Kinetics and Mechanism of the Redox Reaction of Naphthol Green B with Hydrazine Dihydrochloride in Aqueous Acidic Medium

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Abstract: The kinetics of the redox reaction between naphthol green B and hydrazine dihydrochloride has been studied in aqueous hydrochloric acid medium at an ionic strength, I = 0.50 mol dm⁻³(NaCl), [H⁺] = 1.0×10⁻⁴ mol dm⁻³ (HCl) and T = 21±1°C. The redox reaction displayed a stoichiometry of 1:1 and obeys the rate law: -d[NGB³⁻]/dt=k[NGB³⁻][N₂H₄.2HCl]. Change in hydrogen ion concentration of the reaction medium has no effect on the rate of the reaction. Added cations and anions inhibited the rate of the reaction. The redox reaction showed negative salt effect, with the rate decreasing with increase in ionic strength of the reaction medium. Results of the Michaelis–Menten’s plot show that an intermediate complex was not formed during the course of the reaction. The outersphere mechanism is proposed for this reaction.

Keywords: Kinetic, Naphthol Green B, Redox, Hydrazine Dihydrochloride, Intermediate

1. Introduction

Naphthol green B (NGB³⁻) is used in the production of drugs, cosmetics and for staining purposes. It possesses excellent redox characteristic. A new amperometric glucose biosensor with naphthol green B as a mediator has been reported [1]. It was found that naphthol green B is a good mediator, promoting electron transfer from glucose oxidase to graphite electrode.

Hydrazine dihydrochloride, which is a powerful reducing agent, has similarity to the thiourea by possessing nitrogen in its structure can also be possible inhibitor and similar compounds [2]. Hydrazine and its derivatives have been used in industry, agriculture and other fields, including photographic development, rocketry, explosives, and insecticides and blowing agents for plastics. Kinetic study of the oxidation of hydrazine dihydrochloride by aqueous iodine has been reported [3]. It was found that the reaction is first order in both reactants. Reduction of aqueous silver nitrate by hydrazine dihydrochloride in weakly alkaline solution results in a polydisperser colloid that is stable for many months without addition of any stabilizing compounds [4].

This work is carried out to further understand the reaction of naphthol green B and that of hydrazine dihydrochloride.

2. Materials and Methods

A1.0×10⁻¹ mol dm⁻³ stock solution of naphthol green B (Analar grade) was prepared by dissolving 0.02196g in 25cm³ flask using distilled water. Hydrazine dihydrochloride 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 was standardized titrimetrically. Sodium chloride was used to maintain constant ionic strength of the reaction.

The reaction stoichiometry was determined spectrophotometrically using the mole ratio method [5]. This was accomplished by measuring the absorbance of solutions containing varying concentrations of hydrazine dihydrochloride in the range (0.08-1.40)×10⁻⁴ mol dm⁻³,
$[\text{H}^-] = 1.0 \times 10^{-4}$ mol dm$^{-3}$ and $I = 0.50$ mol dm$^{-3}$ at 700nm, 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 pseudo-first order plots of log(A$^{-3}$) by addition of (1–50)×10$^{-4}$ mol dm$^{-3}$ at 21±1°C and $I = 0.50$mol dm$^{-3}$. A point of inflection on the curve of the absorbance versus time was made at temperature of 21±1°C. A similar run was made for the dye alone in the reaction conditions with which does not change the colour of the reacting mixture.

The linearity of the pseudo-first order plots (Figure 1) suggests a first order dependence of reaction rate on [NGB$^{3-}$] and [N$_2$H$_4$.2HCl] under the experimental conditions employed in this investigation. Similar first order dependence has been reported for the oxidation of hydrazine dihydrochloride by aqueous iodine [3]. The reaction is therefore second order overall at constant hydrogen ion concentration. This may be represented as:

$$-\frac{dN}{dt} = k_2[NGB^{3-}][N_2H_4.2HCl] \quad (2)$$

The rate of reaction showed lack of hydrogen ion concentration dependence in the range (0.1 - 20) ×10$^{-4}$ mol dm$^{-3}$. This independence is in accord with the fact that neither the oxidant nor the reductant undergoes significant protonation changes under the reaction conditions. Similar result has been reported [7]. The redox reaction showed negative salt effect, with the rate decreasing with increase in ionic strength from 0.4-1.0 mol dm$^{-3}$ (NaCl). This observation of negative Bronsted-Debye salt indicates that species that formed the activated complex are of opposite charges. Plot of log$k_2$ against $I^{1/2}$ gave a slope of -1.26 ($R^2=0.98$). (Figure 2)

Lack of spectrophotometric evidence for the formation of intermediate complex suggests an outersphere mechanism. Michaelis–Mentein’s plot of 1/$k_2$ versus 1/[N$_2$H$_4$.2HCl] (Figure 3) had an intercept, suggesting an innersphere. However, ions inhibition as shown in Table 2 and 3 is a characteristic of the outersphere mechanism [8]. This evidence suggests that this reaction is probably operating by the outersphere mechanism. On the basis of the above the following reaction scheme is proposed for this reaction.

