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Oxidation of Fe(III) to Fe(VI) by the $Fe(CN)_6^{3-}$ Ion in Strong Solution of Alkalis

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Abstract—Ferricyanide ions oxidize Fe(III) up to Fe(VI) in 7–11 M KOH solutions and 10–16 M NaOH solutions. The completeness of the oxidation increases with increasing alkali and ferricyanide concentrations. The presence of KNO_2, KAc, and $K_2C_2O_4$ in 7 M KOH solution increases the Fe(VI) yield. Potassium fluoride in the concentration of 0.02 M does not hinder Fe(VI) formation, but in the concentration of 0.1 M completely suppresses Fe(III) oxidation. The attempt to oxidize Fe(VI) up to Fe(VIII) by the disproportionation of Fe(VI) or by the action of $Fe(CN)_6^{3-}$ and ozone was unsuccessful due to a high oxidation potential of the Fe(VIII)/(VI) couple.

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The ferrate ion is a strong oxidizing agent in acid and alkaline media as the potential of the couple $HFeO_4$, H^+/Fe^{3+} (pH 0.0) is 2.07 V, and the potential of the couple $FeO_4^{2-}/Fe(OH)_4$, OH^- (pH 13.996) is 0.64 V [1]. For example, FeO_4^{2-} in the phosphate buffer reacts fast with $Fe(CN)_6^{4-}$ ions [2]. The standard potential of the couple $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ is 0.36 V [3]. The real potential of this couple increases as ionic strength increases; in 1 M NaOH solution it is 0.44 V [4], and reaches the value of 0.486 V in 4 M NaOH solution, as it follows from the value of the equilibrium constant for reaction (1) [5] in view of the facts that in such solution at 10°C the potential of the couple Np(VII)/Np(VI) is close to 0.462 V.

$$\mathrm{Np(VI)} + Fe(CN)_6^{3-} \leftrightharpoons \mathrm{Np(VII)} + Fe(CN)_6^{4-}, \quad (1)$$

$$K = [\mathrm{Np(VII)}][Fe(CN)_6^{4-}][\mathrm{Np(VI)}]^{-1}[Fe(CN)_6^{3-}]^{-1} = 2.7\ [6],$$

$$E[Fe(CN)_6^{3-}/Fe(CN)_6^{4-}] = E[\mathrm{Np(VII)/Np(VI)}] + 0.056 \log K.$$

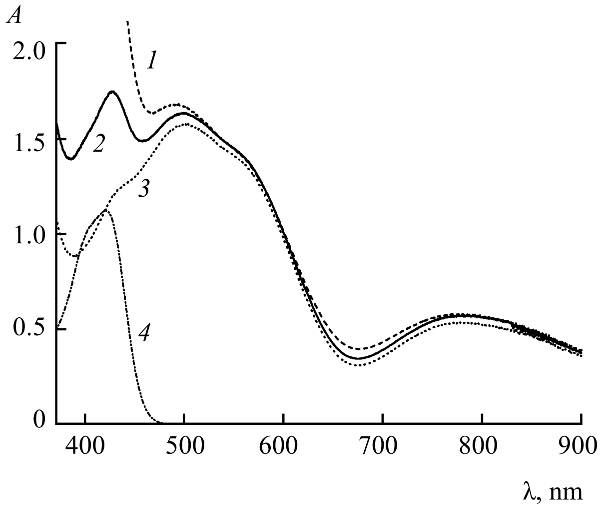
In dilute solutions of alkalis (less than 5 M) the ion $Fe(CN)_6^{4-}$ can reduce FeO_4^{2-}completely, but in strong solutions of alkali the pattern should vary; except for the rise of the potential of the couple $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$, the potential of the couple Fe(VI)/Fe(III) decreases as follows from the equation of reaction (2).

$$FeO_4^{2-} + 4H_2O + 3e^- \leftrightharpoons Fe(OH)_4^- + 4\ OH^-. \quad (2)$$

An estimate shows that ferricyanide ion will oxidize Fe(III) to Fe(VI) in a 10 M NaOH solution. In the present work we have studied conditions for the formation of FeO_4^{2-} by the reaction of Fe(III) with $Fe(CN)_6^{3-}$.

