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# The kinetics of the oxidation of disodium 3, 3'-dioxobi-indolin-2, 2'ylidene-5, 5' disulphonate by heptaoxodichromate(VI) ion in aqueous acidic medium

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## ABSTRACT

The kinetics of the oxidation of disodium 3, 3'-dioxobi-indolin-2, 2'-ylidene-5, 5' disulphonate (IC) by heptaoxodichromate(VI) ion in aqueous acid medium has been studied at  $25\pm1^{0}$ C,  $I = 0.5 \text{ mol } dm^{-3}$ (NaCl). The reaction is first order in [IC] and [ $Cr_2O_7^{2-}$ ] and a stoichiometric mole ratio of IC:  $Cr_2O_7^{2-}$  is 1:1. Variations in ionic strength and added cations did not affect the reaction rate of the reaction. The experiment rate law obtained is:

 $-d[IC]/dt = k[Cr_2O_7^{2-}][IC][H^+].$ 

A plausible mechanism has been proposed on the basis of our experimental results.

## INTRODUCTION

Disodium 3, 3'-dioxobi-indolin-2, 2'-ylidene-5, 5' disulphonate (indigo carmine) here and thereafter referred to as IC 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 IC using peroxydisulphate, hypohalites, acidic iodate [4-6].

The oxidation of IC by  $H_2O_2$ , sulphide, thiourea has been investigated [7-9]. Heptaoxodichromate (VI) ion, an excellent oxidizing agent has been observed to oxidize alcohols, L-cystein, ascorbic acid and thiols [10-11]. Despite its rich chemistry, the redox reaction of this oxidant with IC has not received much attention. In this paper we report our findings on the oxidation of IC by  $Cr_2O_7^{2-}$  in aqueous acidic medium with a view to providing adequate knowledge on the kinetic parameters that characterize this reaction.

#### **MATERIALS AND METHODS**

All chemicals were of high grade quality and were used as received without further purification. A  $1.0 \times 10^{-3} \text{ mol dm}^{-3}$  stock solution of indigo carmine (Analar grade), was prepared by dissolving 4.66g in 100cm<sup>3</sup> volumetric flask using distilled water. 0.10 mol dm<sup>-3</sup> stock solution of potassium dichromate was prepared by accurately weighing 2.42 g of the K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (B.D.H analar) and dissolving in a 100 cm<sup>3</sup> volumetric flask and making up to the mark with distilled water. 1.0 mol dm<sup>-3</sup> solution of hydrochloric acid (BDH) was also prepared (36%, specific gravity 1.18) and standardized titrimetrically [12].

The reaction stoichiometry was determined spectrophotometrically using the mole ratio method [13]. This was accomplished by measuring the absorbance of solutions containing varying concentrations of heptaoxodichromate(VI) ion in the range  $(0.28 - 2.8) \times 10^{-5} \mod \text{dm}^{-3}$ ,  $[\text{H}^+] = 5 \times 10^{-2} \mod \text{dm}^{-3}$  and I = 0.5 mol dm<sup>-3</sup> at 610nm, after the reaction had gone to completion by the observation of a steady zero absorbance value over a period of two days. A point of inflexion on the curve of the absorbance versus mole ratio corresponds to the stoichiometry of the reaction.

The absorption spectra of solutions, containing oxidant alone and the solution of the reaction mixture, under similar conditions, was compared between 400nm and 700nm, to test for the possibility of an intermediate complex formation. There was no observable difference in both spectra with respect to the  $\lambda_{max}$ .

The influence of  $[H^+]$  on the rate was investigated using hydrochloric acid in the range  $(3-20) \times 10^{-2}$  mol dm<sup>-3</sup>, while the [IC] and  $[Cr_2O_7^{2^-}]$  were kept constant. The reaction was carried out at  $25\pm1^0$ C and I = 0.5 mol dm<sup>-3</sup> (NaCl). The results are presented in Table1.

The kinetic runs were performed under pseudo first order conditions with a large excess of the oxidant over IC at  $25\pm1^{\circ}$ C for each run, a required amount of NaCl was added to maintain a total ionic strength of 0.5mol dm<sup>-3.</sup> The reaction was monitored spectrophotometrically by measuring the absorbance at 610nm using Corning Colorimeter 252. The pseudo-first order plots of log (A<sub>t</sub>-A<sub>∞</sub>) versus time, which were linear to about 95% at various reactant concentrations were made (where A<sub>∞</sub> and A<sub>t</sub> are the absorbance at the end of the reaction at time, t respectively). A typical pseudo- first order plot is presented in Fig. 1.

#### RESULTS

One mole of the oxidant was consumed by one mole of IC suggesting the overall stoichiometry shown in equation (1).



