Kinetics and Mechanism of Oxidation of *iso*-Propanolamine and *iso*-Butanolamine by Potassium ferrate

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The kinetics of oxidation of *iso*-propanolamine and *iso*-butanolamine by potassium ferrate(VI) in alkaline liquids at a constant ionic strength has been studied spectrophotometrically in the temperature range of 288.2-308.2 K. The reaction shows first order dependence on potassium ferrate(VI) and each reductant with respect to [OH⁻], the reaction is negative fraction order. The observed rate constant (k_{obs}) decreases with the increase of [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: *Iso*-propanolamine, *Iso*-butanolamine, Potassium ferrate, Kinetics, Mechanism, Oxidation.

INTRODUCTION

Potassium ferrate is an effective and multi-functional water treatment agent, has strong oxidation capacity in aqueous solution[1-4]. Its reductive product Fe(III) does not have toxicity. It integrates the properties, such as oxidation, sterilzation, adsorption, flocculation and deodorization, without causing secondary pollution in wastewater treatment. To understand the utility of ferrate ion, the study of this ion is needed. Ferrate can oxidize many substance, including inorganic compounds such as $S_2O_4^{2-}$, SCN^-, H_2S *etc*.[5-7] and organic compounds such as alcohol, acid, hydroxyl ketone, hydrogen quinonoids, benzene, oxime *etc*.[8-10] without any disturbance of environment because of its strong ability of oxidation,which can be shown from its electrode potential. It is the ideal antioxidant of high efficiency and high selectivity.

To date, relatively few kinetic studies of ferrate oxidations have appeared in the literature. Goff and Murmann published the first kinetic study for the ferrate oxidation of hydrogen peroxide and sulfite along with an oxygen exchange study[11]. Bielski has reported the oxidation of amino acids by ferrate occurs *via* one-electron radical pathways[12]. In this system, the oxidation occurs by a one-electron pathway to produce Fe(V) and then Fe(V) rapidly undergoes a two-electron transfer to form an inner-sphere Fe(III) complex[13]. The exact mechanism by which this occurs is not known. In contrast to the one-electron mechanisms suggested by Bielski, Johnson and Lee have proposed two-electron reductions of ferrate[14]. The proposed bridged species contains an ester linked, Fe-O-S

moiety (S = substrate) accompanied by consecutive two-electron reductions of Fe(VI) that results in Fe(II). Direct oxygen transfer was observed by oxygen tracer studies thereby supporting this mechanism.

Iso-propanolamine can be used as the raw material of surfactant and scouring agent of fiber industry, antistatic agent, dyeing assistant and fiber wetting agent. It can also be used to synthesize detergents, cosmetics, lubricating oil, antioxidants of cutting oils, plasticizer, emulsifier and solvent preparation.

Iso-butanolamine is a well-known multifunctional additive, is appropriated for all types of latex paint, used as pigment dispersant and pH regulator instead of ammonia. As an effective altogether dispersant, *iso*-butanolamine can prevent the aggregation of pigments in the formula and at the same time improve the comprehensive performance of coatings effectively. Also, iso-butanolamine is one of the optional absorbers of CO_2 in chemical absorb, which is widely concerned in the field of CCS (CO_2 capture and storage).

Iso-propanolamine and *iso*-butanolamine don't have strong toxicity, but they are irritating which can cause a certain degree of damage to eyes and skin because of the exist of amino. In this paper, the kinetics and mechanism of oxidation of *iso*-propanolamine and *iso*-butanolamine by potassium ferrate were studied in detail.

EXPERIMENTAL

All the reagents used were of A.R. grade and 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 ($\varepsilon = 1.15 \times 10^3$ L mol^{-1} cm^{-1}). The solution of K_2FeO_4 was always freshly prepared before use. The buffer solution which contained KNO_3 and the Na_2HPO_4 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 (± 0.1 K, Baoding, China).

