Gamma Radiolysis of Phenyl-Substituted TODGAs: Part I

Christopher A. Zarzana*[a], Jack McAlpine[a,b], Andreas Wilden[c], Michelle Hupert[d], Andrea Stärk[d], Mudassir Iqbal[e], Willem Verboom[f], Bruce J. Mincher[a], Gary S. Groenewold[a], Giuseppe Modolo[c]

* Address reprint requests to Christopher A. Zarzana, Idaho National Laboratory, P.O. Box 1625, Idaho Falls, ID 83415-3531, United States of America. E-mail: christopher.zarzana@inl.gov.

[a] Idaho National Laboratory, Idaho Falls, ID 83415, United States of America.

[b] University of Idaho, Moscow, ID 83844, United States of America.

[c] Forschungszentrum Jülich GmbH, Institut für Energie- und Klimaforschung - Nukleare Entsorgung (IEK-6), 52428 Jülich, Germany.

[d] Forschungszentrum Jülich GmbH, Zentralinstitut für Engineering, Elektronik und Analytik (ZEA-3), 52428 Jülich, Germany.

[e.] Department of Chemistry, School of Natural Sciences (SNS), National University of Sciences and Technology (NUST), Islamabad, 44000, Pakistan

[f] Laboratory of Molecular Nanofabrication, Mesa+ Institute for Nanotechnology, University of Twente, 7500 AE Enschede, The Netherlands.

Abstract

The radiolytic stabilities of three phenylated analogs of *N*,*N*,*N'*,*N'*-tetraoctyl diglycolamide (TODGA) were investigated: 2-(2-(di-*n*-octylamino)-2-oxoethoxy)-*N,N*-di-*n*-octyl-2-phenylacetamide (PhTODGA), which has a phenyl substituent bound to a central methylene, 2-(2-(di-*n*-octylamino)-2-oxo-1-phenylethoxy)-*N,N*-di-*n*-octylpropanamide (PhMeTODGA), which also contains a methyl substituent bound to the methylene on the other side of the ether moiety, and, 2-(2-*N*-*n*-hexyl-*N*-phenylamino)-2-oxoethoxy)-*N*-*n*-hexyl-*N*-phenylacetamide (DHDPDGA), which has phenyl substituents located on the amide groups instead of the central methylenes. The objective of Part I of this series of papers covers was to evaluate the contribution of the phenyl group to the stability of diglycolamides when irradiated in a) *n*-dodecane, and b) *n*-dodecane in the presence of a nitric acid-containing aqueous phase. The presence of the phenyl group decreases the overall radiolytic stability compared to unsubstituted TODGA. However, the results also indicate that the phenyl groups interact with nitric acid in a cooperative fashion that enhances the radiation stability of the phenylated diglycolamide (DGA) derivatives in the presence of a nitric acid-containing aqueous phase compared to irradiation in only *n*-dodecane. The results are consistent with the hypothesized formation of nitric acid-phenylated DGA complexes in the *n*-dodecane phase that are significantly more stable with respect to gamma irradiation, compared to the phenylated DGA molecules alone.

Keywords: Radiolysis, Radical chemistry, TODGA, diglycolamides

Introduction

Nuclear energy is a key component of a global, low-carbon energy future. One of the challenges facing large-scale deployment of nuclear power is the long-term disposition of used nuclear fuel.[1] Reprocessing used nuclear fuel can reduce the volume of waste requiring long-term storage, enabling efficient usage of geologic storage repositories.[2] One of the main challenges to efficient use of space in geologic repositories is the heat generated by stored material. Once the plutonium has been removed from the used nuclear fuel, americium and curium represent the largest contributors to the waste heat in the several hundred-to-several thousand year time frame.[3] Thus, partitioning and transmutation schemes that remove the minor actinides americium or curium can reduce heat load, allowing for more efficient use of space in geologic repositories.

Innovative reprocessing technologies offer opportunities to reduce heat load and extract usable americium or curium in reprocessed nuclear fuel. Liquid-liquid extraction is the most common strategy used to separate the elements that comprise used nuclear fuel. The approach relies on organic ligands that selectively interact with a subset of the elements in the used fuel, forming coordination complexes that can partition from the aqueous phase to the organic phase, thus effecting separation. The extractant ligands must operate in an extreme environment of high radiation fields and significant concentrations of nitric acid, which results in degradation of the ligands over time and a loss of separation efficiency. Additionally, radiolytically-produced ligand degradation products can exert a deleterious effect on separation processes resulting from non-specific complexation, further reducing separation efficacy. To maintain separation performance, the degradation products must be removed from the separation solvent and the degraded ligand replaced, which adds to the overall cost of partitioning. Thus, understanding the radiation chemistry of separation ligands in the presence of nitric acid is critical to the development of new, radiation resistant separation ligands and nuclear fuel cycles that can improve the cost competitiveness of nuclear energy.[4–6]

The tetraalkyl diglycolamides (DGAs) are a class of organic ligands that have received significant attention for minor actinide partitioning (Figure 1).[7] Many radiolysis experiments have been conducted by dissolving the DGAs in a paraffinic organic solvent, *e.g.*, *n*-dodecane.[8–12] However, an experimental system in which the organic solvent is in contact with an acidic aqueous phase is a better representation of the process environment, and consequently many studies have compared radiolysis behavior in organic-only solvents with that occurring in organic-acid environments. In the case of the most widely-studied DGA molecule, *N*,*N*,*N'*,*N'*-tetraoctyl diglycolamide (TODGA, Figure 1a), the acid-contact did not make any difference: radiolytic degradation in an *n*-dodecane organic phase was about the

same as that occurring in *n*-dodecane in contact with an aqueous acid.[13–16] For methyl TODGA derivatives, (methyl groups bound to the central methylene moieties on one (MeTODGA) or both sides of the central ether oxygen atom (Me_2TODGA, Figure 1b, c)), the dose coefficients were greater (faster radiolysis) in acid-contacted *n*-dodecane, compared to experiments in organic-only environments.[17,18]

