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Reaction of Np(VI) with Cyclohexanediaminetetraacetic Acid in $HClO_4$ Solutions

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

Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences,
Leninskii pr. 31, korp. 4, Moscow, 119071 Russia
** e-mail: ShilovV@ipc.rssi.ru*

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Abstract—The stoichiometry of the reaction of Np(VI) with *cis*-cyclohexanediaminetetraacetic acid (CHDTA, H_4chdta) in 0.05 M $HClO_4$ solution was studied by spectrophotometry. With Np(VI) in excess, 1 mol of the complexone converts 4 mol of Np(VI) into Np(V). In 0.115–0.98 M $HClO_4$ solutions (the ionic strength of 1.0 was supported with $LiClO_4$) containing 3–29 mM CHDTA at 20–45°C, Np(VI) at a concentration of 0.2–3.3 mM is consumed in accordance with the first-order rate law until less than 40% of Np(VI) remains. After that, the reaction decelerates. The reaction rate has first order with respect to [CHDTA] and the order of –1.2 with respect to $[H^+]$. The activated complex is formed with the loss of one and two H^+ ions. The activation energy is 82.3 ± 3.8 kJ mol^{-1}.

Keywords: neptunium(VI), cyclohexanediaminetetraacetic acid, reduction, kinetics

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Replacement of the ethylene group in the EDTA molecule by the cyclohexane ring leads to different, compared to EDTA, electron density distribution on nitrogen atoms and on terminal carboxy groups. As a result, the dissociation constants and the solubility in water and acid solutions change. As for the reducing power of CHDTA, it is difficult to predict the changes relative to EDTA a priori, and experimental studies are required.

This study deals with the reaction of CHDTA with Np(VI) in perchloric acid solutions.

EXPERIMENTAL

Our experiments were performed with ^{237}Np. Stock solution of Np(VI) was prepared and standardized by the known procedure [1]. 1,2-Cyclohexanediaminetetraacetic acid (pure grade) was recrystallized from water and dried in air. A weighed portion of CHDTA was mixed with a NaOH solution in 1 : 2 molar ratio. The Na_2H_2chdta solution was quantitatively transferred into a volumetric flask. Chemically pure grade $HClO_4$, ultrapure grade NaOH, and pure grade $LiClO_4$ were used. Lithium perchlorate was additionally purified by recrystallization and dried in air. All solutions were prepared in double-distilled water. The solutions were standardized by common procedures.

In the experiments on studying the reaction stoichiometry, into a quartz cell (l = 1 cm) with a solution of Np(VI) in $HClO_4$ we added an aliquot of a Na_2H_2chdta solution. The optical density at 981 nm, corresponding to the Np(V) absorption, was measured at regular intervals with a Shimadzu PC 3100 (Japan) or SF-46 (Leningrad Optical and Mechanical Association, Russia) spectrophotometer. In kinetic studies, we added an aliquot of the Np(VI) stock solution into a temperature-controlled cell with an $HClO_4$ + H_4chdta solution and monitored an increase in the Np(V) content. Each experiment was repeated 2–3 times.

RESULTS AND DISCUSSION

The stoichiometry of the Np(VI) + H_4chdta reaction was studied in 0.05 M $HClO_4$ at 25°C. The initial concentrations of Np(VI) and H_4chdta were 3.6 and 0.5 mM, respectively. The Np(V) concentration was calculated using the Np(V) molar extinction coefficient $\varepsilon_{981} = 403 \pm 3$ L mol^{-1} cm^{-1}. From three experiments, we obtained $\Delta[Np(V)]/\Delta[H_4chdta] = 4$. The results of one of the experiments are given below.

