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KINETICS AND MECHANISM OF THE REDOX REACTION OF ORANGE II WITH THIOSULPHATE ION IN AQUEOUS ACID

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ABSTRACT

The kinetics of the redox reaction of orange II (OR^-) with thiosulphate ion has been studied spectrophotometrically at constant ionic strength, I = 0.50 mol dm^{-3} (NaCl), $[H^+] = 5.0 \times 10^{-2}$ mol dm^{-3} (HCl) and T = $26 \pm 1°C$. The redox reaction displayed a stoichiometry of 1:4 and rate
equation for the reaction is,
$-d[OR^-]/dt = (a + b[H^+])[OR^-][S_2O_3^{2-}]$

The rate of the reaction increases with increase in acid concentration and in the ionic strength of reaction medium. The reaction shows a first order dependence on [oxidant] and [reductant]. Added cations and anions inhibited the rate of the reaction. Michaelis – Menten's plot of $1/k_1$ versus $1/ S_2O_3^{2-}$ and spectrophotometric test suggest absence of an intermediate in the rate determining step. Free radical test did not yield gel formation. Based on the results obtained, this reaction is probably operating through the outersphere mechanism.

Keywords: Thiosulphate; outersphere; kinetics; intermediate

1.0 INTRODUCTION

Azo compounds are a class of chemical compounds that are continuously receiving attention in scientific research (Kirkan, 2008, Seferoglu, 2009). They are usually strongly coloured compounds which can be intensely yellow, red, orange, blue or even green, depending on the exact structure of the molecule. As a result of their colour, azo compounds are tremendous importance as dyes and also as pigments for a long time (Ebenso *et al.,* 2008). In fact, about half of the dyes in industrial use today are azo dyes, which are mostly prepared from diazonium salts (Zollinger, 1991; Robert, 2011). The structural features in organic compounds, that usually produce colour are > C = C <, –N = O, –N=N–, aromatic rings, > C = O and $–NO_2$. Most importantly, the groups that invariably confer colour are the azo (–N=N–) and nitroso (–N=O) while the other groups actually do so under certain circumstances (Otutu, 2013). However, in spite of these and other uses of the dye, the knowledge on its redox kinetics is scanty. The desire to gain further insight into the kinetic behaviour and the mechanisms of the redox chemistry of this dye has prompted the need to carry out this research.

Thiosulphate ($S_2O_3^{2-}$) ion is a moderately strong reducing agent that has been widely used to fix photographic images, extract silver from ore, as an antidote to cyanide poisoning, as a mordant in the dye industry and to determine the oxidizing agents by an indirect procedure that involves iodine as intermediate. With iodine, thiosulphate ion is oxidised to tetrathionate ($S_4O_6^{2-}$) (Patel *et a*l., 2009). Despite its applications, the redox reaction of this reductant with orange II has not been documented in the literature. This prompted the investigation of the electron transfer reaction of thiosulphate ion with orange II in an acidic medium. The kinetic data generated will assist in the better understanding and effective utilisation of its reactions.

2.0 MATERIALS AND METHODS

2.1 Materials and Reagents

Materials and Reagents used for this work are UV-Vis spectrophotometer (JENWAY) 6405, weighing balance, Volumetric flask, FTIR, Orange II (the dye was synthesised in the laboratory), sodium thiosulphate (AR), HCl (BDH), mercury(I) nitrate and distilled water.

2.2 Preparation of solutions:

A 1.0 x 10^{-3} mol dm^{-3} stock solution of orange II was prepared by dissolving 0.0876g in 250 ml volumetric flask using distilled water. A 0.1 M stock solution of sodium thiosulphate as prepared by accurately weighing 3.9525g of $Na_2S_2O_3$ and dissolving in 250 cm^3 volumetric flask; and making up to the mark with distilled water. A 1.0 M solution of hydrochloric acid (BDH) was prepared (36% w/w and specific gravity of 1.18) and standardized titrimetrically (Idris *et al.,* 2005).

2.3 Kinetics measurements:

The stoichiometry of the reaction was determined spectrophotometrically using the mole ratio method by keeping the concentration of the dye constant at 5.0×10^{-5} mol dm^{-3}, $[H^+] = 5.0 \times 10^{-2}$ M, I = 0.50 C^2 M, λ_{max} = 484 nm, T=26 ± 1°C, and $[S_2O_3^{2-}] = 5.0 \times 10^{-6}$- 2.5×10^{-4} M. The stoichiometry was determined from the plot of absorbance versus [reductant]/[oxidant] after the reaction had reached completion by the observation of a steady zero absorbance value over a period of two days.

