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Mechanisms of oxidation of rosaniline hydrochloride by potassium bromate in aqueous perchloric acid medium - A kinetic approach

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ABSTRACT

Bromate oxidizes the methyl group of rosaniline hydrochloride to an aldehyde group in aqueous $HClO_4$ medium. At μ = 0.50M, $NaClO_4$ the oxidation was found to be first-order in [rosaniline] and zero-order in [bromate]. The stoichiometry of reaction determined by spectrophotometric titration was found to be 2 moles of bromate to 5 moles of [rosaniline]. The bromate reaction followed both a first-order acid-dependent and an acid-independent pathway, suggesting that both $HBrO_3$ and BrO_3^- are principal oxidizing species.
The reaction conforms to the rate law:

$$-\frac{d[ROS]}{dt} = (a + b\,[H^+])\,[ROS]$$

The result of this study indicate that the reaction probably occur by the inner-sphere mechanisms.

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INTRODUCTION

There is very scanty report on the oxidation kinetics and mechanisms of rosaniline [1,2]. The study of the kinetics and mechanism of the oxidation of rosaniline is therefore centered mainly on collecting data on this triphenyl methane basic dye, which is widely used as biological dye.

Bromate, a strong oxidant [3], is a very useful analytical reagent [4]. Various acid – dependencies have been reported for reactions involving this oxyanion [4,5,6]. The acid – dependency commonly encountered in reaction of bromate has been attributed to the formation of $HBrO_3$ which reacts with the reductant [7,8,9].

In this paper we report on the kinetics and mechanistic study of the oxidation of rosaniline by bromate in aqueous acid medium.

EXPERIMENTAL

Materials

All chemicals used were BDH (AnalaR Grade) with the exception of rosaniline (Aldrich). Standard salt solutions were made by dissolving known amounts of solutes in given volume of distilled water and the exact concentration determined by standard methods [10]. The rosaniline was determined by gravimetry [1,2].

Stoichiometry of reaction

The stoichiometry of reaction was determined by spectrophotometric titration on a spectronic 20 colorimeter using the mole ratio method. The concentration of rosaniline was kept constant (5.00 x 10^{-5} M) while the concentration of bromate was varied from 2.00 x 10^{-5} M to 6.00 x 10^{-4} M, at constant $[H^+]$ and constant ionic strength, μ = 0.50M, ($NaClO_4$). The reaction was allowed to go to completion indicated by the constancy of absorbance measurements over time at λmax = 545nm, the λmax for rosaniline. The stoichiometry was evaluated from a plot of the absorbance versus the mole ratio (Fig. 1).

Kinetics and order of reaction

At constant ionic strength, μ = 0.50M, ($NaClO_4$) and constant $[H^+]$ = 8.00 x 10^{-3}M $HClO_4$, all kinetic measurements were made under pseudo-first order condition with the concentration of bromate kept in large excess over that of the rosaniline concentration. The decreasing absorbance of the reaction mixture was monitored at λ = 545nm on the colorimeter.

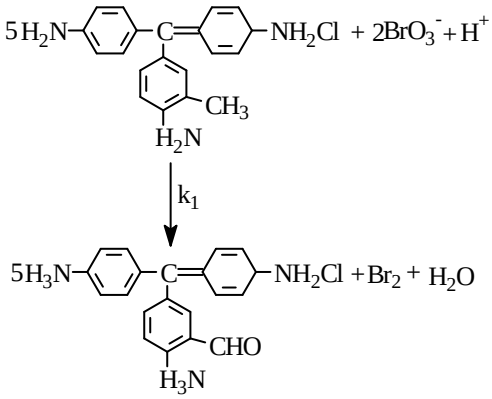
Pseudo-first order rate constants were determined from plots of log ($A_t - A_\infty$) versus time according to the Oswald isolation techniques [2, 11,12].

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RESULTS AND DISCUSSION

Stoichiometry

Two moles of bromate were consumed by five moles of rosaniline. The overall stoichiometric equation can therefore be written as:



Similar stoichiometries were reported for reactions between bromate and aldehyde [9]; between bromate and catechol [4]; between bromate and VO^{2+} [13].

