement of this labile group by solvent. The second stage involves the prolonged oxidation of the nitrosyl complex by oxygen to form the required oxobridged ruthenium dimer. The details of the preparation are outlined below:

(i) Preparation of $[Ru(bpy)_2(NO)Cl]_2(PF_6)_2$

About 0.80g sample of $Ru(bpy)Cl_2.2H_2O$ was suspended in $60cm^3$ of doubly distilled water and the solution boiled for 20 minutes under an inert blanket of purified argon. A red brown solution was formed. Suction filtration of this solution was carried out at room temperature and $5.0cm^3$ of 1.03M HCl was added. $10.0cm^3$ of an aqueous solution containing 0.114g of sodium nitrite was added to the solution while stirring over a period of 10 minutes. The purple solution that resulted was warmed at 50^oC on a water bath for 10 minutes. $8.0cm^3$ of a saturated solution of ammonium hexafluorophosphate was then added giving a

pale brown precipitate. This was filtered under pressure washed with a small portion of cool water and air dried. The precipitate of $\{Ru(bpy)_2(NO)Cl\}_2(PF_6)_2$ obtained was then recrystallized by dissolving it in a minimum amount of acetone and slowly adding an excess amount of isopropyl ether. The whole process was repeated several times to obtain enough sample for the second stage of the preparation.

Equation:

$$(bpy)_2Ru\begin{matrix}Cl\\Cl\end{matrix} + H_2O \rightarrow (bpy)_2Ru\begin{matrix}Cl\\H_2O\end{matrix}$$

$$\xrightarrow[NO_2]{H^+}\left[(bpy)_2Ru\begin{matrix}Cl\\NO\end{matrix}\right](PF_6)_2 \qquad \text{.....(4.14)}$$

The product was confirmed to be the same as reported by and coworkers by taking its IR spectra (Figure 4.4) Typical peak is at $1931cm^{-1}$ which is due to the Nitrosyl stretching fequency.[58a]

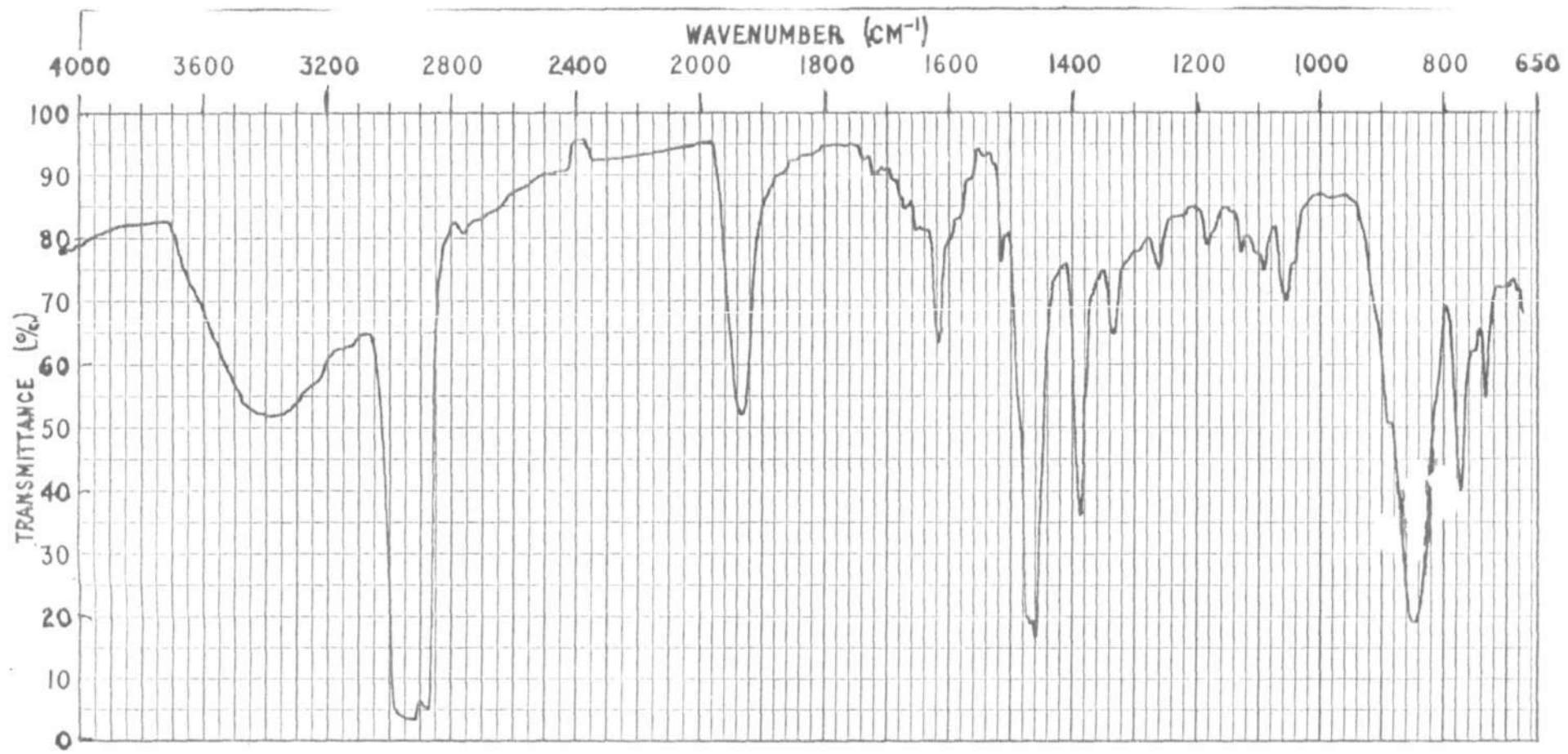
(ii) Preparation of the oxobridged ruthenium(111) dimer.[58]

$\{Ru(bpy)_2(NO)(Cl)\}(PF_6)_2$ prepared as above was dissolved in about $150cm^3$ of acetone in which potassium azide had been suspended. The mixture was stirred under an argon atmosphere for about 6 hours. The resulting solution of the solvento complex, $\{Ru(bpy)_2Cl(S)\}^+$ (s = acetone) was saturated with oxygen at room temperature for 5 days after which the solution was filtered to remove KPF_6 and the product precipitated by a slow addition to a rapidly

Fig. 4.4

I.R. SPECTRA OF $[Ru(Bpy)_2NOCl](PF_6)_2$

REFERENCE : NUJOL



stirred anhydrous iso-propyl ether (750cm^3). The resulting precipitate was isolated by sunction filtration and air dried. It was then washed with small amounts of acetone until the wash was deep blue colour.

The product was then recrystallized by dissolving in acetone and reprecipitating with anhydrous isopropyl ether and this repeated until the pink colour of the filtrate disappeared. The spectrum of the product was then recorded for the wavelengths 300 - 700nm on a Unicam 1750 U.V spectrophotometer (Figure 4.5). A Typical peak representing the Ru - O - Ru moiety[58] is at 648nm.

Equation:

$$\{Ru(bpy)_2(NO)(Cl)\}(PF_6)_2 + KN_3 + S \xrightarrow{(s=acetone)} \{Ru(bpy)_2Cl(S)\}^+ + N_2O + N_2 + KPF_6 + PF_6^- \quad .....(4.15)$$

$$2(Ru(bpy)_2ClS^+) + \tfrac{1}{2}O_2 \xrightarrow{acetone} \left[(bpy)_2ClRuORuCl(bpy)_2\right]^{2+} ..(4.16)$$

Solutions of the oxobridged ruthenium(111) dimer were always prepared by dissolving a known weight of the dimer in known volume of water. These solutions were stable over a period of at least two days and were always kept in the deep freezer when not being used. A fresh solution of the oxobridged ruthenium(111) dimer was always prepared after a period of two days.

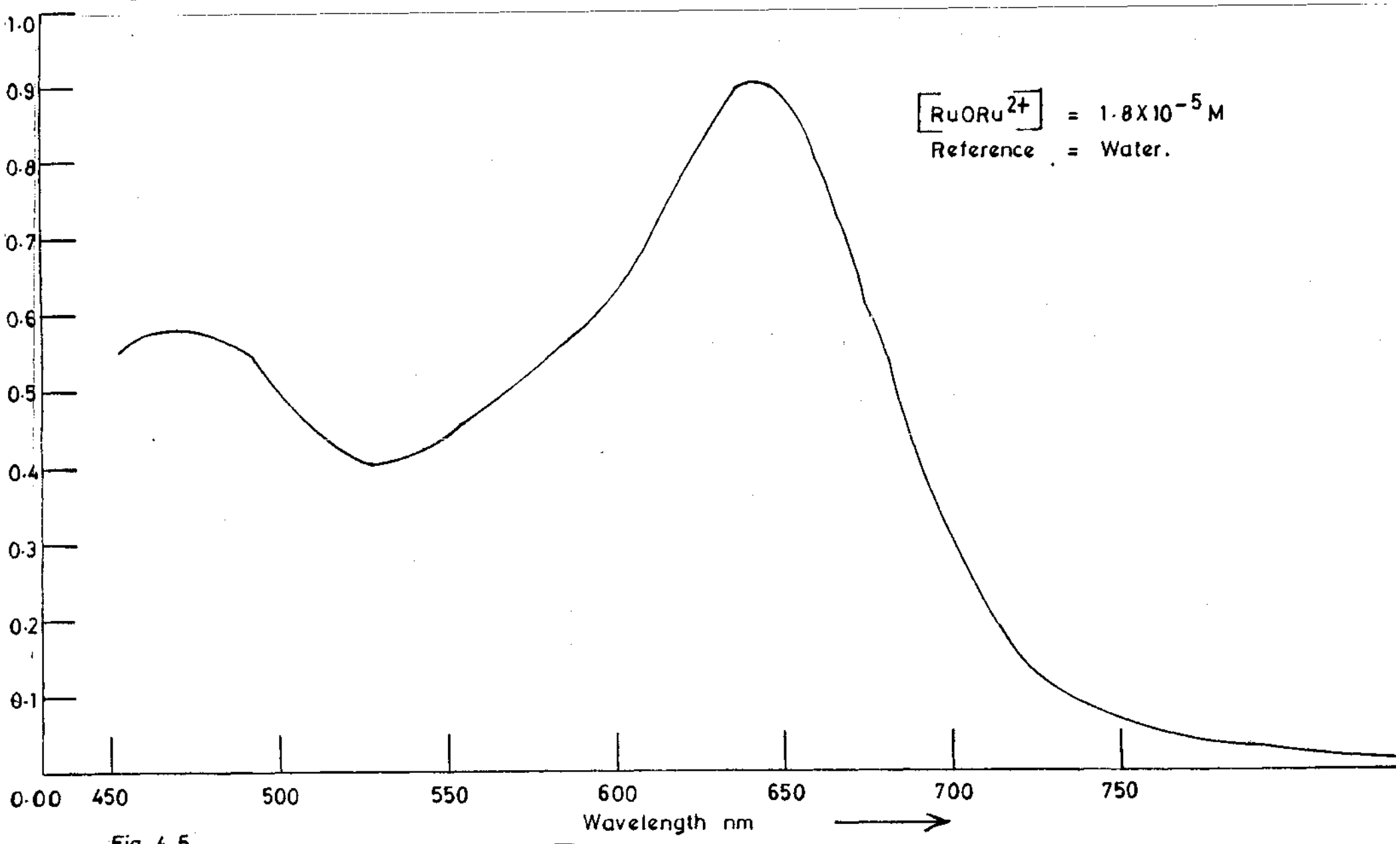


Fig. 4.5
Spectra of $[(bpy)_2\ ClRuORuCl\ (bpy)_2^{2+}]$

Preparation of chloride and thiocyanate solutions.

Solutions of sodium chloride and sodium thiocyanate were prepared by dissolving a known weight of the analar grade of the respective salts in a known volume of doubly distilled water.

Preparation of $LiClO_4$

Standard solutions of $LiClO_4$ was prepared as reported in Chapter one.

KINETICS.

The rate of the anion assisted cleavage of $\{(bpy)_2ClRu-ORuCl(bpy)_2\}^{2+}$ was monitored with the Unicam S.P. 1750 U.V spectrophotometer. This was done by monitoring the decrease in the absorbance of the oxobridged ruthenium(111) dimer at its λ_{max} = 648nm in the visible region. This absorption maximum has been interpreted as being unique to the Ru-O-Ru moiety.[58]

The ionic strength was maintained constant at 2.0M ($LiClO_4$). Pseudo-first-order rate constants were obtained from the plots of log (At-A∞) versus time. (A = Absorbance). The temperature was maintained constant at 25.0 ± 0.1°C for all runs by circulating thermostated water through the cell compartment of the spectrophotometer.

Product analysis:

Hints about the possible pathway of substitution and cleavage of the oxobridged ruthenium(111) dimer could be obtained if it were possible to isolate and characterize the products of the cleavage. However various attempts to separate or isolate the product of the reaction, using different resins, did not succeed. However the spectra of the product of the reaction was monitored in NCS^-, $HClO_4$, Cl^- - ClO_4^- as shown in (4.6a,b). The spectra obtained is also compared with the spectra of the various possible products, i.e. $Ru(bpy)_2Cl_2^+$, $Ru(bpy)_2H_2OCl^{2+}$ $Ru(bpy)(NCS)_2^+$, $Ru(bpy)H_2ONCS^{2+}$ and the oxobridged ruthenium(111) dimer as presented in Table (4.9)

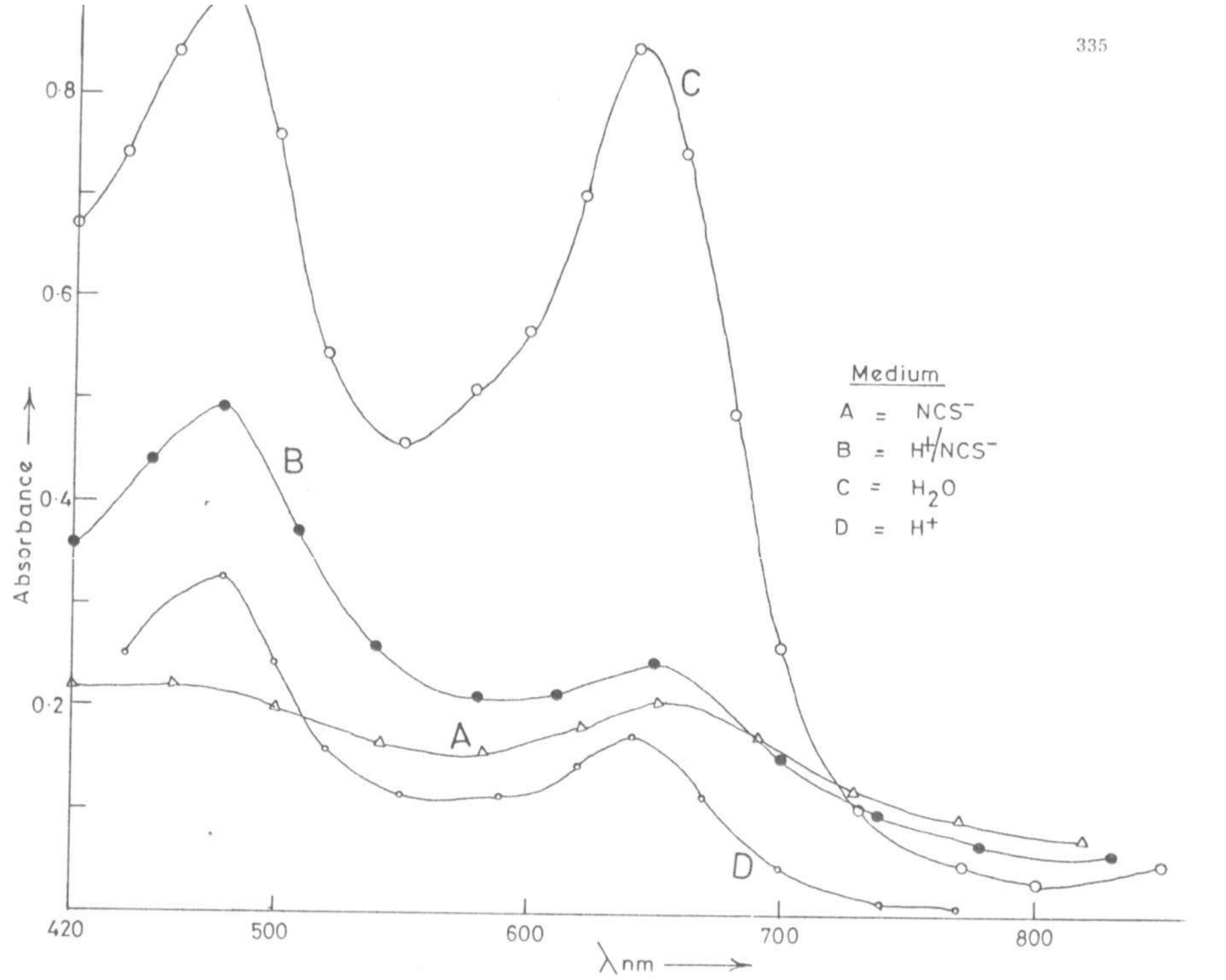


Fig. 4.6a Spectra of the product of the dissociation of $[(bpy)_2ClRuORuCl(bpy)_2]^{2+}$

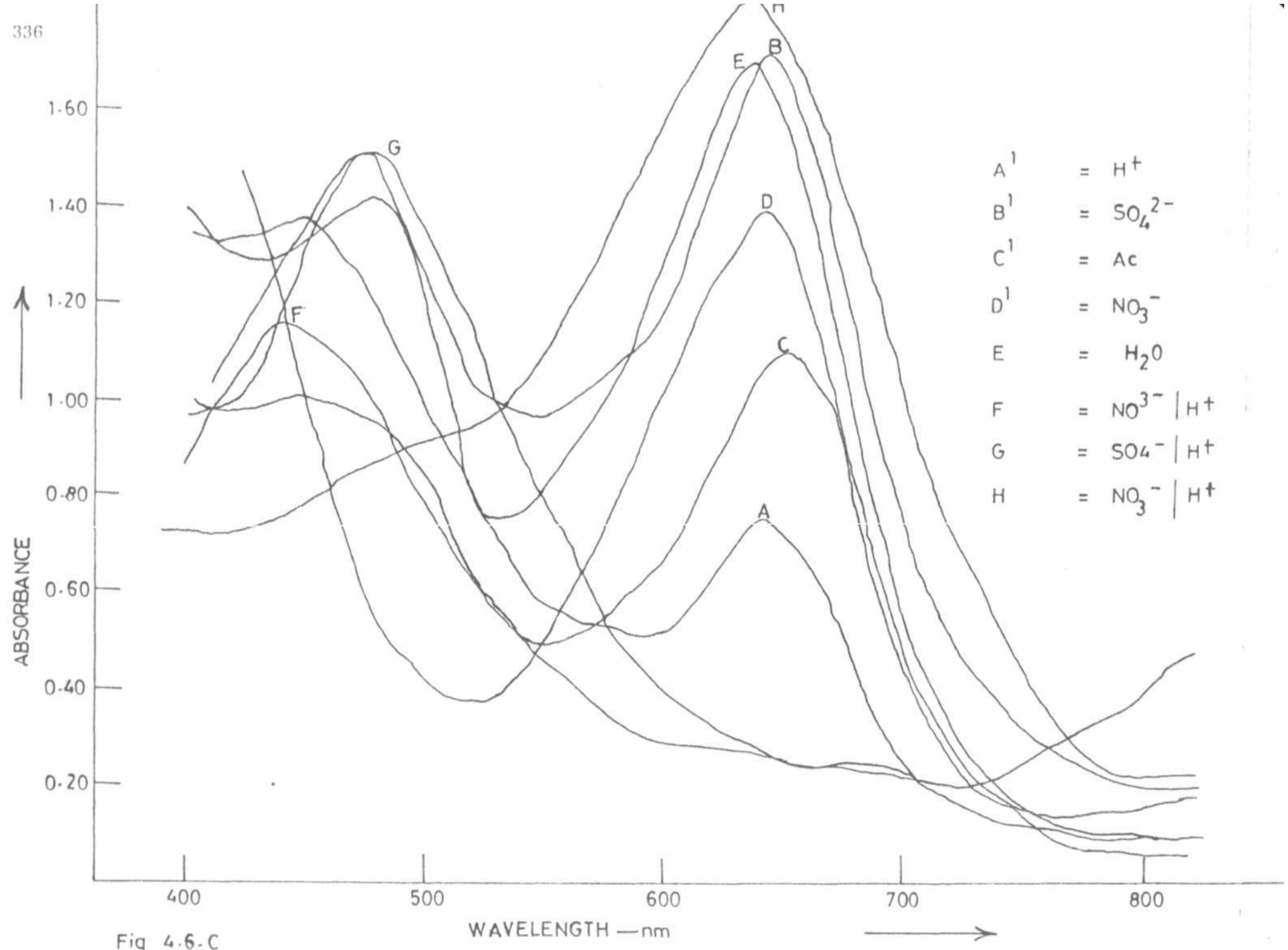


Fig. 4.6.C

Spectra of the Product of the Anion-Assisted dissociation of $[(bpy)_2ClRuORuCl(bpy)_2]^{2+}$

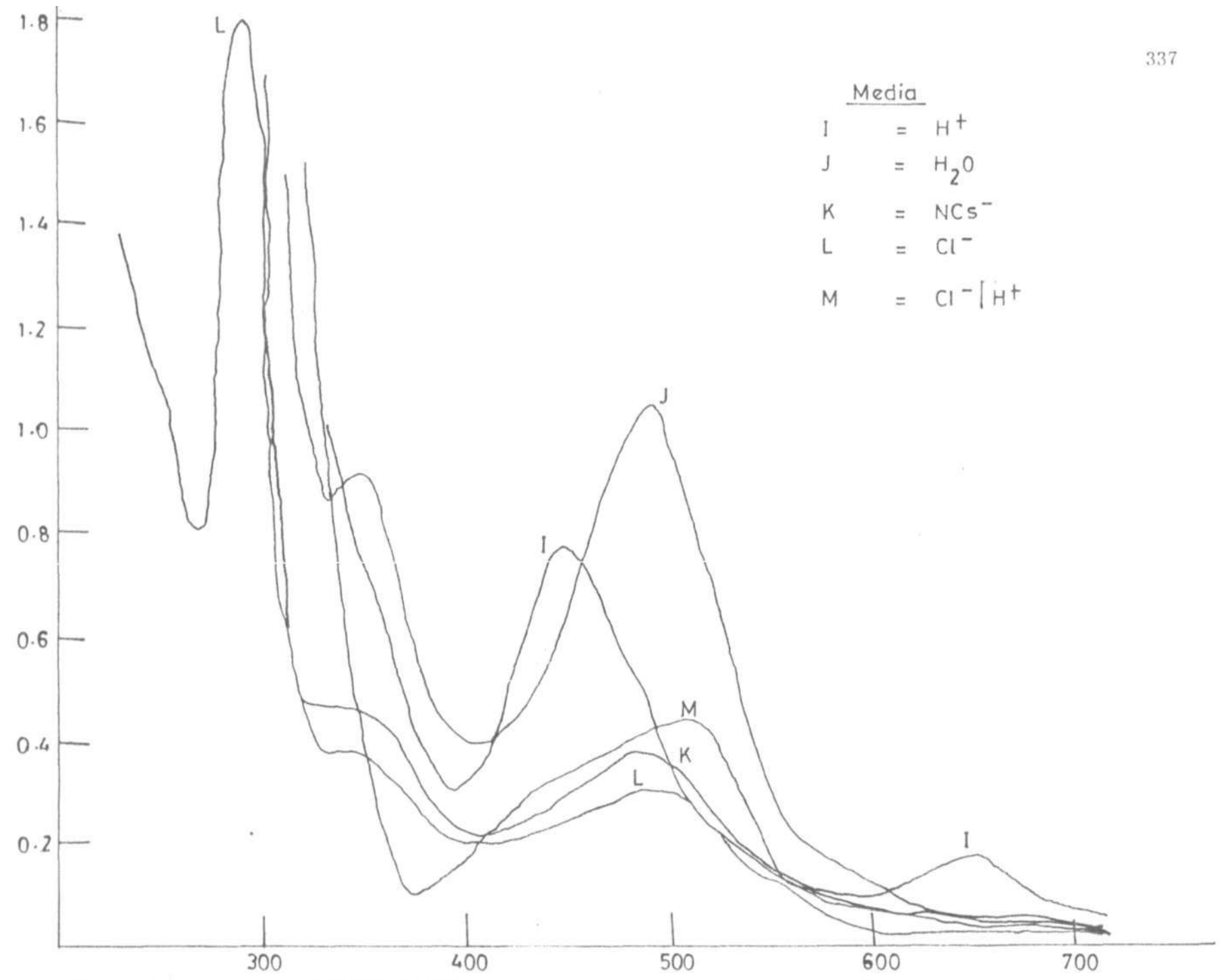


Fig. 4·6b Spectra of the Product of the Anion-Assisted dissociation of $\left[(bpy)_2 ClRuORuCl(bpy)_2\right]^{2+}$.

TABLE 4.9

Absorption peaks of the product of the chloride and thiocyanate ion assisted dissociation of $[(bpy)_2ClRuORuCl(bpy)_2^{2+}]$.

Medium	λ_{max}[a](nm)	λ_{max} nm(litrature value)
H_2O	648	648[58]
H^+	446	
NCS^-	485	
H^+/NCS^-	480	
Cl^-	480	
H^+/Cl^-	510	

a. All the other peaks have relatively low amplitude compared to that of the oxobridged dimer in water.

RESULTS

Effect of $\{H^+\}$

The cleavage of the oxobridged ruthenium(111) dimer was affected by the presence of both acid and anion. However the rate of dissociation of the dimer was found to be very slow either in 2.0M $HClO_4$ or 2M NaCl but was enhanced in the presence of both ions. This confirms an earlier similar observation by Meyer et al.[58] The absorbance of the dimer increased in acidic solutions. $\{Cl^-\}$ was kept constant at 1.0M and 2.0M respectively while investigating the effect of $\{H^+\}$ on the rate of dissociation of the dimer. The acid concentration of the reaction medium was varied from 0.1M to 2.0M which is more than 10^3 times in excess of the oxobridged dimer concentration. The pseudo-first-order plots were linear to about 60% of the extent of the reaction after which it becomes curved in a way suggestive of inhibition. The pseudo-first order rate constants obtained from the initial rates (the linear portion of the curve) are presented in Table (4.10). Each reported rate constant is at least an average of duplicate runs. The pseudo-first-order rate constants obtained were then plotted against $\{H^+\}$ for$\{Cl^-\}$ = 1.0 and 2.0M respectively as shown in Figure (4.7). The points for $\{Cl^-\}$ = 1.0M and 2.0M fall on the same curve with a finite intercept. The curve is linear with a slight deviation at $\{H^+\}$ > 1.5M. A limiting value of k_{obs}, the pseudo-first-order rate constants may

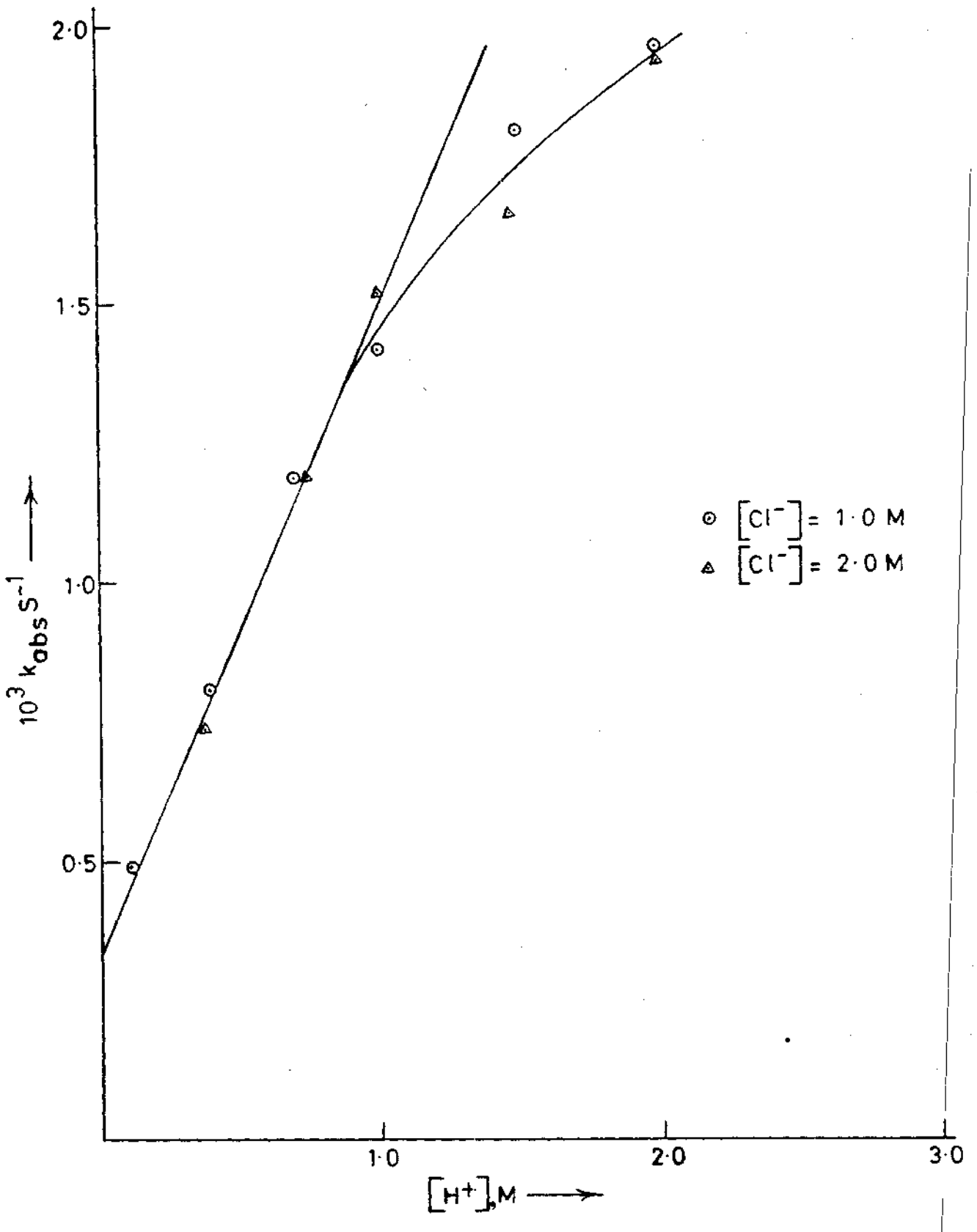


Fig. 4·7 Plot of acid dependent Pseudo-First-Order rate constants against $[H^+]$, M for the Chloride assisted dissociation of $[(bpy)_2ClRuORuCl(bpy)_2^{2+}]$

occur at $\{H^+\} > 2.0M$. The linear part of the k_{obs} versus $\{H^+\}$ plot fits a rate law of the form,

$$k_{obs} = k_o + K_{H^+}\{H^+\} \qquad .....(4.17)$$

with $k_o = 3.5 \times 10^{-4} s^{-1}$

and $k_{H^+} = 1.1 \times 10^{-3} M^{-1} s^{-1}$.

TABLE 4.10

Pseudo-first-order rate constants for the acid dependence of $\{(bpy)_2ClRuORuCl(bpy)_2^{2+}\}$ at constant ClO_4^- - Cl^- concentration.

$I = 2.0M$, $\lambda = 648nm$, $T = 25 \pm 0.1^oC$

$\{(bpy)_2ClRuORuCl(bpy)_2^{2+}\} = 4.5 \times 10^{-5}M$

$\{H^+\}$,M	$\{Cl^-\}$,M	$10^3 k_{obs} S^{-1}$
2.0	1.0	1.96
1.5	1.0	1.81
1.0	1.0	1.42
0.7	1.0	1.19
0.4	1.0	0.82
0.1	1.0	0.49
2.0	2.0	1.94
1.47	2.0	1.66
1.10	2.0	1.52
0.74	2.0	1.18
0.37	2.0	0.74

Since the rate constants obtained at $\{Cl^-\}$ = 1.0M and 2.0M respectively were similar, it was decided that the cleavage of the oxobridged dimer should be studied at constant $\{H^+\}$ while varying the $\{Cl^-\}$ for each set of runs.

Chloride assisted dissociation of $[(bpy)_2ClRuORuCl(bpy)_2^{2+}]$

The chloride dependence of the cleavage of the oxobridged dimer was investigated at constant $\{H^+\}$ values in the range 0.5M $\leqslant \{H^+\} \leqslant$ 2.0M. For each acid concentration investigated, $\{Cl^-\}$ was varied between 0.05 and 2.0M. A known weight of the dimer was always dissolved in water before each set of runs, and the required concentration of the dimer was always injected last into the serum-capped spectrophotometric cell used for these studies. The absorbance of the same concentration of complex was always higher in acid medium than in ordinary water or chloride medium. This is suggestive of a rapid protonated equilibrium preceeding the dissociation step. For each acid concentration investigated, the pseudo-first-order rate constants were linear to about $3t_{\frac{1}{2}}$ at low $\{Cl^-\}$ (< 1.0M). However at higher chloride concentration (1.0M < $\{Cl^-\} \leqslant$ 2.0M) considerable derivation from linearity in a way suggestive of inhibition was observed. Typical plots at low $\{Cl^-\}$ = ($[Cl^-]$=0.25M) and $[Cl^-]$ = 0.8M) are shown in Figures (4.8) and (4.9) respectively. Initial rates were obtained in cases where deviation was observed.

