Redox Chemistry of Neptunium in Solutions of Nitric Acid

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Neptunium Redox Chemistry

- Coexistence of three oxidation states in acidic solutions
  - NpO$_2^+$, NpO$_2$$^2+$, Np$^4+$

- Disproportionation of NpO$_2^+$ in strongly acidic solutions
  \[
  \text{NpO}_2^+ + 4\text{H}^+ \leftrightarrow \text{NpO}_2^{2+} + 2\text{H}_2\text{O}
  \]

- In UREX reprocessing solutions
  - NpO$_2$$^2+$ and Np$^4+$ are readily extracted
  - NpO$_2^+$ remains in the aqueous phase
    - Oxidize Np to NpO$_2$$^2+$ with V(V)
    - Reduce/Scrub NpO$_2$$^2+$ with AHA
$\text{Np(III, IV, V, VI)} = f(\text{HNO}_3)$


- Np(V)
- Np(IV)
Vanadium (V) with Np(V)

- Reduction potentials: $\text{VO}_2^+/\text{VO}^{2+} = 1.0 \, \text{V}$ and $\text{NpO}_2^{2+}/\text{NpO}_2^{+} = 1.15 \, \text{V}$
- This redox reaction is reversible:

$$
\text{NpO}_2^+ + \text{VO}_2^+ + 2\text{H}^+ \leftrightarrow \text{NpO}_2^{2+} + \text{VO}^{2+} + \text{H}_2\text{O}
$$

$$
\text{Np(VI)} + V(IV) \leftrightarrow \text{Np(V)} + V(V)
$$

$$
\frac{dx}{dt} = - \frac{d[Np(V)]}{dt} = k_1'' \cdot [Np(V)]^\alpha \cdot [V(V)]^\beta
$$

$$
+ \frac{d[Np(V)]}{dt} = k_2'' \cdot [Np(VI)]^\gamma \cdot [V(IV)]^\delta
$$

$$
\frac{dx}{dt} = k_1'' \cdot [Np(V)] \cdot [V(V)] - k_2'' \cdot [Np(VI)] \cdot [V(IV)]
$$
Reaction order with respect to concentration of Np(V) and V(V)

Effect of increasing initial \([\text{V}(5^+)]\) on reaction rate

- \(c_{\text{V(V)}} = 0.375 \text{ mM}\); \(c_{\text{Np(V)}} = 0.113-0.504 \text{ mM}\)
- \(c_{\text{Np(V)}} = 0.360 \text{ mM}, c_{\text{V(V)}} = 0.266-6.91 \text{ mM}\)
Initial rates of oxidation of Np(V) as f(H⁺)

Initial rates of oxidation

\[ \text{Initial rate (M·s}^{-1} \right) \]

Effect of [H⁺]

\[ \text{NpO}_2^{+} + \text{VO}_2^{+} + 2H^{+} \leftrightarrow \text{NpO}_2^{2+} + \text{VO}^{2+} + H_2O \]
Hydrolysis of Vanadium (V) in Acid

- Fast protonation equilibria of VO$_2^+$
- Transformation into two additional forms VO(OH)$^{2+}$ and VO$^{3+}$:

\[
VO_2^+ + H^+ \leftrightarrow VO(OH)^{2+}
\]

\[
VO_2^+ + 2H^2+ \leftrightarrow VO^{3+} + H_2O
\]

A simple electron transfer to VO$^{3+}$ leads to oxidation of Np(V):

\[
NpO_2^+ + VO^{3+} \rightarrow NpO_2^{2+} + VO^{2+}
\]

Speciation of V(V) =f[H$_3$O$^+$], [VO$_2^+$], VO(OH)$^{2+}$ and VO$^{3+}$ are given by:

\[
K_1 = \frac{[VO(OH)^{2+}]}{[VO_2^+][H^+]}
\]

\[
K_2 = \frac{[VO^{3+}]}{[VO_2^+][H^+]^2}
\]
Constant rate of oxidation

Assuming:
• NpO₂⁺ is the only form of Np(V) in acidic (HClO₄ or HNO₃) solution
• Speciation/hydrolysis of V(V) to VO³⁺

