CHAPTER-II

EXPERIMENTAL TECHNIQUES

Experimental Techniques:

In following the kinetics of oxidation of benzoic acid hydrazide by bromate catalyzed by metal ions vanadium (IV) and Selenium (IV) in aqueous acidic medium, the experimental results obtained include:

1. Effect of variation of reactants on the rate of reaction and determination of order of the reaction.
2. Effect of variation of catalyst concentration on the rate of reaction and determination of order with respect to it.
3. Effect of variation of hydrogen ion and determination of order with respect to it.
4. Effect of variation of solvent composition.
5. Effect of variation of ionic strength.
6. Effect of temperature variation and to evaluate thermodynamic parameters for the reaction.
7. Stoichiometry.

Preparation and standardization of solution:

The double distilled water was used throughout the work. All the chemicals used for experiments were of reagent grade.

The stock solution of $KBrO_3$ was prepared by dissolving $KBrO_3$ (BDH) in water standardized iodometrically. The benzoic acid hydrazide was prepared by using prescribed procedure [1]. Initially ethyl ester of benzoic acid was prepared by esterification. An equilimolar mixture of ethylester of corresponding acid and hydrazine hydrate (BDH 99%) was refluxed for 15 minutes. Then enough absolute ethanol was added through the condenser to get clear solution and further refluxed for 2 - 3 hours.

The excess of hydrazine hydrate, solvent ethanol and other unreacted material were removed by distilling the solution under reduced pressure. The hydrazide was recrystallised from ethanol. The dry hydrazide was stored in amber coloured bottle, kept in dark place and purity was checked by determining its physical constant. Hydrazide solution was prepared by dissolving it in water.

The catalyst vanadium (IV) was prepared by dissolving vanadyl sulphate (BDH) in water and standardized by titrating against potassium

permanganate. The solution of vanadium (V) was prepared by dissolving ammonium metavanadate (BDH) in hot water.The solution of catalyst selenium (IV) was obtained by dissolving selenium dioxide (SD fine) in distilled water.

The stock solution of sodium thiosulphate was prepared by dissolving calculated quantity in double distilled water. The resulting solution was standardized iodometrically [2] with $K_2Cr_2O_7$ using starch indicator. The stock solution was diluted to the required concentration and then used.

For the reaction of benzoic acid hydrazide catalyzed by vanadium (IV), ionic strength was maintained using KCL solution and for the reaction catalyzed by selenium (IV), $NaClO_4$ solution was used to maintain ionic strength. To vary hydrogen ion concentration HCL (BDH) was used. Acetic acid, Acrylonitrite were used directly as received to study the effect of solvent polarity on the reaction medium and free radical formation respectively.

5% KI was prepared everyday by dissolving calculated amounts of it in double distilled water. 2M H_2SO_4 solution was prepared by dissolving appropriate amount of it in double distilled water. Starch solution was prepared fresh by dissolving it in boiling water and little CCl_4 was added to it. Sodium perchlorate solution was prepared by neutralization of perchloric acid with sodium carbonate.

Kinetic studies:

The ionic strength was maintained at 0.5 M using potassium chloride (KCL) solution for vanadium (IV) catalyzed reaction and sodium perchlorate for selenium (IV) catalyzed reaction respectively.

The main features of experimental method used to follow the kinetics of oxidation of benzoic acid hydrazide by potassium bromate catalyzed by metal ions are as follows:

1. The standard pyrex glassware were used throughout the experimental work.
2. The temperature of the reaction mixture was maintained constant using autothermostated water bath ($\pm$ 0.1^{0}C).
3. The reactions were carried out in a stopped conical flask.

4. The reactions were carried out under pseudo first order conditions keeping hydrazide concentration large excess than potassium bromate.
5. Flask1: The calculated quantities of standard solution of hydrazide solution of catalyst, hydrochloric acid and water.
6. Flask 2: The calculated quantities of potassium bromate solution, hydrochloric acid and water.
7. The conical flasks were thermostated for 30 minutes.
8. The reaction was initiated by adding the thermostated solution from flask 2 to flask 1. The time at initiation of reaction i.e. time of mixing the solutions were recorded as zero time.
9. After mixing immediately 5 ml of this reaction mixture was transferred to conical flask containing 5 ml of 5% KI and 5 ml of 2 mol. dm^{-3} H_2SO_4.
10. The solution was titrated against $Na_2S_2O_3$ using starch as indicator.Then at definite time intervals, 5ml of this reaction mixture were titrated adopting same procedure.
11. The reactions were usually followed up to 90% completion.

The pseudo first order rate constants were determined from pseudo first order plots of log [oxidant] against time. The pseudo first order plots were linear for more than 90% completion of the reaction and the rate constants were reproducible within ± 6%. The example runs are shown in table 2.1 and Table 2.2 for V (IV) and Se (IV) catalyzed reactions respectively. The corresponding pseudo first order plots are shown in figure 2.1 and 2.2.

