ISSN 1066-3622, Radiochemistry, 2010, Vol. 52, No. 3, pp. 245–249. © Pleiades Publishing, Inc., 2010.
Original Russian Text © V.P. Shilov, A.M. Fedoseev, 2010, published in Radiokhimiya, 2010, Vol. 52, No. 3, pp. 209–212.

Reaction of Np(VI) with H_2O_2 in Carbonate Solutions

V. P. Shilov and A. M. Fedoseev*

Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences,
*Leninskii pr. 31, block 4, Moscow, 119991 Russia; * e-mail: fedosseev@ipc.rssi.ru*

Received July 22, 2009

Abstract—The kinetics and stoichiometry of the reaction of Np(VI) with H_2O_2 in carbonate solutions were studied by spectrophotometry. In the range 1–0.02 M Na_2CO_3, the reaction $2Np(VI) + H_2O_2 = 2Np(V) + O_2$ occurs, as $\Delta[Np(VI)]/\Delta[H_2O_2] \approx 2$. In Na_2CO_3 + $NaHCO_3$ solutions, the stoichiometric coefficient decreases, which is caused by side reactions. The reduction at low (1 mM) concentrations of Np(VI) and H_2O_2 follows the first-order rate law with respect to Np(VI), which suggests the formation of a Np(VI) peroxide–carbonate complex, followed by intramolecular charge transfer. Addition of Np(V) in advance decreases the reaction rate. An increase in the H_2O_2 concentration leads to the reaction deceleration owing to formation of a complex with two peroxy groups. In a 1 M Na_2CO_3 solution containing 1 mM H_2O_2, the first-order rate constant k increases with a decrease in [Np(VI)] from 2 to 0.1 mM. For solutions with $[Np(VI)] = [H_2O_2] = 1$ mM, k passes through a minimum at $[Na_2CO_3] = 0.5$–0.1 M. The activation energy in a 0.5 M Na_2CO_3 solution is 48 kJ mol^{-1}.

Key words: neptunium(VI), hydrogen peroxide, redox reactions

DOI: 10.1134/S1066362210030045

Carbonate and bicarbonate solutions are interesting in that, firstly, they simulate to a certain extent natural media. Secondly, these solutions are used for stabilization of higher valence states of actinides. Radiation from radionuclides in aqueous solutions gives rise to radiolysis products, including H_2O_2. This fact makes it necessary to study the behavior of Np(VI) and Np(V) in the presence of H_2O_2 in Na_2CO_3–$NaHCO_3$ solutions.

EXPERIMENTAL

The ^{237}Np sample was purified by anion exchange. From the resulting nitric acid solution, we precipitated Np(IV) oxalate. After centrifugation and washing, the precipitate was dissolved in 16 M HNO_3, concentrated $HClO_4$ was added, and the mixture was boiled for 1 h in a quartz beaker covered with a watch glass. After that, the watch glass was removed and the heating was continued until white vapors appeared. Concentrated $HClO_4$ was added to the residue, and the evaporation was repeated. The wet salts were dissolved in 0.01 M $HClO_4$. A spectrophotometric analysis showed that more than 99% of Np was in the hexavalent state. A part of the Np(VI) solution was reduced with sodium nitrite. The resulting Np(V) was precipitated with ammonia. The precipitate of Np(V) hydroxide was separated by centrifugation and, after washing with double-distilled water cooled to 0°C, was dissolved in a minimal amount of $HClO_4$. The Np concentration in stock solutions was determined by complexometric titration after reduction of Np to the tetravalent state [1]. We used chemically pure grade Na_2CO_3 and analytically pure grade $NaHCO_3$. For additional purification, Na_2CO_3 was recrystallized from double-distilled water. The Na_2CO_3 concentration was determined by acid titration. Medical grade H_2O_2 stabilized by a NaH_2PO_4 additive was distilled at reduced pressure. The H_2O_2 concentration in the resulting solution was found by permanganate titration. All the solutions were prepared in double-distilled water.

