CHAPTER - I

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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 electron loss (oxidation) and electron concept of gain (reduction). Oxidation reduction reactions are also defined involving changes in oxidation states or oxidation as numbers. The assignment of oxidation numbers is based on the following rules : (i) The oxidation number of an atom in an elements is zero; (ii) The oxidation number of monoatomic ions is its charge; (iii) The oxidation number of each atom a covalent compound of known structure is in the charge remaining on the atom when each shared electron pair is assigning completely to the more electronegative of two atom sharing it. An electron pair shared by like atoms is split between them and (iv) The oxidation number of an element in compound of uncertain structure is usually obtained a 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

1

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 reactions are now known which proceed in one step through the transfer of a hydride ions or an oxygen atom $[e.g NO_2^- + OCI \longrightarrow NO_3^- + CI]^{2,3}$.

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 1equivalent reductants or 2-equivalent oxidants and 2equivalent reductants). Examples are the slow reduction of $T1^{3+}$ by Fe²⁺ or Ce⁴⁺ by T1⁺ compared with the rapid reduction of T1³⁺ by Sn²⁺ and of Ce⁴⁺ by Fe²⁺. This can be interpreted in terms of the following types of mechanism for a

2

typical non-complementary reaction in which 'A' is oxidised to ' A^+ ' and ' B^{2+} ' is reduced to 'B':

- I) $2A + B^{2+} 2A^{+} + B$
- II) $A + B^{2+} \longrightarrow A^{+} + B^{+}$ slow $A + B^{+} \longrightarrow A^{+} + B$ fast III) $A + B^{2+} \longrightarrow A^{2+} + B$ slow $A + A^{2+} \longrightarrow A^{+} + A^{+}$ fast

The first of these mechanism 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 Tl(I) - Tl(III) exchange⁶.

The observation expressed by shaffer, for noncomplementary 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 $Tong^{10}$ 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.

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

involving steps of 1(a) to 1(c). The first is a rapid. $Ce(IV) + Cr(III) \longrightarrow Ce(III) + Cr(IV)$ fast1(a) $Ce(IV) + Cr(IV) \longrightarrow Ce(III) + Cr(V)$ slow1(b) $Ce(IV) + Cr(V) \longrightarrow Ce(III) + Cr(VI)$ fast1(c)

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 6occurs¹⁰. The existance 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 stiocheiometric 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 $(2a, 2b)^{14}$.

 $Fe^{2+} + S_2 O_8^{2-} \longrightarrow Fe(III) + SO_4^{2-} + SO_4^{-} \dots (2a)$ As(III) + SO_4^{-} \longrightarrow As(IV) + SO_4^{2-} \dots (2b)

INNER-SPHERE AND OUTER-SPHERE MECHANISM

Two general classes of transition states emerge for redox reactions involving metal complexes, the 'Outerand 'Inner-Sphere'. In the first of these, Sphere' 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 There must also be sufficient orbital overlap two sites. 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 and their coordination spheres, without in any way ions 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 $LxM^{+n+1}XM^{+n}Wx$ 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 м⁺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

6

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 evidance for the mechanism from isolation of the indicated products, which is comes 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 spectrophotometrically, prior detected to their dissociation 15-17. 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 $Co(NH_3)_6^{3+}$ oxidations and $Cr(bipy)_3^{2+}$ reductions; certain reactions of $V(H_2O)_6^{2+}$, which undergoes substitution more slowly than most divalent ions; electron exchange of $Fe(C_5H_5)_2$ and $Fe(C_5H_5)_2^{+}$; and reactions such as electron exchange of $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$.

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 stoicheiometric 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 $[NH_4^+]$ and $[H^+]$. The concentrations of NH_3 , being quite small, is controlled only indirectly. Similarly, when VCl_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 Fe³⁺ in a solution is lowered appreciably by the addition of even small quantities of HF owing to the formation of the rather stable complex FeF²⁺, and the partial ionization of H_3PO_2 lowers the concentration of this species below the added quantity.

formulate the reaction rate as a function То of species concentrations, therefore, requires a knowledge of existence of such equilibria and, generally speaking, the 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 fractions of 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 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 rate 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 sulphate. This shows, in agreement with theory, of 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 Hg(II)/Hg(I), oxidation potentials of the complexes Fe(III)/Fe(II) and Tl(III)/Tl(I) are decreased considerably in presence of chloride ion^{15-17} .

LITERATURE SURVEY

The oxidation of tolune and nitrotolunes to aldehydes catalysed by vanadium (V) in acid solution was studied by Radhakrishna and Patil S.C. and found to be 1^{st} order²⁰ with oxidant and substrate. The reaction was acid catalysed, the active species being pervanadyl ion, VO_2^+ . Mn^{++} also catalyzes the reaction. In solution of acidity 8.1 N, the following rate constants were detd. at 60°C tolune 0.3446, m-nitrotolune 0.000772, p-nitrotolune 0.000581 $mole^{-1}min^{-1}$. The activation energy was 19.68 kcal. The rate increased with decreasing dielectric constant at constant acidity (use of HOAc or H_2SO_4), which was appropriate for a pos. ion dipole reaction. The mol. radius of the activated complex was calculated as 6.4 A. Use of Bunnett's relation (1961) gave an w value of 0.3162, while the reaction constant p had a value of -3.75. Because of the low w and the high p value, the reaction was detd. to be SN_2 , tending toward SN_1 . The rate detg. step was abstraction of the hydride ion.

Vanadium (V) oxidises $(Ta_6Br_{12})^{2+}$ in $HClO_4$ solution in two steps to $(Ta_6Br_{12})^{3+}$ and to $(Ta_6Br_{12})^{4+}$ was studied by Espenson²¹. The second stage reaction follows the rate equation $-d[(Ta_6Br_{12})^{3+}]/dt = [(Ta_6Br_{12})^{3+}] (K_{34} + K'_{34}[H^+][VO_2^+]) [VO_2^+];$ at 25° and $\mu = 0.500$ M, $K_{34} = 1.4 \pm 0.07$ M⁻¹sec⁻¹ and $K'_{34} = 1.17 \pm 0.05 \times 10^4$ M⁻³sec⁻¹. The novel second term in this rate expression suggest either participation of a rapidly equilibrating vanadium (V) dimer or else involvement of a cluster species of net ionic charge

74+. The relative laws for the first step of oxidation was $-d[(Ta_6Br_{12})^{2+}]/dt = K_{23}[(Ta_6Br_{12})^{2+}] [VO_2^+] [H^+] + Ke[(Ta_6Br_{12})^{3+}]$ with Ke = $(K_{34}+K'_{34}[H^+][VO_2^+]) [VO_2^+]$. A method based on the Guggenheim procedure was developed for treating the autocatalytic kinetic data. The value of K_{23} was 2.1 X $10^2 M^{-2}sec^{-1}$ at 20° and $\mu = 0.50 M$. Autocatalysis results from a pathway involving the rate detg. oxidation of the product $(Ta_6Br_{12})^{3+}$ by VO_2^+ , followed by the rapid reproportionation reaction of 4 + and 2 + cluster ions.

