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The Influence of Ag(I) Ions on the Kinetics of Oxidation of Safranine by Peroxodisulphate

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The influence of silver ions on the kinetics of safranine, an azine dye, by peroxodisulphate has been ivestigated in the presence of sulphuric acid colorimetrically. It was found that the rate is independent of the concentration of safranine but first order dependent with respect to the concentration of $S_2O_8^{2-}$ and Ag(I). The reaction exhibits negative salt effect. Acrylonitrile greatly inhibits the rate. A radical mechanism has been proposed to explain the observed results.

INTRODUCTION

Potassium peroxodisulphate is a powerful oxidising agent in aqueous media. Oxidation reactions of the inorganic and organic substrates have been extensively studied and reviewed by House[1], Wilmarth *et al.*[2] and Wilson[3]. In addition to the elucidation of oxidation reaction mechanism, catalytic reduction of peroxodisulphate have been sucessfully used in determining the micro amounts of silver, iron and vanadium[4]. New reactions involving the oxidation of ethylene diaminetetra acetato cobaltate(II)[5], fluoroscein[6] and malachite green[7] substrates with peroxodisulphate catalysed by silver ion have been investigated. The title reaction was chosen to elucidate the reaction mechanism by a kinetic approach.

EXPERIMENAL

All the reagents were high purity chemicals and stock solutions were prepared by dissolving the requisite quantity of the reagents in double distilled water. Standard solution of $K_2S_2O_8$ was prepared afresh just before use by dissolving known quantities of oxidant into redistilled water. The ionic strength was maintained with the use of sodium perchlorate solution.

To the safranine solution in the reaction vessel all the requisite reagents were added and the reaction was initiated by the addition of separately thermostated silver (I) ion solution. The progress of the reaction was followed colorimetrically using green filter having a range 480–560 nm. The λ_{max} of the substrate was located at 535 nm and it obeyed Beer's law in the range of dye concentration used. All the kinetic measurements were carried out in the excess of the $[S_2O_8^{2-}]$ in relation to that of safranine.

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Reaction stoichiometry and product analysis

The stoichometry ratio between safranine and peroxodisulphate was found as 1 : 1 and the overall reaction is

$$\text{Safranine} + S_2O_8^{2-} + 2H_2O \xrightarrow{Ag(I)} P + 2SO_4^{2-} + 2H^+$$

The safranine gave a polymeric resinous material of unknown composition. Shrivastava *et al.*[8] have found the similar type of polymeric products.

RESULTS AND DISCUSSION

The preliminiary experiments have shown that the reaction is rather slow in the absence of the catalyst. However, the reaction proceeds with the measurable velocity in the presence of silver (I). The reaction was investigated at several concentrations of reactants (Table 1). Plots of the optical density *vs* time were linear for the least three half lives suggesting a zero order dependence in [dye].

TABLE-1

EFFECT OF VARYING [$S_2O_8^{2-}$], [SAFRANINE] AND [Ag(I)] ON k_0 IN CATALYSED OXIDATION OF SAFRANINE BY $S_2O_8^{2-}$ ION.

Temperature = 303 K; [H_2SO_4] = 1.0 M, [$NaClO_4$] = 0.33 M

[$S_2O_8^{2-}$] × 10^3 mol dm^3	[Safranine] × 10^5 mol dm^3	[Ag(I)] × 10^4 mol dm^3	k_0 × 10^7 mol dm^3 min^{-1}
0.66	3.30	83.30	1.00
1.60	3.30	8.30	3.00
3.30	3.30	8.30	5.00
5.00	3.30	8.30	8.00
6.60	3.30	8.30	10.50
8.30	3.30	8.30	13.00
3.30	0.83	8.30	5.45
3.30	1.60	8.30	5.30
3.30	2.50	8.30	5.25
3.30	3.30	8.30	5.12
3.30	4.17	8.30	5.50
3.30	5.00	8.30	5.00
3.30	3.30	5.00	3.25
3.30	3.30	8.30	5.50
3.30	3.30	11.60	8.00
3.30	3.30	16.60	11.00
3.30	3.30	25.00	16.50
3.30	3.30	33.00	21.00

In order to examine the effect of $[S_2O_8^{2-}]$ on the rate, the reaction was carried out at various initial concentration of the oxident. The plot of pseudo zero rate constant, k_0 against $[S_2O_8^{2-}]$ is linear. This shows the first order kinetics with respect to $[S_2O_8^{2-}]$.

Furthermore, it was confirmed that the oxidation rates were first order with respect to the [Ag(I)] (Table 1). The rate law for this reaction is thus represented by

$$-\frac{d}{dt}[\text{Safranine}] = k_0\,[\text{Ag(I)}]\,[S_2O_8^{2-}]$$

The rate of the reaction was not appreciably altered by change in acid concentraction.

The influence of ionic strength on the rate of catalytic oxidation of safranine was examined at different ionic strengths by varying the concentractions of sodium perchlorate. The rate constants for various $[NaClO_4]$ are given in Table 2.

