The formation of neptunium peroxo complexes upon reduction of neptunium(VI) by hydrogen peroxide in concentrated solutions of alkalis

Vladimir P. Shilov, Andrei V. Gogolev and Alexei K. Pikaev*

Institute of Physical Chemistry, Russian Academy of Sciences, 117915 Moscow, Russian Federation. Fax: +7 095 335 1778

Kinetic studies have shown that the formation of Np^V peroxo complexes upon reduction of Np^{VI} by hydrogen peroxide in concentrated solutions of alkalis occurs *via* the intermediate appearance of Np^{VI} peroxo complexes.

In our previous work,[1] it was shown that for reactions of hydrogen peroxide with Np^{VI} and Am^{VI} in 0.1 mol dm^{-3} solutions of $HClO_4$, or with Np^{VII} within the pH range 9–14, there is a linear dependence of $\lg k$ (k is the reaction rate constant) on potential difference $\Delta E = E(An^{n+1}/An^n) - E(O_2/H_2O_2)$ (An = = actinide). These reactions proceed *via* an outer sphere mechanism. However, rate constants for reactions of hydrogen peroxide with Np^{VI} in solution at pH 5 or in alkaline medium are higher by 4 orders of magnitude than those expected from the respective ΔE values. Such behaviour indicates an intrasphere reaction mechanism, *i.e.*, the formation of an Np^{VI} peroxo complex. Note that peroxo complexes were also described in the case of U^{VI}.[2]

Earlier[3] we investigated the kinetics of the reaction between Np^{VI} and hydrogen peroxide in slightly alkaline solutions (pH 9.2–13.7). It was found that the reaction rate decreased with increasing pH value. Continuing the study with concentrated solutions of alkalis (1–8.4 mol dm^{-3}), we observed that in these solutions, the product of reduction is Np^V peroxo complex. The respective data are briefly described in the present paper.

A solution of $^{237}NpO_2(ClO_4)_2$ in perchloric acid prepared *via* a standard procedure was used as a stock solution. A solution of Np^V was also utilized. The neptunium concentration in the solutions was determined by a complexonometric method with its preliminary reduction to tetravalent state.[4] Hydrogen peroxide was produced by decomposition of BaO_2 (high-purity grade) by 1 mol dm^{-3} perchloric acid solution. The addition of concentrated K_2SO_4 solution was used to precipitate $BaSO_4$ and $KClO_4$. The analysis of H_2O_2 was conducted by a permanganatometric method. The LiOH and NaOH used were high-purity grade (the content of iron in the 17 mol dm^{-3} NaOH solutions supplied was less than 3×10^{-5}%). The solutions were prepared with twice distilled water.

The study on the reaction of Np^{VI} with hydrogen peroxide was carried out by recording the change in the intensity of its wide charge-transfer band of optical absorption in the near UV region using spectrophotometers SF-46 (Russia) and ‘Shimadzu UV-3100’ (Japan). To investigate this reaction, the solution of alkali was placed in a quartz cell (optical path lengths 1 or 5 cm), the spectrum was recorded, an aliquot of the stock Np^{VI} solution was added upon vigorous stirring, and the spectrum was recorded again. The solution of hydrogen peroxide was then inserted, and the spectrum or absorbance at the chosen wavelength (usually at 320 nm) were periodically measured.

Note that hydrogen peroxide in alkaline solutions exists in the form of HO_2^- or O_2^{2-}. For simplicity, the designation HO_2^- is used in this paper.

It was found that alkaline Np^{VI} solutions became yellow-brown as a result of the addition of hydrogen peroxide. Optical absorption spectra of ~ 8 mol dm^{-3} NaOH solutions containing various amounts of Np^{VI} and hydrogen peroxide which were recorded 20–40 s after mixing the solutions are analogous to the spectrum obtained by us upon the addition of hydrogen peroxide to alkaline Np^V solutions and coincide with those described in the literature[5–7] for Np^V peroxo complex. The molar absorption coefficient of the complex obtained from the measurements of absorbance of ~ 8 mol dm^{-3} NaOH solution at different ratios of Np^V and HO_2^- concentrations is equal to 3.8×10^2 m^2 mol^{-1} at 320 nm.

