

Evaluation of Thermodynamic Constants of the Oxidation of Ferrous to Ferric by RAPOX

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Ferrous solution undergoes oxidation in presence of ammonium acetate and forms a soluble complex with resacetophenone oxime. The oxidation is rapid at higher temperature. Kinetics of oxidation of ferrous was studied at various temperatures, at constant [RAPOX] and [Amm. Acetate] and the thermodynamic constants are evaluated.

INTRODUCTION

In the earlier studies¹, it was observed that Fe^{3+} forms a water soluble 1 : 1 complex with resacetophenone oxime or 2, 4-dihydroxyacetophenone oxime, abbreviated as RAPOX, which remains stable for a long time in the pH range 5.4-7.0. No complex formation was observed with Fe^{2+} at $\text{pH} \leq 3.0$. However, a colour gradually develops if the pH of the ferrous solution is increased by the addition of dilute ammonium hydroxide. Ferrous solution gets hydrolysed if pH of the solution goes beyond 7.0. The hydrolysis could be prevented by buffering the solution at pH 5.5 with ammonium acetate. The colour of the complex so developed is purple, identical to the one formed with Fe^{3+} having a maximum absorption at 500 nm. The absorption spectra of the complex thus obtained from ferrous solution and the one obtained from ferric solution are identical. It was suggested that Fe^{2+} solution undergoes oxidation to 3+ state at $\text{pH} \geq 5.0$ in presence of ammonium acetate and RAPOX. A kinetic study of the oxidation of Fe^{2+} to Fe^{3+} , by the use of ammonium acetate and RAPOX and the influence of their concentration on the system was undertaken and the rate constants for oxidation were obtained at ambient temperature². The present investigation is an extension of the previous study, carried out at various temperatures and from the data thus obtained, various thermodynamic constants were evaluated.

EXPERIMENTAL

Material and Reagents

1×10^{-3} mol dm^{-3} ferrous solution was prepared using B.D.H. AnalaR ferrous ammonium sulphate. Dilute sulphuric acid was added to the solution. RAPOX was synthesized from resorcinol and glacial acetic acid in presence of anhydrous zinc chloride. It was recrystallised from alcohol. Aqueous solution of RAPOX was prepared by dissolving a known quantity of the reagent in distilled water. Known quantity of ammonium

acetate was added to the RAPOX solution ($0.125 \text{ mol. dm}^{-3}$) so as to make it $0.25 \text{ mol. dm}^{-3}$ with respect to ammonium acetate.

Absorbance was recorded at 500 nm as a function of time on Cary 17D spectrophotometer using 10 mm quartz cuvettes.

A known volume of ferrous solution was added to the cuvette directly to which the mixture solution of RAPOX and ammonium acetate was added. The cuvette was shaken vigorously for few seconds and the absorbances were recorded at 500 nm as a function of time. The final molarity of the ferrous solution was $9.5 \times 10^{-5} \text{ mol dm}^{-3}$ and that of RAPOX = $0.1095 \text{ mol dm}^{-3}$ and ammonium acetate, 0.23 mol dm^{-3} . The cuvettes were maintained at constant desired temperature by circulating water through a thermostat controlled water bath.

The ferrous solution initially showed no coloration, but a purple colour gradually developed with time till a constant absorbance was reached. The experiments were repeated at various temperatures, up to 57°C .

RESULTS AND DISCUSSION

The colour developed in the ferrous solution on addition of the mixture of RAPOX and ammonium acetate was undoubtedly due to the oxidation of $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ as seen from the identical absorption spectrum obtained from ferric RAPOXimate. The previous study² has shown the dependence of RAPOX and ammonium acetate concentrations at ambient temperature. Those experiments were carried out as a function of [RAPOX] and [Amm. acetate], keeping one of the components constant and the other varying, The rate constant of oxidation varied with increase in [RAPOX] and [Amm. acetate], at constant temperature. A linear correlation was obtained in the log-log plots rate constant versus RAPOX and ammonium acetate concentrations. In the present investigation, in order to evaluate the activation energy, activation enthalpy and entropy, these two parameters, i.e. [RAPOX] and [Amm. Acetate] were kept constant and temperature varied.

The increase in the absorbance is proportional to $[\text{Fe}^{3+}]$. The reaction of oxidation of Fe^{2+} to Fe^{3+} is pseudo first order with respect to Fe^{2+} .

Thus, the integral equation of the first order reaction between the limits 0 and t times is as follows

$$\int_0^t \frac{d[\text{Fe}^{2+}]}{[\text{Fe}^{2+}]} = - \int_0^t k dt = \log \frac{[\text{Fe}^{2+}]_0}{[\text{Fe}^{2+}]_t} = kt \quad (1)$$

where $[\text{Fe}^{2+}]_0$ and $[\text{Fe}^{2+}]_t$ denote Fe^{2+} concentrations at the start and at time t respectively. The concentration of Fe^{2+} is dependent on Fe^{3+} complex concentration. Thus,

$$[\text{Fe}^{3+}]_t = [\text{Fe}^{2+}]_0 - [\text{Fe}^{2+}]_t \quad (2)$$

$$[\text{Fe}^{3+}]_{\infty} = [\text{Fe}^{2+}]_0 - [\text{Fe}^{2+}]_{\infty} = [\text{Fe}^{2+}]_0 \quad (3)$$

as $[\text{Fe}^{2+}]_0$ is negligible at infinite time. $[\text{Fe}^{3+}]_t$ and $[\text{Fe}^{3+}]_{\infty}$ are the ferric complex concentrations at times t and infinity, respectively. Substituting for ferrous concentrations in equation (1),

$$\log_e \frac{[\text{Fe}^{3+}]_{\infty}}{[\text{Fe}^{3+}]_{\infty} - [\text{Fe}^{3+}]_t} = kt \quad (4)$$

