Kinetics and Mechanism of Np(IV) Oxidation with Nitric Acid

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Abstract—Neptunium (IV) is oxidized to Np(V) with nitric acid in the presence of U(VI) under conditions of low acidity (<~0.1 M). The reaction rate is described by the equation $d[Np(V)]/dt = k_1[Np(IV)]/[H^+]^2 + k_2[Np(IV)]^2[U(VI)]/[H^+]^3$, in which $k_1 = (2.0\pm0.3)\times10^{-5} \text{ mol}^2 \text{ l}^{-2} \text{ min}^{-1}$ and $k_2 = (5.50\pm0.47)\times10^{-2} \text{ mol}^{-1} \text{ min}^{-1}$ at 50°C and solution ionic strength $\mu = 0.5$. The activation energies of the two pathways are 148±31 and 122±12 kJ mol⁻¹. The reaction along the main pathway (with the rate constant k_2) is limited by disproportionation of Np(IV) involving NpOH³⁺ and Np(OH)₂UO₂⁴⁺ complex ions.

It was shown in [1, 2] that Np(IV) in the absence of catalytic impurities is fairly stable in HNO₃ solutions at moderate acidity (~1 M) even at elevated temperatures (50°C) and in the presence of HNO₂. Sokhina *et al.* [3] observed Np(IV) oxidation to Np(V) at 50–100°C and [HNO₃] < 0.3 M; however, no data on the reaction rate were reported.

In this study we examined the kinetics and mechanism of Np(IV) oxidation in dilute HNO_3 solutions.

EXPERIMENTAL

The kinetics of Np(IV) oxidation with HNO₃ was studied spectrophotometrically as the time dependence of the NpO₂⁺ optical density at 980 nm, taking into account small absorption of Np⁴⁺ (extinction coefficient $\varepsilon \sim 30 \ 1 \ mol^{-1} \ cm^{-1}$).

Preliminary experiments showed that the reaction is strongly decelerated as the solution acidity is increased. For instance, in 0.5 M HNO₃ at 50°C the reaction does not start, at least in 6 h after mixing the reactants, while in 0.02 M HNO₃ it is completed within ~1 h (at [U(VI)] = 0.042 M). On the contrary, UO_2^{2+} ions accelerate Np(IV) oxidation with HNO₃. Taking into account these facts, we studied the reaction kinetics within the ranges of [H⁺] 0.018–0.103 M and [U(VI)] 0–0.113 M at 30–50°C (mainly 50°C). The ionic strength of the solution was kept constant with NaNO₃. Under these conditions, the extinction coefficient of Np(V) does not depend on the concentrations of H⁺ and UO_2^{2+} ions; however, it decreases at [U(VI)] > ~0.15 M because of formation of a Np(V) · U(VI) cation–cation complex [4, 5]. The Np(IV) stock solution was prepared by dissolution of a weighed portion of NpO₂ in 7 M HNO₃ at reflux, followed by reduction of Np(VI) to Np(IV) with hydrazine at ~90°C. Then, Np(IV) was purified by sorption on an anion-exchange resin, scrubbing with 7.5 M HNO₃, and desorption with 0.5 M HNO₃. The UO₂(NO₃)₂ stock solution was purified by peroxide precipitation as in [6]. Recrystallized NaNO₂ was used as a source of HNO₂. Distilled water and distilled HNO₃ were used to prepare both stock and working solutions.

The total Np concentration in the stock solution was determined by γ -ray spectrometry, and the content of its valence forms, spectrophotometrically, by characteristic bands of Np(IV) at 723 and Np(V) at 980 nm. The U(VI) concentration was determined by titration with ammonium vanadate solution. The H⁺ concentration in stock solutions was established by potentiometric titration, and in working solutions (after reaction completion), pH-metrically with an MP-220 pH meter (Mettler Toledo). The HNO₂ concentration in the working solutions was determined by UV absorption at 372 nm. In the presence of U(VI), HNO₂ was analyzed colorimetrically by the Griess–Ilosvay method after dilution of the solution samples to U(VI) concentrations less than ~1 × 10⁻⁴ M.

