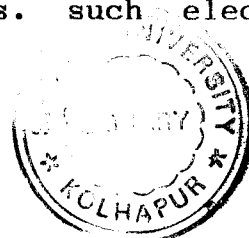

CHAPTER - I

INTRODUCTION, LITERATURE SURVEY AND PRESENT WORK

INTRODUCTION

There has been considerable interest in recent years in oxidation-reduction reaction. The classical definition of oxidation and reduction in terms of gain or loss of oxygen has in modern times been abandoned in favour of the concept of electron loss (oxidation) and electron gain (reduction). Oxidation reduction reactions are also defined as involving changes in oxidation states or oxidation numbers. The assignment of oxidation numbers is based on the following rules: (i) The oxidation number of an atom in an element is zero; (ii) The oxidation number of monoatomic ions is its charge; (iii) The oxidation number of each atom in a covalent compound of known structure is the charge remaining on the atom when each shared electron pair is assigned completely to the more electronegative of two atoms sharing it. An electron pair shared by like atoms is split between them and (iv) The oxidation number of an element in a compound of uncertain structure is usually obtained by assigning reasonable oxidation numbers to the other elements in the compound. Generalisations are also made depending on the position of an element in the periodic table.

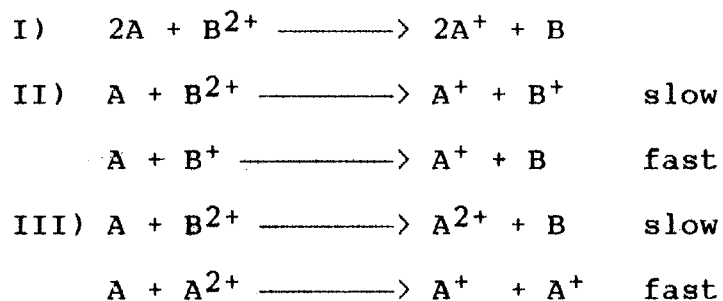
Oxidation-reduction reactions may involve one or more electron transfer. Depending upon the number of electron transferred between the oxidant and reductant, the reaction may proceed in one or more steps. such electron



transfers are governed by two classical principles:

i) The first of these is the Michaelis principle of "Compulsory univalent oxidation steps"¹ This hypothesis involves the principle that takes place in one or more successive single electron transfer steps. this principle involved from a consideration of restricted field of redox reactions, of which the oxidation of hydroquinones to quinones through semiquinone intermediate is typical and is now generally recognised as being without universal validity. Apart from reactions involving metal ions, many 2 - equivalent redox reaction are now known which proceed in one step through the transfer of a hydride ions or an oxygen atom [e.g $\text{NO}_2^- + \text{OCl}^- \longrightarrow \text{NO}_3^- + \text{Cl}^-$] ^{2,3}.

ii) Shaffer's principle of "equivalence change"^{4,5} refers to the observation that non-complementary reactions (i.e., those between 1-equivalent oxidants and 2-equivalent reductants or vice-versa) are often slow compared with complementary ones (those between 1-equivalent oxidants and 1-equivalent reductants or 2-equivalent oxidants and 2-equivalent reductants). Examples are the slow reduction of Tl^{3+} by Fe^{2+} or Ce^{4+} by Tl^+ compared with the rapid reduction of Tl^{3+} by Sn^{2+} and of Ce^{4+} by Fe^{2+} . This can be interpreted in terms of the following types of mechanism for a typical non-complementary reaction in which 'A' is oxidised to 'A⁺' and 'B²⁺' is reduced to 'B':



The first of these mechanisms is expected to be slow because it involves a termolecular step and the last two because they involve the formation of unstable intermediates (B^+ and A^{2+}).

One of the implications of the comparison on which the principle of equivalence change is based is that reactions between 2-equivalent oxidants and 2-equivalent reductants occur by a concerted 2-equivalent step. This may well be the case for reactions such as the $\text{Tl(I)} - \text{Tl(III)}$ exchange⁶.

The observation expressed by Shaffer, for non-complementary reactions, is based on the low probability of termolecular mechanisms as one possibility or the formation of the unstable valence states as the other possibility⁷. Another expected feature of these reactions will be the frequent occurrence of catalysis since the normal paths will be slow.

