Research Article

Kinetics and Mechanisms of Toluidine Blue Reduction by Dithionite Ion in Aqueous Acidic Medium

*S. A. Hamza, J. F. Iyun, S. O. Idris

Department of Chemistry, Ahmadu Bello University, Zaria. Nigeria

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ABSTRACT

Kinetics of reduction of toluidine blue (hereafter referred to as TB^+) by sodium dithionite in aqueous hydrochloric acid medium has been studied spectroscopically at $\lambda = 600$ nm. The order of the reaction with respect to TB^+ and dithionite ion was found to be one and 1.39 respectively. The rate of the reaction increased with increase in $[H^+]$. Variation of the ionic strength and dielectric constant of the medium altered the rate of the reaction, addition anions $(X = SO_4^{2-}, NO_3^-)$ to the reaction mixture decreased the rate of the reaction. Spectroscopic and kinetic investigation showed no sign of intermediate complex formation; free radical polymerisation test showed the presence of free radicals. A plausible mechanism which accommodates all the experimental data was proposed. The rate law for the reaction conforms to the equation:

Rate $= k_4 K_2 [TB^+][S_2O_4^{2-}][H^+] + k_5 k_3 K_1^{\frac{1}{2}}[TB^+][S_2O_4^{2-}]^{\frac{1}{2}}[H^+]$

Key words: Kinetics, Mechanism, Toluidine blue, Dithionite ions.

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INTRODUCTION

Dithionite ion is a strong and versatile reducing agent, which is mechanistically complex, two electron reducing agent. It is used for bleaching, chemicals manufacture [1-3] and as a biochemical reductant [4]. Dithionite ion produces sulphonyl radical SO_2^{-} by reversible dissociation, both dithionite ion and its dissociation radicals are strong reducing agents. Redox potential of SO_2^{-} shows that it is stronger reducing agent than $S_2O_4^{2-}$. Redox reactions of flavodoxin [5], neutrophil cytochrome b-558 [6], and some haemoproteins [7-9] with dithionite occur mainly by a mechanism consistent with participation of SO_2^{-}.

Toluidine blue is a basic dye which finds much application in the biological system [10], and it is also used in textile industry for dyeing cotton [11]. Since toluidine blue and dithionite ion are important redox compounds in the biological system, then understanding the mechanisms of their redox reaction seems to be of significance so that their full potential can be harnessed.

EXPERIMENTAL SECTION

Commercially available reagents were used throughout this work without further purification, stock solution of the reagents were prepared by weighing appropriate amount and dissolving with distilled water and then made up to the mark in volumetric flask. Hydrochloric acid (Analar) was used to investigate the effect of $[H^+]$ on the rate of the reaction, the effect of ionic strength and dielectric constant of the reaction medium on the rate of the reaction was investigated by sodium chloride and acetone respectively.

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Preparation of toluidine blue solution
Toluidine blue dye, analar grade, was obtained from BDH chemical company. Stock solution of 1×10^{-3} mol dm^{-3} of the dye was prepared by accurately weighing 0.0077g using Mettler analytical balance, and dissolving in a 25 cm^3 volumetric flask and making up to the mark with distilled water. The electronic spectrum of the solution was obtained by measuring its absorbance using Corning 253 colorimeter, within a wavelength range of 400 - 700 nm. From the spectrum the wavelength of maximum absorption (λ_{max}) of 600 nm was obtained.

Preparation of sodium dithionite solution
Fresh solution of 1.0 mol dm^{-3} sodium dithionite was prepared each day, by accurately weighing 17.4110 g of sodium dithionite (B.D.H) and dissolving in a 100 cm^3 volumetric flask and made up to the mark with distilled water to make 1.0 mol dm^{-3} solution.

Kinetics

The course of the reaction was monitored by following the decrease in the absorbance of the solution at $\lambda_{max} = 600$ nm which is characteristic of toluidine blue, using Corning 253 colorimeter, all kinetic runs were conducted under pseudo - first order condition with the concentration of the reductant in at least 50fold excess over that of the oxidant. [H^+], ionic strength, I and temperature, T, were kept constants at 0.1, 0.5 mol dm^{-3} and 28 ± 1 ℃ respectively.