The solution spectra were measured on Lambda-40 (Perkin–Elmer) and UV-1201 (Shimadzu) spectro-photometers.

RESULTS AND DISCUSSION

Since the kinetic experiments were performed in the presence of uranyl, let us consider its effect on the Np(IV) spectrum. We found that the Np(IV) extinction coefficients at 723 and 960 nm are unchanged within the [HNO₃] 0.05–0.2 M range, but decrease at higher solution acidity. This follows from the data presented below (at 20°C and $\lambda = 723$ nm):

[HNO ₃], M	ϵ_{IV} , 1 mol ⁻¹ cm ⁻¹
0.05	72.0
0.10	73.0
0.20	72.4
0.35	66.2
0.50	57.2
1.00	43.5

The Np(IV) extinction coefficient also decreases with increasing U(VI) concentration (at 20° C and [HNO₃] = 0.2 M):

U(VI), M	ε_{IV} , 1 mol ⁻¹ cm ⁻¹		
0	72.4		
0.042	69.1		
0.10	64.6		
0.21	55.7		
0.42	46.5		

which can be ratonalized by formation of a cationcation complex Np(IV) · U(VI). This suggestion is confirmed by appearance of a new absorption band at 977 nm with $\varepsilon = \sim 45 \ 1 \ mol^{-1} \ cm^{-1}$ in the Np(IV) spectrum, whose intensity is proportional to the U(VI) concentration.

Using the above dependence of the observed Np(IV) extinction coefficient at 723 nm on U(VI) concentration and the equation of the balance of the optical density at this wavelength, we can estimate the stability constant of this complex, i.e., the equilibrium constant of the reaction

$$Np^{4+} + UO_2^{2+} \rightleftharpoons NpUO_2^{6+}$$
. (1)

 $K_1 = [\text{NpUO}_2^{6+}]/[\text{Np}^{4+}][\text{UO}_2^{2+}] = 1.3 \pm 0.2 \text{ l mol}^{-1}$ at 20°C and [H⁺] = 0.2 M.

The stoichiometry of the reaction between Np(IV) and HNO₃ is of particular interest. The changes in the spectrum of the reaction mixture during the reaction and after its completion show that Np(V) is one of the reaction products. Further oxidation of Np(V) to Np(VI) can be ruled out, taking into account the high rate of the Np(IV) reaction with Np(VI) [7].

Presumably, HNO_3 is reduced with Np(IV) to HNO_2 . However, after reaction completion (and during the reaction progress), the characteristic peaks of HNO_2 at 360–385 nm do not appear in the spectrum.

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The absence of HNO_2 is confirmed by the negative results of its determination with the Griess–Ilosvay colorimetric method.

Thus, the actual oxidant species in this reaction remains to be elucidated. We will return to this problem further.

One of the features of the reaction between Np(IV) and HNO_3 is its high rate in the initial stage and strong deceleration in the final stage of the reaction. The treatment of the kinetic data under various experimental conditions showed that they are well described by the equation

$$d[Np(V)]/dt = k'_1[Np(IV)] + k'_2[Np(IV)]^2, \qquad (2)$$

taking into account the occurrence of the process along two parallel pathways with the first and the second reaction orders with respect to Np(IV).

Denoting the Np(IV) initial concentration as a and its concentration after time t from the start of the reaction as (a - x), we have

$$-d(a - x)/dt = k'_1(a - x) + k'_2(a - x)^2, \qquad (3)$$

and after integration,

$$\ln \frac{k'_2(a - x) + k'_1}{a - x} = \ln \frac{k'_2 a + k'_1}{a} + k'_1 t, \qquad (4)$$

or, in another form,

$$\ln \left[(a - x)^{-1} + K \right] = \ln (a^{-1} + K) + k'_1 t, \qquad (5)$$

where $K = k_2/k_1$. The treatment of the kinetic data by Eq. (5) consists in choosing *K* for each experiment so as to attain the highest regression coefficient of linear function (5). In most experiments, Eq. (5) describes the reaction progress to conversion no less than 75% with R > 0.999. The adequacy of Eq. (5) to the experimental data is illustrated by Fig. 1.

