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SUMMARY

The radiation chemistry of CMPO has been investigated using a combination of irradiation and analytical techniques. The α-, and γ-irradiation of CMPO resulted in identical degradation rates (*G*-value, in μmol Gy^{-1}) for both radiation types, despite the difference in their linear energy transfer (LET). Similarly, variations in γ-ray dose rates did not affect the degradation rate of CMPO. The solvent extraction behavior was different for the two radiation types, however. Gamma-irradiation resulted in steadily increasing distribution ratios for both forward and stripping extractions, with respect to increasing absorbed radiation dose. This was true for samples irradiated as a neat organic solution, or irradiated in contact with the acidic aqueous phase. In contrast, α-irradiated samples showed a rapid drop in distribution ratios for forward and stripping extractions, followed by essentially constant distribution ratios at higher absorbed doses. These differences in extraction behavior are reconciled by mass spectrometric examination of CMPO decomposition products under the different irradiation sources. Irradiation by γ-rays resulted in the rupture of phosphoryl-methylene bonds with the production of phosphinic acid products. These species are expected to be complexing agents for americium that would result in higher distribution ratios. Irradiation by α-sources appeared to favor rupture of carbamoyl-methylene bonds with the production of less deleterious acetamide products.

CONTENTS

FIGURES

ACRONYMS

CMPO	Octylphenyl-N, N-diisobutylcarbamoylmethylphosphine oxide
LET	Linear Energy Transfer
TRUEX	TRansUranic EXtraction
TBP	Tributylphosphate
INL	Idaho National Laboratory
NDRL	Notre Dame Radiation Laboratory
HPLC	High Performance Liquid Chromatography
ESI-MS	Electrospray Ionization Mass Spectrometry
UV	Ultraviolet
DIBFA	Diisobutylformamide
DIBAA	Diisobutylacetamide
DIBA	Diisobutylamine
MDIBA	Methyldiisobutylamine
PDIBA	Propyldiisobutylamine
DMDOHEMA	dimethyl dioctyl hexylethoxymalonamine
BTBP	bistriazinyl bipyridine

SEPARATIONS CAMPAIGN

COMPARING THE ALPHA AND GAMMA RADIOLYSIS OF CMPO

1. Introduction

The successful deployment of any solvent extraction ligand proposed for use in fuel cycle separations will depend upon the stability of that ligand in an acidic, radioactive environment. [1] Irradiation of the ligand occurs due to the decay energy of actinides and fission products in the dissolved nuclear fuel solution. The radiation types are predominantly low linear energy transfer (LET) beta/gamma radiation from fission product decay, and high LET alpha radiation from actinide decay. Due to relatively low ligand concentrations employed most decay energy is absorbed by the diluent and ligand radiolysis is expected to occur by indirect, rather than direct mechanisms. [1] For example, the proposed TRUEX solvent contains 0.2 M octylphenyl-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) as the ligand, while the dodecane diluent and tributylphosphate (TBP) modifier concentrations are about 3 M and 1 M, respectively. Consequently, most ligand damage will be due to reaction with reactive species created by energy deposition in the balance of the organic phase, or in the acidic aqueous phase in contact with that organic phase.

The LET of the incident radiation affects the reactive species produced during diluent radiolysis. Using the radiolysis of water as an example, the yields of reactive species due to irradiation with low LET β^-/γ radiation are shown in Equation 1:[2]

$$\mathrm{H_2O} \rightsquigarrow [0.28]\ \bullet\mathrm{OH} + [0.27]\ e^- + [0.06]\ \bullet\mathrm{H} + [0.07]\ \mathrm{H_2O_2} + [0.27]\ \mathrm{H_3O^+} + [0.05]\ \mathrm{H_2} \qquad (1)$$

The numbers shown in brackets are yields (*G*-values) given in μmol Gy^{-1}. These yields change with LET mode, to favor increased production of the molecular species and decreased production of the radical species, as LET increases. For example, Equation 2 gives the yields of the same species for irradiation of water using ^{210}Po α particles: [3]

$$\mathrm{H_2O} \rightsquigarrow [0.05]\ \bullet\mathrm{OH} + [x]\ e^- + [0.06]\ \bullet\mathrm{H} + [0.15]\ \mathrm{H_2O_2} + [x]\ \mathrm{H_3O^+} + [0.16]\ \mathrm{H_2} \qquad (2)$$

It can be seen that the •OH radical yield dropped, while the yield of H_2O_2 and H_2 increased with α irradiation. This is due to the deposition of large amounts of energy in a small solution volume by the higher LET radiation, which results in high localized concentrations of radicals, allowing for their recombination into molecular species prior to their reaction with the ligands.[4] Given the low •OH radical yields and high H_2O_2 yields for α irradiation, it might be expected that the *G*-value and products of CMPO degradation would vary for irradiation by the two radiation types.

Alpha-radiolysis studies are rare in the literature, mainly due to the institutional prohibitions generally associated with analyzing α-contaminated samples. We are aware of only one study that investigated the α-radiolysis of CMPO, however, the CMPO degradation yields and products were not investigated. [5] Therefore we have initiated an investigation of α-radiolysis of CMPO for comparison to results using conventional γ-irradiation using the ^{60}Co irradiator at Idaho National Laboratory (INL). Two α-sources were used. The first was a He ion beam at the Notre Dame Radiation Laboratory (NDRL). The second was irradiation at INL using the α-emitting isotope ^{244}Cm. Samples irradiated by γ-rays or He ion beam were later analyzed using a combination of solvent extraction, high performance liquid chromatography

(HPLC) and electrospray ionization mass spectrometric (ESI-MS) techniques. Samples irradiated by curium were curium contaminated and could only be analyzed by the solvent extraction techniques due to institutional prohibitons against running contaminated samples on the HPLC and ESI-MS instruments.

2. Experimental Methods

2.1 Gamma-ray irradiations

Gamma-irradiation studies were conducted using ^{60}Co-γ-irradiation of 0.1 M CMPO/dodecane solutions. The INL irradiator was a Nordion GammaCell 220E (Ottawa, Canada) with a current center-line sample chamber dose rate of 7.7 kGy h^{-1}, and temperature of 38^{o}C. These irradiations were performed for both neat organic phase solutions, and for solutions in contact with an acidic aqueous phase. Samples were irradiated in a series of absorbed doses based at the known dose rate as determined by standard decay-corrected Fricke dosimetry, and the duration of irradiation. For experiments at which varying γ-dose-rates were desired a ^{60}Co facility with three different γ-irradiators at NDRL was used.