The oxidation of 2-mercaptosuccinic acid by the oxy-ions of vanadium (V) was studied²² at pH 2.4-4.4 X 0-25° with a stopped flow technique. The reaction proceed via the formation of a coloured intermediate complex followed by a slower electron transfer step. The intermediate has а stability const. of 10 and at 15° the observed rate const. for its formation may be expressed as $K_{obs} = [44.5 + 465(T)]$ sec^{-1} where T = 2-mercaptosuccinic acid. At 15°, the rate const. for the redox process was $K'_{obs} = [5.0 + 40(T)] \sec^{-1}$. The acid dissocn. const. for 2-mercaptosuccinic acid were also measured. Reaction of the intermediate leads to the formation of the disulfide, and a mechanism for the process was proposed. In the range studied, temperature has no significant effect on the rates.

13

The oxidation of propane-1,3-and butane-1,4 diols by vanadium (V) ion was studied in the presence of H_2SO_4 and perchloric acid²³. The reaction, which was acid catalysed, depends on the activity of water for the entire range of acid concentration used. The tentative reactive vanadium (V) species is discussed and the experimental evidence in support of an acyclic mechanism of oxidation was put forward.

The kinetics of the oxidation of citric acid by quinquevalent vanadium ion in H_2SO_4 and $HCIO_4$ and in the absence of these acids were studied. The reaction was first²⁴ order with respect to quinquevalent vanadium ion and citric acid. The reaction was acid catalysed, the rate was faster in $HCIO_4$ than in H_2SO_4 , though at lower concentration of these acids, the rates are almost equaland were found to be measurable in the absence of these acids. The inadequacy of the different relations corelating the rate with the acid concentration was brought out. The mechanism was discussed and the activation parameters were reported.

Kinetics of oxidation of Ph_2CH_2 , Ph_3CH , flurene and cyclohexane by vanadium (V) in aq-acetic acid²⁵ medium were reported. The experimental findings were rationalized on the basis of previously postulated mechanism. The oxidation of I⁻ with V(V) in H_2SO_4 medium was studied by Nikolov and Mikhailova²⁶ and in an atm. of N proceeds according to the kinetic equation, $d[I_2]/dt = (K'[H^+] + K"[H^+]^2) [V(V)] [I^-]$, where K' = 1.6 X $10^{-2}I^2$. mole⁻²sec⁻¹ and K" = 8.31 X $10^{-2}I^3$ mole⁻³sec⁻¹ for 20° and 1 mole NaHSO₄. The temperature dependence of K" has shown $\triangle Ea =$ 11.7 kcal/mole and $\triangle Sa^{293} = -12.5$ entropy unit. A mechanism was proposed, including as rate detg. stage, the reorganization of the initial complex between V(V) and I⁻.

The kinetics of oxidation of atrolactic acid with V(V) has been studied. The oxidation was 1st order²⁷ with respect to V(V) and atrolactic acid. The activation energy, frequency factor and entropy of activation were 15.56 kcals, 5.9 X 10^7 sec⁻¹ and -20.18 entropy unit. The oxidation was acid dependent, the rate increasing with increasing concentration of the acid. This acid dependence was related to $[H_3O^+]$ but no to Hammett's ho. Addition of some metal sulphate did not indicate any primary salt effect. The oxidation appeared to proceed through an initial complex formation and subsequently through free radicals. The equillibrium const. for the formation of complex and its rate of decomposition has been calculated.

The kinetics of the oxidation of D-fructose with V(V) reaction was studied in H_2SO_4 , HCl and HClO₄

15

solution²⁸. The reaction was 1^{st} order both with respect to V(V) and D-fructose. At low acid concentration the reaction rate was independent of the concentration it was 1^{st} order over part of the range. At higher acid concentration logarithms of 1st order const. depend linearly on the concentration tion of the acids.

The oxidation rate of cycloalkanols by V(V) was studied by Radhakrishna and Murti²⁹ in 50% ag.HOAc at a constant acidity of 8.1N H_2SO_4 and in the dark was a 2nd order reaction with the following rate const. (Alc. rate consts. at 40, 50 and 60° X 10^{-1} mole⁻¹ min⁻¹ given) cyclopentanol, 2.16, 6.56, 11.56, cyclohexanol, 1.25, 2.27, 4.16, cyloheptanol, 4.61, 12.38, 36.49, cyclooctonol, 7.46, 27.19, 53.31. For cyclohexanol at 60° the rate const. at acidities of 8.1, 9.45 and 10.8 N were 4.16, 7.18 and 17.90 moles 1min^{-1} respectively. At 2.7 N H₂SO₄ acidity the following rate const. X 10^{-2} moles $^{-1}$ min $^{-1}$ were obtained at 40, 50 and 60° respectively borneol, 4.04, 10.4, 19.08, isoborneol, 12.50, 44.6, 112.70. The oxidation therefore, although not completely a carbonium ion process has predominantly SN1 character.

The stiochiometry of the Sn(II)-V(V) reaction in $HClO_4$ was investigated by using titrimetric and spectrophotometric methods³⁰. Under the conditions used, the stiochi-

ometry of the reaction was given by $Sn(II) + 2 V(V) \longrightarrow Sn(IV) + 2V(IV)$. The rate law for the reaction indicates that two important activated complexes of different components were formed by parallel paths the formation of the 2 activated complexies were : $Sn^{II} + V^V \longrightarrow [V^V - Sn^{II}]^*$ and $Sn^{II} + V^V \longrightarrow [(V^V)_2 Sn^{II}]^*$.

