Asian Journal of Chemistry Vol. 4, No. 4 (1992) 715-725

Silver Ion Catalysed Oxidation of Phenosafranine by Peroxodisulphate—Catalytic Kinetic Determination of Micro Amounts of Silver

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The silver ion catalysed oxidation of phenosafranine, an azine dye, by peroxodisulphate in sulfuric acid and perchloric acid media is studied by following the reaction at 520 nm. The reaction was found to be of zero order in substrate concentration, first order with respect to peroxodisulphate concentration and silver ion concentration. A mechanism and rate law in consistent with these results have been proposed. The results of this investigation are utilized for the determination of microgram amounts of silver ion.

INTRODUCTION

The kinetics of peroxodisulphate oxidation of a number of organic and inorganic substrates have been reported and reviewed[1,2]. Silver (I) ion has the property of catalyzing oxidation reactions of peroxodisulphate ion and this property has been utilised for the determination of micro amounts of the silver (I) ion. Rao et. al[3]. investigated the silver ion catalysed oxidation of indigo carmine and determined silver ion in microgram amounts from the linear relationship existing between the pseudo-zero-order rate constant and silver ion concentration. In this paper we report our results on the silver ion catalysed oxidation of phenosafranine by peroxodisulphate ion in perchloric acid medium and the method for the microgram determination of silver ion.

Phenosafranine, an azinedye which was reported as a redox indicator, acid-base indicator and a complexing agent for the determination of various metal ions such as palladium[4], indium[5], uranium[6], tin[7], mercury[8], silver[9] and gold[10,11] by solvent extraction method, phenosafranine is recently reported as a substrate in the kinetic method of determination of iron (III), where in iron (II) gets as a catalyst in the photochemical oxidation of phenosafranine[12].

EXPERIMENTAL

All the chemicals used in this investigation are of analytical reagent

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grade quality. Solutions are prepared by dissolving the requisite amounts of the substances in double distilled water.

The course of reaction is followed spectrophotometrically by measuring the optical density of the unreacted phenosafranine at 520 nm using double beam schimadzu spectrophotometer with thermostat arrangement. At this wave length Beers law is obayed in a range of the concentration of substrate and also in the range of the concentration of hydrogen ion. All other materials concerned negligible absorption at this wave length. In all the kinetic runs, the ionic strength is maintained constant by the addition of sodium perchlorate solution. Under the experimental condition employed perchlorate ion is not found to oxidise phenosafranine.

The stoichiometry of the reaction is determined by mixing a known concentration of peroxodisulphate ion solution with known exess of phenosafranine solution and silver nitrate solution in 0.01 mol dm^{-3} perchloric acid. After the completion of the reaction (indicated by the constancy of optical density of the reaction mixture with time). The decrease in the value of the optical density of phenosafranine was measured at 520 nm. From the knowledge of molar extinction coefficient of the dye, the number of moles of phenosafranine reacted in the one gram ion of peroxodisulphate ion is found to be two.

RESULTS AND DISCUSSION

Several kinetic runs have been carried out keeping the concentration of phenosafranine very low in comparison with the concentration of peroxodisulphate ion so as to isolate the former. Plots of optical density versus time under these conditions are found to be linear for atleast 90% of the reaction showing that the reaction obeys zero order kinetics with respect to phenosafranine. These straight lines are found to be parallel (Fig. 1) for the runs carried out at different initial concentrations of the dye confirming the zero order behaviour. The results are presented in Table 1.

To study the dependence of rate on peroxodisulphate ion concentration kinetic runs are carried out at different initial concentrations of peroxodisulphate under the condition $[S_2O_8^{2-}] \gg [dye]_0$. Plots of optical density versus time for different initial concentrations of peroxodisulphate ion and at constant concentrations all other reagents are found to be linear (Fig. 2) and the zero order rate constants calculated in each case are presented in Table 2. A plot of the pseudozero order rate constant, k_0, varsus peroxodisulphate ion concentration is found to be a straight line passing through the origin indicating the first order dependence of rate on the concentration of peroxodisulphate ion.