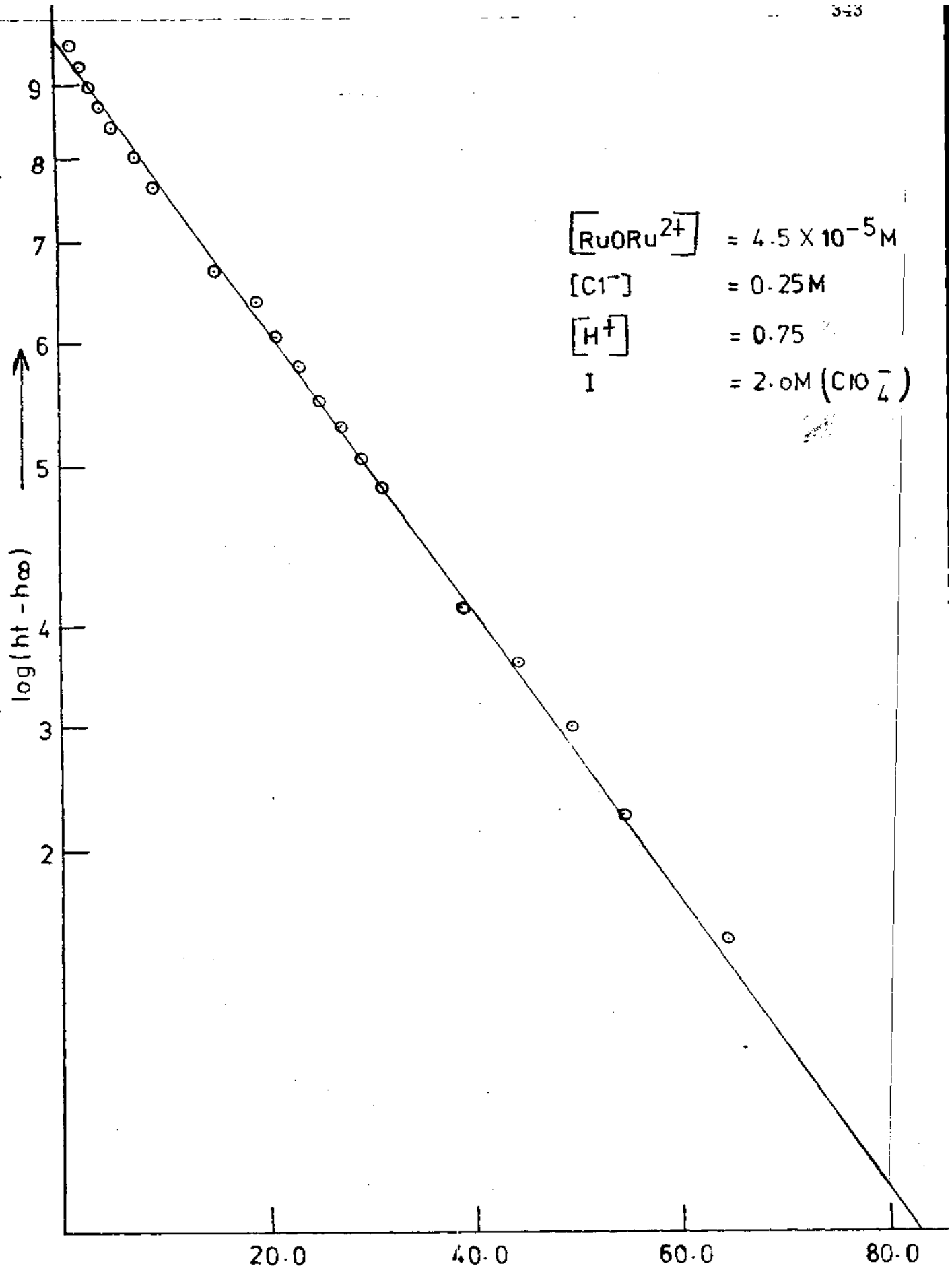
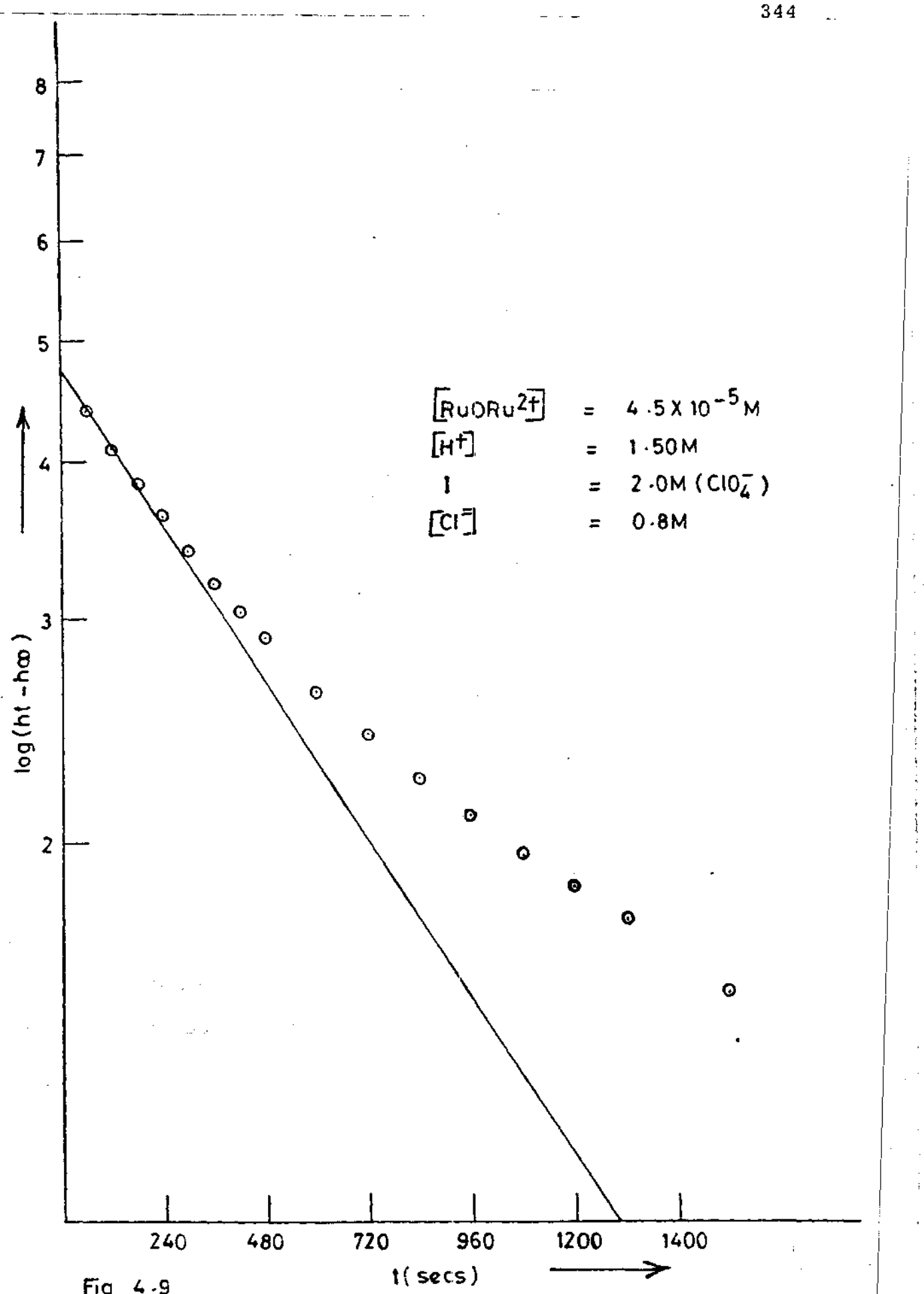


Fig. 4.8

Typical Pseudo-First-order Plot for the Chloride assisted dissociation of $[(bpy)_2 ClRuORuCl(bpy)_2^{2+}]$ at low chloride concentration



$[RuORu^{2+}]$ = 4.5×10^{-5} M
$[H^+]$ = 1.50 M
I = 2.0 M (ClO_4^-)
$[Cl^-]$ = 0.8 M

Fig. 4-9
Typical Pseudo-First-Order Plot for the chloride assisted dissociation of $\left[(bpy)_2ClRuORuCl(bpy)_2\right]^{2+}$ at high chloride concentration.

The rate constants obtained are presented in Table (4.11).

For each acid concentration investigated, k_{obs} increased with increasing $\{Cl^-\}$. For each $\{H^+\}$ a limiting value of k_{obs} was obtained for $\{Cl^-\}$ > 1.0M. A plot of k_{obs} against $\{Cl^-\}$ for each acid concentration investigated is presented in Figure (4.10).

These plots are non linear. The slope of each curve increased with increase in $\{H^+\}$. The plots of $1/k_{obs}$ versus $1/\{Cl^-\}$ for $\{Cl^-\}$ < 1.0M were however linear with positive intercepts and are shown in Figure (4.11). The intercept, a, and slope b, obtained by least - mean-square analysis of these plots are presented in Table (4.12)

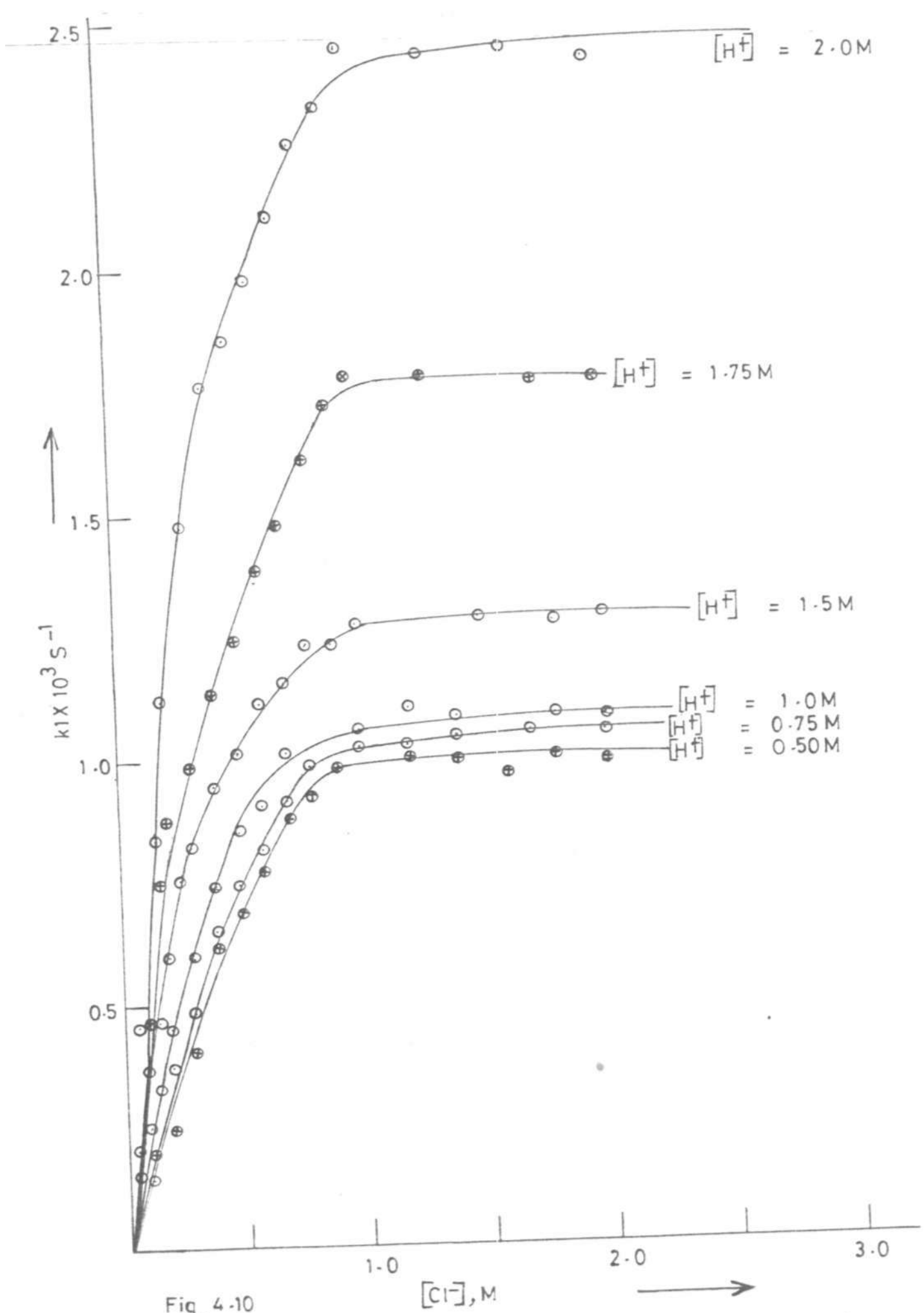


Fig. 4.10

Chloride dependent Pseudo - First - Order rate constant for the dissociation of $\left[(bpy)_2 ClRuORuCl(bpy)_2\right]^{2+}$: Plot of k_{obs} versus $[Cl^-]$

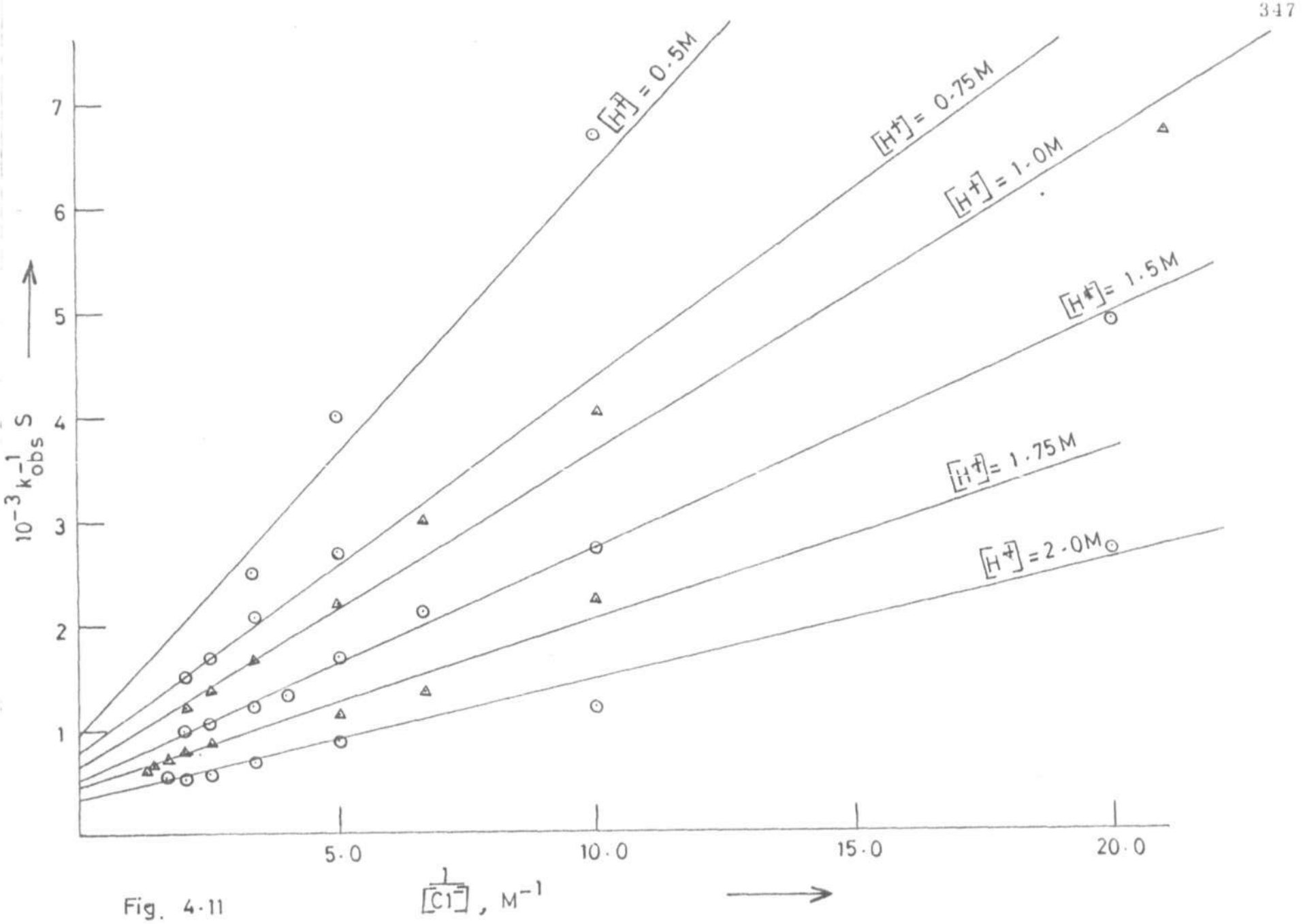


Fig. 4.11

Plot of $\frac{1}{k_{obs}}$ vs $\frac{1}{[Cl^-]}$ for the chloride assisted dissociation of $\left[(bpy)_2ClRuORuCl(bpy)_2\right]^{2+}$

TABLE 4.11

Pseudo-first-order rate constants for the chloride-assisted dissociation of $\{(bpy)_2ClRuORuCl(bpy)_2^{2+}\}$ at constant acid concentrations.

λ = 648nm I = 2.0M(L, ClO_4)

$\{(bpy)_2ClRuORuCl(bpy)_2^{2+}\} = 4.1 \times 10^{-5}M$

$\{H^+\}M$	0.50	0.75	1.0	1.5	1.75	2.0
$[Cl^-]$ ←			$10^3 k_{obs}\ s^{-1}$			→
0.05	-	-	0.15	0.21	-	0.46
0.10	0.15	0.14	0.25	0.37	0.45	-
0.15	-	-	0.33	0.47	0.74	0.84
0.20	0.25	0.37	0.45	0.6	0.88	1.12
0.25	-	-	-	0.75	-	-
0.30	0.4	0.48	0.60	0.83	-	1.48
0.40	0.61	0.65	0.74	0.94	1.13	1.77
0.50	0.69	0.74	0.85	1.01	1.24	1.86
0.60	0.77	0.81	0.91	1.11	1.39	1.98
0.70	0.88	0.91	1.01	1.15	1.47	2.10
0.80	0.93	0.99	0.96	1.24	1.61	2.25
0.90	0.98	-	1.06	1.23	1.71	2.32
1.0	-	1.02	1.10	1.27	1.78	2.44
1.20	1.0	1.02	-	-	-	-
1.33	-	-	-	-	1.78	2.43
1.40	0.99	1.04	1.08	-	-	-
1.50	-	-	-	1.28	-	-
1.60	0.96	-	-	-	-	-
1.67	-	-	-	-	-	2.46
1.70	-	1.05	-	-	1.76	-
1.80	1.0	-	1.09	1.27	-	-
1.90	-	-	-	-	-	-
2.0	1.0	1.05	1.08	1.29	1.76	2.42

TABLE 4.12

Intercepts(a) slopes(b) obtained in the least-mean-square analysis of the plots of $1/k_{obs}$ versus $1/\{Cl^-\}$.

$\{H^+\}$,M	a $x10^{-3}$s	b x 10^{-2}Ms
0.5	0.95	6.16
0.75	0.80	3.95
1.0	0.65	5.1
1.5	0.50	2.2
1.75	0.45	1.6
2.0	0.35	1.18

The linearity of the $1/k_{obs}$ versus $1/_{\{Cl^-\}}$ plots suggests that the empirical rate law for the chloride asissted cleavage of the oxobridged ruthenium(111) dimer is

$$1/k_{obs} = a + \frac{b}{\{Cl^-\}} \qquad .....(4.18)$$

The values of the intercept (a) and the slopes b obtained from the $1/k_{obs}$ versus $1/_{\{Cl^-\}}$ plots were plotted against $\{H^+\}$ (Figures (4.12)and (4.13) respectively).

The former graph was linear with a finite intercept and obeys the expression of the form,

$$a = c + d\{H^+\}^{-1} \qquad .....(4.19)$$

The values of c and d were obtained by least-mean square analysis as

$$c = 1.2 \times 10^2 s$$

$$d = 5.70 \times 10^2 Ms$$

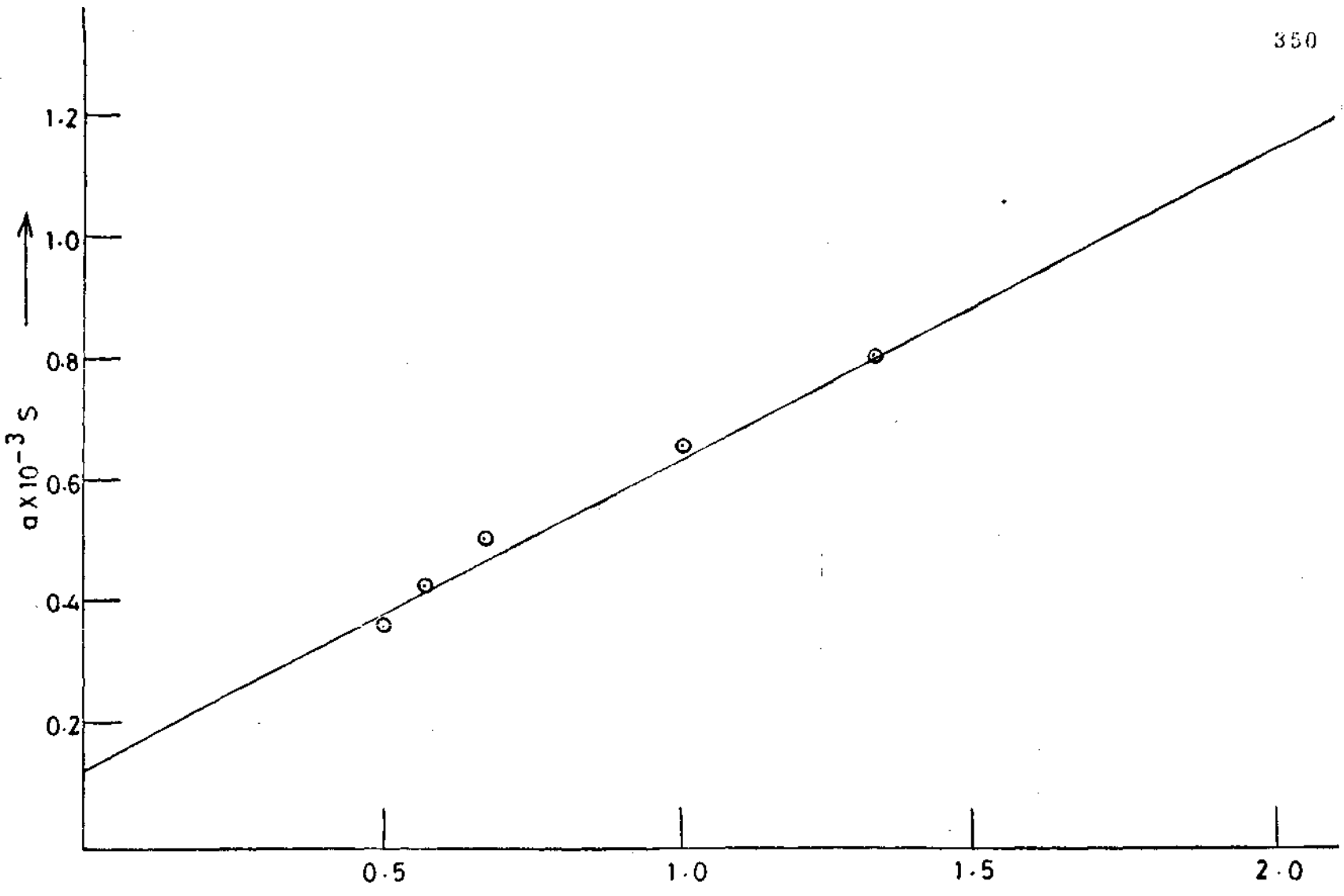


Fig. 4·12

Plot of the intercept (a) $\left\{ \text{of } \frac{1}{k_{obs}} \text{ vs } \frac{1}{[Cl^-]} \text{ plot} \right\}$ against $[H^+]^{-1}$

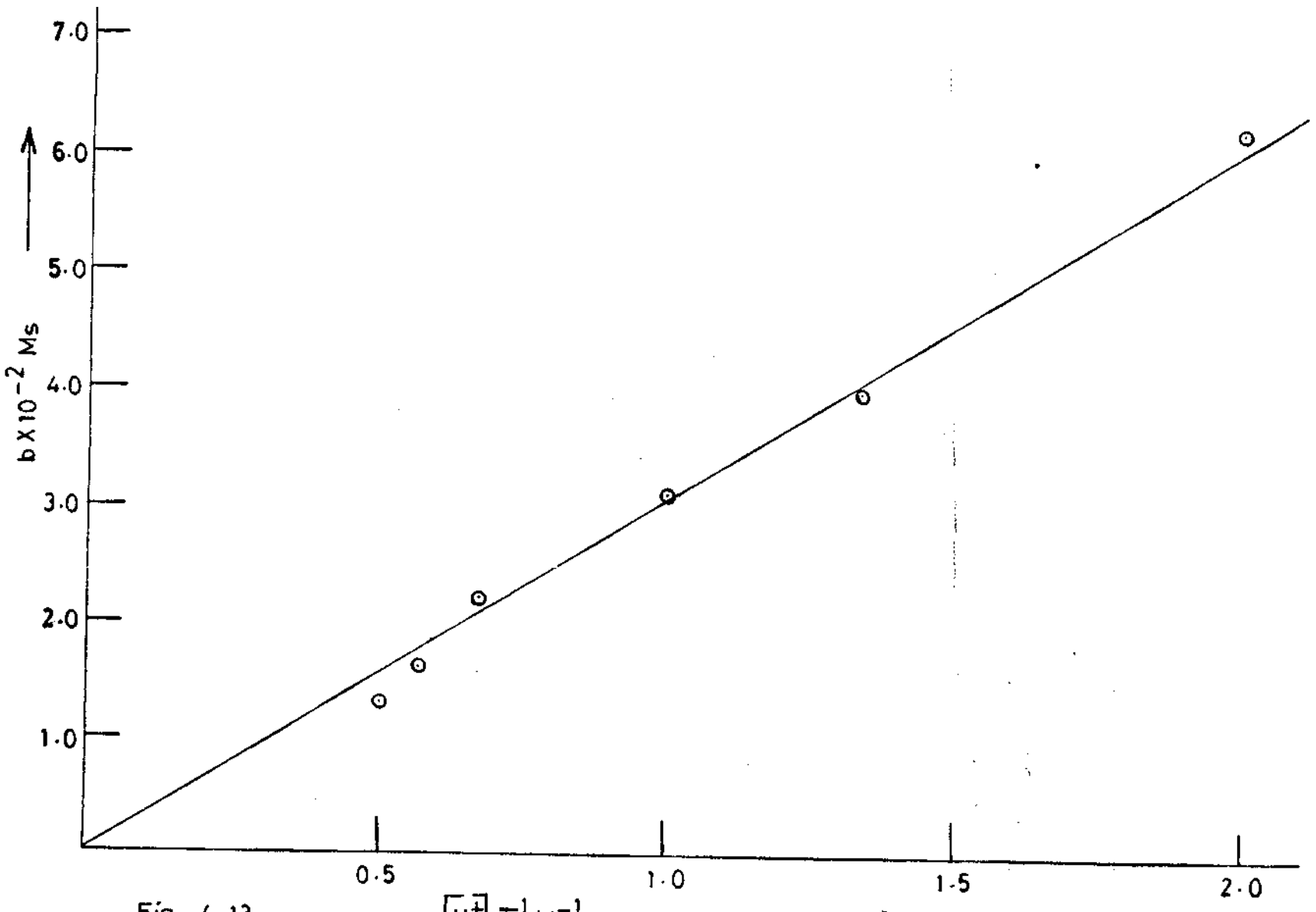


Fig. 4·13

Plot of the slope (b) $\left\{\text{of } \frac{1}{k_{obs}} \text{ vs } \frac{1}{[Cl^-]} \text{ plot}\right\}$ against $[H^+]^{-1}$

The plot of b versus $\{H^+\}^{-1}$ was also linear with zero intercept, and fits an expression of the form,

$$b = e\{H^+\}^{-1}$$

The value of e was calculated as

$$e = 3.02 \times 10^2 \ M^2s$$

Since $1/k_{obs} = a + \frac{b}{\{Cl^-\}}$

and $a = c + d\{H^+\}^{-1}$

from Figure (4.12)

and $b = e\{H^+\}^{-1}$ from Figure (4.13) then the

$$k_{obs} = \frac{\{Cl^-\}}{a\{Cl^-\} + b}$$

$$= \frac{\{Cl^-\}}{\{Cl^-\}\{c + d\{H^+\}^{-1}\} + e\{H^+\}^{-1}}$$

The overall rate law is there

$$\text{Rate} = \frac{\{Cl^-\}}{\{Cl^-\}\{c + d\{H^+\}^{-1}\} + e\{H^+\}^{-1}} \{(bpy)_2ClRuORuCl(bpy)_2^{2+}\} \quad \text{.....(4.20)}$$

NCS⁻ assisted dissociation of $\{(bpy)_2ClRuORuCl(bpy)_2^{2+}\}$

The dissociation of the oxobridged ruthenium(111) dimer in NCS^--ClO_4^- medium was also investigated at varying NCS^- concentration and at constant concentration of acid and $\{(bpy)ClRuORuCl(bpy)_2^{2+}\}$.

Thiocyanate concentrations were always in more than twenty fold excess over $\{(bpy)_2ClRuORuCl(bpy)_2^{2+}\}$.

$[NCS^-]$ was varied from 0.0167M to 0.167M. This was repeated for four different acid concentrations. Ionic strength was maintained at 2.0M($LiClO_4$) and temperature kept constant at 25°C. The pseudo-first-order plots were non-linear but biphasic as shown by the typical plot in Figure (4.14). The observed deviation of the pseudo-first-order plots suggests a catalysis of the reaction.

On the assumption that the two phases of the pseudo-first-order plots represent a consecutive reaction of the form:

$$A \xrightarrow{a} B \xrightarrow{b} C \qquad \text{.....(4.21)}$$

two approaches have been employed in an attempt to separate the rate constants a and b.

1st Approach.

This was done by drawing straight lines through the initial and final parts of the pseudo-first-order plots as shown in Figure (4.14.) The pseudo-first-order rate constants obtained from these lines were assumed to be equal to a and b respectively. The values of a and b so obtained are presented in Table (4.13).

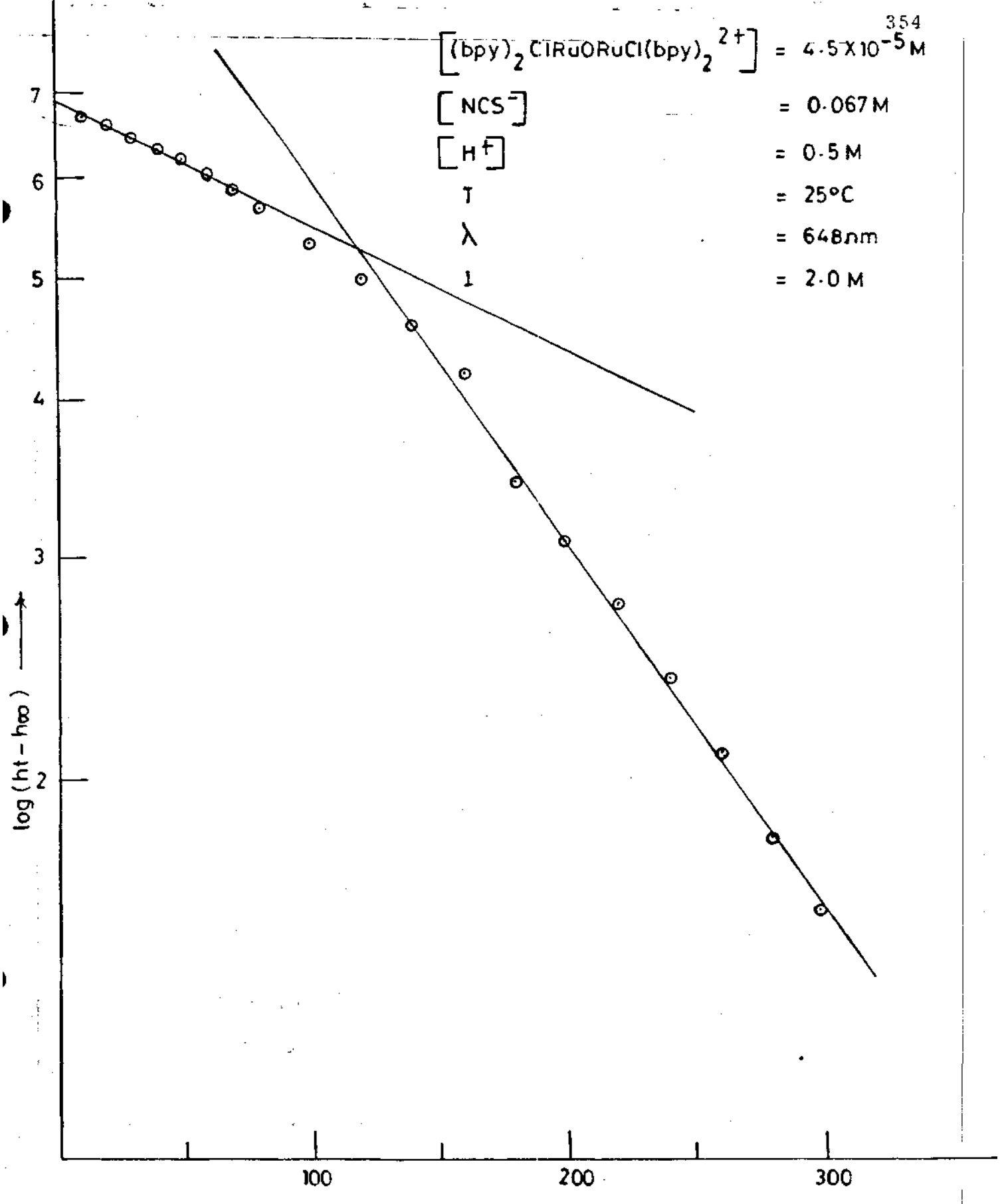


Fig. 4-14

Typical Pseudo -First -Order plot for the thiocyanate assited dissociation of $\left[(bpy)_2ClRuORuCl(bpy)_2{}^{2+}\right]$

TABLE 4.13

Rate constants a and b obtained from the first and second phases of the pseudo-first-order plots of the NCS^- assisted dissociation of the oxobridged ruthenium(111) dimer. $\{(bpy)_2ClRuORuCl(bpy)_2^{2+}\} = 4.5 \times 10^{-5}M$, I, = 2.0M($LiClO_4$)

$\{H^+\}$,M	$\{NCS^-\}$,M	$10^3 a_s^{-1}$	$10^3 b_s^{-1}$
0.50	0.167	2.99	7.14
0.50	0.12	2.30	6.68
0.50	0.067	1.29	2.76
0.50	0.0167	0.23	0.81
0.50	0.0066	0.17	0.35
0.50	0.0033	0.20	0.35
0.735	0.167	3.85	10.25
0.735	0.12	2.93	7.62
0.735	0.067	1.57	4.05
0.735	0.0167	1.13	2.3
0.735	0.0066	0.55	0.55
1.0	0.167	5.76	16.8
1.0	0.12	4.15	10.9
1.0	0.067	2.33	6.0
1.0	0.0167	0.76	1.81
1.0	0.0066	0.62	0.94
1.0	0.0033	0.28	0.39
1.5	0.167	8.89	20.1
1.5	0.12	6.17	15.4
1.5	0.0167	1.47	2.3
1.5	0.0066	0.58	0.58

The values of a and b obtained for the different acid concentrations studied in this work were plotted against $\{NCS^-\}$ as shown in Figure (4.15) and (4.16).

The a versus $\{NCS^-\}$ plots were linear with a common intercept of $1.0 \times 10^{-4} s^{-1}$ and least-mean-square analysis gave the slopes M_1 as presented in Table (4.14).

TABLE 4.14

Slopes, m_1, obtained from the mean-square analysis of the a versus $\{NCS^-\}$ plots.

