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Ferrite Formation from the Intermediate, Green Rust II, in the Transformation Reaction of γ-FeO(OH) in Aqueous Suspension

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The Zn(II)-, Cd(II)-, Ni(II)- and Co(II)-bearing ferrites with spinel structure were synthesized from the intermediates (green rust II) that had been formed from γ-FeO(OH) in aqueous suspensions. These intermediates were obtained when Fe(II) ion was added to the γ-FeO(OH) suspension containing SO_4^{2-} and the metal ions at 25 °C (pH 8.5). This reaction is considered to be initiated by the adsorption of Fe(II) ions to γ-FeO(OH). X-ray diffractometry showed that the metal ions were incorporated into the lattice structure of green rust II during the transformation. The intermediates were stable at temperatures below 4 °C but transformed into the ferrites at 65 °C without any oxidants. From the measurements of the Mössbauer effect, chemical composition, and the lattice constant, it was concluded that the metal ions were incorporated into the lattice structure of the ferrites having nearly stoichiometric chemical composition. The metal ion contents in the ferrites increased with an increase in those in the γ-FeO(OH) suspension. The order of the metal ion content in the ferrites obtained at a fixed metal ion content in the reaction suspension was Zn > Co $\simeq$ Ni > Cd.

Introduction

Ferrites are formed by air oxidation of the $Fe(OH)_2$ suspension containing other metal ions at pH 9–11 and at the temperatures above 50 °C (air-oxidation method).[1-11] In the oxidation reaction of the Fe(II) ion in aqueous solutions, the oxidation rate, the structure and composition of the initial and intermediate species, the pH, and the temperature determine what products are formed.[12-25] Green rusts are formed by 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. Green rust I is formed in the presence of Cl^-, Br^-, and F^- ions, and green rust II, in the presence of the SO_4^{2-} ion. Bernal et al.[15] reported an X-ray crystallographic study of the green rusts: Green rust II has a hexagonal cell with a = 0.317 nm and c = 1.09 nm and is presumably built up of four close-packed oxygen–hydroxyl layers in an ABAC sequence. Green rust I gives various dimensions assigned to the hexagonal unit cell.

Recently we found two new ferrite-formation reactions in an aqueous system where no oxidation reactions are involved: (1) γ-FeO(OH) is transformed into ferrites by the adsorption of Fe(II) and other metal ions[23-24] and (2) green rust II is spontaneously transformed into Fe_3O_4 without any oxidants.[25] These new reactions yielded important information on the mechanism of ferrite formation in the air-oxidation method; they are considered to be elementary reactions.[23-25] However, the relationship between these two reactions has not been well understood yet. This paper is concerned with a new reaction of ferrite formation from green rust II, which is formed as an intermediate in the course of the transformation reaction of γ-FeO(OH). Information yielded by the present study is of considerable interest, since the ferrites are formed by the above reaction (2) using γ-FeO(OH) as a starting material.

Experimental Section

Chemicals. All the chemicals were of analytical grade, and distilled water was used for the preparation of chemical solutions. γ-FeO(OH) was prepared according to the method described in a previous paper.[24]

Apparatus. The reaction vessel used in a previous paper was adopted.[2]

Chemical Analysis. The Fe(II) and total Fe contents were determined by means of the 2,2′-bipyridyl method[26] after dissolving the samples in an HCl solution (1/1). The total Fe was determined after reducing Fe(III) to Fe(II) with hydroxylamine. The contents of other metal ions were determined with an atomic absorption spectrometer (Varian Model AA-875).

Synthesis of the Intermediate (Green Rust II) from γ-FeO(OH) (Step 1). Throughout the experiments, we tried to avoid leakage of oxygen into the reaction system. After nitrogen gas was passed through a suspension of γ-FeO(OH) [0.7 dm^3; 1.4 mmol of γ-FeO(OH); 1.0 g of Na_2SO_4] containing M(II) ions [M(II) = Cd(II), Ni(II), Co(II), Zn(II)], 1.2 g of $FeSO_4 \cdot 7H_2O$ was added, and then the reaction pH was raised to 8.5 at 25 °C by adding an NaOH solution. When the pH was adjusted to 8.5, the reaction was initiated, and a greenish precipitate (intermediate) was formed in 10–30 min. To complete the reaction, the reaction suspension was allowed to stand for 2 h under a nitrogen atmosphere at 25 °C. The intermediate thus obtained was stable under a nitrogen atmosphere at a temperature below 4 °C. For 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. The X-ray powder diffraction pattern was taken by a Rigaku X-ray diffractometer Model RAD-2A.

