CHAPTER 4

DISCUSSION
Two different reaction paths were proposed by the research workers\textsuperscript{1–5}, who were involved in the preparation of carbonyl compounds by the oxidation of oximes with metal ions. McKillop et al\textsuperscript{5} suggested a mechanism involving the formation of a complex which decomposes into the products. Including McKillop et al, others have proposed that the intermediate complex formed gives rise to an iminoxy radical and this free radical dimerizes to yield the products. Santappa et al\textsuperscript{6–9} who have studied the oxidation kinetics of a number of aldoximes and ketoximes with thallium(III) acetate proposed that the corresponding carbonyl compounds are formed via the formation of an intermediate complex and an iminoxy radical, the formation of the radical being the rate determining step. They further suggested that an iminoxy radical may be formed via an inner-sphere mechanism or an outer-sphere mechanism and if the radical is formed via an inner-sphere mechanism the increase in $[H^+]$ will have to decrease the rate. The author did not come across any studies on the oxidation kinetics of cyclohexanone oxime by metal ions. Santappa et al also used V(V) as an oxidant in their studies on the kinetics of the
oxidation of acetophenone oxime and reported that the reaction is first order in each with respect to \([V(V)]\) and \([\text{oxime}]\). In the present study the reaction between cyclohexanone oxime and V(V) initiated vinyl polymerization indicating the formation of a free radical as an intermediate. The reaction is acid-catalysed. According to Santappa et al, this observation suggests that the iminooxy radical is formed via an outer-sphere mechanism. But here \(\text{H}^+\) ions are involved in the protonation of the vanadium species before forming the intermediate complex. The increase in the rate of reaction with increase in \([\text{H}^+]\) cannot be solely attributed to the outer-sphere mechanism. If the formation of an iminooxy radical is through an inner-sphere mechanism then it must involve in two-electron reduction of metal ion. During the product analysis it was found that vanadium(V) being reduced to blue, \(\text{VO}^{2+}\) ion. This suggests that the reaction is proceeding through one-electron process. This observation supports that the formation of iminooxy radical is through outer-sphere mechanism. It was reported in literature\(^{10-12}\) that the active species in sulphuric acid and perchloric acid media are \([\text{V(OH)}_3\text{HSO}_4]^+\) and \([\text{V(OH)}_3]^2+\), respectively. The following scheme for a one-equivalent process\(^{13}\) in vanadium oxidations has been proposed.
\[ \text{VO}_2^+ + H^+ + H_2O \xrightleftharpoons[K_1]{K_1} \text{V(OH)}^{2+}_3 \text{(in perchloric acid)} \]
\[ \text{VO}_2^+ + H_2SO_4 + H_2O \xrightleftharpoons[K_1]{K_1} \text{V(OH)}_3\text{HSO}_4^+ \text{(in sulphuric acid)} \]
\[ \text{V(OH)}^{2+}_3 + S \xrightarrow[K_2]{\text{slow}} \text{S} \xrightarrow{} \text{V(OH)}^{2+}_3 \]
\[ \text{S} \xrightarrow{} \text{V(OH)}^{2+}_3 \xrightarrow[k]{\text{fast}} \text{R}^* + \text{VO}^{2+}_2 + 2H_2O \]

and the rate expression for the disappearance of V(V) is derived as

\[ -\frac{d[V(V)]}{dt} = \frac{k K_1 K_2 [S][H^+][V(V)]_T}{1 + K_1 [H^+] + K_1 K_2 [S][H^+]} \]

On similar lines the following mechanism has been proposed for the oxidation of cyclohexanone oxime by V(V) in perchloric acid medium.
$VO_2^+ + H^+ + H_2O \rightleftharpoons V(OH)_3^{2+}$

$$\text{Cyclic N=O} + V(OH)_3^{2+} \quad \xrightarrow{k_2} \quad \text{Cyclic N-O}$$

$$\text{Cyclic N=O} + V^{2+} + H_2O \quad \xrightarrow{k_1 \text{ (slow)}} \quad \text{Cyclic N-O}$$

$$2 \text{Cyclic N=O} \rightarrow 2 \text{Cyclic CO} + H_2N_2O_2$$
and a similar rate expression is derived, viz.,

\[ \frac{-d[V(V)]}{dt} = \frac{k K_2 K_{oxime} [H^+][V(V)]}{1 + K_1 [H^+]} \]

A similar mechanism can be proposed in the sulphuric acid medium also.