The concentrations of ferric-RAPOXimate complex are proportional to the variations in absorbances at 500 nm.

$$[\text{Fe}^{3+}]_t = \alpha(A_t - A_0) \quad (5)$$

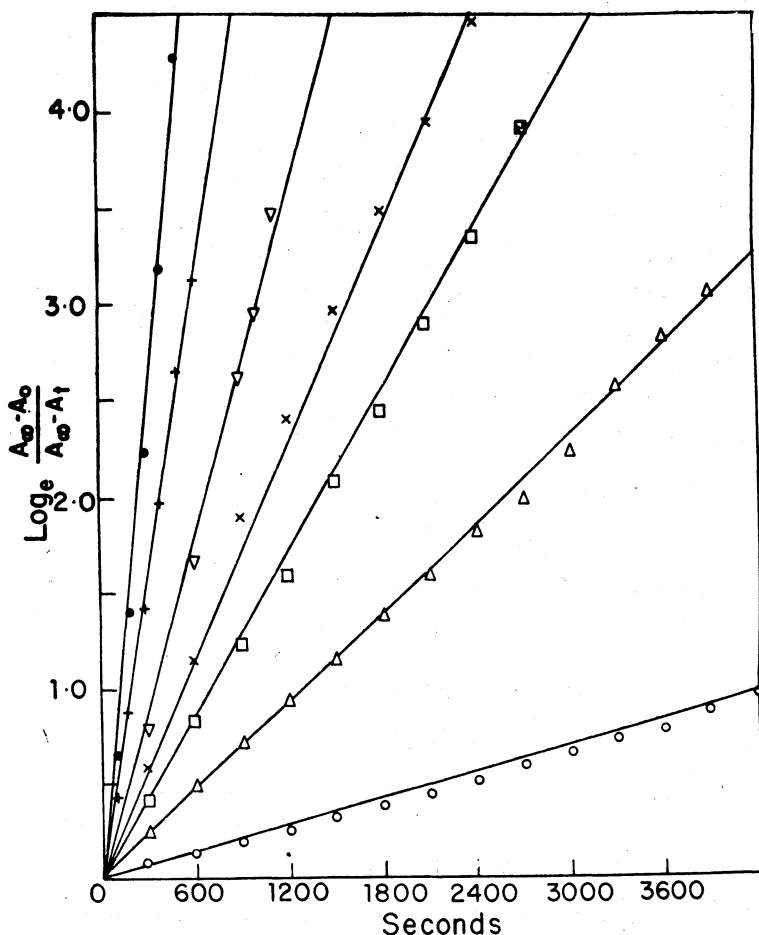


Fig. 1. Plots of $\log_e (A_{\infty} - A_0)/(A_{\infty} - A_t)$ vs. time in seconds at various temperatures (24°C, 30°C, 35°C, 40°C, 46.5°C, 53°C and 57°C). $[\text{Fe}^{2+}] = 9.5 \times 10^{-5}$ M; [RAPOX] = 0.1 M; [Amm. Acetate] = 0.23 M.

$$[\text{Fe}^{3+}]_{\infty} = \alpha(A_{\infty} - A_0) \quad (6)$$

Substituting equations (5) and (6) in equation (4),

$$\log_e \frac{(A_{\infty} - A_0)}{(A_{\infty} - A_t)} = kt \quad (7)$$

$\log_e (A_{\infty} - A_0)/(A_{\infty} - A_t)$ when plotted against time for various temperatures at constant [RAPOX] and [Amm. Acetate] yields a family of straight lines (Fig. 1). The figure shows that the rate of oxidation of Fe^{2+} to Fe^{3+} is first order and it increases with increase in temperature. The rate constant for oxidation is very low at ambient temperature but increases rapidly with the increase in temperature. At temperature higher than 57°C , the oxidation is almost instantaneous. At ambient temperature, it took more than two hours for complete oxidation of the ferrous solution, whereas at 57°C , the oxidation was complete in less than 10 minutes. The values of oxidation rate constants at various temperatures are given in Table 1.

TABLE I
OXIDATION RATE CONSTANTS AT VARIOUS
TEMPERATURES

$[\text{Fe}^{2+}] = 9.5 \times 10^{-5} \text{ M}$; [RAPOX] = 0.1 M
[Amm. Acetate] = 0.23 M.

Temperature ($^{\circ}\text{K}$)	Rate constants $\times 10^4$
297	2.34
303	6.77
308	14.24
313	18.85
319.5	30.00
326	52.90
330	75.75

The Arrhenius plot was constructed by plotting $\log k$ versus $1/T$ and the activation energy E_a and the preexponential factor, A , were calculated from its slope and the vertical intercept, respectively. From these values, activation enthalpy, ΔH^{\ddagger} and activation entropy, ΔS^{\ddagger} were calculated. They are as follows.

$$E_a = -59.66 \text{ KJ mol}^{-1}, \Delta H^{\ddagger} = -62.17 \text{ KJ mol}^{-1}$$

and

$$\Delta S^{\ddagger} = -83.9 \text{ J mol}^{-1} \text{ deg}^{-1}.$$

Thus, it is concluded that temperature also plays a very important

role in carrying out oxidation in the ferrous solution along with RAPOX and ammonium acetate concentrations.

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[Received: 12 May 1988; Accepted: 15 September 1988]