$$N_2H_4.2HCl \overset{K_1}{\rightarrow} N_2H_3^++H^++2Cl^- \quad (3)$$

$$\text{NGB}^{3-} + N_2H_4^+ \underset{k_2}{\overset{k_3}{\rightleftharpoons}} \text{[NGB}^{3-}.N_2H_4^+] \quad (4)$$

$$\text{[NGB}^{3-}.N_2H_4^+] \rightarrow \text{Products (slow)} \quad (5)$$

$$\text{Rate} = k_3[\text{NGB}^{3-}][N_2H_4^+] \quad (6)$$

From equation (4),

$$K_2 = \frac{[\text{NGB}^{3-}.N_2H_4^+]}{[\text{NGB}^{3-}][N_2H_4^+]} \quad (7)$$

$$[\text{NGB}^{3-}.N_2H_4^+] = K_2[\text{NGB}^{3-}][N_2H_4^+] \quad (8)$$

Substituting equation (8) into (6) gives

$$\text{Rate} = k_3[\text{NGB}^{3-}][N_2H_4^+] \quad (9)$$

$$\text{Rate} = k'[\text{NGB}^{3-}][N_2H_4^+] \quad (10)$$

Where $k_3K_2 = k'$.  

3. Results and Discussion

The stoichiometric studies showed that one mole of naphthol green B was consumed by one mole of N$_2$H$_4$.2HCl. The overall stoichiometry equation is shown in equation (1).

$$\text{NGB}^{3-} + N_2H_4.2HCl \rightarrow \text{Products} \quad (1)$$

Organic product of the reaction of NGB$^{3-}$ with N$_2$H$_4$.2HCl gave a yellow precipitate with 2, 4-dinitrophenylhydrazine, confirming the presence of carbonyl group. Ketone was further distinguished by the addition of acidified potassium dichromate, which does not change the colour of the reacting mixture.
Figure 1. Typical pseudo-first order plot for the redox reaction of napthol green B with N\textsubscript{2}H\textsubscript{4}.2HCl at [NGB\textsuperscript{3-}]=4.0×10\textsuperscript{-5} mol dm\textsuperscript{-3}, [N\textsubscript{2}H\textsubscript{4}.2HCl]=20.0×10\textsuperscript{-2} mol dm\textsuperscript{-3}, [H\textsuperscript{+}]=1.0×10\textsuperscript{-4} mol dm\textsuperscript{-3}, I=0.50 mol dm\textsuperscript{-3}, λ=700 nm and T=21±1°C.

Figure 2. Plot of log\textsubscript{10}(A\textsubscript{t} - A\textsubscript{0}) versus Time [s] for the redox reaction of napthol green B with N\textsubscript{2}H\textsubscript{4}.2HCl at [NGB\textsuperscript{3-}]=4.0×10\textsuperscript{-5} mol dm\textsuperscript{-3}, [N\textsubscript{2}H\textsubscript{4}.2HCl]=20.0×10\textsuperscript{-2} mol dm\textsuperscript{-3}, [H\textsuperscript{+}]=1.0×10\textsuperscript{-4} mol dm\textsuperscript{-3}, I=0.50 mol dm\textsuperscript{-3}, λ=700 nm and T=21±1°C.

Figure 3. Michaelis–Menten’ s plot for the redox reaction between napthol green B and N\textsubscript{2}H\textsubscript{4}.2HCl at [NGB\textsuperscript{3-}]=4.0×10\textsuperscript{-5} mol dm\textsuperscript{-3}, [N\textsubscript{2}H\textsubscript{4}.2HCl]=20.0×10\textsuperscript{-2} mol dm\textsuperscript{-3}, [H\textsuperscript{+}]=1.0×10\textsuperscript{-4} mol dm\textsuperscript{-3}, I=0.50 mol dm\textsuperscript{-3}, λ=700 nm and T=21±1°C.

Table 1. Pseudo-first order and second order rate constants for the reaction of napthol green B and N\textsubscript{2}H\textsubscript{4}.2HCl at [NGB\textsuperscript{3-}]=4.0×10\textsuperscript{-5} mol dm\textsuperscript{-3}, λ=700 nm and T=21±1°C.