The Pseudo-first order plots of log  $(A_t-A_{\infty})$  versus time for these reactions were linear for about 95% of the reactions. The linearity of these plots indicates that this reaction is first order with respect to [IC]. A plot of log k<sub>1</sub> versus log  $[Cr_2O_7^{2-}]$  was linear with a slope of 0.99 showing that the reaction is also first order with respect to  $[Cr_2O_7^{2-}]$ . The rate equation for the reaction is

 $-d[IC] / dt = k_2[IC][Cr_2O_7^{2-}]....(2)$ 

Changes in ionic strength in the range (0.1-1.0) mol dm<sup>-3</sup> of the reaction medium had no effect on the rate of the reaction.

The effect of added cations  $Ca^{2+}$  and  $Mg^{2+}$ , on the rate of the reaction was studied and the results are presented in Table 2.

Acrylamide solution was added to initiate polymerization if free radicals were present. The lack of polymerization even after adding excess methanol indicates the absence of free radicals in the reaction mixture.

The spectroscopic studies indicated no significant shift from the absorption maxima of 610nm characteristic of IC.

The second order rate constant of the reaction increases with increase in  $[H^+]$ . The plot of  $\log k_{H^+}$  versus log  $[H^+]$  was linear with a unit slope.

Therefore  $-d[IC]/dt = k [Cr_2O_7^{2-}][IC][H^+]....(3)$ 

## DISCUSSION

One mole of the oxidant was consumed by one mole of IC. Similar stoichiometry has been reported for the reaction of sodium hypochlorite and indigo carmine [14].Similar stoichiometry has been reported for the oxidation of ethanolamine by quinolinium dichromate [15]. Water (1968) also reported in his review that the stoichiometry of the oxidation of benzaldehyde by chromic acid was 1;1 [16]

The presence of  $Cr^{3+}$  was confirmed by the addition of NaOH solution [17]. This gave a steel green colouration as a result of the formation of chromium (III) hydroxide which dissolves in excess NaOH to give a deep green colored solution of the hydroxyl complex suggesting the presence of  $Cr^{3+}$  as one of the reaction products. Several researchers have reported that the main organic product obtained from the oxidation of indigo carmine carmine is Isatin-5-monosulphonic acid [3-7, 14,].

The Pseudo-first order plots of log  $(A_t - A_{\infty})$  versus time for this reaction was linear for about 95% of the reactions; the linearity of these plots indicates that these reactions are first order with respect to [IC]. A plot of log  $k_1$  versus log  $[Cr_2O_7^{2-}]$  was linear with a slope of 0.99 showing that the reaction is also first order with respect to  $[Cr_2O_7^{2-}]$ . This is also supported by the constancy of  $k_2$  values. Therefore the reaction is second order overall at constant  $[H^+]$ . The order of one in both reactants in the reaction conforms to some already reported redox reaction of indigo carmine by sodium hypohalite, acidic bromate and peroxydisulphate [5-6, 13].

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Changes in ionic strength in the range (0.1-1.0) mol dm<sup>-3</sup> of the reaction medium had no effect on the rate of the reaction. The observed zero Brownsted-Debye salt effect suggests that charged and neutral specie is reacting at the rate determining step. The result is presented on Table1. This is a common feature of most reactions of indigo carmine [4, 6, 14,].

There was no effect of added cations on the rate of the reaction. This further supports the result obtained from the effect of changes in ionic strength as one of the reactants in the rate determining step is a neutral specie [18-19]

The acrylamide did not polymerize either the reactant alone or the reaction mixture. This suggests that the free radicals are not involved in this reaction and suggests an outer-sphere mechanism.

The result from the spectroscopic studies indicated no significant shift from the absorption maxima of 610nm characteristic of IC. This suggests the formation of an intermediate complex during the reactions is very unlikely. Plots of  $1/k_1$  versus  $1/[Cr_2O_7^{2-}]$  gave a straight line which passed through the origin (Fig 4). This further suggests the absence of the formation of intermediate complex thereby supporting the outer-sphere mechanism.

The plot of  $k_H$  versus [H<sup>+</sup>] (Fig.3) gave a straight line that passes through the origin. A graph of this nature indicates that an equilibrium exist between the protonated forms of the reactant prior to the rate determining step.

Plots of  $k_1^{-1}$  versus [Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>] gave no intercept, suggesting no detectable binuclear intermediate. That a binuclear-bridged intermediate was not detected indicates that the reaction does not occur by the inner-sphere mechanism. Therefore, the outer-sphere mechanism is proposed for the reaction.

## **Reaction Mechanism**

Various equilibria have been established for  $Cr_2O_7^{2-}$  in aqueous solution [20-21]



The only reactive species of heptaoxodichromate(VI) ion available in large concentration in dilute mineral acid solutions are  $HCrO_4^-$  and  $Cr_2O_7^{2-}$  which are in equilibrium with each other. However  $HCrO_4^-$  has been reported to be the predominant active oxidizing species of these two ions [22]

$$H^{+} + HCrO_{4}^{-} \qquad \stackrel{\kappa_{4}}{\longrightarrow} \qquad H_{2}CrO_{4}....(7)$$