$\{H^+\}$, M	$10^2 M_1$
0.5	1.7
0.735	2.27
1.0	2.91
1.5	5.17

The a versus $\{NCS^-\}$ plots fit an empirical equation of the form,

$$a = c + m_1\{NCS^-\}$$

where $c = 1 \times 10^{-4} s^{-1}$ and m_1 values are as reported in Table (4.14). A plot of M_1 against $\{H^+\}$ (Figure 4.17), was linear with zero intercept and a slope of 3.2×10^{-2} $M^{-2}s^{-1}$. Therefore $M_1 = 3.2 \times 10^{-2}\{H^+\}$. It thus means that

$$a = 1 \times 10^{-4} s^{-1} + 3.2 \times 10^{-2}\{H^+\}\{NCS^-\}\ s^{-1} \quad \ldots\ldots\ldots(4.22)$$

The plot of b versus $\{NCS^-\}$ was linear with zero intercept and least-mean-square analysis gave the slopes m_2 as presented in Table (4.15)

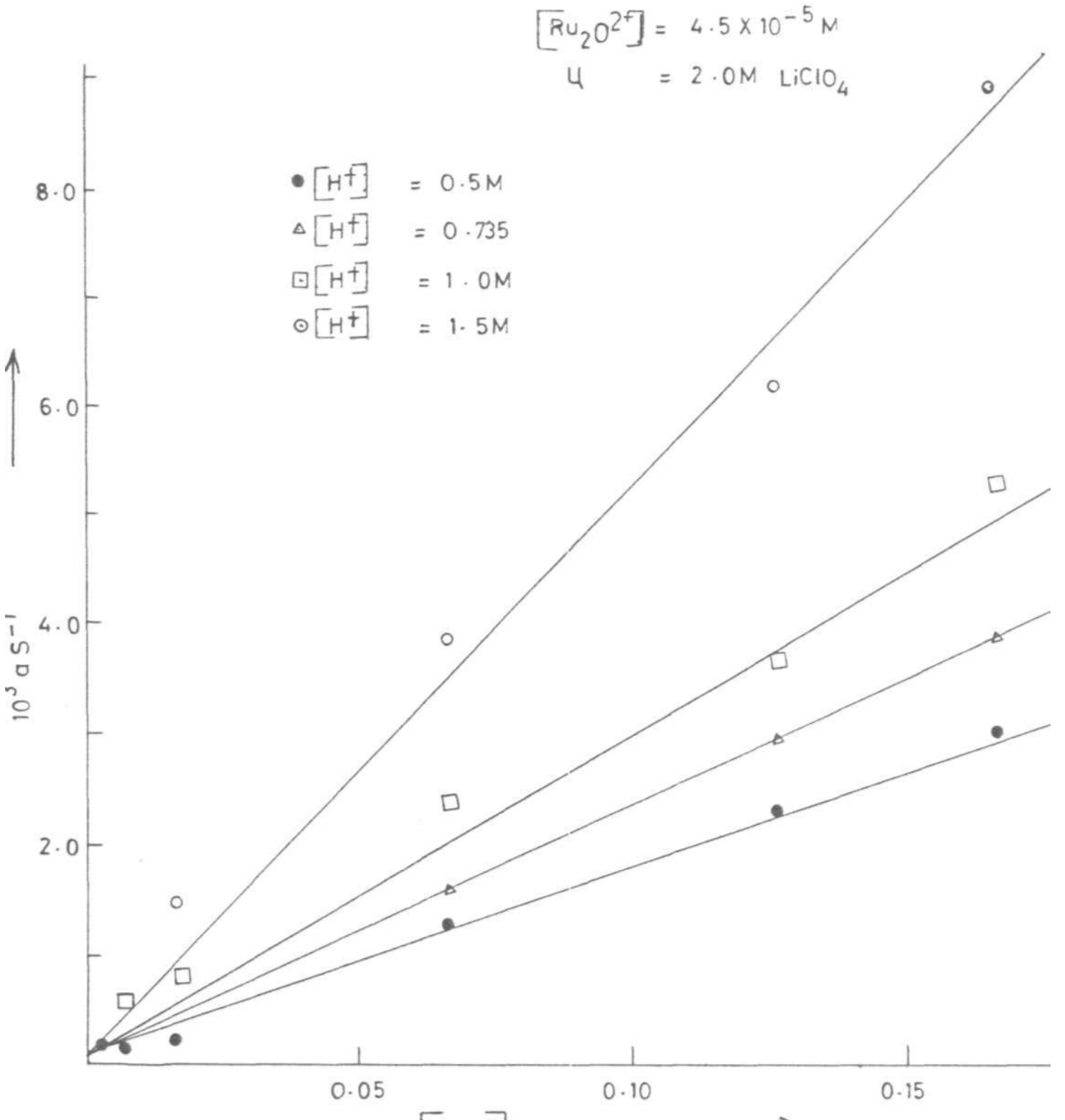


Fig. 4.15

$[NCS^-]$ assited dissociation of $\left[(bpy)_2 \underset{Cl}{Ru} - O - \underset{Cl}{Ru}(bpy)_2\right]^{2+}$

Plot of a versus $[NCS^-]$

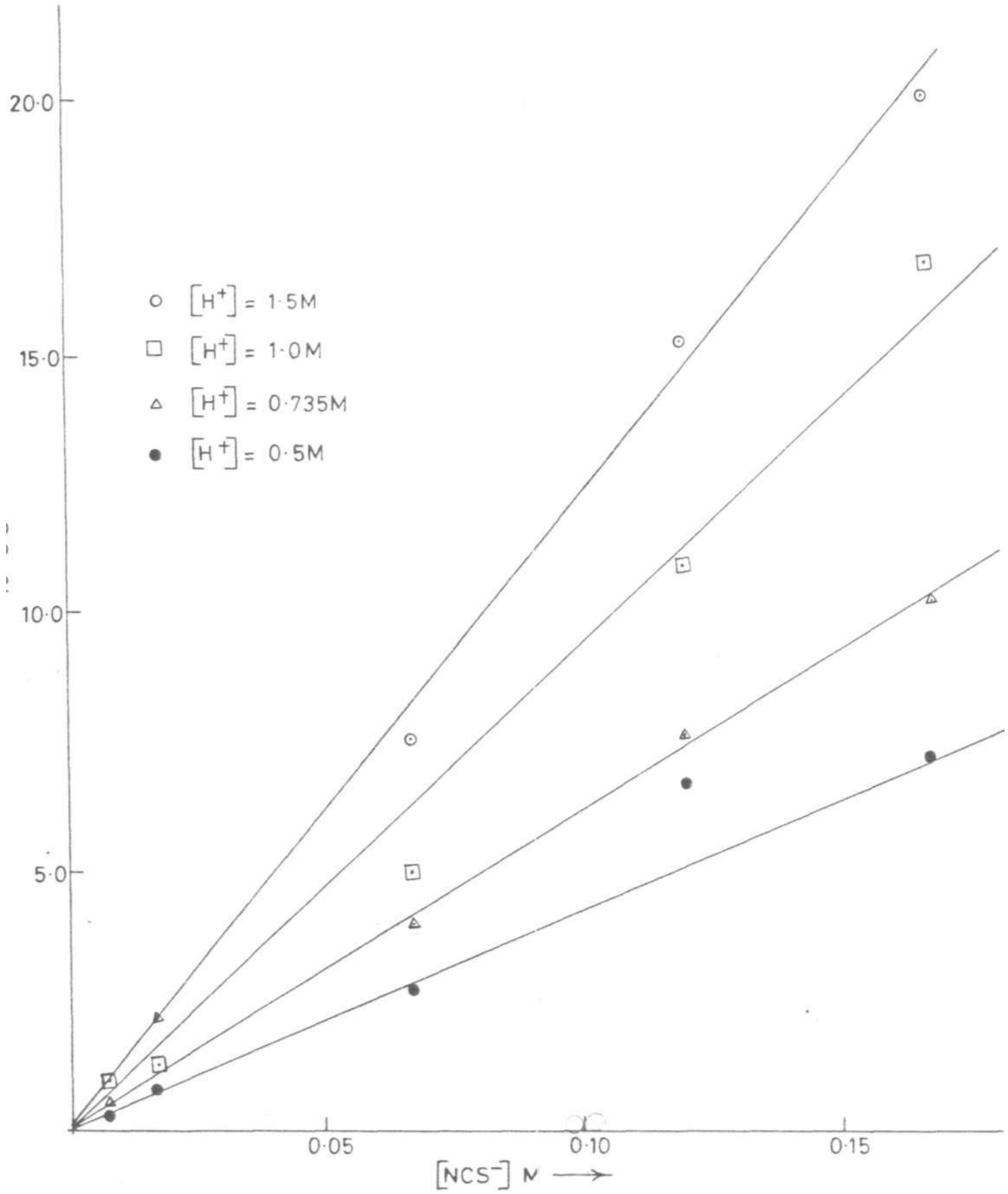


Fig. 4·16 $[NCS^-]$ assisted dissociation of $\left[(bpy)_2Ru(Cl)-o-Ru(Cl)(bpy)_2\right]^{2+}$

Plot of b versus $[NCS^-]$

TABLE 4.15

Slopes, m_2 obtained from the least-mean-square analysis of the b versus $\{NCS^-\}$ plots

$\{H^+\}$,M	$10^2 m_2$
0.5	4.22
0.735	6.17
1.0	9.14
1.5	12.35

Empirically, the dependence of b on $\{NCS^-\}$ can be represented by the equation,

$$b = m_2\{NCS^-\} \qquad \text{.....4.23}$$

A plot of m_2 versus $\{H^+\}$ (Figure 4.18) gave a linear plot which can be represented by the equation,

$$m_2 = 8.2 \times 10^{-2} \{H^+\} \ M^{-2} \ s^{-1}$$

Therefore

$$b = 8.2 \times 10^{-2}\{H^+\} \{NCS^-\} \ s^{-1}$$

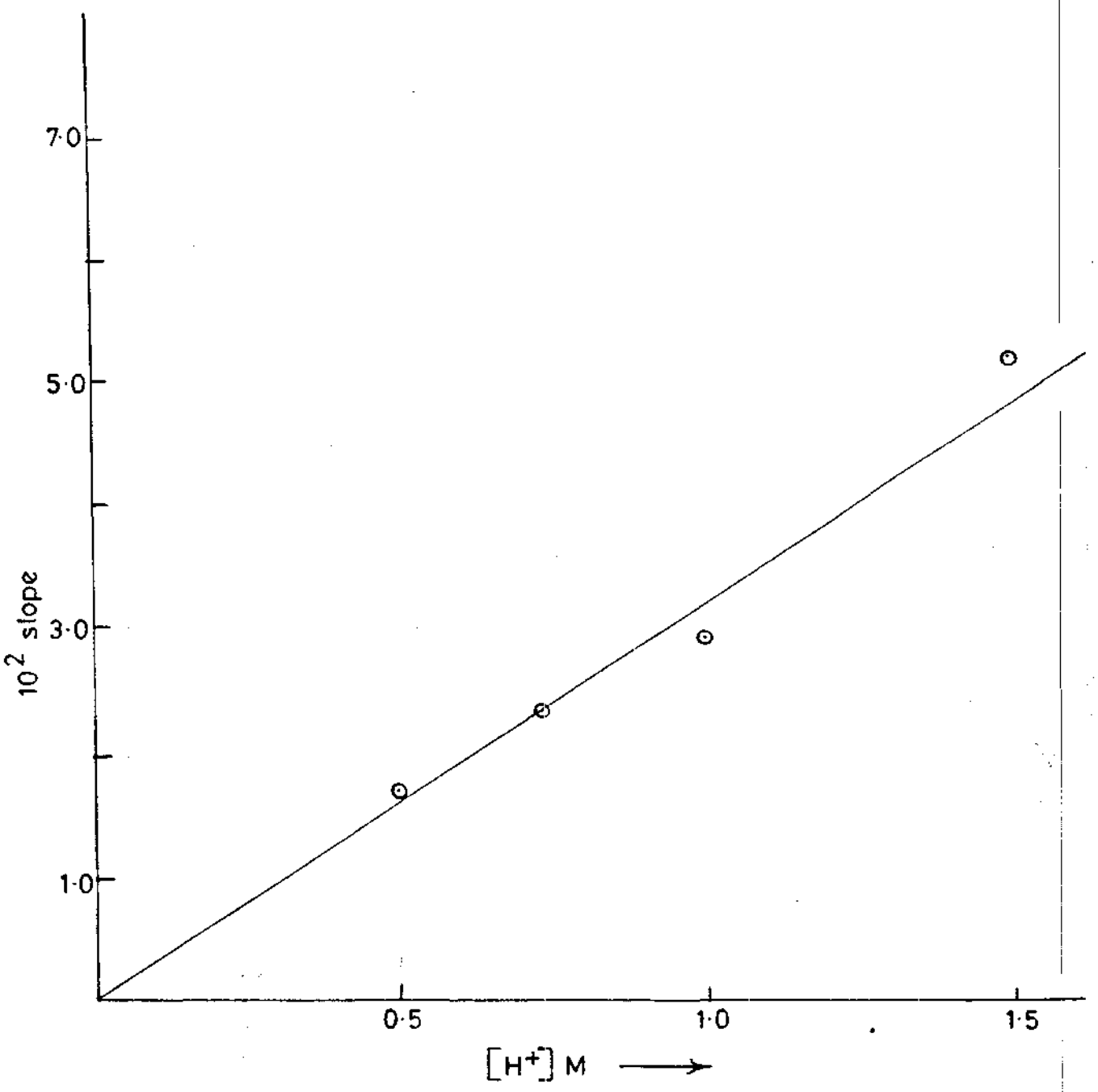


Fig. 4·17 Plot of slope of {a versus H^+} plots against $[H^+]$

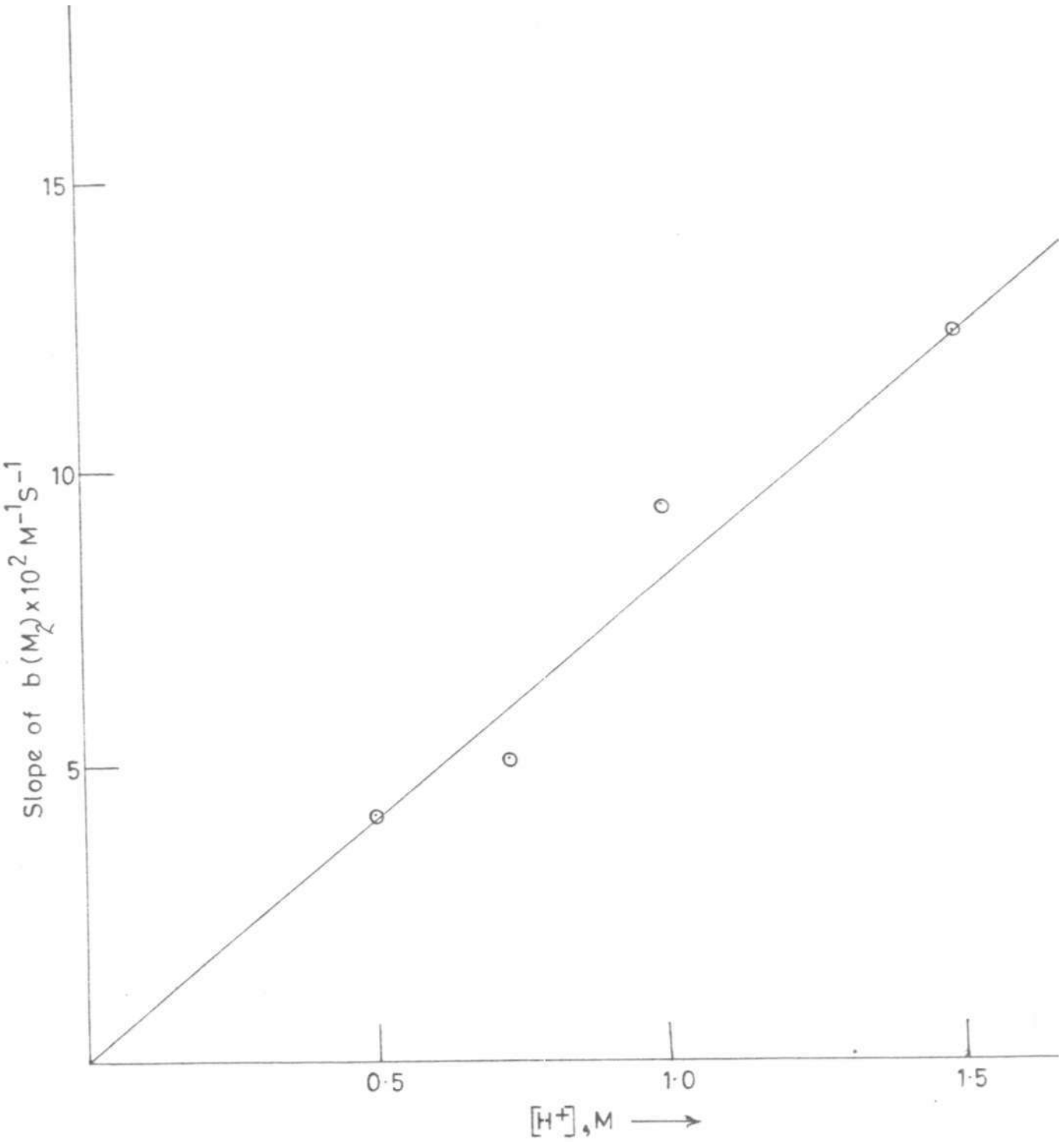


Fig. 4·18 Plot of slope of b vs $[H^+]$

2nd Approach

The closeness of the values of a and b obtained in the first approach suggested that a more rigorous analysis of this reaction scheme was necessary. If we consider the reaction

$$A \xrightarrow{k_1} B \qquad \text{.....(4.24)}$$

$$B \xrightarrow{k_2} C \qquad \text{.....(4.25)}$$

then,

$$-d\{A\}/dt = k_1\{A\} \qquad \text{.....(4.26)}$$

$$-d\{B\}/dt = k_1\{A\} - k_2\{B\} \qquad \text{.....(4.27)}$$

$$-d\{C\}/dt = k_2\{B\} \qquad \text{.....(4.28)}$$

The equation of A (equation(4.26) integrates readily into,

$$A = A_o\, e^{-k_1 t} \qquad \text{.....(4.9)}$$

When this is substituted into equation (4.27) we obtain,

$$d\{B\}/dt = k_1\{A_o\}e^{-k_1 t} - k_2\{B\} \qquad \text{.....(4.29)}$$

This linear first-order equation may be integrated by the usual integrating factor method to give (if $\{B_o\} = 0$)

$$B = \frac{\{A_o\}k_1}{k_2 - k_1}\,(e^{-k_1 t} - e^{-k_2 t}) \qquad \text{.....(4.30)}$$

C may be found most conveniently from the stoichiometric relation obtained by integrating the sum of equations (4.26) to (4.28) i.e.

$$d\{A\}/dt + d\{B\}/dt + d\{C\}/dt = 0 \qquad \text{.....(4.31)}$$

Therefore $A + B + C = A_o$.

If neither B nor C is present initially, then,

$$C = A_o - A - B$$

or

$$C = A_o \left(1 + \frac{1}{k_1 - k_2}\right) (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \qquad .....(4.32)$$

If we assume that the optical absorbance D of the reaction solution at time t, in a cell of pathlength 1cm is additive, i.e.

$$D = \varepsilon_a\{A\} + \varepsilon_b\{B\} + \varepsilon_c\{C\} \qquad .....(4.33)$$

where ε_a is the molar absorptivity of A and so on.

Substituting the values of {A}, {B} and {C} from equations (4.26a), (4.30) and (4.32) into equation (4.33) and rearranging terms leads to the expression

$$D - D_e = a_1 \exp(-k_1 t) + a_2 \exp(-k_2 t) \qquad .....(4.33)$$

where $D_e = \varepsilon_c\{A_o\}$ and a_1 and a_2 are composed of rate constants and molar absorptivities

$$a_1 = \varepsilon_a\{A_o\} + \frac{\varepsilon_b\{A_o\}k_1}{k_2 - k_1} + \frac{\varepsilon_c\{A_o\}k_2}{k_1 - k_2} \qquad .....(4.34)$$

$$a_2 = \frac{k_1\{A_o\}(\varepsilon_b - \varepsilon_c)}{k_1 - k_2} \qquad .....(4.35)$$

Therefore the semilog plot of $D-D_e$ versus time at longer times yields k_s the first-order rate constant for the slow reaction (2.3 x slope). The logarithm of the difference between the extrapolated straight line portion and the experimental curve is then plotted against time and the straight line yields k_f, the rate constant for the fast part of the reaction. A typical analyzed plot is shown in Figure (4.19).

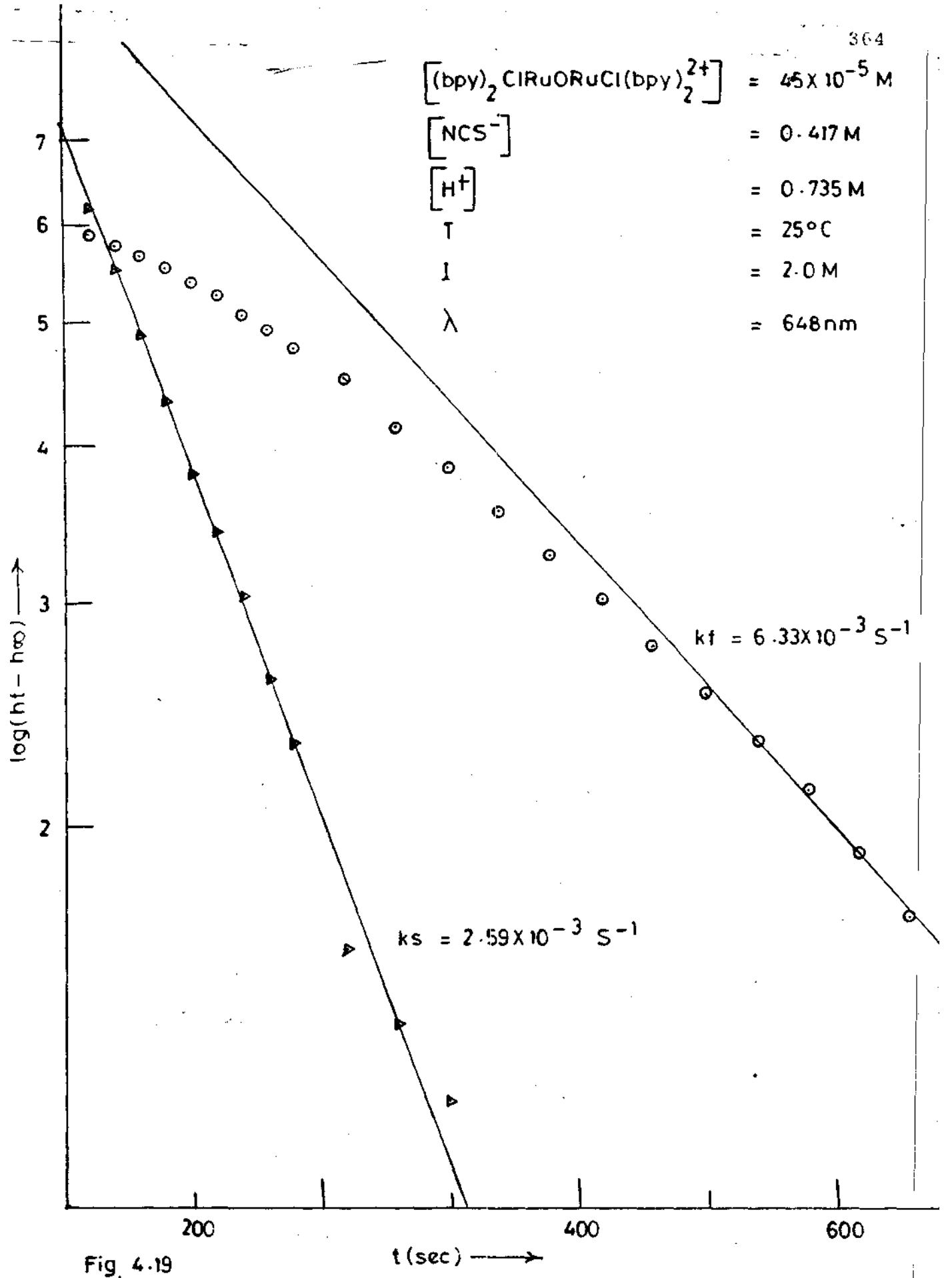


Fig. 4.19

Typical analysed Pseudo-First-Order plot (for k_f and k_s) of the thiocyanate assited dissociation of $\left[(bpy)_2\,ClRuORuCl(bpy)_2^{2+}\right]$

This procedure of analysis is based on the additivity of the exponential terms in equation (4.33).

The results of such analysis for all the acid concentrations investigated are presented in Table (4.16). We can however not assign k_1 and k_2 to k_f and k_s or k_s and k_f respectively since such an assumption was not made in the derivations. To be able to do this we need further information.

TABLE 4.16

k_f and k_s values obtained from the analysis of the pseudo - first-order plots of the NCS^- assisted dissociation of $\{(bpy)_2ClRuORuCl(bpy)_2^{2+}\}$ at for different acid concentrations.

$\{H^+\}$,M	$\{NCS^-\}$,M	$k_f \times 10^2 s^{-1}$	$k_s \times 10^2 s^{-1}$
0.50	0.167	2.34	1.08
0.50	0.12	2.22	0.71
0.50	0.0667	1.32	0.29
0.50	0.0417	0.54	0.086
0.50	0.0066	0.30	0.038
0.50	0.0033	0.12	0.038
0.735	0.167	2.88	1.14
0.735	0.12	2.24	0.94
0.735	0.0667	1.05	0.48
0.735	0.0147	0.63	0.26
0.735	0.0167	0.21	0.095
1.0	0.167	5.11	2.45
1.0	0.12	2.43	1.36
1.0	0.067	1.57	0.88
1.0	0.0167	0.48	0.15
1.0	0.0066	0.26	0.13
1.5	0.167	5.03	2.32
1.5	0.12	2.92	1.75
1.5	0.067	1.67	0.86
1.5	0.0167	0.15	0.15
1.5	0.0066	0.031	0.031

For each acid concentration investigated k_f and k_s increases as$\{NCS^-\}$ increases, with $k_f > k_s$ for each $\{NCS^-\}$ investigated. Also for constant $\{NCS^-\}$ k_f and k_s increases with $\{H^+\}$. The values of k_f and k_s obtained were plotted against $\{NCS^-\}$, for each acid concentration investigated (Figures (4.20-4.23)) graphs were all linear with slopes and intercepts obtained by least-mean-square analysis presented in Table (4.17).

TABLE 4.17

Intercepts and slopes obtained from the k_f and k_s versus $\{H^+\}$ plots for four acid concentrations.

$\{H^+\}$,M	k_f plots intercept x $10^2(s^{-1})$	slope$(M^{-1}s^{-1})$	k_s plots intercept(s^{-1})	x10^2 slope$(M^{-1}s^{-1})$
0.5	0.15	0.144	0	0.05
0.735	0.13	0.157	0	0.06
1.0	0.15	0.19	0	0.12
1.5	0.15	0.256	0	0.13

The k_f versus $\{NCS^-\}$ plots had a constant intercept of 1.5×10^{-3} s^{-1} while k_s versus $\{NCS^-\}$ plots had zero intercept. The slopes of the k_f and k_s versus $\{NCS^-\}$ plots were also plotted against $\{H^+\}$ (Figure 4.24). These plots were linear with the former having a positive intercept of $0.10 s^{-1}$ and slope of 0.082 $M^{-1}s^{-1}$ while the latter plot had a zero intercept but slope of 0.10 M^{-1} $^{-1}$.

The above results can be represented by the following equations:

$$k_f = a + b\{NCS^-\}\{H^+\} \quad \text{.....(4.36)}$$

and

$$k_s = c\{NCS^-\}\{H^+\} \quad \text{.....(4.37}$$

where a = 0.1015 s^{-1}

b = 0.082 $M^{-1}s^{-1}$

c = 0.01 $M^{-1}s^{-1}$

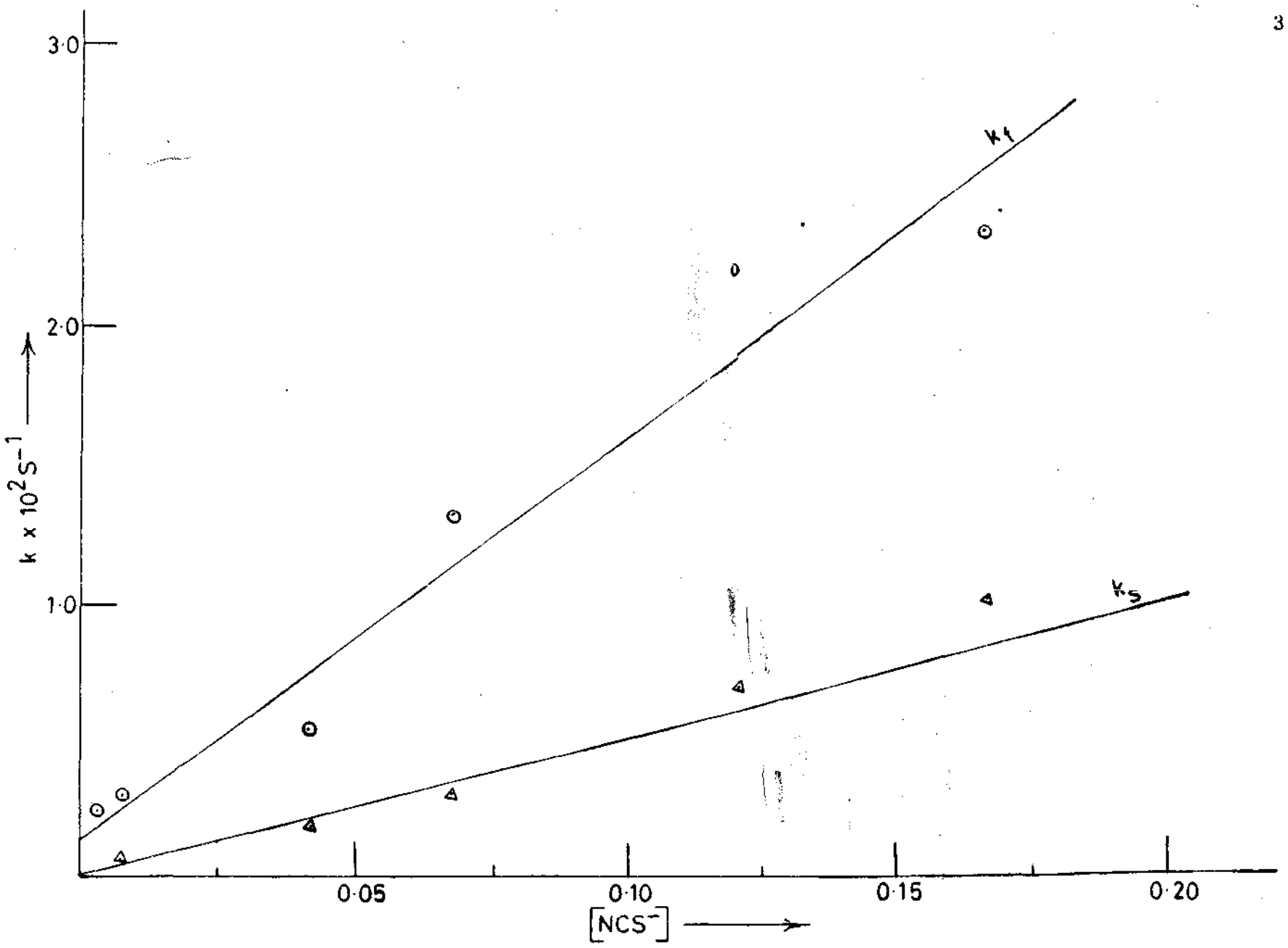


Fig. 4·20 Plot of k_f and k_s versus $[NCS^-]$ for the NCS^- assisted dissociation of $[(bpy)_2ClRuORuCl(bpy)_2]^{2+}$ at $[H^+] = 0.5M$

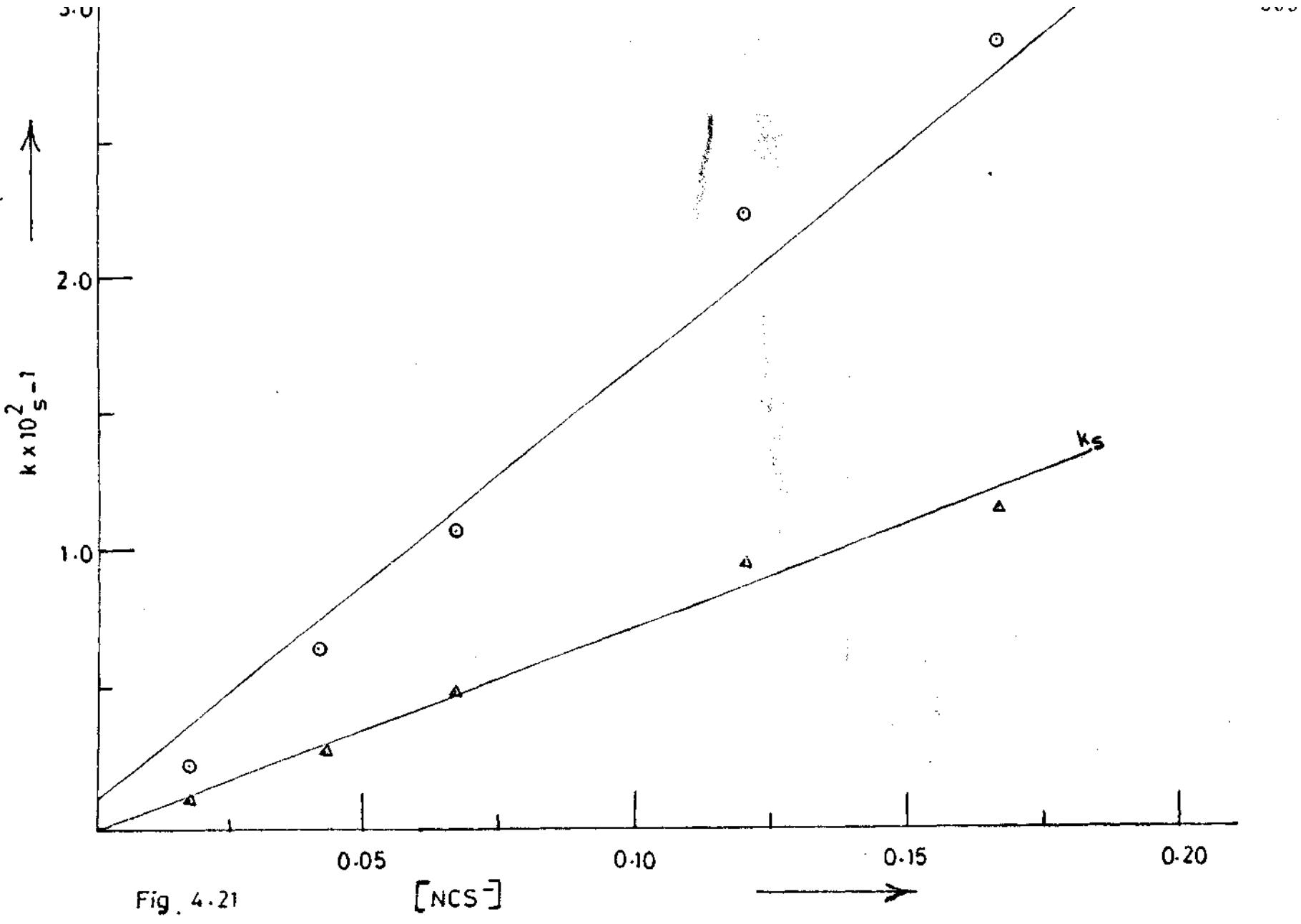


Fig. 4.21

Plot of k_f and k_s versus $[NCS^-]$ for the thiocyanate assisted dissociation of $[(bpy)_2ClRuORuCl(bpy)_2]^{2+}$ at $[H^+] = 0.735$

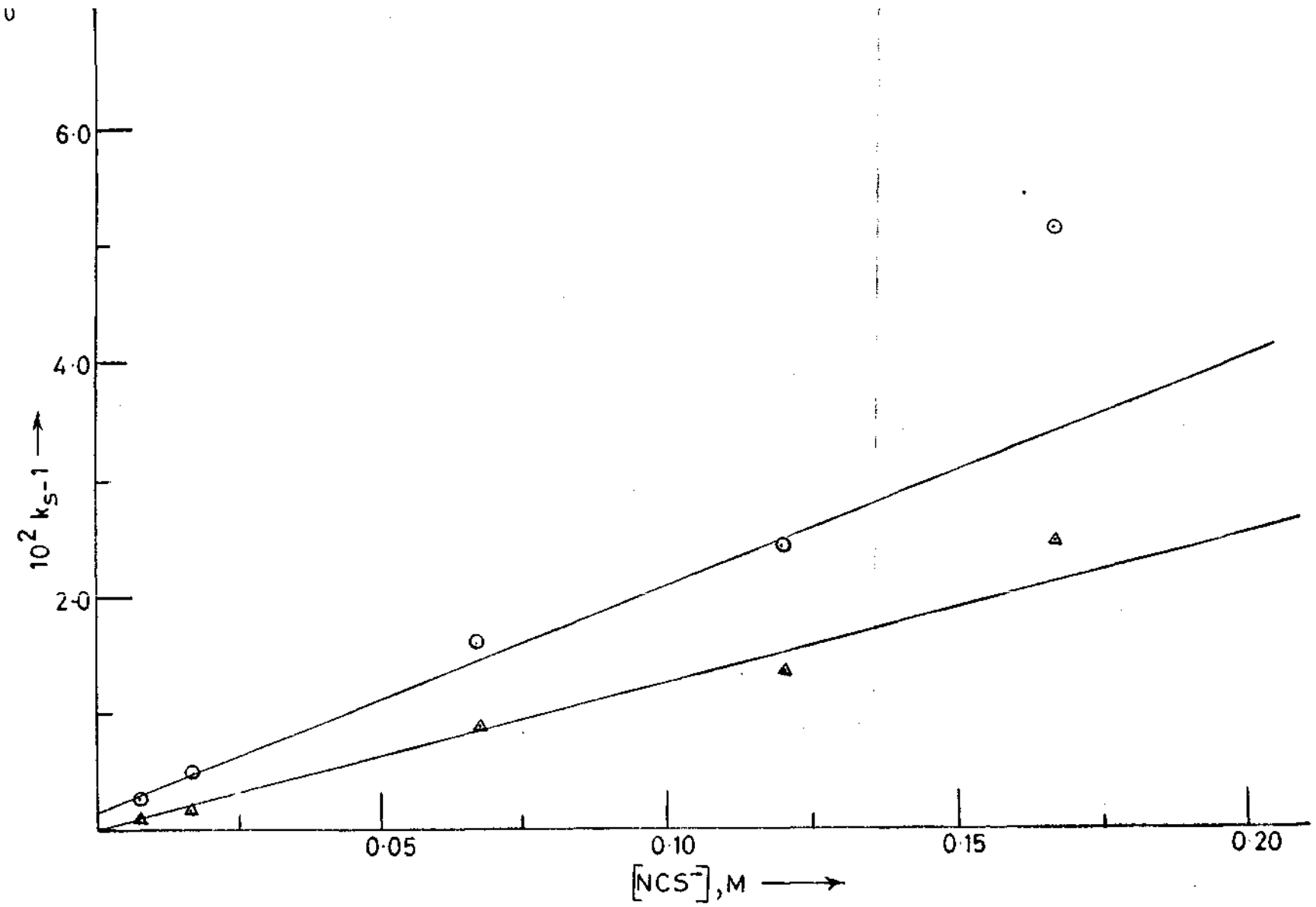


Fig. 4.22 Plot of k_f and k_s versus $[NCS^-]$ for the thiocyanite assisted dissociation of $[(bpy)_2ClRuORuCl(bpy)_2]^{2+}$ at $[H^+] = 1{\cdot}0\,M$

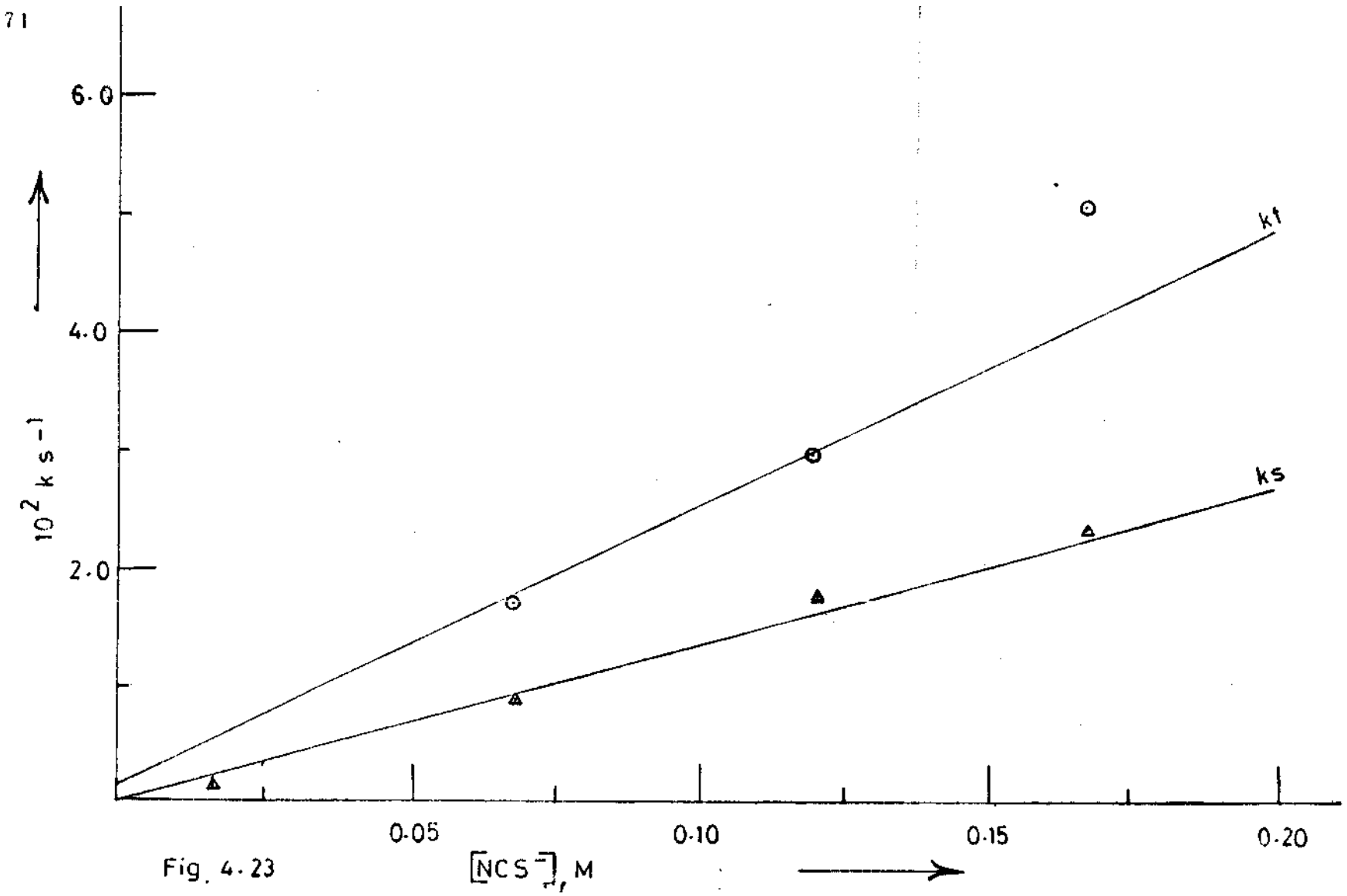


Fig. 4·23

Plot of k_f and k_s versus $[NCS^-]$ for the thiocyanate assisted dissociation of $[(bpy)_2 ClRuORuCl_2]^{2+}$ at $[H^+]$ = 1·50M.

