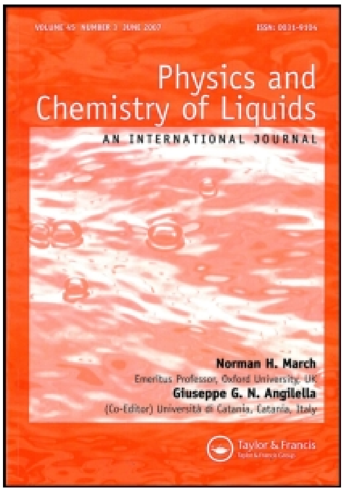

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THERMODYNAMIC AND KINETIC STUDIES ON OXIDATION OF PYROGALLOL RED BY HYDROGEN PEROXIDE IN THE ABSENCE AND PRESENCE OF MOLYBDENUM(VI)

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The oxidation of pyrogallol red (PGR) by hydrogen peroxide has been studied both in the absence and presence of molybdenum(VI) at pH of 7.0 by spectrophotometric detection. The reaction rate was studied with a fix-time method from 0.5 to 4.5 min. The effect of reagents concentration, ionic strength and temperature was studied to give the optimum conditions. At the optimizing conditions the rate constant, energy and entropy of activation and frequency factor have been calculated using the Arrhenius and Eyring plots.

Keywords: Oxidation; Pyrogallol; Molybdenum(VI); Hydrogen peroxide

1. INTRODUCTION

This paper takes further the measurement of thermodynamic properties of solutions [1–3]. Molybdenum is an essential trace element required by both plants and animals in very small amounts [4]. Various methods such as spectrophotometry [5, 6] and atomic absorption spectrophotometry [7] have been utilized in its determination. But these methods suffer from many drawbacks; long analysis times, high limits of detection, or the need for expensive instrumentation. Many

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catalytic procedures were also used but they mostly have high limits of detection or limited linear dynamic range [8–10]. In the present work, a new catalytic–kinetic method was used, which is both sensitive and rapid, based on its catalytic effect on the oxidation of pyrogallol red (PGR) with hydrogen peroxide.

2. EXPERIMENTAL PROCEDURES AND TECHNIQUES

2.1. Materials

Analytical-reagent grade chemicals and doubly distilled water were used throughout.

Stock Mo(VI) solution (1000 $\mu g \cdot ml^{-1}$) was prepared by dissolving 0.184 g of MoO_3 (Merck) in about 100 ml of 3 $mol \cdot dm^{-3}$ $NaNO_3$ solution and diluted to 100 ml with deionized water in a 100 ml volumetric flask.

PGR solution ($4.78 \times 10^{-4} mol \cdot dm^{-3}$) was prepared by diluting 8.5 ml H_2O_2 (27%, Merck) with deionized water in a 250 ml volumetric flask.

2.2. Apparatus

Absorption spectra were recorded with a Shimadzu Model UV,160. A Model 550-SE spectrophotometer (Perkin–Elmer) with 1.0 cm glass cuvettes was used to measure the absorbance change at 543 nm. A thermostat water bath (Memmert) was used to beep the reaction temperature at 303.15 K. A stop-watch was used to record the reaction time.

2.3. Recommended Procedure

To a series of 10 ml volumetric flasks, different amounts of Mo(VI) (0.10–5.0 μg), 1.0 ml buffer solution, phosphate, pH 7.0 and 1.0 ml of 0.3 $mol \cdot dm^{-3}$ hydrogen peroxide were added. The solution was diluted to ca. 8 ml with water. Then 1.0 ml of $4.78 \times 10^{-4} mol \cdot dm^{-3}$ PGR solution was added and the solution was diluted to the mark with deionized water. The zero time was taken as the moment at which the last drop of PGR had been added. Then an appropriate quantity of the solution was transferred into the spectrophotometric cell within 30 s. The decrease in absorption as a function of time ΔA_s was measured against a water reference for 0.5–4.5 min from initiation of the reaction. The blank reaction was performed according to the same procedure without the addition of Mo(VI) and the change in absorbance was labelled as ΔA_b. For each sample or blank, three determinations were made and the average signals were used.

3. RESULT AND DISCUSSION

Pyrogallol Red (PGR) is a dye that can be oxidized by a strong oxidizing agents [11]. In this paper, the catalytic effects of Mo(VI) on the oxidation of PGR with hydrogen peroxide was used for the determination of rate constant and activation parameters. In the absence of Mo(VI) there is only a slow reaction. However, rapid oxidation occurred when Mo(VI) was added. This oxidation process was observed by means of the decrease in absorbance of the characteristic band of PGR (543 nm) at pH = 7.0.

