The Radiolysis of CMPO: Effects of Acid, Metal Complexation and Alpha vs. Gamma Radiation

5th International ATALANTE Conference on Nuclear Chemistry for Sustainable Fuel Cycles

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May 2016

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National Laboratory
operated by
Battelle Energy Alliance

Idaho National Laboratory

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Abstract

The organophosphorus amide octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO) is proposed for use in fuel cycle separations as a group actinide/lanthanide extractant. Alternative compounds such as the monoamides and diglycolamides (DGAs) proposed for actinide and/or actinide/lanthanide extraction also contain the amidic functional group, but do not contain the CMPO aromatic or phosphoryl groups. Their radiation stability is in the order monoamides > CMPO > DGA for irradiation under similar conditions. Although they produce similar radiolysis products, the kinetics of degradation for CMPO are completely different than for the other amides. CMPO degradation occurs in a zero-order fashion, and the $-G$-value for the change in [CMPO] is much lower when in the presence of acid. The DGAs and monoamides degrade with pseudo-first-order kinetics and are not protected by acidity. Possible mechanistic reasons for the differences between CMPO and the other amides are discussed, as are the effects of the diluent and metal complexation on CMPO free radical reaction rates. Finally, it is also shown that α-irradiation has much less adverse effects on CMPO degradation than β/γ irradiation, both with respect to $-G$-values, and radiolysis product generation.

Keywords: amides; free radicals; mass spectrometry; pulse radiolysis; radiation chemistry; solvent extraction

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1. Introduction

Compounds with the amidic functional group [R(C=O)NR'R''] are being increasingly used as ligands for *f*-element separations. Among the best studied for fuel cycle applications are monoamides such as diethylhexylbutyramide (DEHBA), diglycolamides such as tetraoctyldiglycolamide (TODGA) and octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO). The monoamides are simple compounds with only alkyl substitution on the amide N and C atoms. The diglycolamides are composed of two monoamides, joined by an ether linkage. They may be symmetrical or non-symmetrical. Finally, CMPO contains the amide group at one end of the molecule, while a substituted phosphoryl group occurs at the other side of a methylene linkage. These structures are shown in Fig. 1. All these compounds have been proposed for use in applications with exposure to high radiation dose rates, and therefore they have been studied for their radiation stability at several laboratories. Earlier studies often involved only the measurement of before-and-after irradiation extraction and stripping distribution ratios for metal partitioning as the metric for radiation damage. Recent studies have become more sophisticated, and have measured the degradation yields of the parent amides either as *G*-values (μmol J^{-1}) or dose constants (kGy^{-1}), as well as the identification and yields of the daughter products and kinetics of the reactions with radiolytically-produced free radicals. These parameters may vary with the solution conditions, and therefore effects on extraction performance may be altered by the nature of the aqueous phase, the amount of dissolved oxygen in irradiated solution, and the linear energy transfer (LET) of the incident radiation. Because of these factors not all studies are comparable, but there are now enough amide radiolysis papers in the literature to allow us to begin to discuss the effects of the disparate structures of these molecules on their radiation chemistry. Such a discussion is presented here, with especial reference to CMPO, which has been intensely studied at the Idaho National Laboratory.
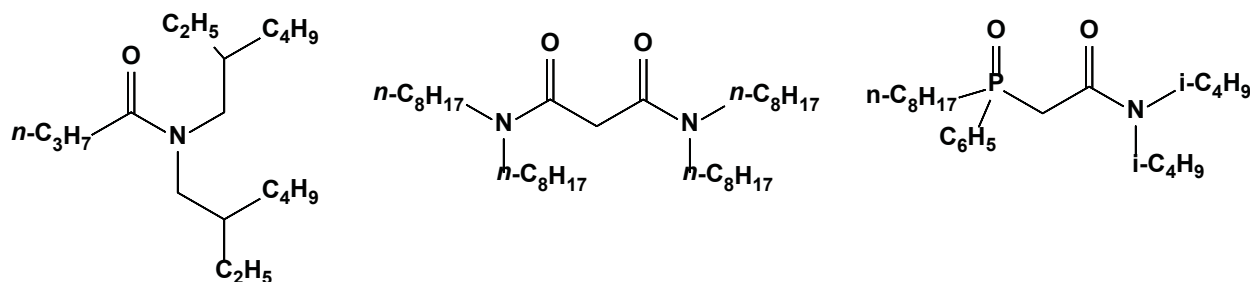