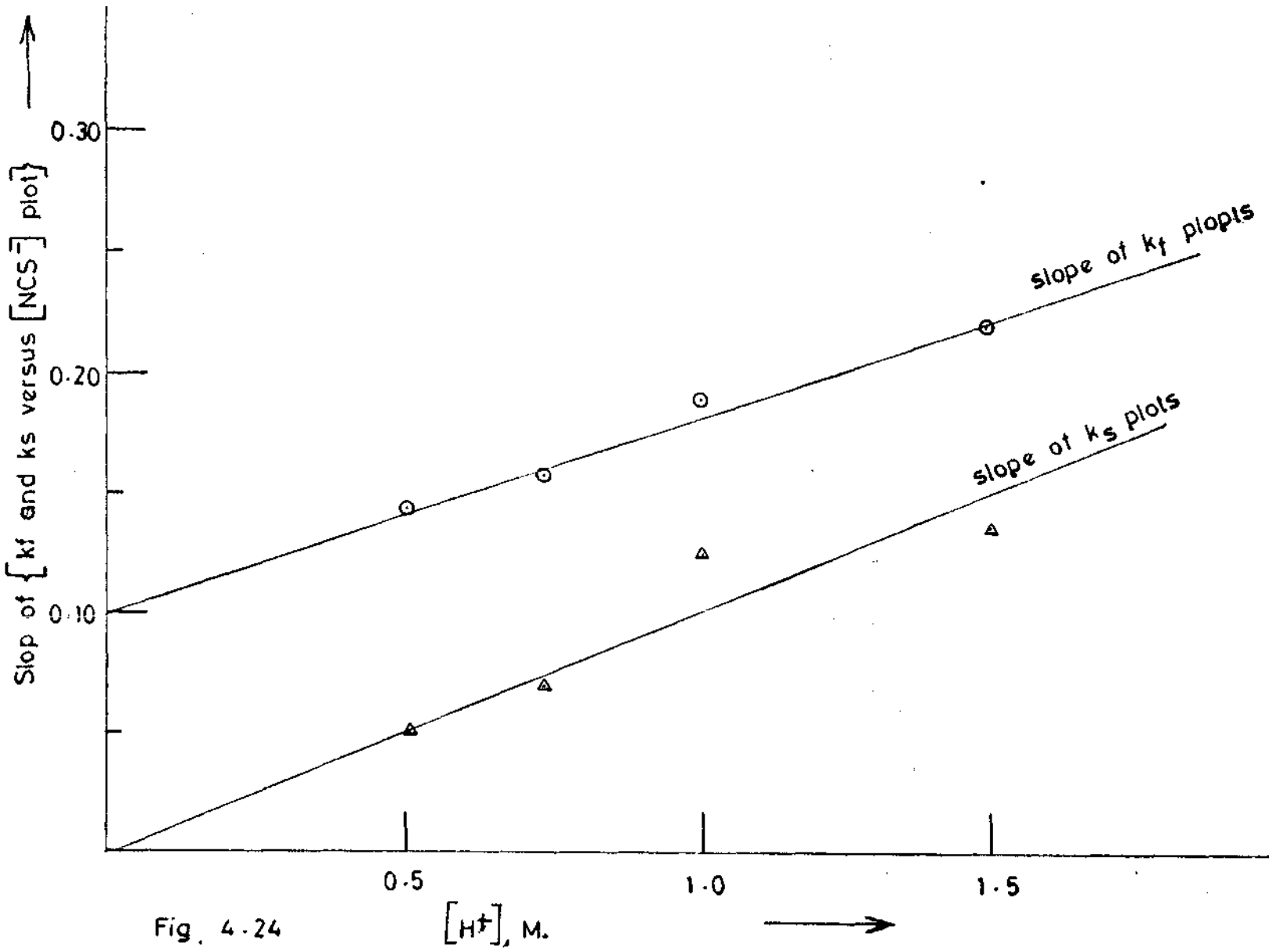


Fig. 4·24

Plot of the slopes of the $\{k_f$ and k_s versus $[NCS^-]\}$ plots against $[H^+]$

D I S C U S S I O N

The increase in the absorbance of the oxobridged ruthenium(lll) dimer in acid medium can be attributed to the protonation of the oxide bridge. Investigation of the effect of acid at $[Cl^-]$ = 1.0M and 2.0M showed that the dissociation of the dimer in HCl - $ClO4^-$ medium follow a linear dependence of the form

$$k_{obs} = k_o + k_{H^+}[H^+]$$

in the range H^+ < 1.0M. Such a dissociation by parallel acid independent and acid dependent paths has previously been observed in the dissociation of some oxo- and hydro-bridged metal ion dimers.[82] For example the dimer $Fe(OH)_2Fe^{4+}$ dissociates by parallel acid-independent and acid-dependent paths.[83]

The chloride assisted dissociation of the oxobridged ruthenium(lll) dimer increases with increasing chloride ion concentration up to about $[Cl^-]$ = 1.0M after which a limiting pseudo-first-order rate constant was obtained for subsequent increase in $[Cl^-]$. Such limiting rate constants have characterized the substitution reactions of some mononuclear complexes. The result of the chloride - assisted dissociation of the ruthenium(lll) oxobridged dimer is consistent with the following proposed mechanism:

$$RuORu^{2+} + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru\text{-}\overset{+}{\underset{H}{O}}\text{-}Ru^{2+} \qquad ....(4.38)$$

$$Ru\text{-}\overset{+}{\underset{H}{O}}\text{-}Ru^{2+} + Cl^- \xrightarrow{k_2} \text{Products} \qquad ...(4.39)$$

($Ru\text{-}O\text{-}Ru^{2+}$ = $[(bpy)_2ClRuORuCl(bpy)_2]^{2+}$)

The application of the steady state approximation of $[Ru \overset{+}{O}\underset{H}{} Ru^{2+}]$ in the above scheme gives,

$$[Ru \overset{+}{O}\underset{H}{} Ru^{2+}] = \frac{k_1 [RuORu^{2+}][H^+]}{k_{-1} + k_2 [Cl^-]} \qquad ...(4.40)$$

Therefore,

$$\text{Rate} = k_2 [Ru \overset{+}{O}\underset{H}{} Ru^{2+}] [Cl^-] \qquad ...(4.41)$$

$$= \frac{k_2 k_1 [Ru\ O\ Ru^{2+}] [H^+] [Cl^-]}{k_{-1} + k_2 [Cl^-]}$$

$$\text{Hence, } k_{obs} = \frac{k_2 k_1 [H^+][Cl^-]}{k_{-1} + K_2 [Cl^-]} \qquad ...(4.42)$$

$$\text{or } 1/k_{obs} = \frac{1}{Kk_2[H^+][Cl^-]} + \frac{1}{k_1 [H^+]} \qquad ...(4.43)$$

It follows that a plot of $1/k_{obs}$ versus $1/[Cl^-]$ should be linear with a slope of $1/Kk_2[H^+]$ and intercept equal to $1/k_1[H^+]$

Such a plot shown in figure (4.11) for all the acid investigations investigated and for $[Cl^-] \leq 1.0M$ was very linear. Equations (4.43) is similar to equation (4.18) with $a = 1/k_1 [H^+]$ and $b = 1/k_2K[H^+]$.

Another implication of the proposed mechanism is that the slop of the $1/k_{obs}$ versus $1/[Cl^-]$ plots should decrease with increase in $[H^+]$.

The slopes of these plots actually decreased with increase in $[H^+]$and a plot of the slopes against $[H^+]$ was very linear with a slope equal to $1/Kk_2$. The value of Kk_2 was thus found from least-mean square analysis to be $3.02 \times 10^2 M^2 s$. The proposed mechanism is further confirmed by the fact that the intercepts of the $1/k_{obs}$ versus $1/[Cl^-]$ decreased with $[H^+]$ as expected and follow a linear relationship of the form.

$$a = c + d[H^+]^{-1}$$

The limiting pseudo-first-order rate constants obtained at $[Cl^-] > 1.0M$ and for all the acid concentrations investigated can also be rationalized on the basis of the propose d mechanism.

At high $[Cl^-]$ i.e. $[Cl^-] \gg 0$

if $k_2 [Cl^-] >> k_{-1}$ then equation (4.42) becomes

$$k_{obs} = \frac{k_2 k_1 [H^+][Cl^-]}{k_2 [Cl^-]}$$

$$= k_1 [H^+] \qquad \ldots(4.44)$$

Therefore,

$$k_{obs}(Lim) = k_1 [H^+] \qquad \ldots(4.45)$$

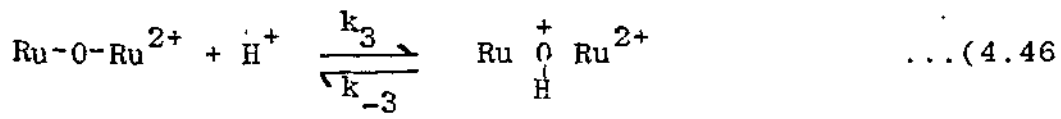
This is very much in line with the observed result that the limiting pseudo-first-order rate constants for the six acid concentrations investigated are independent of $[Cl^-]$ but increases with increasing $[H^+]$. Based on equation (4.45), the k_1 values calculated for the acid concentrations investigated are as follows:

$[H^+]M$	$k_1 M^{-1}s^{-1}$
2.0	1.22
1.75	1.03
1.5	1.2
1.0	1.08
0.75	1.31
0.5	2.0

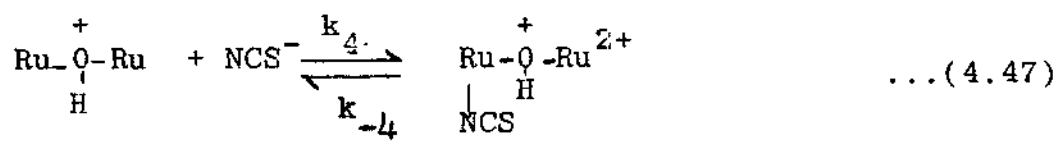
But for $[H^+] = 0.5M$, the k_1 values above are internally consistent and gave an average value,

$$k_1 = 1.2 \times 10^{-3} \quad M^{-1}s^{-1}$$

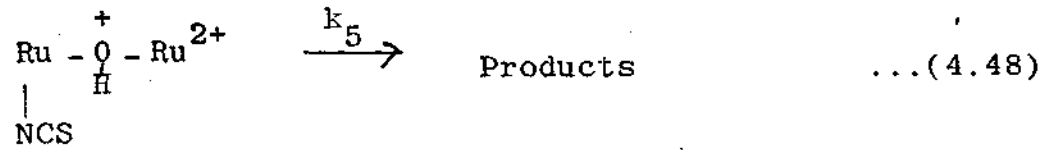
The NCS^- assisted dissociation of the oxobridged ruthenium(111) dimer was a bit more complicated than its chloride assisted dissociation. The observed result was consistent with both protonation of the oxide bridge and substitution on the ruthenium(111) center preceeding dissociation. The pseudo-first-order plots curved in a way suggestive of a consecutive reaction taking place. Generally the NCS^- assisted dissociation was both $[H^+]$ and $[NCS^-]$ dependent. The following reaction sequence is therefore proposed to account for the observed results:



...(4.46)

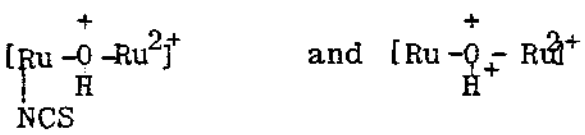


...(4.47)



...(4.48)

The application of the steady-state hypothesis to



and



gives,

$$k_{obs} = \frac{k_3 [H^+] (k_4 + k_5[NCS^-])}{k_4 + k_5[NCS^-](k_{-3} + k_4[NCS^-])} \left[\frac{k_4[NCS^-] - k_4[NCS](k_4+k_5)}{k_4 + k_5[NCS]} \right]$$

...(4.49)

If $k_3 >> k_{-3}$ and $k_4 >> k_{-4}$

then

$$k_{obs} = \frac{k_3[H^+]}{k_4 + k_5[NCS^-]} (1 - k_4 + k_5)$$

$$= \frac{k_3[H^+]}{k_4 + k_5[NCS^-]} - \frac{k_3[H^+](k_4 + k_5)}{k_4 + k_5[NCS^-]} \quad ...(4.50)$$

However from the analysis of the results it was only possible to separate the observed rate constant into two k_f and k_s although it wasn't possible to ascribe k_f or k_s to any

particular reaction step. However a plot of k_f and k_s versus NCS^- were linear, the slope of which depended on $[H^+]$.

The various possible products of the reaction are, $Ru(pby)_2Cl_2^+$, $Ru(bpy)_2ClH_2O^{2+}$, $Ru(bpy)_2(H_2O)_2^{3+}$ in $Cl^- - ClO_4$ medium and $Ru(bpy)_2ClNCS^+$, $Ru(bpy)_2(NCS)_2^+$ in $NCS^- - ClO_4$ medium. Meyer et al[58] reported $Ru(bpy)_2Cl)_2^+$ as the product of dissociation in the $Cl^- - ClO_4$ medium.

Our attempts to try and separate the product of the reaction by ion - exchange did not succeed. The λ_{max} of 485nm and 510nm that we obtained in $Cl^- - ClO_4$ medium did not correlate with that ealier reported by Meyer et al,[58] thus possibly ruling out $Ru(bpy)_2Cl_2^+$ as a product of the reaction. The similarity in the λ_{max} = 485nm obtained in the $NCS^- - ClO_4$ medium with that obtained in the chloride medium may thus mean that it is the diaquoruthinum(111) bis bipyridine complex that is the eventual product of reaction.[84] However a peak of ~480nm had earlier been reported for the thiocyanate ion of bisbipyridyl ruthenium(111).

As in the cases of ligand bridged iron(111) dimer[82] one is tempted to propose that the anion-assisted cleavage of the oxobridged ruthenium(111) dimer proceed by a dissociative mechanism. This is a mechanism consistent with the chloride assisted dissociation of the dimer and also supported by the $kNCS^-/kCl^-$ ratio in the range 1 - 3, which does not reflect the discrimination expected of these ligands in respect of their position in the spectrochemical series if an

associative mechanism were operating. Such a mechanism has been proposed for the anion assisted aquation of dinuclear $Ru_2OCl_{10}^{4-}$ anion[59].

This mechanism which is very common to binuclear metal complexes[82] seem to be as a consequence of the bulkiness of such complexes. The result of the NCS^- assisted dissociation show that there is some participation of the entering ligand. This may however be rationalized as an initial substitution of NCS^- for Cl^- on the dimer and an eventual dissociation.

From literature, it can be seen that the rate constants for the dissociation of cxobridged dimers are much more acid-dependent than are the rate constants of dihydroxy-bridged dimers.[82] The enhanced acid sensitivity of the former dimer may be due, in part to electrostatic factors and to the ease with which the oxybridged species are protonated.[82f] Hence the acid sensititivity of the dissociation of the dimer as observed in this investigation goes to confirm the ruthenium(lll) dimer as being an oxy-and not a hydroxy-bridged dimer, as earlier reported by Meyer et al.[58]

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C H A P T E R 5

Orbital Symmetry Restrictions in Electron Transfer Reactions: Reduction of $[(bpy)_2ClRuORuCl(bpy)_2^{2+}]$ by $V^{2+}_{(aq)}$, $Cr^{2+}_{(aq)}$, $Eu^{2+}_{(aq)}$, $U^{3+}_{(aq)}$, $Ru(NH_3)_6^{2+}$, $TiOH^{2+}$ and Ti^{III}-edta.

E X P E R I M E N T A L

Preparation of $[(bpy)_2ClRuORuCl(bpy)_2^+]$

The ruthenium(111) oxobridged dimer, $[(bpy)_2ClRuORuCl(bpy)_2^{2+}]$ was prepared as reported in Chapter 4.

Preparation of Eu^{3+}/Eu^{2+} solution

Eu^{3+}_{aq} solution was made by dissolving a known weight of Eu_2O_3 in a known excess of perchloric acid calculated from the stoichiometry of the reaction:

$$Eu_2O_3 + 6H^+ = 2Eu^{3+} + 3H_2O \qquad .....(5.1)$$

Europous solution (Eu^{2+}_{aq} solution) was then generated by zinc amalgam reduction of the Eu^{3+}_{aq} solution in an anaerobic atmosphere maintained with a blanket of purified nitrogen gas. The concentration of Eu^{2+} solution was determined by adding a known volume the Eu^{2+}_{aq} solution into excess dearated triiodide solution and determining the excess triiodide by titration against $Na_2S_2O_3$.

Preparation of Uranium(111) solution

Uranium(111) solution was prepared by zinc amalgam reduction of Uranium(V1) perchlorate in a serum-capped bottle under an anaerobic atmosphere of scrubbed nitrogen gas.

Equation:

$$2UO_2^{2+} + 3Zn + 8H^+ = 3Zn^{2+} + 4H_2O + 2U^{4+} \qquad ...(5.2)$$

Preparation of Ruthenium(111) trichloride

Commercial $[Ru(NH_3)_6]Cl_3$ (Johnson and Mathey) was purified by recrystallization as follows:

1g of the commercial sample was dissolved in $40cm^3$ of $10^{-3}M$ hydrochloric acid. The solution was filtered from insoluble impurities and the filtrate cooled to 0^oC in an ice bath. An equal volume of chilled concentrated hydrochloric acid was added to the cold filtrate. The recrystallized $Ru(NH_3)_6Cl_3$ was filtered and washed with cold HCl and dried.

Preparation of $Ru(NH_3)_6^{2+}$ solution

$Ru(NH_3)_6^{2+}$ was prepared from $Ru(NH_3)_6Cl_3$ purified as above by reducing it with Eu^{2+}_{aq} in an anaerobic atmosphere maintained by bubbling carbon dioxide gas. About 5 - 10% less than the stoichiometric amount of Eu^{2+} needed to reduce the $Ru(NH_3)_6Cl_3$ was transferred into an air - tight syringe previously flushed with argon gas. The Eu^{2+}_{aq} solution was then injected into the $Ru(NH_3)_6Cl_3$ solution contained in a serum - capped bottle under an inert atmosphere of carbon dioxide.

Preparation of Chromium(11) solution

2.0g of electrolytic chromium metal was dissolved in $180cm^3$ of 5.0M perchloric acid. The solution was then stirred for 6 hours under an inert atmosphere of nitrogen gas. $80.0cm^3$ of doubly distilled and properly dearated water was then added to the solution under aneorobic conditions. The concentration of the chromium(11) solution was determined by adding a known volume into excess ceric sulphate solution. The excess ceric sulphate was determined iodometrically.

Preparation of Vanadium(lV) solution

About 10g of ammonium metavanadate was dissolved in sodium hydroxide. Perchloric acid (12M) was added to the solution until it turned yellow. The V(V) solution was then reduced to V(lV) by adding Na_2SO_3. The resulting solution was deep blue in colour. The solution was then boiled to remove excess SO_2. A saturated solution of $(NH_4)_2CO_3$ was added until there was no further precipitation (indicated by the ceasation of effervensence). The precipitate V_2O_4 was filtered quickly and washed with distilled water to get rid of any sulphate ions. The oxide was dissolved in $11cm^3$ of 12M perchloric acid. The resulting solution was blue vanadyl solution:

Equation:

$$VO_3^- + 2H^+ \rightarrow VO_2^+ + H_2O \quad ...(5.3)$$

$$2VO_2^+ + SO_2 \rightarrow 2VO^+ + SO_4^= \quad ...(5.4)$$

$$2VO^{2+} + 4OH^- \rightarrow V_2O_4 + 2H_2O \quad ...(5.5)$$

$$V_2O_4 + 4H^+ \rightarrow 2VO^{2+} + 2H_2O \quad ...(5.6)$$

The concentration of V(lV) solution was determined by titration against acidified potassium permanganate and the free acid determined by cation exchange resin as in the Ti(lll) case, but with the assumption that 1 mole of VO^{2+} displaces 2 moles of H^+.

To prepare $V^{2+}aq$, the blue VO^{2+} solution was first pipetted into capped serum bottles and the solution was reduced to $V^{2+}(aq)$ by stirring the solution with freshly prepared zinc amalgam for about 30 minutes.

Determination of the stiochiometry of the reactions.

The stoichiometry of the reactions involving the oxobridged ruthenium(111) dimer and M^{n+} (M^{n+} = $U^{3+}(aq)$, $V^{2+}(aq)$) was determined by spectrophotometric titration as outlined for titanium(111) reactions in chapter 2. The plots of absorbance against the volume of titrant added are presented in Figures (5.1) and (5.2).

For the reaction of the oxobridged ruthenium(111) dimer with $U^{3+}(aq)$, 1.45×10^{-4} mole of the oxobridged complex were consumed by 3.0×10^{-4} moles of U^{3+} at the equivalence point. For the reaction of the oxobridged dimer with vanadium(11), 1.45 mole of the oxobridged dimer were consumed by 2.91 mole of vanadium(11) aquoion at the equivalence point. The above results show that the average stiochiometry of these reactions is 2.0 $\pm$ 0.03 mole of $M^{n+}(aq)$ consumed per mole of oxobridged dimer. This stoichiometry was assumed for all the other reactions investigated in this work. The general equation of the reactions is therefore as in equation (5.7):

$$[(bpy)_2ClRuORuCl(bpy)_2]^{2+} + 2M^{n+} \rightarrow \text{Products} \qquad ...(5.7)$$

(M^{n+} = Cr^{2+}, V^{2+}, $Ru(NH_3)_6^{2+}$, Eu_{aq}^{2+}, U_{aq}^{3+}, Ti^{3+} and Ti^{III}- edta).

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The rates of these reactions were monitored by following the absorbance decrease at λ = 648nm, the absorbance maximum of the oxobridged ruthenium(111) complex. At this wavelength, none of the other species has an effective absorbance. All rate measurements were carried out under pseudo-first-order

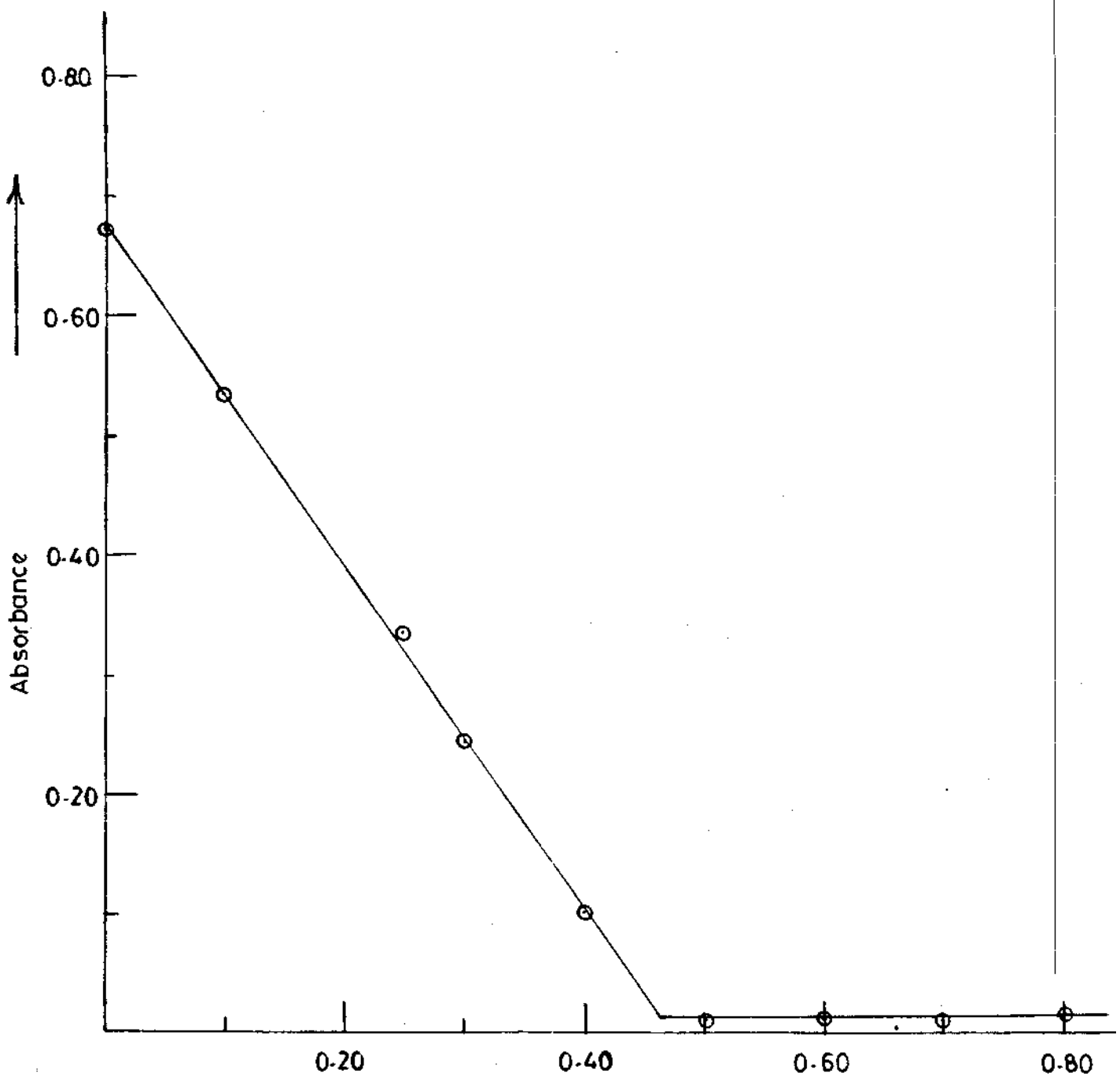


Fig. 5·1 Determination of the stoichiometry of the $\left[(bpy)_2ClRuORuCl(bpy)_2\right]^{2+}$ —$V^{2+}(aq)$ reaction. Plot of absorbance against volume of $V^{2+}(aq)$ added.

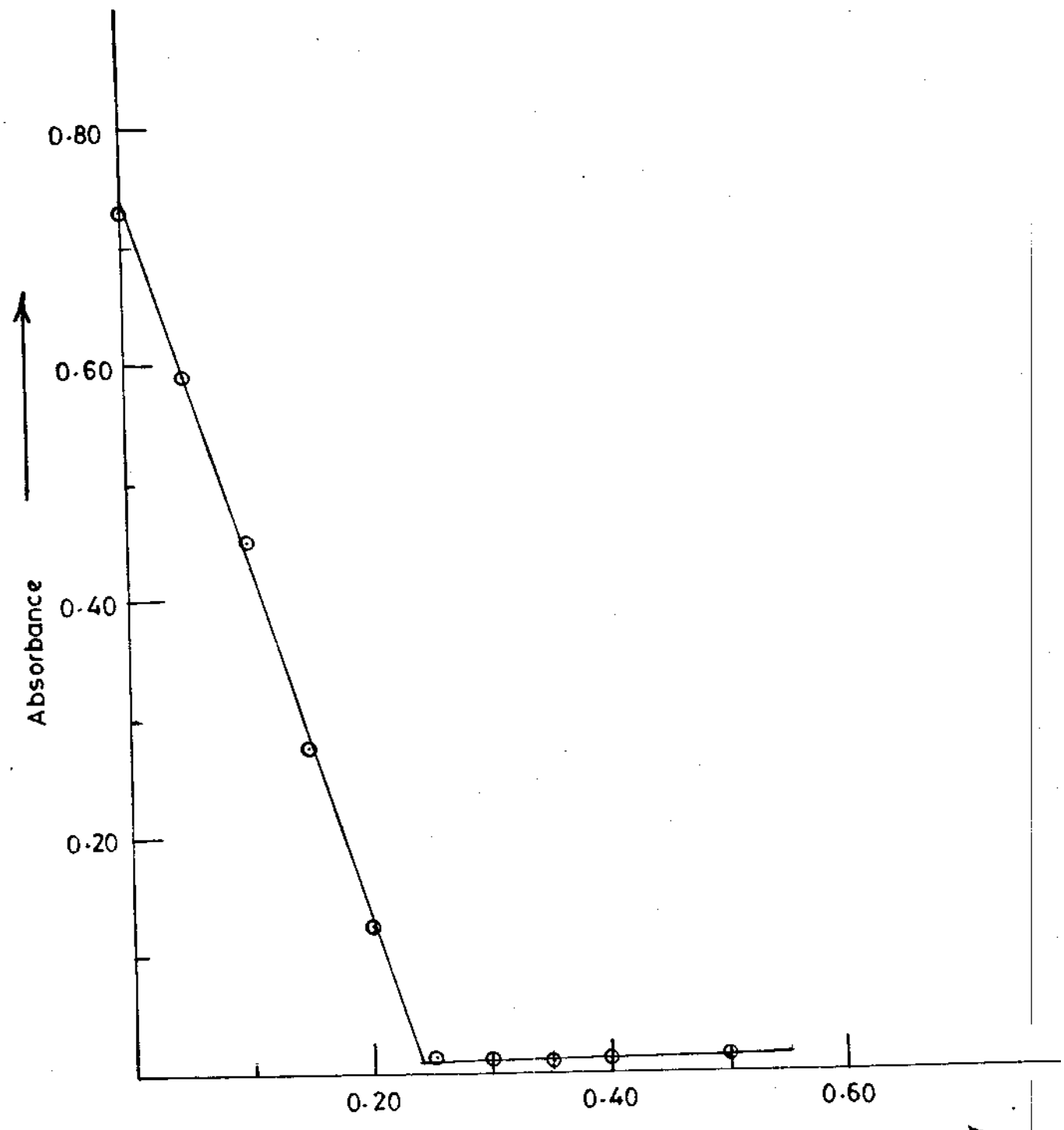


Fig. 5·2 Determination of the stoichiomery of the $[(bpy)_2ClRuORuCl(bpy)_2]^{2+}$ — $U^{3+}(aq)$ reaction. Plot of absorbance versus volume of U^{3+}(aq) added.

conditions with the reductant concentration always in more than twenty-fold excess over that of the oxobridged dimer. Ionic strength was always maintained constant at 0.5M with $LiClO_4$, $NaClO_4$, or $CF_3SO_3^-Li^+$. The non-complexing ability of ClO_4^- or $CF_3SO_3^-$ with the reductant of interest makes either anion a suitable choice as the medium for these reaction.

Temperature was maintained constant at $(26 \pm 1)^oC$ for all runs by circulating thermostated water through the reaction chambers of the spectrophotometer. All solutions were properly dearated before each run. Syringes fitted with platinum needles and flushed properly with nitrogen gas were used for transferring the air-sensitive metal ions involved in this investigation.

Preliminary runs to determine the rates of the reduction of the Ru(lll) oxobridged complex by the reductants: $V^{2+}(aq)$, Cr^{III}_{-edta}, Eu^{3+}, Cr^{2+}, $Ru(NH_3)_6^{2+}$ and U^{3+} showed that the rates of these reactions were too fast to be monitored by the usual conventional techniques and hence, all rate measurements were made on the Durrum - Gibson stopped - flow spectrophotometer.

RESULTS:

Determination of order with respect to $[(bpy)_2ClRuORuCl(bpy)_2]^{2+}$ and $[M^{n+}]$

The reactions were shown to be first-order in $[(bpy)_2ClRuORuCl(bpy)_2^{2+}]$ and $[M^{n+}]$ as follows. Rates of the reactions were measured under conditions in which $[M^{n+}]$ was in at least 20 fold excess over the oxobridged dimer concentrations. Pseudo-first-order plots in $[(bpy)_2ClRuORuCl(bpy)_2^{2+}]$ were linear to more than 90% completion of reaction. Typical plots of log $(A_t - A\infty)$ versus time (A_t and A_∞ are the absorbance of the complex at time t, and the end of the reaction respectively) are shown in figures (5.3) to (5.7) for five of the reactions of interest in this investigation.

