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Silver(I) catalyzed oxidation kinetics of the crystal violet dye by peroxydisulphate in aqueous and micellar media

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The kinetics of the oxidative decolcourisation of crystal violet (CV^+) as a cationic dye by peroxydisulphate using silver(I) catalyst in aqueous acidic medium has been studied. The effects of different parameters like hydrogen ion, silver(I), reactants concentration, micelles and temperatures are investigated. The reaction between $[CV]^+$ and persulphate is investigated under pseudo-first-order kinetics by taking a large excess of $[S_2O_8^{2-}]$ over $[CV^+]$. The effect of surfactant micelles such as SDS and Triton X-100 on the reaction rate is investigated. The rate of reaction decreases with increasing [SDS] but had no effect with Triton X-100. Heat and entropy of activation and are calculated. An outer-sphere process for the electron transfer is the proposed mechanism for this reaction.

Keywords: Crystal violet, Catalysis by silver(I), Oxidative decolcourisation, Outer-sphere mechanism, Pseudo phase model

Organic dyes are one of the biggest environmental problems that cause pollution because organic dyes can form highly toxic compounds for soil and water[1]. The synthetic dyes are toxic and carcinogenic compounds; harmful for human, animals and environment even at low concentrations[2,3]. Environmental pollution caused by organic dyes due to its formation of hazardous aromatic amines through metabolic action in animals and plants. Some tools have been already investigated for treatment to the coloured wastewater such as physico-chemical techniques[4,5]. Amongst all these methods, the oxidative decolonization technique has a great potential for the removal of dyes without introducing any impurities, and also several advantages, such as simplicity and low-cost effectiveness over the methods[6-8]. In acid medium methylene blue oxidized by Ce(IV)[6], phenothiazine dye oxidized by Mn(III)[7] and iron(III) oxidized by malachite green[8] have been reported. In these reactions, the oxidation rate increases with decreasing pH.

The oxidation of dyes by heated persulphate has been studied in the previous studies as an effective and inexpensive process[9,10]. It has high oxidation potential (E_0 = 2.70 V) and low cost. Recently, persulphate is one of the best oxidants for the oxidative degradation of organic dyes. It needs activation through thermal[9] or chemical activation[11]. Powerful sulphate radicals $SO_4^{-\bullet}$ produced via thermal[9] ($T > 30$ °C) (Eqn. (1)) or chemical (Eqn. (2)) processes[11].

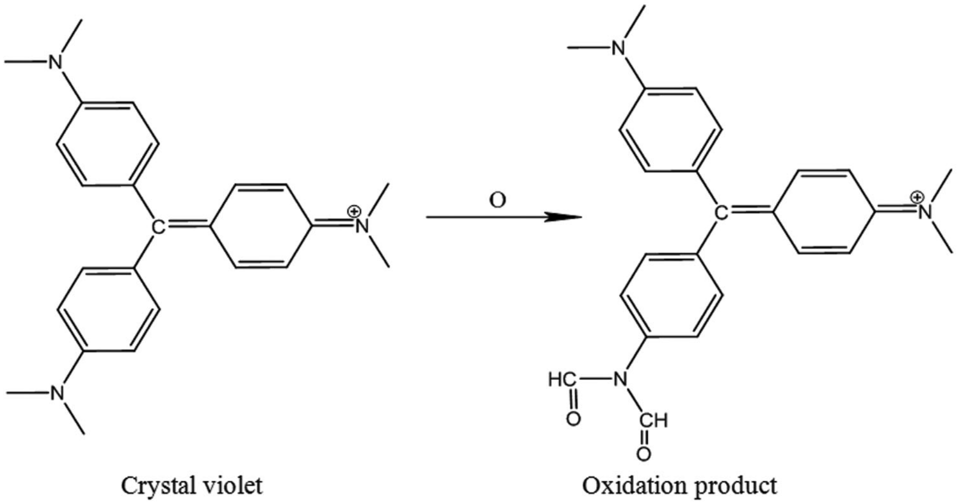
$$S_2O_8^{2-} \xrightarrow{\text{(Thermal activation)}} 2SO_4^{-\bullet} \qquad \ldots (1)$$

$$S_2O_8^{2-} + Ag^+ \xrightarrow{\text{(Chemical activation)}} Ag^{2+} + SO_4^{\bullet} + SO_4^{2-} \qquad \ldots (2)$$

Persulphate is used as a potent and stable oxidant in acid and alkaline medium. So, it is used in the oxidation of both organic and inorganic compounds[12,13].