2.2 Alpha-irradiations

Alpha-irradiation was performed using two main techniques. The first was by He-ion beam irradiation at the NDRL. Helium ions were produced using a 9 MV FN-Tandem Van de Graaff generator with a 20 KeV plasmatron source. Particle energy was selected by varying the accelerator terminal voltage, with sufficient energy such that after passing through the cell window into the sample their energy was 5 MeV. This was designed to simulate the α-particle energies produced by actinide decay. The dose rate was determined as the product of the integrated beam current and particle energy. Samples were stirred continuously to ensure uniform dose deposition. For this technique, only neat organic samples of 0.1 M CMPO in dodecane have so far been irradiated.

In the second technique, samples were irradiated using ^{244}Cm, in a glovebox at INL. Curium decays by emission of a 5.8 MeV α-particle with an 18.1 y half-life. To perform the irradiations, 0.6 mg of ^{244}Cm was dissolved in 0.1 M HNO_3 and then contacted with the organic solution to be irradiated for amounts of time appropriate to deliver the desired absorbed dose. The contact was accompanied by constant stirring. The low acid concentration was selected to minimize the extraction of curium into the organic phase, however, post-extraction organic solutions were still found to be severely contaminated and it was not institutionally possible to perform convention chemical analyses for degradation products or to determine a CMPO *G*-value for these samples. They were used for solvent extraction experiments, however, following dilution to provide adequate volumes for extraction.

Additionally, samples of neat organic 0.1 M CMPO in dodecane were irradiated with ^{211}At at Chalmers University, Göteborg, Sweden. [6] Astatine-211 decays with the emission of an average 6.8 MeV α-particle and a 7.2 h half-life. Thus the absorbed dose to the sample is readily calculated assuming that all atoms of astatine decay prior to the analysis of solutions that are then considered non-contaminated. Astatine was prepared at Rigshospitalet, Copenhagen, Denmark, using a Scanditronic MC32-NI cyclotron, and delivered to Chalmers by courier. Upon receipt of the solid target it was dissolved in acid, and extracted into isoctanol solution. Small volumes of this solution were used to spike the 0.1 M CMPO/dodecane samples for irradiation over a series of absorbed doses. These samples have not yet been analyzed, but should eventually provide for mass spectrometric identification of CMPO degradation products and a *G*-value for CMPO degradation, for comparison to the He ion beam samples above.

2.3 Solvent extraction experiments

Post-irradiation 0.1 M CMPO/dodecane solutions were used to perform ^{243}Am solvent extraction experiments to evaluate the effect of α–, and γ-irradiation on solvent performance. Following irradiation, each sample was diluted with fresh dodecane resulting in a final CMPO concentration of 0.016 M. This was necessitated by the small volumes of solvent that could be curium irradiated. For ease of comparison, the same dilution factors were used consistently for all solvent extraction samples, regardless of irradiation by curium or γ-rays. Equal volume, room-temperature (21 ± 2°C) contacts were then performed from americium-spiked 2 M HNO_3 for forward extractions, and the loaded organic phase was then stripped with 0.1 M HNO_3. The distribution ratios were determined as the ratio of the americium activity in the organic phase and aqueous phase, as measured by γ-ray counting.

2.4 Analytical chemistry of CMPO and radiolysis products

The CMPO concentration for *G*-value determinations in pre-, and post-irradiation samples was determined by HPLC, using a C-18, RP, 25 cm, 4.6 x 5 μ Supelcosil column and guard column. The solvent was 60:40 pH 2.7, 30 mM phosphate buffer and 2-propanol containing 3.6 % 1-octanol at a flow rate of 1 mL min^{-1}. The column temperature was 50 °C with a run time of 45 min. Samples were diluted 1:100 with 2-propanol prior to analysis and analyzed in triplicate with absorbance detection at 220 nm. It should be noted that for samples irradiated in the presence of a HNO_3 aqueous phase the production of the $CMPO•2HNO_3$ complex suppresses the apparent CMPO concentration.

Mass spectrometric analysis of products was conducted with a modified Thermo LCQ-DECA XP Max quadrupole ion trap electrospray ionization mass spectrometer, on samples of 1 mM CMPO irradiated in dodecane. The ESI source was re-positioned from the conventional orthogonal orientation such that the ESI spray was co-axial with the aperture of the sampling cone of the ESI source. Distance between the ESI spray capillary and the sampling cone aperture was approximately 3.5 mm. The ESI source was fitted with a gas flow meter that enabled measurement of the sheath gas flow. Sheath gas (N_2) was admitted together with the ESI flow in a coaxial arrangement such that upon exiting the ESI capillary, the ESI flow was jacketed by the sheath gas. Typical settings for the ESI source were sheath gas flow = 900 cm^3/min, and ESI flow = 7 – 8 μL/min. The transfer capillary temperature was typically operated at 125°C.

For positive ion analysis, ESI potential V_{ESI} was 3.5 – 4.2 kV, adjusted up or down by a few hundred V to stabilize the Taylor cone (a conical volume that forms at the end of the ESI capillary during the ESI-MS process). Key parameters for the ion trap mass spectrometer included the $V_{transfer\ capillary}$ = 46 V, $V_{tube\ lens\ offset}$ = 35 V.For negative ion analysis, ESI potential V_{ESI} was 2.75 kV, $V_{transfer\ capillary}$ = -90 V, $V_{tube\ lens\ offset}$ = – 100 V. Experiments were conducted using the automatic gain control, with a target full value of 2.1 x 10^7 ions. The maximum ion injection time = 200 ms, summing 5 scans.

3. Results- neat organic phase irradiations

The samples of Section 3 were irradiated as neat organic solutions in the absence of the aqueous phase. This allowed for the isolation of the reactions of the predominantly reducing radicals and ions produced in the irradiated organic phase.

3.1 Gamma-ray dose rate effect

Solutions of 0.1 M CMPO in dodecane were irradiated in the absence of an aqueous phase over a series of absorbed doses at varying gamma-ray dose rates using three adjacent ^{60}Co irradiators at the NDRL. The dose rates varied over an order of magnitude from 0.175 to 15.9 kGy h^{-1}. Following irradiation the samples were analyzed at INL using HPLC with UV detection. The results are plotted as CMPO concentration versus absorbed dose in Figure 1. It can be seen that the concentration decrease for CMPO is linear with absorbed dose, and that it is the same for all dose rates. The resulting *G*-value for CMPO degradation is 0.14 μmol Gy^{-1}. It may be concluded that dose rate, at least over the range to be typically encountered using isotopic sources, does not affect the degradation rate of CMPO by γ-radiolysis.

