Radiation Chemistry of the Hydrophilic DGAs

Fuel Cycle Research & Development

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SUMMARY

Short chain diglycolamides (DGAs) are water soluble, and have been used as aqueous stripping and hold back agents in both European and American fuel cycle solvent extraction proposals. An understanding of the influence of radiation on these ligands is critical to the development and implementation of robust separation processes. Therefore, the rates of degradation under radiolysis were measured for four hydrophilic DGAs and compared to the organic-soluble DGAs. Water soluble DGAs were degraded at a faster rate than lipophilic DGAs, but were more stable with increasing molecular weight. The degradation products of the tetraethyldiglycolamide (TEDGA) were also identified and found to be analogous to those produced for lipophilic DGAs in irradiated alkanes. It was concluded that similar products are obtained since reactions in both diluents are by oxidation followed rupture of the weak ether linkage. The fast rate constants of the reactions of two hydrophilic DGAs with the oxidizing •OH radical product of water radiolysis are also shown. Since water-soluble DGAs have been proposed for use as stripping or holdback agents in both European and American fuel cycle scenarios this work was performed in collaboration with colleagues at Forschungszentrum Jülich (FZJ).

CONTENTS

ACRONYMMS

AA	acetic acid
ACN	acetonitrile
ALSEP	Actininde Lanthanide SEparation Process
CHON	Carbon, Hydrogen, Oxygen, Nitrogen
CMPO	octylphenyldiisobutyl carbamoylmethylphenyl phosphine oxide
D^3DODGA	*N*,*N*-didodecyl-*N'*,*N'*-dioctyl-diglycolamide
DGA	diglycolamide
ESI-MS/MS	ElectroSpray Ionization Mass Spec/Mass Spec
FA	formic acid
FIA	Flow Injection Analysis
FTICR	Fourier-Transform Ion Cyclotron Resonance
FZJ	Forschungszentrum Jülich
HPLC	High Performance Liquid Chromatography
LC-MS	Liquid Chromatography Mass Spec
LINAC	LINear Accelerator
LTQFT	Linear Tandem Quadrupole Fourier Transform
MRM	Multiple Reaction Monitoring
TEDGA	*N*,*N*,*N'*,*N'*-tetraethyl-diglycolamide
TEHDGA	*N*,*N*,*N'*,*N'*-tetra-2-ethylhexyl-diglycolamide
TMDGA	*N*,*N*,*N'*,*N'*-tetramethyl-diglycolamide
TODGA	*N*,*N*,*N'*,*N'*-tetraocyl-diglycolamide
TBP	tributylphosphate
UK	United Kingdom

UPLC	Ultra-Pure Liquid Chromatography

HYDROPHILIC DGA RADIOLYSIS

1. INTRODUCTION

The tetraalkyldiglycolamides (DGAs) exhibit excellent extraction efficiency for the trivalent *f*-elements and contain only carbon, hydrogen, oxygen, and nitrogen (CHON); they can be easily incinerated, reducing the volume of waste generated from reprocessing. When their N-alkyl substituents are varied, it is found that long chain derivatives have decreased solubility in water and increased solubility in aliphatic hydrocarbon diluents such as *n*-dodecane. [1] Short chain compounds are water soluble, and have been used as aqueous stripping and hold back agents in both European and American proposals. For example, the American ALSEP (Actinide Lanthanide Separation) process uses the branched DGA *N,N,N',N'*-tetra(2-ethylhexyl)digylcolamide (TEHDGA) as the organic-phase extractant, and the water soluble *N,N,N',N'*-tetraethyldiglycolamide (TEDGA) as a lanthanide stripping agent. [2]

An understanding of the influence of radiation on separation ligands is critical to the development and implementation of robust separation processes. Additionally, the influence of acid hydrolysis is important, especially for water-soluble ligands. In previous work, the short chain, water soluble DGA: TEDGA was investigated for its hydrolytic stability in HNO_3 solution, with comparisons to the less oxidizing mineral acid HCl. [3] The TEDGA was found to be susceptible to acid hydrolysis, with increasing rates at elevated temperature and nitric acid concentration. In contrast, increasing HCl concentration did not result in faster rates of hydrolysis, suggesting that degradation of TEDGA in HNO_3 is due to oxidation by nitric acid. In the same previous study initial measurements of the radiolysis of TEDGA in aqueous solution showed that the kinetics of degradation were first order and the rate constant was about 3x faster than for the longer chain, dodecane soluble DGAs. [3] The degradation of DGAs in water is also expected to be dominated by oxidation reactions, probably involving mainly $^{\bullet}OH$ radical reactions.

