INL/CON-24-78780-Revision-0

Investigating the impacts of used nuclear fuel direct dissolution on the radiolytic longevity of solvent and butyramide extractants

June 2024

Stephen Mezyk, Anh Dang, Gregory Peter Holmbeck, Amy Elizabeth Kynman

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Material Recovery & Waste Form Development

NTRD Nuclear Technology Research & Development

NORM 2024 Breaking Borders: Building Bonds

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Investigating the impacts of used nuclear fuel direct dissolution on the radiolytic longevity of solvent and butyramide extractants

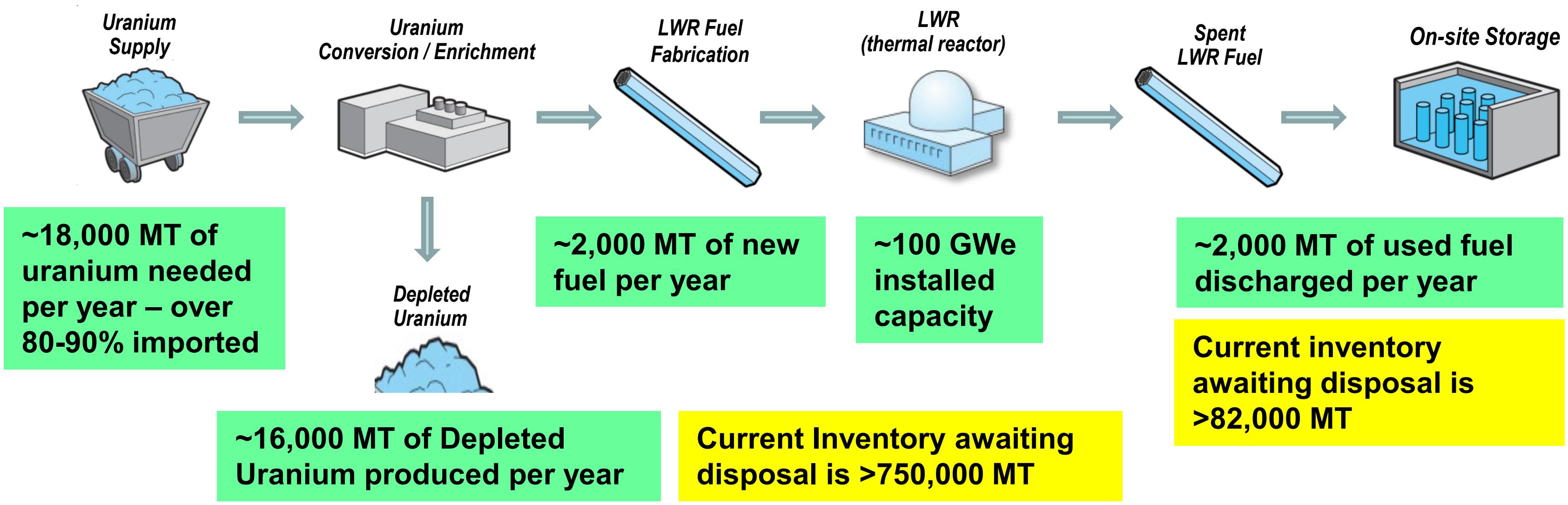
Stephen Mezyk,[1] Anh Dang,[1] Amy Kynman,[2] Gregory Holmbeck[2]

1. California State University at Long Beach, CA
2. Idaho National Laboratory, ID

California State University LONG BEACH

INL Idaho National Laboratory

Current U.S. Open Fuel Cycle



Uranium Supply

~18,000 MT of uranium needed per year – over 80-90% imported

Uranium Conversion / Enrichment

Depleted Uranium

~16,000 MT of Depleted Uranium produced per year

LWR Fuel Fabrication

~2,000 MT of new fuel per year

LWR (thermal reactor)

~100 GWe installed capacity

Current Inventory awaiting disposal is >750,000 MT

Spent LWR Fuel

On-site Storage

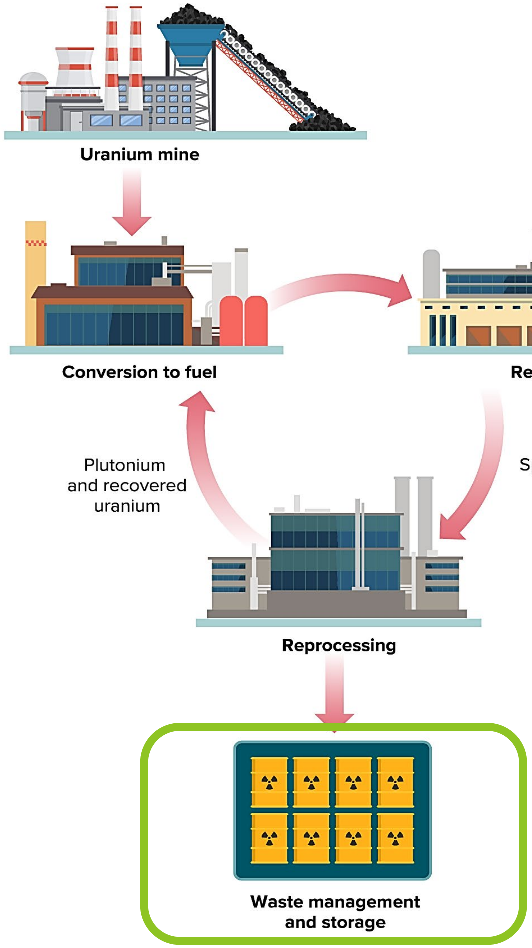
~2,000 MT of used fuel discharged per year

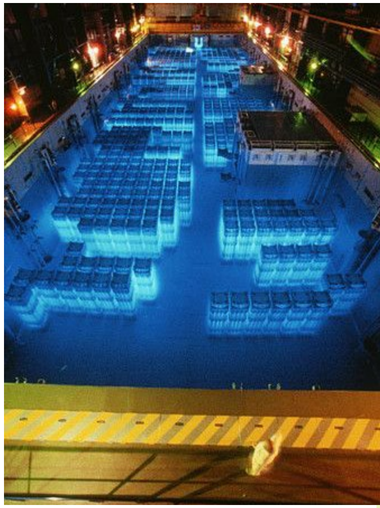
Current inventory awaiting disposal is >82,000 MT

- **The current U.S. fuel cycle generates two major waste streams requiring geologic disposal or similar isolation, along with LLW***
  - 2,000 MT per year of used fuel – planned disposal path: repository
  - 16,000 MT per year of depleted uranium – no disposal path identified, but also requires long-term isolation due to buildup of radioactive decay products

*Todd, T. IAEA Technical Meeting on Advanced Fuel Cycles for Waste Burden Minimization. 2016

Used Nuclear Fuel





🟦 1 H																	2 He
3 Li	4 Be											5 B	🟨 6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 A
19 K	20 Ca	21 Sc	22 Ti	23 V	🟨 24 Cr	🟨 25 Mn	🟨 26 Fe	🟨 27 Co	🟨 28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	🟦 34 Se	🟦 35 Br	🟦 36 Kr
🟦 37 Rb	🟦 38 Sr	🟦 39 Y	🟦 40 Zr	🟦 41 Nb	🟦 42 Mo	🟦 43 Tc	🟦 44 Ru	🟦 45 Rh	🟦 46 Pd	🟦 47 Ag	🟦 48 Cd	🟦 49 In	🟦 50 Sn	🟦 51 Sb	🟦 52 Te	🟦 53 I	🟦 54 Xe
🟦 55 Cs	🟦 56 Ba	🟦 *Ln*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Ti	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	*An*	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun								

Lanthanides	🟦 57 La	🟦 58 Ce	🟦 59 Pr	🟦 60 Nd	🟦 61 Pm	🟦 62 Sm	🟦 63 Eu	🟦 64 Gd	🟦 65 Tb	🟦 66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	89 Ac	90 Th	91 Pa	🟪 92 U	🟥 93 Np	🟪 94 Pu	🟥 95 Am	🟥 96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

