



Kinetics and Mechanism of Oxidation of Diethanolamine and Triethanolamine by Potassium Ferrate

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Abstract: The kinetics of oxidation of diethanolamine and triethanolamine by potassium ferrate(VI) in alkaline liquids at a constant ionic strength has been studied spectrophotometrically in the temperature range of 278.2 K-293.2 K. The reaction shows first order dependence on potassium ferrate(VI), first order dependence on each reductant, The observed rate constant (k_{obs}) decreases with the increase in $[OH^-]$, the reaction is negative fraction order with respect to $[OH^-]$. A plausible mechanism is proposed and the rate equations derived from the mechanism can explain all the experimental results. The rate constants of the rate-determining step and the thermodynamic activation parameters are calculated.

Keywords: Diethanolamine, Triethanolamine, Potassium ferrate, Kinetics and mechanism, Oxidation

Introduction

Potassium ferrate is a powerful oxidizing agent in the whole pH range, it is widely used as a water treatment agent¹⁻³ in 1970s. It can remove the phenolic, sulfide and other organic pollutants⁴⁻⁶ which are residual in wastewater and also can oxidize the cyanide into NO_2^- , NO_3^- and HCO_3^- which are harmless to environment⁷⁻¹⁰. Ferrate as a very effective, selective oxidant which can remove effectively H_2S , CH_3SH_2 and NH_3 etc¹¹ odor substances in biological sludge. The treated sludge can be used as chemical fertilizer and soil conditioner, it is propitious to waste resource utilization.

Applied prospects of ferrate oxidation are becoming hotspot of research¹². Oxidability of ferrate is stronger than potassium permanganate, ozone and chlorine. As a new water treatment agent, it has a trend to replace chlorine-atom. In recent years, James Carr *etc.* used potassium ferrate as water treatment agent, while they studied self-decomposition of potassium ferrate in a wide pH range (pH=2.53-9.31)¹³ and the reaction of oxidizing a variety of organic matters¹⁴. They had proposed rate equation which is applicable to the majority systems. The rate equation includes self-decomposition of potassium ferrate and the

reaction of potassium ferrate with the substrate. They also established new methods to deal with kinetic data of such reaction systems¹⁵. However, all studies were not put forward the reaction mechanism to explain the experimental facts.

Diethanolamine and triethanolamine have a very wide range of uses, they can be directly used as surfactants for detergents and cleaning agent formulations; they also can be used for gas purification agent to remove carbon dioxide or hydrogen sulfide gas. In addition, diethanolamine is raw materials to synthesize drugs and it is also a cross linking agent for production of high resilience polyurethane foam. Triethanolamine is also used as preservatives, water repellent, analytical reagent and PH value regulators. In this paper, the kinetics and mechanism of oxidation of diethanolamine and triethanolamine by potassium ferrate were studied in detail.

Experimental

All the reagents used were of A.R. grade. All solutions were prepared with doubly distilled water. Potassium ferrate (K_2FeO_4) was prepared by the method of Thompson *et al*¹⁵. The concentration of K_2FeO_4 was derived from its absorption at 507 nm ($\epsilon = 1.15 \times 10^3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$). The solution of K_2FeO_4 was always freshly prepared before use. KNO_3 and the Na_2HPO_4 buffer solution were used to maintain ionic strength and acidity of the reaction, respectively. Measurements of the kinetics were performed using a TU-1900 spectrophotometer (Beijing, China) fitted with a DC-2010 thermostat ($\pm 0.1 \text{ K}$, Baoding, China).

Kinetics measurements

All kinetics measurements were carried out under pseudo-first order conditions. The oxidant and reductant were dissolved in buffer solution which contained required concentration of KNO_3 and Na_2HPO_4 . The reaction was initiated by mixing the Fe(VI) to reductant solution. The reaction process was monitored automatically by recording the concentration decrease of all the Fe(VI) species with time (t) at 507 nm with a TU-1900 spectrophotometer. All other species did not absorb significantly at this wavelength.

