

Kinetics and Mechanism of the Redox Reaction of Orange II with Sulphite Ion in Aqueous Acid

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ABSTRACT

A chemical oxidation method is the most acceptable promising alternative for the degradation of persistent pollutants such as an azo dye with limited ability to accumulate in the environment. It is the only degradation method that has the potential to completely convert harmful organic pollutant into biodegradable harmless products. The redox reaction of orange (OR⁻) with sulphite ion in aqueous hydrochloric acid has been studied at an ionic strength of I = 0.50 mol dm⁻³ (NaCl), [H⁺] = 5.0 × 10⁻² mol dm⁻³ (HCl), T = 21 ± 1°C and λ = 484 nm. The redox reaction showed that one mole of OR⁻ reacted with two moles of SO₃²⁻. The reaction showed a first order dependence on [OR⁻] and [SO₃²⁻]. Changes in ionic strength of the reaction medium indicated that the rate constant increases with increase in ionic strength. The reaction was found to be independent of [H⁺] in the range investigated, indicating that the reaction occurs through an acid-independent pathway. Spectroscopic evidence and Michaelis - Mentens plot of 1/k₁ versus 1/SO₃²⁻ suggest the possible absence of an intermediate in the rate determine step. Free radical test did not yield gel formation during the course of the reaction. Added cations and anions accelerated the rate of the reaction. This effect exerted by the ions suggested that the reaction might be operating via the outersphere mechanism.

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INTRODUCTION

Sulphite ion has received a lot of attention as a powerful reductant in the past decade. It has been observed to reduce metal ions and other oxidants by a variety of mechanisms and with varying stoichiometry (Babatunde, 2009). The kinetics of sulphite ion in acidic aqueous media has been reported by several researchers. Iyun and coworkers studied the oxidation of sulphite ion by diaquotetrakis (2,2'-bipyridine)-μ-oxodiruthenium(III) ion in perchloric acid. The reaction was found to be first order with respect to sulphite and oxidant and second order overall. Added anions catalyzed the reaction. There was no evidence for intermediate complex formation and non-conformity of the observed kinetics data with the Michaelis-Menton plot suggested that the reaction most probably occur by the outersphere mechanism. The stoichiometry was found to be 1:1 (Iyun *et al.*, 1992). The rate of the reaction was given by equation 1.

$$-d[\text{H}_2\text{ORuORuH}_2\text{O}]^{4+}/dt = k_2[\text{H}_2\text{ORuORuH}_2\text{O}]^{4+}[\text{SO}_3^{2-}] \quad (1)$$

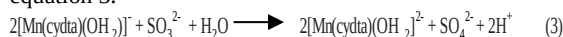
Jonnalagadda and Gollapalli (2000) studied the kinetics of the reduction of toluidine blue (TB⁺) with sulphite ion. The observed stoichiometry is 1:1 which is illustrated in equation (2).



The rate determining steps involves a two electron transfer. The first order dependence of the reaction rate on the reactants and observed negative kinetic salt effect suggests that the rate limiting involves one mole each of SO₃²⁻ and TB⁺. Thus, the rate limiting steps of the reaction is a nucleophilic attack of sulphite ion on TB⁺. The activated complex subsequently hydrolyses to toluidine white (TBH) and sulphate.

The kinetics and mechanism of the oxidation of sulphite ion by the Mn(III)-cydta complex ion have been studied. The study showed that S(IV) is oxidised in two parallel paths; the order with respect to [S(IV)] is one in one of the paths and

two in the other. Increase in [H⁺] was found to decrease the reaction rate. However, the rapid scan of the reaction mixture and the measurement of the initial absorbance of the reaction mixture at different wavelengths at the beginning of the reaction suggest the outersphere mechanism which is further supported by the Marcus cross relation (Utra *et al.*, 1995). The stoichiometry of the reaction was found to be 2:1 as in equation 3.



Despite the several reactions of sulphite ion in aqueous acid, its redox reaction with OR⁻ has not received much attention. This prompted the research to be carried out to explore more on its redox reaction with orange II.

