Sonochemical Redox Reactions of Pu(III) and Pu(IV) in Aqueous Nitric Solutions

Matthieu Virot †, Laurent Venault ‡, Philippe Moisy ‡, Sergey I. Nikitenko†

Proposed mechanism for hydroxylamine formation:

In the presence of hydrazinium nitrate:

\[
\text{NH}_2\text{-NH}_3^+ + \text{HO}^+ + \text{H}^+ \rightarrow \text{NH}_2\text{OH}_2^+ + ^\circ\text{NH}_3^+
\]

\[
^\circ\text{NH}_3^+ + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{HO}^+
\]

In the presence of sulfamic acid:

\[
\text{NH}_2\text{SO}_3\text{H} + \text{HO}^+ + \text{H}^+ \rightarrow \text{NH}_2\text{OH}_2^+ + ^\circ\text{SO}_3\text{H}
\]

\[
^\circ\text{SO}_3\text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3 + \text{HO}^+
\]
Figure S1: Sonolysis (20 kHz, Ar, 26°C, 0.52 W.mL\(^{-1}\)) of a -10 mM Pu(III) solution in 1 M HNO\(_3\) – 0.1 M [N\(_2\)H\(_5\)][NO\(_3\)] evidencing its sonochemical oxidation to Pu(IV) with \textit{in-situ} generated H\(_2\)O\(_2\).
Figure S2: Regression evidencing the first order reaction mechanism observed for the sonochemical reduction of Pu(IV) in 1 M HNO$_3$ – 0.1 M NH$_2$SO$_3$H.

\[
k' = 5.7 \times 10^{-3} \text{ min}^{-1}
\]
Figure S3: Comparison of \( W_0(\text{Pu}^{IV}) \) and \( W_0(\text{H}_2\text{O}_2) \) as a function of \( P_{ac} \). Linear extrapolation for plutonium decrease allow to determine a \( P_{ac} \) threshold of 0.17 W.mL\(^{-1}\) required to observe Pu(IV) reduction.
Figure S4: Regression evidencing the first order reaction mechanism observed for the sonochemical reduction of Pu(IV) in 1 M HNO$_3$ – 0.1 M [N$_2$H$_5$][NO$_3$].

\[ k' = 7.5 \times 10^{-3} \text{ min}^{-1} \]
Figure S5: Comparison of Pu(IV) reduction and Pu(III) appearance in 1 M HNO₃ / 0.1 M [N₂H₅][NO₃] in the presence or absence of 0.1 M [N₂H₅][NO₃] under ultrasound (20 kHz, Ar, 0.52 W.mL⁻¹, 26°C) or stirring.