$$Cr(NH_3)_3(O_2)_2 + 2OH^- = CrO_4^{2-} + 3NH_3 + H_2O + {}^1/_2O_2 \quad (1)$$

with probably only a small contribution if any from the alternative reaction

$$Cr(NH_3)_3(O_2)_2 + 2OH^- = CrO_4^{2-} + 3NH_3 + H_2O_2 \quad (2)$$

since the latter does not fully account for the following observations: (a) considerable gas is evolved in the decomposition of $Cr(NH_3)_3(O_2)_2$ either at ~22 or 102°; (b) Table II shows a slow loss of oxidizing power rather than the rapid initial loss expected if H_2O_2 were rapidly formed with subsequent rapid reduction of some CrO_4^{2-} *via* the reaction

$$Cr_2O_7^{2-} + 3H_2O_2 + 8H^+ = 2Cr^{3+} + 7H_2O + 3O_2 \quad (3)$$

on acidification for the Fe^{2+} titration;[24] (c) no visual evidence of formation of dark peroxychromates is observed upon acidification of any of the solutions of Table II. The additional *ca.* 5% of fast reaction associated with the $Cr(NH_3)_3(O_2)_2$ decomposition itself is one in which CrO_4^{2-} and an N-containing species other than NH_3 is formed. This N-containing species (0.17 ± 0.04 g-atom of N per formula weight of $Cr(NH_3)_3(O_2)_2$ decomposed) probably is slowly oxidized by the CrO_4^{2-}, thus accounting for the gradual loss of oxidizing power up to a maximum of perhaps 0.5 oxidation equiv (*ca.* 0.2 mol) of CrO_4^{2-} lost. Alternatively, this N-containing species may simply act as a catalyst for the oxidation of water by CrO_4^{2-} (thermodynamically unfavorable at 25°, but possibly favorable at 102°) but in that case would have to decompose slowly into species which were noncatalytic and nonoxidizable by CrO_4^{2-}. This N-containing species is not NO_2^- and its nature was not experimentally investigated further.

Decomposition by Explosion.—The explosive decomposition of solid $Cr(NH_3)_3(O_2)_2$ appears to require shock or sudden heating (see Experimental Section). This is in accord with our previous comments[4] that $Cr(NH_3)_3(O_2)_2$ is probably the most stable of the known diperoxoaminechromium(IV) compounds because of a high degree of hydrogen bonding in the crystal.

The explosive decomposition appears to go *ca.* 90% *via* the over-all reaction

$$Cr(NH_3)_3(O_2)_2(s) = {}^1/_2Cr_2O_3(s) + 3NH_3(g) + {}^5/_4O_2(g) \quad (4)$$

The apparent molecular weight of the gas produced was 22.5. The above equation would produce a gas of apparent molecular weight 21.4. The difference is probably within the experimental error but if taken at face value suggests the presence of one or more higher molecular weight constituents. Condensation of the NH_3 in a calibrated vacuum system indicated the gas contained *ca.* 85–90% of the NH_3 expected from the stoichiometry of eq 4. The infrared spectrum of the gas indicated the presence of *ca.* 5% N_2O (ν 2220 cm^{-1}) and *ca.* 1–2% H_2O in the background of a considerable quantity of NH_3 and O_2. No NO, NO_2, or O_3 was observed in the infrared spectrum. The mass spectrum of the gas gave mass peaks corresponding to NH_3, O_2, and H_2O, as well as a mass peak at 44 (N_2O) distinct from another at 44 (CO_2) noted in the background and a peak for N_2 (perhaps 1%). The N_2O mass peak was also observed when $Cr(NH_3)_3(O_2)_2$ was decomposed at *ca.* 150° on a hot filament directly in the mass spectrometer.[25] The mode of formation of N_2O is unknown.

Thus, in each mode of decomposition of $Cr(NH_3)_3(O_2)_2$ examined the decomposition products are not formed by a single stoichiometric reaction.

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[24] Control experiments with solutions 0.03 *F* in H_2O_2, 0.05 *F* in Na_2CrO_4, and 1 *F* in NaOH showed that 15–50% of any H_2O_2 formed would have remained after 2–3 min at 102°, whereas the 2-min value of Table II shows no loss of oxidation equivalents at that time.

[25] N_2O has also been observed as a product of nonexplosive thermal decomposition of $[Co(NH_3)_5]_2O_2^{5+}$ salts: R. G. Hughes and E. A. V. Ebsworth, unpublished observations.