Catalysis of persulphate oxidation of dyes by some transition metals in aqueous medium was studied[11,14,15]. The rate of decolourisation of orange dye by persulphate in the presence of iron(II) catalyst was found to be greater than that obtained with Fenton's reagent[14]. Silver(I) catalyzed persulphate oxidative degradation of Direct violet 31(Ref. 11), Acid red 14(Ref. 16) and methylene blue[9]. In these reactions persulphate activated by Ag^+ to produced $SO_4^{-\bullet}$ and Ag^{2+} which acts as a strong oxidizing agent than $S_2O_8^{2-}$ ions[11,12]. Oxidative decolourisation of $[CV]^+$ by chlorate ion in aqueous acidic solution was investigated[17] as shown in Scheme 1.

In this work, the kinetics and mechanism of the oxidative decolourisation of crystal violet by peroxydisulphate in the absence and presence of Ag(I) catalyst were studied. The effect of Ag(I) and surfactants in the oxidation rate at constant optimum conditions was investigated.



Scheme 1 — Oxidative decolourisation of $[CV]^+$ by chlorate ion in aqueous acidic solution

Materials and Methods

Materials

Crystal violet and ammonium persulphate were supplied by Sigma-Aldrich. Other chemicals and reagents used were of analytical reagent. Freshly prepared of a peroxydisulphate solution was kept in the non-transparent bottle to avoid its decomposition. Stock solutions of silver nitrate ($AgNO_3$), HNO_3, sodium nitrate ($NaNO_3$) were prepared. $NaNO_3$ was used to the adjusted ionic strength of the reactant solution to remain constant. All solutions were prepared using deionised water.

Instruments

The spectra of the oxidation product of crystal violet were recorded using A Lab Med, INC, UVD-2960 spectrophotometer. The reaction mixtures were prepared by adding the amount of each reactant and complete the total volume up to 40 mL using double distilled water. The reaction mixtures except persulphate were thermostated in an automatic circulation water bath for 20 min. The reaction started by adding the amount of peroxydisulphate solution to the reactants mixture. The reaction followed by monitoring the change of the absorbance of oxidation product at 575 nm using Perkin Elmer Lambda EZ-150 spectrophotometer. Jenway pH-meter 3510 was used for measuring of pH of the reaction mixture.

Kinetic procedures

The conditions of the reaction under pseudo-first kinetics were investigated by taking a large excess in peroxydisulphate concentration over $[CV^+]$. The ionic strength of the reaction was adjusted using $NaNO_3$ solution. Pseudo-first order rate constant, k_{obs}, were determined from the plots of $\ln(A_\infty - A_t)$ *versus* time, where A_t and A_∞ are the absorbances at time t, and at the end of reaction, respectively. The heat of activation ΔH^* and entropy of activation ΔS^* were calculated by plotting ln(k/T) against 1/T using the Eyring equation:

$$\frac{\ln k}{T} = \frac{\ln k}{h} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \qquad \dots (3)$$

Where, k is rate of reaction, T is absolute temperature, h is Plank's constant, K is Boltzmann constant and R is universal gas constant. The standard errors for results are calculated using the Origin program 9.0.

Results and Discussion

Kinetics of the oxidation of crystal violet by peroxydisulphate in the absence of catalyst

The absorption spectra of the oxidative decolourisation of $[CV]^+$ by peroxydisulphate were recorded on a LABOMED, INC UVD-2960 spectrophotometer at 575 nm as shown in Fig. 1. From Fig. 1, clear that the $[CV]^+$ has a strong absorption band at 575 nm which decreased with time as $[CV]^+$ got oxidized with peroxydisulphate to form the oxidation products. The kinetics of oxidation of the crystal violet by peroxydisulphate was studied over the temperature range (25–45) °C, ionic strength (0.2–0.7) mol dm^{-3}, $[H^+]$ (0.5 – 4.0) x 10^{-3} mol dm^{-3} at different concentration of $[CV]^+$ and $S_2O_8^{2-}$. The observed rate constant, k_{obs}, values were determined from the plots of $\ln(A_\infty - A_t)$ against time which are linear up to more than 85% of the reactions. Pseudo-first order rate constants, k_{obs}, calculated from the

