A Kinetic Investigation of Non-catalysed Reduction of NpO$_2^+$ by Hydrazine

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The kinetics of reduction of Np(V) to Np(IV) by hydrazine has been studied. The effect of different factors such as H$^+$ ion, hydrazine and nitrate ion concentrations have been investigated. The order of the reduction reaction is found to be 1 with respect to [H$^+$]. No nitrate ion dependence is noticed. On the basis of the results obtained a plausible mechanism for the reduction process has been suggested.

The separation of the actinide elements depends largely on the different chemical behaviour of the various oxidation states of the ions concerned. The reduction of neptunium(VI) by hydrazine has been used in the process of its recovery from irradiated uranium fuel$^1$. Recently Koltunov et al. has studied the reduction of NpO$_2^+$ (ref. 3) and PuO$_2^+$ (ref. 4) by hydrazine in a solution containing HNO$_3$.

The present paper reports the kinetics of the reduction of NpO$_2^+$ by hydrazine. The effect of hydrazine nitrate ion, hydrogen ion and temperature on the reaction rate have been studied and a plausible mechanism for the reduction of the neptunyl ion, (Np V), suggested.

Materials and Methods

Neptunium(V) in the form of the isotope $^{237}$Np or $^{237}$Np + $^{239}$Np was prepared by electrolytic reduction as described earlier$^4,5$. The purity of the isotope was checked using a Carry-17 spectrophotometer. Only the 980 nm peak was detected.

The $\alpha$-activity of neptunium was measured using $\alpha$-scintillation (ZnS$_2$) crystal connected to an ELA counter. The $\gamma$-activity of the isotope $^{239}$Np was measured using a well-type NaI(Tl) crystal connected to a counting set-up.

Hydrazine and nitric acid were of analytical grade. The spectrophotometric method$^7$ was found to be satisfactory for the determination of hydrazine using $p$-dimethylaminobenzaldehyde as a colour developing reagent. The detection and determination of hydrazoic acid was carried out following known procedures. The acid concentration was determined using a Metrohm LTD Herisau E-366 potentiograph.

Reaction unit — A schematic diagram for the reaction unit is given in Fig. 1. The reaction vessel consisted of two parts. The lower part was a double walled container surrounded by a water thermostat. The upper part was fitted to the lower part and was supplied with ethylene glycol to bring about the condensation of any vapour from the lower container. This upper part was fitted with

Fig. 1 — Schematic diagram of the experimental set-up with gas purification system

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five capillary tubes for the passage of argon gas (tube 1), for the withdrawal of organic or aqueous samples (tubes 2, 3), for the introduction of the neptunium solution (tube 4) and finally tube 5 for pressure equilibration in the whole system. This was achieved by connecting this tube to a well-lubricated syringe (Fig. 1).

Procedure — For every set of experimental conditions, the TBP solution in dodecane or xylene was pre-equilibrated with nitric acid and hydrazine. The aqueous phase, the extractant and the reductant were introduced in the lower part of the reaction vessel. Argon gas was allowed to pass and the thermostat allowed to reach a given temperature. The system was then allowed to stay for 10 min to attain thermal equilibrium.

To start the reaction, aliquots of Np(V) were introduced into the reaction vessel. The phases were stirred using a magnetic stirrer and after definite time intervals, samples of both the organic and aqueous phases were withdrawn and subjected to analysis for the calculation of the distribution coefficient.

At the end of the experiment, the Np(V) was completely reduced to the tetravalent state by the addition of a few drops of Fe" solution in the form of ferrous sulphamate and the distribution coefficient of Np(IV) determined for a certain specified set of experimental conditions.

Results and Discussion

The process of reduction of NpO_4^2- ion by hydrazine has been followed at different [reductant], [H^+] and temperature.

In the process of reduction of NpO_4^2- ion by hydrazine, Np(IV) is formed which is extracted from the nitric acid by TBP in kerosene or dodecane. Under these conditions NpO_4^2- ion is not extracted, i.e. \( D_{Np(V)} = 0 \). The amount of Np(IV) produced and subsequently extracted at various time intervals was used as a parameter indicative of the kinetics of the reduction process.

In all the cases, the rate of reduction is measured by following the decrease in [Np(V)]. In order to determine the rate constant and the order of the reduction reaction, some parameters connected with the distribution coefficient were related using appropriate equations — to the time parameter of the reaction. As already stated, the Np(IV) formed during the reduction reaction is extracted in TBP layer and an apparent distribution coefficient (\( D_{app} \)) is obtained which is given by Eq. (1).

\[
D_{app} = \frac{IV_o}{IV_o + V_a + V_a}
\]

IV_o represents Np(IV) in the organic phase, IV_a represents Np(IV) in the aqueous phase and VA represents Np(V) in the aqueous phase.

Since \( D_{IV} = IV_o/IV_a \), \( D_{app} \) is then given by Eq. (2) or Eq. (3)

\[
V_a = \frac{D_{IV} - D_{app}}{D_{app}}
\]

Since for TBP the value of \( D_{Np(V)} = 0 \), then the total initial concentration of neptunium, \([Np]_i\), at a given time is given by Eq. (4)

\[
[Np]_i = IV_o + IV_a + V_a
\]

From Eqs. (4) and (3) it follows that

\[
\frac{[Np]_i/V_a}{IV_o} = 1 + \left( \frac{D_{app}}{D_{IV} - D_{app}} \right)(1 + D_{IV})
\]

\[
\frac{[Np]_i}{V_a} = \frac{D_{IV} (1 + D_{app})}{D_{IV} - D_{app}}
\]

\[
Z = \frac{D_{IV} - D_{app}}{D_{IV} (1 + D_{app})}
\]

From a knowledge of both the distribution coefficient of Np(IV) which acquires a certain value for every set of experimental conditions and \( D_{app} \) obtained from Eq. (1), the parameter \( Z \) indicative of the relative amounts of Np(V) present at a given time during the reduction experiment can be calculated and from this the rate constant \( k \) given
by the equation $2\cdot303 \log Z = kt$ can also be calculated.