TABLE-2
EFFECT OF $[NaClO_4]$, ON THE REACTION RATE AT 303 K

[Safranine] = 3.3×10^{-7} mol dm^{-3}; $[S_2O_8^{2-}] = 3.3 \times 10^{-3}$ mol dm^{-3},
[Ag(I)] = 8.3×10^{-4} mol dm^{-3}; $[H_2SO_4] = 1.0$ M

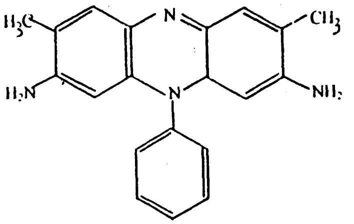
$[NaClO_4] \times 10^{T}$ mol dm^{-3}	$\sqrt{\mu}$	$k_0 \times 10^{7}$ mol dm^{3} min^{-1}
0.66	0.26	15.00
1.33	0.36	12.50
2.00	0.45	10.00
2.66	0.51	7.50
3.30	0.58	5.25
4.00	0.63	4.00

The added sodium perchlorate shows a decrease in the rate of the reaction. This indicates that the rate determining step involves interaction between the positive and negative ions. Similar results have been obtained in the case of silver(I) catalysed oxidation of other organic substrates[9–11]. The reaction mixture with acrylonitrile yielded a white turbidity showing that the reaction initiates vinyl polymerisations.

The reaction was studied in the temperature range 293–308 K. Based on the Arrhenius plot, the values of activation parameters were computed. The values of Ea, $\Delta H^{\neq}$, $\Delta G^{\neq}$ and $\Delta S^{\neq}$ are 56.48 kJ mol^{-1}, 54.56 kJ mol^{-1}, 110.22 kJ mol^{-1} and −185.21 JK^{-1} mol^{-1} respectively.

Safranine is an azine dye. It consists of two aromatic amine groups of similar natue.

The Ag(I) ion catalysed oxidation of safranine by peroxydisulphate in the presence of sulphuric acid is studied colorimatrically. The reaction was found to be of zero order in dye concentration and first order each with respect to peroxodisulphate concentration and Ag(I) ion concentration.



Safranine

It has been reported that with aromatic amines, *o*-aminoaryl sulphonate are produced irrespective of amine being primary, secondary or tertiary[12, 13] and the orienting influence of the functional group[14].

Behrman[15] has suggested a mechanism for this type of 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*-amine aryl sulphate or gets oxidised to humic acid and ammonia.

The stoichiometry is 1 : 1 and there is a strong inhibitory effect by acrylonitrile. On the basis of the kinetic results obtained and the products of oxidation, it is believed that the initial oxidation of the dye leads to the formation of dye free radical in a one electron reaction. The dye radical formed will be oxidised to a stage of extended conjugation.

The following scheme is proposed for the oxidation of safranine by $S_2O_8^{2-}$ in presence of Ag(I).

$$\mathrm{Ag(I)} + S_2O_8^{2-} \xrightarrow[\text{Slow}]{k_1} \mathrm{Ag(II)} + \overset{-}{SO_4^{\bullet}} + SO_4^{2-} \qquad (1)$$

$$\mathrm{Ag(II)} + \text{Safranine} \xrightarrow{k_2} \overset{\bullet}{1} + \mathrm{Ag(I)} \qquad (2)$$

$$\mathrm{I} + S_2O_8^{2-} \xrightarrow[H_2O]{k_3} \mathrm{P} + \overset{-}{SO_4^{\bullet}} + SO_4^{2-} + 2H^+ \qquad (3)$$

$$\mathrm{Ag(I)} + \overset{-}{SO_4^{\bullet}} \xrightarrow{k_4} \mathrm{Ag(II)} + SO_4^{2-} \qquad (4)$$

$$\overset{-}{SO_4^{\bullet}} + \mathrm{I} \xrightarrow[H_2O]{k_5} \mathrm{P} + SO_4^{2-} + 2H^+ \qquad (5)$$

Where I is the dye radical and P is the product.

The rate of disappearance of $[S_2O_8^{2-}]$ is given by equation (6):

$$-\frac{d\,[S_2O_8^{2-}]}{dt} = k_1\,[\mathrm{Ag(I)}][S_2O_8^{2-}] + k_3\,[\mathrm{I}][S_2O_8^{2-}] \qquad (6)$$

The application of steady state approximation to Ag(II) $\overset{-}{SO_4^{\bullet}}$ and [I] and also assuming that

$$k_1\,[S_2O_8^{2-}] \ll k_4\,[\overset{-}{SO_4^{\bullet}}]$$

and $\text{sub3}\,[S_2O_8^{2-}] \ll k_5\,[SO_4^{\bullet-}]$

one gets

$$[I] = \frac{k_4}{k_5}\,[Ag(I)] \qquad (7)$$

From equations (6) and (7), final rate expression is obtained as:

$$-\frac{d\,[S_2O_8^{2-}]}{dt} = k_1\,[Ag(I)][S_2O_8^{2-}] + \frac{k_3k_4}{k_5}\,[Ag(I)][S_2O_8^{2-}]$$

$$= k\,[Ag(I)][S_2O_8^{2-}]$$

where $k = k_1 + \dfrac{k_3k_4}{k_5}$

Thus the rate law derived satisfy all the kinetic features observed in the oxidation of safranine studied.

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