To study the dependence of rate on silver ion concentration, kinetic runs have been performed at different initial concentrations of silver ion

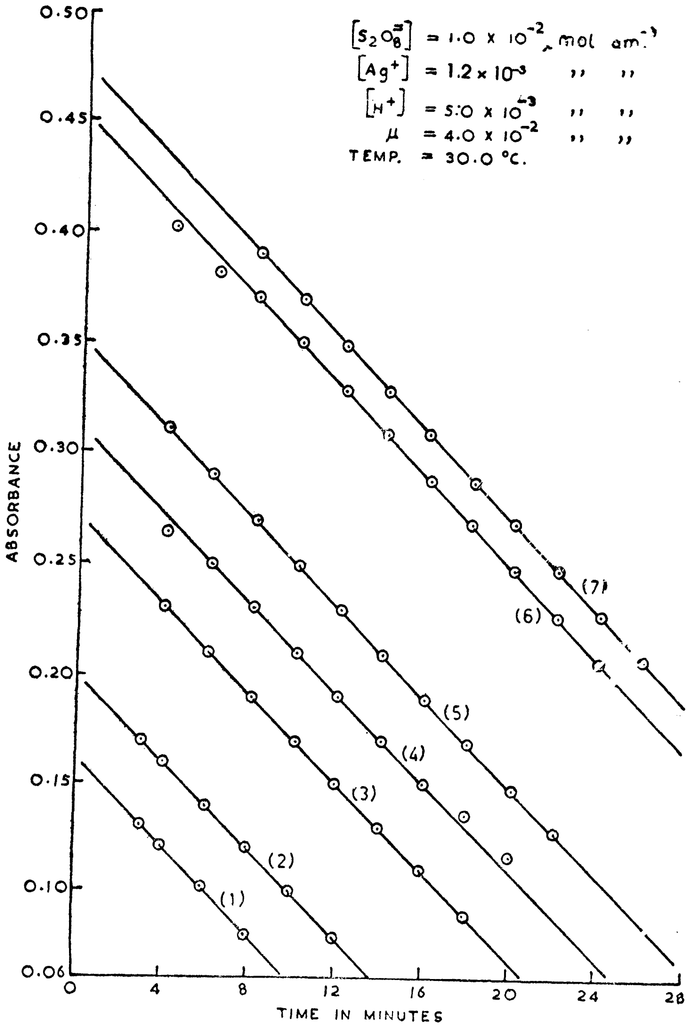

Fig. 1. Effect of Phenosafranine on rate.

keeping the concentrations of all other reagents fixed under the condition that $[S_2O_8^{2-}] \gg [\text{Phenosafranine}]_0$. The pseudozero order rate constants, k_0, have been calculated from the plots of optical density versus time for different initial concentrations of silver ion. The rate data comprising the values of the rate constants for different concentrations of the silver ion are presented in Table 3. A plot drawn between silver ion concentration and the corresponding value of the rate constant is found to be linear, passing through the origin indicating the first order dependence of the rate on silver ion concentration.

