



KINETICS AND MECHANISM OF REDOX REACTION OF NEUTRAL RED AND BROMATE ION IN AQUEOUS ACIDIC MEDIUM



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Abstract: The kinetics and mechanism of redox reaction of neutral red, NR^+ , and bromate ion, BrO_3^- , was studied in aqueous hydrochloric acid medium under pseudo-first order conditions at $25 \pm 1^\circ\text{C}$, $[\text{H}^+] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}$ (NaCl) and $\lambda_{\text{max}} = 525 \text{ nm}$. The reaction was first order with respect to both $[\text{NR}^+]$ and $[\text{BrO}_3^-]$, and second order with respect to $[\text{H}^+]$. The rate of the reaction displayed a positive Bronsted-Debye salt effect. There was no evidence of the formation of an intermediate complex of significant stability and free radicals were probably not present in the reaction. The observations above, coupled with the result of Michaelis-Menten plot suggests an outer sphere mechanism for the reaction. The reaction obeys the rate equation: $-d[\text{NR}^+]/dt = k[\text{NR}^+][\text{BrO}_3^-][\text{H}^+]^2$. A plausible mechanism has been proposed for the reaction.

Keywords: Kinetics, mechanism, neutral red, bromate ion.

Introduction

Bromate ion is a very useful analytical reagent (Clarke, 1970; Iyun *et al.*, 1992). It has been used in the oxidation of both inorganic and organic substrate (Firozabadi, 1995). Redox reactions involving bromate ion has been attributed to the formation of its various protonated species including HBrO_3 , H_2BrO_3^+ and BrO_2^+ which reacts directly with the reductant (Birk, 1973; Lohdip *et al.*, 1996). Various mechanistic studies involving bromate ion have been studied (Ayoko *et al.*, 1991; Iyun *et al.*, 1992; Lohdip *et al.*, 1996; Jonnalagadda and Musengiwa, 1998; Keith *et al.*, 2006).

Neutral red is a eurhodin dye which finds a variety of applications in the biological system (Winckler, 1974; Repetto *et al.*, 2008). It is also used for the dyeing of silk, paper and cotton as well as for the production of inks (Salem, 2002). Redox reactions of neutral red were investigated in aqueous media (Salem, 2002; Khan *et al.*, 2008). Owing to the redox potential of both bromate ion and neutral red, it will be interesting to understand the dynamics of their reaction. In this work effort was made to study the kinetics of the redox reaction of bromate ion and neutral red to provide data for understanding the mechanistic pathway for the reaction.

Materials and Methods

Experimental

All reagents used were Analar grade. Neutral red (Gurr) and potassium bromate (BDH) were used without further purification. Sodium chloride (M&B) was used to maintain the ionic strength of the reaction medium. Hydrochloric acid was standardized titrimetrically using sodium carbonate. All other reagents were used as supplied.

Stoichiometry

The Stoichiometry of $[\text{NR}^+] - [\text{BrO}_3^-]$ system was determined by spectrophotometric titration using the mole ratio method (Iyun *et al.*, 1995). The concentration of $[\text{NR}^+]$ was kept constant while that of $[\text{BrO}_3^-]$ was varied in the reaction mixtures after which excess $[\text{NR}^+]$ was determined by measuring the absorbances of the solutions at 525 nm until a constant value was obtained. A point of

inflection on the curve of plot of absorbance versus mole ratio indicates the stoichiometry of the reaction (Hamza *et al.*, 2012).

Kinetic study

The kinetic study was carried out under pseudo-first order conditions with the $[\text{BrO}_3^-]$ in at least 10-fold excess over the $[\text{NR}^+]$ at 525 nm, $[\text{H}^+] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}$, $T = 25 \pm 1^\circ\text{C}$.