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A Study of the Kinetics of Complex Formation between Hexacyanoferrate(III) Ions and Iron(III) to Form $FeFe(CN)_6$ (Prussian Brown)

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The kinetics of the reaction between iron(III) ion and hexacyanoferrate(III) ion to form the neutral complex $FeFe(CN)_6$ (Prussian Brown) have been investigated by the stopped-flow method. The complexation rate constant was determined over a $[H^+]$ range of 0.02–0.71 *M* at 25° and was found to increase with increase in basicity. Evidence of an autoreduction reaction to form $KFe^{III}Fe^{II}(CN)_6$ (Prussian Blue) and evidence of a very slow reaction (10–70 sec) were also observed.

Introduction

In an investigation by DeWet and Rolle[1] on the structure of $Fe^{III}Fe^{II}(CN)_6$, Prussian Green, and $Fe^{III}Fe^{III}(CN)_6 \cdot 2H_2O$, Prussian Brown, Prussian Green was found to contain mixed hexacyanoferrates with divalent iron predominating and the amount of divalent iron present depended on the method of preparation; how-

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[1] J. F. DeWet and R. Rolle, *Z. Anorg. Allgem. Chem.*, **336**, 96 (1965).

ever, it even varied for different samples prepared in the same manner. In Prussian Brown a very small amount of hexacyanoferrate(II) was found present in the solid precipitated 1.5 min after mixing with essentially all of the complex ion in the form of iron(III) hexacyanoferrate(III). As the sample aged, the amount of hexacyanoferrate(II) increased (by a path involving Prussian Green). Their X-ray diffraction studies showed Prussian Brown to be of the same cubic structure type as the other Prussian Blue type hexacyanoferrate compounds.[2–5] DeWet and Rolle[1] postulated a mechanism whereby the electrons required for the reduction of the iron(III) ions are produced (with the attack of water molecules presumably built into the cell octants as suggested by Van Bever[6]) during precipitation

$$\mathrm{Fe^{3+} + Fe^{III}(CN)_6{}^{3-} + 2H_2O = Fe^{2+} + Fe^{II}(CN)_5{}^{3-} + NH_4{}^+ + CO_2} \quad (1)$$

It should be noted that all the Prussian dyes listed in the references tend to go to the stable Prussian Blue form.

The present investigation was undertaken to determine the kinetics involved in the formation of Prussian Brown and to see to what degree Prussian Blue was being formed in the Prussian Brown solution at very short times (less than 1 min).

Experimental Section

The stopped-flow apparatus used is similar to that used by Spencer and Sturtevant[7] and enables the measurement of reaction times as short as 2 msec. The apparatus was kept at a temperature of 25 ± 0.1° by circulating water from a constant-temperature bath through it.

Stock solutions of sodium perchlorate and iron(III) perchlorate (containing perchloric acid) were prepared from reagent grade chemicals obtained from G. F. Smith and Co. The iron(III) perchlorate was analyzed by titrating with standard thiosulfate[8] and by gravimetric methods, and the sodium perchlorate was analyzed gravimetrically. Reagent grade potassium hexacyanoferrate(III) was obtained from Mallinckrodt Chemical Works. Stock solutions of perchloric acid and sodium hydroxide were prepared from Baker analyzed reagent grade chemicals and analyzed by titrating against sodium carbonate and potassium acid phthalate, respectively.

Solutions of iron(III) perchlorate were prepared by adding a calculated volume of iron(III) perchlorate stock solution from a buret into a volumetric flask, adjusting the acidity with perchloric acid, adding sodium perchlorate to adjust the ionic strength, and adding distilled water to adjust the volume. Solutions of potassium hexacyanoferrate(III) were prepared from a stock solution by pipetting out the desired volume of stock solution into a volumetric flask, adjusting the acidity with perchloric acid, adding sodium perchlorate to adjust the ionic strength and double-distilled water to adjust the volume. Both the stock solution and the solution of potassium hexacyanoferrate(III) for each experiment were prepared and used within 1 hr.

The pH was measured with a Corning Model 12 pH meter using a calomel electrode containing NaCl in place of KCl to avoid erratic readings due to the precipitation of $KClO_4$. The pH meter was standardized against solutions of known iron(III) and perchloric acid concentrations at an ionic strength of 0.6 *M* and the $[H^+]$ values given in Table I represent total concentrations of perchloric acid added.