Product analysis

After completion of the reaction, adding $K_3Fe(CN)_6$ to the solution have non-experimental phenomena, while adding $K_4Fe(CN)_6$ prussian blue precipitate was generated; by adding 2,2-bipyridyl methanol solution have non- experimental phenomena also. It proves that the final reduction product of Fe(VI) is Fe(III)¹⁶. After completion of the reaction, the oxidation product was identified as aldehyde which was precipitated as 2, 4-dinitrophenylhydrazone derivative.

Reaction intermediate

1,10-Phenanthroline was added to the reductant solution, then it was mixed with K_2FeO_4 solution, purple disappears and at the same time orange appears, which indicates that $Fe(phen)_3^{2+}$ has generated in the process of the reaction¹⁶. It proves that Fe(II) has once appeared in the reduction process of Fe(VI) to Fe(III).

Results and Discussion

Evaluation of pseudo-first order rate constants

Under the conditions of $[reductant]_0 \gg [Fe(VI)]_0$, the plots of $\ln(A_t - A_\infty)$ versus time t gives straight lines, details of the evaluation were described in our previous work¹⁷.

Rate dependence on [reductant]

At fixed $[Fe(VI)]$, $[OH^-]$, ionic strength I , the values of k_{obs} were determined at different temperatures. The k_{obs} were found to be increased with the increase of reactant concentration. The plots of k_{obs} versus [reductant] were linear. For the plots passed through the grid origin (Figure 1 and Figure 2), the reaction was first order with reductant.

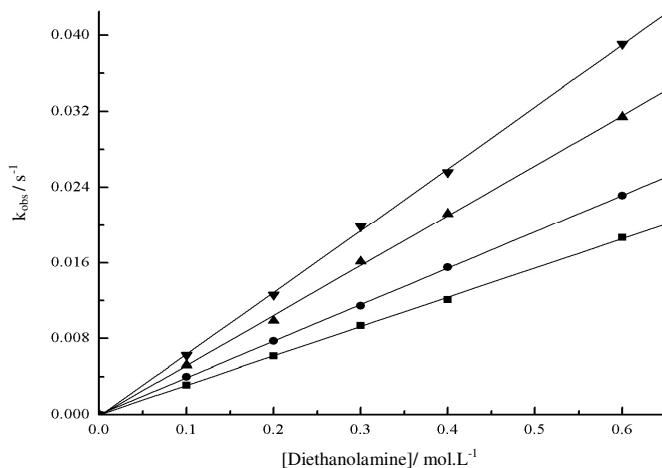


Figure 1. Plots of k_{obs} versus [Diethanolamine] at different temperatures($r \geq 0.999$), $[Fe(VI)] = 1.03 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[OH^-] = 6.76 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$, $I = 1.00 \text{ mol}\cdot\text{L}^{-1}$

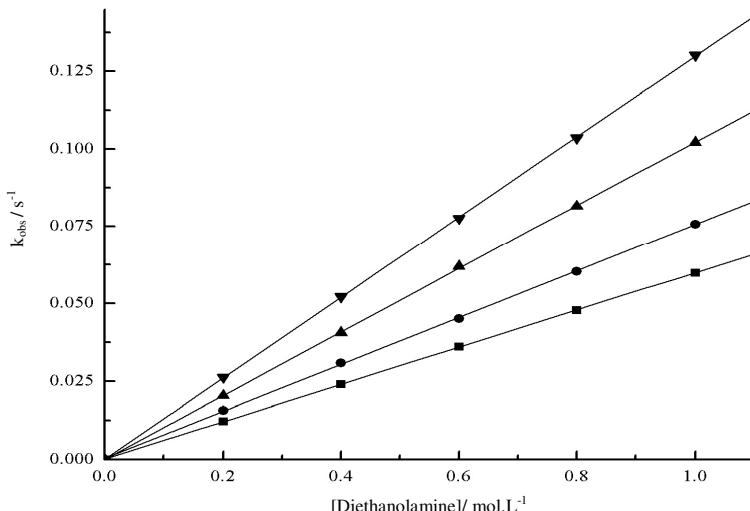


Figure 2. Plots of k_{obs} versus [Triethanolamine] at different temperatures($r \geq 0.999$), $[Fe(VI)] = 1.11 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[OH^-] = 1.38 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $I = 1.00 \text{ mol}\cdot\text{L}^{-1}$

