

CHAPTER -II



**Experimental
Technique**

Kinetics and mechanism of oxidation of ethanediol and propanediol by 6-molybdocobaltate(III) ion has been studied in perchloric acid medium under pseudo-first-order condition.

The experimental results obtained include:

1. Effect of variation of reactant concentration on the rate of reaction and determination of order with respect to it.
2. Effect of oxidant concentration on the rate of reaction and determination of order with respect to it.
3. Effect of variation of hydrogen ion concentration.
4. Effect of temperature variation and to evaluate thermodynamics parameters for the reaction.
5. Product analysis for stoichiometry determination.
6. Effect of ionic strength, solvent polarity and acrylonitrile.

Preparation and standardization of solutions

The doubly distilled water was used throughout the work. The entire chemicals used for experiments were of reagent grade. The cobalt complex 6-molybdocobaltate(III) was prepared by the literature method [1] and standardized spectrophotometrically (at 602 nm $\epsilon = 16.9 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) [2] by dissolving it in water using an Elico SL177 UV-Visible spectrophotometer.

The solution of ethanediol (BDH) and propanediol (BDH) were prepared by dissolving requisite volume in water. The ionic strength was maintained using sodium perchlorate and in order to vary hydrogen ion concentration HClO_4 was used. The distilled water was used for the preparation of stock solutions.

The stock solutions of oxidant of $0.05 \text{ moles dm}^{-3}$ were prepared by appropriate amounts in distilled water. Also the stock solutions of perchloric acid were prepared by dissolving them in double distilled water. The stock solution was diluted to the required concentration and then used.

The stock solutions used were of the following concentrations.

1. Ethanediol	0.5 mol dm ⁻³
2. Propanediol	0.5 mol dm ⁻³ .
3. Perchloric acid.	0.5 mol dm ⁻³
4. 6-molybdocobaltate(III)	0.05 mol dm ⁻³
5. Sodium perchlorate	1 mol dm ⁻³

Methods of following kinetics

The main features of the experimental method used to follow the kinetics of oxidation ethanediol and propanediol 6-molybdocobaltate(III) ion are as follows

1. Through out experimental work standard Pyrex glass were used.
2. The reaction mixture was placed in thermostated water bath and its temperature maintained constant ($\pm 0.1^{\circ}\text{C}$)
3. The reactions were carried out under pseudo-first order conditions keeping concentration of diols excess to that of molybdocobaltate.

The reaction between ethanediol and propanediol oxidized by 6-molybdocobaltate(III) in acid medium was followed under pseudo-first-order conditions. The previously thermally equilibrated solution of 6-molybdocobaltate(III) and ethane diol also containing required quantities of perchloric acid were mixed and transferred to one of the matched 1 cm quartz cells which was then placed in a thermostated cell compartment of a Elico SL-177 UV-VIS spectrophotometer and absorbance of hexamolybdocobaltate(III) at 602 nm was followed. The application of Beers law under the reaction condition had earlier been verified in the concentration range of 4×10^{-3} to 50×10^{-3} mol dm⁻³ of hexamolybdocobaltate(III) (ϵ at 602nm = $16.9 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). The data for Beers plot for hexamolybdocobaltate (III) are given in Table 2.1 and corresponding plot is shown in Figure. 2.1.

The rate constants were obtained by plotting $\log a/a-x$ against time plots. The first order plots in almost all cases were linear to about 75 % of the reaction and the rate constants were reproducible to within $\pm 4\%$.

The reaction between propanediol and hexamolybdocobaltate(III) was also followed under pseudo-first order condition where concentration of propanediol is greater than concentration of hexamolybdate at 25 ± 0.1 °C. The previously thermally equilibrated solutions of propanediol and hexamolybdocobaltate(III) also containing required quantities of perchloric acid were mixed and transferred to one of the matched 1 cm quartz cell which were then placed in a thermostated cell compartment of an elico-SL-177 UV VIS spectrophotometer and the absorbance was followed spectrophotometrically at 602 nm and pseudo-first order rate constant was calculated by plotting $\log a/a-x$ Vs time respectively. The pseudo-first order plots in almost all cases were linear.

Preparation and characterization of hexamolybdocobaltate (III)

The oxidant hexamolybdocobaltate (III) was prepared by the previously reported method.[2-4].

