Radiochemistry Webinars

Nuclear Fuel Cycle Series

• Radiation Chemistry at the Back End of the Nuclear Fuel Cycle

In Cooperation with our University Partners
Meet the Presenters...

Dr. Bruce Mincher

Bruce Mincher, Ph.D., is a Directorate Fellow Scientist in the Aqueous Separations and Radiochemistry Department at Idaho National Laboratory (INL). He holds a Ph.D. and an M.S. in chemistry from the University of Idaho and a B.S. in biology from State University of New York, Albany. He designs and conducts experimental research in radiation chemistry, including solvent extraction ligands in organic solution, reactions of organic compounds with nitrogen-centered radicals in aqueous solution, and the use of irradiation to destroy persistent environmental pollutants in drinking and natural waters. He also designs and conducts experimental research in radiochemistry, especially actinide chemistry, including the use of higher oxidation states of americium, and spectroscopic observation of those oxidation states. Dr. Mincher currently represents the INL on the DOE σ-team investigating actinide/lanthanide separations for the Fuel Cycle R&D program. He is an affiliate faculty member at the University of Idaho and Oregon State University, where he serves on the committees of, and directs research for, graduate students. Dr. Mincher has 70 publications in peer-reviewed journals and has contributed to 17 books. He was a recipient of the Idaho National Laboratory Director’s Distinguished Scientific Achievement award in 2009 and was named the Idaho Academy of Science Distinguished Scientist of the Year in 2014. He also received an Emmy for his on-camera work in instructional television for the series, “Understanding Chemistry in our World,” in 2010.

Dr. Stephen Mezyk

Dr. Mezyk earned his doctorate in Physical Chemistry from the University of Melbourne, Australia, in 1989. Following three postdoctoral appointments at the University of Calgary, Canada, the University of Notre Dame, Indiana, and the University of Saskatchewan, Canada, he joined Atomic Energy of Canada Ltd. (AECL) in 1992. Following 8 years of work as a radiation and reactor research chemist at AECL he accepted a Research Associate position at University of North Carolina in Wilmington, before joining the Department of Chemistry and Biochemistry at CSULB in 2001. He is now a Full Professor at CSULB, with current research interests based in the free radical kinetic, mechanistic, and thermodynamic chemistry occurring in the remediation of chemically contaminated water/soil systems, and in nuclear waste separation, storage and remediation. Dr. Mezyk has been very active in research, particularly with undergraduate and Masters students, with now over 150 peer-reviewed articles and 250 conference presentations. Much of his research has been conducted at Department of Energy Laboratories, where he holds concurrent scientist/contract appointments. He designs and conducts experiments in radiation chemistry, which investigate radical chemistry in the aqueous and organic phases. This research has been funded by multiple Department of Energy, National Science Foundation, Water Research Foundation, and Research Corporation external grants. Dr. Mezyk was awarded the Outstanding Professor Award by CSULB in 2014. He also received an Emmy for his on-camera work in instructional television for the series, “Understanding Chemistry in our World,” in 2010.

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Radiation Chemistry at the Back End of the Nuclear Fuel Cycle

Dr. Steve Mezyk, California State University Long Beach
Dr. Bruce Mincher, Idaho National Laboratory
Radiation chemistry

- The study of the effects of radiation on materials: in our case, the aqueous and organic solutions used in solvent extraction for the nuclear fuel cycle.

- **Aqueous solution**: aqueous nitric acid.

- **Organic solution**: an alkane diluent containing a metal complexing agent, or ligand.
Different types of radiation

- Difference between $\alpha$ and $\beta/\gamma/e^-$ radiation based on Linear Energy Transfer (LET)

**Low LET $\beta/\gamma/e^-$**
Sparse deposition of energy
Radical species formed far apart

**High LET $\alpha/n/Recoil$**
Dense deposition of energy
Radical species formed close together

Why do we care about radiation chemistry?

- Reduction in ligand concentrations are accompanied by decreases in extraction efficiency.

- Radiolysis products are often new complexing agents and may decrease separation factors.

- Products are often hydrophilic complexing agents that impair stripping.

- Radiolytically-produced reactive species may alter metal valence states.

*EXAMPLES OF EACH WILL BE SHOWN THAT ARE RELEVANT TO THE FUEL CYCLE...*
Direct vs. Indirect Radiolysis

- **Direct**: The direct interaction of the particle formed with the compound (ligand). This happens more for high LET and in proportion to the abundance of the ligand.

