# Reduction of Am(IV) with Water in KHCO<sub>3</sub> + K<sub>2</sub>CO<sub>3</sub> Solutions

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Abstract—Reduction of Am(IV) with water in KHCO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> solutions (pH 8.5–10.5) was studied spectrophotometrically at 54–70°C. The Am(IV) concentration decreases, following the first-order rate law. The reduction rate increases with pH ( $\Delta \log k/\Delta pH = 0.4$ ), but decreases with increase in (HCO<sub>3</sub> + CO<sub>3</sub><sup>2-</sup>) concentration. It was assumed that the thermally excited Am(IV) ion forms a dimer with unexcited Am(IV). The dimer dissociates into two Am(III) ions and H<sub>2</sub>O<sub>2</sub>. Hydrogen peroxide reduces two more Am(IV) ions. In this process, the excited Am(III) ion appears, which transfers the excitation to Am(IV) at collision. Thus, a chain process is initiated. This scheme can also explain the kinetics of Am(VI) and Np(VII) reduction in carbonate solutions.

In bicarbonate–carbonate solutions, Am(IV) gradually disappears because of disproportionation and reduction with water [1, 2]. Disproportionation is important at pH higher than 10.The mechanism of this reaction was studied in [3]. The data on Am(IV) reduction with water are fragmentary and do not discover the reaction mechanism. In this work, we studied the kinetics of Am(IV) reduction under various conditions and the reaction mechanism.

## EXPERIMENTAL

<sup>243</sup>Am containing 0.15 wt % <sup>241</sup>Am was used. Accordingly to α-ray spectrometry, the contribution of <sup>241</sup>Am and <sup>244</sup>Cm to the α-activity were 2.6 and 2.4%, respectively. The Am(ClO<sub>4</sub>)<sub>3</sub> solutions were prepared and purified as in [4, 5]. KHCO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> were twice recrystallized. Double-distilled and, in some cases, triple-distilled water was used.

The electronic absorption spectrum of Am(IV) in KHCO<sub>3</sub> + K<sub>2</sub>CO<sub>3</sub> solutions has a band at 369–370 nm with the extinction coefficient  $\varepsilon$  = 2840 l mol<sup>-1</sup> cm<sup>-1</sup> [6], which allows spectrophotometric monitoring of the Am(IV) reduction. For instance, in a 2-cm optical cell,  $5 \times 10^{-5}$  M solutions of Am(IV) can be studied. At such low concentrations, the disproportionation of Am(IV) is minimal.

To avoid introduction of any additional substances into the solution, Am(IV) was prepared photochemically [7]. An  $1 \times 10^{-4}$  M Am(ClO<sub>4</sub>)<sub>3</sub> solution containing KHCO<sub>3</sub> or KHCO<sub>3</sub> + K<sub>2</sub>CO<sub>3</sub> was added into a cylindrical quartz cell, which was placed under the UV beam generated by a VIO-1 device equipped with two super-high-pressure Hg lamps and cylindrical quartz focusing lens. Under the action of UV light, the colorless solution became yellow, suggesting Am(III)  $\rightarrow$  Am(IV) transformation (confirmed spectrophotometrically). The rate of Am(IV) accumulation depends on the solution composition. To obtain (4–6)×10<sup>-5</sup> M Am(IV), 1–3 h is required. In the process, a part of Am remained in the trivalent state.

The cell with the solution was placed in a brass holder temperature-controlled with circulated water from a U-10 thermostat (Germany). In turn, the holder was placed in the cell compartment of the spectrophotometer. After 20–30 min temperature stabilization, the light absorption was measured at 370 nm and in the 400–600 nm range. After the measurements, the temperature in the cell was checked, and after cooling the cell to 20°C the pH of the solution was measured with an OP-211/1 pH meter (Hungary) with a glass electrode.