Rate dependence on $[OH^-]$

Under fixed $[Fe(VI)]$, [reductant], ionic strength I and temperature, k_{obs} values were decreased with an increase of $[OH^-]$. The order with respect to OH^- was found to be negative fractional. The plots of $1/k_{obs}$ versus $[OH^-]$ were liners (Figure 3 & 4).

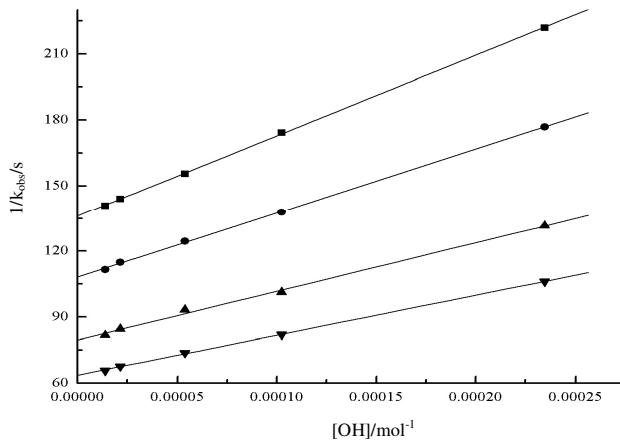


Figure 3. Plots of $1/k_{\text{obs}}$ versus $[\text{OH}^-]$ at different temperatures ($r \geq 0.998$) $[\text{Fe(VI)}] = 1.01 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $[\text{Diethanolamine}] = 0.20 \text{ mol} \cdot \text{L}^{-1}$, $I = 1.00 \text{ mol} \cdot \text{L}^{-1}$

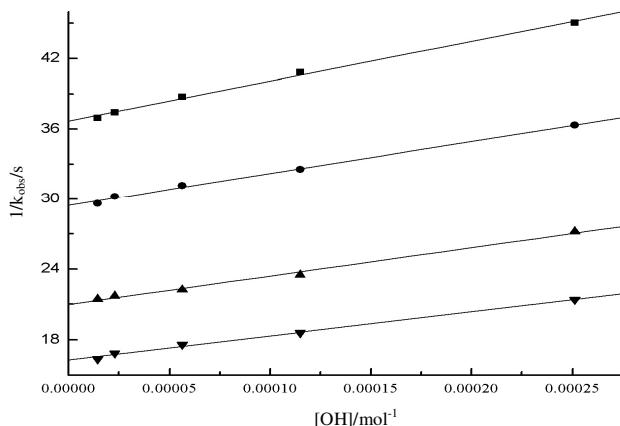
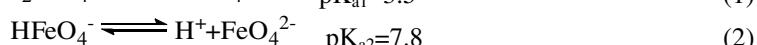
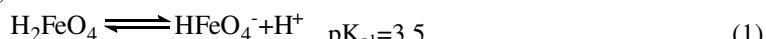


Figure 4. Plots of $1/k_{\text{obs}}$ versus $[\text{OH}^-]$ at different temperatures ($r \geq 0.997$) $[\text{Fe(VI)}] = 1.04 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $[\text{Triethanolamine}] = 0.40 \text{ mol} \cdot \text{L}^{-1}$, $I = 1.00 \text{ mol} \cdot \text{L}^{-1}$