3.2 He ion beam and *G*-value

Solutions of 0.1 M CMPO in dodecane were also irradiated using a He ion beam in the absence of an aqueous phase for three absorbed doses. These samples were then also analyzed by HPLC, with the results plotted in Figure 1. It can be seen that the He ion irradiation data falls on the same line as that for the γ-irradiations, resulting in a *G*-value for α-radiolysis of 0.14 μmol Gy^{-1}. The initial concentration for the 75 kGy - He ion datum was originally 0.09 M and the result was normalized here to a starting concentration of 0.1 M for comparison to the other data.

Based on the LET arguments presented in Section 1, the same *G*-value for α and γ-irradiation was an unexpected result. The recombination of radicals to produce molecular species during high LET irradiation should have resulted in a lower *G*-value for ligand loss.

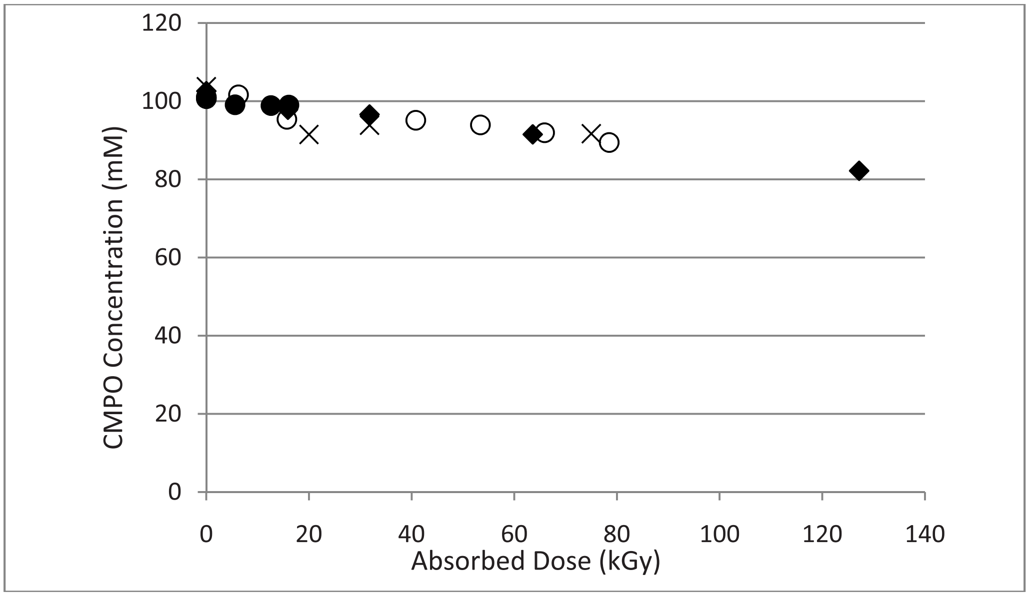

Figure 1. The radiolytic concentration decrease for CMPO in dodecane, irradiated at three gamma-ray dose rates. (solid circles) 0.175 kGy h^{-1} γ, (open circles) 3.14 kGy h^{-1} γ, and (solid diamonds) 15.9 kGy h^{-1} γ, (x) He ion beam. The initial concentration was nominally 0.1 M CMPO, except for the 75 kGy - He ion datum, which sample was originally 0.09 M, for which the results were normalized here to a starting concentration of 0.1 M.

3.3 Solvent extraction experiments

Solvent extraction experiments were performed on 0.1 M CMPO/dodecane solutions, γ-irradiated in the absence of an aqueous phase. Following irradiation, the samples were diluted and then contacted with an equal volume of americium-spiked 2 M HNO_3, for forward extractions. The loaded organic was next stripped with 0.1 M HNO_3. A steady increase in both forward and stripping extraction distribution ratios with absorbed dose was found, over the absorbed dose range 0-600 kGy. At very high absorbed doses of

> 400 kGy, stripping distribution ratios actually exceeded those of the forward extractions. These results are shown in Figure 2.

For both forward extraction and stripping the increase in distribution ratios is approximately linearly correlated to the decrease in CMPO concentration, as shown in Figure 3. This suggests that one or more decomposition products are stronger americium complexing agents than is CMPO itself, and the stripping results indicate that the species is probably an organic-soluble acidic species.

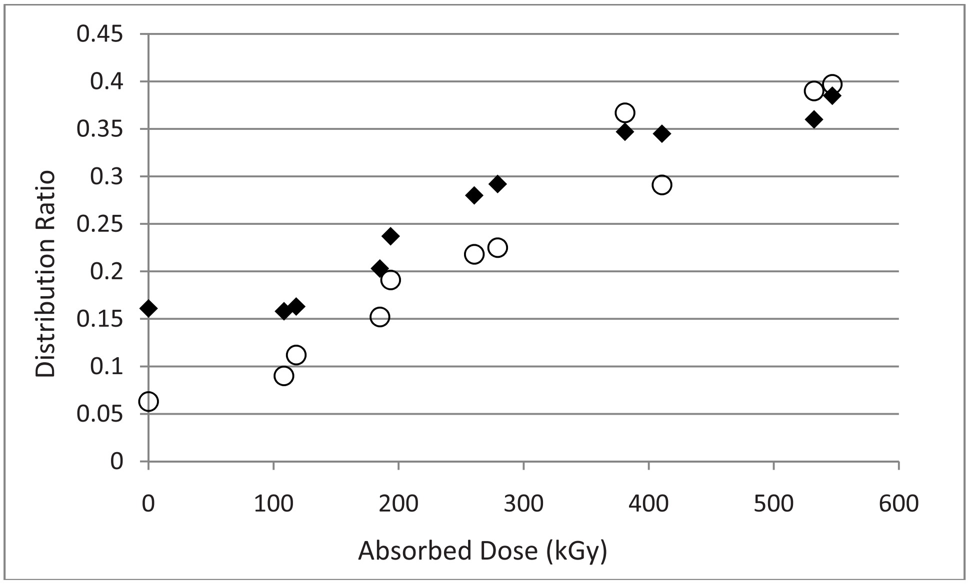

Figure 2. The forward extraction distribution ratio (solid diamonds) and stripping distribution ratio (open circles) for americium extraction from γ-irradiated CMPO solution.

