

## **Key Words**

uranyl complexation

reaction kinetics

dodecane radical cation

extraction ligands

tributyl phosphate (TBP)

N,N-Di-(2-ethylhexyl)butyramide (DEHBA)

N,N-Di-(2-ethylhexyl)isobutyramide (DEHiBA)

radiolytic behavior

second-order rate coefficient (k)

electron transfer

## **Objective**

1. Investigate the Influence of Uranyl Complexation: The primary objective is to evaluate how the complexation of uranyl ions ( $\text{UO}_2^{2+}$ ) with extraction ligands affects the reaction kinetics of the dodecane radical cation ( $\text{RH}^+$ ).
2. Measure Reaction Kinetics: To determine the second-order rate coefficients for the reaction between  $\text{RH}^+$  and both free and complexed forms of the ligands TBP, DEHBA, and DEHiBA.
3. Compare Ligands: To compare the reactivity and radiolytic stability of TBP, DEHBA, and DEHiBA both in their free form and when complexed with uranyl ions.
4. Evaluate Radiolytic Behavior: To understand the radiolytic behavior of these ligands under conditions simulating those found in nuclear fuel reprocessing, particularly focusing on how metal ion complexation influences this behavior.
5. Provide Data for Predictive Models: To provide essential kinetic data that can be used to develop

## REFERENCE: 20026

predictive computer models for ligand radiolysis under reprocessing conditions.

6. Identify Reaction Mechanisms: To elucidate the reaction mechanisms, particularly focusing on electron transfer and proton transfer processes in the presence of uranyl ions.

7. Assess Impact on Process Performance: To assess the potential impact of radiolytic degradation on the performance and recyclability of solvent extraction systems used in nuclear fuel reprocessing.

8. Explore Structural Changes: To investigate the structural changes in the ligands upon complexation with uranyl ions using computational methods, including density functional theory (DFT).

9. Determine Electron Density Distribution: To understand how the distribution of electron density in the ligands is affected by complexation with uranyl ions and how this influences their reactivity.

10. Support Alternative Ligand Development: To support the development of alternative extraction ligands that may offer better radiolytic stability and selectivity compared to the current industrial standard, TBP.

## Methodology

### Materials

#### 1. Chemical Sources

- Uranyl nitrate crystals ( $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) from Idaho National Laboratory's Radiochemistry Laboratory.

- TBP (99.0%), n-dodecane (99% anhydrous),  $\text{HNO}_3$  (99.999% trace metals basis), dichloromethane (DCM, 99.8%), and potassium thiocyanate (KSCN, 99.0% ACS Reagent Grade) from MilliporeSigma.

- DEHBA (99%) and DEHiBA (99%) from Technocomm Ltd.

- Ultra-pure water (18.2 M $\Omega$  cm) for aqueous solution preparation.

## REFERENCE: 20026

### Uranium Extraction Conditions

#### 1. Preparation of Uranium Stock Solution

- Dissolution of uranyl nitrate crystals in 3.97 M HNO<sub>3</sub> to prepare a standardized uranium stock solution.

#### 2. Ligand Extraction

- Ligands (1.1 M in 0.5 M DCM/n-dodecane solution) were pre-equilibrated with 3.97 M HNO<sub>3</sub> three times.
- The extraction involved contacting this solution with 0.21 M uranium in 3.97 M HNO<sub>3</sub> solution at a 1:1 organic-to-aqueous volume ratio for 1 minute using a vortex mixer.
- Post-extraction, phases were left to settle overnight and diluted with 0.5 M DCM/n-dodecane to achieve desired uranium ligand complex concentrations.

#### 3. Measurement of Uranium Concentration

- Liquid scintillation counting (LSC) of uranium-loaded ligand stock solutions was performed using a PerkinElmer Tri-Carb 3180TR/SL Low Activity LSC to determine uranium activity and calculate distribution ratios (DM).

