Radiation Chemistry Research for Improved Nuclear Fuel Cycles

May 2020

Christopher A Zarzana, Gregory P Horne, Bruce J. Mincher, Cathy Rae, Gary S Groenewold
DISCLAIMER

This information was prepared as an account of work sponsored by an agency of the U.S. Government. Neither the U.S. Government nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness, of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. References herein to any specific commercial product, process, or service by trade name, trade mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the U.S. Government or any agency thereof.
Radiation Chemistry Research for Improved Nuclear Fuel Cycles

Christopher A Zarzana, Gregory P Horne, Bruce J. Mincher, Cathy Rae, Gary S Groenewold

May 2020

Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

Prepared for the
U.S. Department of Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517, DE-AC07-05ID14517, DE-AC07-05ID14517
 Radiation Chemistry Research for Improved Nuclear Fuel Cycles

Idaho National Laboratory: Christopher A. Zarzana, Gregory P. Horne, Bruce J. Mincher, Cathy Rae, Gary S. Groenewold
Nuclear Energy

• Part of low-carbon energy portfolio
• Challenges related to disposal of used fuel
• Global inventory of near 250,000 tons of spent nuclear fuel
Deep Geologic Storage

- Often, there are political difficulties with siting repositories for spent fuel
- Question becomes: How do we most efficiently utilize nuclear repositories?
  - Minimize volume that requires deep geologic storage
  - Reduction of the heat produced by the waste forms will allow more efficient utilization of the repository
Deep Geologic Storage

• Often, there are political difficulties with siting repositories for spent fuel
• Question becomes: How do we most efficiently utilize nuclear repositories?
  – Minimize volume that requires deep geologic storage
  – Reduction of the heat produced by the waste forms will allow more efficient utilization of the repository
Processes in a nuclear reactor

FISSION

Splits a larger atom into 2 or more smaller ones.

Neutron Capture

- Neutron capture
- Compound nucleus
- Prompt-gamma radiation
- Radioactive decay
- Decay gamma radiation

235U
T_{1/2} = 4.5 \times 10^9 \text{ years}

239U
T_{1/2} = 23.5 \text{ min}

239Np
T_{1/2} = 2.4 \text{ days}

- β-particle

https://www.energy.gov/ne/downloads/infographic-fission-vs-fusion-whats-difference
https://www.bnc.hu/?q=radiative_neutron_capture
Composition of Used Fuel

- ~96% U
- ~1% Pu
- ~3% FP

- Uranium-238
- Uranium-235
- Uranium-236
- Uranium-234
- Other

- Plutonium
- Neptunium
- Americium
- Curium
- Fission Products
Plutonium Uranium Redox EXtraction (PUREX)

Organic Phase

Aqueous Phase

Tributylphosphate
In kerosene

Spent Nuclear Fuel (SNF) dissolved in nitric acid

UO$_2^{2+}$, Pu$^{4+}$, Cs$^+$, Sr$^{2+}$, Am$^{3+}$
Plutonium Uranium Redox EXtraction (PUREX)

Organic Phase

Aqueous Phase

Tributylphosphate in kerosene

Spent Nuclear Fuel (SNF) dissolved in nitric acid

\[ \text{UO}_2^{2+}, \text{Pu}^{4+}, \text{Cs}^+, \text{Sr}^{2+}, \text{Am}^{3+} \]

\[ \text{NO}_3^- \]

\[ \text{NO}_3^- \]
Problem: the fuel is highly radioactive!

**Organic Phase**

- Tributylphosphate in kerosene

**Aqueous Phase**

- Spent Nuclear Fuel (SNF) dissolved in nitric acid
- UO$_2^{2+}$
- Pu$_4^{+}$
- Sr$^{2+}$
- Am$^{3+}$
- NO$_3^-$
Radiation Degrades TBP, Reduces Process Efficiency

• TBP breaks down into dibutylphosphate and monobutylphosphate

• TBP radiolysis results in loss of process efficiency
  – Loss of TBP
  – Degradation products also reduce extraction efficiency

• Research Goal: Understand fundamentals of organic-phase radiation chemistry
  – Rates of degradation
  – Products of degradation
  – Leads to new, more radiation-resistant molecules and processes
  – Separation process models
Diethylhexyl butyramide (DEHBA) as TPB Replacements

• Benefits over TBP\textsuperscript{[1]}:
  – Greater U selectivity
  – Consist only of Carbon Hydrogen Oxygen, and Nitrogen (CHON)
  – Uranium extraction processes based on monoamides exhibit higher radiolytic stability
    • Based on a comparison of extraction efficiencies as a function of absorbed radiation dose