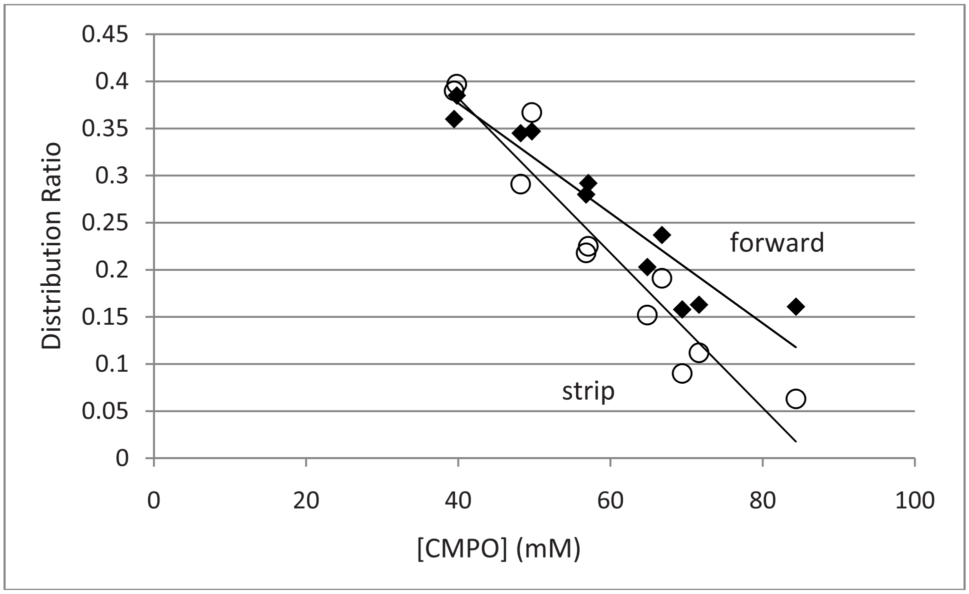

Figure 3. The distribution ratio for americium as a function of [CMPO] for initially 0.1 M CMPO/dodecane irradiated with γ-rays in the absence of an aqueous phase. Forward extractions are represented by closed diamonds with stripping extractions represented by open circles.

3.4 Mass spectrometric analysis of products

The structure of CMPO is shown in Figure 4.

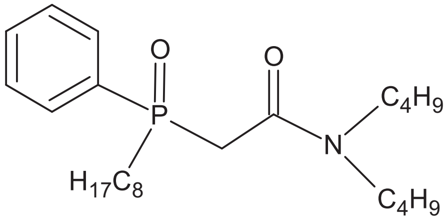

Figure 4. Structure of CMPO.

The products of CMPO irradiated under a number of conditions have been measured by ESI-MS at INL. Selected examples are provided in this report allowing for a comparison of γ-, and He ion beam irradiated samples. In one example, a sample of 0.1 M CMPO in dodecane was irradiated to an absorbed γ-dose of 71.2 kGy using the INL ^{60}Co irradiator. The solution was serially diluted from dodecane using 18% octanol-ethanol in the first dilution, and ethanol in subsequent dilutions to a working concentration of 10 μM. The positive ESI-MS showed only CMPO-derived ions, with little evidence of decomposition products. However, the negative ESI-MS analysis produced a number of significant ions (Figure 5). The negative *m/z* values had a mass measurement error of ~ 0.5 u, which would make the ion at *m/z* 254 actually 253. This would correspond to the conjugate base of octylphenylphosphinic acid. This species, shown in Figure 6, would be produced by fission of the phosphoryl-methylene bond and could account for the increased forward extraction and stripping distribution ratios in the solvent extraction experiments using γ-irradiated CMPO/dodecane solutions above.

The ion at *m/z* 293 was hypothesized to correspond to deprotonated CMPO with elimination of an octyl radical. Solid hypotheses for *m/z* 350, 378 and 420 have not yet been developed.

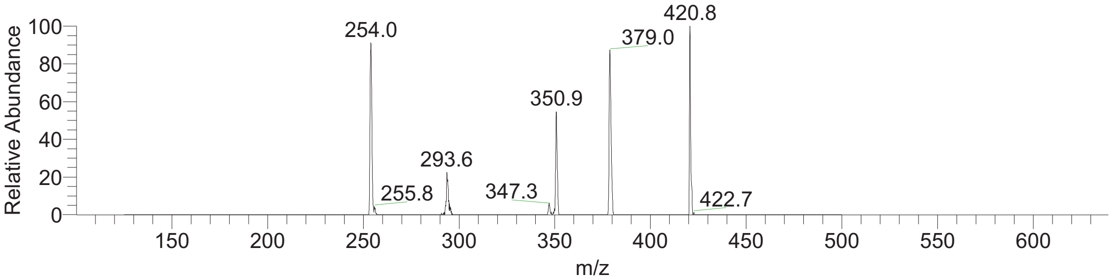

Figure 5. Negative ESI-MS of 1 mM CMPO/dodecane, γ-irradiated to 71.2 kGy in the absence of an aqueous phase.

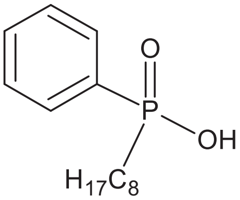

Figure 6. Structure of octylphenylphosphinic acid.

The same concentration of CMPO in dodecane was also irradiated using the NDRL He ion beam to absorbed doses of 20 and 38.3 kGy. In addition to CMPO dimers and sodium adducts (also seen in unirradiated samples), lower abundance peaks at *m/z* 630, 283 and 153 were seen (Figure 7), probably derived from radiolysis products. A low-abundance ion is seen at *m/z* 565, which may correspond to an adduct having the composition $[(\mathrm{CMPO})(\mathrm{DIBFA})\mathrm{H}]^+$, where DIBFA = N,N-diisobutylformamide, shown in Figure 8. DIBFA would be a radiolysis product produced by cleavage of the methylene-carbonyl bond of CMPO.