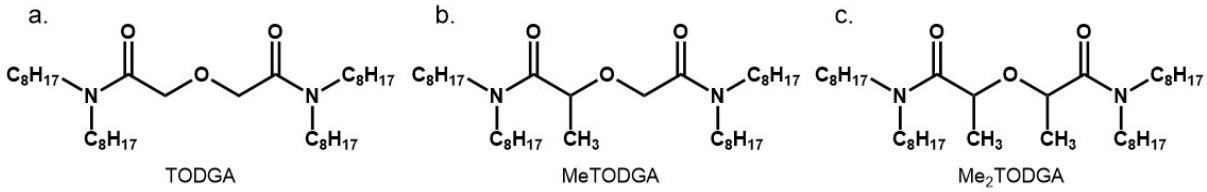

Figure 1. Structures of (a) *N,N,N',N'*-tetraoctyl diglycolamide (TODGA), (b) methyl TODGA (MeTODGA), and (c) dimethyl TODGA (Me_2TODGA).

In contrast to the DGAs, octyl(phenyl)-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO), an organophosphorous aromatic amide extractant, exhibits gamma radiolysis degradation kinetics with rates that are significantly lower when the CMPO-organic phase is irradiated in contact with an aqueous nitric acid phase, compared to radiolysis rates in organic-only experiments. Higher nitric acid concentrations were observed to result in lower radiolysis rates, suggesting the nitric acid provides a protective effect.[19] This radiation protection has been hypothesized to arise from the formation of a strongly bound CMPO-nitric acid complex in the organic phase;[20,21] thus, identification of the CMPO functional groups responsible for the formation of this complex could allow the design of separation ligands with significantly enhanced radiation resistance in the presence of high concentrations of nitric acid.

The two major functional group differences between the DGAs and CMPO are the phosphoryl group and the phenyl ring. Recent comparisons of trioctylphosphine oxide (TOPO) and dioctyl(phenyl)phosphine oxide (DOPPO) demonstrate that DOPPO exhibits nitric acid-induced radiation protection similar to that of CMPO, while TOPO does not,

suggesting that the phenyl group is responsible for conferring radiation protection.[21] Thus, we have begun to systematically modify the structure of TODGA, which does not exhibit any enhanced radiation resistance in the presence of nitric acid,[13] to determine if the addition of a phenyl group can confer a similar nitric acid-induced radiation protection.

The effect of the phenyl groups on the radiolytic stability of diglycolamide ligands has not been studied; however, two reports support the idea that phenyl groups can augment the radiation stability of DGA and related molecules. Sugo and coworkers synthesized *N,N,N′,N′*-tetra(*p*-octylphenyl) diglycolamide (T(OPh)DGA), and observed that it was more radiation stable than TODGA when irradiated in nitrobenzene.[22] Galán and coworkers observed that 2,2'-((((1,3-phenylenebis(methylene))bis(azanediyl))bis(2-oxoethane-2,1-diyl))bis(oxy))bis(*N,N*-dioctylacetamide) (two TODGA molecules with a *m*-xylene spacer between the two DGA subunits) had higher radiation stability in the presence of nitric acid.[23] The molecules studied in these two reports had phenyl groups either attached to, or in close proximity to, the amide nitrogen atoms.

Here we report on the radiation chemistry of two phenyl-substituted versions of TODGA: 2-(2-(di-*n*-octylamino)-2-oxoethoxy)-*N,N*-di-*n*-octyl-2-phenylacetamide (trivially, *N*,*N*,*N'*,*N'*-tetraoctyl phenyldiglycolamide, PhTODGA, Figure 2a), and 2-(2-(di-*n*-octylamino)-2-oxo-1-phenylethoxy)-*N,N*-di-*n*-octylpropanamide (trivially, *N*,*N*,*N'*,*N'*-tetraoctyl phenylmethyldiglycolamide, PhMeTODGA, Figure 2b), with phenyl groups in proximity to the central ether oxygen of the DGA backbone. Iqbal et al. reported on the extraction properties of these two ligands for Am and Eu.[24] Both ligands were shown to extract Am and Eu from highly concentrated nitric acid solutions, albeit with lower distribution ratios than TODGA, likely due to steric hindrance from the presence of the phenyl groups[25,26] and possible modification of the electron density around the oxygens.[24] We also report on preliminary investigations into the radiation chemistry of 2-(2-*N*-*n*-hexyl-

N-phenylamino)-2-oxoethoxy)-*N*-*n*-hexyl-*N*-phenylacetamide (trivially, *N*,*N'*-dihexyl-*N*,*N'*-diphenyl diglycolamide, DHDPDGA, Figure 2c), which has phenyl groups directly bound to the amide nitrogen atoms. This gives a set of TODGA analogs with a phenyl-substituent at different positions, allowing for investigation of both the presence and position of the phenyl group on the radiation chemistry of the diglycolamides. In Part I of this manuscript series, we report on the influence of phenyl substitution on the rates of gamma-radiation-induced degradation of TODGA analogs. The identity and behavior of the degradation products of these three compounds is discussed in Part II of this manuscript series.[27]

