INL/CON-23-72577-Revision-0

Insight into the Radiolytic Degradation Mechanism of TODGA

June 2023

Christopher A Zarzana

Changing the World's Energy Future

INL is a U.S. Department of Energy National Laboratory operated by Battelle Energy Alliance, LLC

INL/CON-23-72577-Revision-0

Insight into the Radiolytic Degradation Mechanism of TODGA

Christopher A Zarzana

June 2023

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

Insight into the Radiolytic Degradation Mechanism of TODGA

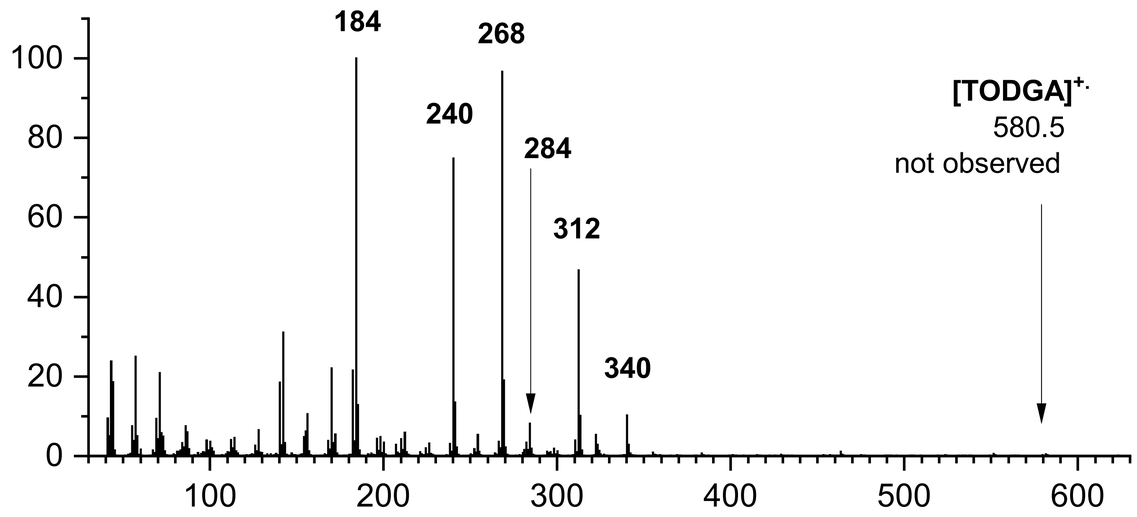
Christopher Zarzana[1], Samuel Tyndall[1,2], Cathy Rae[1]

[1]Idaho National Laboratory, Idaho Falls, ID, USA; [2]Currently affiliation: Northwestern University, Evanston, IL, USA

Background & Motivation

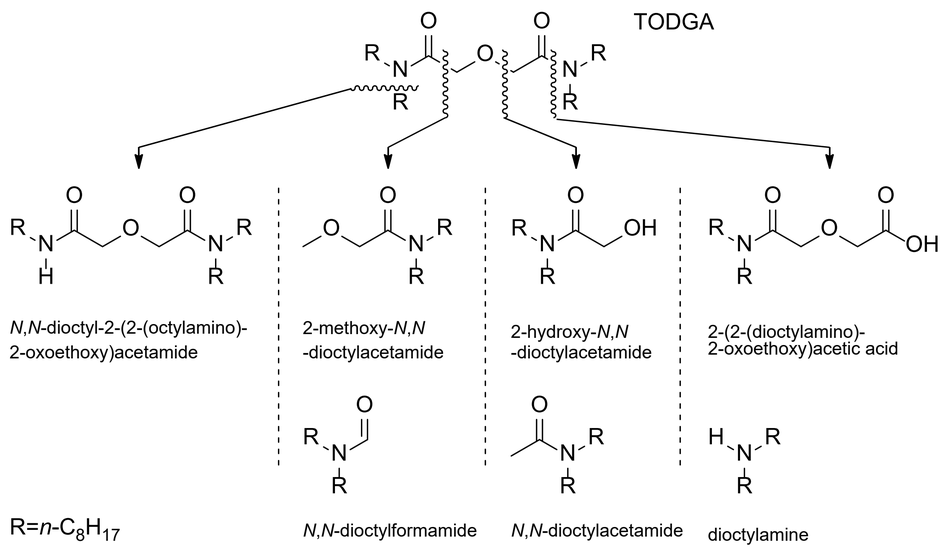
- Safe processing and disposal of spent nuclear fuel is a major step required for wide-spread use of nuclear power
- N,N,N',N'-tetraoctyldiglycolamide (TODGA) has been studied as a ligand for lanthanide/minor actinide extraction for partitioning and transmutation schemes.
- The mechanism of initial energy transfer from products of solvent radiolysis to TODGA is still under debate:
  - hydrogen abstraction from reaction with a neutral radical
  - electron abstraction from reaction with a radical cation
- Hydrogen abstraction is expected to occur adjacent to the central ether of TODGA, and result in formation of N,N-dioctylacetamide
- However, TODGA radiolysis in dodecane results in products from cleavage at all sites on the TODGA backbone
- We hypothesize that TODGA radiolytic fragmentation is driven by both mechanisms
- Irradiation of TODGA in hexane should reduce the influence of electron abstraction from diluent radical cations, since the lifetime of the radical cation in hexane is approximately one order of magnitude less than in dodecane [1]

