Compliance to learned referee‘s suggestions and comments
COMPLIANCE TO LEARNED REFEREE’S SUGGESTIONS AND COMMENTS

At the outset I wish to thank the learned referee for his valuable suggestions made for the improvement of the thesis.

Page No.56:

I do agree that the best fitting plots may not be appropriate for all measurements but still it is felt that they are valuable tools in many cases for better understanding of the data. The correlation coefficients have been computed and presented in all the linear graphs at right hand side as suggested by the learned referee.

Page No.68:

The learned referee has sought clarification with regard to the fractional order on catalyst. Plot of log k vs log[catalyst] lead to plots which have slope of one indicating the first order dependence on catalyst. In some cases these plots gave linear line without any slope indicating zero order dependence on catalyst. I wish to submit that in some cases a fractional slope is obtained. Such plots suggest that the reactions are dependent on both the above mentioned first and zero order reactions and these cumulatively lead to apparent fractional slope. This is reported as fractional order in many kinetic processes.

But the learned referee suggested that presentation of fractional orders shall be avoided. In accordance with the suggestions of honorable referee such statements were changed and the term fractional slope is used in place of fractional order to avoid ambiguity.

Page No.71:

Experiments have been conducted at other conditions to get more kinetic data. I am very much grateful to the suggestions of learned referee which lead for obtaining better correlation coefficient

Page No.72

The four decimal places have been corrected to two decimal places as advised by referee. This data of four decimal places have been obtained by logarithmic tables. Hence they are corrected as suggested.
Page No.76

It is presented that a complex is formed between sugar molecule and Os (VIII). Honorable referee has suggested to clarify the nature of complex. The Os (VIII) which is a catalyst remains unchanged finally due to following reasons. These complexes are mostly outer sphere complexes between the substrate and catalyst. In monohydric alcohols it is easy to visualize a complex as follows

\[
\begin{align*}
\text{H}_3\text{C} & \text{C} \text{H} + \text{OsO}_4 \\
\text{H}_3\text{C} & \text{C} \text{OH}
\end{align*}
\]

Such complexes have been suggested by number of earlier workers viz.
4. M.Prasadrao, B.Sethuram and T.Navaneetha Rao,
   Curr. Sci. (India)., 48(22) (1979) 990
   Indian.J.chem. 20A (1981) 301
7. G.Sarala,P.Jayaprakasa Rao,B.Sethuram and T.Navaneeth Rao

and many others. This may be the case with many organic reactions. In the present case elaboration on complex formation is avoided as it has number of hydroxyl groups. It may be acyclic or cyclic mechanism. Hence it postulated as a complex in a general sense as suggested by many workers. In this process complex breaks down in such a manner that Os (VIII) becomes Os (VI) along with formation of products and the co-oxidant converts Os (VI) to Os(VIII) finally. Hence Os (VIII) remains unchanged.

Page No.77

Such complexes have been postulated by previous workers\(^1-7\) between the substrate and higher valent Ru(V) species. In this reaction the oxidant reacts with Ru(III) converts into higher valent Ru(V) species which forms a complex. The
complex breaks down to give the products and Ru(III) is reformed. Thus Ru(III) remains unchanged finally.

References:

Page No.84
More experiments have been conducted to get more kinetic data for getting better correlation coefficient.

Page No.85
The explanation already given under page 68 correction mentioning fractional slope in place of fractional order holds good as is being advised by learned referee.

Page No.86
The rate constants and Arrhenius parameters which have four decimal places have been approximated to two decimal places as is done earlier.

Page No.90
The same explanation given for Page-76 holds good that Os(VIII) finally remains unchanged.

Page No.91
The concentrations used in the kinetic conditions lead to minute amounts of product and these are identified by various chromatographic techniques generally but the learned referee desires to have additional proof. Hence the experiments have been conducted on macro scale and physical constants are given in the text.

Arabinonic acid - M.P:- 115°C
Erythronic acid - M.P:- 215°C
More experiments have been conducted to get more kinetic data for getting better correlation coefficient.

More experiments have been conducted for getting more kinetic data to get better plot and better correlation coefficient.

More experiments have been conducted to get better correlation coefficient.

The reaction sequence is better presented along with evidence from other similar investigations.

More experiments have been conducted for getting more kinetic data as suggested for getting better correlation coefficient.

The mistake is very much regretted and proper structure is given with four bonds at carbon. Work on deuterated cyclohexanone by Ce(IV) carried out by J.S.Littler confirms the mechanistic process. (Ref. 1) J.S.Littler, J. Chem. Soc., (1962) 832. 2) Oxidation in Organic Chemistry by K.B.Wiberg Part A, Academic Press (1965) 256

The reaction sequence is now presented correctly.

The conditions for the preparation of buffer solution are now given for clarity. The table now contains both pH and various buffer solutions used at neutral and alkaline pH's or strong acids used at higher pH's (Table-5, Page 133).

