

Mechanistic Investigation of Micelle Effects on the Oxidation of Indigo Carmine by Quinolinium Dichromate in Perchloric Acid Media: A Kinetic Approach

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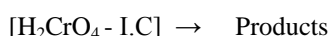
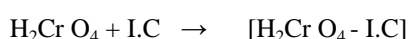
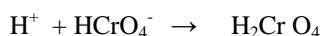
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Abstract: The kinetics of the oxidation of disodium 3,3'-dioxobi-indolin-2,2'-ylidene-5,5' disulphonate (I.C) by quinolinium dichromate(QDC) in aqueous acid medium has been studied at $30 \pm 1^\circ\text{C}$. The reaction is first order in [IC],[monomeric QDC] and [acid].A stoichiometric mole ratio of IC:QDC is 3:2.Variations in ionic strength did not affect the rate of reaction. The mechanism involved the attack of protonated monomeric QDC (QMC) on the substrate in the rate determining step. The effect of anionic micelle (SDS) and neutral micelle (TX-100) on the system was studied using Berezin's kinetic model and the binding constant for both the reactants with the micelle have been computed. The thermodynamic parameters like enthalpy, entropy, and Gibbs free energy are determined. A mechanism confirming to the kinetic observations is suggested.

Keywords: Indigo Carmine, QDC, protonated QMC, SDS,TX-100, binding constant.

1. INTRODUCTION

Disodium 3,3'-dioxobi-indolin-2,2'-ylidene-5,5' disulphonate (Indigo Carmine) here and there after referred to as I.C is an anionic dye [1]which is employed as a redox indicator in analytical chemistry and as a microscopic stain in biology [2].The chemistry of Indigo Carmine compound has been reviewed by Rodd [3].Several studies have been made on the oxidation kinetics of I.C using peroxy disulphate [4],hypohalites [5],acidiodate[6]. The oxidation of I.C by H_2O_2 [7]sulphide[8],Thiourea[9] has been investigated. The oxidants also include N-halo arene sulphanamides[10], H_2O_2 in the presence of sulphides[11] is studied. Recently Edokapayi etal investigated the oxidation of I.C. by aqueous Cr (VI)[12]. The reaction obeys first order kinetics each in dye, Cr (VI) and H^+ . These authors proposed a mechanism involving an intermediate complex formation between H_2CrO_4 and Indigo Carmine.



The present authors have taken up the kinetic studies of I.C by complexed chromium(VI) reagent, quinolinium dichromate(QDC) $(\text{C}_9\text{H}_7\text{N}^+\text{H})_2\text{Cr}_2\text{O}_7^{2-}$ in aqueous HClO_4 medium and the micelle effects of SDS and TX-100 on the kinetics .The results are discussed in detail with a view to provide an adequate knowledge on the kinetic parameters that characterize this reaction.

2. EXPERIMENTAL

2.1 Materials:

All chemicals were of high grade quality and were used as received without further purification. A 0.1 mol dm^{-3} solution of Indigo Carmine (BDH Analar) was prepared in double distilled deionized water. The solution was standardized by the method of GopalaRao and VenkateswaraRao[13]. Quinolinium dichromate (QDC) was prepared by the reported method [14] and standardized [15]. Its purity was checked by spectral analysis. The infrared spectrum (KBr) exhibited bands at 930, 875, 765 and 730 cm^{-1} , characteristic of the dichromate ion. A fluka sample of sodium dodecyl sulphate (SDS) has been used in the preparation of 0.1 mol dm^{-3} solution and its purity was tested by determining the CMC [16] conductometrically, and has been reported to be $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ [17, 18]. Triton X-100 (TX-100) (Fluka) was cleared of any low-boiling impurities by exposure to vacuum for 3h at 70°C following the procedure given by Kumar and Balasubrahmanium[19]. The CMC of TX - 100 has been reported as $2.4 \times 10^{-4} \text{ mol dm}^{-3}$ [20]. Sodium perchlorate (Fluka) and perchloric acid were used without purification and enabled variation of hydrogen ion concentration at a constant ionic strength (1.0M).

2.2 Kinetic methods:

The reaction was followed by measuring the absorbance of the unreacted I.C at 610 nm using Perkin Elmer Lambda 25 UV/ VIS spectrophotometer. The experiments were carried out in a temperature controlled ($\pm 0.1^{\circ}\text{C}$) water bath. The reaction was initiated by injecting, QDC ($2.0 \times 10^{-3} \text{ mol dm}^{-3}$) into Indigo Carmine ($1.0 \times 10^{-5} \text{ mol dm}^{-3}$) and perchloric acid (0.2 mol dm^{-3}) system. Absorbance was measured within 45 seconds by means of spectrophotometer. Log (absorbance) versus time plots is perfectly linear for at least 95% of the reaction. The reactant concentrations have been chosen such that Beer's law is strictly obeyed. The pseudo first order rate constants were determined in duplicate and found to agree with in $\pm 5\%$.