Fig. 1. The structures of DEHBA (left), TODGA (center), and CMPO (right). Note the common [R(C=O)NR'R''] functional group.

2. A brief review of CMPO radiolysis

2.1 Low LET irradiation

The earliest studies of CMPO radiolysis reported decreased extraction distribution ratios and increased stripping distribution ratios, for γ-irradiation experiments conducted in the presence of the acidic aqueous phase.[1] These results suggested that the parent CMPO was degraded, and that the products of CMPO degradation interfered with stripping. Continued studies using GC and GCMS techniques to examine irradiated solutions identified products such as octylphenylphosphinic acid and octylphenylphosphinylacetic acid, compounds shown to deprotonate under low acid conditions and thus to interfere with back extraction.[2,3]

Building on these pioneering studies we initiated a program at INL to examine CMPO γ-irradiation using HPLC, ESI-MS and solvent extraction techniques, using absorbed doses as high as 500 kGy.[4,5,6] The decrease in [CMPO] for initially 0.1 M dodecane solutions irradiated in the presence and absence of the aqueous phase was measured by

HPLC with UV detection at 220 nm.[4] The decrease in [CMPO] was found to be linear with respect to absorbed dose, implying zero-order kinetics and therefore probably a multi-step mechanism.[6] The linear decrease in [CMPO] indicates that the rate (-G-value, μmol J^{-1}) did not change with [CMPO] and that the G-value is an adequate metric for comparing irradiation experiments under differing conditions and for solutions of differing initial [CMPO]. It was found that when CMPO/dodecane was irradiated without an aqueous phase, or in the presence of an aqueous phase containing only 0.1 M HNO$_3$, the -G-value was constant, at ~ 0.18 μmol J^{-1}. However, as the acid concentration of the aqueous phase increased, the -G_{CMPO} decreased, until for irradiations in contact with 5 M HNO$_3$, there was almost no loss in [CMPO] with absorbed dose. This was attributed to the formation of CMPO•HNO$_3$ complexes,[6] which were thought to also be responsible for the decrease in UV absorbance during HPLC analysis of unirradiated samples after acid contact.[4] Sealed, irradiated samples are considered to be de-aerated, due to the scavenging of dissolved oxygen by produced solvated electrons and hydrogen atom.[7] When the samples were aerated during irradiations similar results were found, excepting that -G-values were even lower in the presence of air. For example, the -G-value for aerated 1 M CMPO/dodecane with and without 0.1 M HNO$_3$ contact was 0.11 μmol J^{-1}.