The forward (oxidation) reaction in a non-complexing acid is:

\[- \frac{d[Np(V)]}{dt} = k'' \cdot [NpO₂⁺] \cdot [VO³⁺] = \frac{k \cdot [H⁺]^2}{1 + K₁ \cdot [H⁺] + K₂ \cdot [H⁺]^2} \cdot [Np(V)] \cdot [V(V)]\]

Koltunov:  \( K₁ = 0.79 \text{ M}^{-1} \) and \( K₂ = 0.30 \text{ M}^{-2} \)
"true" rate constant \( k = 245 \pm 15 \text{ M}^{-3} \cdot \text{min}^{-1} \) (4.08 ± 0.25 M⁻³.s⁻¹)

Precek [OSU]:  "true" rate constant \( k = 4.35 \pm 0.18 \text{ M}^{-3} \cdot \text{s}^{-1} \)

where \( K₁, K₂ \) are constants for V(V)
Thermodynamic of activation reaction \( \text{Np(V)} + \text{V(V)} \)

<table>
<thead>
<tr>
<th>Data source</th>
<th>°C</th>
<th>( E_A ) kJ/mol</th>
<th>( \Delta H^* ) kJ/mol</th>
<th>( \Delta S^* ) J/K.mol</th>
<th>( \Delta G^* ) kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>4M HNO(_3) [OSU]</td>
<td>10-50</td>
<td>55±1</td>
<td>53 ± 1</td>
<td>-55.8±1.3</td>
<td>69.3±1.6</td>
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<tr>
<td>4M HClO(_4) [Koltunov]</td>
<td>25.5-46</td>
<td>56 ± 6</td>
<td>53± 6</td>
<td>-59±21</td>
<td>71.4± .2</td>
</tr>
<tr>
<td>2M HNO(_3) [Dukes]</td>
<td>24-50</td>
<td>49±12</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Eyring equation:

\[
\ln k_1'' = \frac{-E_A}{R \cdot T} + \ln A
\]

\[
k_1'' = \frac{k_B T}{h} \cdot e^{\frac{\Delta G^*}{RT}} = e \cdot \frac{k_B T}{h} \cdot e^{\frac{\Delta S^*}{R}} \cdot e^{\frac{-E_A}{RT}}
\]

Boltzmann=\( k_B = 1.38 \cdot 10^{-23} \) J K\(^{-1}\)
Planck = \( h=6.63 \cdot 10^{-34} \) J
\( R =8.314 \) J-K\(^{-1}\)mol\(^{-1}\)
\( T = 298.15K = 25°C \)
Reduction of Np(VI) by HNO₂

\[ \text{NpO}_2^{2+} + \frac{1}{2} \text{HNO}_2 + \frac{1}{2} \text{H}_2\text{O} \xrightleftharpoons[catal. \text{HNO}_2]{\rightleftharpoons} \text{NpO}_2^{+} + \frac{3}{2} \text{H}^+ + \frac{1}{2} \text{NO}_3^- \]