Synthesis of the Ferrites from the Intermediate (Step 2). The temperature of the reaction suspension of the intermediate prepared according to step 1 was raised to 65 °C, and the pH was adjusted to 10.5. The reaction suspension was allowed to stand for 2 h under a nitrogen atmosphere. The greenish precipitate changed to a black one. The product thus obtained was isolated by transferring the reaction suspension

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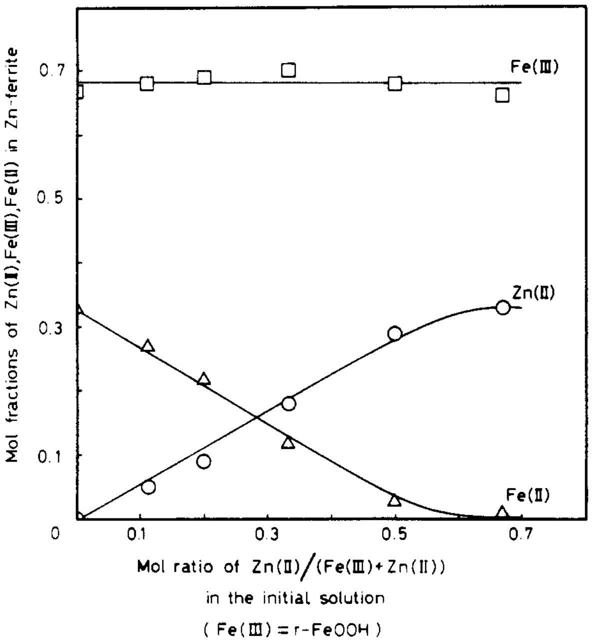

Figure 1. Relationship between the metal ion contents in the Zn(II)-bearing ferrites formed from the intermediate (green rust II) in the γ-FeO(OH) transformation reaction and those in the γ-FeO(OH) suspension in step 1.

to an oxygen-free acetate buffer solution (pH 4.1, 0.05 mol dm^{-3}) to dissolve the Fe(II) and M(II) ions released during the reaction. The product was collected by centrifugation under a nitrogen atmosphere using a 0.1-dm^{-3} centrifuging tube, washed successively with oxygen-free water (two times) and acetone (three times) by repeating centrifugation, and dried by passing nitrogen gas (0.3 dm^3 min^{-1}) into the centrifuging tube at room temperature. The dried product was examined by means of X-ray diffractometry and IR and Mössbauer spectroscopy. The 2θ angles of the diffraction peaks were calibrated against the standard Si powder by using Mn-filtered Fe Kα radiation. The particle size of the ferrites estimated by the Scherrer equation from the main X-ray line (311) ranged from 100 to 160 nm. This magnitude of the particle size was enough to determine the lattice constant with a precision of ±0.00015 nm. The IR spectra were measured by the KBr-disk technique (Shimazu IR spectrometer, Model IR 400). Mirror-image Mössbauer spectra were recorded in 1024 channels by using an ELSINT spectrometer with ^{57}Co source at room temperature. The spectrometer was calibrated by using iron foil. The spectra were fitted to pure Lorentzian line shapes. The two lines of each doublet were constrained to have the same line width and intensity. The chemical composition was determined after dissolving it in an HCl solution (1/1).

