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Gamma-radiolytic stability of new methylated TODGA derivatives for minor actinide recycling

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The stability against gamma radiation of MeTODGA (methyl tetraoctyldiglycolamide) and Me_2TODGA (dimethyl tetraoctyldiglycolamide), derivatives from the well-known extractant TODGA (*N*,*N*,*N*',*N*'-tetraoctyldiglycolamide), were studied and compared. Solutions of MeTODGA and Me_2TODGA in alkane diluents were subjected to ^{60}Co γ-irradiation in the presence and absence of nitric acid and analyzed using LC-MS to determine their rates of radiolytic concentration decrease, as well as to identify radiolysis products. The results of product identification from three different laboratories are compared and found to be in good agreement. The diglycolamide (DGA) concentrations decreased exponentially with increasing absorbed dose. The MeTODGA degradation rate constants (dose constants) were uninfluenced by the presence of nitric acid, but the acid increased the rate of degradation for Me_2TODGA. The degradation products formed by irradiation are also initially produced in greater amounts in acid-contacted solution, but products may also be degraded by continued radiolysis. The identified radiolysis products suggest that the weakest bonds are those in the diglycolamide center of these molecules.

Introduction

Current nuclear reactors consume less than 1% of their natural uranium, which is obviously a low efficiency. In order to achieve long-term sustainability of nuclear energy from fission, new technological solutions which are able to use more than 80% of this natural uranium are being developed. The new technology is based on the combination of fast neutron systems with multi-recycling of the fuel in advanced fuel cycles. The advanced fuel cycles are being designed to re-use most of the uranium, plutonium, and the minor actinides (Am, Np, Cm).[1] To recover the minor actinides from used fuel it is necessary to develop suitable separation processes. Up to now, hydrometallurgical (i.e. solvent extraction) processes have been the reference technology for recycling the major actinides uranium and plutonium from used fuel. The recycling of minor actinides, particularly americium, is currently of high R&D interest due to its major contribution to waste radiotoxicity and heat generation. Several processes for americium recovery are under development in national and international projects. Most proposals rely on the pre-separation of a major uranium and plutonium stream by a conventional PUREX (Plutonium Uranium Redox EXtraction) process with the minor actinides then consecutively separated by multi-step (DIAMEX-SANEX concept)[2,3] or single step processes (1-cycle SANEX,[4] innovative-SANEX,[5] ALSEP,[6] and/or EXAm[7]) from the PUREX raffinate, which still also contains lanthanides, activation products and other fission products.

The diglycolamides (DGAs) are alkyl-3-oxapentane-1,5-diamide derivatives, emerging as promising candidates for the separation of minor actinides which, unlike tributyl phosphate (TBP, extractant of the PUREX process), can extract actinide ions in the trivalent state.[8] Unfortunately, this ligand family, made up of CHON (carbon, hydrogen, oxygen and nitrogen) elements and therefore completely incinerable, cannot discriminate between trivalent actinides (An(III)) and lanthanides (Ln(III)). Nevertheless, the DGAs have many favorable properties, such as high actinide extraction affinity, fast mass transfer, high loading capacities and reasonable stability under relevant process conditions.

It is realized that the extraction and stripping of An(III) and Ln(III) and ions strongly depends on the nature of the alkyl group attached to the DGA nitrogen atoms.[9] The n = 8 and 10 derivatives are soluble in alkane diluents, and these compounds complex and extract actinides and lanthanides with distribution ratios that increase with increasing aqueous nitric acid acidity, and that follow the order M(III)/M(IV)>M(VI)>M(V). Particularly the octyl derivative, *N*,*N*,*N*',*N*'-tetraoctyldiglycolamide (TODGA, Fig. 1) has thus received detailed study for its potential applications at the

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back end of the nuclear fuel cycle for the extraction of lanthanides and actinides.[10-13] In continued European research within the FP 7 ACSEPT project, TODGA was modified by the addition of one or two methyl groups on the methylene carbon positions to produce MeTODGA and Me_2TODGA, respectively (Fig. 1).[14-16] Extraction efficiency decreased with increasing methyl substitution, probably due to steric considerations. Among them, the most interesting extractant is MeTODGA, particularly for the GANEX (Group ActiNide Extraction) process, since it was found that the extraction efficiency of the undesired fission products decreased while the distribution ratios and loading capacity of the desired Ln(III) and An(III) remained acceptable under relevant conditions. Subsequent stripping at low nitric acid concentrations might also be improved.[16]

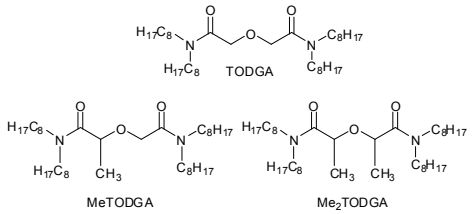

Fig. 1 Structures of TODGA, MeTODGA and Me_2TODGA.