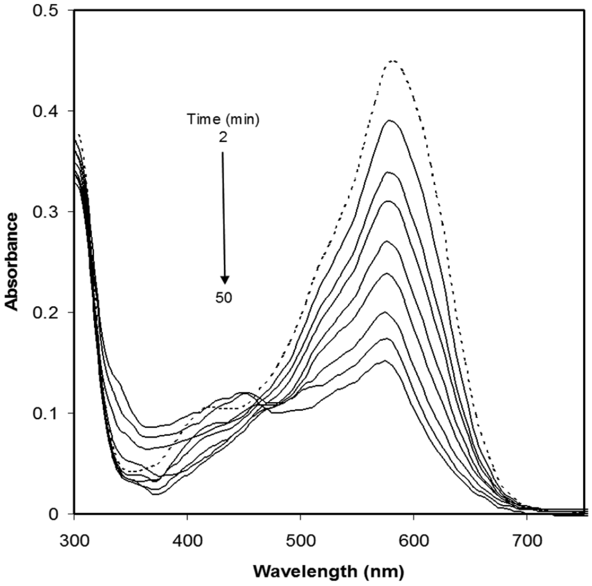


Fig. 1 — Change of absorbance as a function of time. Curves ( ) were recorded at intervals time from (2.0 – 50) min. $[CV^+] = 2.50 \times 10^{-5}$ mol dm^{-3}, $[S_2O_8^{2-}] = 0.01$ mol dm^{-3}, pH = 1.0×10^{-3} mol dm^{-3} and I = 0.20 mol dm^{-3}. Curve (…….) represents the $[CV^+] = 2.50 \times 10^{-5}$ mol dm^{-3}at the same condition

slopes of $\ln(A_\infty - A_t)$ against time graphs are summarized in Table 1. Values of k_{obs} in Table 1 are constant with varying of the $[CV]^+$ at constant peroxydisulphate concentration, indicating first-order dependence on the dye concentration and the rate law is given by Eqn. (4).

$$Rate = k_{obs}[CV^+]_0 \quad \text{... (4)}$$

The dependence of observed rate constant, k_{obs}, on $S_2O_8^{2-}$ was carried out over the (0.5–3.0) x 10^{-2} mol dm^{-3} concentration range of peroxydisulphate at fixed reaction conditions as represented in Table 1 and Fig. 2. Plot of k_{obs} versus $[S_2O_8^{2-}]$ is linear and this relation obeys Eqn (5).

$$k_{obs} = [S_2O_8^{2-}] \quad \text{... (5)}$$

The effect of $[H^+]$ on the rate constant, k_{obs}, was studied over the (0.5–4.0)x 10^{-3} mol dm^{-3} $[H^+]$ range under fixed reaction conditions. It is noticed that the reaction rate was independent on $[H^+]$ as indicated by the nearly constant values of k_{obs} (Table 1).

Table 1 — Values of the observed rate constant for the oxidation of $[CV]^+$ by $S_2O_8^{2-}$ at different parameters

$10^3[H^+]$ (mol dm^{-3})	Temp. (°C)	I (mol dm^{-3})	10^5 $[CV^+]$(mol dm^{-3})	10^2 $[S_2O_8^{2-}]$ (mol dm^{-3})	10^4 k_{obs} (s^{-1})
1.00	35.0	0.20	2.50	0.50	1.51 ± 0.02
				0.75	2.30 ± 0.01
				1.00	3.35 ± 0.02
				1.50	5.02 ± 0.04
				2.00	6.29 ± 0.03
				2.50	8.38 ± 0.06
				3.00	9.57 ± 0.08
			1.25	1.00	3.23 ± 0.03
			3.75		3.46 ± 0.02
			5.00		3.51 ± 0.05
			6.25		3.32 ± 0.04
0.50			2.50		3.39 ± 0.01
1.50					3.27 ± 0.04
2.00					3.49 ± 0.03
2.50					3.42 ± 0.02
3.00					3.31 ± 0.06
4.00					3.40 ± 0.05
1.00	25.0				1.02 ± 0.01
	30.0				1.86 ± 0.03
	40.0				5.82 ± 0.05
	45.0				8.00 ± 0.07
	35.0	0.30			3.02 ± 0.02
		0.40			2.45 ±0.04
		0.50			2.04 ± 0.01
		0.60			1.61 ± 0.05
		0.70			1.18 ± 0.03

