CHAPTER IX

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In the present investigation, an attempt has been made to highlight the kinetic features of oxidation of oximes of aromatic, aliphatic and alicyclic ketones and also that of semicarbazones of aromatic ketones by acid dichromate in aqueous acetic acid medium. The rates were measured under pseudo-first order conditions in the presence of sulphuric acid for oximes. Studies with semicarbazones were carried out in the absence of sulphuric acid. The main theme is to suggest a mechanistic pathway of these oxidation reactions in order to account for the structure reactivity correlations.

The introductory chapter includes a special mention about the role of Cr(VI) as an oxidant and a concise review of the oxidation kinetics of various substrates by Cr(VI).

A literature survey of the reactions of oximes and semicarbazones with various reagents along with the postulated mechanisms are presented in the second chapter.

The scope and main objectives of the title investigation are mentioned in brief as the subject matter of the third chapter. A list of the various substrates chosen for study is also enclosed in this chapter.

Materials used, method of purification of the solvent and the various procedures adopted for the preparation of substrates are described in the fourth chapter. It also includes the actual rate measurements under various experimental
conditions to know the effect of different parameters on the rate law and mechanism and finally the non-kinetic methods.

The experimental results of the oxidation kinetics of various substrates by Cr(VI) are presented in fifth, sixth, seventh and eighth chapters with relevant tables and graphical representations.

The discussion of the results is based on the observations derived from the studies of kinetic order, rate law, acid dependence, effect of solvent polarity, influence of ionic strength and activation parameters.

All the three classes of oximes have similar kinetic behavior. The reactions of oximes with Cr(VI) are found to obey a first order kinetics each with respect to [Cr (VI)] and [Oxime] and a fractional order dependence on [H⁺]. A positive dielectric effect is observed in the oxidation of all types of oximes by Cr(VI) indicating the participation of ion-dipole species in the rate-determining step. It is of interest to note that the added NaClO₄ has negligible influence on the reaction rate. Therefore on the basis of absence of salt effect, it was concluded that it is an acid catalysed reaction. Various activation parameters are computed by running the reactions at four different temperatures. The oxidation of oximes by Cr(VI) is presumed to go via an ionic mechanism since the reaction mixture fails to induce polymerisation of added acrylonitrile.

The oxidation of semicarbazones of aromatic ketones with acid dichromate also exhibits first order dependence each in [substrate] and [oxidant]. As the reactions were immeasurably fast in the presence of sulphuric acid, the oxidation kinetics was followed in aqueous acetic acid medium only. The rates are dielectric dependent. The rate decreases with decrease in solvent polarity. This and the
observed marginal influence of ionic strength on the rate together indicate the probability of dipole - dipole interaction. The thermodynamic parameters have been calculated. Absence of induced polymerisation with added acrylonitrile monomer suggests that free radicals are not involved in the reaction.

The final product was identified as the corresponding ketone in each of the oxidation reactions of oximes and semicarbazones in accordance with the reaction stoichiometry 1:1 in all the cases.

Based on the experimental facts suitable mechanisms have been proposed and the corresponding rate law has been derived for the Cr(VI) oxidation of aromatic ketoximes, aliphatic ketoximes, alicyclic ketoximes and aromatic semicarbazones as in fifth, sixth, seventh and eighth chapters respectively.

The fifth chapter gives an idea about structure reactivity correlation among the aromatic ketoximes. A good correlation was observed in Okamoto - Brown plot when σ+ values are used. The reactivity sequence is found to be

\[ p-\text{NO}_2 > m-\text{NO}_2 > p-\text{Cl} > p-\text{H} > p-\text{Et} > p-\text{Me} > p-\text{OMe} \]

in acetophenone oxime and

\[ p-\text{Cl} > p-\text{H} \]

in benzophenone oxime. The observed trend can be rationalised on the basis of –I and –M effects. The electron – withdrawing substituents in the para position increase the positive charge density on the carbonium ion thus facilitating the nucleophilic attack by the dipole, water in the rate determining step. The electron-releasing substituents retard the reaction through their polar and hyperconjugative
effects. Para – hydroxy and para-amino substituted acetophenone oximes do not undergo oxidation reaction with acid dichromate which may be accounted for, by the formation of an intermediate quinonoid compound. This observation provides a clear supportive evidence for the mechanism proposed.

The effect of varying the alkyl substituent on the rate of oxidation of aliphatic ketoximes can be explained with steric and polar effects as discussed in the sixth chapter.

The seventh chapter presents the effect of ring size on the oxidation which is notable. As the cyclohexanone ring is either increased or decreased by one carbon atom, the rate is decreased. The observed reactivity order cyclohexanone > cycloheptanone > cyclopentanone has been ascribed to their conformational differences. This can be rationalised on the basis of I-strain.

Attention is focussed on the relation between chemical reactivity and molecular structure of aromatic semicarbazones in the eighth chapter. The reactivity trend observed among the semicarbazones is

\[
p^{-\text{Me}} > p^{-\text{Et}} > p^{-\text{H}} > p^{-\text{Cl}} > p^{-\text{OMe}}
\]

A good linear correlation obtained in the Hammett plot supports the observed reactivity sequence. The electron releasing substituents favour the polarisation of carbon-nitrogen double bond of the semicarbazone fragment enhancing the reaction rate. However, the \(p\)-OMe has the lowest value of the rate constant and it deviates from the linear plot. This is because the \(p\)-OMe goes out of plane form the carbon-nitrogen double bond due to large steric interactions preventing the extended conjugation.
In this investigation, an attempt has been made to bring together much of the experimental results of the acid dichromate oxidation kinetics of three chosen categories of oximes by suggesting a hydride-ion transfer mechanism for all the three types of substrates. The divergence of reactivity has been accounted to the possible extent.

As the acetophenone oxime was characterised to be only the syn isomer, the investigation can be extended further with anti alkyl aryl ketoxime also to probe into the configurational aspects of the oxidation studies which is a pioneering field of investigation. The well established conformation of heterocyclic and bicyclic ketone oximes such as piperidone oxime, oxanone oxime and camphor oxime opens out into a novel area of research.