To evaluate the applicability of solvents based on DGAs for process development, it is necessary to prove not only their good extraction properties, but also their degradation resistance, since the organic phase is in contact with highly radioactive solutions and high nitric acid concentrations. Solvent degradation may lead to undesirable effects such as decreases in solvent extraction efficiency, decreases in selectivity, and/or third phase formation.

While the long-chain DGAs appear to be hydrolytically stable, radiolytic degradation of DGAs has been observed.[17-26] The decrease in ligand concentration is exponential with dose, and has been mainly attributed to electron-transfer reactions between radiolytically-produced diluent radical cations.[17,19] The presence of nitric acid during irradiation has been reported to have variable effects. For example, for irradiation experiments to absorbed doses as high as 400 kGy in *n*-dodecane, the presence of the acidic aqueous phase had little effect on the dose constants for the degradation of TODGA.[19] However, when Galán *et al.*[18] irradiated TODGA in the alkane diluent hydrogenated tetrapropene (TPH, used in AREVA's reprocessing plant) that had been pre-contacted with nitric acid to an absorbed dose of 1000 kGy, a slight protective effect was measured when taking into account the remaining concentration of TODGA. In that same work a clear protective effect was seen for irradiations in a diluent composed of TPH and 1-octanol. Thus nitric acid protection occurs depending on the diluent. It has also been demonstrated that the major sites for degradation effects are the bonds within the diglycolamide functional group, specifically the $C{-}O_{ether}$ and $N{-}C_{carbonyl}$.[18,19]

Recently, several studies have appeared regarding the effects of DGA irradiation on solvent extraction metal distribution ratios.[20-24] Initially, DGA degradation was inferred based on the decrease in distribution ratios.[21-23] However, studies of the main degradation products have since shown that the new species have extraction properties that markedly differ from those of the original ligands.[18,24] Thus distribution ratios cannot be used as a metric for ligand degradation.

Since the ether DGA linkage is especially susceptible to radiolytic attack, efforts to reduce degradation should naturally focus on protecting these bonds. In addition to their solvent extraction advantages, the new class of methyl TODGA derivatives (Fig. 1) may offer such stability. Herein we describe an investigation of the γ-radiolytic stability of methyl TODGA derivatives in both *n*-dodecane and TPH using LC-MS techniques. Stability was assessed based on the decrease in DGA concentration with absorbed dose and the generation of degradation products, as measured at three different laboratories as part of a collaborative effort. Irradiations were performed for the organic solutions in the presence and absence of an aqueous nitric acid phase and the results are compared to previous work with un-substituted TODGAs.

Results and discussion

Degradation of MeTODGA in TPH

The mono-substituted MeTODGA at 0.1 M was irradiated in TPH after acid preequilibration over a series of absorbed doses to a maximum of 1000 kGy. For comparison, similar MeTODGA solutions were stored at 25°C for 56 days, to investigate the stability of unirradiated DGAs (ageing effects) and hydrolysis. Fig. 2 shows the exponential concentration decrease as measured by HPLC-DAD for these samples. The effects of ageing and hydrolysis were negligible for this length of exposure and temperature. Also shown in Fig. 2 is that a 50% reduction in MeTODGA concentration takes place by an absorbed dose of 250 kGy.

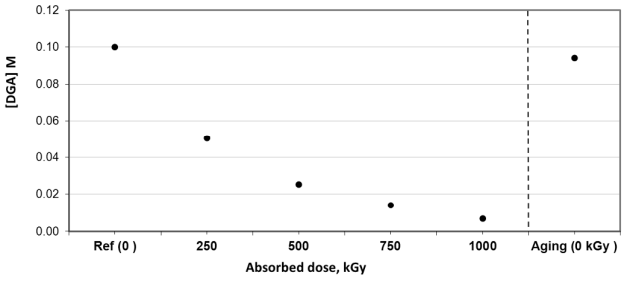

Fig. 2 Quantitative determination of the MeTODGA concentration of fresh (Ref), aged (aging, 0 kGy) and irradiated MeTODGA solutions (250-1000 kGy). Ligand concentration was initially 0.1 M in TPH diluent.