A UV-Vis spectrophotometer 6405 was used to follow the decrease in absorbance of the dye at 484nm, =26±1°C, I = 0.5 C^2mol dm^{-3} (NaCl), and $[H^+]= 5.0 \times 10^{-2}$ $moldm^{-3}$ (HCl). The kinetic runs were conducted under pseudo-first-order conditions with $[S_2O_3^{2-}]$ in at least 90-fold excess over$[OR^-]$.The pseudo-first-order plots of log (A_t - A_∞) versus time were made , (where A_∞ and A_t are the absorbance at the end of the reaction and at time, t respectively). From the slope of the plots, the pseudo-first-order rate constant (k_1) was determined (Mohammed *et al.*, 2009).

2. 4 Effect of hydrogen ion concentration and ionic strength on the reaction rate

The effect of acid on the rate of reaction was investigated by varying [H^+] in the range (0.5–7.0) × 10^{-2} M while [OR^-]and [$S_2O_3^{2-}$] were kept constant at 26 ± 1°C and I = 0.5 C^2M (NaCl). This range was chosen because acid was stable at such range. The effect of ionic strength on the rate of the reaction was studied in the range of 0.2– 10.0 M (NaCl) while the concentrations of other reagents were kept constant at 26 ± 1°C.

2. 5 Effect of added ions on the reaction rate

The effect of added ions on the reaction rate was observed by addition of various amount of ions (Ca^{2+}, Mg^{2+}, SO_4^{2-} and CH_3COO), while the concentrations of OR^-, the oxidant, hydrogen ion, temperature and ionic strength of reaction medium were kept constant (Myek *et al.,* 2020).

2.6 Test for free radicals

About 5cm^3 of acrylonitrile was added to a partially oxidised reaction mixture containing various concentrations of oxidant, reductant and hydrogen ion. This was followed by addition of an excess of methanol. The same treatment was applied to the solution of oxidant and reductant separately as a control.

2.7 Products analysis

At the completion of the reaction, the reaction mixture was analysed for possible formation of organic and inorganic products in the reaction. The products were confirmed by both chemical test and infrared spectroscopy as follows:

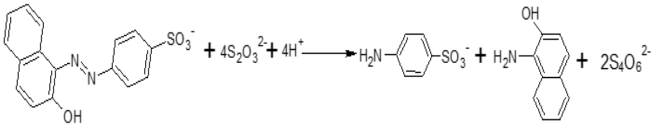
To test for the presence of sulphanilic acid as one of the expected products; conc. HCl (4 cm^3) was added to the reaction mixture in a 50 cm^3 beaker and cooled in an ice-bath to 4 ^{0}C. Few drops of sodium nitrite solution were added to the mixture while keeping the contents on beaker in the ice-bath. A diazonium salt was formed. A solution of 2-naphthol prepared in 0.1 mol dm^{-3} NaOH was added to the diazonium salt and stirred for 30 minutes. To test for the presence of 2-naphthol, a few drops of $FeCl_3$ solution was added to the reaction mixture and a faint green colour was observed (Stephanie, 2008).

The reaction mixture was extracted six times with diethyl ether. The ether extract was dried with anhydrous $MgSO_4$ and evaporated using water-bath. The product was separated using column chromatography and FTIR spectra of the fractions was obtained using Shimadzu FTIR-8400S and recorded as product 1 and 2 in figures 4 and 5. Inorganic products was confirmed by qualitative inorganic analysis (Jeffery *et al.,* 1991., Svehla and Sivasankar's, 2012;).

3. 0 RESULTS AND DISCUSSION

3.1 Stoichiometry and products analysis

The result of stoichiometric studies reveals that one mole of OR^- reacted with four moles of $S_2O_3^{2-}$. Hence the overall equation for the reaction is shown in equation (1).



(1)

Sulphanilic acid and 2-naphthol were confirmed as an organic product as determined by chemical test and FTIR (Figures 4 and 5). A stoichiomerty of 1:1 has been reported for the oxidation of thiosulphate by hexacyanoferrate(III) in aqueous perchloric acid medium (Patil *et al.,* 2009). Presence of $S_4O_6^{2-}$ was confirmed qualitatively by the addition of mercury(I) nirate to the reaction solution which produced a yellow precipitate, which became black on heating, indicating the presence of tetrathionate as one of the product (Patil *et al.,* 2009).