**Diethylhexyl butyramide (DEHBA) as TPB Replacements**

- **Benefits over TBP**\(^1\):
  - Greater U selectivity
  - Consist only of Carbon Hydrogen Oxygen, and Nitrogen (CHON)
  - Uranium extraction processes based on monoamides exhibit higher radiolytic stability
    - Based on a comparison of extraction efficiencies as a function of absorbed radiation dose

- **We want to directly measure the effect of radiation on the ligand.**
  - Irradiate samples to various absorbed radiation doses and directly quantify amount of ligand remaining

---

**Simplified Solvent Extraction Process**

**Extraction**
- High [HNO$_3$]
- $\text{UO}_2^{2+}$
- $\text{Pu}^{4+}$
- FP
- Am$^{+3}$

**Strip**
- Low [HNO$_3$]
- $\text{UO}_2^{2+}$
- $\text{Pu}^{4+}$
- FP
- Am$^{+3}$

→ Next Process
Gamma Irradiation Experiments

- **Irradiate samples**
  - $^{60}\text{Co}$ Gamma Cell source- 5.4 kGy h$^{-1}$

- **Typical Samples**
  - Ligand in dodecane
    - Organic only: control
  - Ligand in dodecane irradiated in contacted with 3 M HNO$_3$
    - Simulates extraction
  - Ligand in dodecane irradiated in contact with 0.1 M HNO$_3$
    - Simulates strip

![Diagram showing control, extraction, and strip samples](image-url)
Sample Analysis: Quantification

- Gas chromatography with flame ionization detection (GC-FID)
  - Very stable detector: High precision
  - Usually < 2% relative standard deviation
Radiolytic Degradation of DEHBA

- **Pseudo-zeroth order degradation for all conditions**
  - Describe degradation with G-value: µmol of ligand destroyed per joule of absorbed radiation

<table>
<thead>
<tr>
<th>DEHBA Sample</th>
<th>G-value (µmol/J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic Only</td>
<td>0.31 ± 0.02</td>
</tr>
<tr>
<td>0.1 M HNO₃ contact</td>
<td>0.53 ± 0.02</td>
</tr>
<tr>
<td>3.0 M HNO₃ contact</td>
<td>0.49 ± 0.02</td>
</tr>
<tr>
<td>TBP in contact with acid</td>
<td>0.37 ± 0.02</td>
</tr>
</tbody>
</table>

- **DEHBA is actually less radiolytically stable than TBP**
  - The difference in process performance is due to the degradation products
Measuring Separation Performance

- Contact irradiated organic phase with tracer-loaded aqueous phase
- Use $^{233}$U and $^{239}$Pu as tracers
- Measure amount of tracer in both phases
  - $D_U = \frac{[U]_{\text{org}}}{[U]_{\text{aqu}}}$
Uranium Extraction Behavior

\[ D_U = \frac{[U]_{\text{org}}}{[U]_{\text{aqu}}} \]

- For extraction:
  - Want \( D_U > 1 \)

- Organic Phase Irradiation Conditions
  - (■) Organic Only
  - (▲) 3.0 M HNO_3 contact

- Aqueous Phase:
  - 4.0 M HNO_3
Plutonium Extraction Behavior

- $D_U = \frac{[Pu]_{\text{org}}}{[Pu]_{\text{aqu}}}$
- For extraction:
  - Want $D_U > 1$
- Organic Phase Irradiation Conditions
  - (■) Organic Only
  - (▲) 3.0 M HNO$_3$ contact
- Aqueous Phase:
  - 4.0 M HNO$_3$

Something is enhancing Pu extraction under organic-only conditions
Sample Analysis: Identification

- Ultra-high pressure liquid chromatography with electrospray ionization mass spectrometry (UHPLC-ESI-MS)
  - Ligand systems are liquid making UHPLC a natural method
  - Common functional group ionizes efficiently
  - UHPLC-ESI-MS –identify nonvolatile compounds not detectable using GC-MS
  - Degradation products identified by exact mass and MS²
DEHBA Radiation Chemistry

$N,N$-di-(2-ethylhexyl)butyramide
DEHBA

$N$-(2-ethylhexyl)butyramide
MEHBA

2-ethylhexyene

bis(2-ethylhexyl)amine
b2EHA

butyric acid
Quantification of MEHBA

(B)  

\[ \text{N-(2-ethylhexyl)butyramide} \]