Results

Formation of the Intermediate, Green Rust II, and Its Transformation into Zn(II)-Bearing Ferrite. X-ray diffractometry showed that the greenish precipitates formed in the γ-FeO(OH) suspension containing Fe(II), Zn(II), and SO_4^{2-} ions (pH 8.5, 25 °C) (step 1) were green rust II.[15] The X-ray diffraction pattern of the black precipitates formed in step 2 (pH 10.5, 65 °C) from the greenish precipitates obtained in step 1 corresponded to that of a spinel type compound. When the Zn(II) content in the reaction suspension was varied in step 1 [Zn(II)/γ-FeO(OH) = 0–2.0], spinel type compounds having various Zn(II) contents were formed. Figure 1 shows the relationship between the Zn(II) contents in the spinel type compounds and those in the reaction suspension. As can be seen here, the amount of Zn(II) ions, which replaced Fe(II) ions, linearly increased with an increase in the Zn(II) content in the reaction suspension. Figure 2 shows the ternary diagram ($FeO–Fe_2O_3–ZnO$ system) of the chemical composition of those spinel type compounds. The broken line connecting Fe_3O_4 and $ZnFe_2O_4$ indicates the stoichiometric composition of the solid solutions between those components. As seen here, the chemical composition of the spinel type compounds formed in step 2 are nearly equal to the stoichiometric ones of the solid solution between Fe_3O_4 and $ZnFe_2O_4$ [Zn(II)-bearing ferrites]. Figure 3 shows the relationship between the lattice constant of the spinel type compounds and their Zn(II) contents. The lattice constant increased with an increase in the Zn(II) content in the ferrites. The lattice constant of the spinel type compound having the highest Zn(II) content [Zn(II)/total Fe = 0.50] agrees with that of $ZnFe_2O_4$ formed by the solid-state reaction (0.8441 nm).[27] The Mössbauer spectrum of this spinel type compound showed a typical pattern of the normal spinel of the $ZnFe_2O_4$ (quadrupole-splitting lines).[28] These results show that the spinel type compounds formed in step 2 are the Zn(II)-bearing ferrites with nearly stoichiometric chemical compositions.

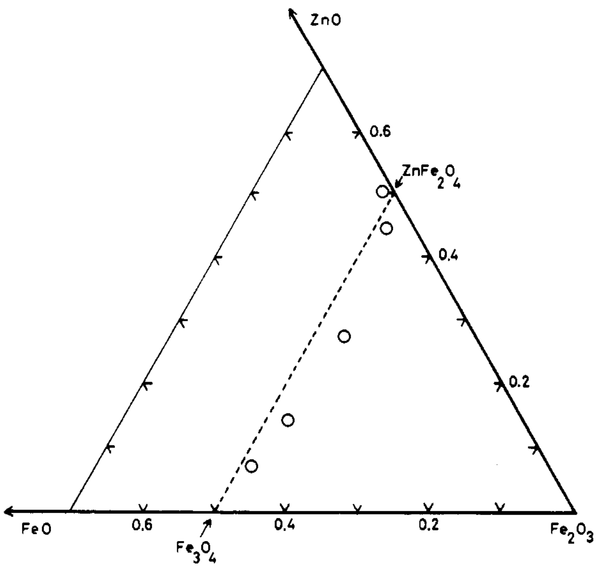

Figure 2. Chemical compositions ($FeO–Fe_2O_3–ZnO$ system) of the Zn(II)-bearing ferrites formed from the intermediate (green rust II) in the γ-FeO(OH) transformation reaction.

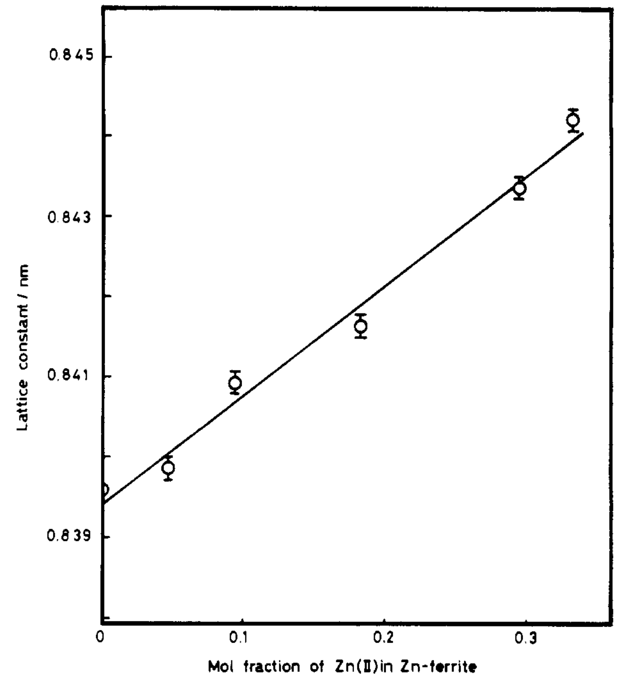

Figure 3. Relationship between the lattice constant of the Zn(II)-bearing ferrites and their Zn(II) contents.