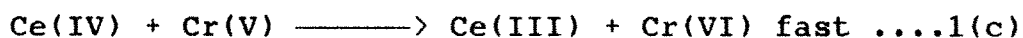
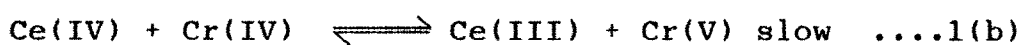
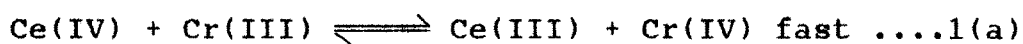
UNSTABLE OXIDATION STATES

The formation of unstable oxidation states during the course of non-complementary reactions has been now anticipated in a number of such reactions with sufficient proofs. The reductions, for examples, of Tl(III) by Fe(II)⁸, V(III) or V(IV)⁹ can only be explained through the formation of unstable Tl(II) species.

The interconversions between Cr(III) and Cr(VI) always appear to involve the unstable states Cr(IV) and Cr(V). In a classic study, King and Tong¹⁰ have worked out the details of the redox reaction between Ce(IV) and Cr(III) in aqueous sulphuric acid. The rate law was found to be as in (1) which is very reasonably explained by the mechanism.

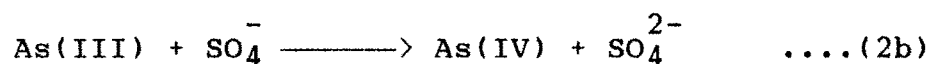
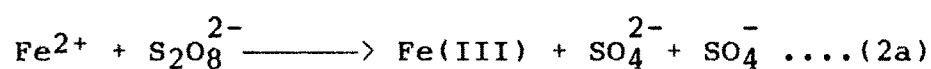
$$\text{Rate} = \frac{k [\text{Ce(IV)}]^2 [\text{Cr(III)}]}{[\text{Ce(III)}]} \quad \dots\dots(1)$$

involving steps of 1(a) to 1(c). The first is a rapid.



equilibrium, and the second step, the interconversion of Cr(IV) and Cr(V), is rate determining. Excellent support comes from the studies of related reactions such as the

oxidation of vanadyl ion by acid chromate ion (HCrO_4^-)¹¹ and the analytically important oxidation of ferrous ion by acid chromate ion¹². It is significant that in the above example, the change over from Cr(V) to Cr(IV) or vice versa, is rate determining. This may be related to the likelihood that, at this stage, a change in coordination number from 4 to 6 occurs¹⁰. The existence of the intermediates, Cr(IV) and Cr(V), is sustained by the observation of induced oxidations. The direct reaction of acid chromate and iodide ion is slow, but the addition of Fe^{2+} to VO^{2+} will cause rapid oxidation of iodide¹³. The stoichiometric examination of the reaction between acid chromate and Fe^{2+} or VO^{2+} in presence of iodide leads to the conclusion that the rapid oxidation of iodide is because of its reaction with Cr(V). A related phenomenon is seen in the oxidation of As(III) by persulphate ion. This slow reaction is accelerated or oxidation is induced by adding Fe(II) and the reaction is postulated to go by the formation of As(IV) from the reaction (2a, 2b)¹⁴.



INNER-SPHERE AND OUTER-SPHERE MECHANISM

Two general classes of transition states emerge for redox reactions involving metal complexes, the 'Outer-Sphere' and 'Inner-Sphere'. In the first of these, the inner coordination shells of both the metal ions are intact in the transition state. In the second case, the two metal ions are connected through a bridging ligand common to both coordination shells. From Franck-Condon principle, it follows that before electron transfer between two ions is possible, the energy of the electron must be the same in the two sites. There must also be sufficient orbital overlap between the two sites to provide for a reasonable probability of a transfer.

In the case of a reaction of outer-sphere type, the electron must wait for an appropriate fluctuation of the ions and their coordination spheres, without in any way being able to influence the changes required in the site to which it will be transferred. For reactions of inner-sphere type, an activated complex of the type $LxM^{n+1}XM^nWx$ may be formed, where L, X and W are ligands. In arriving at a configuration having X as bridging group, either M^{n+1} or M^n (or both) has undergone substitution in the first coordination sphere. Delocalisation of an electron over the two sites will lower the energy needed for the formation of the activated complex and the electron will be able to

effect the energy required to produce a fluctuation at the site to which it is going to be transferred. Presumably the reaction is consummated by some fluctuation which cause the separation of M^{n+1} and M^n and may well require other changes in the coordination spheres as well. A feature of the bridged activated complex is that the bridging group may move from the oxidising agent to the reducing agent, i.e., in the opposite direction to that of the electron.