3.2 Kinetic studies

Plot of logk$_1$ versus log[$S_2O_3^{2-}$] gave a slope of one (Figure 1), indicating that the reaction is first order with respect to [$S_2O_3^{2-}$]. Similar first order dependence with respect to [$S_2O_3^{2-}$] was reported in its reaction with ferrate ions (Johnson and Read, 1996) and chlorine dioxide (Pan and Stanbury, 2014).

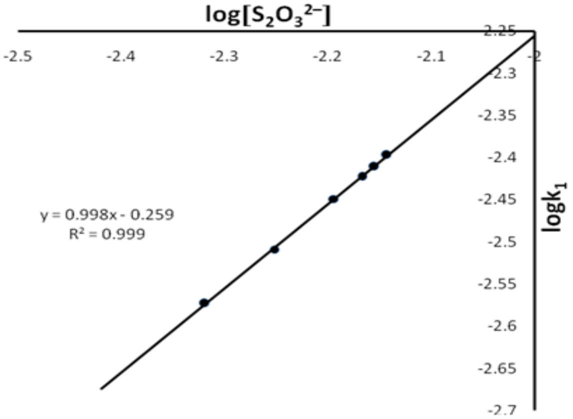


Figure 1: Plot of log k$_1$ versus log[$S_2O_3^{2-}$] for the redox reaction of OR^- with $S_2O_3^{2-}$ at [OR^-] = 5.0 × 10^{-5} M, [$S_2O_3^{2-}$] = (4.8 – 7.2) × 10^{-3} M, [H^+] = 50.0 × 10^{-3} M, I = 0.50 C^2M, λ = 484 nm and T = 26 ± 1°C

3.3 Effect of changes in ionic strength on reaction rate

Effect of changes in ionic strength of the reaction medium indicated that the rate of the reaction increases with increase in ionic strength. This obeyed a positive Bronsted-Debye salt effect, implying that the rate determining step is composed of reactants of like charges (Patil *et al;* 2009). Plot of logk$_2$ against $I^{1/2}$ (Figure 2) gave a slope of 0.66 (R^2 = 0.94).

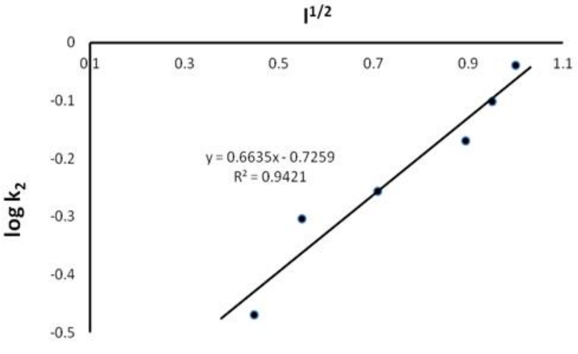


Figure 2: Plot of logk$_2$ versus $I^{1/2}$ for the redox reaction between orange II and $S_2O_3^{2-}$ at [OR^-] = 5.0 × 10^{-5} M, [$S_2O_3^{2-}$] = 6.8 × 10^{-3} mol, dm^{-3}, [H^+] = 5.0 × 10^{-2} M, I = 0.50 M, λ = 484 nm and T= 26 ± 1 °C

3.4 Effect of hydrogen ion on the reaction rate

The reaction increases with increase in [H^+] in the range of (0.5 – 7.0) × 10^{-2} mol dm^{-3} investigated (Table 1). Plot of logk_{obs} versus log[H^+] gave a slope of one indicating that the reaction is first order with respect to [H^+]. Similar result has been reported for the redox reaction of $S_2O_3^{2-}$ (Patil *et al.,* 2009). The plot of k_2 versus [H^+] was linear with an intercept in the acid concentration range investigated. This indicate that a pre-equilibrium between protonated and deprotonated forms of a reactant is rapid, that the protonation equilibrium constant is small, that both the forms are reactive, but the protonated form is more reactive (Gupta and Gupta, 1984)
The rate equation for the reaction is shown in equation 2.

