

Kinetics and Mechanism of Oxidation of 2-amino-1-Butanol and 3-Amino-1-propanol by Potassium Ferrate

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Abstract

The kinetics of oxidation of 2-amino-1-Butanol and 3-Amino-1-propanol by potassium ferrate(VI) in alkaline liquids at a constant ionic strength has been studied spectrophotometrically in the temperature range of 293.2 K-313.2 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 $[\text{OH}^-]$, the reaction is negative fraction order with respect to $[\text{OH}^-]$. 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 activation parameters are calculated.

Keywords: 2-amino-1-Butanol, 3-Amino-1-propanol, Oxidation, Kinetics and mechanism, Potassium ferrate

1. Introduction

As early as 1702, ferrate was found by Starl, then in 1841, Fremy first synthesized out potassium ferrate. Ever since a long time ago, people know little about potassium ferrate because it is unstable in water and humid air. In 1948, high purity potassium ferrate crystal was prepared by oxidizing trivalent iron salt in presence of sodium hypochlorite by Schreye and Thompson (Thompson, G. W., Ockerman, L. T., & Schreye, J. M. 1951). After that, with further research on potassium ferrate, its properties and applications are arousing more and more attention.

Potassium ferrate is a powerful oxidizing agent in the whole pH range; it is widely used as a water treatment agent (Duan, Y. F., Ding, Y., & Zhang, Y. Q. 1998; Wu, L. P. 1994; Zhang, J., Shi, Q. L., & Yang, G. M. 2000) in 1970s. It can remove the phenolic, sulfide and other organic pollutants (Michael, E., Duane, R. C. 1994) which are residual in wastewater, and also can oxidize the cyanide (Waite, T. D., Gray, K. A. 1984) into NO_2^- , NO_3^- and HCO_3^- which are harmless to environment. Ferrate as a very effective, selective oxidant which can remove effectively H_2S , CH_3SH_2 , and NH_3 etc (Virender, K. S., John, T. B., & Vishwas, N. J. 1998) 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 research (Stuart, L., Wang, B. H., & Susanta, G. 1999). 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) (James, Carr. 1985) and the reaction of oxidizing a variety of organic matters (James, 1986). 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 systems (Thompson, G. W., Ockerman, L. T., & Schreyer, J. M. 1951). However, all studies were not put forward the reaction mechanism to explain the experimental facts.

2-amino-1-Butanol is a mixture of optical isomers which is a colorless liquid with ammonia odor. It is mainly used for preparing emulsifiers, surfactants, resinifyingagent, polishing agent, vulcanization accelerator and pharmaceutical raw materials. It is also absorbance of acid gas for removing sulfureted hydrogen and carbon dioxide. D-structure of this product is also used as raw materials of antimicrobial agents and uterine contraction hemostat. 3-Amino-1-propanol is colorless liquid with hygroscopicity and causticity. It can mixed dissolve with water, ethanol, acetone and chloroform. It is an important organic synthesis intermediates. It can synthesize DL-Panthenol and drugs such as cyclophosphamide and segontin.

In this paper, the kinetics and mechanism of oxidation of 2-amino-1-Butanol and 3-Amino-1-propanol by potassium ferrate were studied in detail.

2. Experimental

2.1 Materials and apparatus

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 (Thompson, G. W., Ockerman, L. T., & Schreyer, J. M. 1951). 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).

2.2 Kinetics measurements

All kinetics measurements were carried out under pseudo-first order conditions. The oxidant and reductant were both dissolve 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.

2.3 Product analysis

After completion of the reaction, adding $K_3Fe(CN)_6$ to the solution have non-experimental phenomena, while adding $K_4Fe(CN)_6$ is generated Prussian blue precipitate; by adding 2,2-bipyridyl methanol solution have non-experimental phenomena also. It is prove that the final reduction product of Fe(VI) is Fe(III) (Dong, X. W. 1984). After completion of the reaction, the oxidation product was identified as aldehyde alcohols which was precipitated as 2, 4-dinitrophenylhydrazone derivative.

2.4 Reaction intermediate

Added 1,10-phenanthroline to reductant solution, then mixed with the K_2FeO_4 solution, purple disappeared at the same time orange appeared, indicating that $Fe(phen)_3^{2+}$ have generated in the process of reaction (Dong, X. W. 1984). It is prove that Fe(II) stage have once appeared in the process of Fe(VI) reduction to Fe(III).

