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Chaochao Chen

College of Chemistry and Environmental Science, Hebei University, Key Laboratory of Analytical Science and Technology of Hebei Province, Baoding, 071002 Hebei, China

Jinhuan Shan

College of Chemistry and Environmental Science, Hebei University, Key Laboratory of Analytical Science and Technology of Hebei Province, Baoding, 071002 Hebei, China

Hong Zhang

College of Chemistry and Environmental Science, Hebei University, Key Laboratory of Analytical Science and Technology of Hebei Province, Baoding, 071002 Hebei, China

Yannan Mao

College of Chemistry and Environmental Science, Hebei University, Key Laboratory of Analytical Science and Technology of Hebei Province, Baoding, 071002 Hebei, China

Xiaofang Li

College of Chemistry and Environmental Science, Hebei University, Key Laboratory of Analytical Science and Technology of Hebei Province, Baoding, 071002 Hebei, China

Dan Su

College of Chemistry and Environmental Science, Hebei University, Key Laboratory of Analytical Science and Technology of Hebei Province, Baoding, 071002 Hebei, China

Correspondence**Chaochao Chen**

College of Chemistry and Environmental Science, Hebei University, Key Laboratory of Analytical Science and Technology of Hebei Province, Baoding, 071002 Hebei, China

Kinetics and mechanism study of oxidation of sodium thiosulfate and sodium sulfite By Potassium ferrate (VI) in alkaline media

Chaochao Chen, Jinhuan Shan, Hong Zhang, Yannan Mao, Xiaofang Li and Dan Su

Abstract

In the temperature range of 288.2K-308.2K, the kinetics of oxidation of Sodium thiosulfate and Sodium sulfite by Potassium Ferrate (VI) has been studied spectrophotometrically. All data was obtained from the pseudo-first order reaction. It was found that the reaction is a first-order for reactant. The observed rates constants (k_{obs}) increase with the increase of [reductant], however, the k_{obs} decrease with the increase of $[OH^-]$. The reaction is negative fraction order with respect to $[OH^-]$. A plausible mechanism involving a slow reaction as the rate-controlling step is proposed and the rate equations derived from the mechanism can explain all the experimental results. The rate constants of the rate-controlling step and the thermodynamic activation parameters at 298.2K were also calculated.

Keywords: Mechanism, kinetics, oxidation, Potassium ferrate (VI), sodium thiosulfate, sodium sulfite

1. Introduction

Sodium thiosulfate is one of the antidotes to cyanide, with the participation of enzymes, which can be combined with the free (or combined with the hemoglobin) cyanide ions in the body, making the non-toxic thiocyanate excreted outside the body and detoxification. In addition, topical sodium thiosulfate has been recently used as an alternative treatment for dystrophic calcinosis cutis, with no adverse effects^[1-2].

Sodium sulfite is mainly used in industry to make cellulose sodium sulfite ester, sodium thiosulfate, organic chemicals, bleaching fabrics and so on. It can also serve as reductant^[3], preservatives, chlorine removal agent. However, it stimulates the eyes, skin and mucous membranes, especially, it may contaminate the water.

Fe (VI) sorts are strong oxidizing agents with an oxidation potential of 2.2V in acidic media and 0.72V in alkaline media^[4]. Because of the characteristics of oxidative sterilization, adsorption, flocculation deodorization and without secondary pollution in sewage treatment, it is popularly used to control water pollution^[5-10]. There is disagreement about the oxidation mechanism of whether Fe (VI) is a single^[11] or a two-electron^[12] transfer. In this paper, we aim to study the kinetics and reaction mechanisms of oxidation of sodium thiosulfate and sodium sulfite.

2. Experimental**2.1. Materials**

Potassium Ferrate (VI) was synthesised and purified based on the reported method of Thompson et al [13]. All the matters used were of AR reagent grade. Solutions were prepared with water that had been doubly distilled. Buffer solution is prepared by mixing Na_2HPO_4 and NaOH proportionally. KNO_3 and the buffer solution are used to adjust the ionic strength and hydroxide ion strength of the reaction system. K_2FeO_4 solution is always freshly prepared before use by adding solid samples of K_2FeO_4 to buffer solutions. A molar absorption at 508 nm [14] ($\epsilon = 1150 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) was used to calculate the concentration of potassium ferrate where other species did not absorb significantly at this wavelength. The reducing agent is also dissolved in the buffer solution.