The current report extends that preliminary work by quantitatively measuring the radiolysis rates of several water-soluble DGAs in aqueous solution and comparing those rates to the organic-soluble DGAs. Degradation products of the water soluble DGAs were also identified. Since water-soluble DGAs have been proposed for use as stripping or holdback agents in both European and American fuel cycle scenarios this work was performed in collaboration with colleagues at Forschungszentrum Jülich (FZJ). This document was prepared to meet FCR&D level 3 milestone M3FT-17IN030104032 under the FY17 Fundamental Radiation Chemistry FCR&D work package.

2. EXPERIMENTAL

2.1 Reagents

The TEDGA was supplied by Technocom (UK) and used as received. The remaining hydrophilic DGAs were *N*,*N*,*N'*,*N'*-tetramethyl-diglycolamide (TMDGA), 2-(2-(diethylamino)-2-oxoethoxy)-*N*,*N*-diethylpropanamide (Me-TEDGA), and 2,2'-oxybis(*N*,*N*-diethylpropanamide) (Me_2-TEDGA), and were synthesized by the FZJ collaborator. The structures of these compounds are shown in Fig. 1. The water used as a diluent was nanopure water demineralized to a resistivity of 10 MOhm cm^{-1} prior to use.

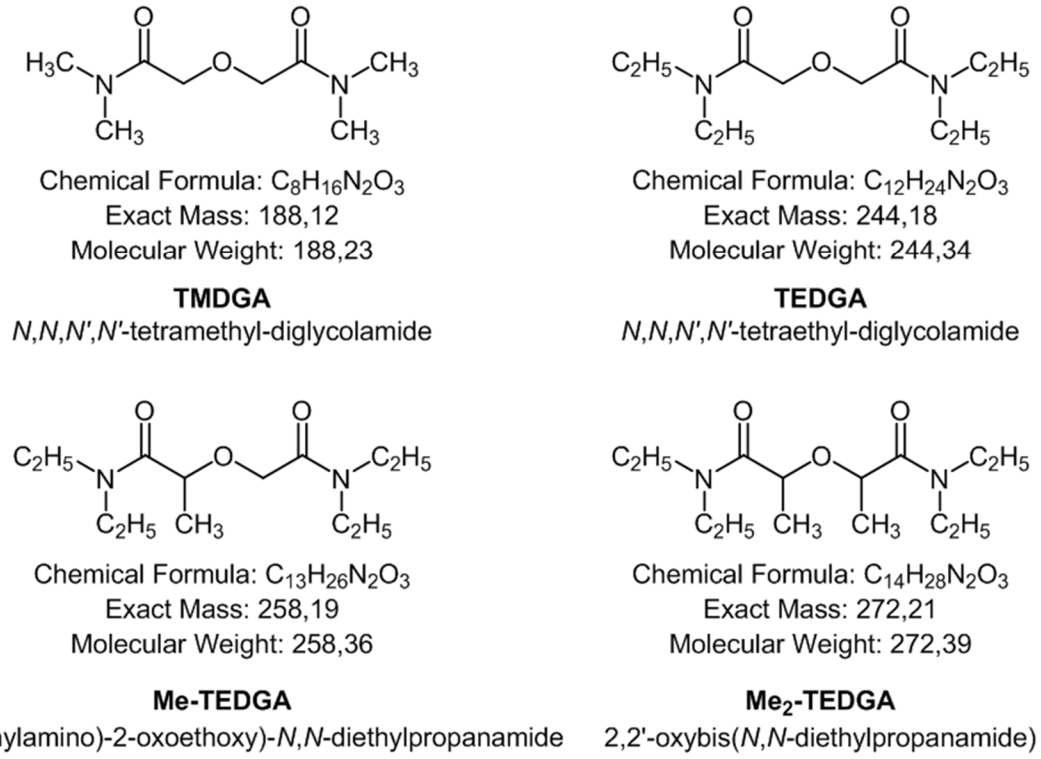


Figure 1. Chemical structures of the irradiated hydrophilic DGAs used in this study.

2.2 Radiolysis

Steady state irradiations were performed at INL using a ^{60}Co-Nordion Gammacell 220, at a dose rate of 4 kGy h^{-1}, as initially measured using standard Fricke procedures, and then subsequently corrected for decay. The DGA solutions were irradiated as initially 0.05 M solutions in nanopure

water to target absorbed doses of 0, 25, 75, 100, 125 and 150 kGy, in sealed containers. Neutral water was chosen to allow for the study of radiolysis in the absence of confounding hydrolysis effects. After irradiation the samples were shipped to FZJ for analysis.

2.3 Mass Spectrometry

Separation methods for the analytes preceded quantification and identification of radiolysis products.

2.3.1 Chemicals and reagents

UPLC-grade acetonitrile (ACN) was purchased from VWR (Langenfeld, Germany), UPLC-grade water from Merck (Darmstadt, Germany), formic acid (FA) in UPLC-MS grade from Biosolve (Valkenswaard, Netherlands), acetic acid (AA) in UPLC-MS grade from Biosolve (Valkenswaard, Netherlands), and ammonium acetate in LC-MS grade from Honeywell Fluka (Schwerte, Germany).