More experiments have been conducted for getting more kinetic data which lead to obtain better correlation coefficient.
Page No 146

The reaction sequence is simplified for clarity as suggested by learned referee.

Page No 151

More experiments have been conducted for getting more kinetic data for obtaining better correlation coefficient.

Page No 156 and 164

More experiments have been conducted for getting more kinetic data for obtaining better correlation coefficient and better plots

Page No 166

The reaction sequence is corrected

Page No 170 and 174

More kinetic experiments have been carried out for getting better plots and correlation coefficient

Page No 176 and 177

The reaction sequence is corrected. The error is highly regretted.

Page No 180

More experiments have been conducted for getting better plots.

Page No 181

The conditions for preparation of buffer solutions are now given for clarity.

More experiments have been done to have not less than four points in the ranges where the first order dependence is observed and also where the second order dependence is observed. The dotted line in the graph indicates the second order dependence in the range pH 2.8 to 3.5. The graph given is especially between log (first order rate constant) Vs. pH. Hence the second order rate constants in the range are not indicated between pH 2.8 to 3.5 in the graph. A separate graph between log (second order rate constant) Vs. pH is also linear. But the plot is not given as it is felt unnecessary as all the experiments have been conducted in the
present investigation in the pH range 0.63 to 0.30 where first order dependence has been observed.

**Page No 182**

The reaction sequence is better explained and unnecessary presentation is omitted. The error is regretted.

**Page No 187**

More experiments have been conducted for getting better plots and correlation coefficient.

**Page No 188**

The reaction sequence gets support from the work of V.J. Shiner except that it is now adopted for one electron oxidant like Ce(IV).


**Page No 191**

More experiments have been conducted for getting better plots and correlation coefficient.

**Page No 192**

Same explanation given for Page-188 holds good as V(V) is also one electron oxidant. The evidence is from the work of V.J.Shiner.


More experiments have been conducted for getting more kinetic data for better correlation coefficient and better plots

**Page No 195**

The reaction course is better explained.

**Page No 198 and 199**

More experiments have been conducted for getting more kinetic data for better correlation coefficient and better plots
Page No202 and 209

There is earlier work regarding the oxidation of disulphide bridge of cystine to cystine monosulphoxide and cystine disulphoxide. The references are as follows.

Ref:

3) M.M.Chau and J.L.Kice, J. Am. Chem. Soc. 98 (1976) 7711

The same thing holds for further oxidation to disulphone as these compounds are isolated and characterized by earlier workers.

Page No 215

More experiments have been conducted for getting more kinetic data for better correlation coefficient and better plots

Page No 216

Unnecessary elaborations were removed as per learned referee's suggestions in order to avoid too much elucidation.

Comments on Summary

The learned referee wanted proof for geometry of formed complexes.

I am highly thankful to learned referee for suggesting that the catalysis observed may be due to synergistic effect of two or more oxidants participating in reactions. This is now included in the summary text as suggested by the referee. Normally in kinetics complex formation is proven as follows. 1/k vs.1/[S] plots yield a linear line going through origin and it is taken as loose complex which
cannot be characterized by stability constants but in some cases \(1/k \text{ vs.} 1/[S]\) plots yield intercepts and slopes. Then it is possible to compute the stability constants indicating complex formation. Experiments for proving the geometry were not attempted but the evidence from literature suggests that transition metals can form complexes using d-orbitals.

Similarly it is already mentioned that the term fractional order is replaced with fractional slope to avoid ambiguity as suggested by learned referee.

With the regard to other suggestions of honorable referee, dielectric constants with various percentages of mixtures of solvents were presented and incorporated in the Table-4A (Page 71A).

With the permission of learned referee I wish to submit the following to explain the influence of dielectric constants.

Chemical reactions occur generally through the following steps:- Initial state (reactants), Transition state and Final product state. Theories of Ingold and Hughes indicate the following regarding solvent effect. The solvents influence the reaction by preferential stabilization of either a transition state or initial state. When initial state is stabilized by solvation the reaction rate is retarded but on contrary if the transition state is stabilized the reaction goes faster. Hence the role of solvent gives an idea of the preferential stabilization with respect to initial and transition states. Thus when the polarity of the system is decreased or the polarity of the system is increased there will be differential results due to the above reason. Hence the word dielectric constant is used which indicates the polarity of the medium. Thus the summary is revised by omitting too many statements. As per the suggestions of honorable referee all the graphs in the revised thesis were presented with more than three points based on experimental evidences. An attempt has been made to explain all mechanisms as best as possible as is understood based on literature survey. It is submitted that best efforts were made in addressing the presentation in light of all suggestions indicated by learned referee which helped in improvement of quality of the thesis.

I am very much grateful to learned referee and profusely thank for all the corrections suggested which lead for better presentation of the thesis.