2.2. Kinetics measurements and apparatus

The reaction rates were measured by following the decay of the ferrate peak at 508 nm on the SFM-2000 (Bio-Logic, France), which has a cell holder kept at constant temperature ($\pm 0.1^\circ\text{C}$) by circulating water from a thermostat (DC-2006, Baoding, China) and the experiments were under pseudo-first order conditions with Sodium thiosulfate and Sodium sulfite in excess. The reaction contains two major substances, potassium ferrate (VI) is serving as oxidant, Sodium thiosulfate and Sodium sulfite as reductant. The concentration of Fe (VI) in the experiments was kept approximately constant at $2.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ [15], while [Sodium thiosulfate] and [Sodium sulfite] were ranged from 2×10^{-3} to $1 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$.

2.3. Product analysis

When the reaction was run under the phosphate-buffered aerobic condition, there is no ferric oxy hydroxides precipitate in the solution. The presence of the Fe (III) was detected by adding the potassium thiocyanate to the waste solutions to produce the red ferric thiocyanate complex. Under the anaerobic conditions, the Fe (III) was therefore found to be the only iron species [16].

2.4. Reaction intermediate

First add 1, 10-phenanthroline to the reductant solution before the reaction begins, then mix it with the Ferrate (VI) solution.

The experimental phenomena is that purple colour faded and orange colour appeared, showing that $\text{Fe}(\text{phen})_3^{2-}$ has once appeared in the reaction process [17]. It is obviously that the process of Fe (VI) reduced to Fe (III) with Fe (II) stage.

3. Results and Discussion

By measuring the absorbance of Fe (VI) at 508 nm wavelength as a function of time to investigate the reaction. Under the conditions of $[\text{reductant}]_0 \gg [\text{Fe (VI)}]_0$, the plots of $\ln(A_t - A_\infty)$ versus t were straight line, where A_t is the absorbance at time t and A_∞ at infinite time. It indicates that the reaction is first order based on the characteristic of pseudo-first order. The pseudo-first order rate constants k_{obs} were calculated by the method of least squares ($r \geq 0.998$). The k_{obs} values were calculated by an average method on the basis of at least three parallel experiments, and the reproducibility was within $\pm 5\%$.

3.1. The effect of [reductant] on the reaction rates

In the temperature range of 288.2K-308.2K, When [Fe (VI)] and $[\text{OH}^-]$ were fixed concentrations and ionic strength was $0.80 \text{ mol}\cdot\text{L}^{-1}$. The k_{obs} of the reaction were measured as a function of [reductant]. It was found that the values of k_{obs} increase linearly with the increase of the reductant concentrations. The plots of k_{obs} versus [reductant] were linear and passed through the origin (Fig.1 and Fig.2). Besides, the linear dependence observes a first-order term with reductant.