### Time-Resolved Pulsed Electron Irradiations

#### 1. Kinetics Measurement Setup:

- Dodecane radical cation reaction kinetics were measured for UO<sub>2</sub><sup>2+</sup>-loaded TBP, DEHBA, and DEHiBA in 0.5 M DCM/n-dodecane solutions using the Brookhaven National Laboratory (BNL) Laser Electron Accelerator Facility (LEAF).
- An FND-100Q silicon photodiode, LeCroy WaveRunner 66Zi transient digitizer, and optical interference filters were used for direct measurement of RH + decay kinetics at 800 nm over 200 ns.

## REFERENCE: 20026

### 2. Data Analysis

- Second-order rate coefficients ( $k$ ) were determined by pseudo-first-order double-exponential fits to the RH + decay traces.
- Corrections for free ligand and corresponding  $\text{UO}_2^{2+}$  complex concentrations were made, and data were plotted as a function of solute concentration.

### Computations

#### 1. ElectronicStructure Calculations

- Gaussian16 and Gaussview6 programs were used for density functional theory (DFT) calculations with the B3LYP functional, 6-31+G(d) basis set, and Grimme et al. s empirical D3 corrections for dispersion effects.
- Solvation effects were included using the polarizable continuum model for n-dodecane.
- Reaction free energies were determined using corrections for standard states.

#### 2. Quantum Chemical Calculations

- The ADF engine within the AMS2021 suite was used for density-based quantum chemical calculations.
- Geometry optimizations were performed using the GGA functional, PBE, with the STO-TZP basis set, considering scalar relativistic effects using the ZORA Hamiltonian.
- Natural bond orbital (NBO) analysis was used to obtain localized molecular orbitals and assess reactivity.

#### 3. Reactivity Assessment

- Fukui functions and local softness were calculated to predict reactive sites in the ligand molecules.
- Free ligands and their  $\text{UO}_2^{2+}$  complexes were studied in their neutral and radical cation states.

### Key Findings

## REFERENCE: 20026

### 1. TBP

- Finding: The second-order rate coefficient ( $k$ ) for the reaction of RH + with free TBP was determined to be  $1.3 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$
- Observation: The reaction rate increased with higher ligand concentrations, indicating that the complexation state of TBP influences the rate.
- Kinetic Data: The decay data fitted a double-exponential decay function, suggesting both geminate and non-geminate recombination processes.

### 2. DEHBA and DEHiBA

- Finding: The second-order rate coefficients for RH + reactions with DEHBA and DEHiBA were significantly higher upon uranyl complexation, with  $2.5 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$  for  $[\text{UO}_2(\text{NO}_3)_2(\text{DEHBA})_2]$  and  $1.6 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$  for  $[\text{UO}_2(\text{NO}_3)_2(\text{DEHiBA})_2]$ .
- Comparison: Free DEHBA and DEHiBA had lower rate coefficients, indicating that uranyl complexation enhances their reactivity.
- Reanalysis: Revised rate coefficients for free DEHBA and DEHiBA were provided due to new fitting procedures.

### 3. Mechanistic Insights

- Reaction Pathways: The study suggested different reaction pathways for TBP and the butyramides (DEHBA and DEHiBA). TBP primarily underwent proton transfer, while DEHBA and DEHiBA were more inclined towards electron/hole transfer.
- Energetic Feasibility: Computational results indicated that electron/hole transfer is energetically unfavorable for TBP but favorable for DEHBA and DEHiBA.

#### 4. Computational Analysis

- Electronic Structure: Density functional theory (DFT) calculations were used to understand the electronic structure of the ligands and their complexes. The study found differences in electron density distribution upon uranyl complexation, influencing their reactivity.
- Fukui Functions: Fukui function calculations were used to predict reactive sites in the ligand molecules, providing insights into their reactivity with  $\text{RH}^+$ .

