Recent Advances in
Radiation-Induced Actinide
Redox Chemistry

September 2022

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Actinide Radiation Chemistry

\[ \text{H}_2\text{O} \rightleftharpoons e^-, H^+, \cdot\text{OH}, H_2, \text{H}_2\text{O}_2, \text{H}_{\text{aq}}^+ \]

\[ \text{NO}_3^- + e^-/H^+ \rightarrow \rightarrow \rightarrow \text{HNO}_2 \]

\[ \text{HNO}_3 + \cdot\text{OH} \rightarrow \text{NO}_3^- + \text{H}_2\text{O} \]
Reprocessing Used Nuclear Fuel

Solvent Extraction Reprocessing
Ligands/organic diluent: $\text{HNO}_3/\text{H}_2\text{O}$
($\pm$ additives)

Reprocessing Used Nuclear Fuel

Complexation Effects

Fig 1. Results of the Fukui function calculations performed on M-TEDGA complexes. Color scales depict the values of the Fukui function calculated in Å³. (a) [Nd(TEDGA)₃(NO₃)]₃, (b) [Nd(TEDGA)₃]Cl₃, (c) [Am(TEDGA)₃(NO₃)]₃, and (d) [Am(TEDGA)₃]Cl₃.

“...in the presence of macroconcentration of lanthanides and actinides, TODGA degradation by radiolysis is minimal and does not generate problematic degradation products.” Kimberlin et al., PCCP, 2022, 24, 9213.
Research Goals

1. Understand the basic radiation chemistry of the actinides in formally non-complexing media.

2. Elucidate the mechanisms underpinning the impact of actinide complexation on ligand radiolysis.

3. Develop multiscale modeling codes for the prediction of radiation-induced chemistry, speciation, and transport of the actinide series in any media.

• https://cr2.inl.gov/SitePages/Home.aspx
• https://inl.gov/article/center-for-radiation-chemistry-research-takes-a-forgotten-science-into-the-future/
Radiation Chemistry Techniques
Electron Pulse Radiolysis

Transients are detected by optical absorption changes.

0 V
Time
Light Intensity
Radical Isolation

- **Hydrated Electron (e_{aq}^-):** HClO₄/0.5 M tBuOH/N₂-saturated.
- **Hydrogen Atom (H•):** ~ 100 μM PCB/HClO₄/50 mM tBuOH/N₂-saturated.
- **Hydroxyl Radical (•OH):** ~ 100 μM KSCN/10 mM HClO₄/N₂O-saturated.
- **Nitrate Radical (•NO₃):** ~ 6.0 M HNO₃/N₂O-saturated.
- **Dodecane Radical Cation (RH•⁺):** 0.5 M DCM/n-dodecane.

> Transients are detected by optical absorption changes.
Radiation-Induced Actinide Redox Chemistry
Non-Traditional Oxidation States…

Impact of $f$-element Complexation on Radiolytic Behavior
**f-element Complexes of HEH[EHP]**

- **Methodology:** $\Delta[\text{HEH}[\text{EHP}]]/[\text{M} \{\text{HEH}[\text{EHP}]\}_2\text{_3}]$ in 0.5 M DCM/$n$-dodecane; $\text{RH}^{++}$ decay measured at 800 nm over 200 ns using the BNL Laser Electron Accelerator Facility (LEAF).

Size Matters…

- **Computations:** Geometry optimization using ADF2020 (*GGA OPBE functional + ZORA/STO-TZP basis set for all atoms*); Wave functions using ORCA (*Hybrid PBE0 functional + DKH-def2-SVP/DKH-def2-TZVP/SARC-DKH-TZVP*); and QTAIM metrics obtained from DFT wave functions using the AIMALL software.

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Steady-State Impact?

- **Steady-State Gamma Irradiations**: Cobalt-60 irradiation of 30 mM HEH[EHP] under organic only (■) and loaded with 2.5 mM La(III) from PIPPS/HNO$_3$ solution (●). Dose constants (d) were calculated from linear fits to $[\text{La}([\text{HEH}[\text{EHP}]]_2)_3]$ vs. absorbed gamma dose.

\[
d(\text{HEH}[\text{EHP}]) = 4.75 \times 10^{-4} \text{ kGy}^{-1}
\]
\[
d([\text{La}([\text{HEH}[\text{EHP}]]_2)_3]) = 6.55 \times 10^{-4} \text{ kGy}^{-1}
\]
Uranyl Complexes of TBP, DEHBA, and DEHiBA

- $\text{UO}_2^{2+}$ complexation had negligible effect on the reaction of TBP with RH•+, $k(T\text{BP} + RH\cdot+) = (1.3 \pm 0.1) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.
- For DEHBA and DEHiBA, $\text{UO}_2^{2+}$ complexation afforded a $2.6\times$ and $1.4\times$ increase in their respective rate coefficients, respectively.

Changes in Reaction Mechanism

Electron/Hole Transfer

\[ \text{RH}^{\bullet^+} + \text{Ligand} \rightarrow \text{RH} + [\text{Ligand}]^{\bullet^+} \]

Proton Transfer

\[ \text{RH}^{\bullet^+} + \text{Ligand} \rightarrow \text{R}^\bullet + [\text{Ligand} (+\text{H})]^+ \]

Table 1  Electronic structure calculation free energy (\( \Delta G \)) values for the reaction of RH\(^{\bullet^+} \) with TBP, DEHBA, and DEHiBA for electron/hole transfer and proton transfer scenarios

<table>
<thead>
<tr>
<th>Ligand</th>
<th>( \Delta G_{\text{electron/hole transfer}} ) (eV)</th>
<th>( \Delta G_{\text{proton transfer}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBP</td>
<td>0.16</td>
<td>-0.36</td>
</tr>
<tr>
<td>DEHBA</td>
<td>-0.88</td>
<td>-0.60</td>
</tr>
<tr>
<td>DEHiBA</td>
<td>-0.90</td>
<td>-0.57</td>
</tr>
</tbody>
</table>
Transuranic Complexation…

- **NpO$_2^{2+}$** complexation by **TBP** afforded ~3× faster rate of reaction with **RH•+**, and over an order of magnitude increase for complimentary **DEHBA** and **DEHiBA** complexes.
- Evidence for electron transfer with the complexed metal center?

What about Pu complexes?

Conclusions

• Actinide radiation chemistry is as fundamental to the actinides as their $5f$ electrons.

• “Unbound” actinides attain exotic radiation-induced transient oxidation states with lifetimes sufficient to propagate chemistry.

• Actinide complexation has significant effects on the radiation robustness of their complexes.

• Overall, the presented data provide important missing information that will augment current and future studies into the unique chemistry of these elements and their periodicity.
Acknowledgements
The INL *Aqueous Separations and Radiochemistry* group and the *Center for Radiation Chemistry Research* are seeking to add an enthusiastic, self-motivated Post-Doctoral Research Fellow and/or Staff Scientist to their team.

An ideal candidate(s) would have previous experience with:

- organic and/or inorganic synthesis as well as characterization techniques used for validation;
- previous familiarity with vitrification, radiation, and/or actinide chemistry is favorable;
- and seeking funds through grant proposal writing.

If interested, please contact either Colt Heathman (colt.heathman@inl.gov), Corey Pilgrim (corey.pilgrim@inl.gov), Melissa Warner (melissa.warner@inl.gov), and/or myself (gregory.horne@inli.gov) for more information.