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$H_{2}CrO_{4} + IC \xrightarrow{K_{5}} [H_{2}CrO_{4}, IC](8)$ $[H_{2}CrO_{4}, IC] \xrightarrow{K_{6}} Products(9)$
Based on the rate determining step,
$Rate = k_6 [H_2 CrO_4, IC].$ (10)
from equation 8 $K_5 = \frac{[H_2 CrO_4, I \cup ]}{[H_2 CrO_4][IC]}$ (11)
$[H_2CrO_4, IC] = K_5[H_2CrO_4][IC](12)$
Substitute equation 12 into 10 $Rate = k_6 K_5 [H_2 CrO_4] [IC](13)$
From equation 7 $K_{4} = \frac{[H_{2}CrO_{4}]}{[H_{2}CrO_{4}^{-}][H^{+}]}(14)$
$[H_2 CrO_4] = K_4 [H^+] [HCrO_4^-].$ (15)
Substitute equation 15 into 13 $Rate = k_6 K_5 K_4 [H_2 CrO_4] [IC] [H^+](16)$
$Rate = K'[H_2CrO_4][IC][H^+](17)$
where $K' = k_6 K_5 K_6$

$10^{3}[Cr_{2}O_{7}^{2}],$	$10^2 [\mathrm{H}^+],$	$10^{1}$ I,	$10^3 k_{1.}$	k <sub>2.</sub>
mol dm <sup>-3</sup>	$mol dm^{-3}$	mol dm <sup>-3</sup>	s <sup>-1</sup>	$dm^3 mol^{-1} s^{-1}$
1.68	5.0	5.0	1.77	1.05
1.96	5.0	5.0	2.00	1.03
2.24	5.0	5.0	2.15	0.96
2.52	5.0	5.0	2.30	0.91
2.80	5.0	5.0	2.73	0.98
3.08	5.0	5.0	2.84	0.92
3.36	5.0	5.0	3.15	0.94
4.20	5.0	5.0	3.90	0.93
2.80	3.0	5.0	2.20	0.79
2.80	5.0	5.0	2.76	0.99
2.80	7.0	5.0	3.65	1.30
2.80	10.0	5.0	4.61	1.65
2.80	15.0	5.0	5.37	1.92
2.80	18.0	5.0	6.53	2.33
2.80	20.0	5.0	7.68	2.74
2.80	5.0	1.0	2.76	0.99
2.80	5.0	2.0	2.97	1.06
2.80	5.0	3.0	2.88	1.03
2.80	5.0	4.0	2.68	0.96
2.80	5.0	5.0	2.76	0.99
2.80	5.0	6.0	2.76	0.99
2.80	5.0	7.0	2.88	1.03
2.80	5.0	10.0	2.97	1.06

Table 1: Pseudo first order and second order rate constants for the IC-Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> reaction at  $[IC] = 2.8 \times 10^{-5} \text{ mol dm}^{-3}, T = 25 \pm 1^{0}C$ 

Table 2: Rate data for the effect of added cation (Ca<sup>2+</sup> and Mg<sup>2+</sup>) on the rate of reaction of indigo carmine with Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> at [IC] = 2.8 x 10<sup>-5</sup> mol dm<sup>-3</sup>, [Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>] = 2.80 x 10<sup>-3</sup> mol dm<sup>-3</sup>, [H<sup>+</sup>] = 5.0 x 10<sup>-2</sup> mol dm<sup>-3</sup>,  $\mu$  = 0.50 mol dm<sup>-3</sup>,  $\lambda$  = 610nm and T = 25 ± 1°C

Ion	$10^{3}$ [ion], mol dm <sup>-3</sup>	$10^3 k_{1,} s^{-1}$	$k_2$ , $dm^3 mol^{-1}s^{-1}$
$\overline{\mathrm{Ca}^{2+}}$	1.0	2.83	1.01
	5.0	2.83	1.01
	10.0	3.18	1.14
	30.0	2.95	1.05
	40.0	2.75	0.99
	40.0	3.00	1.07
	150.0	3.08	1.07

$Mg^{2+}$	1.0	3.08	1.07
-	5.0	2.79	1.15
	10.0	2.86	1.02
	20.0	3.02	1.08
	50.0	2.72	0.97
	85.0	3.18	1.14
	100.0	3.02	1.08



Figure 1: Typical pseudo-first order plot for the redox reaction of Indigo Carmine with  $Cr_2O_7^{2-}$  at  $[IC] = 2.8 \times 10^{-5}$  mol dm<sup>-3</sup>,  $[Cr_2O_7^{2-}] = 2.25 \times 10^{-3}$  mol dm<sup>-3</sup>,  $[H^+] = 5.0 \times 10^{-2}$  mol dm<sup>-3</sup>, I = 0.50 mol dm<sup>-3</sup>,  $\lambda = 610$ nm and  $T=25 \pm 1^0$ C



Figure 2: Plot log  $k_1$  versus log  $[Cr_2O_7^{2-}]$ 



Figure 4: Michaelis-Menten's plot of 1/k<sub>1</sub>, s versus 1/[Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>] dm<sup>3</sup> mol<sup>-1</sup>

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