2.2 Radiolysis product identification

   Electrospray mass spectrometry (ESI-MS) and liquid chromatography mass spectrometry (UPLC-TOF-MS) have been used to identify the products of CMPO radiolysis.[4,5] Among the important produced species are dealkylation products, including loss of an amidic butyl group (mono-isobutyl-CMPO, Fig. 2a), and loss of the phosphoryl octyl group, ((phenyl)-N,N-diisobutyl-CMPO, Fig 2b). The mono-isobutyl-CMPO appears with the highest signal strength and was produced in higher yields for samples irradiated in contact with aqueous solutions at higher acidities and also for higher absorbed doses. It is apparently less soluble in dodecane than CMPO itself, and a mixture of CMPO and mono-isobutyl-CMPO dropped out of irradiated organic-only solutions as a white precipitate.[6] This did not occur for samples in contact with an aqueous phase, and the protonated mono-isobutyl-CMPO was found in aqueous solution. Based on this it can be postulated that the mono-isobutyl species would act as a complexing agent in aqueous solution that could decrease metal distribution ratios. However, it should be noted that in the actual solvent extraction process, tributylphosphate is used as a phase modifier to improve CMPO solubility in dodecane, and its presence probably mitigates the production of mono-isobutyl-CMPO by radical scavenging reactions, and may improve its solubility in the organic phase as well.
   Other important CMPO radiolysis products included octylphenylphosphinic acid (OPPA, Fig. 2c), resulting from rupture of the methyl-carbon P-C bond. This species was also reported in previous work[2,3,8] where it was shown to interfere with stripping.[2,3] However, for irradiations in the presence of the acidic aqueous phase, the preferred product was octylphenylphosphinylacetic acid (OPPAA, Fig. 2d), resulting from rupture of the C-N amide bond. The corresponding amine was also identified. Both of the acidic products are thought be formed through intermediate radicals that are capped by a hydroxyl radical. The yield of OPPAA increased with acidity and absorbed dose, and apparently has a deleterious effect on the stripping of irradiated solutions.[6] Also for acid-contacted samples, nitro-, and nitrohydoxy-substituted CMPOs were generated, and they produced an oily, red third phase at the interface. This third phase also contained detectable OPAA and OPPAA. The nitro-substituted species were likely produced by reactions of CMPO with •NO$_2$ and/or •NO$_3$ radicals rather than HNO$_2$, since they also occurred in air-sparged solution.[6] This third phase may not occur in the presence of the TBP phase modifier.
   Finally, it should be noted that for samples irradiated in the absence of an aqueous phase, higher molecular weight CMPO addition products were generated by apparent addition of methyl, ethyl and even dodecyl radicals to the parent molecule.[6]
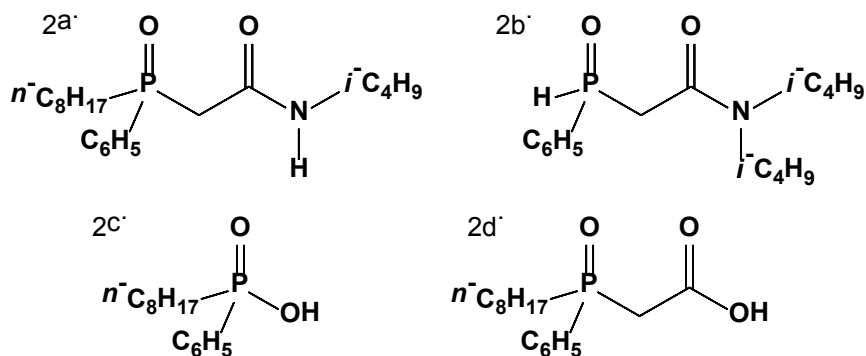
Fig. 2. Structures of radiolysis products formed from CMPO. Note that 2a and 2b require capping of the initially formed radical by a hydrogen radical, while 2c and 2d require capping by a hydroxyl radical.