To determine the stoichiometry of reaction between HO_2^- and Np^{VI}, HO_2^- solution was added to a 1 mol dm^{-3} solution of LiOH, containing 1×10^{-3} mol dm^{-3} Np^{VI}, up to a concentration 4×10^{-4} mol dm^{-3}. The solution became turbid over several minutes, and a precipitate was formed. The latter was separated by centrifugation, then it was dissolved in a 0.1 mol dm^{-3} solution of $HClO_4$. $HClO_4$ was added to the supernatant to adjust the pH to approximately 1. Absorption spectra were recorded in both solutions. They showed the presence of Np^V. The total content of Np^V in both solutions allowed us to conclude that ratio $\Delta[Np^{VI}]/[HO_2^-]_0 \sim 1.8$, where $\Delta[Np^{VI}]$ designates the difference between initial and final Np^{VI} concentrations, *i.e.*, the total reaction that took place in the solution can be described as:

$$2Np^{VI} + HO_2^- + OH^- \longrightarrow 2Np^V + O_2 + H_2O \qquad (1)$$

The stoichiometry of reaction (1) was also studied for NaOH solutions. In this case, excess Np^{VI} was also used, and alkaline Np^{VI} solutions, stored for 1–2 days in the dark to finish the partial reduction of Np^{VI} by organic impurities present in stock NaOH solution (it was supplied from the manufacturer in a polyethylene vessel), were utilized. The data obtained are shown in Table 1, where $n = \Delta[Np^{VI}]/[HO_2^-]_0$. It is evident that hydrogen peroxide is consumed in Np^{VI} reduction and also in side reactions; their fraction increases with increasing NaOH concentration.

The dependence of absorbance of 8.4 mol dm^{-3} NaOH solutions, containing 1×10^{-4} mol dm^{-3} Np^{VI} and different HO_2^- amounts, at 320 nm (A_{320}) on time was investigated. The data obtained are shown in Figure 1. The analysis of the data allows us to draw the following conclusions.

At $[HO_2^-]_0/[Np^{VI}]_0 > 1$, absorbance for 23–25 s reaches 93–95% of the maximal value, *i.e.*, $4\tau_{1/2}$ ($\tau_{1/2}$ is the half-life of one of the reagents, for example, Np^{VI}) elapsed to this moment, and $\tau_{1/2} = 6$ s. The constancy of $\tau_{1/2}$ within the range of HO_2^- concentrations from 1×10^{-4} to 1×10^{-3} mol dm^{-3} requires us to accept the following reduction mechanism at these concentration ratios.

Initially, the complex of Np^{VI} with HO_2^- of $1:m$ composition where $m > 1$ is formed. The increase in A_{320} values for the next 30–40 s at $[HO_2^-] = 10^{-3}$ mol dm^{-3} obeys the rate law for a first-order reaction but $\tau_{1/2} = 12$ s. At present, we can not

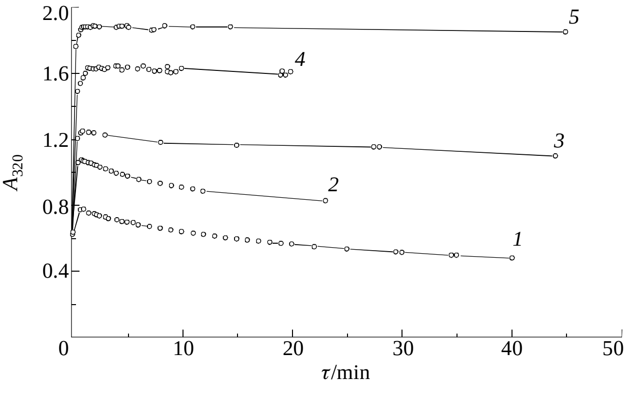

Figure 1 Dependence of A_{320} on time for an 8.4 mol dm^{-3} NaOH solution containing 1×10^{-4} mol dm^{-3} Np^{VI} and various HO_2^- concentrations (mol dm^{-3}): *1*, 4.2×10^{-5}; *2*, 1×10^{-4}; *3*, 2.04×10^{-4}; *4*, 3.97×10^{-4}; *5*, 1.03×10^{-3} (temperature 25 °C, optical path length 5 cm).

explain the increase in $\tau_{1/2}$ value. After reaching the maximum, A_{320} decreases.

