Preliminary Study on the Kinetics and Mechanism of the Oxidation of Naphthol Green B by Dichromate Ion in Aqueous Hydrochloric Acid Medium

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Abstract - The kinetics of the oxidation of naphthol green B (NGB^{3-}) by $Cr_2O_7^{2-}$ has been studied in aqueous hydrochloric acid medium at an ionic strength, $I = 0.50$ mol dm^{-3} (NaCl), $[H^+] = 1.0 \times 10^{-4}$ mol dm^{-3} (HCl) and $T = 25 \pm 1°C$. The redox reaction displayed a stoichiometry of 1:1 and obeys the rate law: $-d[NGB^{3-}]/dt = k_2[NGB^{3-}][Cr_2O_7^{2-}]$. The second order rate constant increases with increase in acid concentration and in the ionic strength of reaction medium. The rates of reaction displayed a positive salt effect. Addition of acrylonitrile to a partially reacted mixture in the presence of excess methanol did not lead to gel formation. Added cations and anions inhibited the naphthol green B - $Cr_2O_7^{2-}$ reaction. Results of the Michaelis – Menten plot gave no evidence of intermediate complex formation during the course of the reaction. Based on the results obtained, the reaction is believed to proceed through the outersphere mechanistic pathway.
Keywords: Intermediate; Redox; Pseudo-octahedral; Michaelis – Menton; Outersphere

Introduction

Naphthol Green B (or naphthol Green, Acid Green 1) an important commercial dye is a pseudo-octahedral Fe^{3+} complex, which contains 1-nitroso- 2-naphthol-6-sulphonate (NNSH) in the deprotonated state (NNS^-) as a bidentate ligand (Zollinger, 1991). As an iron(III) compound it might undergo a photoredox reaction in analogy to numerous other Fe^{3+} complexes (Balzani and Carassiti, 1970; Horvath, and Stevensen, 1992). Kinetics of the oxidation of disodium 3,3'-dioxobi-indolin-2,2'-ylidine-5,5'disulphate (indigo carmine) by dichromate ion in aqueous acidic medium has been reported (Edokpayi *et al.,* 2010). The reaction was found to be first order in both the reactants. Some studies have been shown that NGB^{3-} is used for staining wool, nylon, paper, and soap (Horobin and Kiernan, 2002). Despite the uses of this dye and several other applications, there is need for detail investigation of the kinetics of its electron transfer reaction.

Dichromate ion, an excellent oxidizing agent has been observed to oxidize alcohols, L-cystein, ascorbic acid and thiol (Idris *et al.*, 2001). Despite its rich chemistry, the redox reaction of this oxidant with naphthol green B has not received attention. In this present work we report our preliminary finding on the oxidation of NGB^{3-} by $Cr_2O_7^{2-}$ in aqueous hydrochloric acid medium with a view to providing adequate knowledge on the kinetic parameters that characterize this reaction.

Materials and Methods

A total of 0.001 mol dm^{-3} stock solution of naphthol green B (Analar grade) was prepared by dissolving 0.02196 g in 25 cm^3 flask using distilled water. Potassium dichromate solution was

prepared by dissolving known quantities in distilled water. 1.0 mol dm^{-3} solution of hydrochloric acid (BDH) was prepared (36%, specific gravity 1.18) and standardized titrimetrically (Idris *et al.*, 2005). The reaction stoichiometry was determined spectrophotometrically using the mole ratio method (Mohammed *et al.*, 2009). This was accomplished by measuring the absorbance of solutions containing varying concentrations of dichromate ion in the range (0.20 - 1.80) × 10^{-4} mol dm^{-3}, [H$^+$]=1.0 × 10^{-4} mol dm^{-3} and I= 0.50 mol dm^{-3} at 700 nm, 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 inflection on the curve of the absorbance versus mole ratio corresponds to the stoichiometry of the reaction.

The kinetic runs were performed under pseudo - first order conditions with the concentration of dichromate ion at least 500-folds greater than that of the dye at 25±1°C and ionic strength of 0.50 mol dm^{-3} (NaCl). The reaction was monitored spectrophotometrically by measuring the absorbance at 700nm using Corning Colorimeter 252. The pseudo first order plots of log (A$_t$ - A$_\infty$) versus time, which was linear to about 80% at various reactant concentrations were made (where A$_\infty$ and A$_t$ are the absorbance at the end of the reaction at time, t respectively).