🟪 **Major Actinides** 🟥 **Minor Actinides (MA)**

🟦 **Fission products** 🟨 **Activation products**

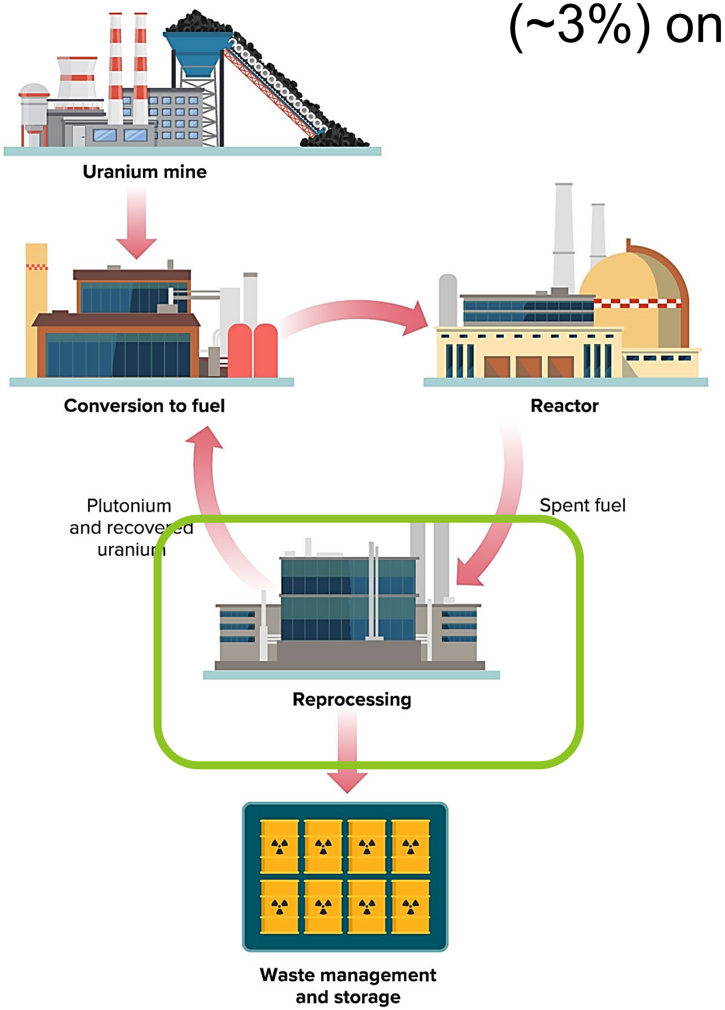
Reprocessing Used Nuclear Fuel

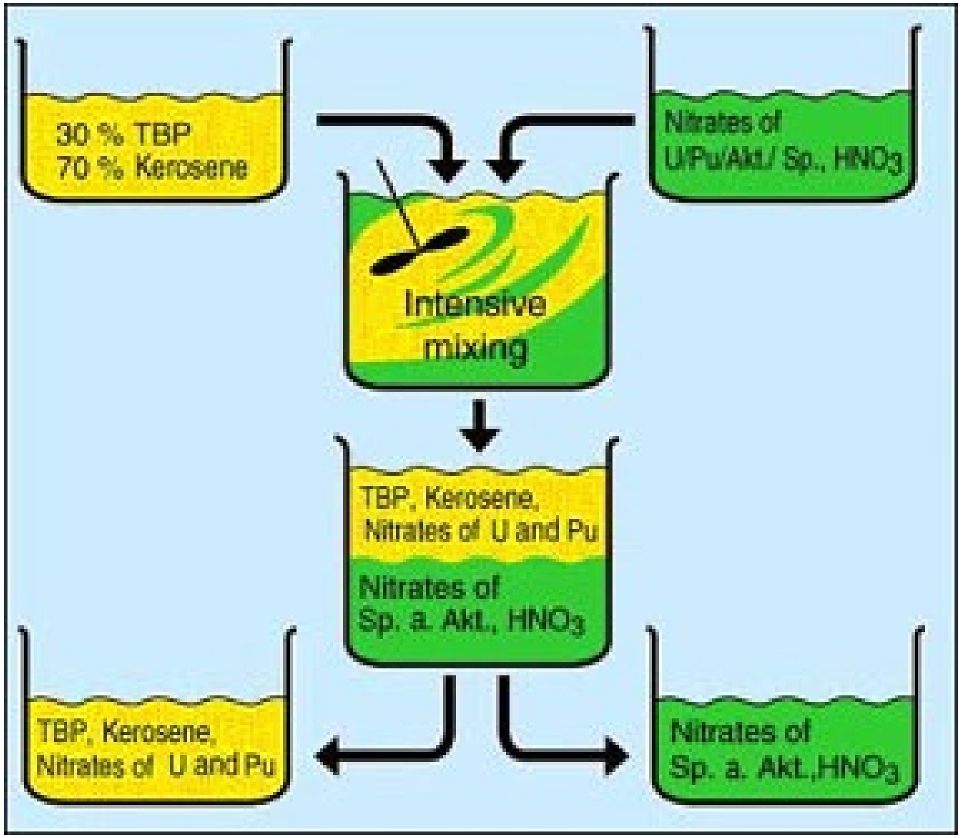
What's in used nuclear fuel?

- **95.6 % UO_2 (< 1% ^{235}U)**
- 2.9% stable fission products
- 0.9% Pu
- 0.3% Cs and Sr
- 0.1% I^- and Tc
- 0.1% other long-lived fission products
- 0.1% minor actinides (Am, Cm, Np)

Reprocessing Used Nuclear Fuel

Actinide recycling has relatively low impact (~3%) on overall final cost of nuclear electricity

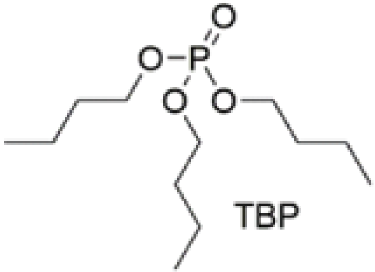


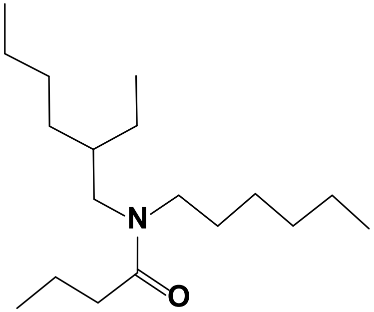


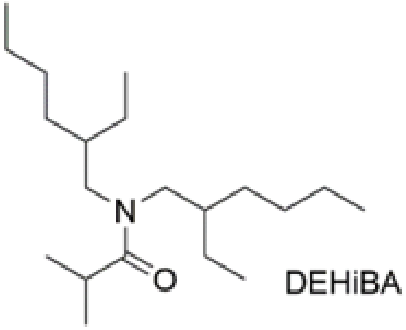
Poinssot *et al.*, Reprocessing and Recycling of Spent Nuclear Fuel, Elsevier, pp. 27–48, (2015).

Coordination-Driven Actinide Control

- We have decades of development of novel reagents to address all technical challenges of actinide separations.
- **Metal ligation** offers opportunity to separate metal ions by variation of thermodynamic stabilities of formed complexes, adducts or ion pairs.
- Separation of U and Pu by TBP/DEHBA based extraction
- Minor actinides/other species can then be separated from PUREX type raffinate

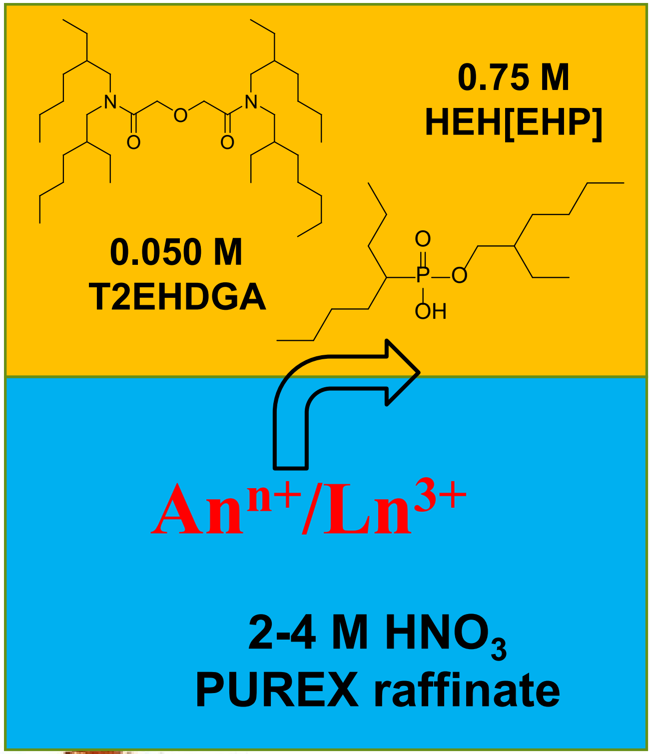

TBP


DEHBA


DEHiBA

Solvent-extraction based separation systems

- ALSEP: Actinide Lanthanide SEparation Process
- Following ALSEP Ln and An extraction can strip back actinides using a citric acid buffered aminopolycarboxylic acid solution

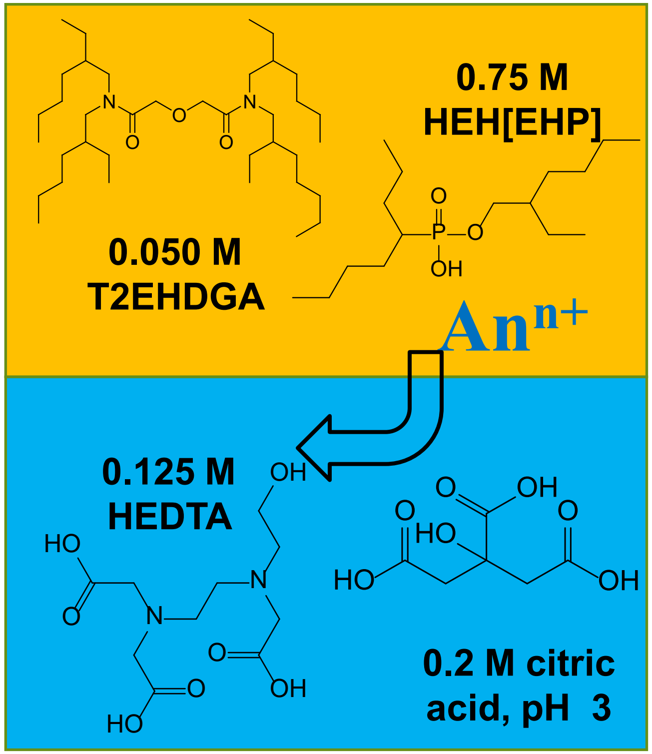


0.75 M HEH[EHP]

0.050 M T2EHDGA

An^{n+}/Ln^{3+}

2-4 M HNO_3 PUREX raffinate



0.75 M HEH[EHP]

0.050 M T2EHDGA

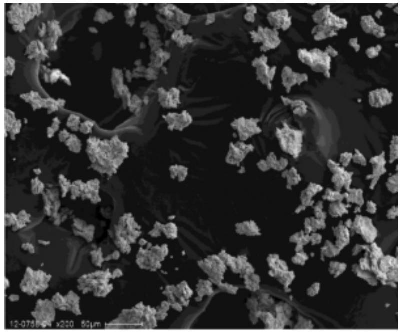
An^{n+}

0.125 M HEDTA

0.2 M citric acid, pH 3

How do we *simplify* solvent-based separations?

