CHAPTER - II

EXPERIMENTAL TECHNIQUES

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The kinetics of oxidation of n-butanol and ethylene glycol by cerium(IV) catalysed by chromium(III) (in H_2SO_4 and $HClO_4$ mixture) has been studied. The experimental results obtained includes.

i) Effect of variation of oxidant Ce(IV) and alcohol concentration on the rate of reaction and determination of order of the reaction with respect to each reactant.

ii) Effect of perchloric acid concentration on the reaction rate and determination of order with respect to $HClO_4$.

iii) Effect of Cr(III) concentration on the reaction rate and determination of order with respect to Cr(III).

iv) Effect of temperature variation and to evaluate temperature coefficient, frequency factor and other thermodynamic parameters for the reaction.

v) Free radical detection.

vi) Identification of end product and stoichiometry.

MATERIALS AND PURITY

The double-distilled water was used through out the work.

All the chemical used for experiments were of BDH/AR grade. All the alcohol(BDH) were first purified by fractional distillation and were used to prepare solution.

Ferrous ammonium sulphate (BDH/AR), cerium ammonium sulphate (BDH/AR), cerium(III) acetate (BDH), potassium chromium (III) sulphate (BDH/AR), perchloric acid (Analar 60%) and sulphuric acid (Glaxo Excel R) were used directly as received.

2.2 PREPARATION AND STANDARDIZATION OF SOLUTIONS

The doulbe-distilled water was used for preparation of stock solutions. The stock solution were stored in air-tight amber coloured bottles and kept in the dark.

The stock solution used were of the following concentration.

1) Alcohol solution   0.5M

2) Cerium(IV) solution   0.1M

3) Chromium(III) solution   0.01M

4) Ferrous ammonium sulphate solution   0.1M

5) Perchloric acid solution   BDH

6) Sodium perchlorate solution   2.0M

7) Sulphuric acid solution   2.0M

8) Cerium(III) solution   0.01M

9) Ferroin indicator solution.

The 0.5M stock solutions of alcohols were prepared by dissolving appropriate amounts of them in double-distilled water.

The stock solution of cerium(IV) was prepared by dissolving a calculated quantity of cerium(IV) ammonium sulphate in 2M sulphuric acid and allowed to stand over-night. The resulting solution was standardised against ferrous ammonium sulphate solution using ferrion as an indicator. The stock solution was diluted to the required concentration and then used.

Ferrous ammonium sulphate was prepared by dissolving calculated quantity of ferrous ammonium sulphate in 2M sulphuric acid. This can be standardised by using potassium dichromate using Barium diphenyl ammonium sulphonate as an indicator solution of requisite concentration $(2.0 \times 10^{-3}M)$ was prepared by diluting stock solution.

Chromium(III) solution was obtained by dissolving calculated quantity of potassium chromium sulphate, in double-distilled water. The concentration of chromium(III) to chromium(VI) with excess persulphate in the presence of a drop of 0.01M silver nitrate as follows.

To the chromium(III) solution excess persulphate was added followed by a drop of 0.01M silver nitrate was boiled for five minutes. The excess persulphate remained after the oxidation was destroyed by further boiling the solution. The chromium(VI) thus obtained was titrated against ferrous ammonium sulphate solution using diphenyl ammonium sulphonate.

Sodium perchlorate solution was prepared by neutralization of perchloric acid with sodium carbonate.

Cerium(III) solution was obtained by dissolving appropriate amount of cerium(III) acetate in double-distilled water. The concentration of cerium(III) was asscertained by oxidising it to cerium(IV) with persulphate using silver nitrate as catalyst and titrating against ferrous ammonium sulphate solution.