Determination of binding constant of quinolinium dichromate (QDC) with SDS and TX- 100 micelles:

The binding constant values of QDC with SDS micelles at $[\text{H}^+] = 2.0 \times 10^{-1} \text{ mol dm}^{-3}$ and $\mu = 0.5 \text{ mol dm}^{-3}$ under the conditions $[\text{SDS}] \gg [\text{QDC}]$ are determined at 330 nm, for various SDS concentrations. The binding constant of QDC has been found to be $41.0 \pm 0.5 \text{ dm}^3 \text{ mol}^{-1}$. Similar experiments are carried out at different TX-100 concentrations above CMC under the conditions $[\text{TX-100}] \gg [\text{QDC}]$ at 330nm where $[\text{QDC}] = 2.5 \times 10^{-5} \text{ mol dm}^{-3}$. The binding constant with respect to TX-100 has been found to be $(1.46 \pm 5) \times 10^2 \text{ dm}^3 \text{ mol}^{-1}$.

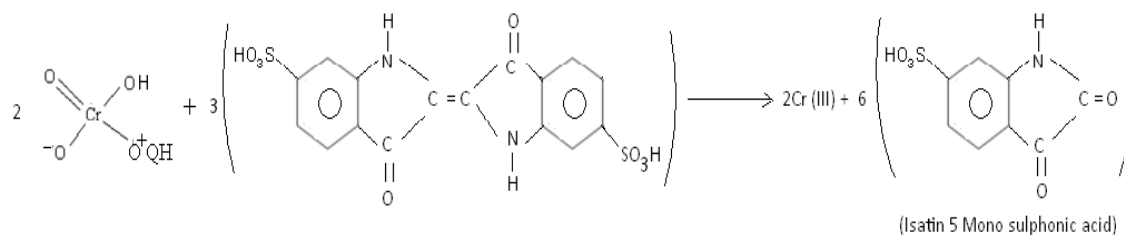
Determination of binding constant of Indigo Carmine with SDS and TX- 100 micelles:

For determining the binding constants of I.C with SDS micelles at $[\text{H}^+] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $\mu = 0.1 \text{ mol dm}^{-3}$ is adjusted with NaClO_4 . Spectra of these substances have been scanned at different SDS concentrations above CMC under the conditions $[\text{SDS}] \gg [\text{I.C}]$ at $\lambda = 610 \text{ nm}$, where $[\text{I.C}] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$. The results shown that the interaction of Indigo Carmine with SDS is negligibly small. The binding constant of I.C with TX-100 in perchloric acid medium has also been observed at similar conditions, was found to be negligibly small.

3. RESULTS

3.1 Stoichiometry:

To determine the stoichiometry of the reaction a known concentration of QDC [$1.0 \times 10^{-3} \text{ mol dm}^{-3}$] was mixed with different concentrations of Indigo Carmine at $[\text{H}^+] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$ in water. The reactions were kept overnight for the completion of the reaction and the absorbance was measured at 610 nm. The results confirm that 2 moles of QDC is reacting with 3 moles of Indigo Carmine. (Scheme 1)



Scheme 1.

3.2 Product analysis:

In the case of oxidation of Indigo Carmine by QDC, $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ I.C was mixed with an equivalent amount of QDC in the presence of perchloric acid ($2 \times 10^{-2} \text{ mol dm}^{-3}$). In the present study the end product was found to be isatin-5-mono sulphonic acid as confirmed by the spot test. [21] (2, 3 – dioxindoline – 5- sulphonic acid). A drop of alcoholic solution of 4 – nitro phenyl hydrazine was added to the product and it was heated in a micro test tube for about five minutes. After cooling, one drop of 10% NaOH and Ag (NO₃) were added. The formation of a blue coloured precipitate indicates the oxidation product is Isatin -5- mono sulphonic acid. The spectra of product obtained (Fig.1) was also confirmed with the authentic sample of Isatin -5- sulphonic acid. The presence of Cr⁺³ was confirmed by the addition of NaOH solution[22]. This gave a green colouration as a result of the formation of chromium(III) hydroxide which dissolves in excess NaOH to give a deep green coloured solution of the hydroxyl complex suggesting the presence of Cr⁺³ as one of the reaction products.

