A Kinetic Study on the Oxidation of Ferrous Ion with Dissolved Molecular Oxygen

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The Kinetics of the oxidation reaction of ferrous ions with dissolved molecular oxygen in hydrochloric acid solutions have been studied at FeCl_2 concentration of 0.2 mol dm^{-3} or below, over the range of HCl $3\text{--}6 \text{ mol dm}^{-3}$, and at various oxygen partial pressures and temperatures. It was found that reaction rate is expressed by the following expression.

$$R = kK_1K_2a_{\text{H}^+}a_{\text{Cl}^-}[\text{Fe}^{2+}] \cdot p_{\text{O}_2}$$

The activation energies were found to be 78.2 kJ mol^{-1} in 3 mol dm^{-3} hydrochloric acid solution and 70.7 kJ mol^{-1} in 3 mol dm^{-3} hydrochloric acid solution containing 2.5 mol dm^{-3} sodium chloride, suggesting the overall reaction rate is controlled by chemical reaction steps. It has been presumed that the species of HFeCl_2^{2+} is thought to be controlled by the activities of hydrogen ion and chloride ion.

1 Introduction

Studies on the oxidation reaction of Fe(II) with dissolved molecular oxygen in hydrochloric acid solutions are interesting in connection with the treatment of waste liquors containing Fe(II) chlorides, which are commonly discharged from the processes, such as the pickling of iron and steel, the upgrading of ilmenite or pentlandite ores, the ferric chloride leaching of copper concentrates, *etc.*

Much work has been carried out in the past on the autoxidation of ferrous sulphate solutions, but only a few papers are available for chloride systems.

Posner¹⁾ studied the kinetics of the autoxidation of ferrous chloride solutions and found that the reaction was of first order with respect to the concentrations of ferrous ion and dissolved oxygen but a more complex function of HCl . On the other hand, Yano and his co-workers²⁾ reported that the reaction was of second order with respect to the concentration of ferrous chloride and of first order to the partial pressure of oxygen. Also, they stated that the reaction rate was independent of the concen-

tration of hydrogen ion as far as the concentration of chloride ion was kept constant. Posner's conclusion of the effect of hydrochloric acid concentration on the reaction rate is quite different from that of Yano *et al.* The controversial conclusions by these previous investigators may be partly attributed to the difference in the experimental conditions employed.

However, it might be the easiest way to work kinetic experiments on the autoxidation of Fe(II) over the wide range of experimental conditions to reach a general understanding of its mechanism.

This study deals with the kinetics of the oxidation reaction of Fe(II) with dissolved molecular oxygen in hydrochloric acid solutions, aiming to get a better understanding of the reaction mechanism.

2 Experimental Procedures

The apparatus used for the oxidation experiments is shown in Fig. 1. The separable flask used as a reaction vessel was 1000 cm^3 in volume.

In each test, 1000 cm^3 of aqueous ferrous chloride solution, whose acid and chloride concentrations were adjusted with hydrochloric acid and various salts, respectively, was charged to the reaction vessel. The temperature of the water bath was controlled within $\pm 0.2^\circ\text{C}$. The apparatus had provision for vigorous agitation

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Fig. 1 Experimental apparatus

- A : Water bath, B : Reaction vessel
 C : Impeller, D : Thermometer
 E : Sampling tube, F : Gas inlet
 G : Manometer, H : Oxygen reservoir

of the reaction mixture at the constant speed of 1000 rpm. Gas phase was sucked at the rate of $5 \text{ dm}^3 \text{ min}^{-1}$ until 10^{-1} Torr is achieved. Then pure oxygen gas was allowed to flow into the reaction system. During each test the oxygen partial pressure was maintained at one atm. At given time intervals, 10 cm^3 of sample solution was removed and was subjected to chemical analysis. The extent of oxidation was determined by titration to the diphenylamine sulphonate end-point with a standard dichromate solution.

The activities of hydrogen ion as well as chloride ion were determined by the *emf* measurements of the following cells:

A silver-silver chloride electrode (3.33 mol dm^{-3} KCl) was used as a reference electrode in this study. The hydrogen electrode and the silver chloride electrode were prepared according to the methods described by Ives and Janz¹⁹.

