A study of the kinetics and mechanism of reaction of (7-amino-8-methyl-phenothiazin-3-ylidene)-dimethyl-ammonium chloride by perchlorate ion in acidic medium

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ABSTRACT

The kinetics of the reaction of (7-amino-8-methyl-phenothiazin-3-ylidene)-dimethyl-ammonium chloride (herein referred to as TB) by Perchlorate ion has been studied at $30 \pm 1°C$, $[H^+] = 1 \times 10^{-2}$ mol dm^{-3} and ionic strength (I) = 0.5 mol dm^{-3} (NaCl). The reaction is first order in both the oxidant and the reductant. The redox reaction displayed a 1:1 stoichiometry and obeys the rate law:

$$-\frac{d[TB^+]}{dt} = (a + b\,[H^+])\,[TB^+][ClO_4^-]$$

Where $a = 3.1 \times 10^{-2}$ dm^3 mol^{-1} s^{-1}, and $b = 1.63 \times 10^3$ dm^3 mol^{-1} s^{-1}

The second-order rate constant increases with increase in acid concentration. It decreases with increasein ionic strength and dielectric constant. Added anions inhibited the reaction rate while spectroscopic investigation and Michaelis-Menten plot showed no evidence of intermediate complex formation in the course of the reaction. A plausible mechanism has been proposed for the reaction.

Key words: Kinetics, Mechanism, Perchlorate, (7-amino-8-methyl-phenothiazin-3-ylidene)-dimethyl- ammonium chloride.
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INTRODUCTION

Perchlorate as a reducing agent can undergo a variety of intramolecular redox reactions that lead to the release of gaseous products. Through such reactions, it acts as a thrust booster.It is used extensively in pyrotechnics industry. It used on a large scale as a component of air bag inflators.it is also used in nuclear reactors and electronic tubes, as additives in lubricating oils, in tanning and finishing leather, as a mordant for fabrics and dyes, in electroplating, in aluminium refining, in rubber manufacture, in the production of paints and enamels and in pharmaceuticals. Perchlorate has also been used medically to control hyperthyroid condition and grave disease [1 ,2].

(7-Amino-8-methyl-phenothiazin-3-ylidene)-dimethyl-ammonium chloride (TB), a phenothiazine dye, that has been widely used for different purposes in several fields such as medicine science. For example, in clinical identification of malignant and premalignant lesion in the oral cavity, effective screening modality for the assessment of intraoperative margins in resource limited environments and reducing the number of frozen section biopsies performed [3].It can be used as mediator for various chemical or biochemical reactions, colorant for cloths, photosensitizer for determining the actions of photo activated microorganism and labelling agent for identifying organisms [4, 5].For effective use and application of both the reductant and oxidant in industries and laboratories, the kinetics and mechanisms of their reactions is therefore reported in this paper.

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MATERIALS AND METHODS

Stocksolution of TB and sodium perchlorate were prepared with distilled water. Hydrochloric acid (Analar grade) was used as a source of hydrogen ions while the ionic strength of the medium was maintained constant at 0.5 mol dm^{-3} using sodium chloride. Standard salt solutions were made by dissolving known amounts of the solute in a given volume of distilled water and the exact concentration determined by standard methods [6].

Stoichiometry
The stoichiometry of the reaction was determined by spectrophotometric titration using the moleratio method [7]. Solutions containing a known concentration of the dye and varying concentrations of perchlorate ion were reacted at $[H^+] = 1 \times 10^{-2}$ mol dm^{-3} and I = 0.50 mol dm^{-3} (NaCl).This was ascertained by a steady absorbance value over a period of two days [8]. The absorbance of the solutions were then measured at λ_{max} = 600 nm, after the reaction had gone to completion. The stoichiometry was evaluated from the plot of the absorbance versus different concentration of the reductant.

Kinetics Studies
A Corning 252 colorimeter was used to monitored the decrease in absorbance of the reaction mixture at λ_{max} = 600 nm. The kinetics runs were conducted under pseudo-first order conditions with the concentration of perchlorate ion20-fold in excess [TB]. Under this conditions, pseudo-first order rate constants were obtained from plots of $\log(A_t-A_\infty)$ versus time (A_t and A_∞ are absorbance at time t and at the end the reaction respectively) which were linear to greater than 90% of the reaction The reaction was carried out at 30±1°C with $[H^+] = 1 \times 10^{-2}$ mol dm^{-3} (HCl) and I = 0.50 mol dm^{-3}(NaCl). The results are presented in Table 1.