Time, min	[Np(V)], mM	Time, min	[Np(V)], mM	Time, min	[Np(V)], mM
1	0.82	15	1.80	150.4	2.12
2	1.342	42.2	1.95	187	2.14
3	1.515	68	2.02	236	2.16
5	1.652	105.4	2.09		

The reaction between Np(VI) and H_4chdta is complete in 50–55 min. Further accumulation of Np(V) is caused by slow reaction of Np(VI) with CHDTA decomposition products. As can be concluded from the data obtained, the following reactions occur in $HClO_4$ solutions containing Np(VI) and H_4chdta:

$$\text{Np(VI)} + \text{H}_4\text{chdta} \rightarrow \text{Np(V)} + \text{R}_1 \text{ (slow)}, \quad (1)$$

$$\text{Np(VI)} + \text{R}_1 \rightarrow \text{Np(V)} + \text{R}_2 \text{ (fast)}, \quad (2)$$

$$\text{Np(VI)} + \text{R}_2 \rightarrow \text{Np(V)} + \text{R}_3 \text{ (fast)}, \quad (3)$$

$$\text{Np(VI)} + \text{R}_3 \rightarrow \text{Np(V)} + \text{low-active products (fast)}, \quad (4)$$

$$\text{Np(VI)} + \text{low-active products} \rightarrow \text{Np(V)} + \text{inactive products (slow)}. \quad (5)$$

The kinetics of the Np(VI) + H_4chdta reaction was studied in 0.115–0.98 M $HClO_4$ solutions at an ionic strength $I = 1.0$, supported by adding $LiClO_4$. Figure 1 shows the kinetic curves in the coordinates time–$\log(D_\infty - D)$ for 0.115 M $HClO_4$ + 0.875 M $LiClO_4$ + 0.010 M $NaClO_4$ solutions containing 5 mM H_4chdta and 3.3, 1.0, and 0.23 mM Np(VI). For the first two Np solutions, the kinetic dependences are linear up to 80% conversion, after which the reaction decelerates. In the case of the third solution, the linear portion of the kinetic curve has a smaller slope than the slope of the kinetic curves of the first and second solutions. Deviation from the linearity starts at the moment corresponding to 60% Np(VI) conversion. Similar character of kinetic curves in [1] was attributed to the fact that the radicals arising in reactions (1)–(3) react with dissolved O_2. We performed an experiment in which argon was passed for 20 min through a 0.48 M $HClO_4$ + 0.5 M $LiClO_4$ + 0.02 M $NaClO_4$ + 10 mM H_4chdta solution at 25°C, after which Np(VI) was added to a concentration of 1.2 mM. The hole in the cell lid was closed with a Teflon stopper, and the Np(V) accumulation was monitored. Similar experiment was repeated with saturation of the solution with O_2. We found that the kinetic curves obtained in solutions saturated with argon and O_2 did not differ from those for the aerated solutions. Hence it follows that dissolved O_2 influences the reaction course insignificantly.

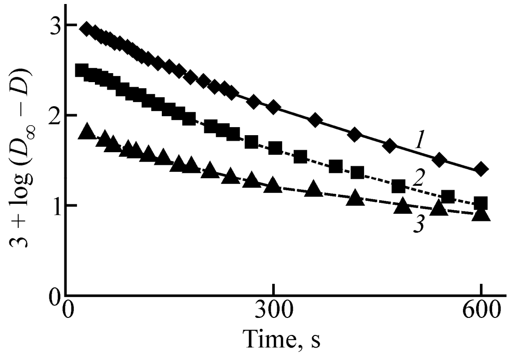

Fig. 1. Kinetic curves of the Np(VI) reduction with CHDTA molecules. [$HClO_4$] = 0.115 M, [$LiClO_4$] = 0.875 M, [$NaClO_4$] = 0.010 M, [H_4chdta] = 5 mM; 24°C. [Np(VI)], mM: (*1*) 3.3, (*2*) 1.0, and (*3*) 0.23.

The linearity of the kinetic curves in semilog coordinates and equal slope of these curve portions in the case of 1.0 and 3.3 mM Np(VI) indicate that the reaction is first-order with respect to Np(VI). The reaction rate is described by the equation

$$-d[\text{Np(VI)}]/dt = k'[\text{Np(VI)}] = k'([\text{Np(V)}]_\infty - [\text{Np(V)}]), \quad (6)$$

where k' is the first-order rate constant. In the integral form, after the replacement of [Np(V)] by the quantity D proportional to the concentration, Eq. (6) transforms into Eq. (7):

$$2.3\log(D_\infty - D) = -k't + \text{const}. \quad (7)$$

The first-order rate constant increases with increasing H_4chdta concentration. This can be illustrated by the example of 1 M $HClO_4$ solutions containing 1 mM Np(VI) and 3–29 mM H_4chdta at 22°C.