MATERIALS AND METHODS

Orange II (0.0876 g) was dissolved in 250 cm³ volumetric flask containing distilled water and made up to the mark with distilled water. A 1.2604 g of Na₂SO₃ (BDH) was dissolved in 250 cm³ flask containing distilled water and made up to the mark with distilled water. A stock solution of hydrochloric acid (0.1 mol dm⁻³ HCl) was made by diluting 2.15 cm³ of 36% HCl (specific gravity 1.18) in 250 cm³ volumetric flask and made up to the mark with distilled water. The solution was then standardised against weighed amount of sodium carbonate using methyl orange as indicator. Standard solutions, 1.0 mol dm⁻³ each of these compounds was prepared by dissolving 1.46g (NaCl), 3.15 g (Na₂SO₄), 0.059 g (CaCl₂·2H₂O), 2.38 g(MgCl₂) and 2.05 g(CH₃COONa) in distilled water and made up to the mark in 25 cm³ volumetric flask. All the reagents were BDH grade.

Stoichiometric Studies

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method

(Idris *et al.*, 2015). The concentration of the OR^- was kept constant while that of the oxyanion was varied as follows: $[\text{OR}^-] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{SO}_3^{2-}] = (0.1 - 2.0) \times 10^{-4} \text{ mol dm}^{-3}$, $T = 21 \pm 1^\circ\text{C}$, $[\text{H}^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 0.50 \text{ mol dm}^{-3}$ (NaCl) and $\lambda_{\text{max}} = 484 \text{ nm}$. The absorbance of the reaction mixture was measured at 484 nm until the completion of the reaction as indicated by a constant absorbance value (A_∞) over a period of two days. Plots of absorbance versus mole ratio $[\text{OR}^- : \text{reductants}]$ was made. Point of inflection in these plots gave the stoichiometry of this reaction.

Kinetic Studies

The rate of the reaction was monitored using UV-Vis spectrophotometer (JENWAY) 6405. The rate of reaction of SO_3^{2-} with OR^- was studied by monitoring the decrease in absorbance of OR^- at 484 nm. All kinetic measurements were carried out under pseudo - first order condition with oxoanion concentration in excess over OR^- concentration. The $[\text{H}^+]$, ionic strength and temperature of each of the reaction systems were maintained constant. Pseudo - first order rate constants for the reactions were obtained from the plot of logarithm of absorbance difference against time (i.e., $\log (A_t - A_\infty)$ where A_t is the absorbance at time, t and A_∞ is the absorbance at infinity. The second order rate constants, k_2 , was determined from k_1 as $k_2 = k_1/[\text{oxidant}]$ (Onu *et al.*, 2009).

Effect of Hydrogen Ion Concentration on the Reaction Rate

The effect of changes in the hydrogen ion concentration on the reaction rate was investigated by keeping the concentration of the reactants constant while varying the hydrogen ion concentration in the range $(3.0 - 20.0) \times 10^{-2} \text{ mol dm}^{-3}$. The ionic strength of the reaction medium was maintained at 0.50 mol dm^{-3} for the system investigated. The order of reaction with respect to hydrogen ion concentration was obtained from the slope of the plot of $\log k_1$ versus $\log [\text{H}^+]$. Variation of acid dependent second order rate constants with $[\text{H}^+]$ was obtained by plotting k_2 against $[\text{H}^+]$.

Effect of Ionic Strength and Dielectric Constant of the Reaction Medium on the Reaction Rate

The effect of ionic strength on the rate of reaction was investigated over the range of $1.0 - 10.0 \text{ mol dm}^{-3}$ while other reaction conditions were kept constant.

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 (Idris *et al.*, 2014).

Test for Free Radicals

About 5 cm^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.

Spectrophotometric Test for Intermediate

Test for the presence of stable, detected intermediate formed during the course of the reaction was carried out spectrophotometrically using UV-Vis spectrophotometer (JENWAY) 6405. Electronic spectra of partially reacted reaction mixtures were obtained in the region 400-700 nm and compared with the spectrum of the dye.

