Part - A

OXIDATION OF INORGANIC SUBSTRATES
Chapter I

GENERAL INTRODUCTION AND SUMMARY
OF THE WORK UNDERTAKEN
Chemistry can be thought of, at the simplest level, as the science that concerns itself with making new substances from other substances. Or, one could say, chemistry is taking molecules apart and putting the atoms and fragments back together to form new molecules. All of this is to say that chemical reactions are the core of chemistry. If Chemistry is making new substances out of old substances (i.e., chemical reactions), then there are two basic questions that must be answered:

1. Does the reaction want to go? - This is the subject of chemical thermodynamics.

2. If the reaction wants to go, how fast will it go? - A branch of chemistry, which addresses such questions, is chemical kinetics.

Here are some examples. Consider the reaction,

$$2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$$

We can calculate $\Delta G^\circ$ for this reaction from tables of free energies of formation (actually this one is just twice the free energy of formation of liquid water). We find that $\Delta G^\circ$ for this reaction is very large and negative, which means that the reaction wants to go very strongly. A more scientific way to say this would be to say that the equilibrium constant for this reaction is very large. However, we can mix hydrogen gas and oxygen gas together in a bulb or other container, even in their correct stoichiometric proportions, and they will stay there forever without reacting. (If we drop in a catalyst - say a tiny piece of platinum - or introduce a spark, or even illuminate the mixture with sufficiently high frequency UV light, the mixture will explode.) The problem is not that the reactants do not want to form the products, they do, but they cannot find a "pathway" to get from reactants to products.

How can this thing be?
The answer is that thermodynamics is not the whole story in Chemistry. Not only do we have to know whether a reaction is thermodynamically favored, we also have to know whether the reaction can or will proceed at a finite rate. The study of the rate of reactions is called chemical kinetics. Thermodynamics tells us what should happen. It does not tell us what will happen. For what does happen, we need to know the rates of a reaction. How fast, and how the rate changes with time, for a given reaction, reveals what is happening at the atomic scale.

Svante Arrhenius (Nobel laureate in Chemistry 1903), inspired by Van't Hoff (the first Nobel laureate in Chemistry, 1901) presented a simple formula for reaction speed as a function of temperature. But this referred to macroscopic systems and relatively long times. It was not until the 1930’s that Henry Eyring and Michael Polanyi formulated a theory based on reactions in microscopic systems of individual molecules. The theoretical assumption was that the transition state was crossed very rapidly, on the time scale that applies to molecular vibrations.

But until very recently little was known about the molecule's path up over the energy barrier and what the molecule really looks like when it is exactly at the top, its 'transition state'. This is exactly what Ahmed Zewail, the 1999’s Nobel laureate set out to do. At the end of the 1980’s he performed a series of experiments that were to lead to the birth of the research area called 'femtochemistry'. This involves the capturing of pictures of molecules just at the transition state. From a phenomenon described in relatively vague metaphors such as 'activation' and 'transition state', we can now see the movements of individual atoms we imagine them.
The work of Henry Taube\textsuperscript{1} in redox systems unequivocally demonstrated the transport of electron from reductant to oxidant. This discovery certainly added many important features in the syntheses of coordination complexes and organometallics. It is such a subject, which has manifestations in almost all walks of life. As a result, oxidation-reduction reaction needs at least two reactants, one capable of gaining electrons (oxidant) and the other capable of losing electrons (reductant), i.e., a reducing agent (reductant) by losing electrons, gets oxidized and an oxidizing agent (oxidant), by gaining the electrons, gets reduced. Electron transfer reactions play a central role in physical, chemical and biological processes. Because of the ubiquity of electron transfer processes, the study of electron transfer reactions, perhaps more so than that of any other area of chemistry is characterized by a strong interplay of theory and experiment\textsuperscript{2}. Nonetheless the importance of electron transfer in transition metal redox chemistry has been recognised\textsuperscript{3} and more recently it has become increasingly obvious that many reactions in organic chemistry once thought to be concerted in nature also occur via sequential one electron steps\textsuperscript{4}.