#### 5. Radiolytic Stability

- Impact of Radiolysis: The findings suggested that radiolytic damage to TBP is predominantly due to direct ionization or reactions with degradation products rather than oxidation by  $\text{RH}^+$ . In contrast, DEHBA and DEHiBA showed increased reactivity upon complexation, making them potentially better alternatives to TBP in radiolytic environments.

#### 6. Practical Implications

- PUREX Process: The results indicated that in the PUREX process, DEHBA and DEHiBA could be more effective than TBP due to their enhanced reactivity with  $\text{RH}^+$  upon uranyl complexation. This has implications for the design and selection of ligands in nuclear fuel reprocessing.

#### Conclusion

1. Negligible Effect on TBP: The study found that uranyl ( $\text{UO}_2^{2+}$ ) complexation has a negligible effect on the reaction of the dodecane radical cation ( $\text{RH}^+$ ) with TBP. The second-order rate coefficient for TBP remained essentially unchanged upon complexation.
2. Increased Reaction Rates for DEHBA and DEHiBA: Uranyl complexation significantly increases the rate of reaction between  $\text{RH}^+$  and both DEHBA and DEHiBA. The second-order rate

## REFERENCE: 20026

coefficients for the reactions of  $\text{RH}^+$  with  $[\text{UO}_2(\text{NO}_3)_2(\text{DEHBA})_2]$  and  $[\text{UO}_2(\text{NO}_3)_2(\text{DEHiBA})_2]$  were found to be higher than those for the free ligands.

3. Different Reaction Pathways: The difference in kinetic enhancement between TBP and the butyramides (DEHBA and DEHiBA) is attributed to different reaction pathways. TBP interacts with  $\text{RH}^+$  primarily via proton transfer, which is not amenable to inner-sphere processes conferred by complexation. In contrast, DEHBA and DEHiBA undergo electron/hole transfer, which is energetically more favorable and enhanced by complexation.

4. Energetic Favorability: Computational results showed that electron/hole transfer is energetically unfavorable for TBP but favorable for DEHBA and DEHiBA, explaining the observed differences in reaction kinetics.

5. Shielding Effect of Nitrate Ligands: The study also found that the attendant nitrate counter anions in the uranyl complexes effectively shield TBP from  $\text{RH}^+$  electron transfer processes, whereas this shielding effect is less pronounced for the butyramides, allowing for increased reaction rates.

6. Radiolytic Damage Implications: These findings suggest that in the PUREX process, most of the radiolytic damage to TBP is by direct ionization or reaction with degradation product radicals, rather than oxidation by  $\text{RH}^+$ . Conversely, the butyramides may experience more radiolytic damage through reactions with  $\text{RH}^+$ , impacting their potential as TBP substitutes.

7. Future Research Directions: The study indicates that further research is needed to explore the steady-state influence of metal complexation on ligand integrity, including gamma irradiation studies and investigations into higher-order structures such as ligand trimers and oligomers.

## Relevance to Study

### Assessment of Radiolytic Stability

- The article investigates the radiolytic stability of TBP, DEHBA, and DEHiBA, crucial for their

## REFERENCE: 20026

performance in the intense radiation fields present in nuclear fuel reprocessing.

- DEHBA and DEHiBA show enhanced reaction rates upon uranyl complexation, suggesting they are more reactive and potentially more susceptible to radiolytic damage compared to TBP

### Reaction Pathways

- The study identifies different reaction pathways for TBP versus DEHBA and DEHiBA, with TBP primarily undergoing proton transfer and the butyramides undergoing electron/hole transfer.
- This difference in pathways indicates that uranyl complexation enhances the radiolytic reactivity of DEHBA and DEHiBA more than TBP, impacting their suitability for long-term use in reprocessing systems

### Kinetic Data for Predictive Models

- The second-order rate coefficients for reactions of  $RH +$  with both free and uranyl-complexed ligands provide essential kinetic data.
- These coefficients are critical for developing predictive models for ligand radiolysis under reprocessing conditions, aiding in the selection of ligands with optimal performance