3. Results and discussion

3.1 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 were straight line, indicating the reaction is first order with respect to the Fe(VI) complex, where A_t and A_∞ are the absorbance at time t and at infinite time, respectively. The pseudo-first-order rate constants k_{obs} were calculated by the method of least squares ($r \geq 0.997$). Generally, to calculate k_{obs} 8-10 A_t values within there times of the half-lives were used. The k_{obs} values were the average values of at least there independent experiments, and reproducibility is within $\pm 5\%$ (Shan, J. H., Qian, J., & Gao, M. Z. 2004).

3.2 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.

3.3 Rate dependence on $[OH^-]$

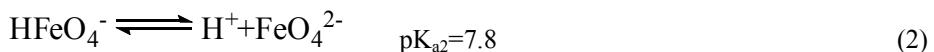
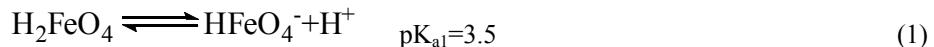
Under fixed $[Fe(VI)]$, [reductant], ionic strength I and temperature, k_{obs} values were decreased with an increase of $[OH^-]$. The order with respect to OH^- was found to be negative fractional. The liners of $1/k_{obs}$ versus $[OH^-]$ were done (**Figure 3** and **Figure 4**).

4. Reaction mechanism

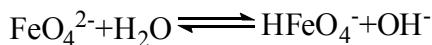
James Carr (James, Carr. 1986) has given the rate equation as follows: rate= $k_1 [FeO_4^{2-}] + k_2 [FeO_4^{2-}]^2 + k [FeO_4^{2-}][S]$

where $[S]$ represents substrate concentration. James Carr thinks: the first two terms is 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: rate= $k[FeO_4^{2-}][R]$. In essence, the results were consistent with James Carr.

Ferrate(VI) is a dicarboxylic acid(James, Carr. 1985), where:



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



Hence:

$$K_h = \frac{[HFeO_4^-][OH^-]}{[FeO_4^{2-}]} = \frac{K_w}{K_{a2}} = 6.31 \times 10^{-7}$$

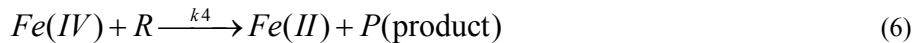
This experiment is performed at pH = 10.10 and 10.42, then there is

$$\frac{[HFeO_4^-]}{[FeO_4^{2-}]} = \frac{K_h}{[OH^-]} = 5.01 \times 10^{-3} \text{ and } \frac{[HFeO_4^-]}{[FeO_4^{2-}]} = \frac{K_h}{[OH^-]} = 2.40 \times 10^{-3}$$

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:





Reaction (4) is the rate-determining step, where R stands for reductant. As the rate of the disappearance of $[FeO_4^{2-}]$ was monitored, the rate of the reaction can be derived as:

$$\begin{aligned} -\frac{d[FeO_4^{2-}]}{dt} &= k_2[HFeO_4^-][R] - k_{-2}[X] \\ &= \frac{k_2 k_3 [HFeO_4^-][R][OH^-]}{k_{-2} + k_3[OH^-]} \end{aligned} \quad (8)$$

Equation (9) can be obtained from (3):

$$[HFeO_4^-] = \frac{K_h[FeO_4^{2-}]}{[OH^-]} \quad (9)$$

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

$$-\frac{d[FeO_4^{2-}]}{dt} = \frac{k_2 k_3 K_h [FeO_4^{2-}][R]}{k_{-2} + k_3[OH^-]} = \frac{k_2 k_3 K_h [R]}{k_{-2} + k_3[OH^-]} [FeO_4^{2-}] \quad (10)$$

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

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

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

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 $[OH^-]$ 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 $[OH^-]$ were liner at different temperatures. From their slopes and equation (12), the rate-determining step constants (k_2) were evaluated, and the activation parameters date were obtained (**Table 1**) (Shan, J. H., Liu, T. Y. 1994).

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 $[OH^-]$ 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.

5. Conclusion

Based on the above discussion and results, we can know that the reaction of potassium ferrate with 2-amino-1-Butanol and 3-Amino-1-propanol both are completed by double-electron transfer and we also observed the rate of the rate-determining step of 3-Amino-1-propanol is quicker than that of 2-amino-1-Butanol, the rate constants of the rate determining step for 3-Amino-1-propanol are larger than those for 2-amino-1-Butanol. The effect of $[OH^-]$ 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 literature (Fu, X. C., Shen, W. X., & Yao, T. Y. 1990), it is reasonable that the reaction rate is not too fast.

