KINETICS OF OXIDATION OF BIVALENT IRON BY CHLORATE

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Kinetics of Fe(II) oxidation by chlorate was studied in homogeneous systems (pH < 1, $HClO_4$) and in heterogeneous systems involving precipitate of Fe(III) hydrolysis products (pH 1 to 5·5). The stoichiometry (6 Fe^{2+} : 1 ClO_3^- : 6 H^+) as well as the rate equation ($-d[Fe^{2+}]/dt = k_{exp} . [Fe^{2+}][ClO_3^-]$) is the same in the two cases. Also the differences in the experimental activation energies and entropies for the two pH regions are insignificant. The $[OH^-]/[Fe^{3+}]$ ratio passes a maximum during the spontaneous change of pH (pH_0 5), whereas if the pH is maintained constant (pH 5) the ratio increases monotonically throughout the whole time interval followed. The balance of the Fe^{2+} and Fe^{3+} showed that part of the Fe^{2+} ($\sim 10^{-3}$ mol l^{-1}) was present during the reaction in the precipitate of the Fe(III) hydrolysis products, while part of the Fe^{3+} ($5 . 10^{-3}$ mol l^{-1}) existed outside this precipitate; the latter dropped by approximately two orders of magnitude only several tens of hours after the finishing of the Fe(II) oxidation.

Study of the kinetics and mechanism of the oxidation of bivalent iron by various oxidizing agents is not only of theoretical interest, but also of practical importance in view of the utilization of some ferric oxides and hydroxide-oxides as pigments or electrotechnical materials.

The oxidation of Fe(II) can be controlled, *i.e.* conducted in conditions leading to the desired product solely, only if an insight is gained into the mechanism of the elementary processes involved in the Fe(II) oxidation and formation of the Fe(III) hydrolysis products in different conditions.

Oxidation of Fe(II) by chlorate in aqueous solution can proceed in dependence on the pH either in the homogeneous phase, or with simultaneous precipitation of solid Fe(III) hydrolysis products. The kinetic data on the oxidation of Fe(III) by chlorate in strongly acidic medium (pH < 1, $HClO_4$) have been treated in detail by Mitzner and coworkers[1], who also have suggested a scheme of the possible mechanism. The authors consider an ionic-radical mechanism, where Cl(V) passes to the final product, Cl^-, *via* a series of lower oxidation degrees, *i.e.* ClO_2, ClO_2^-, ClO^-, and Cl_2. The reaction rate is proportional to the concentration of the activated complex $[Fe; HClO_3^{2+}]^{\neq}$. The effect of neutral salts on the rate of this reaction was studied before by Vronska and Banas[2]. The kinetics of the Fe(II) oxidation by chlorate has not been studied in the pH region where the Fe(III) hydrolysis products precipitate.

In the present work the kinetics of the Fe(II) oxidation by chlorate has been studied both in the homogeneous system at pH < 1 and in a heterogeneous system at pH 1 to 5·5, where $Fe(OH)_2$ does not yet precipitate.

EXPERIMENTAL

The oxidation was conducted at constant (but different in the various experiments) temperature, concentration of H^+ ions, and ionic strength, always in nitrogen inert atmosphere. The constant pH ($\pm 0{\cdot}05$) was maintained by means of an automatic titration apparatus (Radiometer, Copenhagen); for pH > 1 a solution of Na_2CO_3 or NaOH was added, the constant pH < 1 was ensured by using excess $HClO_4$. The constant ionic strength was established by a twenty-fold excess of $KClO_3$ with respect to the remaining constituents of the reaction solution. The experimental layout for the kinetic measurements is shown in Fig. 1.

The kinetic data were obtained from the time dependences of the concentration of Fe(II), as determined in the reaction system samples manganometrically or, in the presence of the Fe(III) hydrolysis products, dichromatometrically using diphenylamine as the redox indicator. The sum of the Fe(II) and Fe(III) concentrations, both in the liquid phase of the reaction mixture and in the solid phase, was determined chelatometrically. The concentration of Fe(II) in the liquid phase only, $[Fe^{2+}]_l$, was determined after removing the solid phase by centrifugation; in the sediment was determined the sum $[Fe^{2+})_s + [Fe^{3+}]_s$. The chlorate was determined by manganometric retitration of excess $FeSO_4$, the chloride ions argentometrically using potentiometric indication.