- Want to **reduce** processing steps and costs
- Minimize waste generation
- Could we **remove aqueous dissolution/extraction steps**?
- **Directly dissolve** used fuel directly into organic solvent (*n*-dodecane)?
- What form of fuel would directly dissolve in liquid organics containing organic ligands?
- Can voloxidize uranium oxide using NO_2/O_3 to create ε-UO_3[1,2] which can dissolve in organic liquids!

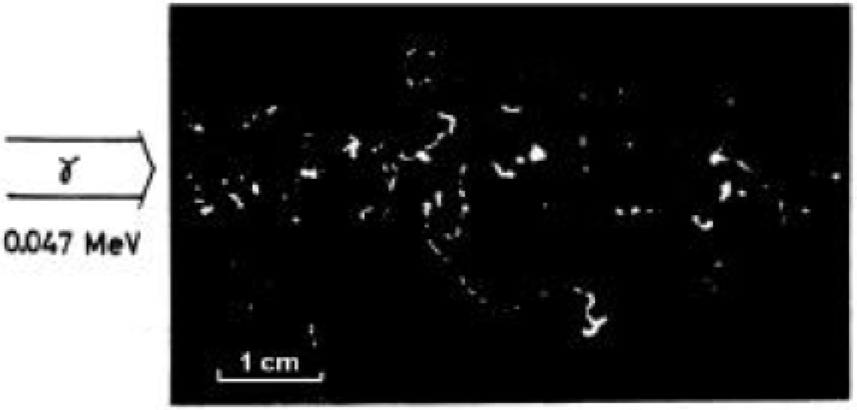


[1] Johnson *et al*, J. Nucl. Mater. 490, 211-215 (2017)

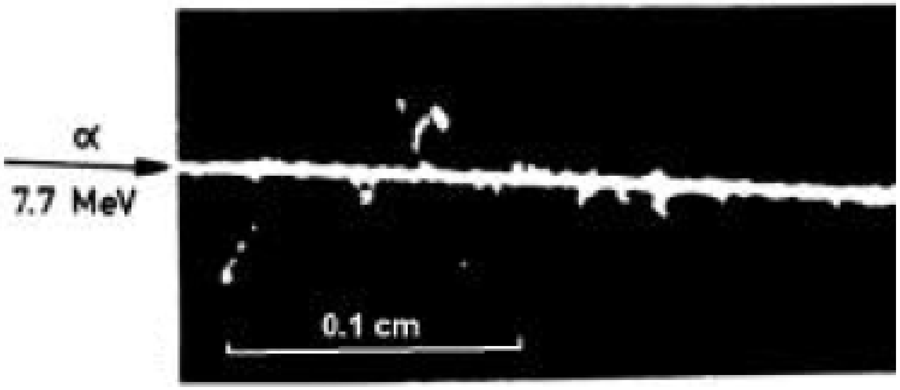
[2] Collins *et al*., US Patent 8,574,523 B2

What about system radiation stability?

- Ubiquitous throughout the fuel cycle
- Two main types of radiation in solvent processes
- Difference between a and b/g/e^- radiation based on Linear Energy Transfer (LET)



Low LET b/g/e^-
Sparse deposition of energy
Radical species formed far apart

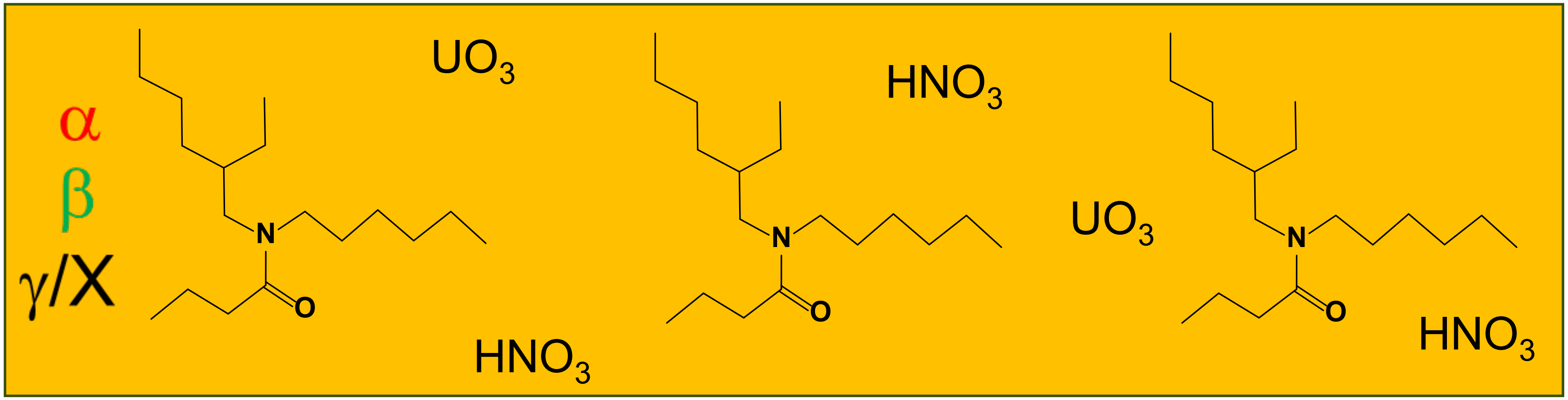


High LET a/n/Recoil
Dense deposition of energy
Radical species close together

Choppin, G.; Liljenzin, J., Rydberg, J., 2002, Radiochem and nuclear chemistry, Butterworth-Hienemann, Woburn, MA

What impacts will radiation have on direct dissolution separations?

- Will radiation-induced solvent/ligand degradation prevent us from achieving our simplified separation process?
- What radiation-induced products will be formed – will they be detrimental or helpful?
- **Goal of this work**: Investigate the impacts of used nuclear fuel direct dissolution on the *radiolytic longevity* of solvent and butyramide extractants.

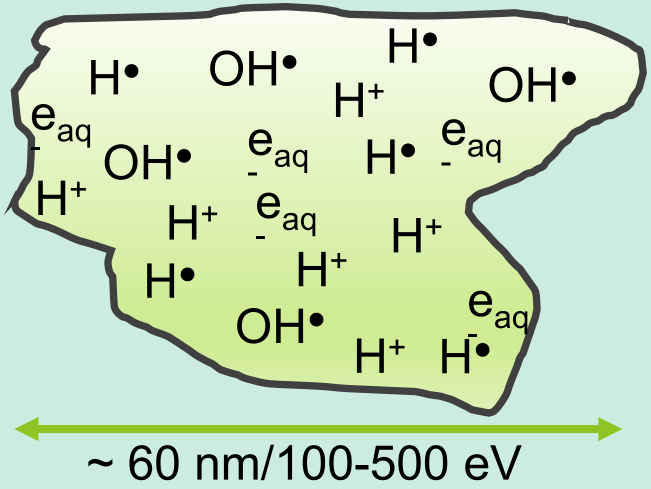


Radiolysis of condensed phases

$CH_3(CH_2)_nCH_3$

Organic

H_2O -\/\/\→



Spur chemistry

$2\ {}^{\bullet}OH \rightarrow H_2O_2$

$2\ H^{\bullet} \rightarrow H_2$

$H^{\bullet} + OH \rightarrow H_2O$

${}^{\bullet}OH + e^- \rightarrow OH^-$

$H^+ + e^- \rightarrow H^{\bullet}$

Aqueous

Spinks, J. W. T.; Woods, R. J. An Introduction to Radiation Chemistry, 3rd Edition, John-Wiley and Sons, Inc., New York, Toronto 1990. ISBN 0-471-61403-3

Radiolysis of organic and aqueous phases

$$CH_3(CH_2)_nCH_3 \;\text{-}\backslash/\backslash/\backslash\!\rightarrow\; e^-_{sol} + [CH_3(CH_2)_nCH_3]^{\bullet+}$$

$$+ CH_3(CH_2)_nC{\bullet}H_2 + {\bullet}CH_3 + H{\bullet} + H_2$$

Organic

$$H_2O \;\text{-}\backslash/\backslash/\backslash\!\rightarrow\; {\bullet}OH + e^-_{aq} + H{\bullet}$$

$$+ H_2O_2 + H_3O^+ + H_2$$

Aqueous

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Spinks, J. W. T.; Woods, R. J. An Introduction to Radiation Chemistry, 3rd Edition, John-Wiley and Sons, Inc., New York, Toronto 1990.
ISBN 0-471-61403-3

Under anticipated reprocessing conditions:

$CH_3(CH_2)_nCH_3$ -\/\/\→ $[CH_3(CH_2)_nCH_3]^{\bullet +}$

HNO_3 -\/\/\→ $NO_3\bullet$

Organic

In presence of HNO_3/O_2

H_2O -\/\/\→ $\bullet OH$ + H_2O_2

HNO_3 -\/\/\→ $NO_3\bullet$

Aqueous

Spinks, J. W. T.; Woods, R. J. An Introduction to Radiation Chemistry, 3rd Edition, John-Wiley and Sons, Inc., New York, Toronto 1990. ISBN 0-471-61403-3

Under reprocessing conditions:

$$CH_3(CH_2)_nCH_3 \rightsquigarrow [CH_3(CH_2)_nCH_3]^{\bullet+}$$

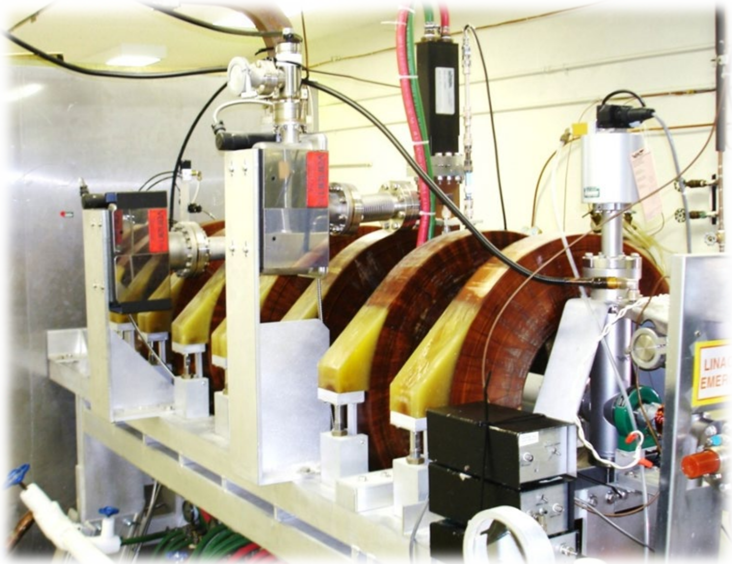
$$HNO_3 \rightsquigarrow NO_3^{\bullet}$$

Organic

Focus on the Organic phase – two major radicals

How do we understand this radiation-induced chemistry?

- Study radiation chemistry of ligands/metal-ligand complexes under anticipated process conditions
- Need **accelerators**, **steady-state gamma irradiators**, **analyses instrumentation**, **theory**….



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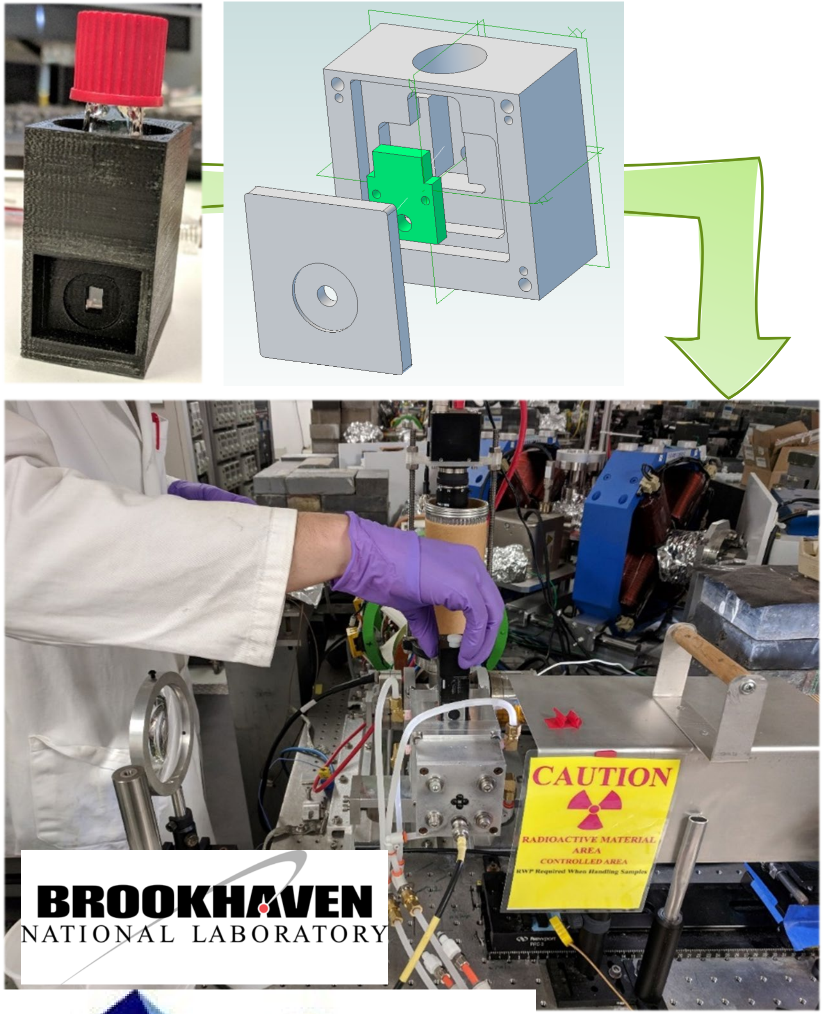
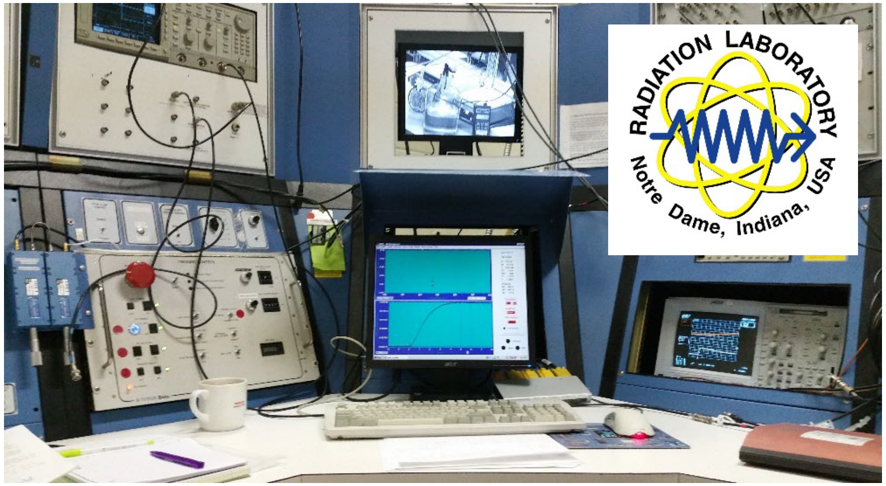
Electron Pulse Radiolysis





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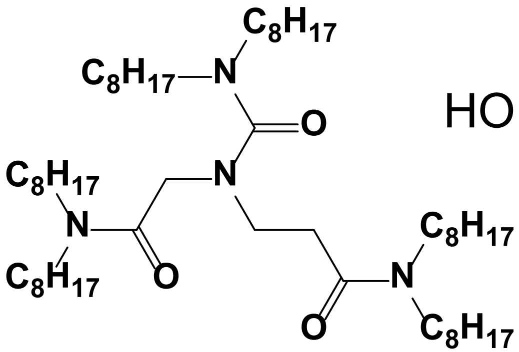
HONTA, hexa-n-octylnitrilotricetamide



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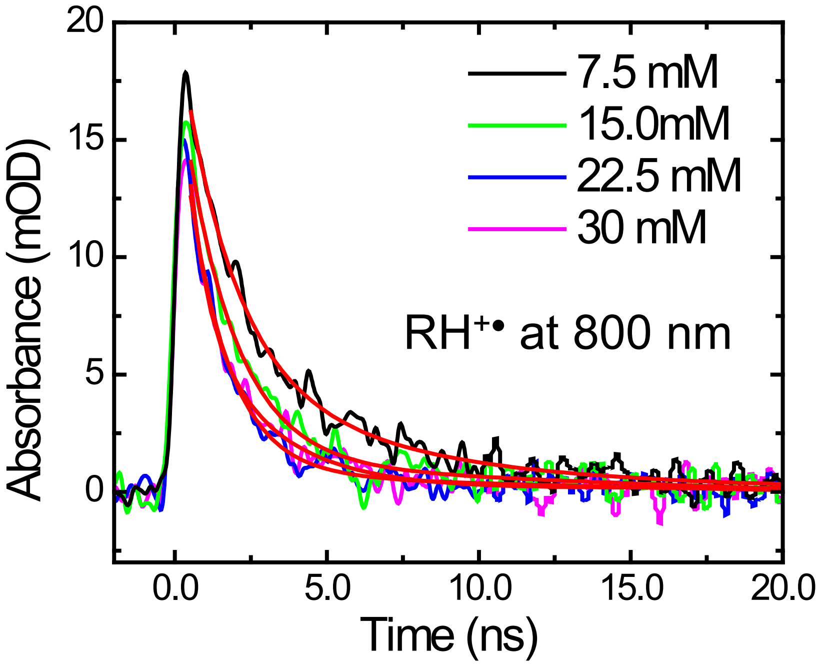