However, as follows from the calculation results, the use of Eq. (5) is incorrect in case when K substantially exceeds 1/(a - x), i.e., at small values of the rate constant k'_1 . Therefore, the rate constants k'_1 and k'_2 we determined by numerical differentiation of Eq. (3) using the minimal sum of deviation squares as a criterion for choosing k'_1 and k'_2 . This method of data treatment allowed satisfactory description of the kinetic curves to conversion no less than 90%. An example of data treatment with Eq. (3) is presented in Fig. 2.

The results of treatment of the experimental data showed that the main contribution (more than 80%) to



Fig. 1. An example of treatment of kinetic curves by Eq. (5). $[Np(IV)]_0 = 1 \times 10^{-3}$ M, 50°C, [U(VI)] = 0.041 M, $\mu = 0.5$, $[H^+]$, M: (1) 0.033, (2) 0.050, and (3) 0.084. Points: experiment; lines: calculation.



Fig. 2. Kinetic curves of Np(V) formation in solutions containing 0.042 M U(VI) at $[H^+] = 0.02$ M, 50°C, $\mu = 0.5$. $[Np(IV)]_0 \times 10^3$, M: (1) 1.24, (2) 11.0, (3) 0.87, and (4) 0.51. Points: experiment; lines: calculation by Eq. (3).

the Np(IV) oxidation rate is made by the reaction pathway with the rate constant k'_2 . As for the second reaction pathway with the rate constant k'_1 , it becomes noticeable in the final stage of the process, where the change of the solution optical density is very small, and correspondingly the error of k'_1 is high. Therefore, we could not reliably find k'_1 at low solution acidity ([H⁺] = 0.018-0.043 M, as in the majority of kinetic experiments).

As seen from the data listed below (at 50°C, [U(VI)] = 0.042, $[Np(IV)]_0 = 1 \times 10^{-3}$ M, and $\mu = 0.5$):

[H ⁺], M	$k'_1 \times 10^3$, min ⁻¹
0.050	8.0
0.065	5.2
0.084	2.6
0.103	1.75

at higher concentration of H^+ ions, the rate constant k_1

decreases in inverse proportion to H^+ concentration squared. Thus, the rate of Np(IV) oxidation along the pathway with the rate constant k'_1 is described by the equation

$$d[Np(V)]/dt = k_1[Np(IV)]/[H^+]^2,$$
(6)

where $k_1 = (2.0 \pm 0.3) \times 10^{-5} \text{ mol}^2 \text{ l}^{-2} \text{ min}^{-1}$ at 50°C, [U(VI)] = 0.042 M, and $\mu = 0.5$.

The rate of the reaction along its main pathway also decreases with increasing $[H^+]$. As seen from the table, the reaction order with respect to hydrogen ion is approximately –3. Thus, at constant [U(VI)] and μ , the Np(IV) oxidation along the pathway with the rate constant k_2 obeys the kinetic equation

$$d[Np(V)]/dt = k_2^{"}[Np(IV)]^2/[H^+]^3,$$
(7)

where $k_2'' = (2.20 \pm 0.22) \times 10^{-3} \text{ mol}^2 \text{ l}^{-2} \text{ min}^{-1}$ at 50°C, [U(VI)] = 0.042 M, and $\mu = 0.5$.

As expected, the rate constant $k_2^{"}$ is virtually independent of the Np(IV) concentration in the initial solution (see table), which additionally confirms the second-order reactin with respect to Np(IV).

