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Oxidation of Sarcosine by potassium ferrate (VI) in alkaline media: Kinetics and mechanism study

Chaochao Chen[1], Jinhuan Shan[2*], Xiaofang Li[3], Dan Su[4]
[1, 3, 4] Chemistry and Environmental Science, Hebei University, Key Laboratory of Analytical Science and Technology of Hebei Province, Baoding, 071002 Hebei, China
[2] College of Chemistry and Environmental Science, Hebei University, China

Abstract
In this work, the kinetics of oxidation of Sarcosine by Potassium Ferrate (VI) has been studied by using stop–flow spectrometer under alkaline media. The results show that the oxidation-reduction reaction is a first-order to reactant and a negative fraction order to [OH^-]. A plausible mechanism involving a slow response as the rate-controlling step is proposed and the rate equations derived from the mechanism was shown to fit all the experimental observations. The rate constants of the rate-controlling step and the thermodynamic activation parameters were calculated.

Keywords: mechanism, kinetics, *Oxidation*, potassium ferrate, sarcosine

1. Introduction

Potassium Ferrate, which is a non-chlorine typed water treatment agent, has been widely used to control water pollution. It has the characteristics of oxidative sterilization, adsorption, flocculation and deodorization, and will not cause secondary pollution in sewage treatment [1-6]. Fe (VI) sorts are strong oxidizing agents with an oxidation potential of 2.2V in acidic media and 0.72V in alkaline media [7]. Fe (VI) ion has maximum absorption wavelength at 508nm in aqueous solution ($\varepsilon = 1150\ L \cdot mol^{-1} \cdot cm^{-1}$) [8], while other species did not absorb significantly at this wavelength.

Sarcosine can be used as a stabilizer for industrial dyes, daily chemicals, amino acid surfactants and has recently become a health care drug fatigue recovery agent. Sarcosine can improve people's intelligence and prevent damage caused by cerebral lesion. In addition, it can effectively improve exercise performance and increase muscle anaerobic strength and explosive power. However, it has a slight hazard to water.

In 1974, Goff and Murmann [9] first published a kinetic study of ferric oxide oxidation of hydrogen peroxide and sulfite along with oxygen exchange. In his paper, oxidation occurs through a single electron pathway, after which Johnson and Lee propose a two-electron reduction of ferrate [10]. Thus, depending on the reaction system, the reaction mechanism will be different and needs to be further studied. In this work, we report the oxidation of sarcosine by potassium ferrate, furthermore, the kinetics and reaction mechanisms were studied.

2. Experiment

2.1 Materials

Potassium Ferrate (VI) was prepared according to the method reported in the literature [11]. Each matter used is of AR reagent grade. Solutions were prepared with doubly distilled water. Combinations of Na_2HPO_4/NaOH is utilized to prepare a series of buffer solution, the role of KNO_3 is to adjust an ionic strength of $0.8 mol \cdot L^{-1}$. K_2FeO_4 solution is always freshly prepared before use by adding the needed amount of solid samples in a buffer of specific pH. It was found by ultraviolet spectral scanning that K_2FeO_4 has a strong absorption at 508nm ($\varepsilon = 1150\ L \cdot mol^{-1} \cdot cm^{-1}$) [8] and the absorption change is large before and after the reaction, so we use 508nm as its characteristic absorption wavelength. The reducing agent is also dissolved in the buffer solution.

2.2 Methods

Kinetics measurement were monitored by recording the absorbance of Fe(VI) at 508nm on the SFM-2000 (Bio-Logic, France) equipment with a DC-2010 thermostat (±0.1k, Baoding, China). Pseudo-first-order conditions were fulfilled by using $[\text{Sarcosine}]_0 > 10\ [\text{Fe (VI)}]_0$, [Fe (VI)] in this experiment approximately at $2.0 \times 10^{-4} mol \cdot L^{-1}$ [12], meanwhile, [Sarcosine] was ranged from 1.00×10^{-2} to $5.00 \times 10^{-2} mol \cdot L^{-1}$.

