Mechanisms of Pu(VII) Reduction in Aqueous Alkaline Solutions in the Presence of Catalysts

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Abstract—Published data on the Pu(VII) stability in alkaline media suggest that one-electron oxidation of OH\(^-\) ion or H\(_2\)O with Pu(VII) ions is thermodynamically impossible. The more probable pathway of Pu(VII) reduction is formation of a dimer from thermodynamically excited and nonexcited Pu(VII) ions, followed by decomposition of the dimer into two Pu(VI) ions and H\(_2\)O\(_2\), molecule, which reacts with Pu(VI) and Pu(VI). The released energy is spent for Pu(VI) excitation. In the presence of sufficiently soluble hydroxides of Fe(III), Co(III), and other \(d\) elements, and also of Pt and PbO\(_2\) hydroxides of elements in higher oxidation states appear at the surface of colloidal particles and electrode materials under the action of Pu(VII). The neighboring OH groups dimerize and are eliminated in the form of H\(_2\)O\(_2\).

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The formal potential of the Pu(VII)/Pu(VI) couple in 0.97 and 0.61 M NaOH solutions is 0.850 and 0.868 V (standard hydrogen electrode), respectively [1], i.e., it significantly exceeds the potential of oxygen evolution from an alkaline solution (the standard potential of the O\(_2\)/OH\(^-\) couple is 0.401 V at pH 14 [2]). Therefore, Pu(VII) is thermodynamically unstable in aqueous alkaline solutions. The Pu(VII) reduction in KOH + NaNO\(_3\) solutions in the absence and in the presence of impurities was studied previously [3]. It was noted that the formal reaction order with respect to [Pu(VII)] is close to 1.2–1.3 and with respect to [OH\(^-\)] it is close to –1. Microamounts of Fe(III), Cu(II), and Ni(II) and nanoamounts of Co(III) accelerate Pu(VII) reduction. The kinetic curves of a decrease in the Pu(VII) concentration in an 0.15 M KOH solution at 25°C in the presence of Fe(III) are shown in [3, Fig. 4]. To gain insight into the reaction order with respect to the reactant concentrations, we estimated the time of Pu(VII) disappearance from the decrease in the optical density at 635 nm by 50 and 75%.

\[
\begin{align*}
[\text{Fe(III)}] \times 10^6, \text{ M} & \quad 0.77 & 1.58 & 3.1 \\
50\% D_0, \text{ min} & \quad 6.25 & 3.12 & 1.54 \\
25\% D_0, \text{ min} & \quad 14.0 & 7.3 & 3.75
\end{align*}
\]

These data show that the second period of Pu(VII) disappearance by half is longer than the first period, i.e., the reaction order with respect to [Pu(VII)] is higher than 1, but the periods decrease in proportion to increase in the Fe(III) concentration, which suggests the first reaction order with respect to [Fe(III)].

The kinetic curves of Pu(VII) reduction in 0.15 M KOH at 25°C in the presence of 2.4–9.07 nM Co(III) have an induction period after which the reaction proceeds by the rate law close to zero order with respect to Pu(VII) concentration (in [3, Fig. 5], the captions and numbering of the curves are confused). With increasing [OH\(^-\)], the sensitivity of Pu(VII) to the presence of Co(III) decreases and the curves of Pu(VII) consumption become similar to those obtained in the presence of Fe(III).

Komkov and Krot [3] believe that, in the absence of impurities, the first stage of reduction is elimination of OH radical from hydrolyzed Pu(VII) ion, followed by conversion of OH into HO\(_2\), and that acceleration of the reaction in the presence of \(d\)-element ions is caused by their oxidation with Pu(VII) ion to higher-valence species which rapidly react with water.

The behavior of Pu(VII) in 0.3–1.96 M NaOH solutions was studied in [4]. To detect OH radicals, Pu(VII) was introduced into 0.5 and 1.0 M NaOH solutions saturated with benzene. It is well known that OH radicals and their alkaline forms O\(^-\) rapidly react with \(C_6H_6\). The arising compound reacts with dissolved O\(_2\) to give phenol as final product. However, phenol was not found in the solutions after Pu(VII) reduction.

