

ALPHA RADIOLYSIS RESEARCH FY14

Stephen P. Mezyk

September 2014



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

ALPHA RADIOLYSIS RESEARCH FY14

Stephen P. Mezyk

September 2015

Idaho National Laboratory

Idaho Falls, Idaho 83415

<http://www.inl.gov>

**Prepared for the
U.S. Department of Energy
Office of Nuclear Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517**

Bruce Mincher milestone report

Alpha Radiolysis Research FY14

Received from prof. Steve Mezyk, Sept 2, 2014

To obtain a full understanding of the overall radiation chemistry involved in large-scale Ln(III)-An(III) separation processes, the impacts of both gamma and alpha radiolysis on the radical-induced ligand degradations for both free and metal-complexed species have to be quantitatively determined. In this reporting period, we have continued our alpha-radiolysis studies into various ligand-solvent systems. These experimental measurements are difficult to perform, with no single reported method being optimal. Therefore, studies have been conducted using three concomitant approaches: internal isotope studies, ion-beam measurements and neutron-induced alpha decays in a TRIGA reactor.

The initial system studied this year by alpha radiolysis was 0.10 M CMPO (octylphenyl-N,N-diisobutylcarbamoylmethylphosphine oxide) in dodecane. Post irradiated samples were analyzed for the radiolytically-induced decrease in CMPO concentration (by HPLC), the appearance of degradation products (MS) and their Am solvent extraction distribution ratios. Results for the He ion-beam irradiation for both aerated and de-aerated solutions showed no CMPO loss up to a maximum absorbed dose of 50 kGy. Contact with 3.0 M HNO₃ prior to irradiation showed similar results. However, for higher doses, obtained by either ²⁴⁴Cm irradiation or using the TRIGA reactor, the results differed. No CMPO loss was found in the isotope irradiation, but a definite degradative loss was seen for the reactor measurements. Although the reactor-generated 1.4 MeV He is also accompanied by a 0.85 MeV Li ion (based on the neutron capture of ¹⁰B) the two particles have similar LETs, and thus should be directly comparable to the isotope data. Distribution measurements showed that the distribution ratio for Am did not change with absorbed dose within the error of measurement. ESI-MS measurements on He-ion beam irradiated solutions (the only ones that did not have residual activity) showed that the main products were the amides N,N-diisobutylformamide, N,N-diisobutylacetamide and diisobutylamine formed by cleavage reactions on either side of the central methylene moiety of CMPO or by cleavage of the amide bond. These data have been summarized in a published journal article: Mincher, B.J.; Mezyk, S.P.; Elias, G.; Groenewold, G.S.; LaVerne, J.A.; Nilsson, M.; Pearson, J.; Schmitt, N.C., *The radiation chemistry of CMPO: Part 2. Alpha radiolysis. Solv. Ext. Ion Exch.*, 32, 167-178, (2014).

The discrepancy in the degradative loss G-values in the ²⁴⁴Cm and TRIGA He ion generation data for CMPO, and the inability of the ion-beam and ²¹¹At approaches to obtain sufficiently high doses for direct comparison to these two techniques, resulted in a new standardization experiment being performed. Our system was 16 μM methylene blue in water at natural pH. The advantage to this system was that it only required 1kGy of dose to get measurable degradation, allowing it to be investigated by all approaches. To date, both the ion-beam and the reactor experiments have been completed. The ion-beam reproduced an earlier literature value for alpha radiolysis within experimental error, with a G_α value of -0.065 μmol J⁻¹. However, the mixed-field TRIGA reactor values could only accurately reproduce the gamma loss G_γ-value (-0.71 μmol J⁻¹): their deduced alpha value was significantly lower at G_α = -0.023 μmol J⁻¹. We

are still waiting on the isotope measurements to be performed at INL and in Sweden (^{211}At) at this time.

Lastly, reactor measurements have also been made for TODGA degradation in dodecane, where a concentration-dependent value of $G_{\alpha} = -0.022 \mu\text{mol J}^{-1}$ (10 mM TODGA) or $G_{\alpha} = -0.06 \mu\text{mol J}^{-1}$ (100 mM TODGA). These values are in contradiction with previous literature data, showing the opposite trend for the concentration-dependence. We have just completed ion-beam irradiations of these systems, but these data have yet to be analyzed. Again, isotope experiments are being planned in the next few months.