Preliminary experiments have shown that the addition of NaOH solutions to a mixture of $Fe(NO_3)_3$ and $K_3Fe(CN)_6^{3-}$ solutions up to a concentration about 10 M gives rise to the appearance of lilac coloring characteristic for FeO_4^{2-} ions. These experiments formed a basis for planning the whole subsequent work.

It is known [4] that $Fe(CN)_6^{3-}$ slowly disappears in 1 M NaOH solution. Therefore first we studied the $Fe(CN)_6^{3-}$ stability in solutions of alkalis. The loss of optical density at 419–420 nm, where the maximum of a $Fe(CN)_6^{3-}$ absorption band is located, allowed us to estimate the rate of the ferricyanide ions disappearance. In a 5 M NaOH solution at 18–20°C the initial rate of $Fe(CN)_6^{3-}$ decomposition is close to 1.7% per 1 min, but after consuming approximately 5–7% of $Fe(CN)_6^{3-}$ the reaction rate was slowed down. The rate of the decomposition of ferricyanide ions increased as the alkali concentration increased, the loss of $[Fe(CN)_6^{3-}]$ not obeying the first- or second-order rate law. In the 11.6 M NaOH solution an initial $Fe(CN)_6^{3-}$ concentration has decreased by half in 110 min. The decomposition of $Fe(CN)_6^{3-}$ was caused by the reaction with H_2O, which was probably accelerated due to nickel and cobalt trace admixtures and also due to a reaction



Spectrum of the aqueous suspended matter containing 5 mmol of $K_3Fe(CN)_6$ + 1 mmol of $Fe(NO_3)_3$ + 8.8 M KOH. (*1*) 5 min after mixing components, (*2*) 34 min after centrifugation for 5 min and (*3*) after repeated centrifugation for 107 min; and (*4*) spectrum of 8.8 M KOH solution containing 1 mmol of $K_3Fe(CN)_6$.

with OH^- ions. To avoid undesirable $Fe(CN)_6^{3-}$ decomposition, we added the initial alkali solution to a mixture of $Fe(NO_3)_3$ and $K_3Fe(CN)_6$ solutions, or added $K_3Fe(CN)_6$ with Fe(III) hydroxide to an alkaline solution.

In 7–11.3 M KOH solutions containing 1 mmol of Fe(III) and 3.3 mmol of $K_3Fe(CN)_6$ a lilac coloring appeared right after mixing. Within 3–5 min a solution became turbid. A precipitate was separated by centrifugation. The spectra of $K_3Fe(CN)_6$ solutions and Fe(III) and $K_3Fe(CN)_6$ mixtures are given in the figure. As a result of the Fe(III) reaction with $Fe(CN)_6^{3-}$ a band with a maximum at 510 nm has appeared in the electronic spectrum of the solution. According to [7], such absorption belongs to the FeO_4^{2-} ion. We used the molar extinction coefficient of 1150±25 l mol^{-1} cm^{-1} at pH 10 [7] to estimate FeO_4^{2-} concentrations, though it is not excluded that in concentrated alkaline solutions it could be a little less.

Table 1. Effect of alkali concentration on the formation of FeO_4^{2-}, [Fe(III)] 1 M

[KOH], M	$[Fe(CN)_6^{3-}]$, M	$[FeO_4^{2-}]$, M
7.0	3.33	0.20[a]
8.0	3.33	0.48
9.0	3.33	0.83
10	3.33	0.95[b]
11.3	3.33	–[c]
10	5.0	0.88[d]

[a] Slow appearance of coloring. [b] $K_3Fe(CN)_6$ was added to an alkaline Fe(III) solution. [c] It was not possible to determine, turbid lilac solution. [d] After separating suspended matter.

The results of some experiments are given in Table 1.