Formation of Cd(II)-, Co(II)-, and Ni(II)-Bearing Ferrites from the Intermediate. When the reaction suspension used in step 1 contained the Cd(II), Co(II), or Ni(II) ion [M(II)/γ-FeO(OH)

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Table I. Parameters of Room-Temperature Mössbauer Spectra

ferrite[a]	hyperfine pattern[b]	internal field, kOe	isomer shift,[c] mm/s	line width, mm/s	area ratio B/A	quadrupole splitting, mm/s
$Cd_{0.12}Fe_{2.88}O_4$	A	480	0.31	0.35	1.0	0.04
	B	447	0.60	0.96	2.2	0.02
$Co_{0.58}Fe_{2.42}O_4$	A	484	0.32	0.47	1.0	0.03
	B	456	0.58	1.15	1.2	0.09
$Ni_{0.32}Fe_{2.67}O_4$	A	484	0.34	0.47	1.0	0.03
	B	452	0.66	1.10	1.2	0.09

[a] Chemical composition was evaluated from Table II by assuming that ferrites are stoichiometric. [b] Obtained by a computer curve fit assuming two Lorentzian sextets of A and B sites. [c] Relative to iron foil.

Table II. Metal Ion Contents (Mole Fraction) in the Ferrites Formed at a Fixed Content of the Metal Ions in the γ-FeO(OH) Suspension [M(II)/γ-FeO(OH) = 1.0]

ferrites	M(II)	Fe(II)	Fe(III)
Zn(II) ferrite	0.29_6	0.02_8	0.67_6
Cd(II) ferrite	0.04_1	0.27_8	0.68_1
Co(II) ferrite	0.19_4	0.13_5	0.67_1
Ni(II) ferrite	0.10_9	0.22_7	0.66_4

= 0–2.0] instead of the Zn(II) ion, greenish precipitates (green rust II) were also formed in step 1, as in the case of Zn(II) ion. X-ray diffractometry showed that the greenish precipitates (green rust II) formed in step 1 were spontaneously transformed into the spinel type compounds in step 2. Chemical analyses showed that they were the spinel type ferrites having nearly stoichiometric chemical compositions. The metal ion contents in the ferrites increased with an increase in those in the γ-FeO(OH) suspension. Parts a and b of Figure 4 show the Mössbauer spectra of the Cd(II)- and Co(II)-bearing ferrites, respectively, formed at M(II)/γ-FeO(OH) = 1.0 in the reaction suspension. The Mössbauer spectrum of the Ni(II)-bearing ferrite formed at Ni(II)/γ-FeO(OH) = 1.0 showed a pattern similar to that of Figure 4b. Table I shows the parameters of the Mössbauer spectra, which were obtained by a computer curve fit assuming two Lorentzian sextets of A and B sites. The results of the chemical analysis of these ferrites are given in Table II. The chemical compositions evaluated from the table are $Cd_{0.12}Fe_{2.88}O_4$, $Co_{0.58}Fe_{2.42}O_4$, and $Ni_{0.33}Fe_{2.67}O_4$, assuming that they are stoichiometric ferrites. The lattice constants of these ferrites were 0.8416 nm [Cd(II)], 0.8394 nm [Co(II)], and 0.8383 nm [Ni(II)]. These values are different from that of Fe_3O_4 (0.839 67 nm),[29] indicating that those metal ions were incorporated into the lattice structure.

Discussion

When no Fe(II) ions were present in the reaction suspension in step 1, IR spectroscopy showed that all of γ-FeO(OH) remained unreacted; no greenish precipitates were formed in step 1. Thus, the reaction of step 1 requires the Fe(II) ions. Furthermore, even though the Fe(II) ions were present, no reactions took place at pH below 6.0, where the Fe(II) ions are not adsorbed to γ-FeO(OH).[24,30] This suggests that the reaction in step 1 is initiated by the adsorption of Fe(II) ions onto γ-FeO(OH).

When we carried out the step 1 reaction at 65 °C, γ-FeO(OH) was directly transformed into the ferrites, and no intermediates were formed. However, at 25 °C, γ-FeO(OH) was not directly transformed into the ferrites but gave rise to the metastable intermediate (green rust II). Since the particle shapes of γ-FeO(OH) (rod type) and green rust II (hexagonal plate type) are different, it is assumed that the intermediate is formed from γ-FeO(OH) by a dissolution–precipitation process. In the dissolution step, some dissolved species, which is considered to be readily transformed into the ferrites at 65 °C, would be released. However, at 25 °C its transformation rate seems to be very slow, and therefore the dissolved species will be deposited as a different precipitate. This would be the case of the formation of the intermediate (green rust II). From the fact that the X-ray diffraction peaks of the intermediate shifted depending on the Zn(II) content in the reaction suspension, it is assumed that the metal ions are incorporated into the lattice structure of green rust II in step 1.