Assuming that \( l \) is far greater than the remaining factors in the denominator of the rate expression, the results of the kinetics of the oxidation of the organic substrates by vanadium(V) by various workers are shown to follow first order kinetics with respect to vanadium(V) and the substrates. In the present investigation, vanadium followed first order kinetics initially in both the acids and fractional order in the remaining course of the reaction. Since the rate of disappearance of \( V(V) \) is followed in determining the pseudo-first order rate constants \( k_1 \), this observation shows that the vanadium consumption becomes faster after sometime of the reaction started. Since vanadium(V) is involved in the conversion of iminoxyl radical into an hydroxy intermediate, it may be assumed that this particular reaction may not be started until sufficient amount of free radical is formed. This is supported by the decrease in time interval of the slow disappearance region with the increase in concentration of the mineral acid and with the increase of the temperature, where the rate of formation of free radical increase is
expected. Surprisingly the rate of disappearance of V(V) is found to decrease with increasing concentration of oxime with a negative order of about 0.5 in both the acids. This observation, instead of increasing the rate of formation of iminoxy radical with the increase of oxime concentration which is normally expected, suggests that the rate of iminoxy radical formation is actually decreasing. This observation further supported by the increase in time interval of initial slow rate region in the concentration-time plots. At present the author is not able to explain how this increase in oxime concentration is decreasing the rate of formation of iminoxy radical and there by the decrease in the pseudo-first order rate constants. It may be that two oxime molecules are involved in the formation of intermediate complex reducing the capability of the cleavage of O-H bond in forming the iminoxy radical from the decomposition of the intermediate complex. This proposition includes a square term in substrate concentration in the rate expression suggested. If the value of $K_2$ is comparatively larger to neglect 1 and $K_1[H^+]$ in the rate expression, a negative value of about 0.5 could be understood.

**Oxidation of resacetophenone oxime:**

Prasanna Chith investigated the properties of resacetophenone oxime complexes of metal ions including vanadium(V) in solution employing spectrophotometric, pH metric and polarographic techniques in this laboratories.
He reported 1:2 brown complex formation between V(V) and resacetophenone oxime at pH 1.1, with the release of two protons. He has made the studies in aqueous ethoxy ethanol medium.

In the present investigation an instantaneous development of brown colour was observed on adding vanadate solution to the acidic oxime solution to start the reaction and the intensity of the colour was found to decrease with time. This suggests that a 1:2 complex is being formed instantaneously and this complex is decomposing with simultaneous reduction of V(V). During the product analysis it was observed that V(V) is being reduced to V(III) (green) in both the acid media. The reaction between V(V) and resacetophenone oxime did not induce vinyl polymerization. Based on these facts, it is supposed that a 1:2 chelate complex between one metal ion species and two oxime molecules with the formation of two covalent bonds through ortho phenolic oxygen atoms with the metal ion species and through two co-ordinate bonds between oxime nitrogen atoms and metal ion species. This complex is protonated immediately at ortho phenolic oxygen atoms. This protonation causes cleavage of V-O bonds yielding a carbocation, V(III) and two protons. The carbocation formed reacts with water and forms an hydroxy compound. The hydroxy compound dimerises and yield 2 molecules of resacetophenone and hyponotrous acid. Based on these foregoing arguments, the following mechanism may be proposed.
\[
\text{VO}_2^+ + H^+ + H_2O \rightleftharpoons V(OH)_3^{2+}
\]
Since the formation of carbocation occurs with the cleavage of V-O bonds, this step may be considered as rate determining step. The zero order kinetics with respect to oxime suggest that the formation of complex is involved in a non-equilibrium step; that means a stable 1:2 complex is instantaneously formed whose formation is independent of the excess concentration of the oxime. Since the protonation is involved in the formation of active vanadium species and in all most all the subsequent reactions, it is very difficult to comment on the order of the reaction with respect to the mineral acid. Had the author studied this oxidation reaction by taking small concentration of the substrate and excess of V(V), the order with respect to oxime might have been one and with respect to V(V) might have been zero, which means the rate of the reaction is dependent on the effective concentration of the complex which in turn is dependent on the concentration of the reactant present in smaller amounts than the other.

Finally the increase in rate for the same concentration of the two mineral acids, in sulphuric acid medium compared to perchloric acid medium, in case of the oxidations of both the oximes is attributed to the different nature of the active species of V(V) in the two acid media.
REFERENCES

14. B.S. Prasannachith, Ph.D. Thesis, SV University, Tirupati (India).