3. Results

Under pseudo-first-order conditions, In (A_t-A_∞) versus t were a straight line, where A_t stand for the absorbance at time t and A_∞ at infinite time, indicating that the reaction is first order for Fe (VI). The pseudo-first-order rate constants k_{obs} were calculated by using at least 3 half-lives. The final k_{obs} values were the average of three parallel experiments, which relative deviation is among ±5%.

3.1 Rate dependence on [Sarcosine]

Keep [Fe (VI)], [OH^-] at certain concentrations and I = 0.80 $mol \cdot L^{-1}$, measuring a series of k_{obs} in the temperature range of 288.2 K-308.2 K. The direct relationship between k_{obs} and [sarcosine] can be seen in Figure 1 where the plots of k_{obs} versus [sarcosine] were linear and across the origin, demonstrating that the reaction is first order to [sarcosine].

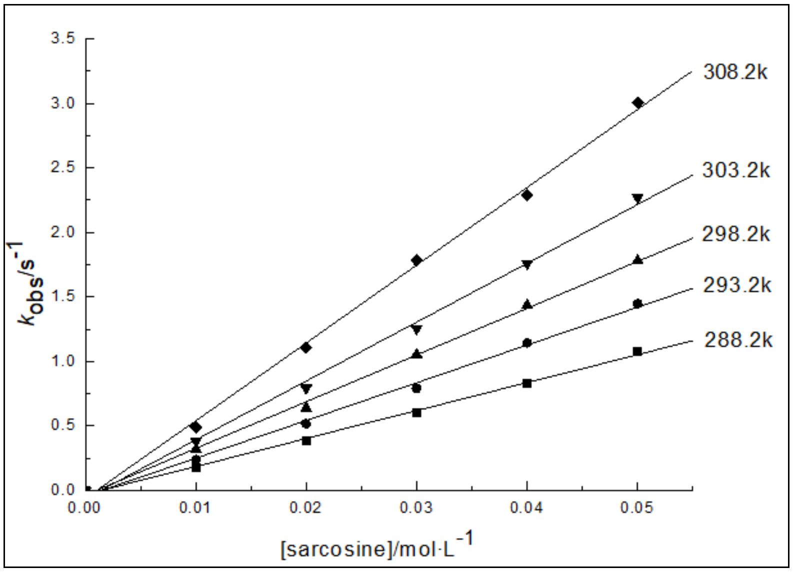

Fig 1: Plots of k_{obs} versus [Sarcosine] at diffirent temperatures. [Fe(VI)] = 2.00×10^{-4}mol·L-1, [OH$^-$] = 8.51×10^{-5}mol·L^{-1}, I=0.80mol·L^{-1}, r≥0.999.

3.2 Rate dependence on [OH$^-$]

Keep [Fe (VI)], [Sarcosine] at fixed concentrations and I = 0.8mol·L^{-1}, measuring a series of k_{obs} in the temperature range of 288.2 K-308.2 K. The direct relationship between k_{obs} and [OH$^-$] can be seen in the figure2 where 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. Obviously, the reaction is negative fractional for [OH$^-$].