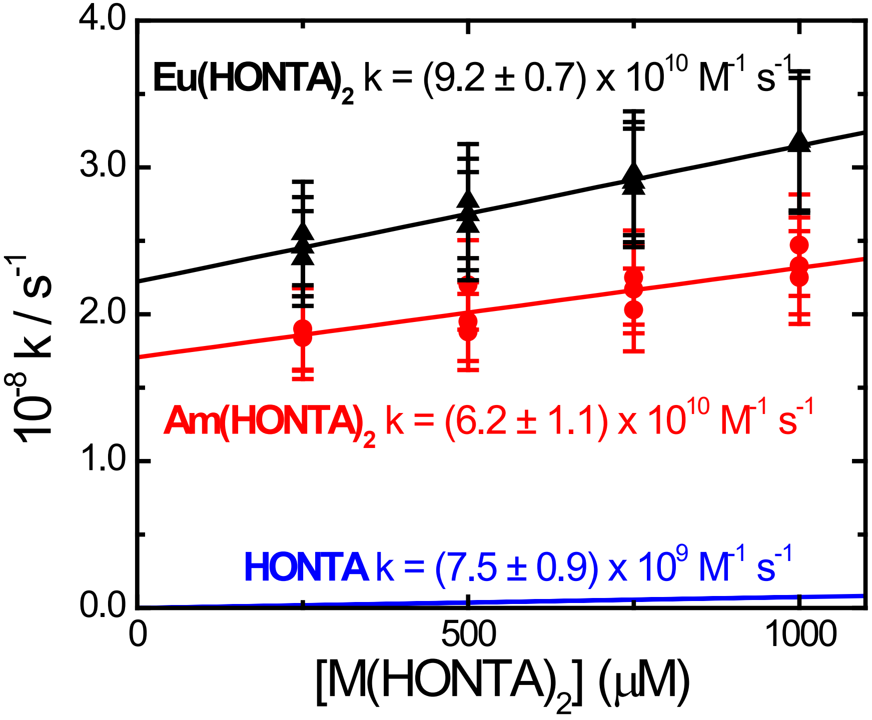

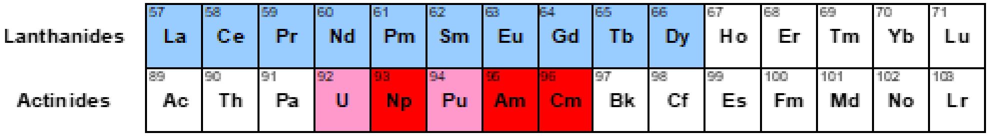

Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Coordinated ligand ~**10x** faster

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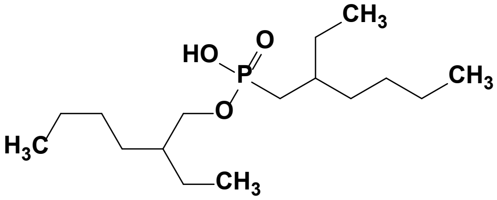
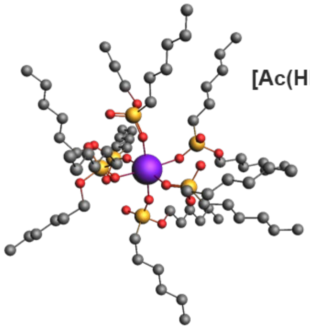
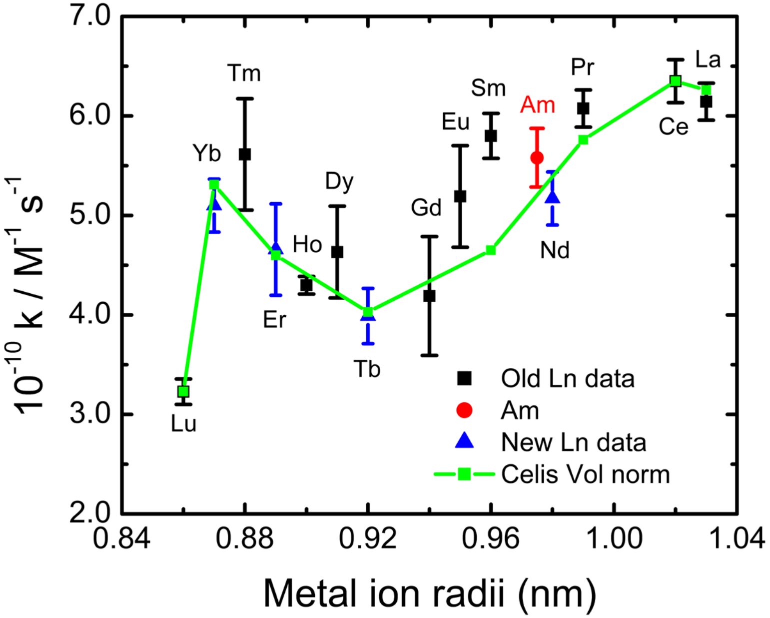
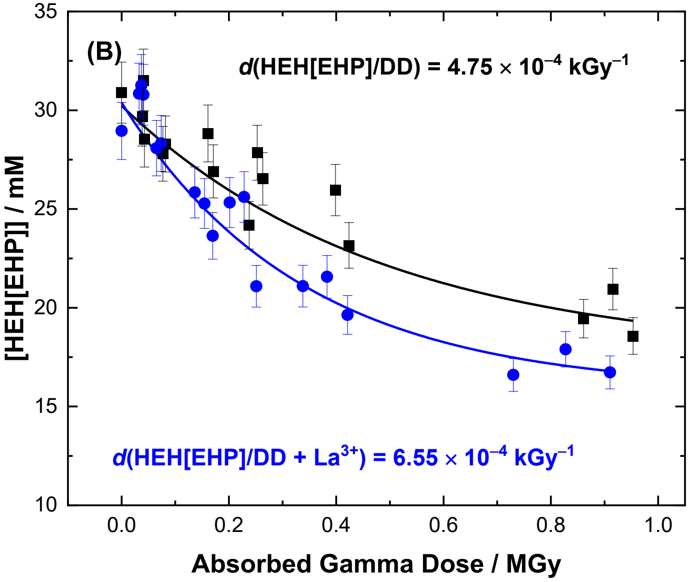
Toigawa, *et al*, PCCP 23, 1343-1351 (2021)

HEH[EHP]





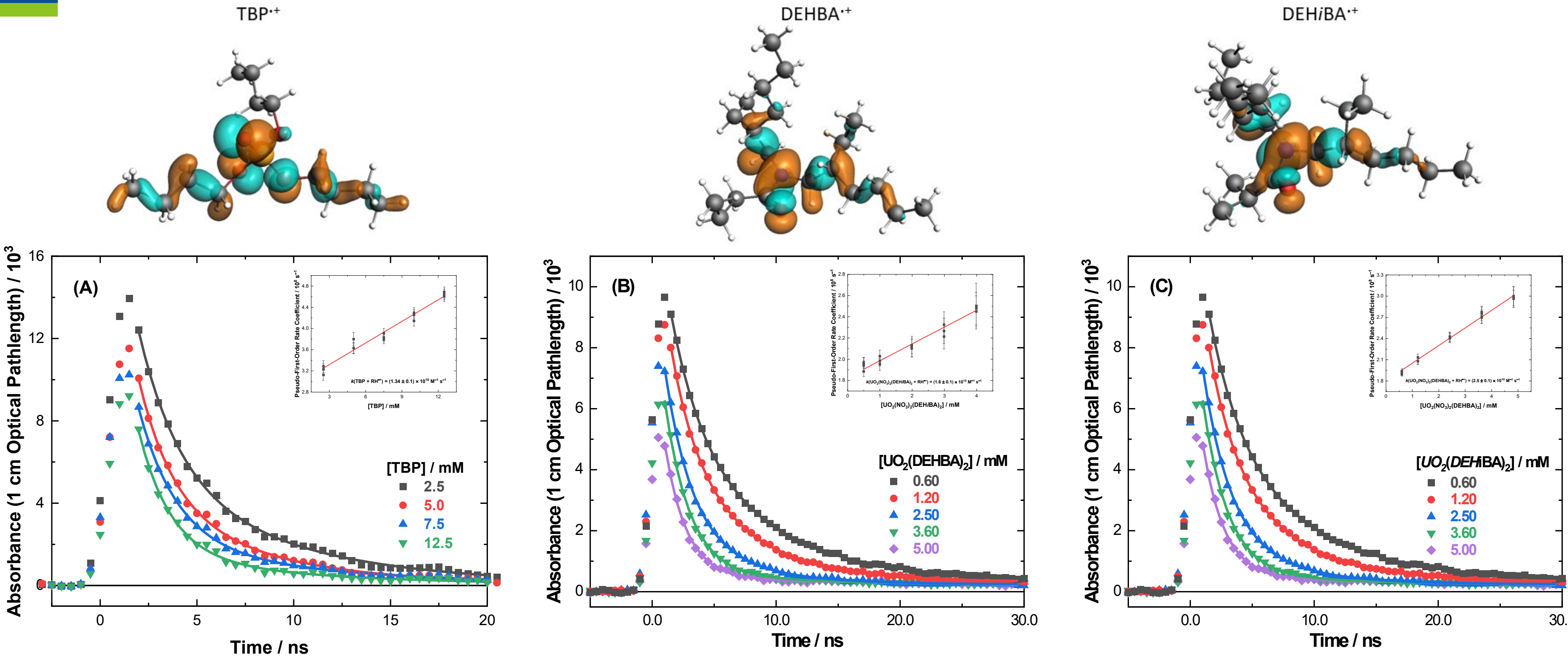




Computations: Geometry optimization using ADF2020 (*GGA OPBE functional* + *ZORA/STO-TZP basis set for all atoms*); Wave functions using ORCA (*Hybrid PBE0 functional* + *DKH-def2-SVP/DKH-def2-TZVP/SARC-DKH-TZVP*); and QTAIM metrics obtained from DFT wave functions using the AIMALL software.