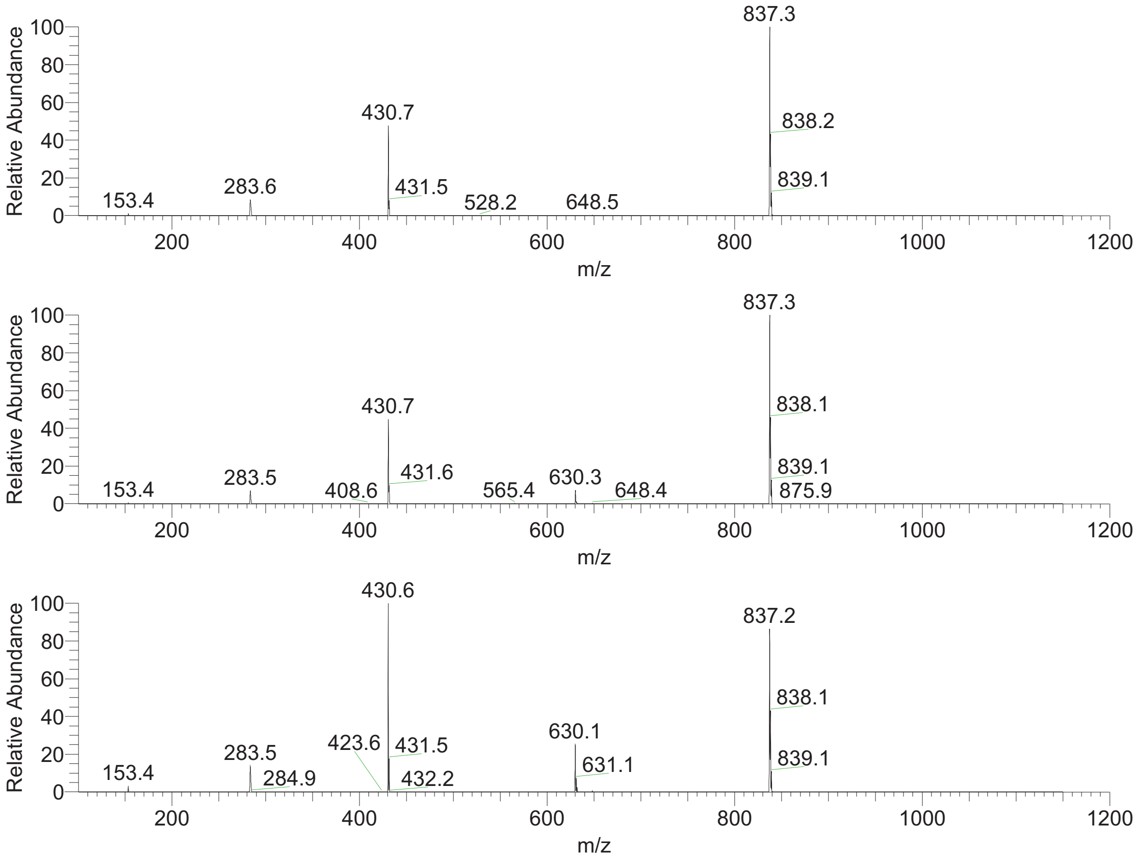

Figure 7. Positive ESI-MS of sample CMPO samples, ESI of organic phase for samples irradiated in the absence of an aqueous phase: top, unirradiated CMPO, middle, 20 kGy He ion beam, bottom, 38.3 kGy He ion beam.

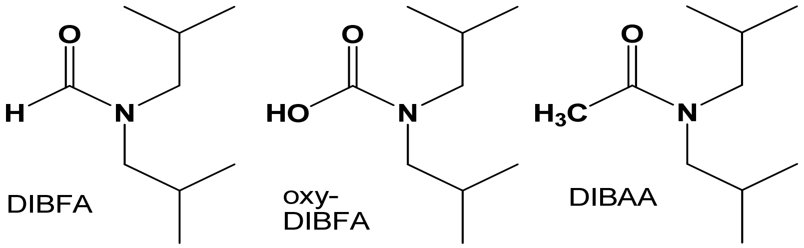

Figure 8. Structures of di-isobutylformamide (DIBFA), an oxygenated DIBFA derivative, and di-isobutylacetamide (DIBAA), possible radiolysis products in the He ion beam 20 kGy sample.

The lower abundance natiated CMPO ions at *m/z* 153 and 283 become much more pronounced when the trap is limited to collect ions with < *m/z* 400. In addition, ions are observed at *m/z* 337 and 353 that were not seen in unirradiated samples. A good hypothesis for the *m/z* 337 ion is a complex having the composition $[(DIBFA)_2Na]^+$, while $[(DIBFA)(oxy\text{-}DIBFA)Na]^+$ may account for *m/z* 353.

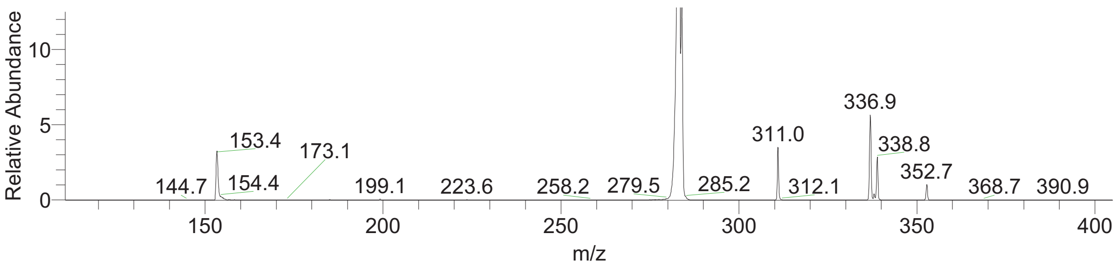

Figure 9. Positive ESI-MS of 20 kGy He ion beam sample, mass range restricted to < m/z 400.

Further analysis limiting ion trapping to < *m/z* 200 (Figure 10) produced an ion at *m/z* 158 which likely corresponds to $[(DIBFA)H]^+$. This assignment would be consistent with the observation of DIBFA complexes noted above. The ion at *m/z* 172 may be protonated N,N-diisobutylacetamide (DIBAA), a compound that could arise by radiolysis of the methylene-phosphoryl linkage. The ion at *m/z* 186 is the most abundant of this group, but a good hypothesis for this ion has not yet been formulated; although recombination of a methyl radical with DIBAA may account for the ion.

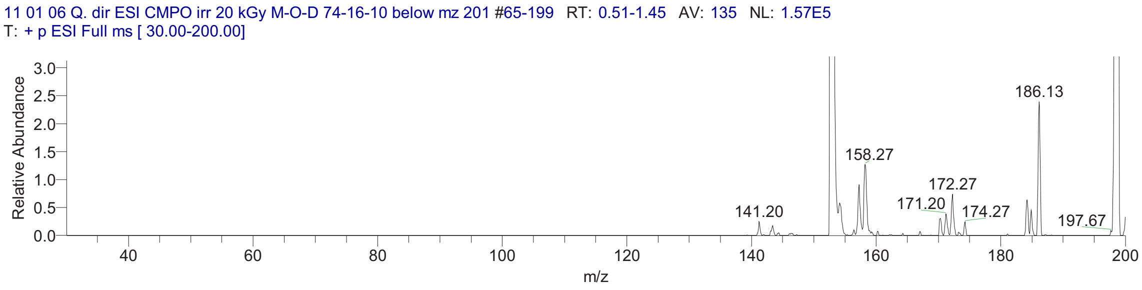

Figure 10. Positive ESI-MS of 20 kGy He ion beam sample, mass range restricted to < m/z 200.

4. Results- biphasic irradiations

The samples of Section 3 were irradiated as neat organic solutions in the absence of the aqueous phase. This allowed for the isolation of the reactions of the predominantly reducing radicals and ions produced in the irradiated organic phase. However, in the solvent extraction process, an aqueous acidic phase is also present, and this results in the generation of additional, usually oxidizing reactive species during irradiation.[1] Therefore, samples of 0.1 M CMPO in dodecane were also irradiated in the presence of an acidic aqueous phase, and the results are presented in Section 4.