Kinetics of oxidation of chloro, bromo and iodotolunes in aqueous acetic acid at high acidities $(8.1 - 10.8 \text{ N} \text{H}_2\text{SO}_4)$ was discussed³¹. The reaction was 2nd order. The results were analyzed in the light of electronic effects. The reactivity decreases in the order I > Br > Cl. The enthalpy of activation was approximately equal in all the halotolunes but the frequency factor and entropy of activation are different. The role of solvent was also discussed and mol radii were evaluated.

The kinetics of oxidation of PhCH(OH) Me by V(V) was studied at 50° in 50% HOA c contg. varying amounts of H_2SO_4 . The reaction was 1st order in alc., first order in V and IInd order in $H_2SO_4^{32}$ up to 3 M H_2SO_4 . According to Bunnett's criteria (CA 57 : 1598 d) the slope of 2 indicates that a H_2O mol was involved in the transition state as a nucleophile and not as a proton abstracting agent. The reaction did not exhibit any free radical character.

Extensive graphic data were presented for support of the conclusion that the oxidation of D-Glucose and D-Xylose with V(V) in acid medium was 1st order³³ with respect to V to reducing sugar in agreement with findings of Littler and Waters (CA 54 : 9459 f) for noncarbohydrates. Energies of activation were 22.95 and 16.79 kcal for D-glucose and D-xylose respectively. K_1 was 4.16 X 10^{-3} min⁻¹ for 0.25 M D-glucose in 6N H₂SO₄ and 0.04 M NaVO₃ at 40°. Logs of the 1st order K were linearly dependent on [H⁺]. The α and β anomers could not be distinguished.

Oxidation of PhOH with V(V) in the system $H_2^{O-H_2SO_4}$ proceeds as 2 competing reactions³⁴. A complex of phenol and V(V) was generated and transformed through the phenoxy radical structure. For the oxidation of 1 mole. PhOH 2 moles V(V) were reduced. Values of effective reaction const. were measured at 40-60°. Influence of ion strength was observed. Values of thermodynamic functions of the transition state are given. ΔE^{\neq} 16.8 kcal/mole. ΔH_{313}^{\neq} 15.8 kcal/mole. ΔS^{*} -9eu, ΔG_{313}^{\neq} 18.5 kcal/mole.

The kinetics of oxidation of isopropyl alcohol, sorbitol, diglycolic acid and tetrahydrofuran were investigated³⁵ in aqueous H_2SO_4 (<2M). The total order of the reaction was 2 for all the redox system. The rate of oxidation increases with $[H^+]$, $[H_2SO_4^-]$ and ionic strength. Oxidation of aniline by V(V) proceeds by complex mechanism³⁶. In the first step radical from aniline were formed which quickly react further with excess PhNH₂ and then with the V to give complex dyes. The reaction was 1st order in PhNH₂ and in H⁺ and of complex order with respect to V(V) due to equil. between various v-contg. cations.

The kinetics of homogeneous oxidation of phenols and amines by vanadium (V) in aqueous AcOH at acidity 0.025 - 2M (H_2SO_4) was reported³⁷. The reaction were 1st order in substrate and 1st order in the oxidant, p values are -4.3 and -1.8 for phenols and amines respectively. Oxidation of phenol was ionic bat that of amines was a free radical process.

A kinetic study of the oxidation of butane 1,3 diols by quinquevalent V ion in H_2SO_4 and $HClO_4$ was reported³⁸. The rate was faster in H_2SO_4 and was proportional to the square of H_2SO_4 and HSO_4^- and H^+ ion concentration. The plot of the log of the rate measured in $HClO_4$ medium of const. ionic strength against $-H_0$ yields a straight line with a slope much less than unity. The mechanism consist of an attack by the H_2O mol. on the transient acylic V(V) diol complex for which kinetic evidence was presented. The salt effects on the rate of oxidation of tolunes by vanadium (V) were observed³⁹. The rate was dependent on the cation type and its concentration. The rate was independent on the ionic strength. The rate decreased in the order,

 $Mg > Cr > NH_4 > UO_2 > Na \approx Co \approx Mn > Al$

The Olson-Simonson effect agreed with ion-dipole reaction.

In the oxidation of hypophosphorous acid by V(V)increase in H⁺ ions increased the oxidation rate⁴⁰. The activation energy, the frequency factor and the activation entropy were calculated to 18.8 ± 0.5 kcal/mole (4.4 ± 0.8) X 10¹¹ 1 mole⁻¹ and -5.3 ± 0.35 entropy units respectively. A free radical mechanism for the reaction was suggested.

The oxidation of H_3PO_2 by V(V) in perchlorate pnedia was investigated. The formation quotient of the 1:1 $VO_2^+ - H_2PO_2^-$ complex was measured⁴¹. The rate law of the redox reaction indicates that several V(V) - P(I) complexes were kinetically significant and a mechanism consistent with this was proposed.

Kinetic data for the oxidation of AS(III) by V(V) at 42-55° were reported⁴². The rate of oxidation increases with increase in the concentration of H^+ . The energy of activation, entropy and free energy of activation were

evaluated. The kinetic evidence does not indicate the formation of an intermediate complex between AS(III) and V(V). Some possible steps for the reaction were proposed.

Catalytic effect of Os(III) in oxidation of N_2H_4 by Na vanadate was related with the change of the oxide state of O_g ion in the course of the reaction⁴³. The reaction proceeds via the formation of a 1:1 O_g (VIII) : N_2H_4 complex, which decomps to N_2H_2 , $2H^+$ and O_g (VI). The mechs. of oxidation was derived and rate const. were given for the individual steps of the reaction. The activation energy for the non-catalytic and the catalytic step of the reaction was 11.5 ± 1.5 and 9.6 ± 1.0 kcal/mole respectively. The rates were studied spectroscopically. The catalytic oxidation of N_2H_4 gives N.

The rate of oxidation of $p-EtOC_6H_4NH_3^+(I)$ to $p-EtOC_6H_4NH_2^+$ by aqueous V(V) reached a maximum with no induction period at pH 2.2 where V(V) exist as an indeterminate intermediate (II) formed during the depolymn, of $H_2V_{10}O_{28}^{4-1}$ to $HOVO^{2+}$, polynuclear V(V) ions were unreactive toward (I). The rate of association of I and II was comparable to that of H transfer from II to I, both rates greatly exceeds those for the reverse reaction⁴⁴.

