

Oxidation of U(VI) with Oxygen in Weakly Acidic and Neutral Solutions

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Abstract—The kinetics of U(IV) oxidation with atmospheric oxygen in solutions with pH 2–7 was studied. In the kinetic curves there is an induction period, which becomes shorter with increasing pH. The induction period is caused by accumulation of U(VI), whose initial presence in the working solution accelerates oxidation. The pseudo-first-order rate constants and bimolecular rate constants of U(IV) oxidation with oxygen were evaluated. The mechanism of U(IV) oxidation is considered. At pH higher than 3, formation of a polymer of hydrolyzed U(IV) with U(VI) plays an important role in oxidation of U(IV), since this prevents formation of U(V). Heating accelerates oxidation of U(IV) at pH 2–2.5, but at a higher pH the process becomes difficultly controllable.

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The stability of U(IV) with respect to molecular oxygen was studied predominantly in solutions of HClO₄ or NaClO₄ + HClO₄ [1–4], or of H₂SO₄ [5]. The range of H⁺ concentrations was varied from 0.01 to 3 M. Oxidation of U(IV) with atmospheric oxygen in 1 M NaHClO₄ + 0.25 M Na₂CO₃ solution was also studied [6]. However, the behavior of U(IV) with respect to O₂ in media with pH 2–8 remains poorly understood. These media are of interest in the context of the problems of migration of actinides in the environment, waste disposal, and storage of sub-standard uranium blocks with aluminum cladding. In this study we examined the kinetics and mechanism of U(IV) oxidation with atmospheric oxygen in weakly acidic and neutral aqueous solutions.

EXPERIMENTAL

The initial material was UO₃ (synthesized and purified by published procedures), which was dissolved in HClO₄ or HCl. The U(VI) content was determined spectrophotometrically ($\lambda = 414$ nm) and gravimetrically. Uranium(VI) was reduced on a mercury cathode in a cell with cathode and anode compartments separated by a cation-exchange membrane in a flow of high-purity Ar. The U(IV) concentration was determined by complexometric titration with Xylenol

Orange as an indicator and also spectrophotometrically at $\lambda = 648$ nm. The acid concentration was estimated by titration of an aliquot of the solution with a reference NaOH solution with phenolphthalein and subtraction of the fourfold content of U(IV) from the resulting value. The U(IV) solution was kept in a flask equipped with a ground-glass stopper. Argon was passed through the flask at regular intervals. In some experiments we used a freshly prepared solution of U(IV) with a minimal content of U(VI). We also used the dry salt Cs₂UCl₆ prepared by addition of a CsCl solution in concentrated HCl to a hydrochloric acid solution of UCl₄. The precipitated crystals were separated, washed with dry ethanol, and dried in a vacuum desiccator.

HClO₄, HCl, NaCl, and NaHCO₃ were of chemically pure grade, and NaOH, of ultrapure grade; NaClO₄ of pure grade was recrystallized two times. In addition, we used K₁₀P₂W₁₇O₆₁·*n*H₂O synthesized by the procedure described in [7]. The heteropoly compound was used for determination of the U(IV) concentration in the working solutions in the presence of U(VI). All solutions were prepared using double-distilled water.

Experimental procedure. A temperature-controlled cell was charged with a 10–50-ml portion of

water or dilute NaOH solution. An aliquot of a U(IV) solution or, in some experiments, an accurately weighed portion of Cs_2UCl_6 was added into the solution with air bubbling (flow rate $100 \pm 10 \text{ ml min}^{-1}$; air was prepurified and saturated with water vapor by passing through a Tishchenko bottle filled with water having the temperature of the experiment). Samples were withdrawn at regular intervals; at uranium concentration of $(1-3) \times 10^{-3} \text{ M}$, their volume was 0.5 ml. A sample was introduced into an ampule or quartz cell ($l = 1 \text{ cm}$) with 2.5 ml of 0.5 M HClO_4 containing $2 \times 10^{-3} \text{ M K}_{10}\text{P}_2\text{W}_{17}\text{O}_{61}$. When the uranium concentration in the working solution did not exceed 10^{-4} M , the sample volume was 3.0 ml and it was introduced into an ampule with 0.5 ml of 3.5 M $\text{HClO}_4 + 6 \times 10^{-3} \text{ M K}_{10}\text{P}_2\text{W}_{17}\text{O}_{61}$. Uranium(IV) forms a very stable red-violet complex with unsaturated heteropolytungstate:



In the electronic absorption spectrum of the U(IV) complex, there is a narrow band with a maximum at 510 nm, $\epsilon = 1000 \text{ l mol}^{-1} \text{ cm}^{-1}$ [8]. In acidic medium, U(VI) forms with $\text{P}_2\text{W}_{17}\text{O}_{61}^{10-}$ only weak complexes; therefore, even at U(VI) concentration exceeding U(IV) concentration by a factor of several hundreds U(VI) does not interfere with the determination of U(IV).