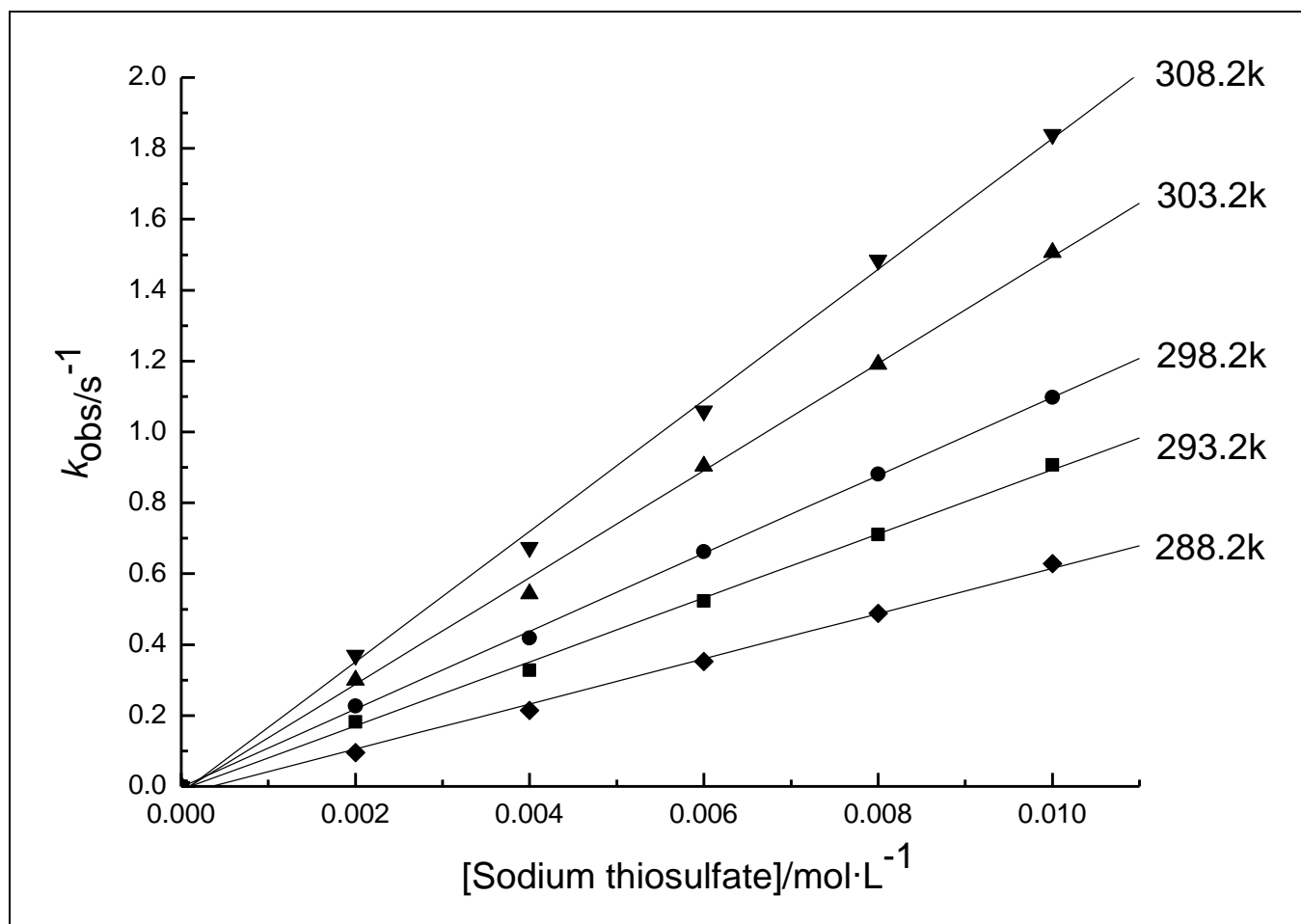


Fig 1: Plots of k_{obs} versus [Sodium thiosulfate] at different temperatures. [Fe (VI)] = $2.00 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[\text{OH}^-]$ = $8.91 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$, $I = 0.8 \text{ mol}\cdot\text{L}^{-1}$, $r \geq 0.999$.