The most conclusive evidence for the mechanism comes from isolation of the indicated products, which is possible only if the appropriate solvolysis reaction occurs slowly. However, the reactions of Cr^{2+} and some of the reactions of V^{2+} and Fe^{2+} are convincingly characterized as following the inner-sphere mechanism. In the latter case, the immediate $V(III)-X$ or $Fe(III)-X$ products have often been detected spectrophotometrically, prior to their dissociation¹⁵⁻¹⁷. Therefore, probably the inner-sphere mechanism is the most favourable provided, (a) suitable ligand is available in the coordination sphere of the oxidising complex and (b) substitution of a water molecule in the reducing agent occurs sufficiently rapidly to permit the transition state $M-X-M'$ to form rapidly¹⁸.

The most common instance of outer-sphere mechanisms are found when the nature of the coordination sphere of one reactant or the other contains ligands unsuited for

bridging or when exchange occurs too slowly to permit bridge formation. Among such reactions¹⁸ - are $\text{Co}(\text{NH}_3)_6^{3+}$ oxidations and $\text{Cr}(\text{bipy})_3^{2+}$ reductions; certain reactions of $\text{V}(\text{H}_2\text{O})_6^{2+}$, which undergoes substitution more slowly than most divalent ions; electron exchange of $\text{Fe}(\text{C}_5\text{H}_5)_2$ and $\text{Fe}(\text{C}_5\text{H}_5)_2^+$; and reactions such as electron exchange of $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$.

THE PREDOMINANT SPECIES

The rate equation that can be interpreted in terms of mechanistic proposals expresses the rate as a function of the concentrations of species in their predominant forms. The experimental data, however, are originally formulated in terms of laboratory concentrations, variously referred to as stoichiometric or total concentrations. One case to be considered is when a reactant is converted to an entirely different species by reaction with the solvent or with the other substrates. In many instances this is almost a trivial situation: the addition of a small concentration of NH_3 to aqueous mineral acid converts it almost entirely to NH_4^+ , and the real laboratory variables are $[\text{NH}_4^+]$ and $[\text{H}^+]$. The concentration of NH_3 , being quite small, is controlled only indirectly. Similarly, when VOCl_4 is dissolved in water, VO^{2+} is formed, and when cyanogen is dissolved in base, it undergoes complete conversion to CN^- and CNO^- .

The species involved in many overall chemical reactions may be subject to other equilibria, which are maintained rapidly relative to main reaction. These equilibria serve to reduce the concentration of a reacting species from the value of the formal concentration for example the concentration of Fe^{3+} in a solution is lowered appreciably by the addition of even small quantities of HF owing to the formation of the rather stable complex FeF^{2+} , and the partial ionization of H_3PO_2 lowers the concentration of this species below the added quantity.

To formulate the reaction rate as a function of species concentrations, therefore, requires a knowledge of the existence of such equilibria and, generally speaking, the knowledge or determination of one or more equilibrium constants. The distinction between the species and laboratory concentrations is particularly critical in the cases of partially displaced equilibria, because the rate equations, if cast in the form of reaction rate as a function of laboratory concentrations, quite often resemble the equations applicable to entirely different mechanisms.

A familiar and frequent incident where preequilibria are important has to do with the pH dependence of a reaction rate. The case where an acid-base reaction converts a significant fraction of a reactant into a different form

(which may be more reactive than the original) and the case where only a very small fraction is converted to a highly reactive form often lead to rate laws of the same algebraic form. In general, one must be able to evaluate the approximate equilibrium constants to distinguish the alternatives.

EFFECT OF IONS ON THE RATE

The rates of redox reactions of complex ions are very sensitive to the presence of other ions in the solutions. Usually, added anions have the greatest influence on the reaction of two cations with each other, and added cations influence the rate of two anions with each other. Large effects of anions on the rate are usually attributed to the formation of bridged species if labile complexes are involved.