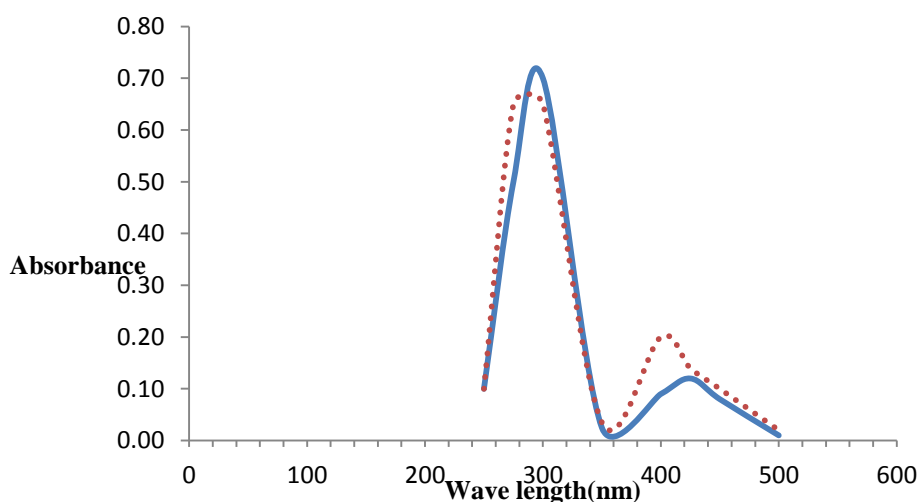


Fig.1 Spectra of the product of the reaction and an authentic sample of Isatin -5- sulphonic acid at $[I.C] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[QDC] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[H^+] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$, $\mu = 0.1 \text{ mol dm}^{-3}$ and $\text{Temp} = 30^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$

Where — = Spectrum of Isatin -5- sulphonic acid ($1.2 \times 10^{-5} \text{ mol dm}^{-3}$)

..... = Spectrum of product of the reaction

3.3 Effect of varying [Indigo Carmine]: The effect of variation of Indigo Carmine concentration on the reaction rate was investigated under the conditions $[QDC] \gg [I.C]$ and plots of $\log(\text{absorbance})$ vs time are good straight lines and at least 95% of reaction obeys the first order kinetics with respect to I.C. The pseudo – first order rate constants, k_1 were calculated from the slopes of the plots. The value of k_1 , determined at different [I.C] but at constant concentration of QDC, H⁺ are invariant to change in concentrations of I.C further confirming the first order with respect to Indigo Carmine (Table 1).

3.4 Effect of varying [QDC] on reaction rate: Pseudo – first order rate constants, k_1 were evaluated by keeping $[QDC] \gg [I.C]$ at different concentrations of QDC and constant concentrations of I.C, acid, and ionic strength. The k_1 values increased with increase in [QDC] (Table 1). The pseudo first order rate constant k_1 , has been calculated from the slopes of

plots of the log(absorbance) versus time. The plot of k_1 versus [QDC] is linear passing through origin at lower [QDC], but deviation from linearity was absent at higher concentrations of QDC. (Fig. 2)

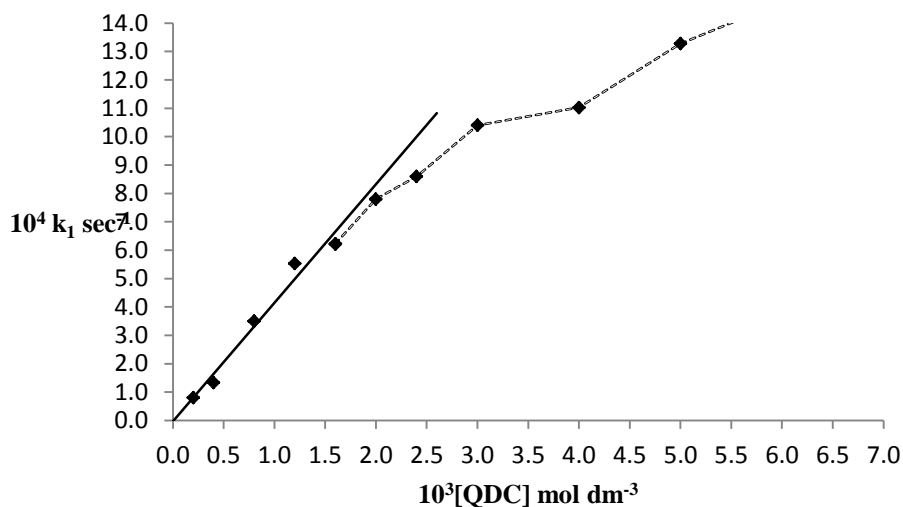


Fig 2. Plot of effect of varying [QDC] on reaction rate (conditions as in Table 1)

3.5 Effect of varying $[\text{H}^+]$ Kinetic runs were performed at constant [QDC] and [I.C] varying the concentration of perchloric acid. The results show that the rate of the reaction increases with an increase in acid concentration indicating that the reaction is accelerated by hydrogen ion. The plot of k_1 versus $[\text{H}^+]$ is a straight line passing through origin showing the first order kinetics with respect to H^+ ion. (Fig. 3) The ionic strength is always adjusted to 0.1 mol dm^{-3} using standard sodium perchlorate solution. The results are presented in the table (Table 2).