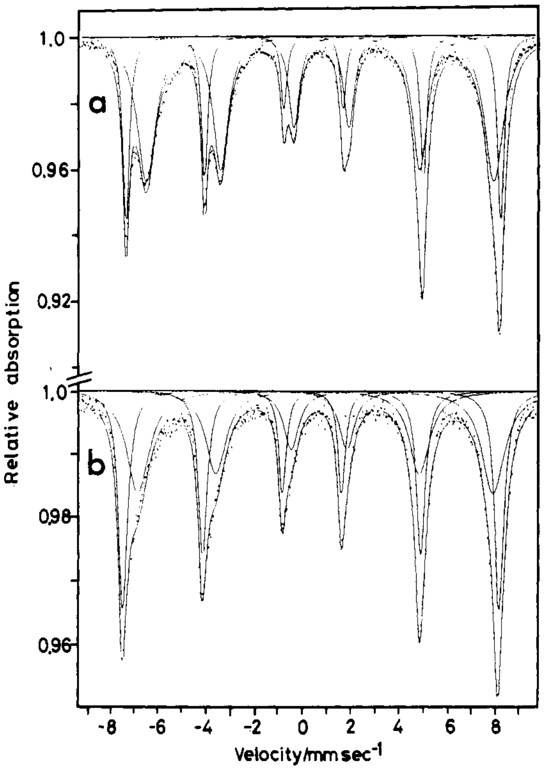

Figure 4. Room-temperature Mössbauer spectra of (a) Cd(II)-bearing ferrite ($Cd_{0.12}Fe_{2.88}O_4$) and (b) Co(II)-bearing ferrite ($Co_{0.58}Fe_{2.42}O_4$). Spectra were fit to pure Lorentzian lines by assuming two Lorentzian sextets of A and B sites.

To see which metal ions are mor readily incorporated into the ferrites in the γ-FeO(OH) transformation reaction, we compared the metal contents in the ferrites that had been formed at a fixed metal content in the reaction suspension [M(II)/γ-FeO(OH) = 1.0]. As can be seen from Table II, although the metal ion contents in the reaction suspensions were the same, those in the ferrites were different. The order of the metal ion content in the ferrites is Zn > Co ≃ Ni > Cd, while the order of the first hydrolysis constant[31] is Zn (p*K* = −8.96) > Co (−9.65) ≃ Ni (−9.86) > Cd (−10.08). This suggests that hydrolysis of the metal ions is required for the incorporation into the lattice structure in the transformation reactions in step 2. In the dissolution–precipitation process in step 2, the hydrolyzed species of the metal ions would be preferentially incorporated into the lattice structure.

The broadening of the B lines of the Mössbauer spectra for the Co(II) and Ni(II) ferrites suggests that the B part of the spectra could be split into several sextets for different hyperfine fields at the B-site Fe nuclei, as reported by Franke and Rosenberg.[32,33]

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The Co^{2+} or Ni^{2+} statistical distribution in the B site gives rise to a distribution of the Fe^{2+} ions with, on average, more Fe^{2+} ions in the Co^{2+}- (Ni^{2+}-) poor regions and less Fe^{2+} ions in the Co^{2+}- (Ni^{2+}-) rich regions. This would cause the different hyperfine fields at the B-site Fe nuclei.[32,33] For the Cd(II) ferrite, the area ratio (B/A) in Table I and the chemical composition (Table II) suggest that the broadening of the B line of the Mössbauer spectrum (Figure 4a) would be due to the slight oxidation of the Fe^{2+} ions in the B site or due to the incorporation of some of the Cd^{2+} ions into the B site (the Cd^{2+} ions would be distributed in both A and B sites.)

