OXIDATION OF SOME COHPLEXONES BY THREE TRANSITION METAL COMPLEXES: A COMPARATIVE MECHANISTIC STUDY

BY

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DECLARATION

I hereby declare that this thesis contains the report of my research work and has not been presented in any previous application for a higher degree. Information from other sources has been acknowledged by means of reference.

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6/4/92

DATE

CERTIFICATION

This thesis entitled "Oxidation of some complexones by three transition metal complexes: A comparative mechanistic study" by Saratu Mamman, meets the regulations governing the award of the degree of Master of Science of Ahmadu Bello University and is approved for its contribution to scientific literary presentation.

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DEDICATION

To my parents, Hajiya Hajara and Alh. Mammam, for their love and prayers.

QUOTATION

"Allah knoweth best (who are) your enemies. Allah is sufficient as a Friend and Allah is sufficient as a Helper".

Quran 4:45

ACKNOWLEDGEMENT

I am grateful to Allah, the Most Merciful, the Most High and the Most knowledgeable, who taught man how to read and revealed to him what is previously unknown And May Peace and Blessings of Allah be upon His Messenger, Muhammad, who was selected by Allah to invite and educate people of the way of Allah.

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ABSTRACT

The kinetics and mechanisms of the oxidation of HEDTA, EDTA and NTA by $Co^{1II}W$, $Fe(bipy)_3^{3+}$ and $Fe(5\text{-}H0_2\text{-}phen)3^{3+}$ respectively have been studied in aqueous perchloric acid media.

One mole of the complexone was found to reduce two moles of the complex in each case. Each reaction is first-order with respect to oxidant and reductant. For all the reactions studied, the empirical rate law is given by

$$\frac{d[Ox]}{dt} = 2k_2[0x][Red]$$

at 25.0 ± 0.1-C, I = 2.0M(5aC10_4) and $[H^+]$ range of (0.25-1.0)M. Where 'Ox' is $Co^{IXI}W$, $Fe(bipy)3^{3+}$ or $Fe(5\text{-}N0_2\text{-}phen)3^{3+}$ and 'Red' is HEDTA, EDTA or NTA.

The rates of reactions decrease with increasing $[H^+]$. This is attributed to the dissociation of the hydrogen of the -CO2H group in the complexones prior to electron transfer.

Similar mechanisms have been proposed for these reactions on the basis of the similarities in their stoichiometries and oxidation products.

Both spectrophotometry and kinetic evidence in these reactions indicate that an inner-sphere complex formation prior to the electron transfer step is absent. The outer-sphere mechanism is therefore the most plausible for the title reactions. The inertness of these oxidants to substitution is advanced as the major reason for the operation of the outer-sphere mechanism in these reactions.

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ABBREVIATIONS

ABBREVIATION	NAME
aq	Aqueous
B.D.H	British Drug House
bipy	2,2'-Bipyridine
Calc.	Calculated
E°	Redox potential
EDTA	Ethylenediaminetetraacetic acid
en	ethylenediamine
E.S.R	Electron magnetic resonance
G.P.R	General purpose Reagent
HEDTA	(Hydroxoethyl) ethylenediamine triacetic acid
I.S	Inner-sphere
K	Equilibrium constant
k	Rate constant
N.T.A	Nitrolotriacetic acid
obsd	Observed
O.S	Outer-sphere
Ox	Oxidant
phen	1,10-phenanthroline
Red	Reductant.

CHAPTER 1

1.1 Introduction

1.1 Oxidation-Reduction (Redox) Reactions

A redox reaction involves the transfer of one or more electrons between oxidants and reductants. This reaction is often accompanied by changes in the oxidation states of at least two of the reactants. A particular oxidation state is said to be stable only when its redox reaction invloves an unfavourable free energy change, or the activation energy for the intra molecular electron-transfer processes are too large (Sutin, 1966; Taube, 1968; Chaffee and Edwards, 1970; and Earley, 1970).

Redox reactions are very important in many chemical, biochemical and technological processes. The investigation of the mechanisms of a large number of these electron-transfer reactions have been reported, (Sutin, 1962; Hunt, 1963; Sykes, 1966; Wilkins, 1974; and Burgess, 1978). A range of experimental techniques have been used in the study of redox reactions, (Sykes, 1966; 1967; Rosseinsky, 1972; Wilkins, 1974; Haque, 1972 and Burgess, 1978). These techniques vary from conventional spectrophotometric methods for slow redox reactions to continuous flow and stopped-flow methods for fast reactions. These methods have been extensively reviewed, (Stranks, 1960; Caldin, 1974; and Wilkins, 1974).

Recent developments in redox chemistry have shown that the basic principles which are applicable to simple systems involving metal ions in solution extend with some modification to biological important processes such as metalloproteins. Other systems to which the principles are applicable are intervalence transfer and reactions of hydrated electrons.

These reactions may occur by the outer- or inner-sphere pathway, (Taube, Rich and Meyer, 1963).

1.2 Types of Electron-transfer Reactions

Redox reactions can be classified on the basis of their thermodynamic parameters.

1.2.1 Homonuclear electron exchange

The basic underlying factor here is that electron transfer takes place between two ions of the same element in the same environment, e.g.

$$^{*}Fe(CN)_6^{4-} + Fe(CN)_6^{3-} \longrightarrow {}^{*}Fe(CN)_6^{3-} + Fe(CN)_6^{4-} \quad \ldots 1.1$$

where * is an Isotopically labelled element. In this exchange, there is no net chemical change and rate constant for the forward reaction equals that of the reverse reaction, so that $K_{equilibrium} = 1$, $\Delta H = 0$, $\Delta G = 0$ and $\Delta S > 0$. Such reaction can therefore be studied only by Isotopic labelling.

1.1.2.2 Heteronuclear electron exchange

These reactions are called "Chemical" (or "Cross") reactions, in which the products are usually chemically distinct from the reactants. The rate constant can be measured by chemical method. Here, $\Delta H \neq 0$ and $\Delta G < 0$, e.g.

$$Fe(CN)_6^{4-} + IrCl_6^{2-} \longrightarrow Fe(CN)_6^{3-} + IrCl_6^{3-} \quad \ldots\ldots 1.2$$

This class of redox reactions could be complimentary or non-complimentary. It is complimentary, if the number of electrons lost by the reductant equals that gained by the oxidant. This type of reaction must always involve 1:1 stoichiometry, e.g.

$$Co^{III} + Cr^{II} \longrightarrow Cr^{III} + Co^{II} \quad \ldots\ldots 1.3$$

On the other hand, a redox reaction is said to be non-complimentary when the number of electrons lost by the reductant is not the same as that gained by the oxidant, and therefore, 1:1 stoichiometry is not possible, e.g.

$$2Fe^{3+} + Sn^{2+} \longrightarrow 2Fe^{2+} + Sn^{4+} \quad \ldots\ldots\ldots 1.4$$

These reactions must almost certainly involve the formation of a reactive intermediates in which unstable oxidation state of metals are formed.

1.3 Franck-Condon Principle

The electron transfer process must satisfy the Franck-Condon restriction, which states that, "the motion of nuclei is so slow (10^{-13}sec) compared to that of the electron (10^{-15}sec) that electron transfer occurs without any appreciable movement of the nuclei". In other words, nuclear position remain essentially unchanged during the act of electron transfer, (Platzman and Frank, 1954; Sutin, 1966). There are two major consequences of this principle of electron transfer reactions;

(a) The oxidant and reductant must undergo reorganization before the act of electron transfer in a way that ensures that their energies in the transition state are identical. This minimizes the energy change on electron transfer.

(b) No significant amount of change in spin angular momentum of the activated complex must occur during electron transfer. Spin inversion when it occurs is found to inhibit the overall redox rate.

1.4 Electron-Tunneling theory

In addition to the above contributions, it has been noted that electronic energy is not as high in either the 'reactants' or the 'products' activated complex as the classical potential energy barrier to electron migration between these complexes. Therefore, electron migration is viewed as a tunneling process in which the electron passes through the potential energy barrier

rather than over it, (Basolo and Pearson, 1967). the result is that the electron can be transferred to distances much greater than would correspond to the actual collision of reactants. Figure 1.1 illustrates a potential energy barrier leakage.

Where u_1 and u_2 = ground states of the electrons in cations 1 and 2 respectively,

d = width of barrier at height of penetration,

W = kinetic energy of the electron,

U_o = height of the barrier.

This situation has led some theoreticians to attempt calculations of the electron transmission coefficient (Marcus et al, 1954). Their results were expressed in terms of transition state theory of chemical kinetics and could be written in the form:

$$k = \frac{KT}{h} k' \exp\left(-\frac{Gr^*}{RT} - \frac{Ge^*}{RT}\right) \quad \ldots\ldots 1.5$$

where k = rate constant

k' = the transmission coefficient which includes the probability of barrier penetration.

T = absolute temperature

K = Boltzman's constant

Ge* = activation free energy for overcoming electronic repulsion between the ions.

Gr* = activation free energy for rearrangement of the hydrated and coordination shells.

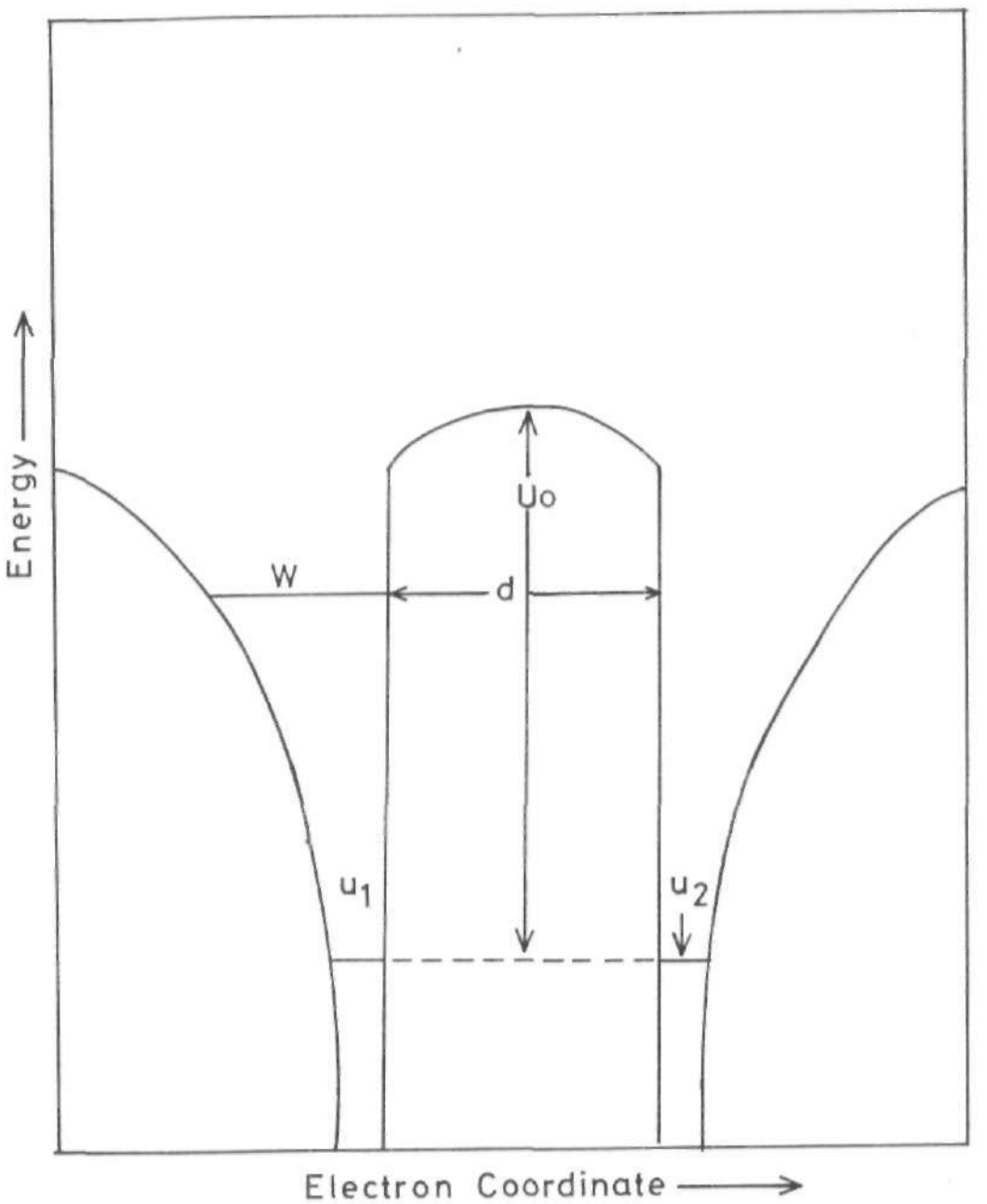


FIG. 1·1 ELECTRON TRANSFER BY PENETRATION
A POTENTIAL ENERGY BARRIER

The transmission coefficient which is always close to one, increases (tending to increase the rate constant) as the exchanging partners come closer together. The energy of activation also increases because of electrostatic repulsion, and this tends to decrease the rate constant. However, at an optimum distance, a maximum exchange rate is obtained. Similar theories for electron transfer by an electron tunneling mechanism have been proposed, (Wess, 1954; and Marcus, 1956). Of recent, Lewis (1980), discussed the question of potential energy as a conceptual tool in the study of electron transfer reactions. He concluded like Taube and Gould (1969), that electron tunneling is probably involved in most electron transfer processes, although the tunneling step may not be the rate determining in most cases.

1.5 Mechanism of Redox Reactions

The study of the mechanism of electron-transfer processes can be discussed broadly under four main points of mechanistic interest;

(a) Stoichiometry of the reaction

(b) Kinetics (including the different factors that may affect the rate of reaction)

(c) Spectrophotometric studies of the different species that may be involved

(d) Product analysis.

In trying to understand the pathway of electron transfer processes, two distinct mechanisms have been established (Taube, 1959; Taube, Meyer and Rich, 1953) namely, the outer- and inner-sphere mechanisms. In principles, either of the mechanisms is possible for both Isotope exchange and chemical reactions. There are two important aspects of each of these mechanisms; the spatial and the energetic aspects.

1.5.1 The outer-sphere mechanism

(A) Spatial aspect: This involves the electron transfer between two species whose coordination sphere remain intact although, not completely undisturbed during the act of electron transfer. The outer-sphere mechanism occurs when both reactants are inert with respect to substitution or when one is relatively inert and it does not present a bonding site for the labile reactant, e.g

$$*Fe(phen)_3^{2+} + Fe(phen)_3^{3+} \rightleftharpoons *Fe(phen)_3^{3+} + Fe(phen)_3^{2+} \quad \ldots 1.6$$

This reaction qualifies for an outer-sphere redox category since the phenanthroline could not become detached from the inert Iron(II) and Iron(III) centres during the course of the rapid redox process. Therefore, the coordination shells of the two

reactants remain essentially intact even after electron transfer (Larsen and Wahl, 1965).

Similarly, outer-sphere mechanism operates for the self-exchange reaction of $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_6^{3+}$ (Meyer and Taube, 1968), and the cross-reaction between $Fe(CN)_6^{4-}$ and $IrCl_6^{2-}$ (Sutin, et al, 1964). the electron exchange between substitution inert $Co(NH_3)_6^{3+}$ and $Cr(H_2O)_6^{2+}$ has been found to proceed via an outer-sphere mechanism because coordinated ligands such as ammonia and ethylenediamine cannot form bridges even though Cr(II) is labile.

(B) Energetics: The mechanism in outer-shere reactions can be illustrated with the following example:

Step I: Formation of precursor complex

$$M_1^{II}(H_2O)_6^{n+} + M_2^{III}(NH_3)_5L^{m+} \dashrightarrow [(H_2O)_6M_1^{II}-LM_2^{III}(NH_3)_5]^{(n+m)+} \quad \ldots 1.7$$

Step II: Activation of the precursor complex.

$$[H_2O)_6M_1^{II}-LM_2^{III}(NH_3)_5]^{(n+m)+} \rightarrow (H_2O)_6M_1^{II}-LM_2^{III}(NH_3)_5]^{*(n+m)+} \quad \ldots. 1.8$$

Step III: Electron transfer and formation of successor complex.

$$[(H_2O)_5M_1^{II}\text{-}LM_2^{III}(NH_3)_5]^{*(n+n)+} \longrightarrow [(H_2O_5)M_1^{III}\text{-}LM_2^{II}(NH_3)_5]^{(n+m)+} \quad \ldots\ldots 1.9$$

This is the rate determining step.

Step IV: Decomposition of the successor complex

$$[(H_2O)_5M_1^{III}\text{-}LM_2^{II}(NH_3)_5]^{(n+m)+} \longrightarrow M^{III}(H_2O)_6^{(n+1)+} + M_2^{II}(NH_3)_5L^{(m-1)+} \quad \ldots\ldots 1.10$$

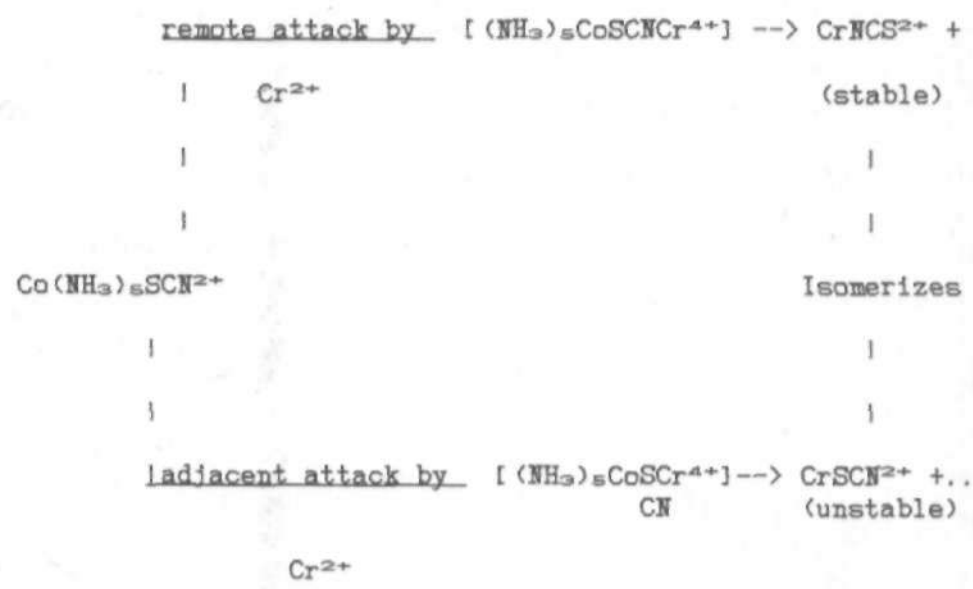
In outer-sphere mechanism, the interaction between the oxidants and reductants is relatively weak on the time scale of the redox reactions and therefore, effect of breakage and formation of bonds are not normally considered, but can only be subjected to theoretical treatments.

1.5.2 The Inner-sphere mechanism

(A) Spatial aspects: The main feature of this mechanism is that substitution occurs at one of the metal centres to give a binuclear ligand-bridged species prior to the transfer of electron. In such a situation, the two reactants are linked by

at least one bridging ligand common to their inner coordination shells. The bridging pattern could be grouped into three systems.

(a) Mono-bridge system: There is one bridge between metal and ligand. The ligand could be unidentate (i.e it has one bonding site) e.g halides, or ambidentate (it has more than one bonding site), most common are CN^- and NCS^-. The use in the oxidant of an ambidentate ligand that presents more than one potential donor site towards the reductant introduces the concept of remote and adjacent attack, (Taube, 1965). This can be illustrated by the reaction scheme (Shea and Haim, 1971);



Adjacent attack occurs when there is only one nucleus separating the two metal centres, and remote attack occurs when

there are two or more intervening atoms between the metal centres, i.e there is a bond with one ligand atom which is not directly connected with the second metal centre. Some factors that governs the site of attack are; steric hindrance to remote attack, favourable bonding at the adjacent site and the ease of electron transfer from the site of the attack to the central metal atom.

(b) Double bridge system: The possibility of two or more bridging groups in the activated complex of an inner-sphere reaction was suggested by Taube and Meyer, (1954). The implication of a double bridge in a redox reaction can only be via product characterization. The Isotopic exchange,

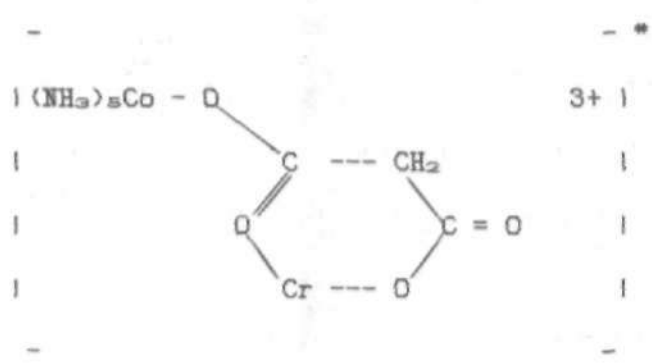
$$Cis\text{-}Cr(N_3)_2 + {}^*Cr^{2+} \rightleftharpoons Cis - {}^*Cr(N_3)_2^{+} + Cr^{2+} \quad \ldots\ldots \quad 1.11$$

can only occur via a double bridge. The rate constant for the exchange is 31 times large at 0^{o} than the rate constant for the net chemical reaction,

$$Cis - Cr(N_3)_2^{+} + Cr^{2+} \longrightarrow Cr(N_3)^{2+} + Cr^{2+} + N_3^{-} \quad \ldots\ldots \quad 1.12$$

which goes through a single bridge (Snellgrove and King, 1964).

(c) Chelated system: The ligand which is bonded to a metal centre forms a chelate with the second metal centre. Here, remote attack occurs although the intervening ligand may not actually take part in the act of electron transfer, e.g the product for the reduction of $Co(NH_3)_5OCOCH_2COOH$ by Cr^{2+} is the chelated Co(III) complex, which could have arisen only from the redox process involving a chelated intermediate, (Huchital and Taube, 1965);



(B) Energetics: The steps that are involved in the inner-sphere mechanism are illustrated with the following examples:

Step I: Formation of encounter complex

$$L_5M_1^{III}X^{m+} + M_2^{II}(H_2O)_6^{n+} \longrightarrow L_5M_1^{III}XM_2^{II}(H_2O)_5]^{(m+n)+} \quad ...1.13$$

Step II: Formation of precursor complex

$$L_sM_1^{III}XM_2^{II}(H_2O)_s]^{(m+n)+} \rightarrow [L_sM_1^{III}\text{-}X\text{-}M_2^{II}(H_2O)_s]^{(m+n)+} \quad ..1.14$$

Step III: Activation of the precursor complex.

$$[L_sM_1^{III}\text{-}X\text{-}M_2^{II}(H_2O)_s]^{(m+n)+} \rightarrow [L_sM_1^{III}\text{-}X\text{-}M_2^{II}(H_2O)_s]^{\#(m+n)+} \quad ..... 1.15$$

Step IV: Formation of successor complex

$$[L_sM_1^{III}\text{-}X\text{-}M_2^{II}(H_2O)_s]^{\#(m+n)+} \rightarrow [L_sM_1^{II}\text{-}X\text{-}M_2^{III}(H_2O)_s]^{\#(m+n)+} \quad ..... 1.16$$

Step V: Deactivation of the successor complex

$$[L_sM_1^{II}\text{-}X\text{-}M_2^{III}(H_2O)_s]^{\#(m+n)} \rightarrow [L_sM_1^{II}\text{-}X\text{-}M_2^{III}(H_2O)_s]^{(m+n)+} \quad .... 1.17$$

Step VI: Decomposition of the successor complex

$$[L_sM_1^{II}\text{-}X\text{-}M_2^{III}(H_2O)_s]^{(m+n)+} \rightarrow L_sM_1^{II}H_2O^{(m-1)+} + XM_2^{III}(H_2O)_s^{n+} \quad .... 1.18$$

In theory, any of the six steps could be the rate determining step, but in practice ony three special cases have been reported as the rate determining steps, the electron transfer within the bridge complex being the most commonly observed in the inner-sphere reactions.

(i) Electron transfer within the bridge is the rate determining step: this operates when there is at least one reactant that is sufficiently labile to form the bridged complex at a very fast rate and the decomposition of the successor complex is also fast. In such reactions, the rate depends on the nature of bridging ligand and on the overall free energy change of the system.

Examples

Rate constants when electron transfer within the bridge is the rate determining step

Reductant	Oxidant	Bridge	$k_2, M^{-1}s^{-1}$	Reference
Cr^{2+}	$Cr(NH_3)_5X^{2+}$	Cl^-	6×10^5	a
"	"	Br^-	$(1.4\pm0.4) \times 10^5$	a
$Co(CN_5)^{3-}$	"	Cl^-	5×10^7	b
"	"	Br^-	2×10^7	c
Fe^{2+}	"	Cl^-	1.4×10^{-3}	d
"	"	Br^-	0.726×10^{-3}	d

a = Candlin and Halpern, (1965)

b = Candlin and Halpern, (1963)

c = Tobe, (1972)

d = Espenson, (1965).

(ii) Decomposition of the successor complex is the rate determining step

This situation arises when both metal ions in the successor complex are substituted inert or when the reactants and the successor complex are in equilibrium, so that the latter is long-lived to the extend that it can be identified or isolated as salt. An example is the reaction (Haim and Wilmarth, 1961) of $Co(CN)_5^{3-}$ with $Fe(CN)_6^{3-}$, when the isolation of the complex anion $[(CN)_5Co^{III}\text{-}NCFe^{II}(CN)_5]^{6-}$, was possible and formation of very small and equal amounts of $Fe(CN)_6^{4-}$ and $Co(CN)_5H_2O^{2-}$ (the result of aquation of the successor complex) was observed. Thus, the reaction is not accompanied by bridge transfer.

(iii) Formation of precursor complex is the rate determining step

This is observed when $k_{redox} > k_{substitution}$, but for some reasons outer-sphere mechanism does not operate. In this case, the rate and activation parameterss of such reactions do not always depend on the nature of oxidant or the overall free energy change for the total reaction. Below, are examples of some reactions of $V_{(aq)}^{2+}$(d^3-substitution inert) in which the format-

ion of the precursor is thought to be rate determining step, because the rate of the redox reactions seem independent of the nature of oxidant.

Second-order rate constants for the oxidation of $V_{(aq)}^{2+}$

Oxidant	$k_2, M^{-1}s^{-1}$	Reference
$Co(NH_3)_5N_3^{2+}$	13.0	a
$Co(NH_3)_5C_2O_4H^{2+}$	12.5	b
$Co(en)_2(HCO_2)^{2+}$	13.0	c

a = Candlin, Halpern and Trimm, (1964)

b = Taube and Gould, (1969)

c = Przystals and Haim, (1972).

Factors that affect the reactivity of the outer- and inner-sphere mechanisms

(A) Effect of Electronic configuration:

(a) outer-sphere mechanism

The removal or addition of electrons from (or to) t_{2g} orbitals is easier than in e_g orbitals. This is because t_{2g} orbitals are non-bonding orbitals while e_g orbitals are antibonding, and addition or removal of electrons leads to large effect on bond lengths. as a general rule, the ease of electron transfer can be represented in the following order;

$(t_{2g} \dashrightarrow t_{2g}) > (e_g \dashrightarrow t_{2g}) > (t_{2g} \dashrightarrow e_g) > (e_g \dashrightarrow e_g)$

e.g V^{2+} ions generally react faster than Cr^{2+} ions with the same oxidant despite the difference of 0.16volts in their E°. This is because, it is much easier to transfer electrons from t_{2g} orbitals in V^{2+}, than transfering electrons from e_g orbitals in Cr^{2+}.

(b) Inner-sphere Mechanism

In this case, an entirely different order is obtained. This is because apart from the symmetry of the metal orbitals the symmetry of the bridging ligand has to be taken into consideration in determining the reactivity sequence. Thus,

(i) e_g ---> e_g is faster than t_{2g} --> t_{2g} transition, in contrast to the outer-sphere mechanism.

(ii) e_g ---> e_g transition is favoured when the bridging ligand is of σ symmetry, e.g Cl^- will be a better bridging group in such inner-sphere reactions than N_3^-.

(iii) t_{2g} ---> t_{2g} transition is favoured when the bridging ligand is of π symmetry. Thus, N_3^- will be a better bridging group in reactions involving donor and acceptor orbitals of t_{2g} symmetry.

(B) Effect of non-bridging ligand

In outer-sphere mechanism, all ligands belong to the group of ligands that are not involved in the act of bridging during redox process.

For the inner-sphere reactions, the influence of non-bridging ligands on the rate of redox reactions could be related to a case in which electronic states in the activated complex are comparable to changing bond distances and therefore the ligand fields of the reactants. For an example, in the reduction of Co(III) and Cr(II) complexes, an electron from the reductant would appear in an empty e_g orbital directed towards 'X' (the bridging group) and 'Y' in trans-$Co(NH_3)_4XY$. The energy of this orbital will obviously be more sensitive to changes in the trans-Y group than to changes in the cis-NH_3 ligands, (Orgel, 1956), and the orbital will be stabilized by a weak field ligand 'Y'. The availability of the orbital is further enhanced by the simultaneous motions of the bridging ligand and the field ligand in opposite directions, (Taube, 1959). in other words, bonds are shortened for the reductants and lengthened for the oxidants in forming the activated complex. e.g the replacement of H_2O by ethylenediamine in Cr(II) increases its rate of reduction of Co(III) complexes, (Williams and Garner, 1971; Diaz and Taube, 1970). Since the ethylenediamine has a stronger field, less shortening is required. Inversely, increasing substitution of

NH_3 for H_2O in $Cr(NH_3)_n(H_2O)_{6-n}Cl^{2+}$ reduces the rate of oxidation of Cr(II), (Carlyle and Espenson, 1969).

(c) Effect of bridging ligand

In the outer-sphere mechanism, there is instantaneous electron transfer between the two orbitals of the metal. Such reactions are said to involve adiabatic electron transfer because, the probability of electron transfer is very close to one.

For the inner-sphere mechanism the effect of the bridging group can be discussed under two mechanisms.

(i) Resonance mechanism. This involves instantaneous transfer between the metal centre through the bridging ligand, it therefore does not involve the formation of free radical binuclear intermediate.

(ii) Chemical mechanism. Either of two things can happen.

(1) a low-lying empty orbital in the bridging ligand receives electron from the reductant and retains it for a reasonable period of time, before passing it to the oxidant or (2) a field ligand (non-bridging ligand) orbital of high energy could pass an electron to an oxidant and remain for sometimes as transient free radical intermediate before it receives electron from the reductant. This mechanism, therefore, involves

transitory reduction or oxidation of a ligand to give a free radical binuclear intermediate. The stepwise process may be illustrated by the following examples;

$$A^{m+}-X-B^{n+} \rightleftharpoons A^{(m+1)+}-X^{\circ}-B^{n+} \quad \ldots\ldots\ldots \quad 1.19$$

$$A^{(m+1)+}-X^{\circ}-B^{n+} \rightleftharpoons A^{(m+1)+}-X-B^{(n-1)+} \quad \ldots\ldots\ldots \quad 1.20$$

1.6 Diagnosis of Redox mechanisms

One of the primary objectives of the redox kinetics is to be able to assign one (or both) of the established redox mechanisms to a redox reaction. The assignment is sometimes obvious, but often difficult and in certain cases impossible. Some of the criteria for diagnosis are discussed below.

1.6.1 k_{redox} (k_{red}) Versus $k_{substitution}$ (k_{sub})

The inner-sphere mechanism involves substitution at one of the metal ions before electron transfer, therefore if $k_{red} >> k_{sub}$, such reaction can only occur by the outer-sphere mechanism because, by the time electron transfer takes place substitution has not occured. For example, the reaction below is proposed to occur through the outer-sphere pathway;

$$Fe^{*}(CN)_6^{4-} + Fe(CN)_6^{3-} \longrightarrow Fe^{*}(CN)_6^{3-} + Fe(CN)_6^{4-} \quad \ldots\ldots \quad 1.21$$

$$k_{red} = 10^{3} M^{-1}s^{-1}$$

while,

$$Fe(CN)_6^{3-} + {}^*CN \dashrightarrow Fe({}^*CN)(CN)_5^{3-} + CN^- \quad \ldots\ldots\ldots\ldots \quad 1.22$$

$$k_{sub} = 2 \times 10^{-7} M^{-1}s^{-1}$$

and

$$Fe(CN)_6^{4-} + {}^*CN \longrightarrow Fe({}^*CN)(CN)_5^{4-} + CN^- \quad \ldots\ldots\ldots\ldots \quad 1.23$$

$$k_{sub} = 7.8 \times 10^{-6} M^{-1}s^{-1}$$

1.6.2 Product analysis

Product analysis (the original method by which Taube recognised the inner-sphere mechanism) may be used to distinguish the mechanisms, e.g in the reaction,

$$Cr^{2+} + Co(NH_3)_5Cl^{2+} \longrightarrow CrCl^{2+} + Co^{2+} + 5NH_4^+ \quad \ldots\ldots \quad 1.24$$

The reaction was carried out in the presence of radioactive Cl^- in solution and it was found that less than 1% of the radioactive Cl^- were incorporated in the product, $CrCl^{2+}$. This proves conclusively that the Cl^- has been transferred from Co to Cr and that the transfer occured via the inner-sphere mechanism in which a Cl^- bridge complex was formed between Co(III) and Cl^- prior to electron transfer (Taube, 1970; Taube and Meyer, 1954).

Similarly, in the reaction between $Co(CN)_6^{3-}$ and $Co^{III}(NH_3)_5X$, the product, $Co(CN)_5X^{3-}$ has been associated with a bridge intermediate, $[(CN)_5Co^{II}\text{-}X\text{-}Co^{III}(NH_3)_5]$, and a rate law sensitive to the nature of 'X'. The inner-sphere mechanism was proposed,

where X = Cl^-, N_3^-, NCS^- or OH^-. But for X = PO_4^{3-}, CO_3^{2-}, SO_4^{2-} NH_3 or OAc^-, the reaction between $Co^{III}(CN)_5^{4-}$ and $Co^{III}(NH_3)_5X$ proceded with a rate law depend on $[CN^-]$ but independent of the nature of X.

However, this criterion must be applied with caution because,
(i) atom transfer does not necessarily occur in all inner-sphere pathway reactions.
(ii) the products of reactions of some reductants (like Fe^{2+}, V^{2+} and Eu^{2+}) in which atom transfer have already taken place, hydrolyse so rapidly to give products in which atom transfer may be effected.

1.6.3 Identification of binuclear intermediate in the inner-sphere mechanism

Sometimes the binuclear intermediate may be detected, if short-lived, by stopped-flow spectrophotometry or if long-lived (when both metal ions are inert) by ordinary spectrophotometry or by isolation.

Some examples of detected intermediates are shown below.

	Reactants	Intermediate
(i)	$V^{2+} + VO^{2+}$	VOV^{4+}, (Newton and Baker, 1964)
(ii)	$Cr(H_2O)_6^{2+} + UO_2^{2+}$	$[(H_2O)_5Cr^{III}\text{-}OU^{V}O]^{4+}$, (Newton and Baker, 1962)

However, it must be noted that the observation of the binuclear intermediate does not imply that the product(s) is

obtained by the inner-sphere pathway. In principle, it can revert to the reactants and product(s) could then be obtained through the outer-sphere mechanism.

1.6.4 Activation parameters

There seems to be no direct correlation between the activation parameters such as ΔS^{*}, ΔH^{*}, ΔG^{*} and the type of mechanism but it is suggested, (Taube, 1970), that the entropy of activation which has a more direct connection with the molecularity, structure and charge of the activated complex, could be helpful in distinguishing between the inner-sphere and the outer-sphere mechanisms. But despite the difference in mechanism, the values of ΔS^{*} for the reaction of Cr^{2+} and $V(H_2O)_6^{2+}$ with Ru^{3+} complexes are almost the same, and we must conclude that a superficial use of the values of ΔS^{*} does not lead to a safe classification of mechanism.

The use of ΔV^{*} has been suggested but its applicability is extremely narrow, thus this criterion is of little use.

1.6.5 Reactivity pattern

Attempts have been made to assign mechanism using the reactivity pattern and comparing this with those for a reagent of a known mechanism. For examples, Cr^{2+} in most cases, reacts by an inner-sphere mechanism (from evidence of atom transfer in the product), while $Ru(NH_3)^{2+}$ reacts by the outer-sphere mechanism

(from the fact that $k_{red} >> k_{sub}$). Some of the reactivity patterns are explained below.