The Pseudo-first order rate plots of $\log(A_t - A_\infty)$ versus time were made (where A_∞ and A_t are the absorbance at the end of the reaction and at time, t) and from the slopes of the plots, the pseudo-first order rate constants (k_1) were determined. The second order rate constants (k_2) were obtained from;

$$k_2 = k_1/[\text{BrO}_3^-] \dots\dots\dots 1$$

Effect of $[\text{H}^+]$ on the reaction rate

The effect of changes in $[\text{H}^+]$ on the reaction rate was investigated by varying the $[\text{H}^+]$ between $(1.8 - 4.2) \times 10^{-2} \text{ mol dm}^{-3}$ while concentration of the dye and bromate ion were kept constant at 5.0×10^{-5} and $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ respectively at $25 \pm 1^\circ\text{C}$ and $I = 0.50 \text{ mol dm}^{-3}$.

Effect of ionic strength and dielectric constant

The effect of varying the ionic strength of the reaction medium on the rate of the reaction was investigated in the range of $(0.3 - 0.8) \text{ mol dm}^{-3}$ while the concentration of other reactants were kept constant at $25 \pm 1^\circ\text{C}$. The effect of dielectric constant (D) on the reaction rate was determined at different dielectric constants in the range 80.1 – 77.14 at constant $[\text{NR}^+]$, $[\text{BrO}_3^-]$, $[\text{H}^+]$ and ionic strength.

Effect of added cation and anion

The effect of added cation and anion were investigated for $[\text{X}] = (5.0 - 9.0) \times 10^{-4} \text{ mol dm}^{-3}$ for SO_4^{2-} and $(1.0 - 5.0) \times 10^{-5} \text{ mol dm}^{-3}$ for Ca^{2+} at constant $[\text{NR}^+]$, $[\text{BrO}_3^-]$, $[\text{H}^+]$ and ionic strength.

Test for intermediate complex

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The spectra of the reaction mixture were obtained after the commencement of the reaction. These were compared with the spectra of the dye alone over a wavelength range of 400 – 700 nm. Michaelis-Menten plot of 1/k₁ versus 1/[BrO₃⁻] was also made.

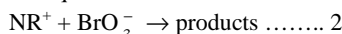
Test for Free Radical

Test for free radicals was investigated by the addition of acrylamide to partially reacting mixtures of neutral red and the bromate ions followed by excess methanol (Adetoro *et al.*, 2011).

Results and Discussion

Stoichiometric study

From the stoichiometric study, the mole ratio of the reaction was found to be 1:1 (Fig. 1) and is represented by the equation:



Similar stoichiometry has been reported in the reaction of toluidine blue with acidic bromate (Jonnalagadda and Musengiwa, 1998).

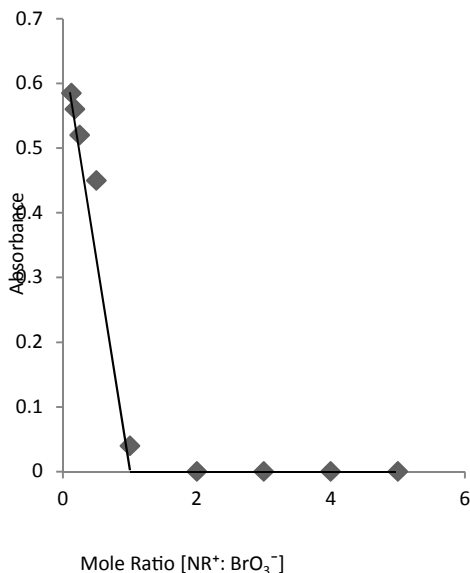


Fig. 1: Plot of Absorbance versus mole ratio for the redox reaction of NR⁺ with BrO₃⁻ at [NR⁺] = 5.0 × 10⁻⁵ mol dm⁻³, I = 0.5 mol dm⁻³, [H⁺] = 2.0 × 10⁻² mol dm⁻³, T = 25 ± 1 °C and λ_{max} = 525 nm