2.3.2 Chromatographic conditions

2.3.2.1 TMDGA

The column Phenomenex Kinetex-HILIC (100 × 4.6 mm; 2.6 µm particle size) was used with a gradient of acetonitrile + 0.1% formic acid (A) in 10 mmol/L ammonium acetate buffer in H_2O at pH 5.5, 40°C and a flow-rate of 900 µL/min. The gradient is described in Table 1. The calibration was done using the unirradiated TMDGA samples by dilution. The linearity was found to be good in the region from 5 nmol/L to 500 nmol/L with $R^2 = 0.9998$. The variation coefficient of a 100 nmol/L standard of TMDGA was 2.5%. All samples were diluted 1:500,000 and measured in triplicates.

Table 1. Gradient for the quantitative analysis irradiated TMDGA samples

Run-time	Composition
0 – 2 min	90% A
2 – 7 min	Decrease to 50% A
7 – 10 min	50% A
10 – 10.5 min	Increase to 90% A
10.5 – 15 min	90% A

2.3.2.2 TEDGA

The column Thermo Phenyl-X (100 × 4.6 mm; 2.6 µm particle size) was used with a gradient of acetonitrile + 0.1% formic acid (A) in 0.1% formic acid in H_2O at 35°C and a flow-rate of 800 µL/min. The gradient is described in Table 2. The calibration was done using the unirradiated TEDGA samples by dilution. The linearity was found to be good in the region from 10 nmol/L to 500 nmol/L with $R^2 = 0.995$. The variation coefficient of a 100 nmol/L standard of TEDGA was 7.4%. All samples were diluted 1:500,000 and measured in triplicates.

Table 2. Gradient for the quantitative analysis irradiated TEDGA and Me-TEDGA samples

Run-time	Composition
0 – 2 min	5% A
2 – 6 min	Increase to 95% A
6 – 12 min	95% A
12 – 12.5 min	Decrease to 5% A
12.5 – 15 min	5% A

2.3.2.3 Me-TEDGA

The column Thermo Phenyl-X (100 × 4.6 mm; 2.6 µm particle size) was used with a gradient of acetonitrile + 0.1% formic acid (A) in 0.1% formic acid in H_2O at 35°C and a flow-rate of 800 µL/min. The gradient is identical to the one used for the analysis of TEDGA, described in Table 2. The calibration was done using the unirradiated Me-TEDGA samples by dilution. The linearity was found to be good in the region from 10 nmol/L to 500 nmol/L with $R^2 = 0.999$. The variation coefficient of a 100 nmol/L standard of Me-TEDGA was 6.2%. All samples were diluted 1:500,000 and measured in triplicates.

2.3.2.4 Me_2-TEDGA

The column Phenomenex Luna Omega C18 Polar (100 × 4.6 mm; 2.6 µm particle size) was used with a gradient of acetonitrile + 0.1% formic acid (A) in 0.1% formic acid in H_2O at 35°C and a flow-rate of 800 µL/min. The gradient is described in Table 33. The calibration was done using the unirradiated Me_2-TEDGA samples by dilution. The linearity was found to be good in the region from 1 nmol/L to 500 nmol/L with $R^2 = 0.9997$. The variation coefficient of a 100 nmol/L standard of Me_2-TEDGA was 8.2%. All samples were diluted 1:500,000 and measured in triplicates.

Table 3. Gradient for the quantitative analysis irradiated Me_2-TEDGA samples

Run-time	Composition
0 – 2 min	5% A
2 – 12 min	Increase to 95% A
12 – 17 min	95% A
17 – 17.5 min	Decrease to 5% A
17.5 – 20 min	5% A

2.3.3 Quantitative Analysis of DGA Degradation

HPLC-ESI-MS/MS for quantification was performed with a Qtrap6500 instrument (ABSciex, Darmstadt, Germany) coupled with an Agilent 1260 HPLC system consisted of a binary pump system, an autosampler and a thermostated column compartment. The MS-parameters used for all methods were optimized performing a Flow Injection Analysis (FIA) with standards and led to the following settings for all analysis: curtain gas (N_2) 40 arbitrary units (au), temperature of

the source 350°C, nebulizer gas (N_2) 40 a.u. and heater gas (N_2) 80 a.u.. Quantification of TMDGA, TEDGA, Me-TEDGA, and Me_2-TEDGA after HPLC separation 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 4.