Degradation of MeTODGA and Me_2TODGA in *n*-dodecane

The two substituted DGAs, MeTODGA and Me_2TODGA, were also irradiated in *n*-dodecane to facilitate a comparison to previous work with TODGA and T(EH)DGA (*N*,*N*,*N*',*N*'-tetra-2-ethylhexyldiglycolamide).[19] The change in the concentration of DGAs versus absorbed dose for samples irradiated as only the organic phase, or as the organic phase in contact with 2.5 M HNO_3 is shown in Fig. 3. The concentration change for each was exponential, suggesting pseudo-first-order kinetics, as has been previously shown for the other TODGAs.[19] Therefore, the radiolytic degradation as a function of absorbed dose can be described by a dose constant.[27]

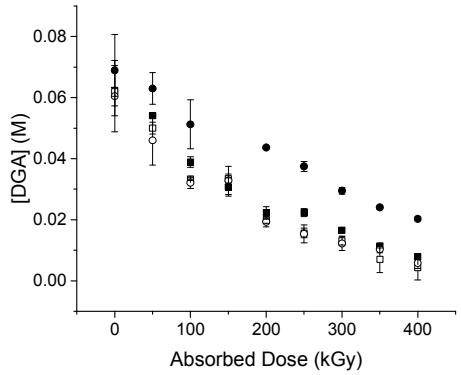

Fig. 3 The change in initially nominal 0.05 M DGA concentration versus absorbed dose. MeTODGA (solid squares), Me_2TODGA (solid circles) MeTODGA/HNO_3 (open squares) and Me_2TODGA/HNO_3 (open circles). There were instrumental difficulties measuring the Me_2TODGA sample at 150 kGy absorbed dose, so those data have been omitted.

Calculated dose constants for the systems studied here are given in Table 1. Dose constants for uncontacted and nitric acid contacted TODGA are reproduced from Zarzana *et al.*[19] for comparison.

Table 1 Dose constants for the degradation of TODGA, MeTODGA and Me_2TODGA (kGy^{-1}) calculated as the exponential constants for fits to the plots of concentration versus absorbed dose. Uncertainties are at the 99% confidence interval. MeTODGA and Me_2TODGA and MeTODGA/TPH from this work. TODGA/*n*-dodecane from.[19]

	Dose constant (10^{-3} kGy^{-1})		
Sample	**0.05 M in *n*-dodecane**	**0.05 M in *n*-dodecane 2.5 M HNO_3**	**0.1 M in TPH, 3 M HNO_3 pre-equilibration**
TODGA	4.1±0.3	3.8±0.3	
MeTODGA	5.0±0.3	5.8±0.4	2.6 ±0.3
Me_2TODGA	3.0±0.2	5.3±0.4	

It is well known that ether bonds are susceptible to scission under radiolysis. According to Belevskii *et al.*,[28] the electron deficiency in an ionized methylamide is most pronounced at the H-atoms of the methyl groups. The analogous situation for diglycolamides would suggest that electron deficiency is localized on the methylene H-atoms, thus facilitating loss of the H-atom to produce a carbon-centered radical. This could favor C-O bond rupture as has been observed for DGAs [15, 18,19] and bis-DGA.[24] Substitution of a methylene H-atom by a methyl group, as in MeTODGA, might be expected to protect that bond, improving the radiolytic stability of the molecule. However, single methyl substitution here instead increased the degradation rate of MeTODGA in *n*-dodecane compared to TODGA. A second methyl substitution (Me_2TODGA) does result in increased radiolytic stability in *n*-dodecane over TODGA.

Previously, we reported that the dose constants for unsubstituted TODGA and T(EH)DGA were unchanged in *n*-dodecane upon acid contact.[19] However, in this case, the presence of nitric acid definitely increased the degradation rate of MeTODGA and Me_2TODGA. Nitric acid does not provide a protective effect for Me_2TODGA, at least in nonpolar solvents where the extraction of nitric acid is low.[29] Thus, if methylation of the DGA protects the ether linkage, these results suggest that another bond is susceptible in the presence of the acid. Several reports have indicated that the amide C-N linkages are susceptible to radiolytic rupture in the presence of nitric acid.[30,31]

