September, 1984] *Bull. Chem. Soc. Jpn.*, *57*, *2411—2416 (1984)* 2411

The Synthesis of Green Rust II(Fe^{III}_1-Fe^{II}_2) and Its Spontaneous Transformation into Fe_3O_4

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(Received December 20, 1983)

Conditions for the synthesis of a pure green rust II with a definite chemical composition and its transformation reaction to Fe_3O_4 under a nitrogen atmosphere were studied. A pure green rust II with the composition of $(Fe^{3+})_1(Fe^{2+})_2(SO_4^{2-})(OH^-)_{5-2n}(O^{2-})_n$ was obtained by the air oxidation of an aqueous solution containing (0.05 mol dm^{-3}) Fe^{II} and (0.3 mol dm^{-3}) SO_4^{2-} ions at pH 6.8 and 25 °C. This iron composition differs from those estimated previously; therefore, the green rust II synthesized here is designated as green rust II(Fe^{III}_1-Fe^{II}_2). This green rust II is spontaneously transformed into Fe_3O_4 under a nitrogen atmosphere at 50—75 °C. It has been accepted that green rust II is transformed to Fe_3O_4 by oxidation. The above evidence suggests that the green rust II can be transformed into Fe_3O_4 not only by oxidation but also spontaneously without oxidants.

The atmospheric rusting of mild steel or low-alloy steel occurs when the steel surface comes into contact with atmospheric water. The Fe^{II} ion dissolved from the steel surface in the course of the rusting is oxidized by oxygen, and iron oxides and hydroxide oxides are formed. In the thin aqueous layer on the steel surface, the oxygen and water react with the iron or intermediates of the rusting process. Eventually, the steel surface is covered with oxides and hydroxide oxides(corrosion products). In the oxidation reaction of the Fe^{II} ion in the aqueous solution, the oxidation rate, the structure and composition of the initial and intermediate species, the pH, and the temperature determine what products are formed.[1–13] The influence of dissolved oxygen has been studied by Foroulis.[6] The significance of the oxidation rate of the dissolved Fe^{II} ion in the corossion of iron and steel in an aqueous solution was pointed out by Gilroy and Mayne.[7] The formation or transformation of iron oxides, hydroxide oxides, and green rusts in aqueous solutions have been studied by Kiyama,[2] Bernal *et al.*,[8] Misawa *et al.*,[1,4] and other workers.[9–13] The transformation reaction of γ-FeO(OH) to α-FeO(OH) has been studied by Schwertmann and Taylor,[9] Oosterhout,[10] and Inoue *et al.*[11] Recently, we have reported that γ-FeO(OH) is transformed to Fe_3O_4 by the adsorption of Fe^{II} ions.[12–13] Other intermediates in the corrosion process and in the oxidation of aqueous solutions containing Fe^{II} ions are greenish precipitates called "green rusts." They are formed by the air oxidation of a dissolved Fe^{II} ion in the presence of SO_4^{2-} or halogen ions, such as Cl^-, Br^-, and F^-, at neutral or slightly alkaline pH values, and are transformed to iron oxides or hydroxide oxides by further oxidation. A green rust I is formed in the presence of Cl^-, Br^-, and F^- ions, and a green rust II, in that of the SO_4^{2-} ion. Bernal *et al.*[8] reported on an X-ray crystallographic study of the green rusts. Misawa *et al.*[14,15] studied dissolved species, called "green complexes," of the Fe^{II} and Fe^{III} complexes.

This paper will describe a new reaction in which a green rust II is transformed to Fe_3O_4 without any oxidation reaction. At the beginning of this work, we undertook to prepare a green rust II with a definite chemical composition. However, the methods reported so far[2,8,14] were inadequate for the synthesis of such a green rust II. As a first report, this paper will describe the reaction conditions for the synthesis of the green rust II with a definite chemical composition, besides the new reaction. A detailed discussion of the relationship between the new reaction and the oxidation reaction of the green rust II will be presented in the subsequent paper.