The *emf* measurements were carried out using Takeda Riken-TR-6855 Digital Multimeter. The *emf* measurements using the above cells should include the liquid junction potential at the junction of the test solution and 3.33 mol dm^{-3} KCl solution of the reference electrode. It is known that the activity of hydrochloric acid increases remarkably with the increase in its concentration⁴¹. The addition of strong electrolyte to a hydrochloric acid solution changes the activity of hydrochloric acid⁴². In general, the value of liquid junction potential is affected

by the concentration of electrolytes added to the solution. However, the magnitude of variation in *emf* due to the activity change of hydrochloric acid is thought to be far greater than that of liquid junction potential, when the concentrated solutions are subjected for the measurements. Thus we may assume that the ion activities measured using the cells described above is useful for the analysis of autoxidation reaction.

Activities of hydrogen ion and chloride ion were calculated from the following equations:

$$\log a_{\text{H}^+} = (E_1 + 0.206) / (2.303 RT/F) \quad (1)$$

$$\log a_{\text{Cl}^-} = (-E_2 + E_0 - 0.206) / (2.303 RT/F) \quad (2)$$

where E_1 and E_2 are the observed electromotive forces of cell(a) and cell(b), respectively, and E_0 is the standard potential of the silver chloride electrode.

3 Experimental Results and Discussion

A typical example of rate curves for the autoxidation of Fe(II) is presented in Fig. 2 as a plot of $\log[\text{Fe(II)}]$ vs. time. The observed linear relationship agrees with the fact that the reaction rate is of first order with respect to Fe(II) concentration. This relationship was observed in all the kinetic experiments done throughout the present study, thus confirming the results of Posner¹⁹. Therefore, at constant temperature, oxygen pressure and

Fig. 2 Typical example of rate curves for the autoxidation of Fe(II)

FeCl_2 : 0.2 mol dm^{-3} , Temp.: 45°C , p_{O_2} : 1 atm,
 I: 3 mol dm^{-3} HCl, 2.5 mol dm^{-3} NaCl, II: 4 mol dm^{-3} HCl, 2 mol dm^{-3} NaClO₄, III: 5.5 mol dm^{-3} HCl

Fig. 3 Effect of oxygen pressure on rate constant

HCl : 3 mol dm⁻³, FeCl₂ : 0.2 mol dm⁻³
NaCl : 2 mol dm⁻³, Temp. : 45°C

hydrochloric acid concentration, we may calculate the rate constant k' from the rate equation $-d[\text{Fe(II)}]/dt = k'[\text{Fe(II)}]$.

To examine the effect of variation in the oxygen partial pressure on the rate constant k' , the oxidation rates of Fe(II) were measured at 0.2 and 1.0 atm, in 0.2 mol dm⁻³ FeCl₂ solution containing 3 mol dm⁻³ HCl and 2 mol dm⁻³ NaCl at 45°C, and the experimental results are shown in Fig. 3. This shows that the reaction rate is directly proportional to the oxygen partial pressure. Therefore, at constant temperature and hydrochloric acid concentration, we may calculate the overall second order rate constant k'' from the rate equation, $-d[\text{Fe(II)}]/dt = k'' \cdot [\text{Fe(II)}] \cdot p_{O_2}$.

Next, the rate of oxidation reaction was measured at various temperatures with the solutions, whose composition were 0.2 mol dm⁻³ FeCl₂ and 3 mol dm⁻³ HCl, and 0.2 mol dm⁻³ FeCl₂, 3 mol dm⁻³ HCl and 2.5 mol dm⁻³ NaCl, respectively, at 1 atm of oxygen partial pressure. By plotting the logarithm of k'' value against the reciprocal of the absolute temperature, the Arrhenius plots shown in Fig. 4 were obtained. From the Arrhenius plots, values of 78.2 and 70.7 kJ mol⁻¹ were obtained as the apparent activation energies, showing a slight decrease in apparent activation energy by the addition of sodium chloride.

The values of the apparent activation energy obtained in this work are in agreement with the value of 61.1 kJ mol⁻¹ determined in HCl

Fig. 4 Effect of temperature on rate constant
HCl : 3 mol dm⁻³, FeCl₂ : 0.2 mol dm⁻³,
 p_{O_2} : 1 atm

Fig. 5 Effect of HCl concentration on rate constant

FeCl₂ : 0.2 mol dm⁻³, Temp. : 45°C,
 p_{O_2} : 1 atm

solutions by Posner¹³, and that of 72.8 kJ mol⁻¹ obtained by George⁶ using perchlorate solutions. These values of activation energy suggest that the chemical reaction controls the overall reaction rate.