For each experiment, iron(III) perchlorate with a certain $[H^+]$ and at an ionics trength of 0.6 *M* was placed in one syringe and freshly prepared potassium hexacyanoferrate(III) with the same $[H^+]$ and ionic strength was placed in the other syringe. The reaction was observed at a wavelength of 500 mμ and the trace was stored on and photographed from a Tektronix 564 storage oscilloscope. The error in the rate constant is believed to be no more than ±10%.

The concentration of both the iron(III) perchlorate and the potassium hexacyanoferrate(III) was varied over ranges of 5.00×10^{-4} to 2.26×10^{-2} *M* and 5.00×10^{-4} to 1.00×10^{-2} *M*, respectively, one or the other always being in large excess. A $[H^+]$ range of 0.02–0.71 *M* was examined.

Results

Hydrolysis.—The pH of the iron(III) perchlorate solutions remained steady after a period of a few hours. The hydrolysis of iron, once complete, did not seem to have a significant effect on changing the pH at these high hydrogen ion concentrations; however, all of the calculations for concentrations were corrected for the hydrolysis of iron.[9]

Formation Constant.—The principal equilibrium between iron(III) ion and hexacyanoferrate(III) ions in aqueous solutions to form Prussian Brown

$$\mathrm{Fe^{3+} + Fe(CN)_6{}^{3-} = FeFe(CN)_6} \quad (2)$$

has been studied by Ibers and Davidson[10] spectrophotometrically, and a formation constant of 36 was obtained in a 0.5 *M* perchloric acid solution (ionic strength of about 0.6 *M* at 26 ± 2°). The extinction coefficient for Prussian Brown was determined to be 611 at a wavelength of 500 mμ. These values were used in this investigation.

Rate Law.— As a working assumption, the mechanism of reaction was considered to be

$$\mathrm{Fe^{3+}(aq) + Fe(CN)_6{}^{3-}(aq)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{FeFe(CN)_6(aq) + H_2O} \quad (3)$$

Using the relationship, $K = k_1/k_{-1}$ in the rate expression, one obtains

$$\mathrm{d[FeFe(CN)_6]}/\mathrm{d}t = k_1\mathrm{[Fe^{3+}][Fe(CN)_6{}^{3-}]} - \{k_1/K\mathrm{[FeFc(CN)_6]}\} \quad (4)$$

In all of the experiments the iron(III) ion or the hexacyanoferrate(III) ion is in large excess and for purposes of deriving a rate expression the ion in large excess is considered to be constant (the iron(III) ion concentration is corrected for hydrolysis and complex formation in the final equation). If one assumes the concentration of $[Fe^{3+}]$ to be constant and expresses $[Fe(CN)_6{}^{3-}]$ in terms of $[Fe^{3+}]$ and $[FeFe(CN)_6]$ and defines $[FeFe(CN)_6]_0$, $[FeFe(CN)_6]$, and $[FeFe(CN)_6]_{eq}$ as the concentration of the complex at the beginning of the reaction, at any time during the reaction, and at the end of the reaction, respectively, the above rate expression may be integrated giving

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[2] J. F. Keggin and F. D. Miles, *Nature*, **137**, 57 (1936).

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[8] N. H. Furman, Ed., "Scott's Standard Methods of Chemical Analysis," Vol. I, 5th ed, D. Van Nostrand Co., Inc., Lancaster, Pa., 1939, p 482.

[9] R. M. Milburn and W. C. Vosburgh, *J. Am. Chem. Soc.*, **77**, 1352 (1955).

[10] J. A. Ibers and N. Davidson, *ibid.*, **73**, 476 (1951).

$$k_1t = \frac{-2.303}{[\mathrm{Fe}^{3+}] + (1/K)} \log \frac{[\mathrm{FeFe(CN)_6}]_{\mathrm{eq}} - [\mathrm{FeFe(CN)_6}]}{[\mathrm{FeFe(CN)_6}]_{\mathrm{eq}} - [\mathrm{FeFe(CN)_6}]_0} \quad (5)$$