- **Indirect**: Interaction of the radiation with the diluent to produce reactive radical and ionic species that then diffuse into solution to react with ligands. This is more common in our systems.
Aqueous phase reactive species

The water:
- $\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + e^-_{\text{aq}}$
- $\text{H}_2\text{O}^+ \rightarrow \text{H}^+ + \cdot\text{OH}$
- $\text{H}_2\text{O} \rightarrow \cdot\text{H} + \cdot\text{OH}$
- $\cdot\text{H} + \cdot\text{H} \rightarrow \text{H}_2$
- $\cdot\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2$

The acid:
- $\text{HNO}_3 \rightarrow \cdot\text{HNO}_3^+ + e^-_{\text{aq}}$
- $\cdot\text{HNO}_3^+ \rightarrow \text{H}^+ + \cdot\text{NO}_3$
- $\text{NO}_3^- + e^-_{\text{aq}} \rightarrow \cdot\text{NO}_3^{2-}$
- $\cdot\text{NO}_3^{2-} + \text{H}^+ \rightarrow \cdot\text{NO}_2 + \text{OH}^-$
- $\text{HNO}_3 \rightarrow \text{HNO}_2 + \cdot\text{O}$

*It’s not as bad as it looks... trust us...*
Organic phase reactive species

- Dodecane as an example:

\[ \text{CH}_3(\text{CH}_2)_{10}\text{CH}_3 \rightarrow \text{e}^-_{\text{aq}} + \cdot\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3^+ \]

- The positively charged species is the dodecane radical cation—we will hear much more about it!

- \[ \text{CH}_3(\text{CH}_2)_{10}\text{CH}_3 \rightarrow \cdot\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2 + \cdot\text{H} \]

- \[ \text{CH}_3(\text{CH}_2)_{10}\text{CH}_3 \rightarrow \cdot\text{CH}_3 + \cdot(\text{CH}_2)_{10}\text{CH}_3 \]

- A suite of carbon-centered radical reaction possibilities. These can even add to each other to produce higher molecular weight alkanes.
What do we want to know?

Need to quantitatively understand:

• Radical reaction kinetics
  - rate constants

• What are the products formed?
  - are they a problem?

• Reaction mechanisms
What do we want to know?

Need to quantitatively understand:

• Radical reaction kinetics
  - rate constants

• What are the products formed?
  - are they a problem?

• Reaction mechanisms
Ionization produces electrons

- The common product of every direct radiolysis reaction was electrons.
- But they really are not important in aerated, acidic solutions:

\[ \text{e}^-_{\text{aq}} + \text{H}^+ \rightarrow \text{H} \quad k = 2.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \]
\[ \text{e}^-_{\text{aq}} + \text{NO}_3^- \rightarrow \text{NO}_3^{2-} \quad k = 9.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \]
\[ \text{e}^-_{\text{aq}} + \text{O}_2 \rightarrow \text{O}_2^- \quad k = 1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \]

These fast reactions remove electrons from consideration as a species that might attack ligands.
What are the important radical reactions?

In order of their usual reactivity, \( \cdot \text{OH} > \cdot \text{NO}_3^- > \cdot \text{H} > \cdot \text{NO}_2 \)
Radicals react similarly:

Using \( \cdot \text{NO}_3 \) radical reactions as the example:

Electron transfer (fast): \( \cdot \text{NO}_3 + \text{CMPO} \rightarrow \text{NO}_3^- + [\text{CMPO}]^+ \)

Hydrogen atom abstraction (intermediate): \( \cdot \text{NO}_3 + \text{CMPO} \rightarrow \text{HNO}_3 + [\text{CMPO}]^- \)

Radical addition reaction (slow): \( \cdot \text{NO}_3 + \text{CMPO} \rightarrow [\text{CMPO}]\text{NO}_3 + \text{H}^- \)

The first two reactions lead to continued decomposition. The last reaction is why solutions turn yellow or orange when irradiated in contact with nitric acid. But its not the only way to nitate things in irradiated solution.
Hydrogen atom abstraction: TBP

- *H*-atom abstraction:
  \[(C_4H_9O)_3P=O + \cdot OH \rightarrow (C_4H_9O)_2(\cdot C_4H_8O)P=O + H_2O\]

- Oxygen addition to carbon-centered radical (peroxyl radical formation):
  \[(C_4H_9O)_2(\cdot C_4H_8O)P=O + O_2 \rightarrow (C_4H_9O)_2P(=O)-O-C_4H_8(OO)\cdot\]

