Research Article

Kinetics and Mechanism of the Oxidation of Naphthol Green B by Peroxydisulphate Ion in Aqueous Acidic Medium

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The kinetics of the oxidation of naphthol green B (NGB³⁻) by peroxydisulphate ion has been carried out in aqueous acidic medium at $\lambda_{\max}$ of 700 nm, $T = 23 \pm 1^\circ\text{C}$, and $I = 0.50 \text{ mol dm}^{-3}$ (NaCl). The reaction shows a first-order dependence on oxidant and reductant concentration, respectively. The stoichiometry of the NGB— $\text{S}_2\text{O}_8^{2-}$ reaction is 1 : 2. Change in hydrogen ions concentration of the reaction medium has no effect on the rate of the reaction. Added cations and anions decreased the rate of the reaction. The results of spectroscopic and kinetic investigation indicate that no intermediate complex is probably formed in the course of this reaction.

1. Introduction

Naphthol green B is used in histology to stain collagen. The dye is a lake, in which the mordant metal is ferric iron. However, the iron appears to play no part in its staining ability [1]. Naphthol green B is very soluble in water and has an absorption maximum of 714 nm. As an anion, it acts as an acid dye [2]. Kinetic spectrophotometric method for the determination of cerium (IV) with naphthol green B has been studied [3]. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of naphthol green B at 710 nm. It was found that the reaction rate is very slow when the temperature is below 60°C , but the rate of the catalyzed reaction increases rapidly when the reaction temperatures are above 70°C .

Peroxydisulphate ion is one of the powerful oxidizing agents known [4, 5]. A large number of investigations have been carried out in the oxidation of metal ions [6, 7], metal complex [8, 9], and various organic compounds [10] by $\text{S}_2\text{O}_8^{2-}$. Most electron transfer reactions of $\text{S}_2\text{O}_8^{2-}$ occur by the outer-sphere mechanism [11–13]. However, reactions with some positively charged metal complexes such as $\text{Fe}(\text{bpy})_3^{2+}$, $\text{Fe}(\text{Phen})_3^{2+}$, and $\text{Os}(\text{bpy})_3^{2+}$ occur by both the outer-sphere and the inner-sphere mechanisms [5, 9]. Except when the reducing agent can be protonated, the redox reaction of

$\text{S}_2\text{O}_8^{2-}$ was found to be independent of hydrogen ion concentration [14]. Despite its reactions with other compounds, the redox reaction of this oxidant with naphthol green B is scanty.

It is our hope that this investigation will help to gain more insight into the redox reaction of naphthol green B with peroxydisulphate ion.

2. Materials and Methods

The chemicals used were of analytical grade and were used without further purification. Standard solution of NGB³⁻ was prepared by dissolving 0.088 g in 100 cm^3 volumetric flask using distilled water. Sodium peroxydisulphate solution was prepared by dissolving known quantities in distilled water. All other reagents used were of analytical grade.

The stoichiometry of the reaction was determined spectrophotometrically using the mole ratio method by keeping the concentration of the dye constant at $4.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, $I = 0.50$, $\lambda_{\max} = 700 \text{ nm}$, $T = 23 \pm 1^\circ\text{C}$, and $[\text{S}_2\text{O}_8^{2-}] = (0.08\text{--}1.4) \times 10^{-4} \text{ mol dm}^{-3}$. The stoichiometry was evaluated from the plot of absorbance versus $[\text{reductant}]/[\text{oxidant}]$ after the reaction had reached completion by the observation of a steady zero absorbance value over a period of two days.

TABLE 1: Pseudo-first-order and second-order rate constants for the reaction of naphthol green B and $\text{S}_2\text{O}_8^{2-}$ at $[\text{NGB}^{3-}] = 4.0 \times 10^{-5} \text{ mol dm}^{-3}$, $\lambda = 700 \text{ nm}$, and $T = 23 \pm 1^\circ\text{C}$.