Generally, oxidation of Co(II) in presence of molybdate gives a mixture of blue-green $[[H_6CoMo_6O_{24}]^{3-}$ (the monomer) and olive green $[H_4Co_2Mo_{10}O_{38}]^{6-}$ (the dimer) and care is required to obtain the pure samples of each species by judicious choice of oxidant, pH, temperature. The product distribution is however somewhat dependent on pH with increasing amount of monomer produced at lower pH, which is in agreement with previously observed instability of dimer towards H^+ . With reference to literature procedure of preparation of hexamolybdocobaltate(III) is as follows. 5 gm of $CoSO_4$ and 40 gm of Ammonium heptamolybdate were dissolved in minimum amount of water then 5 ml of 1 M H_2SO_4 was added and 5 gm of potassium persulphate was added. The solution was boiled for some a minute on waterbath. Reddish brown color changes to green colour. The solution was filtered. The filtrate was concentrated on waterbath. After cooling green shiny crystals were obtained. Recrystallization takes place in hot water. Green shiny crystals were obtained.

The FT-IR spectrum of hexamolybdocobaltate (III) was recorded on Perkin-Elmer-783 instrument in KBr is shown in Figure 2.4. The FT-IR spectrum shows the peaks at 939.56 cm^{-1} Mo-O stretching, peak at 641.76 cm^{-1} corresponding

to NH_4^+ ion. The peak at 1421 cm^{-1} corresponding to Mo-O-Co stretching. The broad peak at 3181 cm^{-1} and 1626.77 cm^{-1} indicates water associated with Anderson structure.

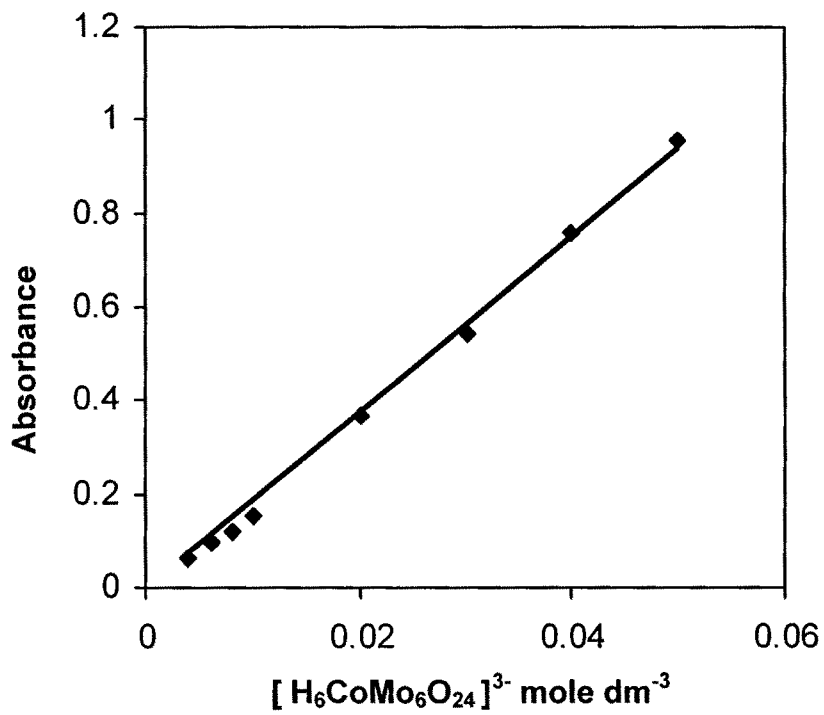
Table 2.1

Beer's Law verification for hexamolybdocobaltate (III) at 602 nm

$[\text{H}_6\text{CoMo}_6\text{O}_{24}]^{3-}$ mole dm^{-3}	Absorbance
0.004	0.064
0.006	0.098
0.008	0.121
0.01	0.154
0.02	0.369
0.03	0.545
0.04	0.759
0.05	0.959

Figure 2.1

Beer's Law verification for hexamolybdocobaltate (III) at 602 nm
Conditions as in Table 2.1



The example runs are shown in Table 2.2 and Table 2.3 for oxidation of ethanediol by hexamolybdocobaltate(III) and propanediol by hexamolybdocobaltate(III) respectively. The corresponding pseudo-first-order plots are shown in Figures 2.2 and Figure 2.3.