For the kinetic measurements, the following procedure was usually applied: 500 ml of the aqueous solution of 0·01—0·05M-$FeSO_4$, freed from the precipitate of Fe(III) hydrolysis products, was thermostated in the reaction vessel to 25°—50°C and freed from traces of oxygen using a nitrogen stream. After adjusting the pH as described above, the oxidation of Fe(II) was commenced by adding $KClO_3$ so that its concentration was 0·03—0·15 mol l^{-1}. The reaction conditions were chosen for the reaction half life not to be shorter than 5 min. In preselected time intervals, samples of the reaction system (10—25 ml) were taken and added to 200 ml of aqueous titration solution chilled to —5°C, containing 10 ml of concentrated H_3PO_4 and 10 ml of concentrated H_2SO_4. The reaction was slowed down owing to the low temperature and high dilution so that its rate was negligible with respect to that in the system examined. This slowing-down was verified by determining Fe(II) in different time intervals after the sampling. In the course of the reaction at pH > 1, the proceeding dependence of the volume of the alkaline solution required to maintain the constant pH upon time was recorded.

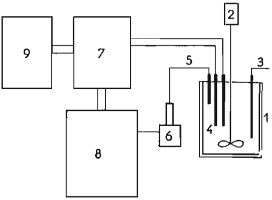

FIG. 1

Scheme of the Apparatus for the Investigation of the Fe(II) Oxidation

1 Thermostated glass reaction vessel, 2 rotating stirrer, 3 inert gas inlet, 4 electrodes for the pH measurement, 5 input of the solution from the automatic burette, 6 automatic burette of the pH-stat, 7 Titrator TTT 1c, 8 Titrigraph SBUR 2, 9 pH recorder TZ 21 S.

The results were statistically tested by using a table computer Compucorp 326 Scientist. The experimental dependences were treated by the least squares method, the fitting of the experimental variables was characterized by the correlation coefficient r and the precision of the values calculated from these dependences by the standard deviation[3].

RESULTS AND DISCUSSION

Kinetics of Oxidation at pH < 1

At pH < 1 and temperature up to 50°C, when the reaction proceeds in solution, the stoichiometry of the Fe(II) oxidation by chlorate was found, in accordance with[1], to be represented by the ratio $6\,Fe^{2+} : 1\,ClO_3^-$. The course of the reaction

$$6\,Fe^{2+} + ClO_3^- + 6\,H^+ = 6\,Fe^{3+} + Cl^- + 3\,H_2O \qquad (1)$$

can be described by the 2nd order kinetic equation

$$-d[Fe^{2+}]/dt = k_{exp}[Fe^{2+}][ClO_3^-]\,, \qquad (2)$$

where the empirical rate constant k_{exp} in the H^+ concentration region 0·2–0·8 mol l^{-1} is a linear function of $[H^+]$, expressed by the equation $k_{exp} = 0.247\,[H^+] - 0.022$ with the correlation coefficient $r = 0.9914$, which indicates a very good fit to the linear dependence.

The dependence of the rate constant on the temperature, obeying the Arrhenius relation, afforded the activation parameters – the activation energy E_a, activation enthalpy $\Delta H^{\neq}$, and activation entropy $\Delta S^{\neq}$ – as given in Table I.