- Peroxyl radical formation is fast in water (\(\sim 3-5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}\)), and is the common fate of carbon-centered radicals in oxygenated solution.
Peroxyl radical decay

- There are multiple mechanisms for peroxyl radical decay, shown here is superoxide elimination:

\[
(C_4H_9O)_2P(=O)-O-C_4H_8(OO)\cdot \\
\rightarrow \cdot O_2^- + [(C_4H_9O)_2P(=O)-O-C_4H_8]^+
\]

- The produced cation then hydrolyses
TBP Cation Hydrolysis

- \[ ((C_4H_9O)_2P(=O)-O-C_4H_8]^+ + H_2O \rightarrow (C_4H_9O)_2P(=O)-O^- + C_3H_7CHO + 2H^+ \]

- Dibutylphosphoric acid (HDBP) and butyraldehyde are the measured products.

- HDBP is a complexing agent that interferes with separation factors for uranium, and precipitates plutonium. It partitions between the phases.

- HDBP is why caustic scrub steps are used to clean up irradiated PUREX solvent.

- Continued irradiation generates monobutylphosphoric acid (MDBP) and even phosphate (PO_4^{3-}).
Peroxyl radical decay

- Other mechanisms for peroxyl radical decays:

- Let $(C_4H_9O)_2P(=O)-O-C_4H_8(OO)\cdot = RCH_2OO\cdot$

- $2RCH_2OO\cdot \rightarrow RCH_2OH + RCHO + O_2$ (Russell)
  $\rightarrow RCHO + RCHO + H_2O_2$ (Bennett)
  $\rightarrow RCHO\cdot + RCHO\cdot + O_2$
Aqueous kinetics of •H-atom abstraction

<table>
<thead>
<tr>
<th></th>
<th>TBP</th>
<th>HDBP</th>
</tr>
</thead>
<tbody>
<tr>
<td>•OH</td>
<td>5.0 x 10^9 M^{-1} s^{-1}</td>
<td>4.4 x 10^9 M^{-1} s^{-1}</td>
</tr>
<tr>
<td>•H</td>
<td>1.8 x 10^8</td>
<td>1.1 x 10^8</td>
</tr>
<tr>
<td>•NO_3</td>
<td>4.3 x 10^6</td>
<td>2.9 x 10^6</td>
</tr>
<tr>
<td>•NO_2</td>
<td>&lt; 2 x 10^5</td>
<td>&lt; 2 x 10^5</td>
</tr>
</tbody>
</table>

•OH is very fast, •NO_2 is too slow to be measured. Most TBP degradation is due to the reactions with •OH.

Trend is the same, but slower for HDBP- this reflects less sites for radical reaction.
Generally the •OH and •NO$_3$ reactions are fast... e.g. for Cs-7SB modifier

- $\text{•NO}_3 \quad k = 2.90 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
- $\text{•NO}_2 \quad k < 10^6 \text{ M}^{-1} \text{ s}^{-1}$
- $\text{•OH} \quad k = 2.19 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
- $\text{•H} \quad k = 1.88 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$
How do we make these measurements?

If the produced radical species has an absorbance in the UV/Vis spectral region we can measure the decrease in absorbance with time, at different ligand concentrations ($A = \varepsilon c l$).

*Example is $\cdot\text{NO}_3$ in $t$-butanol solution*
LINAC UV/Vis at University of Notre Dame

Note flow-through cell...
Control panel at NDRL LINAC
Measuring Rate Constants

\[ \text{•NO}_3 + \text{Cs-7SB} \rightarrow \text{product} \]

Slope of the curve is the bimolecular rate constant \((k)\) in \(M^{-1} \text{s}^{-1}\)

\[
\text{Rate} = k [\bullet \text{NO}_3][\text{Modifier}]
\]

The rate at any given time is the \(G\)-value (umol J\(^{-1}\)), which is not a constant.
But what if the radical has no useful UV/vis absorbance? (like •OH)

- **Use competition kinetics** - add a chemical (KSCN) that generates a known absorbance by reaction with •OH in competition with your ligand.