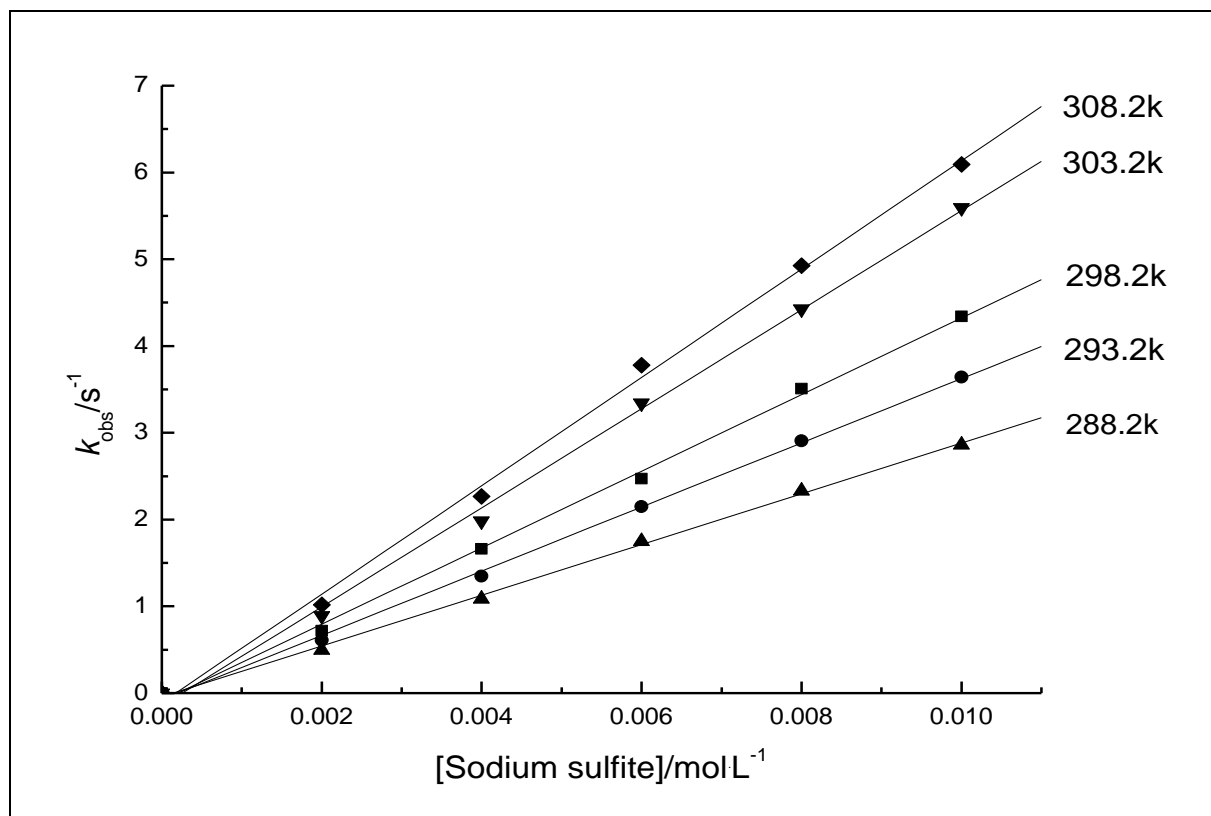


Fig 2: Plots of k_{obs} versus [Sodium sulfite] at different temperatures. $[Fe(VI)] = 2.00 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[OH^-] = 8.13 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$, $I = 0.8 \text{ mol}\cdot\text{L}^{-1}$, $r \geq 0.999$.

3.2. The effect of $[OH^-]$ on the reaction rates

In the temperature range of 288.2K-308.2K, when $[Fe(VI)]$, [Sodium thiosulfate], [Sodium sulfite] and ionic strength were fixed, the k_{obs} decreased with the increase of $[OH^-]$. The plot

of $1/k_{obs}$ versus $[OH^-]$ was linear and the trendlines of the line show that the plots didn't pass through grid origin. The reaction order of $[OH^-]$ was found to be negative fractional (Fig.3 and Fig.4).