Kinetics of Oxidation in the pH *Range* 1–6·5

During the oxidation of Fe(II) by chlorate at pH > 2 and at the temperature 25° to 50°C, hydrolysis products of the formed Fe(III) precipitate; the process can be described by the equation

$$m\,Fe^{3+} + n\,H_2O \rightleftharpoons Fe_m(OH)_n^{3m-n} + n\,H^+\,. \qquad (3)$$

In the range of pH 1–5, the same ratio of the reacting components was observed as in the range of pH < 1, and the reaction rate can be also represented by Eq. (*2*). At pH > 5·5, Fe(II) hydrolysis products precipitate as well, thus the rate constant can be defined according to Eq. (*2*) only for pH < 5·5. The overall change of the H^+ concentration in a time interval Δt obeys the equation

$$\Delta[H^+]_t = \Delta[H^+]_t^h - \Delta[H^+]_t^{ox}\,, \qquad (4)$$

where $-\Delta[H^+]_t^{ox}$ represents the consumption of H^+ during the oxidation of Fe(II) and $\Delta[H^+]_t^h$ the increase of $[H^+]$ accounted for by the hydrolysis of Fe(III). The dependence of pH on time during the spontaneous course of the reaction is represented in Fig. 2 by the curve (*s*), showing that the H^+ concentration increases in the course of the reaction, hence $\Delta[H^+]_t^{ox} < \Delta[H^+]_t^h$. From this it follows that in this case a constant pH has to be maintained with an alkaline solution, as described in the experimental part.

TABLE I

Activation Parameters of the Oxidation of Fe(II) by Chlorate

A: pH < 1, $[Fe^{2+}]_0 = 0{\cdot}009 \text{ mol l}^{-1}$, $[ClO_3^-]_0 = 0{\cdot}033 \text{ mol l}^{-1}$, $[H^+]_0 = 0{\cdot}442 \text{ mol l}^{-1}$; *B*: pH 5, $[Fe^{2+}]_0 = 0{\cdot}05 \text{ mol l}^{-1}$, $[ClO_3^-]_0 = 0{\cdot}166 \text{ mol l}^{-1}$, $[H^+] = 1 . 10^{-5} \text{ mol l}^{-1}$.

T K	$(k_{exp} \pm \sigma_k)$ $10^{-4}\text{l mol}^{-1}\text{s}^{-1}$	$\ln(k_{exp}) + 9$	E_a kJ mol^{-1}	$\Delta H^{\ddagger}$ kJ mol^{-1}	$\Delta S^{\ddagger}$ J mol^{-1} K^{-1}
			A		
288·15	292·3 ± 5·1	5·467			
298·15	749·5 ± 4·3	6·409	75·88 ± 3·68	65·69 ± 3·19	—43·98 ± 2·14
303·15	1 121·4 ± 6·6	6·812			
323·15	8 820·1 ± 46·2	8·874			
			B		
298·15	3·07 ± 0·04	0·912			
313·15	12·88 ± 0·06	2·346	80·35 ± 4·88	78·24 ± 4·73	—49·74 ± 3·01
323·15	38·28 ± 0·21	3·435			

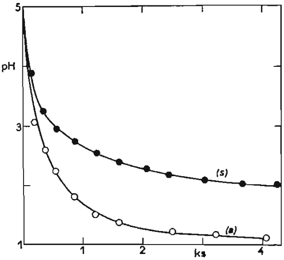

FIG. 2

Time Dependence of pH

$[Fe^{2+}]_0 = 0{\cdot}051 \text{ mol l}^{-1}$, $[ClO_3^-]_0 = 0{\cdot}166 \text{ mol l}^{-1}$, pH_0 5, 40°C; (*s*) spontaneous pH variation, (*a*) apparent pH variation at pH 5 = const.

Dependence of the Rate Constant on the pH *and on the Temperature*

In the region of pH 1 – 6·5, too, the reaction rate was proved to depend considerably on the H^+ concentration; the plot of the rate constant logarithm *versus* pH in the interval 1 – 5·5 is shown in Fig. 3. The dependence in the region of pH 0·07 – 0·58 and the rate constant values for pH 6 and 6·5 calculated from the initial rates are given for a comparison too. At these higher values the reaction deviates considerably from the 2nd order course, the $Fe(OH)_2$ precipitate appears, and the rate constant does not conform to Eq. (*2*) in the whole extent of reaction course. From the dependence given it is seen that in the H^+ concentration extent of six orders of magnitude the rate constant varies in the limits of nearly 4·5 orders of magnitude in such a manner that with the pH increasing up to approximately 3 the rate decreases, passes a minimum, and beginning from pH approximately 4 to 5·5 it increases and then it is almost constant. The empirical equations of the linear parts of this dependence are for the descending branch $\ln k_{\mathrm{exp}} = -2{\cdot}04\,\mathrm{pH} - 1{\cdot}85$ and for the ascending branch $\ln k_{\mathrm{exp}} = 1{\cdot}46\,\mathrm{pH} - 14{\cdot}01$.