All of the quantities in the above equation are known or determined experimentally except k_1. A plot of log $[[\mathrm{FeFe(CN)_6}]_{\mathrm{eq}} - [\mathrm{FeFe(CN)_6}]]$ *vs.* time yields a straight line, confirming the assumption of first-order dependence on the concentration of $[\mathrm{Fe(CN)_6}^{3-}]$. A similar derivation and plot for experiments in which $[\mathrm{Fe(CN)_6}^{3-}]$ is in excess show a first-order dependence on the concentration of $[\mathrm{Fe}^{3+}]$. The optical density of each mixture and its components was measured shortly after mixing so the concentration of Prussian Brown could be determined. After each experiment a measurement was made to determine how much transmittance each division on the oscilloscope screen represented at that particular setting. The oscillographs could then be analyzed for $[\mathrm{FeFe(CN)_6}]$ at any time by subtracting the transmittance (distance in millimeters from the finish line of the reaction curve) from the transmittance for $[\mathrm{FeFe(CN)_6}]_{\mathrm{eq}}$ obtained from the optical density measurement.

The data for the kinetic runs made at 25° are given in Table I. The rate constant varies by less than 10% for a given $[\mathrm{H}^+]$ and is considered adequate to show a first-order dependence on the ion present in the least amount. The average rate constant for a $[\mathrm{H}^+]$ of 0.19 M is 1.2×10^3 M^{-1} sec^{-1}.

TABLE I

KINETIC DATA AT 25° AND $\mu = 0.6$ M

Expt	$\Sigma[\mathrm{Fe(ClO_4)_3}]$, $M \times 10^2$	$\Sigma[\mathrm{Fe(CN)_6}^{3-}]$, $M \times 10^3$	$[\mathrm{H}^+]$, $M \times 10$	k_1, M^{-1} sec^{-1}
1	2.43	1.00	7.05	8.4×10^2
2	2.43	1.00	3.82	9.3×10^2
3	2.26	2.00	1.90	1.1×10^3
4	2.26	1.50	1.90	1.1×10^3
5	2.26	1.00	1.90	1.1×10^3
6	2.26	0.50	1.90	1.2×10^3
7	1.41	2.50	1.90	1.2×10^3
8	1.41	2.00	1.90	1.2×10^3
9	1.41	1.00	1.90	1.1×10^3
10	0.943	2.00	1.90	1.3×10^3
11	0.943	1.00	1.90	1.1×10^3
12	0.943	0.50	1.90	1.2×10^3
13	0.100	10.00	1.90	1.1×10^3
14	0.050	10.00	1.90	1.1×10^3
15	0.100	5.00	1.90	1.2×10^3
16	1.886	1.00	1.24	1.6×10^3
17	1.20	0.50	1.24	1.2×10^3
18	0.943	2.00	0.705	2.3×10^3
19	1.886	0.50	0.705	2.1×10^3
20	1.886	2.00	0.705	2.2×10^3
21	1.886	1.00	0.705	1.8×10^3
22	1.886	1.00	0.496	2.2×10^3
23	1.20	0.20	0.496	2.0×10^3
24	1.886	1.00	0.382	2.6×10^3
25	1.20	0.50	0.382	2.6×10^3
26	1.886	1.00	0.201	3.6×10^3
27	1.20	0.50	0.201	4.0×10^3

Dependence on $[\mathrm{H}^+]$.—In order to determine if the rate of complexation is influenced by a change in $[\mathrm{H}^+]$, a series of experiments was made over a $[\mathrm{H}^+]$ range of 0.02–0.71 M. The data for these experiments are given in Table I. A plot of k_1 *vs.* $1/[\mathrm{H}^+]$ yielded a straight line (see Figure 1) corresponding to a rate law of the form (showing only the forward rate constants)

$$d[\mathrm{FeFe(CN)_6}]/dt = k_1^*[\mathrm{Fe}^{3+}][\mathrm{Fe(CN)_6}^{3-}] + \{k_2^*[\mathrm{Fe}^{3+}][\mathrm{Fe(CN)_6}^{3-}]/[\mathrm{H}^+]\} \quad (6)$$

with $k_1 = k_1^* + (k_2^*/[\mathrm{H}^+])$.