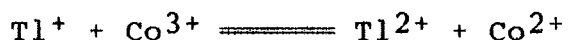
In the redox reactions between two cations, if the reducing agent is complexed, it will be more stabilized in the oxidised form and hence the reaction is speeded up in presence of anion. Also a negative ion should enable two positive ions to approach each other more easily. This will be most effective if the negative ion is between the two cations in the transition state.

If the oxidising agent is complexed first, the anion may stabilise it and slow down its rate of reaction. For example, the rate of reactions of Ce^{4+} oxidations are

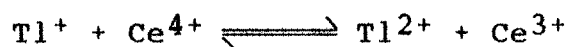
reduced strongly by forming sulphate complexes¹⁹ in presence of sulphate. This shows, in agreement with theory, that coulombic repulsions between the reactants do not play a dominant role. The conclusion to be drawn is not that electrostatic factors do not exist, but that other factors (reorganization energies) are of greater importance. Some significant effects of chloride ion are particularly noticeable in redox reactions. The redox reactions, in which the reductant is able to form complexes with chloride, are found to be accelerated by chloride ion. Among the reductants that can form complexes with chloride are Tl(I), Sn(II) and Sb(III). Presumably because of the complex formation, the oxidation potentials of such redox systems are changed. **The** oxidation potentials of the complexes Hg(II)/Hg(I), Fe(III)/Fe(II) and Tl(III)/Tl(I) are decreased considerably in presence of chloride ion¹⁵⁻¹⁷.

LITERATURE SURVEY

The reaction in which Tl(I) is oxidised to Tl(III) can also proceed via the intermediate formation of Tl(II). The oxidation of Tl(I) with Co(III) proceeds according to the scheme²⁰:



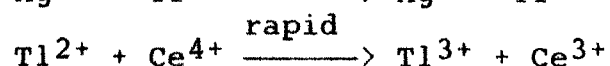
The reaction is independent of the hydrogen-ion concentration in perchlorate ion solutions of hydrogen-ion concentration 0.25 to 2.50 M. In 6.2 M nitric acid, the reaction of Tl(I) and Ce(IV) follows a similar reaction sequence²¹:



but there are additional reactions involving hydroxyl radicals. The reaction between Tl(I) and Ce(IV) in sulphuric acid is catalysed by platinum(IV) chloride. This reaction is first order in cerium(IV) sulphate and zero order in thallium(I) sulphate²². The suggested mechanism is a rapid first step in which Tl(I) is oxidised by the Pt(IV) followed by a two-stage oxidation of Pt(II) by the Ce(IV):

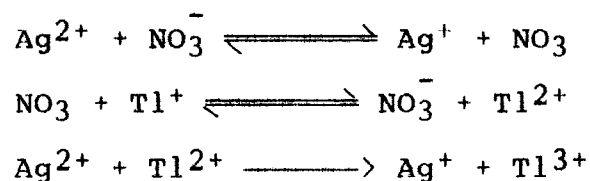


In perchloric acid, with Ag(I) as catalyst²³ the reaction sequence has been proposed as:

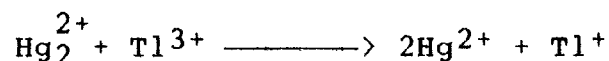


In nitric acid, the same mechanism holds, except that the Ce(IV) is now probably in the form of a complex²⁴ $\text{Ce}(\text{NO}_3)_6^{2-}$.

The reaction between Tl(I) and Ag(II) has been studied in 6.2 N nitric acid and it is believed that a nitrate radical is formed as an intermediate which then oxidises the Tl(I) to Tl(II)²⁵.



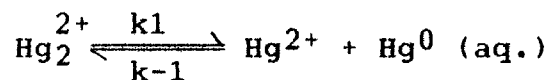
The reaction of the mercury(I) dimer with Tl(III)^{26,27} is:



The rate law found was:

$$\frac{d[\text{Hg}_2^{2+}]}{dt} = \frac{k_1 k_2 [\text{Hg}_2^{2+}] [\text{Tl}^{3+}]}{k_{-1} [\text{Hg}^{2+}]}$$

Pointing to the mechanism



With k_2 (10^6 liters mole⁻¹ sec⁻¹ at 25°C) being at least 10^6 times greater than the rate constant for the direct reaction between the mercury(I) dimer and Tl(III).