RESULTS AND DISCUSSION

Rate law
Under pseudo - first order condition, with [$S_2O_4^{2-}$] in a large excess over [TB^+], plots of log (A_∞ - A_t) against time, t were linear to about 90% extent of reaction (Fig. 1), this point to the first order kinetics on [TB^+], pseudo - first order rate constants k_1 were calculated from the gradients of these plots and these are presented in Table one. A logarithmic plot of pseudo - first order rate constants k_1 versus log [$S_2O_4^{2-}$] (Fig.2) was linear with a gradient of 1.39; this indicates fractional order kinetics with respect to dithionite ion, therefore the reaction is approximately five – half order overall. The five – half order rate constants $k_{5/2}$ obtained from = k_1 / [$S_2O_4^{2-}$]$^{1.39}$ are presented in Table one.

Reactions of toluidine blue were found to proceed through complex mechanisms involving varying order either with respect to toluidine blue or with respect to the other reactants. In the reaction of TB^+ with thiourea [12], the reaction is first order with respect to TB^+ and an order of 1.22 with respect to thiourea. The slightly higher reaction order was interpreted to mean that there existed a major pathway in which one molecule each of reductant and oxidant was involved in the rate determining step giving primarily first order kinetics, but a minor pathway was also present that was second order with respect to thiourea. Similarly reactions of dithionite ion were reported to display fractional order kinetics. This was explained to be due to the dissociation of dithionite ion in aqueous solution yielding either sulphonyl ion or sulphonyl radical according to equations (1) and (2):

$$S_2O_4^{2-} \rightleftharpoons 2SO_2^- \tag{1}$$
$$S_2O_4^{2-} \rightleftharpoons 2SO_2^{\bullet-} \tag{2}$$

Both dithionite ion and its dissociation product would then take part in a parallel reaction with the other reactant [13-16].

Effect of [H^+] on the reaction
The study of the effect of [H^+] on the reaction rate revealed that only the protonated form of the reactant is reactive. This was obtained by varying [H^+] within the range 0.05 – 0.4 mol dm^{-3}. The order with respect to [H^+] is one (Fig. 3), and plot of $k_{5/2}$ versus [H^+] gave a straight line which with no intercept (Fig. 4) suggesting that the $k_{5/2}$ varies with [H^+] according to equation (4), and that only the protonated form of the reactants are reactive.

$$k_{5/2} = a [H^+] \tag{3}$$

where a = 100.40 dm^6 mol^{-2} s^{-1}

Effect of ionic strength on the reaction
The effect of ionic strength on the reaction was investigated by varying the ionic strength of the medium within the range 0.2 – 0.8 mol dm^{-3}. The result implies that positive and negatively charged species are participating in the rate

determining step. This was evident from the observed decrease in the rate of the reaction with increase in ionic strength (figure 5) [17]. The trend portrayed by the variation of ionic strength was verified by investigating the effect of the changes in dielectric constant of the reaction medium. Decrease in dielectric constant of the medium enhanced the rate of the reaction.

Effect of Added ions

The rate constants of the reaction were found to be independent of added Ca^{2+} and Mg^{2+}. Addition of SO_4^{2-} and NO_3^- ions to the reaction mixture within the range $(1.0 - 100) \times 10^{-3}$ mol dm^{-3} significantly inhibit the rate constants of the reaction (Table 2). This is expected on the ground of simple electrostatic laws. The inhibitive effect of these ions suggests that the outer - sphere mechanism might be operating [18-19].
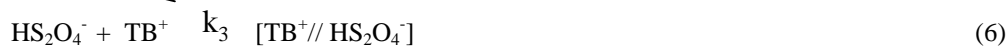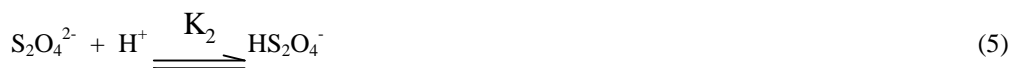
Test for Intermediate complex Formation

The results of the spectroscopic studies indicated no shift of the absorption maxima of 600 nm characteristic of TB^+. This suggests that an intermediate complex formation of significant stability during the reactions is very unlikely. Michaelis - Menten plot of $1/ k_1$ versus $1/ [S_2O_4^{2-}]^{1.39}$ gave a straight line which passed through the origin (Fig. 6). This further proved that this reaction involves no intermediate complex formation [20].

Test for Free Radical

Acrylamide which acts as a radical scavenger was added to the partially oxidized reaction mixture, followed by large excess of methanol to initiate free radical polymerisation. Formation of a layer of gelatinous precipitate indicates the presence of free radicals.