(a) Reactivity pattern with a wide range of reactants

If a range of similar complexes, e.g. $Co(NH_3)X^{2+}$ ($X = Cl^-$, F^-, Br^-, I^- or NO_3^-) are compared with a particular reductant, and the rates are found to be similar, the outer-sphere mechanism is presumed to be operating, since this mechanism does not depend on the identity of the bridging ligands, but when the rates depend on the nature of the bridging group, inner-sphere mechanism is predicted, (Sykes, 1967; Shea and Haim, 1973).

(b) Relative rates of reactions of hydroxo and aquo complexes

The OH^- group is a better bridging ligand than H_2O, so it is expected that hydroxo complexes react faster via inner-sphere mechanism, thus, where $k_{OH^-} << k_{aquo}$, the outer-sphere mechanism is thought to operate.

(c) Comparison of the relative rates of reactions of the azides and Isothiocyanato complexes

e.g $(NH_3)_5Co\text{-}N{=}N{=}N^{2+} + M^{2+} \xrightarrow{k_{N_3^-}} [(NH_3)_5CoNNN\text{-}M]^{4+}$ 1.25

$(NH_3)_5Co\text{-}N{\equiv}C\text{-}S^{2+} + M^{2+} \overset{k_{NCS^-}}{\dashrightarrow} [(NH_3)_5CoN{\equiv}C\text{-}S\text{-}M]^{4+}$ 1.26

If the reaction is occuring by the inner-sphere mechanism and M^{2+} is a hard centre, then $k_{N_3^-} > k_{NCS^-}$ or $k_{N_3^-}/k_{NCS^-} >> 1$, since bond formation is important in this case. This is because metal ions are hard acids and would prefer to associate with the hard N_3^- centre. But if $k_{N_3^-} \approx k_{NCS^-}$ or $k_{N_3^-}/k_{NCS^-} \approx 1$, it means bond formation is not important thus, the reaction occurs by outer-sphere mechanism.

1.6.6 Marcus theory

In the outer-sphere mechanism, the weak interaction between the reactants has permitted its theoretical treatments and correlation between kinetic and thermodynamic parameters (Sutin, 1966). The most widely used of the treatments is the Marcus theory, (Marcus, 1956). when there is little rearrangement before electron transfer takes place, the theory predicts that for the reaction;

$$Ox_1 + Red_2 \underset{}{\overset{K_{12}}{\rightleftharpoons}} Red_1 + Ox_2 \quad \ldots\ldots\ldots\ldots \quad 1.27$$

and related Isotopic exchange reactions;

$$*Ox_1 + Red_1 \xrightarrow{k_{11}} *Red^1 + Ox_1 \quad \ldots\ldots\ldots \quad 1.28$$

$$*Ox_2 + Red_2 \xrightarrow{k_{22}} *Red_2 + Ox_2 \quad \ldots\ldots\ldots \quad 1.29$$

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 1.30$$

where f, usually assumed to be 1, is given by

$$\text{Log}f = \frac{(\text{Log}K_{12})^2}{4\log(k_{11}k_{22}/Z^2)} \quad \ldots\ldots\ldots\ldots\ldots\ldots 1.31$$

k_{12} and K_{12} are the rate and equilibrium constants respectively for the cross reaction, k_{11} and k_{22} are the homonuclear electron exchange rate constants respectively, and Z = $10^{11}M^{-1}s^{-1}$, is the collision frequency for the homogenous reaction. Thus, from Marcus equation, the theoretical rate constants for the redox reactions can be calculated from the expression (1.32) by considering the solvent reorganisation occuring outside the inner coordination shells of each reacant.

$$k = Z\exp^{-\Delta G^*/RT} \quad \ldots\ldots\ldots\ldots\ldots 1.32$$

ΔG^* = the change in free energy of ion-ion and ion-solvent interactions accompanying the formation of the activated complex.

$$\Delta G^* = wr + \Delta G^*in + \Delta G^*out \quad \ldots\ldots\ldots 1.33$$

where, wr = work needed to bring the two reactants together.

ΔG^*in = inner-sphere reorganisation term.

ΔG^*out = outer-sphere reorganisation term.

Using equations 1.30 and 1.31, relations (Marcus and Sutin, 1975) between the kinetic parameters for a cross reaction and the component. Self-exchange reaction can be derived:

$$\Delta G_{12}^{*} = 0.5\Delta G_{11}^{*} + 0.5\Delta G_{22}^{*} + 0.5\Delta G_{12}^{o}(1 + \alpha) \quad \ldots\ldots\ 1.34$$

and

$$\alpha = \frac{\Delta G_{12}^{o}}{4(\Delta G_{11}^{*} + \Delta G_{12}^{*})} \quad \ldots\ldots\ 1.35$$

ΔG_{12}^{*} = the free energy of activation

ΔG_{12}^{o} = the overall free energy in the medium used.

ΔG_{11}^{*} and ΔG_{22}^{*} are the free energies of activation for the self-exchange reactions. α is usually small when f = 1. Thus equation (1.34) becomes,

$$\Delta G_{12}^{*} = 0.5\Delta G_{11}^{*} + 0.5\Delta G_{22}^{*} + 0.5\Delta G_{12}^{o} \quad \ldots\ldots\ 1.36$$

It is negative in reactions of negative ΔG_{12}^{o} and becomes increasingly so with decreasing ΔG_{12}^{o}.

The differentiation of equation (1.34), (Marcus and Sutin 1975) gave related equations for enthalpies and entropies of activation;

$$\Delta H_{12}^{*} = (0.5\Delta H_{11}^{*} + 0.5\Delta H_{22}^{*})(1-4\alpha^{2}) + 0.5\Delta H_{12}^{o}(1 + 2\alpha) \quad \ldots.\ 1.37$$

and

$$\Delta S_{12}^{*} = (0.5\Delta S_{11}^{*} + 0.5\Delta S_{22}^{*})(1 - 4\alpha^{2}) + 0.5\Delta H_{12}^{o}(1+2\alpha) \quad \ldots.\ 1.38$$

So, for a reaction proceeding via the outer-sphere mechanism, a linear relationship between the free energy of activation and standard free energy change of the reaction is predicted with a

slope of the straight line being 0.50. From Marcus theory, $k_{calc} = k_{obs}$, indicates the outer-sphere mechanism, but the reverse does not give absolute evidence for the inner-sphere mechanism. On the other hand, if $k_{obs} >> k_{calc}$, then it can be presumed that the inner-sphere mechanism is operating.

It must be noted that, none of the above criteria, individually, gives conclusive prove about the mechanism, however, when two or more criteria point to the same conclusion, the mechanism can be assigned with some degree of certainity.

1.7 Solvated electron theory

One further possibility of mechanism of electron transfer in solution is that of solvated electron. In this mechanism, the reductant ejects an electron into the solvent, which then solvates it and holds it until the oxidant picks it up. The redox process involved is thought to occur as illustrated below:

$$A + S \rightleftharpoons A^{+} + S^{-} \quad \ldots\ldots\ldots\ldots\ldots \quad 1.39$$

$$S^{-} + B \longrightarrow [S^{-} + B]^{*} \longrightarrow S + B^{-} \ldots. \quad 1.40$$

where, A = reductant

B = oxidant

S = solvent

Although this process occurs readily in non-aqueous media such as liquid ammonia, it is highly unlikely that a solvated electron

with an estimated potential at -2.7v (latimer 1952) will exist in water without rapidly reducing water according to this equation;

$$e_{(aq)} + H_2O \text{ ------> } \tfrac{1}{2}H_{2(g)} + OH^- \quad \ldots\ldots\ldots 1.41$$

Thus, the possibility that this mechanism operates in aqueous media is remote.

1.8 Objectives of the project

(a) The polyanion, 12-tungostocobaltate(III) is important in photochemical reduction of oxygen and water, both of which are useful potential pathways for the conversion and storage of solar energy (Darwart and Akid, 1985). And the complexes $Fe(LL)_3^{3+}$ (LL = 2,2'-bipyridine or 1,10-phenanthroline) are very important in analytical studies.

(b) The aminopolycarboxylic acids, ethylenediaminetetraacetic, (hydroxyethyl)ethylenediaminetriacetic and nitritotriacetic acids (herein abbreviated as EDTA. HEDTA and NTA respectively) are popular complexing agents and are thus often referred to as complexones. They are particularly important in complexometric titrations (Vogel, 1978), as analytical reagents (Belcher, Wilson and West, 1964) and as masking agents in the analysis of metal ions (Ringbom, 1963).

(c) However, the redox reactions of complexones with any of the complexes employed in this research so far appears to have received no attention.

(d) In recent past, some studies of EDTA and HEDTA have been reported. However, no such report have been published concerning NTA. NTA is therefore included in this study to widen the scope of the present investigation for broader comparison.

(e) It would also be of interest to note any complexation along with the redox processes, since the complexones are well known for this function.

(f) Finally, most work reported so far seem to have been done with substitution labile complexes (Palei and Udal'tsona, 1960; Palei, Kabanona and Danushenhora, 1960), whereas all complexes used in this study are apparently substitution inert,, so it would be of interest to examine the behaviour of complexones with such complexes.

Therefore, as part of the continuing interest in the reactions of complexones (and redox reactions in general), and in view of the importance of these species, this research is carried out to accumulate more data on the kinetics and mechanism of these species.

Chapter 2

2.0 LITERATURE REVIEW

12-tungstocobaltate(III) anion is a part of the large family of inorganic polynuclear complexes. This anion and its salts which contain both cobalt and hexavalence tungten in the anion have been able to exhibit a number of unique features (Keggin, 1933, Baker and McCutcheon, 1956), as have been reported of 12-tungstates of Cr(III), Fe(III), Cu(I), Mn(IV) and Zn(II) (Brown and Mair, 1958).

The salts of 12-tungstocobaltate(III) (henceforth designated as $Co^{III}W$) fall into the class of hetetropolyanions referred to as 12-heteropolytungstates. The prefix 12-depicts the ratio of tungsten atom to hetero atom in the compound.

Reports have been made (Dermer, 1973; Jasmin et al, 1974; Graquinta and Dilley, 1975; Berg and Izawa, 1977; Goldfield et al, 1978), of the use of heteropolymolybdaytes and tungstates as electron stains for electron microscopy, antiviral agents and as electron acceptors in the studies of photosynthesis, as well as their use for photochemical generation of hydrogen in the presence of a great variety of organic reagents, (Constantinou and Ioannidis, 1985; Banerjee et al, 1987). This polyanion is known to undergo multi-electron reduction by chemical and electrochemical means (Pope and Varge Jr, 1966; Pope and Papaconstantinou, 1967 and Varge et al, 1977). The reduced forms

of the heteropolytungstates is the blue compounds which are moderate reducing agents.

The anion, $Co^{III}O_4W_{12}O_{36}^{5-}$, (sometimes named as dodecatungstocobaltate(III) or 12-Wolframocobalt(III)ate), is yellow crystalline and has the keggin structure with tetrahedral cobalt(III) ion surrounded by four oxygen atoms, CoO_4. The cobalt(III) ion is deeply burried within a shell of WO_6 octahedral (Figure 2.1) and is completely shielded from contact with external species, (Keggin, 1933, 1934, and Rasmussen, 1967). The WO_6 shell has been reported to be very stable (Baker and Simmons, 1959; Rasmussen and Brubaker, 1964; Geier and Brubaker, 1966), and hence the cobalt(III) ion in $Co^{III}W$ is effectively caged, and there is no distortion of the central CoO_4 tetrahedral except that introduced by the electronic structure of the cobalt.

The interest in this complex has been in the high molecular weight, high charge and extra-ordinary solubility in both aqueous and various oxygenated organic solvents (such as ether, alcohols and ketones). Moreover, the structure and stability of this anion tends to render the tungstate group substitution inert. It therefore represent an ideal complex for the study of outer-sphere electron transfer redox reactions in solution. The metal centre in the tungstocobaltate ion (unlike in many octahedral Co^{III} complexes) is the oxidizing agent and is reduced reversibly.

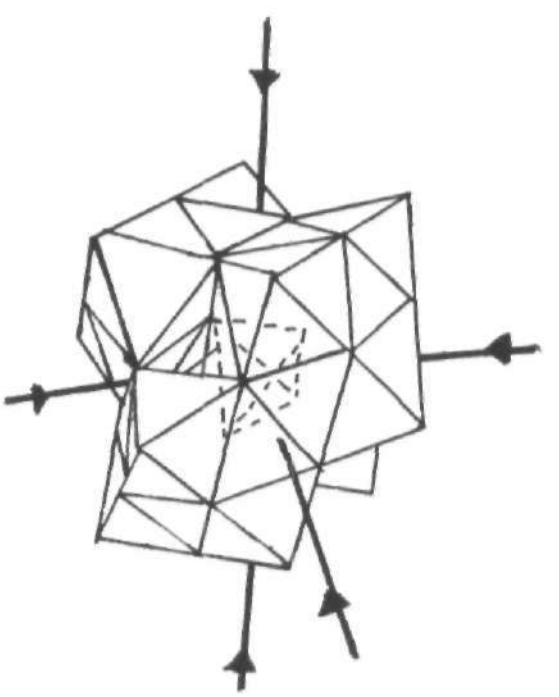


FIG. 2·1 KEGGIN STRUCTURE OF THE 12- TUNGSTO-COBALT (III) ATE ION THE Co(III) ION IS SITUATED IN THE CENTRE OF THE TETRA-HEDRON AND THE TUNGSTEN ATOMS ARE SITUATED IN THE OCTAHEDRON CENTRES EACH CORNER OF AN OCTAHEDRON REPRESENTS AN OXYGEN ATOM

In kinetic studies, $Co^{III}W$ is expected to behave as a one-electron oxidant, which is free from complexities of other cobalt(III) species, (Eberson, 1983). $Co^{III}W$ has been reported to have oxidized many oxygen and nitrogen containing organic compounds, (Billman et al, 1965; Olatunji and Ayoko, 1983; 1984; 1985; and Banerjee et al, 1987).

The chemical reduction of $Co^{III}W$ by both organic and inorganic substrates has been the subject of recent studies, (Banerjee et al, 1988; 1990;Ayoko and Olatunji, 1983; 1984; 1985; 1990). The processes involve the reduction of tetrahedral cobalt(III) ion with a ground state configuration of $e^3t_2^3(^5E)$, by electron to the low energy e orbital. The result is the ground state tetrahedral cobalt(II) ion with the configuration $e^4t_2^3(^4A_2)$.

2.1 Redox reactions of $Co^{III}W$ Anion with organic substrates

The reduction of aromatic hydrocarbons by $Co^{III}W$ has been reported, (Heiba et al, 1969) and the reaction was proposed to have occurred via an intermediate formation of aromatic radical cation.

The oxidation of alkyl aromatic hydrogens by $Co^{III}W$ reported by Chester, (1970), proposed the outer-sphere formation of a radical cation, in which the electron is removed from the aromatic π system and conducted through the tungstate framework of the Co^{III} ion.

McAuley et al (1977) reported the stoichiometries for the oxidation reactions of $Co^{III}W$ with ascorbic acid, hydroquinone and catechol to be 2:1 (oxidant reductant), in each case. The outer-sphere mechanism consisting free radical intermediates was proposed.

The kinetic studies of $Co^{III}W$ with p-methoxytoluene (PMT), (Eberson, 1983) reaction in acetic acid/water with added acetate salt, showed a simple rate law with a 1:1 stoichiometry.

Ayoko and Olatunji, (1983), proposed outer-sphere pathway for the oxidation of glutathione, L-cysteine, Mercaptoacetic acid and Marcapto ethylamine by $Co^{III}W$, with an inverse acid dependence for glutathione, and an inverse second-order acid dependence for L-cysteine and Marcaptoacetic acid.

In the oxidation of Butane-1,4- and pentane-1,5-diols by $Co^{III}W$ (Ayoko and Olatunji, 1985), the overall reaction was reported to depend on the type of diol. The reduction of $Co^{III}W$ with these diols is an exceptional case in which the inner-sphere mechanism was proposed for this caged complex. This is probably due to the presence of hydroxyl group which act as a bridging group.

The kinetics of $Co^{III}W$ by oxalate (pH 2.0-5.0) with a 2:1 oxidant/reductant ratio has been reported (Banerjee et al, 1986). This was also the case with the oxidation reaction of formate with $Co^{III}W$ (Banerjee, et al 1987).

The kinetics of the oxidation of alicyclic cyclohexane, aliphatic 2-butanone and substituted aliphatic 1,3-dihydroxy-2-propanone (dhp), ketones have been investigated (Banerjee et al, 1988) and the outer-sphere mechanism which consists of enol and a free radical intermediate was proposed.

The oxidation of citric acid to formic acid by $Co^{III}W$ was recently reported (Banerjee et al, 1990). An outer-sphere mechanism was proposed, the rate law depending on the nature and concentration of the cation present, with an inverse acid dependence.

2.2 Redox Reactions of $Co^{III}W$ with Inorganic substrates

The oxidation of nitrous acid by $Co^{III}W$ has been reported (Olatunji and Ayoko, 1984), the rate was acid independent in the range, $[H^+]$ = 0.1 - 1.0M and the outer-sphere mechanism was proposed.

The outer-sphere mechanism was also proposed for the oxidation reactions of Iodide and thiocyanate ions by $Co^{III}W$ (Olatunji and Ayoko, 1984), with 1:1 stoichiometry. Anion catalysis was observed for the iodide reaction.

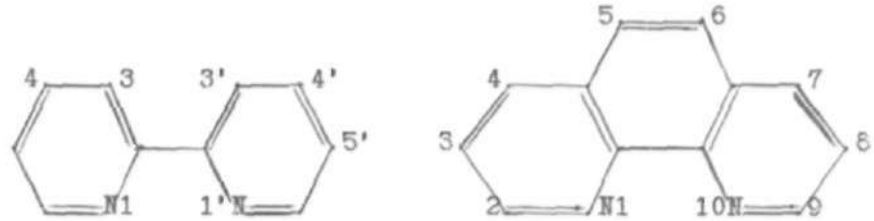
Ayoko and Olatunji, (1985) reported the reaction between hydroxylammonium and $Co^{III}W$ with a simple second-order rate law. The proposed mechanism involves free radical interaction with the oxidant.

Recently, the oxidation reaction of Hydrazine ion, and Arsenous acids by $Co^{III}W$ were reported (Ayoko, 1990). The rate law was second-order and an outer-sphere pathway was postulated for the reactions.

2.3 Complexes of Bipyridyl and Phenanthroline

The organic molecules 2,2'-bipyridyl (or α,α'-bypyridyl), and 1,10-phenanthroline (or o-phenanthroline) are well known and frequently used ligands. Their structures and the numbering of their ring positions are shown in figure 2.2 (Emelens and Sharpe, 1969). Throughout this review the abbreviation bipy and phen will be adopted for these ligands and an analogous set of abbreviations for their substituted derivatives.

Figure 2.2



(a) 2,2'-Bipy (b) 1,10-phen

In Figure 2.2a, 2,2'-bipy is presented as having a cis-planar conformation as is usual in its complexes, the free ligand exists in a trans-planar conformation in the solid state, as shown by x-ray studies, (Merrit and Schroeder, 1956). Dipole moment studies

show that the molecule is still transoid rather than cisoid in benzene solution, but that there now appears to be a net interplanar angle of between 20° and 30°. In contrast, 1,10-phen is rigidly held in a cis conformation, and is almost always found as a planar ligand. The dipole moment is therefore larger being 3.64D as compared to 0.69D for bipy in benzene at 25°C (Cumper and Ginman 1962), and the stable monohydrate usually obtained exhibits solely intramolecular hydrogen bonding between both protons of the water moiety and the ligand N-atoms.

With the exception of the mono-2,9-(methyl)phen complex of Cu(II) where steric factors are important, variation in the dimensions of first-row transition-metal complexes on changing the metal ion, ligands or the coordination number of the metal are not marked.

Bipy and phen behave as weak bases, usually farming monoprotonated species. There are few reported data for the rates of electron transfer of large complexes of these ligands. However, because of their convenient analytical properties, bipy and phen complexes have received much attention in their oxidation-reduction reactions.

2.4 Reduction of $Fe(L\text{-}L)_3^{3+}$ complexes

(L-L = 2,2'-bipy or 1,10-phen).

$Fe(LL)_3^{3+}$ complexes have been extensively investigated as outer-sphere redox reactants with several inorganic metal ions

and complexes (Fordsmith and Sutin 1961; Halpern, Legare and Lumry, 1963; Dulz and Sutin, 1963; Shakhashari and Gordon 1969; Keeton and Sykes 1972, Ng and Henry, 1975). Mentasti and Pelizzetti (1977) have also investigated the kinetics of the oxidation of many substituted quinols, using a series of tris-phen complexes. Other works include organic systems such as benzene-1,2-diols (catechols), benzene-1,4-diols (quzinols) and biphenyl-4,4'-diol using these oxidants. (Pelizzetti, Mentasti and Gurauchi, 1975; Peizzetti and Baiocchi, 1976; Pelizzetti and Mentasti, 1976; Pelizzetti, Mentasti and Saini, 1976). In all cases, the reactions were found to occur by the outer-sphere mechanism. Ligand substitution do not occur rapidly in these oxidants, (Shakhashare and Gordon, 1969; Burgess and Prince, 1963). It is therefore likely that they react via the outer sphere activated complex in their reactions with the organic substrates. Thus, Marcus theory (Marcus, 1968; Reynolds and Lumry, 1966) should be applicable.

The rate constants for the reduction of several complexes in perchloric and sulphuric acid media have been measured (Gordon, Williams and Sutin, 1961). The log of the rate constant or ΔG^{*} was observed to vary with the oxidation-reduction potential, or ΔG°, of the complex ion, which was interpreted as showing that Marcus theory may be applied. The Ag(II) data were also consistent if their oxidation-reduction potentials are of the order of -1.4 volts. A similar variation of kinetics with

thermodynamic parameters was found for the ferrous ion reduction of various substituted Fe(III) complexes (Ford-Smith and Sutin, 1961). In a comparison of this reaction with other Iron(II) oxidation, the existence of a linear relationship between the free energy of activation and the standard free energy changes of the reaction was observed. It was found that rate constant determined for the oxidation of Iron(II) by 2,2'-bipy complex of Iron(III) did not satisfy the linear relationship found for the phenanthroline complexes, (Gordon, Williams and Sutin, 1961). The oxidation, of Fe(II), a reducing agent of intermediate strength (Birk, 1973), by $Fe(phen)_3^{3+}$ proceeds in a single step.

Grammer et al (1974) in their work found unusual activation parameters when $Fe(H_2O)_6^{2+}$ was oxidized by Iron (III) polypyridine or Ru(III)polypyridine complexes (Braddock and Meyer, 1973). There reactions could be represented as,

$$Fe(H_2O)_6^{2+} + M(III) \longrightarrow Fe(H_2O)_6^{3+} + M(II) \quad \ldots\ldots \quad 2.1$$

(M = Iron or Ruthenuim polypyridine complex)

were necessarily outer-sphere, at least in the sense that a mechanism involving a ligand bridge between normal coordination positions of both reacting ions, can be ruled out. Both M(III) complexes are substitution inert on the time scale for electron transfer. Negative ΔH^* values for the oxidation of $Fe(H_2O)6^{2+}$ by Ru(III) polypyridine complexes led to the suggestion that reactions occur by a "non-Marcus path, which includes at least

one distinctive feature not considered in the Marcus model for outer-sphere electron transfer, (Braddock and Meyer 1973) and since the reported activation parameters for the Fe(III) reactions were similar to those of Ru(III) reactions, they occur by the same non-Marcus" path.

In many electron transfer reactions, aggreement between observed and calculated rates have been obtained using the Marcus free energy correlation (Marcus, 1966; Earley, 1970; Linck, 1971; Reynolds and Lumry, 1966; Sutin, 1972). For some redox reactions (Meyer and Taube, 1968) the Marcus model appears to account satisfactorily for the mechanistic details of the activation process. However, the agreement does not extend to the oxidation of $Fe(H_2O)_6^{2+}$ by the Iron(III) and Ru(III)-polypyridine complexes (Braddock and Meyer, 1973; Dulz and Sutin, 1963).

The oxidation of $Fe(H_2O)_6^{2+}$ by the Fe(III)- and Ru(III) polypyridine complexes appears to occur by a distinct path, characterized by the negative or small positive ΔH^* values. It may therefore be possible by experimental means to identify a series of paths for outer-sphere electron transfer which differ in detail from the normal Marcus-Hush path. Similar "non-Marcus paths have been reported by Lavalle et al (1973) in the oxidation of Np(III) by $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_5H_2O^{3+}$. Thus, Rillema and Enclicott (1972) have inferred that certain key factors which make major contributions to such reactions are not considered in current theoretical models of outer-sphere electron transfer.

The full mechanistic details of a "non-Marcus" path are not clear. However, the oxidation of $Fe(H_2O)_6^{2+}$ by Fe(III)polypyridine complexes has been studied in detail by Sutin and co-workers. From their work, certain factors are known which allow inferences to be drawn. These are;

(i) The pattern of activation parameters:-

Negative or small positive ΔH^* values, large negative ΔS^* values is paralled by the thermodynamic parameters for the overall reactions. For

$$Fe(H_2O)_6^{2+} + Fe(bipy)_3^{3+} \longrightarrow Fe(H_2O)_6^{3+} + Fe(bipy)_3^{2+} \quad ...2.2$$

ΔH_{12} = -23kcal/mol; ΔS^*_{12} = -47eu, (George, Hanania and Irovine, 1959).

(ii) Ford-Smith and Sutin (1961) found no evidence for specific steric effects in the reactions of the 5,6- and 3,4,7,8-methyl substituted Iron(III) phen complexes with $Fe(H_2O)_6^{2+}$. The absence of these effects led them to suggest that in the activated complex for electron transfer, $Fe(H_2O)_6^{2+}$ is located in the space between phen groups, rather than at the periphery of a phen group.

(iii) In other solution reactions, where negative ΔH^* (or Ea) values have been observed, Mechanisms have been involved in which enthalpically favourable pre-equilibrium exist (Patal et al, 1970; Pignataro et al 1970; Werner et al, 1971). For the reactions considered by Crammer and Meyer (1974), an equilibrium invloving ion-pair formation between the reacting ions must

exist. Electron transfer presumably follows ion-pair formation, e.g

$$Fe(H_2O)_6^{2+} + Fe(phen)_3^{3+} \underset{}{\overset{K}{\rightleftharpoons}} Fe(H_2O)_6^{3+}.Fe(phen)_3^{2+} \quad .... \ 2.3$$

$$Fe(H_2O)_6^{2+},Fe(phen)_3^{3+} \xrightarrow{k} Fe(H_2O)_6^{3+} + Fe(phen)_3^{2+} \quad .... \ 2.4$$

For reactions involving unlike charged ions, direct evidence has been obtained that ion-pair formation preceeds electron transfer. Hemmers (1972) has calculated that ion-pairing between large cations can be thermodynamically favourable. From attempts to observe ion-pairing between $Co(H_2O)_6^{2+}$ and $Ru(bipy)_3^{3+}$ spectrophotometrically it was concluded that $K < 0.5$ (Braddock and Meyer, 1973). Ion-pairing preceding electron transfer could make a negative contribution to the observed enthalpy of activation (Halpern, Legare and Lumry, 1963).

In media of high ionic strength electrostatic effects are small and expected to make a minor contribution (Reynolds and Lumry, 1966). However, non-electrostatic effects may be important, such effects might include charge fluctuation forces or the effect of solvent structure which has been suggested to enhance ion-pairing when both ions are large (Diamond, 1963). The existence of important non-electrostatic effects could also explain the poor agreement obtained. Marcus (1963) has suggested that this result may be due to a failure of non-electrostatic terms to cancel in the work done in bringing the reactants together.

(iv) The reactions between $Fe(H_2O)_6^{2+}$ and the Fe(III)Polypyridine complexes show strong specific anion effects (Sutin and Farmann, 1971). The specific anion effects for anions like SCN^- or N_3^- may arise as a consequence of prequilibria involving complex ion formation e.g. $FeNCS^+$, however, with other anions, like ClO_4^-, energetically favourable ion-pairing with the polypyridine complex may be an important part of the overall electron transfer reaction.

There is no specific pattern of acid dependence in the redox reactions of these Fe(III)polypyridine complexes. In the reaction of $Fe(phen)_3^{3+}$ and thiocyanate (Ng and Benry, 1975), the value of k_{obsd} was found to decrease with increasing $[H^+]$. This acid inhibition is consistent with protonation of SCN^- to give an inactive HSCN species. The substituted tris (1,10-phen) complexes gave a similar kinetic behaviour.

In the oxidation of several substituted quinols by a series of tris phenanthroline-Iron(III) complexes (Mentasti and Pelizzetti, 1977) the reactions were found to be independent of acidity. Akinyugha et al (1978) have shown that in the reduction of $Fe(phen)_3^{3+}$ by titanium(III) in aqueous solution, the reaction was second order, first order in both reactants. The dependence of the second order rate constant, k_{ob} on $[H^+]$ was given as

$$1/k_{ob} = a + b[H^+] \quad ..... \quad 2.5$$

The magnitude of a and b, however, do not indicate precursor complex formation. Observed catalytic effects of added anions and calculations based on the Marcus theory suggest that the reaction occurs by the outer-shpere mechanism.

The reactions of these oxidants are usually second order, first-order in both reactants. There are however, cases where the reaction might be second order in reactant and first order in oxidant giving overall third-order (Ng and Henry, 1975). The rate constant was shown to vary linearly with the reduction potential of the complexes. This indicates a direct dependence of the standard free energy of the reaction on the free energy of activation (Ford-Smith and Sutin, 1961). Redox reactions of substituted inert polypyridine complexes of Iron(II) or (III) have been employed in most cases to investigate linear free energy relations in redox reactions (Irvine, 1959; Sutin and Gordon, 1961; Ford-Smith and Sutin, 1961; Dulz and Sutin, 1963; Campain, Purdie and Sutin, 1964; Braddock and Meyer, 1973; Crammer and Meyer, 1974; Braddock, Crammer and Meyer, 1975), which usually occur by the outer-sphere mechanism. However, Davies and Earley (1976) have found, using the oxidation of various polycyclic amino acid Cr(II) complexes by $Cr(NH_3)_5Cl^{2+}$, that such linear free energy relationship also exist for reactions of the inner-sphere mechanism and surprisingly did obtain 0.5 as the ΔG^* VsΔG° plots. The dependence of ΔG^* (the free energy of activation for the redox reaction) on ΔG° (the

standard free energy of reaction) has been given a semi-theoretical treatment by Marcus and Sutin, (1963; 1973) and also in a less elaborate manner independently by Newton (1968) and Earley et al (1976). The predicted linearity of such plot and the slope of 0.5 are a consequence of the assumptions that are inherent in these semi-theoretical treatment and these assumptions are essentially equivalent in all the above treatment.

The kinetic data for the oxidation of ascorbic acid by one electron acceptor complexes of Fe(III) and other transition metals have been reported (Pelizzetti et al, 1978). The data suggested that two paths, involving the undissociated or mono anionic substrates were operative. The rate constants were discussed in terms of Marcus theory and an electron-transfer mechanism has been suggested.

Apart from Irvine's (1959) work and the oxidation of ascorbic acid (Pelizzetti, Mentasti and Pramaure, 1976, 1978) by these Iron III complexes and $IrCl_6^{2-}$ redox reactions that have been subjected to this free energy correlation are characterized by, possession of the thermodynamically favourable rate-controlling electron-transfer steps, and transfer of an equal number of electrons (in most cases an electron) between reactants to form final products.

In the study of $Fe(LL)_3^{3+}$ (LL = 1,10-phen or 2,2'-bipy) with iodide, the outer-sphere mechanism was proposed based on

favourable correlation with Marcus equation for cross reactions, (Adegite and Adedensewo, 1979).

In the reaction of $Fe(phen)_3^{3+}$ with iodide Ige et al. (1979) showed that this exhibit strictly second-order behaviour over a very large concentration range and thus obtained the following rate law:

$$-\frac{d[Fe(phen)_3^{3+}]}{dt} = k[Fe(phen)_3^{3+}][I^-] \quad \ldots\ldots 2.6$$

They postulated the outer-sphere mechanism based on the relative inertness of the oxidant and supported by the observed catalysis of reaction by added chloride and bromide ions. The reaction was independent of $[H^+]$. It is interesting to note that the rate law is of a simple form. In contrast, complicated rate laws have been obtained in the reduction of aquo Iron(III) (Sykes, 1952) and Ferric Cyanide ions (Indelli et al, 1964; Majid et al, 1968) by the same reductant, and inhibition by added Cl^- and Br^- (Sykes, 1952) was also observed in the case of aquo Iron (III) reaction. These results have been attributed to inner-sphere complex formation between the oxidant and the added halide ion in the primary step, with FeX^{2+} being less reactive than aquoIron(III).

The reduction of these Fe(III) polypyridine complexes by OH^- ions has been reported (Nord and Wernberg, 1972). The stoichiometry was found to be 1:1, (eq. ...2.7)

$$4\ Fe(LL)_3^{3+} + 4OH^- \longrightarrow 4Fe(LL)_3^{2+} + O_2 + 2H_2O \quad \ldots\ 2.7$$

where LL = 2,2'-bipy, or 1,10-phen. The Fe(II) products were reoxidized slowly and observed by the use of oxygen electrode. Schmid et al (1977) have investigated the oxidation of Iron(II) complexes in acetonitrile, with $Fe(bipy)_3^{3+}$ and hexakis-(N,N-DMF). They proposed the outer-sphere reduction of $Fe(phen)_3^{3+}$ by $Fe(DMF)_6^{2+}$ in MeCN with both salts added as the perchlorates and a reaction order of three with respect to the reductant at constant ionic strength.

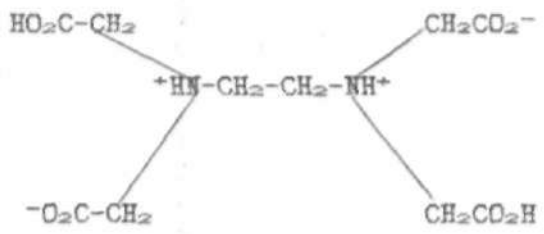
In the report of the reduction of Iron(III) phen complexes by aquo Iron (II) (Schmid and Han, 1983). It has been shown that, the reduction of $Fe(phen)_3^{3+}$ by Fe^{2+} aq occurs via an inner-sphere path mediated by water molecules coordinated at the carbon atom adjacent to the ring nitrogen of the phen-ligands. Water thus, acts as a catalyst. The mechanism proposed included acid dependence, substitutents and activation parameters.

2.3 Oxidation reactions of complexones

The aminopolycarboxylic acids are excellent complexing agents and are often referred to as complexones. These include ethylenediaminethetraacetic acid. Hydroxyethylenediaminetriacetic acid and Nitrilotriacetic acid, for convenience, the abbreviations EDTA, HEDTA and NTA respectively will be utilized in this investigation.

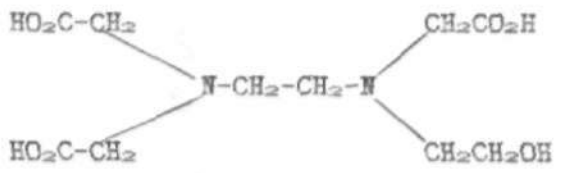
Their actual structures (Vogel, 1978) are shown below.

(a)



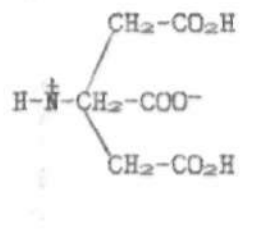
(EDTA)

(b)



(HEDTA)

(c)



(NTA)

Very few redox reactions seem to have been investigated with complexones. The kinetic investigations into the mechanisms and activity patterns of redox reactions involving complexones have been reported in most cases, in the form of metal-complexone being oxidized.

The reduction of Iodine by Fe^{II}-EDTA was found to be first-order with respect to Iodine and Fe^{II}-EDTA and was also directly proportional to the EDTA concentration. The rate was inversely proportional to the fourth power of $[H^+]$, and the ionic strength, but directly proportional to dieletric constant of the medium, (Varm, Srivastara and Saxena, 1975). Kasim and Sulfab, (1977), reported a rate law;

$$\text{Rate} = \frac{k_3 K_1 [CoEDTA^{2-}][L^-]}{1 + K_1[L^-]} \quad \ldots\ldots\ldots 2.8$$

where k_3 = rate constant for the electron transfer process

K_1 = Pre-equilibrium formation constant

$[L^-]$ = total Periodate concentration, for the kinetics of $CoEDTA^{2-}$ by periodate.

