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

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**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 $E = E(An^{n+1}/An^n) - E(O_2/H_2O_2)$ (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 $E$ 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 $3\times10^{-5}$ %). 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 $3.8\times10^2$ 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 $1\times10^{-3}$ mol dm$^{-3}$ $Np^{VI}$, up to a concentration $4\times10^{-4}$ 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:

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

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 $1\times10^{-4}$ 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 $1\times10^{-4}$ to $1\times10^{-3}$ 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

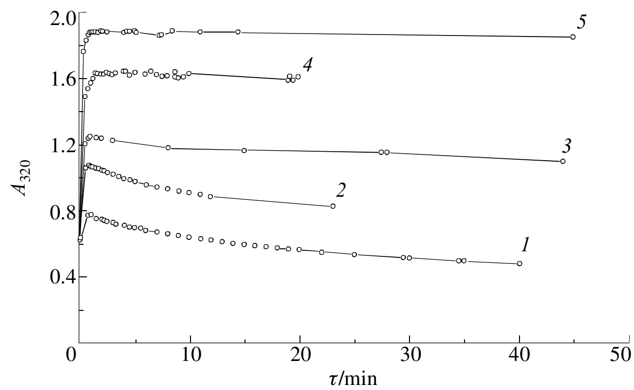


**Figure 1** Dependence of $A_{320}$ on time for an 8.4 mol dm$^{-3}$ NaOH solution containing $1\times10^{-4}$ mol dm$^{-3}$ $Np^{VI}$ and various $HO_2^-$ concentrations (mol dm$^{-3}$): *1*, $4.2\times10^{-5}$; *2*, $1\times10^{-4}$; *3*, $2.04\times10^{-4}$; *4*, $3.97\times10^{-4}$; *5*, $1.03\times10^{-3}$ (temperature 25 °C, optical path length 5 cm).

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

At $[HO_2^-]_0/[Np^{VI}]_0$ = 1–1 0, 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:

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

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

$$HO_2 + OH^- \rightleftharpoons O_2^- + H_2O \quad (4)$$

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

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:

$$Np^{VI}(HO_2^-) + HO_2^- \rightleftharpoons Np^{VI}(HO_2^-)_2 \quad (6)$$

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

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

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

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):

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

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$^{-3}$ | $[Np^{VI}]_0$/ $10^{-4}$ 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:

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

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

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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