Experimental

Chemicals. All the chemicals were of an analytical grade, and distilled water was used for the preparation of chemical solutions. The α- and β-FeO(OH) were perpared according to the methods of Kiyama[2] and of Kiyama and Takada[3] respectively. Fe_3O_4 and γ-FeO(OH) were synthesized by a method reported perviously.[13,16]

Apparatus. The reaction vessel used in previous papers was adopted.[16–18]

Chemical Analysis. The Fe^{II} and Fe_{total} contents were determined by means of the 2,2′-bipyridyl method[19] after dissolving the samples with a HCl solution (1 : 1). The Fe_{total} was determined after reducing Fe^{III} to Fe^{II} with hydroxylamine. The SO_4^{2-} content was determined using a X-ray fluorescence instrument (Toshiba X-ray Spectrometer Model AFV 777) from the intensity of sulpher in $BaSO_4$ precipitate collected on a glass fiber filter paper (Toyo Roshi GA 100 type).

Green Rust II Synthesis. A solution [0.7 dm^3, $FeSO_4 \cdot 7H_2O$ (10.0 g), Na_2SO_4 (25 g)] was oxidized with a mixed gas of air and nitrogen gas[air/N_2=1 : 1(atm), flow rate; 1.6 dm^3 min^{-1}] at pH 6.8±0.05 and 25 °C. During the oxidation, an alkaline solution (0.10 mol dm^{-3} NaOH) was added to maintain the reaction pH constant, and the volume of the alkaline solution consumed was read. When about 25 mol% of the Fe^{II} ion has been oxidized, nitrogen gas was passed through in place of the mixed gas; the reaction vessel was then cooled in a water bath chilled with ice. If the Fe^{II} ions are oxidized over 25 mol%, by-products such as α-FeO(OH) are produced. The greenish precipitate was collected by centrifugation under a nitrogen atmosphere, washed with a distilled water freed from oxygen (4 °C), and suspended in the distilled water (4 °C). The green rust II thus prepared is stable under a nitrogen atmosphere at a temperature below 4 °C.

For the measurement of the Fe^{II} and Fe^{III} contents of the green rust II formed in the course of the synthesis, 0.005 dm^3 of the reaction suspension was transferred under a nitrogen atmosphere to a 0.05 dm^3 centrifuging tube chilled in ice water, and nitrogen gas was immediately flushed into the sample suspension to stop the reaction instantly. After 10 min, the sample was centrifuged under a nitrogen atmosphere at a low temperature (4 °C) at 3000 min^{-1} for 5 min. After the precipitate has been washed with cold distilled water freed from oxygen, the Fe^{II} and Fe^{III} contents were determined.

Electron Microscopy, IR Spectroscopy, and X-ray Diffractometry for the Green Rust II. A small portion of the reaction suspension was taken into a glass capillary tube whose inside was a vacuum; the capillary was then sealed and kept in cold water. The inside sample was mounted under a nitrogen atmosphere on a sample holder for electron microscopy. For the X-ray diffractometry, the precipitate obtained by centrifugation was mounted on a glass plate under a nitrogen atmosphere, and sealed with cellophane-tape to prevent oxidation. For the IR spectroscopy, the green-rust-II precipitate was washed with acetone freed from oxygen (4 °C), dried under a nitrogen atmosphere, and suspended in Nujol. The IR spectrum was taken by a Shimadzu IR spectrometer, Model IR 400, using a KBr cell under a nitrogen atmosphere.

Transformation Reaction of Green Rust II under a Nitrogen Atmosphere. The green-rust-II suspension (0.05 dm^3, 25 °C) was transferred into a 0.4-dm^3 portion of distilled water freed from oxygen. The temperature of the distilled water had been adjusted to get a given temperature after the mixing. The pH of the reaction suspension was adjusted by adding a NaOH solution during the reaction. After 4 h, the product was isolated by transferring 0.2 dm^3 of the reaction suspension to 0.1 dm^3 of an oxygen-free acetate buffer solution (pH 4.1, 0.05 mol dm^{-3}) to dissolve the Fe^{II} ions released during the transformation reaction. The product was collected by centrifugation under a nitrogen atmosphere, washed successively with oxygen-free water and acetone, and dried under a nitrogen atmosphere. The dried product was examined by means of X-ray diffractometry, electron microscopy, and IR spectroscopy. The chemical composition was determined after dissolving it with the HCl solution(1:1).