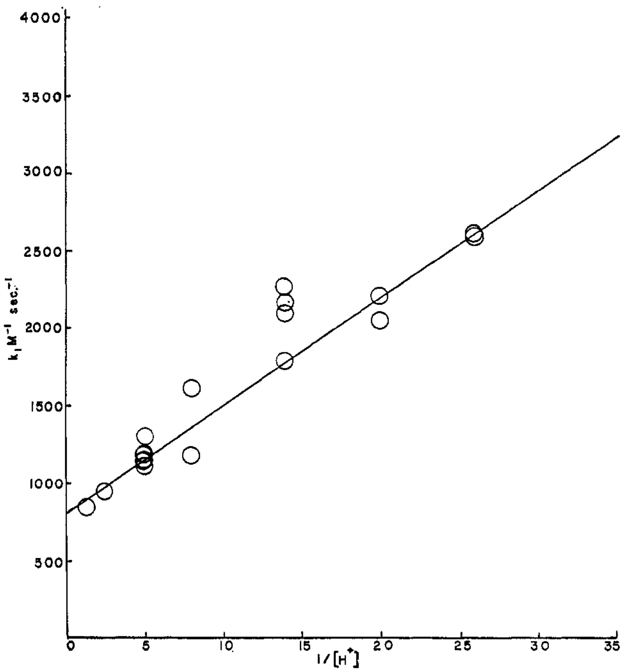

Figure 1.—Dependence of the forward rate constant on the $[\mathrm{H}^+]$ at 25° and $\mu = 0.6$ M.

Other Reactions.—Two reaction curves besides that due to the formation of Prussian Brown were observed. If potassium hexacyanoferrate(III) solutions that were not fresh (exposed to the air and light for more than 30 min) were mixed with iron(III) perchlorate, a reaction curve was observed in the 0.1–0.8-sec range. This curve was in the direction corresponding to an increase in transmittance at 500 mμ indicating the formation of a blue substance. The size of the curve increased with the age of the solution and it disappeared when the solutions of potassium hexacyanoferrate(III) were used immediately after preparation.

It was observed that a solution of potassium hexacyanoferrate(III) which was allowed to stand for several hours became discolored, and a fine bluish green precipitate (probably Prussian Blue) was obtained where the material air evaporated on the volumetric stopper. A check on the optical density of the Prussian Brown complex formed under the conditions used in this study revealed no precipitate and no "significant" change in optical density over a period of 1 hr; however, exposure for longer periods of time indicated the formation of a mixture of Prussian Green and Blue.

The other reaction curve was observed to finish in the range of 10–70 sec. This slower reaction became faster as the pH was raised and is believed to be due to a hydrolysis reaction of the iron(III) ion. This reaction is presently under investigation.

Discussion

The over-all rate constant which was determined in this investigation is based on eq 5. Equation 5 is derived from the working assumption, eq 3, which is a combination of two equations that are often used to explain the over-all rate of complexation for many metal ions. For monovalent and divalent ions, the formation of a complex by substitution of a ligand into the inner coordination sphere of the metal ion consists of at least two well-defined steps.[11] The first step is a rapid diffusion-controlled formation of an ion pair (activated complex with seven sites). In the second step, which is rate determining, a water molecule is dissociated from the aquated metal complex and ligand substitution then occurs. The proposed steps for this system are

$$\mathrm{Fe^{3+}(aq) + Fe(CN)_6{}^{3-}(aq) \overset{K_0}{\rightleftharpoons} FeH_2O,\ Fe(CN)_6(aq)}$$

$$\mathrm{FeH_2O,\ Fe(CN)_6(aq) \overset{k_0}{\rightleftharpoons} FeFe(CN)_6(aq) + H_2O} \qquad (7)$$

where $k_0 = k_1/K_0$. If the two steps of eq 7 are added, one obtains eq 3 which was used in this study as a working assumption. The rate constant for replacement of a water molecule in the hydrated iron(III) ion has been shown to be primarily dependent on the rate of water exchange rather than the nature of the ligand.[12] Only the rate of dissociation is affected by the type of ligand.

The greater rate of complexation realized in more basic solutions is similar to that found with the $FeSCN^{2+}$ complex.[13] The increase in the rate of reaction as the $[H^+]$ decreases may be due to the weakening of the bonding of the hybrid waters around the Fe^{3+} by OH^- making substitution of the ligand easier (see reaction 8a) or to the formation of a hydrolyzed species, $FeOH^{2+}$, which has a considerably higher over-all rate of reaction for complex formation than Fe^{3+} [12,14] (see reaction 8b). For eq 8a it is necessary

$$\mathrm{Fe(H_2O)_6{}^{3+} \rightleftharpoons Fe(H_2O)_5{}^{3+} + H_2O}$$

$$\mathrm{Fe(H_2O)_5{}^{3+} + Fe(CN)_6{}^{3-} \xrightarrow{k} Fe(H_2O)_5Fe(CN)_6} \qquad (8a)$$