Kinetics of the oxidation of crystal violet by peroxydisulphate in the presence Ag(I) catalyst

The kinetics of oxidation of the crystal violet by peroxydisulphate were catalysed by silver(I) using a concentration range (1.25–10.00) × 10^{-4} mol dm^{-3} of silver(I) at $I = 0.20$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3} for the different values of temperatures and $[S_2O_8^{2-}]$. The kinetic data in Table 2 indicated that the reaction rate increases with increasing of [Ag(I)] as a catalyst. Plots of k_1 versus [Ag(I)] at different temperatures, gave a straight line with intercept as represented in Fig. 3 and this relation is given by Eqn (6).

$$k_1 = k_2 + k_3[Ag^+] \qquad ...(6)$$

The values k_3 and k_2 were obtained at 25, 30, 35, 40, and 45 °C from the slopes and intercepts of Fig. 3, respectively, are summarized in Table 3. The heats of activation ΔH_2^* and ΔH_3^* which corresponding to k_2 and k_3, were determined the transition-state theory equation as 89.20 ± 3.20 and 16.91 ± 0.36 kJ/mol, respectively. The activation entropies, ΔS_2^* and ΔS_3^* were determined as 8.97 ± 1.0 and -158.38 ± 0.11 J/K mol, respectively. Ionic strength effect was carried out for a range (0.20 – 0.70) mol dm^{-3} as shown in Table 1. The results in Table 1 show that the observed rate constant, k_{obs}, decreases as the ionic strength increases. From Eqns 4, 5, and 6, the rate of the oxidative decolourisation of $[CV]^+$ by $S_2O_8^{2-}$ in the presence of Ag^+ as catalyst is given by Eqn (7),

$$Rate = (k_2 + k_3[Ag^+][CV^+][S_2O_8^{2-}] \qquad ...(7)$$

$$k_{obs} = k_3[Ag^+][S_2O_8^{2-}] \qquad ...(8)$$

Recently persulphate is used in the water treatment for the oxidation and removal of organic contaminants from aqueous medium due to its stability, high solubility, and relatively low cost[10,12]. Chemical treatment for industrial waste and hazardous contaminants by its oxidation with peroxydisulphate was investigated[4]. Peroxydisulphate can be thermally activated by heat[9,18] and chemically activated by some

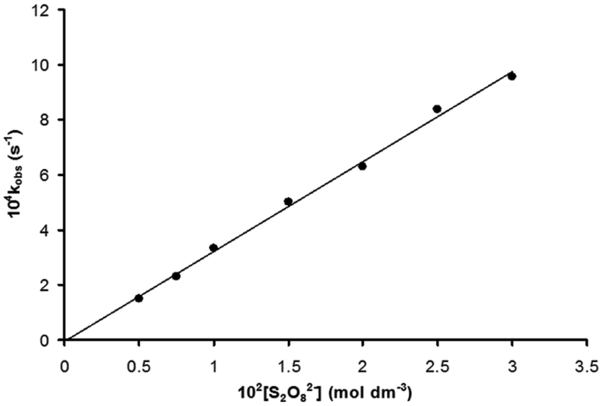


Fig. 2 — Variation of k_{obs} versus $[S_2O_8^{2-}]$ at T = 35 °C

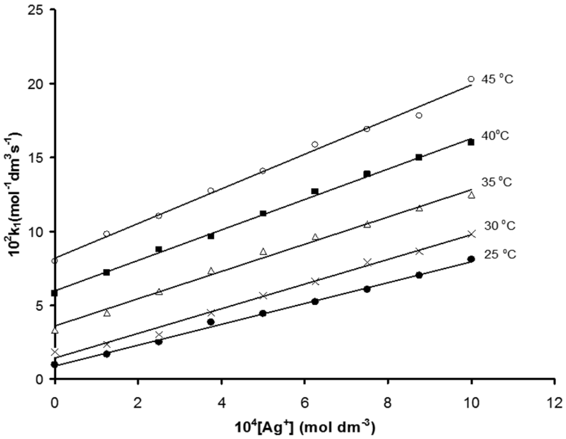


Fig. 3 — Variation of k_1 with $[Ag^+]$ at different temperatures

Table 2 — Variation of k_1 with $[Ag^+]$ at $[CV^+] = 2.50 \times 10^{-5}$ mol dm^{-3}, $[S_2O_8^{2-}] = 1.0 \times 10^{-2}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, $I = 0.20$ mol dm^{-3} and at different temperatures