The values of the activation energy E_a, activation enthalpy $\Delta H^{\ddagger}$, and activation entropy $\Delta S^{\ddagger}$ calculated from the plot of the rate constant on the temperature, obeying the Arrhenius relation, are given in Table I. Their comparison with the corresponding values for pH < 1 exhibits differences which either lie within the limits of random errors of measurement or are insignificant.

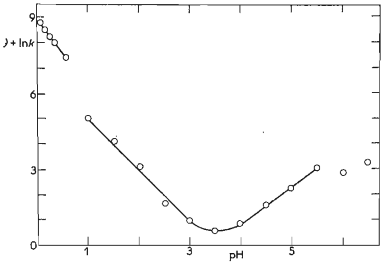

FIG. 3

Dependence of the Rate Constant Logarithm on pH

Hydrolysis of Fe(III) *in the Course of the Reaction*

The comparison of the time dependences of the $[OH^-] : [Fe^{3+}]$ ratio for the reaction course with a spontaneous change of pH (pH_0 5) and for a constant pH (pH 5) showed that the amount of OH^- consumed for the hydrolysis corresponded in every instant to the amount of H^+ released during the hydrolysis of Fe(III). The concentration of Fe(III) corresponds to the oxidized Fe(II), which was determined in the course of the reaction. The difference in the course of the time variation of $\ln([Fe^{2+}]_0/[Fe^{2+}]_t)$ for the pseudomonomolecular reaction is shown for the two cases in Fig. 4. The overall change of the H^+ concentration has been expressed for a general case by Eq. (*4*). In the case of spontaneous variation of pH, $\Delta[H^+]_t^{(s)} = [H^+]_t^{(s)} - [H^+]_0$, $\Delta[H^+]_t^h = [H^+]_t^h - [H^+]_0^h$, and $\Delta[H^+]_t^{ox} = [H^+]_t^{ox} - [H^+]_0^{ox}$, the H^+ concentrations for the oxidation and hydrolysis in the time $t = 0$ being zero, so that

$$[H^+]_t^h = [H^+]_t^{(s)} - [H^+]_0 - [H^+]_t^{ox} . \qquad (5)$$

From this equation, $[H^+]_t^h$ can be calculated, since $[H^+]_t^{(s)}$ and $[H^+]_0$ are directly measurable and $[H^+]_t^{ox}$ corresponds, based on the stoichiometry, to the quantity of $[Fe^{2+}]$ consumed. Since for the case pH = const (pH 5) (superscript (c)) there is $[H^+]_t^{(c)} = [H^+]_0$, we obtain similarly the equation

$$[H^+]_t^h = [H^+]_t^{ox} + [H^+]_t^{(a)} , \qquad (6)$$

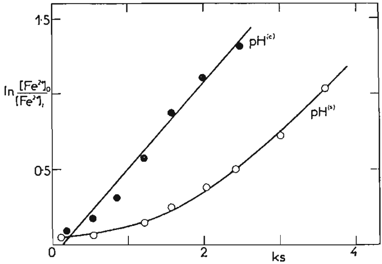

FIG. 4

Dependence of $\ln([Fe^{2+}]_0/[Fe^{2+}]_t)$ on Time

$[Fe^{2+}]_0 = 0{\cdot}051 \text{ mol l}^{-1}$, $[ClO_3^-]_0 = 0{\cdot}166 \text{ mol l}^{-1}$, 40°C, pH_0 5; $ph^{(s)}$ spontaneous variation of pH, $pH^{(c)}$ pH 5 = const.

where the superscript (a) refers to the apparent H^+ concentration calculated from the consumption of the alkaline solution constant pH. The time dependence of the apparent course of pH for this case is depicted in Fig. 2, curve *a*. The time dependences of the $[OH^-]/[Fe^{3+}]$ ratio expressing the degree of the Fe(III) hydrolysis for the spontaneous changes of pH ($pH^{(s)}$) and for constant pH ($pH^{(c)}$) are given in Fig. 5. In the latter case, the ratio $[OH^-]/[Fe^{3+}]$ is seen to steadily increase within the whole time interval followed, whereas in the former case it attains a maximum of approximately 1·4 followed by a slow decrease.