Standard redox potentials (in volts) for U, Pu, Np and 1M HNO₂/HNO₃

[Miles, 1990; Drake, 1990]
<table>
<thead>
<tr>
<th>REDUCTANT</th>
<th>T (°C)</th>
<th>Rate Const (s(^{-1}))</th>
<th>Source</th>
<th>Rate constant</th>
</tr>
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<tbody>
<tr>
<td>Acetohydroxamic Acid</td>
<td>10</td>
<td>2500</td>
<td>1</td>
<td>2nd order</td>
</tr>
<tr>
<td>Formohydroxamic Acid</td>
<td>22</td>
<td>1174</td>
<td>2</td>
<td>2nd order</td>
</tr>
<tr>
<td>Phenyl hydrazine</td>
<td>22</td>
<td>44</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>U(IV)</td>
<td>22</td>
<td>15.7</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>N,N-ethyl(hydroxyl)ethyl hydroxylamine</td>
<td>22</td>
<td>4.5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Hydroxyethyl hydrazine</td>
<td>22</td>
<td>4</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Hydroxylamine</td>
<td>22</td>
<td>3.5</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Dimethyl hydroxylamine</td>
<td>22</td>
<td>3.2</td>
<td>3</td>
<td></td>
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<tr>
<td>Acetaldoxime</td>
<td>22</td>
<td>3</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>1,1-dimethyl hydrazine</td>
<td>22</td>
<td>1.6</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Methyl hydrazine</td>
<td>22</td>
<td>0.69</td>
<td>3</td>
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<tr>
<td>Isopropyl hydroxylamine</td>
<td>22</td>
<td>0.52</td>
<td>3</td>
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<tr>
<td>Methyl hydroxylamine</td>
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<tr>
<td>Diethyl hydroxylamine</td>
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<td>0.28</td>
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<tr>
<td>Hydrazine</td>
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<td>0.17</td>
<td>3</td>
<td></td>
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<tr>
<td>Isobutyaldehyde</td>
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<td>0.05</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Butyraldehyde</td>
<td>22</td>
<td>0.001</td>
<td>7</td>
<td></td>
</tr>
</tbody>
</table>

1  A Study of the Kinetics of the Reduction of Neptunium(VI) by Acetohydroxamic Acid in HClO\(_4\), Mat Sci Eng, 2009
2  A Preliminary Study of the Reduction of Np(VI) by Formohydroxamic Acid using Stopped-Flow Near-Infrared Spectrophotometry, Radioch Acta, 2000
5  The Reduction of Plutonium(IV) and Neptunium(VI) Ions by N,N-ethyl(hydroxyl)ethyl hydroxylamine in Nitric Acid, Radiochimica Acta.
6  The Reduction of Neptunium and Plutonium Ions by Acetaldoxime in Nitric Acid, Radiochimica Acta.
7  Nuclear Technology, 102, 341, 1993.
Reduction of Np(VI) by HNO$_2$

\[
NpO_2^{2+} + \frac{1}{2} HNO_2 + \frac{1}{2} H_2O \xrightleftharpoons[\text{catal. HNO}_2]{\text{NpO}_2^{+}} \rightarrow NpO_2^{+} + \frac{3}{2} H^+ + \frac{1}{2} NO_3^{-}
\]

Radiolysis of HNO$_3$, $aq$ $\rightarrow$ mainly gaseous compounds: H$_2$, O$_2$ and N$_2$
significant amounts of HNO$_2$ and H$_2$O$_2$

\[
HNO_2 + H_2O_2 \rightarrow HNO_3 + H_2O
\]

Hydrogen peroxide:
• not present in post-irradiated solutions, if the production of HNO$_2$ is significantly higher
• i.e., it happens in solutions with concentration of [HNO$_3$] $>$ 0.5 M
Rad Production of HNO$_2$

Radiation yield of HNO$_2$ in aq solutions:

• proportional to concentration of nitrate anion
• decreases with acidity [H+]
• In 0.1M HNO$_3$ + 5.9M NaNO$_3$ 3 x higher than in 6M HNO$_3$
• low LET radiation like β and γ has radiation yields around 0.25 mM/kGy in 1M HNO$_3$
• α radiation yields are approximately two times lower$^a, b$

Managing Np Oxidation State

\[ NpO_2^{2+} + \frac{1}{2} HNO_2 + \frac{1}{2} H_2O \xrightleftharpoons[catal. HNO_2]{\text{catal. HNO}_2} NpO_2^+ + \frac{3}{2} H^+ + \frac{1}{2} NO_3^- \]