The influence of [H$^+$] on the rate of reaction was investigated by using hydrochloric acid in the range (0.1 - 4.0) × 10^{-4} mol dm^{-3}, while the [NGB^{3-}] and [Cr$_2$O$_7$$^{2-}$] were kept constant at 25 ± 1°C and   I = 0.50 mol dm^{-3} (NaCl).

The effect of ionic strength of the reaction medium on the rate of the reaction was also investigated in the range of 0.2 - 0.9 mol dm^{-3} (NaCl) while the concentration of other reactants were kept constant at 25 ± 1°C. The spectra of solutions containing Cr$_2$O$_7$$^{2-}$ alone and those containing the reaction mixture were compared under similar condition between 400 – 700nm.

Results and Discussion

A stoichiometric study showed that one mole of the dye was consumed by one mole of the oxidant suggesting the overall equation as (1).

$$NGB^{3-} + Cr_2O_7^{2-} + 2H^+ \longrightarrow Cr^{3+} + \text{other products} \qquad (1)$$
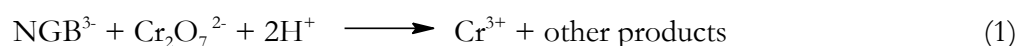
A similar stoichiometry has been reported for the oxidation of indigo carmine by dichromate ion and the oxidation of ethanolamine by quinolinium dichromate (Edokpayi *et al.*, 2010; Reddy *et al.*, 1996).

Presence of Cr^{3+} in the reaction product was confirmed qualitatively by the addition of NaOH solution (Vogel, 1978). This gave a green colouration as a result of the formation 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.

The pseudo - first order plots of log (A$_t$ - A$_\infty$) versus time for these reactions were linear to about 80% of the reactions. The linearity of these plots indicates that these reactions are first order with respect to [NGB^{3-}]. The pseudo – first order rate constants, k$_1$ were obtained from the slopes of these plots. A plot of log k$_1$ versus log [Cr$_2$O$_7$$^{2-}$] was linear with a slope of 1.04 showing that the reaction is also first order with respect to [Cr$_2$O$_7$$^{2-}$]. This is also supported by the constancy of k$_2$ values in Table 1. Thus the reaction is second order at constant [H$^+$] and the rate equation for the reaction is:

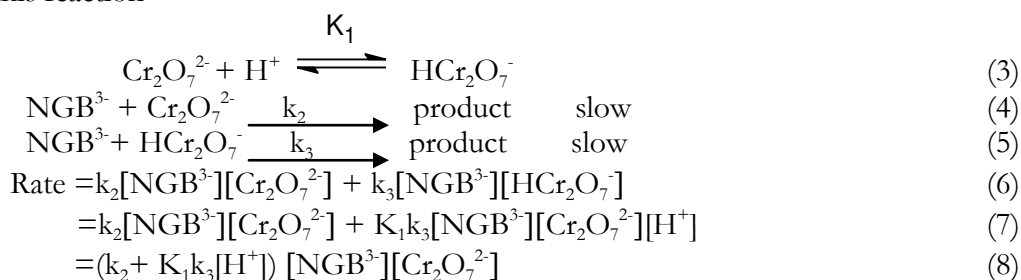$$-d[NGB^{3-}]/dt = k_2[NGB^{3-}][Cr_2O_7^{2-}] \qquad (2)$$

The order of one in both reactants in the reaction conforms to some reported redox reactions of indigo carmine with dichromate ion (Edokpayi *et al.*, 2010). Example of pseudo- first order plot is presented in Figure 1.

The result in Table 1 shows that increase in [H$^+$] speed up the rate of the reaction in the range investigated. Graph of k$_2$ against [H$^+$] was linear with an intercept (Figure 2). The acid dependence of this nature shows that there is a rapid preequilibrium between the protonated and

non-protonated forms in which both the protonated and unprotonated forms are reactive (Myek *et al.,* 2013).The range of hydrogen ion concentration was narrow because the complex was stable at such range.

