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Kinetics and Mechanism of Oxidation of Crystal Violet by Oxone

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ABSTRACT

The waste water treatment of dye bath involve degradation and removal of color by oxidation processes. These oxidative processes are useful for the treatment of waste water from the textile industries which allows it for reuse. The reaction was studied for crystal violet dye under pseudo first order condition at constant temperature 25 ± 0.1°C The stoichiometry was found to be one mole of crystal violet requires two moles of oxone. There was no effect of acrylonitrile observed .The mechanism of the reaction involves interaction between the substrate and the oxidant in prior equilibria. The present reaction might also involve such an ion-pair formation.

Keywords: ion-pair, degradation.

INTRODUCTION

Waste water from textile industry is highly coloured and of a complex and variable nature [1]. Due to their refractory nature it is matter of environmental concern. [2,3] A substantial amount of dyestuff is lost during dyeing process in textile industry [4], which poses major problem for industry as well as threat to environment [4-9]. Hence waste water treatment of dye bath is needed. It involves electrodegradation, photocatalytic degradation [10] and oxidative degradation etc. These oxidative processes are useful for the treatment of waste water from the textile industries which allows it for reuse. In the present work oxidation of crystal violet by peroxomonosulphate(oxone) was undertaken and mechanism of the reaction is deduced.

MATERIALS AND METHODS

Reagent grade chemicals and doubly distilled water were used throughout. The solution of crystal violet and oxone were prepared by dissolving crystal violet (BDH) and oxone

(Lancester) in distilled water respectively.The solutions of oxone were freshly preparaed and standardised iodometrically.The pH of the solutions is mantained by using buffer solution .The buffer of pH 4 was prepared by mixing quantity of 0.2mol dm^{-3} sodium acetate and 0.2 mol dm^{-3} acetic acid.The pH of the solution was measured on Elico GI -10T pH meter .

Kinetic studies

The reaction was studied under pseudo first order condition at constant temperature 25 ± 0.1^oC and pH = 4 of the solution is maintained . The reaction was initiaed by mixing previously thermostated solution of crystal violet and oxone which also contained required amount of distilled water and pH = 4 was maintained. The reaction was followed spectophotometrically by measuring the decrease in absorbance of crystal violet at 588 nm as a function of time b an Elico SL 159 UV-VIS spectrophotometer.

The stoichiometry was found to be one mole of crystal violet requires two moles of oxone. The pseudo first order rate constant goes on increasing with increase in oxone concentration. The order with respect to oxone is 0.6.

The effect of pH was studied by using buffer solutions of pH 3.45, 4.0, 5.0, and 5.9. The reaction rate goes on decreasing slightly with increase in pH value.

The effect of solvent polarity was studied . Acetonitrile is used to vary the solvent polarity. There was no effect of acrylonitrile observed and no free radical formation was detected . The relative permitivity of the medium was computed from the values of relative permitivities of pure liquids using the equation

$$D = V_1 D_1 + V_2 D_2$$

Where V_1 and V_2 are volume functions ; and D_1 and D_2 are dielectric constants of water and acetonitrile respectively . The rate of the reaction decrease with decrease in permittivity

The effect of temperature was studied at 25,30,35,40C and rate constants for the reaction were $4.8x\ 10^{-4}$,$5.54x10^{-4}$,$6.91\ x10^{-4}$,$7.68\ x10^{-4}s^{-1}$ respectively. The values of activation parameters $\Delta H^{\#} = 22.8 \pm 5K\ J\ mol^{-1}$ and $\Delta S^{\#} = -232.1 \pm 4K\ J\ mol^{-1}$