2.3 Reactions with free radicals

The kinetics of the reactions of CMPO with radiolytically-produced free radicals provide important clues toward the elucidation of degradation mechanisms. The $^\bullet NO_3$ radical is a reactive species produced by HNO_3 radiolysis, and we have measured its reaction rate constants with CMPO under various conditions, using the LINAC facility at the University of Notre Dame. The techniques used to measure the aqueous phase $^\bullet NO_3$ rate constants have been previously described.[9] Acetonitrile was used as a co-solvent to improve the solubility of CMPO in aqueous solution. The $^\bullet NO_3$ radical is a neutral species and is also expected to cross the interface to react with both free and metal complexed CMPO in organic solution. We created $^\bullet NO_3$ radical in organic solution by dissolving tetrabutylammonium nitrate to its solubility limit of 1.5 M in *t*-butanol. Upon pulse radiolysis, the $^\bullet NO_3$ UV/Vis spectrum was observed at a slightly lower wavelength than in aqueous solution, with a maximum at 630 nm, allowing kinetic measurements to be made in *t*-butanol. As shown in Table 1, the reaction is about 2.5x faster in the organic phase. The rate constants were also measured for the Nd and Eu CMPO complexes in *t*-butanol. Since the free CMPO rate constant is fast, it was ensured that no free CMPO was present by ensuring an excess of the metal ion. This was performed by measuring the UV/Vis spectrum of 50 mM Nd in *t*-butanol solution, followed by the incremental addition of CMPO. In the presence of CMPO the maximum Nd absorbance shifted to longer wavelengths with higher intensity, as shown in Fig. 3. At the expected ratio of 3:1 CMPO:Nd^{3+}, the spectrum stabilized, and this ratio was used in pulse radiolysis experiments to ensure no free CMPO was present. Metal complexation increased the rate of reaction of CMPO with $^\bullet NO_3$ by an order of magnitude. This is also shown in Table 1. This result highlights the importance of understanding all species present when modeling radiolytic reactions.
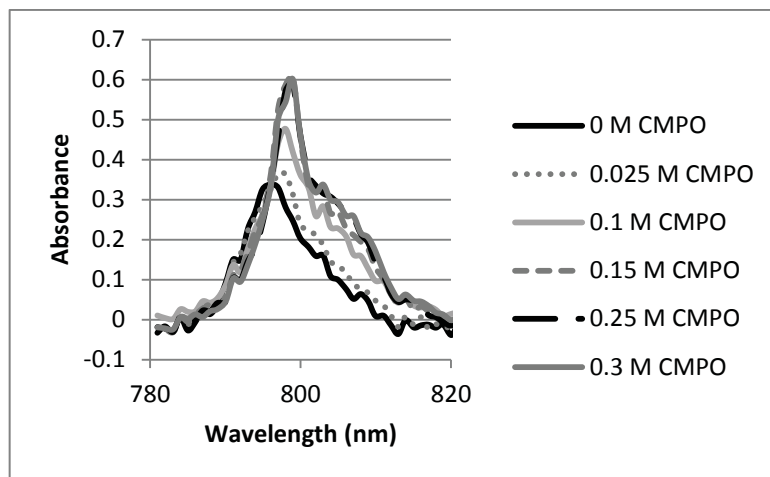
Fig. 3. The UV/Vis spectra of Nd^{3+} in *t*-butanol, as affected by the sequential addition of CMPO. A ratio of 3:1 CMPO:Nd ensures that there is no free CMPO in solution during kinetic analysis.

Table 1. Bimolecular rate constants (*k'*, M^{-1} s^{-1}) for the reaction of the $^{\bullet}NO_3$ radical with CMPO under various conditions.

Condition	Rate Constant
Free CMPO (aqueous)	$(1.28\pm0.13) \times 10^8$
Free CMPO (t-butanol)	$(3.24\pm0.17) \times 10^8$
$Nd(CMPO)_3^{3+}$	$(3.37\pm0.05) \times 10^9$
$Eu(CMPO)_3^{3+}$	$(2.52\pm0.05) \times 10^9$

In recent work, the kinetics of the reaction of free CMPO with the dodecane radical cation in dodecane solution was also measured, using pico-second pulse radiolysis at Brookhaven National Laboratory.[10] A very fast value of 1.2 x 10^{10} M^{-1} s^{-1} was obtained. With a rate constant nearly two orders-of-magnitude faster than the fastest $^{\bullet}NO_3$ radical reaction it is expected that this is an important reaction for CMPO degradation in the organic phase.