Kinetics measurements: The oxidant and reductant were both dissolved in buffer solution which contained required concentration of KNO_3 and Na_2HPO_4. The reaction was initiated by mixing 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 where other species did not absorb significantly (Fig. 1). All kinetics measurements were carried out under pseudo-first order conditions.
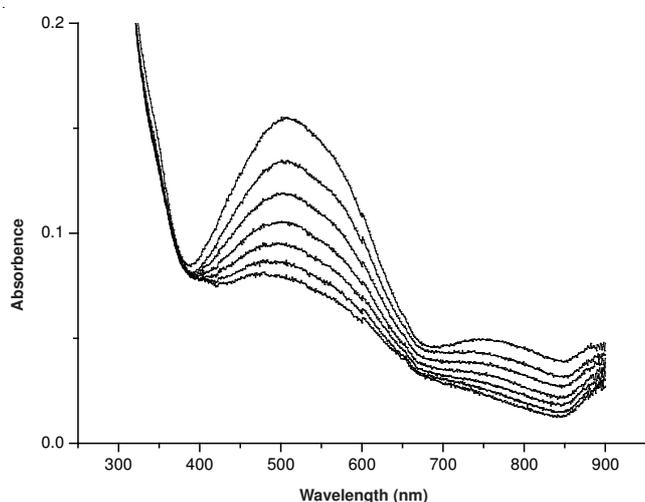
Fig. 1. Plots of reduction of oxidant absorption peak through the reaction

Product analysis: After completion of the reaction, by adding $K_3Fe(CN)_6$ to the solution, there was no experimental phenomena, while added $K_4Fe(CN)_6$, prussian blue precipitate generated by adding methanolic solution of 2,2-bipyridyl. It proves that the final product of Fe(VI) is Fe(III)[16]. At the same time the oxidation product was identified as aldehyde alcohols which was precipitated as 2,4-dinitrophenylhydrazone derivative.

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

Oxidation product of reductant: Compared to reductant solution, ammonia was detected through the reaction using the method of Dong[17], which proved that amino group of the reductant was oxidized to ammonia.

RESULTS AND DISCUSSION

Evaluation of pseudo-first order rate constants: Under the conditions of [reductant]$_0$ >> [Fe(VI)]$_0$, the plots of ln (A$_t$ - A$_\infty$),where A$_t$ and A$_\infty$ are the absorbance at time t and infinite time, respectively *versus* time t were straight line (Fig. 2), which indicats the reaction is first order with respect to the Fe(VI) complex. The pseudo-first-order rate constants k$_{obs}$ were calculated by the method of least squares (r = 0.999). Generally, to calculate k$_{obs}$, A$_t$ values within three times of the half-lives were used. The k$_{obs}$ values were the average values of at least three independent experiments and reproducibility is within ± 5 %.
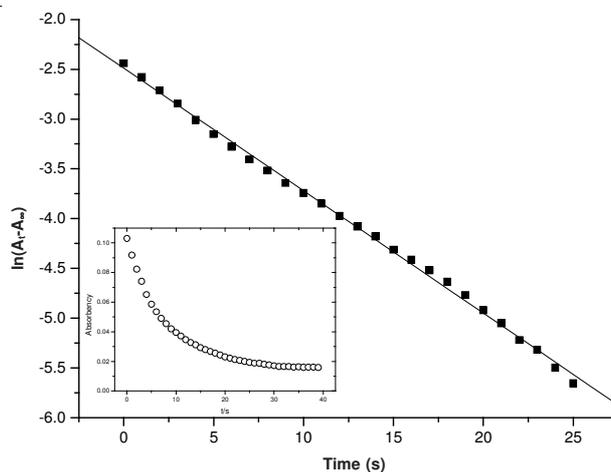
Fig. 2. Plots of ln (A$_t$ - A$_\infty$) *versus* time t, r = -0.998

Rate dependence on [reductant]: At fixed [Fe(VI)], [OH$^-$] and 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 (Figs. 3 and 4), the reaction was first order with reductant.
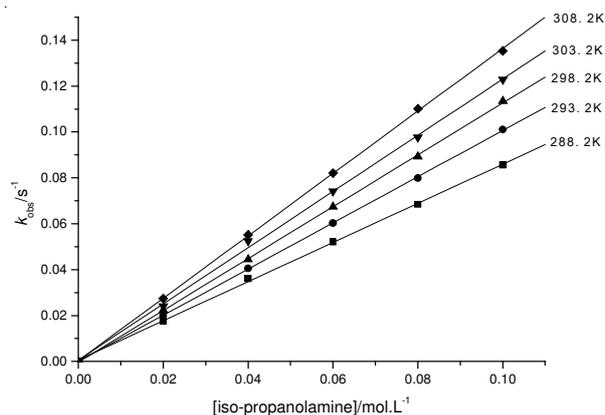
Fig. 3. Plots of k$_{obs}$ *versus* [*iso*-propanolamine] at different temperatures (r = 0.999) [Fe(VI)] = 1.44 × 10^4 mol L^{-1}, [OH$^-$] = 9.77 × 10^{-5} mol L^{-1}, I = 1.00 mol L^{-1}