The linearity of these plots demonstrates that the reactions are first order in $[(bpy)_2ClRuORuCl(bpy)_2^{2+}]$

Pseudo-first-order rate constants k_1 were determined at different initial concentrations of each metal ion. A plot of log k_1 versus log $[M^{n+}]$ is drawn for each aquoion and are presented in Figures (5.8) to (5.12). From the slopes of these linear plots, the order with respect to $[M^{n+}]$ was determined and the results are as follows:

M^{n+}	order with respect to $[M^{n+}]$.
$Cr^{2+}(aq)$	0.97 ± 0.02
$Eu^{2+}(aq)$	1.0 ± 0.01
$Ru(NH_3)_6^{2+}$	0.96 ± 0.02
$V^{2+}(aq)$	1.04 ± 0.03
$Ti^{3+}(aq)$	0.96 ± 0.01

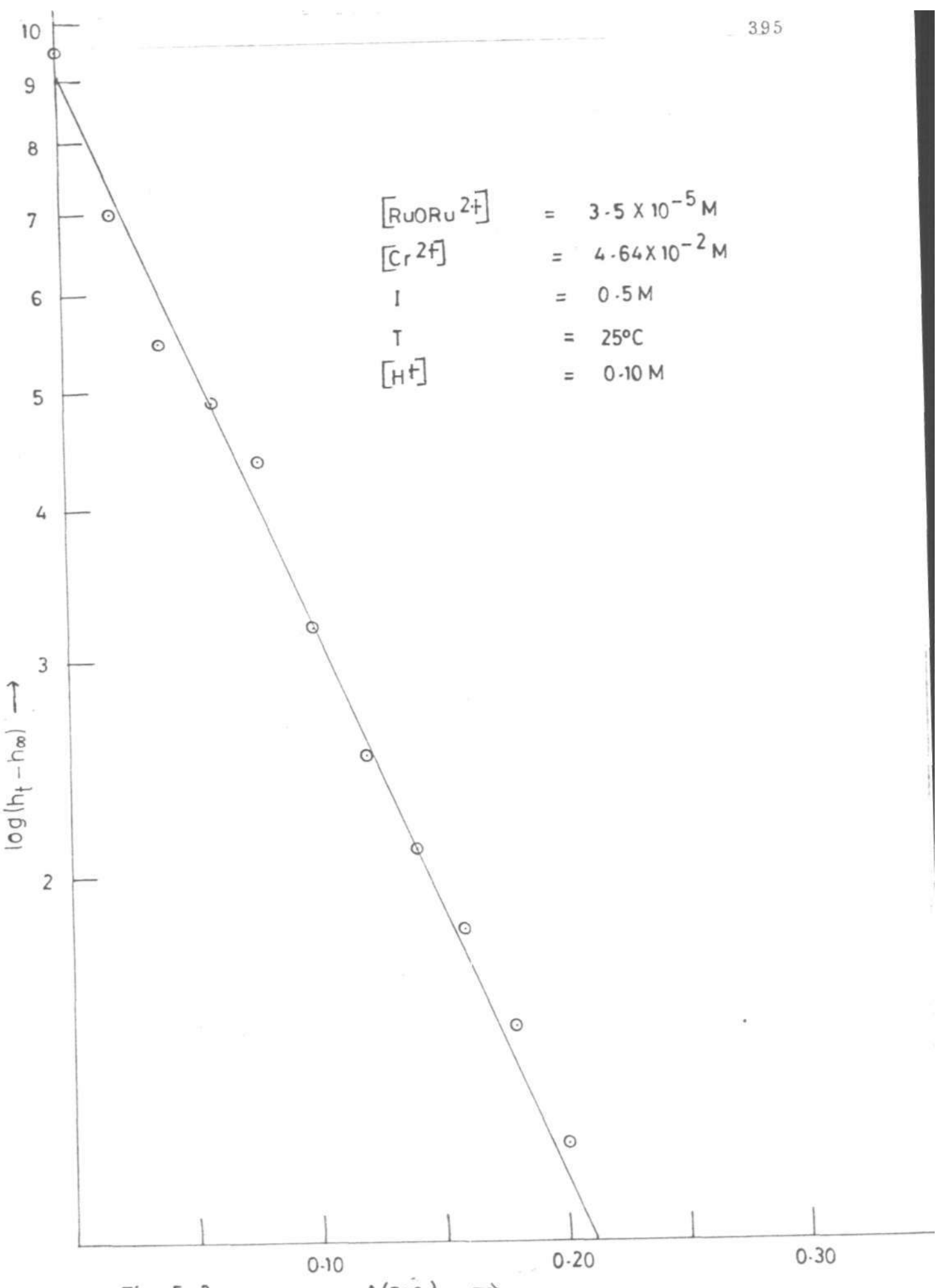


Fig. 5·3 Typical Pseudo – First – Order plot for the $\left[(bpy)_2 ClRuORuCl(bpy)_2\right]^{2+}$ — $Cr^{2+}(aq)$ reaction.

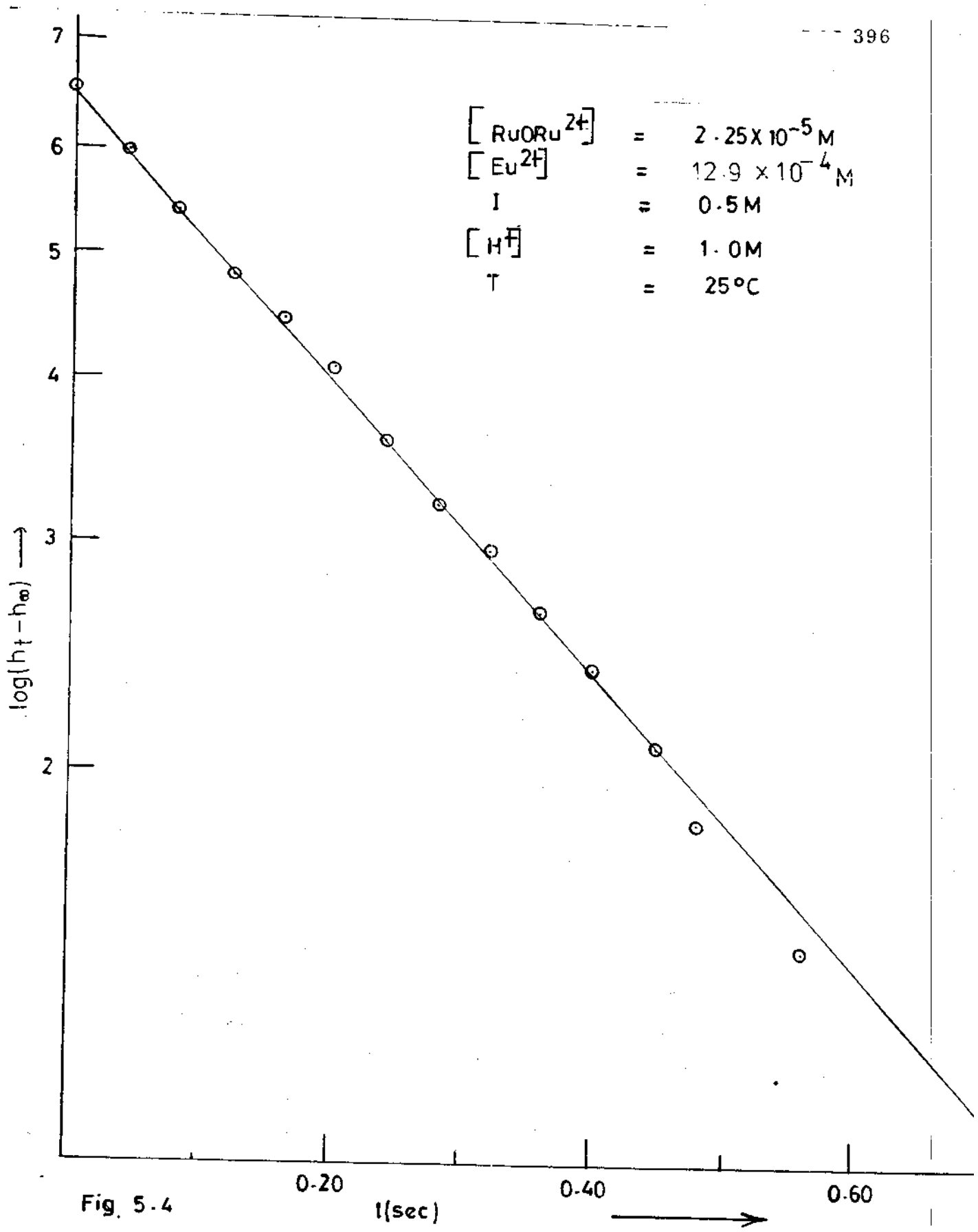


Fig. 5.4 Typical Pseudo-First-Order plot for the $\left[(bpy)_2\,ClRuORuCl(bpy)_2\right]^{2+}$ —$Eu^{2+}(aq)$ reaction.

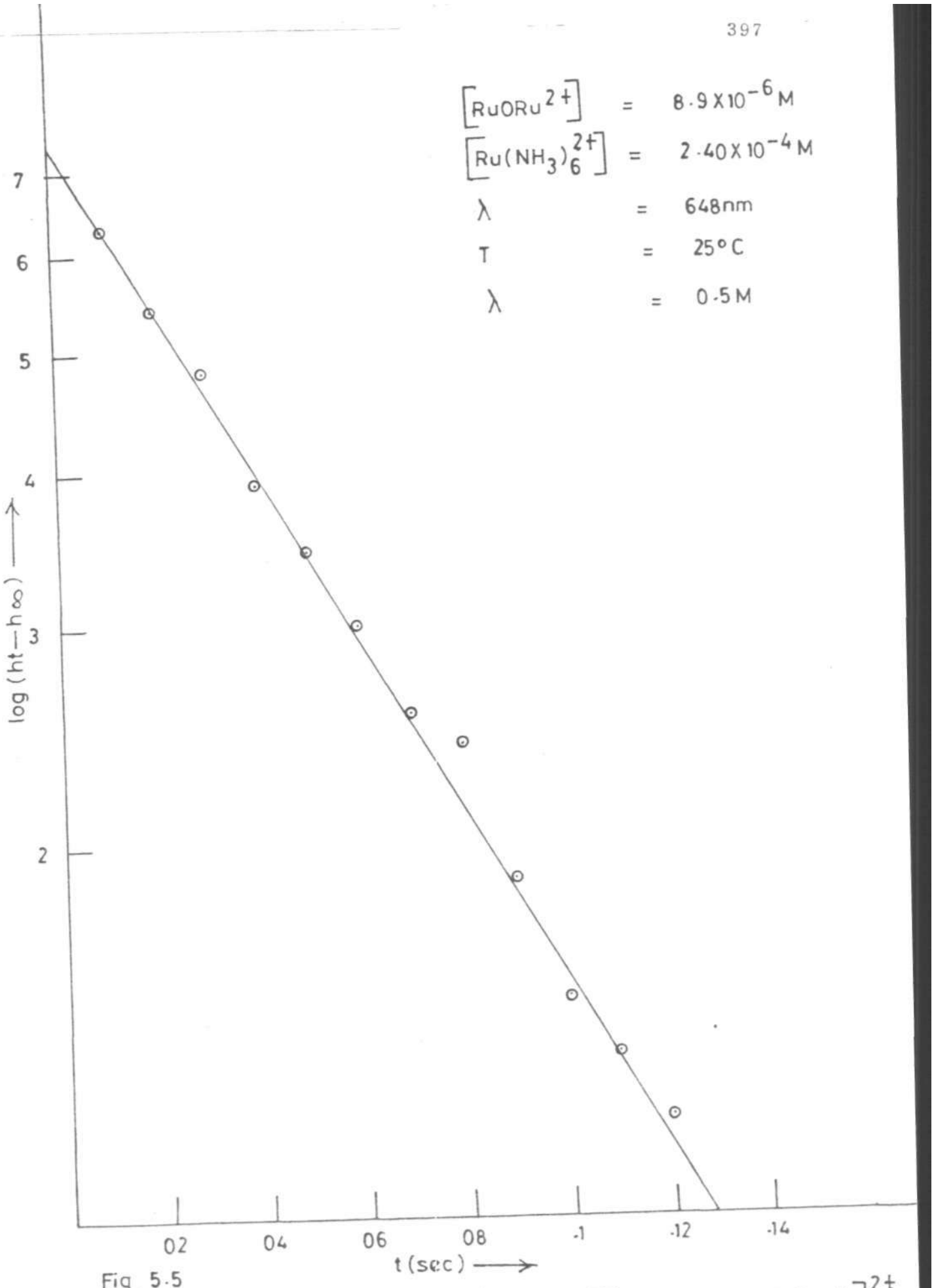


Fig. 5.5

Typical Pseudo-First-Order plot for the $[(bpy)_2ClRuORuCl(bpy)_2]^{2+}$ — $Ru(NH_3)_6^{2+}$ reaction.

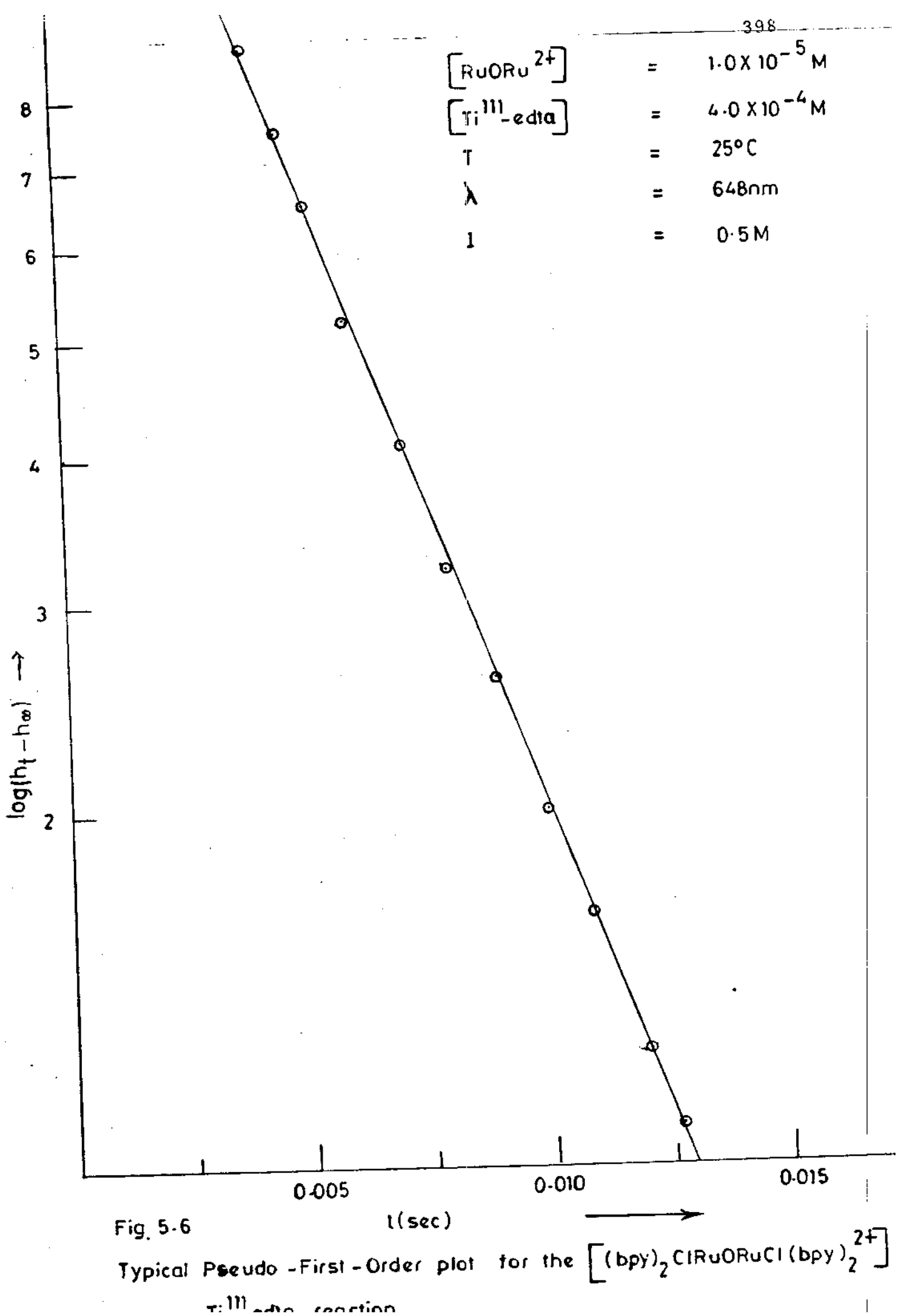


Fig. 5-6

Typical Pseudo-First-Order plot for the $\left[(bpy)_2ClRuORuCl(bpy)_2^{2+}\right]$

Ti^{III}-edta reaction

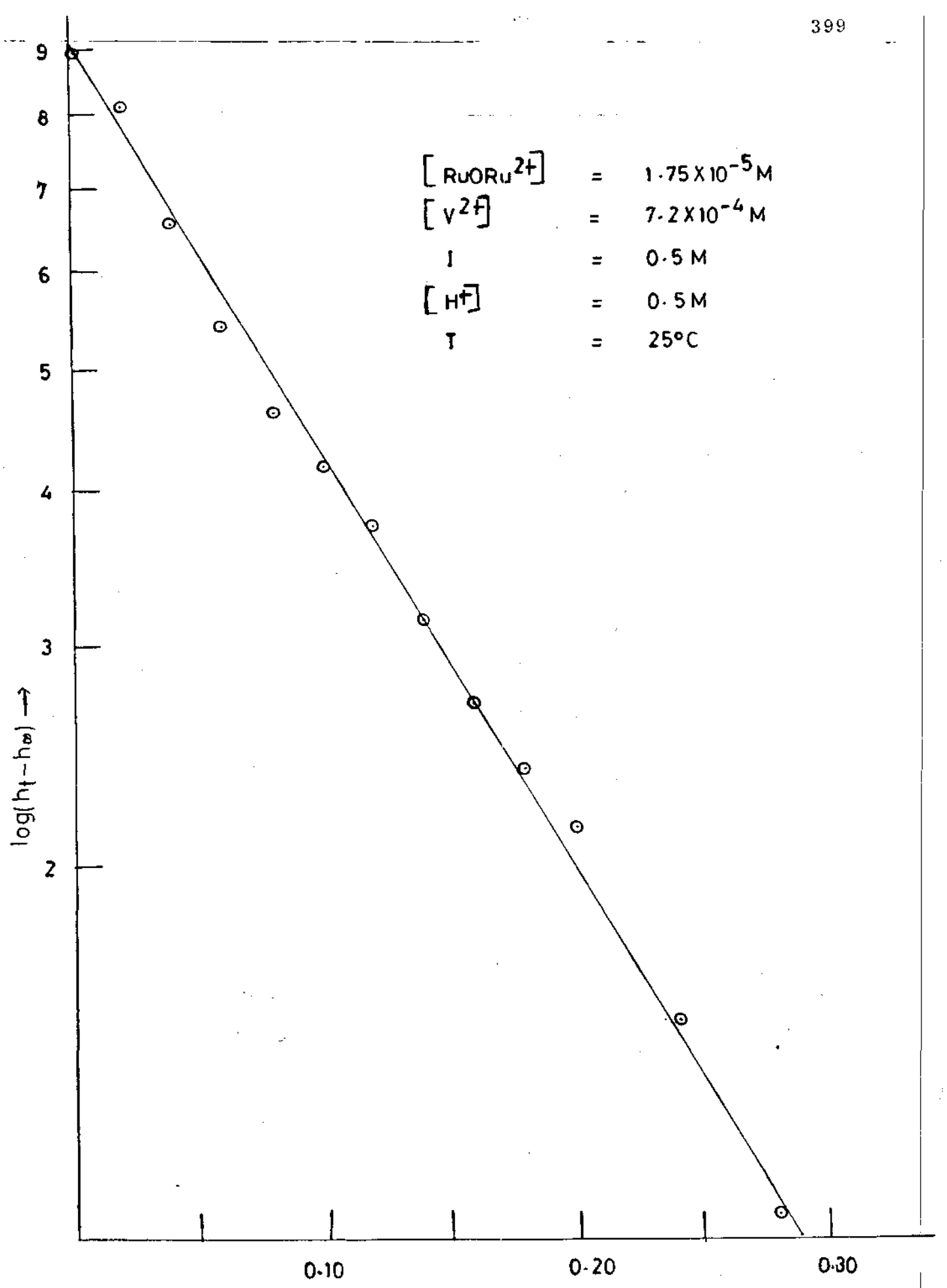
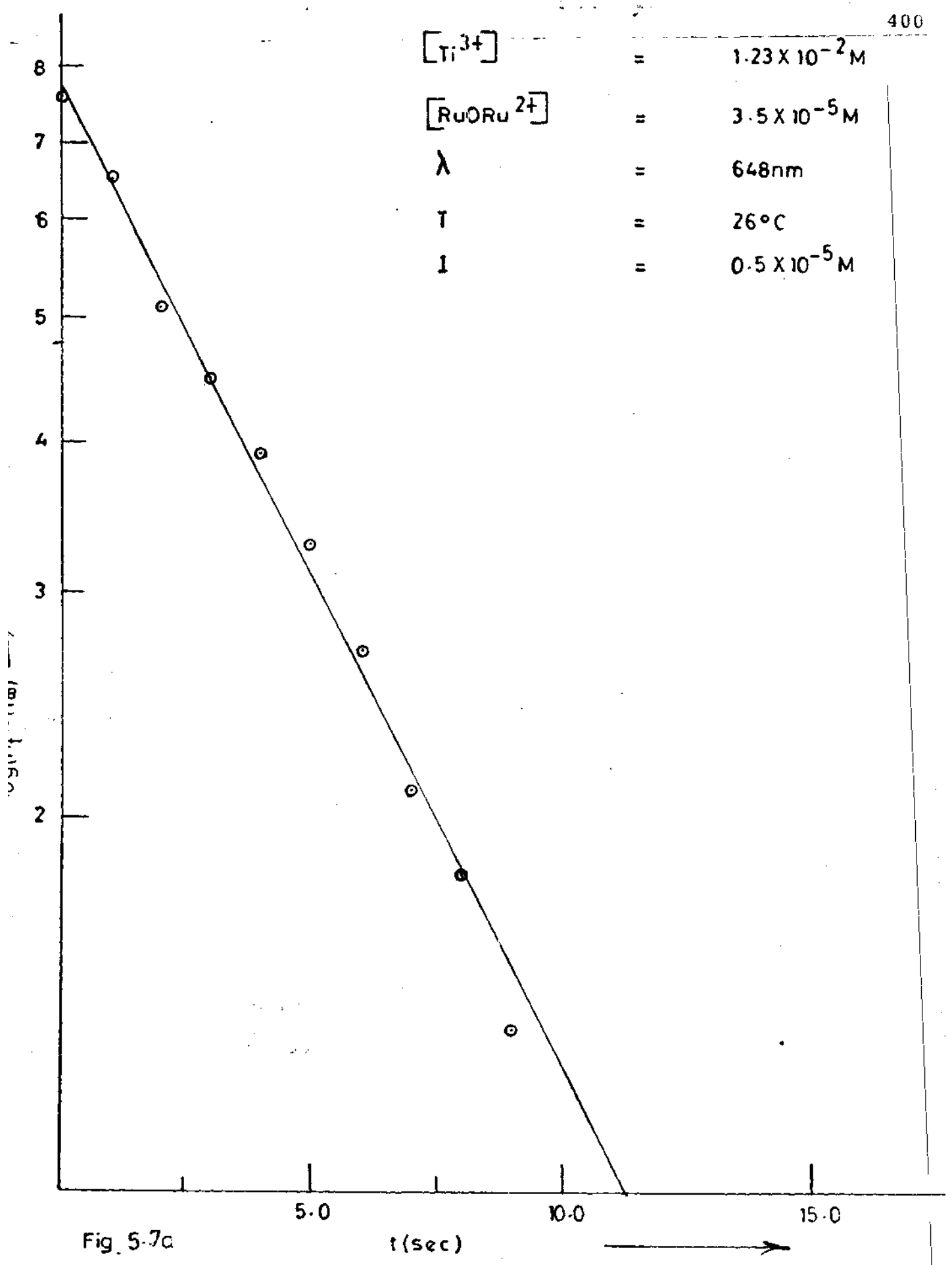


Fig. 5·7

Typical Pseudo-First-Order plot for the $\left[(bpy)_2\,ClRuORuCl\,(bpy)_2\right]^{2+}$



$[Ti^{3+}]$ = 1.23×10^{-2} M

$[RuORu^{2+}]$ = 3.5×10^{-5} M

λ = 648nm

T = 26°C

I = 0.5×10^{-5} M

Fig. 5.7a

Typical Pseudo-First-Order plot for the $[(bpy)_2ClRuORuCl(bpy)_2^{2+}]$ + $Ti^{3+}(aq)$ reaction.

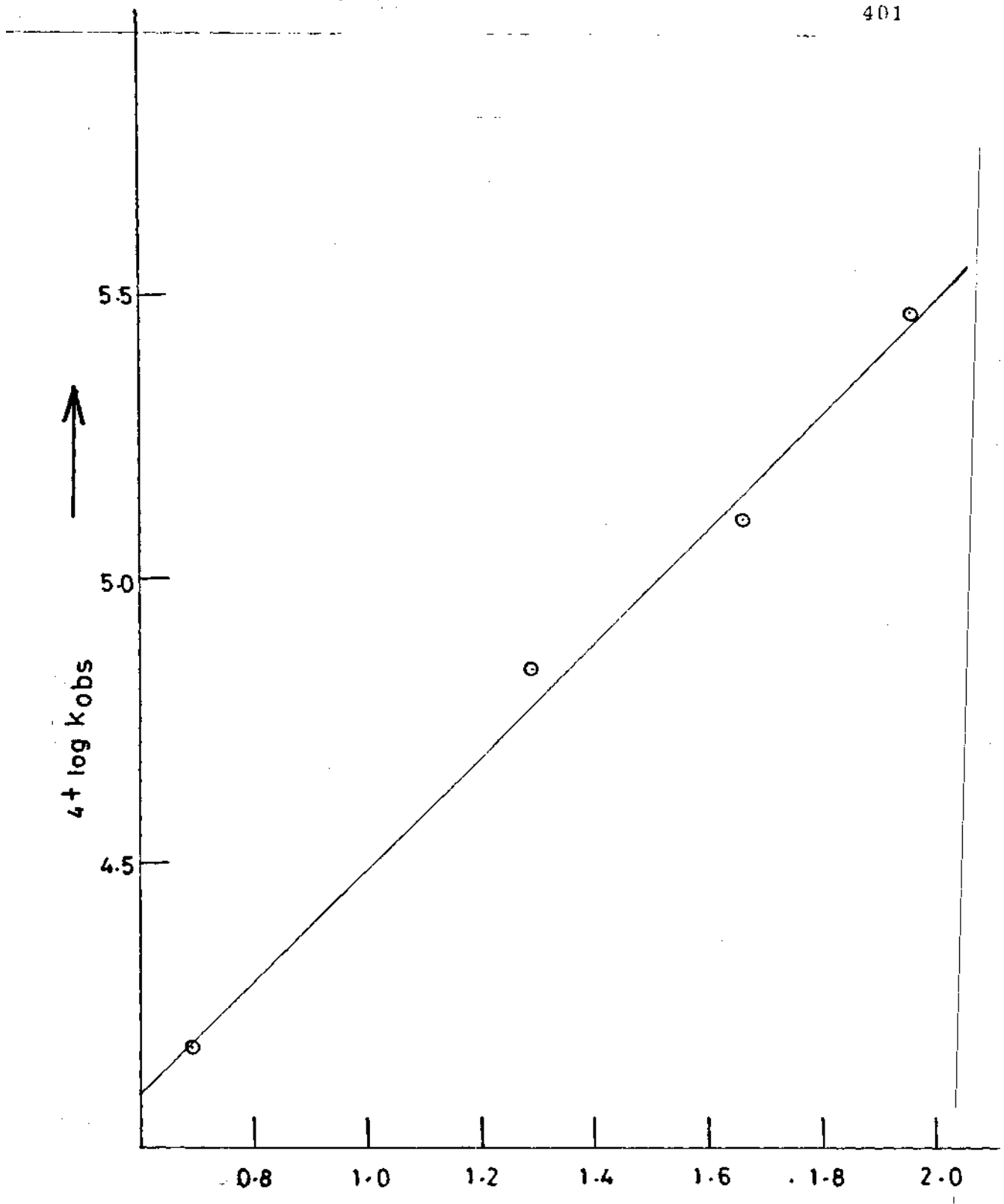


Fig. 5.8 Determination of the order of the $\left[(bpy)_2ClRuORuCl(bpy)_2\right]^{2+}$ — $Eu^{2+}(aq)$ reaction. Plot of log k_{obs} versus log $\left[Eu^{2+}\right]$

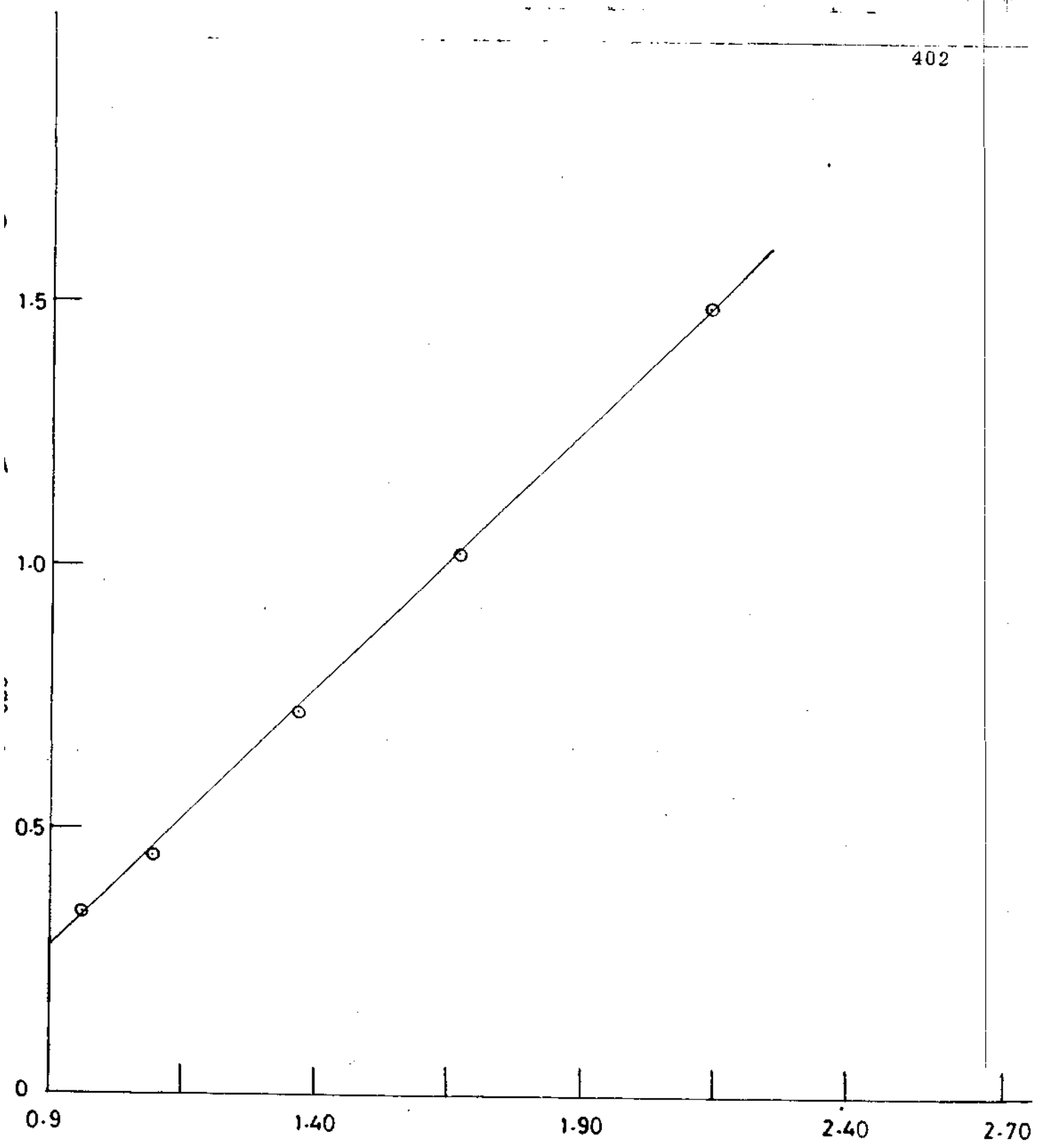


Fig. 5·9 Determination of the Order of the $\left[(bpy)_2 ClRuORuCl(bpy)_2\right]^{2+}$ — $Cr^{2+}(aq)$ reaction. Plot of log k_{obs} versus log $[Cr^{2+}]$

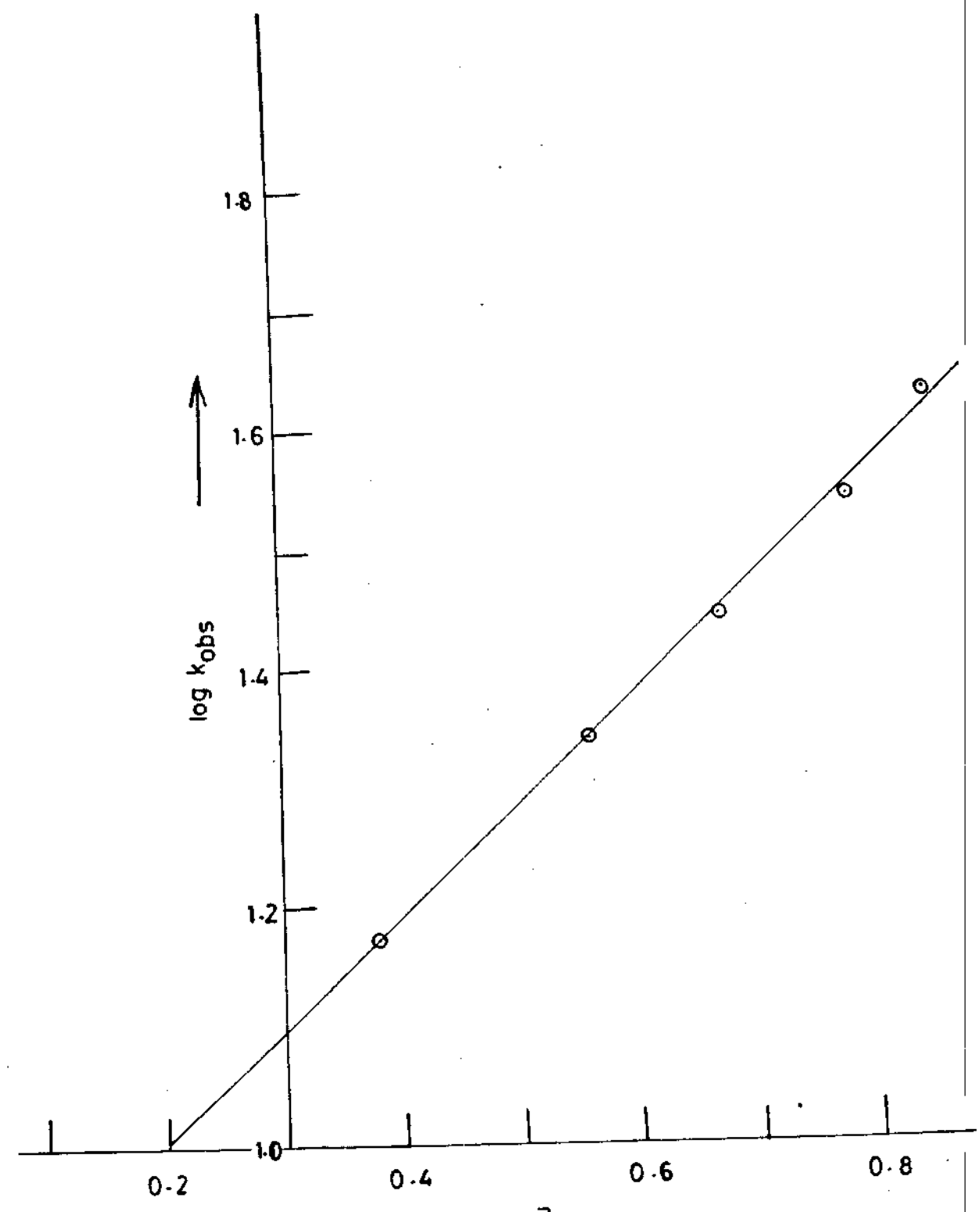


Fig. 5.10

Determination of the order of the $[(bpy)_2\ ClRuORuCl\ (bpy)_2]^{2+}$ — $Ru(NH_3)^{2+}$ reaction. Plot of log k_{obs} versus 4+ log $[Ru^{3+}]$