A modified mechanism of the reaction between Tl^+ and Ce^{4+} ion in aq. H_2SO_4 medium was studied by B.P. Sinha²⁸. The active form of Ce^{4+} was $Ce(SO_4)_2$, and HSO_4^- was the main inhibitor. The rate law was

$$\frac{-d[Ce^{4+}]}{dt} = k' ([Ce^{4+}]/[HSO_4^-])^2$$

The kinetics of the reaction between Ce^{4+} ion and Tl^+ catalysed by Ag^+ in aq. HNO_3 medium was studied by B.P. Sinha²⁹. The overall order of reaction was 2, and 1 with respect to each reactant. The catalytic effect of both H^+ and NO_3^- was examined. A mechanism was suggested according to which the rate equation was

$$\frac{-d[Ce^{4+}]}{dt} = k' ([Tl^+] [Ce(NO_3)_6^{3-}]^{-1}).$$

The reaction between persulphate and thallium(I) was³⁰ found to be 1st order and zero order with respect to $S_2O_8^{2-}$ and $Tl(I)$ respectively in a reaction mixture containing $K_2S_2O_8$, Tl_2SO_4 , and H_2SO_4 and heated at 45° . The oxidation rate varied with the square root of acidity. From the temperature dependence of the reaction, the temperature coefficient, activation energy, frequency factor and activation entropy were 3.54, 24.55 K.Cal. 1.62×10^{11} l/mole sec. and -8.19 e.u. respectively. A chain mechanism was

proposed which involves the thermal decomposition of $S_2S_8^{2-}$ into $2SO_4^-$ as the initial step.

The Ag(I) catalysed $S_2O_8^{2-}$ - Tl(I) reaction was also studied by Singhal R.K. and coworkers³¹. The title $Tl^+ \longrightarrow Tl^{3+}$ reaction was first order with respect to $S_2O_8^{2-}$ and Ag^+ . The reaction proceeds by propagation of a chain initiated by decomposition of $S_2O_8^{2-}$ by Ag^+ giving free SO_4^{2-} and Ag^{2+} . The chain also involves the formation of Tl^{2+} as an intermediate product.

The empirical form of the rate law for the reaction between Np(VII) and Tl(I) in acid perchlorate³² media was

$$\frac{-d[Np(VII)]}{dt} = k' [Np(VII)] [Tl(I)],$$

where $\ln k' = \ln k + n \ln [H^+]$. At 25° in 1 M perchloric acid $K = 4.46 M^{-1} Sec^{-1}$ and $n=0.901$. The apparent activation energy was 7.73 k cal./mole. Results of ^{18}O tracer studies were presented.

The kinetics of oxidation of Tl^+ ions by Ce^{4+} ion catalysed by Os^{VIII} in aq. H_2SO_4 medium³³ was investigated by Singhal R.K. and coworkers. The total order of reaction was 2, viz. 1 for Ce^{4+} and 1 for Tl^+ . The magnitude of the rate also depends from initial concentration of Ce^{4+} and Tl^+ sulfates. The rate was directly proportional to Os^{VIII}

concentration. Bisulfate ions act as the main inhibitor ion and rate varies inversely with the square of their concentration. Tl^{3+} and Ce^{3+} ions do not exert any influence on the rate. The thermodynamic parameters were evaluated and a tentative mechanism was proposed.

the kinetics of oxidation of $Tl(I)$ by $Ce(IV)$ catalysed by $Os(VIII)$ in perchloric acid³⁴ medium (0.75-2M) have been described. The rate law as a function of both $Tl(I)$ and $Ce(IV)$ concentration as well as the $Os(VIII)$ concentration. H^+ ion inhibits the reaction. The effect of ionic strength has been investigated and Arrhenius parameters have been evaluated. The oxidation kinetics conform to the expression:

$$\frac{d[Ce(IV)]}{dt} = k' [Ce(IV)] [Tl(I)] [Os(VIII)]/[H^+]$$

$Mn(III)$ reacted with $Tl(I)$ only when MnO_2 from decomposition or added Cl^- was present³⁵. Observed rates in the presence of Cl^- agreed with reversible reaction of $MnCl_2^{2+}$ with Cl^- to give Cl_2^- which oxidized $Tl(I)$ slowly and $Tl(II)$ rapidly. All $Tl(III)$ appeared as $TlCl_4^-$.