Reaction mechanism

James Carr¹⁴ has given the rate equation as follows $\text{rate} = k_1[\text{FeO}_4^{2-}] + k_2[\text{FeO}_4^{2-}]^2 + k[\text{FeO}_4^{2-}][\text{S}]$ where $[\text{S}]$ represents substrate concentration. According to James Carr¹⁴, the first two terms are contribution of K_2FeO_4 self-decomposition rate to the reaction system when there is no substrate. In this article, under the experimental conditions, the self-decomposition rate of K_2FeO_4 is far less than oxidation rate of reductant reaction, so we get the rate equation: $\text{rate} = k[\text{FeO}_4^{2-}][\text{R}]$. In essence, the results were consistent with James¹³ findings Ferrate(VI) is a dicarboxylic acid, where:



Under the experimental conditions of this paper, FeO_4^{2-} will be partial hydrolysis:

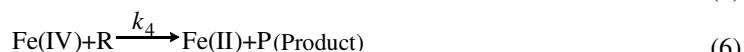
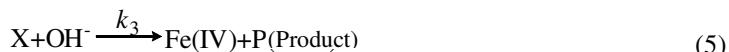


$$\text{Hence: } K_h = \frac{[\text{HFeO}_4^-][\text{OH}^-]}{[\text{FeO}_4^{2-}]} = \frac{K_w}{K_{a2}} = 6.31 \times 10^{-7}$$

This experiment was performed at pH = 9.83 and 10.14, then there is

$$\frac{[\text{HFeO}_4^-]}{[\text{FeO}_4^{2-}]} = \frac{K_h}{[\text{OH}^-]} = 9.33 \times 10^{-3} \text{ and } \frac{[\text{HFeO}_4^-]}{[\text{FeO}_4^{2-}]} = \frac{K_h}{[\text{OH}^-]} = 4.57 \times 10^{-3}$$

Obviously, HFeO_4^- both have a small percentage in the system. The concentration of HFeO_4^- is small, but it is very easy to form complex with reductant in the presence of hydrogen atom and the complex has higher activity. Under the attack of hydroxyl, the complex dissociates into Fe(IV) and product, then Fe(IV) with another molecule of reductant further react to generate Fe(II) and product. Therefore, reaction is mainly through HFeO_4^- to realize. According to discussion, the following reaction mechanism is proposed:



Equation (4) is the rate-determining step, where R stands for reductant. As the rate of the disappearance of $[\text{FeO}_4^{2-}]$ was monitored, the rate of the reaction can be derived as

$$-\frac{d[\text{FeO}_4^{2-}]}{dt} = k_2 [\text{HFeO}_4^-] [\text{R}] - k_{-2} [\text{X}] = \frac{k_2 k_3 [\text{HFeO}_4^-] [\text{R}] [\text{OH}^-]}{k_{-2} + k_3 [\text{OH}^-]} \quad (8)$$

$$\text{Equation (9) can be obtained from (3): } [\text{HFeO}_4^-] = \frac{K_h [\text{FeO}_4^{2-}]}{[\text{OH}^-]} \quad (9)$$

Substituting equation (9) into (8), we can get the following equation (10):

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

$$k_{\text{obs}} = \frac{k_2 k_3 K_h [\text{R}]}{k_{-2} + k_3 [\text{OH}^-]} = \frac{k_2 k' K_h [\text{R}]}{1 + k' [\text{OH}^-]} \quad (11)$$

in the equation $k' = k_3/k_{-2}$

$$\frac{1}{k_{\text{obs}}} = \frac{1 + k' [\text{OH}^-]}{k_2 k' K_h [\text{R}]} = \frac{1}{k_2 k' K_h [\text{R}]} + \frac{[\text{OH}^-]}{k_2 k' K_h [\text{R}]} \quad (12)$$

Equation (10) suggests that the reaction should be first order with respect to Fe(VI); equation (11) suggests that the order with respect to R is unity. The plot of $1/k_{\text{obs}}$ versus $[\text{OH}^-]$ derived from equation (12) at constant [R] is linear with positive intercept. These are consistent with the experimental phenomena.