| 10\textsuperscript{-2}[N\textsubscript{2}H\textsubscript{4}.2HCl], mol dm\textsuperscript{-3} | 10\textsuperscript{-4}[H\textsuperscript{+}], mol dm\textsuperscript{-3} | 10\textsuperscript{-3}I, mol dm\textsuperscript{-3} | 10\textsuperscript{3}k\textsubscript{1}, s\textsuperscript{-1} | k\textsubscript{2}, dm\textsuperscript{3} mol\textsuperscript{-1}s\textsuperscript{-1} |
|-------------------------------|-----------------|-----------------|-----------------|-----------------|
| 3.6                           | 1.0             | 5.0             | 1.15            | 0.032           |
| 6.0                           | 1.0             | 5.0             | 1.67            | 0.029           |
| 8.0                           | 1.0             | 5.0             | 2.39            | 0.030           |
| 12.0                          | 1.0             | 5.0             | 3.85            | 0.032           |
| 16.0                          | 1.0             | 5.0             | 4.61            | 0.029           |
| 20.0                          | 1.0             | 5.0             | 5.95            | 0.030           |
| 20.0                          | 0.1             | 5.0             | 5.37            | 0.027           |
| 20.0                          | 0.5             | 5.0             | 5.78            | 0.029           |
| 20.0                          | 1.0             | 5.0             | 5.76            | 0.029           |
| 20.0                          | 1.5             | 5.0             | 5.94            | 0.030           |
| 20.0                          | 4.0             | 5.0             | 6.08            | 0.030           |
| 20.0                          | 5.0             | 5.0             | 6.20            | 0.031           |
| 20.0                          | 20.0            | 5.0             | 6.03            | 0.030           |
| 20.0                          | 1.0             | 4.0             | 7.60            | 0.038           |
| 20.0                          | 1.0             | 5.0             | 5.94            | 0.030           |
| 20.0                          | 1.0             | 6.0             | 5.37            | 0.027           |
| 20.0                          | 1.0             | 7.0             | 4.21            | 0.021           |
| 20.0                          | 1.0             | 8.0             | 3.55            | 0.018           |
| 20.0                          | 1.0             | 9.0             | 3.45            | 0.017           |
| 20.0                          | 1.0             | 10.0            | 2.30            | 0.012           |
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 N$_2$H$_4$.2HCl at [NGB]$^-$=4.0×10$^{-5}$ mol dm$^{-3}$, [N$_2$H$_4$.2HCl]=20.0×10$^{-2}$ mol dm$^{-3}$, [H$^+$]=1.0×10$^{-4}$ mol dm$^{-3}$, $\lambda$=700 nm and $T$=21±1°C.

| Ion  | 10$^3$[ion], mol dm$^{-3}$ | 10$^3$k, s$^{-1}$ | k$_2$, dm$^3$ mol$^{-1}$ s$^{-1}$ |
|------|----------------------------|------------------|-------------------------------|
| Ca$^{2+}$ | 1.0                         | 4.19             | 0.021                         |
|       | 5.0                         | 3.62             | 0.018                         |
|       | 10.0                        | 3.07             | 0.015                         |
|       | 20.0                        | 2.79             | 0.014                         |
|       | 30.0                        | 2.46             | 0.012                         |
| Mg$^{2+}$ | 1.0                         | 4.45             | 0.012                         |
|       | 5.0                         | 3.53             | 0.018                         |
|       | 10.0                        | 3.13             | 0.016                         |
|       | 20.0                        | 2.56             | 0.013                         |
|       | 30.0                        | 2.06             | 0.010                         |

Table 3. Rate data for the effect of added anions (SO$_4^{2-}$ and CH$_3$COO$^-$) on the rate of reaction of naphthol green B with N$_2$N$_4$.2HCl at [NGB]$^-$=4.0×10$^{-5}$ mol dm$^{-3}$, [N$_2$N$_4$.2HCl]=20.0×10$^{-2}$ mol dm$^{-3}$, [H$^+$]=1.0×10$^{-4}$ mol dm$^{-3}$, I=0.50 mol dm$^{-3}$, $\lambda$=700 nm and $T$=21±1°C.

| Ion    | 10$^3$[ion], moldm$^{-3}$ | 10$^3$k, s$^{-1}$ | k$_2$, dm$^3$ mol$^{-1}$ s$^{-1}$ |
|--------|----------------------------|------------------|-------------------------------|
| SO$_4^{2-}$ | 1.0                         | 4.26             | 0.021                         |
|        | 5.0                         | 3.45             | 0.017                         |
|        | 10.0                        | 3.19             | 0.016                         |
|        | 20.0                        | 2.86             | 0.014                         |
|        | 30.0                        | 2.44             | 0.012                         |
|        | 1.0                         | 4.42             | 0.022                         |
|        | 10.0                        | 3.54             | 0.018                         |
| CH$_3$COO$^-$ | 20.0                        | 3.13             | 0.016                         |
|        | 30.0                        | 2.80             | 0.014                         |
|        | 40.0                        | 2.30             | 0.012                         |
|        | 50.0                        | 2.18             | 0.011                         |

4. Conclusion

The redox reaction of naphthol green B and hydrazine dihydrochloride in acidic medium showed a stoichiometry of 1:1, a first order was observed for NGB$^-$ and [N$_2$H$_4$.2HCl]. The rate of reaction had no effects with increase in acid concentration. Increase in ionic strength decreases the rate of the reaction. 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 mechanism.

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