The effect of uranyl nitrate on the rate of Np(IV) oxidation was studied at U(VI) concentration not exceeding 0.15 M, which is caused by the necessity to avoid complications in calculation of [Np(V)] from the optical density at 980 nm, due to formation of a Np(V) · U(VI) complex. It follows from the table that the rate constant of the main reaction pathway increases approximately in proportion with the U(VI) concentration. With regard to this dependence and Eqs. (6), (7) for both reaction pathways, the kinetic equation of the overall reaction is

$$d[Np(V)]/dt = k_1[Np(V)]/[H^+]^2 + k_2[Np(IV)]^2[U(VI)]/[H^+]^3,$$
(8)

where $k_1 = (2.0 \pm 0.3) \times 10^{-5} \text{ mol}^2 \text{ l}^{-2} \text{ min}^{-1}$ and $k_2 = (5.50 \pm 0.47) \times 10^{-2} \text{ mol} \text{ l}^{-1} \text{ min}^{-1}$ at 50°C and $\mu = 0.5$.

To determine the activation energies for these reaction pathways, we studied the temperature dependences of k_1 and k_2 . The results are presented below.

$t_1 \times 10^3$, mol ² l ⁻² min ⁻¹	$k_2 \times 10^2$, mol l ⁻¹ min ⁻¹
0.047	0.262
0.175	0.548
0.450	1.048
0.875	2.500
2.00	5.24
	$\begin{array}{c} 0.047\\ 0.175\\ 0.450\\ 0.875\\ 2.00\end{array}$

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[H ⁺], M	[U(VI)], M	$[Np(IV)]_0 \times 10^3, M$	k'_2 , 1 mol ⁻¹ min ⁻¹	$k_2^{"} \times 10^3$,* mol ² l ⁻² min ⁻¹	$k_2 \times 10^2$,** mol l ⁻¹ min ⁻¹	
0.033	0	1.0	2.0	0.07	_	
0.027	0.0105	1.0	37.6	0.74	7.05	
0.029	0.021	1.0	37.0	0.90	4.30	
0.033	0.042	1.1	62.6	2.25	5.33	
0.023	0.063	1.0	300	3.65	5.79	
0.019	0.084	1.0	830	5.70	6.78	
0.023	0.113	1.0	630	7.66	6.78	
0.018	0.042	1.0	320	1.97	4.45	
0.033	0.042	1.1	62.0	2.23	5.30	
0.043	0.042	1.0	32.0	2.54	6.01	
0.050	0.042	0.95	20.0	2.50	5.95	
0.065	0.042	1.1	7.0	1.92	4.58	
0.084	0.042	1.1	2.75	1.63	3.90	
0.103	0.042	1.0	2.00	2.19	5.20	
0.019	0.042	0.48	370	2.54	6.04	
0.018	0.042	0.51	400	2.33	5.55	
0.019	0.042	0.87	275	1.90	4.52	

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The dependence of the second-order rate constant k_2' on the concentrations of H⁺ and UO₂²⁺ ions and Np(IV) initial concentration at 50°C and $\mu = 0.5$

* $k_2^{"} = k_2^{"}[\mathrm{H}^+]^3$. ** $k_2 = k_2^{"}/[\mathrm{U}(\mathrm{VI})]$.

0.042

0.021

The activation energies calculated from these data by the least-squares method are as follows: $E_1 = 148 \pm$ 31 and $E_2 = 122 \pm 12$ kJ mol⁻¹. As for the probable reaction mechanism, it should be noted that HNO₃ (nitrate ions) cannot be the actual oxidant species, since (as follows from special experiments) Np(IV) is oxidized also in HClO₄ solutions. HNO₂ (nitrite ions) is not the oxidant for Np(IV) either, since the reaction rate is independent of its concentration and, furthermore, the oxidation is observed in the presence of hydrazine, a reagent rapidly reacting with HNO₂ [8]. In a separate experiment we found that Np(IV) is oxidized in an argon atmosphere at the same rate as in air, and hence oxygen cannot be the actual Np(IV) oxidant.