The kinetic data will be the source of a great deal of detailed insight into the mechanism of a reaction. Although, other types of experimental evidences are also sought for purpose of formulating a reaction mechanism, the study of reaction kinetics generally forms the backbone of a thorough mechanistic investigation. Finally, as an area of pure science in itself, the study of rates and mechanism is one of rich varieties, concerned with the chemistry of every element and full of experimental challenge.
Nearly all the oxidizing agents are inorganic compounds; they contain elements that belong to nearly all parts of the periodic classification, but fortunately theories of organic chemist have been developed so rationally that it is a much simpler task to elucidate oxidation mechanisms in terms of modes of degradation of molecules of distinctive types than to consider them to consider separately each available oxidizing agent.

**Oxidation-reduction in inorganic reactions**

**Probable ways of electron transfer reactions**

Oxidation-reduction reaction may involve one or more electron transfer. Depending upon the number of electrons transferred between oxidant and reductant, the reaction may proceed in one or more steps. Transition metals such as iron and cobalt and several others usually exhibit stable oxidation states differing by one electron and react with each other through one equivalent steps. However, the stable oxidation states in post transition elements such as arsenic, antimony etc., differ by two electrons. Thus, on the basis of their pattern of reactivity, the reactions of these elements are classified into two main categories.

**Complementary and non-complementary reactions**

**Complementary reactions**

The oxidant and reductant change their oxidation state by an equal number of units. These are termed as complementary electron transfer reactions.

e.g. (i) One equivalent – One equivalent reactions

These are the electron reactions in which there occurs the transfer of one
electron from one species to the other. These simple reactions serve as models for more complicated systems and their study has proved invaluable in developing and understanding of the electron transfer in solution\textsuperscript{6}. e.g.,

(ii) Two-equivalent - Two-equivalent reactions\textsuperscript{6,7}

\[
\begin{align*}
\text{U(IV) + Tl(III)} & \quad \rightarrow \quad \text{U(VI) + Tl(I)} \\
\text{Sn(II) + Hg(II)} & \quad \rightarrow \quad \text{Sn(IV) + Hg(0)}
\end{align*}
\]

A large number of complementary reactions have been explained by assuming the formation of bridged activated complexes between the oxidant and the reductant for the facile transfer of electron through the bridging ligand.

**Non-complementary reactions**

The oxidant and the reductant change their oxidation states by a different number of units. These are termed as non-complementary electron transfer reactions. Most non-complementary reactions proceed via elementary steps each involving one electron transfers. The most commonly observed kinetic scheme\textsuperscript{8} is

\[
\text{Cr(VI) + Fe(II)} \quad \leftrightarrow \quad \text{Cr(V) + Fe(III)}
\]

Subsequently, chromium(V) reacts with ferrous ion in a rate determining step by one of the following schemes.

(A) \[
\begin{align*}
\text{Cr(V) + Fe(II)} & \quad \rightarrow \quad \text{Cr(IV) + Fe(III)} \quad \text{slow} \\
\text{Cr(IV) + Fe(II)} & \quad \rightarrow \quad \text{Cr(III) + Fe(III)} \quad \text{rapid}
\end{align*}
\]

(B) \[
\begin{align*}
\text{Cr(V) + Fe(II)} & \quad \rightarrow \quad \text{Cr(III) + Fe(IV)} \quad \text{slow} \\
\text{Fe(IV) + Fe(II)} & \quad \rightarrow \quad 2\text{Fe(III)} \quad \text{rapid}
\end{align*}
\]

According to Tong and King, mechanism (A) is more appropriate because, the slowest step corresponds to the change in the coordination number four of
chromium(V) to six of chromium(III).

**Electron transfer reactions**

Electron transfer reactions may occur by either of two mechanisms: outer and inner sphere mechanisms\(^9\).

