Reduction of Pu(IV) and Np(VI) with Carbohydrazide in Nitric Acid Solution

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Abstract—The reduction of Pu(IV) and Np(VI) with carbohydrazide $(NH_2NH)_2CO$ in 1–6 M HNO₃ solutions was studied. The Pu(IV) reduction is described by a first-order rate equation with respect to Pu(IV). At $[HNO_3] \ge 3$ M, the reaction becomes reversible. The rate constants of the forward and reverse reactions were determined, and their activation energies were estimated. Neptunium(VI) is reduced to Np(V) at a high rate, whereas the subsequent reduction of Np(V) to Np(IV) is considerably slower and is catalyzed by Fe and Tc ions. The possibility of using carbohydrazide for stabilizing desired combinations of Pu and Np valence states was examined.

Keywords: carbohydrazide, nitric acid, solutions, plutonium, neptunium, ions, reduction, kinetics, catalysis, technetium, iron

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One of important lines of improving aqueous technology for reprocessing irradiated fuel, primarily highburn-up spent nuclear fuel, is search for new reagents, more convenient for performing redox operations involving Pu and Np ions. Organic compounds show promise for this purpose. Their use allows the amount of salt-containing radioactive wastes to be sharply reduced [1]. Carbohydrazide (NH₂NH)₂CO can be one of such reagents. Preliminary experiments showed that it rapidly reduces Pu(IV) and Np(VI) in nitric acid solutions at ambient temperature.

In the literature, carbohydrazide was mainly examined as ligand for bi- and trivalent element ions [2–5]. Its reducing properties have been studied in considerably less detail. It is known that carbohydrazide reduces the Cu²⁺ and Fe³⁺ ions to Cu⁺ and Fe²⁺, respectively. Both reactions occur at high rate and are accompanied by the evolution of gases: CO₂ and N₂ [6]. We found no data in the literature on interaction of actinide ions with carbohydrazide in nitric acid solutions. In this study we measured the rate of reduction of Pu(IV) and Np(VI) with carbohydrazide in HNO₃ solutions and examined the possibility of stabilizing Pu and Np in desirable valence state combinations using this reagent.

EXPERIMENTAL

Procedure. A temperature-controlled cell of a spectrophotometer was charged with the calculated amounts of stock solutions of HNO₃ and carbohydrazide and kept to attain the preset temperature. After that, a small aliquot of a Pu(IV) or Np(VI) solution was added, and the absorption spectra of the working solution were recorded at definite time intervals in the wavelength (λ) range 350–1100 nm. The concentration of the Pu and Np valence forms was calculated from the optical density (*D*) at $\lambda = 475$, 602, 980, and 710 nm, corresponding to the absorption maxima of the Pu⁴⁺, Pu³⁺, NpO₂⁺, and Np⁴⁺ ions, respectively.

Chemicals and analysis. The Pu stock solution was prepared by dissolving PuO_2 in a boiling mixture of HNO₃ and HF. After the complete dissolution of PuO_2 , Al(NO₃)₃ was added to bind F⁻ anions in a complex. The resulting solution was acidified with HNO₃ to a concentration of 7 M and purified by sorption on VP-1Ap anion exchanger. The desorbate was evaporated, and Pu was stabilized in the tetravalent state by adding H₂O₂. The solution thus prepared contained 440 g l⁻¹ Pu and 6.6 M HNO₃.

The 90 g l^{-1} Np stock solution was prepared by dis-



Fig. 1. Kinetic curve of Pu(IV) reduction and its linearization in semilog coordinates. [Pu(IV)] = 0.010, $[HNO_3] = 1$, and $[(NH_2NH)_2CO] = 0.05$ M; ~10°C.



Fig. 2. Kinetic curves of Pu(IV) reduction with carbohydrazide. [Pu(IV)] = 0.012 and [(NH₂NH)₂CO] = 0.2 M; 35°C. [HNO₃], M: (*1*) 1, (*2*) 4, (*3*) 3 {+ 5×10^{-3} M [Tc(VII)]}, and (*4*) 6.

solving a weighed portion of 98% pure NpO₂ in boiling 7 M HNO₃, followed by reduction of Np(VI) to Np(IV) with hydrazine and Np purification by sorption on VP-1Ap anion-exchange resin. In the purified solution, Np(IV) was oxidized to Np(VI) by repeated evaporation to wet salts. The Pu and Np concentrations in the stock solutions were determined by γ -ray spectrometry, and the content of valence forms of these elements in working solutions was found from the absorption spectra recorded with a UV-1201 spectrophotometer (Shimadzu).