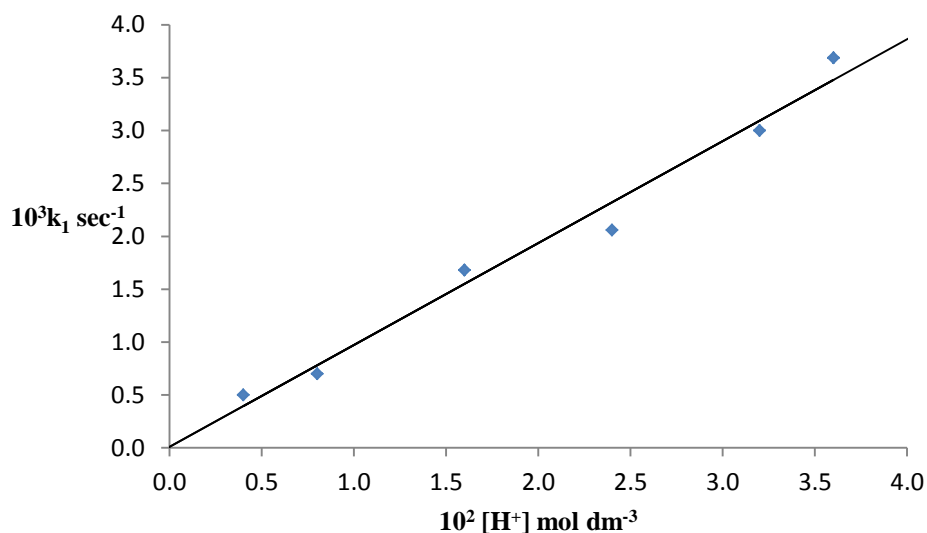


Fig 3. Plot of effect of varying $[\text{H}^+]$ on the reaction rate. (Conditions as in Table 1)

3.6 Activation parameters:

The pseudo- first order rate constants were calculated at different temperatures keeping all other parameters constant. The analysis of temperature effect was not attempted because k_1 being overall pseudo first order rate constant, involves the equilibrium constant, K. However, the apparent activation energy from these data (Table 1).has been obtained by using

the equation
$$\ln \frac{k_1(T_2)}{k_1(T_1)} = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \dots\dots\dots (4)$$

Table 1

$[I.C] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$; $[QDC] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[H^+] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$; $\mu = 0.1 \text{ mol dm}^{-3}$;

Temp (K)	$10^3 k_1 \text{ sec}^{-1}$
303	0.72
313	1.39
323	2.06

$E_a = 57.44 \text{ KJ/mol}$; $\Delta H = 54.992 \text{ KJ/mol}$; $\Delta S = -122.15 \text{ J/mol/K}$;

Table 2 : Effect of variation of [QDC], [I.C], $[H^+]$ on the oxidation kinetics of Indigo Carmine by quinolinium dichromate at 298K and $I = 0.1 \text{ mol dm}^{-3}$.

$10^3 [QDC]$ mol dm^{-3}	$10^5 [I.C]$ mol dm^{-3}	$10^3 [H^+]$ mol dm^{-3}	$10^4 k_1$ sec^{-1}
0.2	2.0	8.0	0.40
0.4	2.0	8.0	1.33
0.8	2.0	8.0	3.50
1.2	2.0	8.0	5.53
2.0	2.0	8.0	7.80
2.4	2.0	8.0	8.60
3.0	2.0	8.0	10.40
4.0	2.0	8.0	11.03
5.0	2.0	8.0	13.28
6.0	2.0	8.0	14.74
2.0	0.8	8.0	6.61
2.0	1.6	8.0	6.52
2.0	2.0	8.0	6.20
2.0	2.4	8.0	6.84
2.0	3.2	8.0	6.95
2.0	2.0	4.0	2.80
2.0	2.0	8.0	6.60
2.0	2.0	16.0	13.80
2.0	2.0	24.0	20.50
2.0	2.0	32.0	27.40
2.0	2.0	36.0	36.80

3.7 Effect of varying [sodium dodecyl sulphate] SDS:

To study the micelle effect of sodium dodecyl sulphate (SDS) on the rate, the kinetic runs were carried out in the presence of varying concentration of SDS, keeping the concentration of I.C, QDC and H^+ , μ constant. From the pseudo first order slopes the specific rate constants k_1 are determined. The results (Table 3.) show that there is a small acceleration by SDS.