**Outer sphere electron transfer reactions**

Electron transfer reactions may occur by either of both of two mechanisms: outer or inner sphere mechanisms. In principle all outer sphere mechanism involves electron transfer from reductant to oxidant with the coordination shells or spheres of each staying intact. That is one reactant becomes involved in the outer or second coordination sphere of the other reactant and an electron flows from the reductant to oxidant. Such a mechanism is established when rapid electron transfer occurs between two substitution-inert complexes.

\[
\begin{align*}
\left[\text{CN}^{-} \text{Fe}^{3+} \text{CN}^{-}\right]^{4-} + \left[\text{CN}^{-} \text{Fe}^{3+} \text{CN}^{-}\right]^{2-} & \rightarrow \left[\text{CN}^{-} \text{Fe}^{3+} \text{CN}^{-}\right]^{3-} + \left[\text{CN}^{-} \text{Fe}^{3+} \text{CN}^{-}\right]^{3-} \\
k &= 4.1 \times 10^{4} \text{ mol}^{-1} \text{ s}^{-1}
\end{align*}
\]

**Inner sphere electron transfer reactions**

An inner sphere mechanism is one in which the reactant and oxidant share a ligand in their inner or primary coordination spheres the electron being transferred across a bridging group.

\[
\begin{align*}
\left[\text{Co(NH}_{3}\right]_{2}\text{NCS}]^{2+} + \left[\text{Cr(H}_{2}\text{O}_{6}]^{2+} & \rightarrow \left[\text{Co(NH}_{3}\right]_{2}\text{NCS}]^{4+} + \left[\text{Cr(H}_{2}\text{O}_{6}]^{2+} + 5\text{NH}_{4}^{+} \\
& + \left[\text{Cr(H}_{2}\text{O}_{6}]^{2+} \text{SCN}]}^{2+}
\end{align*}
\]
Multi equivalent reactions

Oxidising agents such as Cr(VI) and Mn(VII) undergo net changes of 3 and 5 units in oxidation number respectively during their reactions in acidic solution. For the most part, these reactions occur by one or two electron steps, with the necessary intervention of unstable intermediate oxidation states of Cr or Mn. The reactions of Cr(VI) with transition metal complexes generally proceed by sequential one-electron step\textsuperscript{10}, but with post transition metal ions and with non-metallic compounds, two electron steps appear to be preferred.

Electron transfer reactions are found to be governed by two classical principles

(a) Michaelis principle of compulsory univalent oxidation steps\textsuperscript{11}
(b) Shaffer's principle of equivalent change\textsuperscript{12}

Michaelis hypothesis involves the principle that an oxidation-reduction reaction takes place in one or more successive single electron transfer steps. This principle evolved from a considerations 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 the reactions involving metal ions, many two equivalent redox reactions are now known which proceed in one step through the transfer of hydride ion or an oxygen atom\textsuperscript{13}.

E.g., \( \text{NO}_2^- + \text{OCl}^- \rightarrow \text{NO}_3^- + \text{Cl}^- \)

The second principle\textsuperscript{12} refers to the observation that non-complementary reactions are often slow compared with complementary one’s. Examples are the slow reduction of Tl(III) by Fe(II) or Ce(IV) by Tl(I) as compared to the rapid reduction of Tl(III) by Sn(II) and Ce(IV) by Fe(II).
The observations expressed by Shaffer, for non-complementary reactions, are based on the low probability of termolecular mechanisms as one possibility or the formation of the unstable valence states as the other possibility\textsuperscript{14}.

Another expected feature of these reactions will be the frequent occurrence of catalysis since the normal paths will be slow.

**Oxidation-reduction in organic reactions**

The oxidation-reduction concepts, however, are not so clearly applicable in organic chemistry, for when carbon compounds are oxidized their component atoms are very seldom deprived of their surrounding complete electron shells. Covalent bond fission is an essential feature of organic reactions and it can be effected by two different pathways\textsuperscript{15}, viz., "homolytic reactions" in which electron pairs are symmetrically disrupted and "heterolytic reactions" in which electron pairs are transferred from one molecule to another as an undivided entity. Electron removal by these two pathways has clearly distinguishable characteristics.