1.24

The second order with respect to Np(IV) found for the main reaction pathway suggests that, in this pathway, Np(IV) is oxidized by disproportionation:

$$2Np^{4+} + 2H_2O \rightleftharpoons Np^{3+} + NpO_2^+ + 4H^+.$$
(9)

From the thermodynamic point of view, reaction (9) is more probable in solutions of low acidity, since the redox potential of the Np(V)/Np(IV) couple rapidly decreases with increasing pH.

This study, apparently, gave the first experimental confirmation for the above hypothesis.

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There are no published data on the kinetic features of Np(IV) disproportionation. Nevertheless, we can make some conclusions on the kinetic equation of this reaction considering the expression for the constant of equilibrium (9)

2.45

Average

$$K_{\rm eq} = [\rm Np(V)][\rm Np(III)][\rm H^+]^4/[\rm Np(IV)]^2$$
 (10)

5.84

 5.50 ± 0.47

and kinetic equation for reverse reaction between Np(V) and Np(III) [9]

$$-d[Np(V)]/dt = k_r[Np(V)][Np(III)][H^+].$$
(11)

Since the equilibrium constant is the ratio of the rates of the reverse and direct reactions, we can obtain the kinetic equation for reaction (9) by dividing Eq. (11) by Eq. (10), i.e.,

$$d[Np(V)]/dt = k_{f}[Np(IV)]^{2}/[H^{+}]^{3}.$$
 (12)

This equation formally coincides with Eq. (7) describing the Np(IV) oxidation rate for the main pathway. This can be considered as an indirect confirmation that the Np(IV) disproportionation is the slow stage of this reaction pathway.

The fact that H^+ ions inhibit this reaction and UO_2^{2+} ions accelerate it suggests the participation of hy-

drolyzed Np(IV) ions and complex Np(IV) \cdot U(VI) ions in the slow stage of the reaction. Taking into account the reaction order of -3 with respect to H⁺ ions, we can suggest that both reacting species contain hydroxy groups.¹ Correspondingly, the scheme of Np(IV) oxidation for the main reaction pathway can be presented as follows:

$$Np^{4+} + H_2O \rightleftharpoons NpOH^{3+} + H^+,$$
 (13)

$$Np^{4+} + 2H_2O \rightleftharpoons Np(OH)_2^{2+} + 2H^+,$$
 (14)

$$Np(OH)_2^{2+} + UO_2^{2+} \stackrel{\rightarrow}{\leftarrow} Np(OH)_2 UO_2^{4+},$$
 (15)

$$Np(OH)_2UO_2^{4+} + NpOH^{3+} \rightarrow NpO_2H^{2+} + UO_2^{2+}$$

+ $Np^{3+} + H_2O$, (16)

$$NpO_2H^{2+} \stackrel{\rightarrow}{\leftarrow} NpO_2^+ + H^+.$$
 (17)

The charge transfer in the reaction slow stage (16) proceeds as transfer of a hydrogen atom from the $Np(OH)_2UO_2^{4+}$ complex ion to the $NpOH^{3+}$ ion. The rate of this stage and, correspondingly, the rate of Np(IV) oxidation is

$$d[Np(V)]/dt = \chi[Np(OH)_2UO_2^{4+}][NpOH^{3+}].$$
(18)

Obviously, because of low concentration of $Np(OH)_2^{2+}$ ions, equilibrium (15) is virtually completely shifted to the left. Therefore, the concentration of $Np(OH)_2UO_2^{4+}$ species is low and equal to

$$[Np(OH)_2UO_2^{4+}] = K_2[Np(OH)_2^{2+}][UO_2^{2+}],$$
(19)

where K_2 is the constant of equilibrium (15).

Let us express the concentrations of hydrolyzed Np(IV) species through the Np(IV) analytical concentration ([Np(IV)]) and constants of the first (β_1) and second (β_2) steps of Np⁴⁺ hydrolysis. It should be taken into account also that a part of Np⁴⁺ ions are bound into the cation–cation complex NpUO₂⁶⁺ [reaction (1)], which does not participate in the slow step of the reaction. We can neglect small decrease in the UO₂²⁺ concentration because of formation of this complex, since U(VI) occurs in the reaction mixtures in a large excess as compared to Np(IV).