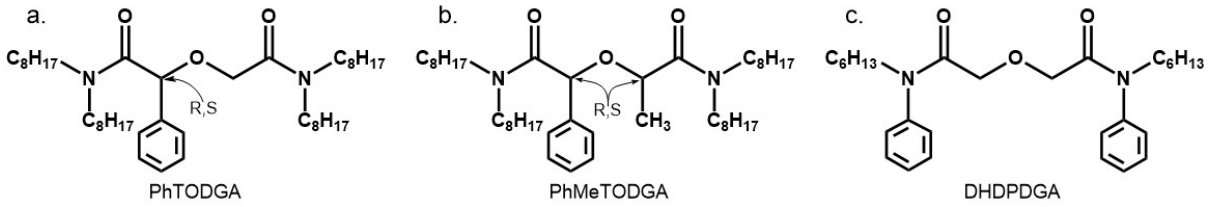

Figure 2. Structures of a) PhTODGA, b) PhMeTODGA, and c) DHDPDGA. Note that PhTODGA has a stereogenic carbon center, yielding two enantiomers (labeled R,S in the figure), and that PhMeTODGA has two stereogenic carbons, yielding four stereoisomers.

Experimental

Ligand preparation

PhMeTODGA and PhTODGA were prepared following the methodology described before.[24] TODGA (~98% purity) was sourced from Marshallton Research Laboratories, Inc. (King, North Carolina, USA, http://www.marshalltonlabs.com), and was used as received. *N*,*N'*-di-*n*-hexyl-*N*,*N'*-diphenyl diglycolamide (DHDPDGA) was prepared as an oil in 84% yield by reaction of diglycolyl chloride with *N*-*n*-hexyl-N-phenylamine under Schotten-Baumann conditions according to the general procedure described in Leoncini et al.[28] Peaks from nuclear magnetic resonance (NMR) spectroscopy confirming the identity of the product as DHDPDGA are as follows:

^{1}H NMR ($CDCl_3$): δ 7.45-7.3 (m, 6H), 7.15-7.1 (m, 4H), 3.93 (s, 4H), 3.65-3.6 (m, 4H), 1.5-1.35 (m, 4H), 1.3-1.2 (m, 12H), 0.84 (t, J = 7.1 Hz, 6H); ^{13}C NMR ($CDCl_3$), δ 168.9, 140.9, 130.0, 128.4, 128.3, 69.1, 49.4, 31.6, 27.6, 26.5, 22.7, 14.1.

Gamma-Ray irradiation

Samples of PhMeTODGA, PhTODGA, and DHDPDGA were irradiated as 0.05 M solutions in *n*-dodecane to facilitate comparison to previous studies of TODGA.[13] Aliquots of these solutions were irradiated as the pure organic phase, or in contact with either 0.1 M HNO_3 or 3.0 M HNO_3 to simulate stripping and extraction conditions. Prior to irradiation, the biphasic samples were vigorously mixed and allowed to sit for 24 hours at room temperature (20-23 °C) to ensure equilibration. Irradiations were conducted at Idaho National Laboratory (Idaho Falls, ID, USA) using a Nordion GammaCell 220E (Ottawa, Canada) ^{60}Co source, with a centerline sample chamber dose rate of 4.5 kGy h^{-1}, as determined by decay corrected Fricke dosimetry.[29,30] Samples were placed as close to the centerline position as possible to reduce deviation between the measured centerline dose rate and the sample position dose rate. However, based on prior measurements, the dose rate at any given point where samples were irradiated can vary by approximately ±10% from the centerline value.

Samples were irradiated in clear glass 20 mL scintillation vials sealed with screw tops. Under these conditions, it is expected that the samples are deareated after absorption of a small dose. The temperature inside the irradiator is uncontrolled. However, based on prior measurements of temperature inside the irradiator, and the decay of the irradiator ^{60}Co source over time, the temperature during irradiation was not expected to have deviated much more than a few degrees °C from room temperature (20-23 °C). Between removal from the irradiator and analysis with UHPLC-ESI-MS (see below), samples were stored in a refrigerator at approximately 5 °C.

UHPLC-ESI-MS

PhMeTODGA and PhTODGA Quantification

Quantification of the concentrations of PhMeTODGA and PhTODGA in irradiated samples was conducted at Idaho National Laboratory. Irradiated PhMeTODGA- and PhTODGA-containing samples in *n*-dodecane were diluted in Optima® LC/MS 2-propanol (Fisher Scientific, Pittsburgh, PA, USA) prior to analysis to generate a concentration in the low micromolar ($\mu mol \cdot L^{-1}$) range (i.e., in the middle of the response versus concentration curve). A spike of TODGA was added as an internal standard. Calibration standards were constructed from unirradiated PhMeTODGA and PhTODGA in *n*-dodecane diluted to appropriate concentrations with Optima® LC/MS 2-propanol. All the diluted samples and calibration solutions were analyzed using a Dionex (Sunnyvale, CA, USA) ultra-high-performance liquid chromatograph (UHPLC) with an Ultimate 3000 RS pump, 3000 RS autosampler, 3000 RS column compartment and a 3000 RS diode-array detector, coupled to a Bruker (Billerica, MA, USA) microTOFQ-II electrospray ionization quadrupole time-of-flight mass spectrometer with Hystar 3.2 software.