The kinetics of oxidation of $PhP(OH)_2$ by V(V) in H_2SO_4 and $HClO_4$ at 40-55° indicated that an intermediate complex was not formed⁴⁵. The rate of oxidation increased with H^+ concentration. The effect of AcOH on the rate showed the reaction to be of the ion dipole type. Activation parameters were calculated.

Kinetics curve were given for the oxidation of EDTA and $HO_2(CH_2N[CH_2CH_2N(CH_2-CO_2H)_2]_2$ by V(V) in the form of solution of NaVO₃ in NaClO₄ solution of desired ionic strength⁴⁶. The oxidation was of 1st order in respect to the oxidising agent and the acid being oxidized. Rate constant and activation energy data were calculated.

The kinetics of oxidation of H_3PO_3 by V(V) was studied at 40-50° and activation parameters detd. The reaction was acid catalysed faster in H_2SO_4 than in $HClO_4^{47}$. The order of reaction was 1st with respect to H_3PO_3 and V(V). The reaction was initiated by formation of free radical in the slow rate-detg. step.

The kinetics of oxidation of glycerol by vanadium (V) in H_2SO_4 and $HClO_4$ was detd⁴⁸. The rate constant were detd. at several temps. and activation parameters was calculated. A reaction mechanism was discussed.

The kinetics of oxidation of lactic acid by v^{5+} was studied⁴⁹ in presence and absence of Cu^{+2} in H_2SO_4 solution at 58°. At ionic strength μ 0.4 M and 0.04 M H_2SO_4 the pseudo 1st order rate const K increased with increasing H⁺ concentration in the presence and absence of Cu^{+2} .

The kinetics of the oxidation of acetophenone by v^{5+} ion was studied using uv spectroscopy⁵⁰. The apparent primary kinetic isotope effect (k_H/k_p) was 1.76. This observed value was explained by assuming a primary kinetic isotope effect of 5.0 and a secondary isotope effect of 1.46.

The oxidation of kinetics of SCN⁻ by V(V) in aqueous $HClO_4$ -NaClO_4 were detected at 35° with 0.2-1.0 M H⁺ concentration V(IV) slowed there action considerably but HSO_4^- had no efect⁵¹. The data was consistent with the rate law

 $-d [V(V)]/dt = K[V(V) [SCN^{-}]^{3} [H^{+}]^{2} / K'[VOSCN^{+}] + [SCN^{-}]$

A suitable mechanism was proposed. The detection of radical formation and other observations ruled out the possibility of the formation of V(III) intermediate in this reaction.

The rate of oxidation of cyclohexanone by V^{5+} in various acid media was in the order $H_2SO_4 > HC1 > HNO_3 >$ $HClO_4^{52}$. In HCl medium an intermediate of the type $[V(OH)_{3}Cl]^{+}$ reacts with the keto form of cyclohexanone in the rate detg. step.

Vanadium (V) in aqueous perchloric acid oxidised 2-ethylcylobutenols and 2-2 dimethyl \approx cyclobutenol to 4hydroxyhexanol and 4 hydroxy-4-methylpentanal respectively⁵³. The oxidation of the cyclobutenols follows the 'rate law U = K[V(V)] [ROH]ho with the relative reactivities for the cyclobutenol and 2-2 dimet-hylcyclobutenol are equally reactive. Methyl cyclobutyl ether was 10⁴ times less reactive than cyclobutenol. The mechanism was discussed. This suggest that the ester mechanism was generally applicable to vanadium (V) oxidations of alcohols.

The kinetics of reaction of V^{5+} with pyrocatechol (I) in 0.1-1M HClO₄ at ionic strength 1, detd. by a stopped flow technique indicated that a complex formed rapidly and quant the complex slowly decomposed to give 0-benzoquinone. The overall decayrate 1st order⁵⁴ each in V⁵⁺ and I, increased with increasing acidity. The data were consistent with the rapid formation of a stable 1:1 V⁵⁺ I which with more I gave a 2:1 complex which decomposed, in a redox reaction. The protonation of the intermidiate complexes was discussed.

Rate constants and activation parameters were detd.⁵⁵ for the V(V) oxidation of 1' and 2' acetonapthones. The rate constant ratio for 1'-acetonaphthone/2'-acetonapnthone was 1.7 which agree well with their ionic radii ratio (1.5) and indicates on absence of the steric interference by the H in the 8 position which characterized Ce(IV) oxidation.

The kinetics for the oxidation of cinnamic acid with NaVO₃ to give PhCH:CHCH:CHPh were 2nd order⁵⁶. Complexation and concurrent reaction was indicated, Michaelies-Menton type of kinetics were not observed. The rate constant did not correlate with the dielectric constant of the medium.

The kinetics of Sb(III) oxidation, by V(V) in aq.HClO₄ and aq.H₂SO₄ was 1st order in each reactant⁵⁷. The rate increases with increasing acid concentration and is greater with H₂SO₄ than with HClO₄. Addition of ACOH reduce the dielectric constant of the solvent and increases reaction rate. Activation enthalpies and entropies were detd. and compared with those for the other oxidations by V(V).

The kinetics for the oxidation of mandelic acid ester $PhCH(OH)CO_2R$ (R = C_1-C_4 alkyl, $PhCH_2$) by $NH_4VO_3-HClO_4$ was studied⁵⁸ and were 1st order in oxidant and substrate and 2nd order in H⁺. The reactivity of the title cycloalknones towards oxidation by V(V) in aqueous AcOH or Me_2SO solution contatining H_2SO_4 was in the stated order⁵⁹. Added Mn (II) retards the rate significantly. The rate acceleration by $(NH_4)_2SO_4$, NH_4OH and $CoSO_4$ was attributed to specific salt effect. The V(V) oxidation of cycloalkanones in acid medium was postulated to occure via their keto forms by single electron transfer in the rate detg. step.