Experiments were performed using Shimadzu UVPC-3100 (Japan) and SF-46 (Leningrad Optical and Mechanical Association, Russia) spectrophotometers as follows. A temperature-controlled quartz cell was charged with a solution of Na_2CO_3 or Na_2CO_3 + $NaHCO_3$, and the absorption spectrum in the wavelength range 300–800 nm was recorded. Then we added a Np(VI) solution and an H_2O_2 solution, and every time we recorded the spectrum or monitored the loss of the optical density at the chosen wavelength. In some experiments with an excess of H_2O_2, at the end

Table 1. Influence of component concentrations (M) on the stoichiometry of the reaction Np(VI) + H_2O_2 ($\alpha = \Delta[Np(VI)]/\Delta[H_2O_2]$)

$[Na_2CO_3]$	$[NaHCO_3]$	$[Np(VI)] \times 10^3$	$[Np(V)] \times 10^3$	$[H_2O_2] \times 10^3$	α
1.0		1.0		0.47	1.97 ± 0.03
1.0		1.0	1.0	0.47	1.93 ± 0.03
1.0		1.0		1.0	1.95 ± 0.10
0.1		1.0		0.47	1.95 ± 0.05
0.1		1.0		1.2	1.82
0.02		1.1		0.35	1.97 ± 0.03
0.75	0.25	1.0		0.47	1.80
0.5	0.5	1.0		0.47	1.71
0.5	0.5	1.0		1.0	0.94

of the reaction, when Np(VI) disappeared virtually completely, the solution was transferred into a beaker and acidified with perchloric acid with vigorous stirring (this was done in an exhaust cabinet because of evolution of gas bubbles), and the sum of H_2O_2 and Np(V) was determined by permanganate titration. The H_2O_2 consumption was calculated as $\Delta[H_2O_2] = [H_2O_2]_0 - (V_1N/V_0 - 2[Np(VI)]_0)$, where V_1 is the volume of the $KMnO_4$ solution spent for the titration; N, its concentration, g-equiv l^{-1}; and V_0, solution volume in the cell.

From the amount of Np(VI) introduced into the carbonate solution, we calculated the extinction coefficient ε required for estimating the Np(VI) concentration in the course of the reduction. To make sure that the carbonate solution contained no reductants, we checked the Np(VI) content. To a cell with a 0.02 M Na_2CO_3 solution containing 0.5–1 mM of Np(VI), we added 10–20 mg of solid $K_4Fe(CN)_6 \cdot 3H_2O$ and recorded the $Fe(CN)_6^{3-}$ absorption. At this concentration of Na_2CO_3, the following reaction occurs:

$$Np(VI) + Fe(CN)_6^{4-} = Np(V) + Fe(CN)_6^{3-}.$$

The $Fe(CN)_6^{3-}$ and, correspondingly, Np(VI) concentrations were calculated using the $Fe(CN)_6^{3-}$ extinction coefficient $\varepsilon_{420} = 1030$ l mol^{-1} cm^{-1} [2]. The ε values found for Np(VI) slightly increase with an increase in the Na_2CO_3 concentration, e.g., ε_{350} increases from 1620 to 1690–1700 l mol^{-1} cm^{-1} in going from 0.02 to 1.0 M Na_2CO_3.

RESULTS AND DISCUSSION

The stoichiometry of the reaction of Np(VI) with H_2O_2 was studied in Na_2CO_3 and Na_2CO_3 + $NaHCO_3$ solutions at 19–20°C. The data obtained for solutions of various compositions are given in Table 1.