[MEHBA] / mM

Absorbed Gamma Dose / kGy

(■) Organic Only
(●) 0.1 M HNO₃ contact
(▲) 3.0 M HNO₃ contact
Quantification of b2EHA

(A) Organic Only
(○) 0.1 M HNO₃ contact
(▲) 3.0 M HNO₃ contact
Radiolytic Degradation of DEHBA Degradation Products

- **b2EHA** much more stable to *radiolysis* than DEHAB
- **MEHBA** much more stable to *radiolysis* than DEHAB
- **b2EHA** degrades rapidly when contacted with acid
- **MEHBA** degrades rapidly when contacted with high concentrations of acid

### Table: G-value (µmol/J)

<table>
<thead>
<tr>
<th>Sample</th>
<th>G-value (µmol/J)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>b2EHA</strong></td>
<td></td>
</tr>
<tr>
<td>Organic Only</td>
<td>0.12 ± 0.01</td>
</tr>
<tr>
<td>0.1 M HNO₃ contact</td>
<td>Hydrolysis</td>
</tr>
<tr>
<td>3.0 M HNO₃ contact</td>
<td>Hydrolysis</td>
</tr>
<tr>
<td><strong>MEHBA</strong></td>
<td></td>
</tr>
<tr>
<td>Organic Only</td>
<td>0.08 ± 0.01</td>
</tr>
<tr>
<td>0.1 M HNO₃ contact</td>
<td>0.12 ± 0.01</td>
</tr>
<tr>
<td>3.0 M HNO₃ contact</td>
<td>Hydrolysis</td>
</tr>
</tbody>
</table>
Probably due to acid hydrolysis

![Graph showing the relationship between absorbed gamma dose and [b2EHA] / mM. The graph includes data points for organic only contact and 0.1 M HNO₃ and 3.0 M HNO₃ contact. The molecule bis(2-ethylhexyl)amine (b2EHA) is also shown.](graph.png)
b2EHA Enhances Pu Extraction

- (■) 1 M DEHBA
- (●) 0.8 M DEHBA + 80 mM b2EHA
- (▲) 0.8 M DEHBA + 80 mM butanoic acid
- (▼) 0.8 M DEHBA + 20 mM MEHBA
- (◆) 0.8 M DEHBA + 20 mM 2-ethylhexene

b2EHA is likely responsible for enhanced Pu extraction in organic-only conditions
What can we (eventually) do with this information?

- Process modeling
  - Extraction behavior
  - Radiolysis Rates
- Solvent clean-up
Deep Geologic Storage

- Often, there are political difficulties with siting repositories for spent fuel
- Question becomes: How do we most efficiently utilize nuclear repositories?
  - Minimize volume that requires deep geologic storage
  - Reduction of the heat produced by the waste forms will allow more efficient utilization of the repository
Heat Contributions of Used Fuel Components

Am is the largest contributor to decay heat from a few hundred to a few thousand years.
Fast Neutron Reactors for Actinide Burning

• Use high-energy neutrons to fission the minor actinides
  – Convert them to short-lived fission products
  – Reduce the size requirements for a deep geologic storage repository

Effect on Repository Size of Different Fuel Cycles

High-Level Partitioning and Transmutation Schemes

1. Removal of uranium and/or plutonium
2. Separation of fission products (Cs and Sr)
3. Co-extraction of trivalent lanthanides and minor actinides
4. Separation of trivalent actinides from trivalent lanthanides
Am recycling reduced repository volume at the expense of more liquid waste

(Pu Multi-recycling)

CMPO

• Originally designed to co-extract Pu, U, Am, and Cm
• Can also be used after PUREX-like process to co-extract An$^{3+}$ and Ln$^{3+}$
• Radiation resistance increases in the presence of nitric acid

CMPO: octylphenyl-$N,N$-diisobutylcarbamoylmethylphosphine oxide
Tetra-Octyl Diglycolamides: Another An/Ln Ligand

- High affinity for An(III)/Ln(III)
- High distribution ratios of An(III)/Ln(III) at process relevant nitric acid concentrations
- Easy/inexpensive synthesis with various possible modifications
- CHON
- Good hydrolytic/radiolytic stability
- Nitric acid has minimal influence on radiolytic stability.
• CMPO and the diglycolamides share amide functional groups

• Phenyl-phosphine oxide group is unique to CMPO
Hypothesis: Phenyl-phosphine oxide is responsible for nitric acid-enhanced radiation protection.