4.1 Gamma ray dose rate effect and *G*-value of biphasic solutions

Solutions of 0.1 M CMPO in dodecane were irradiated in the presence of a 3 M HNO_3 aqueous phase over a series of absorbed doses at two gamma-ray dose rates at the NDRL. The dose rates were 3.14 and 15.9 kGy h^{-1}. Following irradiation the samples were analyzed at INL using HPLC with UV detection.

The results are plotted as CMPO concentration versus absorbed dose in Figure 11. It can be seen that although the initial CMPO concentration was 0.1 M, the zero dose samples were found to contain < 60 mM free CMPO. This is due to formation of the CMPO•2HNO$_3$ complex upon contact with nitric acid. [7] This complex is not detected as free CMPO during the HPLC-UV analysis, although it is seen during ESI-MS analysis. Once again, the γ-dose rate had no effect on the degradation yield of CMPO, with a *G*-value reported here as 0.04 μmol Gy^{-1}. This degradation yield is about a factor of 3.5 less than that for the neat organic solution.

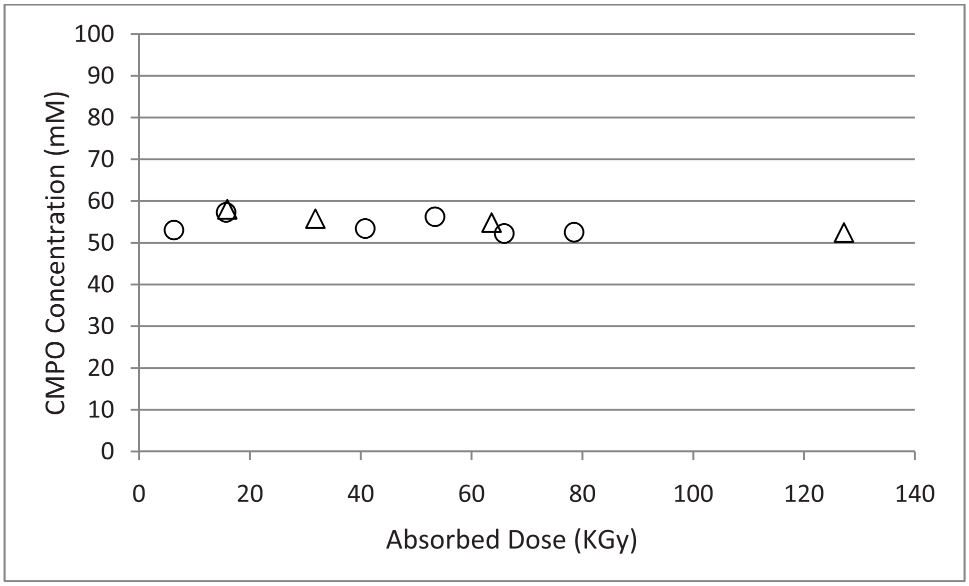

Figure 11. The concentration decrease for CMPO in dodecane, irradiated at two gamma-ray dose rates. (open circles) 3.14 kGy h^{-1}, and (open diamonds) 15.9 kGy h^{-1}. The initial concentration was nominally 0.1 M CMPO.

4.2 Solvent extraction experiments

Solvent extraction experiments were performed on 0.1 M CMPO/dodecane solutions, irradiated in the presence of a 0.1 M HNO$_3$ aqueous phase. This lower nitric acid concentration was chosen to facilitate the curium irradiated samples as described in Section 4.2.2. Following irradiation, the samples were diluted and then contacted with an equal volume of americium-spiked 2 M HNO$_3$, for forward extractions. The loaded organic was next stripped with 0.1 M HNO$_3$.

4.2.1 Gamma irradiated biphasic solutions

Samples of 0.1 M CMPO in dodecane were γ-irradiated in contact with 0.1 M HNO$_3$ using the INL ^{60}Co source. Following irradiation the samples were diluted with fresh dodecane to a CMPO concentration of 0.016 M, to be consistent with the curium irradiated samples in Section 4.2.2. The americium distribution ratios for forward and stripping extractions are shown versus absorbed γ-dose in Figure 12. The results are similar to those for the irradiation of the neat organic phase in the absence of an aqueous phase shown in Figure 2. In both cases, the distribution ratios are little affected until an absorbed dose of about 100 kGy, after which a gradual increase in both forward extraction and stripping distribution ratios occurs.

However, in the neat organic system the strip distribution ratios met or exceeded the forward extraction distribution ratios, while in the presence of the aqueous phase the increasing strip distribution ratios never exceeded those of the forward extraction at the same absorbed dose.

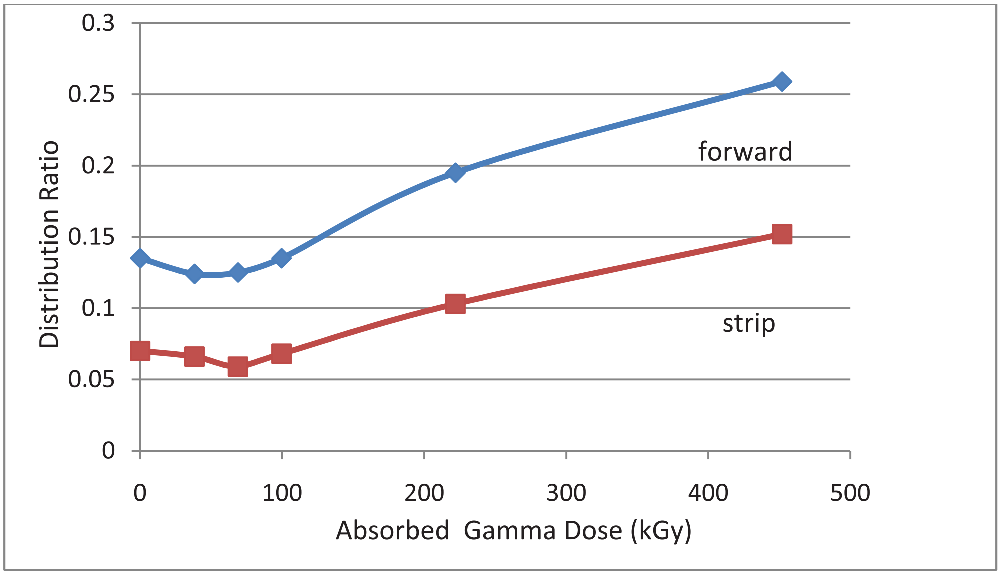

Figure 12. The americium distribution ratios for forward (solid diamonds) and strip extraction (solid squares) from γ-irradiated 0.1 M CMPO/dodecane when irradiated in the presence of 0.1 M HNO_3.