A kinetic study of reduction of $Ce(IV)$ by $Tl(I)$ was made in presence of Pt as heterogeneous catalyst in a H_2SO_4 medium³⁶. Order of reaction, kinetic and thermodynamic parameters, importance of surface area influence of stirring and of concentration of reactants and pH.

The kinetics of electron transfer reaction between Tl^{1+} and Tl^{3+} was investigated³⁷ in the presence of Ce^{4+} by use of radioactive tracer ^{208}Tl . The apparent rate constant of reaction k_{app} was dependent upon $[H^+]$ and $[Ce^{4+}]$ ($< 0.6 \times 10^{-3} M$) and can be expressed by

$$k_{app} = k_A + k_B/[H^+] + (k_C + k_D)/[H^+][Ce^{4+}].$$

k_{app} was gradually satd. to a limiting value according to $[H^+]$ at higher $[Ce^{4+}]$. The observed values are

$$k_A = 4.70 \text{ M}^{-1} \text{ hr}^{-1},$$

$$k_B = 2.13 \text{ hr}^{-1},$$

$$k_C = 1.30 \times 10^3 \text{ M}^{-2} \text{ hr}^{-1} \text{ and}$$

$$k_D = 2.61 \times 10^3 \text{ M}^{-1} \text{ hr}^{-1} \text{ at } 50^\circ$$

Since Ce^{4+} was a 1-electron oxidant Tl^{1+} was oxidized by 1-electron transfer to produce Tl^{2+} as an intermediate. However in the absence of 1-electron oxidant or reductant, 2 electrons are transferred from Tl^{1+} to Tl^{3+} not through double step of 1-electron transfer but predominantly through a single step of 2 electron transfer.

The kinetics were studied³⁸ of the oxidation of $Tl(I)$ by $Ce(IV)$ in H_2SO_4 media containing Mn in different oxidation states as possible catalyst. The proposed mechanism involves Mn(IV) as catalyst, initiating the reaction by oxidation of $Tl(I)$ to $Tl(II)$ with $[TlMn(SO_4)_3]^-$ as the activated complex.

The influence of NaClO_4 , Na_2SO_4 , $\text{Ce}_2(\text{SO}_4)_3$, H_2SO_4 and HClO_4 on the oxidation of Tl(I) by Ce(IV) in presence of Mn(IV) as catalyset was investigated³⁹. In presence of NaClO_4 and HClO_4 the existence of CeSO_4^{2+} facilitated the reaction progress. An increase of the SO_4^{2-} concentration favours the formation of negative complexes of Ce(IV) and Ce(III) such as $\text{Ce}(\text{SO}_4)_3^{2-}$, $\text{HCe}(\text{SO}_4)_3^-$ and $\text{Ce}(\text{SO}_4)_2^-$, inhibiting the course of reaction.

The kinetics of oxidation of Tl(I) by Ce(IV) in aq. HClO_4 medium were investigated by following depletion in concentration of Ce(IV) with time⁴⁰. At a series of equivalent concentrations of the 2 reactants, the total order of the reaction is 2 being 1 in each reactant. The order with respect to $[\text{SCN}^-]$; also 1. The rate was directly proportional to square root of $[\text{H}^+]$. The reaction was having a primary positive salt effect. While the addition of one of the reaction product, viz. Ce(III) retards the rate, the addition of Tl(III) produces no effect. Arrhenius parameters were reported and the reaction scheme which explains the salient features of the reaction were given.