Moreover, the rate of oxidation reaction was measured as a function of acidity in the concentration range 3–6 mol dm⁻³ HCl. The experimental results are shown in Fig. 5, in which rate constant, k'' is plotted against the

concentration of hydrochloric acid. It was evident from Fig. 5 that the reaction rate increases rapidly and non-linearly with the increase in the hydrochloric acid concentration. In this respect, Yano and his collaborators³⁾ reported that the reaction rate was independent of the hydrogen ion concentration in its range 0.2–0.8 mol dm⁻³ as far as the concentration of chloride ion was kept constant, whereas the reaction rate was greatly increased with the increase in chloride ion concentration. Posner¹⁾ also found that in HCl solution at concentrations above 4 mol dm⁻³ an extremely rapid autoxidation of ferrous ions set in, and below this HCl concentration, the reaction was extremely slow. He assumed that in the concentration range of 6–8 mol dm⁻³ HCl, reaction rate was proportional to $(C_{\text{HCl}} - 5.5)$ and pointed out that the formation of associated complex $[\text{HFe}^{2+}\text{Cl}]$ was important to promote the autoxidation. The experimental results shown in Fig. 5 are different in some extent from the conclusion by Posner or by Yano and others.

The concentration of hydrochloric acid used in this work was rather high, so it may be reasonable to use the concept of activity instead of concentration to discuss the role of hydrochloric acid in the autoxidation of Fe(II). Mean activity coefficients of HCl at 25°C cited in the book of Harned and Owen⁷⁾ were used to calculate the value of HCl activity.

Rate constant shown in Fig. 5 is then replotted against the activity of hydrochloric acid, and is depicted in Fig. 6. This figure shows that the rate of oxidation is directly propor-

tional to a_{HCl} . In order to examine the generality of this first order dependence, a set of oxidation experiments was done using the ferrous chloride solutions containing hydrochloric acid and sodium chloride.

The mean activity coefficient of HCl in a mixed HCl–NaCl solution was calculated by using the following equation⁸⁾:

$$\log \gamma_{\pm} = \log \gamma_{\pm}^{\circ} - \beta \cdot m \quad (3)$$

where $\gamma_{\pm}$ and $\gamma_{\pm}^{\circ}$ denote the mean activity coefficients of HCl in mixed solution and in pure HCl solution, respectively, β is the parameter and m is the molality of NaCl expressed in mol solute/kg-H₂O.

The rate constant for the HCl–NaCl mixed solution system is also given in Fig. 6. It is evident that the k'' – a_{HCl} plots for the autoxidation of Fe(II) in HCl–NaCl mixed solutions lie on the same straight line obtained for the oxidation of Fe(II) in HCl solutions. The figure also indicates that the reaction rate is directly proportional to a_{HCl} of the solutions in the HCl–NaCl mixed solution.

Since hydrochloric acid is a strong electrolyte, most of it must dissociate into hydrogen ions as well as chloride ions. Also the activity of HCl is defined as the product of hydrogen ion activity and chloride ion activity. Under these circumstances, the physical meaning of the first order dependency of rate constant upon a_{HCl} must be carefully examined.

Reaction rate might be directly concerned with the activity of undissociated HCl, or otherwise it might be the function of the activities of hydrogen ion and/or chloride ion. It is necessary to investigate which would be the case.

The activities of hydrogen and chloride ions in dilute aqueous hydrochloric acid solutions, which contain neutral chloride salt, have been studied considerably in detail^{8,9)}. However no published data on the activities of hydrogen ion and chloride ion in HCl–MCl_n mixed solutions, whose HCl concentration is over 0.1 mol dm⁻³, are available at this stage.

Therefore, the activities of the hydrogen ion and chloride ion in concentrated HCl solutions containing NaCl were measured in this work through the emf measurements of the following

Fig. 6 Effect of a_{HCl} on rate constant
 FeCl_2 : 0.2 mol dm⁻³, Temp.: 45°C,
 p_{O_2} : 1 atm

Fig. 7 Effect of NaCl concentration on activity of H^+ ion or Cl^- ion in HCl solution at $25^\circ C$

I : 2 mol dm^{-3} HCl, II : 3 mol dm^{-3} HCl

III : 4 mol dm^{-3} HCl

cells at $25^\circ C$:

The experimental results are summarized in the forms of $\log a_{H^+}$ and $\log a_{Cl^-}$ plotted against the concentration of sodium chloride, as shown in Fig. 7. The values of $\log a_{H^+}$ as well as $\log a_{Cl^-}$ increase with the increase in sodium chloride concentration, with approximately the same slopes for the different concentration of hydrochloric acid.

If the oxidation rate of ferrous ion is of first order with respect to each of a_{H^+} and a_{Cl^-} , the plot of $\log(k''/a_{H^+})$ vs. $\log a_{Cl^-}$, or $\log(k''/a_{Cl^-})$ vs. $\log a_{H^+}$ must lie on a straight line whose slope is unity.