On the basis of the evidence obtained from experimental results the following mechanism was proposed for the reaction of TB^+ and $S_2O_4^{2-}$.

$$S_2O_4^{2-} \xrightleftharpoons{K_1} 2^\bullet SO_2^- \tag{4}$$

$$S_2O_4^{2-} + H^+ \xrightleftharpoons{K_2} HS_2O_4^- \tag{5}$$

$$HS_2O_4^- + TB^+ \xrightarrow{k_3} [TB^+// HS_2O_4^-] \tag{6}$$

$$^\bullet SO_2^- + TB^+ \xrightarrow{k_4} [TB^+//^\bullet SO_2^-] \tag{7}$$

$$[TB^+// HS_2O_4^-] \xrightarrow{k_5} Products \tag{8}$$

$$[TB^+//^\bullet SO_2^-] \xrightarrow{k_6} Products \tag{9}$$

Rate law: Equations 6 and 7 are the rate determining step, therefore:

$$Rate = k_4[HS_2O_4^-][TB^+] + k_5[^\bullet SO_2^-] [TB^+] \tag{10}$$

But $\quad [HS_2O_4^-] = K_2[S_2O_4^{2-}][H^+] \tag{11}$

$$[HSO_2^-] = k_3K_1^{\frac{1}{2}}[S_2O_4^{2-}]^{\frac{1}{2}}[H^+] \tag{12}$$

Therefore,
$$Rate = k_4K_2[TB^+] [S_2O_4^{2-}][H^+] + k_5 k_3K_1^{\frac{1}{2}}[TB^+] [S_2O_4^{2-}]^{\frac{1}{2}}[H^+] \tag{13}$$

Equation 13 is consistent with the observed first order with respect to TB^+ and H^+ respectively and the observed fractional order with respect to $S_2O_4^{2-}$. Since the derived rate law is in agreement with the experimental rate law, then the proposed mechanism is plausible.
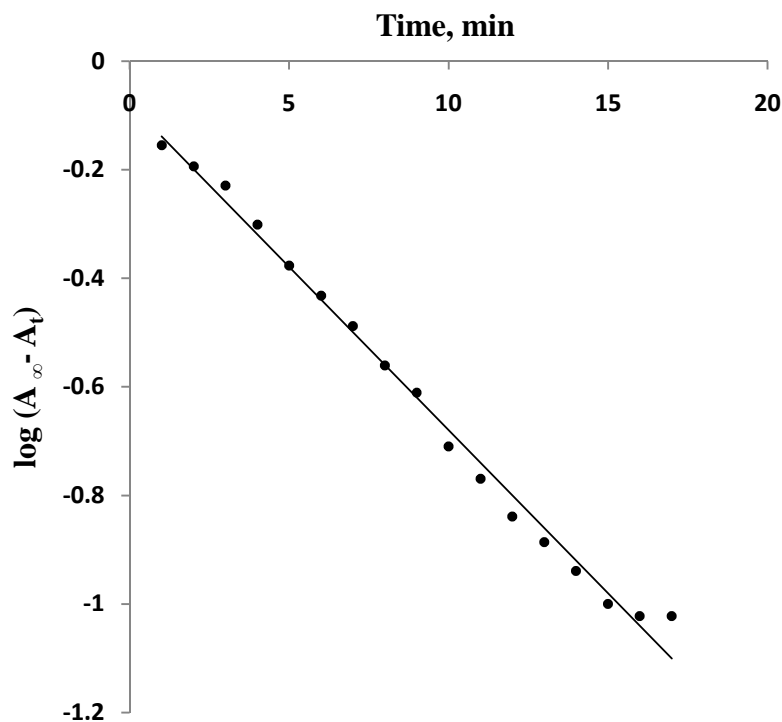
Figure 1: Typical pseudo - first order plot for the toluidine blue reduction by dithionite ions at $[TB^+] = 2.80 \times 10^{-5}$ mol dm^{-3}, $[S_2O_4^{2-}] = 1.40 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-1}$ mol dm^{-3}, I = 0.5 mol dm^{-3} and T = 28 ± 1 ℃

Table 1: Pseudo - first order and five-half order rate constants for the toluidine blue reduction by dithionite ions in aqueous HCl medium at $[TB^+] = 2.80 \times 10^{-5}$ mol dm^{-3}, T = 28 ± 1 ℃ and λ_{max} = 600 nm