4.2.2 Curium irradiated biphasic solutions

Samples of 0.1 M CMPO in dodecane were irradiated using constant stirring in contact with a 0.1 M solution of ^{244}Cm for durations sufficient to deliver the desired absorbed dose. The low nitric acid concentration was chosen to minimize the complexation and extraction of the curium by CMPO. However, due to the macro-amounts of curium necessary for the irradiation, significant contamination of the organic phase nevertheless occurred. Following irradiation, the samples were stripped with 0.1 M HNO_3, to remove much of this curium, and the stripped organic solutions were then used to perform americium extraction experiments, similar to those above in Section 4.2.1. To achieve the high absorbed dose values in the curium irradiated solution, small volume irradiations were necessary. Therefore, the samples were diluted with fresh dodecane to a final concentration of 0.016 M CMPO to achieve the volumes necessary prior to solvent extraction experiments.

The results of both forward and stripping solvent extraction contacts are shown in Figure 13. It can be seen that both the forward and stripping extraction efficiency decreased rapidly with absorbed α-dose, until between about 100-200 kGy the values became relatively constant or slightly increasing with continued irradiation to 673 kGy. This is in contrast to the results of γ-irradiated solutions shown in Figure 12, above. These contrasting results suggest the production of different CMPO degradation products with the two radiation types, as was confirmed by mass spectrometric analysis. Gamma-irradiation produces acidic species that better complex americium and prevent its stripping.

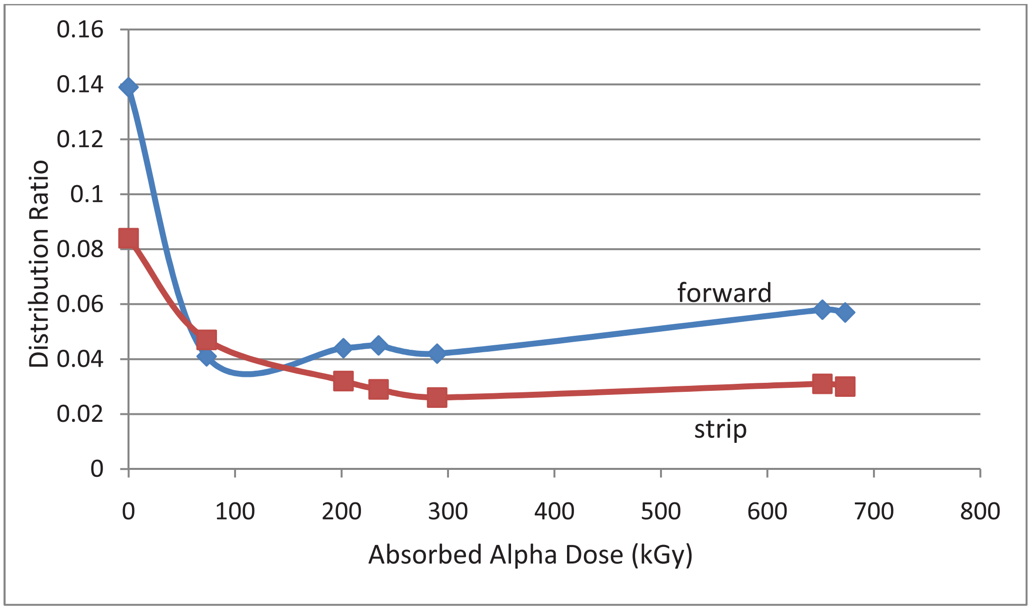

Figure 13. The americium distribution ratios for forward (solid diamonds) and strip extraction (solid squares) from γ-irradiated 0.1 M CMPO/dodecane when irradiated in the presence of 0.1 M HNO_3.

4.3 Mass spec analysis of products- biphasic irradiations

A sample of 0.1 M CMPO in dodecane in the presence of 3 M HNO_3 was irradiated to a γ-absorbed dose of 71.2 kGy. Mass spectrometric analysis of the post-irradiation aqueous phase was conducted and showed significant peaks at *m/z* 130, 144 and 172, when the ion trap was set to accumulate only the low mass peaks (Figure 14). The compound responsible for *m/z* 130 is likely protonated diisobutylamine (DIBA) formed in a straightforward fashion from cleavage of the N-carbonyl bond of CMPO followed by recombination with •H atom. The ion at *m/z* 144 is probably methyldiisobutylamine (MDIBA), formed by recombination with a methyl radical. Similarly, the formation of propyldiisobutylamine (PDIBA) would require recombination of an isopropyl radical with the DIBA radical product of cleavage of the N-carbonyl bond of CMPO, resulting in *m/z* 172. These ion assignments were confirmed by MS/MS fragmentation reactions.

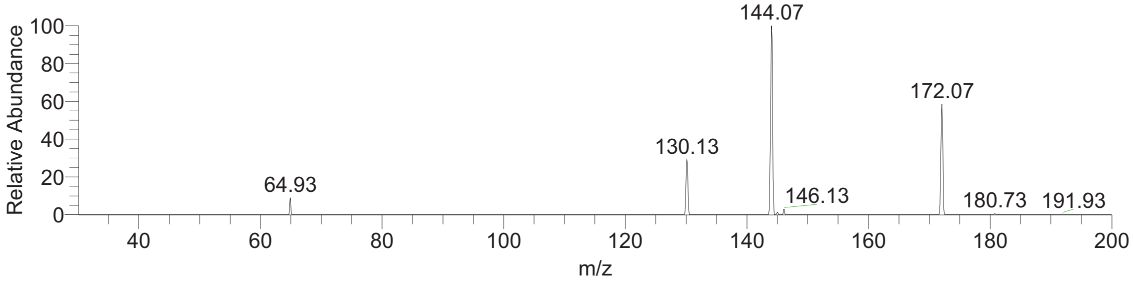

Figure 14. Positive ion mass spectrum of the HNO_3 layer of the biphasic γ-irradiation of 0.1 M CMPO in contact with 3 M HNO_3.

