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The chemistry of separations ligand degradation by organic radical cations

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Abstract

Solvent based extractions of used nuclear fuel use designer ligands in an organic phase extracting ligand complexed metal ions from an acidic aqueous phase. These extractions will be performed in highly radioactive environments, and the radiation chemistry of all these complexants and their diluents will play a major role in determining extraction efficiency, separation factors, and solvent-recycle longevity. Although there has been considerable effort in investigating ligand damage occurring in acidic water radiolysis conditions, only minimal fundamental kinetic and mechanistic data has been reported for the degradation of extraction ligands in the organic phase. Extraction solvent phases typically use normal alkanes such as dodecane, TPH, and kerosene as diluents. The radiolysis of such diluents produce a mixture of radical cations (R^{+}), carbon-centered radicals (R^{\bullet}), solvated electrons, and molecular products such as hydrogen. Typically, the radical species will preferentially react with the dissolved oxygen present to produce relatively inert peroxy radicals. This isolates the alkane radical cation species, R^{+} as the major radiolytically-induced organic species that can react with, and degrade, extraction agents in this phase. Here we report on our recent studies of organic radical cation reactions with various ligands. Elucidating these parameters, and combining them with the known acidic aqueous phase chemistry, will allow a full, fundamental, understanding of the impact of radiation on solvent extraction based separation processes to be achieved.

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1. Introduction and Background

Considerable work has been reported and reviewed¹⁻⁵ on the kinetics and performance impacts of radiation-induced ligand damage in acidic water. Under these conditions the initially-produced radiolysis species, a mixture of oxidizing (hydroxyl radicals, $\cdot\text{OH}$, nitrate radicals, $\text{NO}_3\cdot$) and reducing (hydrated electrons, e_{aq}^- , hydrogen atoms, $\text{H}\cdot$) species is produced. The reducing radicals formed (e_{aq}^- , $\text{H}\cdot$) will primarily react with the dissolved oxygen present, to be rapidly converted to relatively inert $\text{HO}_2\cdot$ radicals. Hence, it is well established that the extraction ligand damage in the acidic aqueous phase is dominated by hydroxyl and nitrate radicals.

Far less kinetic and mechanistic data is available for the radiation-induced degradation of extraction ligands in the organic phase. Recent reports of radiolysis-induced degradation of ligands in organic diluents such as dodecane and octanol have shown vastly different degradation kinetics, which are strongly dependent upon environment. For example, Figure 1a shows the ^{60}Co radiation-induced damage to CMPO (octyl(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide) in dodecane, compared to its loss when the organic phase was irradiated after pre-equilibration with 3.0 M HNO_3 .⁶ When CMPO is pre-equilibrated with acid, a much slower degradation rate is observed. When the loss of CMPO ($-\text{G}_{\text{CMPO}}$, slope of dose dependence) was correlated with the concentration of nitric acid a steep dependence was observed (Figure 1b), showing nearly complete preservation of this ligand for 5.0 M nitric acid pre-contact.

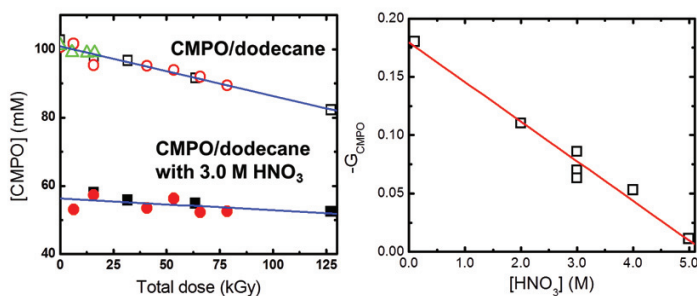
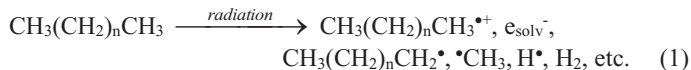


Figure 1. a) left. ^{60}Co -induced loss of irradiated 0.10 M CMPO in dodecane with (filled symbols) and without (open symbols) contact with 3.0 M HNO_3 . Dose rates of 0.175 (triangles), 3.14 (circles) and 15.9 (squares) kGy/hr. b) (right) shows dependence of the CMPO loss as a function of contact HNO_3 acid concentration. Fitted line given by $-\text{G}_{\text{CMPO}} = -0.0347[\text{HNO}_3] + 0.182$.

However, no equivalent protection was observed for acid-contacted TODGA (tetraoctyldiglycolamide) in dodecane (Figure 2).⁸ TODGA is a major component of the U.S. ALSEP process and the Euro-GANEX process for the recovery of minor actinides from PUREX-like raffinates.⁸⁻¹⁰ The different responses of CMPO- and TODGA-containing mixtures demonstrates the existence of a relationship between ligand structure and its radiolytically-induced degradation.

The organic phase in a typical liquid-liquid system uses normal alkanes, such as dodecane, as diluent. The radiolysis of dodecane, $\text{CH}_3(\text{CH}_2)_n\text{CH}_3$, is generically represented by Eqn. 1:¹¹



Under anticipated large-scale processing conditions, the radicals e_{solv}^- , $\text{CH}_3(\text{CH}_2)_n\text{CH}_2\cdot$, $\cdot\text{CH}_3$ and $\text{H}\cdot$ (collectively summarized as $\text{R}\cdot$) will react with dissolved oxygen to ultimately produce peroxy radicals ($\text{RO}_2\cdot$):¹¹



Therefore, reactions of the diluent radical cation, $\text{CH}_3(\text{CH}_2)_n\text{CH}_3^{\bullet+}$ will dominate ligand degradation, Equation 3.



The lifetime of radical cations will be dependent upon its organic structure, but can be relatively long (e.g. ~ 30 ns

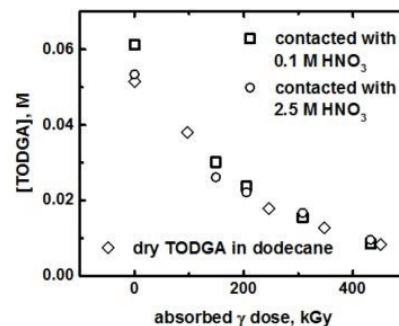


Figure 2: Effect of ^{60}Co γ radiation on the dry and aqueous equilibrated 0.05 M TODGA in dodecane.

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