



Kinetics and Mechanism of Oxidation of 2-Methoxyethanol and 2-Ethoxyethanol by Potassium Ferrate

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The kinetics of oxidation of 2-methoxyethanol and 2-ethoxyethanol by potassium ferrate(VI) in alkaline liquids at a constant ionic strength has been studied spectrophotometrically in the temperature range of 293.2-313.2 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 $[OH^-]$, 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 activation parameters are calculated.

Key Words: 2-Methoxyethanol, 2-Ethoxyethanol, 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. It can remove the phenolic, sulfide and other organic pollutants⁴⁻⁶ which are residual in wastewater and can also 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 etc.¹¹ 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^{13,14}, 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) and the reaction of oxidizing a variety of organic matters. 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.

2-Methoxyethanol and 2-ethoxyethanol both have wide applications. 2-Methoxyethanol is mainly used as solvent for oil, lignin, nitro cellulose, alcohol-soluble dye and synthetic resin. It can also be used as industrial dye penetrant and leveling agent. 2-Ethoxyethanol is mainly used as solvents for nitro-cellulose lacquer and aircraft wing paint. It is also used as varnish plastic, purifying liquid, dye bath and can increase the emulsion stability. It is widely used in formulations of advanced automotive brake fluid and intermediates for preparing ester derivatives.

In this paper, the kinetics and mechanism of oxidation of 2-methoxyethanol and 2-ethoxyethanol by potassium ferrate were studied.

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 ($\epsilon = 1.15 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$). 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 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.

Product analysis: After completion of the reaction, adding $\text{K}_3\text{Fe}(\text{CN})_6$ to the solution have non-experimental phenomena, while adding $\text{K}_4\text{Fe}(\text{CN})_6$ is generated prussian blue precipitate; by adding 2,2-bipyridyl methanol solution have non-experimental phenomena also. It is proved that the final reduction product of Fe(VI) is Fe(III)¹⁶. After completion of the reaction, the oxidation product was identified as aldehyde alcohols which was precipitated as 2,4-dinitro phenylhydrazone derivative.

Reaction intermediate: Added 1,10-phenanthroline to reductant solution, then mixed with the K_2FeO_4 solution, purple colour disappeared at the same time and orange colour appeared, indicating that $\text{Fe}(\text{phen})_3^{2-}$ have generated in the process of reaction¹⁶. It is proved that Fe(II) stage have once appeared in the process of Fe(VI) reduction to Fe(III).

RESULTS AND DISCUSSION

Evaluation of pseudo-first order rate constants: Under the conditions of $[\text{reductant}]_0 \gg [\text{Fe(VI)}]_0$, 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 ($r \geq 0.999$). Generally, to calculate k_{obs} , 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 $\pm 5\%$ ¹⁷.

Rate dependence on [reductant]: At fixed $[\text{Fe(VI)}]$, $[\text{OH}^-]$, 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 $[\text{reductant}]$ were linear. For the plots passed through the grid origin (Figs. 1 and 2), the reaction was first order with reductant.

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

Reaction mechanism: James¹⁴ 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, 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: $\text{rate} = k[\text{FeO}_4^{2-}][\text{R}]$. In essence, the results were consistent with James^{13,14}.

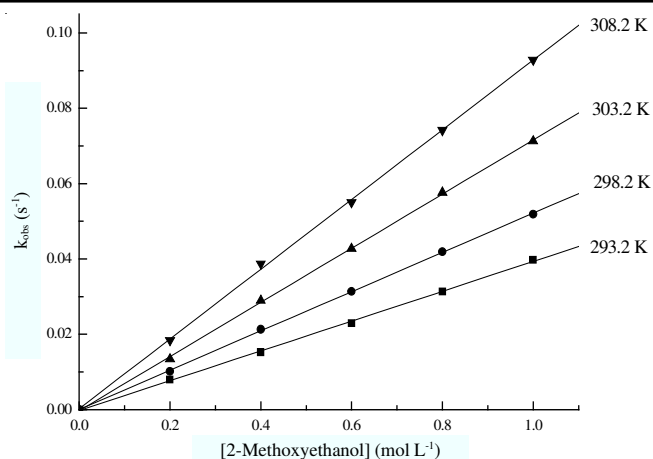


Fig. 1. Plots of k_{obs} versus $[\text{2-methoxyethanol}]$ at different temperatures ($r \geq 0.999$) $[\text{Fe(VI)}] = 2.07 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{OH}^-] = 1.32 \times 10^{-4} \text{ mol L}^{-1}$, $I = 1.00 \text{ mol L}^{-1}$