Table 3

[I.C] = $2.0 \times 10^{-5} \text{ mol dm}^{-3}$; $[\text{H}^+] = 4.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{QDC}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$; $\mu = 0.1 \text{ mol dm}^{-3}$; Temp = $30^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$

$10^3 [\text{SDS}] \text{ mol dm}^{-3}$	$10^3 k_1 \text{ sec}^{-1}$
0.0	2.89
0.4	3.25
1.6	3.27
3.2	3.22
8.0	3.04
16.0	2.94
32.0	2.74
48.0	2.56

3.8 Effect of varying Triton x – 100

To study the effect of TX-100 on the reaction mixture {I.C + QDC+ACID} the concentration of TX – 100 is varied at the fixed concentration of reaction mixture keeping the ionic strength and other reactants as constant. The pseudo first order rate constants are obtained from log absorbance vs. time plots at 610nm.(Table 4) The results show that the rate of reaction increases with [TX-100].

Table 4

[I.C] = $2.0 \times 10^{-5} \text{ mol dm}^{-3}$; $[\text{H}^+] = 4.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{QDC}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$; $\mu = 0.032 \text{ mol dm}^{-3}$; Temp = $30^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$

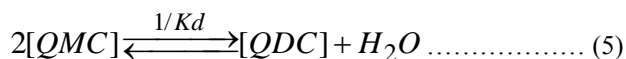
$10^3 [\text{TX-100}] \text{ mol dm}^{-3}$	$10^3 k_1 \text{ sec}^{-1}$
0.0	2.89
6.80	4.37
9.52	4.86
12.20	4.88
17.00	4.92
23.80	5.06

3.9 Test for free radicals: The reaction was conducted in the presence of acrylonitrile in an evacuated Thunberg tube, no perceptible change in the reaction rate was observed and no precipitation of polymer was noticed, indicating the absence of free radical intermediates in the reaction.

4. DISCUSSION

4.1 Kinetic approach:

The kinetics of oxidation of I.C by QDC obeys first order kinetics with respect to substrate (I.C) and H^+ . The plot of k_1 versus [QDC] is linear initially passing through origin, but negative deviation from linearity was observed at higher [QDC]. The order with respect to QDC is calculated, as it is unity initially but becomes fractional at higher QDC concentrations due to rate being less than what it should be directly proportion to QDC. The author calculated concentration of monomeric form of QDC (QMC) assuming a value [23] of $35.5 \text{ mol}^{-1} \text{ dm}^3$ (K_d) for the dimerisation constant for the equilibrium, which is a reported value for aqueous chromic acid system.



The concentration of QMC is calculated using mass balance.

$$\begin{aligned}
 [QDC]_t &= [QDC] + \frac{[QMC]}{2} \\
 &= \frac{2[QDC] + [QMC]}{2} \\
 &= \frac{2K_d[QMC]^2 + [QMC]}{4K_d}
 \end{aligned}$$

Or $2K_d [QMC]^2 + [QMC] - 4K_d[QDC]_t = 0$ and $[QMC] = \frac{-1 + \sqrt{1 + 8K_d[QDC]_t}}{4K_d}$

The corresponding values of QMC and rate constants are presented in Table 5. Plot of k_1 versus $[QMC]$ is linear passing through origin (Fig 4) without deviation even at higher QDC concentration. This establishes that the monomeric form of QDC in protonated form $QH^+H_2CrO_4$ is the active oxidizing species. Quinoline added to the reaction mixture of the QDC and the substrate has no effect on the rates of the reaction and this rules out the presence of the preequilibrium before the rate determining step in the mechanism, and the oxidant reacts only in the form of QMC, $QH^+HCrO_4^-$ after protonation. Pseudo first order rate constants for the I.C-QDC reaction at $[I.C]=2.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[H^+]=8.0 \times 10^{-3} \text{ mol dm}^{-3}$ for various $[QMC]$ are presented in Table 5.

Table 5

$[I.C] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$; $[H^+] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$; $\mu = 0.1 \text{ mol dm}^{-3}$; Temp = $30^0 \pm 0.1^0 \text{C}$

$10^4 [QMC] \text{ mol dm}^{-3}$	$10^4 k_1 \text{ sec}^{-1}$
1.97	0.40
3.89	1.33
7.59	3.50
11.12	6.03
17.76	7.80
20.89	8.60
25.41	10.40

