V. SUMMARY

The research work described in this Thesis is concerned with the investigation of the kinetics of oxidation of certain Uracils by Ce(IV) in aqueous sulphuric and perchloric acid media separately.

Some important aspects on the basic principles relating to the concept of oxidation and reduction, the classification of redox reactions with relevant examples, a literature review encompassing the role of Ce(IV) as an oxidant in the oxidation of organic and inorganic compounds, a note on the structure and properties of the pyrimidine bases and a brief description of their reactions studied by various methods including pulse radiolysis and flash photolysis are outlined in the first chapter.

The active role of Ce(IV) as an oxidant in redox reactions, synthetic transformations, its versatility in effecting the non-enzymatic hydrolysis of nucleotides and as a cofactor implied in the regulation of cell functions, its ability to react with many organic compounds either through complex formation or a direct electron transfer involving radical intermediates and with inorganic compounds, the lack of study on its reaction with the pyrimidine bases (Uracils) and the scope of the present investigation are described in brief as the subject
matter of the second chapter  The experimental conditions and methods employed for the rate measurements, stoichiometry and product analysis are presented in the third chapter.

The experimental results and discussion are provided in the fourth chapter. The results for all the reactions, oxidation of Uracil, thymine, thymidine, 6-methyluracil, 5-bromouracil, 5-chlorouracil, 5-fluorouracil and 5-iodouracil in aqueous \( \text{H}_2\text{SO}_4 \) and that of Uracil, thymidine, uridine, 6-methyluracil, 1,3-dimethyluracil and 6-azathymine in aqueous \( \text{HClO}_4 \) are presented in the form of tables and graphs. The discussion of the results is based on the observations such as the kinetic order, rate law, effect of \([\text{H}_2\text{SO}_4]\) when \( \mu \) not maintained, effect of \([\text{HSO}_4^-]\), effect of \([\text{H}^+]\), effect of ionic strength (\( \mu \)) and activation parameters. The mechanism of oxidation is proposed taking into account all the experimental observations mentioned above.

In aqueous \( \text{H}_2\text{SO}_4 \), the reactions are found to follow a first order dependence each on \([\text{Ce(IV)}]\) and \([\text{pyrimidine base}]\). No evidence for complex formation between Ce(IV) and the pyrimidines was observed. The reaction rate is retarded by increase in \([\text{H}_2\text{SO}_4]\) and attributed to the complexing ability of \(\text{HSO}_4^-\) (from the dissociation of \(\text{H}_2\text{SO}_4\)) with Ce(IV). The effect of \([\text{HSO}_4^-]\) studied by using a mixture of \(\text{H}_2\text{SO}_4\) and \(\text{HClO}_4\) with different initial concentrations of each but at a fixed total concentration, is found to decrease.
the reaction rate. However, the influence \([H^+]\) studied by applying a mixture of 
\(H_2SO_4\) and \(NaHSO_4\) with individual variation of their concentration but a fixed 
total concentration, is seem to enhance the reaction rate. The rate law is

\[
rate = k_1 + \frac{k_2}{K[HSO_4^-]}
\]

The active species of the oxidant Ce(IV) are Ce(IV), Ce(SO_4)_2 and 
HCe(SO_4)_3, while that of the pyrimidines is the keto (lactam) form:

\[
\text{The existence of the protonated forms of the oxidant, Ce(IV) has been}
\]
taken into account. The proposed mechanism consists in the attack of Ce(IV) 
on the \(C_5 - C_6\) double bond in the pyrimidine ring in a successive fashion forming
the radical cations which then react with \(H_2O\) leading to the corresponding glycol
as the product. The values of \(E_a\), \(\Delta H^\circ\) and \(\Delta S^\circ\) are also calculated and discussed.
The reactivity trend, 5-Iodouracil > 5-Bromouracil > 5-Chlorouracil > Thymine
> 5-Fluorouracil > 6-Methyluracil > Uracil is explained in terms of the
activation parameters.
The differences in the reactivity among the pyrimidines observed are attributed to the differing values of $E^\ddagger$ and $\Delta S^\ddagger$. The values of $\Delta S^\ddagger$ are all found to be negative implying electrostriction in the transition state. A correlation between rate constant and the electron density at $C_2$ observed in the case of 5-halouracils has been studied using a theoretical (semiempirical AM1 method) method involving MOPAC 6.0 programme.

The reactions in aqueous $\text{HClO}_4$ are found to follow the same pattern of dependence of reaction rate on $[\text{Ce(IV)}]$ and [pyrimidine base], as in aq $\text{H}_2\text{SO}_4$ involving no complex formation between Ce(IV) and the pyrimidines. The influence of $[\text{HClO}_4]$ is found to enhance the reaction rate. The active species of the oxidant is Ce(IV). The rate law is

$$\text{rate} = k [\text{Ce(IV)}][\text{pyrimidine base}][\text{HClO}_4]$$

The reactivity trend observed, 6-methyluracil $> \text{uracil} > \text{thymidine} \approx 6$-azathymine $> \text{uridine} > 1,3$-dimethyluracil, is explained in terms of the activation parameters. The reactions in aq. $\text{HClO}_4$ are found to follow the same mechanism as observed in aq. $\text{H}_2\text{SO}_4$. The nature of the product formed in aq. $\text{HClO}_4$ is the same as that in aq. $\text{H}_2\text{SO}_4$, namely the corresponding pyrimidine glycol. The reaction in aq. $\text{HClO}_4$ is faster than in aq. $\text{H}_2\text{SO}_4$ and is due to the higher reduction potential of Ce(IV)/Ce(III) in the former.