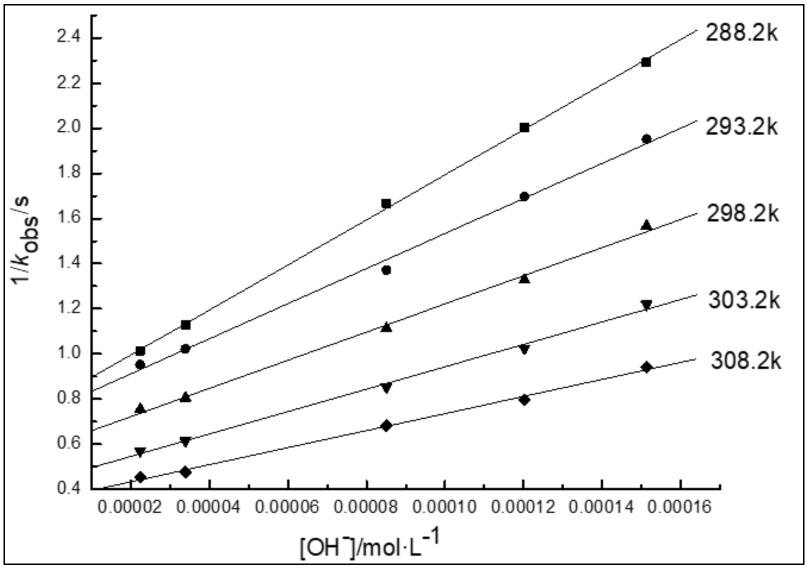

Fig 2: Plots of 1/k_{obs} versus [OH$^-$] at diffirent temperatures. [Fe (VI)] = 2.00×10^{-4} mol·L^{-1}, [Sarcosine] = 3.00×10^{-2} mol·L^{-1}, I = 0.80 mol·L^{-1}, r ≥ 0.998.

4. Reaction mechanism

Ferrate is a dibasic acid, it undergoes two-step ionization:

$$H_2FeO_4 \rightleftharpoons HFeO_4^- + H^+, pK_{a_1} = 3.5 \qquad (1)$$

$$HFeO_4^- \rightleftharpoons FeO_4^{2-} + H^+, pK_{a_2} = 7.8 \qquad (2)$$

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

$$FeO_4^{2-} + H_2O \rightleftharpoons HFeO_4^- + OH^-$$

Thus:

$$K_h = \frac{\left[HFeO_4^-\right]\left[OH^-\right]}{\left[FeO_4^{2-}\right]} = \frac{K_w}{K_{a_2}} = 6.31\times10^{-7}$$

Experiment was carried out under the condition of pH=9.93:

$$\frac{\left[HFeO_4^-\right]}{\left[FeO_4^{2-}\right]} = \frac{K_h}{[OH^-]} = 7.41\times10^{-3}$$

Although the concentration of $HFeO^{4-}$ is very small and decreases when pH increases, it is very easy for $HFeO_4^-$ to form an active complex with reductant in the presence of H atom. With the help of OH^-, the complex decomposes into Fe (IV) and the product, then Fe (IV) reacts further with the reductant to form Fe (II) and the product. Consequently, the reaction is mostly realized through $HFeO^{4-}$.

Based on the above discussion, we can propose the following mechanism:

$$\mathrm{FeO_4^{2-} + H_2O} \overset{K_\mathrm{h}}{\rightleftharpoons} \mathrm{HFeO_4^- + OH^-} \tag{3}$$

$$\mathrm{HFeO_4^- + R} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{X} \tag{4}$$

$$\mathrm{X + OH^-} \xrightarrow{k_3} \mathrm{Fe(IV) + Products} \tag{5}$$

$$\mathrm{Fe\ (IV) + R} \xrightarrow{k_4} \mathrm{Fe\ (II) + Products} \tag{6}$$

$$\mathrm{Fe\ (IV) + Fe\ (II)} \xrightarrow{k_5} \mathrm{2Fe\ (III)} \tag{7}$$

In the equation, R represents a reductant. Since the reaction detects the rate of consumption of $[FeO_4{}^-]$, the rate expression was derived as follows:

$$-\frac{\mathrm{d\,[FeO_4^{2-}]}}{\mathrm{d\,t}} = k_2[\mathrm{HFeO_4^-}][\mathrm{R}] - k_{-2}[\mathrm{X}] \tag{8}$$

According to the equations of (4) and (5), the [X] can be obtained by the approximate steady-state processing method:

$$[\mathrm{X}] = \frac{k_2[\mathrm{HFeO_4^-}][\mathrm{R}]}{k_{-2} + k_3[\mathrm{OH^-}]} \tag{9}$$