Acid dependence studies
The effect of acid on the rate was investigated using hydrochloric acid in the range $(0.5\text{-}2.5) \times 10^{-2}$ mol $dm^{-3}$by keeping all other conditions constant at $[TB^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[ClO_4^-] = 20 \times 10^{-4}$ mol dm^{-3}, I = 0.5 mol dm^{-3} and T = 30 ± 1˚C [9]. The results are presented in Table 1.

Effect of ionic strength
The effect of ionic strength on the rate of the reaction was investigated in the range
I = 0.3 -1.2 mol dm^{-3} (NaCl) at $[TB^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[ClO_4^-] = 20 \times 10^{-4}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-2}$ mol dm^{-3} and T = 30 ± 1˚C,while the concentration of the other reagents were kept constant at 30 ± 1°C. The results are presented in Table 1.

Test for intermediate complex formation
Spectroscopic test was carried out by comparing the electronic spectrum of the reaction mixture five minute after the start of the reaction with that of the dye within a wavelength of 500-650 nm.
Michaelis-Menten's plots of $1/k_1$ versus $1/[ClO_4^-]$ were also made (Fig. 2).

RESULTS AND DISCUSSION

Stoichiometry
The results of the spectrophotometric titration indicate a 1:1 stoichiometry. The overall reaction is given by equation 1.

$TB^+ + ClO_4^- \rightarrow$ Product   -- 1

This is consistent with what has been reported for the reduction of TB with Sn(II) [10], and with sulphite ion [11].
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Kinetics studies
The pseudo first order plots of log A_t -A_∞ versus time were linear to more than 90% of the extent of reaction indicating that the reactionis first order dependent on $[TB^+]$ (Fig 1). The observed pseudo first order rate constant (k_1) evaluated from slopes of the plots increases as the concentration of ClO_4^- increase.while plot of log k_1 versus log $[ClO_4^-]$ gave a slope of 0.93 suggesting that the reaction is approximately first order in $[ClO_4^-]$ (Fig 2). The second order rate constant $[k_2]$ was obtained at constant $[H^+]$ fromk_1 / $[ClO_4^-]$ (Table 1). The constancy of the second rate constant shows that the reaction also first order with respect to$[ClO_4^-]$. Therefore the overall order for the reaction is second order. The rate equation is

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$$- \frac{d[TB^+]}{dt} = k_2 \, [TB^+][\, ClO_4^-] \qquad\qquad -- \; 2$$

at $[H^+] = 1 \times 10^{-2}$ mol dm (HCl), I = 0.5 mol dm^{-3} (NaCl)and T = 30 ±1°C.
$k_2 = 6.56 \times 10^{-2}$ mol dm^{-3}

Similar second order kinetics has been reported in the reaction of TB with Sn (II), phenylhydrazine, and sulphite ion [10, 12, 11] respectively.

Effect of Acid
Within the range of $(0.5 – 2.5) \times 10^{-2}$ mol dm^{-3}, the rate of reaction increases with increase in concentration of hydrogen ions (Table 1). Plots of k_2 versus $[H^+]$ was also linear with a positive intercept (Fig. 3) therefore the acid dependent rate constant k_2 is given as

$$k_2 = a + b \, [H^+] \qquad\qquad -- \; 3$$

The rate equation of the reaction as a function of $[H^+]$ can now be written as:

$$- \frac{d[TB^+]}{dt} = (a + b \, [H^+]) \, [TB^+][ClO_4^-] \qquad\qquad -- \; 4$$

Where $a = 3.1 \times 10^{-2}$ dm^3 mol^{-1} s^{-1}, and $b = 1.63 \times 10^3$ dm^3 mol^{-1} s^{-1}

This nature of acid dependence observed implies that there are two pathways, one which depends on acid and the other which does not depend on acid. This result shows that both the protonated and unprotonated forms of the reactant are reactive. The positive $[H^+]$ dependence on the rate of reduction of ClO_4^- has been explained in terms of protonation of it to form $HClO_4$ which subsequently reacts with the substrate in a slow step to give the product.

Effect of ionic strength
The increase in the ionic strength of medium from 0.3 – 1.2 mol dm^{-3} (NaCl) resulted in a decrease in the rate of reaction (Table 1). Plot of log k_2 versus $\sqrt{I}$ gave a linear graph with a negative slope of – 0.11showing a negative salt effect (Fig. 4).i.e there is most likely no band formation at the transition state and the reaction involves two opposite charges [13].