Time Dependence of the Concentrations of the Iron Species in the Course of the Reaction

Fe(II) as well as Fe(III) can occur during the reaction both in the liquid and in the solid phases of the reaction system. If we know the total iron concentration (determined as the initial concentration of $FeSO_4$), $[Fe^{2+}]_0 = a$, the instantaneous concentration of Fe(II) in the liquid phase, $[Fe^{2+}]_l = b$, the sum $[Fe^{2+}]_s + [Fe^{3+}]_s = d$, and the sum $[Fe^{2+}]_l + [Fe^{2+}]_s = c$, determined as described in the experimental part, we can calculate the concentrations of iron in the various oxidation states in the both phases: $[Fe^{2+}]_s = c - b$, $[Fe^{3+}]_l = a - b - d$, and $[Fe^{3+}]_s = d + b - c$. The time change of these concentrations during the reaction is illustrated in Fig. 6. The increase of the $[Fe^{3+}]_s$ concentration corresponds to the decrease of $[Fe^{2+}]_l$ up to a small difference, given by the low amount of Fe^{2+} found

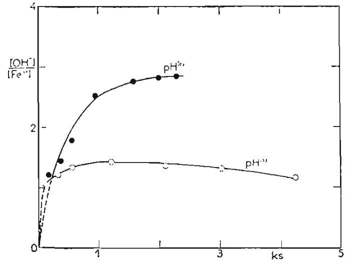

FIG. 5

Dependence of the $[OH^-]/[Fe^{3+}]$ Ratio on Time

$[Fe^{2+}]_0 = 0{\cdot}051$ mol l^{-1}, $[ClO_3^-]_0 = 0{\cdot}166$ mol l^{-1}, 40°C, pH_0 5; $pH^{(s)}$ spontaneous variation of pH, $pH^{(c)}$ pH 5 = const.

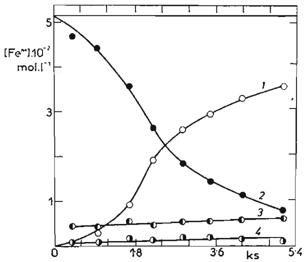

FIG. 6

Dependence of the Concentrations of the Various Iron Species on Time

$[Fe^{2+}]_0 = 0{\cdot}050$ mol l^{-1}, $[ClO_3^-]_0 = 0{\cdot}166$ mol l^{-1}, pH 5, 40°C; *1* $[Fe^{3+}]_s$, *2* $[Fe^{2+}]_l$, *3* $[Fe^{3+}]_l$, *4* $[Fe^{2+}]_s$.

in the solid phase of the reaction system and the low amount of Fe^{3+} that did not pass into the solid phase separated by centrifugation. The concentration of $[Fe^{3+}]_l$ nearly does not change during the reaction, amounting to about $5 . 10^{-3}$ mol l^{-1}, and drops to a value of the order of 10^{-6} mol l^{-1} only after several tens of hours. The concentration of $[Fe^{2+}]_s$ nearly does not change either during the reaction, being of the order of 10^{-3} mol l^{-1}.

Mechanism of Oxidation of Fe(II) *and Separation of Solid Products of* Fe(III)

The results obtained in this work for pH < 1 are in accordance with those reported by Mitzner and coworkers[1] as to the stoichiometry of the reaction ($6\,Fe^{2+} : 1\,ClO_3^-$), 2nd order rate equation, and linear dependence of the rate constant on the H^+ concentration. The differences lie within the limits of the random errors of measurement for determination of the activation energy (compare the E_a value for pH < 1 in Table I with the value $E_a = 70{\cdot}34 \pm 2{\cdot}51$ kJ mol^{-1} obtained by recalculation of the data[1] from kcal to kJ); only the difference in the activation entropies $\Delta S^{\neq}$ exceeds the random error of measurement (compare the value in Table I with the value, $\Delta S^{\neq} = -62{\cdot}38 \pm 9{\cdot}21$ J mol^{-1} K^{-1} recalculated from data)[1].