For the reaction under investigation, a linear relation between $\log Z$ and time was obtained (Fig. 2) at constant [hydrazine nitrate] and for various [nitric acid]. This indicates that the reduction reaction is first order with respect to [neptunyl ion].

**Effect of varying $[H^+]$:** The effect of varying $[H^+]$ on neptunium(V) reduction by hydrazine was studied at constant total nitrate ion and ionic strength of 4 (mixture of HNO$_3$+LiNO$_3$ was used). The variation of $\log Z$ values with time at 60° is shown in Fig. 3 for various $[H^+]$. The order of the reaction ($n$) with respect to $[H^+]$ was deduced from a plot of $k$ values against $[H^+]$. The value of $n$ was found to be 1 (Fig. 4).

**Effect of varying [nitrate ion]:** The nitrate ion dependence was studied at constant $[H^+]$ and ionic strength. The variation of $k$ values with $[NO_3^-]$, given in Table 1, shows that there is no dependence of the $k$ on the $[NO_3^-]$ under the experimental conditions.

**Effect of varying [hydrazine]:** The effect of varying [hydrazine] was studied at three different temperatures (50°, 60°, 70°) and for the [hydrazine] in the range 0·05 to 0·5M. The $k$ values obtained from $\log Z$ relations are plotted as a function of $N_2H_5NO_3$ concentration and are shown in Fig. 5. The linear plots in Fig. 5 give an average slope of 0·5. This means that every hydrazine ion is capable of reducing a couple of NpO$_5^+$ ions. It should be noticed that the results at 70° fit a linear plot of a slope = 0·7. This suggests that the reaction takes place at this temperature by more than one path. This is supported by the fact that hydrazine itself may be oxidized via two different paths yielding one or two electrons according to the following mechanism:

$$N_2H_5^+ \rightarrow NH_3 + \frac{1}{2}N_2 + 2H^+$$

$$2N_2H_5^+ \rightarrow 2NH_3 + N_2H_4 + 3H^+$$

The non-integrality of the order of hydrazine has been reported by Powell and later confirmed by Rossinsky in the course of reduction of Fe$^{III}$ by hydrazine.

In nitric acid media, both the protonated hydrazine species $N_2H_5^+$ and $N_2H_4^+$ exist in solution. For reactions with $N_2H_5^+$, Eqs. (7) and (8) can be used to describe the reduction reaction at 50° and 60°, where reaction (7) is predominating. At 70° both the reactions (7) and (8) are possibly taking place.

$$NpO_5^++N_2H_5^+\rightarrow Np^{4+}+N_2H_3$$  \(\ldots(7)\)

$$NpO_5^++N_2H_4^+\rightarrow Np^{4+}+N_2H_3$$  \(\ldots(8)\)

**Table 1 — Effect of Varying [Nitrate Ion] on Neptunium Reduction in Nitric-Perclooric Mixture of Constant Ionic Strength at 50°**

<table>
<thead>
<tr>
<th>HNO$_3$</th>
<th>HClO$_4$</th>
<th>[NO$_3^-$]</th>
<th>$10^6k$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>M</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>1·25</td>
<td>4·14</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>2·25</td>
<td>4·37</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>4·25</td>
<td>4·14</td>
</tr>
</tbody>
</table>

**Fig. 3 — Effect of varying $[H^+]$ on Np(V) reduction**

**Fig. 4 — Effect of varying $[H^+]$ on Np(V) reduction by 0·25M $N_2H_5NO_3$ in solution**
In the light of the above-mentioned experimental results, an attempt was made to suggest a mechanism for hydrazine reduction of neptunium.

The neptunyl cation $\text{NpO}^{2+}$ is supposed to participate as a protonated cation in several redox and exchange reactions (Eq. 9)

$$\text{NpO}_2^+H^+ = \text{NpO}_2H^{2+} \quad \ldots (9)$$

This cationic protonated form reacts with hydrazine and $H^+$ to yield an activated complex (Eq. 10)

$$\text{NpO}_2H^{2+} + \frac{1}{2}\text{N}_2\text{H}_4^+ + \frac{3}{2}H^+ = [C^+]^{4+} \quad \ldots (10)$$

The activated complex decomposes to give the tetravalent neptunium and oxidation products of hydrazine (Eq. 11)

$$[C^+]^{4+} = \text{Np}^{4+} + \frac{1}{2}\text{N}_2\text{H}_4 + 2\text{H}_2\text{O} \quad \ldots (11)$$

From Eqs. (9), (10) and (11) the overall reaction can be represented by Eq. (12)

$$\text{NpO}_2H^{2+} + \frac{1}{2}\text{N}_2\text{H}_4^+ + \frac{3}{2}H^+ = \text{Np}^{4+} + \text{N}_2\text{H}_4 + 2\text{H}_2\text{O} \ldots (12)$$

where $\text{N}_2\text{H}_4$ can be removed by one or both the reactions (a) and (b)

$$\text{N}_2\text{H}_4 \xrightarrow{(a)} \text{N}_2 + \text{N}_2\text{H}_4 \quad \ldots (13)$$

$$\rightarrow \text{NH}_3 + \text{HN}_3 \quad \ldots (14)$$

Since the presence of $\text{HN}_3$ (hydrazoic acid) could not be experimentally proved, the reaction (b) is accepted for the removal of $\text{N}_2\text{H}_4$ from the reaction medium producing $\text{N}_2$ and $\text{N}_2\text{H}_4$ as the products of hydrazine oxidation.

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References