At the end of the experiment, the solution pH was measured with an OP-211/1 millivoltmeter-pH-meter (Radelkis, Hungary) equipped with a combined glass electrode filled with 1 M KCl solution (in some experiments, with 1 M NaCl). The spectrophotometric measurements were performed on SF-46 (Russia) and UVPC-3100 (Shimadzu, Japan) devices.

RESULTS AND DISCUSSION

The kinetic curve of U(IV) consumption in a solution with pH 1.80 (curve 1) is shown in Fig. 1. It is seen that, after an induction period, the reaction accelerates. The similar autocatalysis was attributed in [4] to accumulation of U(VI), which reacts with hydrolyzed U(IV) species, $\text{U}(\text{OH})_2^{2+}$ ions. Indeed, when U(IV) ($3.28 \times 10^{-3} \text{ M}$) is added into a solution initially containing $3 \times 10^{-3} \text{ M UO}_2(\text{ClO}_4)_2$, the induction period becomes significantly shorter and the reaction follows approximately first-order rate law (curve 2). This dependence is clearly seen in the semilog plots (Fig. 2). The similar pattern is observed in solutions containing $1 \times 10^{-3} \text{ M UO}_2(\text{ClO}_4)_2$ and lower concentrations of U(IV), at least down to

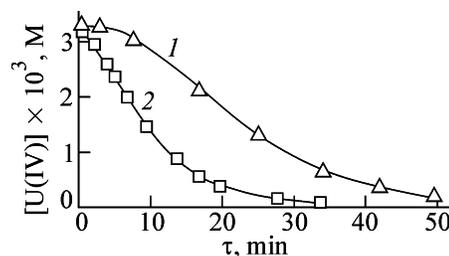


Fig. 1. Kinetic curves of U(IV) consumption in passing of air through a solution with pH 1.80 at 20°C. $[\text{U(IV)}]_0 = 3.28 \times 10^{-3} \text{ M}$; $[\text{U(VI)}], \text{M}$: (1) 0 and (2) 3×10^{-3} .

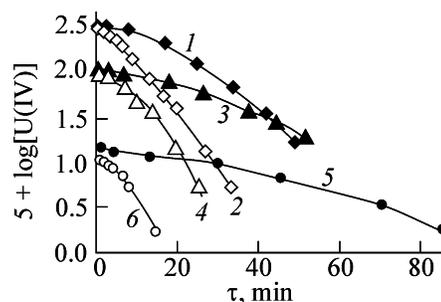


Fig. 2. Semilog plots of U(IV) consumption in passing of air through solutions at 20°C, pH 1.80. $[\text{U(IV)}]_0 \times 10^4, \text{ M}$: (1, 2) 32.8, (3, 4) 11.0, (5) 1.50, and (6) 1.15. $[\text{U(VI)}]_0 \times 10^4, \text{ M}$: (1, 3, 5) 0, (2) 30.0, (4) 31.0, and (6) 28.0.

10^{-4} M . By the end of the experiments, the kinetic curves plotted in the semilog coordinates become linear, which suggests pseudofirst reaction order with respect to U(IV). Let us consider the features of the kinetic curves, i.e., compare the slopes of the initial and final portions of these curves in Fig. 2 (Table 1). From these data we can make the following conclusions.

(1) The slopes of the final portions of the curves are approximately the same for solutions with U(VI) concentrations of $(5.50-6.14) \times 10^{-3}$ and $2.86 \times 10^{-3} \text{ M}$, i.e., an increase in the U(VI) concentration above certain level does not affect the reaction rate. This suggests that the reacting species form complexes undergoing intramolecular transformations.

(2) The slope of the initial portions of curves 2 and 6 is smaller than the slope of the final portion of curve 1 for almost the same concentration of U(VI). This suggests slow formation of the above complex.