Table 2.2

Oxidation of Ethanediol by hexamolybdocobaltate (III) in aqueous acidic medium at 25⁰C

Example run

[Ethanediol] = 0.5 mol dm⁻³

10³[H₆CoMo₆O₂₄]³⁻ = 5.0 mol dm⁻³

[HClO₄] = 0.5 mol dm⁻³

I = 0.6 mol dm⁻³

Time min	Absorbance	log a/a-x
0	0.079	0
5	0.070	0.0525
10	0.062	0.105
15	0.056	0.149
20	0.049	0.207
25	0.044	0.254
30	0.041	0.285
35	0.038	0.32
40	0.035	0.354
45	0.031	0.41
50	0.029	0.435

Figure 2.2

Oxidation of Ethanediol by hexamolybdocobaltate (III) in aqueous acidic medium at 25^oc

Example run

(Condition as in Table2.2)

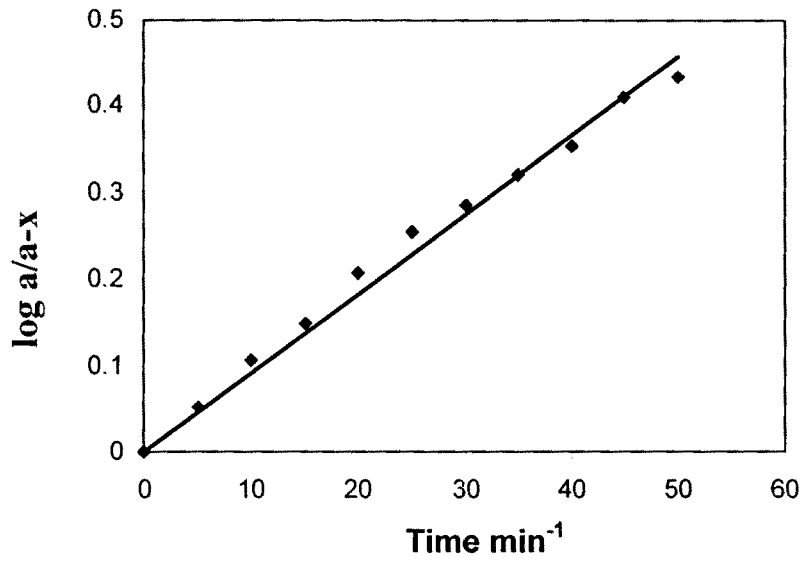


Table 2.3

Oxidation of Propanediol by hexamolybdocobaltate (III) in aqueous acidic medium at 25⁰c

Example run.

[Propanediol]=0.5 mol dm⁻³

10³ [H₆CoMo₆O₂₄]³⁻ =5 mol dm⁻³

[HClO₄]=0.5 mol dm⁻³

I=0.6 mol dm⁻³

Time min	Absorbance	log a/a-x
0	0.079	0
5	0.067	0.0715
10	0.056	0.149
15	0.048	0.216
20	0.043	0.264
25	0.037	0.33
30	0.033	0.379
35	0.029	0.435
40	0.028	0.45
45	0.026	0.48
50	0.024	0.517

Figure 2.3

Oxidation of Propanediol by hexamolybdocobaltate (III) in aqueous acidic medium at 25 °C

Example run.

(Conditions as in Table 2.3)

