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Kinetics of oxidation of azo dyes by Cr^{VI} using oxalic acid in absence and presence of micelle forming surfactants

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Abstract : Kinetic studies on the oxidation of aromatic azo compounds Ponceau-S and Fast Sulphon Black-F using chromic acid catalysed by oxalic acid was investigated in absence and presence of cationic surfactant (CTAB) and anionic surfactant (SDS). An appreciable rate constant obtained from the kinetic investigation revealed the feasibility of the reaction. Mechanism, already reported has been found consistent with the experimental findings. The oxidation reaction of both the dyes were found to be inhibited in presence of CTAB and showed no effect in presence of SDS.

Keywords : Ponceau-S, chromic acid, oxalic acid, kinetic studies, sodium dodecyl sulphate.

Introduction

Study of dye-surfactant interactions has been a subject of intense research activity due to the extensive use of these systems in analytical determinations. The interaction of four ionic dyes, C.I. Mordant Black 11, C.I. Mordant Black 17, C.I. Direct Yellow 50 and C.I. Basic Blue 9, with cationic and anionic surfactants was studied by absorption spectroscopy[1]. The effect of micellar media on the mechanistic paths of reduction of Cr^{VI} to Cr^{III} and also the oxidation of the substrate has been discussed and such studies are important in the understanding of the mechanism of redox activity and toxicity of Cr^{VI} [2]. The chromic acid oxidation of D-galactose in presence and absence of 2,2′-bipyridine (bpy) has been carried out at different temperatures. The observed micellar effects have been explained by considering the hydrophobic and electrostatic interactions between the reactants and surfactants in terms of the proposed mechanism[3].

Many oxidation reactions have been performed but no literature data has been found on kinetic studies of the redox reactions of the two different dyes : Ponceau-S and Fast Sulphon Black-F. The micellar effect on the oxidation of both the dyes was carried out in the presence of anionic surfactant, sodium dodecyl sulphate (SDS) and cationic surfactant, cetyl trimethyl ammonium bromide (CTAB).

Experimental

Chromic trioxide was used and standardized by the improved iodometric method[4]. All the chemicals used were of analytical reagent grade. Kinetic measurements were carried out spectrophotometrically using a Shimadzu-160A micro processor controlled UV-Visible recording spectrophotometer.

Reaction was followed by noting the decrease in absorbance of Ponceau-S (518 nm) and Fast Sulphon Black-F (464 nm) at their visible absorption maximum as a function of time. The product analysis was carried out by using TLC plate using chloroform-methanol as solvents. The presence of nitroso groups in the compounds of both the spots were identified by the spot test prescribed by Feigl[5].

Results and discussion

Kinetics of oxidation of azo dyes by Cr^{VI} using oxalic acid in absence of surfactants :

Kinetic runs were carried out under pseudo-first order conditions keeping the concentration of Cr^{VI} 10 times greater than that of the dyes. All the kinetic runs were carried out at 298 K.

Effect of Ponceau-S concentration :

The dependence of rate constant on Ponceau-S concentration was determined by recording the kinetic runs, keeping the concentrations of Cr^{VI} and oxalic acid constant at 0.5×10^{-2} *M* and 2×10^{-2} *M* respectively and varying the Ponceau-S concentration in the range 0.5×10^{-4} to 2.2×10^{-4} *M*. Plot of log (absorbance) versus time were found to be linear indicating that the reaction is first order with respect to Ponceau-S. At different initial concentrations of Ponceau-S the plots were found to be parallel. The pseudo-first order rate constants obtained from the slopes of the plots are given in the Table 1.

Table 1. Effect of FSBF, Cr^{VI}, oxalic acid and Cl^- concentrations and pH on the rate of oxidation of FSBF by Cr^{VI} at room temp. at pH = 7.0, $[Cr^{VI}] = 0.5 \times 10^{-2}$ *M*, $[FSBF] = 0.5 \times 10^{-3}$ *M* and [oxalic acid] = 0.05 *M*

[FSBF] 10^4 (*M*)	$k \times 10^3$ (s^{-1})	$[Cr^{VI}]$ 10^2 (*M*)	$k \times 10^4$ (s^{-1})	[Oxalic acid] 10^1 (*M*)	$k \times 10^3$ (s^{-1})	$[Cl^-]$ 10^2 (*M*)	$k \times 10^3$ (s^{-1})	pH	$k \times 10^4$ (s^{-1})
0.5	3	0.5	4.5	0.5	2.15	0.5	2.18	4	1.1
0.8	4.5	1	6.7	1	2.66	1	2.07	5.1	1.2
1	3.5	1.5	11.5	2.5	3	1.5	2.27	6.3	1.7
1.2	4.27	2	14.4			2	2.71	7	2.3
1.4	3.95	2.5	19.7			2.5	2.54	8.01	2.3
1.6	5					3	2		
1.8	4.6					3.5	2.29		
2	4					4	2.44		
2.2	4.15								