The Tc(VII) stock solution was prepared by dissolving in water a weighed portion of 97 wt % pure $KTcO_4$. The Tc content in solution was determined by inductively coupled plasma mass spectrometry.

The carbohydrazide stock solution was prepared by dissolving in 0.1 M HNO₃ a weighed portion of the 97 wt % pure product (Acros Organics, USA). The carbohydrazide concentration in stock and working solutions was determined by potentiometric titration with potassium iodate [7].

Nitric acid was of ultrapure grade. The acid concentration in the stock solution was determined by titration of its weighed portion with a 0.1 M alkali solution, and in working solutions containing U and Pu, by potentiometric titration with ammonium oxalate.

RESULTS AND DISCUSSION

Reduction of Pu(IV)

In solutions of low acidity (<1 M HNO₃), carbohydrazide fully converts Pu(IV) to Pu(III) within 1–2 min at room temperature. The Pu(III) formed remains stable against oxidation, including solutions containing 50 g l⁻¹ U(VI) and 100 mg l⁻¹ Tc(VII). Experiments at decreased temperature (~10°C) showed that the reaction is described by a first-order rate equation with respect to Pu(IV) (Fig. 1) and allowed estimation of the rate constant in the rate equation

$$-d[\operatorname{Pu}(\operatorname{IV})]/dt = k_1[\operatorname{Pu}(\operatorname{IV})], \qquad (1)$$

equal to 0.02 min⁻¹ at [HNO₃] = 1 M and [(NH₂NH)₂CO] = 0.05 M.

At higher acidity, the reaction does not go to completion, and equilibrium between Pu(III) and Pu(IV) is attained (Fig. 2). The equilibrium constant

$$K = [Pu(III)]_{e}/[Pu(IV)]_{e}$$
(2)

 ${[Pu(III)]_e \text{ are } [Pu(IV)]_e \text{ are the equilibrium concentra$ $tions of Pu(III) and Pu(IV)} decreases with an increase$ in the solution acidity and increases with temperature.

The kinetic data were processed using equations for reversible first-order reactions [8]. In the case when both the forward [Pu(IV) reduction] and reverse [Pu(III) oxidation] reactions are first-order with respect to Pu ions, the kinetic curves should be linearized in the coordinates $\ln[A/(A - x)]$ -time, where A = Ka/(K + 1), *a* is the initial Pu(IV) concentration, and *x* is the Pu(III) concentration at time *t*.

The slope of the straight line in these coordinates is numerically equal to the sum of the rate constants of the forward (k_1) and reverse (k_{-1}) reactions. Knowing the sum $k_1 + k_{-1}$ and the quantity *K* equal to the ratio k_1/k_{-1} , we can calculate the rate constants of both reactions. An example of processing experimental kinetic data is given in Fig. 3, and the values of k_1 and k_{-1} for separate experiments are given in Table 1.

Table 1 shows that an increase in the HNO₃ concentration leads to a decrease in the rates of both forward and reverse reactions. The rates of both reactions increase with temperature, but for the forward reaction, Pu(IV) reduction, to a greater extent than for the reverse reaction. Estimation of the activation energies from these data gives the values of ~88 and ~34 kJ mol⁻¹ for the forward and reverse reactions, respectively. It should be noted that, in a 3 M HNO₃ solution containing Tc ions, the Pu(III) formed is unstable and starts to be oxidized already in the course of the experiment (Fig. 2).

Reduction of Np(VI) and Np(V)

At low acidity ([HNO₃] < 1 M) and room temperature, carbohydrazide rapidly reduces Np(VI) to Np(V). In a 0.3 M HNO₃ solution, even at low temperature (10–15°C), Np(VI) is fully reduced to Np(V) within the time of mixing the reactants. The rate decreases with an increase in the HNO₃ concentration and, e.g., in a 1 M HNO₃ solution at [(NH₂NH)₂CO] = 0.05 M and ~10°C, the reaction is complete in ~8 min.

With an increase in the solution acidity and temperature, Np(V) undergoes further reduction to Np(IV), accelerated by Fe and Tc ions (Fig. 4). A characteristic feature of the catalytic process is an induction period in the Np(IV) formation curve. A separate study is required to elucidate the origin of the induction period.

