

Kinetics and Mechanism Study of Oxidation of Ethylenediamine and Ethanolamine by Potassium Ferrate (VI) in Alkaline Media

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Abstract

In this work, the kinetics of oxidation of Ethylenediamine and Ethanolamine 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 $[\text{OH}^-]$. A convincing 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, ethylenediamine, ethanolamine

1. Introduction

Ethylenediamine is widely used in industry as a solvent, an additive in some solutions and gels, a corrosion inhibitor, a lubricant, emulsifiers and resin adhesives and for making ethylenediamine derivative (Balato, Cusano, Lembo, & Ayala, 1984). In contrast, it is well-known that most sensitizations are caused by topical preparations containing ethylenediamine as a stabilizer (Angelini, Vena, & Meneghini, 1985). A sharp increase in the incident has been noticed in many countries where they treat the cream including triamcinolone acetonide, neomycin, gramicidin, nystatin and ethylenediamine as a popular dermatological remedy.

Ethanolamine is used as a chemical reagent, solvent, emulsifier, rubber promoter, corrosion inhibitor and degradation agent (Nawrocki, Wetzel, Jones, Woods, & McBride, 2018). It is also commonly served as a purifying solution for extracting acid components from gases such as natural gas. However, the ethanolamine waste liquid produced by this process, after preliminary analysis, has a COD of $60\sim 80 \times 10^4$ mg/L and high concentration of organic nitrogen is separated, which seriously impacts the normal operation of the biochemical system of sewage.

Therefore, we urgently need to understand the oxidation of ethanolamine and ethylenediamine in an aqueous environment. Ethanolamine and ethylenediamine are typical alcohol amine and diamine, knowing their oxidation mechanism is of great importance for understanding both alcohol amine and diamine.

Fe (VI) sorts are strong oxidizing agents with an oxidation potential of 2.2V in acidic media and 0.72V in alkaline media (Liu, Wang, & Shan, 2016). Due to the characteristics of oxidative sterilization, adsorption, flocculation deodorization and without secondary pollution in sewage treatment, it is popularly used to control water pollution (Graham, Jiang, & Li, 2004; Jiang, Alex, & Mike, 2006; Ma & Liu, 2002; Ruben & Frank, 2000; Sharma, Radek, & Varma, 2015; Wilharm, Chin, & Pliskin, 2014). There is a disagreement about the oxidation mechanism of whether Fe (VI) is a single (Sharma & Bielski, 1991) or a two-electron (Bielski & Thomas, 1987) transfer. In this paper, we aim to study the kinetics and reaction mechanism of oxidation of ethylenediamine and ethanolamine.

2. Experiment

2.1 Materials

Potassium Ferrate (VI) was prepared according to the method reported in the literature (Goff & Murmann, 1971). Each matter used is of AR reagent grade. Solutions were prepared with doubly distilled water. Combinations of $\text{Na}_2\text{HPO}_4/\text{NaOH}$ is utilized to prepare a series of buffer solution, the role of KNO_3 is to adjust an ionic strength of $0.8\text{mol}\cdot\text{L}^{-1}$. 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 508 nm ($\epsilon = 1150 \text{ L mol}^{-1} \text{ cm}^{-1}$) (Sharma, Wayne, & Joshi, 1999) 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 ($\pm 0.1\text{k}$, Baoding, China). Pseudo-first-order conditions were fulfilled by using $[\text{reductant}]_0 > 10 [\text{Fe(VI)}]_0$, $[\text{Fe(VI)}]$ in this experiment approximately at $2.0 \times 10^{-4} \text{ mol L}^{-1}$ (Wang & Liu, 2016), meanwhile, $[\text{ethylenediamine}]$ was ranged from 2.5×10^{-3} to $1.25 \times 10^{-2} \text{ mol L}^{-1}$ and $[\text{ethanolamine}]$ was ranged from 5×10^{-3} to $2.5 \times 10^{-2} \text{ mol L}^{-1}$.

3. Results

Under pseudo-first-order conditions, $\ln(A_t - A_\infty)$ 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 $\pm 5\%$.