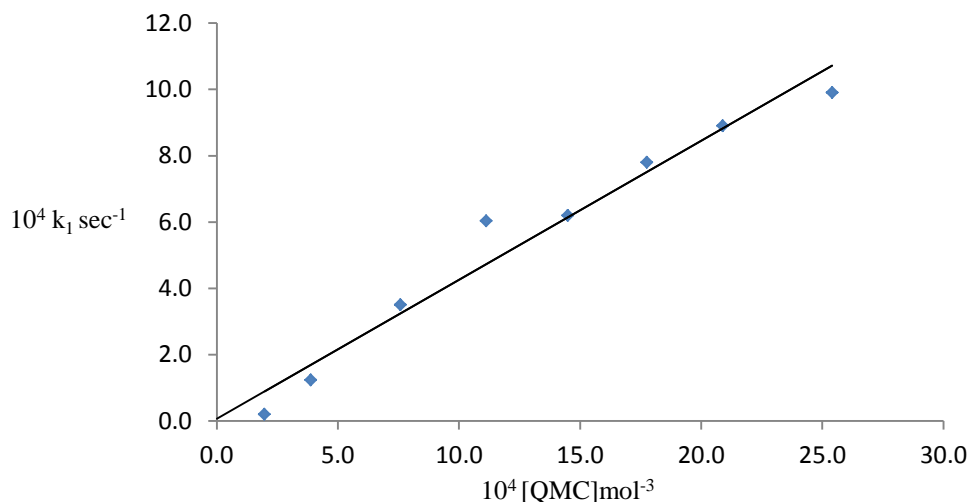
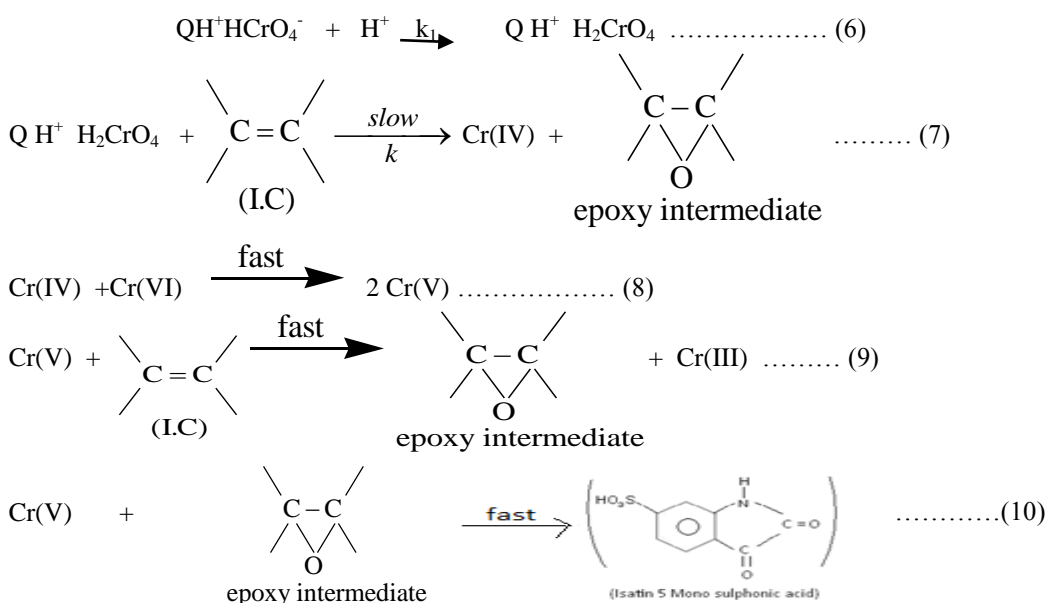


Fig. 4: Effect of varying QMC on the reaction rate. (Conditions as in Table 5)

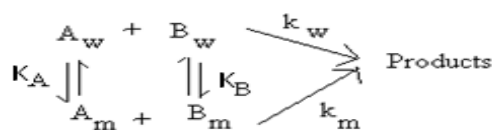
The author assumes that the site of oxidation is C=C double bond in I.C which first gives epoxy type of compound. This epoxy type of intermediate is oxidized to Isatin 5- mono sulphonic acid in the fast step and reacting with QH⁺H₂CrO₄ or Cr (V). This is fast step and not rate determining is shown by very good first order plots. If the oxidation of epoxy intermediateto Isatin 5- mono sulphonic acid is slow this would have led to consecutive mechanism and plot of log (absorbance) versus time should have not been a simple straight line but should have two parts.The reaction mixture did not initiate any vinyl polymerization and the author proposes the following mechanism which does not involve any free radical formation.



This mechanism leads to the Rate law $-d[\text{I.C}]/dt = kK_1[\text{I.C}][\text{QH}^+ \text{HCrO}_4^-][\text{H}^+] \dots\dots\dots (11)$

4.2 Micellar effect:

SDS and TX- 100 have modest accelerating effect on the oxidation of I.C. by QDC. There is an increase in rate constants with the increase in SDS and TX -100 concentration and the bimolecular reaction between QDC and I.C. between micelle aqueous pseudo phases can be reported by the Scheme 2.