The standard solutions for calibration had concentrations of 10 nM; 25 nM; 50 nM; 100 nM; 250 nM; 500 nM (TEDGA, Me-TEDGA), 1 nM; 5 nM; 10 nM; 25 nM; 50 nM; 100 nM; 250 nM; 500 nM (Me_2-TEDGA) and 5 nM; 10 nM; 25 nM; 50 nM; 100 nM; 250 nM; 500 nM (TMDGA) in acetonitrile. Samples were measured in triplicate and a 100 nM standard was also measured in triplicate as a quality sample.

In all LC-MS/MS experiments data acquisition and processing were carried out using the Software Analyst 1.6.1 (AB Sciex, Darmstadt, Germany). Quantification was performed with the Software Multiquant (AB Sciex, Darmstadt, Germany).

Table 4. Overview of the experimental conditions used in the MRM method.

Name	Precursor Ion	Product Ion	Declustering potential DP	Collision Engergy CE	Cell Exit Potential CXP
TMDGA_1	189.1	58.1	21	45	14
TMDGA_2	189.1	116.1	21	21	10
TEDGA_1	245.1	144.2	31	25	20
TEDGA_2	245.1	172.2	31	19	18
Me-TEDGA_1	259.2	72.2	96	39	18
Me-TEDGA_2	259.2	158.2	96	19	14
Me_2-TEDGA_1	273.2	172.2	40	19	18
Me_2-TEDGA_2	273.2	72.2	40	37	12

2.3.4 Qualitative Analysis of Degradation Products

Product analysis were performed using a hybrid linear ion trap FTICR (Fourier-Transform Ion Cyclotron Resonance) mass spectrometer LTQFT (Linear Tandem Quadrupole Fourier Transform) Ultra™ (Thermo Fisher Scientific, Bremen, Germany) coupled with an Agilent 1200 HPLC system consisted of a binary pump system, an autosampler, a thermostated column compartment and a Diode-Array detector (Agilent, Waldbronn, Germany). The mass spectrometer was first tuned and calibrated in the positive mode following the standard optimization procedure for all voltages and settings: Source Type: ESI, Ion Spray Voltage: 3.8 kV, Capillary Voltage: 37.00 V, Tube Lens; 130.00 V, Capillary Temp: 275.00°C, Sheath

Gas Flow: 60.00. Mass spectra were recorded in full scan from 100 to 1000 Da with a resolution of 100,000 at *m/z* 400. All data were processed using the Xcalibur software version 2.0.

2.3.5 Pulse Radiolysis

Pulse radiolysis was performed using the LINAC system at the University of Notre Dame Radiation Laboratory, using previously described techniques. [4] Although •OH radical kinetics are typically measured using thiocyanate competition, the direct product of the reaction with hydrophilic DGAs has significant transient absorbance in the UV/Vis region and it was directly observed at 380 nm and 420 nm for TMDGA and TEDGA, respectively.

3. RESULTS AND DISCUSSION

3.1 Degradation Rates

In agreement with the preliminary results reported for TEDGA in [3], the radiolytic decrease in all the hydrophilic DGAs examined here was exponential. This is shown in Fig. 2. This is also in agreement with the kinetics that has been reported for the DGAs in organic solution. [5, 6, 7] Figure 2 shows the natural logarithms of the concentrations of hydrophilic DGAs determined in irradiated samples as a function of the absorbed dose. The change in concentration versus absorbed dose can be fitted using exponential functions (or a linear function using the natural logarithms of these values), suggesting a pseudo-first-order relationship. These exponential functions, or dose constants (d, kGy^{-1}) for the different DGAs are summarized in Table 5 together with the initial G-values (G_0 in μmol/J), which were calculated according to Equation 1. [5]

$$G_0 = d \times [\text{initial DGA concentration}] \times 1{\times}10^3 \quad (1)$$

The factor $1{\times}10^3$ accounts for unit conversions from M to uM for concentration and for kGy to joules. Duplicate runs were performed for TEDGA, resulting in a value of 0.010 ± 0.001 kGy^{-1}, a value in excellent agreement with that reported previously of 0.011 kGy^{-1}. [3] It can be seen in Table 5 that the degradation rates decreased with the increasing number of carbon atoms in a congener, following the trend TMDGA > TEDGA > Me-TEDGA > Me_2-TEDGA.

Table 5. Dose constants for the degradation of hydrophilic diglycolamides

Diglycolamide	Dose constant d (kGy^{-1})	G_0 (μmol J^{-1})
TMDGA	14.9×10^{-3}	0.97
TEDGA1	11.1×10^{-3}	0.72
TEDGA2	$9.8 / 9.5 \times 10^{-3}$ *	0.64 / 0.62 *
Me-TEDGA	7.8×10^{-3}	0.51
Me_2-TEDGA	7.3×10^{-3}	0.47

*The first value included the data point 50 mmol/L TEDGA at 0 kGy, which was not measured, but used according to the preparation of the samples.