Order of reaction

Pseudo-first order rate constants, k_1, were determined at different initial concentration of bromate from plots of log (A_t-A_∞) versus time. The plots were only linear in the initial points, and the rate of reaction was found not to vary with the concentration of bromate as presented in Table 1. Thus, the oxidation reaction was found to be zero-order [3, 14] in [BrO_3^-]. The equation for the rate of the reaction of rosaniline and bromate can therefore be best fitted into equation (2).

$$\frac{-d[ROS]}{dt} = k_1[ROS] \quad .....(2)$$

Effect of Acid

Influence of acid on the rate of reaction was investigated in the range of $[HClO_4] = 5.00 \times 10^{-3} - 1.10 \times 10^{-1}$M at $\mu = 0.50$M, ($NaClO_4$) when concentration of rosaniline and bromate were kept constant. The results are as presented in Table 1. A plot of k_1 versus $[H^+]$ was linear with a positive intercept, suggesting that k_1 vary with $[H^+]$ according to equation (3).

$$k_1 = a + b[H^+] \quad \ldots(3)$$

Therefore,

$$\frac{-d[ROS]}{dt} = (a + b[H^+])[ROS] \quad \ldots(4)$$

Table 1: Pseudo-first order rate constants for the reaction of rosaniline and potassium bromate, λ = 545nm; t = 25^{0}C

10^5[ROS] M	10^3[$HClO_4$] M	μ = [$NaClO_4$] M	10^3 [BrO_3^-] M	$10k_1$ s^{-1}
5.0	10.0	0.50	5.0	2.48
5.0	10.0	0.50	6.0	2.49
5.0	10.0	0.50	8.0	2.50
5.0	10.0	0.50	9.0	2.50
5.0	10.0	0.50	10.0	2.50
5.0	10.0	0.50	11.0	2.52
5.0	5.0	0.50	8.0	2.38
5.0	20.0	0.50	8.0	4.61
5.0	35.0	0.50	8.0	5.85
5.0	50.0	0.50	8.0	7.60
5.0	65.0	0.50	8.0	9.15
5.0	80.0	0.50	8.0	10.08
5.0	95.0	0.50	8.0	9.60
5.0	110.0	0.50	8.0	12.79
50	8.0	0.20	8.0	2.66
50	8.0	0.40	8.0	2.79
50	8.0	0.60	8.0	2.95
50	8.0	0.80	8.0	3.11
50	8.0	0.90	8.0	3.14

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Table 2: Pseudo – first order rate constants for rosaniline – bromate reaction, λ = 545nm, t = 25^{0}C and μ = 0.50M, $NaClO_4$

10^5[ROS]M]	10^2[H^+]M	10^3[BrO_3^-]M	10^3[Anion]M	$10\ ^1k_1S^{-1}$
			Anion = [CO_2^-]	
5.0	8.0	8.0	0.0	9.60
5.0	8.0	8.0	5.0	9.98
5.0	8.0	8.0	10.0	9.74
5.0	8.0	8.0	15.0	9.60
5.0	8.0	8.0	25.0	9.41
			Anion = [$CH_3CO_2^-$]	
5.0	8.0	8.0	0.0	9.61
5.0	8.0	8.0	5.0	9.78
5.0	8.0	8.0	10.0	9.98
5.0	8.0	8.0	20.0	9.73
5.0	8.0	8.0	25.0	9.47

In acid solution, bromate establishes the following equilibra [4,5].

$$BrO_3^- + H^+ \rightleftharpoons HBrO_3$$

$$HBrO_3 + H^+ \rightleftharpoons H_2BrO^{3+}$$

Therefore, the nature of the acid-dependence can be used to suggest the possible bromate species in solution.

In the oxidation of hydrazoic acid by bromate in perchloric acid medium, the observed first-order acid dependence was used to suggest $HBrO_3$ as the oxidizing bromate specie [17]. The observed acid-dependence in this study suggests BrO_3^- and $HBrO_3$ as the probable species involved in this reaction.

Effect of ionic strength

Ionic strength effect on the reaction was investigated over the range of 0.20 – 0.90M, ($NaClO_4$). The results as presented in Table 1, show that the rate constants increase with increase in ionic strength, suggesting a positive Bronsted – Debye [18,19] salt effect

Effect of added anions

Added formate and acetate did not affect the rate of reaction much (Table 2), an indication that the reaction might be via the inner sphere pathway [20].

Michealis – Menten Plot.

Michealis – Menten plot of $1/k_1$ versus $1/[BrO_3^-]$ was linear with a positive slope and a finite intercept on the $1/k_1$ axis, suggesting an intermediate complex formation precedes the rate-determining step.