Meanwhile, the plots of $1/k_{\text{obs}}$ versus $[\text{OH}^-]$ were liner at different temperatures. From their slopes and equation (12), the rate-determining step constants (k_2) were evaluated and the thermodynamic activation parameters date were obtained (Table 1)¹⁸.

Table 1. Rate constants (k_2) and Thermodynamic activation parameters of the rate-determining step (T=298.2K)

T, K →		278.2	283.2	288.2	293.2
$k_2/\text{mol}^{-1}\cdot\text{L}\cdot\text{s}^{-1}$	Diethanolamine	21.61	26.68	35.78	43.57
	Triethanolamine	116.70	144.34	163.90	193.90
Thermodynamic activation parameters	Diethanolamine	$E_a = 32.51 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta H^\ddagger = 30.04 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta S^\ddagger = -110.94 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$			
	Triethanolamine	$E_a = 22.40 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta H^\ddagger = 19.92 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta S^\ddagger = -133.06 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$			

The plots of $\ln k$ vs. $1/T$ have following intercept (a) slope (b) and relative coefficient (r). Diethanolamine: a = 17.12 b = -3910.59 r= 0.997, Triethanolamine: a = 14.46 b = -2694.32; r = 0.996

It is noteworthy that according to equation (12) and Figure 3 & 4, we can get the values of k' under corresponding temperature and then, substituting the k' , k_2 and $[\text{OH}^-]$ into equation (11), we can calculate the rate constants in corresponding [R], we found that the calculated value is very close to the experimental value (Table 2 and Table 3). This also illustrates the equation (12) is correct and the reaction mechanism we supposed is reasonable.

Table 2. The values of k_{obs} experimental and calculated at different temperatures ($[\text{OH}^-] = 6.76 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ R= diethanolamine)

Conc., $\text{mol}\cdot\text{L}^{-1}$ → 0.10	0.20		0.30		0.40		0.60	
T, K	Exp	Cal	Exp	Cal	Exp	Cal	Exp	Cal
278.2	0.00311	0.00311	0.00616	0.00622	0.00936	0.00932	0.0121	0.0124
283.2	0.00398	0.00390	0.00772	0.00779	0.0114	0.0117	0.0155	0.0156
288.2	0.00520	0.00529	0.00987	0.0106	0.0161	0.0159	0.0212	0.0212
293.2	0.00623	0.00659	0.0126	0.0132	0.0199	0.0198	0.0256	0.0264

Table 3. The values of k_{obs} experimental and calculated at different temperatures ($[\text{OH}^-] = 1.38 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ R= triethanolamine)

Conc., $\text{mol}\cdot\text{L}^{-1}$ → 0.20	0.40		0.60		0.80		1.00	
T, K	Exp	Cal	Exp	Cal	Exp	Cal	Exp	Cal
278.2	0.0121	0.0121	0.0240	0.0242	0.0361	0.0362	0.0478	0.0483
283.2	0.0156	0.0150	0.0308	0.0301	0.0451	0.0451	0.0602	0.0601
288.2	0.0204	0.0206	0.0405	0.0411	0.0619	0.0617	0.0815	0.0822
293.2	0.0263	0.0262	0.0521	0.0524	0.0776	0.0785	0.104	0.105

Conclusion

Based on the above discussion and results, we can know that the reaction of potassium ferrate with diethanolamine and triethanolamine both are completed by double-electron transfer. At the same time, we also observe the rate of the rate-determining step of triethanolamine is quicker than that of diethanolamine and the rate constants of the rate-determining step of triethanolamine at different four temperatures are larger than those of diethanolamine. The effect of $[\text{OH}^-]$ and the activation parameters are all in support of the mechanism and consistent with experimental phenomena.

In the reaction system, we also observe that the activation energy of experiment is very small, but the entropy of activation has a big negative value. So according to the literature¹⁹, it is reasonable that the reaction rate is not too fast.

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