$10^3 [\text{S}_2\text{O}_8^{2-}]$, mol dm^{-3}	$10^4 [\text{H}^+]$, mol dm^{-3}	$10^1 I$, mol dm^{-3}	$10^3 k_1$, s^{-1}	k_2 , $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
4.8	1.0	5.0	7.30	1.52
5.2	1.0	5.0	8.22	1.58
5.6	1.0	5.0	8.50	1.52
6.0	1.0	5.0	9.39	1.57
6.4	1.0	5.0	9.79	1.53
6.8	1.0	5.0	10.70	1.57
5.6	0.1	5.0	8.39	1.50
5.6	0.5	5.0	8.50	1.52
5.6	1.0	5.0	8.59	1.53
5.6	1.5	5.0	8.82	1.58
5.6	2.0	5.0	8.64	1.54
5.6	4.0	5.0	8.17	1.46
5.6	10.0	5.0	8.64	1.54
5.6	1.0	0.5	17.7	3.16
5.6	1.0	1.0	15.4	2.74
5.6	1.0	2.0	10.10	1.80
5.6	1.0	5.0	8.58	1.53
5.6	1.0	6.0	6.91	1.23
5.6	1.0	7.0	6.14	1.10

A Corning Colorimeter Model 252 spectrophotometer was used to follow the decrease in absorbance of the dye at 700 nm , $T = 23 \pm 1^\circ\text{C}$, $I = 0.5 \text{ mol dm}^{-3}$ (NaCl), and $[\text{H}^+] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$ (HCl). The kinetic runs were conducted under pseudo-first-order conditions with $[\text{S}_2\text{O}_8^{2-}]$ in at least 120-fold excess over $[\text{NGB}^{3-}]$. The pseudo-first-order plots of $\log (A_t - A_\infty)$ versus time were made (where A_t and A_∞ are the absorbance at time t and at the end of the reaction, resp.). From the slope of the plots, the pseudo-first-order rate constant (k_1) was determined [15].

The effect of acid on the rate of reaction was studied by varying $[\text{H}^+]$ in the range $(0.1\text{--}10.0) \times 10^{-4} \text{ mol dm}^{-3}$, while $[\text{NGB}^{3-}]$ and $[\text{S}_2\text{O}_8^{2-}]$ were kept constant at $23 \pm 1^\circ\text{C}$ and $I = 0.5 \text{ mol dm}^{-3}$ (NaCl). The range was narrow because acid was stable at such range.

The effect of ionic strength on the rate of the reaction was investigated in the range of $0.05\text{--}0.7 \text{ mol dm}^{-3}$ (NaCl) while the concentrations of other reagents were kept constant at $23 \pm 1^\circ\text{C}$.

3. Results and Discussion

The result of stoichiometric studies reveals that one mole of NGB^{3-} reacted quantitatively with two moles of $\text{S}_2\text{O}_8^{2-}$. Hence the overall equation for the reaction is

The presence of SO_4^{2-} was confirmed qualitatively by the addition of BaCl_2 followed by HCl which formed an insoluble white precipitate in excess HCl. Kinetic studies indicated

FIGURE 1: Plot of $\log k_2$ versus $I^{1/2}$ for the redox reaction between naphthol green B and $\text{S}_2\text{O}_8^{2-}$ at $[\text{NGB}^{3-}] = 4.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{S}_2\text{O}_8^{2-}] = 5.6 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, $I = 0.05\text{--}0.7 \text{ mol dm}^{-3}$, $\lambda = 700 \text{ nm}$, and $T = 23 \pm 1^\circ\text{C}$.

first-order dependence of rate of reaction on $[\text{NGB}^{3-}]$ and $[\text{S}_2\text{O}_8^{2-}]$. Under the experimental conditions employed k_2 was found to be $1.55 \pm 0.22 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$.

FIGURE 2: The Michaelis-Menten plot for the redox reaction between naphthol green B and $\text{S}_2\text{O}_8^{2-}$ at $[\text{NGB}] = 4.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{S}_2\text{O}_8^{2-}] = (4.8\text{--}6.8) \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, $I = 0.50 \text{ mol dm}^{-3}$, $\lambda = 700 \text{ nm}$, and $T = 23 \pm 1^\circ \text{C}$.