In homolytic oxidations, electrons are removed singly from organic molecules by active atoms such as chlorine, or by active free radicals. Though, molecules containing unshared electrons can be oxidized in this way, homolytic oxidations usually involve the removal from an organic molecule of one electron together with a hydrogen atom\textsuperscript{16}.

Heterolytic oxidations involve the attack on organic compounds of electrophilic reagents, which can, by a single process gain control of a further electron pair. Heterolytic oxidants therefore attack the exposed electron pairs of
atom such as π oxygen, nitrogen or sulphur or the loosely held π-electrons of olefins, rather than sigma electron pairs of C—H, O—H or N—H bonds. Again, heterolytic reactions yield stable molecular or ionic products in one or at most two consecutive stages and very seldom lead to chain reactions. On the other hand, they usually require higher activation energy than homolytic reactions and so tend to be slower processes. When heterolytic reactions are subjected to catalysis, the mechanism of catalysis is largely different from the catalysis involved in the case of homolytic reactions.

Catalysis

William Ostwald was the first to write down a definition of a catalyst: ‘A catalyst is a substance that changes the rate of a chemical reaction without itself appearing in the products’. It is important to note that a catalyst does not influence the thermodynamic equilibrium of reactants and products. Therefore, the current definition is slightly better, though close to Ostwald’s description: ‘A catalyst is a substance that increases the rate of approach to thermodynamic equilibrium of a chemical reaction without being substantially consumed’17. Catalysts work by providing an alternative mechanism involving a different transition state and lower activation energy. The effect of this is that more molecular collisions have the energy needed to reach the transition state. Hence, catalysts can perform reactions that, albeit thermodynamically feasible, would not run without the presence of a catalyst, or perform them much faster, more specific, or at lower temperatures. The net free energy change of a reaction is the same whether a catalyst is used or not; the catalyst just makes it easier to activate.
Homogeneous catalysis

In homogeneous catalysis the reactants and catalyst are in the same phase. Here catalyst is a molecule, which facilitates the reaction. The reactant(s) coordinate to the catalyst (or vice versa), are transformed to product(s), which are then released from the catalyst.

Examples of homogeneous catalysts are H⁺(aq), which acts as a catalyst in esterification, and chlorine free radicals in the break down of ozone.

Heterogeneous catalysis

In heterogeneous catalysis the catalyst is in a different phase than the reactants and products. A simple model for heterogeneous catalysis involves the catalyst providing a surface on which the reactants (or substrates) temporarily become adsorbed. Bonds in the substrate become weakened sufficiently for new bonds to be created. The bonds between the products and the catalyst are weaker, so the products are released.

Examples of heterogeneous catalysts are finely divided iron in the Haber process to manufacture ammonia, vanadium(V) oxide in the contact process, nickel in the manufacture of margarine, alumina and silica in the cracking of alkanes and platinum rhodium palladium in catalytic converters.

Many catalysts used in refineries and in petrochemical applications are regenerated and reused multiple times to save costs, energy and reduce environmental impact from recycling or disposal of spent catalysts.

Autocatalysis is a form of catalysis in which one of the products of a reaction serves as a catalyst for the reaction. e.g., in the oxidation of oxalic acid by permanganate in acidic medium, Mn(II), one of the products acts as a catalyst.\textsuperscript{18,19}
Since a catalyst alters the rate of a chemical reaction, the effectiveness of various catalysts for accelerating a given reaction can be measured by measuring the velocity constants in the presence of each catalyst in turn. Often, very small quantities of catalysts like Os(VIII), Pd(II), Cr(III), Ru(III), helieds, etc., cause appreciable rate acceleration of particular reactions. The rate increase depends on the catalyst concentration and hence a kinetic-catalytic species becomes available.

Effect of ions on the rate of reaction

The rates of redox reactions of complex ions are highly sensitive to the presence of other ions in the solution. Usually, added anions have the greater influence on the reaction between two cations and vice-versa. Large effects of anions on the rate of reaction are usually attributed to the formation of bridged species if labile complexes are involved.