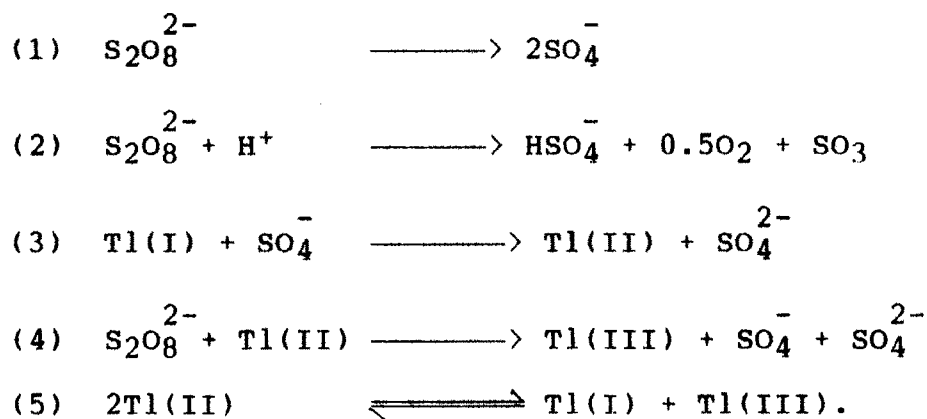
The oxidation kinetics of Tl(I) by Ce(IV) catalyzed by IBr in aq. HClO_4 were studied⁴¹ at constant ionic strength. The total order of reaction was being unity with respect to Ce(IV) and zero in the reductant. The rate was

found to be directly proportional to the square root of catalyst concentration. H^+ ion linearly enhanced the rate. While the reaction product $Tl(III)$ did not influence the rate, $Ce(III)$ produced retardation. The effect of adding neutral electrolytes was investigated and activation parameters were determined. A tentative reaction mechanism was proposed.

A kinetic study was made of the oxidation of $Tl(I)$ by $Ce(IV)$ catalyzed by ICl in aq. $HClO_4$ ⁴². The total order of reaction was 2. The rate was also linearly related to the concentration of ICl . H^+ enhanced the rate but the relation of the two reaction products, thallic ion did not exert any influence on the rate while the cerous ion lead to retardation. The effect of ionic strength was studied and the activation parameters were determined. A reaction mechanism was proposed with rate equation,

$$\frac{-d[Ce(H_2O)_n^{4+}]}{dt} = [Ce(H_2O)_n^{4+}] [Tl^+]$$

The oxidation reaction of the $Tl(I)$ ion to the $Tl(III)$ ion by $S_2O_8^{2-}$ was studied⁴³ in an aq. solution. The reaction constituted a chain reaction initiated by the thermal decomposition of $S_2O_8^{2-}$, the reaction involved no direct reactions between the $Tl(I)$ and $S_2O_8^{2-}$ ions. At $Tl(I)$ ion concentration $> 0.004 \text{ mol dm}^{-3}$, the reaction mechanism was assumed to be:



The rate of reaction was given by

$$\frac{-d[\text{S}_2\text{O}_8^{2-}]}{dt} = (k_1 + k_2 [\text{H}^+][\text{S}_2\text{O}_8^{2-}]) + k_4 (k_1/k_5)^{1/2} [\text{S}_2\text{O}_8^{2-}]^{3/2}$$

The rate constants at an ionic strength of 0.16 mol dm^{-3} were determined to be

$$k_1 = 1.99 \times 10^{19} \exp[-157 \text{ kJ/mol}^{-1}/RT] \text{ s}^{-1}.$$

$$k_2 = 2.75 \times 10^{12} \exp[-103 \text{ kJ mol}^{-1}/RT] \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

and $k_4(k_1/k_5)^{1/2} = 2.81 \times 10^{13} \exp[-108 \text{ kJ mol}^{-1}/RT] \text{ dm}^{3/2} \text{ mol}^{-1/2} \text{ s}^{-1}$ in $0.01 \text{ mol dm}^{-3} \text{ HClO}_4$, the k_4 value being increased with decrease in the H^+ concentration. The ionic strength (μ) dependence was described as

$$\log k_4(k_1/k_5)^{1/2} = 4.17 - 1.05 \mu^{1/2}$$

in $0.01 \text{ mol dm}^{-3} \text{ HClO}_4$ at 40° .

The kinetics of oxidation of Tl(I) by Ce(IV) in aq. HClO_4 were catalyzed by ICl_3 ⁴⁴. The catalysis is attributed to ICl_4^- obtained from ionization of ICl_3 . The oxidation proceeds via the formation of an activated

complex, as the reaction follows 1st order kinetics in oxidant and catalyst. A linear dependence of rate of H^+ and a primary positive salt effect were observed. Reaction products did not influence the rate. Activation parameters were determined and the rate law was given.