3.1 Rate Dependence on [Reductant]

Keep $[\text{Fe(VI)}]$, $[\text{OH}^-]$ at certain concentrations and $I = 0.80 \text{ mol L}^{-1}$, measuring a series of k_{obs} in the temperature range of 283.2 K-303.2 K. The direct relationship between k_{obs} and $[\text{reductant}]$ can be seen in Figure 1 and Figure 2 where the plots of k_{obs} versus $[\text{reductant}]$ were linear and across the origin, demonstrating that the reaction is first order to $[\text{reductant}]$.

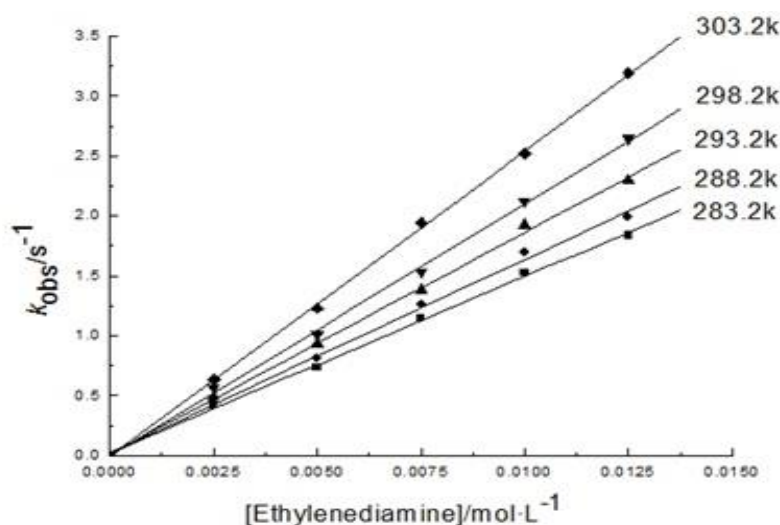


Figure 1. Plots of k_{obs} versus $[\text{Ethylenediamine}]$ at different temperatures. $[\text{Fe(VI)}] = 2.00 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{OH}^-] = 7.24 \times 10^{-5} \text{ mol L}^{-1}$, $I = 0.80 \text{ mol L}^{-1}$, $r \geq 0.999$

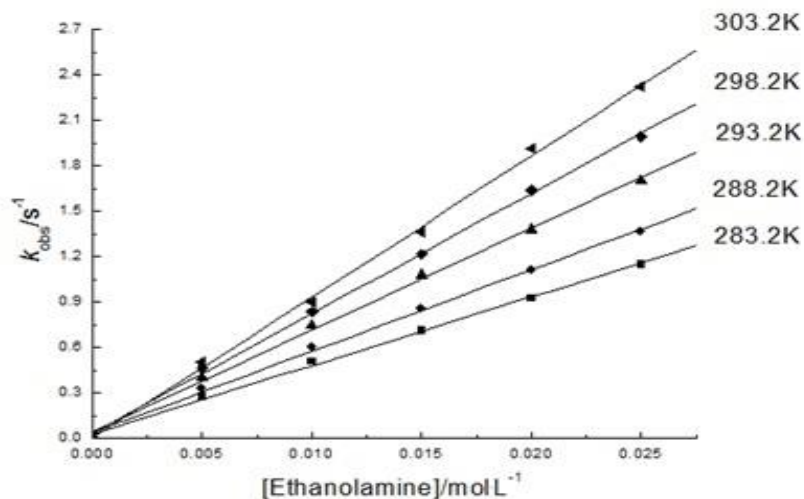


Figure 2. Plots of k_{obs} versus [Ethanolamine] at different temperatures. $[Fe(VI)] = 2.00 \times 10^{-4} \text{ mol L}^{-1}$, $[OH^-] = 7.94 \times 10^{-5} \text{ mol L}^{-1}$, $I = 0.80 \text{ mol L}^{-1}$, $r \geq 0.999$

3.2 Rate Dependence on $[OH^-]$

Keep $[Fe(VI)]$, [Ethylenediamine], [Ethanolamine] at fixed concentrations and $I = 0.80 \text{ mol L}^{-1}$, measuring a series of k_{obs} in the temperature range of 283.2 K-303.2 K. The direct relationship between k_{obs} and $[OH^-]$ can be seen in the figure 3 and figure 4 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 $[OH^-]$.