# **RESULTS AND DISCUSSION**

In 1.5 M KHCO<sub>3</sub> (pH 8.48–8.70), Am(IV) (5 ×  $10^{-5}$  M) completely transforms into Am(III) at 22–68°C. In the 0.75 M KHCO<sub>3</sub> + 0.75 M K<sub>2</sub>CO<sub>3</sub> solution (pH 9.96), Am(IV) ( $n \times 10^{-5}$  M) is almost completely reduced at 20–25°C, but at 55°C 25% of Am(IV) remains unchanged. The other valence states of Am were not observed. Thus, under the conditions studied, Am(IV) is mainly consumed in reduction reactions. The typical kinetic curves of Am(IV) consumption are shown in Fig. 1. Certain distortions of the initial portions of the curves are due to the temperature change in this period. The middle part of the curve is a straight line in semilog coordinates, which indicates the first order of the reaction with respect



**Fig. 1.** Kinetic curves of Am(IV) reduction with water in KHCO<sub>3</sub> + K<sub>2</sub>CO<sub>3</sub> solutions. Cell thickness l = 2 cm,  $T = 54.2^{\circ}$ C. [KHCO<sub>3</sub>], M: (1) 0.75 and (2) 1.5; [K<sub>2</sub>CO<sub>3</sub>], M: (1) 0.75 and (2) 1.5. [Am(IV)]<sub>0</sub>×10<sup>5</sup>, M: (1) 7.5 and (2) 5.4.



Fig. 2. Rate constant of Am(IV) reduction with water as a function of total  $KHCO_3 + K_2CO_3$  concentration. pH 10.01–9.86,  $T = 54.2^{\circ}C$ .

Rate constants of Am(IV) reduction with water in  $KHCO_3 + K_2CO_3$  solutions

<i>T</i> , °C	[KHCO <sub>3</sub> ], M	[K <sub>2</sub> CO <sub>3</sub> ], M	рН	$k' \times 10^4,$ $s^{-1}$
54.2	0.375	0.375	9.86	19.4
54.2	0.75	0.75	9.96	5.24
54.2	1.125	1.125	9.98	2.22
54.2	1.5	1.5	10.01	1.23
54.2	1.5	_	8.50	1.6
54.2	1.25	0.25	9.27	3.14
54.2	1.0	0.5	9.65	4.00
54.2	0.5	1.0	10.26	6.67
63	1.5	_	8.6	4.14
63	1.25	0.25	9.3	7.60
63	1.0	0.50	9.65	9.9
63	0.75	0.75	9.96	12.3
63	0.5	1.0	10.26	15.2
70	1.25	0.25	9.4	14.8
70	1.0	0.5	9.63	15.2
70	0.75	0.75	9.96	22.9
70	0.7	0.8	10.01	29.0
70	0.5	1.0	10.26	28.8



Fig. 3. Effect of pH on the rate constant of Am(IV) reduction with water. *T*, °C: (1) 54.2, (2) 63, and (3) 70.

to Am(IV), and hence, to a first approximation, the kinetic equation is

$$-d[Am(IV)]/dt = k'[Am(IV)].$$
(1)

In the integral form, after substitution of the Am(IV) concentration by the proportional value  $(D - D_{\infty})$  (*D* is light absorption at 370 nm), Eq. (1) transforms into

$$2.3\log(D - D_{\infty}) = k't + \text{const}, \qquad (2)$$

where *D* and  $D_{\infty}$  are the optical densities at the moment and after Am(IV) disappearance, respectively. The constant *k*' was determined graphically. Its average values under various conditions are listed in the table. As seen, at  $[\text{HCO}_3^-]$  :  $[\text{CO}_3^{2-}] = 1 : 1$  and constant temperature Am(IV) becomes more stable with an increase in the total  $\text{HCO}_3^- + \text{CO}_3^{2-}$  concentration. The experimental values of *k*' (in the logarithmic coordinates) fall on a straight line, whose shape  $n = \Delta \log k' \Delta \log [\text{HCO}_3^- + \text{CO}_3^{2-}] = 2.0$ . This indicates that the Am(IV) complex ion eliminates two  $\text{CO}_3^{2-}$  ions

$$\operatorname{Am}(\operatorname{CO}_3)_{n+2}(\operatorname{H}_2\operatorname{O})_x^{2n-} + z\operatorname{H}_2\operatorname{O} \xleftarrow{} \operatorname{Am}(\operatorname{CO}_3)_n(\operatorname{H}_2\operatorname{O})_{x+z}^{(2n-4)-} + 2\operatorname{CO}_3^{2-},$$
(3)

either in the rate determining or preceding stage.