The chromium(VI) oxidation of thallium(I) in 3 M hydrochloric acid at ionic strength 4 M and 25°C was studied⁴⁵ spectrophotometrically and was found to follow a second order rate law. The reaction was understood to occur between the species $ClCrO_3^-$ and $TlCl$ and the possible mechanisms were discussed.

Chromium(VI) oxidation of thallium(I) in 60% acetic acid containing 1.25 mol dm⁻³ hydrochloric acid was found to be a second order reaction⁴⁶, understood to be between CrO_3Cl^- and $TlCl$. Increase in $[H^+]$ and $[Cl^-]$ accelerate the reaction. Added V(V) accelerates the reaction till $[V(V)]$ slightly exceeds $[Tl(I)]$ because of a 1:1 interaction between V(V) and Tl(I). At higher $[V(V)]$, the rate constant was lowered due to a specific cation effect. No interaction between added V(V) and Tl(I) was encountered in the case of the reaction in 40% aqueous acetic acid; however, in 80 and 90% aqueous acetic acid 2:3 and 1:2 interactions between V(V) and Tl(I) were observed.

The hexacyanoferrate(III)-thallium(I) reaction in aqueous acetic acid containing large concentrations of

hydrochloric acid was considerably accelerated⁴⁷ both by hydrogen and chloride ions as well as increasing acetic acid in the medium. The experimental results obey the rate law(1).

$$-\frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = \frac{(\beta_4 k_a [\text{H}^+] + \beta_5 k_b [\text{H}^+]^2) \beta_2 [\text{Cl}^-]^2 [\text{Fe}(\text{CN})_6^{3-}]_T [\text{Tl}^+]_T}{(1 + \beta_4 [\text{H}^+] + \beta_5 [\text{H}^+]^2 + \beta_6 [\text{H}^+]^3 + \beta_1 [\text{Cl}^-] \beta_2 [\text{Cl}^-]^2 + \beta_3 [\text{Cl}^-]^3)}$$

Where β_1 and β_6 are the cumulative stability constants of the species TlCl , TlCl_2^- , TlCl_3^{2-} , $\text{HFe}(\text{CN})_6^{2-}$, $\text{H}_2\text{Fe}(\text{CN})_6^-$ and $\text{H}_3\text{Fe}(\text{CN})_6$ respectively and k_a and k_b are the rate constants associated with the mono- and di-protonated oxidant species. The main active species were $\text{H}_2\text{Fe}(\text{CN})_6^-$ and TlCl_2^- .

Permanganate oxidation of thallium(I) in aqueous perchloric acid has 2:3 stoichiometry⁴⁸ (Oxidant:reductant) and manganese(IV) and thallium(III) were the products. A clean second order kinetics was followed by the reaction with fractional dependence on [acid]. The results were explained by a mechanism involving HMnO_4 as the active oxidant species.

The reaction between V^{V} and Tl^{I} was studied⁴⁹ in 4.0 mol dm^{-3} HCl at an ionic strength of 4.1 mol dm^{-3} at 25°C. The main active species under the reaction conditions were found to be VO_2^+ and TlCl_3^{2-} for the oxidant and reductant respectively. A probable mechanism in terms of these species

was given, and follows the rate law:

$$-\frac{d[V^V]}{dt} = \frac{k\beta_2\beta_5 [H^+]^2 [Cl^-]^3 [V^V] [Tl^I]}{(1 + \beta_1 [H^+] + \beta_2 [H^+]^2)(1 + \beta_3 [Cl^-] + \beta_4 [Cl^-]^2 + \beta_5 [Cl^-]^3)}$$

Where β_2 is the cumulative stability constant of the VO_2^+ ion, formed by stepwise protonation of the VO_3^- ion, and β_5 that for the $TlCl_3^{2-}$ species.

PRESENT WORK

The work for the M.Phil. dissertation consists of study of oxidation of thallium(I) by tetrachloroaurate(III) and pyridinium chlorochromate in hydrochloric acid. The study involves determination of order with respect of oxidant and reductant. Since chloride is known to form complexes with the reductant, thallium(I) in different stoichiometric proportions, its effect on the reaction was studied. Such a study will help to know the reactive species of the reductant. The effect of hydrogen ion concentration on the reaction is also in order to understand the possible prior equilibria of the oxidant species with hydrogen ion. Further, the effect of added product was also studied to a probable mechanism of the reaction in agreement with the experimental results.