In experiments on Np(V) reduction with carbohydrazide, the Np(IV) formation was monitored by an increase in the optical density of the solution at $\lambda =$ 710 nm (Np⁴⁺ absorption maximum). Experimental data were processed assuming that the reaction follows a first-order rate equation with respect to Np

$$-d[Np(V)]/dt = d[Np(IV)]/dt = k[Np(V)].$$
(3)

In this case, with the reductant taken in excess, the kinetic curves should be linearized in the coordinates $\ln(D_{\text{fin}} - D)$ -time, where D_{fin} and D are the final and running optical densities of the solution. Indeed, as seen from Fig. 5, the dependences in these coordinates are linear. From their slopes, we calculated the rate constants k (Table 2).

It follows from Table 2 that the Fe and Tc ions considerably accelerate the Np(V) reduction, with Tc(VII) being approximately 4 times more effective than Fe(III). The catalytic effect of the Fe ions can be accounted for by the occurrence of the reactions

$$Fe(III) + (NH_2NH)_2CO \rightarrow Fe(II) + products,$$
 (4)

$$Np(V) + Fe(II) \rightarrow Np(IV) + Fe(III).$$
 (5)

Apparently, similar scheme can be suggested for catalysis with Tc ions.



Fig. 3. Plot of $\ln[A/(A - x)]$ vs. time in reduction of Pu(IV) with carbohydrazide. [Pu(IV)] = 0.012, [(NH₂NH)₂CO] = 0.2, and [HNO₃] = 6 M. *T*, °C: (*1*) 35 and (*2*) 50.



Fig. 4. Kinetic curves of Np(IV) formation in reduction of Np(VI) with carbohydrazide. [Np(VI)] = 8.4×10^{-3} , [(NH₂NH)₂CO] = 0.2, and [HNO₃] = 3 M. Additives: (1) none, (2) 9 × 10⁻⁴ M Fe(III), and (3) 1 × 10⁻³ M Tc(VII); the same for Fig. 5.



Fig. 5. Plot of $\ln(D_{\text{fin}} - D)$ vs. time in reduction of Np(V) with carbohydrazide. [Np] = 8.4×10^{-3} , [(NH₂NH)₂CO] = 0.2, and [HNO₃] = 3 M.

We also should note strong (approximately quadratic) dependence of the rate constant on the HNO₃ concentration: In the presence of Fe ions, *k* increases by a factor of ~4.5 in going from 3 to 6 M HNO₃.

Table 1. Rate constants of forward (k_1) and reverse (k_{-1}) reactions of Pu(IV) reduction with carbohydrazide. [Pu(IV)] = 0.012, [(NH₂NH)₂CO] = 0.2 M

[HNO ₃], M	<i>T</i> , °C	[Tc(VII)], M	k_1, \min^{-1}	k_{-1}, \min^{-1}
3	35	0.005	0.15	0.020
4	35	0	0.12	0.016
6	35	0	0.011	0.0064
6	50	0	0.054	0.012

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$[Np] \times 10^3$	[HNO ₂]	$[Fe(III)] \times 10^4$	$[Tc(VII)] \times 10^3$	1
	$k \times 10^{3}, \min^{-1}$			
8.4	3	0	0	0.18
8.4	3	9.0	0	1.15
8.4	3	0	1.0	4.5
4.2	6	9.0	0	5.1

Table 2. Rate constants of Np(V) reduction with carbohydrazide. $[(NH_2NH)_2CO] = 0.2 \text{ M}, T = 35^{\circ}C$

Use of Carbohydrazide for Stabilizing Desired Combinations of Pu and Np Valence States

It is of interest to examine the possibility of using carbohydrazide for stabilization of desired combinations of Pu and Np valence states, in particular, of the Pu(III)–Np(V) couple suitable in the extraction technology for separation of these elements from U and of the Pu(III)–Np(IV) couple suitable for mutual separation of Pu and Np by extraction or ion exchange.

Apparently, the Pu(III)–Np(V) couple should be prepared at a low acidity ([HNO₃] \leq 1 M), because under these conditions both Pu(IV) and Np(VI) are rapidly reduced with carbohydrazide and the products, Pu(III) and Np(V), should be stable for a long time.¹ We attempted to stabilize the Pu(III)–Np(V) couple at 35°C in a 1.1 M HNO₃ solution containing (M) 0.012 Pu(IV), 2.1 × 10⁻³ Np(VI), and 0.2 (NH₂NH)₂CO. As seen from Fig. 6, Pu(IV) is very rapidly (within less than 1 min) reduced to Pu(III), whereas Np(VI) is reduced to Np(V) more slowly that it was expected from the results of experiments without Pu and does not remain in this valence state, gradually transforming into Np(IV) (to ~30% within 5.5 h).