Rate constants were detg⁶⁰. for the oxidation by vanadium (V) in 4.0 M H_2SO_4 at 35, 40, 45 and 50° of MeOH, EtOH, PrOH, BuOH, Me₂CHCH₂CH₂OH and Me₃COH. The rate detg. step in the oxidation of primary alcs. appeared to the oxidation to RCHOH which was effected concarrently by VO_2^+ , $V(OH)_3^{2+}$ and $[V(OH)_3HSO_4]$ oxidation of RCHOH by V(V) was rapid. A mechanism for the oxidation of Me₃COH was proposed which involved H⁺ attack to give Me₃C⁺, then Me₂C:CH₂ which was oxidised slowly to products.

The kinetics of oxidation of methyl orange and methyl red by V(V) in aqueous perchloric acid was studied⁶¹ and obey the rate law :

 $-d/dt [V(V)] = K'[VO_2^+][dye] + K''K_1 [VO_2^+] [dye] [H^+]^2$

 $H_2PO_4^-$, HSO_4^- and $C1^-$ accelerate the reaction due to additional V(V) species formed with these anions.

The oxidation kinetics of Np(IV) with $\rm NH_4VO_3$ and $\rm H_2O_2$ in a 1.0 to 4.0 M NHO_3 aqueous solution was studied⁶² at 22-40°. The reaction was 1st order with respect to Np(IV) and its rate was proportional to the HNO₃ concentration. The activation energy is 26.2 kcal/mole.

The rate of oxidation of cyclohexanone and lacticacid by V(V) in HCl increases in the presence of Cu^{++} ions. The order with respect to $[V^{5+}]$ was 1 both in presence and in absence of Cu^{++} ions, that in cyclohexanone and lactic acid was fractional in the presence of Cu^{++} ions. Acid catalysis was observed⁶³ both in presence and in absence of Cu^{++} is H_3O^+ concentration dependent. A mech. was suggested.

The redox reaction between $V(\dot{V})$ and thiourea was investigated⁶⁴ at 25° over the H-ion concentration range $[H^+] = 0.2 - 1.40$ M. using modified stopped flow system. Two mol. of thiourea were consumed per mol. of oxidant, the V(IV) product being considered to be a 1:1 thiourea complex.

The oxidation of I by V(V) catalysed by oxalic acid in aqueous $HClO_4$ at constant ionic strength was 1^{st} order⁶⁵ in both V(V) and I. The reciprocal of rate constant correlates linearly with the reciprocal of the square of the catalyst concentration. H^+ accelerates the reaction. An increase in the ionic strength caused a decrease in the reaction rate, suggesting that the rate detg. step involves a cation and an anion. A 1:2 V(V) oxalic acid complex forms, it was more powerful oxidant than V(V) itself.

The kinetics of oxidation of RCOCO_2H (R = H₁Me) by V(V) was studied⁶⁶ spectrophotometrically in the presence of HClO₄ over a wide temperature range. Each reaction was 1st order both in V(V) and substrate. The order with respect to H ion was significantly < 1 in each reaction. The energy of activation were 18.4 ± 1.0 and 12.8 ± 0.5 KCal mole⁻¹ respectively. The corresponding entropies of activation were 1.5 ± 3.0 and -17.0 ± 1.5 cal mole⁻¹ deg⁻¹. The reaction evidently proceeded via free radical intermediate.

The oxidation of D-xylose, L-arabinose and pribose by V(V) in H_2SO_4 was first order with respect to both oxidant and substrate concentration⁶⁷. The rate of oxidation increases with first power of $[H^+]$ in 2.0 M to 4.5 M acid concentration range and with second power of $[H^+]$ in higher acid range > 4.5 M at constant HSO_4^- concentration. The increase in oxidation rate with HSO_4^- concentration at constant H^+ concentration was also observed. The thermodynamic parameters were evaluated.

The kinetics of oxidation of D-galactose, Dmannose, L-arabinose and D-xylose by V(V) in $HClO_4$ was 1st order with respect to both vanadium (V) and aldose⁶⁸. The reaction were catalysed by acid. The addition of $NaClO_4$ accelerate the reaction. Kinetic evidence for the formation of intermediate comp. between V(V) and aldose was insignificant and a mech. was suggested. The oxidation rates follows the order xylose > arabinose > galactose > mannose. The activation parameters were reported.

The kinetics of oxidation of a aromatic azo compounds by V(V) showed⁶⁹ 1st order kinetics each in NaVO₃ and azo compounds $p-RC_6H_4N_2C_6H_4NMe_2-P$ (R = H, Ci, NO₂, CO₂H) and methyl orange. The results indicates that the active oxidising species was a 1:2 complex between the vanadate and oxalic acid.

The kinetics of oxidation of D-mannose, glucose, galactose-arabinose, -xylose and fructose by V(V) in binary mixture of Me_2SO-H_2O and $AcOH-H_2O$ in H_2SO_4 medium has been studied⁷⁰. The reaction was 1st order in both oxidant and substrate. The effect of acidity on reaction kinetics shows a clear difference. The ketose has a unit dependence where as aldose has a 0.5 dependence in Ho. The role of solvent in these reactions has been detd. A suitable mechanism has been postulated taking all the observed facts into consideration. The EDTA-catalysed oxidation of indigo carmine by V(V) was 1st order with both vanadium and substrate⁷¹ and was markedly inhibited by H⁺ ions. Kinetic evidence for the formation of a 1:1 complex of vanadium and EDTA was obtained. The stability constant of this complex and its thermodynamic parameters were evaluated. A suitable mechanism was proposed.

The oxiation of aro.azo. compounds by VO_2^+ catalysed by EDTA obeys 1st order kinetics each in oxidant and substrate⁷². The plot of 1/k₁ vs 1/[EDTA] was linear with a pos. intercept on the 1/k₁ axis. This shows that a 1:1 VO_2^+ EDTA complex was the reactive oxidising species. The rate of reaction decreases with increase in [H⁺]. The activation parameters of the reaction and the stability const and thermodynamic parameters of the intermediate complex were evaluated. The mechanism of catalysis was discussed.

The oxidation of N-methyldiphenylamine-4-sulfuric acid by NH_4VO_3 was catalyzed by Ir(IV) in 2M H_2SO_4 medium⁷³ W, Co, Ni, and Os do not show any catalytic effect on this reaction. On the basis of this reaction a catalytic method was developed for the detn. of small amounts of Ir(IV).