Kinetics

A plot of log(A_t-A_∞) against time t, gave a straight line graph (a typical plot is depicted by Fig. 2), suggesting that the reaction is first order with respect to [NR⁺]. The slope was calculated and k₁, was determined by multiplying the slope by 2.303. The order of the reaction with respect to [BrO₃⁻] was determined by plotting log k₁ against log [BrO₃⁻]. The gradient of the linear graph was obtained as 0.98 (Fig. 3). The values of second order rate constants k₂ determined as the ratio of k₁ and [BrO₃⁻] were fairly constant (Table 1). The rate equation for the reaction can be written as

$$-d[NR^+]/dt = k_2[NR^+][BrO_3^-] \dots\dots\dots 3$$

This order correlates with what was reported in the redox reaction of bromate with toluidine blue (Jonnalagada and Musengiwa, 1998), 12-tungstocobaltate (II) (Ayoko *et al.*, 1991), methylene blue (Iyun and Asala, 1994), and 4-oxo-4-arylbutanoic acids (Cherkupally *et al.*, 2010).

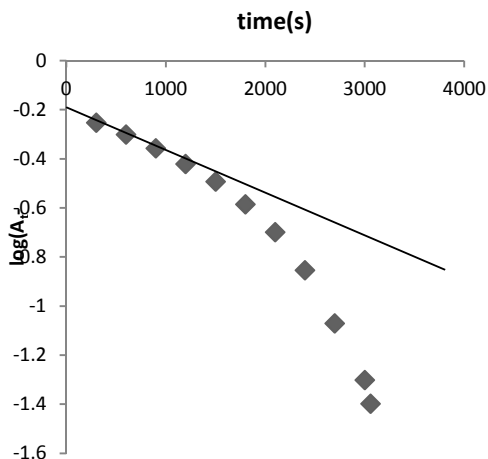


Fig. 2: Typical pseudo-first order plot for the redox reaction of NR⁺ with BrO₃⁻ at [NR⁺] = 5.0 × 10⁻⁵ mol dm⁻³, [BrO₃⁻] = 2.0 × 10⁻³ mol dm⁻³, I = 0.5 mol dm⁻³, [H⁺] = 2.0 × 10⁻² mol dm⁻³, T = 25 ± 1 °C and λ_{max} = 525 nm

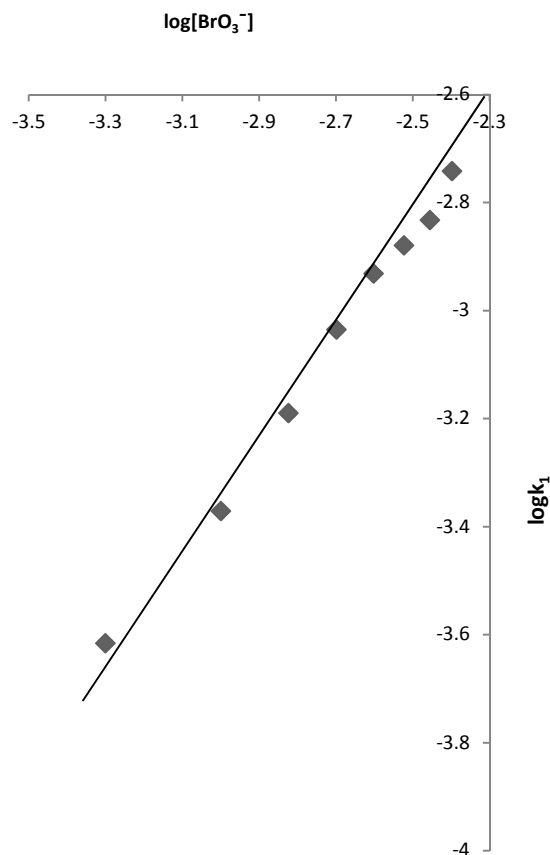


Fig. 3: Plot of log k₁ versus log [BrO₃⁻] for the redox reaction of NR⁺ with BrO₃⁻ at [NR⁺] = 5.0 × 10⁻⁵ mol dm⁻³, I = 0.5 mol dm⁻³, [H⁺] = 2.0 × 10⁻² mol dm⁻³, T = 25 ± 1 °C and λ_{max} = 525 nm

Effect of [H⁺]