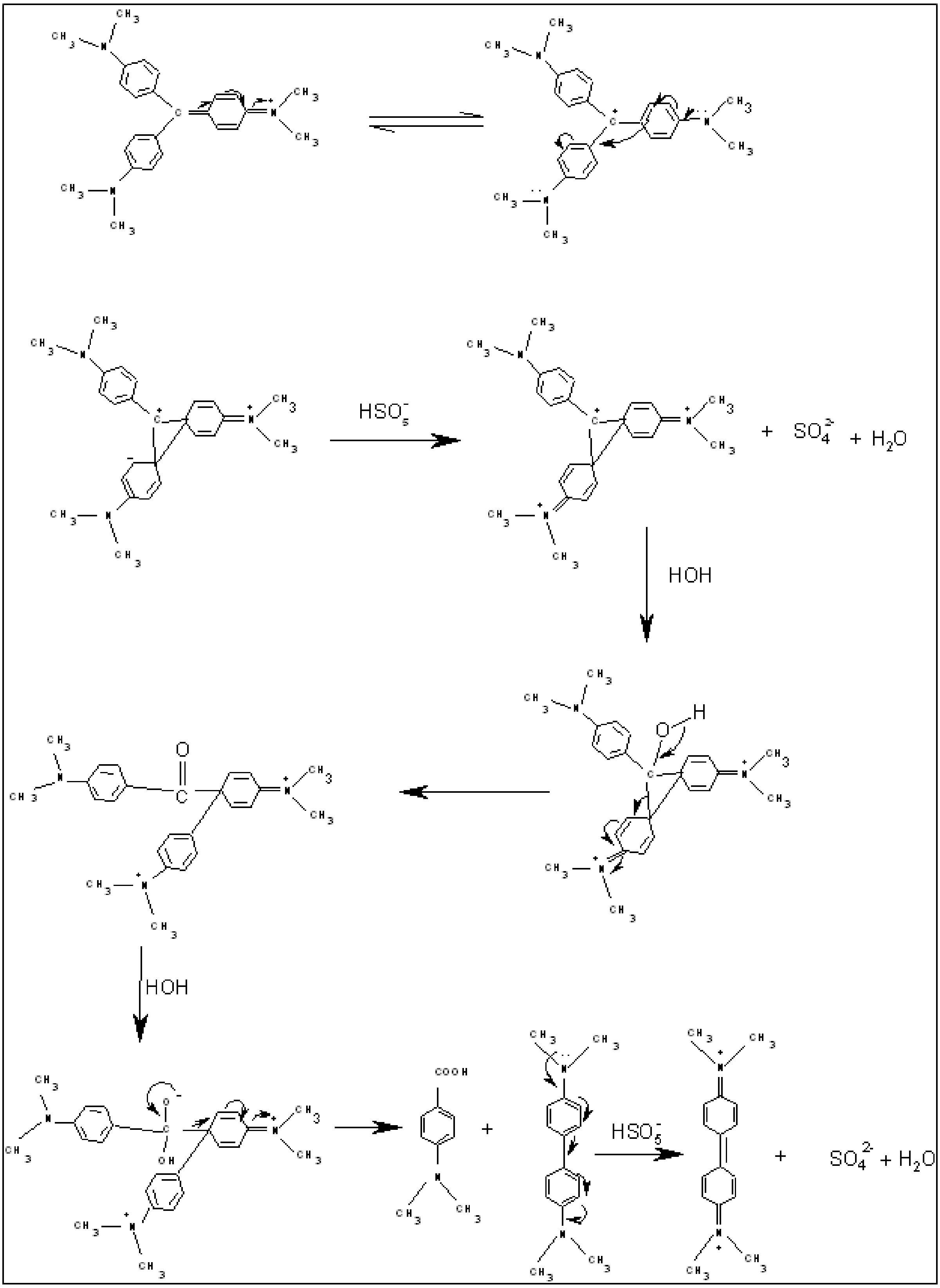
RESULTS AND DISCUSSION

Peroxomonosulphate, Oxone, is a strong two-electron oxidant and its reactions with organic and inorganic substrates have been studied extensively [11, 12]. The oxidations involving peroxocompounds generally involve either their thermal decomposition as the initial step, successive one-electron transfer steps or by direct two-electron transfer step. In earlier work step by step deamination was observed, but we do not get such evidence. The mechanism involving either thermal decomposition or one-electron transfer step to generate sulphate free radicals and in the former case the reaction will be independent of substrate concentration [13] [Table 1] . In the present study, the order in crystal violet concentration is found to be unity as there is no change in the pseudo-first-order rate constants. The pseudo-first-order rate constants also remain unchanged in presence of added acrylonitrile, a free radical scavenger, indicating no formation of any free radicals in the mechanism of the reaction. The order in oxidant concentration is found to be fractional (0.65) If the reaction is initiated by thermal decomposition of Oxone then the order would have been exactly 0.5 [13]. Therefore the mechanism of the reaction involves interaction between the substrate and the oxidant in prior equilibria. The involvement of direct two-electron transfer step in the oxidations by peroxocompounds as the prior equilibria is mainly due to formation of an ion-pair complex as proposed in Ag(I) catalyzed oxidations and oxidation of Au(I) [14]. Increase in the pH of the solution from 3.45 to 5.9 decreases the rate of the reaction indicating HSO_5^- as the active species whose concentration decreases with increase in pH. Therefore, the present reaction might also involve such an ion-pair formation. The substrate, crystal violet, was a chloride salt and in aqueous solution it exists as crystal violet cation and chloride anion. The positive charge on the nitrogen can be delocalized on to the tertiary carbon which undergoes ion pair formation with the Oxone. The oxidant species under the conditions of the pH utilized, the reaction exists mainly as HSO_5^- . Thus the ion pair formation is possible between the crystal violet cation and the active oxidant species. The detailed proposed mechanism of the reaction is shown in Scheme I. The ion pair formed undergoes internal oxidation and reduction to produce a labile cyclopropane derivative (I) with a positive charge on the tertiary carbon atom. This labile cyclopropane derivative, a strong electrophile is attacked by a water molecule, with consequent release of proton in solution. Cyclopropane ring opening occurs due to the strain on the ring as well as restoration of aromaticity to the quinoidly ring systems. The subsequent rapid reaction with another water molecule result in formation of dimethylaminobenzoic acid and the intermediate II (N,N,N',N'-tetramethyl benzidine). Such intermediates are reported in related malchite green oxidation by various oxidizing agents. [15 - 17] The intermediate II further react with another oxidant to give one of the final product diphenoquinone-4-4'(bis)dimythylimine.

Table 1

10^6[Crystal Violet.] $moldm^{-3}$	10^4[OXONE]$moldm^{-3}$	$10^4 k_{obs}$ sec^{-1}
1	1	4.7
3	1	4.6
5	1	4.8
7	1	5.0
10	1	4.8
5	0.25	2.05
5	0.5	3.84
5	1	4.8
5	1.5	6.14
5	2.5	9.11

Scheme I



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