Scheme 2: Bimolecular reaction between QDC and I.C. between micelle , aqueous pseudo phases

For the kinetic analysis of the micellar effects, Berezin’s model[24] involving the partition coefficient of the species between the micellar and aqueous pseudo phases has been applied.According to this the second order rate constant k_2 is related to the micelle concentration expressed as {[TX-100] or [SDS]– CMC} by the equation

$$k_2 = \frac{k_w + k_m K_A P_B C}{(1 + K_A C)(1 + K_B C)} \dots\dots\dots (12)$$

Where K_A = Binding constant of QDC with SDS orTX-100 micelles, K_B =Binding constant of I.C and P_B = Partition coefficient of I.C. SDS has very small accelerating effect on the oxidation of I.C. by QDC. The pseudo first order rate constant in aqueous medium is $2.89 \times 10^{-4} \text{ sec}^{-1}$ slightly increases to a value of $3.27 \times 10^{-4} \text{ sec}^{-1}$ in the presence of [SDS] = $1.6 \times 10^{-3} \text{ mol dm}^{-3}$ and then decreases slowly with further increase in SDS. According to Berezin this corresponds to the case where only one reactant is strongly bound to micelle where as the other is weakly bound it. Under these conditions the rate law according to Berezin is

$$k_2 = \frac{k_w + k_m K_A P_B C}{(1 + K_A C)} \dots\dots\dots (12)$$

Where, K_A = Binding constant of QDC ($41.0 \text{ dm}^3 \text{ mol}^{-1}$), K_B =Binding constant of Indigo Carmine(negligibly small) and P_B =Partition coefficient of I.C. In accordance with this equation plot of, $k_2 (1+K_A C)$ Vs C is linear with an intercept (Fig 6.) From the intercept the k_2 value corresponds to $1.66 \text{ sec}^{-1} \text{ mol}^{-1} \text{ dm}^3$ which is in reasonable agreement with the value of reaction in the absence of micelles ($1.44 \text{ sec}^{-1} \text{ mol}^{-1} \text{ dm}^3$).

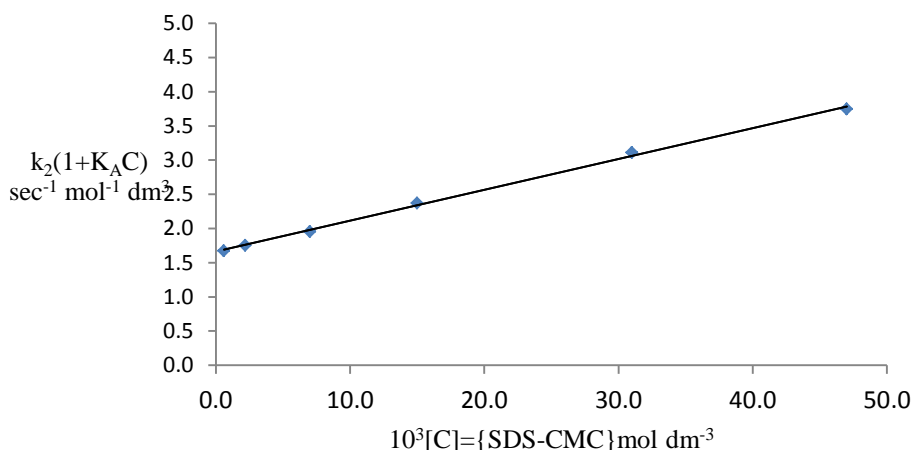


Fig 6. Plot of $k_2(1+K_A C)$ Vs. $\{[SDS]- CMC\}$ (conditions as in Table 3)

The rate of reaction increases with increase in [TX-100]. The value of K_B (binding constant of I.C with TX-100) has been found to be very small as evidenced by very small changes in absorbance of I.C. Hence $(1 + K_B C) \approx 1$ and Berezin equation changes to

$$k_2 = \frac{k_w + k_m K_A P_B C}{(1 + K_A C)} \dots\dots\dots (13)$$

From the value of binding constant of QDC determined from the absorption spectral studies, $k_2(1+K_A C)$ has been calculated and plotted against 'C' and a straight line with a positive intercept has been obtained(Fig .7). From the intercept the k_2 value corresponds to $1.84 \text{ sec}^{-1} \text{ mol}^{-1} \text{ dm}^3$ which is in reasonable agreement with the value in the absence of micelles ($1.44 \text{ sec}^{-1} \text{ mol}^{-1} \text{ dm}^3$).