The rate of the reaction increases with increased in ionic strength of the reaction, which suggests a positive Bronsted - Debye salt effect (Benson, 1969; Birk, 1978). Plot of $\log k_2$ against $I^{1/2}$ gave a slope of 1.20 (R^2= 0.97). This implies that activated complex was formed from reactants with similar charges in the rate determining step and the product of their charges was 1.20. The results are presented in Table 1.

The effect of added Ca^{2+} and Mg^{2+} on the reaction rate was unexpected as the cations were expected to increase the rate of the reaction due to the fact that anions are participating in the rate determining step. Added CH_3COO^- and SO_4^{2-} inhibited the rate of reaction. This inhibited effect by the ions suggested that the reaction might be operating via the outersphere mechanism (Mayer and Taube, 1987). Addition of acrylonitrile to a partially reacted mixture in the presence of excess methanol did not lead to gel formation. This shows that the participation of free radicals in this reaction system is unlikely. Similar result has been reported by Myek *et al.* (2013). A spectroscopic study suggests that the formation of an intermediate complex during the reaction might be unlikely. Plot of $1/k_1$ versus $1/[Cr_2O_7^{2-}]$ (Figure 3) suggests the absence of the formation of intermediate complex in the reaction. On the basis of the above findings, the mechanism below is proposed for this reaction

$$Cr_2O_7^{2-} + H^+ \xrightleftharpoons{K_1} HCr_2O_7^- \tag{3}$$

$$NGB^{3-} + Cr_2O_7^{2-} \xrightarrow{k_2} \text{product} \quad \text{slow} \tag{4}$$

$$NGB^{3-} + HCr_2O_7^- \xrightarrow{k_3} \text{product} \quad \text{slow} \tag{5}$$

$$\text{Rate} = k_2[NGB^{3-}][Cr_2O_7^{2-}] + k_3[NGB^{3-}][HCr_2O_7^-] \tag{6}$$

$$= k_2[NGB^{3-}][Cr_2O_7^{2-}] + K_1k_3[NGB^{3-}][Cr_2O_7^{2-}][H^+] \tag{7}$$

$$= (k_2 + K_1k_3[H^+]) [NGB^{3-}][Cr_2O_7^{2-}] \tag{8}$$

Equation (8) is similar to equation (2) where $a = k_2$ and $b = K_1k_3$

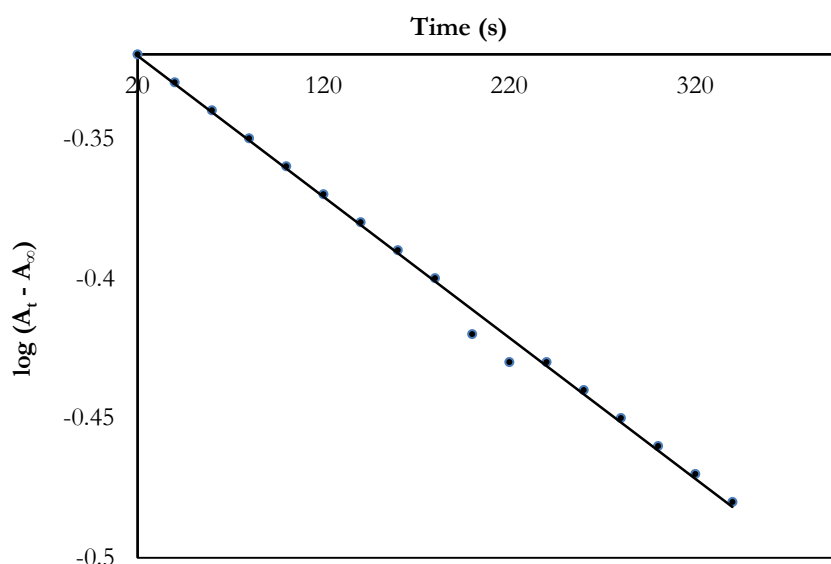
Figure 1. Typical pseudo-first order plot for the redox reaction of naphthol green B with $Cr_2O_7^{2-}$ at $[NGB^{3-}]$= 4.0 × 10⁻⁵ mol dm⁻³, $[Cr_2O_7^{2-}]$= 4.4 x 10⁻² mol dm⁻³, $[H^+]$= 1.0×10⁻⁴ mol dm⁻³, I= 0.50 mol dm⁻³, λ= 700 nm and T=25 ± 1 °C