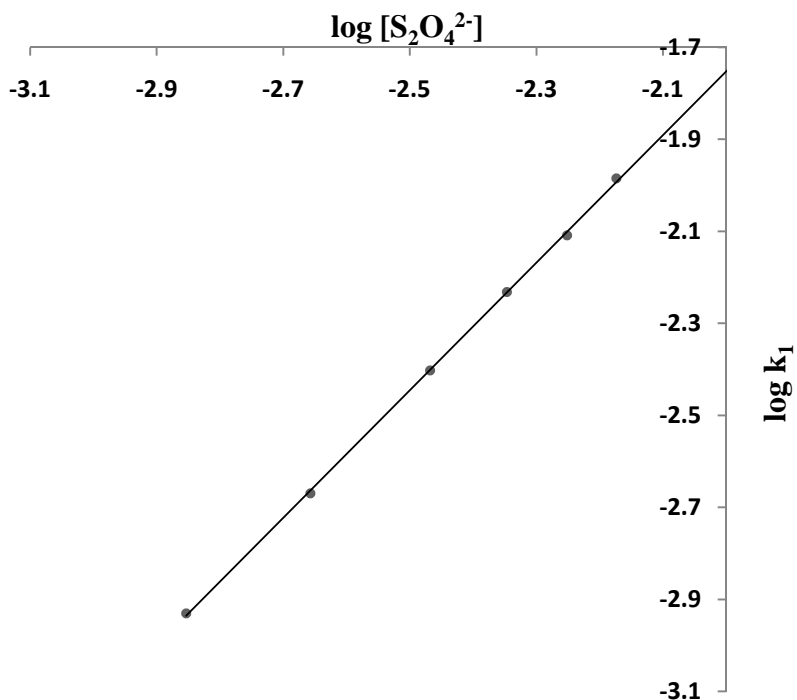| $10^3\,[S_2O_4^{2-}]$, mol dm^{-3}	$[H^+]$, mol dm^{-3}	I, mol dm^{-3}	$10^3\,k_1$, s^{-1}	$k_{5/2}$, dm^3 mol^{-1} s^{-1}
1.4	0.1	0.5	1.18	10.39
2.2	0.1	0.5	2.14	10.14
3.4	0.1	0.5	3.96	10.27
4.5	0.1	0.5	5.87	10.33
5.6	0.1	0.5	7.78	10.13
6.7	0.1	0.5	10.36	10.52
4.5	0.05	0.5	3.29	5.77
4.5	0.1	0.5	5.82	10.24
4.5	0.15	0.5	7.37	12.98
4.5	0.2	0.5	10.93	19.25
4.5	0.3	0.5	16.39	28.56
4.5	0.4	0.5	23.26	40.95
4.5	0.1	0.2	10.01	17.63
4.5	0.1	0.3	7.89	13.91
4.5	0.1	0.4	7.59	13.36
4.5	0.1	0.5	5.81	10.23
4.5	0.1	0.6	4.86	8.55
4.5	0.1	0.8	3.76	6.23
4.5	0.1	1.0	2.86	4.86