  *An electron transfer reaction between •OH and SCN⁻ produces (SCN)₂⁻ which absorbs at 475 nm*

  •OH + 2SCN⁻ → (SCN)₂⁻ + OH⁻ \[ k_{SCN⁻} = 1.05 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \]

  *Can compete with the •H-atom abstraction by •OH from TBP:*

  •OH + (C₄H₉O)₃P=O → (C₄H₉O)₂(•C₄H₈O)P=O + H₂O \[ k_{TBP} \]

- Solve equations to get:

  \[
  \frac{Abs^o (SCN)^{-2}}{Abs (SCN)^{-2}} = 1 + \frac{k_{TBP}[TBP]}{k_{SCN^{-}}[SCN^{-}]}
  \]
• OH competition kinetics

The absorbance of \((SCN)_2^-\) decreases as the ligand concentration increases.

Rearrange integrated equation to give

\[
\frac{1}{\text{Abs}(SCN)_2^-} = \frac{1}{\text{Abs}^o (SCN)_2^-} + \frac{1}{\text{Abs}^o (SCN)_2^-} \ast \frac{k_{TBP}[TBP]}{k_{SCN^-}[SCN^-]}
\]

Plot of \(1/\text{Abs}(SCN)_2^-\) vs \([TBP]/[SCN^-]\),

\[k_{TBP} = \text{slope/intercept} = 5.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}\]
• H competition kinetics

• Use tetracycline as standard probe molecule. Upon addition of ligand, growth kinetics get faster – 49 µM and 221 µM TBP.

• From change in growth kinetics as function of [TBP] get second-order rate constant.

• Slope of second-order plot corresponds to
  \[ k = (1.8 \pm 0.2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \]
Factors affecting rate constants

- For \( \cdot \text{NO}_3 \) as the example:

<table>
<thead>
<tr>
<th>Condition</th>
<th>Rate Constant ((k))</th>
</tr>
</thead>
<tbody>
<tr>
<td>free CMPO (aq)</td>
<td>(1.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1})</td>
</tr>
<tr>
<td>free CMPO ((t\text{-butanol}))</td>
<td>(3.2 \times 10^8)</td>
</tr>
<tr>
<td>(\text{Nd(CMPO)}_3^{3+} (t\text{-butanol}))</td>
<td>(3.4 \times 10^9)</td>
</tr>
<tr>
<td>(\text{Eu(CMPO)}_3^{3+} (t\text{-butanol}))</td>
<td>(2.5 \times 10^9)</td>
</tr>
</tbody>
</table>
Organic Phase Radical Cation Chemistry


“The results showed n-dodecane has a *sensitization effect* on the radiolysis of [TODGA]...”

This is not unique to dodecane...
Organic Phase Radical Cation Chemistry

- Electron transfer from the dodecane radical cation:

\[ \text{CH}_3(\text{CH}_2)_{10}\text{CH}_3 \gamma \rightarrow e^-_{aq} + \cdot \text{CH}_3(\text{CH}_2)_{10}\text{CH}_3^+ \]

- \(\cdot \text{CH}_3(\text{CH}_2)_{10}\text{CH}_3^+ + \text{TODGA} \rightarrow \)

- \([\text{TODGA}]^+ + \text{CH}_3(\text{CH}_2)_{10}\text{CH}_3\)

- Whether this happens depends on the ionization potentials of the reactants

- If it happens, it happens quickly!
TODGA + dodecane radical cation = fast!

• To do reactions on the nanosecond time scale (vs. microsecond) we need picosecond long radiation pulses.

• LASER electron accelerator facility (LEAF) at Brookhaven (10 ps pulses of electrons)

• Same UV/Vis detection system approach
Very fast reactions

- Brookhaven National Laboratory (LEAF)
- For very fast measurements of $[C_{12}H_{26}]^{++}$

Time scale in nanoseconds
Control panel at LEAF
What do we want to know?

Need to quantitatively understand:

• Radical reaction kinetics
  - rate constants

• What are the products formed?
  - are they a problem?

• Reaction mechanisms?
How do we generate these products?

- Steady state irradiation performed using $^{60}\text{Co}$:

  - Shield doors open
  - Doors closed
  - Sample chamber inserted
Solutions irradiated over a series of absorbed doses:

- The irradiated samples are then analyzed with some appropriate technique. Examples:

**Decrease in [CMPO] vs. absorbed dose**

**Production of HNO2 in irradiated nitric acid**

**Loss of anisole and production of nitroanisoles in irradiated nitric acid**
TODGA irradiation under different solution conditions:

- G-value for loss of [TODGA] is the same for:
  - TODGA in dodecane
  - TODGA/dodecane in contact with 0.1 M HNO₃
  - TODGA/dodecane in contact with 2.5 M HNO₃
  - It’s the organic diluent, more evidence of the radical cation’s role in degradation of this ligand.
What do we want to know?