Dose constants have now been reported for many dodecane-soluble DGAs over a range of carbon chain lengths, where it was reported that the degradation rates were statistically identical for samples irradiated under a variety of conditions. [5, 6, 7] For example, the unsymmetrical dodecane-soluble DGA didodecyldioctyldiglycolamide (D^3DODGA) had a reported mean dose constant of 0.0039 ± 0.0003 kGy^{-1} for irradiation in pure dodecane, dodecane solution that was air sparged, or dodecane solution in contact with 2.5 M HNO_3. [6] Similarly, the mean result for tetraoctyldiglycolamide (TODGA) irradiated in pure dodecane, or in dodecane in contact with either 0.1 M or 2.5 M HNO_3 was 0.0041 ± 0.0004 kGy^{-1}, and the mean for tetraethylhexyldiglycolamide (TEHDGA), which also contains eight-carbon chains was 0.0040 ± 0.0004 kGy^{-1} for irradiation in dodecane or dodecane in contact with 0.1 M HNO_3. [5] These dose constants do not appear to vary with total carbon atom content of the congener, however; methylated TODGAs such as Me-TODGA and Me_2-TODGA were reported to have slightly faster values of 0.0058 ± 0.0006 kGy^{-1} and 0.0042 ± 0.0016 kGy^{-1}, respectively, for irradiation in pure dodecane or dodecane in contact with 2.5 M HNO_3. [7] The higher uncertainty for the Me_2-TODGA result makes a definite conclusion difficult, but the trend for greater stability with carbon-content found for irradiation in water is probably not followed for irradiation in alkane solution.

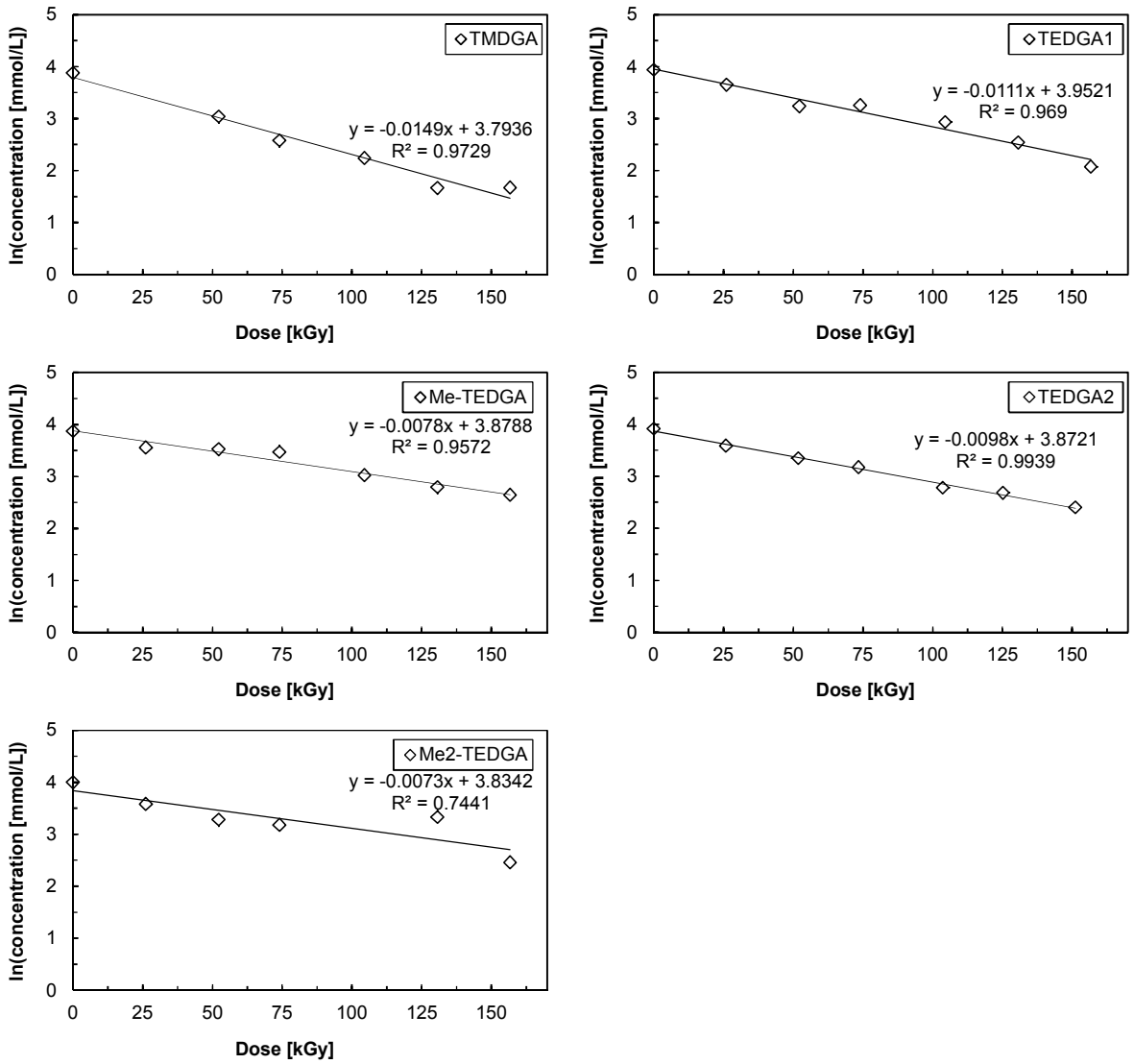
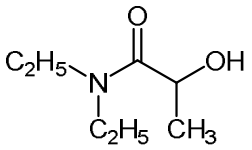