Proposed Mechanism

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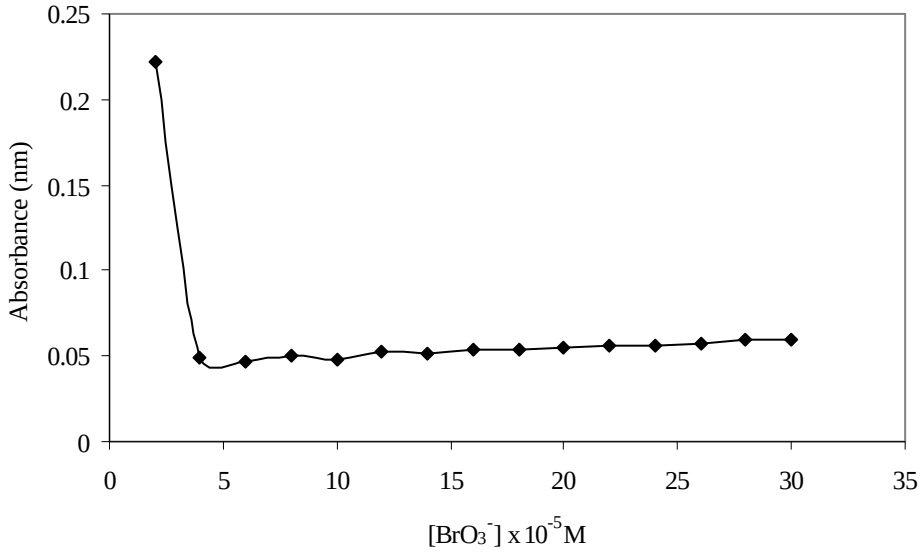
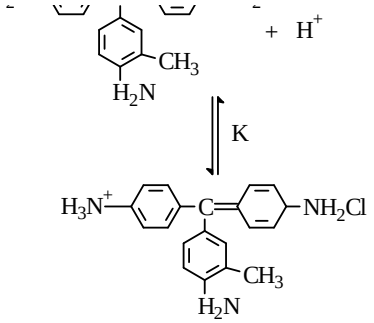


Figure 1: Stoichiometry curve for ROS-Bromate reaction [ROS] = 5.0 x 10^{-5} [H^+] = 7.70 x 10^{-3} μ = 0.50M (NaClO4) λ = 545nm

Based on the observed stoichiometry, order of the reaction, acid-dependence, Michealis-Menten plot, effect of ionic strength and effect of added anions, the following scheme, which accommodates all the experimental findings, is proposed for the mechanisms.



Rate = $\frac{k_3 k_2 \; k_1}{[R^+][H^+][BrO_3^-]}$ ..... (16)

$R^+ + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RH^{2+}$ .....(6)

$RH^{2+} + BrO_3^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HRBrO_3^+$ ....(7)

$HRBrO_3^+ \xrightarrow{k_3} R^{2+} + BrO_2^- + OH$ ....(8)

$OH + OH \longrightarrow H_2O + H$ ....(9)

$H + H \longrightarrow H_2$ ....(10)

$BrO_2^- + 4R^+ + 4H^+ \longrightarrow 4R^{2+} + Br^- + 2H_2O$....(11)

$5Br^- + BrO_3^- + 6H^+ \longrightarrow Br_2 + 6H_2O$ .....(12)

Equation (8) is the r.d.s.

Rate = $k_3 [HRBrO_3^+]$ .....(13)

Substitution from equation (7) gives

Rate = $\frac{k_3 k_2}{k_{-2}} [RH^{2+}][BrO_3^-]$ .....(14)

$= k_3 k_2 [RH^{2+}][BrO_3^-]$

Applying SSH to RH^{2+}

$d[RH^{2+}]/dt = k_1 [R^+][H^+] - k_{-1}[RH^{2+}] - k_2[RH^{2+}][BrO_3^-] = 0$

$\therefore [RH^{2+}] = \frac{k_1[R^+][H^+]}{k_{-1} + k_2 [BrO_3^-]}$ .....(15)

Substituting equation (15) into equation (14) gives

$$\text{Rate} = \frac{k_1 k_3 k_2 [R^+][H^+][BrO_3^-]}{k_{-1} + k_2 [BrO_3^-]}$$

If $k_2[BrO_3^-] >> k_{-1}$ then, $k_{-1} + k_2[BrO_3^-] \cong k_2[BrO_3^-]$

equation (16) becomes,

$$\text{Rate} = \frac{k_1 k_3 k_2 [R^+][H^+][BrO_3^-]}{k_2 [BrO_3^-]}$$