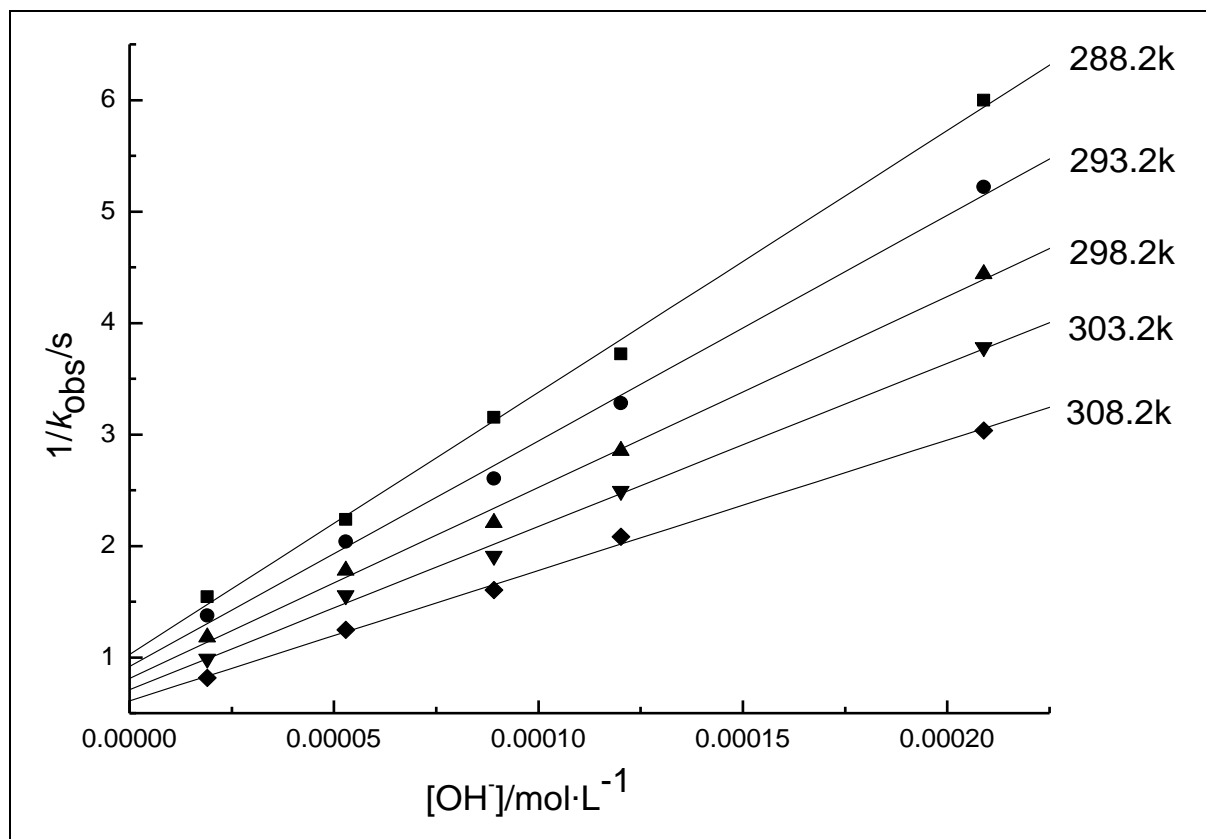


Fig 3: Plots of $1/k_{obs}$ versus $[OH^-]$ at different temperatures. $[Fe(VI)] = 2.00 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, [Sodium thiosulfate] = $6.00 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, $I = 0.8 \text{ mol}\cdot\text{L}^{-1}$, $r \geq 0.998$.

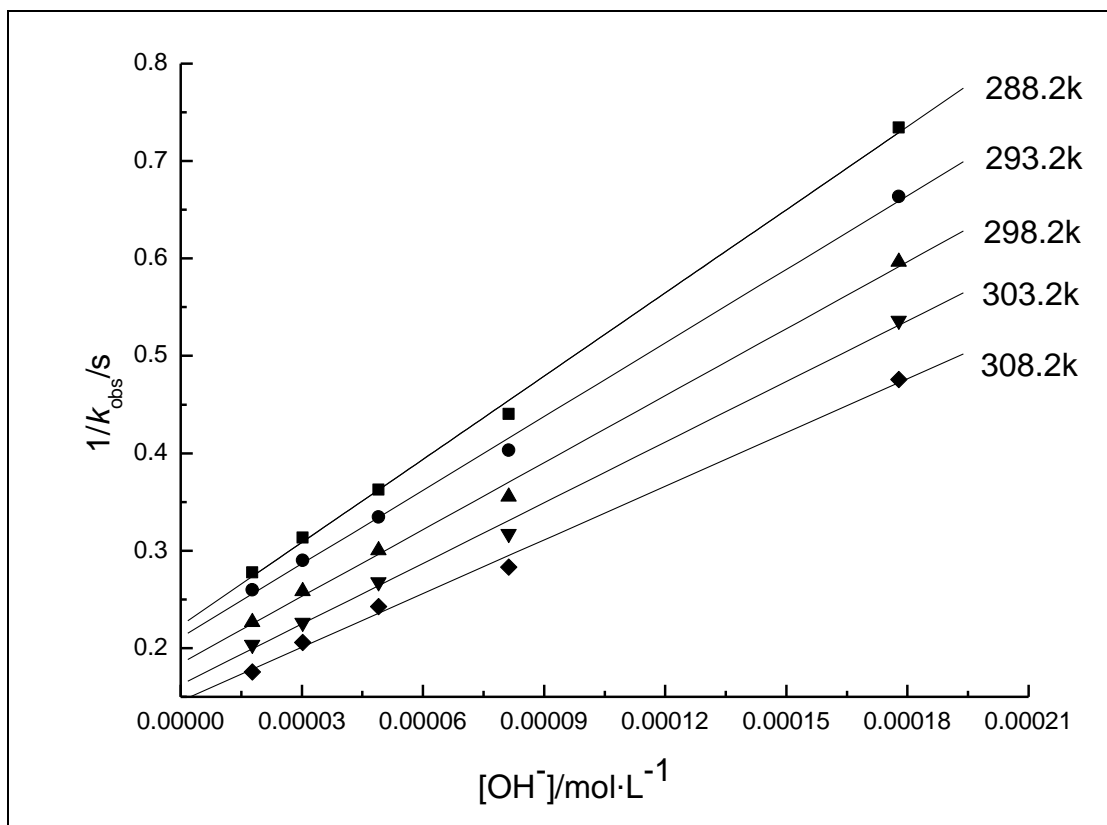
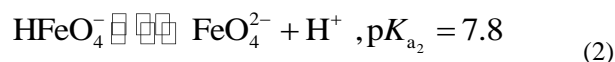
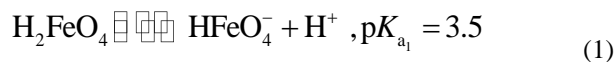