Products Analysis

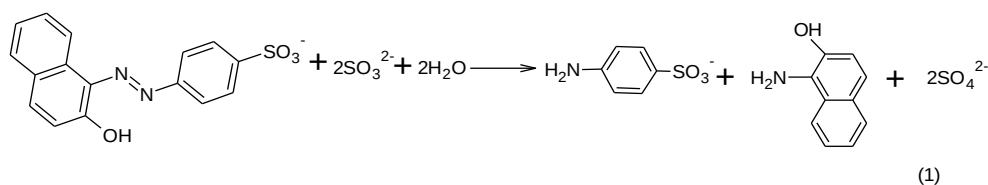
At the completion of the reaction, the reaction mixtures were analysed for possible formation of organic and inorganic products in each of the reactions. The products were confirmed by both chemical test and infrared spectroscopy as follows:

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°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 in Figure 1 and 2. Inorganic products were confirmed by qualitative inorganic analysis (Svehla and Sivasankar's, 2012; Jeffery, Bassett *et al.*, 1991).

RESULTS AND DISCUSSION

The result of stoichiometry study showed that one mole of OR^- reacted with two moles of SO_3^{2-} . Hence the overall equation for the reaction is shown in equation (1).



However, a stoichiometry of 1:1 was reported for the redox reaction of sulphite ion with indigo carmine (Edokpayi *et al.*, 2011). The presence of SO_4^{2-} was confirmed by the addition of BaCl_2 followed by HCl which formed an insoluble white precipitate in excess HCl. Sulphanilic acid and 2-naphthol

were confirmed as an organic products as determined by chemical test. The pseudo - first order plots of $\log (A_t - A_\infty)$ versus time (Figure 1) for this reaction was linear; the linearity of these plots indicates that these reactions are first order with respect to $[\text{OR}^-]$.

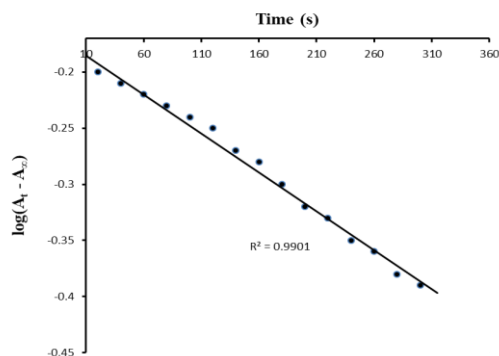


Figure 1: Pseudo-First Order Plot for the Redox Reaction of OR^- with SO_3^{2-} at $[\text{OR}^-] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{SO}_3^{2-}] = 7.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 0.50 \text{ mol dm}^{-3}$, $\lambda = 484 \text{ nm}$ and $T = 21 \pm 1^\circ \text{C}$

Plot of $\log k_1$ versus $\log[\text{SO}_3^{2-}]$ (Figure 2) gave a slope of one, indicating that the reaction is first order with respect to $[\text{SO}_3^{2-}]$. Similar result was obtained in the redox reaction of indigo carmine with sulphite ion in acidic medium (Edokpayi,

2011). First order reaction was also observed in the reaction of malachite green with sulphite ion (Imam *et al.*, 2018).

The rate law for the reaction is shown by Equation 2.

$$-d[\text{OR}^-]/dt = k_2[\text{OR}^-][\text{SO}_3^{2-}] \quad (2)$$

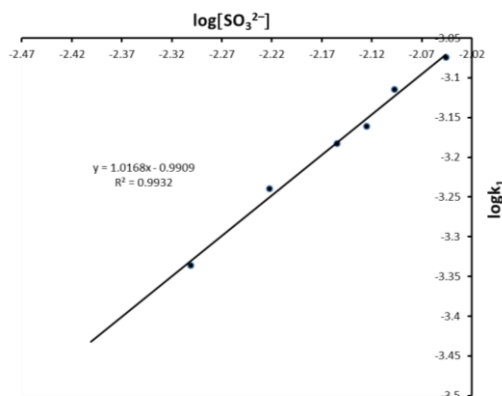


Figure 2: Plot of $\log k_1$ versus $\log[\text{SO}_3^{2-}]$ for the redox reaction of OR^- with SO_3^{2-} at $[\text{OR}^-] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{SO}_3^{2-}] = (5.0 - 9.0) \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 0.50 \text{ mol dm}^{-3}$, $\lambda = 484 \text{ nm}$ and $T = 21 \pm 1^\circ \text{C}$