Results and Discussion

Conditions for Green Rust-II Synthesis. Curves A and A′ in Fig. 1 show the amounts of Fe(OH)$_2$ precipitate which were formed by adjusting the pH of the solutions containing Fe^{II} ions at high (Curve A; 0.3 mol dm^{-3}) and low (0.05 mol dm^{-3}) concentrations of SO$_4^{2-}$ to those indicated in the figure at 25 °C. As may be seen here, most Fe^{II} ions dissolved at pH values below 6.8 at a high SO$_4^{2-}$-concentration. When a mixed gas of air and nitrogen gas was passed into the solution containing Fe^{II} ions at pH 6.8 and at a high SO$_4^{2-}$-concentration, the clear solution became turbid, and a greenish precipitate was formed by the oxidation of the Fe^{II} ions. Figure 2 shows the time variation of the Fe^{II} (Curve A) and Fe^{III} (Curve B) contents of the greenish precipitates formed in the course of air oxidation at pH 6.8. As can be seen here, the Fe^{II}/Fe^{III} mol ratio was maintained at nearly 2:1 during the reaction. This suggests that one mol of the Fe^{III} ions formed by oxidation combines with two mols of the Fe^{II} ions to form the greenish precipitate. The X-ray diffraction pattern of the greenish precipitate formed at an oxidation time of 40 min corresponded to that of the green rust II reported by Bernal *et al.*[8] In the IR spectrum, no bands of iron hydroxide oxides appeared, but a strong band of SO$_4^{2-}$ (1100 cm^{-1}) and weak bands (720, 620 cm^{-1}) did appear. These results indicate the formation of the green rust II containing SO$_4^{2-}$. Figure 3 shows an electron micrograph of the product.

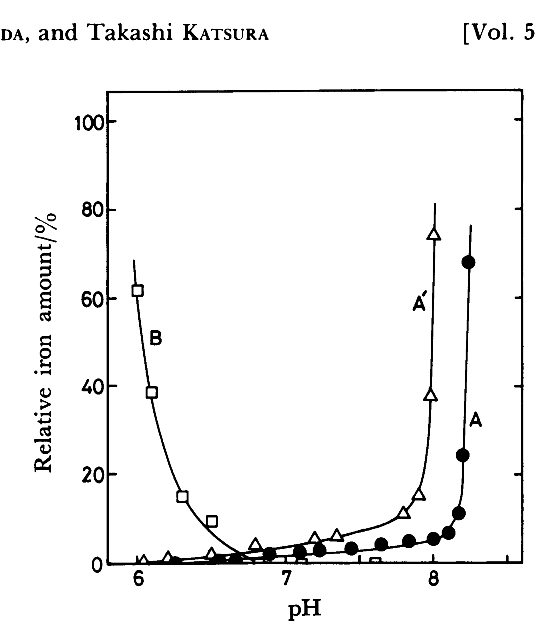

Fig. 1. The amount of Fe(OH)$_2$ precipitates which were formed by adjusting the pH of the solution containing Fe^{II} ion at high (Curve A; 0.3 mol dm^{-3}) and low (Curve A′; 0.05 mol dm^{-3}) concentrations of SO$_4^{2-}$ to those indicated in the figure at 25 °C. The amount was estimated from the Fe^{II} in the precipitates which were formed by allowing the Fe(OH)$_2$ suspension to stand for 30 min after the addition of 0.1 mol dm^{-3} NaOH solution.
Curve B; relationship between the amount of the by-products and the reaction pH. The reaction suspension(0.05 dm^3) was taken and transferred to 0.1 dm^3 of the tartaric acid solution(10 w/v%, pH 6.0). After allowing to stand for 6 h, the amount of the total iron in the precipitate remained undissolved in the tartaric acid solution was determined.