Mezyk *et al.*, *Dalton Trans*, 2024, 53, 6881-6891.

Do these effects occur for all metals/ligands?

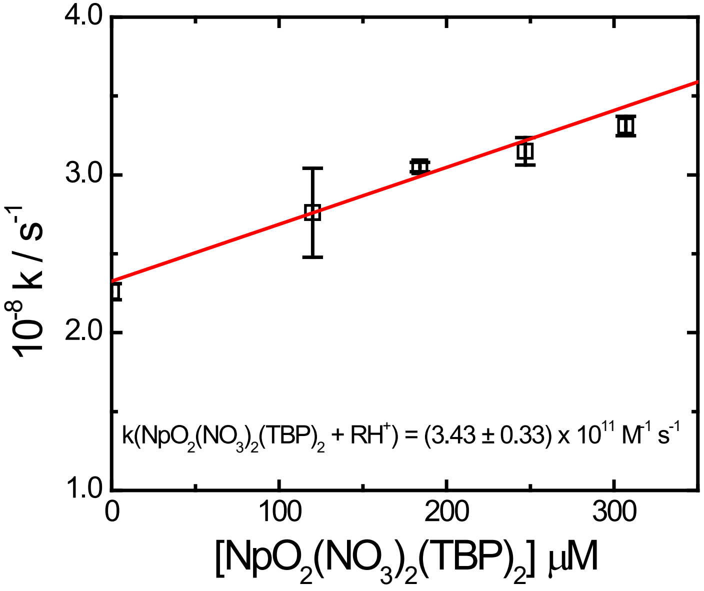


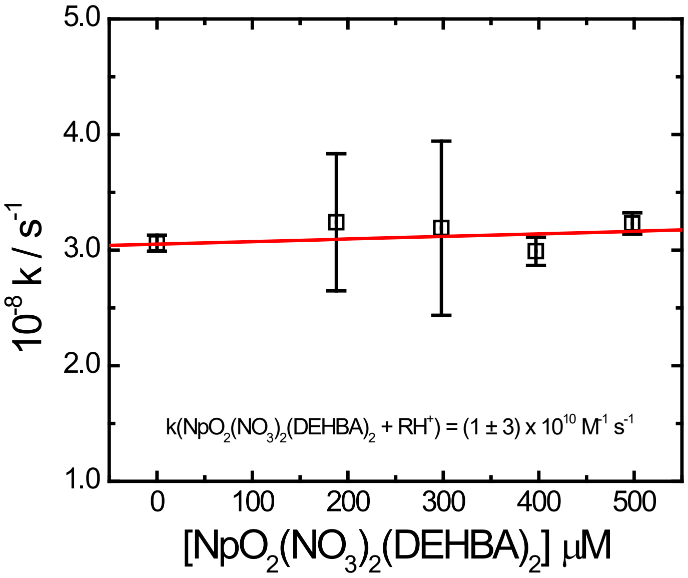
- UO_2^{2+} complexation had no effect on the reaction of **TBP** with **RH•$^+$**, *k*(**TBP** + **RH•$^+$**) = **(1.3 ± 0.1) × 10^{10} M$^{–1}$ s$^{–1}$**.
- For **DEHBA** and **DEHiBA**, UO_2^{2+} complexation afforded only a **2.6x** and **1.4x** increase in their rate coefficients.

Celis-Barros, Pilgrim, Cook, Grimes, Mezyk, and Horne, *PCCP*, **2021**, *23*, 24589.
Tagawa, Hayashi, Yoshida, Washio, and Tabata, *Int. J. Radiat. Appl. Instrum., Part C*, **1989**, *34(4)*, 503.
Yoshida, Ueda, Kobayashi, Shibata, and Tagawa, *Nucl. Instrum. Methods Phys. Res., Sect. A*, **1993**, *327(1)*, 41.
Wishart, Cook, and Miller, *Rev. Sci. Instrum.* **2004**, *75 (11)*, 4359.

Does this occur for all metals/ligands?

- **UO_2^{2+}** complexation had no effect on the reaction of **TBP** with **RH•⁺**, k(**TBP** + **RH•⁺**) = **$(1.3 \pm 0.1) \times 10^{10}$ M⁻¹ s⁻¹**.
- For **DEHBA** and **DEHiBA**, **UO_2^{2+}** complexation afforded a **2.6x** and **1.4x** increase in their rate coefficients.
- What about **NpO_2^{2+}**?



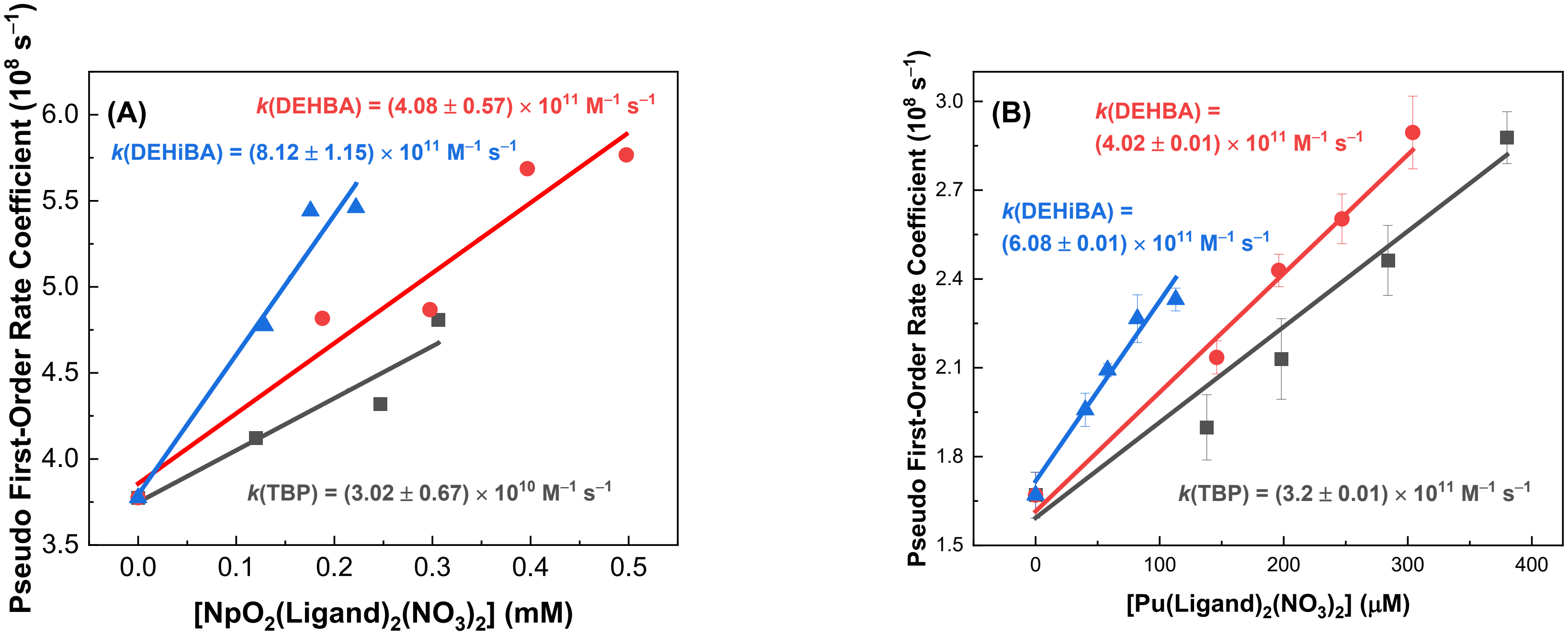


~25x faster

No change?

Opposite chemistry?

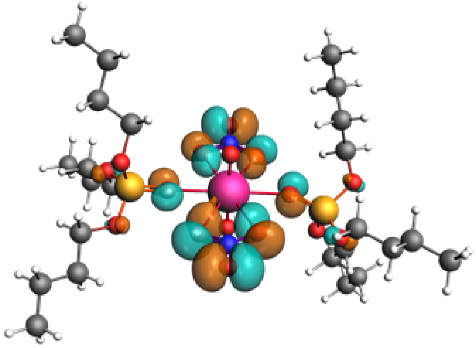
Does this occur for all ligands?



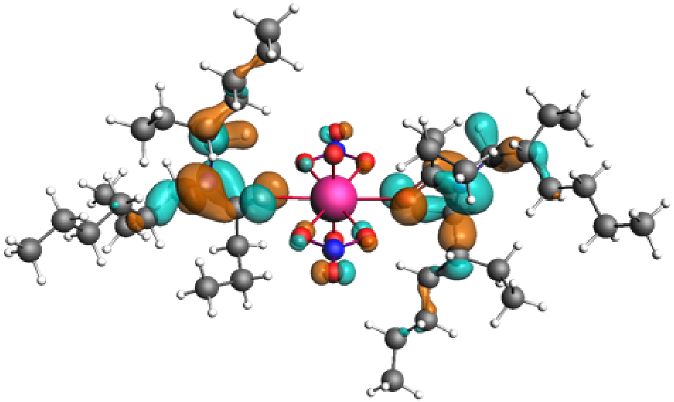
- Np(VI) and Pu(VI) complexation afforded significantly faster rates of reaction with **RH•⁺**, then for the non-complexed **TBP**, **DEHBA** and **DEHiBA** molecules.
- Evidence for electron transfer with the complexed metal center?