Rate dependence on [OH$^-$]: Under fixed [Fe(VI)], [reductant], ionic strength I and temperature, k$_{obs}$ values were decreased with the increase of [OH$^-$], which indicates that there is a balance of [OH$^-$] generation before the speed-control step[18]. The order with respect to OH$^-$ was found to be negative fractional. The straight lines of 1/k$_{obs}$ *versus* [OH$^-$] were observed (Figs. 5 and 6).
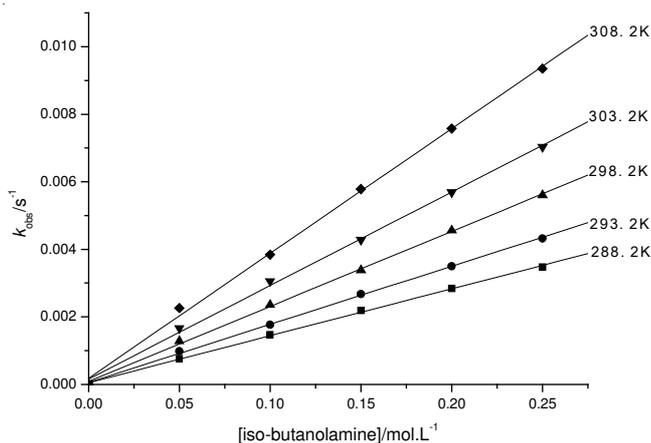
Fig. 4. Plots of k_{obs} *versus* [*iso*-butanolamine] at different temperatures (r = 0.999) [Fe(VI)] = 1.44 × 10⁻⁴ mol L⁻¹, [OH⁻] = 1.07 × 10⁻⁴ mol L⁻¹, I = 1.00 mol L⁻¹
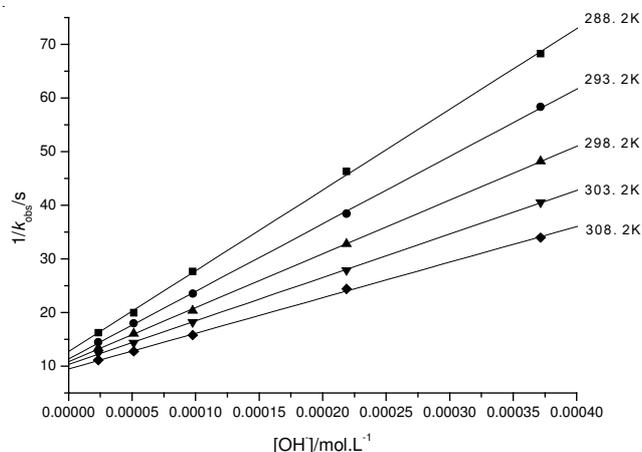
Fig. 5. Plots of $1/k_{obs}$ *versus* [OH0⁻] at different temperatures (r = 0.999) [Fe(VI)] = 1.44 × 10⁻⁴ mol L⁻¹, [*iso*-propanolamine] = 0.04 mol L⁻¹, I = 1.00 mol L⁻¹
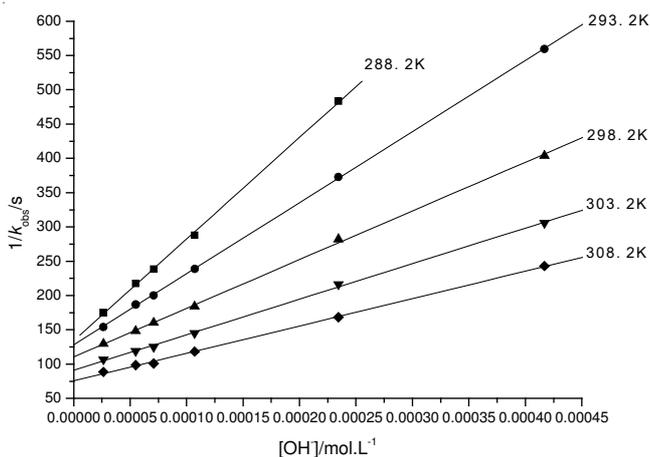
Fig. 6. Plots of $1/k_{obs}$ *versus* [OH⁻] at different temperatures (r = 0.999) [Fe(VI)] = 1.44 × 10⁻⁴ mol L⁻¹, [*iso*-butanolamine] = 0.25 mol L⁻¹, I = 1.00 mol L⁻¹