In the redox reaction between two cations, if the reducing agent is complexed first, it will be more stabilized in the oxidized form and hence the reaction is speeded up in the presence of an anion. Also a negative ion should enable two positive ions to approach each other more easily. This will be more 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 cerium(IV) oxidations is reduced strongly by forming sulphate complexes in presence of sulphate. This shows, in agreement with the theory, that the columbic repulsions between reactants do not play a dominant role. The conclusion to be drawn is not that electrostatic factors do not exist but that the other factors are of greater importance. Chloride ions significantly affect some redox reactions. The redox
reactions, in which the reductant is complexed with chloride, are found able to be accelerated by chloride ions. Reductants that form complexes with chloride are Tl(I)\textsuperscript{26}, Sn(II)\textsuperscript{27}, Sb(III)\textsuperscript{28}, As(III)\textsuperscript{29} and Pd(II)\textsuperscript{30}.

**Active species**

If a particular substance (oxidant, reductant or catalyst) is capable of existence in several forms in aqueous solution, all the species existing may not be active. Those species that are involved in the slow step will primarily influence the reaction. The reaction conditions will determine the nature of the active species. Moore and Anderson\textsuperscript{31} have reported that three or four species of Ce(IV) exist in sulphuric acid depending on its strength and the main active species in dilute solutions is CeSO\textsubscript{4}\textsuperscript{2+}. Harwick and Robertson\textsuperscript{32}, have given the following equilibria amongst various species of Ce(IV) in sulphuric acid solutions. The concentration $\text{H}^+$, HSO\textsubscript{4}⁻ and SO\textsubscript{4}²⁻ would determine the nature of the active species.

\[
\begin{align*}
\text{Ce}^{4+} + \text{H}_2\text{O} & \rightleftharpoons \text{Ce(OH)}^{3+} + \text{H}^+ \quad K_{\text{OH}} \\
\text{Ce}^{4+} + \text{SO}_4^{2-} & \rightleftharpoons \text{Ce(SO}_4^{2+} \quad K_1 \\
\text{Ce(SO}_4^{2+} + \text{SO}_4^{2-} & \rightleftharpoons \text{Ce(SO}_4^{2+} \quad K_2 \\
\text{Ce(SO}_4^{2+} + \text{HSO}_4^- & \rightleftharpoons \text{H}_3\text{Ce(SO}_4^{4+} \quad K_4
\end{align*}
\]

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

**Fast reactions**

The reactions, which go to equilibrium within a few seconds or less, are said to be fast reactions. The half-life range of such reactions is very small. It is of the order of 10 seconds to $10^{-10}$ second. Kinetics of such reactions cannot be studied by usual conventional methods. In recent years various methods like, flow-methods, relaxation methods, flash photolysis etc., have been developed to study the fast reactions.

The study of fast reactions\textsuperscript{33} is on the threshold of exciting developments, since so many reactions of complexes, especially of transition series and biological processes are rapid. Muscle action, self reproduction, the combustion of rocket fuel and gasoline, the action of poisons and nerve gases, appearance of colours on addition of indicators etc. complete within a fraction of second and would thus provide a truly formidable challenge to classical kinetics.

**Five main components of a kinetic investigation are\textsuperscript{34}**

- Intermediate detection and product analysis
- Concentration determination of all species present
- Deciding on a method of following the rate
- The kinetic analysis
- Determination of the mechanism
Present work

In the present investigation, oxidation of some inorganic and organic substances in different media using different oxidants have been studied. These substrates (antimony, palladium, ciprofloxacin, etc.) are mainly considered as water pollutants. The oxidized products formed were found to be less toxic as compared to the non-oxidized substrates. The work done in the thesis can be used for the analysis of these compounds in wastewater successively. The thesis comprises six chapters with a general introduction and summary of the work done as the first chapter. All reactions were followed by spectrophotometer in the UV-vis. region using Varian Cary-50 spectrophotometer and Hitech SFA-12 rapid kinetic accessory.