An intermediate was identified which slowly formed hexadentate $CoEDTA^-$. The stoichiometry was 2:1 complex: ligand, and the inner-sphere mechanism was proposed. The evidence being the formation of an initial Co^{III} product, other than the hexadentate $CoEDTA^-$ which undergoes a slow ring closure.

In the reduction of Neptunium (VI) with disodium ethylenediaminetetraacetic acid (Shastri and Amis, 1968), It was observed that 6moles of Np(VI) was reduced by 1mole of EDTA. The reaction was the second-order type, first-order in each reactants, with a

fractional-order with respect to $[H^+]$. The following mechanism was proposed:

$$NpO_2^{2+} + EDTA + H_2O \text{ -----> } NpO_2(OH)EDTA^+ + H^+ \quad ..... \ 2.9$$

$$NpO_2^{2+} + EDTA + 2H_2O \text{ -----> } NpO_2(OH)_2EDTA + 2H^+ \quad .... \ 2.10$$

$$10NpO_2^{2+} + NpO_2(OH)EDTA^+ \text{ ---> } NpO_2(OH)_2EDTA \xrightarrow{fast} \text{Products} \quad ..2.11$$

It is assumed that at the concentration of $HClO_4$ acid used, the EDTA is in the form of the slightly ionized acid. The fractional dependence upon the $[H^+]$ probably arises from simultaneous reactions of the equations 2.9 and 2.10 in the proposed mechanism above, which are about equally influential in controlling the rate. Formation of the initial complex between NpO_2^{2+} ion and the EDTA is supported by the observed colour changes which take place during the reaction.

Varadarajan and Hossian, (1979), did a comparative study of the oxidation of EDTA and HEDTA by aquocobaltic ions in perchlorate media. A comparison of oxidation rates of HEDTA and EDTA were presented over a wide range of acidities at different ionic strength. The rates varied inversely with acidity from 1.0M to 5.0M at I = 5.0M (I = ionic strength) and directly with acidity from 5.0M to 7.0M at I = 7.0M. The stoichiometries were determined as functions of acidity and time. It was observed that the number of moles of Co^{III} consumed per mole of EDTA and HEDTA varied respectively with these functions.

The observation of a decorboxylation was indicative of a 1:1 complex formation. The products were CO_2, formaldehyde, glycine, ethylenediamine-N,N-diacetic acid and ethylenediamine.

Identical mechanisms were proposed for the two substrates at the two acidity ranges, based on their comparable rate constants and the similarities in their stoichiometries and oxidation products.

Chapter 3

3.1 Experimental

3.1 Materials and Reagents

All reagents and solvents were used without further purification and solutions were prepared with distilled water.

3.1.1 Preparation of potassium 12-tungstocobaltate Anions

Potassium salt of 12-tungstocobaltate(III) anion, $(Co^{III}W_{12}O_{40})^{5-}$, was prepared by the method of Baker and McCutcheon (1956), either by its oxidation with persulphate or by the electrolysis of the $(Co^{II}W_{12}O_{40})^{6-}$ anion and characterized for purity by its uv-visible spectra (Amjad, Brodooitch and McAuley, 1977).

The stock solution of $Co^{III}W$ was standardized using a spectrophotometric titration, carried out with a standard solutions of ferrous mmonium sulphate which quantitatively reduced $Co^{III}W$ to $Co^{II}W$. The ferrous ammonium sulphate was standardised by spectrophotometric titration against Ce(IV) solution.

3.1.2 Preparation of $Fe(L\text{-}L)_3^{2+}$ and $Fe(L\text{-}L)_3^{3+}$ complexes (L-L = 5-NO_2-phenanthroline, or 2,2'-bipyridine)

Either the respective Iron II complex or the ligands were obtained commercially (G.F. Smith). In the latter case, the

Iron(II) complex was prepared by adding an equivalent amount of the appropriate ligand to a solution of ferrous sulphate. The perchlorate of the Iron (II) complex was precipitated by adding sodium perchlorate.

The Iron(III) complexes were generated in aqueous acidic solution by oxidation of the Iron(II) complexes using PbO_2. Solutions of the Iron(III) complexes thus prepared in conc. $HClO_4$, characterized by their blue colouration were stored in the refrigerator and aliquots taken immediately prior to kinetic runs. Uv-visible spectra of the complexes exhibited λmax values in good agreement with those reported in literature.

The concentrations of the $Fe(L\text{-}L)_3^{3+}$ solutions so formed, were determined spectrophotometrically by using literature values of λmax and extinction coefficient as given below.

Absorption spectra of 5-NO_2-phenanthroline and 2,2-bipyridine Iron(III) complexes

Complex	λmax mμ	Molar extinction Coefficient	Reference
$Fe(5\text{-}NO_2\text{-}phen)_3^{3+}$	590 + 5	950cm^3/mol	a, b
$Fe(bipyl)_3^{3+}$	617 + 5	320cm^3/mol	b

a = Brandt and Gullstron (1952)

b = Moss, Mellon and Smith (1942)

It was found that the solutions in the concentrated acids were relatively stable while those in dilute acids decomposed fairly rapidly, however, the decomposition of the complexes were generally of the order 5-10% during a series of six runs (Ford-Smith and Sutin, 1961).

The amount of acid in each of the complex solutions was determined by volumetric titration against $Na_2B_4O_7.10H_2O$ with methyl orange as indicator.

3.1.3 Preparation of 0.1M solution of complexones

A known equivalent weight of each of the complexones (A.R) was accurately weighed and dissolved in distilled water in appropriate volumetric flasks (filled to the mark) to give 0.1M solutions (Vogel, 1978). In all cases except for HEDTA, the disodium salt of the complexones were used.

3.1.4 Preparation of 0.1M $Na_2B_4O_7.10H_2O$ Solution

(Primary standard)

3.746g of $Na_2B_4O_7.10H_2O$ (B.D.H Analar) was occurately weighed and dissolved in 1000cm^3 volumetric flask and made to the mark with distilled water to give a 0.1M solution, (Vogel, 1978).

3.1.5 Preparation of standard perchloric acid solution

A stock solution (about 5.0M) of $HClO_4$ was prepared from concentrated $HClO_4$ (B.D.H Analar). A diluted portion of the

stock solution was then titrated against 0.1M $Na_2B_4O_7.10H_2O$ solution using methyl orange as indicator. The concentration of the $HClO_4$ was calculated according to equation (3.1).

$$B_4O_7^{2-} + 2H^+ + 5H_2O \text{ ------> } 4H_3BO_3 + \text{.....} \quad 3.1$$

3.1.6 Preparation of standard $NaClO_4$ solution

A known weight of $NaClO_4$ (B.D.H, G.P.R) was dissolved in distilled water to prepare a stock solution of about 5.0M. The solution was standardized gravimetrically by evaporating to dryness, $2.0cm^3$ portions of the stock solution in preweighed bottles at 120°C and cooled in a dessicator until constant weights were obtained. The actual concentration was then calculated from the residual weight obtained.

3.1.7 Stoichiometry studies

The stoichiometry of the reactions were determined by spectrophotometric titration. In each case, the concentration of the oxidant, $[Co^{III}W]$, was kept constant while that of the reductant (complexone) was varied. $[Co^{III}W] = 2.0 \times 10^{-4}M$, [Reductant] = $(0.20 - 20.0) \times 10^{-4}M$, $[H^+] = 0.50M$ and I = 2.0M ($NaClO_4$) for all systems. The reactions were allowed to stand for 96 hours at 25.0 ± 0.1°C, and the absorbance of the solutions were measured at 400nm ($\varepsilon = 1180 \pm 20 M^{-1}cm^{-1}$) using the corning 253 colorimeter.

stock solution was then titrated against 0.1M $Na_2B_4O_7.10H_2O$ solution using methyl orange as indicator. The concentration of the $HClO_4$ was calculated according to equation (3.1).

$$B_4O_7^{2-} + 2H^+ + 5H_2O \text{ -------> } 4H_3BO_3 + \text{ ..... } 3.1$$

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A known weight of $NaClO_4$ (B.D.H, G.P.R) was dissolved in distilled water to prepare a stock solution of about 5.0M. The solution was standardized gravimetrically by evaporating to dryness, 2.0cm^3 portions of the stock solution in preweighed bottles at 120°C and cooled in a dessicator until constant weights were obtained. The actual concentration was then calculated from the residual weight obtained.

3.1.7 Stoichiometry studies

The stoichiometry of the reactions were determined by spectrophotometric titration. In each case, the concentration of the oxidant, $[Co^{III}W]$, was kept constant while that of the reductant (complexone) was varied. $[Co^{III}W] = 2.0 \times 10^{-4}M$, [Reductant] = $(0.20 - 20.0) \times 10^{-4}M$, $[H^+] = 0.50M$ and I = 2.0M ($NaClO_4$) for all systems. The reactions were allowed to stand for 96 hours at 25.0 ± 0.1°C, and the absorbance of the solutions were measured at 400nm (ε = 1180 ± 20$M^{-1}cm^{-1}$) using the corning 253 colorimeter.

For the complexes, $Fe(L\text{-}L)_3^{3+}$, the stoichiometries could not be carried out without doubts, since the complexes decompose after a long time. Thus, their stoichiometries were assumed.

3.1.8 Free radical test

Polymerization studies were conducted to investigate the presence of free radicals in the reaction mixtures. Each set of experiment was carried out at I = 2.0M ($NaClO_4$) and T = 25.0 ± 0.1°C. 5.0cm^3 of 10% (w/v) acrylamide was added to partially reduced reaction mixture, and total volume was adjusted to 10cm^3 with distilled water. Methanol was then added in excess. No gel formation was observed in each case.

3.1.9 Spectra Measurements

These measurements were undertaken to determine whether an intermediate complex was formed between the oxidants and the substrates. Solutions of the reactants were mixed and their absorbance noted at a preset wavelength on the corning 253 colorimeter.

The process was repeated for different wavelengths. Similar measurements were made for the solution of each of the oxidants alone.

3.1.10 Kinetic studies

The kinetics of the reaction was studied on a corning colorimeter 253, by monitoring the decrease in absorbance of $Co^{III}W$, $Fe(bipy)_3^{3+}$ and $Fe(5\text{-}NO_2\text{-}phen)_3^{3+}$ (at 400nm, 620nm and 595nm respectively) as a function of time. All kinetic measurements were carried out under pseudo-first order conditions with each of the reductant concentrations in excess of at least 100 folds over those of the complexes (oxidants) at T = 25.0 ± 0.1°C, I = 2.0M ($NaClO_4$), unless otherwise stated.

3.1.11 Product Analysis

The natures of the primary products were determined by spectrophotometric measurements by their absorption characteristic maxima at 625nm, 522nm and 510nm for $Co^{II}W$, $Fe(bipy)_3^{2+}$ and $Fe(5\text{-}NO_2\text{-}phen)_3^{2+}$ respectively (Figures 4.34 - 4.36). Formaldehyde was tested for, from a portion of the neutralized reaction mixtures using Tollen's reagent and Fehling's reagents.

Chapter 4

4.0 Results

4.1 Stoichiometry

The results of the stoichiometry studies determined from the titration curves presented in figures 4.1-4.3, were consistent with two moles of the oxidants being consumed by one mole of the reductant in each case. The 2:1 (oxidant:reductant) stoichiometries were assumed for the reactions between $Fe(LL)_3^{3+}$ and the reductant (LL = 2,2'-bipy or 5-NO_2-phen), the complexes being one electron oxidant like $Co^{III}W$.

On the basis of the stoichiometries determined, the overall reaction can be represented by equations 4.1 and 4.2.

$$2Co^{III}W + H_nY \longrightarrow 2Co^{II}W + CO_2 + \ldots\ldots, \quad 4.1$$

$$2Fe(LL)_3^{3+} + H_nY \longrightarrow 2Fe(LL)_3^{2+} + CO_2 + \ldots, \quad 4.2$$

where H_nY = HEDTA, EDTA or NTA

4.2 Determination of order with respect to reactants

Pseudo-first order plots of $\log(A_t - A_\infty)$ versus time were linear for more than 70% to 80% of the reactions. The linearity of these plots indicate that the reactions are first-order with respect to [oxidant] in each case, (A_t and A_∞ are absorbances of the complex at time 't' and the end of the reaction

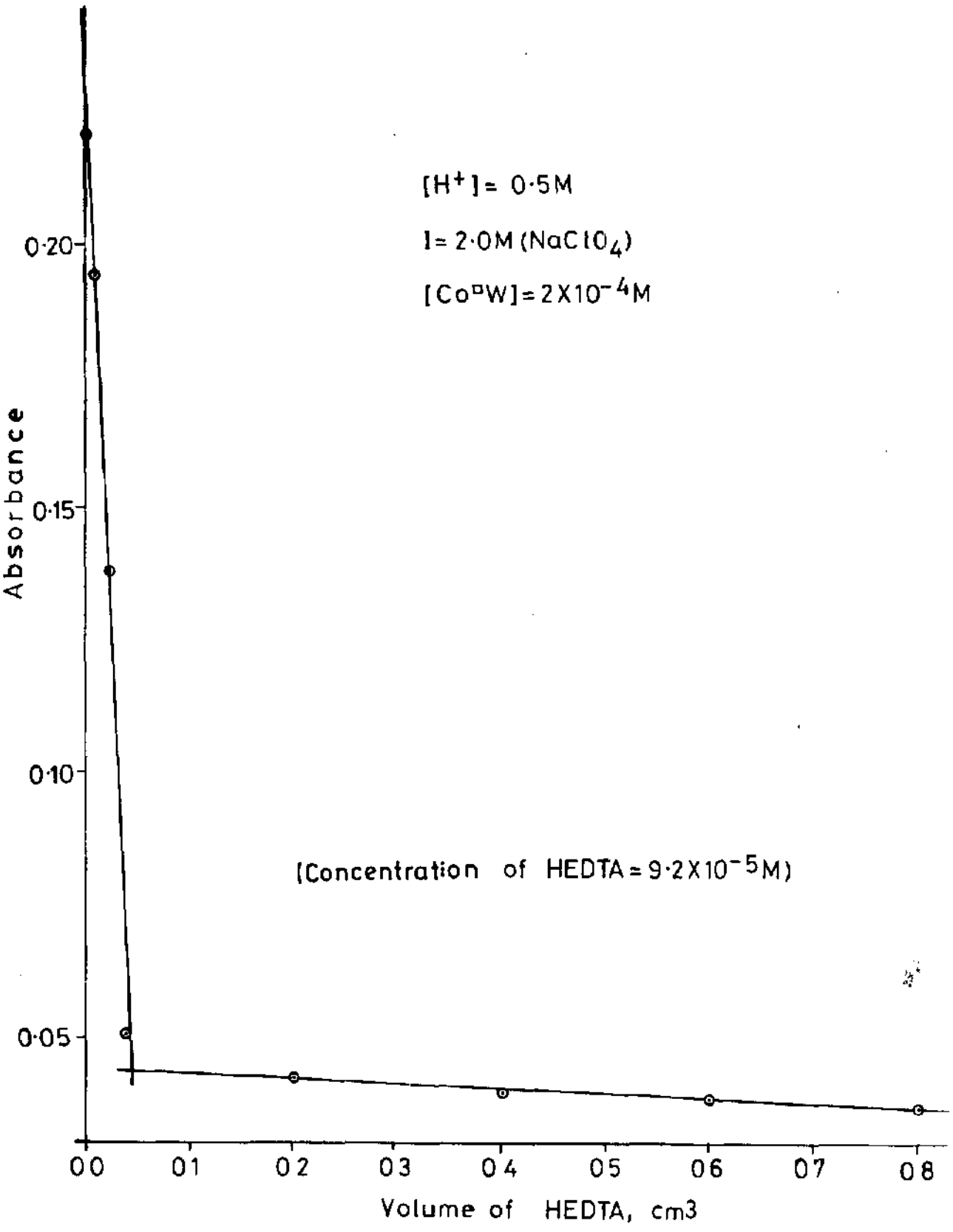


FIG. 4·1 PLOT OF ABSORBANCE VERSUS VOLUME OF HEDTA ADDED TO MIXED REACTING SOLUTIONS OF HEDTA AND $Co^{III}W$.

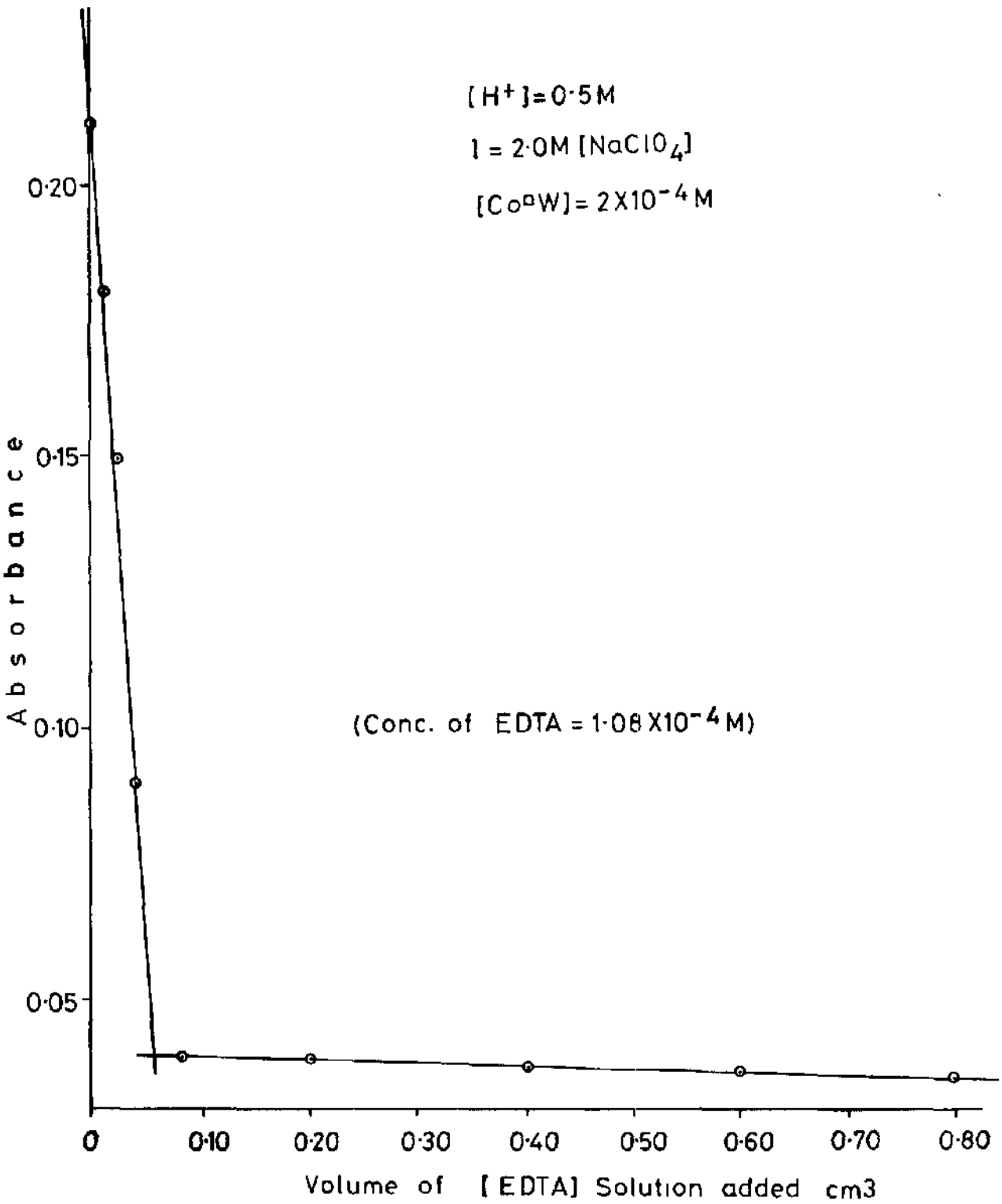
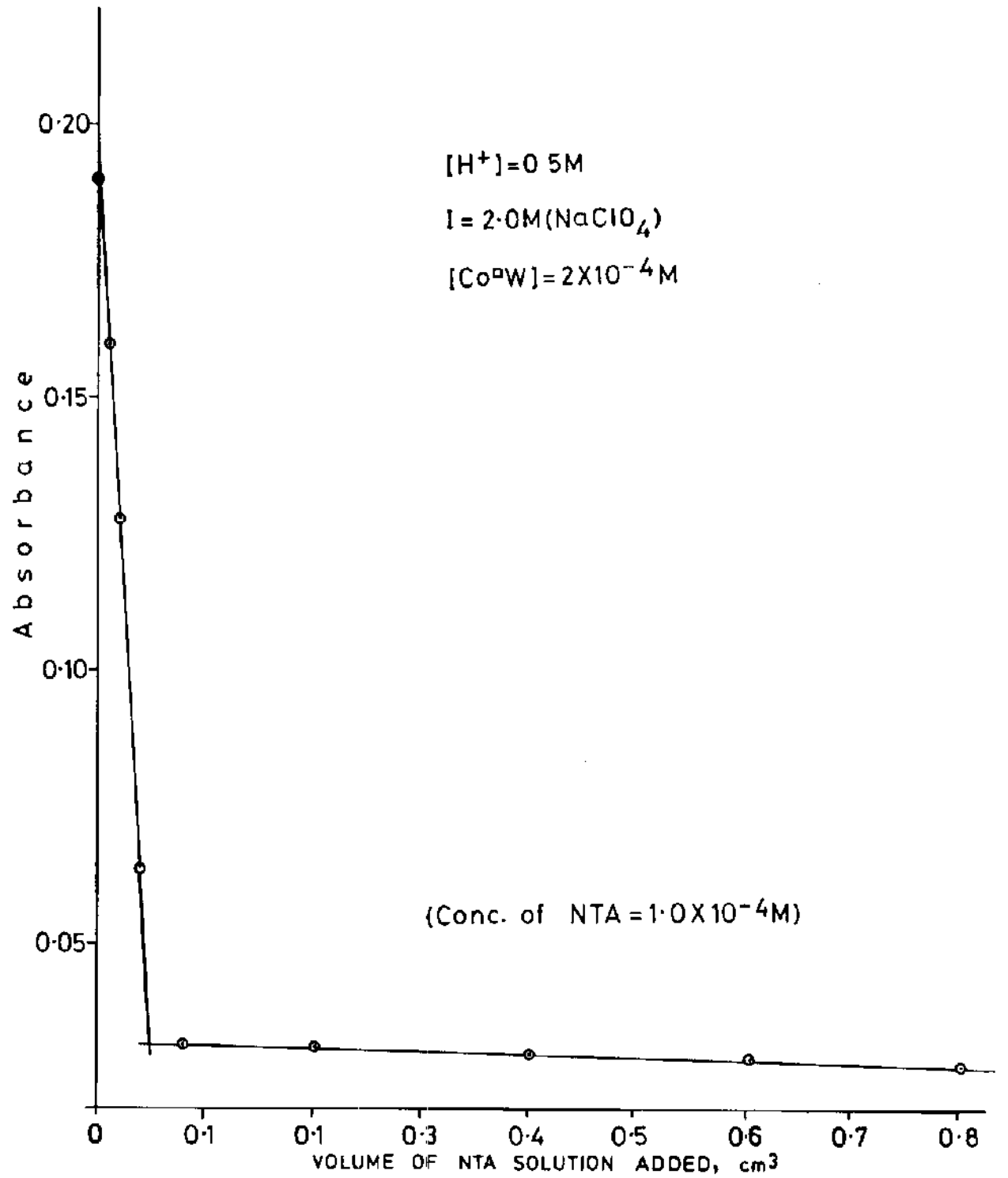


FIG. 4·2 PLOT OF ABSORBANCE VERSUS VOLUME OF EDTA ADDED TO REACTING MIXED SOLUTIONS OF EDTA AND $Co^{II}W$



$[H^+]$=0 5M

I = 2·0M($NaClO_4$)

$[Co^{III}W]$= $2X10^{-4}$M

(Conc. of NTA = $1·0X10^{-4}$M)

FIG. 4·3 PLOT OF ABSORBANCE VERSUS VOLUME OF NTA ADDED TO MIXED REACTING SOLUTIONS OF NTA $Co^{III}W$

respectively). Typical plots are shown in figures 4.4-4.6 from the slopes of such plots the pseudo-first order rate constants k_{obsd} were obtained.

The plots of $\log k_{obsd}$ versus $\log[H_nY]$ gave slopes of 0.99 ± 0.05, (figures 4.7-4.9 are typical examples of such plots), showing the reactions to be first order in $[H_nY]$. The second-order rate constants k_2, were determined from k_{obsd} as $k_{obsd}/[H_nY]$ and reported in tables 4.1-4.9. In view of the reported stoichiometries at constant $[H_+]$, the rate law for the reactions may be represented by equations 4.3 and 4.4.

$$-\frac{d[Co^{III}W]}{dt} = 2k_2[Co^{III}W][H_nY] \quad \ldots\ldots\ldots 4.3$$

$$-\frac{d[Fe(LL)_3^{3+}]}{dt} = 2k_2[Fe(LL)_3^{3+}][H_nY]$$

4.3 The influence of $[H^+]$ on the rates of reaction

The effect of $[H^+]$ on the rates of the reactions between the oxidants ($Co^{III}W$ and $Fe(LL)_3^{3+}$) and reductants were investigated by determining the rate constants in the acid range of 0.2-1.60M, T = 25.0 ± 0.1°C, I = 2.0M $NaClO_4$. The rate constants were found to be inversely dependent on the $[H^+]$ for all the reactions (figures 4.13-4.15). Values of the acid-dependent rate constants are presented in Tables 4.1-4.9.

The plot of k_H versus $[H^+]^{-1}$ were linear with no significant intercepts, typical examples are shown by figures (4.16-4.18).

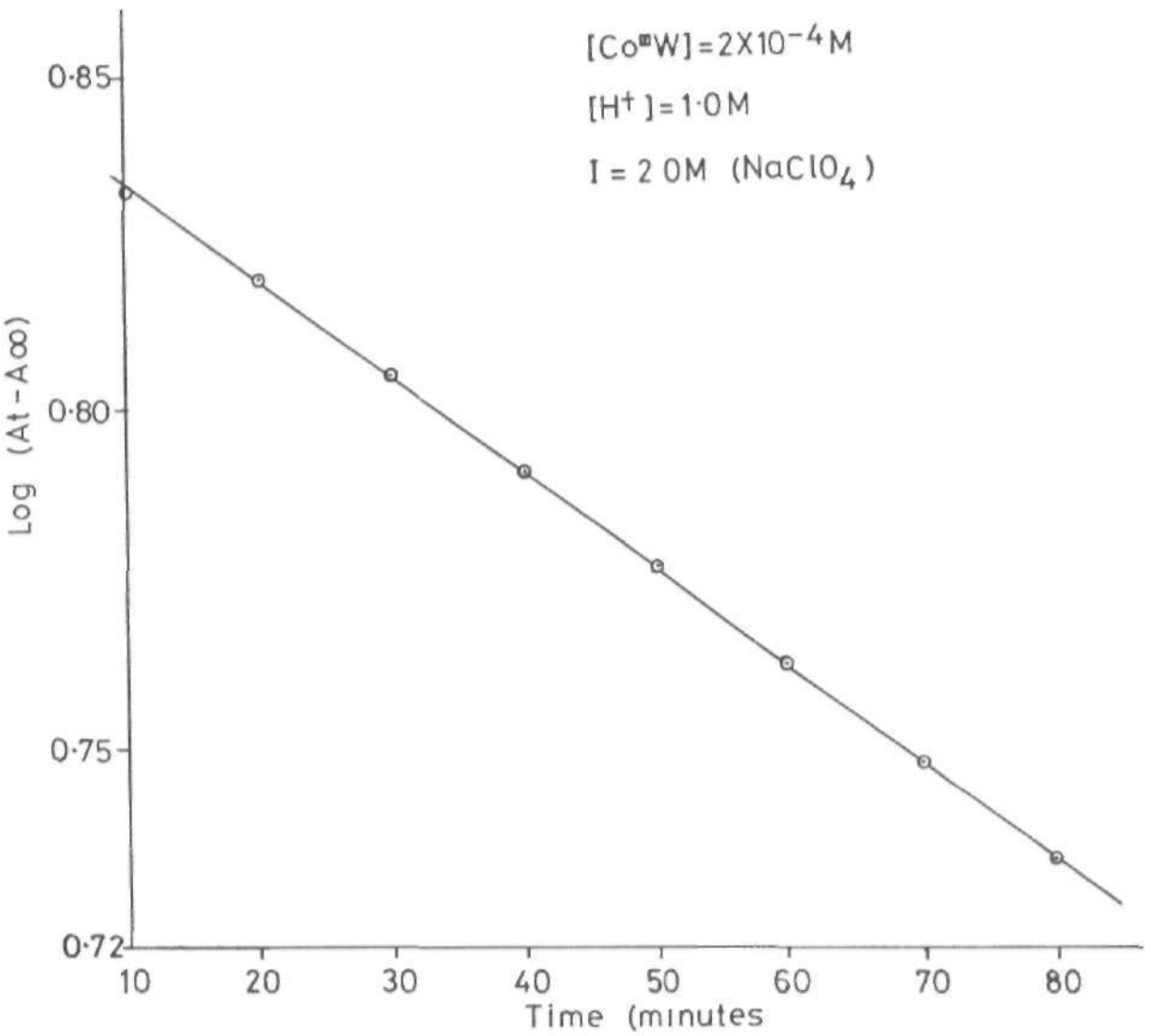


Fig. 4·4 TYPICAL PSEUDO-FIRST ORDER PLOT FOR THE REDOX REACTIONS OF Co^{III}W AND COMPLEXONE

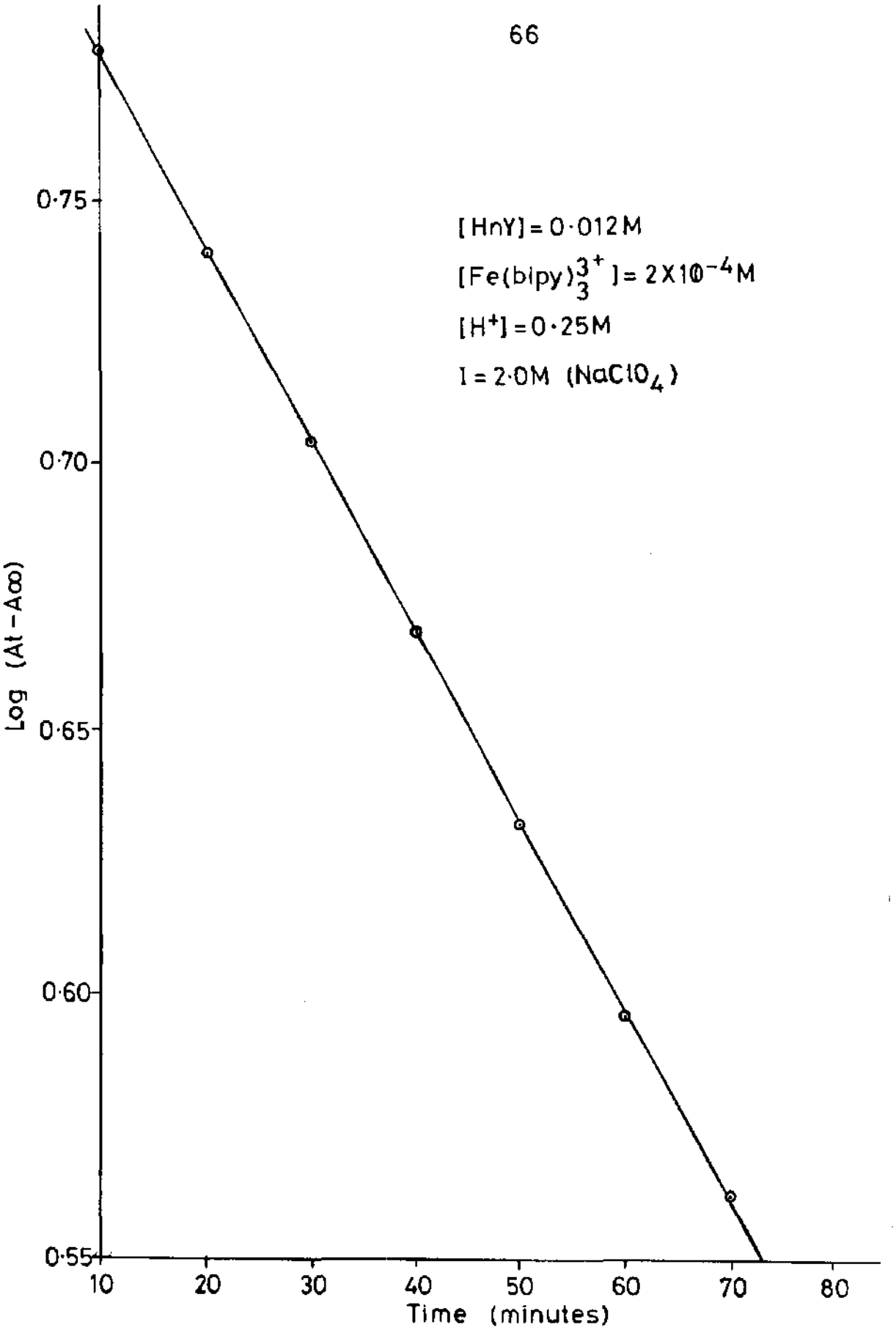


FIG. 4·5 TYPICAL PSEUDO- FIRST-ORDER PLOT FOR THE REDOX REACTIONS OF Fe(bipy)$_3^{3+}$ AND COMPLEXONE

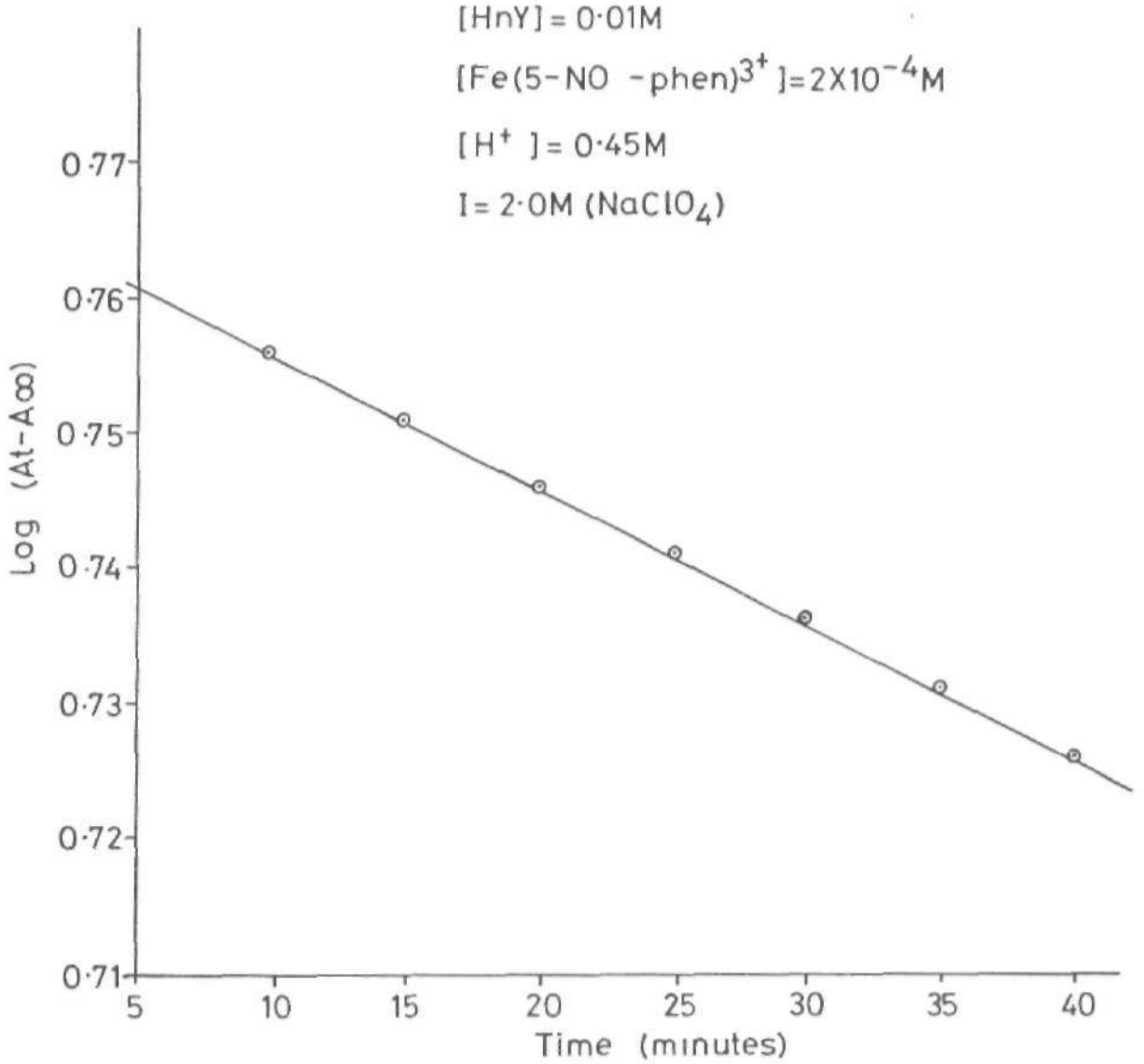


FIG. 4·6 A TYPICAL PSEUDO-FIRST-ORDER PLOT FOR THE REDOX REACTIONS OF $Fe(5\text{-}NO_2\text{-}phen)_3^{3+}$ AND COMPLEXONE