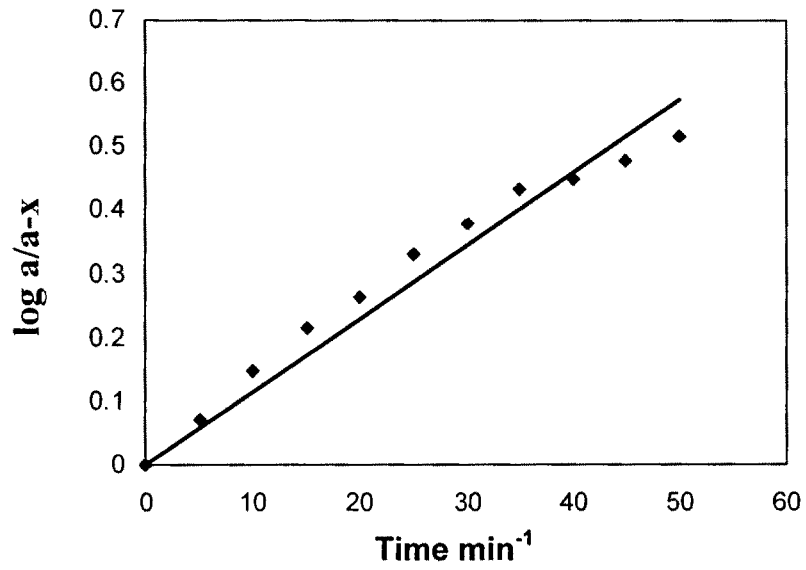
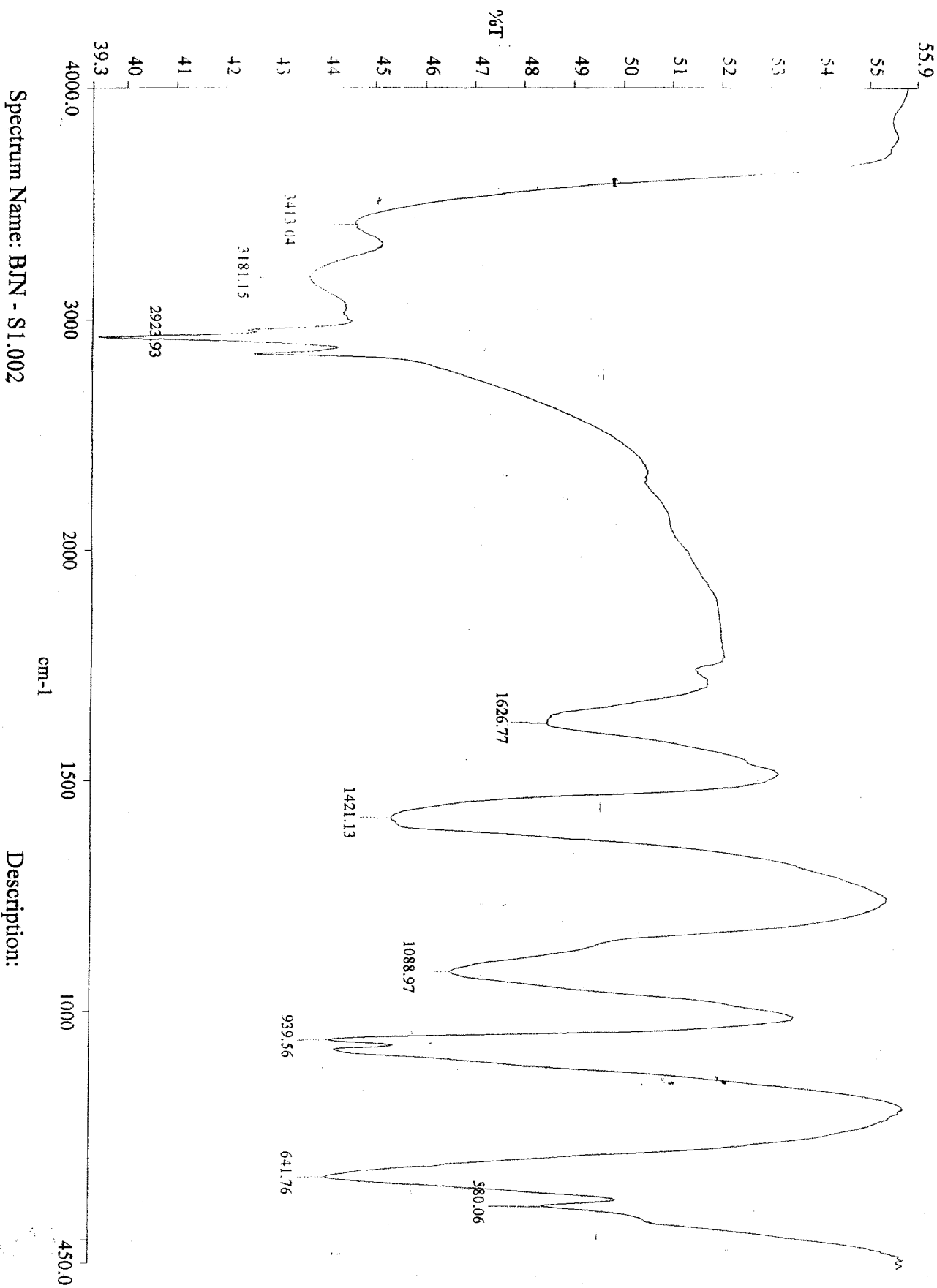


Figure 2.4

FIR Spectrum of 6-molybdocobaltate(III)



Spectrum Name: BJN - S1.002

Description:

4
15876

References:

1. L. C. W. Baker, B. Love, and T. P. McCutcheon, *J. Am. Chem. Soc.* **72**, (1950) 2374.
2. B. Goyal, M. Mehrotra, A. Prakash and R. N. Merotra, *Indian J. Chem.*, **40A**, (2001) 965.
3. L. C. Baker and T. P. McCutcheon, *J. Am. Chem. Soc.*, **78**, (1956) 4503.
4. K. Nomiya, T. Takahashi, T. Sharai and M. Miwa, *Polyhedron* **6**, (1987) 213 - 218.