10^4 $[Ag^+]$ (mol dm^{-3})	10^2k_1 (mol^{-1} dm^3 s^{-1})				
	25 °C	30 °C	35 °C	40 °C	45 °C
0.00	1.02 ± 0.01	1.86 ± 0.03	3.35 ± 0.02	5.82 ± 0.01	8.00 ± 0.01
1.25	1.72 ± 0.03	2.38 ± 0.01	4.51 ± 0.03	7.21 ± 0.05	9.82 ± 0.04
2.50	2.54 ± 0.02	3.06 ± 0.02	5.97 ± 0.01	8.79 ± 0.03	11.03 ± 0.08
3.75	3.86 ± 0.02	4.52 ± 0.05	7.39 ± 0.03	9.66 ± 0.06	12.75 ± 0.12
5.00	4.45 ± 0.04	5.67 ± 0.04	8.65 ± 0.06	11.20 ± 0.04	14.08 ± 0.09
6.25	5.23 ± 0.03	6.63 ± 0.06	9.67 ± 0.06	12.70 ± 0.08	15.86 ± 0.06
7.50	6.10± 0.06	7.92± 0.08	10.48 ± 0.08	13.89 ± 0.10	16.90 ± 0.10
8.75	7.03 ± 0.08	8.67 ± 0.07	11.60 ± 0.10	15.00 ± 0.12	17.82 ± 0.11
10.00	8.11 ± 0.05	9.83 ± 0.10	12.49 ± 0.09	16.01 ± 0.10	19.23 ± 0.14

($k_1 = k_{obs}/ [S_2O_8^{2-}]$)

Table 3 — Values of Ag^+- independent rate constant k_2 and k_3 Ag^+ -dependent rate constant k_3 at different temperatures

Temp. (°C)	10^2k_2 ($mol^{-1}\ dm^3\ s^{-1}$)	k_3($mol^{-2}\ dm^6\ s^{-1}$)
25	0.93 ± 0.01	35.19 ± 0.10
30	1.44 ± 0.01	41.75 ± 0.15
35	3.63 ± 0.02	46.09 ± 0.18
40	5.98 ± 0.01	51.58 ± 0.13
45	8.36 ± 0.02	58.70 ± 0.20

transition metals[19]. Persulphate oxidation catalysed by silver(I) in the aqueous acid medium through the formation of two active species $AgHS_2O_8$ and $AgS_2O_8^-$ (Ref. 20). Several peroxydisulphate oxidations obeyed an outer-sphere mechanism where the electron transfers between two reactants in the redox step without dissociation of the coordination spheres[11].

It is proposed that electron transfer between $[CV]^+$ and $S_2O_8^{2-}$ or $AgS_2O_8^-$ (Eqns 11 and 12) proceeds via an outer-sphere mechanism which is the rate-determining steps without formation the covalent bond between two species[21]. There is no significant shift in the electronic spectra of $[CV]^+$ at 575 nm as shown in Fig. 1, confirming that the intermediate complex formation is maybe not formed previously and the electron transfer passes through an outer-sphere mechanism[22]. The kinetic data in Table 1, shows that the values of k_{obs} unchanged as $[H^+]$ increases whereas the protonation or deprotonation reactant species are not involved. The observed rate constants, k_{obs}, increase as the temperature increases (Table 2). Elevation of temperature is one method for the generation of $SO_4^{-\bullet}$(Ref. 18). From Table 1, it clear that the observed rate constants, k_{obs}, decreases as the ionic strength increases, suggested that the reaction occurs between the reactants of different charges. The sharing of $SO_4^{-\bullet}$ in the oxidative decolourisation of $[CV]^+$ by peroxydisulphate is confirmed by the polymerisation of acrylonitrile in the reaction mixture. The proposed mechanism for this reaction is represented in Eqns (9-14).