The most sensitive catalytic reactions are based on redox mechanisms in which the metal catalyst acts *via* a redox cycle, according to the following scheme:

$$\mathrm{Red_1} + \mathrm{M}^{n+} \longrightarrow \mathrm{Ox_1} + \mathrm{M}^{(n-1)+}$$

$$\mathrm{M}^{(n-1)+} + \mathrm{Ox_2} \longrightarrow \mathrm{M}^{n+} + \mathrm{Red_2}$$

where $\mathrm{Red_1}$ and $\mathrm{Ox_1}$ represent the reduced and oxidized forms of the dye. $\mathrm{Ox_2}$ and $\mathrm{Red_2}$ are those of the oxidized and reduced forms of the added oxidant.

The experimental rate law for the uncatalyzed reaction was found to be

$$k_o = \frac{\Delta A_b}{\varepsilon \cdot L \cdot \Delta t [\mathrm{H_2O_2}]^0 [\mathrm{PGR}]^{0.39}} \quad (1)$$

In the presence of Mo(VI) the experimental rate law is

$$k_c = \frac{\Delta A_s - \Delta A_b}{\varepsilon \cdot L \cdot \Delta t[H_2O_2]^{0.27}[PGR]^{0.79}[Mo(VI)]^{1.09}} \tag{2}$$

where $\varepsilon = 28015.5$ and $L = 1$ cm are the molar absorptivity and cell length, respectively.

3.1. Effects of Variables on the Reaction

The effect of the concentration of each reagent and of temperature on the rate of both the uncatalyzed and the catalyzed reaction was studied with 1.0 $\mu g \cdot ml^{-1}$ of Mo(VI) and with a fixed-time method of 0.5–4.5 min from the initiation of the reaction.

The effect of pH on obtaining a maximum reaction rate was investigated with $4.78 \times 10^{-5} mol \cdot dm^{-3}$ PGR and $0.03 mol \cdot dm^{-3}$ hydrogen peroxide at 303.15 K (Fig. 1). The results show (Tab. I) that by increasing the pH up to 7.0, the catalyzed reaction rate increased, whereas at greater pH-values (> 7.0) the sensitivity decreased. This means that the rate of uncatalyzed reaction increases with pH to a

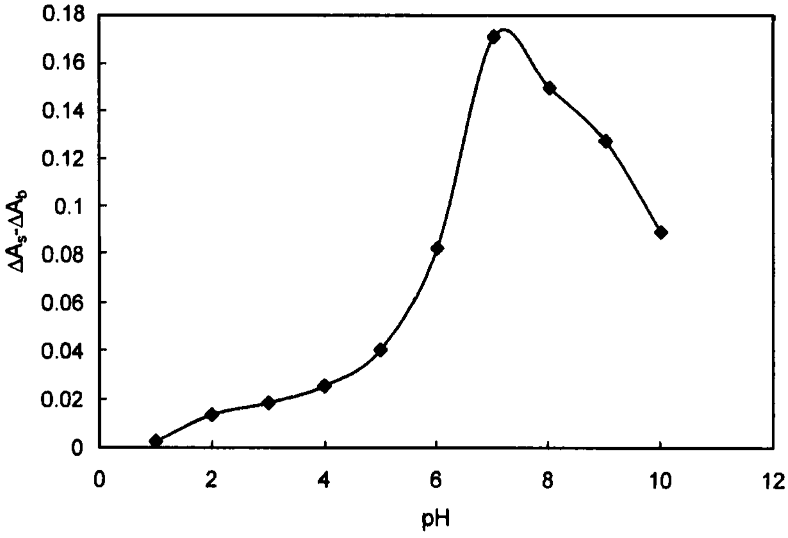

FIGURE 1 Effect of pH on the reaction rate.

TABLE I Effect of pH on the absorption of blank and sample

pH	ΔA_b	ΔA_s	$\Delta A_s - \Delta A_b$
1	0.001	0.004	0.003
2	0.002	0.016	0.014
3	0.002	0.021	0.019
4	0.003	0.029	0.026
5	0.003	0.044	0.041
6	0.003	0.086	0.083
7	0.004	0.175	0.171
8	0.011	0.161	0.150
9	0.022	0.150	0.128
10	0.039	0.129	0.090