Identification and behavior of MeTODGA radiolysis products

Previous TODGA stability studies revealed that the main ruptures take place in the C-O_{ether} and $C_{carbonyl}$-N bonds, giving rise to ten degradation compounds.[18,19,23] In solvent formulations containing 1-octanol, the formation of acids, amines or esters is favored, but the first two can also be observed in alkane diluents when nitric acid is present. As mentioned before, one of the challenges of this family of DGA compounds is to reduce the radiolytic degradation rates by protecting the ether bonds. Therefore, it was of interest to identify and quantify the degradation compounds formed when unsymmetrical MeTODGA was subjected to irradiation. Similar structures were identified both in *n*-dodecane and TPH, and the three mass spectrometric techniques employed at our laboratories produced very consistent results. Fig. 4 shows the structures assigned to the products found after the irradiation of MeTODGA in *n*-dodecane or TPH from the mass analysis spectra. Thirteen mass signals were identified as possible radiolysis products for MeTODGA for which we have assigned the structures 1-10 and 14-16 (Fig. 4). For most of these radiolytic degradation products, reasonable structures were inferred based on simple homolytic cleavage of the parent structure, followed by capping of the resultant radical. The exception to this is product 13 *(m/z* 256.3), which could be assigned to an oxidation of dioctylamine, since a simple cleavage and capping reaction could not produce a satisfactory structural hypothesis, and so the structure of this compound is at present not clear. The rupture of bonds on the carbonyl and alkyl sides of the amides gives rise to products 11-16. Rupture of the ether linkage in non-symmetrical MeTODGA also results in four possible products (1-4), depending on which side of the linkage the break occurs. The ether linkage breaks are shown in Fig. 5.

If the ether break occurs on the side adjacent to the methyl group, the products have protonated masses 300.3 (compound 4 in in Figs. 4 and 5) and 298.3 (compound 3 in Figs. 4 and 5). Compound 4 is the same product as for TODGA radiolysis, namely 2-hydroxy-*N*,*N*-dioctylacetamide. This compound grew in with absorbed dose slightly faster in the samples irradiated in the presence of the acidic aqueous phase. This is shown in Fig. 6, and is in good agreement with previous results on TODGA radiolysis.[18,24]

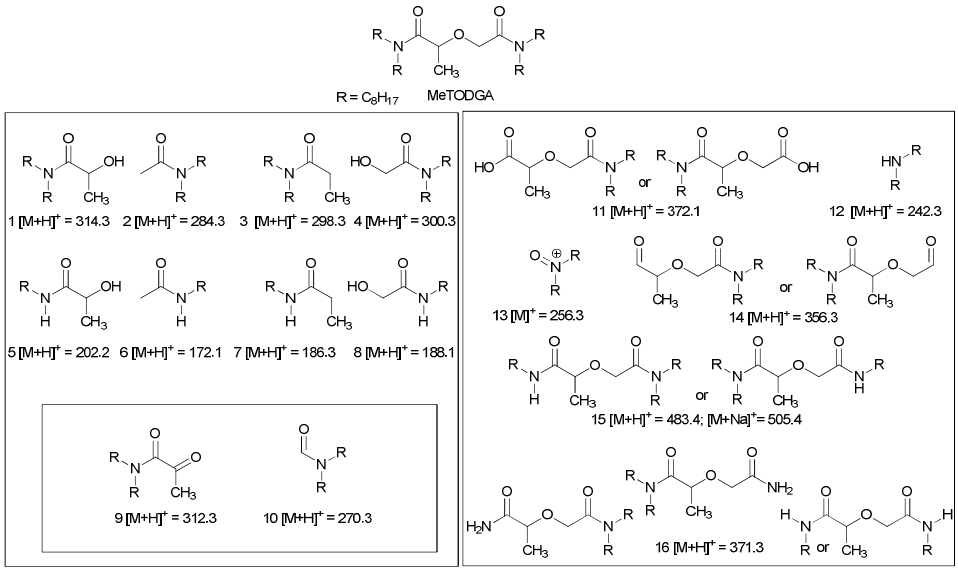

Fig. 4 Proposed structures of the products found in irradiated MeTODGA solution.

If the ether linkage ruptures on the side opposite the methyl group, products at protonated masses 314.3 (compound 1 in Figs.4 and 5) and 284.3 (compound 2 in Figs. 4 and 5) occur. Signals at these masses were detected. Compound 1, with a methylated ether linkage, had a slightly higher signal intensity than the non-methylated hydroxyacetamide compound 4, possibly indicating that pathway a in Fig. 5 is preferred. This would indicate that the methylated ether linkage was somewhat protected, assuming that the mass spectrometric response factors are the same for both fragments. This 2-hydroxy-*N*,*N*-dioctylpropanamide also grew in faster in the presence of the acidic aqueous phase, as also shown in Fig. 6, in agreement with previous studies.[18] In presence of nitric acid compounds with a 2-hydroxyalkylamide structure are always the main products formed, and compound 1 was detected in all samples by all three laboratories. These results again support the hypothesis of different degradation pathways in presence of nitric acid.