The chromatographic separation was achieved using 5 µL injections on a Kinetex 1.7 µm particle size, EVO-C18 stationary phase, 50 mm × 2.1 mm column (Phenomenex, Torrance, CA, USA) held at 50 °C. The aqueous component was Optima® LC/MS water with 0.1% v/v formic acid (Fisher Scientific, Pittsburgh, PA), and the organic component was Optima® LC/MS 2-propanol. A 25-minute isocratic mobile phase profile was initially used to separate the irradiated PhMeTODGA solutions, with a flow rate of 300 $\mu L \cdot min^{-1}$ and a 59% organic composition. A 10-minute gradient mobile phase profile was used to separate the irradiated PhTODGA solutions. The mass spectrometer conditions were: capillary: 4.5 kV, positive mode; temp.: 220 °C; nebulizer gas and dry gas were both N_2, nebulizer pressure: 0.4 bar; dry

gas flow rate: 9 $L \cdot min^{-1}$. The mass spectrometer was operated using standard Bruker "tune low" and "tune wide" tuning parameters. Each sample was injected 3 times.

DHDPDGA Quantification

Irradiated samples containing DHDPDGA were analyzed at Forschungszentrum Jülich GmbH (Jülich, Germany) by high performance liquid chromatography electrospray ionization tandem mass spectrometry (HPLC-ESI-MS/MS). Quantification of DHDPDGA was performed with an Agilent 1260 HPLC system, consisting of a binary pump, autosampler, and thermostated column compartment, coupled to a QTRAP 6500 instrument (ABSciex, Darmstadt, Germany). A Phenyl-X column from Thermo (100 × 4.6 mm; 2.6 µm) was used in a gradient of 0.1% formic acid in HPLC grade water (A) and 0.1% formic acid in acetonitrile (B) with a flow rate of 800 $\mu L \cdot min^{-1}$. After injection, the gradient was held at 40% B for 2 minutes, then ramped from 40% B to 100 % B in 5 min (from minute 2 to 7), and then held at 100% B for 13 min (until minute 20). The gradient was ramped back to 40% B over 30 s to prepare for column equilibration prior to the next injection. The column was held at 35°C. All samples were diluted 1:500,000 and measured in triplicate. The calibration was done using the unirradiated DHDPDGA samples by dilution and the linearity was found to be good in the region from 10 $nmol \cdot L^{-1}$ to 250 $nmol \cdot L^{-1}$ with $R^2 = 0.9990$. The variation coefficient of a 50 $nmol \cdot L^{-1}$ standard of DHDPDGA was 4.0%.

The MS parameters used for all methods were optimized by performing a Flow Injection Analysis with standards and led to the following settings for all analysis: curtain gas (N_2) 40 arbitrary units (a.u.), temperature of the source 350°C, nebulizer gas (N_2) 40 a.u., heater gas (N_2) 80 a.u., ion spray voltage of 4500 V. Quantification after HPLC was performed using ESI-MS/MS detection in the multiple reaction-monitoring (MRM) mode in positive ionization mode. MRM transitions involving precursor ions $(M+H)^+$ and the two most abundant product ions were used for quantification of all analytes as shown in Table S1. All

data acquisition and processing was carried out using the Analyst® Software 1.6.1 (AB Sciex, Darmstadt, Germany). Quantification was performed with the Multiquant™ Software (AB Sciex, Darmstadt, Germany).

Results and Discussion

Decreased Radiolytic stability induced by phenyl-substitution

The radiolytic behavior of PhTODGA and PhMeTODGA exhibited an exponential decay indicative of pseudo-first order kinetics (Figure 3), as has been observed for all previously studied DGAs.[13–17,31] This enabled calculation of the dose coefficients (*d* values) with units of inverse kiloGray (kGy^{-1}) via regression of the natural logarithm of the concentration plotted as a function of absorbed dose.

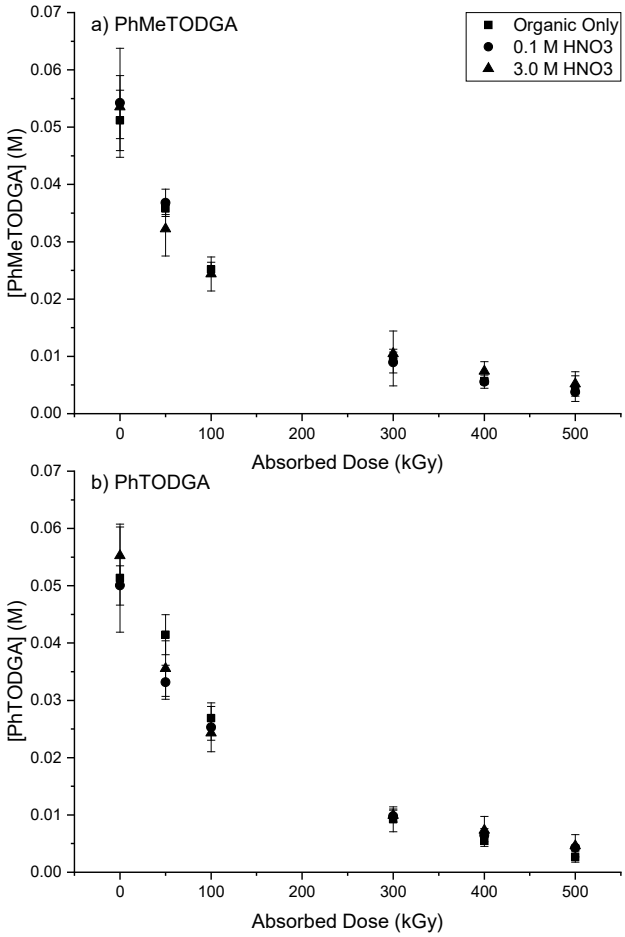

Figure 3. Concentration of a) PhMeTODGA and b) PhTODGA in *n*-dodecane as a function of absorbed dose. Three experiments are presented: organic-only (solid squares), in contact with 0.1 M HNO_3 (solid circles), and in contact with 3.0 M HNO_3 (solid triangles). Each point is the mean of three measurements and the error bars represent 99% confidence intervals.