Electron Impact Mass Spectrum of TODGA

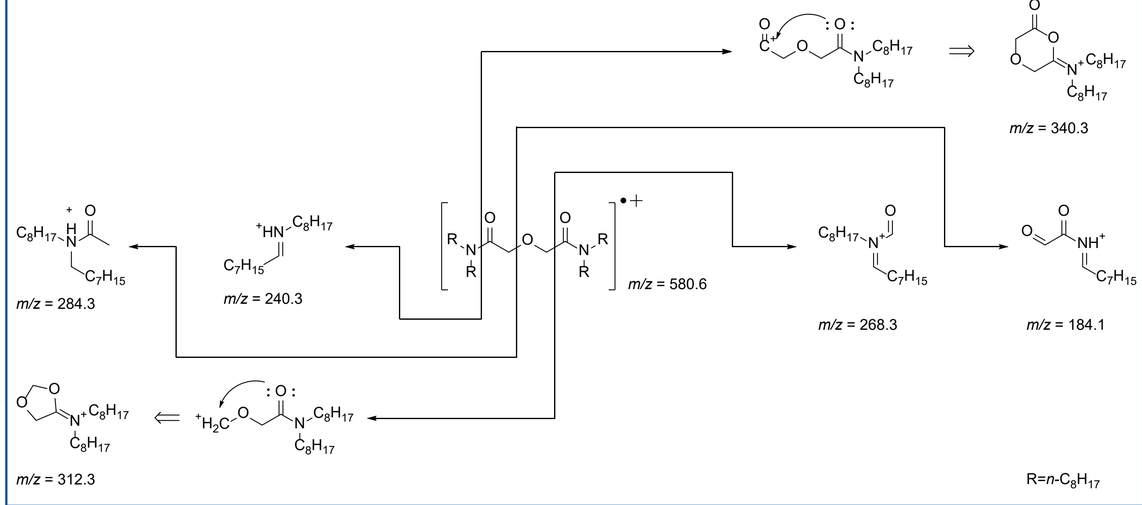


- Electron impact ionization of TODGA in the gas phase produced the TODGA radical cation, which fragments
- Fragments result from bond cleavages from many of the TODGA backbone bonds

TODGA Degradation Products, Dodecane Irradiation



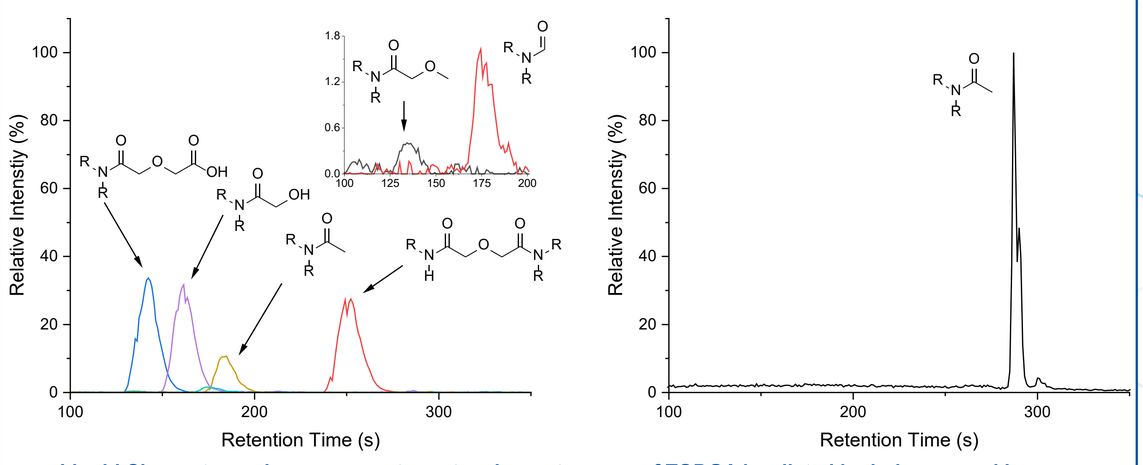
TODGA Radical Cation Fragment Ion Proposed Structures



Results

TODGA Irradiated in Dodecane

TODGA Irradiated in Hexane



Liquid Chromatography mass spectrometry chromatograms of TODGA irradiated in dodecane and hexane

- Irradiation in dodecane results in a well-known suite of degradation products resulting from cleavages across the whole TODGA backbone
- Irradiation in hexane results in only N,N-dioctylacetamide, which results from cleavage adjacent to the central ether

Conclusions

- TODGA degradation is likely a competition between electron abstraction and hydrogen abstraction
  - Electron abstraction likely leads to fragmentation across the TODGA backbone
  - Hydrogen abstraction likely leads to fragmentation adjacent to the ether
- Inhibition of electron abstraction could dramatically reduce degradation product production

Future Work

- Irradiations in other diluents between hexane and dodecane (octane, decane)
- Should see a rise in the abundance of degradation products from other backbone fragmentations besides adjacent to the ether as the diluent chain length gets longer

Acknowledgments

- All experiments were performed at Idaho National Laboratory were supported by the US Department of Energy (US-DOE), Assistant Secretary for Nuclear Energy, under the Fuel Cycle R&D Program, Idaho Operations Office Contract DE-AC07-05ID14517.

References:
[1] F. Sviridenko et al., Chem. Phys. Lett. 1998, 297 (3), 343–349, DOI: 10.1016/S0009-2614(98)01099-9.

www.inl.gov
INL/CON-23-72577

Battelle Energy Alliance manages INL for the U.S. Department of Energy's Office of Nuclear Energy

Idaho National Laboratory