Test with model compounds:

- Trioctyl phosphine oxide (TOPO)
- Dioctylphenyl phosphine oxide (DOPPO)
Model Compound Radiolysis

Phenyl-phosphine oxide group very likely responsible for nitric acid-enhanced radiation protection!
Can we improve the radiation resistance of DGAs?

- Phenylmethyl tetraoctyldiglycolamide
  - PhMeTODGA
- Synthesized by collaborators at the University of Twente, The Netherlands

\[
\begin{align*}
\text{R} &= \text{C}_8\text{H}_{17}
\end{align*}
\]
Can we improve the radiation resistance of DGAs?

- Does the phenyl group increase stability in the presence of nitric acid?

![Chemical structure of DGAs with R = C₈H₁₇]
Can we improve the radiation resistance of DGAs?

• Yes!

<table>
<thead>
<tr>
<th>PhMeTODGA Sample</th>
<th>Dose Constant (kGy⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic Only</td>
<td>(5.0 ± 0.5) × 10⁻³</td>
</tr>
<tr>
<td>0.1 M HNO₃ contact</td>
<td>(5.4 ± 0.4) × 10⁻³</td>
</tr>
<tr>
<td>3.0 M HNO₃ contact</td>
<td>(4.4 ± 0.5) × 10⁻³</td>
</tr>
</tbody>
</table>

\[ R = C₈H₁₇ \]
Can we improve the radiation resistance of DGAs?

• Yes! but…..

<table>
<thead>
<tr>
<th>PhMeTODGA Sample</th>
<th>Dose Constant (kGy⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic Only</td>
<td>(5.0 ± 0.5) × 10⁻³</td>
</tr>
<tr>
<td>0.1 M HNO₃ contact</td>
<td>(5.4 ± 0.4) × 10⁻³</td>
</tr>
<tr>
<td>3.0 M HNO₃ contact</td>
<td>(4.4 ± 0.5) × 10⁻³</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TODGA Sample</th>
<th>Dose Constant (kGy⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic Only</td>
<td>(4.1 ± 0.3) × 10⁻³</td>
</tr>
<tr>
<td>0.1 M HNO₃ contact</td>
<td>(4.5 ± 0.2) × 10⁻³</td>
</tr>
<tr>
<td>3.0 M HNO₃ contact</td>
<td>(3.8 ± 0.3) × 10⁻³</td>
</tr>
</tbody>
</table>
PhMeTODGA Degradation Product Analysis

• Quantification of degradation products gave us information about degradation pathways for DEHBA

• What about PhMeTODGA?

\[ R = C_8H_{17} \]
Characterization of Irradiated Organics

• High Resolution High Mass Accuracy Mass Spectrometry
  – Bruker micrOTOF-Q II:
    • quadrupole time-of-flight
    • Mass range: 3000 m/z
    • Resolution: ~15,000 (full-width half-max)
    • Mass Accuracy: ~±0.002 Da
    • ESI, APCI, APPI ion sources
    • Waters Acquity H-Class Plus UPLC front-end

• Unambiguous molecular formula

• Some structural information from tandem MS

• Decent quantification accuracy (typically better than 10%), but narrow dynamic range (~2 orders of magnitude)
High Mass Accuracy Yields Molecular Formula

Dimethyl phthalate \( \text{C}_{10}\text{H}_{11}\text{O}_{4}^+ \)  
\( m/z: 195.0652 \)  
\( \Delta m: -0.0493 \)  
-253 ppm

2-ethylhexyl phosphonic acid \( \text{C}_8\text{H}_{20}\text{O}_3\text{P}^+ \)  
\( m/z: 195.1145 \)

Polyethylene glycol (n=4) \( \text{C}_8\text{H}_{19}\text{O}_5^+ \)  
\( m/z: 195.1227 \)  
\( \Delta m: +0.0082 \)  
+42 ppm
Orthogonal Quadrupole Time-of-Flight MS

ESI Source

Ion Funnels Quadrupole

Hexapole

Collision cell

TOF

Detector
Collision-induced Dissociation (CID)

http://www.chm.bris.ac.uk/ms/cid.xhtml
Example for PhMeTODGA Cmpd 6

![Mass spectrum diagram with labeled peaks and molecular formulas.]