The calculated dose coefficients are shown in Figure 4 and in Table S2. The *d* values generated by irradiation of PhTODGA and PhMeTODGA in *n*-dodecane are significantly

higher than those measured for unmodified TODGA;[13] this suggests that the addition of a phenyl group makes the ligand more susceptible to radiolytic degradation. Irradiation of systems of ligands dissolved in *n*-dodecane is believed to result in the generation of *n*-dodecane radical cations, which react with ligand molecules through electron transfer, resulting in their degradation.[8,20,32] The overall radiolytic stability of ligands thus depends on the energetics (driven by differences in ionization energy between *n*-dodecane and the ligand) and kinetics of electron transfer from the *n*-dodecane radical cation to the phenyl-substituted DGA. As modification of the TODGA structure, especially through the inclusion of phenyl groups, would be expected to change both the ionization efficiency and the rates of *n*-dodecane radical cation-ligand electron transfer, the observation that the addition of phenyl substituents to TODGA decreases the overall radiolytic stability is unsurprising.

Experiments were also performed using another phenylated diglycolamide derivative, *N*,*N'*-di-*n*-hexyl-*N*,*N'*-diphenyl diglycolamide (DHDPDGA, Figure 2c), which has the same diglycolamide core as TODGA, but differs in that it has a) shorter paraffinic groups (hexyl instead of octyl), and b) phenyl moieties that are situated on the amide N atoms instead of the center methylene carbon atoms. The hexyl-for-octyl variation in DHDPDGA is not expected to result in any significant change in the susceptibility to radiolytic degradation. However, the dose coefficient was 0.0061 ± 0.0001 for DHDPDGA in an organic-only environment, a value ~ 50% greater than that for unmodified TODGA. It is unlikely that the shorter alkyl moieties significantly affect the dose coefficient,[13,14,16] and so it is likely that the reduction in radiolytic stability of DHDPDGA in *n*-dodecane is due to the presence of the phenyl groups attached to the amide nitrogen, which are not present in TODGA.

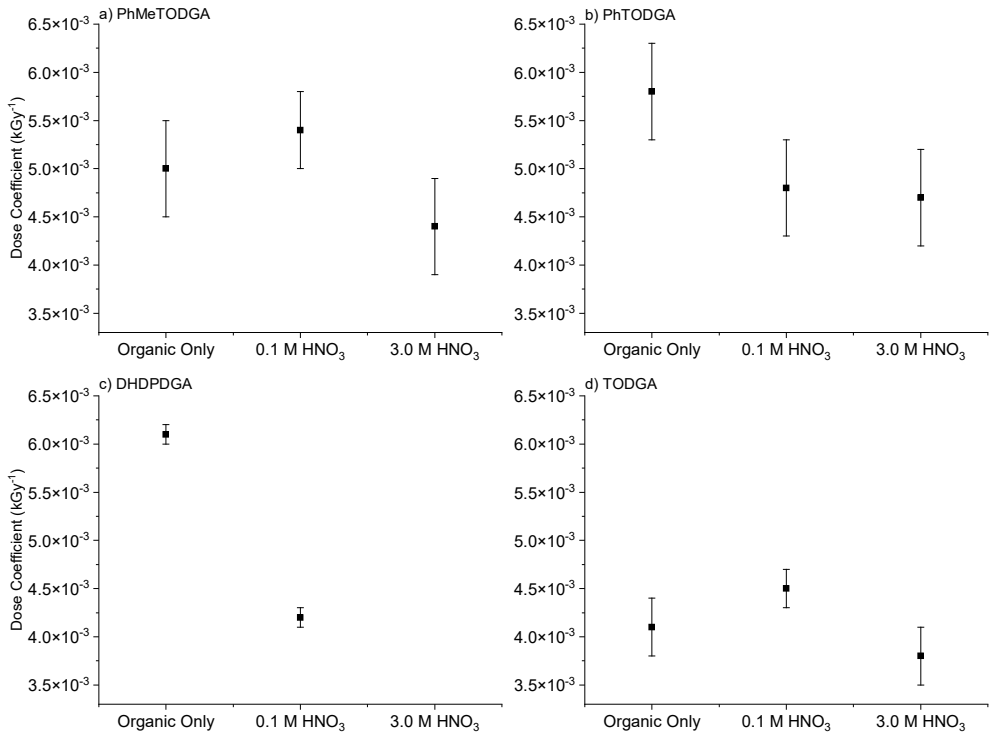

Figure 4. Dose coefficients (d, kGy^{-1}) for a) PhMeTODGA, b) PhTODGA, c) DHDPDGA, and d) TODGA. Values were generated from experiments conducted in *n*-dodecane only (Organic-Only), *n*-dodecane in contact with 0.1 M HNO_3 (0.1 M HNO_3), and *n*-dodecane in contact with 3.0 M HNO_3 (3.0 M HNO_3). The d value for DHDPDGA in contact with 3.0 M HNO_3 is not reported because of difficulty stemming from third-phase formation and the TODGA dose coefficients are taken from Zarzana et al.[13] The uncertainty in the dose coefficients are 99% confidence intervals calculated from the linear fits of the natural log of the concentration of the respective DGA as a function of absorbed dose.