I. General introduction and summary of the work undertaken

In this chapter an introduction to reaction kinetics and mechanism generally relevant to the studies including summary of the thesis is presented.

PART - I

OXIDATION OF INORGANIC SUBSTRATES

II. Mechanistic study of oxidation of palladium(II) by cerium(IV) in aqueous acid

The kinetics of oxidation of palladium(II) by cerium(IV) has been studied spectrophotometrically in HClO₄ media at 40°C. The reaction is first order each in cerium(IV) and palladium(II) concentrations at constant H⁺ ion concentration. Increasing H⁺ ion concentration accelerates the reaction rate with
fractional order in H⁺ ion concentration. The initially added products, palladium(IV) and cerium(III) do not have any significant effect on the reaction rate. At constant acidity, increasing the added chloride concentration enhances the rate of reaction. H₃Ce(SO₄)₄ and PdCl₂⁺ are the active species of oxidant and reductant respectively. The possible mechanism is proposed and the reaction under this condition follows the rate law:

\[
\text{Rate} = \frac{d[Ce(IV)]}{dt} = \frac{k K_9 [Ce(IV)] [Pd(II)] [H^+]}{1 + K_9 [H^+]}
\]

where \(k\) and \(K_9\) are the rate constant with respect to slow step and equilibrium constant, respectively. The reaction constants involved in the mechanism were calculated. There is a good agreement between observed and calculated rate constants under different experimental conditions. The activation parameters with respect to slow step of Scheme were calculated and discussed.

III. Chloride and iodide mediated oxidation of antimony(III) by cerium(IV) in aqueous sulphuric acid medium

The micro amounts of iodide (10⁻⁷ mol dm⁻³) and chloride (10⁻² mol dm⁻³) mediated oxidation of antimony(III) by cerium(IV) in an aqueous sulphuric acid medium has been studied spectrophotometrically at 25°C and \(\mu = 3.10\) mol dm⁻³. The stoichiometry was 1:2 in chloride and iodide mediated reactions. i.e. one mole of antimony(III) required two moles of cerium(IV). In case of chloride mediated reaction, the reaction was first order in cerium(IV) and halide concentrations, whereas in case of iodide mediated reaction the order with respect to [cerium(IV)] was unity and with respect to iodide
concentrations was more than unity (ca. 1.4). In both chloride and iodide mediated reactions the order with respect to antimony(III) concentrations was less than unity. Increase in sulphuric acid concentration increased the rate. The order with respect to H⁺ ion concentration was less than unity. Added products, cerium(III) and antimony(V) did not have any significant effect on the reaction rate. The active species of oxidant was understood to be H₃Ce(SO₄)₄⁻, whereas that of reductant as SbCl₃ in case of chloride and SbI₂⁺ in case of iodide mediated reactions. The possible reaction mechanisms were proposed and the activation parameters were determined and discussed. The proposed mechanism and the derived rate laws are consistent with the observed kinetics.

PART – II

OXIDATION OF ORGANIC SUBSTRATES

IV. Oxidative transformation of ciprofloxacin by alkaline permanganate – a kinetic and mechanistic study

This spectroscopic study presents the kinetics and degradation pathways of oxidation of ciprofloxacin (CF) by permanganate in alkaline medium at constant ionic strength of 0.04 mol dm⁻³. Orders with respect to substrate, oxidant and alkali concentrations were determined. Effect of ionic strength and solvent polarity of the medium on the rate of the reaction was studied. The oxidation products were identified by LC-ESI-MS technique. Product characterization of ciprofloxacin reaction mixtures indicates the formation of three major products corresponding to m/z 263, 306, and 348 (corresponding to
full or partial dealkylation of the piperazine ring). The piperazine moiety of ciprofloxacin is the predominant oxidative site to $\text{MnO}_4^-$.