$$S_2O_8^{2-} + Ag^+ \underset{}{\overset{K_1}{\rightleftharpoons}} AgS_2O_8^- \quad \dots (9)$$

$$AgS_2O_8^- \xrightarrow{\text{(fast)}} Ag^{2+} + SO_4^{2-} + SO_4^{-\bullet} \quad \dots (10)$$

$$[CV]^+ + S_2O_8^{2-} \xrightarrow{\text{(slow) } k_4} \text{Products} \quad \dots (11)$$

$$[CV]^+ + AgS_2O_8^- \xrightarrow{\text{(slow) } k_5} \text{Products} \quad \dots (12)$$

$$[CV]^+ + Ag^{2+} \xrightarrow{\text{(fast)}} \text{Products} \quad \dots (13)$$

$$[CV]^+ + SO_4^{-\bullet} \xrightarrow{\text{(fast)}} \text{Products} \quad \dots (14)$$

According to the previously proposed mechanism, the rate law is expressed by Eqn (15):

$$Rate = k_4[CV^+][S_2 \quad \dots (14)$$

$$Rate = k_4[CV^+][S_2O_8^{2-}] + k_5[CV^+][AgS_2O_8^-] \quad \dots (15)$$

From Eqn (9) we obtain

$$[AgS_2O_8^-] = K_1[S_2O_8^{2-}][Ag^+] \quad \dots (16)$$

By substitution of Eqn (16) into Eqn (15) we then obtain:

$$Rate = k_4[CV^+][S_2O_8^{2-}] + K_1k_5[CV^+][S_2O_8^{2-}][Ag] \quad \dots (17)$$

$$Rate = (k_4 + K_1k_5[Ag^+])[CV^+][S_2O_8^{2-}] \quad \dots (18)$$

$$Rate = (k_4 + K_1k_5[Ag^+])[S_2O_8^{2-}] \quad \dots (19)$$

Comparing Eqns (19) and (8) we get, $k_2 = k_4$ and $k_3 = K_1k_5$

In comparison with the oxidation of some organic dyes such as direct violet-31(Ref. 11) tartrazine[12], methylene blue[23] and safranin-O(Ref. 23) by peroxydisulphate using Ag^+ as a catalyst under the same conditions have been studied. These reactions get enhanced in acid medium and the electron transfer process takes place via a one-electron radical mechanism through outer-sphere mechanism. The rate constant, 10^4k_{obs}, are 5.24, 3.35, 2.30, 2.24 and 1.12 s^{-1} for tartrazine, crystal violet, safranin-O, direct violet-31 and methylene blue, respectively at 35 °C. In all cases during oxidation process, Ag^{2+} and $SO_4^{-\bullet}$ are produced which act as oxidant for these dyes[12,23]. Also, in comparison with its oxidation with permanganate[24] under the same reaction conditions, it is found that at lower temperature the reaction rate for the oxidation of CV^+ by permanganate is higher than its oxidation with peroxydisulphate. This is may be due to peroxydisulphate need the thermal activation by increasing of temperature and chemical activation by using Ag^+ as a catalyst. Another redox system $Fe^{2+}/S_2O_8^{2-}$ Fenton-like process was used for the oxidation of orange dye[14]. It was found that the oxidation rate is more than its oxidation with Fenton's reagent. This is may be due to the fact that the $SO_4^{-\bullet}$ produced during oxidation of dye by $Fe^{2+}/S_2O_8^{2-}$ is more stable in aqueous solution than the $OH^{\bullet}$ generated from Fenton's reagent.

Acoording to the oxidation of $[CV]^+$ by peroxydisulphate, the activation entropy is positive value for uncatalysed reaction and higher negative value for catalysed one. This is attributed to the reaction rate for uncatalysed reaction is lower with the higher activation energy than that of catalysed one. The redox reaction included a larger energy of activation, just like that requiring higher oxidation temperatures. Otherwise, the oxidative decolourisation of $[CV]^+$ in the existence of the catalyst involves a rate determining step which is related to the negative values of activation entropy, thus, suggest a highly structured oxidation product[25]. The intermolecular electron transfer steps are endothermic this is confirmed by positive values of ΔH^*. The values of the heat of activation, ΔH^*, and entropy of activation, ΔS^*, this means that factors controlling ΔH^* and ΔS^* are similar. Plotting of ΔH^* versus ΔS^* for the oxidation of some organic dyes by persulphate was linear suggests that the oxidation mechanism of these dyes[10,11,26-28] are similar as shown in Fig. 4 and Table 4. Similar to previous studies for the redox reactions with linear plots of ΔH^* versus ΔS^* are reported[29,30]. The isokinetic relationship for the oxidation of organic dyes by peroxydisulfate is linear with the general mechanism for these reactions[30]. It is suggested that the electron transfer for these reactions take place via an outer-sphere mechanism.