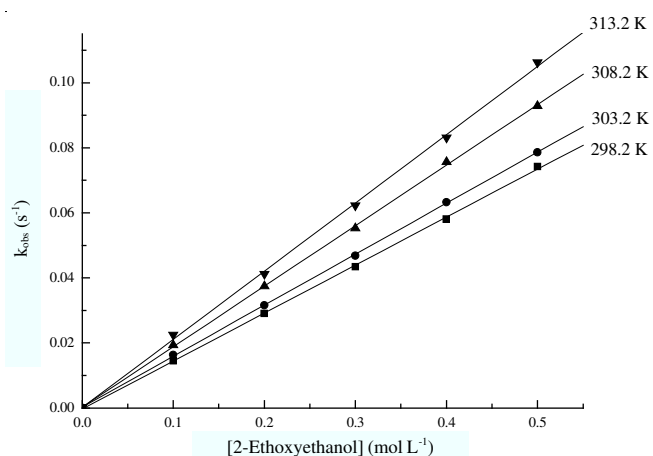


Fig. 2. Plots of k_{obs} versus $[\text{2-ethoxyethanol}]$ at different temperatures ($r \geq 0.999$) $[\text{Fe(VI)}] = 1.15 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{OH}^-] = 3.55 \times 10^{-4} \text{ mol L}^{-1}$, $I = 1.00 \text{ mol L}^{-1}$

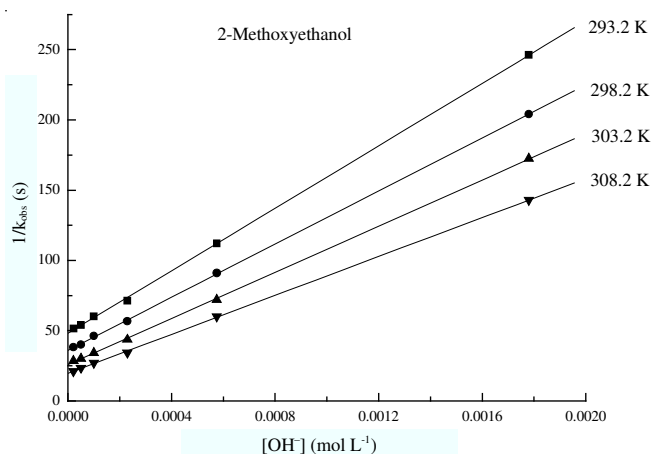
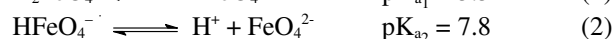
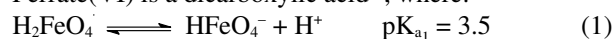


Fig. 3. Plots of $1/k_{\text{obs}}$ versus $[\text{OH}^-]$ at different temperatures ($r \geq 0.999$) $[\text{Fe(VI)}] = 2.07 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{2-methoxyethanol}] = 0.40 \text{ mol L}^{-1}$, $I = 1.00 \text{ mol L}^{-1}$

Ferrate(VI) is a dicarboxylic acid¹³, where:



Under the experimental conditions of this paper, will be partial hydrolysis:

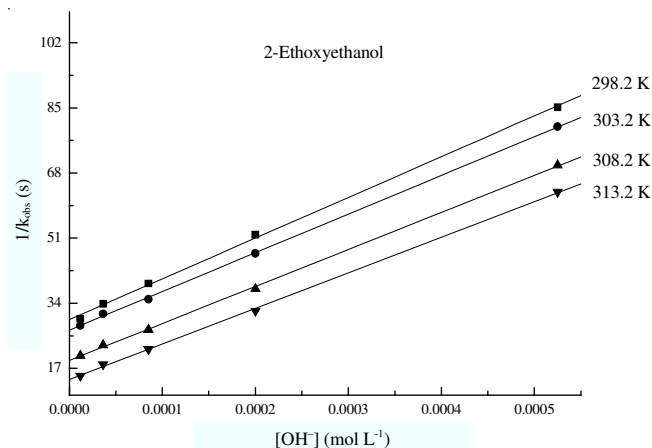
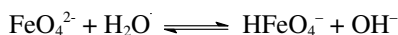


Fig. 4. Plots of $1/k_{\text{obs}}$ versus $[\text{OH}^-]$ at different temperatures ($r \geq 0.999$) $[\text{Fe(VI)}] = 1.18 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{2-ethoxyethanol}] = 0.10 \text{ mol L}^{-1}$, $I = 1.00 \text{ mol L}^{-1}$



Hence:

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

This experiment is performed at pH = 10.12 and 10.55, then there is

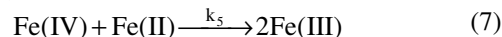
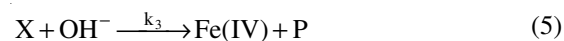
$$\frac{[\text{HFeO}_4^-]}{[\text{FeO}_4^{2-}]} = \frac{K_h}{[\text{OH}^-]} = 4.78 \times 10^{-3}$$

and

$$\frac{[\text{HFeO}_4^-]}{[\text{FeO}_4^{2-}]} = \frac{K_h}{[\text{OH}^-]} = 1.78 \times 10^{-3}$$

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 $[\text{FeO}_4^{2-}]$ was monitored, the rate of the reaction can be derived as:

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

Eqn. 9 can be obtained from (3):

$$[\text{HFeO}_4^-] = \frac{K_h[\text{FeO}_4^{2-}]}{[\text{OH}^-]} \quad (9)$$

Substituting eqn. 9 into 8, we can get the following eqn.