In the solutions with the constant total concentration  $[\text{HCO}_3^-] + [\text{CO}_3^{2-}] = 1.5$  M, the rate constant k' increases with pH. The dependence of log k' on pH is linear (Fig. 3). The shape  $n = \Delta \log k' / \Delta pH$  equal to 0.34 - 0.40 shows that OH<sup>-</sup> ions participate in the consumption of Am(IV). Firstly, this may be due to parallel disproportionation of Am(IV), whose rate is proportional to  $[\text{OH}^-]^2$ . Therefore, the rate of Am(IV) disappearance should be presented as

$$V = k'[Am(IV)] = k_1[Am(IV)] + 2k_2[Am(IV)]^2$$
 or

$$k' = k_1 + 2k_2[\text{Am}(\text{IV})],$$
 (4)

where  $k_1$  is the rate constant of Am(IV) reduction with water and  $k_2$  is the constant of Am(IV) disproportionation. To estimate  $k_1$ , we subtracted from k'the  $2k_2$  values taken from [3] and recalculated to higher temperatures using the activation energy of 100 kJ mol<sup>-1</sup> [2]. The resulting  $k_1$  values increase with pH; in the log  $k_2$ -pH coordinates, the shape of the straight line is 0.44. Thus, Am(IV) is reduced by two pathways; in one of them the reactive species is Am(CO<sub>3</sub>)<sub>n</sub>(H<sub>2</sub>O)<sub>x</sub><sup>2n-4</sup>, and in the second it is the hydrolyzed ion AmOH(CO<sub>3</sub>)<sub>n</sub>(H<sub>2</sub>O)<sub>x-1</sub><sup>(2n-3)-</sup>. These species are formed in the stages preceding the charge transfer.

The activation energy of Am(IV) reduction within the 54–70°C range (pH 9.96) was estimated at 86 kJ mol<sup>-1</sup>, which is close to 96 kJ mol<sup>-1</sup> obtained in [2].

Let us consider the mechanism of the charge transfer. It is usually suggested that the oxidant reacts with water or OH<sup>-</sup> ions to form OH radicals, which then recombine. Then, in our case, the following reactions would proceed:

$$Am(IV) + H_2O \xrightarrow{CO_3^{2-}} Am(III) + OH + HCO_3^{-},$$
 (5)

$$OH + OH \rightarrow H_2O_2$$
,  $2k = 1 \times 10^{10} \ 1 \ mol^{-1} \ s^{-1}$  [8]. (6)

Let us estimate the validity of this scheme. The redox potential of the Am(IV)/Am(III) couple in bicarbonate–carbonate solution is 0.9 V [2, 6]. The standard potential of the OH/OH<sup>-</sup> couple is 1.77 V [9], and at pH 10 the redox potential of the OH radical reaches 2 V. Thus, the concentration of OH radicals corresponding to equilibrium (5) is 20 orders of magnitude lower than the Am(IV) concentration. So low concentration of OH radicals cannot provide the rate of  $H_2O_2$  generation corresponding to the observed rate of Am(IV) consumption.

The mechanism of  $H_2O$  oxidation to  $H_2O_2$  in one stage seems more acceptable. The standard potential of the  $H_2O_2/H_2O$  couple is 1.76 V [10], in the solution with pH 10 the potential of this couple decreases to approximately 1.2 V, i.e., it does not strongly exceed the potential of the Am(IV)/Am(III) couple. However, the participation of two Am(IV) ions is

required to form H<sub>2</sub>O<sub>2</sub>. Nevertheless, the reaction order should remain first, as follows from the experiment. The mechanism similar to the mechanism of excimer formation (i.e., when the photoexcited species reacts with unexcited species to form a dimer termed excimer) meets the above conditions. The mechanism of excimer formation under the action of light quanta considered in [11] assumes that the excited species can be also generated thermally. The fraction of excited molecules \**n* is  $\ln(*n/n) = -\Delta E/(RT)$ , where  $\Delta E$  is the activation energy. Therefore, in our case the Am(IV) excitation proceeds thermally. It should be noted that the number of excited ions is small.