(3) The slope of the final portion of curve 2 is smaller than that of the final portions of curves 2 and 6. This is caused by the fact that all U(IV) is bound in a complex within 300 (curve 6) and 800 s (curve 2), whereas in the case of curve 1 accumulation of $2.95 \times$

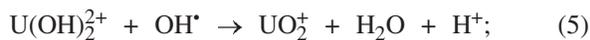
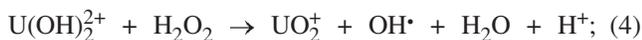
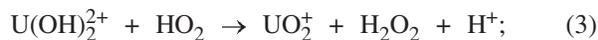
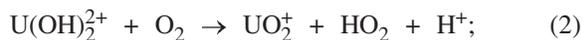
Table 1. Slopes of kinetic curves of U(IV) oxidation with atmospheric oxygen from data presented in Fig. 2

Curve no.	[U(VI)] ₀ × 10 ⁴ , M	[U(IV)] ₀ × 10 ⁴ , M	tan φ _{init} × 10 ³ , s ⁻¹	[U(VI)] _{fin} × 10 ⁴ , M	tan φ _{fin} × 10 ³ , s ⁻¹
1	–	32.8	–	29.5	0.657
2	30	32.8	0.364	55.0–61.4	1.053
5	–	1.5	–	1.2	0.303
6	28	1.15	0.242	28.6	1.16
*	100**	2.48	0.325	102	0.84
*	100***	1.21	0.258	101	1.1

* Additional runs. ** pH 1.79. *** pH 1.85.

10⁻³ M of U(VI) takes 2500 s. Within this period of time, U(IV) partially polymerizes.

In weakly acidic solutions U(IV) exists in the form of hydroxo complexes U(OH)_n⁽⁴⁻ⁿ⁾⁻. To evaluate the hydrolysis constants *K'* and fractions of various species U(OH)_n⁽⁴⁻ⁿ⁾⁻ (*n* = 1–4), we used the standard constants of formation of hydroxo complexes β_n⁰ given in [9]. The log *K'* values evaluated according to SIT (specific ion interaction theory) [10] for the ionic strength *I* = 0.03 are -0.82 ± 0.2, -1.8 ± 1.0, -5.54 ± 1.0, and -12.4 ± 1.0 for *n* = 1, 2, 3, and 4, respectively. In the experiments without additionally introduced U(VI), *I* did not exceed the above value of 0.03. Calculations performed with these values of log *K'* and activity coefficients γ_n = 0.9 show that at pH 1.8–1.85 up to 83.47% of U(IV) occurs in the form of U(OH)₂²⁺. The same results were obtained using the constants β_n⁰ given in [11]. Therefore, in a solution with pH 1.80–1.85 the main part of U(IV) occurs in the form of U(OH)₂²⁺. Proceeding from the scheme of the chain reaction presented in [1], oxidation of U(IV) with oxygen can be described as follows:



$$k_6 = 31.4 \text{ l mol}^{-1} \text{ s}^{-1} \text{ [12];}$$

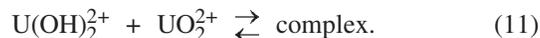


It is well known that in weakly acidic solutions the

following equilibrium takes place:



The equilibrium constant in perchloric and hydrochloric acid solutions was determined in [13]. Our experiments show that in weakly acidic solutions reaction (10) is preceded by reaction (11), formation of a complex from U(IV) and U(VI):



Thus, in oxidation of U(IV) after accumulation of some amount of U(VI) reaction (10) becomes the rate-determining step of the process. Fairly high rate of reaction (10) was demonstrated in individual experiments. For this purpose, a weighed portion of Cs₂UCl₆ was added into a cell filled with a solution containing 0.1 M UO₂(NO₃)₂ and the absorption spectrum in the wavelength range 400–1200 nm was recorded. Within less than 5 min, a band with a maximum at 737 nm appears in the spectrum, suggesting attainment of the equilibrium



and hence the occurrence of reaction (10). At the end of the experiment, the solution pH was 1.46.

Let us consider the initial portions of the curves of U(IV) loss in solutions without additionally introduced U(VI) (pH 1.80–1.85). From the slopes of the curves, the following pseudo-first-order rate constants of *k'* were obtained.

[U(IV)] ₀ × 10 ⁴ , M	1.50	11.0	32.8
<i>k'</i> × 10 ⁴ , s ⁻¹	2.92	2.90	0.27

A decrease in the rate constant with increasing concentration of U(IV) is caused by polymerization of hydrolyzed U(IV).