Effect of added anion species
The results obtained from the effect of added anions on the rate of the reaction were presented in Table 2. The added ions led to decrease on the rate of reaction. This is suggestive of outer –sphere mechanism.

Test for intermediate complex formation
Spectroscopic studies indicate no significant shift from the absorption maxima of 600 nm characteristic of [TB]. This indicated absence of the formation of an intermediate complex suggesting the absence of inner-sphere mechanism in the reaction. Plots of $1/k_1$ versus $1/[ClO_4^-]$ were linear with zero intercept (Fig 5). Both results suggest absence of the intermediate complex formation prior to electron transfer in the reactions. A similar observation was reported for reduction of TB^+ with $S_2O_4^{2-}$ [14].

Test for Free Radical
Acrylamide was added to the partially oxidized reaction mixture of the TB and ClO_4^-. No gel formation was observed even on addition of a large excess of methanol. This suggests absence of free radical in the reaction mixture.

Product Analysis
Product analysis was carried out by reacting equimolar amount of the dye and the perchlorate at $[H^+] = 1.0 \times 10^{-2}$ mol dm^{-3} and I = 0.5 mol dm^{-3} (NaCl) After the completion of the reaction a colourless solution was obtained and UV visible spectra of the product showed no absorption peak at λ_{max}600 nm. This indicates the destruction of the quinoid structure that gives the dye colour.

Qualitative test for chloride ion was carried out. Chloride ion wasidentified by adding drops of $AgNO_3$ solutionfollowed by 1cm^3 HNO_3into the reacted mixture of the reactants.

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Reaction mechanism

Based on the result of our investigation under the acid condition used for the stoichiometry and kinetic studies, the reaction scheme consistent with the observed data proposed for the reaction is as below:

$$ClO_4^- \;+\; H^+ \;\underset{}{\overset{K_1}{\rightleftharpoons}}\; HClO_4 \qquad\qquad\qquad -- 5$$

$$HClO_4 \;+\; TB^+ \;\xrightarrow[\text{Slow}]{k_2}\; Product \qquad\qquad\qquad -- 6$$

$$ClO_4^- \;+\; TB^+ \;\xrightarrow[\text{Slow}]{k_3}\; Products \qquad\qquad\qquad -- 7$$

The equations 6 and 7 are the rate determining steps

$$Rate = k_2 \,[TB^+]\,[HClO_4] + k_3\,[TB^+]\,[ClO_4^-] \qquad\qquad -- 8$$

From equation 5

$$[HClO_4] = K_1\,[ClO_4^-]\,[H^+] \qquad\qquad\qquad -- 9$$

Substitute equation 9 into equation 8

$$Rate = k_2 K_1\,[TB^+]\,[ClO_4^-]\,[H^+] + k_3\,[TB^+]\,[ClO_4^-] \qquad\qquad -- 10$$

$$= k_3 + k_2 K_1\,[H^+]\,[TB^+]\,[ClO_4^-] \qquad\qquad\qquad -- 11$$

Where $k_3 = a$
  $k_2 K_1 = b$

Equation 11 becomes

$$Rate = (a + b\,[H^+])\,[TB^+]\,[ClO_4^-] \qquad\qquad\qquad -- 12$$

Where $a = 3.1 \times 10^{-2}\, dm^3\, mol^{-1}\, s^{-1}$, and $b = 1.63 \times 10^{3}\, dm^3\, mol^{-1}\, s^{-1}$