Changes in ionic strength of the reaction medium indicated that the rate constant increases with increase in ionic strength (Table 1). Plot of $\log k_2$ against $I^{1/2}$ (Figure 3) gave a slope of 1.77 ($R^2 = 0.97$). The reaction was found to be independent of $[\text{H}^+]$ in the range investigated, indicating that the reaction

occurs through an acid-independent pathway. The non-dependence of this reaction on the change in hydrogen ion concentration is uncommon for redox reaction of sulphite ion. However, inverse independent of rate on $[\text{H}^+]$ has been widely reported (Edokpayi, 2011).

Table 1: Pseudo – First Order and Second Order Rate Constants for the Reaction of OR^- and SO_3^{2-} at $[\text{OR}^-] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$, $\lambda = 484 \text{ nm}$ and $T = 21 \pm 1^\circ \text{C}$

$10^3[\text{SO}_3^{2-}]$, mol dm^{-3}	$10^2[\text{H}^+]$, mol dm^{-3}	I , mol dm^{-3}	$10^4 k_1$ s^{-1}	k_2 , $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
5.0	5.0	0.5	4.61	0.092
6.0	5.0	0.5	5.76	0.096
7.0	5.0	0.5	6.91	0.094
7.5	5.0	0.5	7.68	0.092
8.0	5.0	0.5	8.43	0.096
9.0	5.0	0.5	4.01	0.094
7.0	3.0	0.5	6.44	0.092
7.0	5.0	0.5	6.50	0.093
7.0	7.0	0.5	6.72	0.096
7.0	10.0	0.5	6.58	0.094

$10^3[\text{SO}_3^{2-}]$, mol dm^{-3}	$10^2[\text{H}^+]$, mol dm^{-3}	I, mol dm^{-3}	$10^4 k_1$ s^{-1}	k_2 , $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
7.0	15.0	0.5	6.65	0.095
7.0	20.0	0.5	6.58	0.094
7.0	5.0	0.2	2.73	0.039
7.0	5.0	0.4	4.34	0.062
7.0	5.0	0.5	6.58	0.094
7.0	5.0	0.6	7.63	0.109
7.0	5.0	0.8	14.9	0.213
7.0	5.0	0.9	21.1	0.301

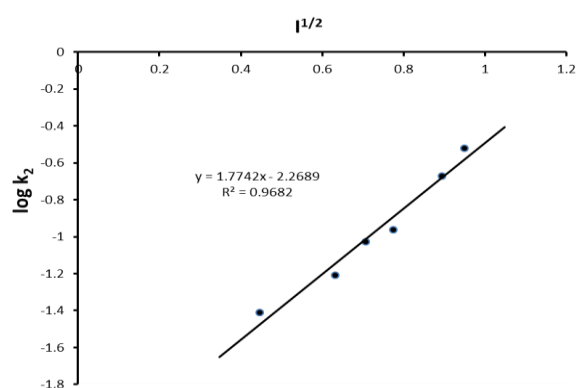


Figure 3: Plot of $\log k_2$ Versus $I^{1/2}$ for the Redox Reaction Between OR^- and SO_3^{2-} at $[\text{OR}^-] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{SO}_3^{2-}] = 7.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 0.50 \text{ mol dm}^{-3}$, $\lambda = 484 \text{ nm}$ and $T = 21 \pm 1^\circ \text{C}$

Added cations and anions accelerated the rate of the reaction (Table 2 and 3). This effect exerted by the ions suggested that the reaction might be operating via the outersphere mechanism (Mayer and Taube, 1987). Spectroscopic evidence and Michaelis - Mentens plot of $1/k_1$ versus $1/\text{SO}_3^{2-}$ suggest the possible absence of an intermediate in the rate determine step. Free radical test did not yield gel formation during the course of the reaction.