The thermally excited Am(IV) complex ion forms with unexcited Am(IV) a dimer (bound by coordinated water molecules)

$$Am(IV) \xrightarrow{\text{heating}} *Am(IV), \tag{7}$$

\*Am(IV) + Am(IV) 
$$\rightarrow$$
 dimer. (8)

The dimer decomposes with the liberation of  $H_2O_2$  and two Am(III) ions. Then, the following reactions occur:

$$\operatorname{Am}(\operatorname{IV}) + \operatorname{H}_2\operatorname{O}_2 \xrightarrow{\operatorname{CO}_3^{2^-}} *\operatorname{Am}(\operatorname{III}) + \operatorname{HO}_2 + \operatorname{HCO}_3^{-}, \quad (9)$$

$$HO_2 + CO_3^{2-} \rightarrow O_2^- + HCO_3^-,$$
 (10)

$$\operatorname{Am}(\operatorname{IV}) + \operatorname{O}_2^- \to \operatorname{*Am}(\operatorname{III}) + \operatorname{O}_2.$$
(11)

The comparison of the redox potentials of Am(IV)/Am(III),  $H_2O_2/H_2O$ , and  $O_2/O_2$  couples (0.20 and -0.33 V for the two latter, respectively [10]) shows that, in reactions (9) and (11), the substantial free energy is released, which can be localized on Am(III) and transfer it into the excited state.

The reaction

$$*Am(III) + Am(IV) \rightarrow Am(III) + *Am(IV)$$
 (12)

proceeds with the diffusion-controlled rate.

The occurrence of reaction (12) is confirmed by the fact that Am(III) is oxidized under irradiation of the Am(III) and Am(IV) mixture in spite of superposition of the Am(IV) and Am(III) charge-transfer bands [7]. Due to reaction (12), the chain process is developed, in which the number of excited Am(IV) species substantially exceeds the number of Am(IV) ions excited thermally. A part of \*Am(III) is deactivated in other reactions.

The decrease in the  $HCO_3^-$  and  $CO_3^{2-}$  concentrations causes the appearance of the low-charged Am(IV) complexes, which favors dimer formation and accelerates the reaction.

It is found in [1, 2] that Am(IV) reduction in carbonate solutions with water obeys the first-order rate law. Probably, in this case the above dimers are also formed, i.e., reactions (13)–(18) and (10) proceed:

$$Am(VI) \xrightarrow{heating} *Am(VI), \qquad (13)$$

\*Am(VI) + Am(VI)  $\rightarrow$  dimer, (14)

dimer 
$$\rightarrow 2\text{Am}(V) + \text{H}_2\text{O}_2,$$
 (15)

 $\operatorname{Am}(\operatorname{VI}) + \operatorname{H}_2\operatorname{O}_2 + \operatorname{CO}_3^{2-} \to \operatorname{*Am}(\operatorname{V}) + \operatorname{HO}_2 + \operatorname{HCO}_3^{-}, (16)$ 

$$\operatorname{Am}(\operatorname{VI}) + \operatorname{O}_2^- \to \operatorname{*Am}(\operatorname{V}) + \operatorname{O}_2, \tag{17}$$

$$*Am(V) + Am(VI) \rightarrow Am(V) + *Am(VI).$$
 (18)

The excimer mechanism can also explain the Np(VII) behavior in bicarbonate–carbonate solutions. At pH 9–11, Np(VII) transforms into Np(VI) by the first-order rate law; increase in pH decelerates the reaction [12]. In this case, reactions (19)–(24) and (10) proceed:

$$Np(VII) \xrightarrow{\text{heating}} *Np(VII),$$
(19)

\*Np(VII) + Np(VII) 
$$\rightarrow$$
 dimer I, (20)

dimer 
$$\mathbf{I} \rightarrow 2Np(VI) + H_2O_2$$
, (21)

$$Np(VII) + H_2O_2 \rightarrow *Np(VI) + HO_2, \qquad (22)$$

$$Np(VII) + O_2^- \rightarrow *Np(VI) + O_2, \qquad (23)$$

$$*Np(VI) + Np(VII) \rightarrow Np(VI) + *Np(VII).$$
 (24)

After Np(VI) accumulation, reactions

$$^{k}Np(VI) + Np(VI) \rightarrow dimer II,$$
 (25)

dimer 
$$\mathbf{II} \rightarrow 2Np(V) + H_2O_2,$$
 (26)

$$Np(VII) + Np(V) \rightarrow 2Np(VI),$$
 (27)

$$Np(VI) + H_2O_2 \rightarrow Np(V) + HO_2, \qquad (28)$$

$$Np(VI) + O_2^- \rightarrow *Np(V) + O_2$$
(29)

can also proceed.

In conclusion, we should note that the proposed scheme of reduction of the metal ions with water can be applicable not only to actinides but also to thermodynamically unstable ions (or molecules) of other elements.

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