Structural degradation analysis was also conducted for irradiated samples of MeTODGA in TPH that were pre-equilibrated with 3 M HNO_3. In fact, an irradiation to 1000 kGy was carried out to maximize the concentrations of degradation products. The HPLC-MS chromatograms for MeTODGA, and also TODGA for comparison, irradiated under these conditions are shown in Fig. 7, where a higher number of signals corresponding to products were found for MeTODGA, as expected for a non-symmetric structure. However, it should be noted that this is not an indication that only these products were generated since the radiolysis products may also undergo radiolytic decomposition. The chromatograms in Fig. 7 also show the products of the rupture of the ether linkage, compounds 4 and 3, and 2 and 1, as the main products in TPH solution after 1000 kGy. The peak heights of these compounds are consistent with increased C-O bond stability on the substituted side of the ether.

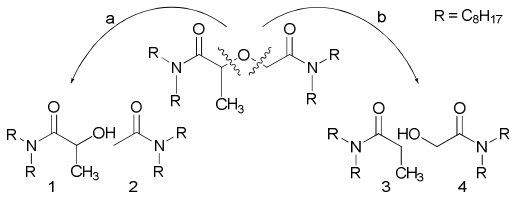

Fig. 5 The four possible products of ether linkage rupture for the unsymmetrical MeTODGA.

Loss of a single alkyl chain also occurred for MeTODGA in both *n*-dodecane and TPH, in analogy with TODGA and T(EH)DGA in *n*-dodecane.[18,19] The single de-octylation (protonated mass 483.4, or sodiated mass 505.4, compound 15 in Fig. 4) was clearly favored by the presence of the acidic aqueous phase; as was previously shown for bis-DGA.[24] This is shown in Fig. 8. These results again support the hypothesis of different degradation pathways in presence of nitric acid.

The product corresponding to the loss of a single octyl group (compound 15, Fig. 4) was also detected for irradiations in TPH, but upon irradiation to 1000 kGy, it was present in only negligible amounts, probably indicating its own radiolytic decomposition. The products of a second de-alkylation were also detected in *n*-dodecane; however, they were present in unirradiated samples, and did not show a clear trend with absorbed dose, and thus may not be radiolysis products.

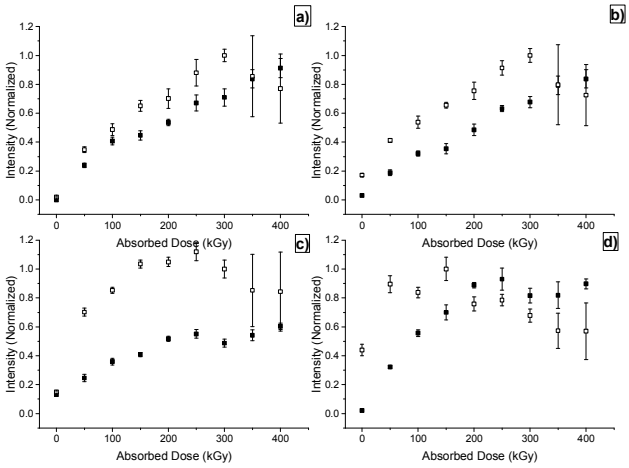

Fig. 6 Formation of compounds a) 4, b) 1, c) 11 and d) 15 (Fig. 4) versus absorbed dose for the irradiation of 0.05 M MeTODGA in *n*-dodecane (solid squares), for pure organic samples, and for samples irradiated in the presence of 2.5 M HNO_3 (open squares). Intensities are normalized to the maximum detected signal for each compound.

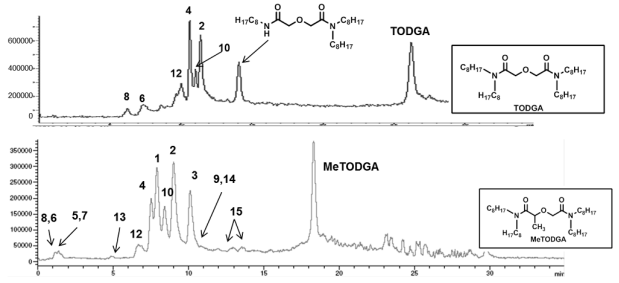

Fig. 7 HPLC-MS(APCI$^+$) chromatograms for TODGA and MeTODGA irradiated to 1000 kGy in acid pre-equilibrated TPH. Peak numbers correspond to compounds in Fig. 4.

Rupture of the amide moiety to produce a carboxylic acid and the corresponding amine (protonated mass 372.1, compound 11, Fig. 4) was found in irradiated MeTODGA/*n*-dodecane samples, again with favored production in the presence of acidic aqueous phase, at least initially (Fig. 6). Following about 200 kGy absorbed dose, the carboxylic acid product concentration dropped below that found in the pure organic samples, for samples irradiated in the presence of the aqueous phase. The formation of the amine (protonated mass 242.3, compound 12, Fig. 4) was not measured in *n*-dodecane at INL due to the conditions of the mass detector selected for these experiments. It was found in the same samples using the parameters adopted at Jülich. The radiolytic generation of the amine was also observed in experiments performed in TPH pre-equilibrated with nitric acid at CIEMAT. Compounds corresponding to rupture of the methylene-carbonyl C-C bonds were also detected in irradiated MeTODGA/*n*-dodecane samples, but only at very low signal strength. Rupture of this bond is not preferred.