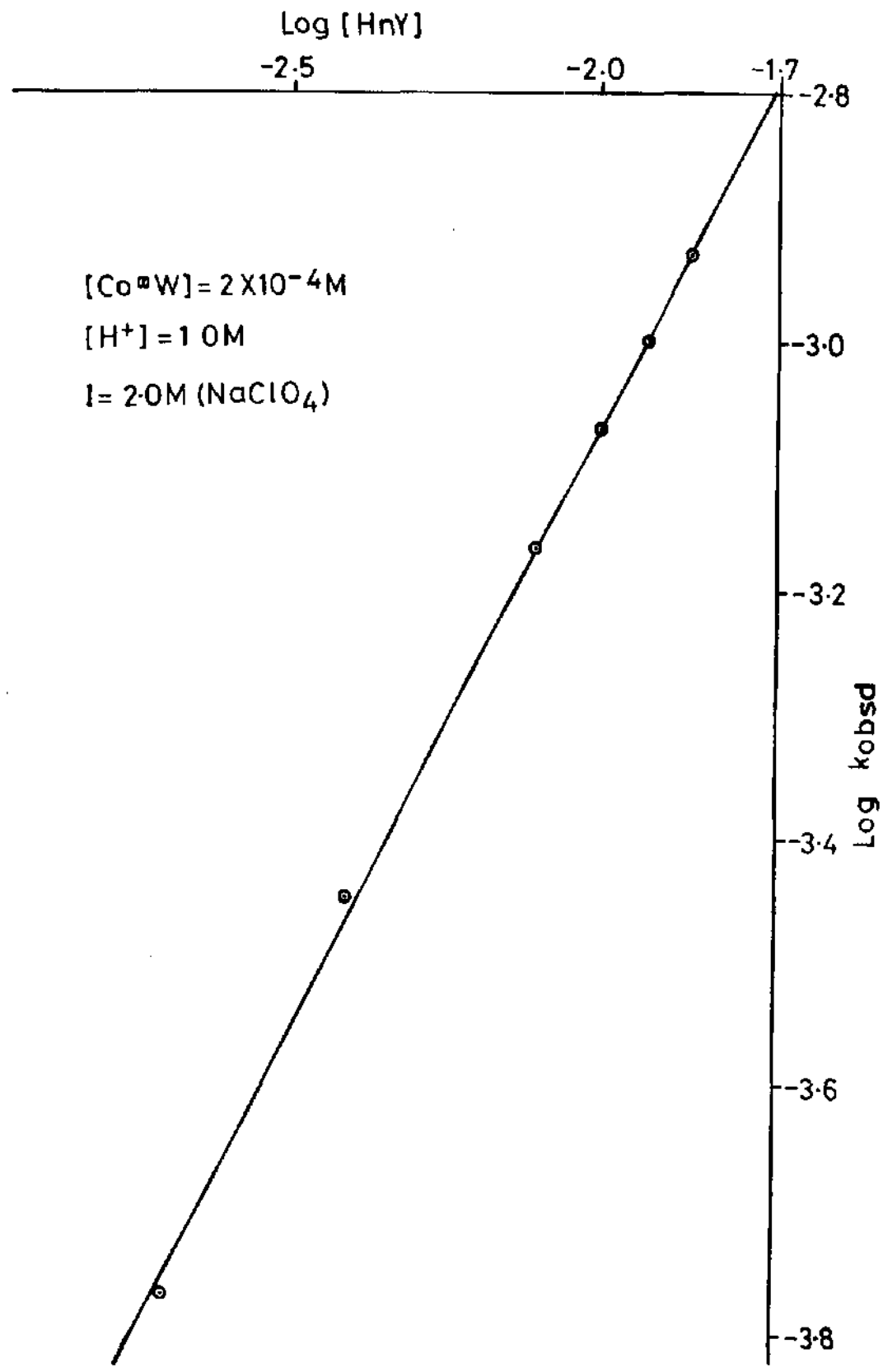


FIG. 4-7 TYPICAL PLOT OF Log k_{obsd} VERSUS Log [HnY] FOR THE REDOX REACTIONS OF $Co^{III}W$ AND COMPLEXONE

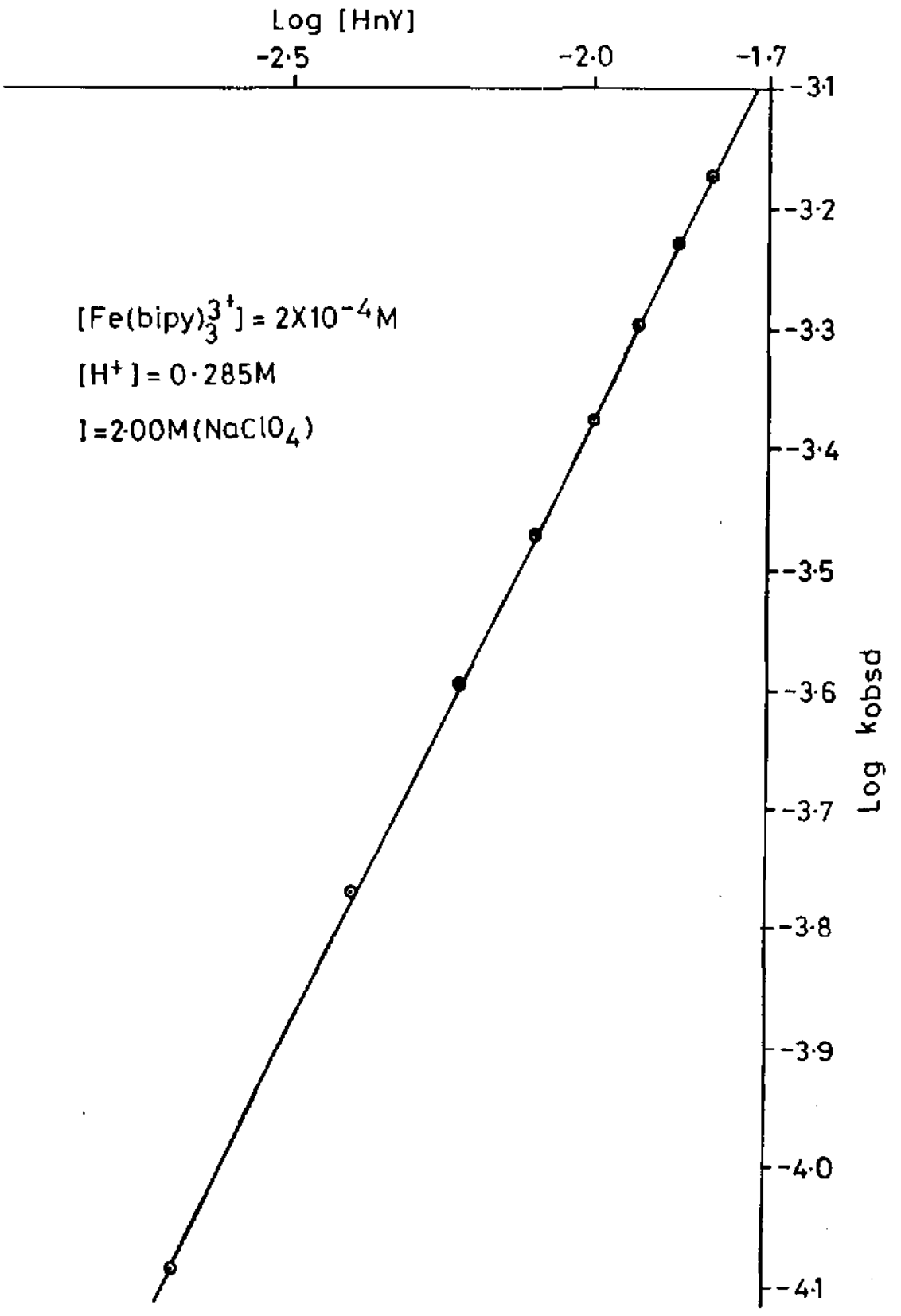


FIG. 4·8 A TYPICAL PLOT OF k_{obsd} VERSUS LOG [HnY] FOR THE REDOX REACTIONS OF $Fe(bipy)_3^{3+}$ AND COMPLEXONE

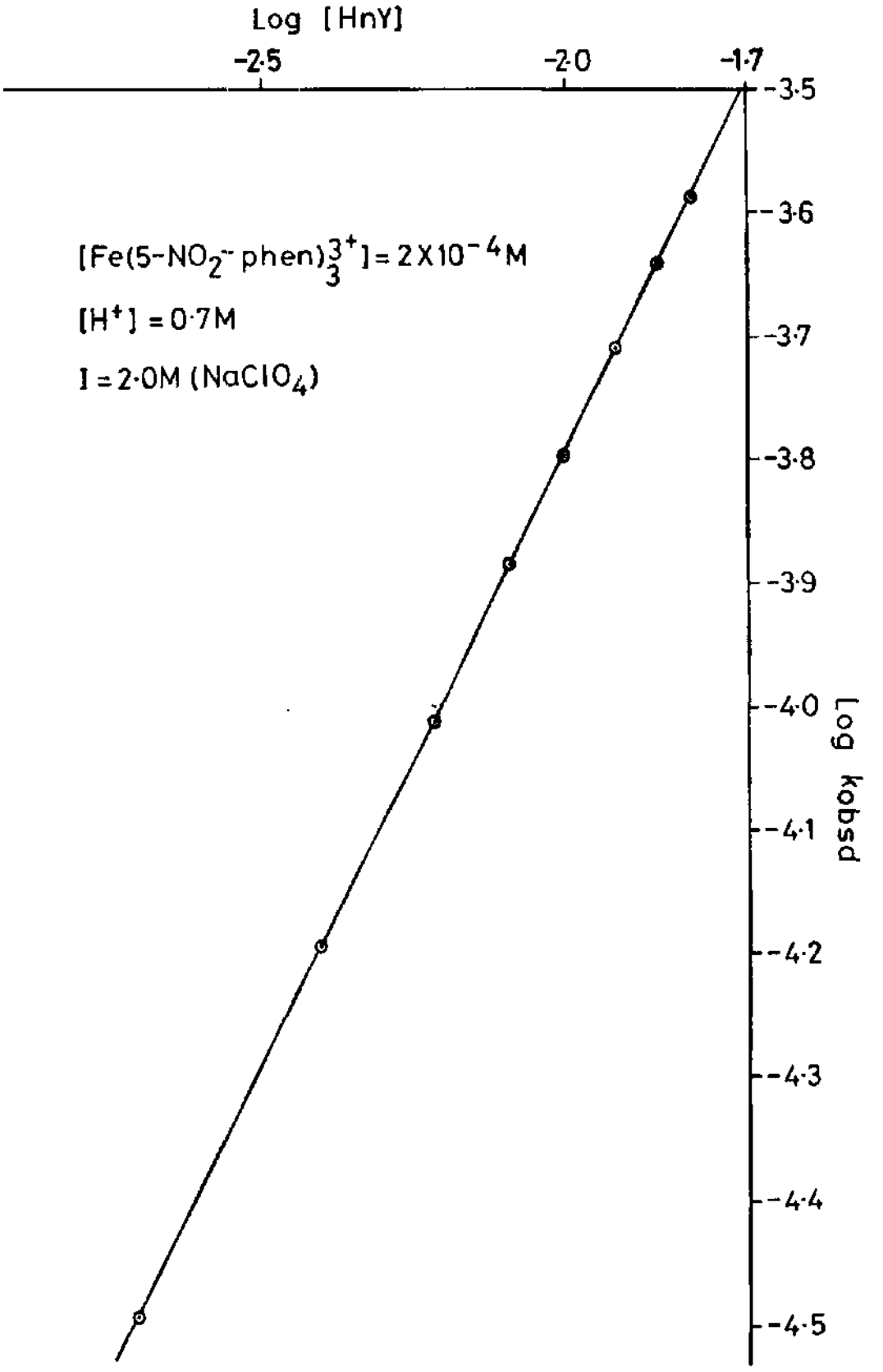


FIG. 4·9 TYPICAL PLOT OF Log kobsd VERSUS Log [HnY] FOR THE REDOX REACTIONS OF $Fe(5\text{-}NO_2\text{-}phen)_3^{3+}$ AND COMPLEXONE

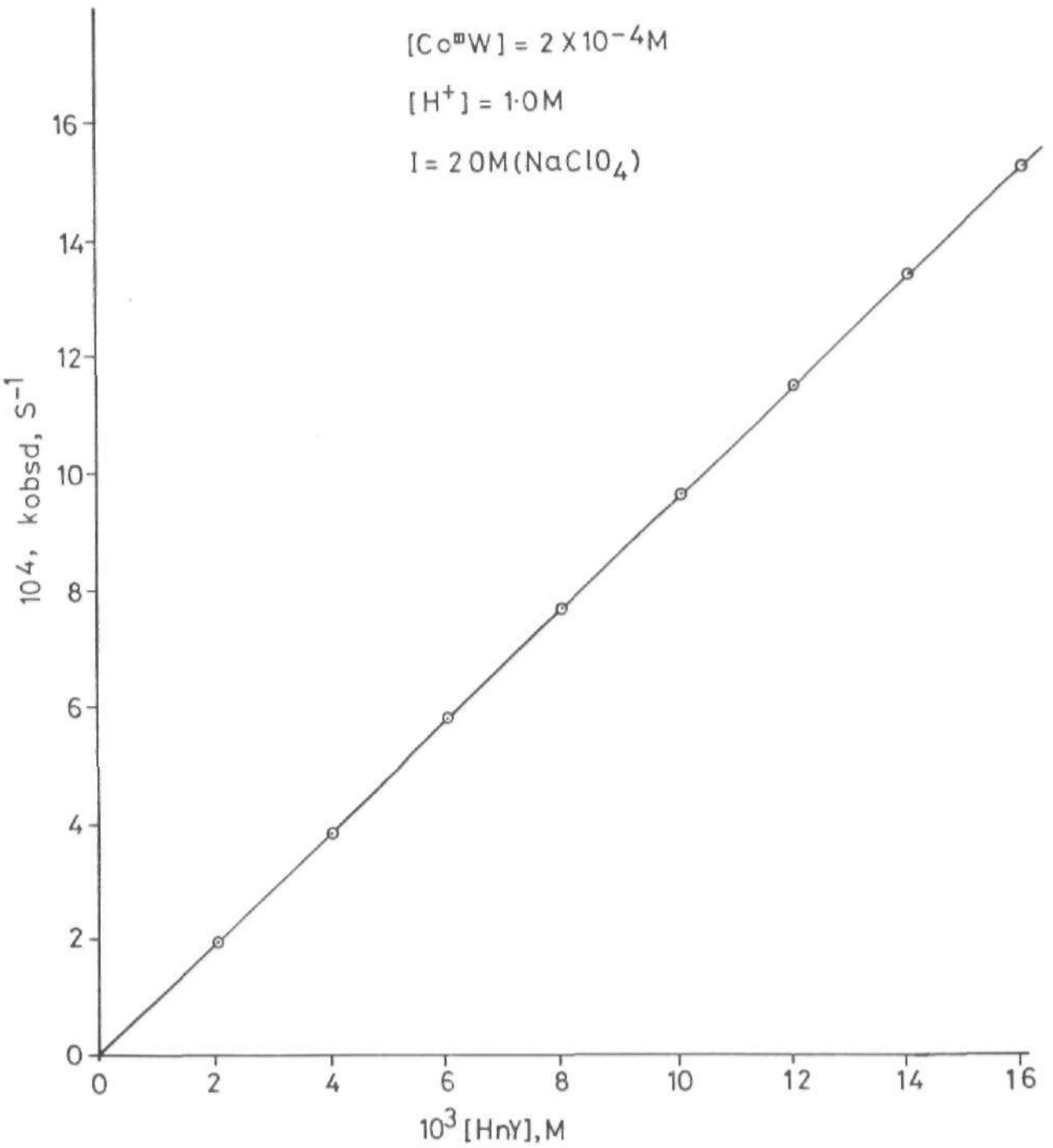


FIG.4-10 TYPICAL PLOT OF k_{obsd} VERSUS [HnY] FOR THE REDOX REACTIONS OF $Co^{III}W$ AND COMPLEXONE

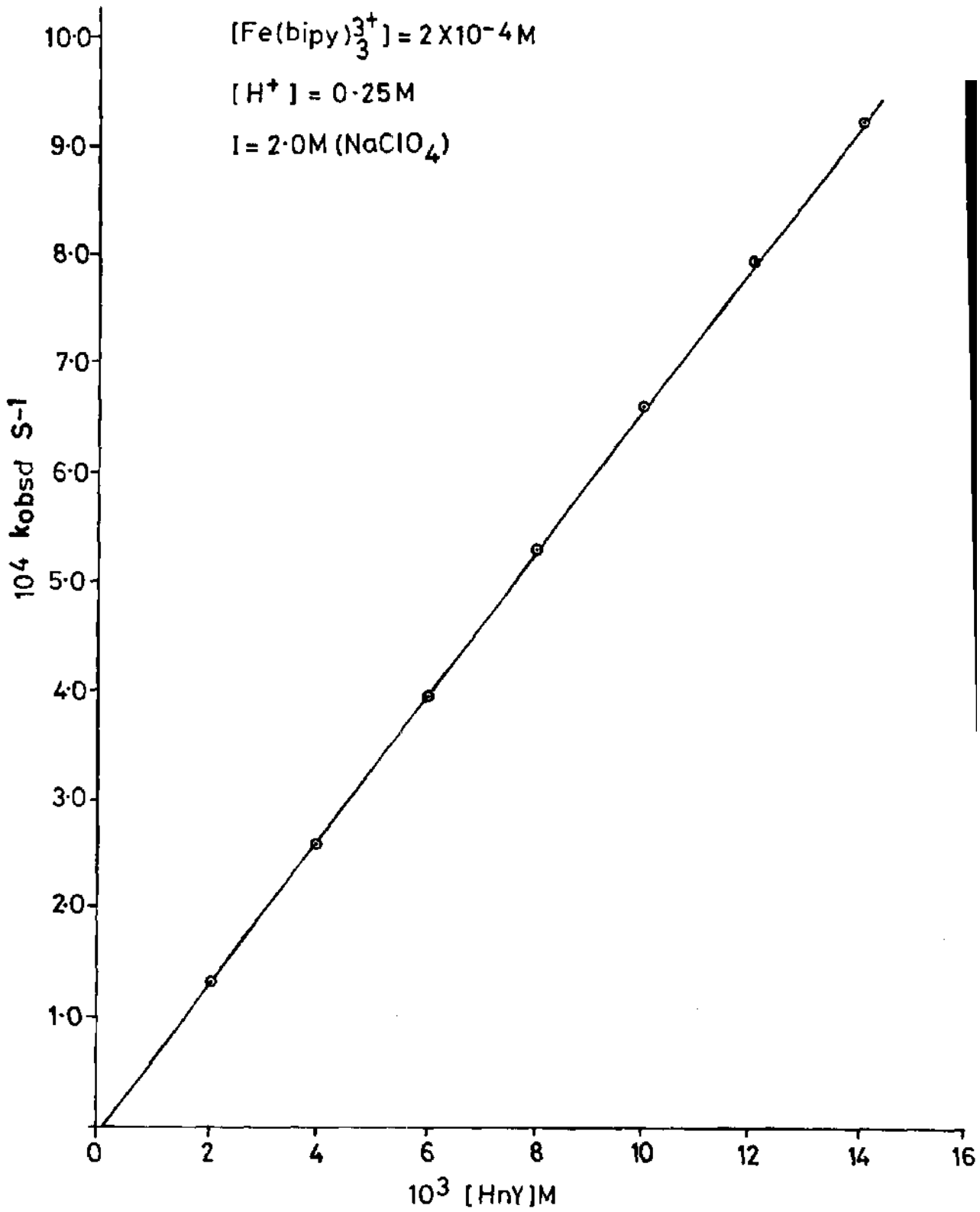


FIG. 4·11 TYPICAL PLOT OF kobsd VERSUS [HnY] FOR THE REACTIONS OF Fe(bipy)$_3^{3+}$ AND COMPLEXONE

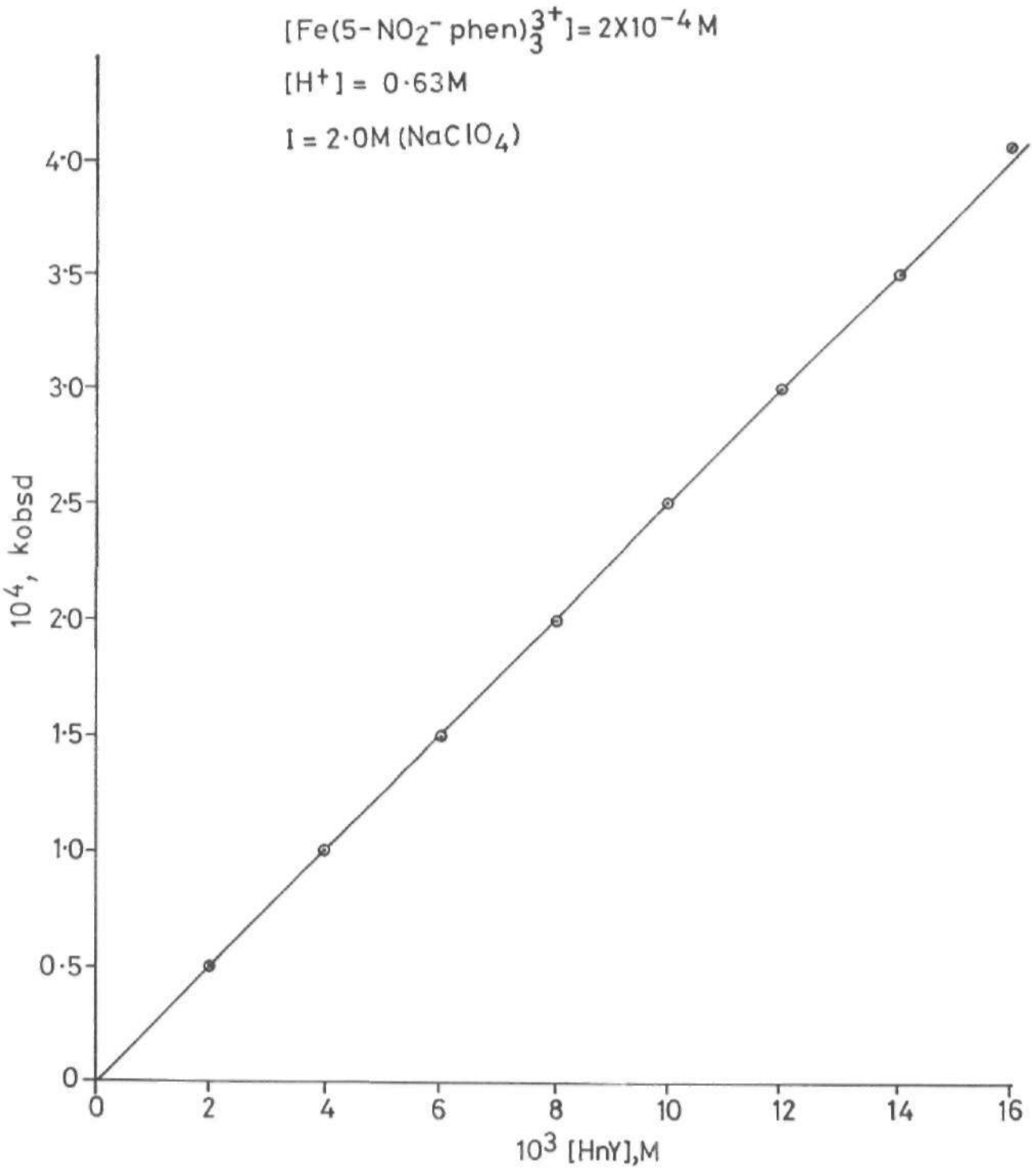


FIG. 4·12 TYPICAL PLOT OF kobsd VERSUS [HnY] FOR THE REDOX REACTIONS OF $Fe(5\text{-}NO_2\text{-}phen)_3^{3+}$ AND COMPLEXONE

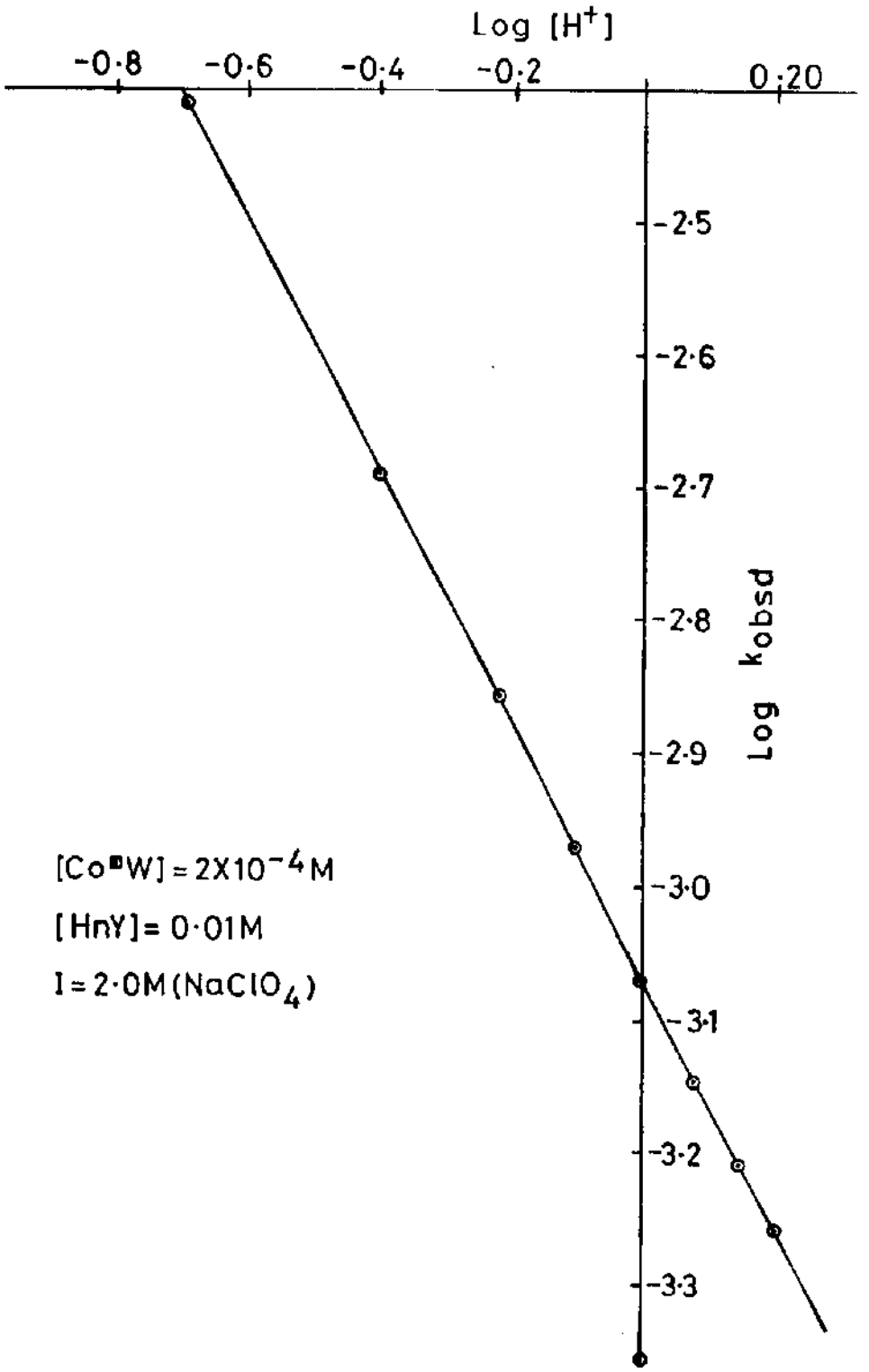


FIG 4 13 TYPICAL PLOT OF Log kobsd VERSUS Log [H+] FOR THE REDOX REACTIONS OF Co■W AND COMPLEXONE

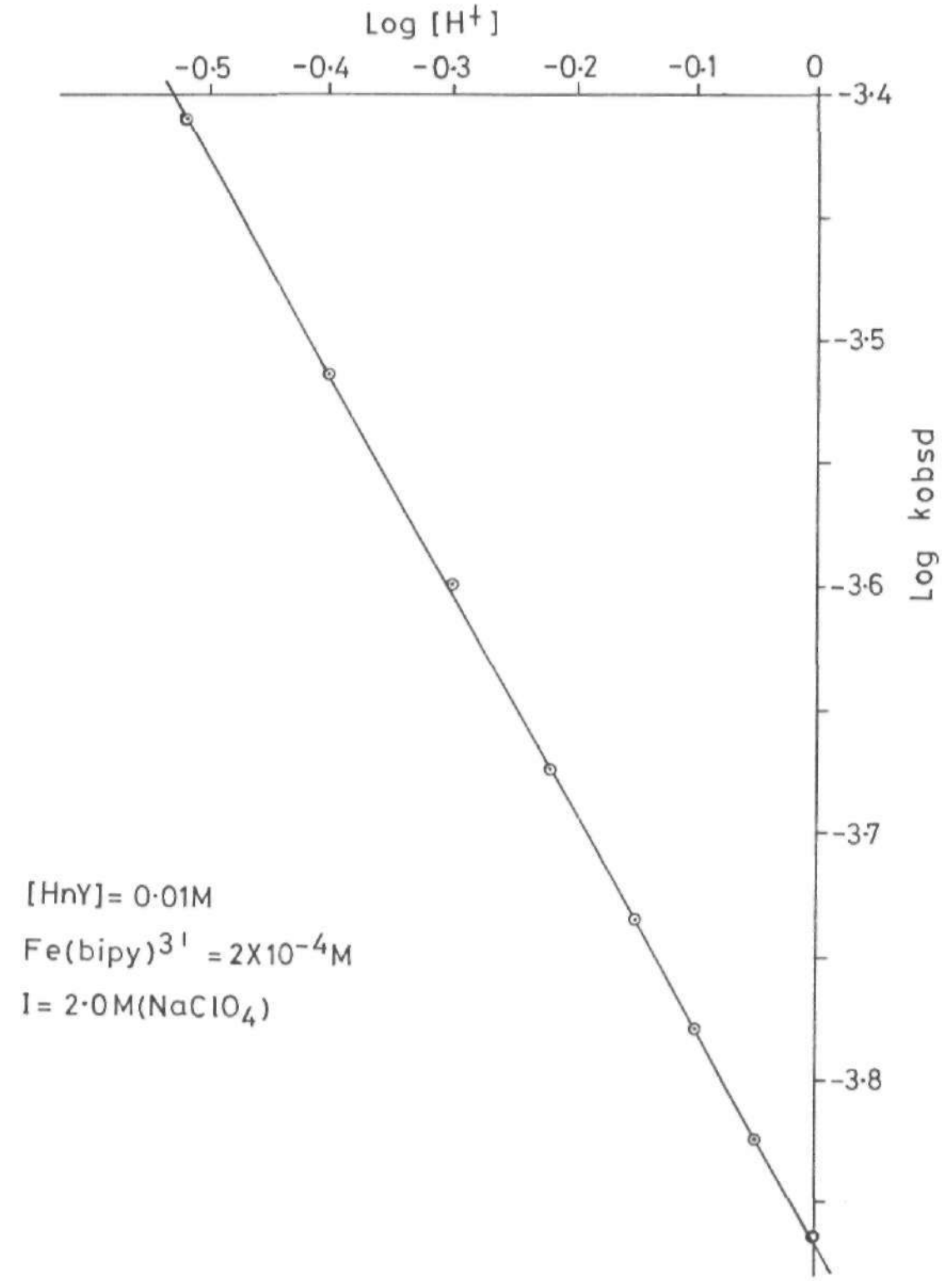


FIG. 4·14 A TYPICAL PLOT OF Log kobsd VERSUS Log [H+] FOR THE REDOX REACTIONS OF $Fe(bipy)_3^{3+}$ AND COMPLEXONE

$[Fe(5\text{-}NO_2\text{-}phen)_3^{3+}] = 2 \times 10^{-4} M$

$[HnY] = 0{\cdot}01M$

$I = 2{\cdot}0M\ (NaClO_4)$

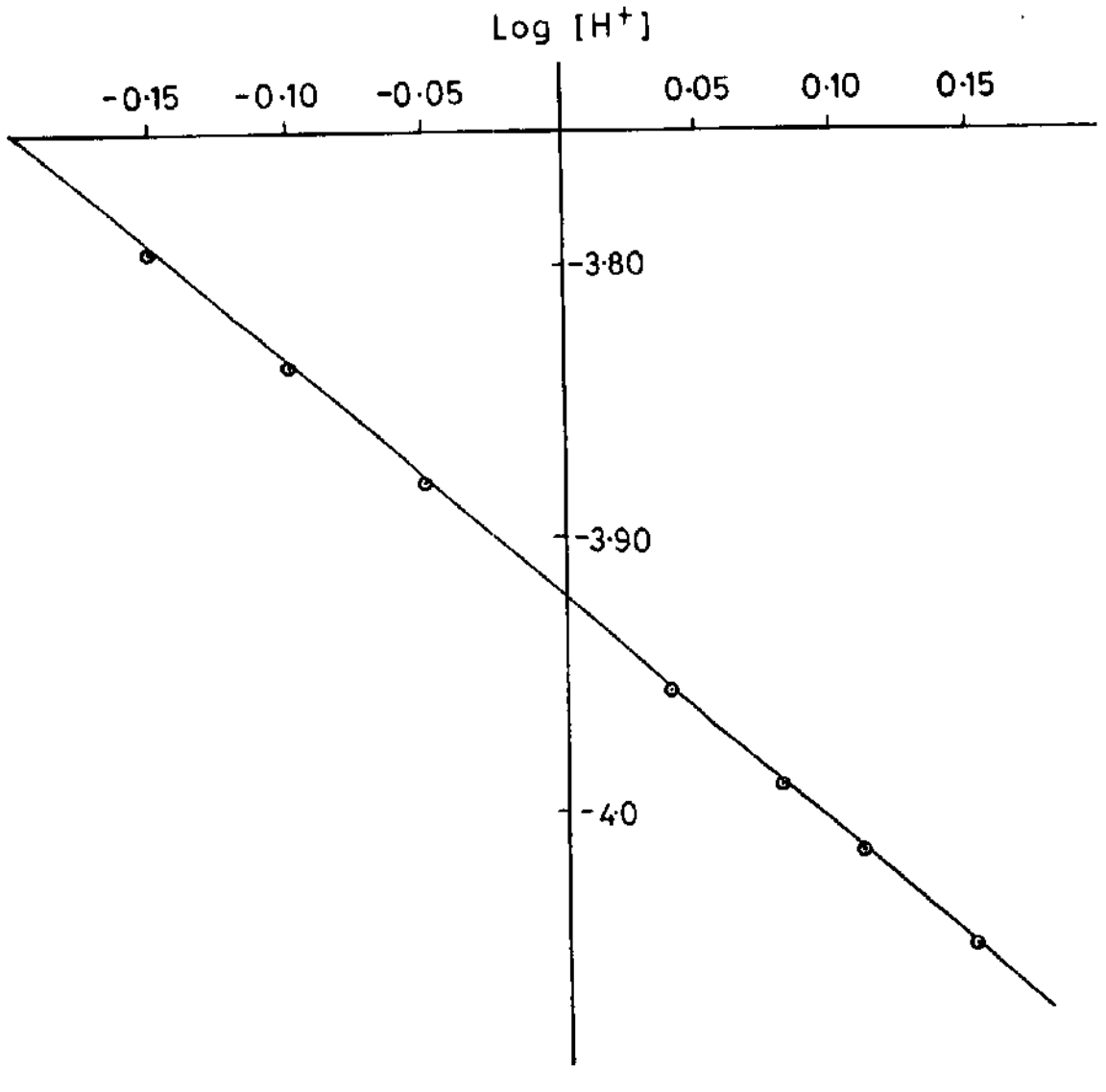


FIG. 4·15 TYPICAL PLOT OF Log k_{obsd} VERSUS Log $[H^+]$ FOR THE REDOX REACTIONS OF $Fe(5\text{-}NO_2\text{-}Phen)_3^{3+}$ AND COMPLEXONE