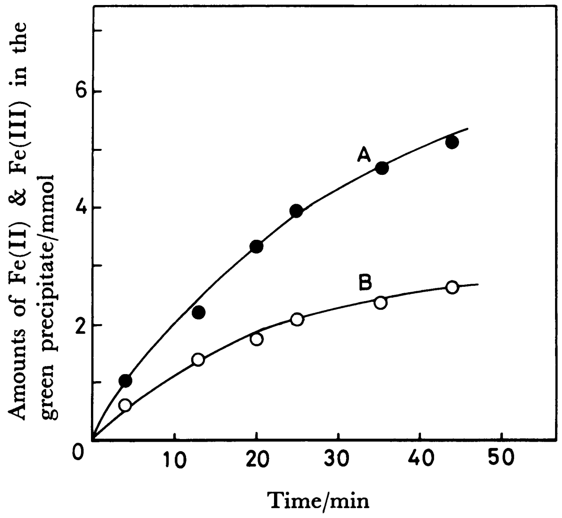

Fig. 2. The time variations of Fe^{II}(Curve A) and Fe^{III} (B) contents in the green rust II formed in the course of the synthesis.

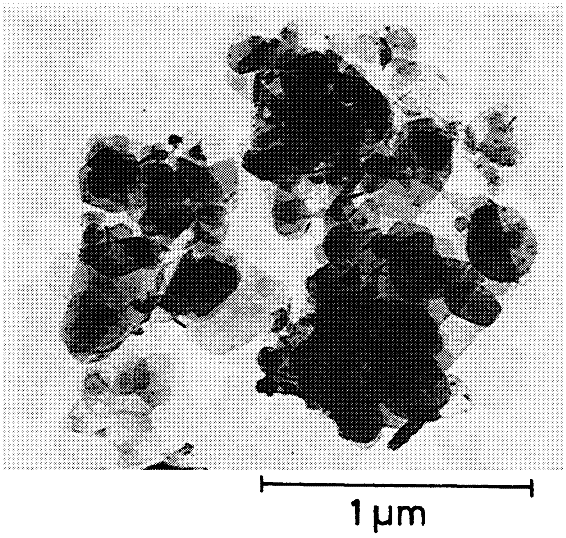

Fig. 3. Electron micrograph of the green rust II(Fe^{III}_1-Fe^{II}_2).

TABLE 1. DISSOLUTION TEST OF THE GREEN RUST II, Fe_3O_4, AND IRON HYDROXIDE OXIDES WITH A TARTARIC ACID SOLUTION (10 w/v%, pH 6.0)

Iron oxides or hydroxide oxides added (7.2×10^{-4} mol; Fe_{total})	Amount of iron dissolved (mol; Fe_{total})
Green rust II	7.2×10^{-4}
Fe_3O_4	4.3×10^{-7}
α-FeOOH	2.9×10^{-7}
β-FeOOH	6.2×10^{-7}
γ-FeOOH	7.1×10^{-7}

After allowing the test suspensions to stand for 6 h under a nitrogen atmosphere, the concentration of the total iron in the supernatant was determined by the atomic-absorption method.

To ascertain the purity of the product, the green rust II obtained at pH 6.8 and at the high SO_4^{2-}-concentration was transferred to a tartaric acid solution (10 w/v%, pH 6.0), and the mixture was allowed to stand for 6 h. The green rust II dissolved completely (Table 1). However, as can be seen from the table, little of the α-, β-, and γ-FeO(OH) dissolved. This suggests that the green rust II contains no by-products such as hydroxide oxides, but is a pure green rust II. However, at pH values below 6.8 (at a high SO_4^{2-}-concentration), some by-products insoluble in the tartaric-acid solution were formed. The relationship between the amounts of the by-products and the reaction pH is given by Curve B in Fig. 1. In the IR spectrum of the by-products, key bands of α-FeO(OH) appeared strongly at 795 and 890 cm^{-1}, along with a very broad absorption over the range of 400—1000 cm^{-1}. The broad absorption could not be assigned, but it seems to be due to the Fe^{III} amorphous hydroxide oxides. Thus, the by-product can be said to be mainly composed of α-FeO(OH).