Equation 12 is consistent with the observed first order with respect to TB^+, ClO_4^- and H^+ respectively. Since the derived rate law is in agreement with the experimental rate law, then the proposed mechanism is plausible.
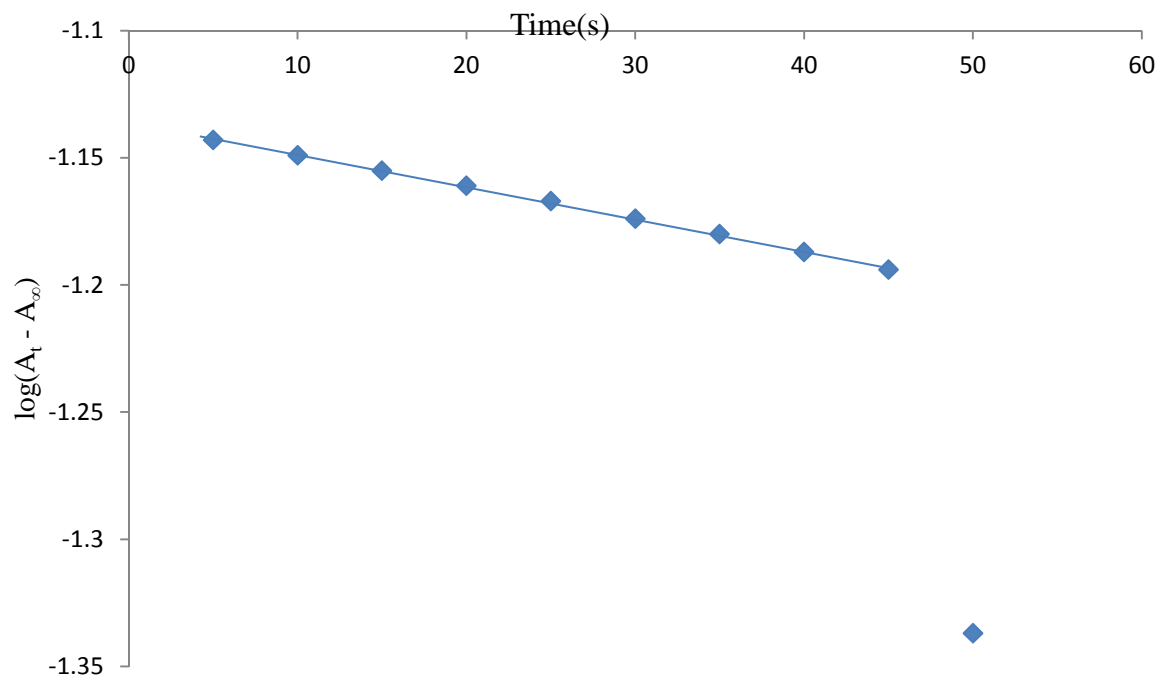

Fig 1: Pseudo-first Order Plot for the Reduction of TB by ClO_4^-

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Table 1: Pseudo – first order and second order rate constants for TBoxidation by ClO_4^- in aqueous HCl medium at $[TB^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, I = 0.5 mol dm^{-3}, T = 30 ± 1°C and $\lambda_{max} = 600$ nm

10^4 [ClO_4^-] mol dm^{-3}	I (NaCl) mol dm^{-3}	10^2 [H^+] mol dm^{-3}	$10^1 k_1$ s^{-1}	$10^1 k_2$ dm^3 mol^{-1} s^{-1}
20	0.5	1.0	1.40	7.00
30	0.5	1.0	2.00	6.50
40	0.5	1.0	2.60	6.50
50	0.5	1.0	3.20	6.40
60	0.5	1.0	3.80	6.40
20	0.5	0.5	1.30	6.50
20	0.5	1.0	1.40	7.00
20	0.5	1.5	1.50	7.40
20	0.5	2.0	1.70	8.40
20	0.5	2.5	2.00	9.90
20	0.3	1.0	1.50	7.20
20	0.5	1.0	1.40	6.90
20	0.7	1.0	1.30	6.70
20	1.0	1.0	1.30	6.50
20	1.2	1.0	1.20	6.20
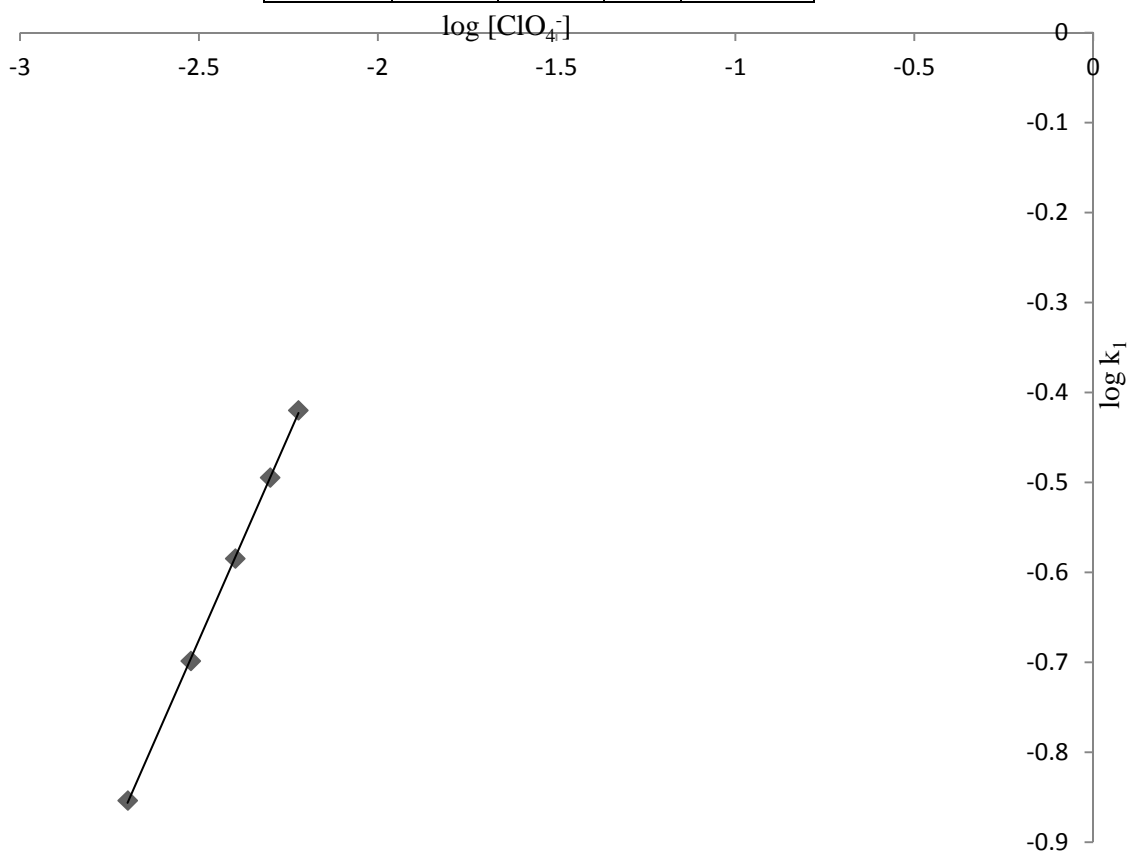
Fig 2: Pseudo - first order plot of log $k_1$versus log [ClO_4^-] for the TB reduction by [ClO_4^-]