After mixing Fe(III) and $K_3Fe(CN)_6$ aqueous solutions with concentrated KOH solutions colorless precipitates are formed within 2–3 min. These precipitates were separated from the solutions and mixed with a CH_3COOH solution. In most cases a resulting mixture immediately became brightly dark-blue that testified to the presence of Prussian blue, i.e. the compound of Fe(III) and $Fe(CN)_6^{4-}$. In separate experiments after adding CH_3COOH a precipitate was dissolved without appearance of a dark blue coloring. However the subsequent adding of a $Fe(NO_3)_3$ solution always resulted in the Prussian blue formation, which pointed to the presence of ferrocyanide ions. Thus, in an alkaline medium reaction (3) occurs between Fe(III) and $Fe(CN)_6^{3-}$.

$$Fe(OH)_4^- + 3\,Fe(CN)_6^{3-} + 4\,OH^- \leftrightharpoons FeO_4^{2-} + 3\,Fe(CN)_6^{4-} + 4\,H_2O. \tag{3}$$

In the case of the incomplete oxidation a part of Fe(III) was bound with $Fe(CN)_6^{4-}$. It is necessary to note that the addition of $K_4Fe(CN)_6$ to a Fe(III) alkaline solution also resulted in the formation of a colorless precipitate, which, however, did not become dark blue on acidification.

The change in the time between preparation of Fe(III) alkaline solution and $K_3Fe(CN)_6$ addition from 5 min to 20 h did not affect the character of the reaction.

The effect of highly soluble potassium salts on the reaction of Fe(III) with $Fe(CN)_6^{3-}$ in a 7 M KOH solution (Table 2) has been checked. It has appeared that K_2CO_3 and KNO_2 slightly increase the yield of FeO_4^{2-}. The addition of KF up to the concentration of 0.02 M did not affect the Fe(VI) formation, but KF in the concentration of 0.1 M completely inhibited the oxidation reaction. The same was observed in the 8–11 M KOH solution.

The formation of FeO_4^{2-} in a NaOH solution also depends on the alkali concentration. For example, in a 10.3 M NaOH solution in the moment of mixing of 1 mmol l^{-1} of Fe(III) and 3.33 mmol l^{-1} of $K_3Fe(CN)_6$ 0.49 mmol l^{-1} of FeO_4^{2-} was formed and within 3 h its concentration has grown up to 0.72 mmol l^{-1}. In a 10.3 M NaOH solution fluoride ions inhibit Fe(III) oxidation. However in a 15 M NaOH solution fluoride ions in the

Table 2. Effect of potassium salts (KX) on the formation of ferrate ions in alkaline solutions

[KOH], M	[Fe(III)], mmol l^{-1}	[$K_3Fe(CN)_6$], mmol l^{-1}	[KX], mmol l^{-1}	Character of lilac coloring of solution
7	1	3.33	KF, 0.02	Slow coloring
7	1	3.33	KF, 0.10	Absence of coloring
5	5.3	26.3	KF, 5.2	Slow coloring
7	1	3.33	KNO_2, 5	Intensive coloring
7.0	1	3.33	K_2CO_3, 2	Intensive coloring
5.6	4.8	23	K_2CO_3, 2.6	Slow coloring
8.8	1	3.33	KSCN, 2.5	Intensive coloring, fast disappearance
7	1	3.33	$KC_2H_3O_2$, 3.2	Intensive coloring
6	1	3.33	$KC_2H_3O_2$, 4.1	Intensive coloring
5	1	3.33	$KC_2H_3O_2$, 4.8	Coloring
10	1	4	$K_2C_2O_4$, 0.04	Intensive coloring
11.2	1	4	EDTA, 0.01[a]	Weak coloring

[a] Entered into solution in the form of $NaFe(EDTA)\cdot 2H_2O$.

concentration of 0.1 M hinder the oxidation within first minutes, and then the coloring develops, but not in full measure.

Under the selected conditions Fe(VI) solutions slowly lose coloring, i.e. Fe(VI) is reduced by water and by products of the decomposition of iron cyanide complexes. With a 5–10-fold excess of $Fe(CN)_6^{3-}$ the red-violet color of solutions is retained within several days.