The observed decrease in the rate of the Np(VI) reduction to Np(V) can be accounted for by the occurrence of fast Np(V) reproportionation in weakly acidic solutions:

$$Np^{4+} + NpO_2^{2+} + 2H_2O \rightleftharpoons 2NpO_2^+ + 4H^+,$$
 (6)

and Np(IV) is apparently formed in the reaction

$$NpO_2^+ + Pu^{3+} + 4H^+ \rightleftharpoons Np^{4+} + Pu^{4+} + 2H_2O.$$
 (7)

Estimation, based on data of [9], of the time τ required for 30% completion of the reaction under the conditions of our experiment {[Pu(IV)] = 0.012, [Np(VI)] = 8.4 × 10⁻³, [HNO₃] = 1.1 M, 35°C} gives

 $\tau \sim 3.5$ h, i.e., the shorter time than that found in the experiment. However, taking into account the fact that the kinetic data given in [9] were obtained in solutions with a higher ionic strength ($\mu = 2$), we can conclude that the calculated and experimental estimations of τ are reasonably consistent.

In any case, the very fact of the Np(IV) formation indicates that, under the examined conditions, the use of carbohydrazide does not allow stabilization of the Pu(III)–Np(V) couple. This may become possible at lower acidity (0.5 M) and lower temperature (20– 25°C), because in this case the rate of the Np(IV) formation by reaction (7) will considerably decrease (according to [9], by a factor of ~14 in going to [HNO₃] = 0.5 M and 25°C).

As for the Pu(III)–Np(IV) couple, it is appropriate to stabilize it at a high acidity. In this case, the rate of the Np(V) reduction to Np(IV) under the action of carbohydrazide increases, as well as the contribution of reaction (7), whose rate increases with the HNO₃ concentration [9], to the Np(V) reduction. However, an increase in the HNO₃ concentration inevitably leads to a decrease in the rate and degree of Pu(IV) reduction to Pu(III). This problem can be solved by elevating the solution temperature simultaneously with increasing the acidity. Indeed, as shown above, the activation energy of the forward reaction [Pu(IV) reduction] considerably exceeds that of the reverse reaction [Pu(III) oxi-



Fig. 6. Kinetic curves of formation of Pu(III) and Np(V) in reduction of Pu(IV) and Np(VI) with carbohydrazide. [HNO₃] = 1.1, [Pu(IV)] = 0.012, [Np(VI)] = 2.1×10^{-3} , and [(NH₂NH)₂CO] = 0.2 M; 35°C.

If we assume that the reaction order of Np(V) reduction with carbohydrazide with respect to HNO₃ without Fe ions is the same as in their presence, calculation from data in Table 2 shows that the conversion of only 10% of Np(V) to Np(IV) requires 97 h at [HNO₃] = 1, [(NH₂NH)₂CO] = 0.2 M and 35°C.

dation], and hence the rate of the forward reaction will increase with temperature considerably more rapidly than the rate of the reverse reaction, which will result in more complete reduction of Pu(IV) to Pu(III).

We performed two experiments on stabilization of the Pu(III)–Np(IV) couple with carbohydrazide in a 6 M HNO₃ solution at two temperatures: 35 and 50°C. The Pu(IV) and Np(VI) concentrations in the starting solution were 0.012 and 2.1×10^{-3} M, respectively, and the carbohydrazide concentration was 0.2 M. The spectrophotometric measurements showed that, in both experiments, Pu(IV) was reduced incompletely, although, as expected, the reduction was more complete at 50°C (81%, against 63% at 35°C) (Fig. 7). On further keeping at room temperature for 18 h, a part of Pu(III) (about 25%) was oxidized back to Pu(IV).

The Np(IV) formation occurred without induction period at a rate exceeding that in the solution without Pu by 1.5–2 orders of magnitude. In the experiment at 35°C, Np transformed into Np(IV) incompletely, because a small peak at ~980 nm, belonging to Np(V) and corresponding to its concentration of ~8 × 10⁻⁵ M (about 4% of total Np concentration), was recorded throughout the observation period. Keeping the solution after the experiment for 18 h at room temperature led to an increase in the Np(V) fraction. In the experiment at 50°C, Np was fully reduced to Np(IV), but after keeping for 18 h at room temperature approximately 1.5% of Np(IV) passed into the pentavalent state.

Presumably, heating to a higher temperature (\sim 70°C) would allow more complete conversion of Pu(IV) to Pu(III), but the instability of Pu(III) and, though to a lesser extent, Np(IV) to oxidation in the course of solution storage makes apparently impossible stabilization of the Pu(III)–Np(IV) couple at very high acidity (6–7 M HNO₃).