Table 2: Rate data for the effect of added cations (Ca^{2+} and Mg^{2+}) on therate of reaction of OR^- and SO_3^{2-} at $[\text{OR}^-] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{SO}_3^{2-}] = 7.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 0.50 \text{ mol dm}^{-3}$, $\lambda = 484 \text{ nm}$ and $T = 21 \pm 1^\circ \text{C}$

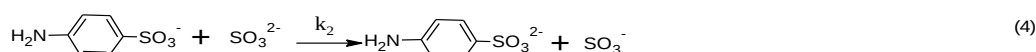
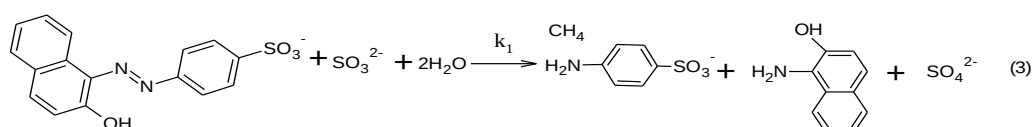
Ion	$10^3 [\text{ion}]$, mol dm^{-3}	$10^4 k_1$, s^{-1}	k_2 , $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
Ca^{2+}	0.0	6.51	0.093
	20.0	8.40	0.120
	40.0	13.0	0.186
	60.0	20.5	0.293
	80.0	23.0	0.328
	100.0	28.1	0.402
	150.0	41.3	0.590
Mg^{2+}	0.0	6.58	0.094
	20.0	8.89	0.127
	40.0	14.8	0.211
	60.0	13.5	0.336
	80.0	27.4	0.391
	100.0	34.2	0.488
	120.0	42.6	0.609

Table 3: Rate Data for the Effect of Added Anions (CH_3COO^- and SO_4^{2-}) on the Rate of Reaction of OR^- and SO_3^{2-} at $[\text{OR}^-] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{SO}_3^{2-}] = 7.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 0.50 \text{ mol dm}^{-3}$, $\lambda = 484 \text{ nm}$ and $T = 21 \pm 1^\circ \text{C}$

Ion	$10^3 [\text{ion}]$, mol dm^{-3}	$10^4 k_1$, s^{-1}	k_2 , $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
CH_3COO^-	0.0	6.58	0.094
	20.0	7.84	0.112
	40.0	13.5	0.193
	60.0	16.5	0.236

Ion	$10^3 [\text{ion}],$ mol dm^{-3}	$10^4 k_1,$ s^{-1}	$k_2,$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
SO_4^{2-}	80.0	23.9	0.341
	100.0	29.5	0.422
	150.0	42.2	0.603
	0.0	6.65	0.095
	20.0	8.26	0.118
	40.0	14.1	0.201
	60.0	24.5	0.350
	80.0	27.6	0.394
	100.0	32.3	0.461
	150.0	41.4	0.592

The reaction mechanism proposed for this reaction is shown in equations 3 – 5



$$\text{Rate} = k_1[\text{OR}^-][\text{SO}_3^{2-}] \quad (5)$$

Equation 5 is analogous to equation 2 where $k_2 = k_1$

CONCLUSION

The redox reaction between OR^- and SO_3^{2-} ion in aqueous acid showed that one mole of OR^- reacted with two moles of SO_3^{2-} . Changes in ionic strength of the reaction medium indicated that the rate constant increases with increase in ionic strength. The rate of the reaction increased with increase in acid concentration as well as in the ionic strength of the reaction medium. Free radical test did not yield gel formation during the course of the reaction. Added cations and anions accelerated the rate of the reaction. This effect exerted by the ions suggested that the reaction might be operating via the outersphere mechanism.

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