2.4 High LET irradiation

High LET radiation such as the α-particle is more rarely studied than β/γ radiation because of the difficulty in handling high-specific activity α-emitting isotopes, and/or the specialized and expensive equipment needed to generate non-isotopic α-particles. High LET radiation deposits large amounts of reactive species in small volumes, allowing for radical and ion recombination and altered solution yields of the primary radiolysis products. This is expected to decrease the *G*-values for the radiolytic degradation of solutes such as amides, and to alter the yields of ligand radiolysis products. This has indeed been demonstrated for CMPO.[11]

When 0.1 M CMPO/dodecane solutions were irradiated with 5 MeV He^{2+} ions, the [CMPO] remained constant to a maximum absorbed dose of 50 kGy, for organic-only samples that were de-aerated or air saturated, and for aerated samples that had been pre-equilibrated with 3 M HNO_3. Solvent extraction and stripping distribution ratios were similarly unaffected. However, given the sensitivity of ESI-MS techniques, radiolysis products were detectable. For non-acid-equilibrated, He-ion irradiated solution, the main products were diisobutylformamide (DiBFA), and diisobutylacetamide (DiBAA), and derivatives thereof.[11] These would be caused by rupture of the CMPO methyl-carbonyl C-C bond, and the methyl-phosphoryl C-P bond, respectively. These species are not expected to have an effect on solvent extraction performance, although the balance of the parent molecule would be OPAA and methyloctylphenylphosphine oxide. These species were not detected, possibly because of their very low yields at these low absorbed doses and low CMPO -*G*-values. It was not possible to produce DiBAA or DiBFA in CMPO solutions that had been treated with H_2O_2 in an attempt to chemically simulate α-irradiation.[11]

Higher absorbed α-doses were achieved in the same study using ^{244}Cm isotopic irradiation in the presence of 0.1 M HNO_3, and with the He ions generated by the (n,α) reaction of ^{10}B using a nuclear reactor.[12] The resulting radioactive solutions were not analyzed by mass spectrometry for products, however, they were measured by HPLC for post-irradiation [CMPO]. For the Cm-irradiated samples, there was no measurable change in [CMPO] to an absorbed dose as high as 550 kGy. In contrast, the reactor-α-irradiated samples did show a slow decrease in [CMPO] for both organic-only samples, and for samples in contact with 0.1 M HNO_3, with *G* ~ 0.05 μmol J^{-1}.[11] The maximum absorbed dose in the reactor experiments was ~ 425 kGy. The disparity in the Cm and reactor results has been speculated to be a dose rate effect, with the dose rate being much higher for the reactor experiments.

In summary, it can be concluded that CMPO radiolytic degradation is very much more severe for low LET irradiation and that high LET α-particles have a very limited adverse effect. The presence of molar amounts of HNO_3 and dissolved oxygen, as would be encountered under process conditions enhances the stability of CMPO when irradiated by low LET irradiation. Aerated CMPO solutions in contact with 2 M HNO_3 showed almost no measurable loss in [CMPO]. Further, the TBP phase modifier is a known radical scavenger.[9] It will further protect CMPO, and probably mitigates precipitation of radiolysis products and their metal complexes. However, very small

amounts of products do interfere with solvent extraction performance; only at high absorbed doses. Thus, the performance of CMPO in an irradiated process would be similar in rate and products to that experienced with TBP, where small amounts of acidic products are removed by washing the solvent with alkaline solutions.

3. Comparing CMPO to other amides

3.1 Diglycolamides

Diglycolamides such as TODGA, tetraethylhexyldiglycolamide (TEHDGA) and methylated TODGAs (Me$_n$TODGA), are under development as group actinide/lanthanide extractants. They serve the same role as CMPO in fuel cycle scenarios with the advantage that they do not contain phosphorous, satisfying the CHON requirement. In recent work it has been shown that TODGA, TEHDGA, Me$_n$-TODGAs, and didodecyldioctyldiglycolamide (D$_3$DODGA) are radiolytically degraded with similar rates in organic solution, and in contact with varying concentrations of nitric acid, with or without air sparging.[13,14,15] This is in contrast to CMPO which was protected by both air and acidity. A further difference is that the loss in [DGA] is exponential with respect to absorbed dose, rather than linear. The -G value therefore depends on concentration and is no longer an appropriate metric. Instead, the dose constant (d, kGy^{-1}) is employed. It is analogous to a pseudo-first-order rate constant except that it is expressed with respect to absorbed dose, rather than time.[16] For direct comparison to the CMPO rate of 0.11 µmol J^{-1}, (aerated CMPO/dodecane in contact with 2 M HNO$_3$) an initial -G_{TODGA} value maybe calculated for any initial TODGA concentration ([TODGA]$_o$) using the expression:

$$-G_{TODGA} = d[TODGA]_o \qquad (1)$$

The -G_{TODGA} for an initially 0.2 M TODGA/dodecane solution is thus 0.76 µmol J^{-1}, based on the reported d = 3.8 x 10^{-3} kGy^{-1},[14] for an initial TODGA degradation rate 7x faster than CMPO, when in dodecane. However, this rate slows as the [TODGA] decreases.

The observed first-order kinetic behavior does not imply that the DGAs are reacting with a single reactive species; the dose constant is most often a composite value for several competing reactions. However, in this case the similar rates found in pure organic solution or in the presence of aqueous acid eliminate the participation of many of the common reactive species. The solvated electron and •H-atom are eliminated given the lack of a protective affect by acidity and dissolved oxygen, which would scavenge these radicals.[7] Additionally, the •OH and •NO$_3$ reactive species produced in the aqueous phase are not important, since degradation rates are unchanged in the absence of water and acid. This does indeed focus attention on the solvent radical cation as the single important species. Recent pico-second pulse radiolysis studies show that the rate of reaction of the dodecane radical cation with TODGA and CMPO are both diffusion limited.[10,13] Pre-equilibration of pulse irradiated dodecane solutions with aqueous nitric acid did not change the rate of the radical cation reaction, thus the CMPO acid radioprotection was not explained. What is the mechanism of this protection for CMPO that is not also active for TODGA?

One hypothesis involves the formation of a CMPO•HNO$_3$ complex, which, when undergoing electron transfer with the dodecane radical cation would then decompose back to CMPO and HNO$_3^+$, thus maintaining the [CMPO] concentration in irradiated, acidic solution.[10] Complexes of varying stoichiometries have been reported for both CMPO and TODGA, thus, the hypothesis requires formation of a CMPO•HNO$_3$ complex that is stronger than that of TODGA. Evidence for such a complex has been reported by Fugi et al.[17] and Elias et al.[4] where contact with HNO$_3$ reduced the UV absorbance for known concentrations of CMPO, and the complex was strong enough that it was apparently not decomposed in the HPLC eluent. The latter workers reported a conditional formation constant for a presumed 1:1 CMPO complex in dodecane of 0.150 ± 0.011.[6] Values reported for TODGA complexes vary widely with diluent. Ansari et al.[18] reported 4.1 ± 0.04 in dodecane, however, McLaughlan et al.[19] reported 0.615 in the alternative alkane diluent odorless kerosene. Thus, although both are actually higher than the single value available for CMPO, their disparity makes it difficult to draw conclusions. A further weakness of the proposed mechanism is that it cannot explain the zero-order kinetics found for CMPO radiolysis. Clearly more work is needed to understand the nature of HNO$_3$ protection of CMPO.

An alternate possibility is that the CMPO phenyl group sufficiently delocalizes the hole (+ charge) formed by the electron transfer reaction that the CMPO radical cation has stability sufficient to persist long enough to undergo reaction with a second reactive species before CMPO is degraded to products. This second reaction must be mitigated by acidity and dissolved oxygen, and be slow such that the rate of degradation is independent of total [CMPO]. This would allow the rate constant for the radical cation reaction to be unchanged by acid, yet provide acid protection and satisfy the requirement for zero-order kinetics. A test of this hypothesis would be to synthesize and irradiate an aromatic DGA.