Fig 4: Plots of $1/k_{\text{obs}}$ versus $[\text{OH}^-]$ at different temperatures. $[\text{Fe(VI)}] = 2.00 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[\text{Sodium sulfite}] = 6.00 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, $I = 0.8 \text{ mol}\cdot\text{L}^{-1}$, $r \geq 0.998$.

4. Reaction Mechanism

Since ferrate is a dibasic acid, it will undergo the following ionization:



Under the condition of this experiment, according to the value of $\text{p}K_{a_2}$, there exists only the form of equation (2). It is assumed that HFeO_4^- is an active reaction component and decreases with the increase of pH. In fact, it has been proved from this study that HFeO_4^- is most likely to be a reactive species.

Under alkaline conditions, FeO_4^{2-} will be partially hydrolyzed:



Hence:

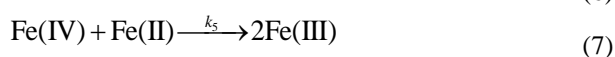
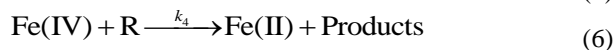
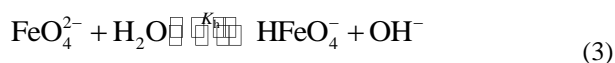
$$K_h = \frac{[\text{HFeO}_4^-][\text{OH}^-]}{[\text{FeO}_4^{2-}]} = \frac{K_w}{K_{a_2}} = 6.31 \times 10^{-7}$$

Therefore:

$$\frac{[\text{HFeO}_4^-]}{[\text{FeO}_4^{2-}]} = \frac{K_h}{[\text{OH}^-]}$$

Obviously, the concentration of HFeO_4^- decreases with the increase of $[\text{OH}^-]$, and was very small, however, HFeO_4^- is very easy to form a highly active complex with reductant through the H atom. Under the attack of the hydroxyl ion, the complex decomposes into Fe (IV) and the product, and then Fe (IV) reacts further with the reductant to form Fe (II) and the product. Therefore, the reaction is mainly achieved by HFeO_4^- .

According to a series of discussions, the mechanism may be written as follows:



The equation (4) is the rate-determining step, where R stands for reductant. The rate law of the reaction was derived as follows:

$$-\frac{d[\text{FeO}_4^{2-}]}{dt} = k_2[\text{HFeO}_4^-][\text{R}] - k_{-2}[\text{X}] \quad (8)$$

$[\text{X}]$ can be got on the basis of static state method and equation of (4) and (5):

$$[\text{X}] = \frac{k_2[\text{HFeO}_4^-][\text{R}]}{k_{-2} + k_3[\text{OH}^-]} \quad (9)$$

According to equation (8) and (9), we get equation (10)

$$-\frac{d[\text{FeO}_4^{2-}]}{dt} = \frac{k_2 k_3 [\text{HFeO}_4^-][\text{R}][\text{OH}^-]}{k_{-2} + k_3[\text{OH}^-]} \quad (10)$$