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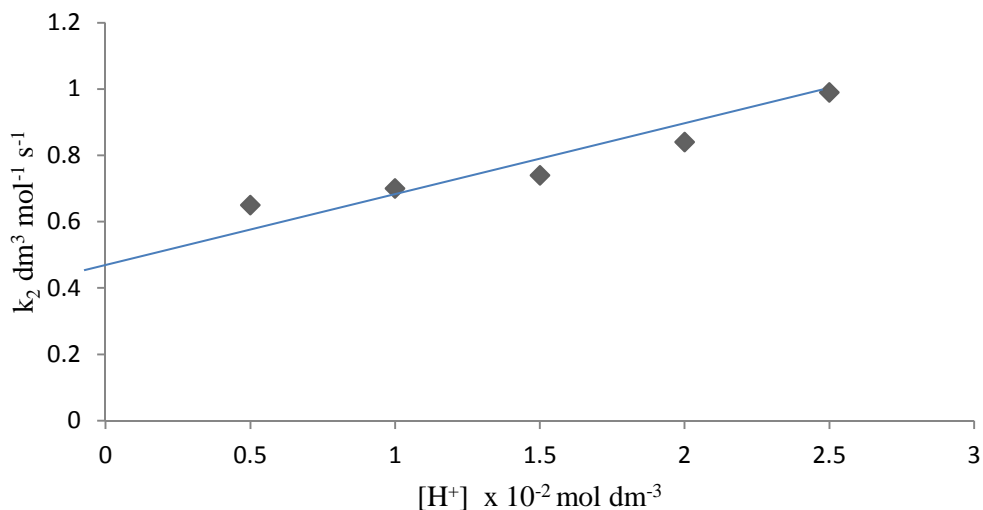
Fig 3: Plot of k_2 versus [H⁺] for the TB reduction by [ClO₄⁻]