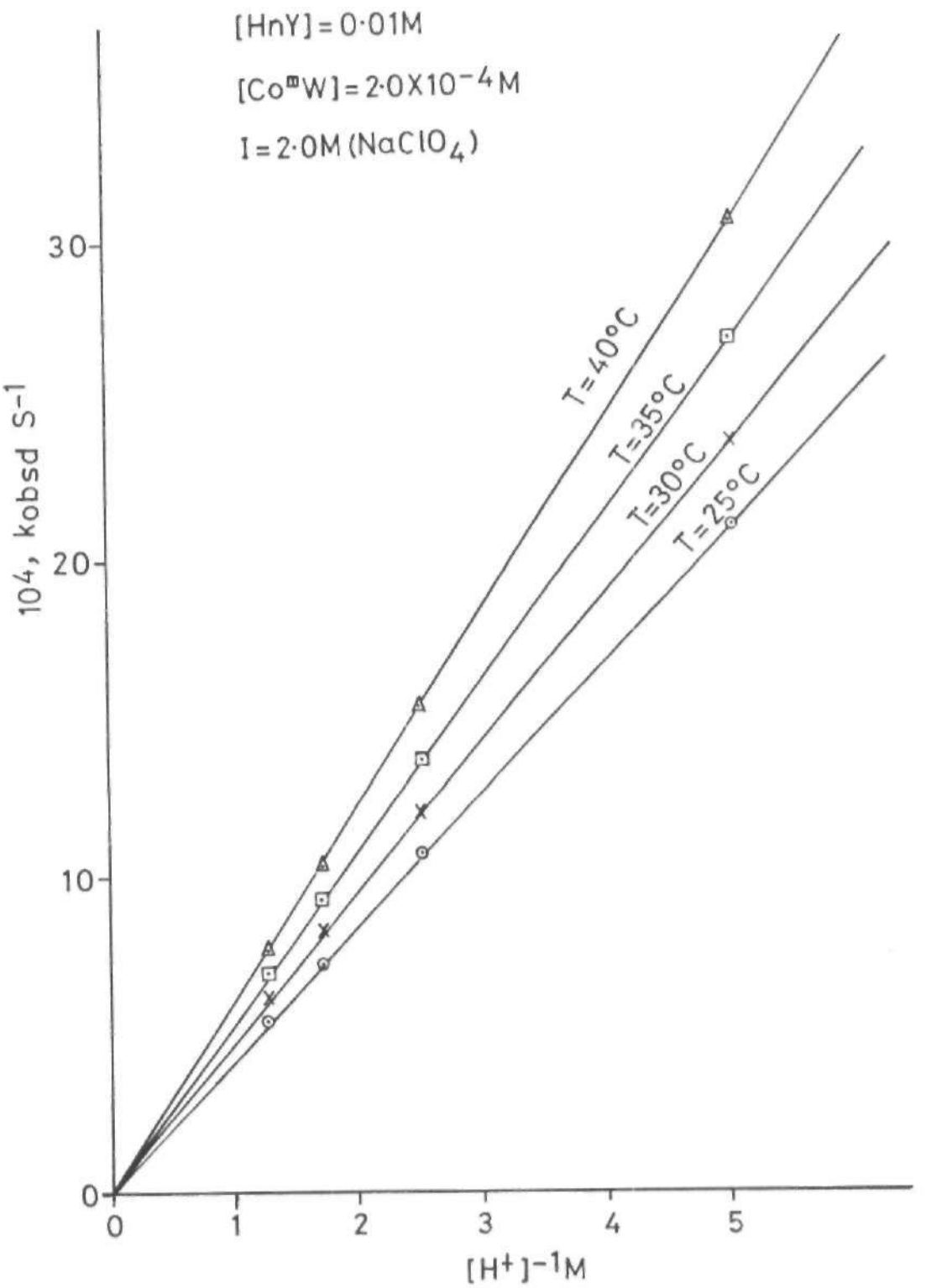


FIG. 4·16 TYPICAL PLOT OF k_{obsd} VERSUS $[H^+]^{-1}$ FOR THE REDOX REACTIONS OF $Co^{III}W$ AND COMPLEXONE

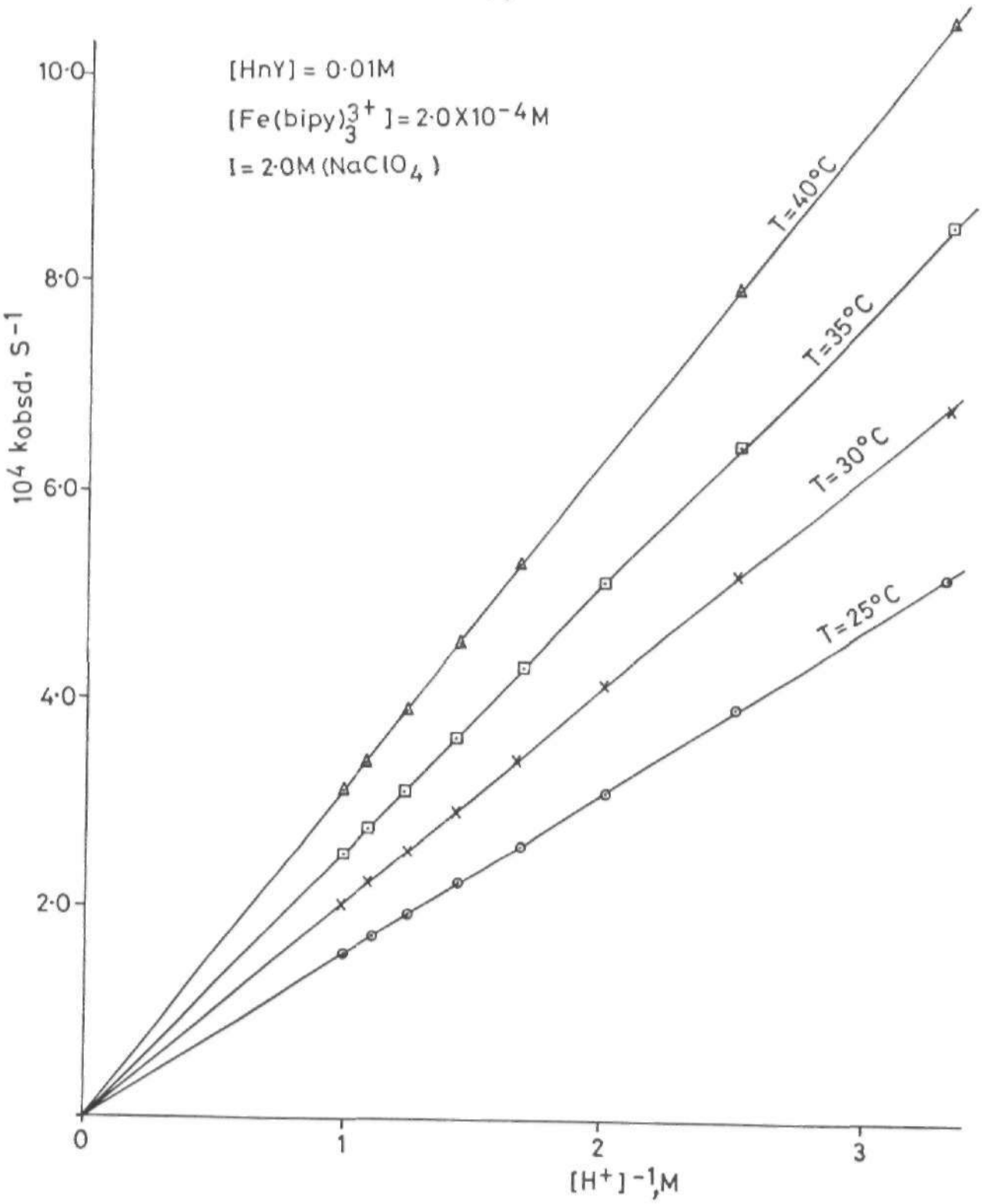


FIG. 4·17 TYPICAL PLOT OF k_{obsd} VERSUS $[H^+]^{-1}$ FOR THE REDOX REACTIONS OF $Fe(bipy)_3^{3+}$ AND COMPLEXONE

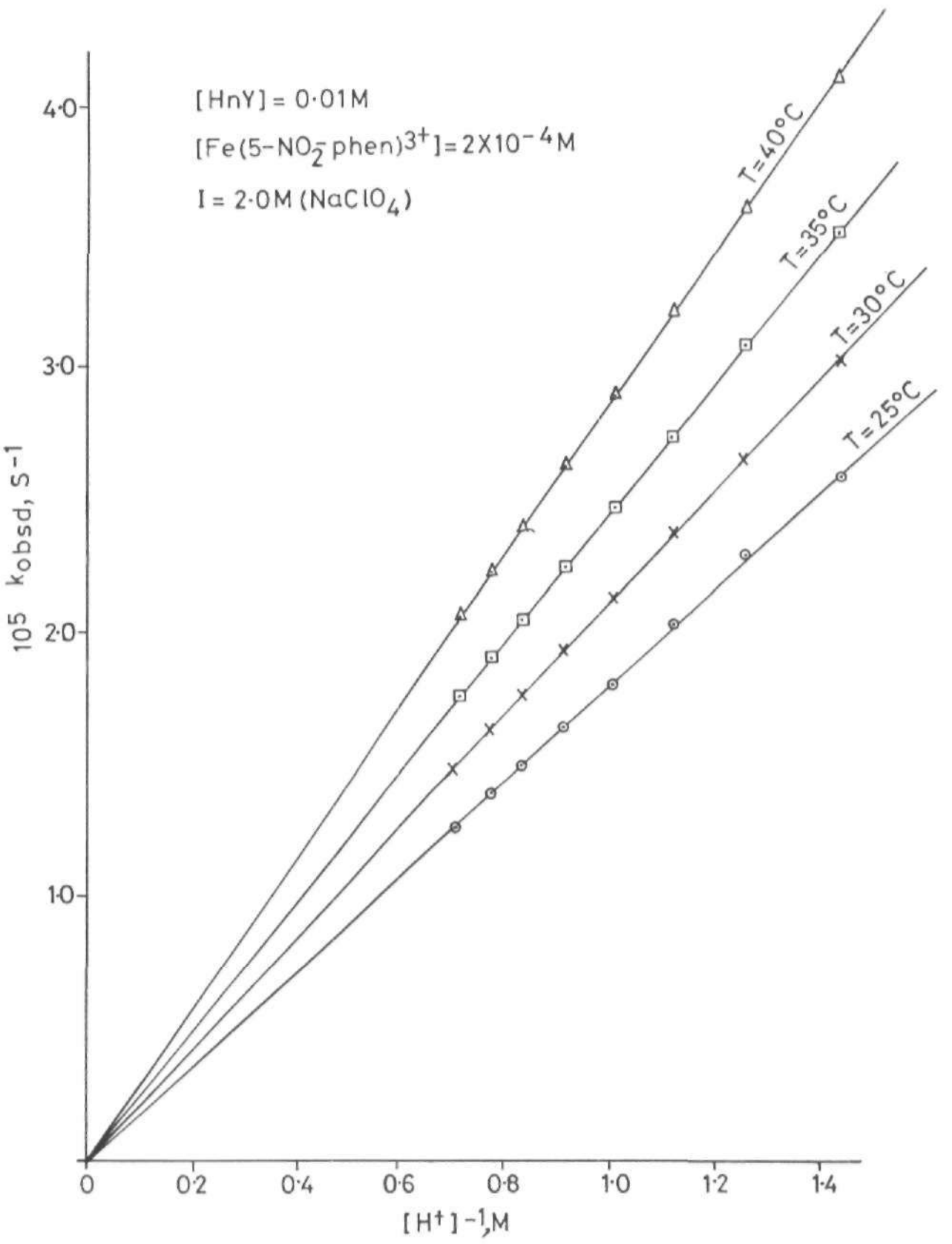


FIG. 4·18 TYPICAL PLOT OF kobsd VERSUS $[H^+]^{-1}$ FOR THE REDOX REACTIONS OF $Fe(5\text{-}NO_2^-\ phen)_3^{3+}$ AND COMPLEXONE

therefore, the acid dependent rate constants can be represented by equation (4.5).

$$k_H = b[H^+]^{-1} \quad \ldots\ldots\ldots\ldots\ldots\ldots 4.5$$

and the overall rate equations can be written as

$$-\frac{d[Co^{III}W]}{dt} = b[H^+]^{-1}[Co^{III}W][H_nY] \quad \ldots\ldots 4.6$$

$$-\frac{d[Fe(LL)_3^{3+}}{dt} = b[H^+]^{-1}[Fe(LL)_3^{3+}][H_nY] \quad \ldots\ldots 4.7$$

At T = 25.0 ± 0.1°C and I = 2.0M $NaClO_4$, the values of 'b' are given as follows; 8.80 x $10^{-4}Ms^{-1}$, 7.5 x 10^{-4} and 4.20 x 10^{-4} for the reaction of $Co^{III}W$ with HEDTA, EDTA and NTA respectively; 1.69 x $10^{-4}Ms^{-1}$, $1.08Ms^{-1}$ and $0.28Ms^{-1}$ for the reactions between $Fe(bipy)_3^{3+}$ and HEDTA, EDTA and NTA respectively; and 1.01 x $10^{-4}Ms^{-1}$, 1.90 x $10^{-4}Ms^{-1}$ and $0.19Ms^{-1}$ for the reactions of $Fe(5\text{-}NO_2\text{-}phen)_3^{3+}$ with HEDTA, EDTA and NTA respectively.

4.4 Effect of ionic strength on the rates of reactions

The effect of ionic strength on the rates of the reactions was investigated in the ranges I = 0.60 - 1.00M and 1.00 - 2.00M for the Co^{III}-H_nY and $Fe(LL)_3^{3+}$-H_nY reactions respectively. At 25.0 ± 0.1°C, constant $[H^+]$, the rate constants were found to be dependent on I (I = ionic strength). Values of the dependent rate constants are presented in tables (4.1-4.9).

The effect of ions on the rate constant of reactions involving two reactants with charges Z_A and Z_B are related by the following equation (Bronsted, 1922).

$$\log k = \log k_o + 2\alpha Z_A Z_B I^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ 4.8$$

k = the rate constant of the reaction,

k_o = hypothetical rate constant in a medium of infinite dielectric constant

I = ionic strength

α = 0.50 at 25°C.

This equation has been used to correlate salt effects with the rate constants for reactions involving ions: thus, plots of logk versus $I^{\frac{1}{2}}$ should be linear with slope $Z_A Z_B$ (at 25°C when $t^{2\alpha}$ = 1) and intercepts values of $\log k_o$ (Bronsted, 1922). The equation predicts a positive salt effect (i.e an increasing rate constant with increasing concentration) when reactants have charges of the same sign and a negative salt effect when charges are of opposite sign (Bronsted, 1922). In the present work, linear plots of $\log k_{obsd}$ versus $I^{\frac{1}{2}}$ were obtained figures (4.22-4.24).

4.5 Activation parameters for the reactions

The energies of activation were obtained from the slopes of the plots of $\log k_{obsd}$ versus 1/T and $\log k_H$ versus 1/T figures (4.19-4.21) from which other activation parameters were

calculated. This was determined by carrying out the reactions at four temperatures (i.e 25.0, 30.0, 35.0 and 40.0) ± 0.1°C. Where k_{obsd} is the temperature dependent rate constant and k_H is the rate constant at varied $[H^+]$, obtained as the slopes of the plots of k_{obsd} versus $[H^+]^{-1}$ at each temperature, (figures 4.25-4.27). Tables 4.10 'a' and 'b' display the values of the activation parameters, calculated using Arrhenius relationship.

4.6 Michaelis-Menten plot

The least square analysis of plots of $1/k_{obsd}$ versus $[H_nY]^{-1}$ were linear with zero intercepts and are shown in figures (4.25-4.27).

From Michaelis-Menten reaction scheme involving a catalyst (e.g an enzymes), the rate is given as

$$\frac{dp}{dt} = k_{obsd}[E_o] \quad \ldots\ldots 4.9$$

$$\text{with } k_{obsd} = \frac{k_1[S]}{K_m + [S]} \quad \ldots\ldots\ldots\ldots 4.10$$

$$1/k_{obsd} = 1/k_1 + \left(\frac{K_m}{k_1}\right)\frac{1}{[S]} \quad \ldots\ldots 4.11$$