The process rate in the initial period, when U(VI)

Table 2. Influence of conditions on the rate constant of U(IV) oxidation with atmospheric oxygen k' . $[U(IV)]_0 = (1-1.5) \times 10^{-4}$ M

$T, ^\circ\text{C}$	pH	$k' \times 10^4, \text{s}^{-1}$	$k = k'/[O_2],$ $1 \text{ mol}^{-1} \text{ s}^{-1}$	$T, ^\circ\text{C}$	pH	$k' \times 10^4, \text{s}^{-1}$	$k = k'/[O_2],$ $1 \text{ mol}^{-1} \text{ s}^{-1}$
20	1.80	2.80	1.01	20	3.20	38.0	13.7
20	1.95	2.40	0.87	20	3.60	15.3	5.52
20	2.10	8.10	2.92	20	4.14	71.8	25.9
20	2.40	7.30	2.64	20	5.55	42.6	15.4
20	2.48	7.20	2.60	20	5.56	62.2	22.5
20	2.81	7.30	2.64	20	6.67	27.1	9.78
20	2.83	18.4	6.64	20	7.38	7.9	2.85
20	2.81	44.8	16.2	30	2.00	8.7	
20	2.88	38.7	14.0	30	2.50	24.2	
20	2.80	14.4	5.20	40	1.98	25.1	
20	3.00	40.0	14.4				

accumulation is insignificant, is described by the expression

$$-d[U(IV)]/dt = k_2[U(IV)][O_2] + k_3[U(IV)][HO_2] + k_4[U(IV)][H_2O_2] + k_5[U(IV)][OH^*].$$

Using the method of steady-state concentrations, we obtained

$$-d[U(IV)]/dt = 4k_2[U(IV)][O_2]$$

or

$$-d[U(IV)]/dt = k'[U(IV)], \quad (13)$$

where $k' = 4k_2[O_2]$. The solubility of O_2 in water at 20°C is 1.385×10^{-3} M [15]; therefore, in a solution saturated with air, $[O_2] = 2.8 \times 10^{-4}$ M. Hence, $k_2 = 0.26 \text{ l mol}^{-1} \text{ s}^{-1}$ for a solution containing $(1-11) \times 10^{-4}$ M of U(IV). The resulting k_2 value is by a factor of approximately 120 smaller than the rate constant of UO_2^+ oxidation. This is caused primarily by the standard oxidation potentials E^0 : for the UO_2^+/UO_2^2+ and UO_2^+/U^{4+} couples they are 0.17 and 0.38 V, respectively [16]. Due to hydrolysis of U(IV), the difference in E^0 becomes larger. In addition, rearrangement of the structure of uranyl ions in passing from tetravalent to higher oxidation states makes a certain contribution to the decrease in the reaction rate.

With increasing pH, the rate of U(IV) oxidation increases (Fig. 3). In this case, the induction period decreases. In a solution with pH higher than 4, the U(IV) consumption follows the first-order reaction law. The acceleration of the process with increasing

concentration of H^+ ions can be easily explained by reaction (2). Disappearance of an induction period is caused by the absence of reaction (10). Hydrolyzed U(IV) forms a polymer into which uranyl ion is incorporated. This phenomenon was studied previously for bonding of uranyl ion to a hydrolyzed polymer of Th(IV) in the pH range 1.5–4.0 [17]. The rate of polymerization and capture of U(VI) depends on pH. At low pH, reaction (10) is complete before formation of the polymer; at pH higher than 4, polymerization prevents formation of U(V). It should be noted that, in deaerated solutions containing U(IV) and U(VI), we observed formation of combined polymer even at pH less than 3. Colloidal particles appearing in this case imparted to the solution the black color. Formation of colloidal particles containing mixed U(IV) and U(VI) hydroxides was observed in [18] in reduction of U(VI) in bicarbonate solutions at a temperature exceeding 50°C .

The pseudo-first-order rate constants k' found from the initial slopes of the kinetic curves in semilog coordinates are presented in Table 2. The values obtained at the same pH vary in a wide range. This is

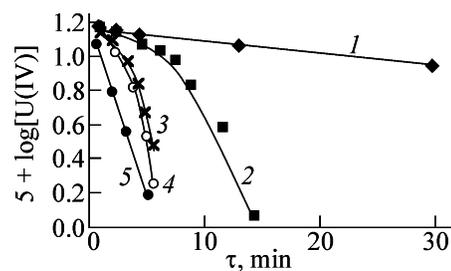


Fig. 3. Influence of pH on the kinetics of oxidation of approximately 1×10^{-4} M U(IV) with atmospheric oxygen. pH: (1) 1.80, (2) 2.48, (3) 2.83, (4) 3.20, and (5) 4.14.