Effect of micelles on the rate of oxidative decolourisation of $[CV]^+$ by peroxydisulphate

Micelles play a significant role in the rate of the chemical reaction. Micelles as a pseudo-phase can be combined with some substrates which lead to an increase in the dissolution of this substrate and can affect the rate of reaction. The interaction of micelles molecules with substrates leads to the increasing or decreasing of the rate of reaction and micelle molecules act as reactants [31,32]. The effect micelle like anionic sodium dodecyl sulphate (SDS) and nonionic Triton X-100 (TX-100) on the oxidation rate of crystal violet by peroxydisulphate was investigated at $[CV^+] = 2.5\text{x}10^{-5}$ mol/dm^3, $[S_2O_8^{2-}] = 1.0 \text{ x } 10^{-2}$ mol/dm^3, $[H^+] = 1.0 \text{ x } 10^{-3}$ mol/dm^3, $I = 0.20$ mol/dm^3 and $T = 35.0$ °C over the concentration range of surfactant (1.25–10.0) x 10^{-4} mol/dm^3. Triton X-100 had no effect on the oxidation rate because TX-100 is a nonionic surfactant, hence it cannot attract reactants to the micellar phase. The effect of SDS as anionic micelles shows a continuous decrease in the observed rate constant, k_{obs}, with increasing SDS concentration as represented in Table 5. Different kinetic models have been proposed to explain the effect of the

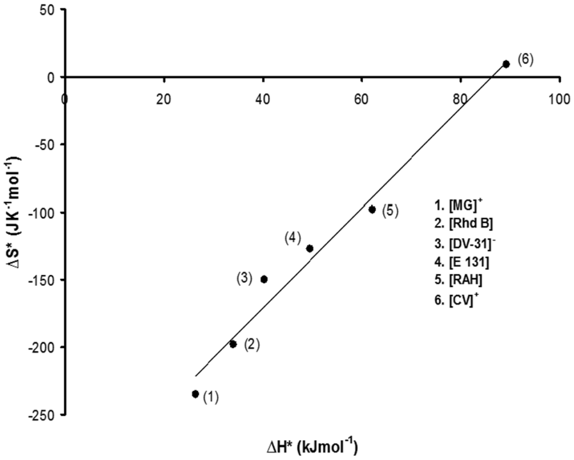


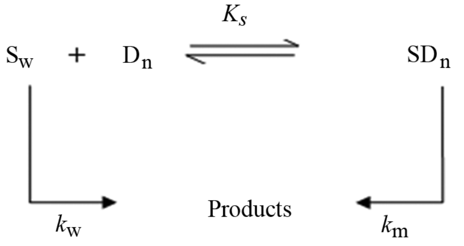
Fig. 4 — Isokinetic relationship for the oxidation of $[CV]^+$ by peroxydisulphate

Table 4 — Values of ΔH^* and ΔS^* for the oxidation of some organic dyes by persulphate

S. No.	Organic dye	ΔH^* (kJ mol^{-1})	ΔS^* (JK^{-1}mol^{-1})	Reference
1.	Malchite green $[MG]^+$	26.4	-235	25
2.	Rhodamine B [Rhd B]	34.0	-198	26
3.	Direct violet 31 $(DV\text{-}31]^-$	40.2	-149.6	11
4.	Food colourant (E131)	49.5	-127	27
5.	Rosaniline hydrochloride [RAH]	62.1	-98.4	22
6.	Crystal violet $[CV]^+$	89.2	8.97	This work

Table 5 — Effect of surfactant micelles on k_{obs} at $[CV^+] = 2.50 \text{ x } 10^{-5}$ mol dm^{-3}, $[S_2O_8^{2-}] = 1.0 \text{ x} 10^{-2}$ mol dm^{-3}, $[H^+] = 1.0 \text{ x } 10^{-3}$ mol dm^{-3}, $I = 0.20$ mol dm^{-3} and T = 35 °C