Figure 2: Pseudo - first order plot of log k_1 versus log $[S_2O_4^{2-}]$ for the toluidine blue reduction by dithionite ions at $[TB^+]$ = 2.80×10^{-5} mol dm^{-3}, $[H^+]$ = 0.1 mol dm^{-3}, I = 0.5 mol dm^{-3}, T = 28 ± 1 ℃ and λ_{max} = 600 nm
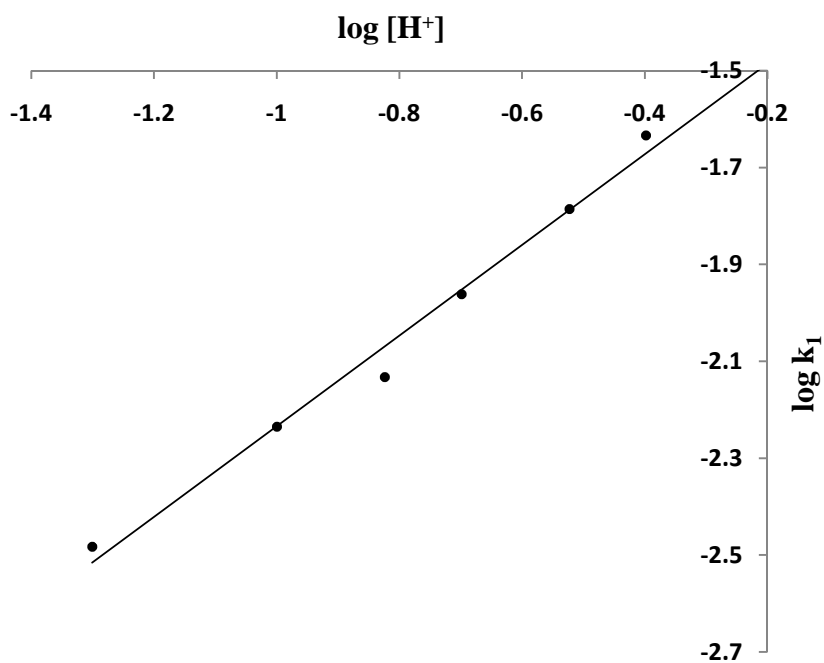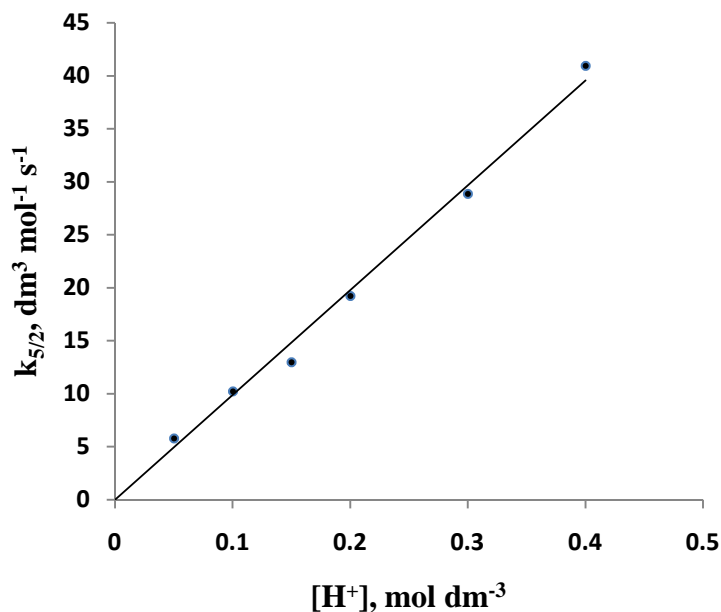

Figure 3: Plot of log k_1 versus log $[H^+]$ for the toluidine blue reduction by dithionite ion at $[TB^+]$ = 2.80×10^{-5} mol dm^{-3}, $[S_2O_4^{2-}]$ = 4.5×10^{-3} mol dm^{-3}, I = 0.5 mol dm^{-3}, T = 28 ± 1 ℃ and λ_{max} = 600 nm

Figure 4: Plot of $k_{5/2}$ versus [H$^+$] for the toluidine blue reduction by dithionite ion at [TB$^+$] = 2.8 × 10^{-5} mol dm^{-3}, [S$_2$O$_4$$^{2-}$] = 4.5 × 10^{-3} mol dm^{-3}, I = 0.5 mol dm^{-3}, T = 28 ± 1 ℃ and λ$_{max}$ = 600 nm