The ion $Fe(CN)_6^{3-}$ is a one-electron oxidizing agent, therefore the process of Fe(III) oxidation up to Fe(VI) passes through sequential stages (4)–(6).

$$Fe(III) + Fe(CN)_6^{3-} \leftrightarrows Fe(IV) + Fe(CN)_6^{4-}. \quad (4)$$

$$Fe(IV) + Fe(CN)_6^{3-} \leftrightarrows Fe(V) + Fe(CN)_6^{4-}. \quad (5)$$

$$Fe(V) + Fe(CN)_6^{3-} \leftrightarrows Fe(VI) + Fe(CN)_6^{4-}. \quad (6)$$

Therefore

$$E[Fe(CN)_6^{3-}/Fe(CN)_6^{4-}] \geq E[Fe(IV)/Fe(III)] \sim E[Fe(V)/Fe(IV)] \sim E[Fe(VI)/Fe(V)].$$

In [8] Fe(VI) solutions obtained by the anodic dissolution of metallic iron in 5–10 M NaOH contacted with CCl_4, and the reaction mixture was distilled under a reduced pressure to give pink condensates. On the basis of these experiments Kiselev et al. asserted that the condensate contained FeO_4, and reaction (7) of the Fe(VI) disproportionation proceeded in the solution.

$$2Fe(VI) \leftrightarrows Fe(IV) + Fe(VIII). \quad (7)$$

The distillation with CCl_4 shifted equilibrium (7) to the side of the Fe(VIII) formation. It follows from these experiments that E[Fe(VI)/Fe(IV)] ≥ E[Fe(VIII)/Fe(VI)]. If an element in a certain oxidation state is able to disproportionate, the higher oxidation state can be obtained by the action of chemical reagents on a lower oxidation state or in another way. For example, Np(VI) and Am(VI) disproportionate in strong NaOH solutions [9] [reactions (8), (9)].

$$2Np(VI) \leftrightarrows Np(V) + Np(VII), \quad (8)$$

$$2Am(VI) \leftrightarrows Am(V) + Am(VII). \quad (9)$$

Septivalent neptunium and americium are readily obtained under the action of ozone or in the radiation-chemical way [9].

We have fulfilled a series of experiments with the aim of possible obtaining Fe(VIII). In one of them to 11.3 M KOH solution containing Fe(VI) and an excess of $K_3Fe(CN)_6$ we added an equal volume of CCl_4 and then checked the presence of iron in the organic phase. It was supposed that reaction (7) proceeds in the system under study and the formed FeO_4 would pass in the organic phase. But our hopes were not justified. No iron was present in the CCl_4 layer.

In the next experiment we bubbled oxygen through an 11 M KOH solution containing Fe(VI) and $K_3Fe(CN)_6$.

It was supposed that Fe(VIII) could be generated by the disproportionation of Fe(VI) or by its oxidation by $Fe(CN)_6^{3-}$ ions. A gas stream should carry along FeO_4, which should be absorbed by HCl solution with the conversion Fe(VIII) → Fe(III). Iron(III) chloride complexes have an absorption band in the nearest UV region of the spectrum and are intensively colored. The barbotage within 2 h has not led to discoloration of the HCl solution. Then we added water in the alkaline Fe (VI) solution and continued the oxygen barbotage. Such operation was repeated several times, KOH concentration being varied from 11 up to 5 M. A bubbler with the alkaline Fe(VI) solution was placed in water at 60–90°C. No discoloration of the HCl solution was observed.

The possibility of detecting a volatile compound has been checked up in the experiment with ruthenium. We loaded 25 mg of metallic ruthenium in the form of a fine powder in a bubbler with 4 M NaOH solution and passed through an ozone-oxygen mixture. Within 1 h an HCl solution in a bubbler connected sequentially turned yellow and then became brown. A black thin coat was formed in connective tubes. Ruthenium was oxidized up to RuO_4, which was transferred by a gas stream, partially reduced, and precipitated on the walls in the form of RuO_2. Remaining RuO_4 was reduced by chloride ions, and ruthenium chloride complexes colored the solution.