[H_4chdta], mM	3	5	10	20	29
$k' \times 10^3$, s^{-1}	0.253	0.406	0.777	1.46	2.20
k, L mol^{-1} s^{-1}	0.082	0.081	0.078	0.073	0.076

The bimolecular rate constant $k = k'/[\text{H}_4\text{chdta}]$ in the examined range of H_4chdta concentrations remains essentially constant, which suggests the first order of the reaction with respect to the reductant. The k values obtained under different conditions are given in the table.

As seen from the table, as the perchloric acid concentration is increased, the Np(VI) reduction rate appreciably decreases. Figure 2 shows the log–log plot of

Influence of conditions on the rate constant of the reaction Np(VI) + H_4chdta. I = 1.0 M, [H_4chdta] = 5–10 mM, [Np(VI)] = 1 mM

T, °C	[$HClO_4$], M	k, L mol^{-1} s^{-1}
25	0.115	1.64
25	0.24	0.648
25	0.48	0.266
25	0.98	0.122
20	0.98	0.064
30	0.98	0.216
35	0.98	0.355
40	0.98	0.59
45	0.98	0.98

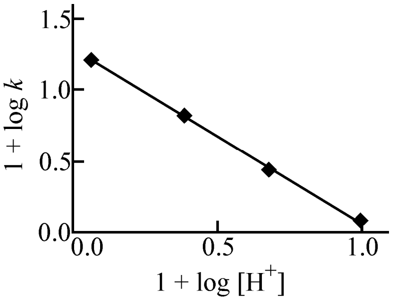

Fig. 2. Influence of the concentration of H^+ ions on the rate constant of the Np(VI) reduction with ions and molecules of H_4chdta in a solution with an ionic strength of 1.0 at 25°C.

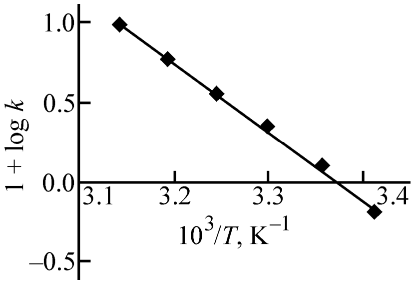

Fig. 3. Logarithm of the rate constant of the Np(VI) reduction with ions and molecules of H_4chdta as a function of reciprocal temperature. [$HClO_4$] = 0.98 M, [H_4chdta] = 10 mM.

k vs. [H^+]. At 25°C, the experimental points are fitted by a straight line with a slope of –1.2. Hence it follows that the reduction occurs via formation of an activated complex with the elimination of one and two protons. For *cis*- and *trans*-cyclohexanediaminetetraacetic acid at an ionic strength of 1.0 and 20°C, pK_1 = 2.4 [2]; therefore, in a dilute perchloric acid solution the complexone exists in the form of the H_3chdta^- ion and H_4chdta molecule. The activated complex is formed by the reactions

$$NpO_2^{2+} + H_3chdta = NpO_2H_2chdta + H^+,$$
$$NpO_2^{2+} + H_4chdta = NpO_2H_2chdta + 2H^+.$$

The charge transfer leads to the formation of Np(V) and radical R.

Figure 3 shows the temperature dependence of k in the Arrhenius coordinates. The activation energy found from this dependence is 82.3 ± 3.8 kJ mol^{-1}.

Variation of the ionic strength only slightly influences the rate of the Np(VI) + H_4chdta reaction. In a 0.115 M $HClO_4$ solution at 25°C, k = 1.99 L mol^{-1} s^{-1}, and in a 0.115 M $HClO_4$ + 0.875 M $LiClO_4$ + 0.02 M $NaClO_4$ solution, k = 1.64 L mol^{-1} s^{-1}. A decrease in the reaction rate with increasing ionic strength is typical of reactions between oppositely charged species, but low extent of this decrease suggests participation of a neutral species also. All these facts indicate that the activated complex is formed with the participation of H_3chdta^- and H_4chdta.

Comparison of the kinetic relationships for the reactions of Np(VI) with H_4edta and with H_4chdta shows that, under equal conditions, the rate constants are close and the mechanisms are similar.

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