CHAPTER VIII

SUMMARY
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In the present investigation an attempt has been made to highlight the kinetic features of oxidation of oximes of various aromatic, aliphatic and alicyclic ketones by two structurally similar oxidants NBSA and NCSA.

First chapter deals with the chemistry of oxidants with special mention about their role in oxidation and halogenation reactions.

A concise review of the chemistry of oximes is discussed in the second chapter. It includes a survey of reactions of oximes along with the postulated mechanisms.

The scope and main objectives of the title investigation along with the list of various substrates and oxidants chosen for the present study are enlightened in brief as the subject matter of the third chapter.

Materials used, preparation of oxidants, and their estimation and the various procedures adopted for the preparation of different types of oximes are described in the fourth chapter. The experimental conditions, actual rate measurements and non-kinetic methods like stoichiometry and product analysis are also illustrated in this chapter.

Fifth, sixth and seventh chapters constitute the experimental results of the kinetics of oxidation of aromatic, aliphatic and alicyclic ketoximes by NBSA and NCSA respectively. Each chapter presents relevant graphical illustrations, discussion of the experimental observations and possible conclusions drawn from them.

The discussion of the results is based on the observations such as the kinetic order, rate law, acid dependence, influence of solvent, effect of ionic strength, activation parameters and reactivity order.
In all the cases the reactions are first order in [oxime], first order in [oxidant] and fractional order in [H⁺]. Influence of ionic strength on the rate of the reaction is negligible.

A negative dielectric effect is observed in the oxidation of aromatic ketoximes while oxidation of aliphatic and alicyclic ketoximes show a positive dielectric effect.

Various activation parameters have been calculated by running reactions at different temperatures.

No induced polymerisation was observed in the reactions.

Stoichiometry of the reaction between the [oxime]: [oxidant] was found to be 1:1 and the products were identified as parent ketones.

In the case of aromatic ketoximes with both the oxidants, the observed order of reactivity is

\[ p\text{-OMeAcPO} > p\text{-EtAcPO} > p\text{-MeAcPO} > AcPO > p\text{-ClAcPO} > p\text{-NO}_2\text{AcPO} > m\text{-NO}_2\text{AcPO} \]

This has been explained on the basis of polar effects of various substituents introduced in the aromatic ring.

Aliphatic ketoximes show the following order in their reactivity.

\[ EMKO > MiPKO > ACO > MnPKO > nBMKO > iBMKO \]

This trend is attributed to inductive effect and steric effect.

The following order is observed in alicyclic ketoximes.

\[ CH\text{exO} >> CH\text{epO} > CPO \]

Such differences in reactivity among different alicyclic ketoximes have been explained with the help of variation in ring size and conformational influences.

On the basis of kinetic data obtained in the present investigation and with the aid of previous literature survey a plausible ionic mechanism has been
proposed for all the three systems with both the oxidants and corresponding rate laws have been derived.

The mechanism envisages the attack of bromonium ion on the oxime molecule in a rate determining step resulting in the formation of resonance stabilized phenonium ion intermediate in the case of aromatic ketoximes.

The aliphatic and alicyclic ketoximes follow a different mechanism which involves the attack of protonated oxidant on the substrate in a slow step leading to the formation of a more stable carbonium ion as an intermediate.

In all the schemes, the intermediate formed is readily attacked by water resulting in the formation of hydroxy nitroso compound which dimerises to yield the respective ketones.

Uniformly, oxidation of all the oximes by N-Chlorosaccharin is faster than those by N-bromosaccharin which gives additional support for the proposed mechanism in each case.

The kinetic study of oxidation of oximes not only provides good procedures for the liberation of ketones from their biological sources but also increase the knowledge about different mechanistic pathways. Oxidation of oximes with other structurally related N- halo compounds provide excellent opportunity for further investigation. As the oximes chosen for the present study are syn aryl oximes, the work can be extended to understand the conformational effect on the reaction by considering anti aryl oximes.