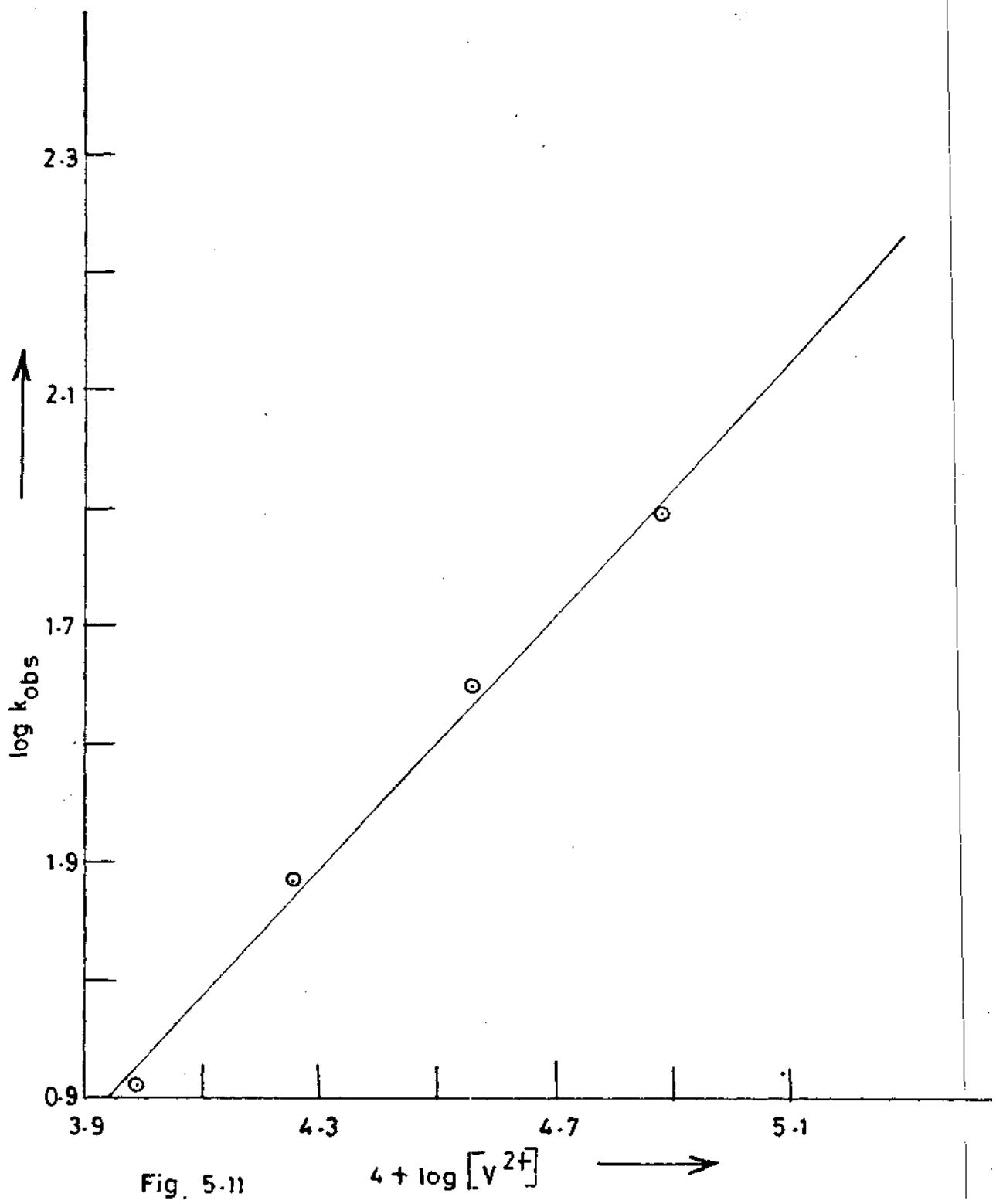


Fig. 5·11

Determination of the order of the $\left[(bpy)_2\ ClRuORuCl\ (bpy)_2\right]^{2+}$ – $V^{2+}(aq)$ reaction. Plot of log k_{obs} versus $4 + \log\left[V^{2+}\right]$

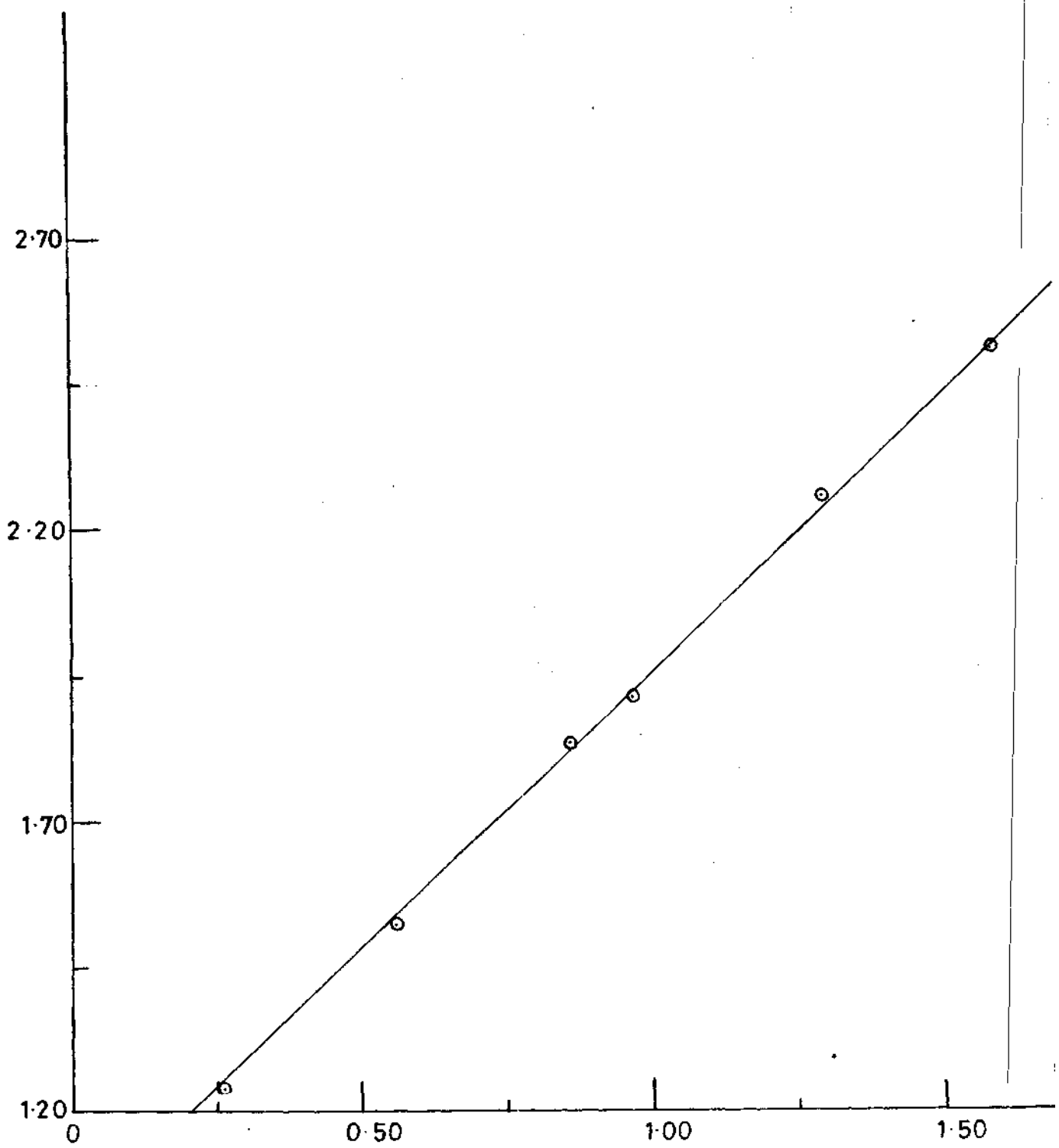


Fig. 5·12 Determination of the order of the $\left[(bpy)_2ClRuORuCl(bpy)_2\right]^{2+}$ $- Ti^{3+}(aq)$ reaction.
Plot of log k_{obs} versus log $\left[Ti^{3+}\right]$

The results do confirm that these reactions are strictly first order in $[M^{n+}]$. Hence, at constant $[H^+]$ and ionic strength, the rate equation for each of these reactions is,

$$\frac{-d}{d_t}[(bpy)_2ClRuORuCl(bpy)_2^{2+}] = k_o[M^{n+}][(bpy)_2ClRuORuCl(bpy)_2^{2+}] \quad ...(5.7)$$

The second-order rate constant k_o was determined for each run as,

$$k_o = k_1/[M^{n+}] \quad ....(5.8)$$

where k_1 is the pseudo-first-order rate constant. The values of k_o are reported in Tables (5.1) to (5.9).

All the values reported are an average of at least duplicate runs. Rate constants obtained from such runs agree within 5%.

Effect of Hydrogen ions on rate.

The influence of $[H^+]$ on the rate of the reactions of each of the metal ions with the oxobridged ruthenium(111) complex was investigated by determining k_2 in the acid range $0.05 \leq [H^+] \leq 0.5M$. Both the $[(bpy)_2ClRuORuCl(bpy)_2]^{2+}$ and $[M^{n+}]$

(M^{n+} - $Cr^{2+}(aq)$, $V^{2+}(aq)$, $U^{3+}(aq)$, $Ru(NH_3)_6^{2+}$, $Eu^{2+}(aq)$ and $Ti^{3+}(aq)$) were kept constant at I = 1.0M ($liClO_4$) and T= 26°C. The results obtained are included in Tables (5.1) to (5.7). Except for $Ti^{3+}_{(aq)}$ it was found out that all the reactions of interest were independent of the acid concentration in the acid range (0.01 - 0.5)M investigated. However, in the reaction of $Ti^{3+}_{(aq)}$ with $[(bpy)_2ClRuORuCl(bpy)_2^{2+}]$

TABLE 5.1

Second-order rate constants for the $[(bpy)_2ClRuORuCl(bpy)_2^{2+}]^{2+}$ Cr_{aq}^{2+} reaction.

$[(bpy)_2ClRuoRuCl(bpy)_2^{2+}]$ = 3.5×10^{-5}M, I = 0.5M($NaClO_4$)

T = 26 ± 1°C

10^2·,$[Cr^{2+}]$,M	$[H^+]$,M	$[X^-]$,M	$10^{-2}k_2M^{-1}s^{-1}$
0.92	0.10	-	2.39
2.32	0.10	-	2.26
4.64	0.10	-	2.28
13.9	0.10	-	2.23
1.23	0.02	-	2.35
1.23	0.10	-	2.31
1.23	0.16	-	2.26
1.23	0.22	-	2.25
		X= Cl	
1.23	0.10	0.05	4.4
1.23	0.10	0.10	7.4
1.23	0.10	0.20	12.7
1.23	0.10	0.30	17.9
1.23	0.10	0.40	24.1
		X = 10^4 NCS^-	
1.23	0.10	2	2.3
1.23	0.10	5	3.2
1.23	0.10	10	5.2
1.23	0.10	25	8.0
1.23	0.10	40	11.4
1.23	0.10	50	13.7

TABLE 5.2

Second-order rate constants for the $[(bpy)_2ClRuORuCl(bpy)_2]^{2+}$ $Eu^{2+}_{(aq)}$ reaction.

$[(bpy)_2ClRuORuCl(bpy)_2^{2+}] = 22.5 - 8.9 \times 10^{-6}M$,

$I = 0.5M$, $T = 26 \pm 1^{\circ}C$

$10^4 \cdot [Eu^{2+}]$, M	$[H^+]$, M	$[X^-]$, M	$10^{-3}k_2 M^{-1}s^{-1}$
4.9	0.05	-	3.1
4.9	0.10	-	3.1
19.6	0.10	-	3.5
12.9	0.10	-	3.8
91.6	0.10	-	3.2
45.8	0.25	-	2.8
45.8	0.50	-	2.7
		X = Cl	
4.24	0.10	0.02	3.6
4.24	0.10	0.06	5.0
4.24	0.10	0.10	5.3
4.24	0.10	0.30	6.9
4.24	0.10	0.50	9.6
		$10^4X = NCS^-$	
1.58	0.10	1.6	2.9
1.58	0.10	6.4	3.8
1.58	0.10	25	4.1
1.58	0.10	100	4.6
1.58	0.10	300	5.0
1.58	0.10	500	6.4

TABLE 5.3

Second-order rate constants for the $[(bpy)_2ClRuORuCl(bpy)_2]^{2+}$ + $Ru(NH_3)_6^{2+}$ reaction.

$[(bpy)_2ClRu\ O\ RuCl(bpy)_2^{2+}] = 8.9 \times 10^{-6}M$, $I = 0.5M$

$T = 26 \pm 1^{o}C$ $\lambda = 648nm$

$10^4\ [Ru(NH_3)_6^{2+}]$,M	$[H^+]$,M	$[X^-]$, M	$10^{-3}k_2M^{-1}s^{-1}$
4.68	0.05	-	60
7.02	0.10	-	61
2.40	0.10	-	63
3.60	0.20	-	61
6.00	0.20	-	66
		X = Cl	
1.23	0.10	8×10^{-5}	59
1.23	0.10	8×10^{-4}	107
1.23	0.10	0.006	117
1.23	0.10	0.02	162
1.23	0.10	0.03	185
1.23	0.10	0.05	262
1.23	0.10	0.10	464
		X = NCS	
1.23	0.10	5×10^{-5}	V. fast.

TABLE 5.4

Second-order rate constants for the $[(bpy)_2ClRuORuCl(bpy)_2]^{2+}$ + U^{3+} reaction

$[(bpy)_2ClRuORuCl(bpy)_2^{2+}] = 5.0 \times 10^{-5} - 9.0 \times 10^{-6}$M

I = 0.5M, T = 26 ± 1°C, λ = 648nm

10^4 [U^{3+}],M	[H^+],M	[X^-],M	$10^{-4}k_2M^{-1}s^{-1}$
1.59	0.01	-	53.0
3.18	0.25	-	52.0
1.59	0.25	-	51.0
1.59	0.50	-	52.0
		X = Cl	
1.2	0.10	1×10^{-4}	V.fast
		X = NCS	
1.2	0.10	1×10^{-4}	V.fast

TABLE 5.5

Second-order rate constants for the $[(bpy)ClRuORuCl(bpy)^{2+}]$ + V^{2+}_{aq} reaction. $[(bpy)_2ClRuORuCl(bpy)_2^{2+}] = (1.75 - 4.1) \times 10^{-5}M$

$T = 26^{o}C$, $I = 0.5M(LiClO_4)$

10^3 ,$[V^{2+}]$,M	$[H^+]$,M	$[X^-]$.,M	$10^{-4}k\ M^{-1}s^{-1}$
0.91	0.25	-	0.91
1.82	0.25	-	1.02
1.82	0.25	-	0.85
3.64	0.25	-	1.09
3.64	0.25	-	0.98
7.28	0.25	-	1.09
7.28	0.25	-	1.01
3.64	0.5	-	0.97
3.64	0.10	-	1.14
3.60	0.10	-	0.97
		X = Cl	
1.82	0.25	8×10^{-5}	0.87
1.82	0.25	2×10^{-3}	1.02
1.82	0.25	0.01	1.0
1.82	0.25	0.02	1.02
1.82	0.25	0.1	1.08
1.82	0.25	0.2	1.1
		X = NCS	
0.72	0.25	0.5×10^{-4}	1.23
0.72	0.25	1×10^{-4}	2.24
0.72	0.25	1.5×10^{-4}	1.47
0.72	0.25	2.5×10^{-4}	3.95
0.72	0.25	3.5×10^{-4}	5.87
0.72	0.25	4.0×10^{-4}	6.45

TABLE 5.7

Second order rate constants for the $[(Ru(bpy)_2Cl)_2O]^{2+}$ + $Ti^{3+}_{(aq)}$ reaction.

$[(Ru(bpy)_2Cl)_2O]^{2+} = 3.5 \times 10^{-5}M$, $T = 26 \pm 1^{o}C$

$I = 0.5M$ ($liClO_4$)

10^3, $[Ti^{3+}]$, M	$[H^+]$, M	$[X^-]$, M	k_2, $M^{-1}s^{-1}$
9.2	0.10	-	8.85
19.6	0.10	-	9.20
39.2	0.10	-	8.26
1.82	0.10	-	9.60
3.64	0.10	-	9.14
7.28	0.10	-	9.34
0.72	0.10	-	9.73
0.92	0.10	-	9.14
34.5	0.10	-	9.46
		X = Cl	
18.0	0.10	8×10^{-4}	30.6
18.0	0.10	0.02	30.5
18.0	0.10	0.06	30.0
18.0	0.10	0.12	30.5
18.0	0.10	0.16	30.1
		$X = NCS^-$	
18.0	0.10	8×10^{-4}	32.5
18.0	0.10	0.01	188
18.0	0.10	0.03	870
18.0	0.10	0.05	218
18.0	0.10	0.07	353
18.0	0.10	0.0025	50.5
18.0	0.10	0.005	88
18.0	0.10	0.015	287
18.0	0.10	0.02	433
18.0	0.10	0.04	1515.

TABLE 5.6

Second-order rate constants for the acid dependence of the $[(bpy)_2ClO^{Ru}RuCl(bpy)_2^{2+}]$ = 3.5 x 10^{-5}M

$[Ti^{3+}]$ = (9.0 - 34.5) x 10^{-3}M, T = 26°C, I = 0.5M.($LiClO_4$)

10^2M, $[H^+]$	k $M^{-1}s^{-1}$
1.0	60.3
2.0	47.6
2.36	40.6
2.76	32.5
3.0	34.3
3.56	28.3
4.0	26.8
4.36	24.9
5.0	24.3
5.16	23.3
5.37	17.3
6.4	14.0
8.0	13.6
8.4	11.0
9.96	11.2
10	9.2
11.56	10.1
12.4	7.8
13.19	8.7
14.76	7.6
15.4	7.2

TABLE 5.8

Second-order rate constants obtained in the range pH 1.0 - 6.0 for the $[(bpy)_2ClRuORu(bpy)_2^{2+}]$ + Ti^{III}- edta reaction.

$[Ti^{III}\text{-edta}] = 3.4 \times 10^{-4}M - 6.1 \times 10^{-4}M$,

$[(bpy)_2ClRuORuCl(bpy)_2^{2+}] = 1.0 \times 10^{-5}M$, $I = 0.5M(LiClO_4)$

$T = 26 \pm 1^{\circ}C$

pH	$10^{-5}k\ M^{-1}s^{-1}$
1.0	2.50
1.2	2.60
1.4	2.40
1.5	2.60
1.6	2.70
1.9	2.90
2.0	2.67
2.5	2.70
2.9	3.00
3.25	3.30
3.65	3.65
4.15	4.05
4.3	4.04
4.5	4.40
4.7	4.90
5.1	5.64
5.4	5.98
6.0	8.20

TABLE 5.9

Second-order rate constants for the anion dependence of the reaction of $[(bpy)_2ClRuORuCl(bpy)_2^{2+}]$ with Ti^{III}.edta.

$[(bpy)_2ClRuORuCl(bpy)_2^{2+}] = 1.75 \times 10^{-5}M$

$T = 26 \pm 1^{\circ}C$ $I = 0.5M (LiClO_4)$

10^3M, $[Ti^{III}$-edta$]$	pH	$[X^-]$mM	$10^5k\ M^{-1}s^{-1}$
		X = Cl	
1.11	2.9	10	3.31
1.11	2.9	50	3.23
1.11	2.9	100	3.23
1.11	2.9	150	3.41
1.11	2.9	200	3.18
		X = NCS	
0.74	3.3	0.5	3.8
0.74	3.3	1.0	3.5
0.74	3.3	5.0	3.37
0.74	3.3	10	3.28
0.74	3.3	15	3.1
0.74	3.3	20	3.7

as in other reactions involving $Ti^{3+}_{(aq)}$ ion, the rate decreases as $[H^+]$ increases. A plot of k_o against $[H^+]^{-1}$ is non-linear as shown in Figure (5.13). However the plot of k_o^{-1} versus $[H^+]$ is linear with a finite intercept (Fig. 5.14) From these results it was deduced that k_o varies with $[H^+]$ according to equation

$$1/k_o = a + b\,[H^+] \qquad \ldots.(5.9)$$

Values of a and b obtained from least-mean-square analysis of the data are

$$a = (3.95 \pm 0.05) \times 10^{-3}\ M^{-1}{}_s{}^{-1}$$

$$b = (9.33 \pm 0.04) \pm 0.02\ s^{-1}$$

The second-order rate constants for the reaction of the oxobridged ruthenium(111) dimer with Ti^{111}-edta was measured as a function of pH in the pH range 1.0 - 6.0 while the initial concentration of the two reactants were kept constant. Formate or acetate buffer were used to maintain a constant pH when necessary. As in the reaction of Ti^{111}-edta with Br_2^- and I_2. these buffers had no effect on the rate of the reaction. pH values were measured by using a pH-meter in a medium containing equal volumes of the reductant solutions. The rate constants obtained are presented in Table (5.8) Below pH=2.5, k_o^{edta} increases with pH. The plot of the second-order rate constant against pH is biphasic as shown in Figure (5.15).

A similar biphasic behavior has been previously obtained for the reaction of Ti^{111}-edta with aqueous solutions of bromine and iodine and some cobalt(111) ammine complexes[1]. As in the reaction of Ti^{111}-edta with aqueous solutions of Bromine and Iodine, the second-order rate constants obtained

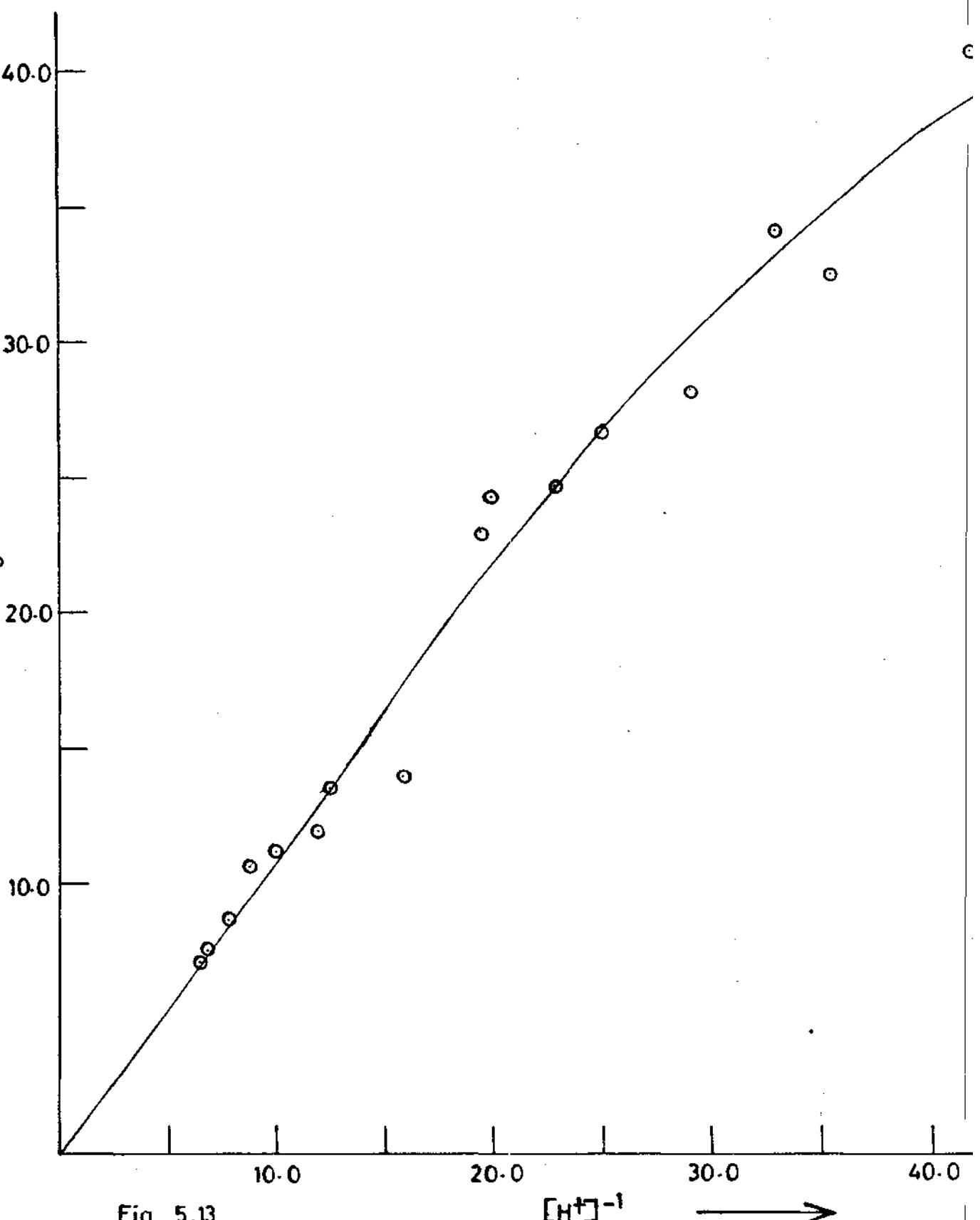


Fig. 5.13

Acid - dependence of the $\left[(bpy)_2\ ClRuORuCl(bpy)_2\right]^{2+}$ - $Ti^{3+}_{(aq)}$ reaction.

Plot of k_o versus $\left[H^+\right]^{-1}$

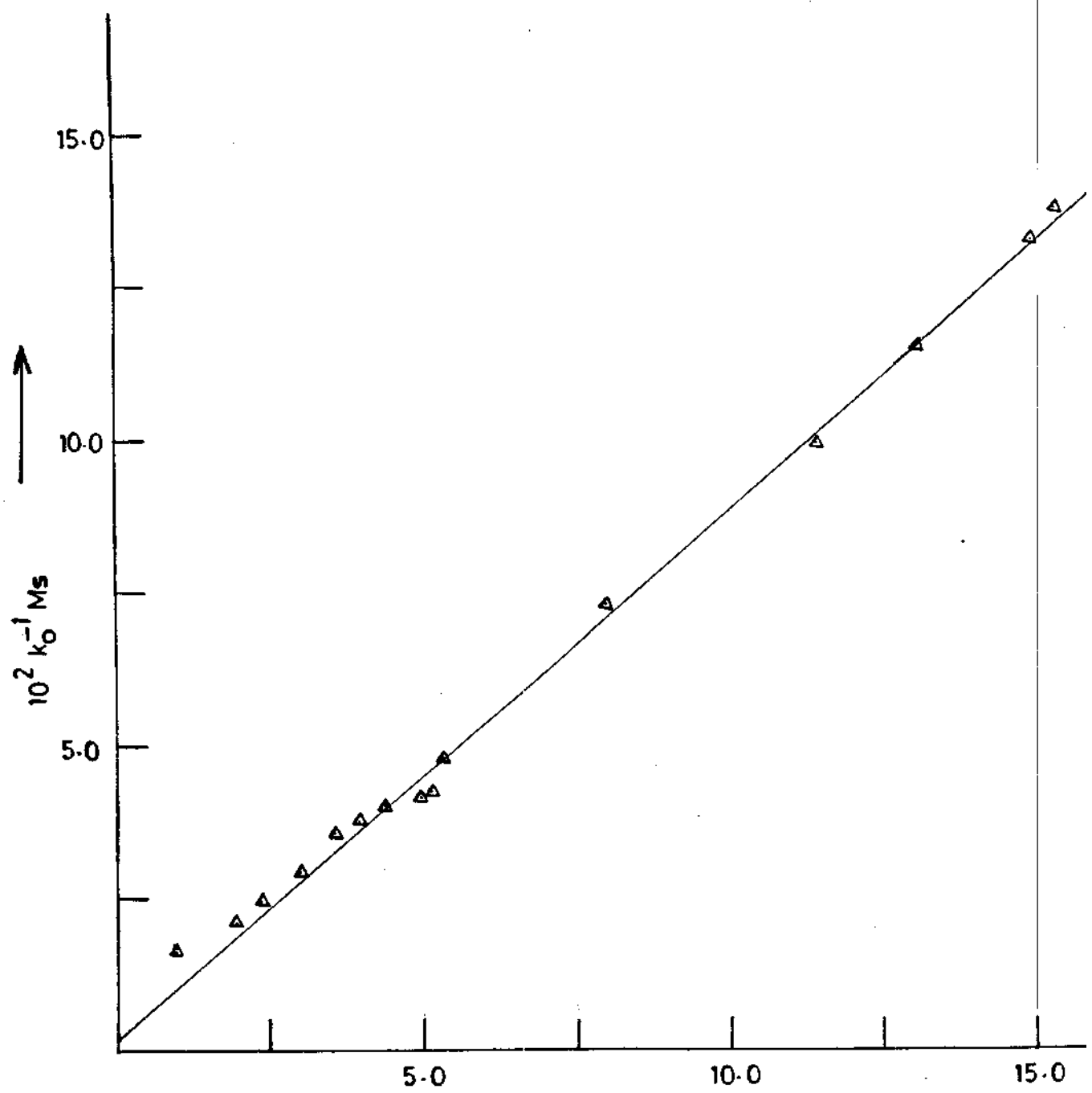


Fig. 5·14

Plot of k_o^{-1} Versus [H+] for the $[(bpy)_2 ClRuORuCl(bpy)_2]^{2+}$ - $Ti^{3+}(aq)$ reaction.

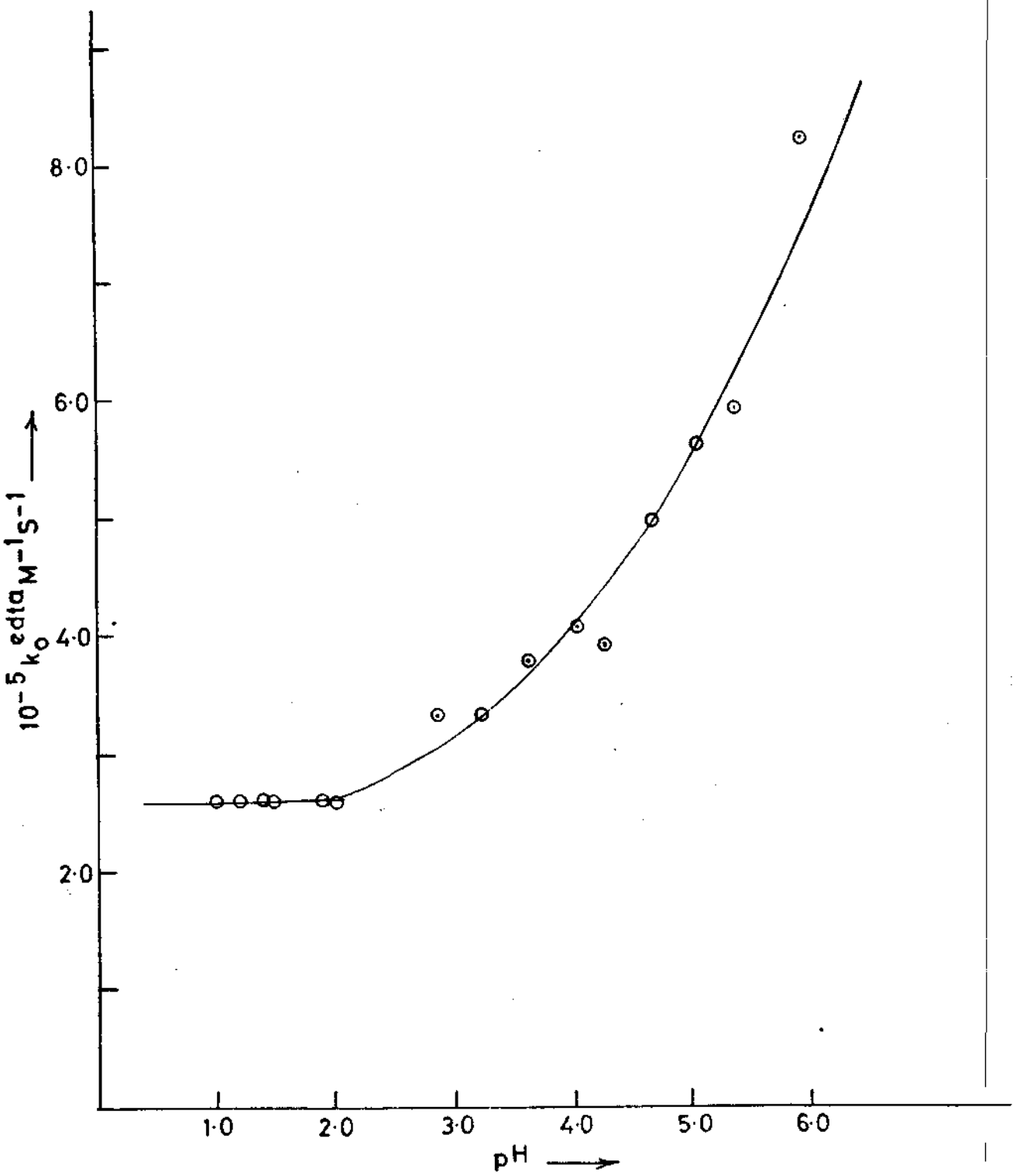


Fig. 5·15 p^H – dependence of the $\left[(bpy)_2ClRuORuCl(bpy)_2\right]^{2+}$ — Ti^{III} edta reation. Plot of k_o^{edta} versus p^H

were fitted into an equation of the form:

$$k_o^{edta} = \frac{k_2 + k_2K_1[H^+]^{-1} + k_3K_1K_2[H^+]^{-2}}{1 + K_1[H^+] + K_1K_2[H^+]^{-2}} \quad \ldots.(5.10)$$

using non-linear least-mean-square computer analysis[2] with $(1/k_o^{edta})^2$ weighting and the values of K_1 and K_2 fixed as determined by Podlahova and Podlaha[3] i.e.

$$pK_1 = 2.02 \pm .01$$

$$pk_2 = 8.64 \pm .02$$

in their titration study of Ti^{III}-edta solutions The values of k_2 and k_3 so determined are as follows:

$$k_2 = (2.96 \pm 0.13) \times 10^5 \ M^{-1}S^{-1}$$

$$k_3 = (3.00 \pm 0.56) \times 10^8 \ M^{-1} \ S^{-1}$$

From the computed values of k_2 and k_3 and the values of K_1 and K_2 as reported by Podlahova and Podlaha[3] was substituted into equation (5.10) and the values of k_o^{edta} was calculated for the various pH values investigated. The value of k_o^{edta} so obtained and the experimental values are presented for comparison in Table (5.10).

TABLE 5.10

Observed and calculated second-order rate constants k_o^{edta} for the Ti^{III}-edta + $[(bpy)_2ClRuORuCl(bpy)_2]^{2+}$ reaction

pH	$10^{-5}k_o^{edta}$(expt)$M^{-1}s^{-1}$	$10^{-5}k_o^{edta}$(calc)$M^{-1}s^{-1}$
1.0	2.5	2.96
1.2	2.6	2.96
1.4	2.4	2.96
1.5	2.6	2.96
1.6	2.7	2.96
1.9	2.9	2.96
2.0	2.67	2.96
2.5	2.70	2.96
2.9	3.00	2.97
3.25	3.30	2.97
3.65	3.65	2.99
4.15	4.05	3.06
4.3	4.04	3.10
4.5	4.40	3.18
4.7	4.90	3.31
5.1	5.64	3.83
5.4	5.98	4.68
6.0	8.20	9.81

A plot of k_o^{edta}(expt) and k_o^{edta}(calc) versus pH is also presented in Figure (5.16)

The pH dependent second-order rate constants for the reaction of Ti^{111}-edta with the oxobridged ruthenium(111) dimer was also fitted by rearranging equation into the form:

$$(k_o^{edta}\ 1 + k_i [H^+] + k_1k_2 [H^+]^{-2} - k_2)\ [H^+] - k_2K_1 = k_3K_1K_2 [H^+] \qquad ...(5.11)$$

Hence a plot of the left-handside of equation against $K_1K_2 [H^+]$ should be linear with a slope equal to k_3 and intercept equal to zero. Such a plot is presented in Figure (5.17) for pH < 5. This plot is linear with a small but finite intercept. The value of k_3 obtained from the least-mean-square of the data is

$$k_3 = (2.41\pm0.2) \times 10^8\ M^{-1}s^{-1}$$

Effect of Chloride ion on the rates of the reactions.