The effect of changes in [H⁺] on the reaction rate was investigated by varying the [H⁺] between (1.8 - 4.2) × 10⁻² mol dm⁻³. The rate of the reaction increased with increase

in [H⁺] (Table 1). The slope obtained from the plot of log k₁ versus log [H⁺], was 2.11, which showed a second order dependence on [H⁺]. A plot of acid dependent second order rate constant k₂ versus [H⁺]² was also linear with no intercept (Fig. 4). This nature of acid dependence effect is expressed as;

$$k_2 = a[H^+]^2 \dots\dots\dots 4$$

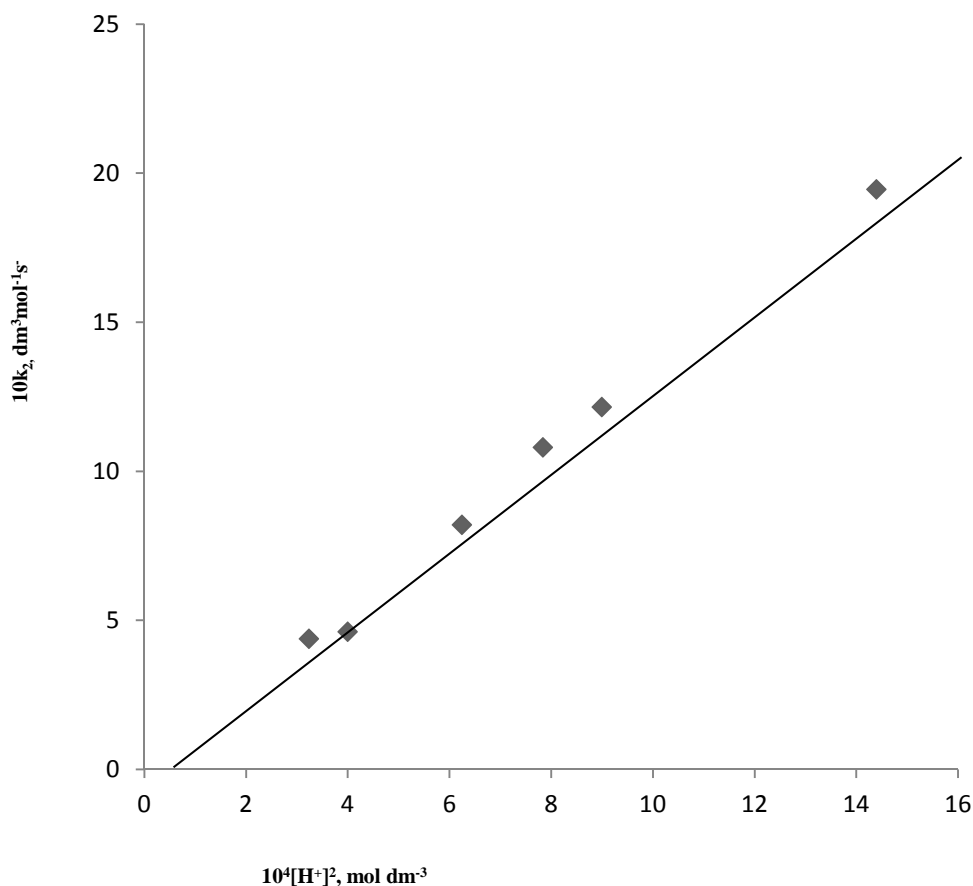
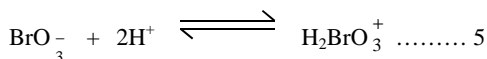


Fig. 4: Plot of 10k₂ versus 10⁴[H⁺]² for the redox reaction of NR⁺ with BrO₃⁻ at [NR⁺] = 5.0 x 10⁻⁵ mol dm⁻³, [BrO₃⁻] = 2.0 x 10⁻³ mol dm⁻³, I = 0.5 mol dm⁻³, T = 25 ± 1 °C and λ_{max} = 525 nm

This suggests that only the protonated species of BrO₃⁻ is involved in the reaction (Birk, 1973; Birk and Kozub, 1973; Lohdip *et al.*, 1996). The second order [H⁺] dependence term was rationalized in term of the pre-

equilibrium double protonation of BrO₃⁻ to give H₂BrO₃⁺ (Birk, 1973; Knight *et al.*, 1973; Ayoko *et al.*, 1991; Iyun *et al.*, 1992).