Effect of Cr^{VI} and oxalic acid concentration on the oxidation of Ponceau-S :

The dependence of rate on Cr^{VI} concentration was studied by maintaining the Ponceau-S, H^+ and oxalic acid concentrations constant at 0.2 *M*, pH 7.0 and 0.05 *M* respectively and varying Cr^{VI} concentration in the range 0.5×10^{-2} to 2×10^{-2} *M*. Plots of log (absorbance) versus time at varying concentrations of Cr^{VI} were found to be linear. The values of rate constants obtained at different Cr^{VI} concentrations are listed in the Table 1. As the concentration of Cr^{VI} increased the rate of the reaction also increased. Plot of rate constant versus Cr^{VI} concentration is found to be linear passing through the origin indicating that the reaction is first order with respect to oxidant (Fig. 1). The dependence of rate on oxalic acid concentration was studied by varying oxalic acid concentration in the range 0.05–0.4 *M* keeping the [substrate], $[Cr^{VI}]$ and pH constant.

Effect of pH and added NaCl concentration on the oxidation of Ponceau-S :

Dependence of the rate of oxidation of Ponceau-S on H^+ concentration was examined in the pH range 4.0 to 10.4. Rate increased with increase in pH up to 7.0 and then decreased. Influence of added [NaCl] on the rate of oxidation of Ponceau-S by Cr^{VI} in the presence of oxalic acid was studied by varying the concentration of NaCl in the range 0.5×10^{-2} to 4×10^{-2} *M*. As the concentration of NaCl is increased the rate of reaction decreased.

Effect of FSBF concentration :

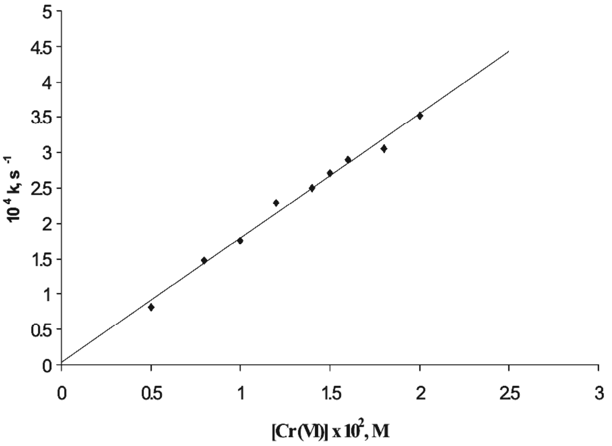

Fig. 1. Variation of rate constant with $[Cr^{VI}]$ for the oxidation of Ponceau-S by Cr^{VI} using oxalic acid.

The dependence of rate constant on FSBF concentration was determined by recording the kinetic runs, keeping the concentrations of Cr^{VI} and pH constant at 0.5 ×

10^{-2} *M* and 7.0 respectively and varying the FSBF concentration in the range 0.5×10^{-4} to 2.2×10^{-4} *M*. Plots of log (absorbance) versus time were found to be linear indicating that the reaction is first order with respect to FSBF. These plots at different initial concentrations of FSBF were found to be parallel. Pseudo-first order rate constants obtained from the slopes of the plots are given in the Table 1.

Effect of Cr^{VI} concentration on the oxidation of Fast Sulphon Black-F :

The dependence of rate on Cr^{VI} concentration was studied by maintaining the FSBF and $H_2C_2O_4$ concentrations constant at 0.5×10^{-4} *M* and 0.1 *M* respectively and varying Cr^{VI} concentration in the range 0.5×10^{-2} to 2.5×10^{-2} *M*. Plots of log (absorbance) vs time at varying concentrations of Cr^{VI} were found to be linear. The values of rate constants determined at different Cr^{VI} concentrations are listed in Table 1. Increase in the concentration of Cr^{VI} increased the rate of the reaction. Plot of rate constant vs Cr^{VI} concentration is found to be linear passing through the origin indicating that the reaction is first order with respect to oxidant.

Effect of added oxalic acid, added NaCl and pH on the oxidation of Fast Sulphon Black-F :

The oxidation of FSBF by Cr^{VI} was studied in the presence of oxalic acid. Kinetic runs were recorded at constant concentrations of FSBF, Cr^{VI} and varying the oxalic acid concentration in the range 0.05 to 0.5 *M*. Effect of varying FSBF, Cr^{VI}, pH and added NaCl in presence of oxalic acid catalyst is investigated. The data is given in Table 1.