The kinetics of glyoxal oxidation by V(V) was studied⁷⁴ spectrophotometrically (760 mµ) in HClO₄ and HNO₃ solution. The oxidation mechanism involved $C_2H_2O_2-VO_2^+-VO_3^{++}$

complex formation and their slow decomposition. The kinetic equation corresponding to the mechanism and various reaction conditions were derived. The activation energies, enthalpies, free energies and entropies were tabulated.

The oxidation of 4-methylpentan-2-one (1) by V(V)in dil. $HClO_4$ to give Me_2CHCHO , was 1^{st} order each in V(V)and I. The reaction was acid catalyzed⁷⁵ and 1^{st} order in acid $NaHSO_4$, $NaClO_4$, NaCl and Na_2SO_4 has a species effect on the reaction which takes place via a free radical mechanism. A mechanism involving the formation of two types of complexes was suggested.

The kinetics were studied⁷⁶ of oxidation of NH_2OH by VO_2^+ (aqueous) at 25-60°, acidity 1-5 mol/dm³HClO₄ and constant ionic strength 5 mol/dm³. The reaction was 1st order in V concentration and between 0 to 1 in NH_2OH concentration. The variation of pseudo-first order rate constant with $[NH_2OH]$ and $[H^+]$ shows that 2-paths operate both via complexes between VO_2^+ and differently protonated NH_2OH . Entropies and enthalpies were determined for each path.

Vanadium (V) oxidation of L-arabinose was 1^{st} order with respect to oxidant and substrate concentration⁷⁷. The order with respect to $[H^+]$ changes from one in 2.5 - 4.5 M acid concentration range to two in 5 to 6.5 M acid concentration. The oxidation rate increases with ionic strength and decrease with dielectric constant of the medium. Thermodynamic 'parameters were evaluted. The reaction was initiated by the formation of free radical in a slow rate detg. step.

The kinetics of oxidation of 3-alkyl and 3-5 • dimethyl substituted 1 methyl 2-6 diphenyl-4-piperidones by V(V) was examined⁷⁸ in aqueous HOAc containing H_2SO_4 . The reaction were 1st order each in oxident and substrate at constant acid concentration. The order with respect to H_2SO_4 was fractional at 0.2-6 M acid. The oxidation of piperidones involves a free radical mechanism. The order of reactivity was 3-Et > 3 Me > 3-Me_2CH > 3,5-di-Me. A tentative mechanism and corresponding rate equation was proposed.

The oxidation of 4-methylpentan-2-one by V(V) in dil. sulfuric acid was found⁷⁹ to 1st order in V(V) and 0.8 in the ketone. The reaction follows both acid dependent and independent paths and the order in acid was 1. At concentration of $V(V) > 1.5 \times 10^{-2}$ M, while the order in acid remains unchanged, the order in V(V) is 2 and that in ketone in 1. Taking into account the formation of free radical during the reaction a mechanism involving 1-electron transfer was suggested.

32

The kinetics of Np(V) oxidation by V(V) was studied⁸⁰ in HClO₄ + NaClO₄ solution and ionic strength (μ) 2-4. The activation entropy and energy were -14 entropy unit and 13.5 kcal/mole respectively. The oxidation mechanism involves a slow electron transfer step between NpO₂⁺ and VO³⁺ ions.

The kinetics of oxidation of Np⁴⁺ by V⁵⁺ was studied spectrophotometrically⁸¹ in HNO₃ and HClO₄ solution at ionic strength (μ) 2 and 4 and a rate equation was derived. The activation energy was 18 and 20 kcal/mole $\mu = 2$ and 4 respectively. The oxidation mechanism involves H atom transfer from NpOH³⁺ to VO₂⁺ and VO³⁺ ions in parallel slow reaction.

The oxidation of butan-2-one by vanadium (V) showed 1^{st} order kinetics each in 2-butanone (I) and oxidant, while the order with respectively to acid approached one⁸². The solvent p isotope effect suggested involvement of the enolic form of I in a reaction occuring via free radical intermediate.

The oxidation kinetics of $ROCH_2CH_2OH$ (I, R = Me, Et) by NH_4VO_3 in H_2SO_4 was 1st order⁸³ each in substrate and oxidant. The reaction involves the formation of an intermediate complex between I and $V(OH)_3HSO_4^+$ the decomposition of which was rate limiting.

33

The oxidation of D-xylose, L-arabinose and Dribose by V(V) in HCl were essentially of the 1st order with respect to both substrate and oxidant concentration⁸⁴. The rate increases with H^+ and Cl^- concentration. A chloro complex of vanadium is assumed to be the active species. The thermodynamic parameters were calculated.

the oxidation of the isoquinoline⁸⁵ by V_2O_5 In reaction occurs either at the heterocyclic N atom to give 1-benzyl-6-7 dimethoxyisoquinoline and 1,3,4-trioxo-1,2,3,4, tetrahydroisoquinoline or at the methoxy gr. to give ring cleavge, the proportion depends on the H_2SO_4 concentration. Conservation of CH₂ was seen in formation of 2-benzyl -3.4pyridinedicarboxylic acid.

of D-soubitol with V(v) in H₂SO₄₄ The kinetics of oxidation⁴ was studied in presence of excess of substrate and acid concentration and by establishing unreacted oxidant titrimetrically⁸⁶. The pseudo-1st order rate constant K_{obs} increases with [D-Sorbitol], $[H_2SO_A]^2$ $[HSO_A^-]^2$, ionic strength and the percentage composition of acetic acid in the binary mixts. of acetic acid-[H⁺] water. However the K_{obs} was not affected by change in at constant $[HSO_{4}]$. The oxidation product was glucose and when the oxidant was in excess, formic acid was obtained as the end product. The suitable mechanistics steps involving the formation of free radical were proposed and thermodynamic parameters were reported.

The oxidation of substituted benzyl alcohols with V(V) was carried out on $HClO_4$ solutions⁸⁷. All rate constant were determined under pseudo 1st order conditions with PhCH₂OH in excess. The rate of oxidation was linearly dependent on [HClO₄] when the concentration strength was held constant. Rate constant and activation parameters were determined.

The kinetics of oxidation of HNO_2 by VO_2^+ were studied spectrophotometrically⁸⁸ at 320 nm in 1M $HClO_4$ medium at 293-308 K. The rate increases with increase in ionic strength. A mechanism was proposed and activation parameters were determined HSO_4^- markedly acelerates the reaction.