$$-d[OR^-] = (a + b[H^+])[OR^-][S_2O_3^{2-}] \quad (2)$$

Table 1: Pseudo – first order and second order rate constants for the reaction of OR^- and $S_2O_3^{2-}$ at [OR^-] = 5.0 × 10^{-5} M, λ = 484 nm and T = 26 ± 1°C

$10^3[S_2O_3^{2-}]$, mol dm^{-3}	$10^2[H^+]$, (M)	I, C^2(M)	10^3k_1, (s^{-1})	k_2, ($M^{-1}s^{-1}$)
4.8	5.0	0.5	2.67	0.556
5.6	5.0	0.5	3.10	0.554
6.4	5.0	0.5	3.56	0.556
6.8	5.0	0.5	3.78	0.556
7.0	5.0	0.5	3.88	0.554
7.2	5.0	0.5	4.01	0.557
6.8	0.5	0.5	2.15	0.316
6.8	2.0	0.5	3.07	0.452
6.8	4.0	0.5	3.39	0.499
6.8	5.0	0.5	3.78	0.556
6.8	6.0	0.5	3.85	0.566
6.8	7.0	0.5	4.03	0.593
6.8	5.0	0.2	2.30	0.338
6.8	5.0	0.3	3.38	0.497
6.8	5.0	0.5	3.77	0.554
6.8	5.0	0.8	4.61	0.678
6.8	5.0	0.9	5.37	0.790
6.8	5.0	1.0	6.22	0.915

3.5 Test for free radicals and effect of added ions on reaction rate

Added cation and anion inhibited the rate of the reaction (Tables 2 and 3). This inhibited effect by the ions suggested that the reaction might be operating via the outersphere mechanism (Mayer and Taube, 1987).

Table 2: Rate data for the effect of added cations (Ca^{2+} and Mg^{2+}) on the rate of reaction of OR^- and $S_2O_3^{2-}$ at [OR^-] = 5.0 × 10^{-5} mol dm^{-3}, [$S_2O_3^{2-}$] = 6.8 × 10^{-3} M, [H^+] = 5.0 × 10^{-2} M, I = 0.50 C^2M, λ = 484 nm and T = 26 ± 1 °C

Ion	10^3 [ion], mol dm^{-3}	10^3 k_1, s^{-1}	k_2, dm^3 mol^{-1} s^{-1}
	0.0	3.78	0.556
Ca^{2+}	20.0	3.62	0.532
	40.0	3.39	0.498
	60.0	3.24	0.476
	80.0	2.67	0.393
	100.0	2.26	0.332
	150.0	1.72	0.253
	0.0	3.77	0.555
Mg^{2+}	20.0	3.68	0.541
	40.0	3.49	0.513
	60.0	3.22	0.474
	80.0	2.65	0.390
	100.0	2.11	0.310
	150.0	1.92	0.282

Table 3: Rate data for the effect of added anions (CH_3COO^- and SO_4^{2-}) on the rate of reaction of OR^- and $S_2O_3^{2-}$ at [OR^-] = 5.0 × 10^{-5} M, [$S_2O_3^{2-}$] = 6.8 × 10^{-3} M, [H^+] = 5.0 × 10^{-2} M, I = 0.50 C^2M, λ = 484 nm and T = 26 ± 1 °C

Ion	10^3 [ion], mol dm^{-3}	10^3 k_1, s^{-1}	k_2, dm^3 mol^{-1} s^{-1}
	0.0	3.78	0.556
CH_3COO^-	20.0	3.45	0.508
	40.0	3.22	0.474
	60.0	2.63	0.387
	80.0	2.13	0.313
	100.0	1.96	0.288
	150.0	1.15	0.169
	0.0	3.78	0.556
SO_4^{2-}	20.0	3.15	0.463
	40.0	2.76	0.406
	60.0	2.30	0.338
	80.0	2.02	0.297
	100.0	1.54	0.226
	150.0	1.08	0.159

Free radical test did not yield gel formation or if present it might be transient. Myek *et al.,* 2020, reported similar results. Spectroscopic evidence and the Michaelis - Menten's plot of $1/k_1$ versus $1/S_2O_3^{2-}$ (Figure 3) suggest that intermediates may be unimportant in the rate determining step.