At $[HO_2^-]_0/[Np^{VI}]_0 = 1–10$, the absorbance tends to the value corresponding to the equilibrium value for a Np^V and HO_2^- solution of a concentration that is equal approximately to $[HO_2^-]_0 - 0.5[Np^{VI}]_0$. Hence, the ligand HO_2^- is already present in the coordination sphere, and a complex $Np^V(HO_2^-)$ appears *via* reduction of $Np^{VI}(HO_2^-)$ complex by the species attacking from outside. At $[HO_2^-]_0/[Np^{VI}]_0 > 0.5$, A_{320} decreases to a value corresponding to Np^{VI} concentration minus the amount consumed in reaction with hydrogen peroxide.

At HO_2^- excess, the $Np^V(HO_2^-)$ concentration calculated *via* molar absorption coefficient is equal to 90–95% of the initial neptunium concentration. If reactions:

$$Np^{VI} + HO_2^- \longrightarrow Np^{VI}(HO_2^-) \qquad (2)$$

$$Np^{VI}(HO_2^-) \longrightarrow Np^V + HO_2 \qquad (3)$$

$$HO_2 + OH^- \rightleftarrows O_2^- + H_2O \qquad (4)$$

$$Np^{VI}(HO_2^-) + O_2^- \longrightarrow Np^V(HO_2^-) + O_2 \qquad (5)$$

proceed, the $Np^V(HO_2^-)$ concentration after reduction should be equal to about $0.5[Np^{VI}]_0$, and then an increase in absorbance should occur because of reaction between Np^V and HO_2^-. Special experiments showed that the Np^V peroxo complex in the reaction of Np^V with hydrogen peroxide is formed slowly. For instance, at $[HO_2^-]_0/[Np^V]_0 = 10:1$, the duration of this reaction is 70 min. Since an increase is not observed, it is most probable that reactions (2), (4), (6), (7) and (5) take place:

$$Np^{VI}(HO_2^-) + HO_2^- \rightleftarrows Np^{VI}(HO_2^-)_2 \qquad (6)$$

$$Np^{VI}(HO_2^-)_2 \longrightarrow Np^V(HO_2^-) + HO_2 \qquad (7)$$

At Np^{VI} excess, reaction (8) should be added to the reactions considered:

$$Np^{VI} + O_2^- \longrightarrow Np^V + O_2 \qquad (8)$$

At $[HO_2^-]_0/[Np^{VI}]_0 < 0.5$, it is necessary to propose as an explanation of the obtained kinetic data (the initial rate linearly decreases with increasing NaOH concentration but slightly depends on Np^{VI} concentration and increases with increasing $[HO_2^-]_0$) that the formed complex $Np^V(HO_2^-)$ participates in reaction (9):

$$Np^V(HO_2^-) + Np^{VI} \longrightarrow 2Np^V + HO_2 \qquad (9)$$

In addition, dissociation of $Np^V(HO_2^-)$ to Np^V and HO_2^- occurs, and released hydrogen peroxide reacts with Np^{VI}.

Table 1 Influence of NaOH concentration and initial Np^{VI} and HO_2^- concentrations on the stoichiometry of reaction $Np^{VI} + HO_2^-$.

[NaOH]/ mol dm^{-3}	$[Np^{VI}]_0$/ 10^{-4} mol dm^{-3}	$[HO_2^-]_0$/ 10^{-4} mol dm^{-3}	$\Delta[Np^{VI}]_0$/ 10^{-4} mol dm^{-3}	*n*
1.0	1.98	0.74	1.29	1.74
1.0	2.48	1.08	1.97	1.82
2.1	2.20	1.01	1.58	1.56
4.1	3.85	1.80	2.73	1.52
4.2	3.50	1.67	2.38	1.43
8.2	8.12	3.28	4.66	1.42
8.2	3.84	1.82	2.36	1.30

As mentioned above, HO_2^- is consumed not only in Np^{VI} reduction but also in side reactions. Reactions (10) and (11) can belong to such processes:

$$HO_2^- + O_2^- \longrightarrow O^- + OH^- + O_2 \qquad (10)$$

$$Np^V(HO_2^-) + O_2^- \longrightarrow Np^V + O^- + OH^- + O_2 \qquad (11)$$

Radical ion O^- formed oxidizes Np^V to Np^{VI}. In reaction (11), radical ion O^- can appear in the Np^V coordination sphere and in the same place can perform its oxidation.

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