Need to quantitatively understand:

• Radical reaction kinetics
  - rate constants

• What are the products formed?
  - are they a problem?

• Reaction mechanisms?
How to form radiolysis products?

- Nitration can occur due to radical and ionic mechanisms:

  \[(\text{C}_4\text{H}_9\text{O})_2(\cdot\text{C}_4\text{H}_8\text{O})\text{PO} + \cdot\text{NO}_3 \rightarrow (\text{C}_4\text{H}_9\text{O})_2(\text{OC}_4\text{H}_8\text{NO}_3)\text{PO}\]

  \[(\text{C}_4\text{H}_9\text{O})_2(\cdot\text{C}_4\text{H}_8\text{O})\text{PO} + \cdot\text{NO}_2 \rightarrow (\text{C}_4\text{H}_9\text{O})_2(\text{OC}_4\text{H}_8\text{NO}_2)\text{PO}\]

- Nitrated TBP derivatives created by radical-radical addition.
N-radicals can also add to phenyl rings:

- OH radical mediated nitration is also known from atmospheric chemistry. These products of this Reaction were detected by mass spec for Cs-7SB.
Ring-opening can also occur:

Reactions like this are important in water treatment using radiation.
Ionic nitrations, catalyzed by HNO$_2$:

- $\text{HNO}_3 \rightarrow \text{HNO}_2 + \bullet\text{O}$
- $\text{HNO}_2 + \text{H}^+ \rightarrow \text{NO}^+ + \text{H}_2\text{O}$
- $\text{ArH} + \text{NO}^+ \rightarrow \text{ArHNO}^+$
- $\text{ArHNO}^+ \rightarrow \text{ArNO} + \text{H}^+$
- $\text{ArNO}^+ + \text{HNO}_3 \rightarrow \text{ArNO}_2 + \text{HNO}_2$

*This is where most aromatic nitration comes from in acidic irradiated solution.*
Nitration can have effects more important than color change:

Nitration sterically hinders the metal complexation site, double nitration completely suppresses extraction.
Dealkylation can be initiated by •H-atom abstractions, or possibly by electron transfer, (but not dissociative electron capture in acidic solution):

\[ \text{•OH} + \text{CMPO} \rightarrow \text{HOH} + [\text{CMPO}]^\cdot \]
\[ [\text{C}_{12}\text{H}_{26}]^{\cdot+} + \text{CMPO} \rightarrow \text{C}_{12}\text{H}_{26} + [\text{CMPO}]^{\cdot+} \]

The produced complexing agents are less soluble in the organic phase. The precipitate found in irradiated organic solution is a mixture of CMPO and its mono-isobutyl derivative.
Acidic products

- More deleterious products include acidic species that are soluble in the organic phase. HDBP was an example.

- For amides, this means C-N bond rupture.

- An acidic CMPO product is octylphenylethiophosphinylacetic acid:

\[
\begin{align*}
\text{Octylphenylphosphinylacetic acid} &\rightarrow \text{Octylphenylphosphinylacetic acid} + \text{Octylamine}
\end{align*}
\]

C-N bond cleavage favored in the presence of HNO₃. Figure shows it growing in at 0, 188 and 482 kGy.
Similar results for other amides

DMDOHEMA

TODGA

CMPO
Ether linkages are weak:

Decomposition of 18C6 crown ether initiated by •H-atom abstraction,

\[
\begin{align*}
\text{O} & \text{O} & \text{O} & \text{O} & \text{O} \\
\text{O} & \text{O} & \text{O} & \text{O} & \text{O} \\
\text{H} & & & & \\
\rightarrow & \text{H} & \rightarrow & \text{H} & \text{H}_2 \\
\end{align*}
\]

Decomposition of the ring next occurs by peroxyl radical formation:

\[
\begin{align*}
\text{O} & \text{H} & \text{O} & \text{O} & \text{O} & \text{O} \\
\text{O} & \text{O} & \text{O} & \text{O} & \text{O} \\
\text{O}_2 & \rightarrow & \text{O}_2 \\
\rightarrow & \text{Non-cyclic ox products}
\end{align*}
\]