Figure 2. Natural logarithms of the concentrations of hydrophilic DGAs determined in irradiated samples as a function of the absorbed dose. Please note that TEDGA1 refers to an initial set of samples and TEDGA2 refers to a replicate set of samples. The first data point of the TEDGA2 data (0 kGy) was inserted manually, as an unirradiated sample was not analyzed. A linear regression is included in the graphs.

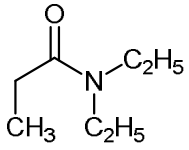
3.2 Radiolysis Products

Analogous products were identified for the radiolysis of all hydrophilic DGAs examined. For the purposes of this report, the products of Me_2-TEDGA are used for illustration. The entire data set will be summarized for publication at a later date. The m/z = 146.12 corresponds to the expected degradation fragment shown in Figure 3. The fragment has a retention time of 5.5 min. This degradation fragment is a glycolamide and can be formed by rupture of the ether C-O bond. Similar products have been found for the degradation of long-chain DGAs in organic diluents. [5, 6, 7] However, the acetamide with a protonated mass of m/z = 130.12, corresponding to the

balance of the molecule has not been identified. This may indicate that it undergoes hydrolysis or rapid radiolysis upon production.



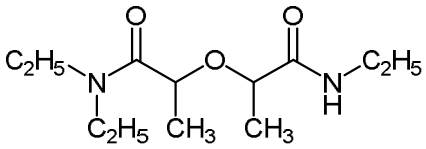
Chemical Formula: $C_7H_{15}NO_2$
Exact Mass: 145,1103



Chemical Formula: $C_7H_{15}NO$
Exact Mass: 129,1154

Figure 3. The detected Me_2-TEDGA degradation compound with protonated mass 146.12 and the corresponding balance of molecule with protonated mass 130.12 that was not detected.

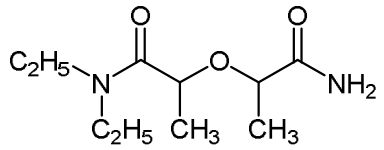
De-alkylation reactions for DGAs [4, 5, 6], CMPO [8] and TBP [9] have been previously reported, and may result from reactions with •OH radical, •H atom or even dissociative electron capture, given the sealed, neutral water samples used here. Products of both single and double de-alkylation reactions were also detected for the hydrophilic DGAs. The mass 245.19 corresponds to the degradation fragment shown in Figure 44 and mass 267.17 to its sodiated analogue. The fragment has a retention time of 6.1 and 6.7 min, due to the existence of two different diastereomers. This degradation fragment can be formed by single dealkylation of an amidic nitrogen atom.



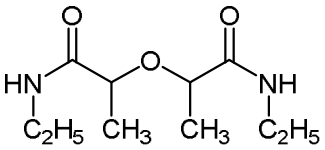
Chemical Formula: $C_{12}H_{24}N_2O_3$
Exact Mass: 244,1787

Figure 4. Me_2-TEDGA degradation compound with protonated mass 245.19.

Double dealkylation products would have m/z = 217.15 corresponding to the two possible degradation fragments shown in Figure 5. The product has a broad retention time of 5.1-6.0 min. There is no clear distinction between the two different diastereomers, the intensity is generally low and overlaps with many different masses. This degradation fragment can be formed by two dealkylations of a single amidic nitrogen atom or two single dealkylations of two different amidic nitrogen atoms.



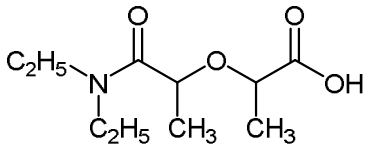
Chemical Formula: $C_{10}H_{20}N_2O_3$
Exact Mass: 216,1474



Chemical Formula: $C_{10}H_{20}N_2O_3$
Exact Mass: 216,1474

Figure 5. Me_2-TEDGA degradation compound with protonated mass 217.15.