2.3 METHODS OF FOLLOWING KINETICS

The main features of the experimental method are as follows.

i) The standard Pyrex glassware was used through out the experimental work.

ii) The temperature of the reaction mixture was adjusted and maintained by using auto-thermostated water bath ($\pm$ 0.1°C).

iii) The reactions were carried out in a stoppered conical flask (100 ml).

iv) The reactions were carried out under pseudo-first order conditions with the alcohol concentration much in excess of that of the cerium(IV).

v) The reaction mixtures in all runs contained a constant amount of H_2SO_4 ($6.0x10^{-2}M$) on account of H_2SO_4 used in the dissolution of cerium(IV) ammonium sulphate to obtain the Ce(IV) stock solution.

vi) Generally where the effect of acidity on the reaction rate was not under examination, a constant quantity of 2.0M perchloric acid was used in addition to $6.0x10^{-2}M$ H_2SO_4 in the reaction mixture.

vii) The ionic strength was maintained of 2.1M by the addition of a solution of sodium perchlorate.

viii) Flask 1 the calculated quantities of standard solution of alcohol, chromium(III) and perchloric acid.

xi) Flask 2 the calculated quantities of cerium(IV), sodium perchloreate, perchloric acid, sulphuric acid and water.

x) Two conical flasks were thermostated at for 30 minutes.

xi) The reaction was initiated by adding the thermostated solution from flask 2 to flask 1. The time of initiation of reaction i.e. time of mixing the solutions was

recorded as zero time.

xii) After mixing, immediately 5 ml aliquot of this reaction mixture was pipetted out in conical flask adding ferroin indicator and titrated against standard ferrous ammonium sulphate. This is an initial reading 'a' then after definite time intervals, 5 ml aliquots of reaction mixture were titrated adopting same procedure.

xiii) The titre values (Tt) so obtained were then subjected to graphical method to determine the order and specific reaction rate.

2.3.1 TEMPERATURE VARIATION

In the preliminary work, experiments were carried in order to decide the range of temperature, concentrations of cerium(IV), alcohol and perchloric acid.

It was observed that the reaction occurred with measurable rate at ordinary temperatures (25°C to 40°C). So this temperature range was employed. The temperature was kept constant using kinetic study of the reaction by means of thermostat with ±0.1°C accuracy.

2.3.2 VARIATION IN CONCENTRATION

It was observed that satisfactory results were not obtained at higher concentration of Ce(IV) solution and rate of oxidation was found to be inversely proportional to the

Ce(IV) concentration. Hence low concentration of Ce(IV) in the range 2.0×10^{-3} to 6.0×10^{-3}M was employed. In case of alcohol, however, the rate of reaction was found to be very low at lower concentration. Hence, higher concentration of alcohol was employed to get consistent results. As such it was decided to elucidate the order of the reaction with respect to Ce(IV) by Ostwald's isolation method by using concentration of alcohol at least 5 to 10 times greater than that of Ce(IV). Hence alcohol in the concentration range 2.0×10^{-2} to 6.0×10^{-2}M was used. In case of $HClO_4$, the rate of reaction was found to be very low at lower concentration range. Hence, $HClO_4$ in the concentration range 1.0 to 2.0M was employed to get consistent results. To study the effect of chromium(III) concentration on rate of the reaction, chromium(III) concentration was varied from 2.0×10^{-4} to 20.0×10^{-4}. To maintain ionic strength constant at 2.1 M, requisite amount of sodium perchlorate solution was used.

2.4 STOICHIOMETRY

The stoichiometry was studied by keeping cerium(IV) concentration excess over alcohol at 60°C for about 8 hours with a condenser. The concentration of unused cerium(IV) was determined by titrating against ferrous ammonium sulphate. This can be used to determine the stoichiometry. The stoichiometry in case of n-butanol and ethylene glycol was found to be one mole of alcohol to 2

mole of cerium(IV). The catalyst, Chromium(III) reamined unchanged at the end of reaction as found by measuring the absorbance at 580 nm, the molar absortivity of chromium(III) at this wavelength being 15.4 ± 0.02.

2.5 DETECTION OF FREE RADICALS

Tests were carried out to decide whether free radicals are formed during the course of the reaction. The reaction was allowed to take place in presence of acryllonitile and tested for polymerisation.

The results obtained on the kinetic studies of n-butanol and ethylene glycol are included in Chapter III and the relevant discussion on these results is included in chapter IV.