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The radiolysis of CMPO: effects of acid, metal complexation and alpha vs. gamma radiation

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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.

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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.

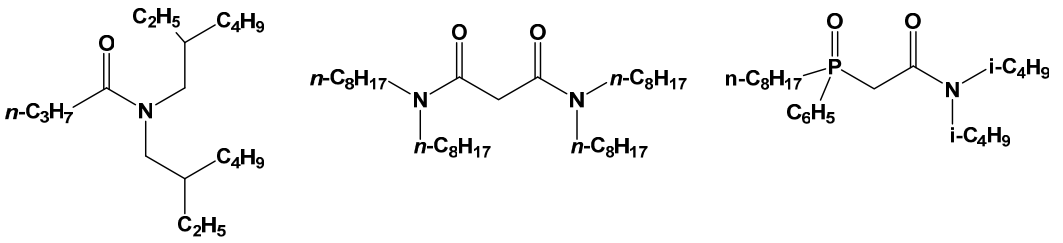

Fig. 1. The structures of DEHBA (left), TODGA (center), and CMPO (right). Note the common [R(C=O)NR'R''] functional group.

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 □-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