One mole of dulcitol was oxidised to galactose by 2 eq. of V(V) at 70° in 1.2 M H_2SO_4 . When V(V) was in excess, 14 equivalent of V(V) are required for the complete oxidation of 1 mol of dulcitol to formic acid⁸⁹. Mechanistic step involving a free radical were proposed on the basis of kinetic and stiochiometric results. The rate expression.

d[V(V)]/dt = K[V(V)] [dulcitol] [H₂SO₄]²

explains the kinetic results. Further solvent effects were

studied and thermodynamic activation parameters calculated.

Rate constant (K_1) for the oxidation of m-cresol were detd. by V(V) in presence of salicylic and substituted salicylic acids were detd⁹⁰. in perchloric acid medium. The reaction was 1^{st} order each in V(V) and m-cresol. Plots of 1/k Vs J/[L] (where L represents salicylic or substituted .salicylic acid) were linear with positive intercepts on log K_1 - axis, suggesting the formation of a 1:1 complex between V(V) ligand which was belived to be a more potent oxidant. The reaction acid catalysed and the plot of $1/k_1$ vs $1/[H^+]$ linear with a positive intercept on 1/k₁ axis. was The applicability of Marcus theory to this reaction was discussed.

The oxidation of glycolic acid by quinquevalent vanadium in sulfuric acid⁹¹ was 1st order each in [oxidant] and [substrate] and 2nd order in [H⁺] with activation energy 13.68 kcal/mole. The acid dependence of oxidation was expressed by log k = 1.2 log $[H_2SO_4] - 3.74$. The rate constant increased with $[HSO_4^-]$ at constant $[H^+]$. A radical mechanism was postulated.

The oxidation of indigo carmine by V(V) studied spectrophotometrically⁹² in perchloric acid medium was 1st order each in V(V) and indigo carmine. The formation of a 1:1 complex between V(V) and the ligand was found. The activation and thermodynamic parameters has been calculated. The applicability of the Marcus relationship between catalytic effectiveness and redox potential of V(V)/V(IV) couple in the presence of different ligands viz. salicylic subsequently salicylic acids was discussed.

The kinetics of the $HO_2(CO_2H)$ (I) catalyzed oxidation of HNO_2 by V(V) in M HClO₄ was 1st order each in V(V), NO_2^- and fractional order in I. NO_3^- retards the reaction⁹³. At low H⁺ concentration the reaction was independent of the H⁺ concentration, at higher concentration, the reaction was retarded by additional H⁺. The kinetics and a spectral detn. support the intermediacy of a 1:1 V(V) -I complex.

The kinetics of the oxidation of tetramethylolmethane and 2,2-diethyl-1-3-propanediol with V(V) was studied⁹⁴ in H_2SO_4 and $HClO_4$ solution. The reaction were 1st order with respect to alc. and V(V) concentration and were faster in H_2SO_4 than in $HClO_4$ solution. Added NaHSO₄ and NaClO₄ both accelerate the reaction, the effect of the 1st salt being greater. At constant H⁺ concentration and at constant ionic strength, the reaction were 1st order with respect to the HSO_4^- concentration. A reaction mechanism was discussed. The kinetics of oxidation of 6-epimeric pairs of piperidin-4-ols by V(V) in AcOH containing H_2SO_4 and $HClO_4$ were studied⁹⁵. The corresponding deuterated piperidin-4-ols were pred. in most of the cases and their rates of oxidation by V(V) were determined. The reaction was 1st order each in oxidnt and substrate at constant acid concentration and 1st order in H_3O^+ at constant ionic strength in $HClO_4$. A mechanism involving a free radical intermediate was proposed. Activation parameters were also determined.

In the oxidation of phenyl substituted alcohols with V(V) were studied⁹⁶ in perchloric acid, acetic acid water (50 vol %) solution, the reactivity decreases in the order: einnamyl alcohol > benzyl alcohol > diphenylmethanol \approx 1-phenylethanol. the activation parameters were determined. The results were discussed in terms of a mechanism involving formation of a radical by H atom clevage in the rate detg. decomposition of an alcohol-vanadium complex.

The oxidation of diethylene glycol by V(V) was carried out in H_2SO_4 and $HClO_4$ media⁹⁷. The reaction was acid catalyzed and first order with respect to V(V) and the substrate. A radical mechanism was postulated.

The reaction $V(V) + ClP_z \longrightarrow V(IV) + ClP_z^+$. (ClP_z) = chlorpromazine) was studied by stopped spectrometry and pulsed radiolysis methods⁹⁸. Oxidation occurs at pH 7.4. The forward and reverse rate constant were given.

The rate of oxidation of amino acids by V(V) in aqueous $HClO_4$ was 1^{st} order with respect to V(V) and amino alcohol⁹⁹. The dependance of the rate on the acidity of the reaction mixture indicates that the active species was $V(OH)^{2+}_{3}$. The influence of substrate structure on the rate of oxidation was studied. In the proposed mechanism for the oxidation the rate determining step was the homolytic decomposition of an amino alcohol -V(V) complex and involves H abstraction from the C-H bond and to the OH group.

The kinetics of the oxidation of D-fructose with V(V) in HClO₄ were studied¹⁰⁰. The reaction was 1st order with respect to [fructose] but values of the rate constant increases slightly with increasing [V(V)]. In the range from 0.002 - 0.02 M V(V) the inverse of the 2nd order rate constant was linearly related to the inverse of [V(V)]. NaHSO₄ and NaClO₄ accelarates the reaction, the effect of the former salt being greater. At constant [H⁺] ionic strength, the reaction was 3rd order with respect to [H⁺]. The activation parameters were determined The data obtained were compared with those for simple mono and polyhydric alcs. A possible 3 step mechanism involving C-H bond fission and yielding glucosones as primary production was suggested.

The oxidation of acetylactone and benzoylacetone

by V(V) was studied¹⁰¹ in aqueous acetic acid in the presence of ammonium metavanadate dissolved in an appro priate concentration of H_2SO_4 . The reaction were 1st order in V(V). An ion-dipole mechanism was postulated.

