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► **To cite this version:**

Matthieu Viot, Laurent Venault, Philippe Moisy, Sergey I. Nikitenko. Sonochemical redox of Pu(IV) and Pu(III) in aqueous nitric solution. 14th meeting of the European Society of Sonochemistry, Jun 2014, Avignon, France. <hal-04765244>

HAL Id: hal-04765244

<https://hal.science/hal-04765244v1>

Submitted on 4 Nov 2024

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

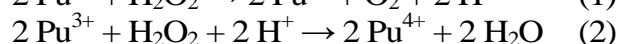
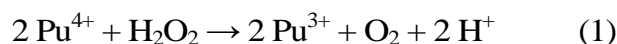
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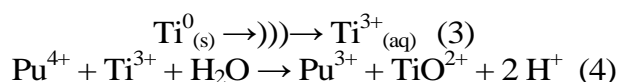
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The redox behavior of Pu(III) and Pu(IV) is investigated in aqueous nitric solutions under 20 kHz ultrasound irradiation (0.28-0.52 W.mL⁻¹). Experiments are carried out in Atalante facility (Marcoule) in a dedicated glove box allowing the control of the various parameters. The experiments are performed under Ar atmosphere (100 mL.min⁻¹) at almost room temperature (25-29°C). Pu(IV) and Pu(III) are analyzed by using a UV-Vis-NIR spectrophotometer connected to the glove box with optic fibers and are respectively followed at 476 nm ($\epsilon = 73 \text{ cm}^{-1} \text{ M}^{-1}$), and 602 nm ($\epsilon = 33 \text{ cm}^{-1} \text{ M}^{-1}$).

In 1 M HNO₃, Pu(IV) solution are chemically stable under ultrasound irradiation while the sonolysis of Pu(III) in similar conditions leads to the rapid accumulation of Pu(IV). The oxidation reaction is complete and results from HNO₂ generation by HNO₃ sonolysis. In the presence of 0.1 M anti-nitrous reagents ([N₂H₅][NO₃], or NH₂SO₃H), the sonication of Pu(IV) in 1 M HNO₃ leads to the accumulation of Pu(III) in solution. The reduction process is found to be highly dependent upon the acoustic intensity and follows a first-order reaction law. The reduction is not complete and leads to a steady-state where Pu(IV) and Pu(III) coexist in solution. The process is attributed to the sonochemical generation of H₂O₂ resulting from the homolytic dissociation of water molecules. The steady state is attributed to the partial back oxidation of Pu(III) with H₂O₂. These observations are in agreement with what already noticed without ultrasound and can be explained by the reactions (1-2).^[1]



In this chemical system, the presence of anti-nitrous reagents allows the scavenging of HNO₂ and the subsequent accumulation of H₂O₂. H₂O₂ can be formed with higher accumulation rates than what observed in pure water due to a different mechanism of formation involving nitrate ions. Kinetics attributed to H₂O₂ accumulation are however found to be stoichiometrically lower than those attributed to Pu(IV) reduction. A complementary reduction step, related to the accumulation of Ti particles in solution, is proposed. Sonotrode tips made out of titanium alloy may liberate particles during sonolysis due to the implosive collapse of acoustic bubbles at the vicinity of the probe.^[2] These particles, normally highly passivated in nitric media, can be solubilized under ultrasound and play a redox behavior in solution particularly with Ti(III), a powerful reducing agent.



References

[1] Cleveland J. M., The Chemistry of Plutonium, American Nuclear Society, La Grange Park. **1979**.

[2] Virot M., Chave T., Nikitenko S. I., Shchukin D. G., Zemb T., Möhwald H. **2010**.

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