Or by disproportionation:

\[
\begin{align*}
\text{O} & \text{H} & \text{O} & \text{O} & \text{O} & \text{O} \\
\text{O} & \text{O} & \text{O} & \text{O} & \text{O} \\
\text{H} & \rightarrow & \text{H} & \text{H} & \\
\rightarrow & \text{CH}_2 & \text{CH} & \text{H} & \\
\rightarrow & \text{O} & \text{O} & \text{O} & \text{O} & \text{O} \\
\end{align*}
\]
Ether linkages are weak:

DMDOHEMA:
An example of ligand design with radiolysis in mind:

If this linkage breaks, it protects the C-N bond and creates inoffensive products.
TODGA/T(EH)DGA radiolysis is similar

Products of C-C bond rupture are lowest abundance
Ionization of amides

- Once the amide has been ionized by electron transfer to the dodecane radical cation:

- “The C-H bonds corresponding to methyl group protons are substantially weakened... The C-N bonds exhibit the largest weakening.”

- *This is consistent with ether and amide bond rupture in DGAs, and amide bond rupture in CMPO.*
But what are the effects on solvent extraction?

- Little change in $D_{Am}$, due to production of new complexing agents from CMPO.

- But acidic radiolysis products interfere with stripping:

Increase in stripping distribution ratios for Am from 0.1 M CMPO irradiated in contact with several nitric acid concentrations.
Separation factors may deteriorate

Note the increase in $D_{\text{Am}}$ is greater than $D_{\text{Eu}}$
Metal Redox Chemistry

- Separations depend on the complexation of metals in preferred valence states.
- Np(VI) and Np(IV) are complexed and extracted by TBP, while Np(V) is not.
- In HNO$_3$, radiolysis promotes a mixture of Np(V) and Np(VI) regardless of the starting mixture.
Radiolytic Redox Chemistry of Np

Overall trend is reduction of Np(VI) to Np(V) by irradiation. But look at those first few kilogram!
A long-lived reactive species - HNO$_2$

\[ \text{HNO}_3 \xrightarrow{\gamma} \text{HNO}_2 + \text{O}^- \]

\[ \text{NpO}_2^+ + \frac{3}{2}\text{H}^+ + \frac{1}{2}\text{NO}_3^- \leftrightarrow \text{NpO}_2^{2+} + \frac{1}{2}\text{HNO}_2 + \text{H}_2\text{O} \]
But that long-lived species is in competition with short-lived oxidizers

- \( \text{NpO}_2^+ + \cdot \text{OH} \rightarrow \text{NpO}_2^{2+} + \text{OH}^- \) \( k = 4.30 \times 10^8 \text{ M}^{-1} \text{s}^{-1} \)

- \( \text{NpO}_2^+ + \cdot \text{NO}_3 \rightarrow \text{NpO}_2^{2+} + \text{NO}_3^- \) \( k = 8.10 \times 10^8 \text{ M}^{-1} \text{s}^{-1} \)

- These radicals are oxidizing but when a sufficient concentration of HNO\(_2\) is produced, after which the system goes reducing!

- It has been suggested that HNO\(_2\) may also be an oxidizing agent via production of \( \cdot \text{NO}_2 \):

- \( \cdot \text{NO}_2 + \cdot \text{NO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{N}_2\text{O}_4 + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{H}^+ + \text{NO}_3^- \)

- We could not oxidize NpV with NO\(_2\) (N\(_2\)O\(_4\)) sparging.
Some Concluding Ideas

• Can an easily ionized co-solvent protect ligands from the radical cation? “Electron donor.”

• Can’t avoid dealkylation products. But how harmful they are depends on their solubility in the respective phases. Co-solvent TBP helps keep dealkylation products in solution.

• Can’t entirely avoid acidic products of C-N bond cleavage. But if we can understand how acid protects CMPO, we may be able to protect other ligands.
What about $\alpha$ radiolysis?

- Little is known about impacts of alpha radiolysis under materials recovery solvent-extraction conditions.

- Important for high burnup fuels, where up to 75% of radiation-induced degradation caused by alpha irradiation.