In a 1 M Na_2CO_3 solution with an excess of Np(VI) relative to H_2O_2, and also with an excess of H_2O_2, the stoichiometric coefficient is close to 2. Thus, there are good grounds to believe that the following reaction occurs in the system:

$$2Np(VI) + H_2O_2 = 2Np(V) + O_2. \qquad (1)$$

Additional introduction of 1 mM Np(V) does not affect the reaction stoichiometry. A decrease in the Na_2CO_3 concentration does not alter the stoichiometric coefficient at $2[Np(VI)] > [H_2O_2]$. However, with an excess of H_2O_2, the coefficient decreases, i.e., H_2O_2 is consumed in side reactions. In the case of Na_2CO_3 + $NaHCO_3$ solutions, an increase in the $NaHCO_3$ concentration leads to a decrease in the stoichiometric coefficient, especially with an excess of H_2O_2. For example, in a 0.5 M Na_2CO_3 + 0.5 M $NaHCO_3$ solution containing 1 mM Np(VI) and 1 mM H_2O_2, 0.04 mM Np(VI) remained in 22 min, but then the optical absorption associated with Np(VI) started to slowly increase, and by the 90th minute of the experiment the Np(VI) concentration was 0.063 mM. It did not change significantly during the subsequent 24 h. By that time, H_2O_2 was fully consumed. Similar phenomenon was observed previously in 1 M $NaHCO_3$ solution [3], when after adding H_2O_2 the Np(VI) concentration first decreased and then increased.

Kinetics of the Np(VI) + H_2O_2 Reaction

The semilog plots in the figure demonstrate the Np(VI) loss with time. In a 1 M Na_2CO_3 solution containing 1 mM Np(VI) and 1 mM H_2O_2, the experimental points are fitted by a straight line (line *1*), which indicates that the reaction is first-order with respect to Np(VI).

The rate equation has the form

$$-d[\mathrm{Np(VI)}]/dt = k[\mathrm{Np(VI)}]. \tag{2}$$

In the integral form, after replacement of the Np(VI) concentration by the proportional quantity $D - D_\infty$, the equation takes the form

$$2.3\log(D - D_\infty) = kt + \mathrm{const}, \tag{3}$$

where k is the first-order rate constant; D and D_∞ are the optical densities of the solution at the given time and after the reduction completion. The constant k was found graphically. Its mean values from experiments performed under various conditions are given in Table 2. The extreme values for solutions with the Np(VI) concentration below 0.5 mM differed by a factor of 3.

A decrease in the H_2O_2 concentration to 0.5 mM in a 1 M Na_2CO_3 solution affects the reaction kinetics insignificantly up to 70% conversion, after which the reaction decelerates (line *2* in the figure). With an increase in the H_2O_2 concentration to 5 mM, the reaction follows the first-order rate law up to consumption of 60% of Np(VI), after which the decelerated reaction also follows a first-order rate law (line *3* in the figure). It should be noted that, in most cases, the reaction deceleration occurred in 40–100 s, and the rate constants k corresponding to this period are given in Table 2 in parentheses.

The independence of the reaction rate from the reductant concentration (in the first half of the process) indicates that Np(VI) and H_2O_2 form a complex in which an intramolecular charge transfer leads to the Np(VI) reduction. In a 1 M Na_2CO_3 solution, pH is 12. Under these conditions, a considerable amount of hydrogen peroxide exists in the form of HO_2^-, because for the equilibrium

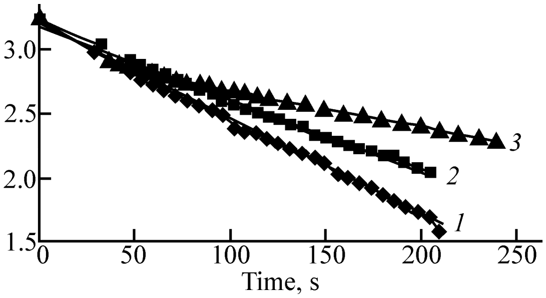
$$H_2O_2 \rightleftarrows H^+ + HO_2^-$$

pK = 11.58 at 30°C [4].