- **148.074**: 
  - $-C_7H_{14}$

- **218.191**: 
  - $27.995 - CO$
  - $C_{27}H_{47}N_2O_3^+$

- **246.186**: 
  - $98.112 - C_7H_{14}$

- **290.212**: 
  - $157.143 - C_9H_{19}NO$

- **394.327**: 
  - $447.355 - C_{11}H_{23}NO_2$

- **447.355**: 
  - $20 eV$

Abundance (%) on the y-axis, m/z on the x-axis.
Proposed Gas-Phase Fragmentation Mechanisms

\[
\text{HN} \quad \text{O} \quad \text{NH} + \text{HN} \quad \text{O} \quad \text{R} \quad \text{mw}: 218.190
\]
\[
\text{m/z: 246.185} \quad \text{CID} \quad \Rightarrow \quad \text{HN} \quad \text{C}+ \quad \text{R} \quad \text{m/z: 290.211} \quad \text{mw: 157.147}
\]
\[
\text{m/z: 447.358} \quad \text{HN} \quad \text{O} \quad \text{NH} + \text{HN} \quad \text{O} \quad \text{R} \quad \text{m/z: 246.185} \quad \text{CID} \quad \Rightarrow \quad \text{HN} \quad \text{CH}+ \quad \text{O} \quad \text{R} \quad \text{m/z: 148.076} \quad \text{mw: 118.042}
\]
\[
\text{m/z: 246.185} \quad \text{HN} \quad \text{CH}+ \quad \text{O} \quad \text{R} \quad \text{m/z: 290.211} \quad \text{mw: 157.147}
\]
\[
\text{m/z: 246.185} \quad \text{HN} \quad \text{CH}+ \quad \text{O} \quad \text{R} \quad \text{m/z: 148.076} \quad \text{mw: 118.042}
\]

\[
\text{m/z: 447.358} \quad \text{HN} \quad \text{O} \quad \text{NH} + \text{HN} \quad \text{O} \quad \text{R} \quad \text{m/z: 246.185} \quad \text{CID} \quad \Rightarrow \quad \text{HN} \quad \text{CH}+ \quad \text{O} \quad \text{R} \quad \text{m/z: 148.076} \quad \text{mw: 118.042}
\]
\[
\text{m/z: 246.185} \quad \text{HN} \quad \text{CH}+ \quad \text{O} \quad \text{R} \quad \text{m/z: 290.211} \quad \text{mw: 157.147}
\]
\[
\text{m/z: 447.358} \quad \text{HN} \quad \text{O} \quad \text{NH} + \text{HN} \quad \text{O} \quad \text{R} \quad \text{m/z: 246.185} \quad \text{CID} \quad \Rightarrow \quad \text{HN} \quad \text{CH}+ \quad \text{O} \quad \text{R} \quad \text{m/z: 148.076} \quad \text{mw: 118.042}
\]
PhMeTODGA Degradation Product Analysis

PhMeTODGA Backbone Cleavages Followed by H-Radical Addition:

- Compound 8, \(N,N\)-dioctylformamide, Monoisotopic MW: 269.3
- Compound 7, 2-hydroxy-\(N,N\)-dioctylpropanamide, Monoisotopic MW: 313.3
- Compound 20, \(N,N\)-dioctyl-2-phenylacetamide, Monoisotopic MW: 359.3
- Compounds 11a and 11b, 2-(2-(dioctylamino)-2-oxo-1-phenylethoxy)propanoic acid, Monoisotopic MW: 447.3
- Compounds 23a and 23b, \(N,N\)-dioctyl-2-(2-(octylamino)-2-oxo-1-phenylethoxy)propanamide, Monoisotopic MW: 558.5
- Compounds 9a and 9b, 2-((1-(dioctylamino)-1-oxopropan-2-yl)oxy)-2-phenylacetic acid, Monoisotopic MW: 447.3
- Compound 2, Dioctylamine, Monoisotopic MW: 241.3
- Compound 15, \(N,N\)-dioctylpropionamide, Monoisotopic MW: 297.3
- Compound 17, 2-hydroxy-\(N,N\)-dioctyl-2-phenylacetamide, Monoisotopic MW: 375.3
- Compound 8, \(N,N\)-dioctylformamide, Monoisotopic MW: 269.3
- Compounds 24a and 24b, 2-(2-(dioctylamino)-2-oxo-1-phenylethoxy)-\(N\)-octylpropanamide, Monoisotopic MW: 559.5
- Compound 19, \(N,N\)-dioctyl-2-phenylacetamide, Monoisotopic MW: 359.3
But wait, there’s more......