The plot of $\log(k''/a_{H^+})$ vs. $\log a_{Cl^-}$ is given in Fig. 8, and the plot of $\log(k''/a_{Cl^-})$ vs. $\log a_{H^+}$ is depicted in Fig. 9. Evidently these figures support the assumption of the first order dependency of reaction rate upon a_{H^+} as well as a_{Cl^-} . Thus, the first order dependency of reaction rate upon a_{HCl} can now be understood as the first order dependency of reaction rate upon both a_{H^+} and a_{Cl^-} .

Regarding the effect of hydrochloric acid

Fig. 8 Relation between $\log(k''/a_{H^+})$ and $\log a_{Cl^-}$

a_{Cl^-}

(1) 4 mol dm^{-3} HCl, 1.5 mol dm^{-3} NaCl

(2) 4 mol dm^{-3} HCl, 1 mol dm^{-3} NaCl

(3) 3 mol dm^{-3} HCl, 2.5 mol dm^{-3} NaCl

(4) 3 mol dm^{-3} HCl, 2 mol dm^{-3} NaCl

(5) 3 mol dm^{-3} HCl, 1.5 mol dm^{-3} NaCl

(6) 4 mol dm^{-3} HCl

(7) 2 mol dm^{-3} HCl, 3 mol dm^{-3} NaCl

(8) 3 mol dm^{-3} HCl, 1 mol dm^{-3} NaCl

(9) 3 mol dm^{-3} HCl

Fig. 9 Relation between $\log(k''/a_{Cl^-})$ and $\log a_{H^+}$

(1) 3 mol dm^{-3} HCl, 2.5 mol dm^{-3} NaCl

(2) 4 mol dm^{-3} HCl, 1.5 mol dm^{-3} NaCl

(3) 4 mol dm^{-3} HCl, 1 mol dm^{-3} NaCl

(4) 3 mol dm^{-3} HCl, 2 mol dm^{-3} NaCl

(5) 3 mol dm^{-3} HCl, 1.5 mol dm^{-3} NaCl

(6) 2 mol dm^{-3} HCl, 3 mol dm^{-3} NaCl

(7) 4 mol dm^{-3} HCl

(8) 3 mol dm^{-3} HCl, 1 mol dm^{-3} NaCl

(9) 3 mol dm^{-3} HCl

concentration, Posner¹³ concluded that the rate had first order dependence on hydrochloric acid concentrations above 5.5 mol dm^{-3} . On

the other hand, Yano *et al.*²⁾ stated no influence of hydrogen ion concentration in dilute hydrochloric acid solution and they observed a remarkable rate enhancement by chloride addition. The present authors' results of the first order dependencies of the reaction with respect to each of hydrogen ion activity and chloride ion activity are quite different from the conclusions of previous investigations. However it might be possible to analyze the experimental results by Posner or by Yano *et al.* according to the same method of this study without any controversy.

As mentioned before, we observed that the rate is first order with respect to the concentration of Fe(II), and this may suggest that the ratio of the activity coefficient, $\gamma_{\text{Fe}^{2+}}/\gamma_{\text{HFeCl}^{2+}}$, stays almost constant during the oxidation reactions.

To interpret the results obtained in this work, the following oxidation mechanism involving chain reactions is proposed:

where K_1 and K_2 are the equilibrium constants for the reactions (4) and (5), respectively, and k_0 is the rate constant for the reaction (6). The above mechanism is similar to the one proposed by Cher and Davidson¹⁰⁾ for the autoxidation reaction of ferrous ion in aqueous phosphoric acid solutions.

Rate equation which satisfies both the experimental results and the mechanism proposed above, can be expressed by eqs. (10)

$$R = k \cdot [\text{HFeCl}^{2+}] \cdot p_{\text{O}_2} \\ = k_0 K_1 K_2 \cdot a_{\text{H}^+} \cdot a_{\text{Cl}^-} \cdot [\text{Fe}^{2+}] \cdot p_{\text{O}_2} \quad (10)$$

The concentration of the species HFeCl^{2+} is thought to be controlled by the activities of hydrogen ion and chloride ion.

4 Conclusion

The oxidation reaction of Fe(II) in aqueous hydrochloric acid solutions by dissolved molecular oxygen is controlled by chemical reaction steps. It is considered that the second order reaction holds between HFeCl^{2+} and dissolved O_2 under the experimental condition studied. The concentration of the former species is determined by the activities of both hydrogen ion and chloride ion.

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