Product analyses showed that oxidation by permanganate results in dealkylation at the piperazine moiety of ciprofloxacin, with the quinolone ring essentially intact. The reaction kinetics and product characterization point to a reaction mechanism that likely begins with formation of a complex between ciprofloxacin and the $\text{KMnO}_4$, followed by oxidation at the aromatic N1 atom of piperazine moiety to generate an anilinyl radical intermediate. The radical intermediates subsequently undergo N-dealkylation. Investigations of the reaction at different temperatures allowed the determination of the activation parameters with respect to the slow step of proposed mechanism. For the proposed mechanisms the rate law is

$$\text{Rate} = -\frac{d [\text{MnO}_4^-]}{dt} = \frac{k K_1 K_2 [\text{MnO}_4^-][\text{OH}^-][\text{CF}]}{1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{OH}^-][\text{CF}]}$$

V. Oxidation of DL-methionine by diperiodatoargentate(III) in aqueous alkaline medium (stopped flow technique)

A. At high OH\textsuperscript{-} ion concentration

The kinetics of oxidation of DL-methionine by diperiodatoargentate(III) (DPA) has been studied spectrophotometrically in higher range, 0.3-1.0 mol dm\textsuperscript{-3}, of alkali at constant ionic strength of 0.50 mol dm\textsuperscript{-3}. The order with respect to oxidant concentration was found to be unity. The order with respect to DL-methionine concentration changes from fractional order to zero order. Where as increase in periodate concentration retarded the rate of the reaction. At constant DPA, DL-methionine, periodate and at constant ionic strength, the
order with respect to OH⁻ ion concentration was found to be positive fractional
(0.44). The increase in dielectric constant of the medium increases the rate of
the reaction. The added products did not have any significant effect on the rate
of reaction. The main products were identified by spot test and IR
spectroscopy. A free radical mechanism has been proposed for the reaction.
The active species of Ag(III) was found to be monoperiodatoargentate(III) in
higher range of OH⁻ ion concentration. The rate constant of the slow step of the
mechanism was determined. The activation parameters were evaluated and
discussed.

B. At low OH⁻ ion concentration

The kinetics of oxidation of DL-methionine by diperiodatoargentate(III)
(DPA) has been also studied spectrophotometrically in lower range, 0.01 – 0.20
mol dm⁻³, of alkali at constant ionic strength of 0.50 mol dm⁻³. As in higher
OH⁻ ion concentration, in lower OH⁻ ion concentration also the order with
respect to oxidant concentration was found to be unity and the order with
respect to DL-methionine concentration changes from fractional order (0.40) to
zero order. In the lower range of OH⁻ ion concentration, periodate have no
significant effect on rate of the reaction. At constant DPA, DL-methionine,
periodate and at constant ionic strength, the order with respect to OH⁻ ion
concentration was found to be negative fractional (-0.36). The increase in
dielectric constant of the medium increases the rate of the reaction. The added
products did not have any significant effect on the rate of reaction. The main
products were identified by spot test and IR spectroscopy. A free radical
mechanism has been proposed for the reaction. The active species of Ag(III)
was found to be diperiodatoargentate(III) in lower range of OH⁻ ion concentration. The rate constant of the slow step of the mechanism was determined. The activation parameters were evaluated and discussed.

VI. Oxidation of tyrosine by hexacyanoferrate(III) in aqueous ethanoic acid medium- a kinetic and mechanistic study

The kinetics of oxidation of tyrosine by hexacyanoferrate(III) has been studied in 40% ethanoic acid – water containing 4.0 mol dm⁻³ hydrochloric acid. The oxidation is made possible by varying the difference in redox potential by adding ethanoic acid to the reaction mixture. The reaction is first order with respect to hexacyanoferrate(III) and fractional (0.72) order with respect to tyrosine concentrations. Increasing the acid concentration at constant chloride concentration accelerates the reaction. The order with respect to acid concentration is nearly two. Amongst the initially added products hexacyanoferrate(II) retards the reaction. H₂Fe(CN)₆⁻ is the active species of hexacyanoferrate(III). A suitable mechanism is proposed and the activation parameters and thermodynamic quantities with respect to slow step of Scheme 1 were calculated and discussed.
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