It was shown [5] that one-electron oxidation of
OH$^-$ ion or H$_2$O with Pu(VII) ion is thermodynamically impossible, because the potential of the OH/OH$^-$ couple is 1.9 V [6, 7]. At the same time, the potential of the OH$_2$/OH$^-$ couple in alkaline media (0.867 V for a solution with pH 14 [2]) is comparable to the potential of the Pu(VII)/Pu(VI) couple. Therefore, the following scheme of reactions is suggested. The Pu(VII) ion is activated thermally:

$$\text{Pu(VII)} \rightarrow ^*\text{Pu(VII)}. \quad (1)$$

Then the excited species forms a dimer with a nonexcited species:

$$\text{Pu(VII)} + ^*\text{Pu(VII)} \rightarrow [\text{Pu(VII)}]_2, \quad (2)$$

and this dimer decomposes to form H$_2$O$_2$ and two Pu(VI) ions:

$$[\text{Pu(VII)}]_2 \rightarrow 2\text{Pu(VI)} + \text{H}_2\text{O}_2. \quad (3)$$

The H$_2$O$_2$ molecule is deprotonated and participates in a series of reactions with Pu(VII) and Pu(VI):

$$\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{HO}_2^- + \text{H}_2\text{O}, \quad (4)$$

$$\text{Pu(VII)} + \text{HO}_2^- \rightarrow ^*\text{Pu(VI)} + \text{HO}_2, \quad (5)$$

$$\text{HO}_2^- + \text{OH}^- \rightarrow \text{O}_2^- + \text{H}_2\text{O}, \quad (6)$$

$$\text{Pu(VII)} + \text{O}_2^- \rightarrow ^*\text{Pu(VI)} + \text{O}_2, \quad (7)$$

$$\text{Pu(VI)} + \text{HO}_2^- \rightarrow \text{Pu(V)} + \text{HO}_2, \quad (8)$$

$$\text{Pu(VI)} + \text{O}_2^- \rightarrow \text{Pu(V)} + \text{O}_2, \quad (9)$$

$$\text{Pu(VII)} + \text{Pu(V)} \rightarrow 2^*\text{Pu(VI)}. \quad (10)$$

In reactions (5), (7), and (10), much energy is released and excited ^*Pu(VI) ions appear. As a result of collisions of ^*Pu(VI) with Pu(VII), the energy exchange takes place:

$$^*\text{Pu(VI)} + \text{Pu(VII)} \rightarrow ^*\text{Pu(VII)} + \text{Pu(VI)}. \quad (11)$$

Reaction (11) actually provides the occurrence of reaction (2).

The similar reaction pattern with the elimination of H$_2$O$_2$ takes place in the presence of Fe(III). Fe(III) hydroxide is difficultly soluble in alkaline media and forms colloidal solutions. In the contact of Pu(VII) with the particle surface, the following reaction takes place:

$$\text{FeOOH} + \text{PuO}_4\text{(OH)}_2 \rightarrow \text{FeO(OH)}_2 + \text{PuO}_4^{2-} + \text{OH}^-.$$  \quad (12)

A part of FeO(OH)$_2$ molecules is excited thermally or in some other way, for example, in collision of *Pu(VI) with the surface of a colloidal particle. The excited Fe(IV) molecule forms with neighboring nonexcited molecule a sort of a dimer:

$$^*\text{FeO(OH)}_2 + \text{FeO(OH)}_2 \rightarrow \text{dimer.} \quad (13)$$

In turn, the dimer decomposes to form H$_2$O$_2$:

$$\text{dimer} \rightarrow 2\text{FeOOH} + \text{H}_2\text{O}_2. \quad (14)$$

Reactions (13) and (14) are fast; therefore, the rate-determining stage is reaction (12).

In the presence of Co(III), the following reactions are possible:

$$\text{CoOOH} + \text{Pu(VII)} \rightarrow \text{CoO(OH)}_2 + \text{Pu(VI)}, \quad (15)$$

$$\text{CoO(OH)}_2 + \text{Pu(VII)} \rightarrow ^*\text{CoO(OH)}_3 \text{ or CoO}_4^{2-} + \text{Pu(VI)}, \quad (16)$$

$$^*\text{CoO(OH)}_3 + \text{CoO(OH)}_3 \rightarrow \text{dimer,} \quad (17)$$

$$\text{dimer} \rightarrow 2\text{CoOOH} + \text{H}_2\text{O}_2. \quad (18)$$

It is difficult to choose the rate-determining stage, but it is other than reactions (15) and (16).

The acceleration of Pu(VII) reduction in aqueous alkaline media was observed on contact of Pu solutions with electrode materials: Pt, PbO$_2$, and graphite [8]. In all cases, reduction of Pu(VII) follows the first-order law with respect to [Pu(VII)]. This fact indicates that oxidation of the surface of the electrode material is the rate-determining reaction. In contact with Pu(VII), oxides (hydroxides) of elements in the higher oxidation state than before the contact are formed at the surface of the electrode material. Then, the molecule of a hydroxide of a metal in a higher oxidation state is excited. The excited molecule forms with a nonexcited molecule a dimer which decomposes with the release of H$_2$O$_2$. With graphite, the process is more complicated.

It should be noted in conclusion that Pu(VII) reduction in the presence of microimpurities of d elements and at the surface of electrode materials has similar features. This is not surprising since in both cases the reactions proceed at the surface, i.e., het-