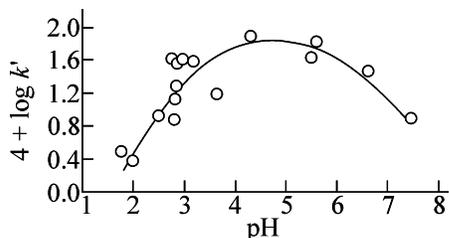


Fig. 4. Pseudo-first-order-reaction constant k' as a function of pH.

apparently caused by nonuniform dilution of an aliquot of the initial acidic solution of $\text{U}(\text{ClO}_4)_4$. Due to the local increase in the U(IV) concentration, a polymer is formed, which decreases the fraction of U(IV) entering into the reaction with O_2 .

The dependence of $\log k'$ on pH is presented in Fig. 4. Despite the scatter of k' values, it is seen that $\log k'$ increases with increasing pH in the range of pH 2–3. At higher pH, $\log k'$ increases more slowly, passes through a maximum at approximately pH 4.5, and then noticeably decreases. This is caused by polymerization of U(IV).

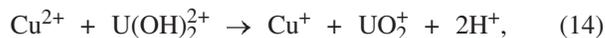
Heating accelerates U(IV) oxidation. The reaction kinetics was studied only in the pH range 2.0–2.5. At higher pH, the procedure used is inefficient.

We studied the influence of additions of NaClO_4 , $\text{Cu}(\text{ClO}_4)_2$, $\text{Pd}(\text{ClO}_4)_2$, NaTcO_4 , NaNO_3 , and NaCl . The influence of the two latter components was studied since NO_3^- and Cl^- ions were added into solutions together with uranium.

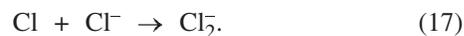
In the solutions with pH 1.8–2.0, addition of NaClO_4 to a concentration of 0.5 M decreases k' . This is caused solely by decreasing solubility of O_2 in this solution. At higher pH, the influence of NaClO_4 was not studied, since increasing concentration of salts should accelerate coagulation of colloids formed by U(IV) polymers. In solutions with pH 2–3, nitrate ion in a concentration of 0.05 M somewhat decreases k' . In a solution with pH 1.95, chloride ion in a concentration of 5×10^{-3} M noticeably decreases k' and increases the induction period. Addition of Cu^{2+} ions (5×10^{-5} M) increased k' several times in solutions with pH 1.6–2.8 and abruptly decreased the induction period. In the range of pH 3–5, Pd(II) and TcO_4^- ions (approximately 10^{-3} M) were reduced with U(IV) to metal and $\text{TcO}_2 \cdot n\text{H}_2\text{O}$, respectively, and formed a dark suspension of colloidal particles.

The role of Cl^- and Cu^{2+} ions in 0.5 M HClO_4 was considered in [1]. It was assumed that in the case of

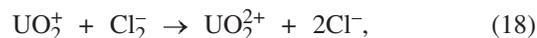
Cu^{2+} reactions (14), (15), and (3)–(9) take place:



In our opinion, the reaction of U(IV) with O_2 is inhibited by chloride ions according to the following mechanism [19]:



Then, the following reactions are possible:



The latter reaction decreases the amount of oxidants and thus decreases the rate of U(IV) oxidation.

Thus, oxidation of U(IV) with oxygen in weakly acidic and neutral solutions proceeds by the pseudo-first-order rate law. In many cases, in the kinetic curves there is an induction period caused by accumulation of U(VI). The presence of U(VI) accelerates oxidation of U(IV), which is confirmed by experiments with solutions initially containing U(IV) in a mixture with U(VI). The oxidation mechanism involves the reaction of hydrolyzed $\text{U}(\text{OH})_2^{2+}$ with O_2 , HO_2 , H_2O_2 , and OH^\bullet , formation of U(V), and its reactions with the above species. After accumulation of some amount of U(VI), the reaction $\text{U(VI)} + \text{U(IV)} \rightarrow 2\text{U(V)}$ becomes the rate-determining step. At a higher pH, formation of a mixed polymer of U(IV) and U(VI) plays an important role. Heating accelerates U(IV) oxidation at pH 2–2.5, but at higher pH the process becomes difficultly controllable.

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