Further, using the equation of Np(IV) balance

$$[Np(IV)] = [Np^{4+}] + [NpOH^{3+}] + [Np(OH)_2^{2+}] + [NpUO_2^{6+}],$$
(20)

we obtain after transformations:

$$[NpOH^{3+}] = \frac{\beta_1[Np(IV)][H^+]}{[H^+]^2 + K_1[H^+]^2[UO_2^{2+}] + \beta_1[H^+] + \beta_2}, \quad (21)$$

$$[Np(OH)_{2}^{2+}] = \frac{\beta_{2}[Np(IV)]}{[H^{+}]^{2} + K_{1}[H^{+}]^{2}[UO_{2}^{2+}] + \beta_{1}[H^{+}] + \beta_{2}}.$$
 (22)

Substitution of these expressions in Eq. (19) and then in (18) gives the overall kinetic equation of the reaction

$$\frac{\mathrm{d}[\mathrm{Np}(\mathrm{V})]}{\mathrm{d}t} = \frac{\chi\beta_1\beta_2K_2[\mathrm{Np}(\mathrm{IV})]^2[\mathrm{UO}_2^{2+}][\mathrm{H}^+]}{\{[\mathrm{H}^+]^2(1+K_1[\mathrm{UO}_2^{2+}])+\beta_1[\mathrm{H}^+]+\beta_2\}^2}.$$
 (23)

This equation can be simplified taking into consideration that the constant of equilibrium (1) is small $(K_1 \sim 1.3 \ 1 \ \text{mol}^{-1})$ and the term $(1 + k_1 [UO_2^{2+}])$ in the denominator exceeds unity by only 15% at the highest U(VI) concentration used and in the most of experiments it amounts to 1.055. The constant of the first stage of Np(IV) hydrolysis is known at the solution ionic strength $\mu = 2$ and 25°C [11] ($\beta_1 = 5 \times$ 10^{-3} M). The values of β_1 under other conditions are unknown. However, we may suggest that in our case β_1 is substantially lower. This conclusion is indirectly confirmed by the fact that the Np⁴⁺ extinction coefficient at 723 nm remains unchanged with increasing HNO₃ concentration from 0.05 to 0.2 M. It is known that the hydrolysis constant of metal ions [12] and, in particular, actinides [13] for the second step is approximately an order of magnitude lower than the those for the first step. Thus, we can believe that $[H^{+}]^{2} \gg (\beta_{1}[H^{+}] + \beta_{2})$, and then Eq. (23) becomes

$$-d[Np(V)]/dt = k_2[Np(IV)]^2[U(VI)]/[H^+]^3, \qquad (24)$$

where $k_2 = \chi \beta_1 \beta_2 K_2$ and $[U(VI)] = [UO_2^{2^+}].$

As seen, the calculated equation of Np(IV) oxidation along its main pathway (24) is identical to Eq. (8).

As regards the minor reaction pathway with the rate constant k_1 , the known experimental data are insufficient for understanding the mechanism of this pathway. The negative second order with respect to H⁺ ions suggests that in the slow stage of the reaction along this pathway Np(IV) reacts probably in the form of Np(OH)₂²⁺ ions. However, the actual oxidant species remains to be elucidated. The reaction mechanism including the Np(OH)₂²⁺ reaction with NO₃⁻ ions in the slow stage formally corresponds to kinetic

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¹ It is interesting that the slow stage of Pu(IV) disproportionation involves the reaction between the hydrolyzed ions $PuOH^{3+}$ and $Pu(OH)_2^{2+}$.

equation (6). Regretfully, we cannot check this hypothesis since the concentration of nitrate ions in all the experiments was constant (0.5 M) because of the constancy of the solution ionic strength ($\mu = 0.5$).

Probably, a special study of the kinetics of the reaction between Np(IV) and NO_3^- ions in HClO₄ at high pH and various NO_3^- concentrations is required to answer this question.

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