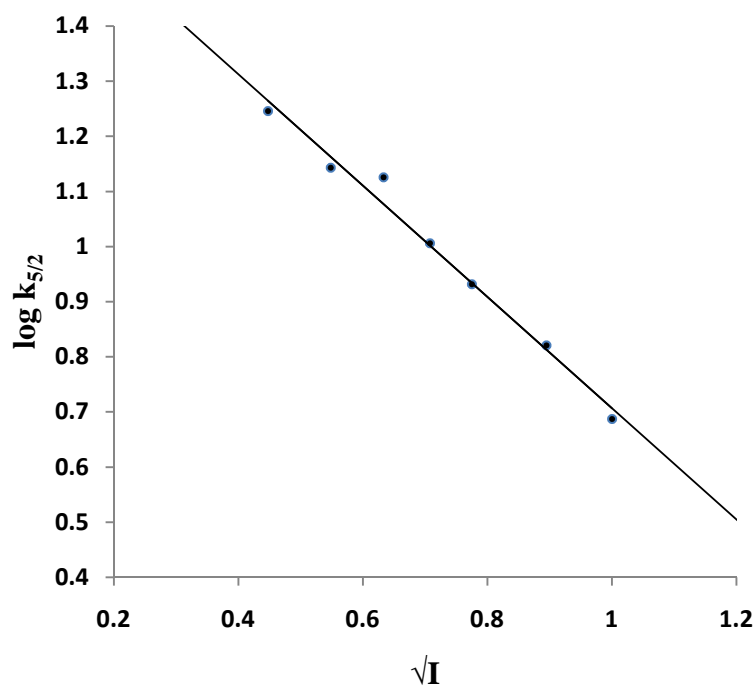**Figure 5: Plot of log $k_{5/2}$ versus √I for the toluidine blue reduction by dithionite ion at [TB$^+$] = 2.80 × 10^{-5} mol dm^{-3}, [S$_2$O$_4$$^{2-}$] = 4.50 × 10^{-3} mol dm^{-3}, [H$^+$] = 0.1 mol dm^{-3}, T = 28 ± 1 ℃ and λ$_{max}$ = 600 nm**
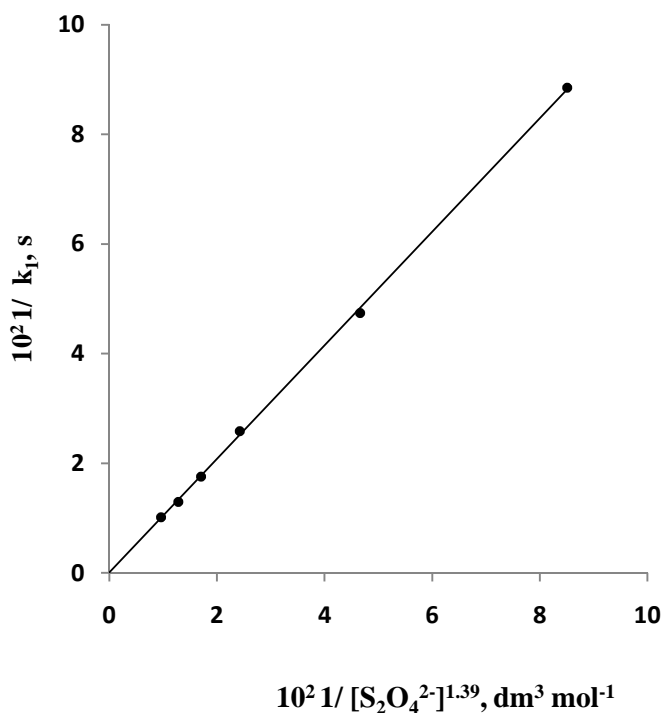
Figure 6: Michaelis - Menten plot of $1/k_1$ versus $1/[S_2O_4^{2-}]$ for the toluidine blue reduction by dithionite ion at $[TB^+] = 2.80 \times 10^{-5}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-1}$ mol dm^{-3}, I = 0.5 mol dm^{-3} and T = 28 ± 1 ℃

Table 2:   Pseudo - first order and five - half order rate constants for the effect of added anions on the toluidine blue reduction by dithionite ion at $[TB^+] = 2.80 \times 10^{-5}$ mol dm^{-3}, $[S_2O_4^{2-}] = 4.5 \times 10^{-3}$, $[H^+] = 1.0 \times 10^{-1}$ mol dm^{-3}, I = 0.5 mol dm^{-3} and T = 28 ± 1 ℃

$10^3[X]$, mol dm^{-3}	$10^3 k_1$, s^{-1}	$k_{5/2}$, dm^3 mol^{-1} s^{-1}
X = $[SO_4^{2-}]$		
	5.24	9.37
10	3.72	6.65
20	2.68	4.79
40	2.14	3.83
80	1.40	2.51
100	0.93	1.66
X = $[NO_3^-]$		
1	5.19	9.28
10	4.11	7.35
20	3.99	7.14
40	3.42	6.12
80	2.64	4.72
100	2.02	3.61

CONCLUSION

The reaction was found to be aproxamately five - half overall at constant $[H^+]$. And the proposed reaction steps point to an outer sphere electron transfer process, considering the fact that addition of foreign ions led to the inhibition of the reaction rates, when the reaction mixture was scanned as the reaction progresses the maximum remains at

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600nm, also Michaelis-Menten plot of $1/k_1$ against $1/[S_2O_4^{2-}]^{1.39}$ passed through the origin. These points greatly favours the outer sphere mechanistic pathway for this reaction

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