Because the degree of Pu(IV) reduction with carbohydrazide and the stability of the Pu(III) formed increase with a decrease in the HNO₃ concentration, it seemed appropriate to decrease the solution acidity for stabilization of the Pu(III)–Np(IV) couple, but the acidity should be, at the same time, sufficient to ensure acceptable rate of the Np(V) reduction to Np(IV). Therefore, in the next experiment the HNO₃ concentration was decreased to 3 M, but the solution temperature was left on the level of 50°C to accelerate the Np(V) reduction. In addition, we added to the starting solution Fe(III) (9 × 10⁻⁴ M), which is present in proc-



Fig. 7. Kinetic curves of Pu(III) formation in reduction of Pu(IV) and Np(VI) with carbohydrazide. [HNO₃] = 6, [Pu(IV)] = 0.012, [Np(VI)] = 2.1×10^{-3} , and [(NH₂NH)₂CO] = 0.2 M. *T*, °C: (*1*) 35 and (*2*) 50.



Fig. 8. Kinetic curves of Pu(III) and Np(V) formation in reduction of Pu(IV) and Np(VI) with carbohydrazide. [P(IV)] = 0.012, $[Np(VI)] = 2.1 \times 10^{-3}$, $[(NH_2NH)_2CO] = 0.2$, $[HNO_3] = 3$, and $[Fe(III)] = 9 \times 10^{-4}$ M; 50°C.

ess solutions and originates from equipment corrosion and impurities in chemicals. The Pu(IV) and Np(VI) concentrations were the same as in the previous experiments (0.012 and 2.1×10^{-3} M, respectively).

The kinetic curves of the Pu(III) accumulation and Np(V) loss are shown in Fig. 8. As can be seen, under these conditions Pu(IV) and Np(V) are reduced to Pu(III) and Np(IV), respectively, to \sim 97–98% in \sim 1.5–2 h, and the content of these forms of Pu and Np does not change in the course of subsequent storage of the solution for, at least, 70 h at room temperature.

Thus, carbohydrazide rapidly reduces Pu(IV) at low acidity (≤ 1 M). The rate of this reaction is comparable with the rate of the reduction with the most kinetically effective reductants of the class of organic derivatives of hydrazine, hydroxylamine, and oximes, which are considered as alternatives to traditional reagents for Pu stripping [1]. Calculation based on the results of this study and on data of [10, 11] shows that, at [HNO₃] = 1 M and 35°C, the time of 99% reduction of Pu(IV) is 1.3, 3.7, 1.3, and 1.1 min with carbohydrazide, hydroxyethylhydrazine, acetaldoxime, and dimethylhydroxylamine, respectively (at reductant concentration of 0.5 M). The remaining Pu(III) is stable against oxidation at low acidity (including solutions containing Tc ions); hence, carbohydrazide acts as antinitrite stabilizer protecting Pu(III) from oxidation with nitrous acid. This conclusion is confirmed by the fact that carbohydrazide reacts with HNO₂ at a high rate (at ~20°C, $[(NH_2NH)_2CO] = 0.1$, $[HNO_2] = 0.014$, and $[HNO_3] =$ 0.5 M, the reaction is complete within the time of reactant mixing). Preliminary data show that the reaction products contain no HN₃. At a high acidity (no less than ~3 M HNO₃), Pu(IV) is reduced with carbohydrazide incompletely, and the forming Pu(III) is unstable and is gradually oxidized in Tc(VII)-containing solutions.

Carbohydrazide, like the majority of the abovementioned organic reductants, rapidly converts Np(VI) to Np(V) at a low acidity (<1 M), but at a high acidity (exceeding \sim 3 M HNO₃) it reduces Np(V) to Np(IV), and this reaction is catalyzed by Fe and especially Tc ions.

An attempt to stabilize with carbohydrazide the Pu(III)-Np(V) couple at low acidity (1.1 M HNO₃) failed because of the formation of Np(IV) in the reaction of Np(V) with Pu(III). It is not improbable that the Pu(III)-Np(V) couple can be stabilized at lower acidity (<1 M HNO₃) and temperature (~20–25°C), at which this side reaction will be decelerated.

The results of the experiment on stabilization of another couple, Pu(III)–Np(IV), with carbohydrazide in 3 M HNO₃ at 50°C [in the presence of 50 mg l⁻¹

Fe(III)] can be considered as positive: up to ~98% of Pu and Np passed into the required valence states whose content did not change in the course of prolonged storage of the solution.

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