For experiments conducted in *n*-dodecane contacted with 0.1 M HNO_3, the d values for PhTODGA were modestly higher compared to TODGA, while those for PhMeTODGA were significantly higher. This behavior supports the conclusion that the phenyl moieties situated on the central methylene carbon atoms de-stabilize the compound. DHDPDGA showed a slightly decreased d value compared to TODGA, indicating that this compound has enhanced resistance to radiolytic degradation in the presence of low-concentration nitric acid. The d values measured in experiments where TODGA-*n*-dodecane solutions were in contact with aqueous, 3 M HNO_3 also indicated lower stability for PhTODGA and PhMeTODGA, compared to TODGA. DHDPDGA formed a third phase in contact with 3.0 M HNO_3, which precluded measurement of radiolytic decay.

Radiolytic stabilization from phenyl-HNO_3 interaction

While the overall effect of phenyl derivatization is to destabilize the DGA ligands, the interactions with HNO_3 indicate a cooperative interaction between the acid and the phenyl moieties that modestly increases ligand stabilization. This is illustrated by all three of the phenylated derivatives. The dose coefficients for PhMeTODGA in *n*-dodecane only and in contact with 0.1 M HNO_3 were the same within experimental uncertainty ($(5.0 \pm 0.5) \times 10^{-3}$ kGy^{-1} and $(5.4 \pm 0.4) \times 10^{-3}$ kGy^{-1}, respectively, Table S2), averaging about $(5.2 \pm 0.4) \times 10^{-3}$ kGy^{-1}; however, contact with 3.0 M HNO_3 decreased the value to $(4.4 \pm 0.5) \times 10^{-3}$ kGy^{-1}, a value comparable to unmodified TODGA (Figure 4a). The *d* values for PhTODGA decrease from $(5.8 \pm 0.5) \times 10^{-3}$ kGy^{-1} when the compound is irradiated in *n*-dodecane only, to an average of $(4.8 \pm 0.4) \times 10^{-3}$ when the solution is in contact with 0.1 M, and 3.0 M HNO_3, respectively (Figure 4b). The *d* value for DHDPDGA also underwent a dramatic decrease – from $(6.1 \pm 0.1) \times 10^{-3}$ kGy^{-1} when measured in *n*-dodecane only, to $(4.2 \pm 0.1) \times 10^{-3}$ kGy^{-1} when contacted with 0.1 M HNO_3 (Figure 4c). In contrast, unmodified TODGA was comparatively unaffected by contact with HNO_3 (Figure 4d).

The results for the phenylated TODGA derivatives are opposite those previously reported for methyl-substituted TODGA derivatives,[17] which exhibited higher dose coefficients when irradiated in an organic phase contacted with a nitric acid-containing aqueous phase, compared to irradiations conducted in organic-only environments. Thus, for the phenylated DGA derivatives, the increase in radiation resistance in the presence of nitric acid must be due to the presence of the phenyl group, rather than just substitution adjacent to the central ether oxygen.

Examining Figure 4, there is evidence that the DGA structure makes a difference in the amount of acid required for observation of a protective effect. There is little difference in the

radiolytic resistance between PhMeTODGA (Figure 4a) in *n*-dodecane only, and in the *n*-dodecane-0.1 M HNO_3-contacted environment (PhMeTODGA was slightly less stable in contact with the dilute acid). However, the *d* value for the PhMeTODGA-*n*-dodecane solution irradiated in contact with the 3.0 M HNO_3 aqueous phase is significantly lower, indicating that the higher HNO_3 concentration in combination with the phenyl group provides a measure of protection. In contrast, while the radiation resistance of PhTODGA-*n*-dodecane solutions is significantly improved in the acid-contacted experiments, the magnitude of the effect is little influenced by the acid concentration (Figure 4b). DHDPDGA (Figure 4c) follows the same trend as PhTODGA, exhibiting significantly more radiation stability when in contact with a 0.1 M HNO_3 aqueous phase compared to the organic-only environment. The dose coefficient for the DHDPDGA – 3.0 M nitric acid experiment could not be measured because of formation of a third phase (*vide infra*), and so we cannot tell if the similarities between DHDPDGA and PhTODGA extend to higher acid concentrations.

The difference in the change in radiolytic stability on going from organic-only to 0.1 M HNO_3-contacted environments, observed in comparing PhMeTODGA and PhTODGA, is likely derived from the two compounds having different ability to solubilize HNO_3 in the organic phase. The nitric acid-induced radiation protection mechanism likely involves formation of a ligand-HNO_3 complex with significant interaction between the HNO_3 and the phenyl group, as has been shown for CMPO.[21] A simple explanation for this difference may be that PhMeTODGA extracts nitric acid into the organic phase less efficiently than PhTODGA and DHDPDGA. Less HNO_3 in the PhMeTODGA-*n*-dodecane phase would be expected to decrease the protective effect of HNO_3 and result in increased *d* values. However, the differences disappear in the 3.0 M HNO_3 environment, since mass action would result in higher HNO_3 concentrations in the organic phase. Higher HNO_3 concentrations may be driven by conformational changes in the DGA:HNO_3 complexes in the organic phase as the