A comparison of equation 4 with equation 2 imparts:

$$-\frac{\mathrm{d\,[FeO_4^{2-}]}}{\mathrm{d\,t}} = \frac{k_2k_3[\mathrm{HFeO_4^-}][\mathrm{R}][\mathrm{OH^-}]}{k_{-2} + k_3[\mathrm{OH^-}]} \tag{10}$$

Based on equation (3), equation (11) can be written as follows:

$$[\mathrm{HFeO_4^-}] = \frac{K_\mathrm{h}[\mathrm{FeO_4^{2-}}]}{[\mathrm{OH^-}]} \tag{11}$$

A comparison of equation (11) with equation (10), we can get equation (12)

$$-\frac{\mathrm{d\,[FeO_4^{2-}]}}{\mathrm{d\,t}} = \frac{k_2k_3K_\mathrm{h}[\mathrm{FeO_4^{2-}}][\mathrm{R}]}{k_{-2} + k_3[\mathrm{OH^-}]}$$

$$= \frac{k_2k_3K_\mathrm{h}[\mathrm{R}]}{k_{-2} + k_3[\mathrm{OH^-}]}[\mathrm{FeO_4^{2-}}] \tag{12}$$

Hence:

$$k_\mathrm{obs} = \frac{k_2k_3K_\mathrm{h}[\mathrm{R}]}{k_{-2} + k_3[\mathrm{OH^-}]} = \frac{k_2k'K_\mathrm{h}[\mathrm{R}]}{1 + k'[\mathrm{OH^-}]} \tag{13}$$

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

$$\frac{1}{k_\mathrm{obs}} = \frac{1 + k'[\mathrm{OH^-}]}{k_2k'K_\mathrm{h}[\mathrm{R}]} = \frac{1}{k_2k'K_\mathrm{h}[\mathrm{R}]} + \frac{[\mathrm{OH^-}]}{k_2K_\mathrm{h}[\mathrm{R}]} \tag{14}$$

This equation (13) shows that the reaction is first-order to Fe (VI) and [reductant], such plots obtained in Figure 1 support the proposed mechanism. In addition, $1/k_\mathrm{obs}$ versus $[OH^-]$ at constant [R] was linear with positive intercept in the equation (14), which was in accordance with the plots which we have been gotten in the figure 2. According to their slopes and equation (14), the rate-determining step constants (*K2*) were evaluated and the relational activation parameters date were calculated (Table 1) [13].

Table 1: Rate constants of (*K2*) and thermodynamic activation parameters of the rate-controlling step

T(K)	**288.2**	**293.2**	**298.2**	**303.2.2**	**308.2**
$k_2 \cdot 10^{-3}(\mathrm{mol^{-1} \cdot L \cdot s^{-1}})$	5.29	6.79	8.46	10.64	13.99
Thermodynamic ctivation arameters (298.2K)	$E_a/(\mathrm{kJ \cdot mol^{-1}}) = 36.04$, $\Delta H^{\neq}/(\mathrm{kJ \cdot mol^{-1}}) = 33.56$, $\Delta S^{\neq}/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = -57.51$				

Taking $\ln k_2$ as the ordinate and 1/T as the abscissa, the graph has its own intercept (a), slope (b) and relative coefficient (r): a = 23.60, b = -4334.49, r = 0.997.

5. Conclusions

The kinetics of oxidation of Sarcosine by Potassium Ferrate (VI) has been studied kinetically and mechanistically by using the stopped-flow techniques, we can draw the following three conclusions. (1) There is a two-electron transfer in each oxidation. 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. Once more, 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) Under pseudo-first order conditions, the reaction is first-order with respect to Fe (VI) and reductant and to $[OH^-]$ is negative fractional. The mechanisms described are in accordance well with experimental observations and provide the basis for kinetics studies.

6. Acknowledgement

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