$$\mathrm{Fe(H_2O)_6{}^{3+} \overset{K_h}{\rightleftharpoons} Fe(H_2O)_5OH^{2+} + H^+}$$

$$\mathrm{Fe(H_2O)_5OH^{2+} + Fe(CN)_6{}^{3-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Fe(H_2O)_4(OH)Fe(CN)_6{}^-}$$

$$(\text{where } k_3 = k_2/K_h) \qquad (8b)$$

that exchange of the coordinated water with a bulk water occur faster than substitution by the ligand can occur, and for eq 8b it is necessary that the splitting of a water molecule into OH^- and H^+ occur faster than the formation of the collision complex. Although both of these assumptions have been considered reasonable for Fe^{3+}, mechanism 8b seems to be more generally supported.[12] In a recent publication by Singleton and Swinehart[15] in which this system was studied by a temperature-jump method, experiments indicate that the first step in expression 7, formation of the ion pair, occurs in less than 1 μsec, whereas the release of a water molecule from the ion pair occurs in the millisecond range indicating that the rate constant for the formation of the ion pair is considerably larger than k_0.

Although Singleton and Swinehart did not find a difference in relaxation time when they changed the acid concentration from 0.5 *M* perchloric acid to 1 *M* perchloric acid, our investigation indicates that a decrease in $[H^+]$ does enhance the rate of reaction. Using the relationship $k_3 = k_2/K_h$, the value of K_h from ref 9, and k_2 from the slope of the plot in Figure 1, a value of $3.6 \times 10^4\ M^{-1}\ sec^{-1}$ is obtained for the rate constant for the $[H^+]^{-1}$ term. This value compares reasonably well with the k_3 value of $10^4\ M^{-1}\ sec^{-1}$ for the $FeSCN^{2+}$ system.[13] As $[H^+]^{-1}$ approaches 0 the rate constant approaches $8.0 \times 10^2\ M^{-1}\ sec^{-1}$ ($k_1 = k_1{}^*$). Singleton and Swinehart found a forward rate constant of $1750 \pm 250\ M^{-1}\ sec^{-1}$, whereas our rate constant under similar conditions was found to be $940 \pm 100\ M^{-1}\ sec^{-1}$; however, if one uses the equilibrium constant of 117 that can be obtained from the slope and intercept of their $1/\tau$ *vs.* $\{[Fe(H_2O)_6{}^3] + [Fe(CN)_6{}^{3-}]\}$ plot instead of 36, the data obtained in our studies indicate a rate constant of $1500 \pm 150\ M^{-1}\ sec^{-1}$ at the same $[H^+]$ concentration which agrees very well with their constant. Using an equilibrium constant of 117 gives a rate constant of $1200\ M^{-1}\ sec^{-1}$ as $[H^+]$ approaches 0 and a k_3 value of $7.9 \times 10^4\ M^{-1}\ sec^{-1}$.

The discoloration of Prussian Brown solutions that were allowed to age to form a bluish green solution and the actual formation of bluish crystals from Prussian Brown solutions that were aged and evaporated furnish some evidence for the autoreduction mechanism proposed by DeWet and Rolle[1] in eq 1.

Two observations indicate that potassium hexacyanoferrate(III) solutions can produce Prussian Green, Prussian Blue, and $Fe(CN)_6{}^{4-}$ upon aging. The first of these observations was the reaction which was observed between iron(III) perchlorate and aged potassium hexacyanoferrate(III) solutions in the 0.1–0.8-sec range. This reaction showed an increase in transmittance at 500 mμ (blue light) indicating the formation of a blue complex. The size of this reaction increased as the solution aged and essentially disappeared when fresh solutions of potassium hexacyanoferrate(III) were used. The observation chamber was bluish green after several experiments. The second observation was the formation of blue crystals on the stopper of the volumetric flask containing the aged potassium hexacyanoferrate(III) and the discoloration of these solutions upon aging.

The slow reaction observed (10–70 sec for completion) is believed to be due to the polymerization of $FeOH^{2+}$ to form $Fe_2(OH)_2{}^{4+}$ or a higher polymer of $FeOH^{2+}$. The reaction time decreased with decreasing $[H^+]$ as one would expect with a hydrolysis reaction of this type.[16]

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