Keeping the concentration of all other reagents constant and maintaining a constant ionic strength of 0.5M ($LiClO_4$), the effect of added chloride ion on the rates of the reaction of each of the metal ions with the oxobridged ruthenium(111) dimer was investigated in the concentration range $0.05 \leq [Cl^-] \leq 0.4M$. With Ti^{111}-edta, the pH was maintained constant at 2.9 using a formate buffer. The results are reported in Tables (5.1 - 5.5), (5.7) and (5.9). With $M^{n+} = V^{2+}$, $Ti^{3+}_{(aq)}$ and Ti^{111}-edta, the rates were found to be insensitive to changes in chloride ion concentration in the concentration

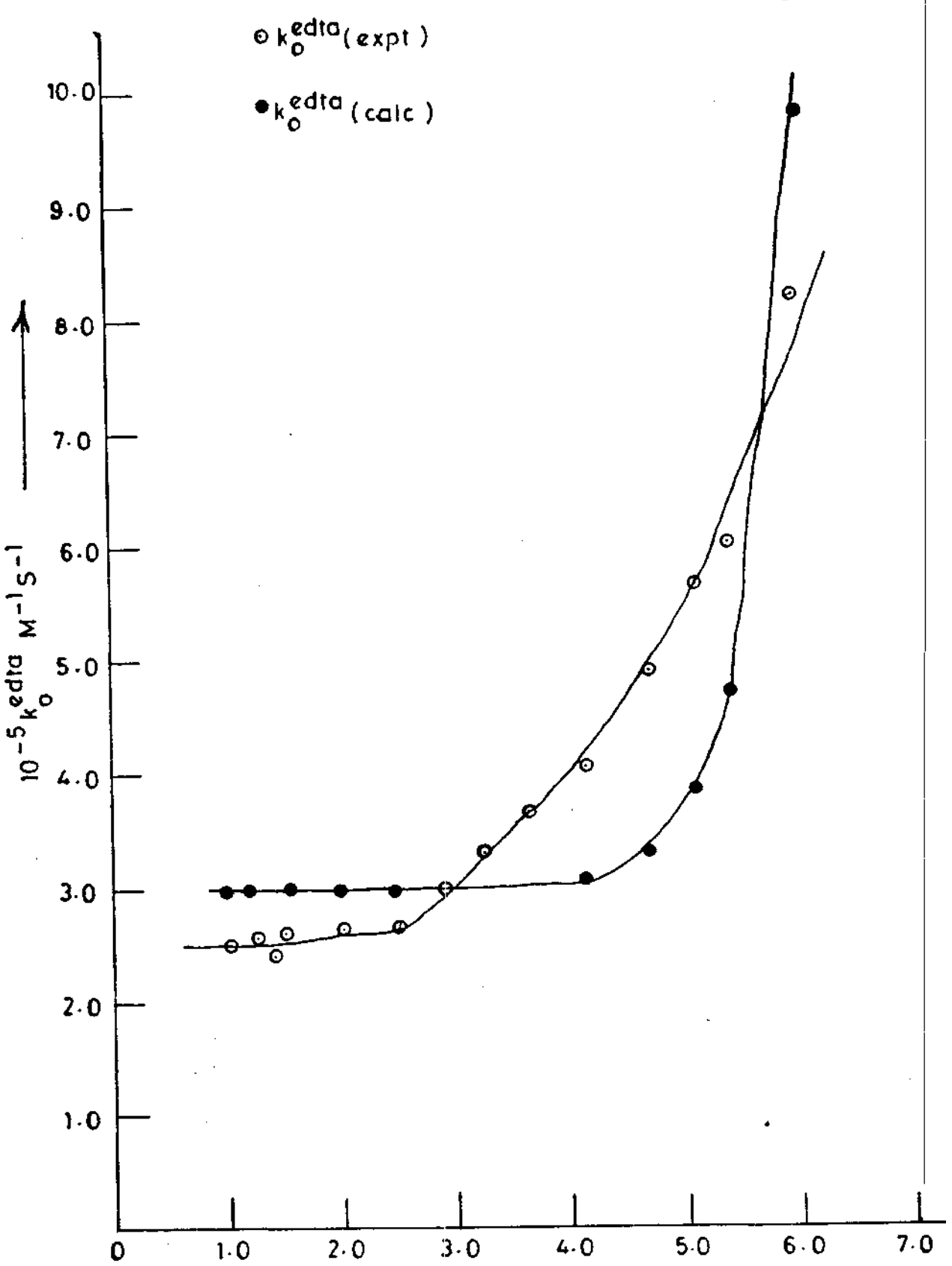


Fig. 5.16

Plot of k_o^{edta} (expt) and k_o^{edta} (calc) versus PH for the $[(bpy)_2 ClRuORuCl(bpy)_2^{2+}]$ — Ti^{III}-edta reaction.

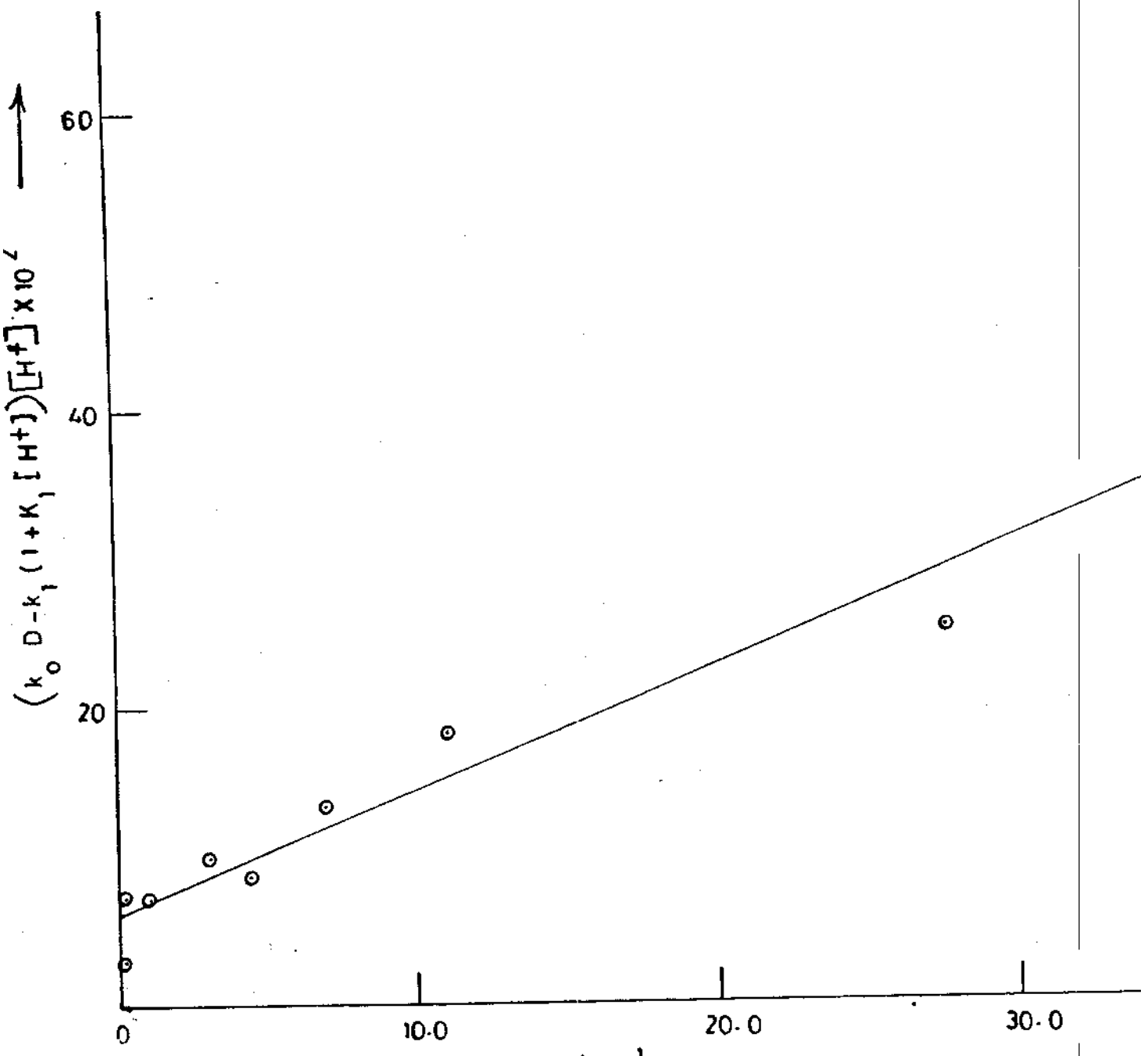


Fig. 5.17

Plot of $\left(k_o(1+K_1[H^+]+K_1K_2[H^+]^2] - k_1(1+K_1[H^+])\right)[H^+]$ versus $[K_1K_2[H^+]$ for the $(bpy)_2ClRuORuCl(bpy)_2^{2+}]-Ti^{III}$ –edta reaction.

range investigated. The reactions of the oxobridged dimmer with $Eu^{2+}_{(aq)}$, $Cr^{2+}_{(aq)}$, $Ru(NH_3)^{2+}_6$ were found to increase with increasing chloride ion concentration of the medium. For each of these ions, the plot of k_o^{Cl} against $[Cl^-]$ is linear as shown in Figure (5.18 - 5.20). Least - mean - square computation of the data gave slopes and intercepts as follows:-

$Eu^{2+}_{(aq)}$

Slope = $(1.7 \pm 0.1) \times 10^4\ M^{-2}\ s^{-1}$

Intercept = $(3.55 \pm 0.2) \times 10^3\ M^{-1}\ s^{-1}$

$Cr^{2+}_{(aq)}$

slope = $(5.55 \pm 0.04) \times 10^3 M^{-1} s^{-1}$

Intercept = $(180.0 \pm 0.50)\ M^{-1}\ s^{-1}$

$Ru(NH_3)^{2+}_6$

Slope = $(4.44 \pm 0.06) \times 10^6\ M^{-2}\ -1$

Intercept = $(1.0 \pm 0.1) \times 10^5\ M^{-1}\ -1$

The reaction of the oxobridged ruthenium(111) dimer with $U^{3+}_{(aq)}$ at $[Cl^-]$ as low as 1×10^{-4}M was too fast to be monitored by the Durrum - Gibson stopped - flow spectrophotometer. From the linear dependence of k_o^{Cl} on $[Cl^-]$, the empirical dependence of these reaction can be written as:

$$k_4 = a + b\ [Cl^-] \qquad \ldots(5.12)$$

(where $k_4 = k_o^{Cl}$)

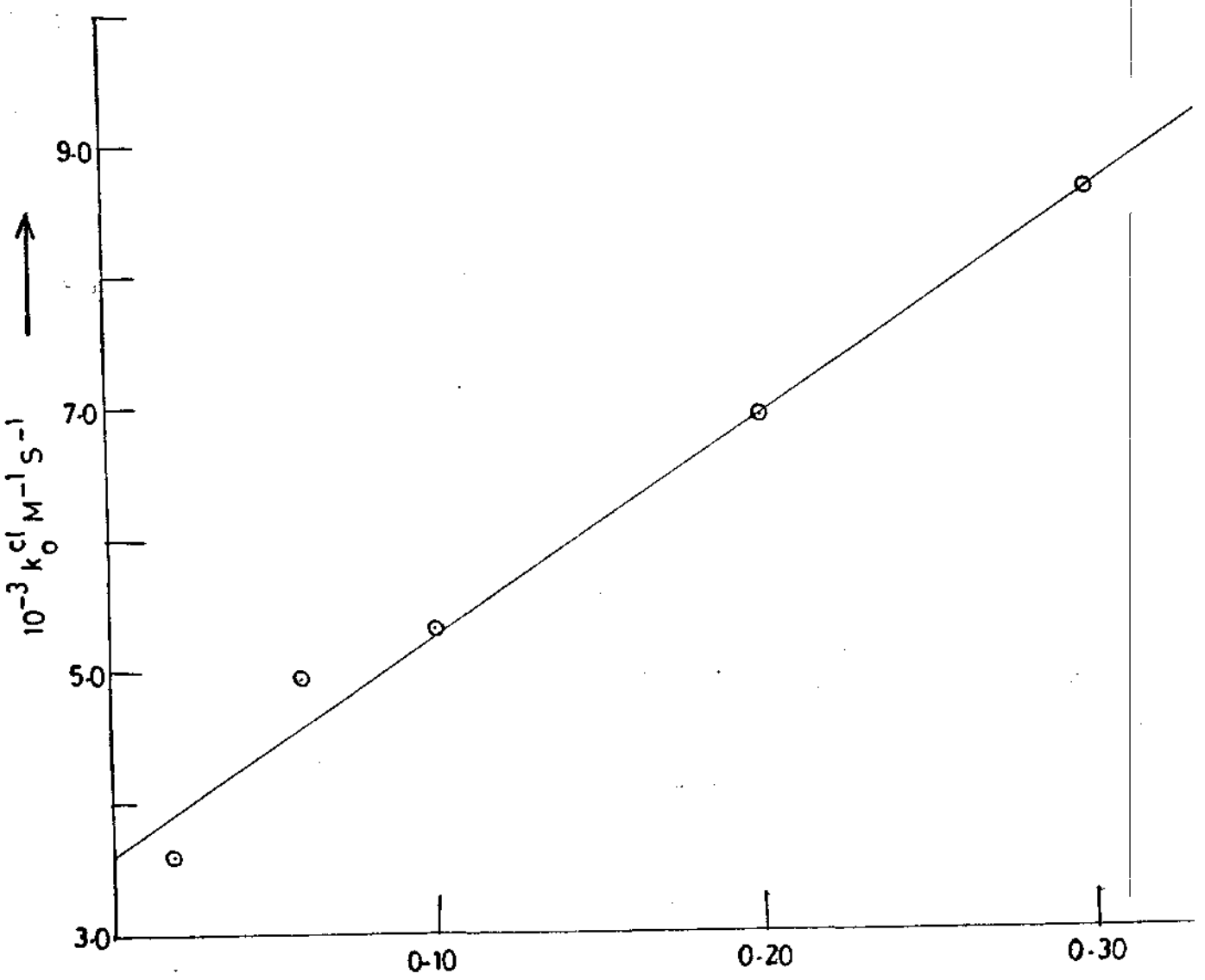


Fig. 5·18

Chloride dependence of the $\left[(bpy)_2\, ClRuORuCl\,(bpy)_2\right]^{2+} - Eu^{2+}$(aq

reaction shown by the plot of k_o^{Cl} versus $[Cl^-]$

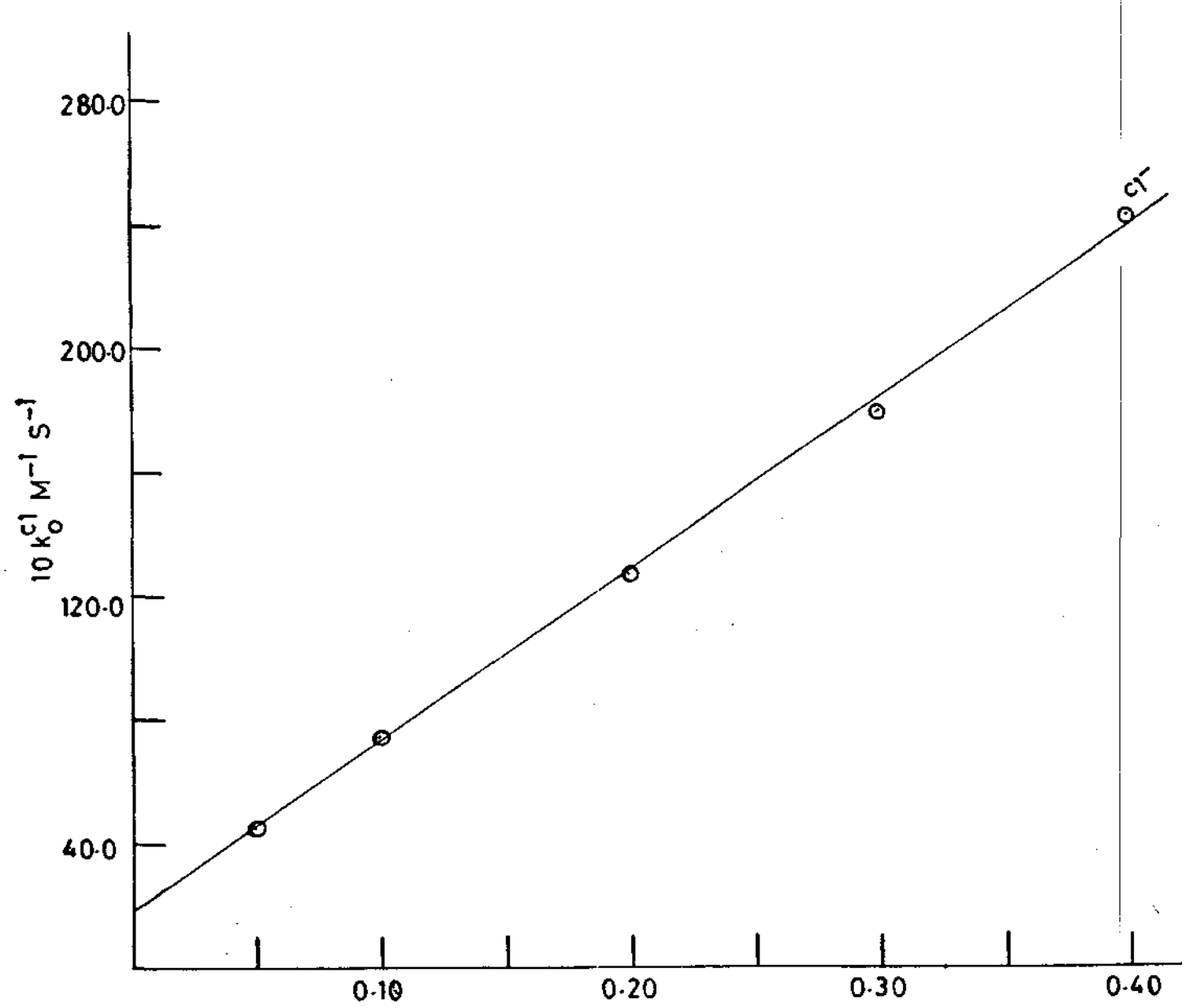


Fig. 5.19

Chloride dependence of the $\left[(bpy)_2\ ClRuORuCl(bpy)_2\right]^{2+} - Cr^{2+}$ reaction.

Plot of k_o^{Cl} versus $[Cl^-]$

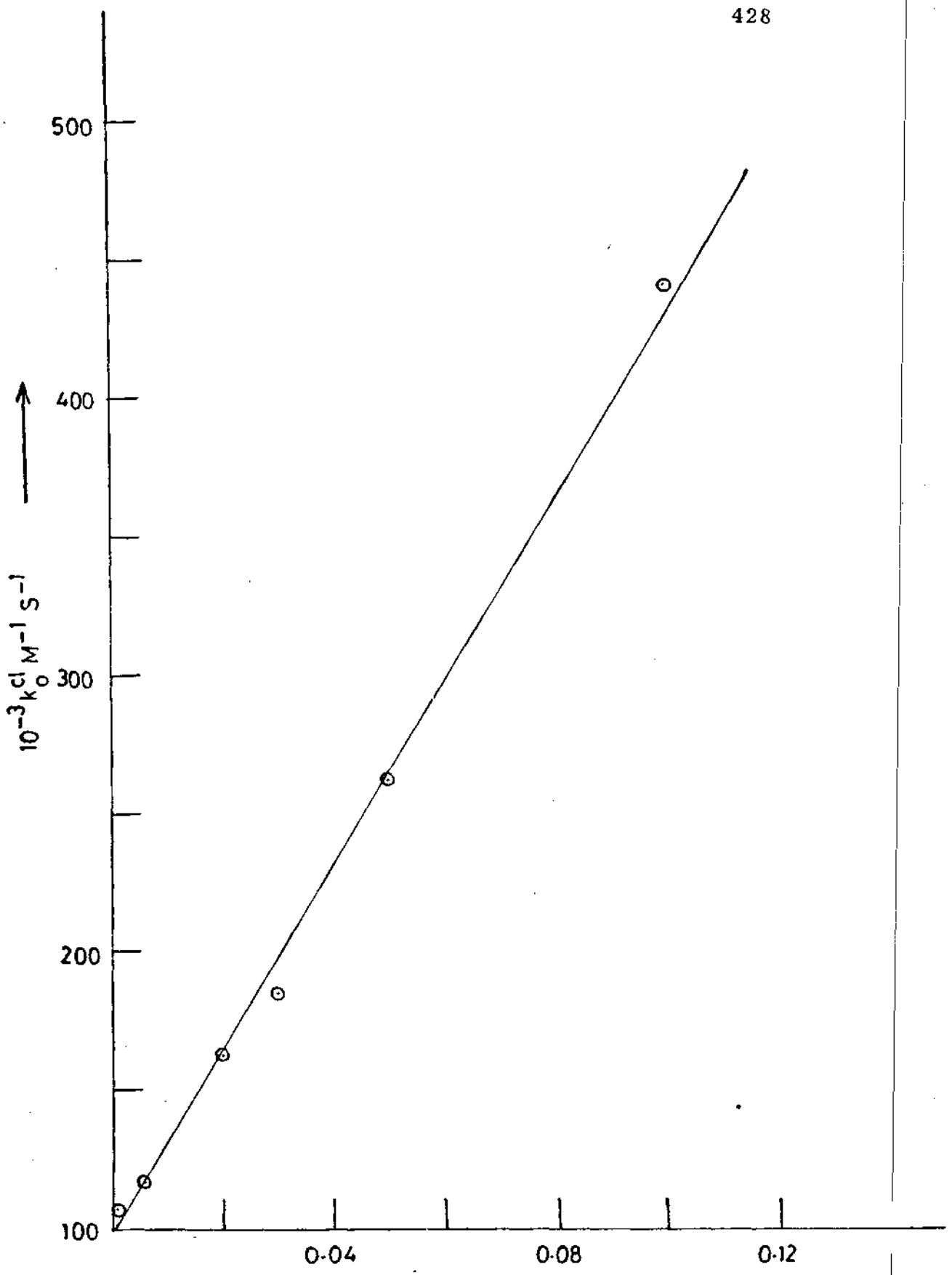


Fig. 5·20

Chloride dependence of the $\left[(bpy)_2\ ClRuORuCl\ (bpy)_2\right]^{2+}$ — $Ru(NH_3)_6^{2+}$ reaction shown by the plot of k_o^{Cl} versus $[Cl^-]$

Effect of added thiocyanate ion on rate.

The second-order rate constant for each of these reactions was determined as a function of $[NCS^-]$. For the range $[NCS^-] = (0.02 - 5.0) \times 10^{-2}M$, a plot of k_5 as a function of $[NCS^-]$ for the reactions involving $V^{2+}_{(aq)}$, $Cr^{2+}_{(aq)}$ and $Eu^{2+}_{(aq)}$ was obtained. The data obtained (Table (5.1), (5.2) and (5.5) showed a linear dependence on $[NCS^-]$. From the linear plots obtained (Figures (5.21) - (5.23) an empirical equation of the form:

$$K_5 = p + q\,[NCS^-] \qquad \ldots(5.13)$$

is obtained.

From the least-mean-square computation of the slopes and intercepts of each curve, the kinetic parameters p and q were obtained as follows:

$V^{2+}_{(aq)}$: $q = (1.51 \pm 0.06) \times 10^{8} M^{-2} s^{-1}$

$p = (5.5 \pm 0.2) \times 10^{3} M^{-1} s^{-1}$

$Cr^{2+}_{(aq)}$ $q = (2.37 \pm 0.5) \times 10^{5} M^{-2} s^{-1}$

$p = (185 \pm 2.0) \quad M^{-1} s^{-1}$

Eu^{2+} $q = (4.4 \pm 0.1) \times 10^{4} M^{-2} s^{-1}$

$p = (3.9 \pm 0.1) \times 10^{3} M^{-1} s^{-1}$

The values of p derived from these plots are in excellent agreement with k_o directly measured for each reaction at zero concentration of added anion. The rates of the reaction of the oxobridged ruthenium(111) dimer with $U^{3+}_{(aq)}$ and $Ru(NH_3)^{2+}_6$ at very low $[NCS^-]$ ($[NCS^-] = 5 \times 10^{-5}$ M) were too fast to be

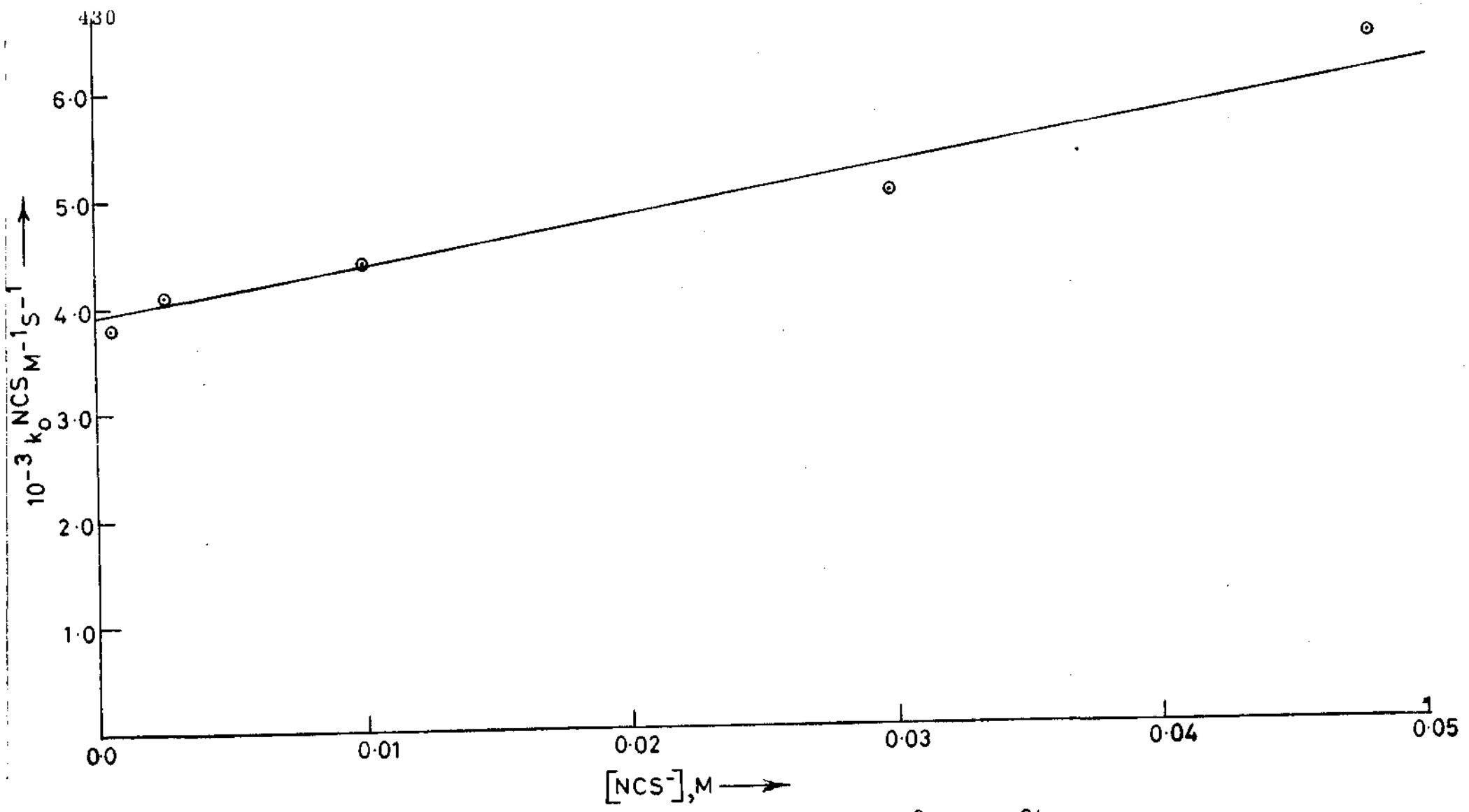


Fig. 5·21 $[NCS^-]$ dependence of the $[(bpy)_2ClRuORuCl(bpy)_2]^{2+}$ — $Eu^{2+}(aq)$ reaction. Plot of k_o^{NCS} versus $[NCS^-]$

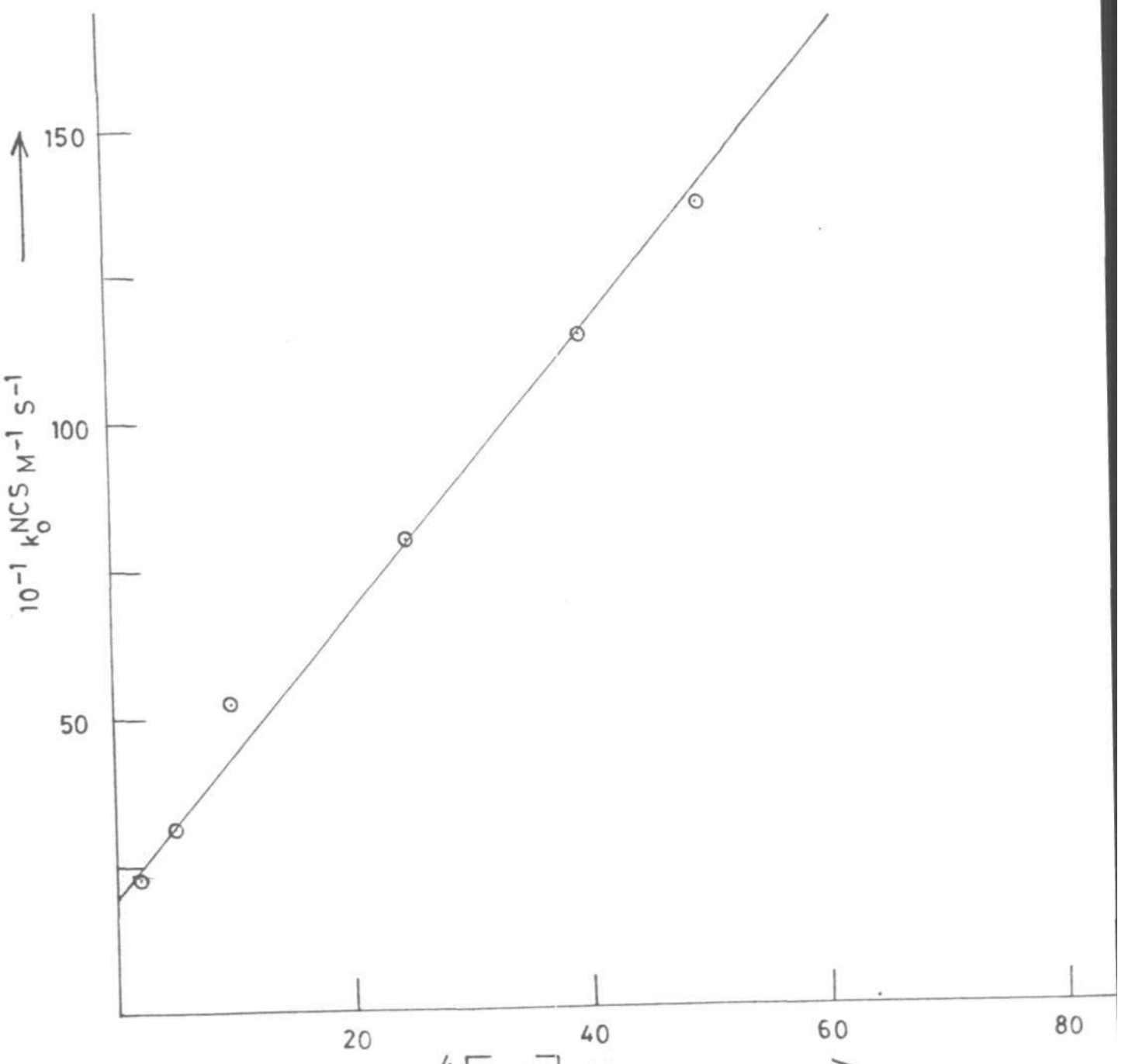


Fig. 5.22 $[NCS^-]$ dependence of the $[(bpy)_2\ ClRuORuCl(bpy)_2]^{2+} - Cr^{2+}(aq)$ reaction.

Plot of k_o^{NCS} versus $[NCS^-]$

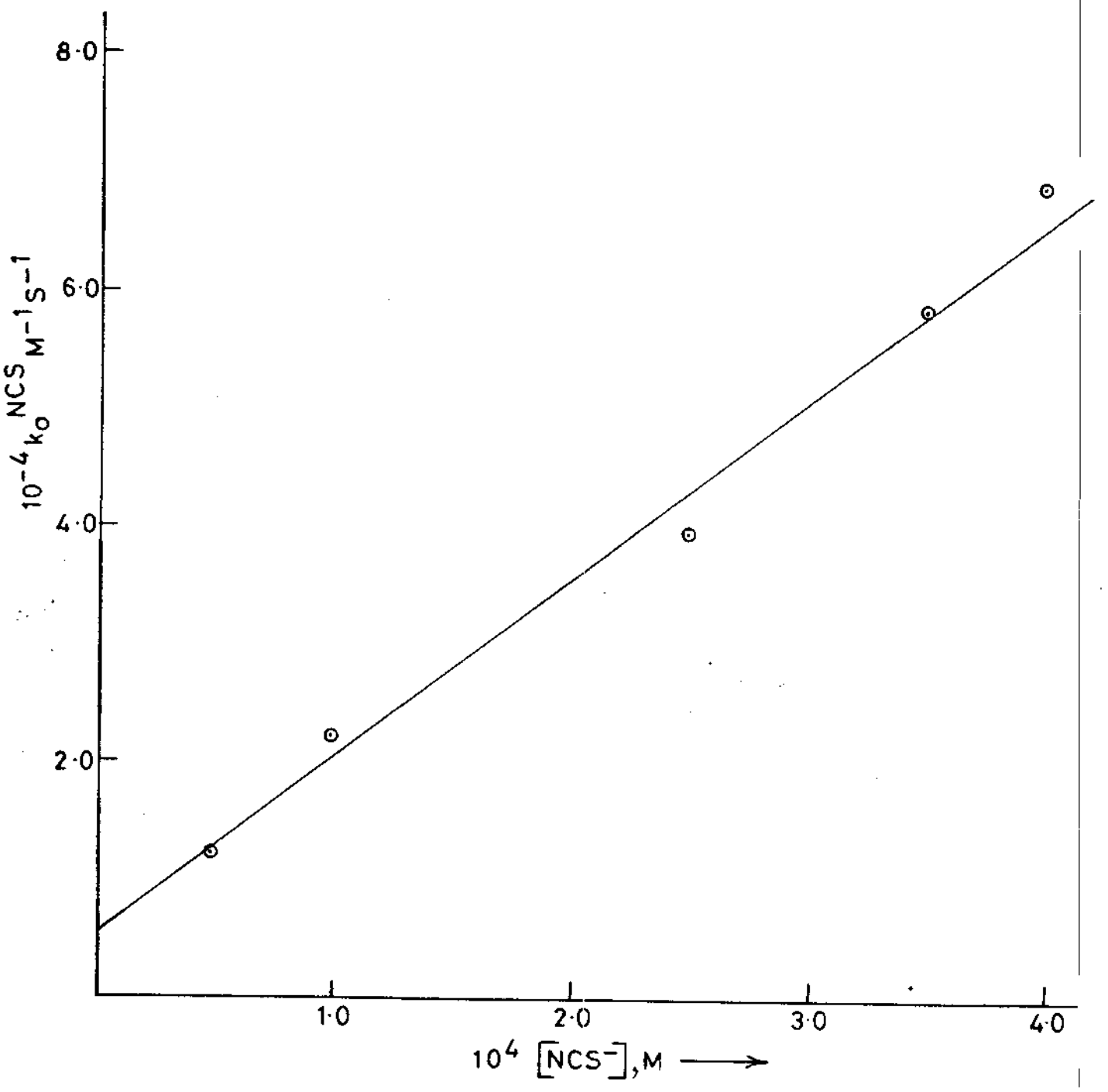


Fig. 5.23 NCS^- dependence of the $[(bpy)_2 ClRuORuCl(bpy)_2]^{2+}$-$V^{2+}$ reaction- Plot of k_o^{NCS} versus $[NCS^-]$

monitored by the Durrum - Gibson stopped-flow spectrophotometer showing that NCS^- also catalyzed the rates of oxidation of these reactions.