Theory says:

$[UO_2(NO_3)_2(TBP)_2]^{\cdot +}$



$[UO_2(NO_3)_2(DEHBA)_2]^{\cdot +}$



$[UO_2(NO_3)_2(DEH\textit{i}BA)_2]^{\cdot +}$

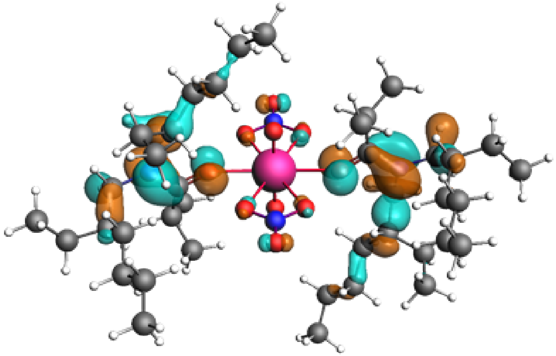


Table 1 Electronic structure calculation free energy (ΔG) values for the reaction of $RH^{\bullet +}$ with TBP, DEHBA, and DEHiBA for electron/hole transfer and proton transfer scenarios

Ligand	$\Delta G_{\text{electron/hole transfer}}$ (eV)	$\Delta G_{\text{proton transfer}}$ (eV)
TBP	0.16	−0.36
DEHBA	−0.88	−0.60
DEHiBA	−0.90	−0.57

Electron/Hole Transfer

$RH^{\bullet +}$ + Ligand → RH + $[\text{Ligand}]^{\bullet +}$

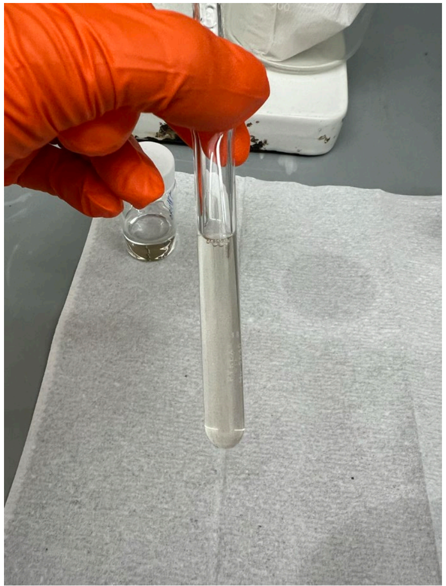
Proton Transfer

$RH^{\bullet +}$ + Ligand → R• + $[\text{Ligand(+H)}]^{+}$

Celis-Barros, Pilgrim, Cook, Grimes, Mezyk, and Horne, *PCCP*, **2021**, *23*, 24589.
Frisch, Trucks, Schlegel, Scuseria, Robb, *et al.*, Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford CT, **2016**.
ADF 2021.1, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.

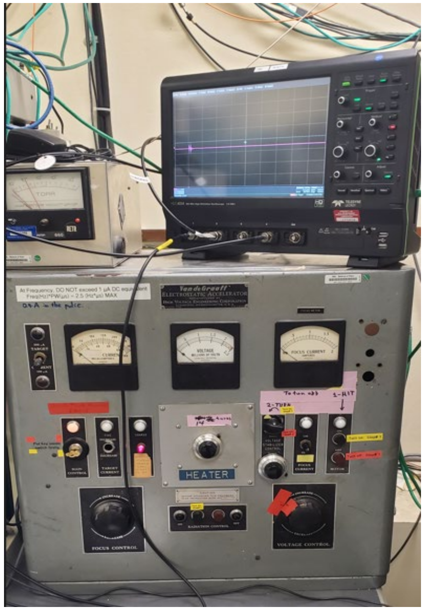
OK – what about the radiation-stability of UO_3 complexes with these ligands?

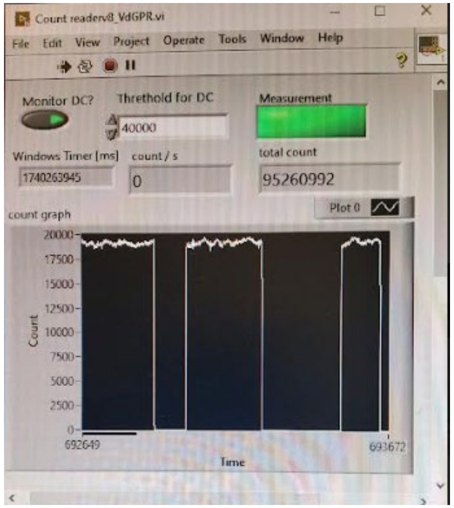
- Want high concentrations of metal in reprocessing systems (as high as possible ideally)
- Would expect radiation effects to be **direct** and **indirect** (through $RH^{+\bullet}$ radical reactions)
- Investigate: 100 mM ReO_3/1.50 M ligand in *n*-dodecane
- [Dodecane] = 4.40 M
- Measure kinetics of $RH^{+\bullet}$ reaction
- Measure loss of ligand with increasing radiation dose



Steady-state irradiations

- Typically done using ^{60}Co systems
- Takes a long time to achieve large doses (typically weeks to months for MGy)
- Try different approach, continuous Van De Graaff (VdG) irradiation
- BNL VdG: 2.0 MeV electron accelerator





Monitor DC?

Threthold for DC: 40000

Measurement

Windows Timer [ms]: 1740263945

count / s: 0

total count: 95260992

count graph

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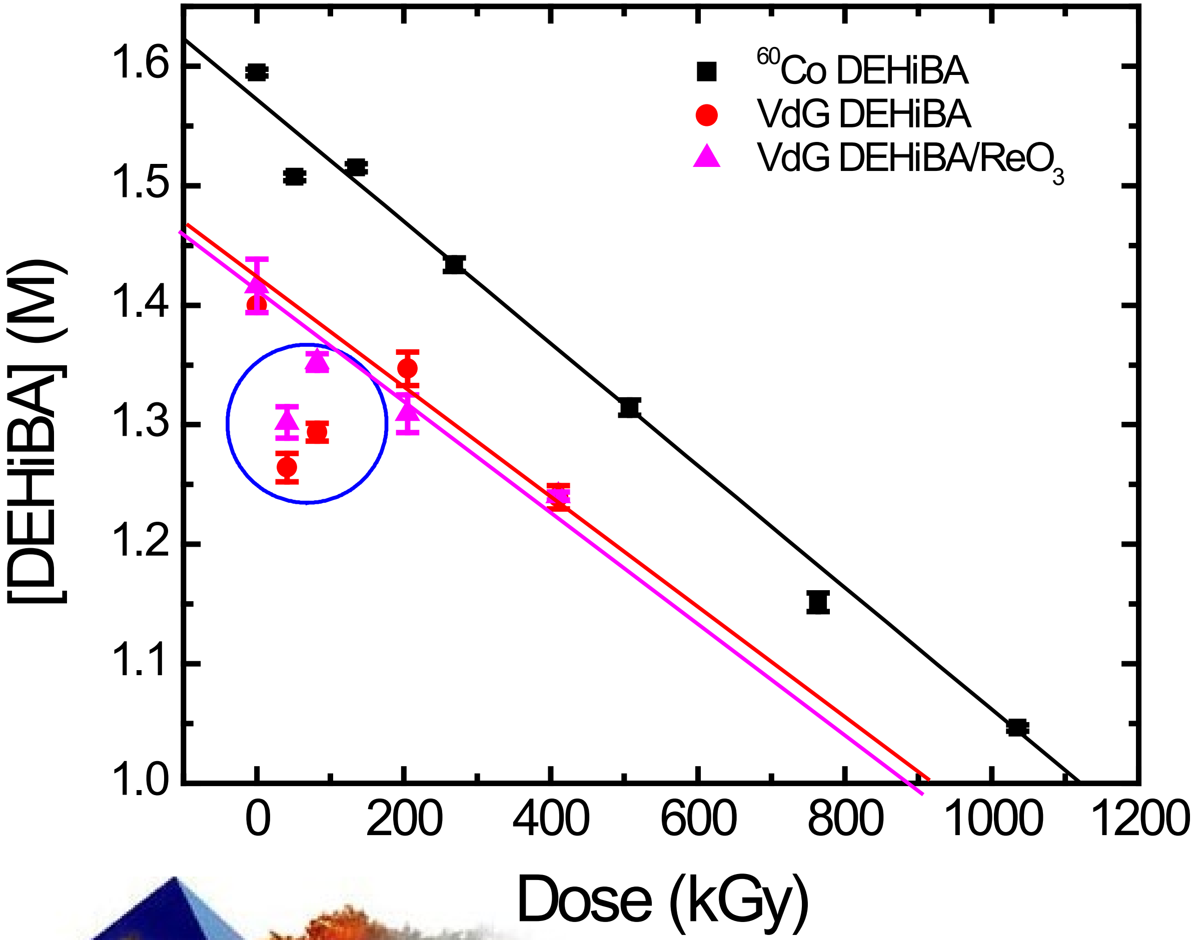
Experimental protocol