Effect of varying Cr^{VI}, H^+, oxalic acid and azo compound concentration on the rate of oxidation in the absence of surfactants indicates that the mechanism of oxidation is consistent with the observed results for the oxidation of the azo compounds, given below.

$$HCrO_4^- + (COOH)_2 \xrightleftharpoons{K_1} HO_2CCO_2CrO_3^- + H_2O$$

$$X^- + H^+ \xrightleftharpoons{K_2} XH$$

$$XH + S \xrightarrow{k_1} \text{Products}$$

Scheme 1

Scheme 1 gives the following expression for the rate of disappearance of the substrate.

$$\frac{-d\,[\text{Azo compound}]}{dt} = Kk_1\,[\text{Azo compound}]\,[HCrO_4^-]\,[(COOH)_2]$$

This mechanism, which is similar to the one, reported earlier[6] leads to the following rate law :

$$\frac{-d\,[\text{Azo compound}]}{dt} = k_1K_1K_2\,[\text{Azo compound}]\,[HCrO_4^-]\,[(COOH)_2]\,[H^+]$$

Kinetics on oxidation of azo dyes by Cr^{VI} using oxalic acid in presence of surfactants :

Kinetic runs were carried out under pseudo-first order conditions keeping the concentration of Cr^{VI} 10 times greater than that of the dyes. All the kinetic runs were carried out at room temperature.

Kinetic studies on the oxidation of Ponceau-S in presence of surfactants :

Effect of anionic micelle forming surfactant sodium dodecyl sulphate (SDS), cationic micelle forming surfactant cetyltrimethylammonium bromide (CTAB), on the rate of oxidation of Ponceau-S by Cr^{VI} has been investigated. Studies were carried out by varying the surfactants concentration in the range 1×10^{-5} *M* to 5×10^{-5} *M* (Table 2) keeping the concentration of Ponceau-S, Cr^{VI} and oxalic acid constant. Anionic surfactant SDS showed no effect on the rate of the reaction. 5×10^{-5} *M* CTAB inhibited the reaction that no appreciable change in the

Table 2. Effect of surfactant on the rate of oxidationof Ponceau-S by Cr^{VI} in presence of oxalic acid at room temperature

[Ponceau-S] = 0.5×10^{-4} M^{-1}, [Cr^{VI}] = 0.5×10^{-2} *M*, [oxalic acid] = 0.05 *M* and pH = 7.0

Surfactant $\times 10^3$ (*M*)	$k \times 10^4$ (s^{-1})	
	CTAB	SDS
0	3.53	3.53
0.01	3.29	3.34
0.05	3.16	3.5
0.1	3.07	3.2
1.0	3.04	3.6
2.0	2.88	3.7
5.0	No reaction	–

Ponceau-S concentration was observed.

Kinetic studies on the oxidation of Fast Sulphon Black-F in presence of surfactants :

Effect of anionic micelle forming surfactant sodium dodecyl sulphate (SDS) and cationic micelle forming surfactant cetyltrimethylammonium bromide (CTAB) on the rate of oxidation of Cr^{VI} has been studied in the range of 1×10^{-5} to 1×10^{-3} *M*. Studies were carried out by varying the surfactants concentration and keeping the concentration of FSBF, Cr^{VI} and pH constant. CTAB inhibited the oxidation reaction so strongly that no appreciable change in the FSBF concentration was observed even after 2 h. Anionic surfactant SDS showed no effect. According to the above results CTAB micelles showed inhibition of the oxidation reaction. The azo compounds bind to cationic micelles of CTAB due to hydrophobic interactions. This can be explained based on the distribution of X^- and $HCrO_4^-$ between CTAB micelles and bulk phase.

The inhibition in CTAB may be attributed to the decrease in XH concentration and lower rate of attack of XH towards micelle bound substrate compared to that in bulk phase. SDS micelles showed no effect on the oxidation reaction. The reason may be due to relatively no binding of azo compounds to SDS micelles as a result of favorable hydrophobic repulsions. Enhanced concentration of substrate (S) and X^- in aqueous phase must be responsible for oxidation reaction outside the Stern layer due to repulsion by the surfactant SDS (anionic).

Conclusion

The oxidation of FSBF and Ponceau-S by Cr^{VI} was studied in the presence of oxalic acid. The reaction rate was appreciable in absence of surfactants. The reaction was inhibited in presence of CTAB and no effect in presence of SDS. These effects were interpreted on the basis of the mechanism and the possible interactions between the reacting species and micelles of different charge type.

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