Examination of the higher mass range (Figure 15) showed a dominant ion at *m/z* 408 which is protonated CMPO, $[(\text{CMPO})\text{H}]^+$. An abundant ion at *m/z* 537 corresponds to the cluster ion $[(\text{CMPO})(\text{DIBA})\text{H}]^+$. What is remarkable about this spectrum is that it does not show CMPO clusters with either MDIBA or PDIBA. We hypothesize that while the secondary amine DIBA readily clusters with CMPO, neither of the tertiary amines do, perhaps on account of steric repulsion caused by the extra alkyl moiety. Additional evidence for DIBA was found in the mass spectrum of the aqueous phase, which showed an abundant ion at *m/z* 130, corresponding to $[(\text{DIBA})\text{H}]^+$. Limiting the mass range so that $[(\text{CMPO})\text{H}]^+$ was excluded resulted in formation of proton-bound clusters of MDIBA and PDIBA, which provided additional evidence for their presence in the HNO_3 layer. Radiolytic cleavage of an isobutyl group draws further support from a low abundance ion at *m/z* 352, which is exactly 56 u lower than protonated CMPO at *m/z* 408.

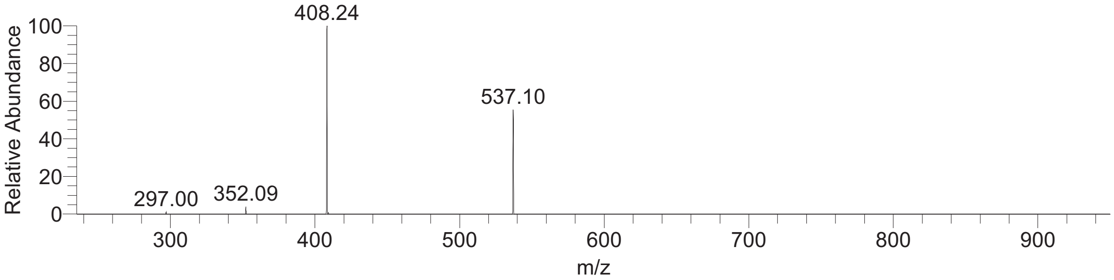

Figure 15. High mass range positive ESI mass spectrum of the HNO_3 layer of the biphasic irradiation of 0.1 M CMPO in contact with 3 M HNO_3.

Another low abundance ion at *m/z* 297 is also clearly above background, and is likely protonated, indicating a molecular weight of 296. This even value precludes incorporation of an odd number of N atoms, suggesting that the diisobutyl amine moiety has been cleaved. Replacement by a hydroxy group would form an acidic compound having a molecular weight of 296, octylphenylphosphinylacetic acid.

5. Discussion

It may be concluded that dose rate, at least over the range to be typically encountered using isotopic sources, does not affect the degradation rate of CMPO by γ-radiolysis. Additionally, the degradation yield of CMPO irradiated in neat dodecane solution is the same for α (He ion beam) and γ-irradiation, at 0.14 μmol Gy^{-1}. Only Nash et al has also used direct CMPO analysis to measure the change in CMPO concentration with absorbed dose. [8] They reported a value for $-G_{\text{CMPO}}$ slightly lower to that reported here of 0.12 μmol Gy^{-1} for a TRUEX solvent formulation containing CMPO, TBP and dodecane. The lower *G*-value reported in that work may be due to the presence of the TBP, which would compete for reaction with radiolytically-produced reactive species.

The result that the *G*-value for CMPO degradation by γ and α radiolysis was the same was unexpected, since the yields of reactive radical species produced by the higher LET α-radiation are lower than for γ-radiation, as was shown for water in Equations 1 and 2. In fact, lower decomposition yields using α-irradiation have been reported for dimethyl dioctyl hexylethoxymalonamide (DMDOHEMA) irradiated in acid pre-equilibrated hydrocarbon solution. [9] However, our results are consistent with recent work performed on the bistriazinyl bipyridines (BTBPs), that behaved similarly whether α or γ irradiated in purely organic solution. [10] The identical *G*-values for CMPO decomposition found here suggest two possible explanations. First, the degradation of CMPO in α-irradiated dodecane solution may be due to reaction with a secondary radiolysis species, produced by recombination of the primary reactive species. In the aqueous phase such a species would be H_2O_2, produced by •OH radical combination. However, the identity of an analogous species responsible for the decomposition of CMPO in the α-irradiated dodecane is not immediately obvious, but may involve organic radical cation species. A second possibility is that the yield and reaction rate of the primary reactive species is high enough that CMPO at 0.1 M concentration is able to compete with geminate recombination to undergo decomposition despite the high LET of α-irradiation. The responsible mechanism is currently unknown.

The product distributions of CMPO irradiation as determined by mass spectrometry are different for the two radiation types. For α-irradiation, a predominant reaction is the fission of the CMPO carbonyl-methylene bond to generate DIBFA. In contrast, radiolysis by γ-irradiation appears to favor cleavage of the CMPO methylene-phosphoryl bond, resulting in formation of octylphenylphosphinic acid. These acidic species are generally believed to be responsible for the difficulties encountered in stripping irradiated CMPO solutions, [8, 11, 12] while the amines generated by α-radiolysis are probably less deleterious to solvent extraction efficiency.

This result is consistent with the solvent extraction results reported here, where increases in stripping distribution ratios accompanied γ-irradiation, while the curium α-irradiated solutions did not show increased stripping distribution ratios with absorbed dose. These solvent extraction experiments, however, are different than the pure organic phase irradiations discussed above in one respect. They were performed using solutions that had been irradiated in the presence of the acidic aqueous phase, due to the experimental requirements of the curium irradiations. Therefore, it should be noted that mass spectrometric analysis of γ-irradiated biphasic samples also showed the production of numerous small amine products indicating that the carbonyl-N bond is also severed in the presence of nitric acid.

Currently, CMPO *G*-values are only available for γ-irradiation in the presence of the aqueous phase, because institutional prohibitions have prevented the HPLC analysis of curium-irradiated samples. However, for solutions γ-irradiated in the presence of the acidic aqueous phase, the rate of CMPO degradation was much lower than in organic solution, at only about 0.04 μmol Gy^{-1}. This suggests that the aqueous solution scavenges the produced reactive species that cause degradation in the organic phase. For γ-irradiation these are likely to be the solvated electron, or •H atom.

6. Conclusions and future direction

The preliminary results here suggest that there is little difference in the rate of CMPO decomposition with absorbed α or γ dose, but that the products of γ-irradiation are different and more deleterious to the solvent extraction process. The *G*-value for samples γ-irradiated in the presence of the aqueous phase was lower. The G-value for α-irradiated samples in the presence of the aqueous phase is unknown, however, samples that were curium α- irradiated in the presence of the aqueous phase have been generated and are currently awaiting analysis. Future experiments will also include continued mass spectrometric analysis of products, including those of the in-progress ^{211}At irradiated samples. Once these analyses are completed the results will be combined with our previous pulse radiolysis work on the free radical reactions of CMPO to produce a comprehensive manuscript on the radiation chemistry of this important ligand.

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