TABLE 2. RESULTS OF THE CHEMICAL ANALYSIS OF THE GREEN RUST II OBTAINED AFTER 30 min OF AIR OXIDATION

Ions	mol	Ratio
Fe^{3+}	7.3×10^{-4}	1.0
Fe^{2+}	1.4×10^{-3}	1.9
SO_4^{2-}	6.1×10^{-4}	0.83
OH^-	3.4×10^{-3}	4.7

The results of the chemical analysis of the green rust II obtained at pH 6.8 and at a high SO_4^{2-}-concentration are given in Table 2, together with the OH^- amount consumed during the reaction. From the values in the table, the chemical formula can be estimated to be $(Fe^{3+})_1(Fe^{2+})_2(SO_4^{2-})(OH^-)_5$. Since Misawa *et al.*[4] suggested that green rusts contain hydroxo-bridges and oxo-bridges, the chemical formula can be generally represented by: $(Fe^{3+})_1(Fe^{2+})_2(SO_4^{2-})(OH^-)_{5-2n}(O^{2-})_n$, where n means the number of oxo-bridges. The iron composition of this green rust II is different from that estimated from the composition of the green complex II by Misawa *et al.*[15] The green rust II synthesized in the present study will hereafter be designated as green rust II(Fe^{III}_1-Fe^{II}_2).

Equilibrium Consideration of the Formation of the Green Rust II. As may be seen in Curve B in Fig. 1, the amount of the by-product, which is mainly composed of α-FeO(OH) as has been mentioned above, increased with a decrease in the pH from 6.8 to 6.0. In the course of the reaction, Fe^{III} ions are formed by the oxidation of the Fe^{II} ions. In this pH range, the main species of the Fe^{III} ion formed by the oxidation is $Fe(OH)_2^+$, one of the hydrolysis species of the Fe^{3+} ion.[20] It is considered that α-FeO(OH) is formed by the polymerization of the $Fe(OH)_2^+$ ions. However, at pH values above 6.8, no such by-products are formed (Curve B in Fig. 1), and the green rust II is formed. This indicates that the $Fe(OH)_2^+$ ions preferentially combine with the Fe^{II} and SO_4^{2-} ions, and that they are transformed to the green rust II. Since the Fe^{2+} ion is more readily hydrolyzed into $FeOH^+$ at a higher pH in the pH range of 6—10,[20] The Fe^{II} ions which take part in the green-rust-II formation are considered to be $FeOH^+$ ions. Thus, the green rust-II formation will be written as:

$$Fe^{2+} + H_2O \rightleftharpoons FeOH^+ + H^+, \qquad (1)$$

$$Fe(OH)_2^+ + 2FeOH^+ + SO_4^{2-} \rightleftharpoons (Fe^{3+})_1(Fe^{2+})_2(SO_4^{2-})(OH^-)_{5-2n}(O^{2-})_n + nH_2O. \qquad (2)$$