### Impact of Complexation on Ligand Performance

- The article highlights that uranyl complexation has a negligible effect on TBP but significantly increases the reactivity of DEHBA and DEHiBA.
- This finding implies that DEHBA and DEHiBA might undergo more rapid degradation in reprocessing environments, influencing their effectiveness as TBP alternatives

### Electronic Structure Insights

- Computational analyses provide insights into the electronic structure and reactivity of the ligands upon uranyl complexation.
- The electron density distribution and reactivity predictions help in understanding how complexation affects ligand performance, guiding the design of more robust ligands



## REFERENCE: 20026

### Potential for Improved Ligand Design:

- The research supports the development of alternative ligands with better radiolytic stability and selectivity than TBP, such as DEHBA and DEHiBA.
- These alternatives could offer improved performance in the nuclear fuel cycle, reducing the generation of problematic degradation products and enhancing process efficiency

### Relevance to PUREX Process

- The findings are directly relevant to the PUREX process, the most common method for reprocessing used nuclear fuel.
- Understanding the radiolytic behavior of these ligands under process conditions helps in optimizing the PUREX process and selecting the most suitable ligands for uranium and plutonium recovery

## Critical Parameters Identified

### High Importance

#### Chemical Stability

- The study evaluates the reaction kinetics and reactivity of TBP, DEHBA, and DEHiBA ligands in the presence of uranyl ions, providing insights into their chemical stability.
- It is noted that uranyl complexation does not significantly alter the reaction kinetics of TBP, suggesting good chemical stability for TBP in these conditions.
- DEHBA and DEHiBA, however, show increased reactivity upon complexation, indicating potential concerns about their chemical stability under these conditions

#### Radiolysis Resistance

- The primary focus of the study is on the radiolytic stability of the ligands in the presence of a radiation field.
- Findings indicate that TBP is less affected by radiolytic conditions compared to DEHBA and

## REFERENCE: 20026

DEHiBA, which show increased reaction rates upon uranyl complexation, potentially reducing their radiolysis resistance

- The study suggests that the degradation of TBP is mainly due to direct ionization or reaction with degradation products rather than RH + oxidation, implying better radiolysis resistance for TBP compared to the butyramides

### Thermodynamics

- The article provides computational insights into the thermodynamic favorability of electron/hole transfer and proton transfer reaction pathways.
- Electron/hole transfer is energetically favorable for DEHBA and DEHiBA but unfavorable for TBP, affecting the thermodynamics of their reactions with RH + and influencing their separation efficiency under reprocessing conditions

### Medium Importance

#### Kinetics (forwards and reverse)

- The study extensively measures the second-order rate coefficients (k) for the reaction of RH + with both free and complexed ligands.
- TBP shows a negligible change in reaction kinetics upon uranyl complexation, while DEHBA and DEHiBA show significantly increased rates, indicating faster kinetics which can impact the speed of the separation process

### Loading Capacity

- While not explicitly measured in the study, the increased reactivity of DEHBA and DEHiBA upon uranyl complexation could influence their loading capacity, as higher reactivity might lead to faster saturation of the ligands

### Operational Condition Range

## REFERENCE: 20026

- The study does not specifically address the operational condition range, but the findings imply that TBP might be more robust under a variety of radiolytic conditions due to its stable reaction kinetics and lower susceptibility to RH + oxidation

### Low Importance

#### Solubility

- Solubility is not directly addressed in the study, though the use of different solvents (DCM/n-dodecane) for ligand preparation indicates an awareness of the importance of solubility in experimental setups

#### Dispersion Numbers

- The study does not discuss dispersion numbers, focusing instead on reaction kinetics and radiolytic stability.

#### Phase Disengagement

- Phase disengagement is not covered in the study, as the focus is on the chemical and radiolytic behavior of the ligands rather than practical separation processes.