The experiment with the assumed FeO_4 distillation was fulfilled with the use of ozone. It is necessary to note that Fe(VI) is not formed if Fe(III) is mixed with $K_3Fe(CN)_6$ not in advance, but in an ozone current. Therefore we used a solution with ready Fe(VI) and an excess of $K_3Fe(CN)_6$ in the experiment with the ozone barbotage. It was supposed that FeO_4^{2-} would be oxidized either by ozone or by ozonide ions. However within a 7 h ozonation a color of HCl solution in the bubbler has not changed.

Let us consider how much the hopes to obtain Fe(VIII) under the experimental conditions were justified. Potentials of the couples with the maximal oxidation state for an element in solution with 1 M OH^- concentration in the series Ti(IV)/Ti(III), V(V)/V(IV), Cr(VI)/Cr(V), and Mn(VII)/Mn(VI) are –1.2, –0.8, 0.1, and 0.56 V [1], i.e. they almost monotonically increase. For the couple Fe(VIII)/Fe(VII) the potential should be no less than 1 V. The potentials of the previous couples are close to the potentials of couples with the maximal oxidation states. For example, for the couple Mn(VI)/Mn(V) the potential is 0.27 V [1]. Therefore E[Fe(VIII)/Fe(VI)] ≥ 1 V. The potentials of the couples Os(VIII)/Os(VII) and Ru(VIII)/Ru(VII) are 0.2 and 0.85 V [1]. The extrapolation to the Fe(VIII)/Fe(VII) couple also gives a value higher than 1 V. The potential of the couple Am(VII)/Am(VI) in 1 M NaOH is 1.05 V [9], but ozone oxidizes Am(VI) at $t < 0°C$ [9]. The absence of the Fe(VI) oxidation, though it goes without restructuring ($FeO_4^{2-} \rightarrow FeO_4$), points to the fact that the potential Fe(VIII)/Fe(VI) ≥ 1.05 V.

The assertion of the authors [8] about Fe(VI) disproportionation is erroneous. Though they determined the oxidative equivalent of the compound distilled with CCl_4, they have not tested this compound for the presence of iron.

EXPERIMENTAL

Concentrated solutions of KOH and NaOH (special-purity grade) and $Fe(NO_3)_3$, $K_3Fe(CN)_6$, $K_4Fe(CN)_6 \cdot 3H_2O$, H_2O, KNO_2, KF, K_2CO_3, $K_2C_2O_4$, KCH_3COO, and $NaFe(EDTA) \cdot H_2O$ (Chemically-pure or analytical grade) were used in the work. The study was carried out using Shimadzu UV 3100 spectrophotometer (Japan). Spectra of solutions were recorded in quartz cells (l 1 cm).

Concentrations of the initial alkali solutions were determined by acidometry, and concentrations of the other reagents, in weighted samples taken analytically.

Experiments on assumed obtaining Fe(VIII). *a.* In a tube with a ground-glass stopper 0.050 ml of 0.1 M $Fe(NO_3)_3$, 0.100 ml of 0.5 M $K_3Fe(CN)_6$, and 2.85 ml of 11.8 M KOH solutions, and 3 ml of CCl_4 were placed. The mixture was shaken for 5 min. After separating phases into layers the upper aqueous layer was red-violet and the lower was colorless. The tube was stored in darkness for 3 days. The higher layer remained brightly colored and the lower, colorless. The phases were mixed again. After separating phases a sample of 1 ml was taken from the lower layer and mixed with an aqueous solution of $NH_2OH \cdot HCl$ + *o*-phenanthroline. It was expected that hydroxylamine would reduce iron in the higher oxidation states up to Fe(II), which gives a bright coloring with *o*-phenanthroline.

b. 3 ml of an 11 M KOH solution containing 3.4 mmol of Fe(III) and 17 mmol of $K_3Fe(CN)_6$ were placed in a bubbler (no. 1) and oxygen was passed through. A bubbler no. 2 was sequentially connected to bubbler no. 1 with a 5 M HCl solution. Variations of the HCl solution color were kept under observation during the experiment.

To study of $Fe(CN)_6^{3-}$ stability, we placed 3.0 ml of 1 M. NaOH solution in a cell, added 0.030 ml of 0.1 M $K_3Fe(CN)_6^{3-}$ solution, and periodically recorded absorption spectra.

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