In the range of pH 1–5·5, where starting from approximately pH 2 the precipitate of the hydrolyzed Fe(III) separates, the same stoichiometry of the Fe(III) oxidation and the same rate equation are held as in the range of pH < 1; the differences between the activation parameters for pH 5 and for pH < 1 are insignificant. The rate constant at pH > 5·5 is not defined by Eq. (*2*) in the whole reaction region beginning from approximately 20% conversion of Fe(II), a considerable deviation from the 2nd order course appears. The change in the slope of the plot of the rate constant logarithm *versus* pH in this region can be explained in terms of the equilibrium $Fe^{2+} + H_2O \overset{K_{h1}}{\rightleftharpoons} Fe(OH)^+ + H^+$ beginning to operate; the K_{h1} value of $3{\cdot}1 . 10^{-7}$ (1M-$HClO_4$, 25°C) has been tabulated[4]. Instead of the hydrated ferrous ion, the $Fe(OH)^+$ ion starts to be oxidized; its concentration rises with increasing pH. The activation energy and entropy (Table I) are in this case approximately the same as at pH < 1, which implies that the formation of the activated complex $[Fe;\ HClO_3^{2+}]^{\neq}$ is of equal probability as that of $[Fe(OH)^+;\ ClO_3^-]^{\neq}$. In this case the reaction rate would obey the equation

$$v = k'_{exp}[Fe(OH)^+][ClO_3^-] . \tag{7}$$

Inserting $[Fe(OH)^+] = K_{h1}[Fe^{2+}][H^+]^{-1}$ in this equation we obtain

$$v = k'_{exp}\, K_{h1}[Fe^{2+}][H^+]^{-1}[ClO_3^-] , \tag{8}$$

and comparing this equation with Eq. (*2*) we find $k_{exp} = k'_{exp}\, K_{h1}[H^+]^{-1} =$

$= k[H^+]^{-1}$, a dependence which was experimentally observed in the region of pH 4 – 5·5.

The concentration ratio $[OH^-]/[Fe^{3+}]$, expressing the degree of hydrolysis for the spontaneous change of pH (curve $pH^{(s)}$, Fig. 5), attains the maximum value of 1·4 and then decreases slowly. This is probably due to the partial dissolution of the Fe(III) hydrolytic precipitate at decreasing pH. In case that a constant pH 5 is maintained, the $[OH^-]/[Fe^{3+}]$ ratio rises further, *i.e.* the system tends towards equilibrium in the sense of maximum hydrolysis of Fe(III).

The balance of the various iron oxidation degrees in the two phases of the system revealed that the increase of the $[Fe^{3+}]_s$ concentration corresponds to the decrease of $[Fe^{2+}]_l$ up to a small difference due to the small amount of Fe^{2+} present in the solid phase ($\sim 10^{-3}$ mol l^{-1}) (probably adsorbed on the precipitate of the Fe(III) hydrolysis products) and the small amount of Fe^{3+} that remains in the liquid phase after the solid phase is removed by centrifugation. The latter amount is during the reaction approximately $5 \cdot 10^{-3}$ mol l^{-1} and after several tens of hours drops to a concentration of the order of 10^{-6} mol l^{-1}. The iron occurs here probably in the form of complex Fe(III) aquo-hydroxo ions, possibly dimerized through OH or O-bridges, which convert to a crystalline precipitate on additional chaining[5–7].

Investigation of the kinetic data on the oxidation of Fe(II) by chlorate in conditions when the Fe(III) created is separated from the reaction solution as the solid hydrolytic products, is of importance in seeking for the dependence of the composition of these products on the reaction conditions, which will be the subject of our further study.

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