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

T(K)		293.2	298.2	303.2	308.2	313.2
$k_2/\text{mol}^{-1}\cdot\text{L}\cdot\text{s}^{-1}$	2-amino-1-Butanol	47.60	64.12	85.95	111.64	
	3-Amino-1-propanol		308.52	351.47	410.06	463.33
Thermodynamic activation parameters	2-amino-1-Butanol	$E_a = 42.98 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta H^\ddagger = 40.50 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta S^\ddagger = -74.54 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$				
	3-Amino-1-propanol	$E_a = 21.33 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta H^\ddagger = 18.85 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta S^\ddagger = -134.02 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$				

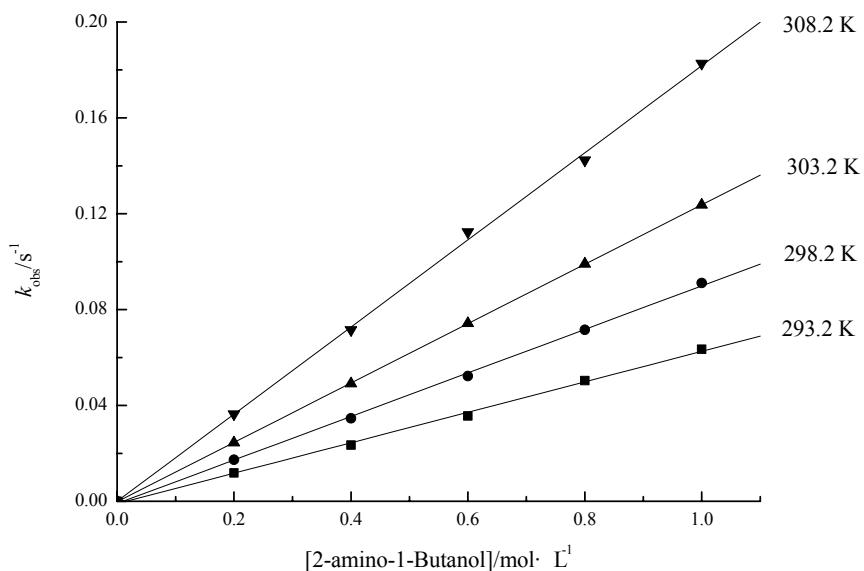
The plots of $\ln k$ vs. $1/T$ have following intercept (a) slope (b) and relative coefficient (r). 2-amino-1-Butanol: a = 21.44 b = -5152.72 r= 0.9999, 3-Amino-1-propanol: a = 14.34 b = -2566.86 r = 0.9992

Table 2. The values of k_{obs} experimental and calculated at different temperatures

		$([\text{OH}^-] = 1.26 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}, R = 2\text{-amino-1-Butanol})$									
c/mol·L ⁻¹		0.20		0.40		0.60		0.80		1.00	
		EXP	CAL	EXP	CAL	EXP	CAL	EXP	CAL	EXP	CAL
293.2		0.0119	0.0129	0.0235	0.0258	0.0357	0.0386	0.0504	0.0515	0.0634	0.0644
298.2		0.0173	0.0181	0.0346	0.0362	0.0523	0.0543	0.0715	0.0724	0.0911	0.0905
303.2		0.0245	0.0248	0.0491	0.0496	0.0743	0.0744	0.0991	0.0992	0.124	0.124
308.2		0.0365	0.0358	0.0715	0.0716	0.112	0.107	0.142	0.143	0.183	0.179

Table 3. The values of k_{obs} experimental and calculated at different temperatures

		$([\text{OH}^-] = 2.63 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}, R = 3\text{-Amino-1-propanol})$									
c/mol·L ⁻¹		0.04		0.08		0.12		0.16		0.20	
		EXP	CAL	EXP	CAL	EXP	CAL	EXP	CAL	EXP	CAL
298.2		0.0108	0.0110	0.0208	0.0221	0.0312	0.0331	0.0427	0.0442	0.0526	0.0552
303.2		0.0152	0.0139	0.0279	0.0278	0.0405	0.0418	0.0554	0.0557	0.0699	0.0696
308.2		0.0183	0.0168	0.0324	0.0335	0.0498	0.0503	0.0656	0.0670	0.0837	0.0838
313.2		0.0225	0.0197	0.0412	0.0394	0.0610	0.0590	0.0798	0.0787	0.105	0.0984

Figure 1. Plots of k_{obs} versus [2-amino-1-Butanol] at different temperatures ($r \geq 0.999$)
 $[\text{Fe(VI)}] = 1.83 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $[\text{OH}^-] = 1.26 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $I = 1.00 \text{ mol} \cdot \text{L}^{-1}$