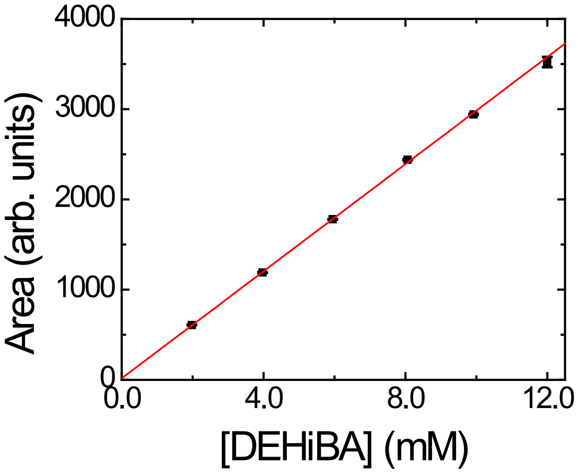
- Make up 1.50 M ligand in n-dodecane, with/out 100 mM ReO_3 in thrice-contacted 6.0 M HNO_3/n-dodecane
- Irradiate to 0,50,100,250,500 kGy
- Each irradiation was 50-100 kGy on *125 uL of solution* in 5 x 5 mm cuvettes (~3 min for 50 kGy!)
- Dosimetry based on Fricke solution for single pulse and extrapolated
- Ligand (TBP, DEHBA, DEHiBA) degradation measured by GCMS

GCMS results:

Degradation of DEHiBA ligand



DEHiBA calibration curve



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GCMS results

Ligand degradation comparison: **Dose Constants**

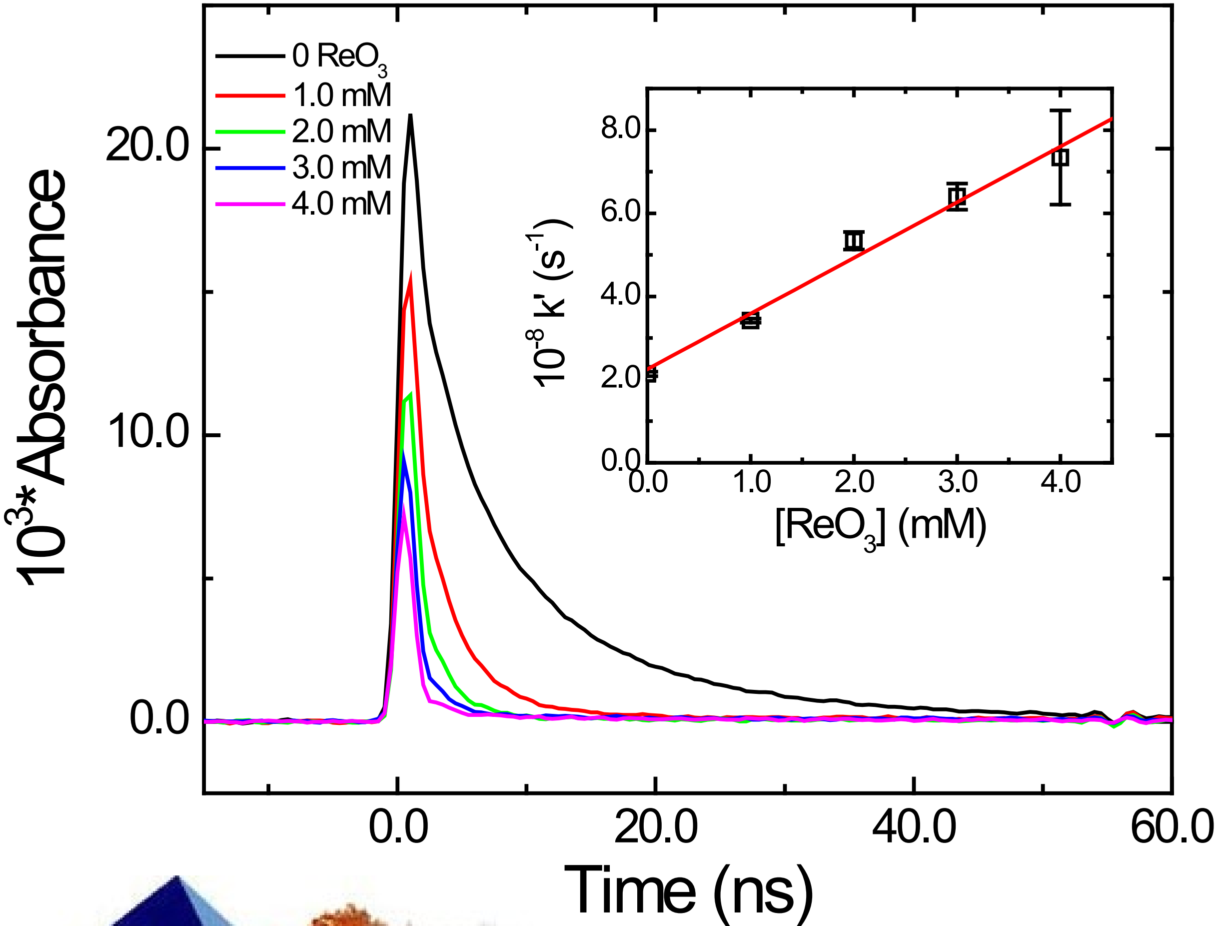
Plot **ln([Ligand]) vs Dose – take slope (for 0, > 200 kGy)**

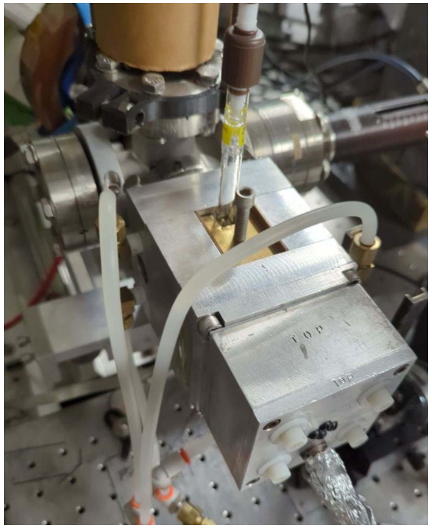
System	Radiation Source	-Dose constant kGy^{-1}
DEHiBA	^{60}Co	$(4.00 \pm 0.18) \times 10^{-4}$
DEHiBA	VdG	$(2.97 \pm 0.62) \times 10^{-4}$
DEHBA	^{60}Co	n.d.
DEHBA	VdG	$(3.21 \pm 0.03) \times 10^{-4}$
TBP	^{60}Co	$(2.60 \pm 0.17) \times 10^{-4}$
ReO_3/DEHiBA	VdG	$(3.23 \pm 0.34) \times 10^{-4}$
ReO_3/DEHBA	VdG	$(4.10 \pm 0.30) \times 10^{-4}$
ReO_3/TBP	VdG	n.d.

Not much change for DEHiBA, some increased degradation for DEHBA?

Kinetic measurements:

- Looking at $RH^{+\bullet}$ kinetics as before





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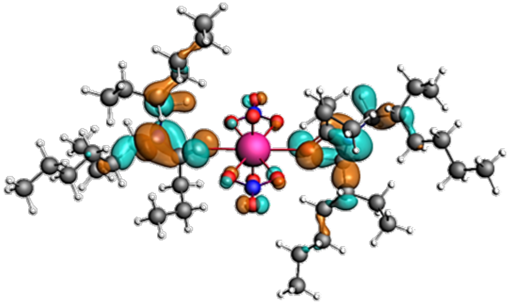
Kinetic measurements

$RH^{+\bullet}$ rate coefficients measured (0.50 M CH_2Cl_2/n-dodecane):

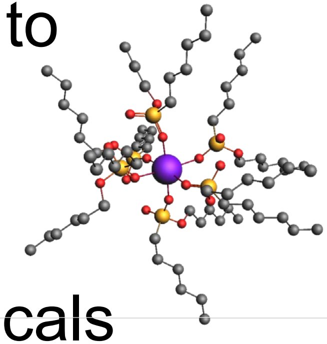
System	k M^{-1} s^{-1}
DEHBA	(1.04 ± 0.02) x 10^{10} [1]
DEHiBA	(1.52 ± 0.11) x 10^{10} [2]
TBP	(1.58 ± 0.08) x 10^{10}
ReO_3/DEHBA	(1.20 ± 0.13) x 10^{11}
ReO_3/DEHiBA	(1.34 ± 0.10) x 10^{11}
ReO_3/TBP	(1.65 ± 0.06) x 10^{11}

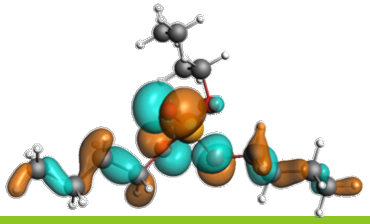
1. Horne *et al*., Dalton Trans. 48, 14450, 2019.
2. Drader *et al*., Solv. Extr. Ion Exch. 35, 480-495, 2017

Where we are/Future work



- Can directly dissolve large concentrations of ReO_3 into n-dodecane using ligands and acid-contacted organics
- Understanding fundamental radiation chemistry is essential for innovating nuclear technology.
- Metals have a significant effect on reaction kinetics, that varies from changes in electron distribution to generally increasing ligand reactivity
- Not so important for overall ligand degradation
- Still need to investigate the impacts of $NO_3^{\bullet}$ radicals
- Want to apply DFT theory to these data





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NTRD Nuclear Technology Research & Development

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Any Questions?