Previously, degradation of TODGA and T(EH)DGA was attributed to the electron transfer reaction with the *n*-dodecane radical cation.[17,19] However, perhaps unsurprisingly the TPH results here suggest that *n*-dodecane is not a unique source of reactive species, and that the ionization of other alkanes also produces radical cations that are capable of participating in electron transfer reactions with the diglycolamides. The smaller dose constant reported in Table 1 for MeTODGA in TPH solution may reflect smaller rate constants for branched alkane radical cation electron transfer reactions, since branched alkane radicals are expected to have a lower ionization potential, resulting in a slower electron transfer reaction between solvent and the DGA molecule. The ionization potential of DGAs was calculated by the semiempirical AM1 method to be less than that of *n*-dodecane by a factor of 1.6 eV.[32] The difference in the ionization potentials supports the charge transfer from radical cations of *n*-dodecane to these amide molecules.

Identification and behavior of Me_2TODGA radiolysis products

The study of structural degradation of Me_2TODGA was performed in the same way as for MeTODGA. In this case a lower number of degradation compounds were identified, shown in Fig. 8. The highest signal intensity product of Me_2TODGA radiolysis occurred at mass 314.3, and corresponds to the product 2-hydroxy-*N*,*N*-dioctylpropanamide (compound 1, Fig. 8); the same as produced by MeTODGA irradiation (compound 1, Fig. 4). It was detected at all three laboratories. Since Me_2TODGA is symmetrical, compound 1 is produced by rupture on either side of the ether. Although small amounts were detected in unirradiated samples, it is also clearly a radiolysis product for which the concentration increases with absorbed dose, until the highest absorbed dose applied of 400 kGy. As shown in Fig. 9, its generation was again enhanced by the presence of the acidic aqueous phase. Rupture of the ether linkage would also be expected to produce *N*,*N*-dioctylmethylacetamide from the balance of the initial molecule and this compound was indeed detected (mass 298.3, compound 3 in Fig. 8), although at fairly low signal intensity. Products generated by loss of alkyl substituents also occurred for Me_2TODGA. Loss of a single octyl group (mass 497.5, compound 19 in Fig. 8) took place in both purely organic and acid contacted conditions, and was again favored by the presence of the acidic aqueous phase. It was detected at all three laboratories.

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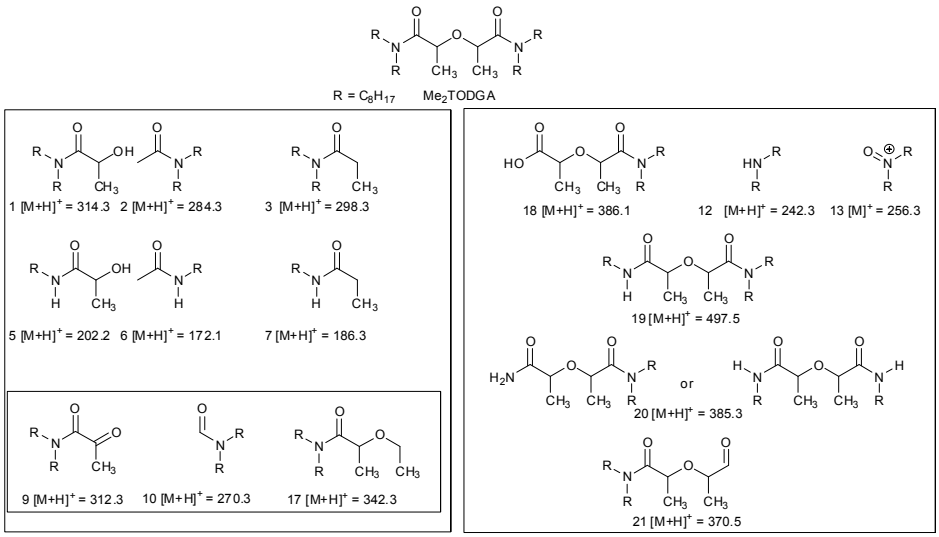

Fig. 8 Proposed structures of the products found in irradiated Me_2TODGA solutions.