10:

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

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

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

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

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

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

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

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 ($\text{mol}^{-1} \text{L s}^{-1}$)	2-Methoxyethanol	35.65	41.94	48.25	57.20	–
	2-Ethoxyethanol	–	149.17	156.97	164.05	170.79
Thermodynamic activation parameters	2-Methoxyethanol	$E_a = 23.14 \text{ kJ mol}^{-1}$, $\Delta H^\ddagger = 20.66 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -144.69 \text{ J K}^{-1} \text{ mol}^{-1}$				
	2-Ethoxyethanol	$E_a = 6.99 \text{ kJ mol}^{-1}$, $\Delta H^\ddagger = 4.51 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -188.15 \text{ J K}^{-1} \text{ mol}^{-1}$				

The plots of $\ln k$ versus $1/T$ have following intercept (a) slope (b) and relative coefficient (r). 2-Methoxyethanol: a = 13.06, b = -2782.95, r = 0.9999, 2-Ethoxyethanol: a = 7.83, b = -841.39, r = 0.9992

TABLE-2
VALUES OF k_{obs} EXPERIMENTAL AND CALCULATED AT DIFFERENT
TEMPERATURES ($[\text{OH}^-] = 1.32 \times 10^{-4} \text{ mol L}^{-1}$ R = 2-METHOXYETHANOL)

T (K)	0.20 (c/mol L ⁻¹)		0.40 (c/mol L ⁻¹)		0.60 (c/mol L ⁻¹)		0.80 (c/mol L ⁻¹)		1.00 (c/mol L ⁻¹)	
	EXP	CAL	EXP	CAL	EXP	CAL	EXP	CAL	EXP	CAL
293.2	0.00800	0.00794	0.0152	0.0159	0.0230	0.0238	0.0314	0.0318	0.0398	0.0397
298.2	0.0102	0.0104	0.0213	0.0207	0.0313	0.0311	0.0419	0.0414	0.0519	0.0518
303.2	0.0134	0.0143	0.0290	0.0286	0.0427	0.0429	0.0576	0.0572	0.0713	0.0715
308.2	0.0184	0.0186	0.0387	0.0372	0.0550	0.0557	0.0742	0.0743	0.0928	0.0929

TABLE-3
VALUES OF k_{obs} EXPERIMENTAL AND CALCULATED AT DIFFERENT
TEMPERATURES ($[\text{OH}^-] = 3.55 \times 10^{-4} \text{ mol L}^{-1}$ R = 2-ETHOXYETHANOL)

T (K)	0.10 (c/mol L ⁻¹)		0.20 (c/mol L ⁻¹)		0.30 (c/mol L ⁻¹)		0.40 (c/mol L ⁻¹)		0.50 (c/mol L ⁻¹)	
	EXP	CAL	EXP	CAL	EXP	CAL	EXP	CAL	EXP	CAL
298.2	0.0145	0.0148	0.0291	0.0296	0.0434	0.0444	0.0580	0.0592	0.0743	0.0740
303.2	0.0164	0.0158	0.0316	0.0316	0.0468	0.0474	0.0633	0.0632	0.0786	0.0790
308.2	0.0193	0.0188	0.0374	0.0376	0.0552	0.0564	0.0757	0.0752	0.0929	0.0940
313.2	0.0225	0.0213	0.0412	0.0426	0.0623	0.0639	0.0831	0.0852	0.106	0.107

Conclusion

Based on the above discussion and results, the mechanism of the reaction of potassium ferrate with 2-methoxyethanol and 2-ethoxyethanol are reported. Both are completed by double-electron transfer. First, Fe(VI) react with a molecule of reductant to form complex X, under the attack of strong base, the X dissociates into Fe(IV) and product, then Fe(IV) with another molecule of reductant further react to generate Fe(II) and product. At last, Fe(IV) react with Fe(II) to generate Fe(III). At the same time we also observed the rate of the rate-determining step of 2-ethoxyethanol is quicker than that of 2-methoxyethanol, the rate constants of the rate determining step for 2-ethoxyethanol are larger than those for 2-methoxyethanol, 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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