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Kinetics of Oxidation of the Chromium(II) Acetate Dimer by Iodine: An Example of Mixed Zero-Order/First-Order Kinetics

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The reaction between $Cr_2(OOCCH_3)_4$ and I_3^- has been studied in acetic acid solution in the presence of sodium iodide. The reaction is rapid and quantitative, and the stoichiometry corresponds to $Cr^{II}_2 + I_2 \rightarrow 2Cr^{III} + 2I^-$. The kinetics support the mechanism $Cr^{II}_2 \rightleftarrows 2Cr^{II}$ (k_1, k_{-1}), $Cr^{II} + I_2 \rightarrow$ products (k_2). At fixed water activity (0.4 M) and 25 °C the rate constants are $k_1 = a' + b'[NaI]^2$ and $k_2^* = k_2(k_1/k_{-1})^{1/2} = c' + d'[NaI]$ with $a' = 0.028\ s^{-1}$, $b' = 59.0\ M^{-2}\ s^{-1}$, $c' = 240\ M^{-1/2}\ s^{-1}$, and $d' = 3.18 \times 10^3\ M^{-3/2}\ s^{-1}$. The iodide dependences are attributed to an intermediate diiododichromium(II) complex $Na_2[Cr_2(OOCCH_3)_4I_2]$.

Introduction

In previous studies, Cannon[1,2] and Stillman[2] have shown that the dimeric chromium(II) acetate reacts with a variety of oxidizing agents in one-electron steps, preceded by dissociation of the dimer into mononuclear chromium(II) species

$$Cr^{II}_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2Cr^{II} \tag{1}$$

$$Cr^{II} + X \xrightarrow{k_2} Cr^{III} + \text{products} \tag{2}$$

In these equations, Cr^{II}_2 and Cr^{II} denote $Cr_2(OOCCH_3)_4$ and $Cr(OOCCH_3)_2$, with additional coordinated solvent and CH_3COO^- ions, according to conditions. Two limiting rate laws have been observed, eq 3 and 4, according to whether step 1 or step 2 is rate-determining

$$R = -d[Cr^{II}_2]/dt = k_1[Cr^{II}_2] \tag{3}$$

$$R = -d[Cr^{II}_2]/dt = k_2(k_1/k_{-1})^{1/2}[Cr^{II}_2]^{1/2}[X] \tag{4}$$

In the previous experiments,[2b] the oxidizing agents X were usually taken in excess over chromium(II), but preliminary observations suggested that, with chromium(II) in excess, varieties of kinetic behavior could be observed intermediate between pseudo zero and pseudo first order, the character of the rate law varying from one to the other in a given experiment, as the concentration of oxidant X decreased with time. We have found this to be true, using iodine as oxidant and using a nonaqueous solvent to minimize the overall dissociation of the dimer (eq 1). We report here the kinetics of the reaction.

Experimental Section

Acetic acid was dried by refluxing over boron triacetate and distilled.[3] All nitrogen used for degassing was deoxygenated by passage through BASF R3-11 catalyst. Reagent solutions were stored and mixed in vessels of the type shown in Figure 1. Iodine and chromium(II) concentrations were determined immediately before mixing in the stopped-flow apparatus, and water concentrations were determined in the mixture, after reaction. Iodine was determined by thiosulfate titration after dilution with water, chromium(II) by direct visual titration with iodine, and water by the Karl Fischer method.[4] Measured water concentrations were converted to activities by using data of Hansen et al.[5]

Chromium(II) acetate solutions were prepared by dissolving $[Cr_2(OAc)_4(OH_2)_2]$[6] in glacial acetic acid. Solutions up to about 10 mM were obtained at first, but when they were allowed to stand over several weeks, brown crystals of formula $[Cr_2(OOCCH_3)_4]\cdot 2CH_3COOH$ were deposited and the concentration fell to $[Cr^{II}_2] = 7.2$ mM. Solutions diluted with acetic acid obeyed Beer's law down to $[Cr^{II}_2] \leqslant 0.1$ mM. All other reagents used were analytical grade. All stopcocks were PTFE, and all solutions were handled in gas-tight syringes with PTFE plungers and needles.

Kinetic measurements were made in the HI-TECH SF-3 stopped-flow apparatus with an MCS-1 data acquisition and processing system. To avoid oxygen diffusion into the PTFE mixing system the thermostated water bath and air spaces were flushed continuously with nitrogen. To avoid stray-light effects[7] the instrument was calibrated by using solutions of iodine and NaI in acetic acid, at typical concentrations used in the kinetic studies, and at the same wavelengths and slit widths, the true transmittance being determined in separate measurements on a UNICAM SP8-200 spectrophotometer at 1-nm bandwidth. The dead time of the apparatus was estimated to be 1.5 ms (see below, Figure 7).

Results

1. The $I_2 + I^-$ Equilibrium. A spectrophotometric study ($\lambda = 410$ nm) of the equilibrium[8]

$$I_2 + NaI \overset{K}{\rightleftharpoons} NaI_3 \tag{5}$$

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