The reversibility of Reaction (2) was also examined. When the pH of the green rust-II suspension containing a high SO_4^{2-}-concentration (0.3 mol dm^{-3}) was lowered to 5.5, the green rust II(Fe^{III}_1-Fe^{II}_2) was decomposed and a brownish precipitate was formed. In the IR spectrum of the precipitate, no key bands of iron hydroxide oxides appeared, but a very broad absorption appeared over the range of 400—1000 cm^{-1}, indicating that some amorphous precipitates of Fe^{III} were formed. Assuming that the reverse process of Reaction (2) takes place upon a lowering of the pH, it is considered that the $Fe(OH)_2^+$ ions released in the reverse process of Reaction (2) form the amorphous precipitates. However, the Fe^{II} ions released in the reverse process dissolve in the solution at pH 5.5, since their solubilities are fairly high at that pH. These considerations suggest that possibility that there exists the reverse process of Reaction (3). When the pH of the brownish suspension obtained above was raised to 8.0, a greenish precipitate was formed almost instantly. X-Ray diffractometry and chemical analysis showed that this greenish precipitate was the green rust II (Fe^{III}_1-Fe^{II}_2). Thus, the direct and reverse processes of Reaction (2) are considered to take place reversibly, and they seem to readily attain equilibrium. From Eqs. 1 and 2, the equilibrium constant for the formation of the green rust II is given by:

$$K = \frac{[H^+]^3}{[Fe(OH)_2^+][Fe^{2+}]^2[SO_4^{2-}]K_1^2K_w} \quad (3)$$

where K_1 and K_w are the hydrolysis constant of Fe^{2+} (Eq. 1) and the dissociation constant of water respectively. In the pH range of 6—7, $[Fe(OH)_2^+]$ is around 10^{-11}—10^{-12} mol dm^{-3}.[20] Equation 3 indicates that the lower values of the Fe^{2+}-concentration, the pH, and the SO_4^{2-}-concentration are unfavorable for the formation of the green rust II(Fe^{III}_1-Fe^{II}_2). When the Fe^{2+}-concentration is lowered as the oxidation reaction proceeds, Reaction (2) attains equilibrium, and the green rust II is no longer formed. The $Fe(OH)_2^+$ ions, which are formed by a further oxidation of the remaining Fe^{2+} ions, polymerize and form α-FeO(OH)(by-product). At a pH lower than 6.8, the formation of the by-product is initiated at an earlier stage of the oxidation reaction. This means that the amount of the by-products will increase with a decrease in the pH from 6.8, as is shown by Curve B in Fig. 1. When the reaction pH was further lowered to 5.5, no green rust II was formed, but only the by-products. In these experiments, the concentrations of Fe^{II} and SO_4^{2-} were 0.05 and 0.3 mol dm^{-3} respectively. For these values, the pH value of 5.5 is too small to form the green rust II in Eq. 3.

Spontaneous Transformation of the Green Rust II to Fe_3O_4 under a Nitrogen Atmosphere. When the green rust II(Fe^{III}_1-Fe^{II}_2)-suspension containing no oxidants was allowed to stand under a nitrogen atmosphere at 75 °C, the suspension spontaneously turns black, and the pH became around 7.8. Figure 4 shows the electron micrograph of the product; no particles of the green rust II are seen, but only the spherical or cubic particles characteristic of Fe_3O_4. The X-ray diffractometry, IR spectroscopy, and chemical analysis showed that the product is Fe_3O_4. In this reaction, no oxidants were used; therefore, the formation of Fe_3O_4 from the green rust II is given by:

$$2[(Fe^{3+})_1(Fe^{2+})_2(SO_4^{2-})(OH^-)_{5-2n}(O^{2-})_n] \longrightarrow$$
$$Fe_3O_4 + 3Fe^{2+} + 2SO_4^{2-} + 2(2-n)H_2O + 2OH^-. \quad (4)$$

As can be seen from Eq. 4, three mols of Fe^{2+} ions and two mols of OH^- ions are released. One out of the three mols of Fe^{2+} ions will form $Fe(OH)_2$, and the remaining two be free. The pH after the mixing of the Fe^{2+} and OH^- ions at this ratio was around 7.6. This value agrees with that where the reaction pH is attained in the early stage of the reaction. At a pH around this pH value, some of the remaining Fe^{2+} ions are hydrolyzed, and the proton is released (Eq. 1). This is the cause of the gradual lowering of the pH in the transformation reaction.