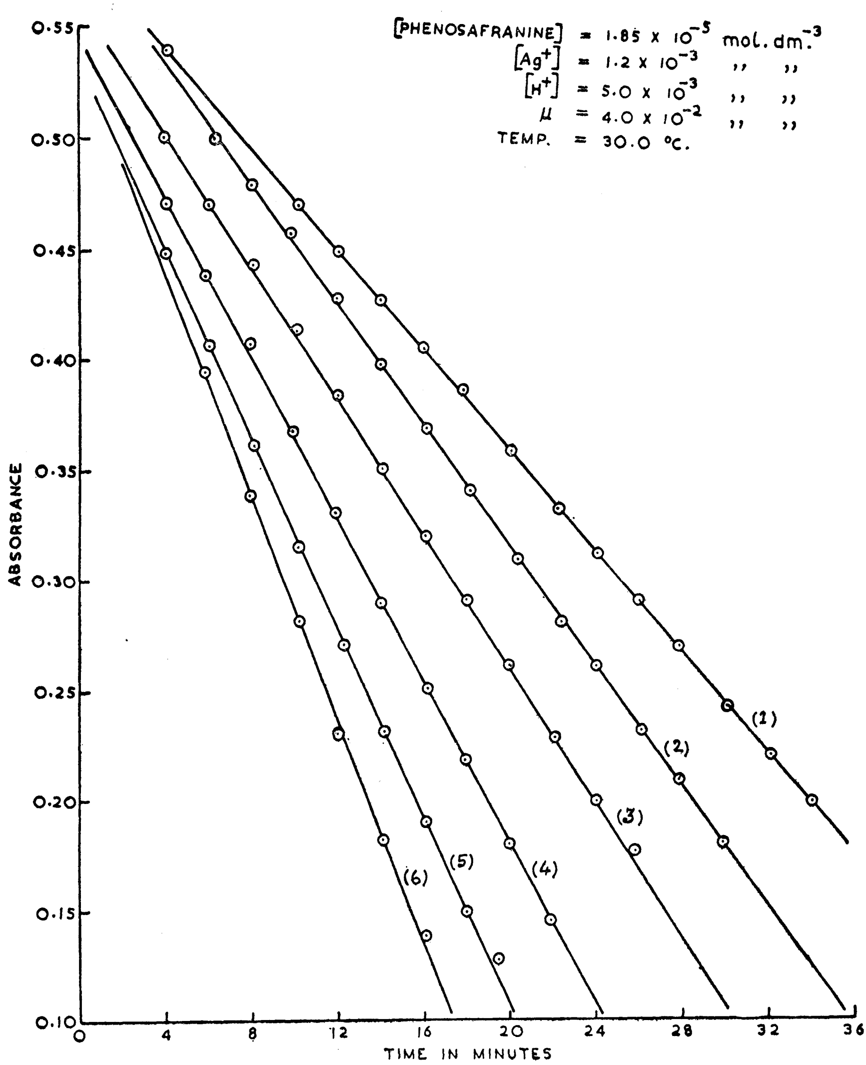

Fig. 2. Plot of absorbance vs time with variation in [$S_2O_8^{2-}$].

To obtain the type of dependence of rate on hydrogen ion concentration, kinetic runs were performed at different initial concentrations of perchloric acid to the range 0.2×10^{-2} mol. dm^{-3} to 5.0×10^{-2} mol. dm^{-3}. The extent of protonation of the dye in this range of acid concentration is negligible. The zero order rate constants are evaluated from the plots of optical density versus time. From the rate data presented in Table 4 it is evident that the hydrogen ion has no effect on the rate of the

TABLE 1

EFFECT OF (PHENOSAFRANINE) ON RATE OF THE REACTION

(Phenosafranine) $\times 10^5$ mol dm^{-3}	$k_0 \times 10^7$ mol dm^{-3} min^{-1}
1.850	11.73
1.549	11.74
1.239	11.75
1.084	11.73
0.9294	11.72
0.6696	11.79
0.4647	11.72

TABLE 2

EFFECT OF PDS ION CONCENTRATION ON RATE OF THE REACTION

(Phenosafranine) = 1.85×10^{-5} mol dm^{-3};
(Ag^+) = 1.2×10^{-3} mol dm^{-3}
(H^+) = $5.0 \times 10^{-3} = 4.0 \times 10^{-2}$ mol dm^{-3}
Temp = 30.0±0.1°C

($S_2O_8^{2-}$) $\times 10^{-2}$ mol dm^{-3}	$k_0 \times 10^7$ mol dm^{-3} min^{-1}
0.60	7.97
0.80	9.67
1.00	11.73
1.20	14.09
1.40	16.38
1.60	18.92

TABLE 3

EFFECT OF SILVER ION CONCENTRATION ON RATE OF THE REACTION

(Phenosafranine) = 1.85×10^{-5} mol dm^{-3};
($S_2O_8^{2-}$) = 1.0×10^{-2} mol dm^{-3}
(H^+) = 5.0×10^{-3} mol dm^{-3}
U = 4.0×10^{-2} mol dm^{-3}
temp = 30.0±0.1°C

(Silver ion) + 10^3 mol dm^{-3}	$k_0 \times 10^7$ mol dm^{-3} min^{-1}
0.8	7.54
1.0	8.96
1.2	11.72
1.4	15.85
1.6	18.46
1.8	22.01
2.0	24.07

reaction in the proposed range of acid concentration employed in the present investigation

TABLE 4

EFFECT OF HYDROGEN ION CONCENTRATION ON RATE OF THE REACTION

(Phenosafranine) = 1.85×10^{-5} mol dm^{-3};
($S_2O_8^{2-}$) = 1.0×10^{-3} mol dm^{-3};
(Ag^+) = 1.2×10^{-3} mol dm^{-3},
U = 4.0×10^{-2} mol dm^{-3}
temp = 30.0°C ± 0.1°C

($HClO_4$) $\times 10^3$ mol dm^{-3}	$k_0 \times 10^7$ mol dm^{-3} min^{-1}
0.2	10.20
1.0	10.00
2.0	9.82
2.6	9.81
3.0	9.92
3.6	9.92
4.2	10.92
5.0	11.73

To understand the nature of dependence of rate on ionic strength, many kinetic runs are performed by maintaining different ionic strengths in the reaction mixture. The rate data determined at different ionic strengths are incorporated in Table 5. A plot between log k_0 versus $(U)^{1/2}$