<table>
<thead>
<tr>
<th>Source</th>
<th>Conditions</th>
<th>G-DBP ($\mu$mol J$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{60}$Co</td>
<td>Degassed/sealed</td>
<td>0.31</td>
</tr>
<tr>
<td>$^{60}$Co</td>
<td>Degassed/N$_2$O</td>
<td>0.23</td>
</tr>
<tr>
<td>$^{60}$Co</td>
<td>No pretreatment</td>
<td>0.15</td>
</tr>
<tr>
<td>Gamma</td>
<td>HNO$_3$ contacted</td>
<td>0.11</td>
</tr>
<tr>
<td>1.25 MeV e$^-$</td>
<td>Water saturated</td>
<td>0.09</td>
</tr>
<tr>
<td>Gamma</td>
<td>HNO$_3$ contacted</td>
<td>0.06</td>
</tr>
<tr>
<td>He ion ($\alpha$)</td>
<td>Sealed in quartz</td>
<td>0.07</td>
</tr>
<tr>
<td>Pu ($\alpha$)</td>
<td>HNO$_3$ contacted</td>
<td>0.002</td>
</tr>
</tbody>
</table>

Typical values for DBP formation for irradiated 30% TBP/n-dodecane show large variation.
How is $\alpha$ radiolysis different?
How is $\alpha$ radiolysis different?

Difference in radical yields:

- **Low LET ($\gamma$ in acidic water):**
  \[
  \text{H}_2\text{O} - \sqrt[3]{\sqrt[3]{\sqrt[3]{\sqrt[3]{\sqrt[3]{\sqrt[3]{}}}}}} \rightarrow 0.28 \cdot \text{OH} + 0.33 \cdot \text{H}^\bullet + 0.07 \text{H}_2\text{O}_2 + 0.05 \text{H}_2
  \]

- **High LET ($^{210}\text{Po}$ 5 MeV $\alpha$):**
  \[
  \text{H}_2\text{O} - \sqrt[3]{\sqrt[3]{\sqrt[3]{\sqrt[3]{\sqrt[3]{\sqrt[3]{}}}}}} \rightarrow 0.05 \cdot \text{OH} + 0.33 \cdot \text{H}^\bullet + 0.15 \text{H}_2\text{O}_2 + 0.16 \text{H}_2
  \]

- $e^-_{\text{aq}} + \text{H}_3\text{O}^+ \rightarrow \text{H}^\bullet$

- Difficult to measure alpha radiolysis yields
- No single technique is optimal
- Perform measurements using multiple techniques
- Pros and Cons for each method used
Alpha Radiolysis

Four complementary approaches used to obtain alpha radiolysis data

- $^{244}$Cm irradiations at Idaho National Laboratory
- $^{211}$At irradiations at Chalmers University of Technology, Sweden
- 5.0 MeV alpha ion-beam at University of Notre Dame
- TRIGA reactor at University of California, Irvine
$^{244}$Cm irradiations at INL

- Dissolved 0.6 mg of $^{244}$Cm ($t_{1/2} = 18.1$ yr, 5.8 MeV a) in 0.10 M HNO$_3$

**Pros:**
- Similar to large-scale extraction conditions
- High doses available

**Cons:**
- Radioactive solutions
211\textsuperscript{At} irradiations at Gothenburg, Sweden

\begin{itemize}
  \item $^{211}\text{At} \ (t_{1/2} = 7.2 \text{ h}, \ 6.8 \text{ MeV a})$
  \item $^{211}\text{At}$ prepared using Bi target: $^{209}\text{Bi} (\text{a, 2n})^{211}\text{At}$
\end{itemize}

**Pros:**
\begin{itemize}
  \item Similar to $^{244}\text{Cm}/$large-scale extraction conditions
  \item Short $t_{1/2}$ means residual $\alpha$ radioactivity is negligible!
  \item Product is $\beta \gamma$-emitter $^{207}\text{Bi} \ (t_{1/2} = 31.6 \text{ yr})$
\end{itemize}

**Cons:**
\begin{itemize}
  \item Only low doses available (GBq)
α ion-beam irradiations at Notre Dame

- Direct alpha ion beam radiolysis of solutions

**Pros:**
- Non-radioactive samples
- Tunable energy of α irradiation

**Cons:**
- Only low total doses available
- Short particle penetration into irradiation cell, makes experiments difficult
Nuclear reactor $\alpha$ irradiation at UCI

- UC – Irvine TRIGA
- $^{10}$B (n,\(\alpha\)) \(\gamma\)Li

Pros:
- Very high doses available
- Easy to perform experiments

Cons:
- Mix of $\alpha$ and $\gamma$ radiation
- B species present in samples
- Final samples can be radioactive
Our approach:

- γ-irradiation
- α-beam
- Reactor n,α
- α-isotopes

α-radiolysis measurements

Radical Kinetics / Stable Products / Extraction Studies

Predictive computer model
System of Interest: CMPO in dodecane

- CMPO (octylphenyl-N,N-diisobutylcarbamoylmethyl phosphine oxide)
- Used in TRUEX formulation, 0.1 – 0.2 M CMPO/1.1 M TBP in alkane diluent
- Designed to extract trivalent lanthanides and actinides
- Formulation used in contact with 3-4 M HNO$_3$ aqueous phase, and high radiation doses (estimated ≥ 2.5 kGy/yr)
- Measure loss of parent compound using different radiation (γ and α) and chemical conditions
- [CMPO] measured by HPLC using UV-detection$^1$

System of Interest: CMPO in dodecane

- $^{60}$Co CMPO irradiation
- No dose rate dependence found for CMPO loss over range $0.18 - 15.9$ kGy hr$^{-1}$
  - $G_1 = 0.145 \pm 0.008$
  - $G_2 = 0.034 \pm 0.017$
- CMPO-HNO$_3$ complex forms, results in apparent lower CMPO yield.
- Lower degradation in presence of nitric acid due to solvent radical cation reaction with HNO$_3$/NO$_3^-$?
System of Interest: CMPO in dodecane

- $\alpha$ radiolysis by ion-beam method (*)
- Shows similar CMPO loss to $\gamma$ measurements
- $-G_1 = 0.145 \pm 0.008$
- $-G_2 = 0.034 \pm 0.017$
System of Interest: CMPO in dodecane

- $^{244}\text{Cm} \alpha$ irradiations
  - Shows similar CMPO loss to $\gamma$ measurements for 3.0 M HNO$_3$ acid contact
  - $G_1 = 0.145 \pm 0.008$
  - $G_2 = 0.034 \pm 0.017$
System of Interest: CMPO in dodecane

- Higher dose irradiations
- Compare $^{244}\text{Cm}$ and reactor based $\alpha$-irradiation values

(□) $^{244}\text{Cm}$ with 0.10 M HNO$_3$
(○) Reactor for CMPO
(▽) Reactor CMPO with 0.10 M HNO$_3$
(△) Reactor CMPO with 3.0 M HNO$_3$

- Why different?
System of Interest: CMPO in dodecane

- CMPO product analyses: ESI-(MS)$^n$

\[ \gamma - \text{radiolysis} \]
\[ \text{green – most} \]
\[ \text{blue – some} \]

\[ \alpha - \text{radiolysis} \]
\[ \text{red – most} \]
\[ \text{pink - some} \]
TBP radiolysis:

- Reactor data for TBP and DBP
- Same $\gamma$ G-value from $^{137}$Cs source and reactor measurements
- No irradiation dose rate dependence

<table>
<thead>
<tr>
<th>Source</th>
<th>Conditions</th>
<th>G-DBP ($\mu$mol J$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{60}$Co</td>
<td>Degassed/sealed</td>
<td>0.31</td>
</tr>
<tr>
<td>$^{60}$Co</td>
<td>Degassed/N$_2$O</td>
<td>0.23</td>
</tr>
<tr>
<td>$^{60}$Co</td>
<td>No pretreatment</td>
<td>0.15</td>
</tr>
<tr>
<td>Gamma</td>
<td>HNO$_3$ contacted</td>
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<tr>
<td>1.25 MeV e$^-$_</td>
<td>Water saturated</td>
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<tr>
<td>Gamma</td>
<td>HNO$_3$ contacted</td>
<td>0.06</td>
</tr>
<tr>
<td>Reactor $\gamma$</td>
<td>Degassed/sealed</td>
<td>0.18</td>
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<tr>
<td>He ion ($\alpha$)</td>
<td>Sealed in quartz</td>
<td>0.07</td>
</tr>
<tr>
<td>Pu ($\alpha$)</td>
<td>HNO$_3$ contacted</td>
<td>0.002</td>
</tr>
<tr>
<td>Reactor $\alpha$</td>
<td>Degassed/sealed</td>
<td>0.047</td>
</tr>
</tbody>
</table>
On-going work

- Trying to resolve results from different alpha radiolysis techniques
- Need more impact at lower doses (TBP, CMPO too “stable”)
- Look at methylene blue dye

References


Great white free radical searches for helpless ligand in aqueous phase diluent. Rate is limited only by diffusion.

THE END
Upcoming Webinars in the Nuclear Fuel Cycle Series

• Pyroprocessing Technology
• Nuclear Waste Management - Application to Technetium
• Nuclear Repository Science and the Waste Isolation Pilot Plant

NAMP website http://www.wipp.energy.gov/namp/