amount of nitric acid in the aqueous phase – and thus the amount of nitric acid extracted into the organic phase – increases. Studies of nitric acid extraction into an organic phase indicate that both the amount of nitric acid and the stoichiometry of the TODGA:HNO_3 complexes changes as the amount of nitric acid in the aqueous phase increases.[33] It seems reasonable that the DGAs studied here would exhibit the same behavior. It also seems reasonable that as the DGA:HNO_3 complex stoichiometry changes, the conformation of the DGA could change. We hypothesize that the presence of the methyl in proximity to the phenyl group in PhMeTODGA could, in certain conformations, partially block access of HNO_3 to the phenyl group, preventing the interaction between the nitric acid and the phenyl group believed to be necessary for complex formation and enhanced radiation resistance. If an increase in the amount of nitric acid in the PhMeTODGA:HNO_3 complex induced by an increase in aqueous nitric acid concentration resulted in a shift of the ligand to a conformation where the methyl group was no longer blocking the phenyl group, HNO_3-phenyl group association would no longer be inhibited, conferring radiation protection. There is no methyl group in PhTODGA to block the phenyl group, and for DHDPDGA the phenyl groups are on the periphery of the molecule, and thus more accessible, so access to the phenyl group for these two DGAs might be assumed to be less dependent on concentration. Easier access to the phenyl groups could also explain why there is a larger radiation protection effect observed for DHDPDGA than for PhTODGA, although an alternative explanation is that there are two times as many phenyl groups in DHDPDGA as in PhTODGA.

Prior irradiations of methyl-substituted TODGA suggested the addition of methyl groups on one side of the central ether oxygen decreases radiation resistance compared to TODGA, while addition of methyl groups on both sides increases radiation resistance compared to TODGA in organic-only environments.[17] It was hypothesized that the substitution of both methylene carbons may protect those vulnerable sites from H-atom abstraction reactions. In

contrast, addition of a phenyl group decreases the overall radiolytic stability of the resultant molecule, even when the second methylene carbon was substituted with a methyl group (TODGA organic-only dose coefficient: $(4.1 \pm 0.3) \times 10^{-3}$;[13] PhTODGA organic-only dose coefficient: $(5.8 \pm 0.5) \times 10^{-3}$; PhMeTODGA organic-only dose coefficient: $(5.0 \pm 0.5) \times 10^{-3}$, see Table S2). The trend of substitution on only one side of the ether linkage resulting in less radiolytic stability compared to substitution on both sides is consistent with the trend observed for MeTODGA.[17]

DHDPDGA third phase formation

A third phase formed after a short time for the unirradiated DHDPDGA solutions in contact with 3 mol L^{-1} HNO_3, which concurrently developed a dark yellow color. Irradiation was conducted as planned, despite the presence of a third phase, which appeared as red droplets of varying sizes. The amount of third phase decreased with increasing absorbed dose. The three different phases present in the samples were separated and analyzed individually. The color of the organic and aqueous phases did not change significantly as a function of the absorbed dose and stayed dark yellow and light yellow, respectively. The third phase was not soluble in 3 mol L^{-1} HNO_3 or *n*-dodecane, but it was dissolved in acetonitrile, which enabled LC-MS analysis. DHDPDGA in contact with 0.1 mol L^{-1} HNO_3 did not show the formation of such a red third phase, whether or not it was irradiated, however, as dose increased, the organic phase changed from bright yellow to red-brown, and the aqueous phase changed from colorless to yellow.

Figure 5 shows the DHDPDGA concentration in the organic phase as a function of the absorbed dose. For samples irradiated without contact with aqueous HNO_3, the initial concentration of DHDPDGA was measured at 0.05 M, in exact agreement with the gravimetrically-prepared solution. As the sample was irradiated, an exponential decrease in

the measured organic phase concentration is observed, indicative of pseudo-first order kinetics. In contrast, for samples irradiated in contact with 0.1 mol L^{-1} HNO_3, a DHDPDGA concentration of 0.008 M was measured at 0 kGy, far less than the expected value of approximately 0.05 mol L^{-1}: this result was reproduced in repeated sample preparations and measurements. The reason for the significantly reduced DHDPDGA concentration in the 0 kGy samples is unclear. However, it may be that most of the DHDPDGA precipitated or formed an unobserved third phase in the unirradiated sample of the 0.1 M HNO_3-contacted experiment, thereby reducing the concentration in the organic phase, which is what was seen in unirradiated samples exposed to 3.0 M HNO_3. Irradiation of the 0.1 M HNO_3-contacted sample resulted in a dramatic increase in the concentration of DHDPDGA in the organic phase, which may be attributed to the third phase breaking up under irradiation. The concentration of DHDPDGA after 50 kGy in this experiment was nearly identical to that measured in the noncontacted experiment after the same dose. The subsequent, exponential decrease in [DHDPDGA] is not quite as steep compared to the experiment in uncontacted *n*-dodecane, consistent with the notion of HNO_3 providing some measure of protection for the ligand. Additionally, in the samples irradiated in contact with 3 mol L^{-1} HNO_3, a decrease in the volume/amount of third phase was observed along with an increase of DHDPDGA in the *n*-dodecane phase. Therefore, we speculate that the partitioning of DHDPDGA between the third phase and the organic phase might shift towards the organic phase with increasing dose. This could be caused by a change in the physicochemical properties of the diluent with increasing dose, due to the formation of diluent degradation products.[34–36]