Allyl alc. (I) oxidation with V(V) in $HClO_4$ solution was 1^{st} order each in V(V), I and H⁺ concentration. Both added $NaClO_4$ and $NaHSO_4$ accelerates the reaction, the effect of the latter salt being greater¹⁰². At constant H⁺ concentration and at constant ionic strength oxidation was 1^{st} order in HSO_4^- . Activation parameters were determined. A reaction mechanism involving radical formation by H cleavge in the rate detg. step, followed by a rapid oxidation of the radical to acrolein is suggested. The main oxidising species in $HClO_4$ solution is $V(OH)_{3}^{2+}$, in HSO_4^- solution, $V(OH)_{3}HSO_4^+$ contributes.

Oxidation of PhCHO and its substrates derivates by V(V) in $HClO_4$ was 1st order in both [V(V)] and $[H^+]$ and $< 1^{st}$ order in substrate¹⁰³. The kinetic and spectrophotometric results indicate the formation of an intermediate 1:1 complex between the reactive V(V) species and hydrated PhCHO prior to electron transfer. Thermodynamic parameters associated with the intermediate complex and activation parameters for the slow step were evaluated. The reaction has a significant D isotope effect. A mechanism consistent with the experimental observation was proposed.

The oxidation kinetics of digol by V(V) were studied¹⁰⁴ in aqueous H_2SO_4 and HCl. The order of reaction with respect to the oxidant and substrate was 1 within the range of the concentration used. Formation of a intermediate complex between V(V) and substrate and free radical formation during the course of reaction were observed. The energy of activation and entropy of activation were calculated. A mechanism was proposed.

Oxidation of L-serine by V(V) in H_2SO_4 medium follows 1st order kinetics in oxidant and substrate each¹⁰⁵. The oxidation rate increases with square of sulfuric acid and bisulfate ion concentration. Bunnett plot indicates that water acts as a proton abstracting agent. The effect of acetic acid on the rate indicates the reaction to be of ion dipole type. Thermodynamic parameters were computed. A mechanism involving decarboxylation followed by deamination was suggested.

The oxidation of RC_6H_4NHPh (I, $R = 2-NO_2$, $3 - NO_2$, 4 - NO_2 , 4 - MeO) by ammonium vanadate¹⁰⁶ (II) in H_2SO_4 was 1st order in H_3O^+ , I and II with activation energies of 37-38 kJ/mol. A common mechanism, involving reaction of protonated I with II was proposed for all I. The kinetics of the oxidation of D-galacturonic acid by vanadium (V) in acid solution were studied 107 . The reaction was of the 1st order with respect to both V and the org. substrate. Formic acid and VO are the final reaction products. The reaction rate was increased with increasing acidity, suggesting that variously protonated vanadium (V) species were active in the substrate oxidation.

The oxidation of $Mo_3O_4(H_2O)_9^{4+}$ by VO_2^+ in aqueous $HClO_4$ was studied¹⁰⁸ sphectrophotometrically at 25°. The stoichiometry was determined to be 1 Mo_3^{IV} : $6V^V$. The effect of $[VO_2^+]$ and $[H^+]$ on the rate constant were determined. A mechanism was proposed.

The kinetics of the oxidation of D-glucose and Dmannose with V(V) were studied¹⁰⁹ in aqueous $HClO_4$ solution and the results were compared with corresponding data for D-fructose. The reaction were of 1st order with respect to the carbohydrate concentration but the values of the rate constant for fructose increases slightly while those for mannose decreases slightly with increasing V(V) concentration. At constant ionic strength the reaction for mannose, like glucose, was of 2nd order, but, that for fructose of 3rd order with respect to the H⁺ ion concentration. Possible mechanism involving c-c bond cleavage for glucose and mannose to arabinose and CH bond cleavage for fructose to dicarbonyl compounds as the 1st reaction products were suggested.

Oxidation of 3-pentanone by V(V) in H_2SO_4 inhibits¹¹⁰ first order kinetics in [oxidant], [substrate] and [H⁺]. Activation parameters were calculated. A radical mechanism was proposed.

The oxidation of trans-stibene and indene by Cr(VI) and V(V) were acid catalysed and strongly dependent on the permittivity¹¹¹ of the medium with Cr(VI) indene (I) reacts faster than trans-stihene (11), with V(V) II reacts faster than I. The mechanism was discussed.

The reaction between VO_2^+ and 2 dimeric Mo(V)complexes, $MO_2O_4^{2+}$ and $MO_2O_4^-$ (EDTA)⁻ was studied¹¹² in HCl and HClO₄ media via stopped flow technique. The overall reaction stiochiometry in which an intermediate was formed correspond to the equation $(MO(V))_2 + 2VO_2^+ \longrightarrow 2MO(VI)$ $+ 2VO^{2+}$. The rate constant and the hydrolysis constant were determined at 25° and ionic strength 1 M HCl. The value for K was unaffected by the products but was retarded by ClO_4^- . An intermediate composed of $(MO(V))_2$ and V(V) was postulated.

The oxidation of ethyl digol by vanadium (V)

reaction was 1^{st} order with respect to V(V) and the substrate and was acid catalyzed¹¹³. The Hammett acidity function (H_o) and Bunnett hypothesis has been applied. The formation of free radicals during the course of the reaction has been indicated and probable reaction mechanism was proposed.

The kinetics of the oxidation of acetoin with V(V)were studied 114 in HClO₄ solutions. This secondary oxoalc. oxidizes faster than hydroacetone. The reaction was of 1st order with respect to the V(V) and acetoin concentration and of 2nd order with respect to the H ion concentration. The proponderant oxidant was supposed to be $V(OH)_2^{3+}$ cation. At a constant H ion concentration and a constant ionic strength the reaction was of 1^{st} order with respect to the HSO₄ ion concentration which points to the $V(OH)_2HSO_4^{2+}$ cation as more powerful oxidant. Activation parameters а were A reaction mechanism involving formation of a determined. radical by H atom transfer in the rate detg. decomposition of an acetoin -V(V) complex was suggested.

PRESENT WORK

The work for M.Phil. dissertation consists of study of oxidation of thiosemicarbazide by vanadium (V) in perchloric acid medium. The results indicated formation of complex between the two. Therefore, the effect of reactants on the formation as well as decomposition was studied along with the effect of perchloric acid. A probable mechanism and the rate law is given based on the results. Similarly the oxidation of hydrazine by vanadium (V) was also studied particularly the effect of sulphuric acid on the reaction. An effort is made to understand the active species of the oxidant.