TABLE 5

EFFECT OF IONIC STRENGTH ON RATE OF THE REACTION

(Phenosafranine) = 1.85×10^{-5} mol dm^{-3}; ($S_2O_8^{2-}$) = 1.0×10^{-2} mol dm^{-3}; (H^+) = 5.0×10^{-3} mol dm^{-3}; (Ag^+) = 1.2×10^{-3} mol dm^{-3}
temp = 30.0 ± 0.1°C

Ionic strength 4 mol dm^{-3}	Rate constant $K_0 \times 10^7$ mol dm^{-3} min^{-1}	$(U)^{1/2}$	6+log k_0
0.017	18.17	0.130	0.2593
0.027	16.15	0.164	0.2081
0.037	14.57	0.192	0.1635
0.047	13.20	0.216	0.1206
0.057	12.08	0.238	0.0824
0.067	11.50	0.258	0.0606

is found to be a straight line with a slope of -1.8 indicating that the rate determining step involves positive and negative ions, the product of the charges[13] being -2.

To understand the nature of the reaction intermediates experiments are conducted in a thumburg tube by taking phenosafranine, perchloric acid, silver nitrate and acrylonitrile in the tube and potassium peroxodisulphate solution in the side arm. The tube is evacuated and then the solutions are mixed thoroughly. A thick solid mass of the polymer has been observed after about two hours indicating that the reaction proceeds via as free radical mechanism.

The values of pseudozero order rate constants, k_0, are determined at different temperatures and the rate data obtained is shown in Table 6. A plot of log k_0 versus I/T is a straight line. From the slope of this straight line, the activation energy is calculated to be 14.80+0.2 kcal mole^{-1}. The entropy of activation $S^{\#}$ of the rate determining step is calculated using the equation

TABLE 6

EFFECT OF IONIC STRENGTH ON RATE OF THE REACTION

(Phenosafranine) = 1.85×10^{-5} mol dm^{-3}; ($S_2O_8^{2-}$) = 1.0×10^{-2} mol dm^{-3}, (H^+) = 5.0×10^{-3} moldm^{-3} (Ag^+) = 1.2×10^{-3} moldm^{-3} temp = 30.0 ± 0.1°C

Ionic strength 4 mol dm^{-3}	Rate constant $k_0 \times 10^7$ mol dm^{-3} min^{-1}	$(U)^{1/2}$	$6 + \log k_0$
0.017	18.17	0.130	0.2593
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0.067	11.50	0.258	0.0606

$$K = \frac{e \cdot k_bT}{h} \cdot e^{\Delta S^{\#}/R} \cdot e^{-E/RT}$$

where k_b is the Boltzman constant and the value is found to be -167.23 JK^{-1} Mol^{-1}.

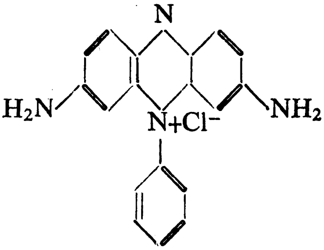
The salient observations of the kinetic investigation of the silver ion catalysed oxidation of phenosafranine by peroxodisulphate ion are:

1. The reaction follows zero order kinetics with respect to phenosafranine.

2. The reaction obeys first order kinetics with respect to peroxodisulphate ion.
3. The reaction rate is proportional to the concentration of silver(I).
4. The rate of reaction is not appreciably altered by a change in the concentration of hydrogen ion at constant ionic strength.
5. The rate of reaction decreases with an increase in ionic strength.
6. The reaction mixture initiates vinyl polymerization.

Since the presence of acrylonitrile in the reaction mixture causes the formation of polymer, the authors believe that the reaction proceeds through the formation of radical intermediates.

The phenosafranine molecules consist of two aromatic amine groups of similar nature.



It has been reported that the reaction between aromatic amines and peroxodisulphate ion in aqueous base results in the formation of a number of products in addition to the sulphate esters.[14,15] Bahraman[16] has suggested a mechanism for Boyland-Sims[17] oxidation involving a nucleophilic displacement by the amine nitrogen on peroxide oxygen to give the corresponding aryl hydroxyl amine-O-sulphonate. This postulated intermediate rearranges to O-amino aryl sulphate or gets oxidised to humic acid and ammonia.