K



Similar acid dependence has been established in the redox reaction of toluidine blue with acidic bromate and 4-oxo-4-arylbutanoic acid respectively (Jonnalagadda and Musengiwa, 1998; Cherkupally and Padma, 2010). It is thought that the protons serve to weaken the bonds between the oxygen atoms and central bromine atom thereby facilitating the reductability of the later (Edwards *et al.*, 1988).

Effect of ionic strength and dielectric constant

The rate constants were observed to increase with increase in ionic strength (Table 1) and a plot of $\log k_2$ against \sqrt{I} gave a positive slope, suggesting positive Bronsted – Debye salt effect (Barton and Wright, 1968; Benson, 1969; Birk, 1978). This indicates that the species at the rate determining step are of similar charges. This result was supported by the observed decrease in the reaction rate as the dielectric constant of the medium was decreased.

Table 1: The pseudo-first order and second order rate constants for the reaction of NR⁺ and BrO₃⁻ at [NR⁺] = 5.0 × 10⁻⁵ mol dm⁻³, T=25 ± 1 °C and λ_{max} = 525 nm

10 ⁴ [BrO ₃ ⁻], mol dm ⁻³	10 ² [H ⁺], mol dm ⁻³	10I, mol dm ⁻³	10 ⁴ k ₁ , s ⁻¹	10 ⁴ k ₂ , dm ³ mol ⁻¹ s ⁻¹
5.0	2.0	5.0	2.42	4.84
10.0	2.0	5.0	4.25	4.25
15.0	2.0	5.0	6.45	4.30
20.0	2.0	5.0	9.21	4.61
25.0	2.0	5.0	11.70	4.68
30.0	2.0	5.0	13.20	4.40
35.0	2.0	5.0	14.70	4.20
40.0	2.0	5.0	18.10	4.53
20.0	1.8	5.0	8.75	4.38
20.0	2.0	5.0	9.21	4.61
20.0	2.5	5.0	16.40	8.20
20.0	2.8	5.0	16.80	8.40
20.0	3.0	5.0	24.30	12.15
20.0	3.8	5.0	38.90	19.45
20.0	2.0	3.0	3.69	1.84
20.0	2.0	4.0	7.14	3.57
20.0	2.0	5.0	9.67	4.84
20.0	2.0	6.0	14.50	7.25
20.0	2.0	7.0	15.40	7.70
20.0	2.0	8.0	22.80	11.40

Effect of added ions

Addition of anion (SO₄²⁻) to the reaction medium increased the reaction rate, while cation (Ca²⁺) inhibited the reaction (Table 2). Similar anion catalysis involving acetate and some carboxylate ions was reported in the bromate oxidation of iodide (Adegite *et al.*, 1977). This is an indication that the reaction might be operating via the outer sphere mechanism (Pennington and Haim, 1967; Ayoko *et al.*, 1991).

Table 2: Effect of added anion and cation on the rate of reaction of NR⁺ and BrO₃⁻ at [NR⁺] = 5.0 × 10⁻⁵ mol dm⁻³, [BrO₃⁻] = 2.0 × 10⁻³ mol dm⁻³, I = 0.5 mol dm⁻³, [H⁺] = 2.0 × 10⁻² mol dm⁻³, T = 25 ± 1 °C and λ_{max} = 525 nm

10 ⁴ [SO ₄ ²⁻], mol dm ⁻³	10 ⁴ k ₁ , s ⁻¹	10 ⁴ k ₂ , dm ³ mol ⁻¹ s ⁻¹
0.0	9.44	4.74
5.0	11.10	5.55
6.0	11.70	5.85
7.0	13.10	6.55

10 ⁵ [Ca ²⁺], mol dm ⁻³	10 ⁴ k ₁ , s ⁻¹	10 ⁴ k ₂ , dm ³ mol ⁻¹ s ⁻¹
8.0	16.10	8.05
9.0	21.40	10.70
0.0	9.21	4.61
1.0	8.98	4.49
3.0	8.75	4.38
5.0	8.52	4.26

Test for intermediate complex formation

There was no clear shift in λ_{max}, 525 nm, recorded when the spectrum of the reaction mixture was compared with that of [NR⁺]. Lack of spectroscopic evidence for the formation of intermediate complex suggests an outer sphere mechanism. The Michaelis-Menten plot of 1/k₁ versus 1/[BrO₃⁻] was linear with no intercept suggesting the absence of an intermediate complex formation (Fig. 5).