Neptunium(VI) in carbonate solutions exists in the form of $NpO_2(CO_3)_3^{4-}$ [5]. Therefore, the first step of the process is the reaction

$$NpO_2(CO_3)_3^{4-} + HO_2^- = NpO_2(O_2)(CO_3)_2^{4-} + HCO_3^-. \tag{4}$$

The second step is the charge transfer



Decrease in the Np(VI) concentration with time. $[Na_2CO_3]$ = 1 M; $[Np(VI)]_0$ = 1 mM; 20°C. $[H_2O_2]$, mM: (*1*) 1, (*2*) 0.5, and (*3*) 5.

$$Np^{VI}O_2(O_2)(CO_3)_2^{4-} \rightarrow Np^{V}O_2(CO_3)_2^{3-} + O_2^-. \tag{5}$$

With an excess of Np(VI), fast reactions occur:

$$NpO_2(CO_3)_3^{4-} + O_2^- \rightarrow NpO_2(CO_3)_2^{3-} + O_2 + CO_3^{2-} \tag{6}$$

Table 2. Influence of conditions on the rate of the Np(VI) + H_2O_2 reaction

T, °C	$[Na_2CO_3]$, M	[Np(VI)], mM	[Np(V)], mM	$[H_2O_2]$, mM	$k \times 10^3$, s^{-1a}
20	1	1	–	1	17.3
20	1	1	–	0.5	16.5 (11.3)
20	1	1	–	2	18 (14.6)
20	1	1	–	3	18 (13.5)
20	1	1	–	4	20 (11.7)
20	1	1	–	5	17.9 (6.6)
20	1.88	1	–	1	19.3
20	0.5	1	–	1	12.6 (7.6)
20	0.1	1	–	1	12.4 (7.2)
20	0.05	1		1	35 (11)
20	0.02	1		1	>100
20	0.1	1	–	4	11.8 (3.4)
20	1	2	–	1	14.9 (12.8)
20	1	0.5	–	1	18.8 (13.9)
20	1	0.2	–	1	32.8
20	1	0.1	–	1	42
20	1	1	0.7	0.46	12.2 (8.8)
20	1	1	1	1	8.7 (5.8)
20	1	1	1	2	10.5 (7)
20	1	0.14	1	1	8 (5.5)
35	0.5	1	–	1	32.7 (15.5)
45	0.5	1	–	1	50 (34)

[a] In parentheses are the k values found after performing the reaction to 50% and higher conversion.

and

$$Np^{VI}O_2(O_2)(CO_3)_2^{4-} + O_2^- + H_2O \rightarrow Np^{V}O_2(CO_3)_2^{3-} + O_2 + HO_2^- + OH^-. \quad (7)$$

In solutions with [Np(VI)] < [H_2O_2], the O_2^- radical ion participates in reactions (7) and (8):

$$H_2O_2 + O_2^- \rightarrow OH + OH^- + O_2. \quad (8)$$

The arising OH radical reacts with H_2O_2 (HO_2^-) and CO_3^{2-}:

$$HO_2^- + OH \rightarrow O_2^- + H_2O,$$

$$CO_3^{2-} + OH \rightarrow CO_3^- + OH^-.$$

Then the following reactions are possible:

$$HO_2^- + CO_3^- \rightarrow O_2^- + HCO_3^-,$$

$$Np(V) + CO_3^- \rightarrow Np(VI) + CO_3^{2-}.$$

At the [Np(VI)] : [H_2O_2] ratio equal to 1 : 1, almost the whole amount of Np(VI) is bonded in a peroxide–carbonate complex, because an increase in the H_2O_2 concentration leads to only a slight increase in the rate of the Np(VI) consumption. Reaction (7) results in the release of HO_2^-, owing to which its concentration increases, and virtually constant fraction of $NpO_2(O_2)\cdot(CO_3)_2^{4-}$ is provided. At [Np(VI)] : [H_2O_2] > 2, the HO_2^- concentration remains low, and starting from a certain moment the relative content of the peroxide–carbonate complex decreases, which leads to the process deceleration (line *2* deviates upwards).

Deviations from the straight line in the case of 2–5 mM H_2O_2 solutions are caused by another factor, namely, by the formation of a complex of Np(VI) with two peroxy groups, similarly to the complexation with uranyl ion [6]. The rate of formation of the second peroxide–carbonate complex is considerably lower than the rate of formation of the first complex, but the second complex is more stable to intramolecular reduction.