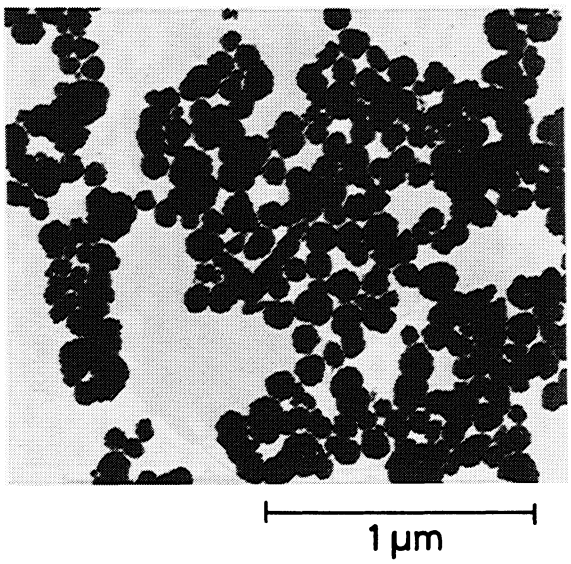

Fig. 4. Electron micrograph of the product which was obtained by allowing the green rust II(Fe^{III}_1-Fe^{II}_2)-suspension under a nitrogen atmosphere at 75 °C for 4 h. Concentrations of SO_4^{2-} and the green rust II; 0.018 mol dm^{-3} and 50 mmol dm^{-3}(Fe^{2+}), respectively.

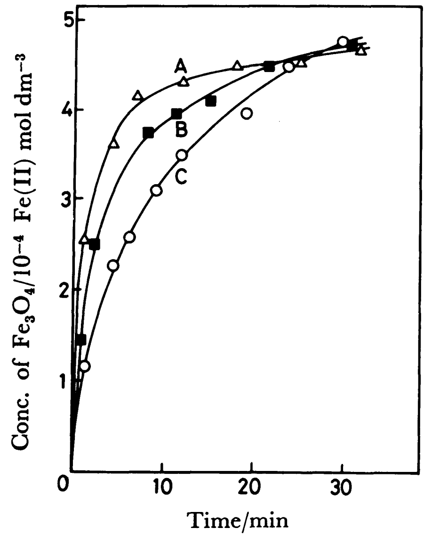

Fig. 5. The time variation of the Fe_3O_4-formation at various pH's(50 °C).
Curve A; pH 7.7, B; 9.8, and C; 10.6. Concentrations of SO_4^{2-} and the green rust II; 0.018 mol dm^{-3} and 50 mmol dm^{-3}(Fe^{2+}). The reaction suspension (0.05 dm^3) was taken and transferred to 0.1 dm^3 of the tartaric acid solution(10 w/v%, pH 6.0). After allowing to stand for 6 h, the amount of Fe^{II} in the precipitate remained undissolved in the tartaric acid solution was determined.

Figure 5 shows the time variation in the Fe_3O_4-formation from the green rust II at various pH's(50 °C) under a nitrogen atmosphere. The reaction pH was maintained by adding an alkaline solution. As may be

TABLE 3. THE RATE OF THE SPONTANEOUS TRANSFORMATION OF THE GREEN RUST II INTO Fe_3O_4 AT VARIOUS TEMPERATURES UNDER A NITROGEN ATMOSPHERE

Temperature °C	Transformation rate to Fe_3O_4 (Fe^{2+} mol dm^{-3} min^{-1})
30	1.51×10^{-6}
50	6.38×10^{-5}
74	1.86×10^{-3}

The rate gradually became slow with time. The values in the table were evaluated from the tangent of the Fe_3O_4-formation curve at 0 time. Concentration of $SO_4{}^{2-}$: 0.018 mol dm^{-3}. Concentration of the green rust II: 50 mmol dm^{-3} (Fe^{2+}).