Table 2.1

oxidation of benzoic acid hydrazide by bromate catalysed by vanadium (IV) in aqueous acidic medium at 25^0 C

Example Run

10^2 [hydrazide] = 1.0 mol dm^{-3} 10^3 [$KBro_3$]= 1.0 mol dm^{-3}

[HCl] = 0.1 mol dm^{-3} 10^4 [V^{IV}] = 1.0 mol dm^{-3}

I = 0.5 mol dm^{-3}

Time min	Burette Reading ml	-log [$KBro_3$]
0	30.0	2.25
5	24.3	2.31
10	21.1	2.37
15	18.1	2.44
20	15.3	2.51
25	13.0	2.58
30	10.6	2.67
35	8.6	2.76
40	7.1	2.84

Figure 2.1

oxidation of benzoic acid hydrazide by bromate catalysed by vanadium(IV) in aqueous acidic medium at 25^0 C

Example Run

Conditions as in Table 2.1

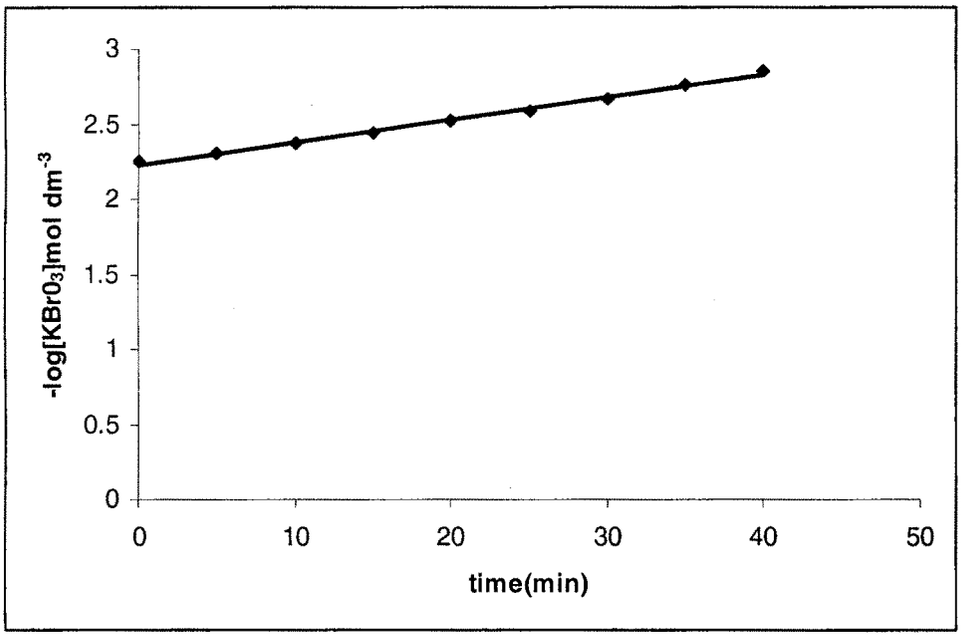


Table 2.2

oxidation of benzoic acid hydrazide by bromate catalysed by selenium(IV) in aqueous acidic medium at 27^0 C

Example Run

10^2 [hydrazide] = 1.0 mol dm^{-3} 10^3 [$KBro_3$]= 1.0 mol dm^{-3}

[HCl] = 0.1 mol dm^{-3} 10^4 [Se^{IV}] = 1.0 mol dm^{-3}

I = 0.5 mol dm^{-3}

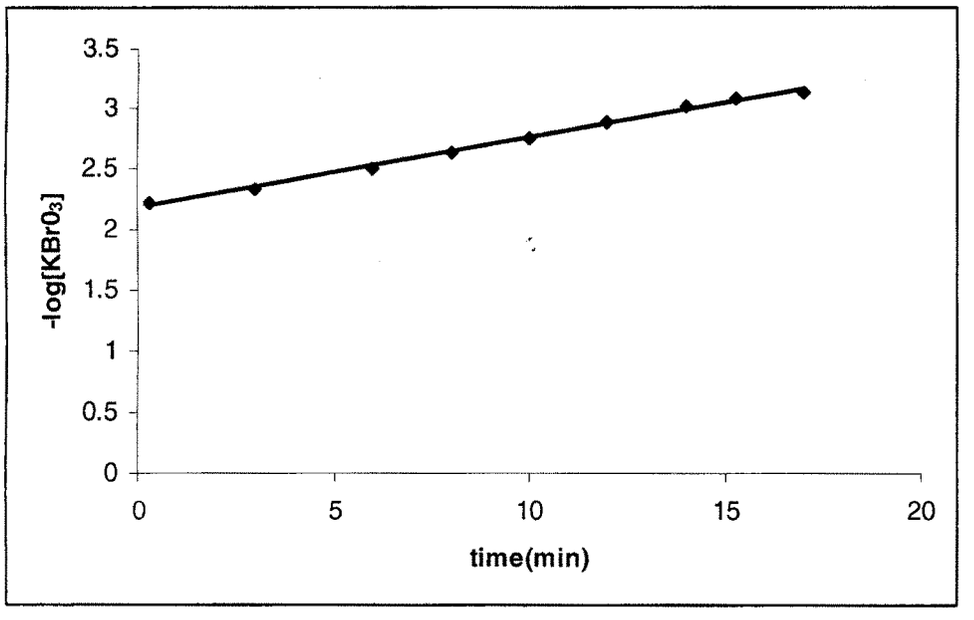
Time min	Burette Reading ml	-log [$KBro_3$]
0.30	29.6	2.22
3.0	23.2	2.33
6.0	15.7	2.50
8.0	11.5	2.63
10.0	8.8	2.75
12.0	6.5	2.88
14.0	4.7	3.02
15.30	4.1	3.08
17.0	3.7	3.13

Figure 2.2

oxidation of benzoic acid hydrazide by bromate catalysed by selenium(IV) in aqueous acidic medium at 27^0 C

Example Run

Conditions as in Table 2.2



References:

1. Vogel, A.I. A Text Book of Practical Organic Chemistry Including Qualitative Organic Analysis, 3rd Edition (E.L.B.S. and Longman Group Ltd. 1975).
2. Vogel, A.I. A Text Book of Quantitative Inorganic Analysis 3rd edition. 1961, 349.