Redox buffering conditions:
- managing concentration \([NO_2^-]\)
- Difficult, \(HNO_2\) also extracted by TBP
- Using \(HNO_2\) scavengers:
  - Acetamide
  - Methylurea
  - Dimethylurea
Acetamide:

- similar to the reaction of other primary amide (e.g. urea)
- production of N\textsubscript{2}(gas)
- rate of the reaction – slow*
- considerably slower scavenger of HNO\textsubscript{2} than methylurea


\[
CH_3CONH_2 + HNO_2 \rightarrow CH_3COOH + N_2 + H_2O
\]
**Nitrosation Reaction**

**Mechanism:**
- protonation of HNO$_2$ $\rightarrow$ intermediate NO$^+$
- NO$^+$ attacks the carbonyl oxygen
- followed by deprotonation and rearrangement of the NO group
- NMU is not reactive towards Np(VI) anymore $\rightarrow$
- MU functions as an efficient inhibitor of Np(VI) reduction by HNO$_2$

Nitrosation and irradiation of MU

Absorption spectrum of HNO₂ and nitrosomethylurea (NMU) in HNO₃ after addition of methylurea (MU). The spectra are clearly distinguished.

Spectrum of 10mM NaNO₂ and variable [MU] after irradiation with 40.5 kGy.

4M HNO₃
Effect of addition of vanadium-V

**Observed:**
- Irradiated, V(V) had no effect on the final redox speciation of neptunium,
- No Np(VI), even with a 5-fold excess of V(V)

**Conclusion:**
- Vanadium (V) was also reduced to V(IV) during the irradiation, but not directly by HNO₂;
- More likely by Np(V) generated by reduction of Np(VI) by HNO₂
- (or another intermediate products of radiolysis)
Effect of combined additives on Np-redox

Irradiated solutions:

- 2 mM Np(VI) in 4 M HNO₃, various [V(V)] and[MU] (10 mM=5x[Np])
- Dose: 0-61 kGy.
- Initial ratio of Np(VI):Np(V) = 95:5.

Synergistic effect expected:

- Scavenging of HNO₂ by MU undergoes simultaneously with oxidizing Np(V→VI) by V(V):
  - If any HNO₂ is produced, it is scavenged by MU
  - If any Np(V) produced/reduced by HNO₂, it is re-oxidized back to Np(VI) by V(V).
Effect of combined additives on Np after irradiation

Observed:

• Neither the presence of MU or V(V), nor their combination did affect the reduction of Np(VI) to Np(V) at all with respect to the case with no MU and V(V) addition.
• The ratio Np(VI):Np(V)=95:5 decreases to 50:50.

Results suggest:

• [HNO]₂ larger than estimated
• studied scavengers interact also with other intermediate products of radiolysis [Kazinjian, 1970]
• Higher concentrations of the selected additives (in the order of 100mM) should be applied to prevent reduction of Np(VI)
Reference: non-irradiated

50 (...) and 100 (-) mM methylurea - reference

Ratio Np(VI):Np(V) dropped to ~75:25
Fig. 4. Absorption spectrum of Np ions in 4.0 M HNO₃ at 22°C. ——, Np(III); . . . ., Np(IV); ———, Np(V); . . . ., Np(VI).
However, higher concentrations of the selected additives (in the order of 100mM) may have an opposite effect than desired: Reduction of Np(VI). At 60kGy Np(VI):Np(V):Np(IV) = 0:10:90
Radiolytic decrease of [MU]
Conclusion

• MU is gradually decomposed with a rate 0.7 mM/kGy (approx.)
• Higher concentration of MU scavenger can promote reduction of Np(VI), even up to Np(IV)
• However, if it is manageable; Np(IV) can work, too.

Acknowledgment

Funding: US DOE/NERI program
1.0 V for $\text{VO}_2^+/\text{VO}^{2+}$ and 1.15 V for $\text{NpO}_2^{2+}/\text{NpO}_2^+$
1.1 V for $\text{PuO}_2^{2+}/\text{Pu}^{4+}$