A product of m/z = 218.11 probably corresponds to the acidic degradation fragment shown in Figure 6. The fragment has a broad retention time of 5.9 and 7.0 min, due to the existence of two different diastereomers. This degradation fragment can be formed by cleavage of the amide C-N bond, followed by oxidation to produce a carboxylic acid. The balance of molecule would be the corresponding amine, although it was not detected here because the mass is too low to be detected by the method. An acidic product such as this could be an important radiolytic complexing agent. Analogous products have also been reported for other DGAs [5, 6, 7] and CMPO. [8]



Chemical Formula: $C_{10}H_{19}NO_4$
Exact Mass: 217,1314

Figure 6. Me_2-TEDGA degradation compound with protonated mass 218.14.

Products with m/z of 160.10, 263.20, and 297.19 were also detected, however, structures have not been assigned to these signals.

3.3 Radical Reaction Kinetics

The reaction kinetics of the $^{\bullet}OH$ radical with the hydrophilic DGAs TMDGA and TEDGA were measured by pulse radiolysis using the LINAC at the University of Notre Dame Radiation Laboratory. The obtained rate constants were $(3.06 \pm 0.09) \times 10^9$ M^{-1} s^{-1} for TMDGA and $(2.91 \pm 0.10) \times 10^9$ M^{-1} s^{-1} for TEDGA. These are fast rate constants typical of $^{\bullet}OH$ reactions with hydrocarbons, and indicate that this species is important in DGA degradation in water.

Kinetic data for the reaction of the hydrophilic DGAs was also collected for H-atom and the $^{\bullet}NO_3$ radical. This data is currently being analyzed and will be reported in a subsequent publication.

3.4 Mechanistic Considerations

DGA degradation in water generated products analogous to those in dodecane. Degradation in alkanes has been attributed to reaction with the alkane radical cation product of direct alkane radiolysis. [5] The reactions of this species occur at diffusion limited rates, possibly explaining the fairly invariant dose constants measured for the various high molecular weight DGAs under various solution conditions. Such fast reactions may be little affected by the structure of the target molecule. However, for irradiation in pure water no radical cations exist and the most likely reactive species accounting for DGA degradation is the •OH radical product of direct water radiolysis, also an oxidative species. This species typically reacts with organic compounds with rate constants over a range of values about an order of magnitude slower than does the alkane radical cation. Since the *d* values reported here were faster in aqueous solution, this may indicate that the electron transfer does not always lead to subsequent degradation in dodecane, or that the higher molecular weight of the lipophilic DGAs slowed down their subsequent decomposition in analogy with aqueous results.

A common reaction of the •OH radical is H-atom abstraction from a DGA molecule. In this case, the rates would be expected to increase with molecular weight, as this also represents an increase in the H-atom content of the molecule, thus representing more sites for •OH radical attack. In spite of this expectation, the rate constants for TMDGA and TEDGA were about the same, suggesting that not all H-atoms are equally vulnerable. In contrast to the rate constants, the dose constants decreased with increasing H-atom content. This may indicate that only H-atom abstraction from a carbon atom adjacent to the ether oxygen results in ether linkage rupture, the most important degradation mechanisms consistently reported for DGAs. [5, 6, 7] Ether rupture is consistent with the production of the product at m/z = 146.12, shown in Figure 3. More H-atom content at other locations in the molecule may preserve a fast rate constant, but decrease the likelihood of attack at the ether linkage H-atoms, resulting in lower *d*-values for the heavier DGAs, as was measured here.

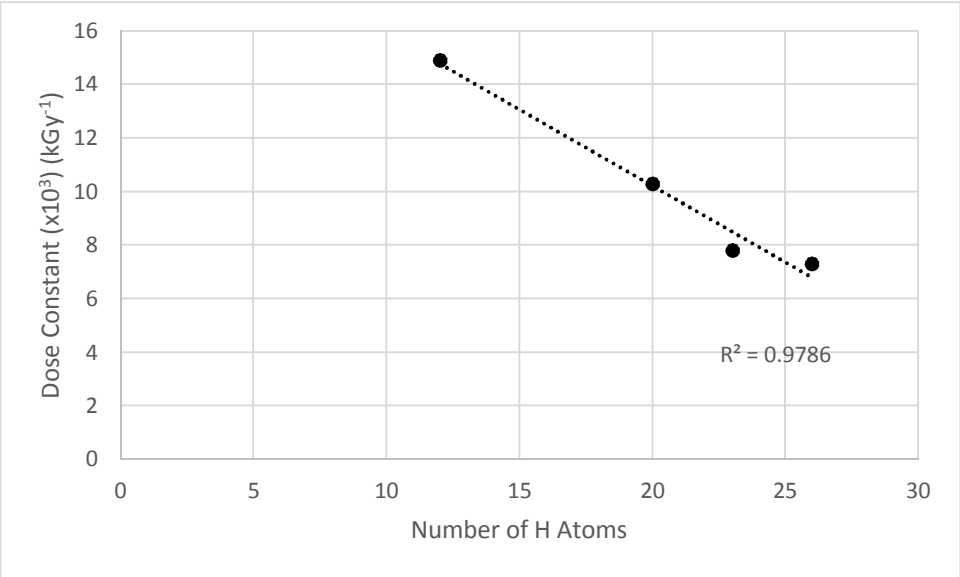


Figure 7. The rate of DGA degradation in neutral, de-aerated water as a function of H-atoms in addition to those on carbon atoms directly adjacent to the ether linkage.