Based on equation (3), equation (11) will be obtained:

$$[\text{HFeO}_4^-] = \frac{K_h [\text{FeO}_4^{2-}]}{[\text{OH}^-]} \quad (11)$$

Substituting equation (11) into equation (10), we can get equation (12)

$$-\frac{d[\text{FeO}_4^{2-}]}{dt} = \frac{k_2 k_3 K_h [\text{FeO}_4^{2-}][\text{R}]}{k_{-2} + k_3[\text{OH}^-]}$$

$$= \frac{k_2 k_3 K_h [R]}{k_{-2} + k_3 [OH^-]} [FeO_4^{2-}] \quad (12)$$

Hence:

$$k_{obs} = \frac{k_2 k_3 K_h [R]}{k_{-2} + k_3 [OH^-]} = \frac{k_2 k' K_h [R]}{1 + k' [OH^-]} \quad (13)$$

$$k' = \frac{k_3}{k_{-2}}$$

Where

Taking reciprocal of equation (13) we get equation (14)

$$\frac{1}{k_{obs}} = \frac{1 + k' [OH^-]}{k_2 k' K_h [R]} = \frac{1}{k_2 k' K_h [R]} + \frac{[OH^-]}{k_2 K_h [R]} \quad (14)$$

It is clear from the equation (12) that the oxidation-reduction reaction is first-order to potassium ferrate; equation (13) predicts that the plot of k_{obs} versus [reductant] should be first-order term. Such plots have been obtained in this work (Figure 1 and 2), which supporting the proposed mechanism. In addition the k_{obs} decreases with the increase of $[OH^-]$ and $1/k_{obs}$ versus $[OH^-]$ was linear by the equation (14), which was consistent with the plots which we have been gotten in the figure 3 and 4. According to their slopes and equation (14), the rate-controlling step constants (k_2) were evaluated and the relational activation parameters data were obtained (Table 1) [18].

Table 1: Rate constants of (k_2) and activation parameters of the rate-determining step

T(K)		288.2	293.2	298.2	303.2	308.2
$k \times 10^{-4} (\text{mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1})$	Sodium thiosulfate	1.12	1.30	1.54	1.80	2.26
$k \times 10^{-4} (\text{mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1})$	Sodium sulfite	9.27	10.48	11.53	12.72	14.36
Thermodynamic activation parameters (298.2K)	Sodium thiosulfate	$E_a/(\text{kJ} \cdot \text{mol}^{-1}) = 26.59, \Delta H^\ddagger/(\text{kJ} \cdot \text{mol}^{-1}) = 24.03, \Delta S^\ddagger/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = -84.19$				
	Sodium sulfite	$E_a/(\text{kJ} \cdot \text{mol}^{-1}) = 15.79, \Delta H^\ddagger/(\text{kJ} \cdot \text{mol}^{-1}) = 13.32, \Delta S^\ddagger/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = -103.80$				

The plot $\ln k$ versus $1/T$ have the following intercepts (a), slope (b) and relative coefficient (r): for

Sodium thiosulfate: $a=20.39, b=-3198.09, r=0.999$, and for Sodium sulfite: $a=18.03, b=-1899.87, r=0.999$.

5. Conclusion

From the former discussed about the experiment, we can get the following conclusion. (1) Each oxidation is assumed to have occurred through a two-electron pathway. First the Fe (VI) reacts with a molecule of reductant to form complex X. Then, the X dissociates into Fe (IV) and products under the attack of hydroxyl. The Fe (IV) with another molecule of reductant to form Fe (II) and products. Finally, the Fe (IV) reacts with Fe (II) to form Fe (III). (2) With the condition of pseudo-first, the reaction is first-order with respect to oxidant and reductant and to OH^- is negative fractional. (3) The rate constant of Sodium sulfite is significantly larger than that of Sodium thiosulfate. Since positive tetravalent sulfur in sodium sulfite loses two electrons, the formed positive hexavalent transition state is more stable than that of positive tetravalent sulfur formed by sodium thiosulfate, which is more likely to form complexes with iron (VI), so the reaction is faster. The mechanisms described are consistent with experimental observations and provide the basis for kinetics studies.

6. Acknowledgement

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