For the $Ti^{3+}_{(aq)}$ + $[(bpy)_2ClRuORuCl(bpy)_2^{2+}]$ reaction, the rate also increases as thiocyanate ion concentration increases in the range $[NCS^-] = (0.08 - 7.0) \times 10^{-2}$ M (Table (5.7) . A plot of k_5' versus $[NCS^-]$ was non-linear as shown in Figure (5.24). However, a plot of

$$\frac{k_5 - k_o}{[NCS^-]}$$

against $[NCS^-]$ (k_o is the observed rate constant in the absence of $[NCS^-]$ was linear as shown in Figure (5.25).

Hence, the $[NCS^-]$ dependent rate constant, k_5, fits an equation of the form

$$k_5 = p + q[NCS^-] + r[NCS^-]^2 \qquad ...(5.14)$$

$$\text{or} \quad \frac{k_5 - p}{[NCS^-]} = q + r[NCS^-] \qquad ...(5.15)$$

least-mean-square computation of the slope (r) and intercept (q) of this plot gave values of these parameters as:

$$p = 32.5\ M^{-1}$$

$$q = 5.6 \pm 0.1 \times 10^3\ M^{-2}s^{-1}$$

$$r = 7.55 \pm 0.30 \times 10^5\ M^{-3}s^{-1}$$

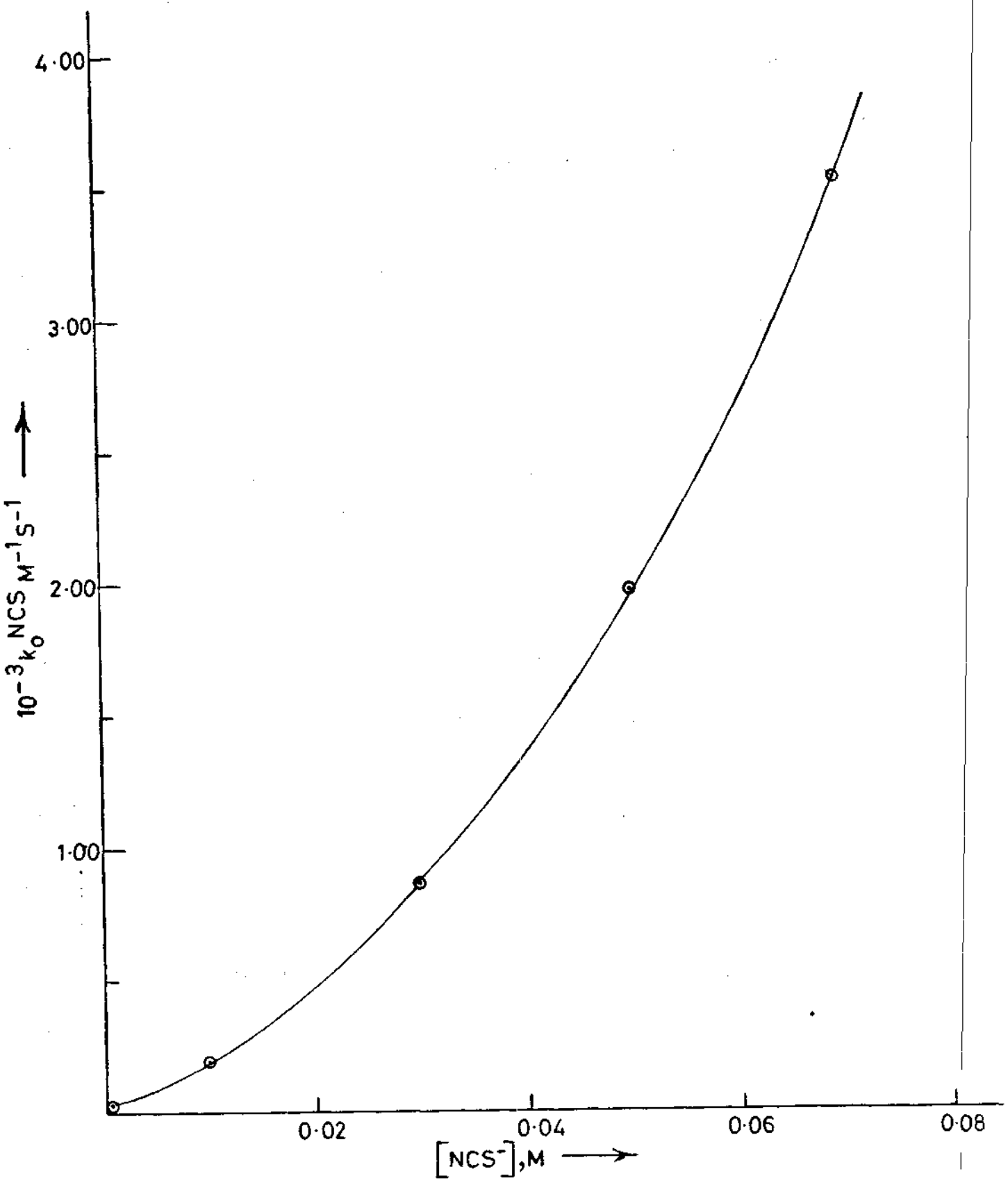


Fig. 5.24 $[NCS^-]$ dependence of the $[(bpy)_2 ClRuORuCl(bpy)_2]^{2+}$ — $Ti^{3+}(aq)$ reaction.
Plot of k_o^{NCS} versus $[NCS^-]$

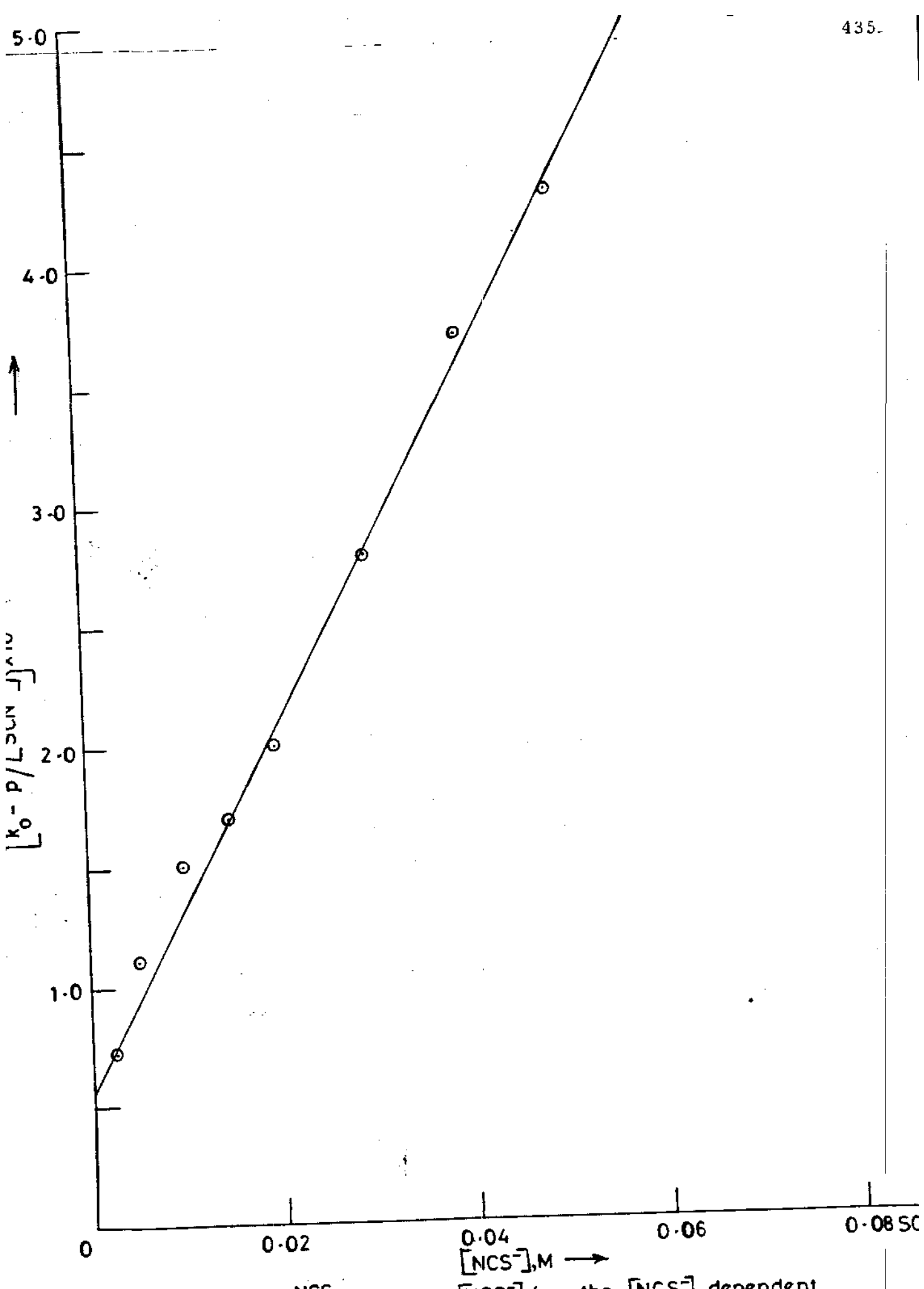


Fig. 5·25 Plot of k_o^{NCS} p versus $[NCS^-]$ for the $[NCS^-]$ dependent

At pH = 2.5 and varying $[NCS^-]$ from 5×10^{-4}M to 2×10^{-2}M, the rate of the Ti^{III} - edta + $[(bpy)_2ClRuORuCl(bpy)_2^{2+}]$ was found to be insensitive to variations in $[NCS^-]$ (Table (5.9)). This suggests that this anion may play no role in the electron transfer process.

D I S C U S S I O N

The pseudo-first-order plots of the reactions involving $[(bpy)_2ClRuORuCl(bpy)_2^{2+}]$ and M^{n+} ($M^{n+} = Cr^{2+}_{(aq)}$, $V^{2+}_{(aq)}$, $Ru(NH_3)_6^{2+}$, $Eu^{2+}_{(aq)}$, $U^{3+}_{(aq)}$, $Ti^{3+}_{(aq)}$ and Ti^{III}-edta) were linear to more than 90% reaction. These reactions are therefore first-order in $[(bpy)_2ClRuORuCl(bpy)_2^{2+}]$. The order of these reactions with respect to $[M^{n+}]$ was also found to be one. The above results show that the reduction of this two-electron oxidant, $[(bpy)_2ClRuORuCl(bpy)^{2+}]$, by these well established one-equivalent reducing ions involves an activated complex formed by a simple bimolecular interaction between the oxidant and the reductant ions. The reactions can be represented by a second-order rate law of the form.

$$\text{Rate} = k_o [(bpy)_2ClORuCl(bpy)_2^{2+}][M^{n+}] \qquad ....(5.16)$$

The 2:1 stoichiometry determined for these reactions shows that two moles of M^{n+} react with one mole of the oxobridged ruthenium(III) dimer. These reactions are therefore non-complementary in redox reaction terminology. The overall reaction can be represented by an equation of the form:

$$[(bpy)ClRuORuCl(bpy)_2^{2+}] + 2M^{n+} \rightarrow \text{Products} \qquad ...(5.17)$$

The 2.1 stoichiometry and the second-order kinetics obtained suggest that these reactions must occur by a series of univalent changes with the formation of a $Ru^{II}ORu^{III}$ dimer as an intermediate. Moreover, the detailed cyclic polarographic investigations by Meyer[4] and co-workers have shown that the proposed mixed valence oxobridged intermediate is a product of the one-electron reduction of the oxobridged ruthenium(III) dimer.

Their results did show that the $[(bpy)_2ClRuORuCl(bpy)_2^{2+}]$ complex ion is a more powerful oxidant (E^o = 1.0V) than the $[(bpy)_2ClRuORuCl(bpy)_2^{+}]$ dimer ($E_{\frac{1}{2}}$ = 0.68V) and that the latter undergoes a further one-electron reduction and subsequent decomposition of the oxo-bridge to give monomeric products.

The reaction scheme for the title reaction can therefore be proposed as follows:

$$[(bpy)_2ClRu^{III}\text{-}O\text{-}Ru^{III}Cl(bpy)_2] + M^{n+} \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} [(bpy)_2ClRu^{II}\text{-}O\text{-}Ru^{III}(bpy)_2] + M^{(n+1)+} \quad ...(5.18)$$

$$[(bpy)_2ClRu^{II}ORu^{III}Cl(bpy)_2] + M^{n+} \xrightarrow{k_7} \text{products} \quad ...(5.19)$$

The application of the steady-state approximation to the concentration of the $Ru^{II}ORu^{III}$ dimer gives the rate expression:

$$\frac{-d}{dt}[(bpy)_2ClRuORuCl(bpy)_2^{2+}] = \frac{k_6k_7[(bpy)_2ClRuORuCl(bpy)_2^{2+}][M^{n+}]}{k_{-6}[M^{(n+1)+}] + k_7[M^{n+}]} \quad ....(5.20)$$

If $k_7 >> k_{-6}$ equation (5.20) reduces to a simple second-order expression:

$$\text{Rate} = k_6[(bpy)_2ClRuORuCl(bpy)_2^{2+}][M^{n+}] \quad ...(5.21)$$

The assumption in the above scheme is justified by the absence of any complexity (such as product inhibition) in the observed rate law. Similar reaction schemes have, in the past, been used to rationalize the kinetic behavior of many non-complementary reactions which display similar kinetic behavior as in the reactions of interest in this

investigation. Some examples of such reactions are $V(11) + I_2^5$, $U^{3+} + Br_2$, $I_2I_3^6$ and $Eu^{2+} + I_2$, I_3^{-7} reactions while the $V(1V) + Cl_2^8$ and $Fe(bpy)_3^{2+} + Br_2$ reactions provide examples of systems in which product inhibition makes the first step in the series of univalent changes a kinetically reversible one.

The values of the ratio[10] $k_{M^{n+}}/kV^{2+}$ for all the reducing ions, $Cr^{2+}_{(aq)}$, $Eu^{2+}_{(aq)}$ $Ru(NH_3)_6^{2+}$ and $U^{3+}_{(aq)}$ employed in this work are as follows:

M^{n+}	Cr^{2+}	Eu^{2+}	$Ru(NH_3)_6^{2+}$	U^{3+}
$\frac{k_{M^{m+}}}{k_{V^{2+}}}$	0.023	0.33	6	54

For reactions of the outer-sphere mechanism, $k_{Cr^{2+}}/k_{V^{2+}} < 0.024$ is well established[10] for the Cr^{2+}aq reduction of $Co(NH_3)_5X^{2+}$ (X = py, NH_2^-, CH_3CN and C_6H_5CN) and also for $Ru(NH_3)_5py^{3+}$[11]. For reactions of the inner-sphere mechanism, the ratio is generally greater than 20 as typified by the reduction of FeX^{2+}(X = N_3^-., NCS^-, Cl^-) and of $Co(NH_3)_5Cl^{2+}$

by these ions. The value of $k_{Cr^{2+}}/k_{V^{2+}} = 0.023$ obtained in this investigation suggests that the reduction of the oxobridged ruthenium(111) dimer by Cr^{2+}aq and V^{2+}aq occur by the outer-sphere mechanism. The rate ratios $k_{Eu^{2+}}/k_{V^{2+}}$ of 23 and 51 have been obtained for some inner-sphere reductions involving these ions. The outer-sphere values of this ratio has been put in the range 0.05 to 0.48.[13]

The value of 0.33 obtained for the reduction of the oxobridged ruthenium(lll) dimer by $Eu^{2+}(aq)$ suggests that this reaction occur by the outer-sphere mechanism. $Ru(NH_3)_6^{2+}$ is a well established outer-sphere reductant. The value $k_{Ru(NH_3)_6^{2+}}/k_{V^{2+}} = 6$ was obtained in this investigation. $k_{U^{3+}}/k_{V^{2+}}$ was also found to be 53.

It must be noted that the mechanism in which reactant species are in equilibrium with post-cursor complexes, a phenomenon common in the reduction of some Ru(lll)[14,15] ammine complexes by $Cr^{2+}(aq)$ is not supported by our kinetic data. This mechanism represented by the equation.

$$RuCl^{2+} + Cr^{2+} \underset{}{\overset{K}{\rightleftharpoons}} [Ru^{II}ClCr^{III}]^{4+} \qquad ....(5.22)$$

$$[RuClCr]^{4+} \xrightarrow{k} RuOH_2^{2+} + CrCl^{2+} \qquad ....(5.23)$$

leads to a rate law of the form:

$$\text{Rate} = \frac{kK[Cr^{2+}][RuCl^{2+}]}{1 + K[Cr^{2+}]} \qquad ...(5.24)$$

in which,

$$k_{obs} = \frac{k\,K}{1 + K[Cr^{2+}]}$$

Implicit in this mechanism are:

(1) that the reaction proceeds by the inner-sphere mechanism

(ii) that the rate should be independent of $[Cr^{2+}]$ at high $[Cr^{2+}]$. Therefore, the absence of saturation kinetics in the range $[Cr^{2+}] = (0.92 - 13.9) \times 10^{-2}M$ investigated rules

out the inner-sphere mechanism for the reduction of the oxo-bridged complex by $Cr^{2+}(aq)$ and thus further confirm that these reactions proceed by the outer-sphere mechanism.

The effect of acid on the rates of these reactions presents some interesting features. Only the rates of the reactions of $Ti^{3+}aq$ and Ti^{III}-edta are dependent on $[H^+]$. The rate of reduction of $[(bpy)_2ClRuORuCl(bpy)_2^{2+}]$ by $Cr^{2+}(aq)$, $V^{2+}(aq)$, $Eu^{2+}(aq)$, $Ru(NH_3)_6^{2+}$ and $U^{3+}(aq)$ are acid - independent in the acid range $0.025 < [H^+] < 0.5M$ investigated. The substitution reaction of the oxobridged ruthenium(III) dimer is acid-catalyzed.[4,16] This has been interpreted in terms of pre-rate-determining step protonation of the oxide linkage leading to the probable formation of the aqua-complex $Ru(bpy)_2ClH_2O^+$ as the decomposition products.

However, that not all the reductants of interest in this investigation exhibit the dependence of rate on $[H^+]$, which usually characterize the reactions of oxo- and hydroxobridged metal dimers[16b] suggests that the $Ru^{III}ORu^{III}$ moiety is not the source of $[H^+]$ dependence where such was observed. It further suggests that it is the post-electron-transfer mixed-valence dimer $Ru^{II}ORu^{III}$, that is protonated after the rate-determining step given by equation (5.18).

The observed complex acid dependence of the reduction of the dimer by $Ti^{3+}(aq)$ is consistent with what is usually observed in the reaction of this ion with monomeric Co(III) and Ru(III) complexes[17,7] and aqueous bromine and

iodine solutions.[18] The observed dependence on $[H^+]$ as in these other systems can be rationalized by the following proposed scheme.

$$Ti(H_2O)_6^{3+} \underset{}{\overset{K_a}{\rightleftharpoons}} (H_2O)_5TiOH^{2+} + H^+ \qquad ...(5.26)$$

$$(H_2O)_5TiOH^{2+} + RuORu^{2+} \xrightarrow{k_8} \text{products} \qquad ...(5.27)$$

From the above reaction scheme the following rate law can be deduced:

$$\text{Rate} = \frac{k_8 K_a [H^+]^{-1} [Ti(III)] [RuORu^{2+}]}{1 + K_a [H^+]^{-1}} \qquad ...(5.28)$$

$$\text{or } k_o = \frac{k_8 K_a [H^+]^{-1}}{1 + K_a [H^+]^{-1}} \qquad ...(5.30)$$

$$\text{or } k_o^{-1} = 1/a + [H^+]/b \qquad ....(5.31)$$

Equations (5.30) and (5.31) are identical with $a = k_8$ and $b = k_8K_a$. Least-mean-square computation of the obtained data gives values of a and b, and hence k_8 and K_a are calculated as:

$$k_8 = (2.53 \pm 0.03) \times 10^2 M^{-1} s^{-1}$$

$$K_a = (4.0 \pm 0.1) \times 10^{-3} M$$

The literature value of K_a lie in the range $(2\text{-}5) \times 10^{-3}M$ for outersphere reactions[19] involving $Ti^{3+}(aq)$. The value of $K_a = 4.0 \times 10^{-3}M$ derived from the obtained kinetic data is in good agreement with the kinetically derived values of K_a

in the reaction of aquotatanium(111) ion with such oxidants as $Co(terpy)^{3+}$, $Co(NH_3)_5Cl^{2+}$, $Co(NH_3)_4Cl_2{}^{+}$[20] and many Ru(111) complexes.[21] This is also consistent with the derived K_a values for the reaction of $Ti^{3+}(aq)$ with I_2 and Br_2.[18] As in earlier reactions involving $Ti^{3+}(aq)$, the derived value of K_a in this investigation confirms $TiOH^{2+}$ as the principal reactant $Ti^{3+}(aq)$ species. In the reactions of $Ti^{3+}(aq)$ such as its oxidation by $Co(NH_3)_5N_3^{2+}$ and $Co(NH_3)_5NCS^{2+}$ where reactivity pattern provided unequivocal evidence for the inner-sphere mechanism, the K_a values are usually in the range 0.01 to 0.2[22-24] and in such cases, deprotonation occurs from the activated complex which is generally binuclear in composition.

The dependence of the rate of the reaction of Ti^{III}-.edta - with $[(bpy)_2ClRuORuCl(bpy)_2^{2+}]$ on pH is biphasic as shown in figure (5.16). Such a dependence has been observed in the reactions of Ti^{III}-edta with Br_2, I_2[18], $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5NCS^{2+}$. In these reactions for the range pH < 3, the rate is not pH dependent while in the range pH > 3, the rate increases with pH. As in earlier investigations, such a dependence on pH can be attributed to differing reactivities of the Ti^{III}-edta species present in solution[3]. These are $[Ti(H_20)(Hedta)]$, $[Ti(H_20)\ edta)^{-}]$and $[Ti(\ OH)(edta)]^{2-}$

Therefore this interpretation is consistent with the polarographic findings that at pH < 3, Ti^{IV}-edta exists as an aquoion while at pH > 3 it exists as an oxo ion[3]. The principal activation paths for these reaction can be proposed as follows:

$$TiY \underset{K_2}{\overset{K_1}{\rightleftharpoons}} TiY^- + H^+ \qquad \ldots(5.32)$$

$$TiY^- \underset{}{\overset{K_2}{\rightleftharpoons}} TiY^2 + H^+ \qquad \ldots(5.32)$$

$$TiY + RuORu^{2+} \xrightarrow{k_1} \text{(Activated complex)} \qquad \ldots(5.34)$$

$$TiY^- + RuORu^{2+} \xrightarrow{k_2} \text{(Activated complex)} \qquad \ldots(5.35)$$

$$TiY^{2+} + RuORu^{2+} \xrightarrow{k_3} \text{(Activated Complex)} \qquad \ldots(5.36)$$

where Y = edta, $RuORu^{2+} = \left[(bpy)_2ClRuORuCl(bpy)_2^{2+}\right]$

The above scheme gives

$$k_o^{edta} = \frac{k_1 + k_2K_1\left[H^+\right]^{-1} + k_3K_1K_2\left[H^+\right]^{-2}}{1 + K_1\left[H^+\right]^{-1} + K_1K_2\left[H^+\right]^{-2}} \qquad \ldots(5.37)$$

From the titration studies of Tl^{III}-edta solutions reported by Podlahova and Podlaha[3], the first two species $\left[(Ti(H_20)(Hedta)\right]$ and $\left[Ti(H_20)\ edta\right]^-$ were identified at pH < 3. Moreover the result of this investigation suggests that the above two species react at the same rate i.e. $k_1 = k_2$. This is consistent with the result of recent investigations. Therefore equation (5.37) becomes,

$$k_o^{edta} \frac{k_2 + k_2K_1\left[H^+\right]^{-1} + k_3K_1K_2\left[H^+\right]^{-2}}{1 + K_1\left[H^+\right] + K_1K_2\left[H^+\right]^{-2}} \qquad \ldots(5.38)$$

Using values of K_1 and K_2 as measured by Podlahova and Podlaha[3] i.e.

$pK_1 = 2.02 \pm 0.01$

$pK_2 = 8.64 \pm 0.02$

non-linear least - mean_square computer fitting of the obtained data into equation (5.37) gave values of k_2 and k_3 as $k_2 = (2.96 \pm 0.13) \times 10^5\ M^{-1}{}_s{}^{-1}$

$k_3 = (3.00 \pm 0.56) \times 10^8\ M^{-1}{}_s{}^{-1}$

The value of $k_{2(calc)} = (2.96 \pm 0.13) \times 10^5 M^{-1}{}^{-1}$ compares favourably with the value of $k_{2(expt)} = 2.7 \times 10^5 M^{-1}{}_s{}^{-1}$ the average value of k_o^{edta} for pH < 3. The agreement between $k_{2(calc)}$ and $k_{2(expt)}$ confirms the proposed mechanism. This mechanism is further confirmed by the linear plot of

$$[k_o^{edta}\ (1 + [K_1\ [H^+] + K_1K_2\ [H^+]^{-2}]) - k_2]\ [H^+] - k_2K_1$$

versus $K_1K_2\ [H^+]$. obtained (Figure (5.17)). The value of $k_3 = (2.41 \pm 0.3) \times 10^8 M^{-1}s^{-1}$ obtained from the least-mean-square analysis of the slope of this plot is comparable with the value $k_{3(calc)} = (3.0 \pm 0.56) \times 10^8 M^{-1}s^{-1}$ obtained from the computer analysis of the data. An additional confirmation of the proposed reaction scheme is the fit obtained between the calculated and observed value of k_o^{edta} as a function of pH with a correlation coefficient of 0.99. The similarity in the k_o^{edta}(calc) and k_o^{edta} is brought out clearly in the rate/pH profile shown in Figure (5.16).

As for whether the reduction by Ti^{111}-edta proceed by the outer-or inner-sphere mechanism the only evidence of mechanism is that the rate constant,

$k_o^{edta} = 10^5\ M^{-1}S^{-1}$

obtained is much higher than the substitution-controlled rate for inner-sphere reactions of Ti^{111}-edta with $Co(NH_3)_5SCN^{2+}$ and $Co(NH_3)_5N_3{}^{2+}{}^1$ and also much greater than the k substitution $= 10^{-2} - 10^{-3}$M for the oxobridged dimer. [16] If we also consider

the rate ratio $k_{TiOH^{2+}}/k_{o}Ti^{III}edta$, the value for Br_2, I_2[18] and $(bpy)_2ClRuORuCl(bpy)_2^{2+}$ are 1.1×10^{-4}, 0.5×10^{-4} and 0.36×10^{-3} respectively. The similarity in these values suggests that these reactions most probably proceed by the same mechanism, i.e. the outer-sphere mechanism. The reduction of the oxobridged ruthenium(III) dimer by $TiOH^{2+}$, $V^{2+}aq$ and Ti^{III}-edta are independent of $[Cl^-]$, while the reduction by Ti^{III}-edta is also independent of $[NCS^-]$. All the other reactions investigated in this work show some dependence of rate on added chloride or thiocyanate ion concentration. Except for the complex dependence on $[NCS^-]$ displayed by the rate of reaction involving $TiOH^{2+}$ and the oxobridged dimer, the observed dependence of the rates of these reactions on added anion concentration fits a general equation of the form:

$$k_o^X = k_o + b[X^-], \quad (X^- = Cl^- \text{ or } NCS^-)$$

The dependence of the rate of the $TiOH^{2+}$ reduction of the oxobridged dimer on $[SCN^-]$ follows a rate law of the form:

$$k_o^{SCN} = p + q[SCN^-] + r[SCN^-]^2.$$

with p the $[NCS^-]$ independent rate constant ($p = 32.5 M^{-1}s^{-1}$)

The linear plot of

$$\frac{k_o^{NCS} - p}{[NCS^-]} \quad \text{versus } [NCS^-] \text{ give}$$

slope and intercept as

$$r = 5.6 \times 10^3 \ M^{-3}s^{-1}$$

$$q = 7.55 \times 10^5 \ M^{-2}s^{-1}$$

respectively.

The linearity of this plot suggests that the complexed Ti(111) species of the form $Ti^{3+}(aq)$, $Ti(SCN^-)^{2+}$ and $Ti(SCN)_2^+$ react at different rate. The following reaction scheme can therefore be proposed:

$$Ti^{3+}(aq) + NCS^- \underset{}{\overset{K_3}{\rightleftharpoons}} TiSCN^{2+} \quad ...(5.39)$$

$$TiSCN^{2+} + NCS^- \underset{}{\overset{K_4}{\rightleftharpoons}} Ti(SCN)_2^+ \quad ...(5.40)$$

$$Ti^{3+}aq + [(bpy)_2ClRuOCl(bpy)_2^{2+}] \xrightarrow{k_9} \text{Products} \quad ...(5.41)$$

$$TiSCN^{2+} + [(bpy)_2ClRuORuCl(bpy)_2^{2+}] \xrightarrow{k_{10}} \text{Products} \quad ..(5.42)$$

$$Ti(SCN)_2^+ + [(bpy)_2ClRuORuCl(bpy)_2^{2+}] \xrightarrow{k_{11}} \text{Products} \quad ..(5.43)$$

Therefore,

$$\frac{k_o^{SCN} - k_9}{[SCN^-]} = k_{10}K_3 + k_{11}K_3K_4[SCN^-] \quad ...(5.44)$$

Thus a plot of the left-hand-side of the above equation against $[SCN^-]$ should be linear as confirmed in Figure (5.25). Since equation (5.44) is identical to equation (5.5) then,

$$p = k_9 = 32.5M^{-1}s^{-1}$$

$$q = k_{10}K_3 = 5.6 \pm 10^3M^{-1}s^{-1}$$

$$r = k_{11}K_3K_4 = 7.55 \pm 0.30M^{-1}s^{-1}$$

The similarity of the measure value of k_o with p and k_9 the $[NCS^-]$ independent rate constant confirms the proposed scheme.

The reactivity order obtained for all the reducing ions employed in this investigation in order to decreasing rate constant is:

$$U^{3+} > Ti^{111}\text{-edta} > Ru(NH_3)_6^{2+} > Eu^{2+} > Cr^{2+} > TiOH^{2+}$$

This order does not paralled the order expected on the basis of their reduction potentials which is,

$U^{3+} > Cr^{2+} > Eu^{2+} > V^{2+} > Ru(NH_3)_6^{2+} > Ti^{III}$-edta $> TiOH^{2+}$

(E^o values[25] are $U^{4+}/U^{3+} = -0.63V$,

$Cr^{3+}/Cr^{2+} = -0.46V$, $Eu^{3+}/Eu^{2+} = -0.42V$,

$Ru^{3+}/Ru^{2+} = 0.088V$, $V^{3+}/V^{2+} = 0.255V$

TiO^{2+}-edta/Ti^{III}-edta $= 0.30V$ and $TiO^{2+}/Ti^{3+} = 0.1V$).

Except for U^{3+}, there is a reversal in the order expected on the basis of the redox potentials of these reducing ions. It is generally accepted that kinetic reactivity, viz in redox systems,is determined by two factors.

The relative significance of each of these factors has attracted some attention. These factors following Marcus[10] and Sutin[26] are,

(i) thermodynamic factors which are determined by E^o.

(ii) non-thermodynamic factors, e.g. homonuclear exchange rates and the nature of the orbitals of the reducing and the oxidizing ions.

Based on the orbitals from which electron is to be transferred, the reducing ions can be divided into two classes, viz:

1. $Cr^{2+}_{(aq)}$, $Eu^{2+}_{(aq)}$ and $U^{3+}_{(aq)}$ where the electron to be transferred is in an orbital that has σ symmetry.

2. $Ru(NH_3)_6^{2+}$, $V^{2+}_{(aq)}$ $TiOH^{2+}$, Ti^{III}-edta where the electron to be transferred is in an orbital with π (t_{2g}) symmetry.

The lowest orbital of $[(bpy)_2ClRuORuCl(bpy)_2^{2+}]$ that can accept the electron transferred is a π^* orbital.[4] Taube and Stritar[27] have used similarities in the oxidant and reductant orbitals to rationalize the reactivity pattern observed in some inner-sphere and outer-sphere reactions involving Co(lll) ammine complexes as oxidants and some divalent metal ions as reductants. Earley et al[28] have also interpreted the observation that the acid-dependent rate constants for some inner-sphere reactions of $Ti^{3+}_{(aq)}$ are consistently larger than for the corresponding Co(lll) oxidants, in terms of the greater cross-bridged electronic interactions through the π-electron system of the bridge in case of Ru(lll) than for Co(lll). The results of the electron-transfer reactions between U(lll) and some ruthenium(lll) ammine complexes,[29] when compared with its Co(lll) analogues also highlight the basic difference in the kinetic reactivity pattern of these complexes in terms of the effect of the electronic configuration of the central metal ion both on the rate of electron transfer and the choice of mechanism.

The general conclusion, therefore, from literature, on orbital symmetry effect on electron transfer rates is that a similarity in the donor-acceptor orbital of an oxidant-reductant pair (i.e. $\sigma \rightarrow \sigma$ or $\pi \rightarrow \pi, \pi^*$) usually lead, to high rates. However, high intrisic barrier to electron-transfer, in terms of mismatch of donor-acceptor orbitals may force reactants to adopt the inner-sphere mechanism, in which case activation energy may be lowered by the exothermicity of the formation

of a precursor binuclear intermediate. When the adoption of the inner-sphere mechanism is not structurally possible, then rates are usually low.

The results of this investigation show, as in earlier works,[27-29] that the symmetry of the orbitals of the oxidizing and reducing ions, to a large extent determine the magnitude and the order of electron transfer rates. Cases where electrons are transferred from a π orbital of the reductant (class 2 above) to the π^* acceptor orbital of the oxobridged ruthenium(111) dimer were of high rates than cases involving $\sigma \rightarrow \pi^*$ transition (Class 1 above).

That $U^{3+}_{(aq)}$ and $TiOH^{2+}$ reduction of the dimer did not conform to the expected order in terms of orbital symmetry, can be attributed to the very low reduction potential ($E^{\circ} = -0.063V$) of the former ion and the drastic structural rearrangement that accompanies the conversion of the later ion ot its oxocation.

That the observed order of reactivity for the reductants of interest reflect the importance of the participating orbitals is further confirmed by the thiocyanate and chloride catalysis observed for these reactions. Sutin and Przstas[30] have shown that the magnitude of catalysis by anions usually observed for reactions that proceed by the outer-sphere mechanism, is determined by the correlation of symmetry of anion orbital with that of the oxidizing and reducing ions. Their model, which assumes that the anion is complexed to the reductant, also assumes that the

coordinated anion is in a position between the oxidant and reductant but it is not directly coordinated to the oxidant. Assuming this model in the rationalization of our observed result suggests that the observed lack of anion dependence of the reductions by $TiOH^{2+}$, V^{2+}_{aq} on $[Cl^-]$ and that by Ti^{III} - edta on $[NCS^-]$ means that $TiCl^{2+}$, VCl^+ are probably reacting at the same rate with the native aquions. It is pertinent to mention that the 'innocence' of Ti^{3+}_{aq} reactions in a chloride medium is not new.[31] For the reductions of the dimer that showed enhancement in rate by added anion, the order of observed chloride catalysis is

$U^{3+} >> Ru(NH_3)_6^{2+} > Eu^{2+} > Cr^{2+}$

and that for thiocyanate is:

$Ru(NH_3)_6^{2+}$, $U^{3+} > V^{2+} > Cr^{2+} > Eu^{2+}$

Thiocyanate is considered as a good π-bridging ligand while chloride is a good σ bridging ligand. Since the acceptor orbital of the dimer is of π^* symmetry[4], it is expected that there should be greater thiocyanate catalysis for $Ru(NH_3)_6^{2+}_{aq}$ than for Cr^{2+}, Eu^{2+} and U^{3+} since the former represents a $\pi \rightarrow \pi \rightarrow \pi^*$ transition while the latter is a $\sigma \rightarrow \pi \rightarrow \pi^*$ transition. Broadly speaking, these results conform with this expectation.

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