Interesting effect is exerted by the reaction product, Np(V). In solutions with Np(VI) and H_2O_2 concentrations of 1 and 0.46 mM, respectively, in the presence of 0.7 mM Np(V) the initial rate constant is lower by approximately 25% than the rate constant in the solution without Np(V) added. In solutions with [Np(VI)] = [H_2O_2] = 1 mM, preliminary introduction of Np(V) to a concentration of 1 mM leads to a decrease in the reaction rate constant by a factor of 2. However, at 2 mM H_2O_2, the same amount of Np(V) decreases *k* to a lesser extent. The effect of Np(V) in the solution with the initial Np(VI) concentration of 0.1 mM is more pronounced.

An increase in the Np(VI) content from 0.1 to 2 mM leads to the reaction deceleration, which is due to an increase in the Np(V) accumulation rate.

In going from 1 to 1.88 M Na_2CO_3, the pH, fraction of HO_2^-, and, correspondingly, the percentage of the Np(VI) peroxide–carbonate complex increase, which leads to a certain increase in the rate constant. In 0.5–0.1 M Na_2CO_3 solutions, the pH and HO_2^- fraction are lower. As a result, the concentration of the Np(VI) peroxide–carbonate complex and, correspondingly, the rate constant decrease. In 0.05 and 0.02 M Na_2CO_3, the rate increases. In the latter case, within the time from reactant mixing to the start of measurements (22–25 s), ≥90% of Np(VI) disappeared. In solutions with a lower concentration of carbonate or bicarbonate, higher rates of Np(VI) reduction are expected, similarly to the results of the reaction of Pu(VI) with H_2O_2 in 0.005–0.1 M $NaHCO_3$ [7].

The activation energy calculated from the initial values of *k* in 0.5 M Na_2CO_3 solution is about 48 kJ mol^{-1}.

Partial replacement of carbonate by bicarbonate affects the Np(VI) reduction insignificantly. Below are the results of separate (not averaged) experiments with solutions containing 1 mM Np(VI).

[$NaHCO_3$], M	[Na_2CO_3], M	[H_2O_2], mM	$k \times 10^3$, s^{-1}
0.25	0.75	0.46	17
0.25	0.75	1	26
0.5	0.5	0.46	24
0.5	0.5	1	17.5

The constants are close to those in 1 M Na_2CO_3 at the same concentrations of Np(VI) and H_2O_2. Certain data scatter is, most probably, due to local effects, because the stirring was manual.

It should be noted in conclusion that, similarly to the reaction of Np(VI) with H_2O_2, the reaction of Pu(VI) with H_2O_2 will decelerate in 0.5–2 M Na_2CO_3 solutions. However, the reduction will be complicated by the disproportionation of Pu(V).

REFERENCES

1. Smirnov-Averin, A.P., Kovalenko, G.S., Ermolaev, N.P., and Krot, N.N., *Zh. Anal. Khim.*, 1966, vol. 21, no. 1, pp. 76–78.
2. Sullivan, J.C., Brown, W., Nash, K., and Thompson, M., *Radiochim. Acta*, 1982, vol. 30, no. 1, pp. 45–47.
3. Shilov, V.P., Yusov, A.B., Gogolev, A.V., and Fedoseev, A.M., *Radiokhimiya*, 2005, vol. 47, no. 6, pp. 512–516.
4. *Spravochnik khimika* (Chemist's Handbook), Moscow: Khimiya, 1964, 2nd ed., vol. 3, p. 78.
5. Clark, D.L., Hobart, D.E., and Neu, M.P., *Chem. Rev.*, 1995, vol. 95, no. 1, pp. 25–48.
6. Runde, W., Brodnax, L.F., Peper, S.M., et al., *Recent Advances in Actinide Science*, May, I., Alvares, R., and Bryan, N., Eds., *Proc. Eighth Actinide Conf. Actinides-2005*, Manchester (UK), July 4–8, 2005, Cambridge (UK): Roy. Soc. Chem., 2006, pp. P174–P176.
7. Nash, K., Noon, M.E., Fried, S., and Sullivan, J.C., *Inorg. Nucl. Chem. Lett.*, 1980, vol. 16, no. 1, pp. 33–35.