Table 1. Pseudo – first order and second order rate constants for the reaction of naphthol green B and $Cr_2O_7^{2-}$ at $[NGB^{3-}] = 4.0 \times 10^{-5}$ mol dm^{-3}, $\lambda = 700$ nm and $T = 25\pm1$ºC

$10^2[Cr_2O_7^{2-}]$, mol dm^{-3}	$10^4[H^+]$, mol dm^{-3}	$10^1 I$, mol dm^{-3}	$10^3 k_1$, s^{-1}	k_2, dm^3 mol^{-1} s^{-1}
2.0	1.0	5.0	1.28	0.064
2.4	1.0	5.0	1.47	0.061
2.8	1.0	5.0	1.72	0.061
3.6	1.0	5.0	1.96	0.054
4.0	1.0	5.0	2.60	0.065
4.4	1.0	5.0	2.75	0.063
4.4	0.1	5.0	2.06	0.047
4.4	0.5	5.0	2.47	0.056
4.4	1.0	5.0	2.83	0.064
4.4	2.0	5.0	3.12	0.071
4.4	3.0	5.0	4.25	0.097
4.4	4.0	5.0	4.61	0.105
4.4	1.0	2.0	1.34	0.030
4.4	1.0	3.0	2.03	0.046
4.4	1.0	4.0	2.49	0.057
4.4	1.0	5.0	2.79	0.063
4.4	1.0	6.0	3.22	0.073
4.4	1.0	8.0	4.61	0.10
4.4	1.0	9.0	6.09	0.14

Table 2. Dependence of rate constant on cations and anions on the redox reaction of naphthol green B with dichromate ion at $[NGB^{3-}] = 4.0 \times 10^{-5}$ mol dm^{-3}, $[Cr_2O_7^{2-}] = 4.4 \times 10^{-2}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, $\lambda = 700$ nm, $T = 25 \pm 1$ºC

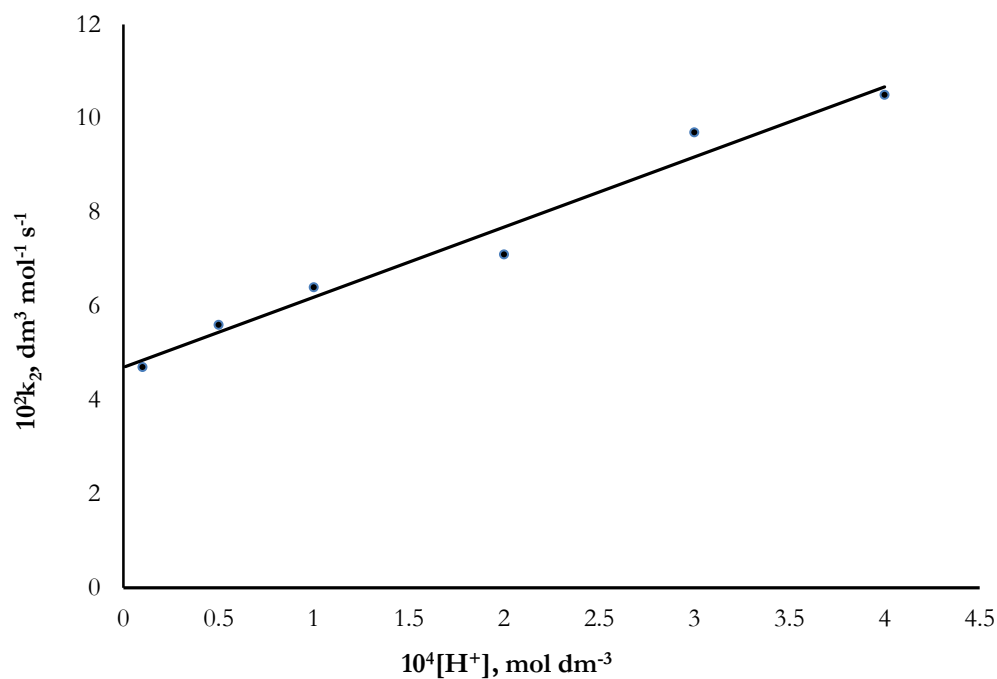| $10^3[Ca^{2+}]$, mol dm^{-3}	10^3, s^{-1}	k_2, dm^3 mol^{-1} s^{-1}
1.0	2.55	0.058
10.0	1.87	0.043
20.0	1.06	0.038
80.0	0.877	0.024
100.0	0.85	0.019
150.0	0.816	0.014
$10^3[Mg^{2+}]$, mol dm^3		
1.0	2.49	0.057
20.0	2.30	0.052
60.0	1.97	0.045
80.0	1.73	0.039
150.0	1.73	0.034
$10^3[SO_4^{2-}]$, mol dm^3		
1.0	2.02	0.046
10.0	1.67	0.038
20.0	1.30	0.029
40.0	1.15	0.026
60.0	0.85	0.019
$10^3[CH_3OO^-]$, mol dm^3		
1.0	2.20	0.050
10.0	1.94	0.044
20.0	1.72	0.039
40.0	1.54	0.035
60.0	1.23	0.028
80.0	0.92	0.021