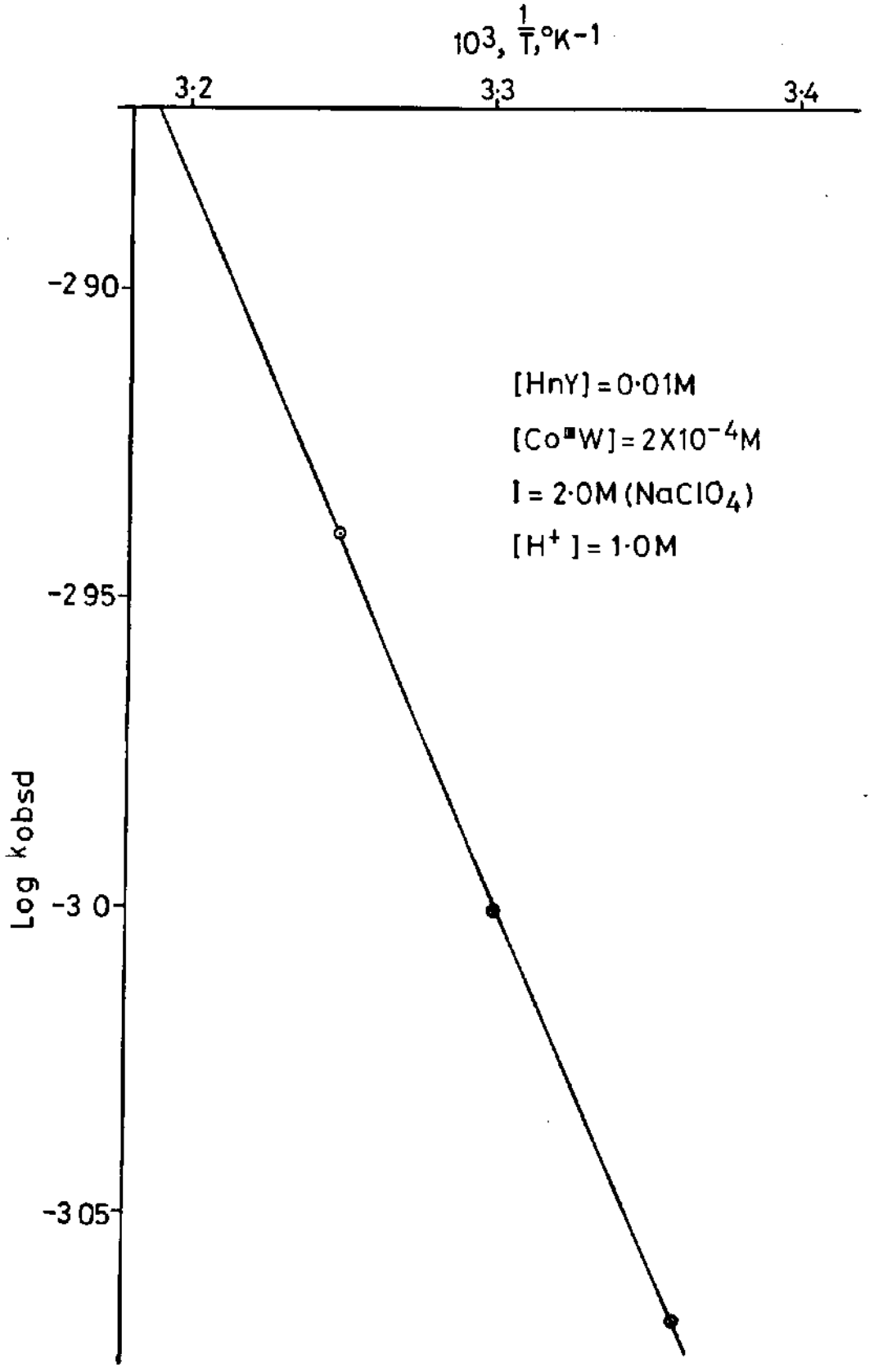


FIG. 4·19(a) TYPICAL ARRHENIUS PLOT FOR THE REDOX REACTIONS OF $Co^{III}W$ AND COMPLEXONE

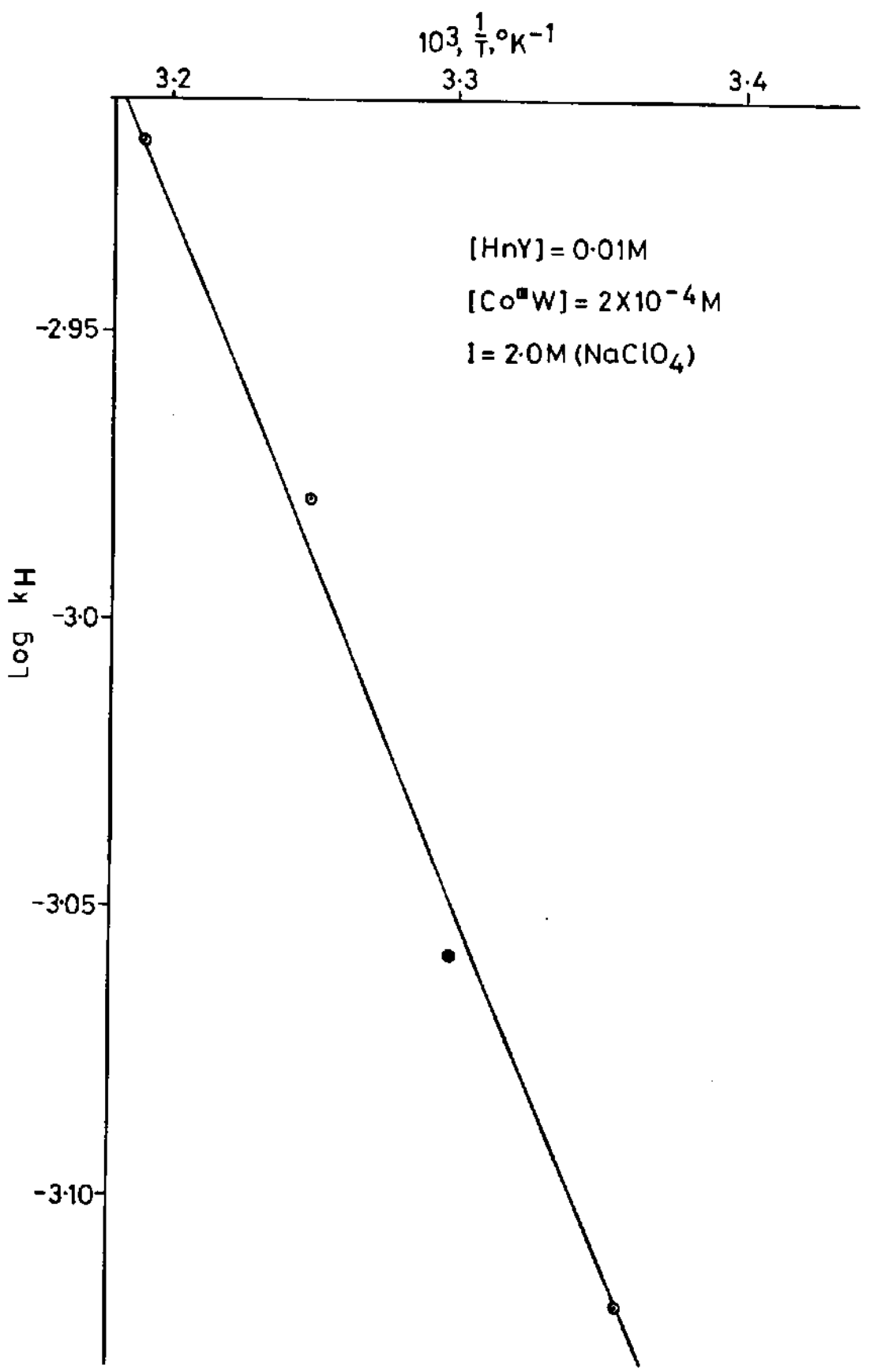


FIG. 4·19 (b) TYPICAL ARRHENIUS PLOT FOR THE REDOX REACTIONS OF $Co^{III}W$ AND COMPLEXONE

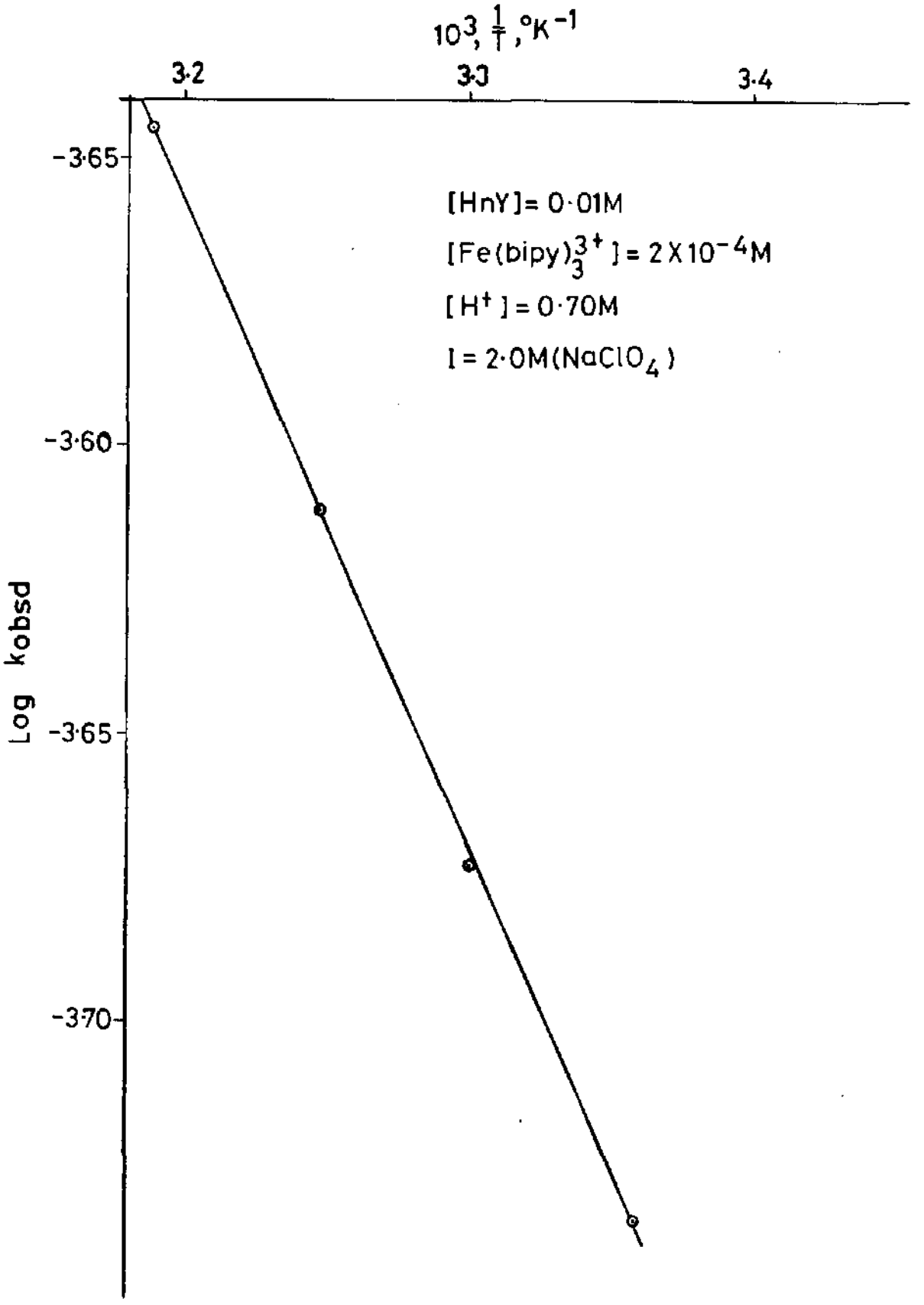


FIG. 4·20(a) TYPICAL ARRHENIUS PLOT FOR THE REDOX REACTIONS FOR Fe(bipy)$_3^{3+}$ AND COMPLEXONE

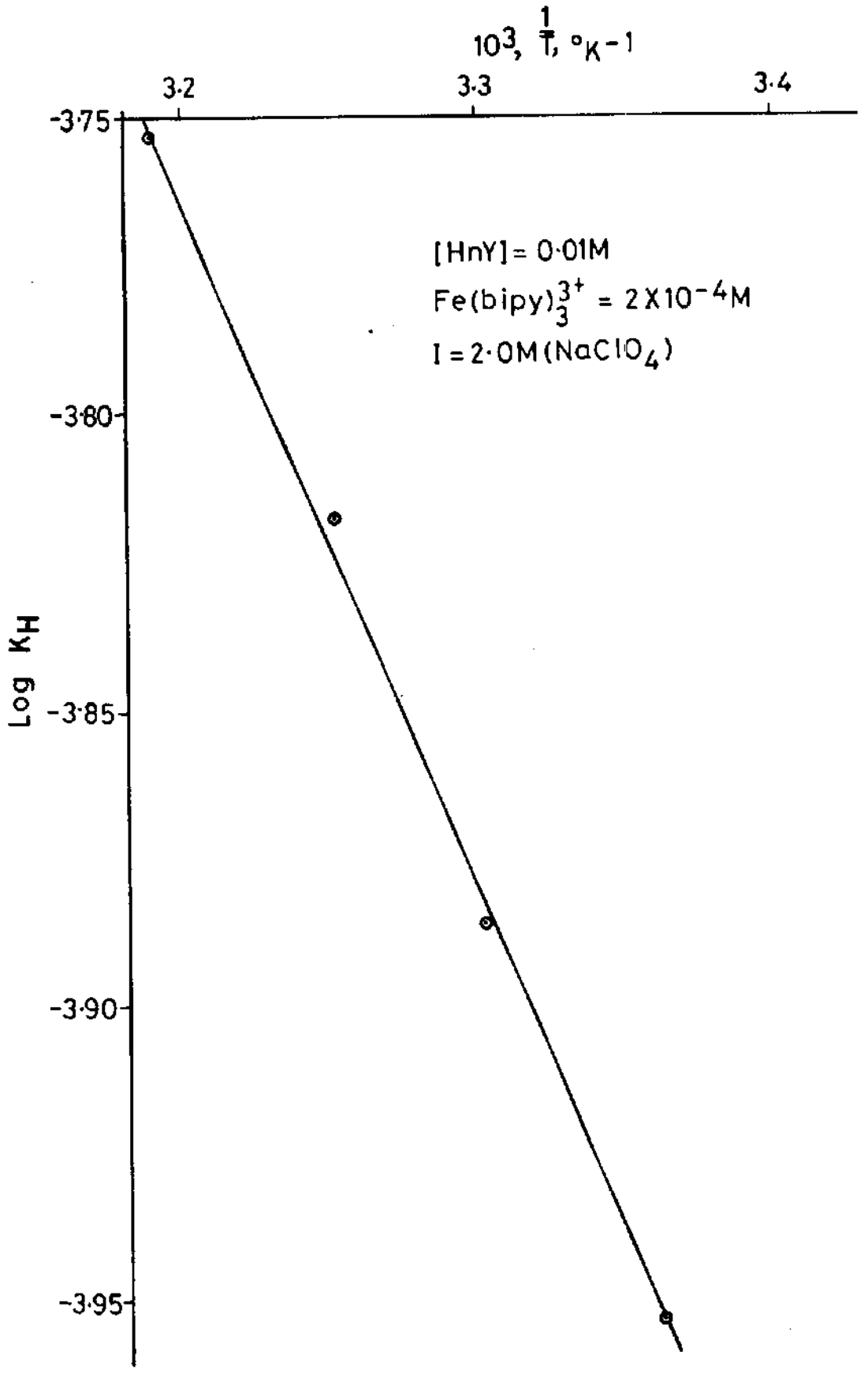


FIG. 4·20(b) TYPICAL ARRHENIUS PLOT FOR THE REDOX REACTIONS OF $Fe(bipy)_3^{3+}$ AND COMPLEXONE

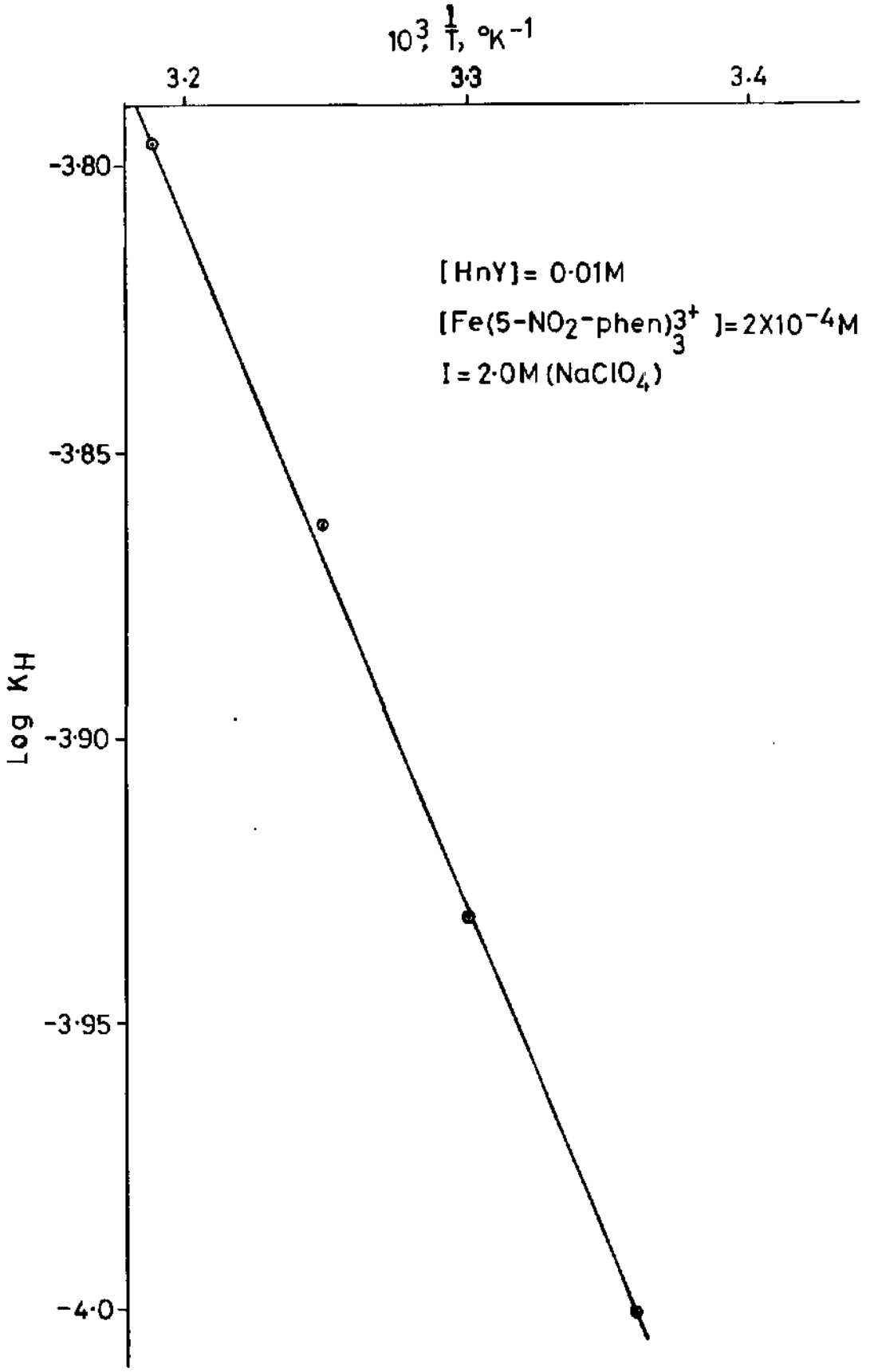


FIG. 4·21(b) TYPICAL ARRHENIUS PLOT FOR THE REDOX REACTIONS OF Fe(5-NO_2^- phen)$_3^{3+}$ AND COMPLEXONE

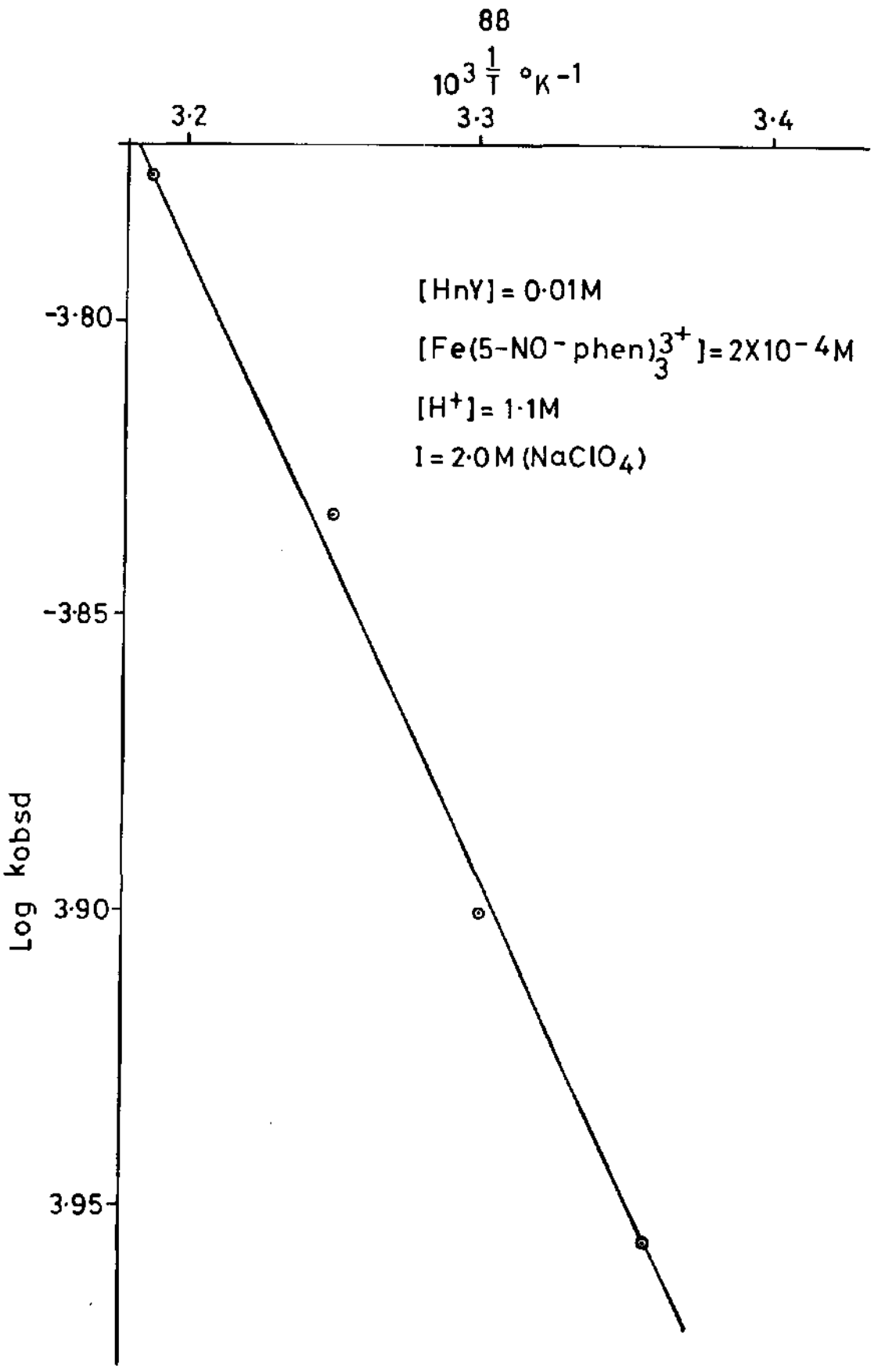


FIG. 4·21(a) TYPICAL ARRAHENIUS PLOT FOR THE REDOX REACTIONS OF Fe(5-NO_2^-Phen)$_3^{3+}$ AND COMPLEXONE

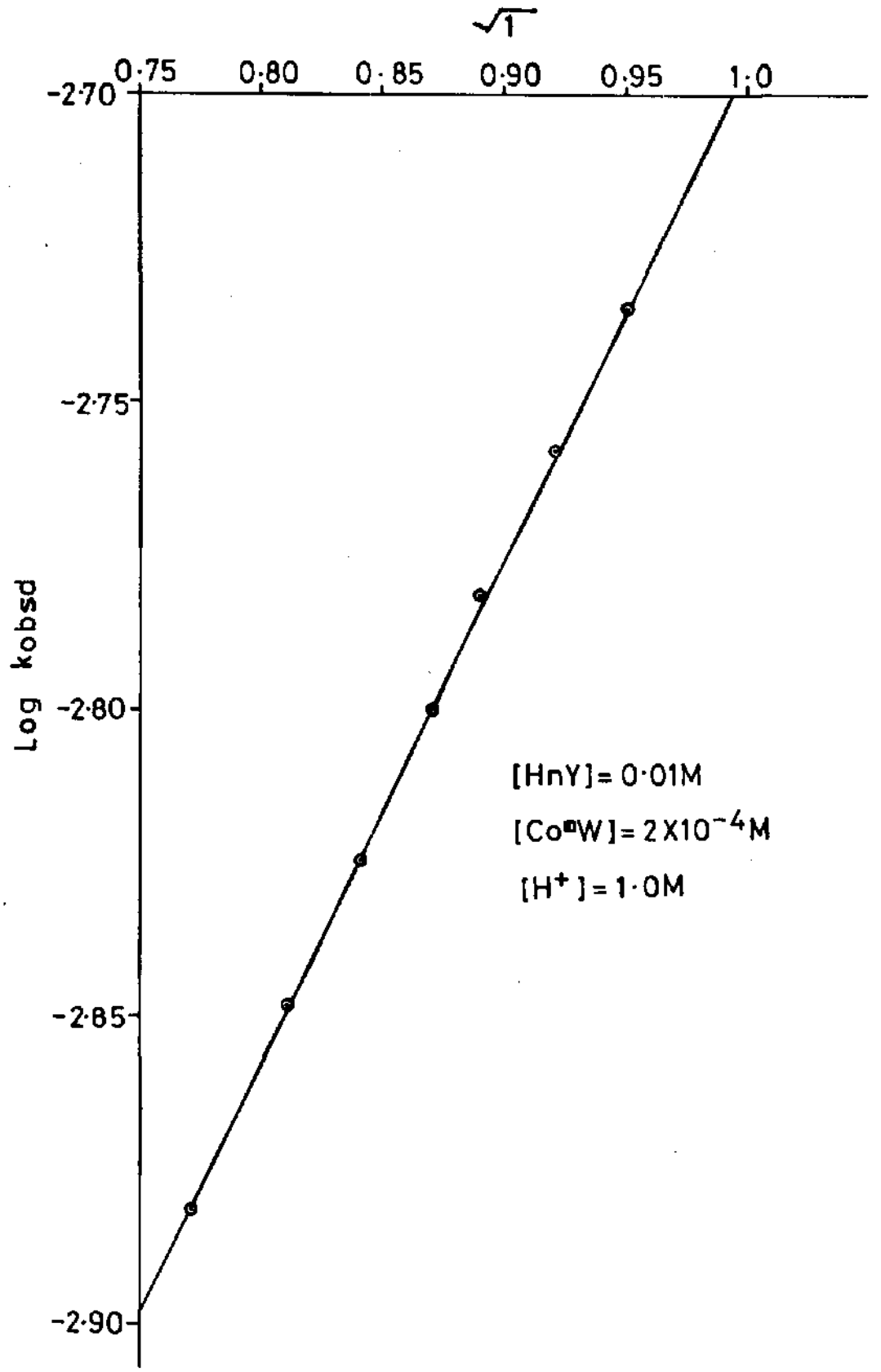


FIG. 4·22 TYPICAL PLOT OF Log kobsd VERSUS $\sqrt{I}$ FOR THE REDOX REACTIONS OF Co^{III}W AND COPLEXONE

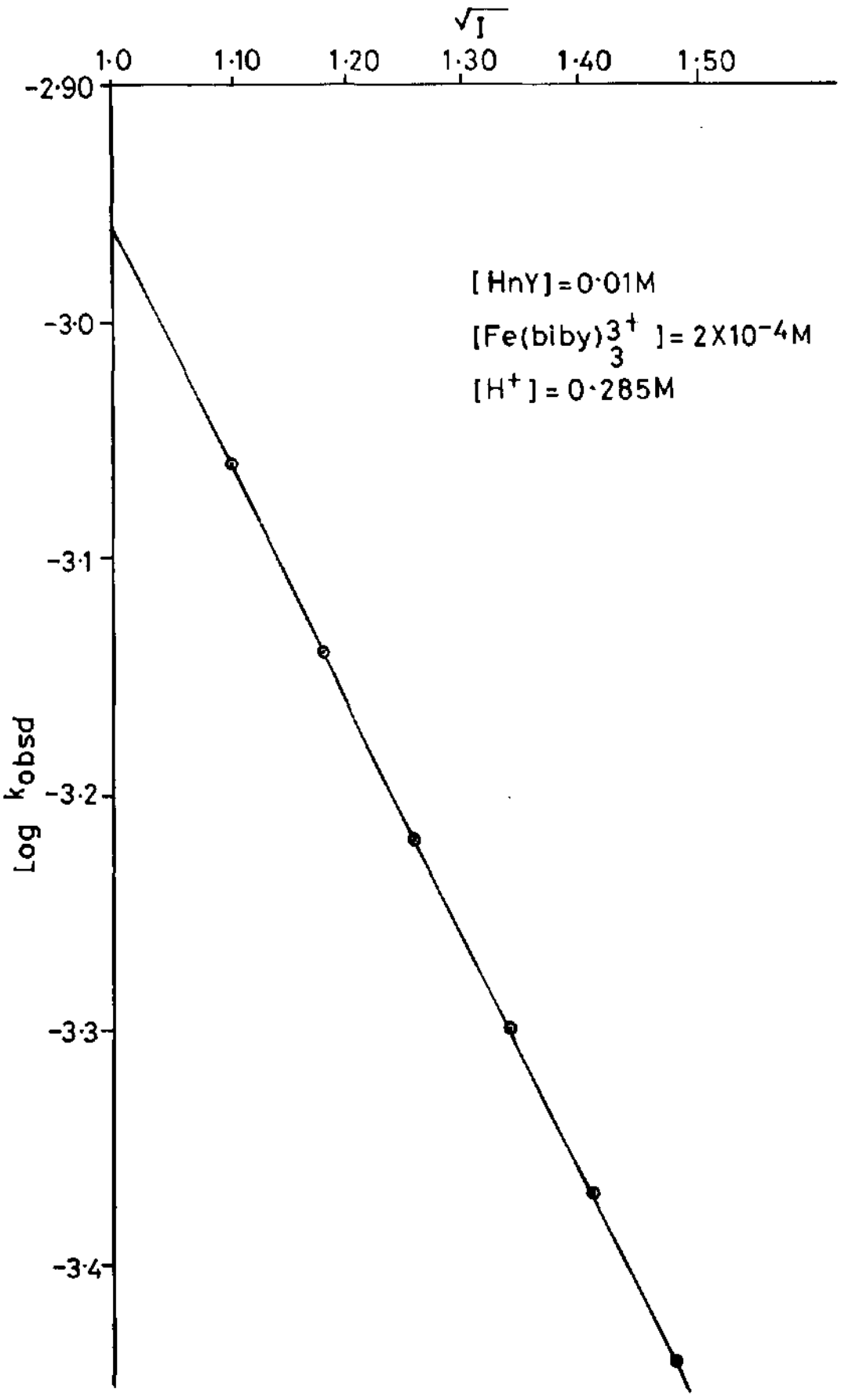


FIG. 4·23 TYPICAL PLOT OF Log k_{obsd} VERSUS $\sqrt{I}$ FOR THE REDOX REACTIONS OF Fe(bipy)$_3^{3+}$ AND COMPLEXONE

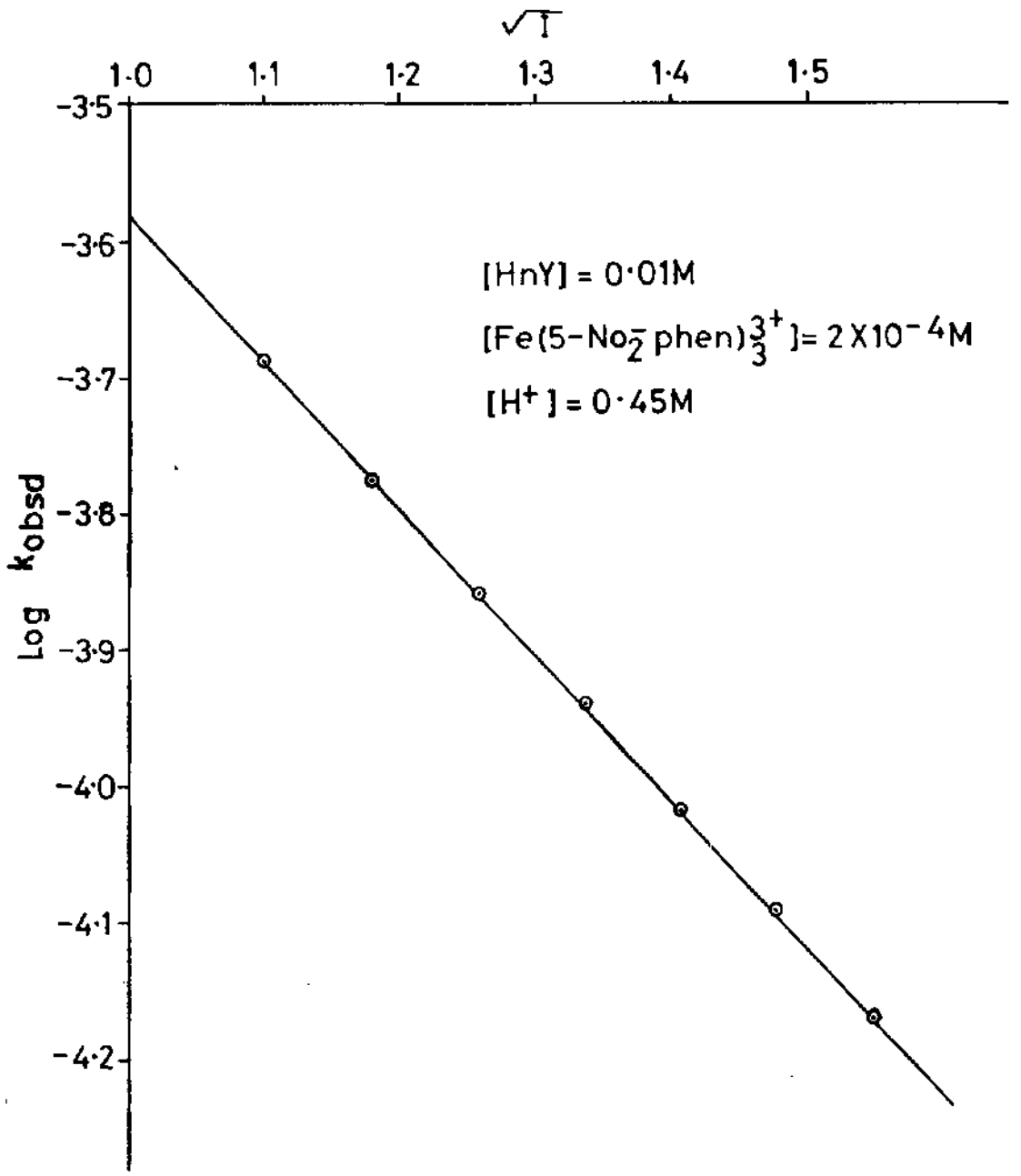


FIG. 4-24 TYPICAL PLOT OF Log k_{obsd} VERSUS $\sqrt{I}$ FOR THE REDOX REACTIONS OF $Fe(5\text{-}NO_2\text{-}phen)^{3+}$ AND COMPLEXONE

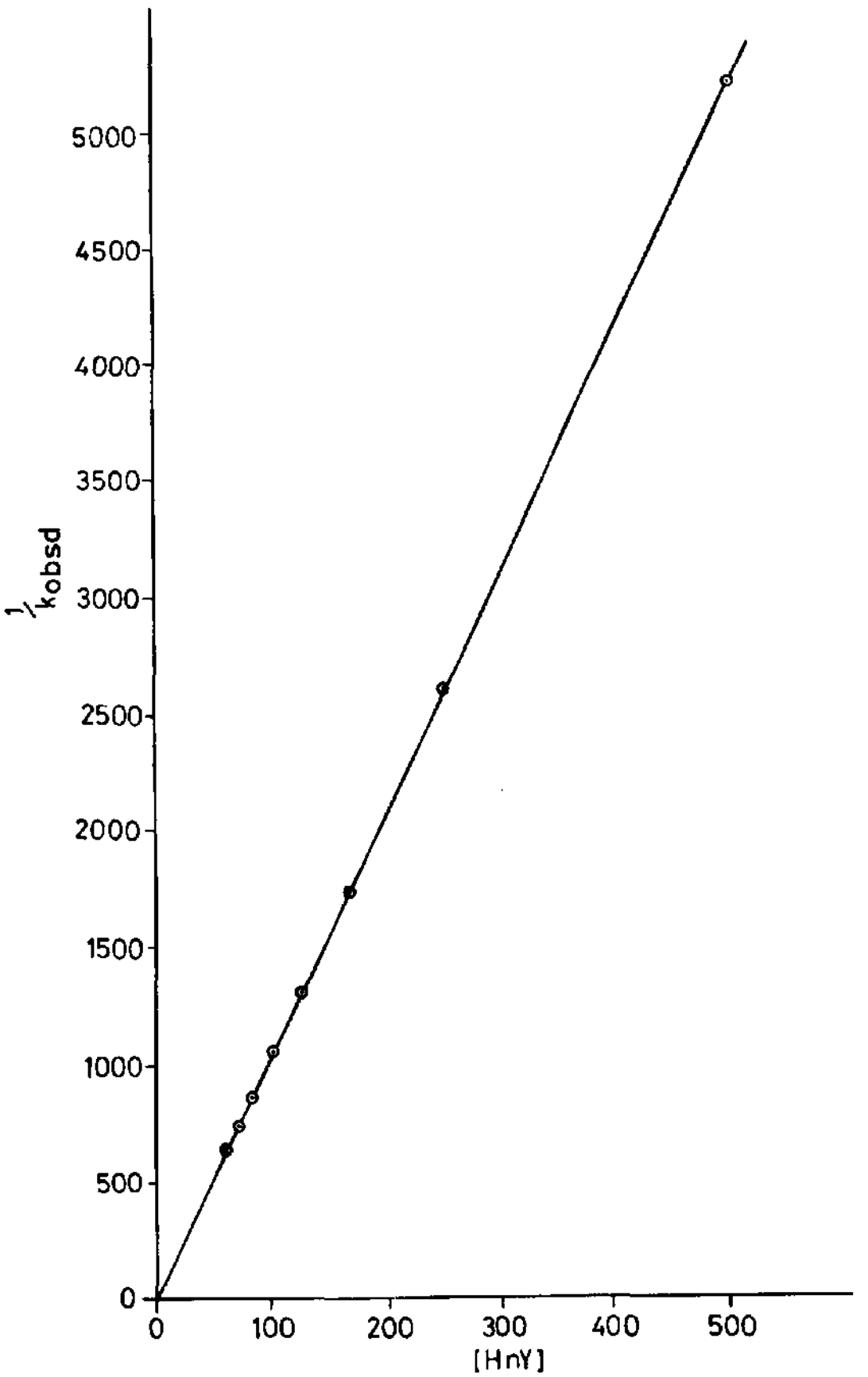


FIG. 4·25 TYPICAL MICHAELIS–MENTEN'S PLOT FOR THE REACTIONS OF $Co^{III}W$ AND COMPLEXONE

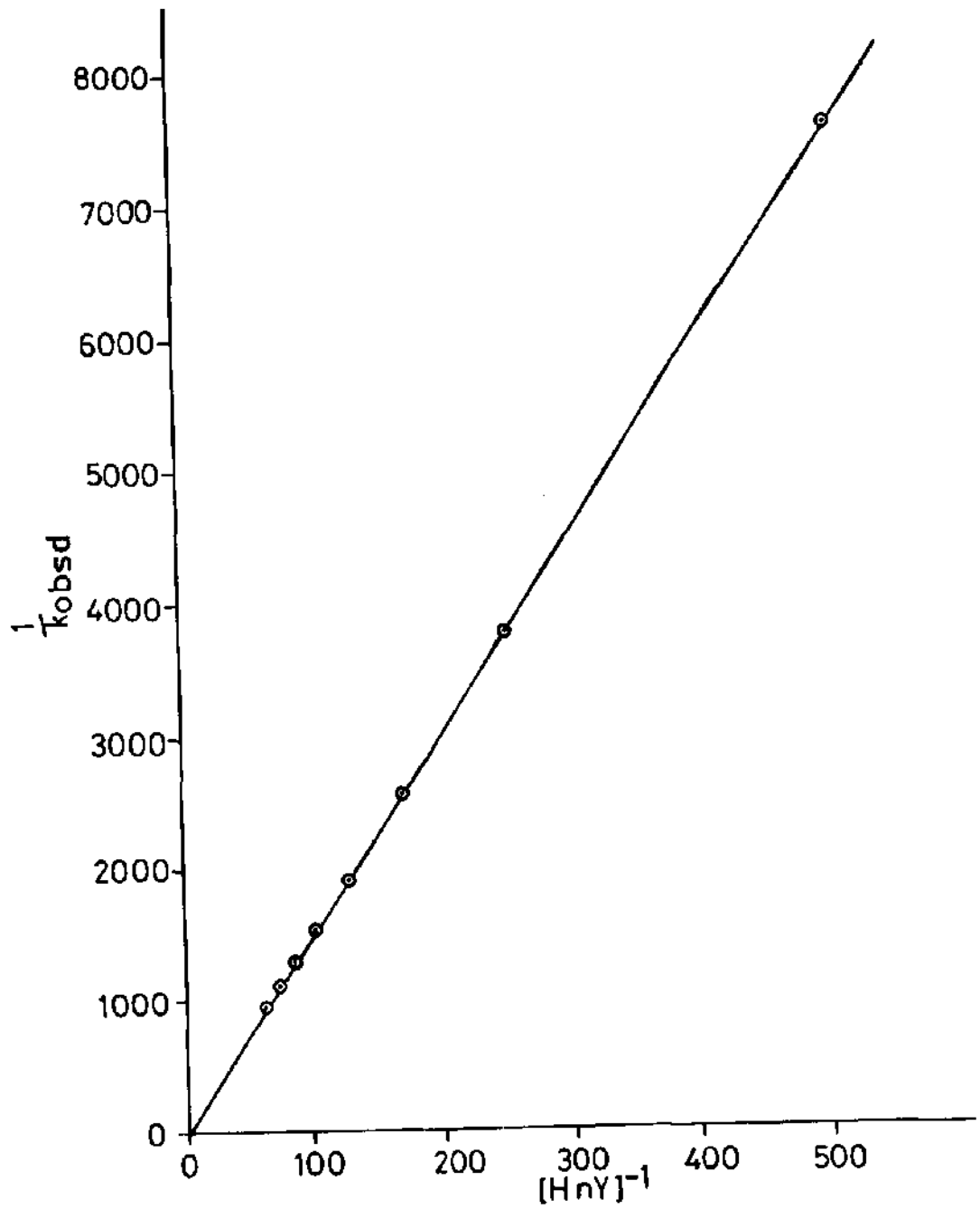


FIG. 4·26 TYPICAL MICHAELIS–MENTEN'S PLOT FOR THE REACTIONS OF $Fe(bipy)_3^{3+}$ AND COMPLEXONE

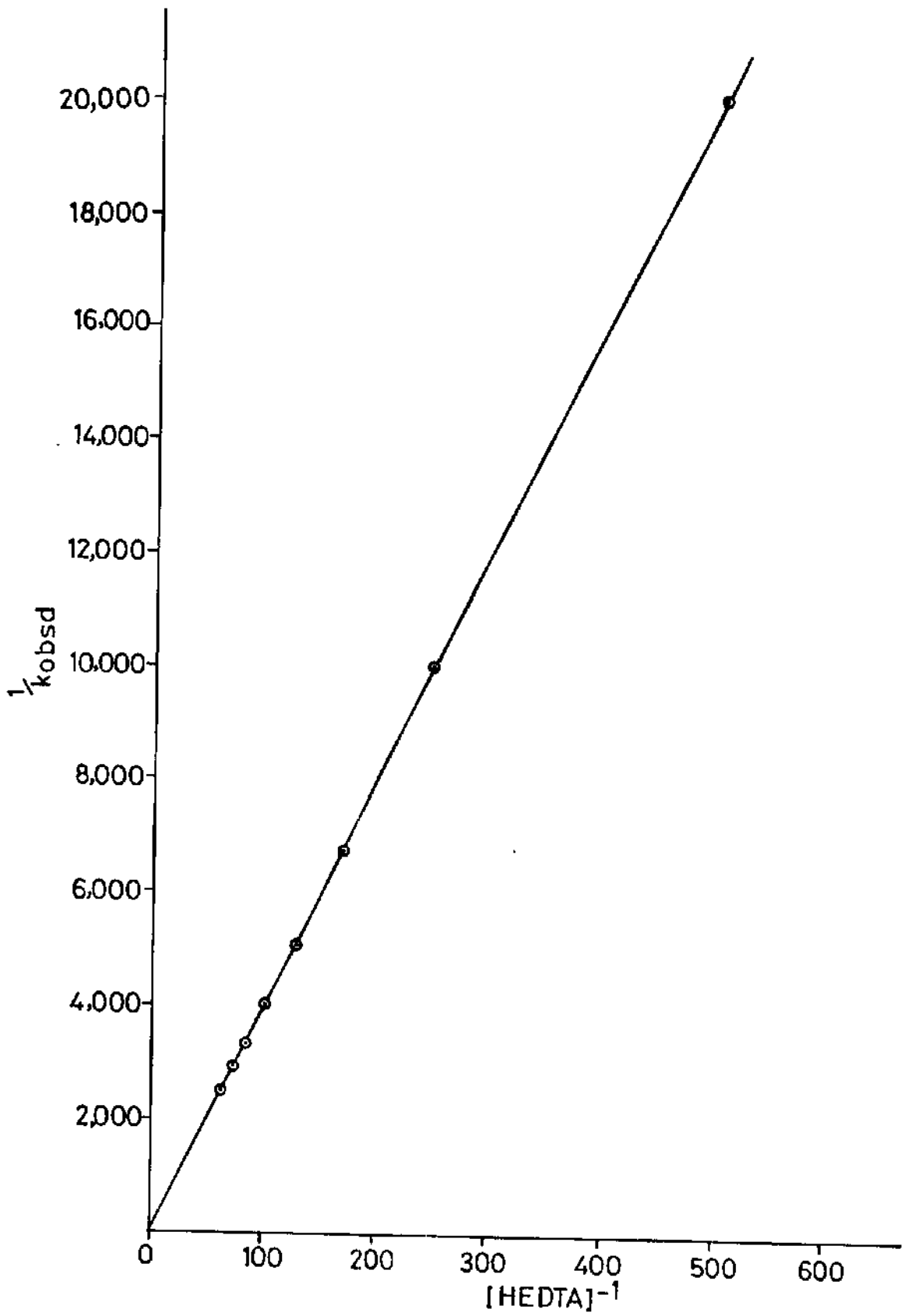


FIG 4·27 TYPICAL MICHAELIS–MENTEN'S PLOT FOR THE REACTIONS OF $Fe(5\text{-}No_2\text{-}Phen)_3^{3+}$ AND COMPLEXONE

where, k_{obsd} = rate constant for the overall reaction

$[E^o]$ = Total catalyst concentration

K_M = Michaelis-Menten constant

k_1 = rate constant for the break up of an active intermediate into products.

S = substrate (S = H_nY above),

plot of $1/k_{obsd}$ versus $1/[S]$ gives $1/k_1$ as intercept. The zero intercepts, therefore, suggest the absence of intermediate complex formation in the reactions.

4.7 Spectra Measurements

The result of the spectrophotometric measurements displayed in figures (4.31-4.33) show that there is no clear shift in λmax of the oxidant on addition of the substrates. Since no shift in λ_{max} was observed in the present investigations, the formation of intermediate complexes with the oxidants has either to be ruled out or the equilibrium constant for the formation of such complexes must be very small.

4.8 Product Analysis

The spectra of the primary products are shown in (figures 4.34-4.36). Carbondioxide was also one of the products in all the reactions as sufficient effervescence occurred when concentrated solutions of the reductants were reacted with excess oxidant solutions. Formaldehyde was expected as a product but could not be detected. This could be due to its oxidation by the oxidants, since its formation is very slow and could only be detected after a prolonged oxidation by the complexones.

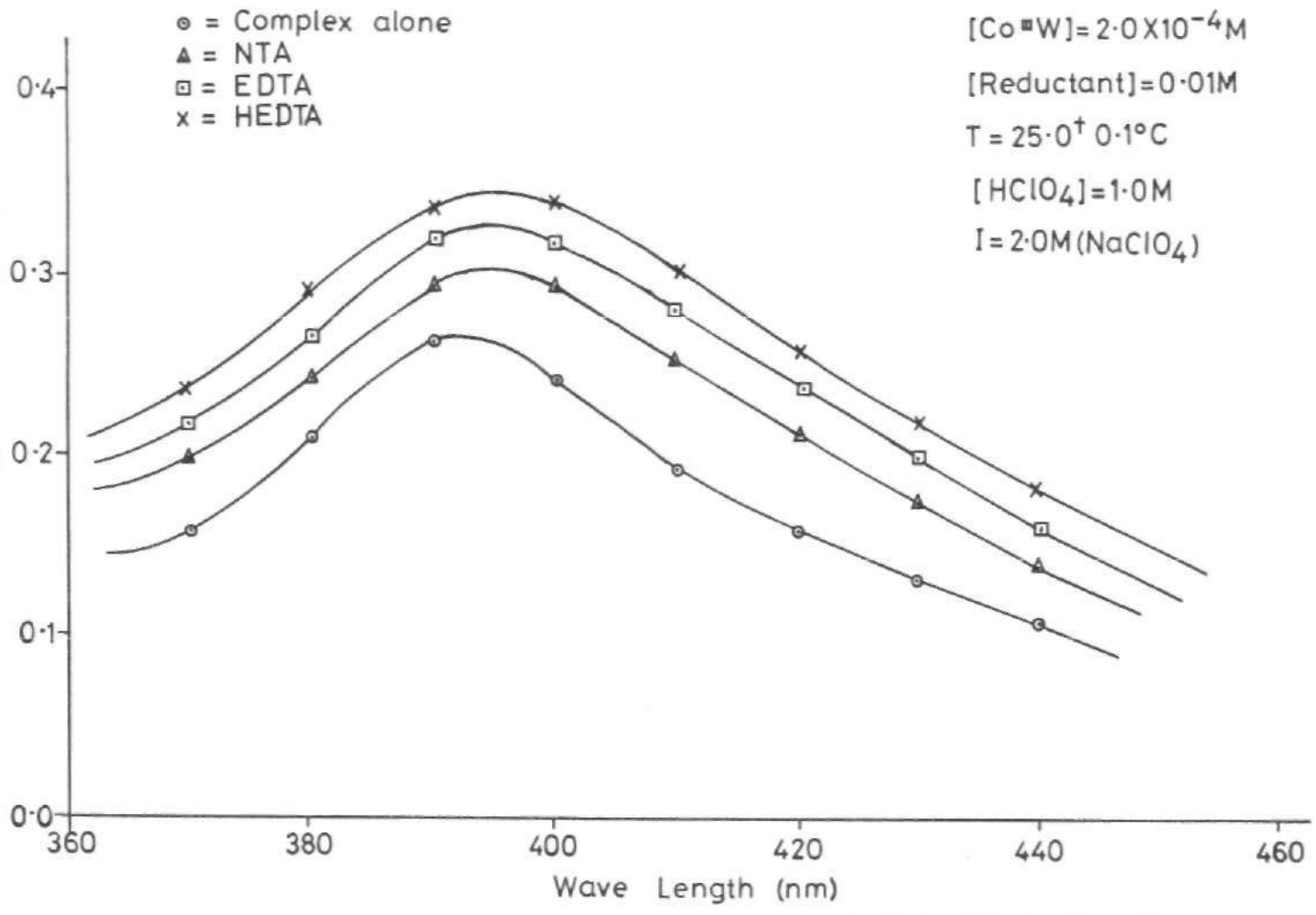


FIG. 4·28 SPECTRA OF Co■W SOLUTIONS AND MIXTURES OF Co■W AND COMPLEXONE SOLUTIONS

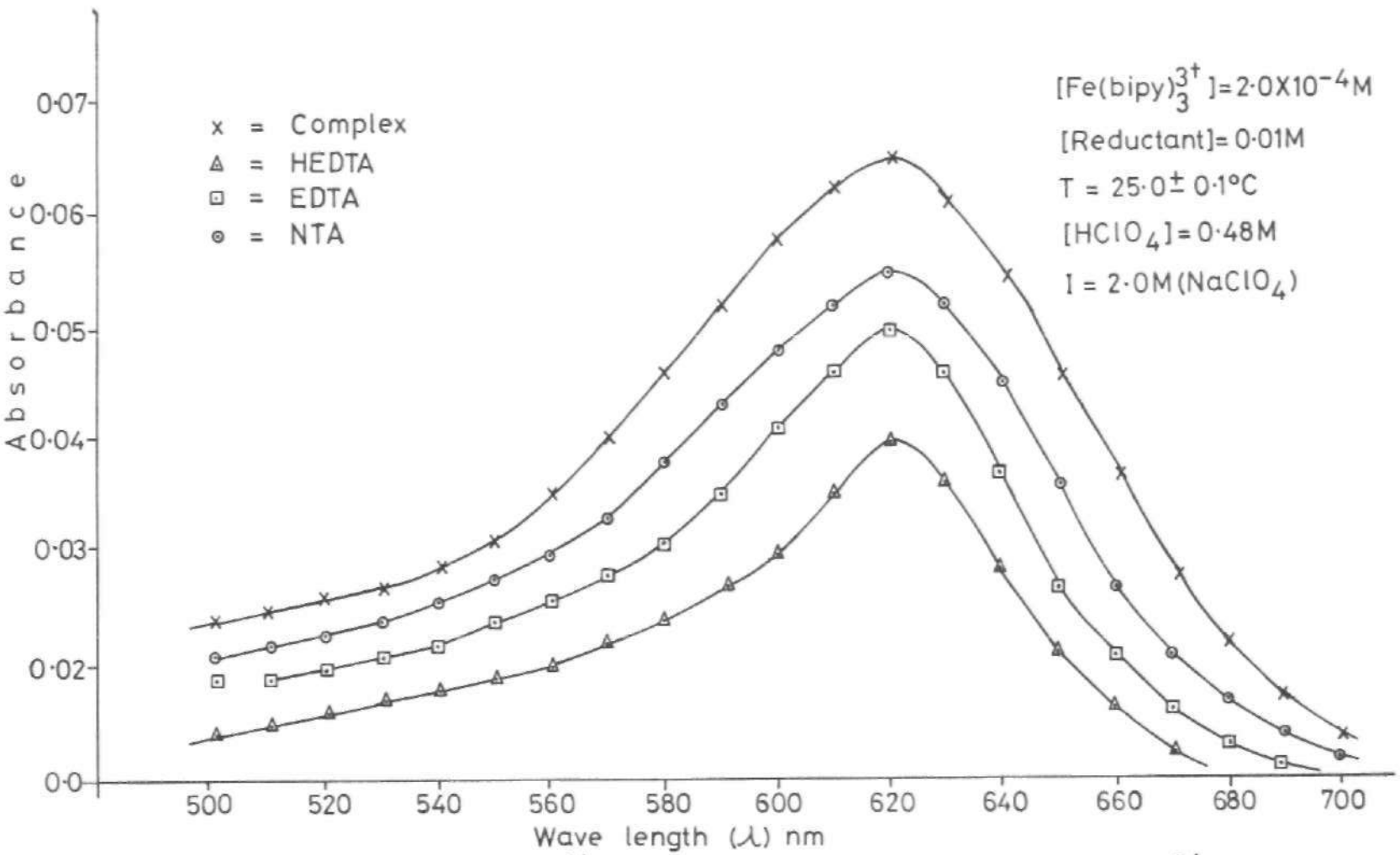


FIG. 4·29 SPECTRA OF Fe(bipy)$_3^{3+}$ SOLUTION AND MIXTURES OF Fe(bipy)$_3^{3+}$ AND COMPLEXONE SOLUTIONS

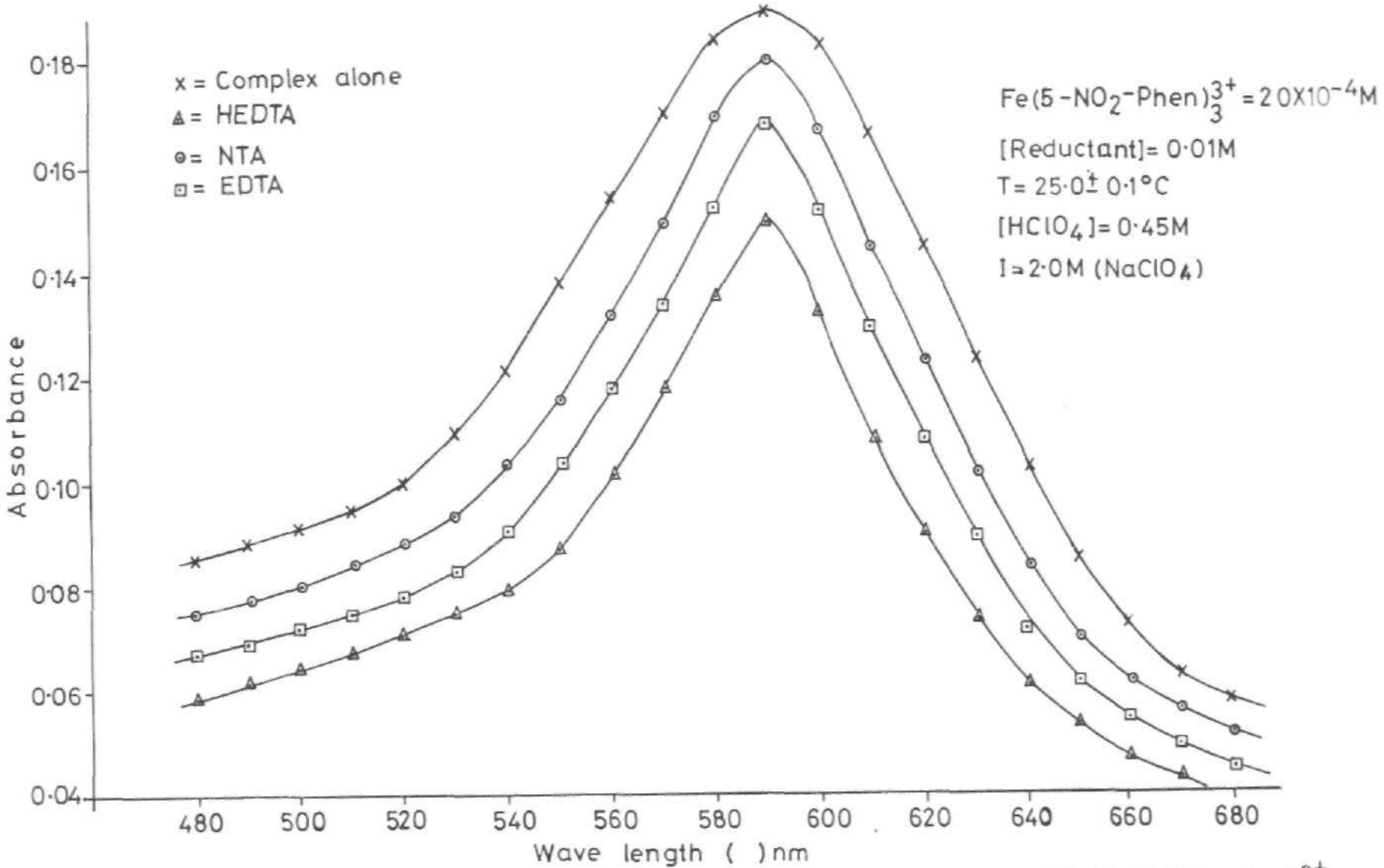


FIG. 4·30 SPECTRA OF $Fe(5-NO_2-phen)_3^{3+}$ SOLUTIONS AND MIXTURES OF $Fe(5-NO_2-phen)_3^{3+}$ AND COMPLEXONE SOLUTIONS