TABLE 4. THE RELATIONSHIP BETWEEN THE CONCENTRATION OF THE GREEN RUST II IN THE SUSPENSION AND THE RATE OF THE SPONTANEOUS TRANSFORMATION OF THE GREEN RUST II INTO Fe_3O_4 UNDER A NITROGEN ATMOSPHERE AT 50 °C

Green rust II conc. in the reaction suspension (Fe^{2+} mmol dm^{-3})	Transformation rate to Fe_3O_4 (Fe^{2+} mol dm^{-3} min^{-1})
4.9	7.07×10^{-6}
11	1.27×10^{-5}
25	3.36×10^{-5}

The rates were evaluated from the tangent of the Fe_3O_4-formation curve at 0 time. Concentration of $SO_4{}^{2-}$: 0.018 mol dm^{-3}.

seen here, the green rust II was transformed spontaneously to Fe_3O_4 without being oxidized, even at a pH above 7.8. However, the reaction pH affects the initial rates of the transformation reaction. The temperature and the $SO_4{}^{2-}$-concentration also affect the rate. The relationship between the initial rate and the temperature is given in Table 3. When the $SO_4{}^{2-}$-concentration became higher, the rate became slower, becoming extremely slow at 0.1 mol dm^{-3}.

The electron microscopy(Figs. 3 and 4) showed that plate particles of the green rust II are transformed to cubic or spherical particles of Fe_3O_4. This indicates that the transformation reaction proceeds through a dissolution-precipitation process. This process seems likely in view of the fact that no transformation occurred when the green rust II was dried under a nitrogen atmosphere after having been washed with a O_2-free acetone to remove as much water as possible. The transformation reaction is considered to involve the dissolution process of the green rust II. In this process, some dissolved species such as the green complex II[14] are released and transformed to Fe_3O_4 without being oxidized. If the transformation rate of the dissolved species is slower than the dissolution rate of the green rust II, the bulk solution is saturated with the dissolved species. In this case, the concentration of the dissolved species is kept constant, even though the number of particles of the green rust II in the suspension(green-rust-II concentration) is increased. This means that the rate of the Fe_3O_4-formation does not depend on the green-rust-II concentration. However, as is shown by Table 4, the rate of the Fe_3O_4-formation depends on the green-rust-II concentration. It is considered that the rate of the transformation of the dissolved species to Fe_3O_4 is fast, and that the dissolution of the green rust II is the rate-determining step of the reaction. At a higher concentration of the green rust II, the dissolution rate of the green rust II becomes faster as a result of the increase in the total surface area of the green-rust-II particles.

If the dissolved species is the green complex II with the composition of $[(Fe^{3+})(Fe^{2+})(OH^-)_x(O^{2-})_y]^{(5-2y-x)+}$,[14] the dissolution process of the green rust II is given by:

$$\begin{aligned}&(Fe^{3+})_1(Fe^{2+})_2(SO_4{}^{2-})(OH^-)_{5-2n}(O^{2-})_n \rightleftharpoons\\&\quad[(Fe^{3+})(Fe^{2+})(OH^-)_{5-2n-m}(O^{2-})_n]^{m+}\\&\quad+Fe^{2+}+SO_4{}^{2-}+mOH^-,\end{aligned}\tag{5}$$

where it is assumed that the oxo-bridges in the green rust II are transformed into the green complex II. The Fe_3O_4-formation from the green complex II may be written as:

$$\begin{aligned}&2[(Fe^{3+})(Fe^{2+})(OH^-)_{5-2n-m}(O^{2-})_n]^{m+}+2(m-1)OH^-\\&\quad\longrightarrow Fe_3O_4+Fe^{2+}+2(2-n)H_2O.\end{aligned}\tag{6}$$

Equation 6 shows that the Fe_3O_4-formation reaction should depend largely on the reaction pH if Reaction (6) is the rate-determining step. However, as is shown by Fig. 5, the reaction rate did not increase with an increase in the reaction pH, but, rather, decreased. This suggests that the transformation step of the dissolved species to Fe_3O_4 is not the rate-determining step, as has been discussed above.

It has been accepted that green rust II is transformed to Fe_3O_4 by oxidation. However, the above evidence suggests that the green rust II can be transformed into Fe_3O_4 not only by oxidation, but also spontaneously without oxidation reaction.

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