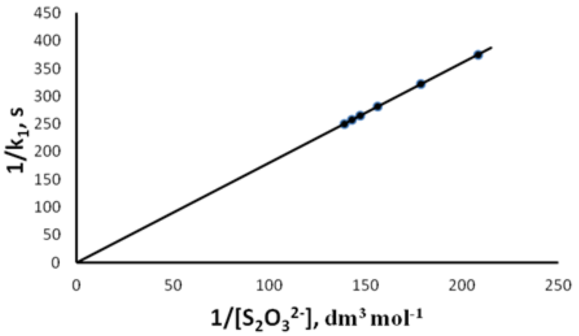


Figure 3: Michaelis - Menten plot for the redox reaction between orange II and $S_2O_3^{2-}$ at [OR^-] = 5.0 × 10^{-5} M, [$S_2O_3^{2-}$] = (4.8 – 7.2) × 10^{-3} M, [H^+] = 5.0 × 10^{-2} M, I = 0.50 C^2M, λ = 484 nm and T= 26 ± 1 °C

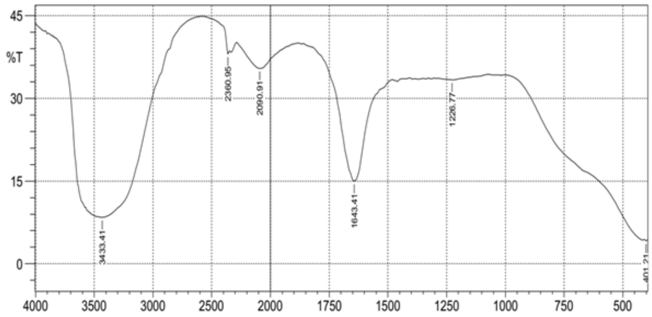


Figure 4: FTIR Result for $S_2O_3^{2-}$ product (1)

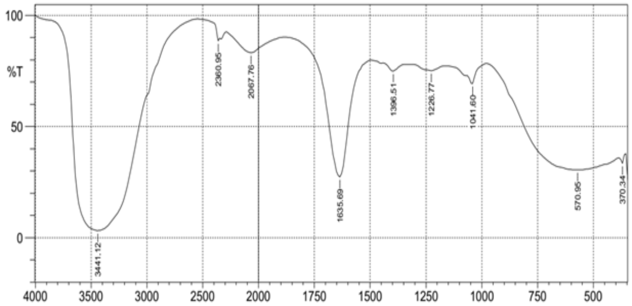
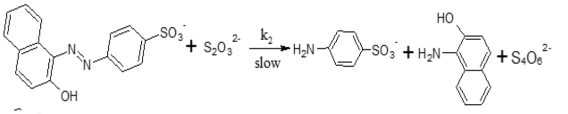


Figure 5: FTIR Result for $S_2O_3^{2-}$ product (2)

On the basis of the above findings, the following mechanisms are proposed for this reaction (equations 3 – 9).

$$S_2O_3^{2-} + H^+ \overset{K_1}{\rightleftharpoons} HS_2O_3^- \qquad (3)$$



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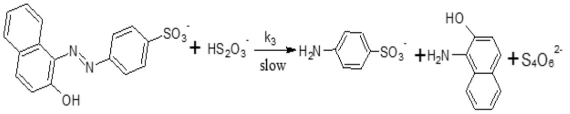

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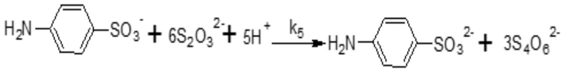

(6)

$$Rate = k_2[OR^-][S_2O_3^{2-}] + k_3[OR^-][HS_2O_3^-] \qquad (7)$$

$$[HS_2O_3^-] = K_1[S_2O_3^{2-}][H^+] \qquad (8)$$

$$Rate = k_2[OR^-][S_2O_3^{2-}] + k_3K_1[OR^-][S_2O_3^{2-}][H^+] \qquad (9)$$

Equation 9 is analogous to equation 2 where a = k_2 and b = k_3K_1

4. Conclusion

The redox reaction of orange II and thiosulphate ions in aqueous acidic medium showed a stoichiometry of 1:4; a first order was observed for OR^- and $S_2O_3^{2-}$ ions. The rate constant increases with increase in acid and ionic strength of the reaction medium. Spectroscopic evidence and the Michaelis-Menten's plot of $1/k_1$ versus 1/ $S_2O_3^{2-}$ suggest that intermediates may be unimportant in the rate determining step. Polymerization test suggests the absence of free radicals in the reaction medium. Based on the above results, it is proposed that the reaction most probably operates through the outer-sphere mechanism

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