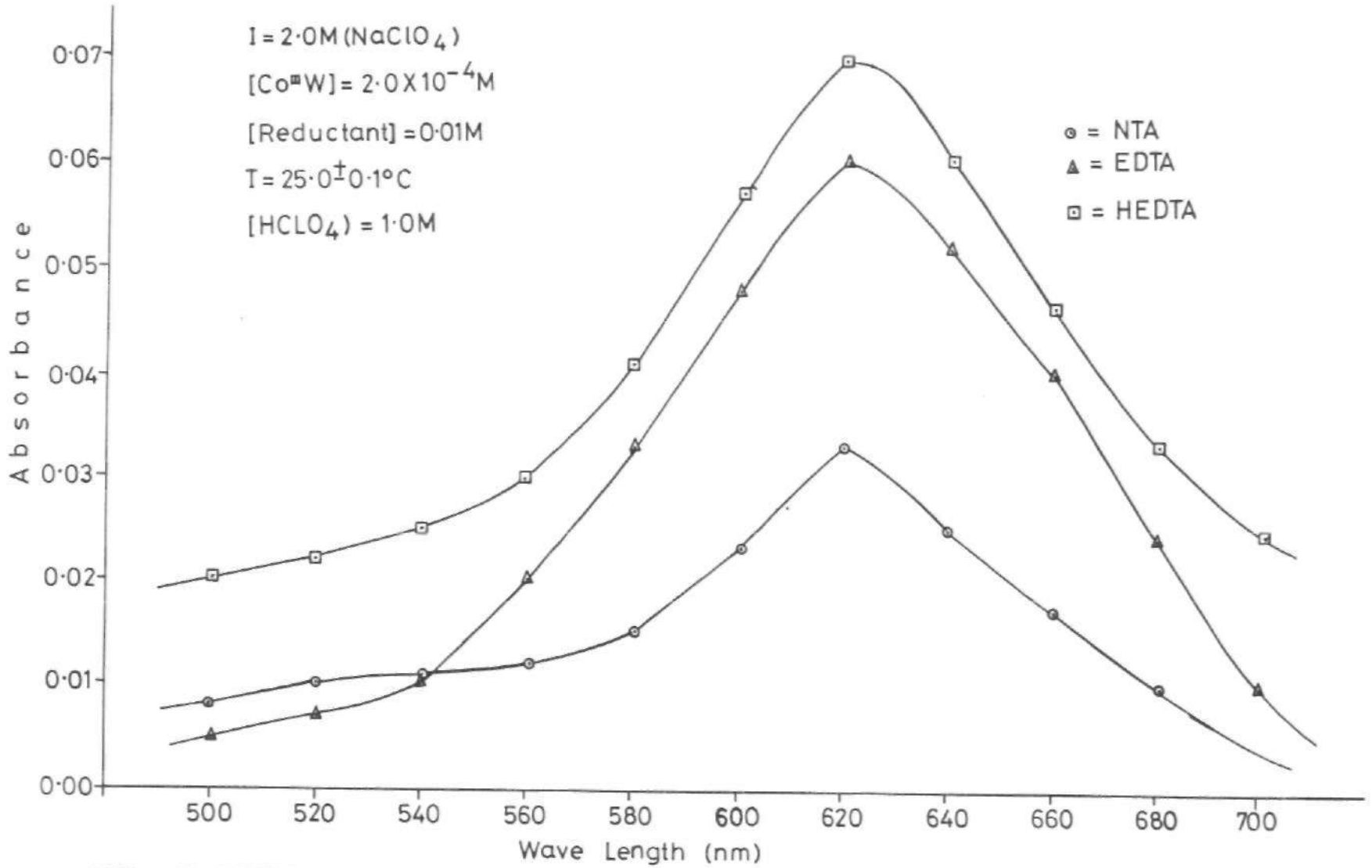


FIG. 4·31 SPECTRA OF THE PRODUCTS FOR THE REDOX REACTIONS OF $Co^{III}W$ AND COMPLEXONE

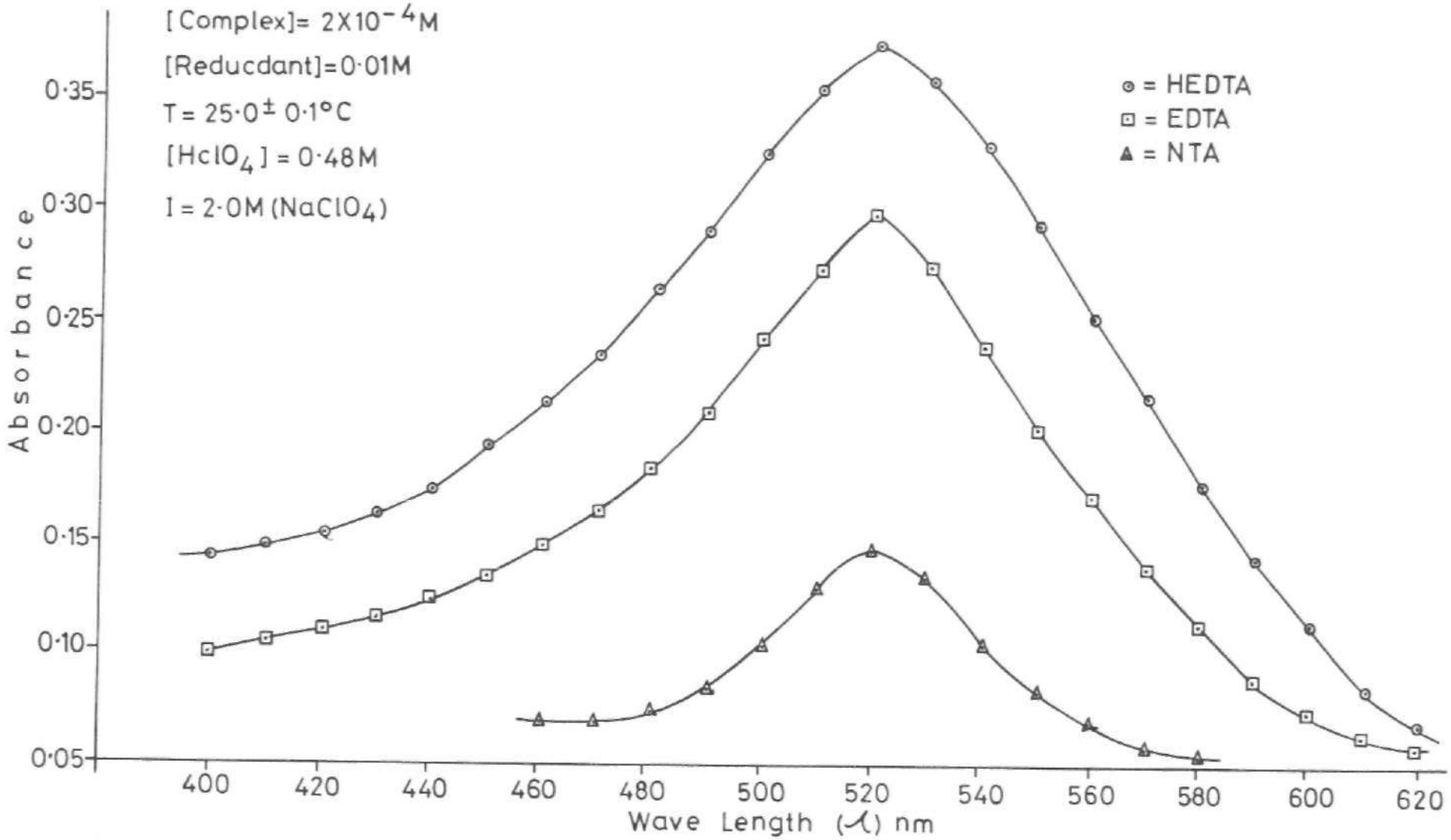


FIG. 4·32 SPECTRA OF THE PRODUCTS FOR THE REDOX REACTIONS OF $Fe(bipy)_3^{3+}$ AND COMPLEXONE

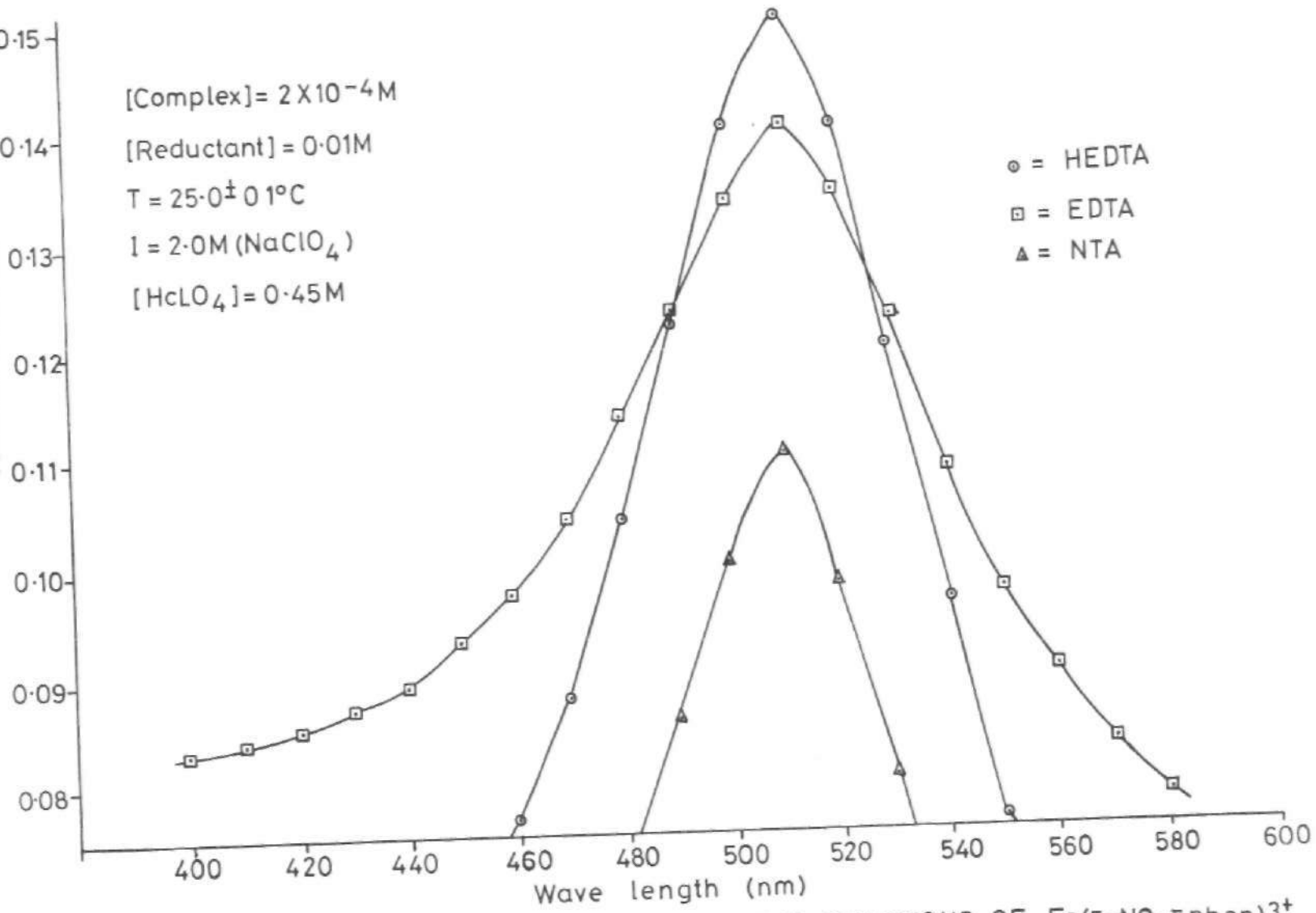


FIG. 4·33 SPECTRA OF THE PRODUCTS FOR THE REACTIONS OF $Fe(5\text{-}NO_2^-phen)_3^{3+}$ AND COMPLEXONE

Table 4.1

Pseudo-first order and second-order rate constants for the reaction between $Co^{III}W$ and HEDTA.

$[Co^{III}W] = 2.0 \times 10^{-4}M$, T = 25.0 ± 0.1°C, λmax = 400nm

10^3[HEDTA], M	$[H^+]$, M	I($NaClO_4$), M	$10^3 k_{obsd}, s^{-1}$	$10^2 k_2, M^{-1}s^{-1}$
2.0	1.0	2.0	0.19	9.60
4.0	1.0	2.0	0.38	9.57
6.0	1.0	2.0	0.58	9.60
8.0	1.0	2.0	0.76	9.55
10.0	1.0	2.0	0.95	9.58
12.0	1.0	2.0	1.15	9.60
14.0	1.0	2.0	1.35	9.57
16.0	1.0	2.0	1.53	9.56
10.0	0.2	2.0	4.40	44.0
10.0	0.4	2.0	2.26	22.6
10.0	0.6	2.0	1.53	15.3
10.0	0.8	2.0	1.17	11.7
10.0	1.0	2.0	0.94	9.43
10.0	1.2	2.0	0.78	7.83
10.0	1.4	2.0	0.67	6.74
10.0	1.6	2.0	0.61	6.10
10.0	1.0	0.60	1.29	12.9
10.0	1.0	0.65	1.39	13.9
10.0	1.0	0.70	1.48	14.8
10.0	1.0	0.75	1.56	15.6
10.0	1.0	0.80	1.67	16.7
10.0	1.0	0.85	1.76	17.6
10.0	1.0	0.90	1.85	18.5
10.0	1.0	1.0	1.99	19.9

Table 4.2

Pseudo-first order and second-order rate constants for the reaction of $Co^{III}W$ and EDTA. $[Co^{III}W] = 2.0 \times 10^{-4}$W, T = 25.0 ± 0.1°C, λmax = 400nm

10^3[EDTA],M	$[H^+]$,M	I($NaClO_4$),M	$10^3 k_{obsd}$,s^{-1}	$10^2 k_2$,$M^{-1}s^{-1}$
2.0	1.0	2.0	0.17	8.45
4.0	1.0	2.0	0.35	8.83
6.0	1.0	2.0	0.51	8.47
8.0	1.0	2.0	0.68	8.51
10.0	1.0	2.0	0.86	8.56
12.0	1.0	2.0	1.00	8.36
14.0	1.0	2.0	1.18	8.44
16.0	1.0	2.0	1.33	8.33
10.0	0.2	2.0	3.88	38.8
10.0	0.4	2.0	2.04	20.4
10.0	0.6	2.0	1.39	13.9
10.0	0.8	2.0	1.07	10.7
10.0	1.0	2.0	0.86	8.58
10.0	1.2	2.0	0.71	7.14
10.0	1.4	2.0	0.62	6.18
10.0	1.6	2.0	0.55	5.54
10.0	1.0	0.60	0.82	8.24
10.0	1.0	0.65	1.00	10.0
10.0	1.0	0.70	1.02	10.2
10.0	1.0	0.75	1.04	10.4
10.0	1.0	0.80	1.05	10.5
10.0	1.0	0.85	1.07	10.7
10.0	1.0	0.90	1.09	10.9
10.0	1.0	1.0	1.12	11.2

Table 4.3

Pseudo-first order and second-order rate constants for the reaction of $Co^{III}W$ and NTA. $[Co^{III}W] = 2.0 \times 10^{-4}M$, T = 25.0 ± 0.1°C, λmax = 400nm.

10^3[NTA],M	[H^+],M	I($NaClO_4$),M	$10^5 k_{obsd}, s^{-1}$	$10^3 k_2, M^{-1}s^{-1}$
2.0	1.0	2.0	0.89	4.45
4.0	1.0	2.0	1.78	4.45
6.0	1.0	2.0	2.69	4.49
8.0	1.0	2.0	3.56	4.45
10.0	1.0	2.0	4.50	4.50
12.0	1.0	2.0	5.22	4.35
14.0	1.0	2.0	6.22	4.44
16.0	1.0	2.0	7.11	4.44
10.0	0.2	2.0	21.1	21.1
10.0	0.4	2.0	10.7	10.7
10.0	0.6	2.0	7.14	7.14
10.0	0.8	2.0	5.47	5.47
10.0	1.0	2.0	4.44	4.44
10.0	1.2	2.0	3.67	3.67
10.0	1.4	2.0	3.17	3.17
10.0	1.6	2.0	2.81	2.81
10.0	1.0	0.60	6.03	6.03
10.0	1.0	0.65	7.59	7.59
10.0	1.0	0.70	8.91	8.91
10.0	1.0	0.75	10.7	10.7
10.0	1.0	0.80	12.0	12.0
10.0	1.0	0.85	14.1	14.1
10.0	1.0	0.95	17.0	17.0
10.0	1.0	1.00	22.4	22.4

Table 4.4

Pseudo-first order and second-order rate constants for the reaction of $Fe(bipy)_3^{3+}$ and HEDTA. $[Fe(bipy)_3^{3+}] = 2.0 \times 10^{-4}M$, $T = 25.0 \pm 0.1^{\circ}C$, $\lambda max = 620nm$

10^3[HEDTA].M	[H^+].M	I($NaClO_4$).M	$10^4 k_{obsd}.s^{-1}$	$10^2 k_2.M^{-1}s^{-1}$
2.0	0.25	2.0	1.32	6.85
4.0	0.25	2.0	2.63	6.58
6.0	0.25	2.0	3.95	6.58
8.0	0.25	2.0	5.27	6.58
10.0	0.25	2.0	6.59	6.59
12.0	0.25	2.0	7.92	6.60
14.0	0.25	2.0	9.22	6.58
16.0	0.25	2.0	10.6	6.60
10.0	0.3	2.0	5.43	5.43
10.0	0.4	2.0	3.98	3.98
10.0	0.5	2.0	3.13	3.13
10.0	0.6	2.0	2.57	2.57
10.0	0.7	2.0	2.16	2.16
10.0	0.8	2.0	1.91	1.91
10.0	0.9	2.0	1.70	1.70
10.0	1.0	2.0	1.50	1.50
10.0	0.25	1.0	14.1	14.1
10.0	0.25	1.2	11.6	11.6
10.0	0.25	1.4	10.1	10.1
10.0	0.25	1.6	8.73	8.73
10.0	0.25	1.8	7.52	7.52
10.0	0.25	2.0	6.59	6.59
10.0	0.25	2.2	5.81	5.81
10.0	0.25	2.4	5.11	5.11

Table 5

Pseudo-first order and second-order, rate constants for the reaction of $Fe(bipy)_3^{3+}$ and EDTA. $[Fe(bipy)_3^{3+}] = 2.0 \times 10^{-4}M$, $T = 25.0 \pm 0.1°C$, $\lambda max = 620nm$.

10^3[EDTA],M	$[H^+]$,M	I($NaClO_4$),M	$10^4 k_{obsd}, s^{-1}$	$10^2 k_2, M^{-1}s^{-1}$
2.0	0.29	2.0	0.84	4.22
4.0	0.29	2.0	1.69	4.22
6.0	0.29	2.0	2.53	4.22
8.0	0.29	2.0	3.38	4.22
10.0	0.29	2.0	4.22	4.22
12.0	0.29	2.0	5.06	4.21
14.0	0.29	2.0	5.91	4.22
16.0	0.29	2.0	6.75	4.27
10.0	0.3	2.0	3.89	3.89
10.0	0.4	2.0	3.05	3.05
10.0	0.5	2.0	2.51	2.51
10.0	0.6	2.0	2.11	2.11
10.0	0.7	2.0	1.84	1.84
10.0	0.8	2.0	1.66	1.66
10.0	0.9	2.0	1.50	1.50
10.0	1.0	2.0	1.37	1.37
10.0	0.29	1.0	11.0	11.0
10.0	0.29	1.2	8.71	8.71
10.0	0.29	1.4	7.24	7.24
10.0	0.29	1.6	6.03	6.03
10.0	0.29	1.8	5.01	5.01
10.0	0.29	2.0	4.27	4.27
10.0	0.29	2.2	3.63	3.63
10.0	0.29	2.4	3.09	3.09

Table 4.6

Pseudo-first order and second-order rate constants for the reaction of $Fe(bipy)_3^{3+}$ and NTA.

$[Fe(bipy)_3^{3+}] = 2.0 \times 10^{-4}$M, T = 25.0 ± 0.1°C, λmax = 620nm

10^3[NTA], M	[H^+], M	I($NaClO_4$), M	$10^5 k_{obsd}$, s^{-1}	$10^2 k_2$, $M^{-1}s^{-1}$
2.0	0.25	2.0	2.39	1.17
4.0	0.25	2.0	4.69	1.17
6.0	0.25	2.0	7.00	1.17
8.0	0.25	2.0	9.42	1.19
10.0	0.25	2.0	11.7	1.17
12.0	0.25	2.0	14.1	1.17
14.0	0.25	2.0	16.3	1.17
16.0	0.25	2.0	18.6	1.16
10.0	0.3	2.0	9.95	0.99
10.0	0.4	2.0	7.76	0.78
10.0	0.5	2.0	6.35	0.63
10.0	0.6	2.0	5.41	0.54
10.0	0.7	2.0	4.71	0.47
10.0	0.8	2.0	4.27	0.43
10.0	0.9	2.0	3.85	0.39
10.0	1.0	2.0	3.49	0.35
10.0	0.25	1.0	30.0	3.0
10.0	0.25	1.2	24.0	2.4
10.0	0.25	1.4	20.0	2.0
10.0	0.25	1.6	16.7	1.67
10.0	0.25	1.8	13.9	1.39
10.0	0.25	2.0	11.7	1.17
10.0	0.25	2.2	10.0	1.0
10.0	0.25	2.4	8.41	0.84

Table 4.7

Pseudo-first order and second-order rate constants for the reaction of $Fe(5\text{-}NO_2\text{-}phen)_3^{3+}$ and HEDTA.

$[Fe(5\text{-}NO_2\text{-}phen)_3^{3+}] = 2.0 \times 10^{-4}$M, T = 25.0 ± 0.1°C, λmax = 595nm

10^3[HEDTA].M	[H^+].M	I($NaClO_4$).M	$10^4 k_{obsd}.s^{-1}$	$10^2 k_2.M^{-1}s^{-1}$
2.0	0.63	2.0	0.50	2.50
4.0	0.63	2.0	0.99	2.49
6.0	0.63	2.0	1.49	2.49
8.0	0.63	2.0	1.98	2.47
10.0	0.63	2.0	2.49	2.49
12.0	0.63	2.0	3.00	2.50
14.0	0.63	2.0	3.50	2.50
16.0	0.63	2.0	4.06	2.53
10.0	0.7	2.0	2.21	2.21
10.0	0.8	2.0	1.93	1.93
10.0	0.9	2.0	1.70	1.70
10.0	1.0	2.0	1.48	1.48
10.0	1.1	2.0	1.33	1.33
10.0	1.2	2.0	1.20	1.20
10.0	1.3	2.0	1.10	1.10
10.0	1.4	2.0	1.00	1.00
10.0	0.63	1.0	4.76	4.76
10.0	0.63	1.2	4.07	4.07
10.0	0.63	1.4	3.60	3.60
10.0	0.63	1.6	3.16	3.16
10.0	0.63	1.8	2.78	2.78
10.0	0.63	2.0	2.49	2.49
10.0	0.63	2.2	2.23	2.23
10.0	0.63	2.4	1.99	1.99

Table 4.8

Pseudo-first order and second-order rate constants for the reaction of $Fe(5\text{-}NO_2\text{-}phen)_3^{3+}$ and EDTA.

$[Fe(5\text{-}NO_2\text{-}phen)_3^{3+}] = 2.0 \times 10^{-4}M$, T = 25.0 ± 0.1°C, λmax = 595nm

10^3[EDTA],M	[H^+],M	I($NaClO_4$),M	$10^4 k_{obsd}, s^{-1}$	$10^2 k_2, M^{-1}s^{-1}$
2.0	0.7	2.0	0.32	1.61
4.0	0.7	2.0	0.64	1.60
6.0	0.7	2.0	0.97	1.62
8.0	0.7	2.0	1.31	1.63
10.0	0.7	2.0	1.60	1.60
12.0	0.7	2.0	1.94	1.62
14.0	0.7	2.0	2.28	1.63
16.0	0.7	2.0	2.59	1.62
10.0	0.7	2.0	1.60	1.60
10.0	0.8	2.0	1.45	1.42
10.0	0.9	2.0	1.32	1.32
10.0	1.0	2.0	1.20	1.20
10.0	1.1	2.0	1.11	1.11
10.0	1.2	2.0	1.02	1.02
10.0	1.3	2.0	0.95	0.95
10.0	1.4	2.0	0.89	0.89
10.0	0.7	1.0	4.22	4.22
10.0	0.7	1.2	3.3	3.33
10.0	0.7	1.4	2.77	2.77
10.0	0.7	1.6	2.29	2.29
10.0	0.7	1.8	1.88	1.88
10.0	0.7	2.0	1.60	1.60
10.0	0.7	2.2	1.33	1.33
10.0	0.7	2.4	1.15	1.15

Table 4.9

Pseudo-first order and second-order rate constants for the reaction of $Fe(5\text{-}NO_2\text{-}phen)_3^{3+}$ with NTA. [$Fe(5\text{-}NO_2\text{-}phen)_3^{3+}$ = 2.0 x 10^{-4}M, T = 25.0 ± 0.1°C, λmax = 595nm

10^3[NTA], M	[H^+], M	I($NaClO_4$), M	$10^5 k_{obsd}, s^{-1}$	$10^3 k_2, M^{-1}s^{-1}$
2.0	0.45	2.0	1.92	9.59
4.0	0.45	2.0	3.83	9.58
6.0	0.45	2.0	5.75	9.58
8.0	0.45	2.0	7.67	9.59
10.0	0.45	2.0	9.58	9.58
12.0	0.45	2.0	11.5	9.58
14.0	0.45	2.0	13.4	9.54
16.0	0.45	2.0	15.4	9.60
10.0	0.70	2.0	2.60	2.60
10.0	0.80	2.0	2.29	2.29
10.0	0.90	2.0	2.04	2.04
10.0	1.00	2.0	1.80	1.08
10.0	1.10	2.0	1.64	1.64
10.0	1.20	2.0	1.50	1.50
10.0	1.30	2.0	1.40	1.40
10.0	1.40	2.0	1.26	1.26
10.0	0.45	1.0	26.3	26.3
10.0	0.45	1.2	20.6	20.6
10.0	0.45	1.4	16.6	16.6
10.0	0.45	1.6	13.8	13.8
10.0	0.45	1.8	11.5	11.5
10.0	0.45	2.0	9.58	9.58
10.0	0.45	2.2	8.13	8.13
10.0	0.45	2.4	6.76	6.76

Table 4.10

(a) Activation parameters for the reactions at constant [H^+]

Oxidant	Reductant	Ea, kj/mol	ΔH, kj/mol	ΔS, j/molK^{-1}	ΔG, Kj/mol
$Co^{III}W$,	HEDTA	21.05	18.58	-308.19	110.42
"	EDTA	22.20	19.73	-309.08	111.83
"	NTA	16.33	13.85	-334.86	113.64
$Fe(bipy)_3^{3+}$					
	HEDTA	33.49	31.02	-318.14	125.83
"	EDTA	21.30	18.83	-322.09	114.81
"	NTA	15.46	12.98	-334.54	112.68
$Fe(5\text{-}NO_2\text{-}phen)_3^{3+}$					
	HEDTA	32.92	30.44	-322.3	126.49
"	EDTA	20.58	18.10	-326.49	115.39
"	NTA	25.26	22.79	-341.68	124.61

(b) Activation parameters for the reactions at varied [H^+]

Oxidant	Reductant	Ea, Kj/mol	ΔH, kj/mol	ΔS, j/molk^{-1}	ΔG, kj/mol
$Co^{III}W$,	HEDTA	22.97	20.49	-308.90	112.55
"	EDTA	22.97	20.49	-309.96	112.86
"	NTA	18.18	15.71	-334.91	115.51
$Fe(bipy)_3^{3+}$	HEDTA	31.91	29.43	-320.72	125.0
"	EDTA	22.97	20.49	-326.05	117.66
	NTA	16.91	14.43	-338.64	115.34
$Fe(5\text{-}NO_2\text{-}phen)_3^{3+}$					
	HEDTA	33.49	31.02	-320.99	126.67
"	EDTA	22.97	20.49	-326.88	117.90
"	NTA	20.67	18.19	-341.37	119.92

Chapter 5

5.0 Discussion

5.1 $Co^{III}W$-H_nY Reactions

(H_nY = HEDTA, EDTA or NTA)

Studies of the stoichiometries of the oxidation of HEDTA or EDTA do not always give definite results. For example, the ratio n(oxidation/reduction) for the reaction of Np(VI) and EDTA was reported to be 6 (Shastri and Amis, 1968), 4 in the oxidation of EDTA by $Ag(OH)_4^-$ (Sun, Kirchenbaum and Kouadio, 1991) and 8 for the reaction of EDTA with MnO_4^- (Palei and Udal'tsona, 1960). A wide range of values of 'n' is also possible when the stoichiometry is carried out as a function of time and acidity (Varadarajan and Hossain, 1979).

In the oxidation of HEDTA and EDTA by $Co^{3+}_{(aq)}$, the value of 'n' was given as two in the rate law, (Varadarajan and Hossain, 1979). Similar 2:1 (oxidant/reductant) stoichiometry has been reported for the oxidation of some organic substrates by $Co^{III}W$, (McAuley, 1977; Banerjee *et al* 1986; 1987). Since the kinetic studies of the present work were conducted under pseudo-first order conditions with H_nY in large excess, 2:1 (oxidant:reductant) stoichiometry is probably maintained throughout the present study, (equation 4.1).

In the reaction (4.1), CO_2 was identified qualitatively, while the appearance of an absorption peak maximum at 625nm (Anijad, Braddock and McAuley, 1977) confirmed the formation of

$Co^{III}W$. The occurrence of CO_2 product was also reported in other reactions of HEDTA and EDTA (Varajaradan and Hossian, 1979; Amis and Shastri, 1968).

Plots of k_{obsd} versus $[H_nY]$ display the first-order dependence on $[H_nY]$ with no significant intercept, showing lack of any appreciable kinetic evidence for more than one kinetic pathway. At constant $[H^+]$, the reaction may therefore be represented by the rate equation (5.1)

$$-\frac{d[Co^{III}W]}{dt} = 2k_2[Co^{III}W][H_nY] \quad \ldots\ldots\ldots \quad 5.1$$

where 'n' in H_nY is the number of hydrogen atoms present per molecule. At $[H^+]$ = 1.0M, I = 2.0M ($NaClO_4$) and T = 25.0 ± 0.1°C, the average value of the second-order rate constant, k_2 = (9.57 ± 0.24) x $10^{-2}M^{-1}s^{-1}$, (4.45 ± 0.01) x $10^{-2}M^{-1}s^{-1}$ and (8.49 ± 0.20) x $10^{-3}M^{-1}s^{-1}$, for the reactions between $Co^{III}W$ and HEDTA, EDTA and NTA respectively.

In this study, the rate of oxidation of H_nY exhibits a first-order inverse dependence on $[H^+]$ in each case and the redox process seems to occur by only the acid-dependence pathway, since the plot of k_H versus $[H^+]^{-1}$ shows no significant intercept. Thus, the rate equation for the reactions is given by,

$$-\frac{d[Co^{III}W]}{dt} = 2b[H^+]^{-1}[Co^{III}W][H_nY] \quad \ldots\ldots\ldots \quad 5.2$$

At 25.0 ± 0.1°C, 'b' has been calculated to be 8.8 x $10^{-4}Ms^{-1}$, 7.50 x $10^{-4}Ms^{-1}$ and 4.20 x $10^{-4}Ms^{-1}$ for the reaction of HEDTA, EDTA and NTA respectively with $Co^{III}W$. The form of acid-dependence obtained in this work is similar to that obtained by Ayoko and Olatunji, (1983) in the oxidation of glutathione by $Co^{III}W$, and in the reaction of HEDTA and EDTA by other oxidants (Shastri and Amis, 1968; Varadarajan and Hossain, 1979). The inverse $[H^+]$ dependence suggests the existence of an equilibrium step prior to the rate-determining step in which hydrogen ion is one of the products (Wilkins, 1977), and this can only be attributed to the slight ionization of the reductants (i.e H_nY).