The rate equation for the reaction is

$$-\frac{d[\text{NGB}]}{dt} = k_2 [\text{NGB}^{3-}] [\text{S}_2\text{O}_8^{2-}]. \quad (2)$$

Effect of changes in ionic strength of the reaction medium indicated that the rate constant decreases with increase in ionic strength. This obeyed a negative Bronsted-Debye salt effect [16]. Plot of $\log k_2$ against $I^{1/2}$ (Figure 1) gave a slope of -0.71 ($R^2 = 0.96$).

The reaction was found to be independent of $[\text{H}^+]$ in the range of $(0.1\text{--}10) \times 10^{-4} \text{ mol dm}^{-3}$ investigated, indicating that the reaction occurs through an acid-independent pathway (Table 1). Similar results have been reported for the redox reaction of $\text{S}_2\text{O}_8^{2-}$ [17–19]. Added cation and anion inhibited the rate of the reaction (Tables 2 and 3). This inhibited effect by the ions suggested that the reaction might be operating via the outersphere mechanism [20].

Spectroscopic evidence and the Michaelis-Menten plot of $1/k_1$ versus $1/\text{S}_2\text{O}_8^{2-}$ (Figure 2) suggest that intermediates may be unimportant in the rate determining step. Free radical test did not yield gel formation or if present it might be transient.

On the basis of the above findings, the mechanism below is proposed for this reaction.

4. Reaction Scheme

The reaction scheme is as follows:

TABLE 2: Rate data for the effect of added cations (Ca^{2+} and Mg^{2+}) on the rate of reaction of naphthol green B with $\text{S}_2\text{O}_8^{2-}$ at $[\text{NGB}^{3-}] = 4.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{S}_2\text{O}_8^{2-}] = 5.6 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, $I = 0.50 \text{ mol dm}^{-3}$, $\lambda = 700 \text{ nm}$, and $T = 23 \pm 1^\circ \text{C}$.

Ion	$10^3[\text{ion}], \text{mol dm}^{-3}$	$10^3 k_1, \text{s}^{-1}$	$k_2, \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
Ca^{2+}	1.0	8.25	1.47
	10.0	7.84	1.40
	20.0	7.30	1.30
	60.0	7.05	1.26
	80.0	6.91	1.23
	200.0	5.57	0.99
Mg^{2+}	1.0	7.42	1.33
	5.0	5.59	1.00
	10.0	4.48	0.80
	20.0	4.11	0.73
	80.0	3.65	0.65
	200.0	2.65	0.47

TABLE 3: Rate data for the effect of added anions (SO_4^{2-} and CH_3COO^-) on the rate of reaction of naphthol green B with $\text{S}_2\text{O}_8^{2-}$ at $[\text{NGB}^{3-}] = 4.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{S}_2\text{O}_8^{2-}] = 5.6 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, $I = 0.50 \text{ mol dm}^{-3}$, $\lambda = 700 \text{ nm}$, and $T = 23 \pm 1^\circ \text{C}$.

Ion	$10^3[\text{ion}], \text{mol dm}^{-3}$	$10^3 k_1, \text{s}^{-1}$	$k_2, \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
SO_4^{2-}	1.0	7.26	1.30
	5.0	6.60	1.18
	10.0	5.60	1.00
	20.0	5.32	0.95
	80.0	3.26	0.58
CH_3COO^-	1.0	6.45	1.15
	2.0	4.19	0.75
	3.0	2.88	0.51
	4.0	2.69	0.48
	5.0	1.77	0.32

$$\text{Rate} = k_1 [\text{NGB}^{3-}] [\text{S}_2\text{O}_8^{2-}] \quad (8)$$

Equation (8) is analogous to (2) where $k_2 = k_1$.

5. Conclusion

The redox reaction of naphthol green “B” and peroxydisulphate ions in aqueous acidic medium showed a stoichiometry of 1:2; a first order was observed for NGB^{3-} and $\text{S}_2\text{O}_8^{2-}$ ions, respectively. The rate constant decreases with increase in

ionic strength and the reaction was found to be independent of $[H^+]$. Spectroscopic evidence and the Michaelis-Menten plot of $1/k_1$ versus $1/S_2O_8^{2-}$ suggest that intermediates may be unimportant in the rate determining step. Polymerization test suggests the absence of free radicals in the reaction medium. Based on the above results, it is proposed that the reaction most probably operates through the outer-sphere mechanism.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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