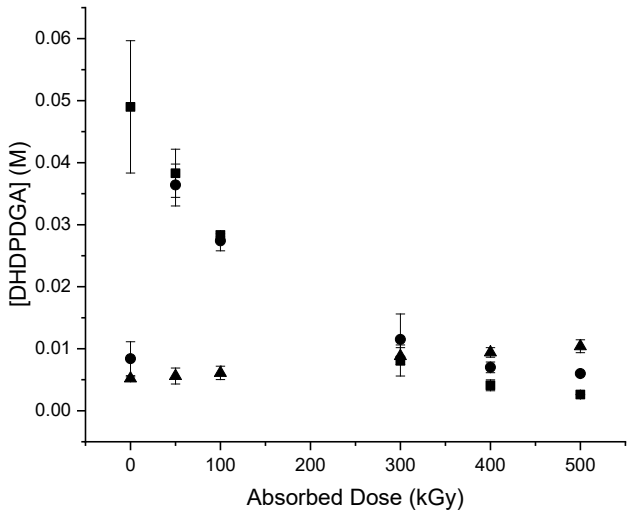

Figure 5. Concentration of DHDPDGA as a function of absorbed dose. Experiments in three *n*-dodecane environments were conducted: organic-only (solid squares), in contact with 0.1 M HNO_3 (solid circles), and in contact with 3.0 M HNO_3 (solid triangles). The initial DHDPDGA concentration was 0.5 M in each experiment. Each point is the mean of three measurements and the error bars represent 99% confidence intervals.

Negligible effect of Stereochemistry on degradation

The UHPLC-ESI-MS chromatogram of PhMeTODGA (Figure S1) shows two peaks eluting at 16.8 and 17.0 min; the mass spectra of both molecules showed abundant peaks corresponding to their respective protonated molecules with the same mass-to-charge ratio (*m/z* = 671.6), and their collision-induced dissociation (CID) spectra were practically identical (Figure S2 and Figure S3). Both chromatographic peaks are derived from a set of two enantiomers. PhMeTODGA has two stereogenic carbon atoms (the two carbons adjacent to the ether oxygen atom), and thus four stereoisomers. These stereoisomers can be divided into two sets of two enantiomers: one with the phenyl and methyl groups on the same side of the plane of the molecule, and one with the phenyl and methyl groups on opposite sides of the molecule. While it is generally difficult to separate stereoisomers with liquid chromatography, the identical *m/z* value of the protonated molecules and identical CID fragmentation patterns indicate two peaks do indeed correspond to the two sets of enantiomers. By way of contrast, PhTODGA only has one stereogenic carbon, and the chromatogram of PhTODGA only has one peak corresponding to the intact molecule, which

is consistent with the above hypothesis for PhMeTODGA. By adjusting chromatographic conditions, we were able to resolve the two PhMeTODGA peaks and measure radiolysis rates for the two peaks separately. There was no statistical difference between the rates for the separated peaks and the combined peaks, so there does not appear to be any stereochemical influence on PhMeTODGA radiolysis rates.

Conclusions

Examination of the radiolytic degradation of phenyl-substituted DGA derivatives indicates that the phenyl substituents destabilize the molecules, with pseudo-first order decay coefficients that are greater compared to those of the non-phenylated TODGA molecule used as a benchmark. However, in molecules containing a phenyl group adjacent to the ether oxygen atom, the presence of HNO_3 serves to decrease decay coefficients, i.e., stabilizes the ligands, compared to environments where no HNO_3 was present. PhMeTODGA could be equivalent to – but is unlikely to be more stable than – TODGA irradiated in contact with the highest HNO_3 concentration aqueous phase, but it is clearly less stable than TODGA under the other conditions; PhTODGA is clearly less stable than TODGA under all conditions. In general, substitution of TODGA with phenyl rings adjacent to the central ether oxygen atom increased radiolytic degradation rates for solutions irradiated under acidic, oxidizing conditions.

Addition of a phenyl group to the amide nitrogen atoms also dramatically decreased the radiolytic stability compared to TODGA. This result is in contrast to the conclusions of Sugo et al., who observed that *N*,*N*,*N'*,*N'*-tetra(p-octylphenyl) diglycolamide was more radiolytically stable than TODGA in nitrobenzene.[22] A direct comparison of our data derived from experiments conducted in *n*-dodecane to data derived from experiments in nitrobenzene is hardly possible, as the formation of diluent-based radicals is different in

nitrobenzene compared to *n*-dodecane.[37–39] However, it is possible that substitution of only one of the alkane side-chains of the amide functional group for a phenyl group weakens one or more of the surrounding bonds, while substitution of both side-chains strengthens the surrounding bonds. This should be readily investigable using computational chemistry but is beyond the scope of this study. Thus, from a radiolytic standpoint, the ligands studied here seem to be less useful for separation of used nuclear fuel than TODGA or CMPO. Further studies of the extraction behavior and phase stability of these ligands is necessary for a complete evaluation.

The three ligands studied here all have lower radiolytic stability than TODGA, especially in the presence of significant amounts of nitric acid, as would be expected during the extraction phase of a separation process, and so do not hold much promise as new ligands for used nuclear fuel separation processes. Additionally, DHDPDGA exhibited significant third phase formation, especially in the presence of 3.0 M HNO_3, further reducing its utility. Prior studies have shown that PhMeTODGA and PhTODGA also have lower extraction distribution ratios than TODGA for lanthanides and the minor actinides,[24] so there seems little use in pursuing these compounds for advanced fuel cycles. However, this research again indicates that increased stability may be achievable by incorporating a phenyl group in the design of new ligands, that results from cooperative protection afforded by interaction of the phenyl moiety and nitric acid.

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Disclosure Statement

The authors report there are no competing interests to declare.

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