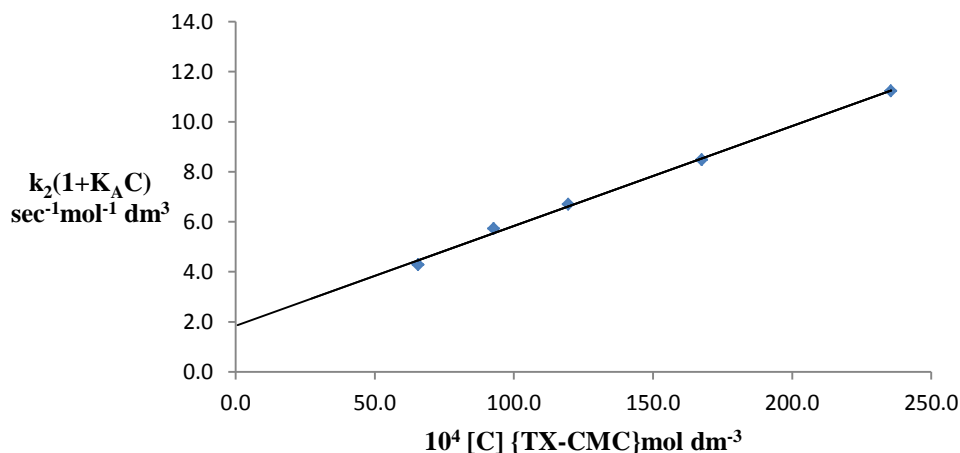


Fig 7. Plot of $k_2(1+K_A C)$ vs $\{[TX-100]- CMC\}$ (conditions as in Table 4)

5. CONCLUSION

QDC in the monomeric form (QMC) on protonation $\{Q H^+ H_2CrO_4\}$ was the reactive oxidising species during the oxidation of Indigo Carmine, giving the cyclic chromate ester which underwent decomposition, in the rate-determining step to yield Isatin-5 mono sulphonic acid as product, where the order with respect to QMC, IC and acid were found to be unity. The effect of micelle on the oxidation reaction can be explained basing on the binding constant of each of the reactant with respect to SDS and triton X-100 at the described wave length in acid media.

REFERENCES

- [1] Yujian, L., Jizhen, L., Xueli, Z., Jie, T., Wei, B., Jainhong, L.: *J. Col. Inter. Sci.*, 292, 210-218 (2005)
- [2] Gurr, E.: *Encyclopedia of Microscopic Stains*, Leonard Hill (Books) LTD., London (1960) pp 235.
- [3] Rodd E.H.: *Chemistry of carbon compounds*, Elsevier, Amsterdam, Vol IV B, 1093 (1960).
- [4] Muthakia G.K. Jonnalagadda S.B.: *Int. J. Chem. Kinet*, 21, 519-533 (1989).
- [5] Rao P.V.S, Murthy P.S.N, Murthy R.V.S, Murthy B.A.N.: *J. Indian Chem. Soc.*, LV 1280 (1978)
- [6] Jonnalagadda S.B, Simoyi R.H., Muthakia A.K.: *J. Chem. Soc. Perkin. Trans II*, 1111-1115 (1988)
- [7] Gemeay, A.H., Ikhlas A., Mansons R.G., El-Sharkawy, Zaki A.B.: *J. Mol. Catal*, 193, 109 - 120 (2003)
- [8] Omura, T., Kayane, Y., Tezuka, Y.: *Dyes and Pigments*, 20, 227-246 (1992)
- [9] Ohura, R., Katayama, A., Takagishi, T.: *Textile Res. J.* 61, 242-246 (1991)
- [10] Puttaswamy, Mahadevappa D.S., Rangappa K.S.: *Bull. Chem. Soc. Jpn.*, 62, 3343-3348 (1989)
- [11] Weisz, H., Pantel S., Marquardt J.: *Anal. Chim. Acta* 143, 177-184 (1982)
- [12] Edokpayi J.N., Iyun J.F and Idris S.O.: *Arch. Appl. Sci. Res.*, 2(5), 126-134 (2010).
- [13] Gopala Rao G and Venkateswara Rao N.: *Talanta*, 8, 539 (1961)
- [14] Balasubramanian K and Prathiba V.: *Indian. J. Chem.*, 25B, 326 (1986)
- [15] Gopalarao G and Viswanatham C.R.: *Curr. Sci* 11, 102-103 (1942)
- [16] Bunton C. A and Savelli G.: *Adv. Phys. Org. Chem* 22, 1015 (1986)
- [17] Bunton C. A and Wolfe B.: *J. Am. Chem. Soc* 95(11), 3742-3749 (1973)
- [18] Pramauro E, Pelizzetti E, Diekmann Sand Frahm.: *J Inorg. Chem* 21, 243 (1982)
- [19] Kumar C and Balasubramanian D. K.: *J. Colloid. Interface. Sci.*, 69 271-279 (1979)
- [20] Lin H Y and Thomas J L *Langmuir* 19, 1098-1105 (2003)
- [21] Feigl F "spot tests in organic Analysis" Elsevier Scientific Publishing Company, London, (1966) p540
- [22] Vogel A.I. *Quantitative Inorganic Analysis*, ELBS and Longman, London, 1978, 4th Edn., 427.
- [23] Michel G and Machiroux R.: *J. Raman Spectrosc* 14(1), 22-27 (1983).
- [24] Berezin I.V, Martinek K and Yatsimirskii A.K.; *Russ. Chem. Rev.*, 42(10), 787-802 (1973).