CHAPTER 9

SUMMARY
Summary

The basic principles pertaining to the concept of kinetics of oxidation and reduction, the classification of redox reactions, a special note on the chemistry of quinolinium dichromate (QDC) mentioning its discovery, preparation and structure and a concise review of the reactions of QDC with the postulated mechanisms are presented in the first chapter.

In the second chapter a review of the reactions of oximes and semicarbazones with different oxidants are presented.

The use of QDC in different fields, along with, their potential ability to undergo reactions exhibiting different types of mechanisms, the lack of study on QDC in relation to the present work and the scope of the present investigation are described in brief as the subject matter of the third chapter.

The experimental conditions and the methods employed for the estimation of oxidant, QDC, rate measurements and stoichiometry determination are described in the fourth chapter. The method of purification of the solvent, acetic acid, used in kinetic studies is also mentioned.

The experimental results and discussion of aromatic, aliphatic and alicyclic oximes and aromatic semicarbazones are presented in the fifth, sixth, seventh and eighth chapters respectively. The results for the oxidation of oximes of

a) aromatic ketones:
   - acetophenone
   - p-methylacetophenone
   - p-ethyacetophenone
   - p-methoxyacetophenone
   - p-chloroacetophenone
- p-nitroacetophenone
- m-nitroacetophenone
- benzophenone
- p-chloroacetophenone

b) aliphatic ketones:
- acetone
- ethylmethylketone
- n-propylmethylketone
- iso-propylmethylketone
- n-butylmethylketone
- iso-butylmethylketone

c) alicyclic ketones:
- cyclohexanone
- cyclopentanone
- cycloheptanone

d) semicarbazones of aromatic ketones:
- acetophenone
- p-methylacetophenone
- p-ethylacetophenone
- p-chloroacetophenone
- p-methoxyacetophenone

are presented in the form of tables and graphs. The discussion of the results is based on the observation such as the kinetic order, rate law, acid dependence, influence of solvent, effect of ionic strength and activation parameters.

In all cases, the reactions are found to follow a first order dependence each on [Substrate] and [QDC]. The reaction rates are independent of [H⁺]. The μ
value has negligible influence on the rate of the reactions. The rate is found to increase when the dielectric constant of the medium is increased.

The mechanism proposed in the case of aromatic ketoximes involves the nucleophilic attack of water over the cationic centre of a very stable carbonium ion and formation of a bodenstein intermediate. This bodenstein intermediate on dimerisation gives the parent ketones.

In the case of aliphatic ketoximes the proposed mechanism involves the formation of chromate ester. In the last step the chromate ester by the nucleophilic attack of water gives an intermediate, which on dimerisation gives the corresponding ketones. A similar mechanism is proposed for aliphatic ketoximes and aromatic semicarbazones.

The reactivity trend seen in the aromatic ketoximes has been explained on the basis of inductive, polar and hyperconjugative effects. Among the aliphatic ketoximes the reactivity trend is explained by steric effect. The reactivity trend observed in the cyclicketoximes may be due to I-strain. The reactivity trend seen among aromatic keto-semicolonbazones may be due to the \(+R\) effect of the phenyl ring. In general the oxidative hydrolyses of keto-semicolonbazones are found to be faster than that of the corresponding ketoximes.