Figure 2. Plot of k_2 versus [H$^+$] for the redox reaction between naphthol green B and $Cr_2O_7^{2-}$
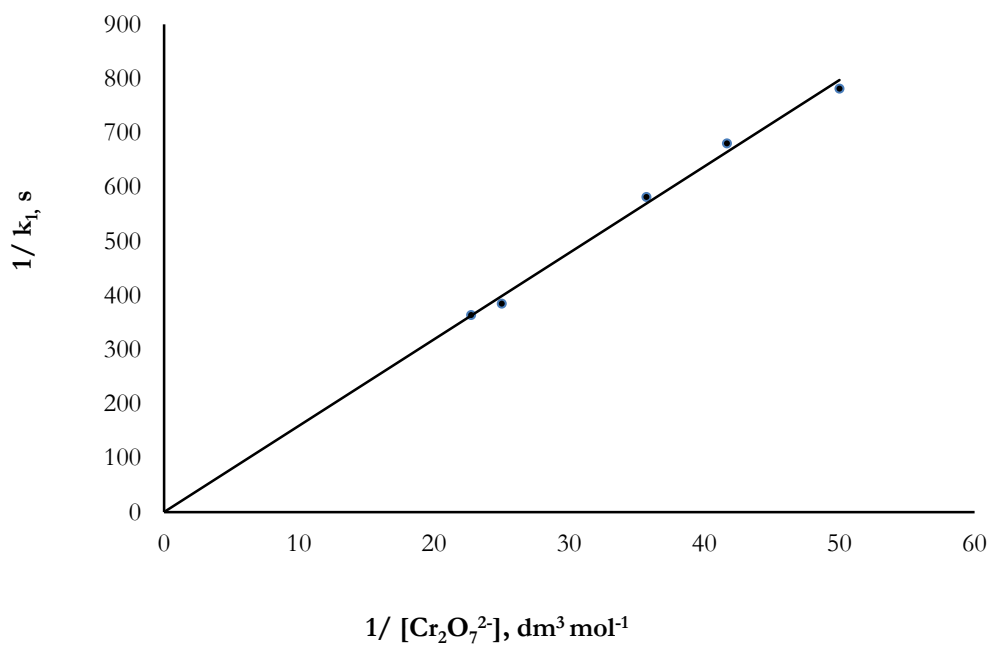

Figure 3. Michaelis - Menten plot of $1/k_1$ against $1/[Cr_2O_7^{2-}]$, for the redox reaction between naphthol green B and $Cr_2O_7^{2-}$

Conclusions

The redox reaction of naphthol green B and dichromate ions in aqueous acidic solution revealed a stoichiometry of 1:1, a first order was observed for NGB^{3-} and $Cr_2O_7^{2-}$ ions respectively. The rate of reaction increases with increase in acid concentration and ionic strength of the reaction medium. Added ions inhibited the rate of the reaction. An intermediate complex was not implicated during the course of the reaction. Based on the above results, it is proposed that the reaction is most probably operates through the outersphere mechanistic pathway.

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