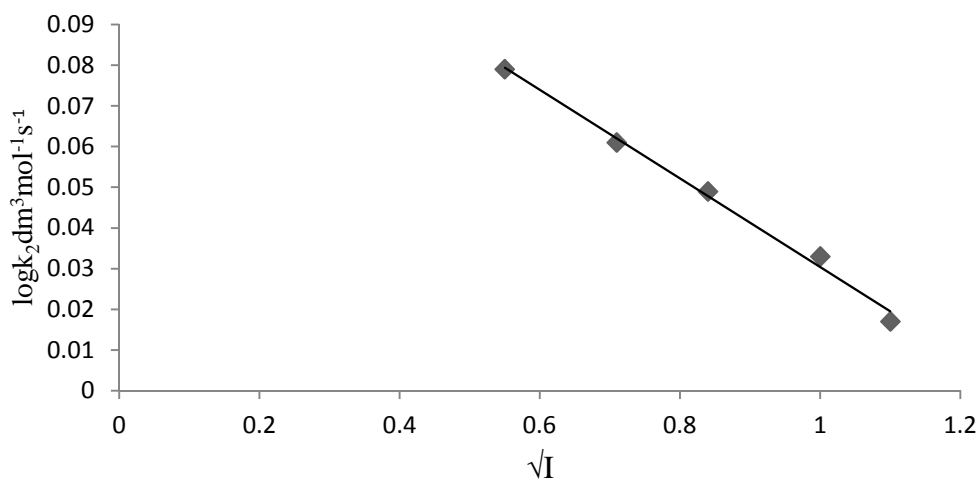**Figure 4:plot of log $k_2$versus √I for the reduction of TB by [ClO₄⁻]**
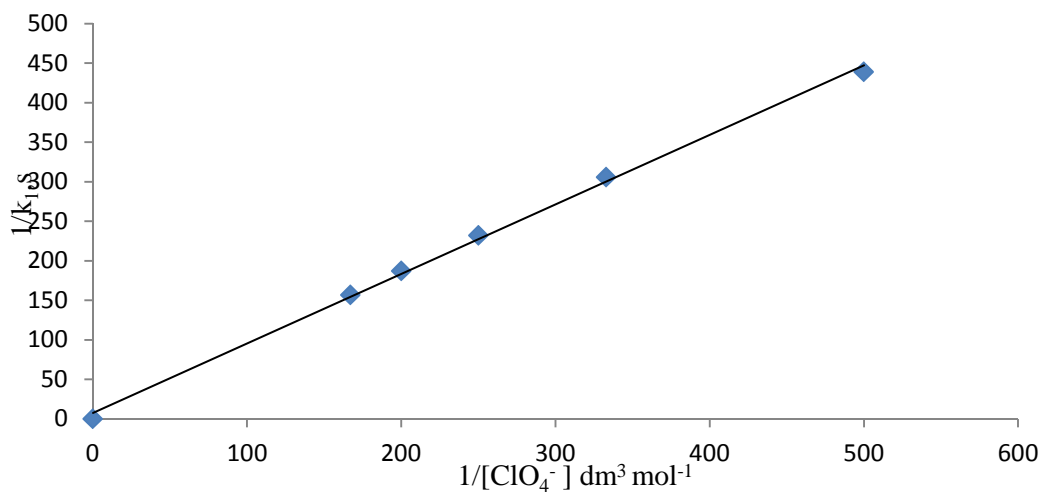
Figure 5: Michaelis - Menten plot of 1/ k_1 versus 1/ [ClO₄⁻] for the TB reduction by [ClO₄⁻]

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Table 4.7: Pseudo – first order and second order rate constants for the effect of added species X⁻ on the TB reduction by ClO₄⁻ at [TB⁺] = 1.0 x 10⁻⁴ mol dm⁻³, [ClO₄⁻] = 20.0 x 10⁻⁴ mol dm⁻³, [H⁺] = 1.0 x 10⁻² mol dm⁻³, I = 0.5 mol dm⁻³ and T = 30± 1˙C, λ_{max} = 600 nm

X⁻	10^4 [X] mol dm^{-3}	10^1 k$_1$ s^{-1}	10^1 k$_2$ dm^3 mol^{-1} s^{-1}
SO_4^{2-}	0.2	1.42	7.14
	0.4	1.41	7.02
	0.6	1.38	6.90
	0.8	1.37	6.84
	1.0	1.35	6.78
NO_3^-	0.2	2.09	10.44
	0.4	1.99	9.96
	0.6	1.90	9.48
	0.8	1.81	9.06
	1.0	1.73	8.64

CONCLUSION

The absence of kinetic and spectrophotometric evidence for intermediate complex formation in this reaction confirms an earlier suggestion that the reaction points towards outer sphere pathway. These views are further supported by the fact that Michaelis- Menten plots was linear with no appreciable intercept. The inhibition of the rate by added anion further confirms the presence of outer sphere mechanism. Outer sphere mechanism has also been Proposed for reactions between TB and ClO₄⁻

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