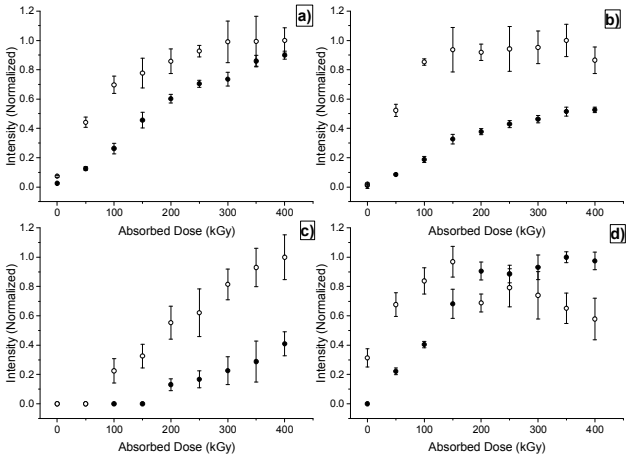

Fig. 9 Formation of compounds a) 1, b) 19, c) 20, and d) 18 (Fig. 8) versus absorbed dose for the irradiation of 0.05 M MeTODGA in *n*-dodecane (solid squares), for pure organic samples, and for samples irradiated in the presence of 2.5 M HNO_3 (open squares). Intensities are normalized to the maximum detected signal for each compound.

Fig. 9 shows as well the ingrowth of this signal for irradiation under both conditions. At higher absorbed doses a signal at mass 385.3 appeared, (compound 20, Fig. 8), attributed to loss of a second octyl group. This species did not appear until sufficient absorbed dose had been accumulated, indicating that it is likely produced from the single dealkylation product. It continued to grow in with continued irradiation, and was favored by the presence of the acidic aqueous phase. This is also depicted in Fig. 9.

The other relatively abundant product was the expected carboxylic acid produced by rupture of the DGA C-N bond (mass 385.1, compound 18, Fig. 8). Initially, the presence of acid seems to have favored rupture of the amide bond to give the carboxylic acid, but the product appears to undergo radiolysis with a declining concentration above about 200 kGy, when irradiated in contact with nitric acid, similarly to that shown for the analogous carboxylic acid produced by MeTODGA radiolysis in Fig. 6. This is shown in Fig. 9.

Conclusions

The results indicate that rupture of the ether linkage is a main pathway for the radiolytic decomposition of all the studied TODGAs in the two alkane diluents investigated. The introduction of a methyl group on only one methylene carbon atom of the ether linkage did not protect MeTODGA. In fact, MeTODGA degraded faster than non-substituted TODGAs, possibly because the unsubstituted C-O linkage was weakened by this structural change. This is supported by the fact that

products of the ether linkage rupture are still very abundant for this compound, and that the products created by rupture on the non-substituted side of the molecule are the most abundant. The substitution of the industrial diluent TPH for *n*-dodecane did not affect this result, indicating that other radical cations besides that derived from *n*-dodecane are capable of electron transfer reactions with the DGAs, although presumably with different rate constants. Reactions of branched alkyl radicals might be expected to be slower, since branched carbon centered radicals are more stable. This is consistent with the slower dose constant found for MeTODGA degradation in TPH. The addition of a second methyl group on the second methylene carbon atom of the ether linkage did protect Me_2TODGA, which had a much slower rate of radiolytic degradation than MeTODGA, and a lower rate than that measured for the unsubstituted TODGAs in our previous work, at least in the organic phase.

Other important degradation products included species produced by loss of an octyl group, and for Me_2TODGA, loss of two octyl groups. Cleavage of the amide C-N bond also occurred to produce carboxylic acids, especially in the presence of nitric acid. This has also been reported for other amidic ligands, including other TODGAs. The presence of the acidic aqueous phase appears to have a greater adverse effect on the stability of MeTODGA and Me_2TODGA than was found in previous work with the non-substituted TODGAs. Especially for Me_2TODGA, the degradation rate of the DGA was much higher in the presence of the acidic aqueous phase. In each case the main degradation products, regardless of which bond was cleaved to produce them, occurred with higher yields for samples irradiated in the presence of the acidic aqueous phase. This suggests that methyl substitution, while possibly protecting the bond hosting the substitution, may activate other bonds in the molecule, especially toward reaction with reactive species produced by acid and water radiolysis. The most likely of these would be reactive $^{\bullet}OH$ and $^{\bullet}NO_3$ radicals, both probably reacting by $^{\bullet}$H-atom abstraction from the susceptible sites on the DGA. The overall dose constants for MeTODGA and Me_2TODGA for irradiation in the presence of the aqueous phase are comparable to those reported for the unsubstituted TODGAs.