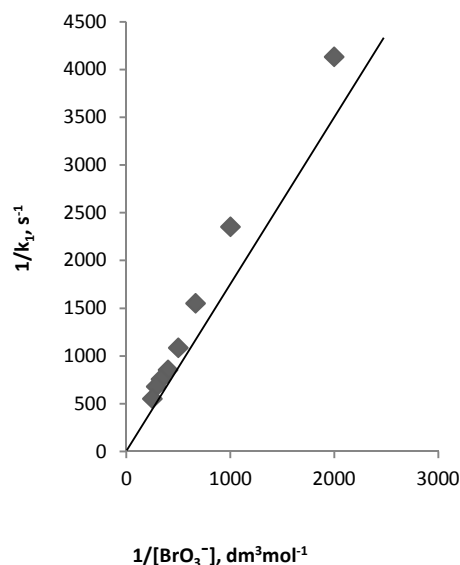


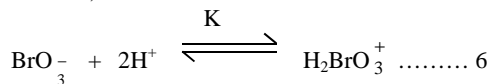
Fig. 5: Michaelis-Menten plot for the redox reaction of NR⁺ with BrO₃⁻ at [NR⁺] = 5.0 × 10⁻⁵ mol dm⁻³, I = 0.5 mol dm⁻³, [H⁺] = 2.0 × 10⁻² mol dm⁻³, T = 25 ± 1 °C and λ_{max} = 525 nm

Polymerization studies

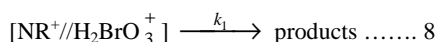
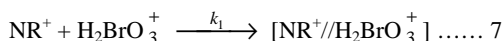
Addition of acrylamide to the partially reacted solution to serve as free radical scavenger in the presence of large excess of methanol did not produce a gelatinous precipitate. This indicates that the involvement of free radicals in the reaction is unlikely.

Reaction mechanism

On the basis of the results above from our investigation, the following reaction scheme is proposed for this reaction;



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Equation 7 is the rate determining step. Therefore, the rate law for the reaction can be written as:

$$\text{Rate} = k_1[\text{NR}^+][\text{H}_2\text{BrO}_3^+] \dots\dots\dots 9$$

From the equilibrium reaction in equation 7;

$$K = \frac{[\text{H}_2\text{BrO}_3^+]}{[\text{BrO}_3^-][\text{H}^+]^2} \dots\dots\dots 10$$

$$[\text{H}_2\text{BrO}_3^+] = K[\text{BrO}_3^-][\text{H}^+]^2$$

Therefore:

$$\text{Rate} = Kk_1[\text{NR}^+][\text{BrO}_3^-][\text{H}^+]^2 \dots\dots\dots 11$$

$$\text{Rate} = k'[\text{NR}^+][\text{BrO}_3^-]$$

Where: $k' = Kk_1[\text{H}^+]^2 = 0.45 \pm 0.02 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at $[\text{H}^+] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$

Conclusion

The redox reaction of neutral red with bromate in aqueous acidic medium showed a stoichiometry of 1:1. The reaction was second order overall. Doubly protonated form of BrO_3^- was found to be the active specie due to the observed second order dependence of the rate of the reaction on $[\text{H}^+]$. The reaction also displayed a positive Bronsted-Debye salt effect. Both kinetic and spectroscopic investigations showed no evidence of intermediate complex formation. Based on the foregoing, the outer sphere mechanism is proposed as the plausible mechanistic pathway for this reaction.

Aknowledgement

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