Reaction mechanism: James Carr[14] has given the rate equation as follows:

$$\text{rate} = k_1[\text{FeO}_4^{2-}] + k_2[\text{FeO}_4^{2-}]^2 + k[\text{FeO}_4^{2-}][S]$$

where [S] represents substrate concentration. James Carr thought that the first two terms were contribution of $K_2\text{FeO}_4$ self-decomposition rate to the reaction system when there was no substrate. In present studies, under the experimental conditions, the self-decomposition rate of $K_2\text{FeO}_4$ is far less than oxidation rate of reductant reaction, so we get the rate equation: rate = $k[\text{FeO}_4^{2-}][R]$. The results were consistent with James Carr suggestions.

Ferrate(VI) is a dicarboxylic acid[19], where:

$$\text{H}_2\text{FeO}_4 \rightleftharpoons \text{HFeO}_4^- + \text{H}^+ \qquad pK_{a_1} = 3.5 \quad (1)$$

$$\text{HFeO}_4^- \rightleftharpoons \text{H}^+ + \text{FeO}_4^{2-} \qquad pK_{a_2} = 7.8 \quad (2)$$
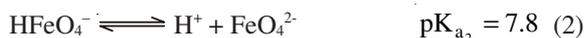
Under the experimental conditions of this paper, FeO_4^{2-} will be partial hydrolysis:

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 = 9.99 and 10.03, then there is

$$\frac{[\text{HFeO}_4^-]}{[\text{FeO}_4^{2-}]} = \frac{K_h}{[\text{OH}^-]} = 6.46 \times 10^{-3}$$

and

$$\frac{[\text{HFeO}_4^-]}{[\text{FeO}_4^{2-}]} = \frac{K_h}{[\text{OH}^-]} = 5.90 \times 10^{-3}$$

Although the concentration of HFeO_4^- is very small, it is easy for it to form a hexatomic-ring complex with the reductant in the presence of hydrogen atom, which has higher activity. Under the attack of hydroxyl ion, 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 takes place mainly through HFeO_4^-.

According to the discussion, the following reaction mechanism is proposed:

$$\text{FeO}_4^{2-} + \text{H}_2\text{O} \xrightleftharpoons{K_h} \text{HFeO}_4^- + \text{OH}^- \qquad (3)$$

$$\text{HFeO}_4^- + \text{R} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{X} \qquad (4)$$

$$\text{X} + \text{OH}^- \xrightarrow{k_3} \text{Fe(IV)} + \text{P} \qquad (5)$$

$$\text{Fe(IV)} + \text{R} \xrightarrow{k_4} \text{Fe(II)} + \text{P} \qquad (6)$$

$$\text{Fe(IV)} + \text{Fe(II)} \xrightarrow{k_5} 2\text{Fe(III)} \qquad (7)$$
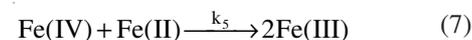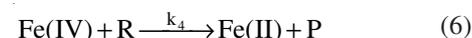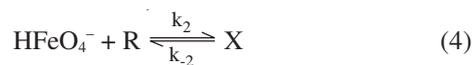
Reaction (4) is the rate-determining step, where R stands for reductant and P stands for product. As the rate of the disappearance of $[\text{FeO}_4^{2-}]$ was monitored, the rate of the reaction can be derived as:

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

$$= \frac{k_2 k_3[\text{HFeO}_4^-][R][\text{OH}^-]}{k_{-2} + k_3[\text{OH}^-]} \qquad (8)$$

Eqn. 9 can be obtained from (3):

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

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

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

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

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

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

The equations indicate that the reaction should be first order both with Fe(VI) and reductant. The plot of $1/k_{obs}$ *versus* $[OH^-]$ derived from eqn. 12 at constant [R] is linear with positive intercept. These are consistent with the experimental phenomena.

As the plots of $1/k_{obs}$ *versus* $[OH^-]$ were shown in Figs. 5 and 6, the rate-determining step rate constants (k_2) could be evaluated and the thermodynamic activation parameters were obtained (Table-1)[20] with the help of their slopes and eqn. 12.