10^4[Micelles] (mol dm^{-3})	$10^4 k_{\text{obs}}$ (s^{-1})	
	[SDS]	[TX-100]
0.00	3.35 ± 0.02	3.35 ± 0.02
1.25	2.97 ± 0.04	3.41 ± 0.01
2.50	2.60 ± 0.03	3.42 ± 0.01
3.75	2.31 ± 0.01	3.29 ± 0.06
5.00	2.04 ± 0.04	3.37 ± 0.02
6.25	1.69 ± 0.02	3.33 ± 0.03
7.50	1.27 ± 0.05	3.48 ± 0.02
8.75	1.03 ± 0.04	3.27 ± 0.04
10.00	0.78 ± 0.02	3.39 ± 0.03



Scheme 2.

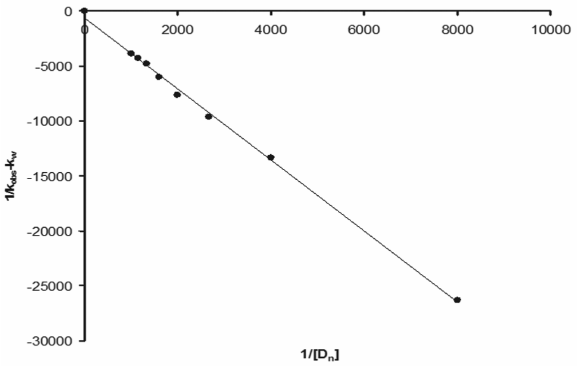


Fig. 5 — Pseudo-phase model at this condition: $[CV^+]$ = 2.50 x 10^{-5} mol dm^{-3}, $[S_2O_8^{2-}]$ = 0.01 mol dm^{-3}, I = 0.2 mol dm^{-3}, $[H^+]$ = 1.0 x 10^{-4} mol dm^{-3} and T = 35 °C.

surfactant on the rate of the chemical reaction. Menger and Portony proposed the model of pseudo-phase where the substrates are distributed between water and micellar phases[32]. Catalysis by micelles occurs when both substrates are attached to the surfactant micelle and hence the effective concentration increase. Furthermore, the suppression takes place when one of the reactant substrates is divided into the surfactant whereas the other residue in bulk solution. In this study, the SDS micelle attracts $[CV^+]$ while, $S_2O_8^{2-}$ stay in the bulk solution and hence the suppression effect is observed. The overall rate of reaction in the pseudo-phase model is to the algebraic sum of the rates in water and micelles, as represented in Scheme 2.

According to the pseudo-phase model, the observed rate constant (k_{obs}) has been derived by the following Eqn (20).

$$\frac{1}{k_{obs}-k_w}=\frac{1}{k_m-k_w}+\frac{1}{k_m-k_w}K_s[D_n]\ \ldots.(20)$$

where k_w is the rate constant in the absence of SDS, k_{obs} is the rate constant in the presence of SDS, K_s is the binding constant of the reactant with the surfactant, k_m is the micellar rate constant and D_n = [D]CMC, [D] is the [micelles]. The value of CMC for SDS was calculated experimentally and has a value of 7.84 x 10^{-3} mol dm^{-3} at 35 °C[33]. The plot of $(1/k_{obs} - k_w)$ against $1/[D_n]$ is linear with intercept as in approval with the pseudo-phase model as shown in Fig. 5. K_s and k_m values were determined from the slope and intercept of Fig. 5, as 193 mol^{-1} dm^3 and 1.27 x 10^{-4} s^{-1}, respectively. The k_m value (1.27x10^{-4} s$^{-1)}$ is less than k_w (3.35 x 10^{-4} s^{-1}), supported that the inhibition effect of SDS[34].

Conclusions

Oxidative decolourisation of $[CV]^+$ by peroxydisulphate in the acid medium was carried out in the absence and presence of Ag^+ catalyst. The reaction rate increases with the elevation of temperature but had no effect with the change of pH. Ag(I) enhanced the rate of decolourisation of $[CV]^+$ by peroxydisulphate. The mechanism of electron transfers for the reaction between crystal violet and peroxydisulphate passes through an outer-sphere mechanism. An anionic SDS inhibited the rate of reaction but Triton X-100 had no effect. The relation between ΔH* and ΔS* values for the oxidation of some organic dyes by peroxydisulphate is linear confirming the isokinetic relationship between enthalpy and entropy of activation for these reactions.

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