3.2 Monoamides

The monoamides also satisfy CHON requirements and are commonly claimed to have good radiation stability. However, the literature reports are actually scarce. They involve post-irradiation studies of the effects on solvent extraction and limited attempts to identify degradation products.[20,21,22,23] Quantitative degradation rates have not been reported. In our own unpublished work, the decreases in [DEHiBA] and [DEHBA] were exponential and about an order-of-magnitude lower than for the DGAs. Preliminary data also suggests that the rates are not affected by acidity or dissolved oxygen, possibly again implicating the dodecane radical cation. The monoamides appear to behave more similarly to the DGAs than to CMPO, and like the DGAs they lack the phosphoryl group and aromatic ring of CMPO. The faster degradation rates for the DGAs are almost certainly a result of their ether linkages, which are known from other work to be radiolytically fragile.[24] Analyses of irradiated DGA solutions inevitably identify glycolamides and acetamides produced by rupture of the ether linkage.[13,14,15]

3.3 Common radiolysis products

Although the mechanism of CMPO degradation is clearly different from that of the DGAs and monoamides, certain products are analogous. All three classes of compounds undergo radiolytic dealkylation at C-N bonds. As was discussed in Section 2.2, the CMPO dealkylation product is mono-isobutyl-CMPO. The analogous products for the DGAs are trialkydiglycolamides,[13,14,15] and secondary amides for the monoamides, detected in our own unpublished work. These products retain the metal-complexing carbonyl functional group, although they will have decreased solubility in the organic phase. Rupture may also occur at the carbonyl C-N bond. For CMPO the product is OPPAA, which interferes with stripping as discussed in Section 2.2. For the DGAs, organic phase-soluble acids are also created. For example, 5-(N,N-dioctyl)amido-3-oxapentanoic acid and 5-(N,N-diethylhexyl)amido-3-oxapentanoic acid have been identified in irradiated TODGA and TEHDGA solutions, respectively.[13] Analogous products have been identified in irradiated MeTODGA and Me$_2$TODGA solution.[14] It is likely that these acids also interfere with stripping, although the appropriate solvent extraction studies are only currently in progress. In contrast, rupture of the carbonyl C-N bond in the monoamide produces the secondary amine, and an organic acid with significant water solubility.[18] These products are relatively innocuous.

This similarity in dealkylation for all the ligand classes is not so much a function of any similarity in the chemistry of the amides but rather that dealkylation can be caused by electron transfer reactions or $^{\bullet}$H-atom abstraction reactions with all the common primary radiolysis products of aqueous and organic diluents. This will also be true for non-amide ligands.

4. Conclusion

Of the amides discussed here the radiation stability is in the order monoamide > CMPO > DGA. Many products of the radiolysis of CMPO and the CHON amides are analogous, with dealkylation derivatives being especially common. These probably have little effect on solvent extraction, except perhaps to maintain distribution ratios even as the parent ligand degrades. The main deleterious products from a solvent extraction point of view are the organic acids. When even small amounts of organic-soluble acidic species are generated they have the potential to interfere with stripping. This is a concern for CMPO and the DGAs. However, the lower molecular weight acids generated during monoamide radiolysis are more likely to be water soluble and thus are more innocuous to the process.

The solvent radical cation is implicated in the degradation of both CMPO and the DGAs, and it is likely that the monoamides also react with radical cations but this has not been explored. The kinetics and acid protection experienced by CMPO indicates that a multi-step mechanism occurs for CMPO, which must be related to strong acid complexes formed by the phosphoryl group, or charge stabilization by the aromatic group. These effects do not occur for the DGAs or monoamides. Investigations of the kinetics of CMPO reactions with the $^{\bullet}NO_3$ radical reveal that the diluent and metal complexation have large effects on reaction rate constants. This indicates the need to thoroughly understand the speciation present in the system to build radiation kinetic models.

Acknowledgements

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