In addition to the ether linkage rupture, products of dealkylations, created by several possible mechanisms, and rupture of the C-N amine bond are probably also initiated by •OH radical H-atom abstraction. It is now well known that amine bond rupture is especially favored in the presence of HNO_3, possibly indicating that the H-atom extraction at this position is favored by the •NO_3 radical.

The irradiations were performed here in the absence of HNO_3 to avoid the confounding effects of acid hydrolysis. It is important to note that in aqueous HNO_3, •OH radical is scavenged to produce •NO_3 radical. Since the reactions of the oxidizing •NO_3 radical are similar, although usually somewhat slower than for the •OH radical, the data collected in pure water are still informative. When the •NO_3 kinetic data has been analyzed, its reactivity will be readily compared to the •OH data presented here.

4. CONCLUSION AND FUTURE WORK

Water soluble DGAs were degraded in aqueous solution at a faster rate than lipophilic DGAs in dodecane, but were more stable with increasing molecular weight. The degradation products of the water soluble DGAs were identified and found to be analogous to those produced in irradiated alkanes. It was concluded that similar products are obtained since reactions in both diluents are by oxidation followed by rupture of the weak ether linkage. The fast rate constants of the reactions of two hydrophilic DGAs with the •OH radical were measured and indicate that it is a likely important oxidative species in pure water. Additional data for •NO_3 radical reactionsand products analysis for additional DGAs is in progress and will be reported in a subsequent publication.

5. REFERENCES

1. Sasaki, Y.; Sugo, Y.; Morita, K.; Nash, K.L. 2015. The effect of alkyl substituents on actinide and lanthanide extraction by diglycolamide compounds. *Solvent Extr. Ion Exch*. 33: 625-641.
2. Moyer, B.A.; Lumetta, G.L.; Mincher, B.J. Minor actinide separation in the reprocessing of spent nuclear fuel: recent advances in the United States, Ch. 11 in: Taylor, R. Reprocessing and recycling of Spent Nuclear Fuel. Woodhead Publishing Series in Energy, Number 79, Elsevier, NY, 2015.
3. Mincher, B.J., Zarzana, C.A. Hydrolysis and radiation chemistry of the DGAs. Report FCRD-MRWFD-2016-000369, Sept. 2016.
4. Cullen, T.D.; Mezyk, S.P.; Martin, L.R.; Mincher, B.J. 2013. Elucidating the radical kinetics involved in the radiolytic destruction of lanthanide-complexed DTPA. *J Radioanal Nucl Chem* 296:717–720.
5. Zarzana, C.A.; Groenewold, G.S.; Mincher, B.J.; Mezyk, S.P.; Wilden, A.; Schmidt, H.; Modolo, G.; Wishart, J.F.; Cook, A.R. 2015. A comparison of the γ-radiolysis of TODGA and T(EH)DGA using UHPLC-MS analysis. *Solvent Extr Ion Exch* 33:431-447.
6. Roscioli-Johnson, K.M.; Zarzana, C.A.; Groenewold, G.S.; Mincher, B.J.; Wilden, A.; Schmidt, H.; Modolo, G. A study of the γ-radiolysis of di-dodecyl di-octyl diglycolamide using UHPLC-ESI-MS analysis. *Solvent Extr. Ion Exch*. 34:439-453.
7. Galán, H.; Zarzana, C.A.; Wilden, A.; Núñez, A.; Schmidt, H.; Egberink, R.J.M.; Leoncini, A.; Cobos, J.; Verboom, W.; Modolo, G.; Groenewold, G.S.; Mincher, B.J. 2015. Gamma-radiolytic Stability of New Methylated TODGA Derivatives for Minor Actinide Recycling. *Dalton Trans* 44:18049-18056.
8. Mincher, B.J.; Mezyk, S.P.; Elias, G.; Groenewold, G.S.; Olson, L.G. 2013. The radiation chemistry of CMPO: Part 1. Gamma radiolysis. *Solvent Extr Ion Exch* 31:715–730.
9. Mincher, B.J.; Modolo, G.; Mezyk, S.P. 2009. The effects of radiation chemistry on solvent extraction: 1. Conditions in Acidic Solution and a Review of TBP Radiolysis. *Solvent Extr Ion Exch* 27:1–25.