Meanwhile, with the help of eqn. 12, the values of k' under corresponding temperature could be calculated using the slopes and intercepts of Figs. 5 and 6. Then, substituting k', k_2 and $[OH^-]$ into eqn. 11, we can calculate the rate constants under corresponding [R], which are closed to the experimental value (Tables 2 and 3). This illustrates that the eqn. 12 is correct and the reaction mechanism is reasonable.

Conclusion

The results and discussion presented in this paper demonstrate that the reaction of potassium ferrate with *iso*-propanolamine and *iso*-butanolamine are completed by two-electron transfer. First, Fe(VI) react with a molecule of reductant to form Fe(IV) and product, then Fe(IV) with another molecule of reductant react further to generate Fe(II) and product. At last, Fe(IV) react with Fe(II) and generate Fe(III). At the same time we also observed the rate of the rate-determining step of *iso*-propanolamine is quicker than that of *iso*-butanolamine and the rate constants of the rate-determining step for *iso*-propanolamine is larger than those for *iso*-butanolamine. The reason for it should be that the resistance of *iso*-butanolamine is bigger than *iso*-propanolamine because of the exist of branch on α-C. The activation parameters are all in support of the mechanism and consistent with experimental phenomena.

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TABLE-1
RATE CONSTANTS (k_2) AND THERMODYNAMIC ACTIVATION PARAMETERS OF THE RATE-DETERMINING STEP

	T (K)	288.2	293.2	298.2	303.2	308.2
k_2 (mol^{-1} L s^{-1})	*iso*-propanolamine	263.37	315.22	394.90	489.08	597.07
	iso-butanolamine	4.28	6.11	8.93	12.24	15.26
Thermodynamic activation parameters	*iso*-propanolamine	E_a= 30.65 kJ mol^{-1}, $\Delta H^{\neq}$ = 28.17 kJ mol^{-1}, $\Delta S^{\neq}$ = -100.73 J K^{-1} mol^{-1}				
	iso-butanolamine	E_a = 47.89 kJ mol^{-1}, $\Delta H^{\neq}$ = 45.41 kJ mol^{-1}, $\Delta S^{\neq}$ = -74.83 J K^{-1} mol^{-1}				

The plots of ln k *versus* 1/T have following intercept (a) slope (b) and relative coefficient (r). *iso*-propanolamine: a = 18.35 b = -3686.63 r = 0.999, *iso*-butanolamine: a = 21.46, b = -5759.64, r = 0.997.

TABLE-2
VALUES OF $10^3 \times k_{obs}$ EXPERIMENTAL AND CALCULATED ATDIFFERENT
TEMPERATURES ($[OH^-]$ = 9.77 × 10^{-5} mol L^{-1} R = *iso*-PROPANOLAMINE)

c (mol L^{-1})	0.02		0.04		0.06		0.08		0.10	
T (K)	EXP	CAL	EXP	CAL	EXP	CAL	EXP	CAL	EXP	CAL
288.2	17.58	17.33	36.12	34.67	52.12	52.00	68.44	69.33	85.62	86.67
293.2	20.10	20.13	40.57	40.26	60.30	60.39	79.89	80.52	101.07	100.65
298.2	22.33	23.14	46.15	46.27	68.07	69.40	91.18	92.54	113.42	115.67
303.2	24.07	26.29	52.39	52.58	77.28	78.87	99.54	105.16	122.84	131.45
308.2	28.63	30.11	57.94	60.22	82.67	90.33	119.63	120.44	135.32	150.56

TABLE-3
VALUES OF $10^4 \times k_{obs}$ EXPERIMENTAL AND CALCULATED AT DIFFERENT
TEMPERATURES ($[OH^-]$ =1.07 × 10^{-4} mol L^{-1} R = *iso*-BUTANOLAMINE)

c (mol L^{-1})	0.05		0.10		0.15		0.20		0.25	
T (K)	EXP	CAL	EXP	CAL	EXP	CAL	EXP	CAL	EXP	CAL
288.2	7.68	6.84	14.48	13.68	21.01	20.52	26.98	27.36	34.75	34.20
293.2	9.85	8.37	17.14	16.73	25.51	25.10	34.32	33.47	41.88	41.84
298.2	12.85	10.73	23.58	21.46	32.05	32.19	42.35	42.92	54.32	53.65
303.2.	16.63	13.66	28.64	27.32	42.79	40.98	56.76	54.64	68.98	68.29
308.2	22.60	17.65	38.44	35.30	57.83	52.96	72.39	70.61	89.04	88.26

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