Experimental

Ligand preparation

MeTODGA and Me_2TODGA were synthesised following the methodology described before[15] or were purchased from TechnoComm Ltd., Wellbrae, Scotland.

Gamma irradiation procedure

Gamma-irradiation was performed at either CIEMAT (Spain) or INL (USA). The CIEMAT irradiations were performed at the Náyade facility, which is a pool of 1.2 m^2 by 4.5 m deep. It consists of 60 ^{60}Co sources distributed in six lots with a total activity of $1.1x10^{14}$ Bq. The irradiation container used provides a homogeneous irradiation flux. Samples were prepared by dissolving ligands in TPH up to 0.1 M and were pre-equilibrated by contacting twice (15 min each) with 3 M HNO_3 at room temperature. The samples were irradiated up to 1000 kGy at dose rate of 1.78 kGy/h. No volume decrease was observed during irradiation, hence evaporation of the solvent is assumed to be negligible. The glass bottles were then stored in a freezer while awaiting further analyses. Reference samples for aging control were kept in the laboratory during the irradiation process.

The INL irradiations were performed using a Nordion (Ottawa, Canada) Gamma Cell 220 ^{60}Co irradiator, with a sample cell, center-line dose rate of 5.4 kGy/h up to a maximum absorbed dose of 400 kGy. The ligands were prepared as 0.05 M solutions in *n*-dodecane, either as the pure organic phase, or in contact with an equal volume of 2.5 M HNO_3. Mixed phase solutions were well-agitated prior to irradiation. It should be noted that sealed vessel irradiations should be considered to be deaerated due to rapid scavenging of dissolved oxygen by produced solvated electrons.

DAD/MS measurement procedure

The chemical composition of the irradiated samples was characterised by LC-DAD/MS or LC-HRMS. The HPLC-DAD measurements were performed by using a reverse phase C-18 column and CH_3CN/H_2O as the mobile phase at 205 nm.

HPLC–MS measurements were performed using three methods. For TPH samples at CIEMAT an Agilent 1100 (Quadrupole detector 6120A) HPLC–MS with a Protonsil C-8 column (50 x 2 mm, 5 µm) at 40 °C using a gradient of mobile phase [(A: 0.1 % v/v CH_3CN/HCOOH), (B: 0.1 % v/v formic acid)] in the $APCI^+$ ionization mode (SCAN 100 a 1500 umas /SIM) was used. The mass spectrometer conditions were: capillary voltage: 2000 V; Corona current: 5 µA; charging voltage: 2000 V; positive mode; dry temp.: 250 °C; vaporization temp 200 °C; nebulizer gas and dry gas were both N_2; nebulizer pressure: 1.4 bar; dry gas flow rate: 5 L/min. Samples were analysed without pre-evaporation and diluted up to 0.5 and 1.0 mM in a (90:10)% v/v MeOH/1-octanol mixture. All measurements were repeated twice.

For *n*-dodecane samples at INL, a Dionex (Sunnyvale, CA) 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) microTOFQ-II electrospray ionization quadrupole time-of-flight mass spectrometer with Hystar 3.2 software was used. The mass spectrometer conditions were: capillary: 4500 V; 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/min. Samples were analysed without pre-evaporation and diluted up to 1:31600 in 2-

propanol prior to analysis. All experiments conducted on the Dionex UHPLC were carried out isocratically using a 30% aqueous, 70% organic mobile phase. The aqueous component was 0.1% v/v formic acid in NanoPure ® water, and the organic component was 4% v/v 1-octanol in 2-propanol. The chromatographic separation was achieved using a 3 µL injection volume onto a C18 reverse-phase (RP-C18) column (Dionex Acclaim® RSCL 120 C18, 10 cm x 2.1 mm, 2.2 µm) with a flow rate of 200 µL/min. The column was maintained at 50 °C. Each sample was injected 5 times. Standards were prepared by serial dilution of unirradiated, non-acid contacted samples with 2-propanol to final concentrations ranging from 0.5 µM to 5 µM.

Also for *n*-dodecane samples, LC-HRMS measurements were performed at Forschungszentrum Jülich using a hybrid linear ion trap FTICR mass spectrometer LTQFT UltraTM (Thermo Fisher Scientific, Bremen, Germany) coupled with an Agilent 1200 system (Agilent, Waldbronn, Germany). A ZORBAX Eclipse Plus C18, 4.6x100 mm, 3.4 µm (Agilent, Waldbronn) column was used using a gradient of mobile phase [(A: 0.1 % v/v CH_3CN/HCOOH), (B: 0.1 % v/v formic acid)]. The mass spectrometer was tuned and calibrated in the positive ion mode. 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.

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