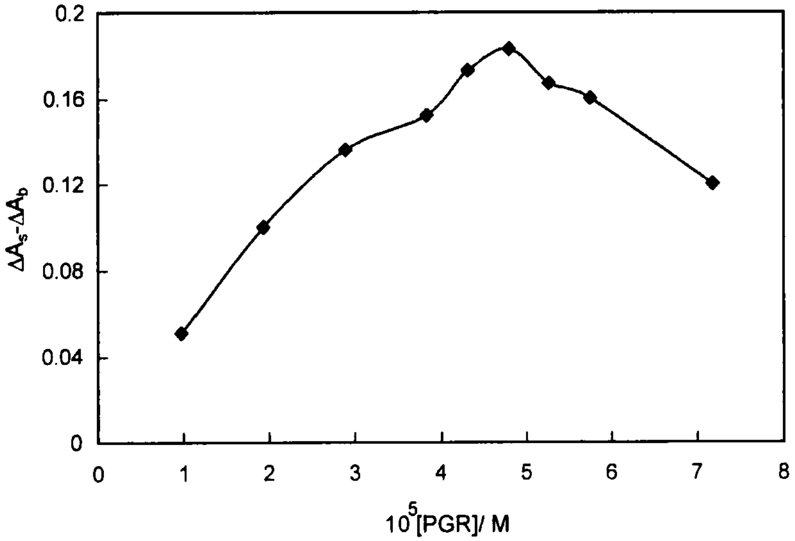

FIGURE 2 Effect of PGR concentration on the reaction rate.

greater extent than the catalyzed reaction and the difference between the rate of the catalyzed and uncatalyzed reaction (equivalent to $A_s - \Delta A_b$) diminished at pH > 7. At lower pH values, the reaction rate decreased due to the protonation of the dye. Thus a pH of the 7.0 was used throughout the study.

The effect of PGR concentration on the reaction rate was studied at pH 7.0 with $0.03\,\mathrm{mol \cdot dm^{-3}}$ hydrogen peroxide at 303.15 K (Fig. 2). The results show (Tab. II) that the optimum concentration of PGR was $4.78 \times 10^{-5}\,\mathrm{mol \cdot dm^{-3}}$. This value was used for further study.

TABLE II Effect of concentration of pyrogallol red on the absorption of blank and sample

$[PGR] \times 10^5$ $(mol \cdot dm^{-3})$	ΔA_b	ΔA_s	$\Delta A_s - \Delta A_b$
0.96	0.004	0.055	0.051
1.91	0.004	0.104	0.100
2.87	0.006	0.142	0.136
3.82	0.006	0.158	0.152
4.30	0.007	0.180	0.173
4.78	0.007	0.190	0.183
5.25	0.006	0.173	0.167
5.73	0.006	0.166	0.160
7.17	0.006	0.126	0.120

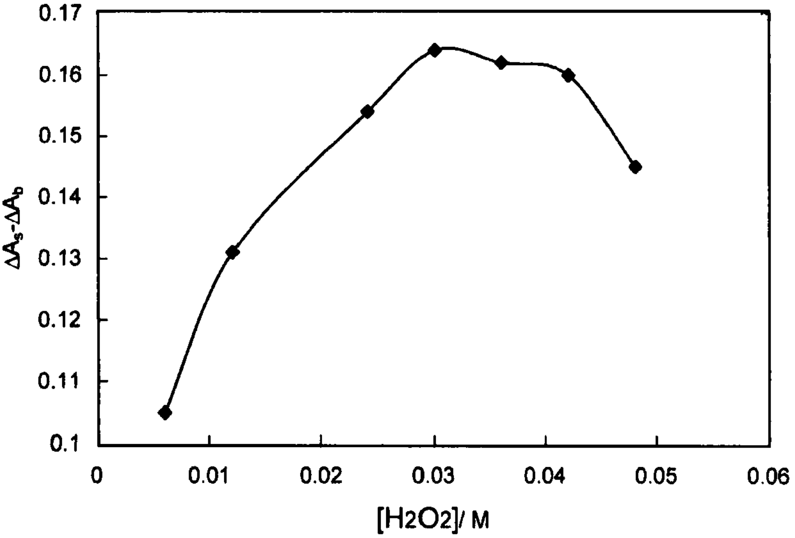

FIGURE 3 Effect of hydrogen peroxide on the reaction rate.

The influence of hydrogen peroxide concentration on the blank and sample reaction rates were studied at pH 7.0 and a PGR concentration of $4.78 \times 10^{-5} \mathrm{mol} \cdot \mathrm{dm}^{-3}$ at 303.15 K. Figure 3 shows (Tab. III) that sensitivity increased up to $0.03 \mathrm{mol} \cdot \mathrm{dm}^{-3}$ whereas higher concentrations of hydrogen peroxide did not affect the sensitivity. Therefore $0.03 \mathrm{mol} \cdot \mathrm{dm}^{-3}$ hydrogen peroxide was selected for the study.

