Chapter - II

Materials and Techniques Used
Experimental

Preparation of solutions:

1. An aqueous solution of sodium metaperiodate (NaIO₄) was prepared always fresh from (E. Merk) sample by direct weighing. The solution was standardised by the iodometric method¹ and was preserved in dark bottles to prevent photochemical deterioration.

2. Aqueous solutions of D(+) glucose (CDH), D(-) fructose, D(+) galactose and D(+) lactose (s.d. Fine), D(+) maltose (Qualikem) were direct prepared from analytical grade samples.

3. The stock solution of ruthenium trichloride (RuCl₃) 15.2 x 10⁻³ mol dm⁻³ was prepared² by dissolving 1.0 gm. of sample of RuCl₃ (Thomas Baker) in 25 ml of HCl (0.01M) and then diluting it to 250 ml with doubly distilled water. The stock solution was stored in black coated bottles to prevent photochemical decomposition.

4. The ruthenium (III)³ content in the stock solution was checked spectrophotometrically from time to time. The hundreds of more time dilute solution of the stock solution of the catalyst was used in the reaction mixtures.

5. Aqueous solution of alkali was prepared by dissolving NaOH (AR, BDH) in doubly distilled water and was standardised by titrating it against standard oxalic acid solution using
phenolphthalein as an indicator.

6. For ionic strength studies, aqueous solution of sodium perchlorate was prepared from A.R. grade sample.

7. An aqueous stock solution of sodiumthiosulphate (A.R. BDH) was used for estimation of sodium metaperiodate. A 10% solution of potassium iodide (Thomas Baker) was always prepared fresh to liberate iodine.

8. Freshly prepared 1% starch solution was used for iodometric titration.

Other reagents used during the course of investigation were of AR grad. All solutions were prepared in double distilled water. Stills used, were all made of Jena orf corning glass. REaction flasks were coated black from outside to avoid photochemical decomposition of reactants.

**Experimental Method:**

Appropriate quantities of the solution of substrate, sodium hydroxide and catalyst (RUCL₃) were taken in a 100 ml Jena glass vessel. Requisite amount of double distilled water was added so that the total volume of reaction mixture would become 50 ml after adding the solution of sodium metaperiodate (in separate flasks) were now placed in a thermostatic water bath maintained at the desired temperature within the range ± 0.1°C. The reaction mixture and oxidant solution solution were allowed to attain the temperature
of the water bath. The reaction was started by adding the requisite amount of sodium metaperiodate solution to the reaction vessel.

The kinetics were followed by determining the unreacted amount of sodium metaperiodate. An aliquot of 5 ml of reaction mixture was withdrawn from reaction vessel at a definite time interval and was transferred to titrating flask containing 5 ml of 3N.H₂SO₄ and 5 ml of 10% KI solution. The solution was then titrated with sodium thiosulphate (hypo) solution using starch as indicator to determine the amount of unreacted sodium metaperiodate.

**Determination of the Order of Reaction:**

During the investigations of concentration of the solution of sodium metaperiodate was always kept at least eight time dilute than the concentration of the reducing substrate solution to maintain pseudoorder conditions.

In rethenium (III) Catalysed reactions, log [sodium metaperiodate] versus time plots were linear suggesting a first order dependence of rate with respect of oxidant. Therefore, the pseudo-first order rate constants in sodium metaperiodate were obtained from the slopes (slope = k_{obs}/ 2.303 of these straight lines plotted between log (a-x) versus time (where (a-x) correspond to unreacted amount of sodium metaperiodate, at any time t). In place of (a - x) the direct titre value i.e. amount of hypo required for titration of 5 ml of reaction mixture of different time intervals has been taken in the various plots.
Effect of [reactants], [catalyst], [OH'], ionic strength, solvent, products and temperature on the rate has been investigated in each case. The products have been identified and the stoichiometry of the reactions has been also studied. The systematic kinetic data are tabulated in each case and mechanism has been discussed in the end of chapter. In some cases e.g. ionic strength effect and temperature effects, the value of observed rate constants have only been given for the sake of brevity.
References:

1. A. Berka, J. Vulterin & J. Zyka: "Newer Redox Titrant"
   Pergamon Press (1955)

   (1977)

3. F.E. Bearmish & J.C. Vanlool: "Recent Advances in the
   Analytical Chemistry of Nobel Metals", P. 1357,