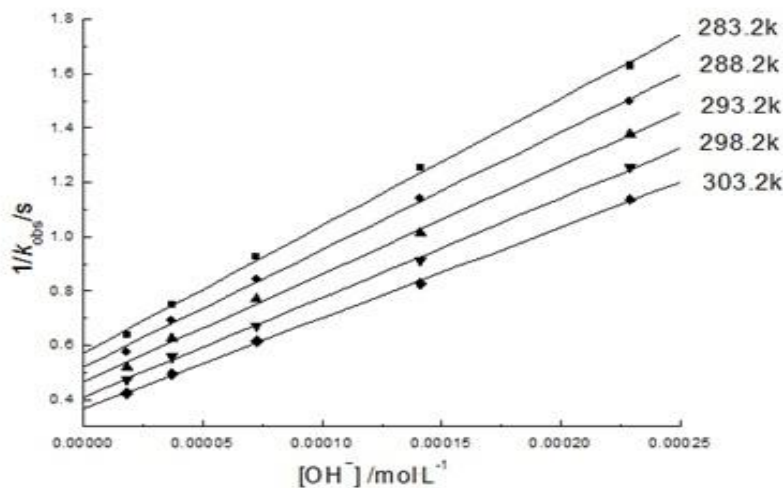


Figure 3. Plots of $1/k_{obs}$ versus $[OH^-]$ at different temperatures. $[Fe(VI)] = 2.00 \times 10^{-4} \text{ mol L}^{-1}$, [Ethylenediamine] = $7.5 \times 10^{-3} \text{ mol L}^{-1}$, $I = 0.80 \text{ mol L}^{-1}$, $r \geq 0.999$

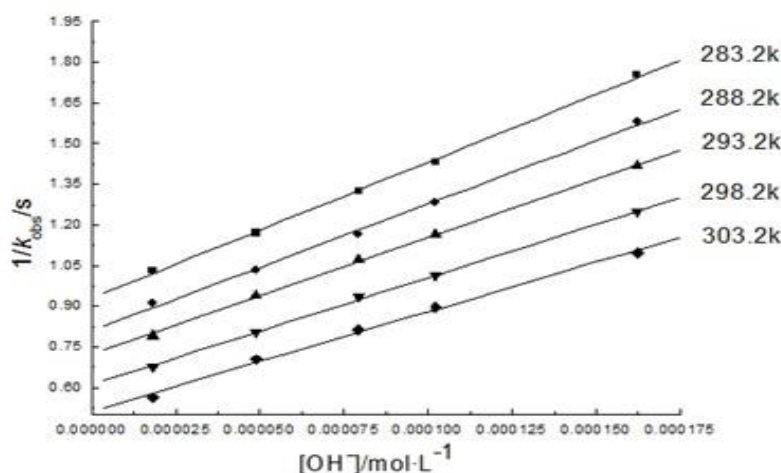
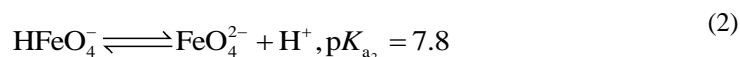
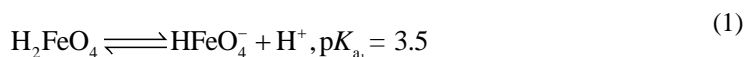


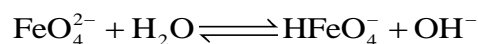
Figure 4. Plots of $1/k_{\text{obs}}$ versus $[\text{OH}^-]$ at different temperatures. $[\text{Fe (VI)}] = 2.00 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{Ethanolamine}] = 1.5 \times 10^{-2} \text{ mol L}^{-1}$, $I = 0.80 \text{ mol L}^{-1}$, $r \geq 0.998$