The lack of free radical as possible intermediate in these reactions is suggested by the absence of gel formation when acrylamide was introduced into the reaction medium. Therefore an equilibrium involving ion-pair formation between the reacting species most probably exist followed by the electron transfer step. The absence of kinetic and spectrophotometric evidence for intermediate complex formation in these reactions, which was further suggested by the absence of any significant intercept in the Michaelis-Menten plots, confirm an earlier suggestion (Amjad, Brodovitch and McAuley, 1977; Baker and McCutcheon, 1956) that the tungstate groups in the $Co^{III}W$ are substitution inert. This implies that a direct bond between the Co^{III} centre and the reductants can be excluded and the reactions occurring most probably by the outer-sphere mechanism.

The positive salt effect observed in this work suggest the involvement of ions of the same charges in the activated complex, further suggesting that at [H^+] = 1.0M, the reductants (H_nY) were in the ionized form during the redox reaction (Shastri and Amis, 19680.

Activation parameters such as ΔH^*, ΔS^* etc seem to have no direct relationship to the type of mechanism occurring in a reaction, (Wilikins, 1977). However, such information could shed some light in support or against a particular mechanism, e.g negative value of ΔH^* (or $\Delta H^* = 0$) shows the presence of a precursor complex which is characteristic of the inner-sphere mechanism (Wilkins, 1977). The activation parameters for these reactions shown in table (4.10) are determined using the Arrhenius relationship.

The values obtained for ΔH^* refer mostly to the strength of the coordination bonds between the metal and the ligands, since only the initial stages of the reactions have been kinetically studied. It is significant that in these reactions the free energy changes are very similar and a mutual compensation of free energies have been maintained by changes in entropies and enthalpies of activation. However, the enthalpies of activation in these reactions are lower than those of the corresponding reactions of the reductants with aquo cobaltic ion, table (5.1). This is because unlike in $Co^{3+}_{(aq)}$, spin-inversion is not expected in the reduction of cobalt atom in $Co^{III}W(e^3t_2^3)$ to

$Co^{III}W(e^4t_2^3)$, thus the lower energies of activation.

Since the values of pseudo-first order rate constants in the same range of acidity are comparable and their stoichiometries and oxidation products are similar, it is reasonable to propose identification mechanism for the reactions of H_nY with $Co^{III}W$. The following reaction scheme is consistent with the experimental results:

$$H_nY \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_{n-1}Y^- + H^+ \quad \ldots\ldots 5.3$$

$$H_{n-1}Y^- + Co^{III}W \underset{\text{r.d.s}}{\overset{K_{IP}}{\rightleftharpoons}} H_{n-1}Y^-, Co^{III}W \ldots\ldots 5.4$$

$$H_{n-1}Y^-, Co^{III}W + Co^{III}W \underset{\text{fast}}{\overset{K'_{IP}}{\rightleftharpoons}} H_{n-1}Y^-, 2Co^{III}W \ldots\ldots 5.5$$

$$H_{n-1}Y^-, 2Co^{III}W \xrightarrow[\text{fast}]{k_3} 2Co^{II}W + CO_2 \ldots\ldots 5.6$$

From the above scheme, the rate law can be represented by equation (5.7);

$$-\frac{d[Co^{III}W]}{dt} = K_{IP}[Co^{III}W][H_{n-1}Y^-] \ldots\ldots 5.7$$

Applying the steady state approximation to the above scheme equation (5.3-5.6), we obtain,

$$-\frac{d[Co^{III}W]}{dt} = \frac{k_1 K_{IP}[Co^{III}W][H_nY]}{k_{-1}[H^+] + K_{IP}[Co^{III}W]} \quad \ldots\ldots\ldots 5.8$$

Provided $k_{-1}[H^+] >> K_{IP}[Co^{III}W]$, equation (5.8) leads to the empirical rate law identical to equation (5.1) where

$$2k_2 = \frac{k_1 K_{IP}}{k_{-1}[H^+]} \quad \ldots\ldots 5.9$$

The Marcus theory for outer-sphere electron transfer reactions predicts a simple relationship (equation 5.10);

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \quad \ldots\ldots\ldots 5.10$$

$$\log k_{12} = 0.5(\log k_{11} + \log k_{22} + \log f) + 8.46n(\Delta E^{o}) \ldots\ldots 5.11$$

where k_{12} is the cross-reaction rate constant, k_{11} and k_{22} are the self-exchange rate constants and K_{12} is the equilibrium constant. Thus, it is expected that a plot of $\log k_{12}$ versus ΔE^{o} for a reaction would be linear with a slope of $8.46v^{-1}$ at 25°C (Marcus, 1963). But Schuster (1979) also predicted a negative slope of $-16.9v^{-1}$ when the electron transfer is the rate determining step. Therefore, using the theory as a further test for possible outer-sphere nature of the reactions, plots of $\log k_2$

versus E° were made (figures 4.31 - 4.433) using the values in table (5.2). The best lines yielded least mean square slopes of $2.88v^{-1}$, $-2.32v^{-1}$ and $-2.88v^{-1}$ for NTA, HEDTA and EDTA reactions respectively. When allowance is made for the low precision with which the various ΔE° values are known, results show that the rate constant correlate qualitatively with the driving force of the reactions supporting an outer-sphere pathway for these reactions. Such quantitative deviations from Marcus prediction are not uncommon in reactions of polytungstate anions (Dennis et al, 1986; Ayoko, 1990; Rasmussan and Brubakar, 1964; McAuley et al, 1977; Banerjee et al, 1990). Banerjee et al, (1990), suggested that since the central ions in these anions are surrounded by WO_6 octahedra rather than by oxygen atoms, the transfer of electron within the tungstate groups may not be identical to that in the simple oxo anions.

Hence, it appears that, from the substitution inertness of the oxidant as well as the absence of spectrophotometric and kinetic evidence for intermediate complex formation in the reactions, that the outer-sphere mechanism is the most likely pathway for the reactions.

5.2 $Fe(LL)_3^{3+}$ - H_nY Reactions

(LL = 2,"2'-bipy or 5-NO_2-phen and H_nY = HEDTA, EDTA or NTA)

Like the $Co^{III}W$ reactions with H_nY, a 2:1 oxidant:reductant ratio has been assumed for these reactions (equation 4.2), the

complexes being one-electron oxidants. The formation of $Fe(LL)_3^{2+}$ in equation (4.2) was confirmed by the appearance of absorption maximum at 522nm and 510nm characteristic of $Fe(bipy)_3^{2+}$ and $Fe(5\text{-}NO_2\text{-}phen)_3^{2+}$ respectively, (Brand and Gullstron, 1952; Moss, Mellon and Smith, 1964).

Kinetic studies of the reactions have shown that the reactions are first-order in both oxidant and reductant in each case as illustrated by equation (5.12).

$$-\frac{dFe(LL)_3^{3+}}{dt} \quad \ldots\ldots\ 2k_2[Fe(LL)_3^{3+}][H_nY] \quad \ldots\ldots\ 5.12$$

The average value of the second-order rate constant, k_2, for the various reactions are as follows;

(a) $Fe(bipy)_3^{3+}$ - HEDTA

$k_2 = (6.62 \pm 0.16) \times 10^{-2}M^{-1}s^{-1}$, at $[H^+] = 0.25M$

$T = 25.0 \pm 0.1^{o}C$, $I = 2.0M$ ($NaClO_4$).

(b) $Fe(bipy)_3^{3+}$ - EDTA

$k_2 = (4.22 \pm 0.10) \times 10^{-2}M^{-1}s^{-1}$, at $[H^+] = 0.29M$

$T = 25.0 \pm 0.1^{o}C$, $I = 2.0M$ ($NaClO_4$)

(c) Fe(bipy) - NTA

$k_2 = (1.17 \pm 0.03) \times 10^{-2}M^{-1}s^{-1}$, at $[H^+] = 0.25M$

$I = 2.0M$ ($NaClO_4$), $T = 25.0 \pm 0.1^{o}C$

(d) $Fe(5\text{-}NO_2\text{-}phen)_3^{3+}$ - HEDTA

$k_2 = (2.49 \pm 0.06) \times 10^{-2} M^{-1}s^{-1}$ at $[H^+] = 0.63M$

$I = 2.0M$ ($NaClO_4$), $T = 25.0 \pm 0.1^oC$.

(e) $Fe(5\text{-}NO_2\text{-}phen)_3^{3+}$ - EDTA

$k_2 = (1.62 \pm 0.04) \times 10^{-2} M^{-1}s^{-1}$, at $[H^+] = 0.70M$

$I = 2.0M$ ($NaClO_4$), $T = 25.0 \pm 0.1^oC$

(f) $Fe(5\text{-}NO_2\text{-}phen)_3^{3+}$ - NTA

$k_2 = (0.96 \pm 0.02) \times 10^{-2} M^{-1}s^{-1}$ at $[H^+] = 0.45M$

$I = 2.0M$ ($NaClO_4$) and $T = 25.0 \pm 0.1^oC$

The rate of reaction in each case was linearly dependent on the $[H^+]^{-1}$ in the range of $[H^+]$ used. Hence, as a function of acidity, the rate law is given by equation (5.13);

$$-\frac{d[Fe(LL)_3^{3+}]}{dt} = 2b[H^+]^{-1}[Fe(LL)_3^{3+}][H_nY] \quad .... \quad 5.13$$

The fact that no significant intercept was observed in the plots of k_H versus $[H^+]^{-1}$ suggests that the reaction probably occur by only the acid-dependent pathway. At 25.0 ± 0.1°C, 'b' has been calculated to be $1.69 \times 10^{-4} Ms^{-1}$, $1.08 \times 10^{-4} Ms^{-1}$ and $0.28 \times 10^{-4} Ms^{-1}$ for the reactions between $Fe(bipy)_3^{3+}$ and HEDTA, EDTA and NTA respectively, and $1.01 \times 10^{-4} Ms^{-1}$, $1.90 \times 10^{-4} Ms^{-1}$ and $0.19 \times$

$10^{-4}Ms^{-1}$ for the reactions between $Fe(5\text{-}NO_2\text{-}phen)_3^{3+}$ and HEDTA, EDTA and NTA respectively. The form of acid-dependence obtained in this work was also obtained in the oxidation of other substrates by $Fe(phen)_3^{3+}$ (Ng and Henry, 1975; Akinyugba et al, 1978). However, there is no specific pattern of acid dependence in the redox reactions of Fe(III)-polypyridine complexes.

The linearity of plots of k_{obsd} versus $[H_nY]$ with no appreciable intercepts suggests only one oxidation pathway for the reactions. The absence of spectrophotometric evidence for intermediate complex formation prior to electron transfer step in the reactions was further supported by the result of Michaelis-Menten plots of $1/k_{obsd}$ versus $[H_nY]^{-1}$, which were linear with zero intercepts.

The activation parameters obtained using Arrhenius relationship shown in table 4.10 are similar for all the reactions, with large negative values of $\Delta S^{\neq}$, suggesting an equilibrium involving ion-pair formation between the reacting ions, (Crammer and Meyer, 1974).

The similarities in the oxidation products of these redox reactions and those of $Co^{III}W$ and H_nY allow for the proposal of the same reaction scheme as follows;

$$H_nY \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_{n-1}Y^- + H^+ \quad \ldots\ldots\ldots 5.14$$

$$H_{n-1}Y^{-} + Fe(LL)_3^{3+} \underset{\text{r.d.s}}{\overset{K_{IP}}{\rightleftharpoons}} H_{n-1}Y^{-},Fe(LL)_3^{3+} \quad \ldots\ldots 5.15$$

$$H_{n-1}Y^{-},Fe(LL)_3^{3+} + Fe(LL)_3^{3+} \underset{\text{fast}}{\overset{K'_{IP}}{\rightleftharpoons}} H_{n-1}Y^{-},2Fe(LL)_3^{3+} \quad \ldots. 5.16$$

$$H_{n-1}Y^{-},2Fe(LL)_3^{3+} \xrightarrow[\text{fast}]{k_3} 2Fe(LL)_3^{2+} + CO_2 + \ldots\ldots 5.17$$

From the above scheme, the rate law can be represented by equation (5.18) with reaction (5.15) being the slowest.

$$-\frac{d[Fe(LL)_3^{3+}]}{dt} = K_{IP}[Fe(LL)_3^{3+}][H_{n-1}Y^{-}] \ldots\ldots 5.18$$

Applying the steady state approximation to the above scheme (5.14-5.17), we obtain,

$$-\frac{d[Fe(LL)_3^{3+}}{dt} = \frac{k_1K_{IP}[Fe(LL)_3^{3+}][H_nY]}{k_{-1}[H^+] + K_{IP}[Fe(LL)_3^{3+}]} \ldots\ldots 5.19$$

Provided that $k_{-1}[H^+] >> K_{IP}[Fe(LL)_3^{3+}$, equation (5.19) leads to the empirical rate law identified to equation (5.12), where

$$2k_2 = \frac{k_1K_{IP}}{k_{-1}[H^+]} \quad \ldots\ldots 5.20$$

Attempt was also made to interprete the results interms of Marcus cross correlation, (Marcus, 1963) using equation (5.11).

However, the vaules of $2.88v^{-1}$, $-2.32v^{-1}$ and $-2.88v^{-1}$ obtained for NTA, HEDTA and EDTA reactions respectively, as the slopes of plots of $\log k_{21}$ versus E^{o}, qualitatively correlate for the reactions, if allowance is given for the low precision with which the values of E^{o} are known. The 'non-Marcus' correlation is not unusual for the reactions of these complexes, e.g the oxidation of $Fe(H_2O)_6^{2+}$ by Fe(III)-polypyridine complexes occur by a distinct path characterized by small positive or negative ΔH^{*} values, the path which differ in detail from the normal Marcus-Hush path, (Broddock and Meyer, 1973; Dulz and Sutin, 1963).

The Marcus theory is an adiabatic theory and thus proceeds from the assumption that, within the activated complex for electron transfer, the probability of electron transfer is unity. Other assumption made in deriving equation (5.11) are that 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 motions of the inner coordination shells are harmonic. Differences in the stabilities of the precursor and successor complexes for the exchange and cross-reactions (including work terms for bringing the reactants together and separating the products were neglected in the derivation of equation (5.11). These are incorporated in equation (5.20) (Przysras and Sutin, 1973).

$$k_{12} = \left[\frac{P_{12}P_{21}k_{11}k_{22}K_{12}f_{12}}{P_{11}P_{22}}\right]^{*} \quad \ldots\ldots\ldots 5.20$$

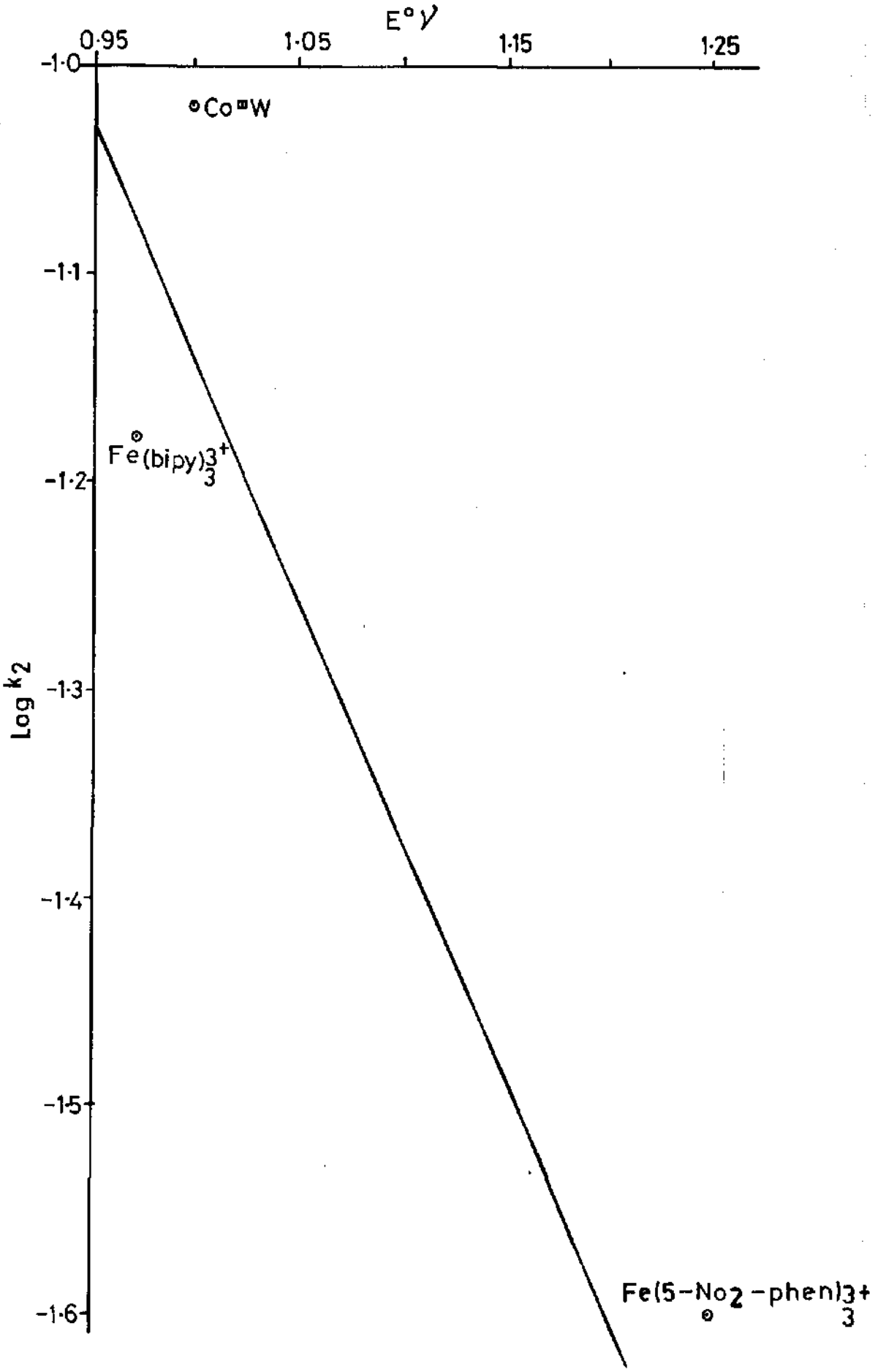


FIG. 5·1 PLOT OF $\log k_2$ VERSUS E° FOR THE REACTIONS OF THE OXIDANTS AND HEDTA

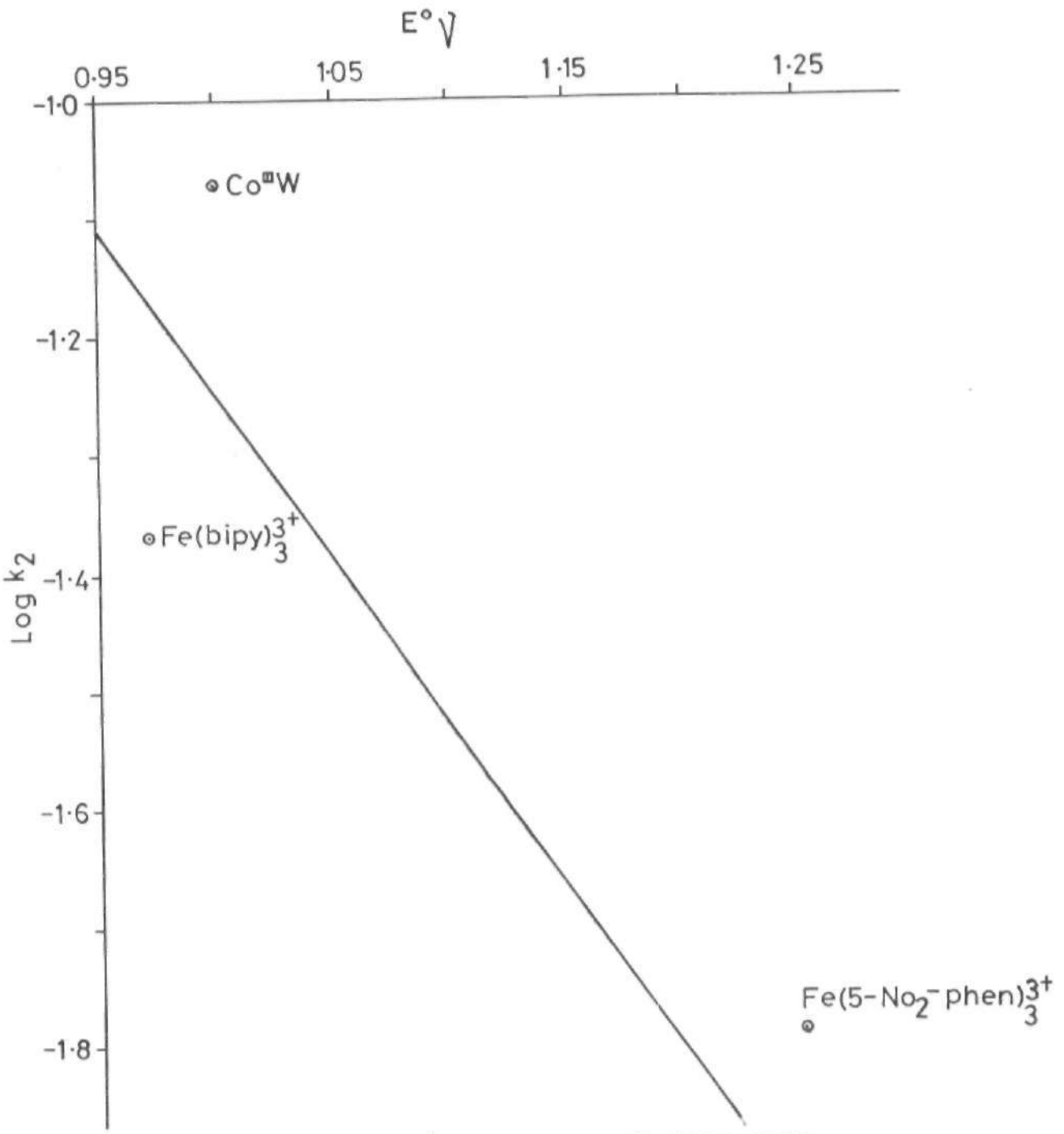


FIG. 5·2 PLOT OF $Log\,k_2$ VERSUS E° FOR THE REACTIONS OF THE OXIDANTS AND EDTA

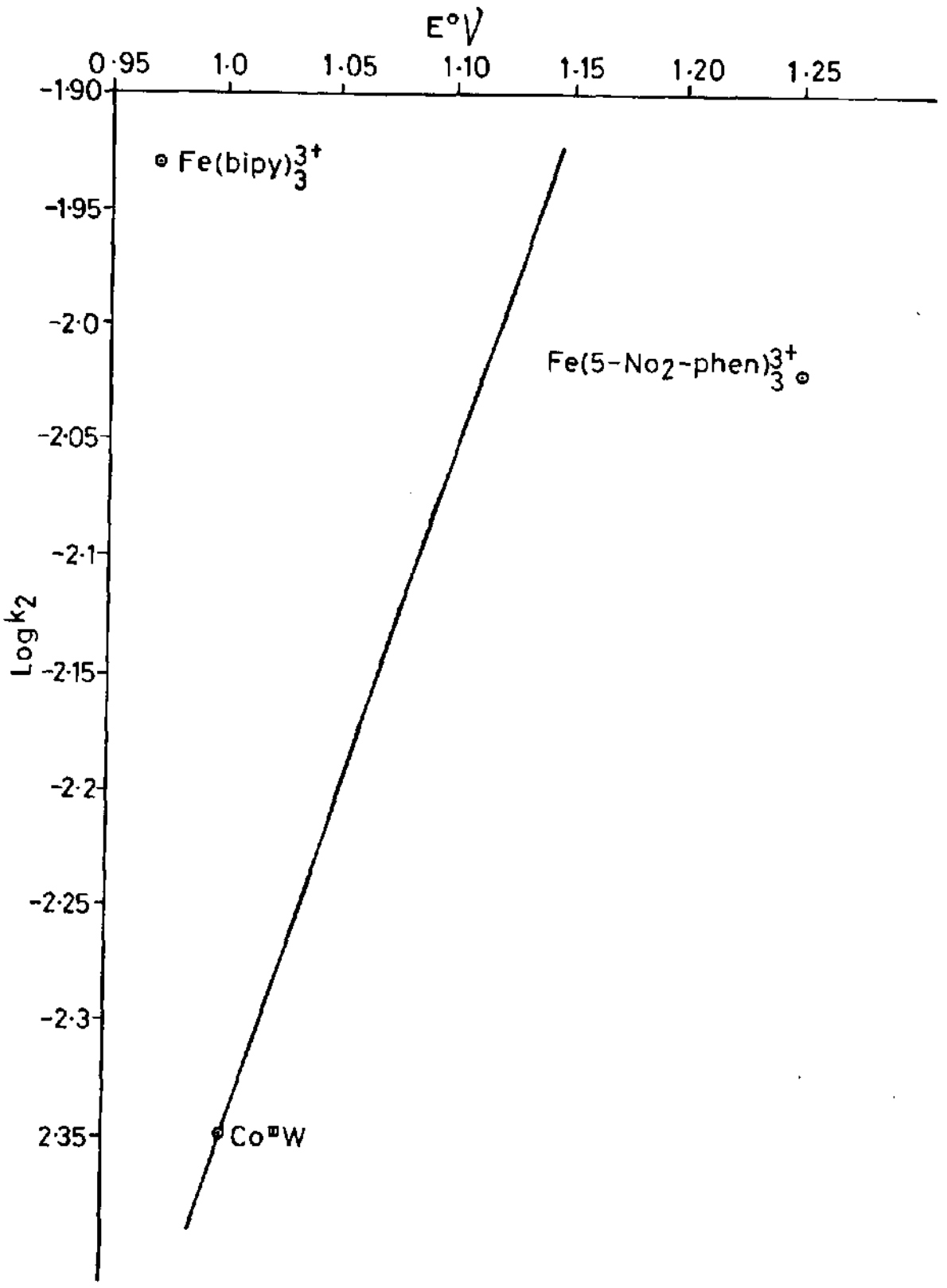


FIG. 5·3 PLOT OF $\log k_2$ VERSUS E° FOR THE REACTIONS OF NTA AND THE OXIDANTS

$$\log f_{12} = \frac{[\mathrm{Log}(K_{12}P_{21}/P_{12})]^2}{4\mathrm{Log}k_{11}k_{22}h^2/P_{11}P_{22}k^2T^2} \quad \ldots\ldots 5.21$$

where P_{11}, P_{22} and P_{12} are the stability constants of the precursor complexes for the exchange and cross-reactions and P_{21} is the stability constant of the successor complex for the cross-reaction. Considering equation (5.21) there are certainly cases where this equation is not expected to reduce to equation (5.11) even when $f_{12} \approx 1$ simply because $P_{12}P_{21} \neq P_{11}P_{22}$. For cross-reactions between oppositely charged ions, as is the case in the reactions under investigation, $P_{12}P_{21}$ will be greater than $P_{11}P_{22}$ since the cross-reaction (and not the exchange reactions) benefits from the electrostatic interaction between the ions. For such cross-reactions k_{12} calculated from equation (5.11) should be less than the observed value. On the other hand, for cross-reactions involving very different kinds of ions, nonelectrostatic contributions to the work terms may give rise to a situation in which $P_{11}P_{22} \gg P_{12}P_{21}$. Under this condition, rate constants calculated from equation (5.11) for these reactions will be too slow by $P_{12}P_{21}/P_{11}P_{22}$.

Although equation (5.20) reduces to equation (5.11) if $P_{12}P_{21} \approx P_{11}P_{22}$ and $f_{12} \approx 1$, if f_{12} becomes small deviations from equation (5.11) may occur even when $P_{12}P_{21} \approx P_{11}P_{22}$. In the not unlikely event that $P_{12}P_{21} \approx 1$, effects from the denominator of the $\log f_{12}$ term (equation 5.21) may dominate. Thus, even for systems in which $P_{12}P_{21} \approx P_{11}P_{22}$ the rate constants should be

larger than those calculated from equation (5.11) when the driving force becomes very large (or small) if $P_{11}P_{22} > 1$. On the other hand, when $P_{11}P_{22} < 1$, rate constants calculated from equation (5.11) should exceed the observed values at very large (or small) driving force.

Another assumption of the Marcus theory to be considered is that of adiabaticity. If P_{11} and P_{22} are the electron-transfer probabilities for self-exchange processes for which k_{11} and k_{22} are the experimentally determined self-exchange rates, the Marcus equation may be modified as follows, (Sutin, 1973).

$$k_{12} = P_{12}\left[\frac{[k_{11}k_{22}K_{12}f_{12}]^{1/2}}{P_{11}P_{22}}\right] \quad \ldots\ldots 5.22$$

$$\log f_{12} = \frac{(\log k_{12})^2}{4\log(k_{11}k_{22}/P_{11}P_{22}Z^2} \quad \ldots\ldots 5.23$$

Equation (5.22) reduces to equation (5.11) if $P_{12} \approx (P_{11}P_{22})^{1/2}$ and $f_{12} \approx 1$, (Sutin, 1973). Thus, even if the self-exchange and cross-reactions are nonadiabatic, the simple Marcus cross-relation equation (5.11) will predict k_{12} values when $P_{12} \approx (P_{11}P_{22})^{1/2}$ provided that the driving force for electron transfer is not so great that f correction becomes substantial. When however, K_{12} does become large, the simple cross-relation (equation 5.11) is expected to break down even though $P_{12} \approx (P_{11}P_{12})^{1/2}$. The use of k_{11} and k_{22}, the observed (nonadiabatic)

exchange rates rather than k_{11}/P_{11} and $k_{22}P_{22}$, the "intrinsic" adiabatic exchange rates, results in f_{12} values which are too large. Consequently, the discrepancy between $k_{12,obsd}$ and $k_{12,calc}$ is expected to increase as the net free energy to change increases if the cross-reaction and one or both of the self-exchange reactions are nonadiabatic. Thus, it would appear that deviations from adiabaticity could be responsible for the discrepancies observed in the Marcus treatment of the reactions under investigation.

Sutin et al (1977) suggest the possible operation of two sources of deviation, one which is important even at small driving force and the other which becomes important only at large driving force. They concluded based on the data from their work, that the large discrepancy observed for the ironpolypyridine complexes cannot result merely from the presence of the polypyridine ligands, but rather depends on properties of the complex as a whole. The Iron complexes manifest several usual properties in the divalent state, there is relatively strong mixing of metal d and ligand π^* orbitals, so that significant metal electron density exists on the ligands. This property is in part responsible for the very high self-exchange rates $\approx 1.2 \times 10^9 M^{-1}s^{-1}$, (Sutin et al, 1977). The back-bonding interaction has the effect of shortening the metal(III)-Nitrogen bonds so that the inner-shell reorganization barrier to electron transfer is lowered. In part, the introduction of the relatively large pyridine into the coordination shell of the metal helps to lower

the outer-shell electron transfer barrier by virtue of the increase in ion size. Moreso, the manipulation of space-filling models of the tris(bipy) and -phenantholine complexes show that "stacked" overlap of a pyridine ring in one complex with one pyridine in another complex is quite favourable. This contact may offer an especially facile pathway for the self-exchange reaction.

Ford-Smith and Sutin, (1961), found no evidence for steric effects in the reaction of some substituted Iron(III)-phen complexes with $Fe(H_2O)_6^{2+}$. The absence of these effects led to the suggestion that in the activated complex for electron transfer, $Fe(H_2O)_6^{2+}$ is located in the space between the phen groups rather than at the periphery of a phen group. Therefore, for reactions involving unlike charge ions, direct evidence has been obtained that ion-pair formation proceeds electron transfer (Garwick and Haim, 1971).

The reactions are therefore necessarily outer-sphere, at least in the sense that a mechanism involving a ligand bridge between normal coordination positions of both reactants can be ruled out, and the fact that the complexes (oxidants) are substitution inert on the time scale for electron transfer supports the mechanism. In this regard, the reactions are similar to other reactions of the complexes with several organic substrates, (Mentaski and Pelizzette, 1977; Pelzzetti and Girauchi, 1975; Pelizzette and Baiocchi, 1976; Pelizzetti and Mentasti, 1976; Pelizzetti, Mentasti and Saini, 1976).

Table 5.1

Activation parameters for the reaction of $Co(H_2O)_6^{3+}$ with HEDTA and EDTA. T = 25°C, I = 5.0M, $[H^+]$ = 2.0M

Oxidant	Reducatant	Ea	ΔS^*	ΔH^*	ΔG^*
		kcal/mol	e.u	kcal/mol	kcal/mol.
$Co(H_2O)_6^{3+}$	HEDTA	23.21	46.66	28.90	15.38 ± 0.6
		±0.40	±1.83	±0.26	
"	EDTA	21.37	37.24	26.40	15.30± 6.26
		±4.12	±18.85	±2.77	

Reference: (Varadarajan and Hossain, 1979).

Table 5.2

Values of E^o for the oxidants and the second-order rate constants for the reactions.

Oxidant	E^o,v	Reductant	$10^2k_2, M^{-1}s^{-1}$	Reference
$Co^{III}W$	1.00[a]	HEDTA	9.57 ± 0.24	This work
"	"	EDTA	8.49 ± 0.21	"
"	"	NTA	0.45 ± 0.01	"
$Fe(bipy)_3^{3+}$	0.97[b]	HEDTA	6.62 ± 0.16	"
"	"	EDTA	4.22 ± 0.10	"
"	"	NTA	1.17 ± 0.03	"
$Fe(5\text{-}NO_2\text{-}phen)_3^{3+}$	1.25[c]	HEDTA	2.49 ± 0.06	"
	"	EDTA	1.62 ± 0.04	"
	"	NTA	0.96 ± 0.02	"

a = Ayoko, Iyun and El-Idris, (1991)

b = G.F. Smith and Richter, (1944)

c = G.F. Smith and Gullstrom, (1952)

5.3 Summary and Conclusion

The redox reactions of $Co^{III}W$, $Fe(bipy)_3^{3+}$ and $Fe(5\text{-}NO_2\text{-}phen)_3^{3+}$ were each studied with HEDTA, EDTA and NTA respectively in aqueous perchloric acid medium. The stoichiometry of the reactions were determined for the reactions of $Co^{III}W$ and was then assumed for the other reactions. The rates of these reactions showed the same form of hydrogen ion dependence. The main products were identified spectrophotometrically.

The rates were found to be dependent on the ionic strength. However, the form of dependence depends on the type of charge present on the species involved, e.g the effect was positive for the $Co^{III}W$ (an anion) reactions and negative for the $Fe(bipy)_3^{3+}$ and $Fe(5\text{-}NO_2\text{-}phen)_3^{3+}$ reactions. The quantitative result (slopes) of the plots of $\log k_{obsd}$ versus $I^{\frac{1}{2}}$ could not be considered reliable because of the high ionic strength at which the reactions were carried out, since the rule holds strictly at very low ionic strengths.

Activation parameters were determined for all the reactions and the results are presented in table (4.10). The parameters are roughly the same at both constant and varied $[H^+]$, further supporting the acid-dependence path as the only pathway for the reactions.

Although these reactions are similar in almost every respect, the nature of a particular oxidant or reductant gives its reaction some characteristic properties. For example, the rates of reaction are fastest for HEDTA reactions and lowerest for NTA reaction for a particular oxidant. This trend of result is not suprising judging from the structure of the different complexones involved (Figure 2.3). The nitrilo group of the NTA is a very powerful electron-withdrawing group therefore, its reducing property (i.e the ease of release of electron) would be very poor compared to the other two reductants. Also, the presence of a lone pair of electrons coupled with an OH^- group (an electron-donating group) in the HEDTA molecule obviously makes its reducing property better than that of EDTA or NTA.

When a particular reductant is considered, the rate of reaction is highest for the reactions with $Co^{III}W$ and lowest for the reactions with $Fe(5\text{-}NO_2\text{-}phen)_3^{3+}$. However, for the NTA reaction with $Co^{III}W$, the k_2 is lowest. The latter observation could be due to the attraction of the nitrilo group in NTA towards the oxygen atoms surrounding the central Co^{III} ion of the $Co^{III}W$ complex. The former observation could be explained in respect of the structures of the complexes. The tetrahedra structure of the central Co^{III} in $Co^{III}W$ complex makes it readily available as an electron acceptor, whereas, the $Fe(5\text{-}NO_2\text{-}phen)_3^{3+}$ and $Fe(bipy)_3^{3+}$ complexes have cis-planar conformation. Moreover, the phen complex has a higher dipole moment than the bipy complex and coupled with the electron rich substituent (-

NO_2^-) present on the phen complex, the k_2 value for its reactions is lower than that of the bipy complex reactions.

Based on the substitution inertness of these oxidants, the lack of intermediate complex formation in the reactions and the results of the application of Marcus theory to these reactions, all the reactions studied are proposed to occur by the outer-sphere mechanism.

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