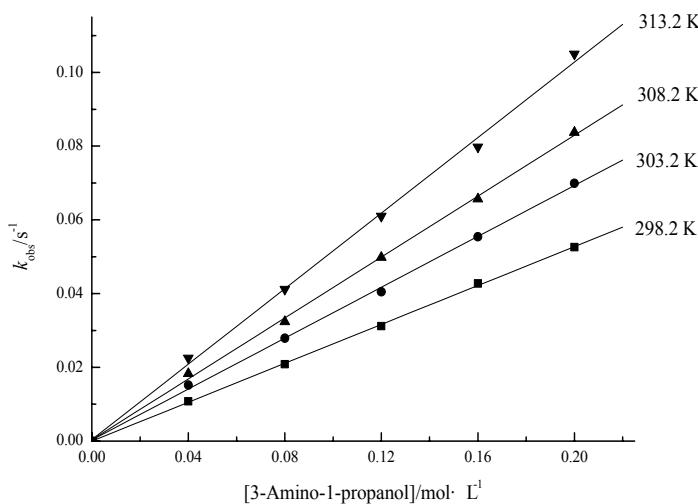


Figure 2. Plots of k_{obs} versus [3-Amino-1-propanol] at different temperatures ($r \geq 0.999$)
 $[\text{Fe(VI)}] = 1.74 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $[\text{OH}^-] = 2.63 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $I = 1.00 \text{ mol} \cdot \text{L}^{-1}$

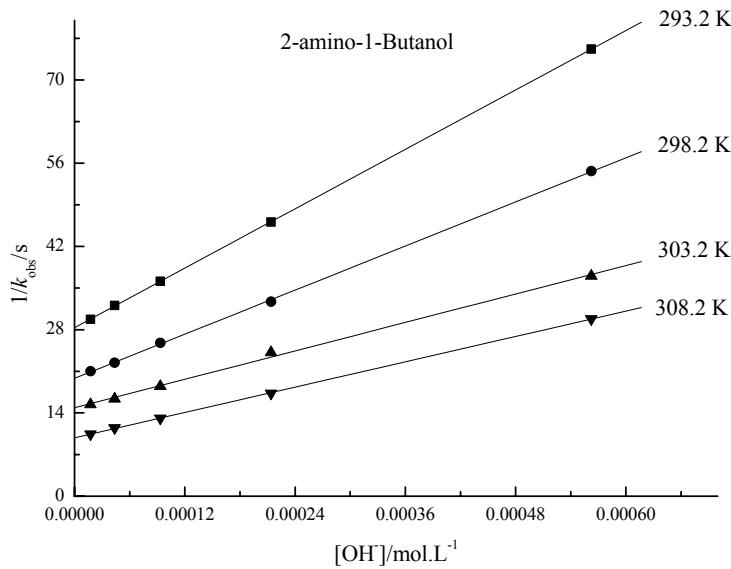


Figure 3. Plots of $1/k_{\text{obs}}$ versus $[\text{OH}^-]$ at different temperatures ($r \geq 0.999$)
 $[\text{Fe(VI)}] = 1.57 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $[2\text{-amino-1-Butanol}] = 0.40 \text{ mol} \cdot \text{L}^{-1}$, $I = 1.00 \text{ mol} \cdot \text{L}^{-1}$

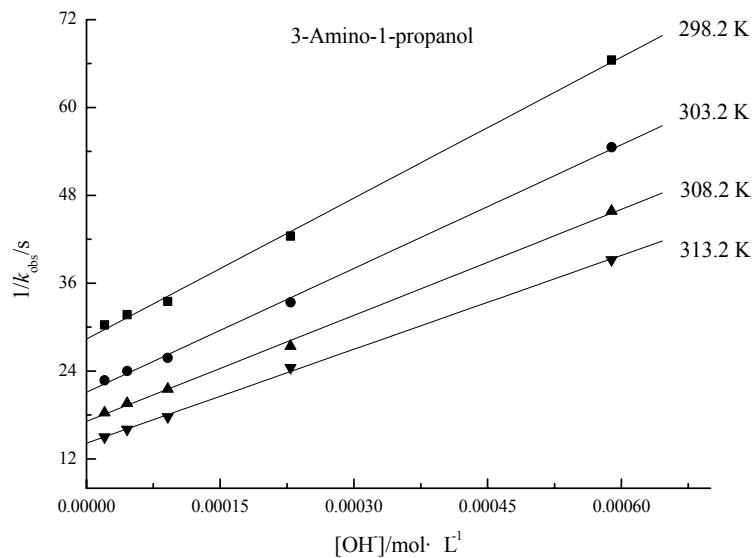


Figure 4. Plots of $1/k_{\text{obs}}$ versus $[\text{OH}^-]$ at different temperatures ($r \geq 0.999$)
[Fe(VI)] = 1.74×10^{-4} mol·L⁻¹, [3-Amino-1-propanol] = 0.08 mol·L⁻¹, $I = 1.00$ mol·L⁻¹