The studies on the stoichiometry of the reaction indicated that two moles of phenosafranine react with one mole of peroxodisulphate ion when the concentration of peroxodisulphate ion is comparable to that of the dye. However at higher concentration of peroxodisulphate ion the stoichiometry varied with time and also with the concentration of peroxodisulphate ion. So the present authors believe that initial oxidation of the dye leads to the formation of dye free radical in a one electron reaction and subsequently the dye free radical will be oxidised to a stage of extended conjugation.

In view of these observations the authors believe that the dye radical formed will result in the formation of products in accordance with scheme-1

SCHEME-1

$$S_2O_8^{2-} \overset{k}{\rightleftharpoons} 2SO_4^{-} \qquad (1)$$

$$Ag^+ + 2SO_4^{-} \xrightarrow[k]{\text{Slow}} Ag^{3+} + 2SO_4^{2-} \qquad (2)$$

$$Ph + Ag^{3+} \xrightarrow{\text{fast}} \text{Products}$$

where Ph is phenosafranine

The rate of the reaction is given by the expression,

$$\frac{-d(S_2O_8^{2-})}{dt} = k\,(Ag^+)\,(SO_4^{-})^2 \qquad (1)$$

From the equilibrium (1) the rate constant k given by the expression

$$k = (SO_4^{-})^2/(S_2O_8^{2-}) \qquad (2)$$

or

$$(SO_4^{-})^2 = k(S_2O_8^{2-}) \qquad (3)$$

Substituting this value of (SO_4^{-}) in the rate expression (1) one gets

$$\frac{-d}{dt}(S_2O_8^{2-}) = kk\,(S_2O_8^{2-})\,(Ag^+) \qquad (4)$$

The above expression is in accordance with the kinetic pattern observed by the present authors. Several other investigators also proposed similar mechanism for the silver ion catalysed oxidation of substrate by peroxodisulphate ion.

Catalytic Kinetic Determination of Silver(I) Ion

The oxidation of phenosafranine by peroxodisulphate ion in the presence of silver(I) does not show any induction period. Hence, in order to determine the concentration of the catalyst either variable time or fixed time procedure may be employed. The authors have determined the amount of silver(I) according to fixed time procedure.

The authors recommended the following procedure for determining ΔX values to measure the extent of reaction at the end of 10th minute.

Calculated quantities of phenosafranine and perchloric acid to give over all concentration of 6.196×10^{-6} mol. dm^{-3} and 1.0×10^{-3} mol. dm^{-3} are mixed with known fixed volume of silver (I) solution and water is added to make a total volume of 25 ml. The reaction mixture is kept in thermostat at 30.0 ± 0.1°C. Potassium peroxodisulphate solution is also kept in the same thermostat. After temperature equilibrium is attained, calculated quantity of peroxodisulphate to give the overall concentration of 2.0×10^{-2}

mol. dm^{-3} is added to the reaction mixture, simultaneously starting a stop watch. Exactly after ten minutes the optical density is measured. The initial optical density is noted by measuring the optical density of the reaction mixture without peroxodisulphate. The difference gives ΔX.

The ΔX values are determined at different known concentration of silver(I), the concentrations of other reactants being kept constant. The plot of ΔX versus [Ag(I)] is a straight line passing through origin which serves as the calibration curve. The ΔX value is determined taking the known volume of silver(I) solution, whose concentration has to be determined and the concentration of the same has to be read from the calibration curve.

In the estimation of silver(I), the interference of various ions were studied. It is observed that 400 fold excess of Bi(II), Co(II), Zn(II) and Ba(II), Ru(III) do not interfere in the determination of silver(I) ion.

The results obtained by this using this new method for the micro determination of silver ion are presented in Table 7, which indicates good reproducibility and accuracy.

TABLE 7

EFFECT OF TEMPERATURE ON RATE OF THE REACTION

(Phenosafranine) = 1.85×10^{-5} mol dm^{-3}, ($S_2O_8^{2-}$) = 1.0×10^{-2} mol dm^{-3} (H^+) = 5.0×10^{-3} mol dm^{-3}: (Ag^+) = 1.2×10^{-3} mol dm^{-3}

Temperature °K	$k_0 \times 10^7$ mol dm^{-3}
303.5	11.72
307.5	15.20
312.5	21.91

ACKNOWLEDGEMENT

K. B. Subhashchandran wishes to thank, U.G.C., New Delhi for the grant of F.I.P. to carry out this work and to Principal, S.V.N.S.S. College, wadackanchery, Trichur, Kerala for his encouragement.

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(*Received*: 30 October 1990; *Accepted*: 12 July 1991) AJC-341