The effect of temperature on the rate of reaction was studied in the range of 303.15–343.15 K with the optimum reagents concentration and $1 \mu\mathrm{g} \cdot \mathrm{ml}^{-1}$ of Mo(VI). The rate constants for the uncatalyzed, k_o and catalyzed, k_c reaction were calculated by applying Eqs. (1) and

TABLE III Effect of concentration of hydrogen peroxide on the absorption of blank and sample

$[H_2O_2] \times 10^5 (mol \cdot dm^{-3})$	ΔA_b	ΔA_s	$\Delta A_s - \Delta A_b$
0.006	0.007	0.112	0.105
0.012	0.007	0.138	0.131
0.024	0.007	0.161	0.154
0.030	0.007	0.171	0.164
0.036	0.007	0.169	0.162
0.042	0.006	0.166	0.160
0.048	0.006	0.151	0.145

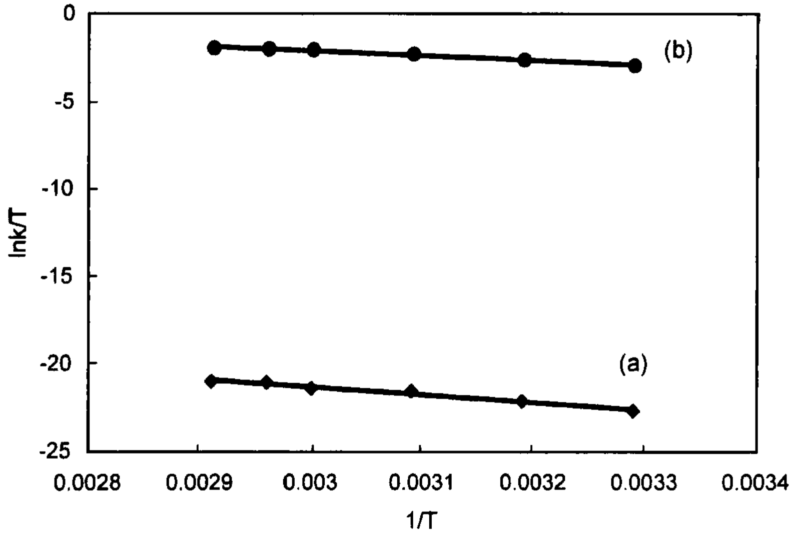

FIGURE 4 Plot of Eyring $\ln k/T$ vs. $1/T$. (a) uncatalyzed (b) catalyzed.

(2). The results shown in Figure 4 (Tab. IV) demonstrate that with increasing temperature the net reaction rate increased. A change in ionic strength has little effect on the sensitivity.

Activation parameters are calculated using the Eyring equation $k = \mathrm{RT/Nh}\ [\exp(-\Delta H^{\neq} + \Delta S^{\neq})]/\mathrm{RT}$. Plots of $\ln k/T$ vs. $1/T$ should be linear. From the intercept and slope, values of entropy, $\Delta S^{\neq}$ and enthalpy, $\Delta H^{\neq}$ of activation were evaluated, respectively. Frequency factor, A and activation energy, E_a were estimated by using the Arrhenius equation $k = A\exp(-E_a/\mathrm{RT})$. Plots of k vs. $1/T$ gave intercept for A and slope for E_a. The results for both uncatalyzed and catalyzed path ways are given in Table V.

TABLE IV Effect of temperature on the rate of reaction for uncatalyzed, k_o and catalyzed, k_c path ways

T/K	ΔA_b	$k_o \times 10^8$	$\Delta A_s - \Delta A_b$	k_c
303.15	0.005	4.13	0.165	16.03
313.15	0.010	7.54	0.234	22.73
323.15	0.019	13.68	0.333	32.34
333.15	0.023	16.52	0.440	42.74
338.15	0.033	23.74	0.465	45.17
343.15	0.035	25.28	0.500	48.57

TABLE V Activation parameters on the oxidation of pyrogallol red by hydrogen peroxide

	$\Delta S^{\neq}$ ($J\ mol^{-1} K^{-1}$)	$\Delta H^{\neq}$ ($kJ\ mol^{-1}$)	E_a ($kJ\ mol^{-1}$)	A
uncatalyzed	− 264.5	36.68	38.55	0.196
catalyzed path	− 147.3	22.33	24.26	252660

3.2. Calibration Graph and Precision

Calibration graphs were obtained using the fixed-time method. The method was applied to the change in absorbance over an interval of 0.5–4.5 min, because it provided the best regression and sensitivity. The oxidation rate of PGR was a linear function of molybdenum concentration in a range of 0.010–1.00 μg · ml^{-1} with the regression equation $\Delta A = -4.78 \times 10^{-3} + 0.15 \times 10^{-3} C$ with $r = 0.995$, where A is $\Delta A_s - \Delta A_b$ and C is the concentration.

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