PhMeTODGA Backbone Bond Cleavage Followed by CH$_3$-Radical Addition:

- Compound 10: N,N-dioctylacetamide
  Monoisotopic MW: 283.3

- Compound 18: N,N-dioctylisobutyramide
  Monoisotopic MW: 311.3

Dodecanol Esterification:

- Compound 25: dodecyl 2-(1-(dioctylamino)-1-oxopropan-2-yl)oxy)-2-phenylacetate
  Monoisotopic MW: 615.5

- Compound 26: dodecyl 2-(2-(dioctylamino)-2-oxo-1-phenylethoxy)propanoate
  Monoisotopic MW: 615.5

Oxidation of Primary PhMeTODGA Radiolysis Products:

- Compound 12: N,N-dioctyl-2-oxopropanamide
  Monoisotopic MW: 373.3

- Compound 19: N,N-dioctyl-2-oxo-2-phenylacetamide
  Monoisotopic MW: 261.2

Oxidation of Secondary PhMeTODGA Radiolysis Products:

- Compound 4: N,N-dioctyl-2-oxo-2-phenylacetamide
  Monoisotopic MW: 261.2

Oxidation of OH-Radical Addition:

- Compound 22: 1-(dioctylamino)-1-oxopropan-2-yl benzoate
  Monoisotopic MW: 417.3

Primary PhMeTODGA Radiolysis Product Bond Cleavages Followed by H-Radical Additions:

- Compound 5: N-octyloctanamide
  Monoisotopic MW: 255.3

Unknown Formation Mechanism:

- Compound 21: 2-(4-nitrophenyl)-N,N-dioctylacetamide
  Monoisotopic MW: 404.3

Nitrate-Radical Additions:

- Compound 21: 2-(4-nitrophenyl)-N,N-dioctylacetamide
  Monoisotopic MW: 420.3

- Compound 14: 2-(4-nitrophenyl)-2-oxo-1-phenylethyl nitrate
  Monoisotopic MW: 358.3

Aromatic Nitration:

- Compound 15: 2-(4-nitrophenyl)-N,N-dioctylacetamide
  Monoisotopic MW: 404.3

Nitrosamine Formation:

- Compound 13: N,N-dioctylnitrous amide
  Monoisotopic MW: 270.3

Unknown Formation Mechanism:

- Compound 1: 2-hydroxy-N-octylpropanamide
  Monoisotopic MW: 201.2

- Compound 3: 2-hydroxy-N-octyl-2-phenylacetamide
  Monoisotopic MW: 263.2

- Compounds 6a and 6b: N-octyl-2-(2-(octylamino)-2-oxo-1-phenylethoxy)propanamide
  Monoisotopic MW: 398.3
Future Directions

• Prepare degradation products by irradiating high concentrations of ligand to high doses

• Separate and purify degradation products using preparative-scale high-performance liquid chromatography (HPLC)
  – Produce amounts for structure conformation with NMR, quantification standards
    • Improve identification
  – Eventually enough for solvent extraction experiments
    • Enable modeling
Future Directions, cont.....

• New methods to statistically reveal which chromatographic peaks are degradation products
Conclusions

• Radiation chemistry studies can provide:
  – Detailed information about the performance of processes for separating used nuclear fuel
  – Identify problematic degradation products
  – Develop process models to predict and control industrial separation
  – Fundamental radiation chemistry can help with ligand design

• Standards greatly enhances obtainable information

![Graph showing radiation chemistry studies](image-url)
Center for Radiation Chemistry Research

• The CR2 mission is to:
  – Address radiation chemistry challenges throughout the nuclear fuel cycle and beyond.
  – Advance our fundamental and applied knowledge of ionizing radiation phenomena.
  – Train the next generation of radiation chemists, to preserve the world's expertise for future generations.

• [https://cr2.inl.gov/](https://cr2.inl.gov/)
Molecular Chromatography and Mass Spectrometry Group

• Personnel
  – Gary Groenewold
    - Gary.Groenewold@inl.gov
  – Brittany Hodges
    - Brittany.Hodges@inl.gov
  – Chris Zarzana
    - Christopher.Zarzana@inl.gov
  – Cathy Rae
  – Dayna Daubaras
• Work funded by the US-DOE Assistant Secretary for NE, under the FCR&D Radiation Chemistry program; DOE-Idaho Operations Office Contract DE-AC07-05ID14517 and Nuclear Energy Universities Program (NEUP) DE-NE0008406 grant.
Landscape of Separations Processes