4. Reaction Mechanism

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



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



Thus:

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

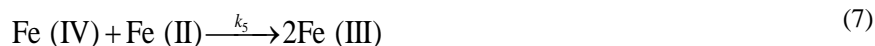
Experiment was carried out under the condition of $\text{pH}=9.90$:

$$\frac{[\text{HFeO}_4^-]}{[\text{FeO}_4^{2-}]} = \frac{K_h}{[\text{OH}^-]} = 7.95 \times 10^{-3}$$

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:





In the equation, R represents a reductant. Since the reaction detects the rate of consumption of $[\text{FeO}_4^{2-}]$, the rate expression was derived as follows:

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

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

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

A comparison of equation 4 with equation 2 imparts:

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

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

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

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

$$\begin{aligned} -\frac{d[\text{FeO}_4^{2-}]}{dt} &= \frac{k_2 k_3 K_h [\text{FeO}_4^{2-}][\text{R}]}{k_{-2} + k_3[\text{OH}^-]} \\ &= \frac{k_2 k_3 K_h [\text{R}]}{k_{-2} + k_3[\text{OH}^-]} [\text{FeO}_4^{2-}] \end{aligned} \quad (12)$$

Hence:

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

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

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

This equation (13) shows that the reaction is first-order to Fe (VI) and [reductant], such plots obtained in this work (Figure 1 and 2) support the proposed mechanism. In addition, $1/k_{\text{obs}}$ versus $[\text{OH}^-]$ 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 3 and 4. According to their slopes and equation (14), the rate-determining step constants (k_2) were evaluated and the relational activation parameters date were calculated (Table 1) (Shan, Liu, Huo, Fan, & Shen, 2006).

Table 1. Rate constants of (k_2) and thermodynamic activation parameters of the rate-controlling step

$T(K)$		283.2	288.2	293.2	298.2	303.2
$k \times 10^{-4}$ ($\text{mol}^{-1} \text{L s}^{-1}$)	Ethylenediamine	4.51	4.89	5.31	5.77	6.32
$k \times 10^{-4}$ ($\text{mol}^{-1} \text{L s}^{-1}$)	Ethanolamine	2.10	2.26	2.45	2.68	2.88
Thermodynam-ic activation parameters (298.2k)	Ethylenediamine	Ea/(kJ mol ⁻¹) = 11.85, ΔH^\ddagger /(kJ mol ⁻¹) = 9.37, ΔS^\ddagger /(J K ⁻¹ mol ⁻¹) = -100.75				
	Ethanolamine	Ea/(kJ mol ⁻¹) = 11.36, ΔH^\ddagger /(kJ mol ⁻¹) = 8.88, ΔS^\ddagger /(J K ⁻¹ mol ⁻¹) = -127.88				

Taking $\ln k_2$ as the ordinate and $1/T$ as the abscissa, each graph has its own intercept (a), slope (b) and relative coefficient (r): for ethylenediamine: a = 15.74, b = -1424.78, r = 0.999 and for ethanolamine: a = 14.77, b = -1366.57, r = 0.999.

5. Conclusions

The kinetics of oxidation of Ethylenediamine and Ethanolamine 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. (2) Under pseudo-first order conditions, the reaction is first-order with respect to Fe (VI) and reductant and to OH⁻ is negative fractional. (3) The rate constant of ethylenediamine is significantly larger than that of ethanolamine, because when the reductant molecule has both amino and hydroxyl groups, the oxidant will first oxidize the amino. Since the electronegativity of the nitrogen atom in the amino group is smaller than that of the oxygen atom in the hydroxyl group then the electron is more easily to transfer and to form complexes with Fe (VI). In addition, ethylene-diamine has two amino, the increase in the number of amino groups of oxidant molecules can increase the probability of the effective collision with Fe (VI). These two reasons make the reaction of ethylenediamine faster. Obviously, the mechanisms described are in accordance well with experimental observations.

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