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

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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 employ designer ligands in an organic phase to extract metal ions from an acidic aqueous phase. These extractions must be performed in highly radioactive environments, and the radiation chemistry of all the complexants and their diluents will play a major role in determining extraction efficiency, separation factors, and solvent-recycle longevity. Extraction solvent organic phases typically use normal alkanes such as dodecane, TPH, and kerosene as diluents. The radiolysis of such diluents produces a mixture of radical cations ($R^{\bullet+}$), 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 peroxyl radicals. This isolates the alkane radical cation species, $R^{\bullet+}$ 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.

Peer-review under responsibility of the organizing committee of ATALANTE 2016.

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

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1. Introduction and Background

Considerable work has been reported and reviewed[1-5] on the kinetics and performance impacts of radiation-induced ligand damage in acidic water. Under these conditions the initially-produced radiolysis species,[6] a mixture of oxidizing (hydroxyl radicals, $^{\bullet}OH$, nitrate radicals, $NO_3^{\bullet}$) and reducing (hydrated electrons, e_{aq}^{-}, hydrogen atoms, $H^{\bullet}$) species is produced. The reducing radicals formed (e_{aq}^{-}, $H^{\bullet}$) will primarily react with the dissolved oxygen present, to be rapidly converted to relatively unreactive $HO_2^{\bullet}$ radicals. Hence, it is well established that 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 findings 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-carbamoyl-methylphosphine oxide) in dodecane, compared to its loss when the organic phase was irradiated after pre-equilibration with 3.0 M HNO_3.[7] When CMPO is pre-equilibrated with acid, a much slower degradation rate is observed. When the loss of CMPO ($-G_{CMPO}$, 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.

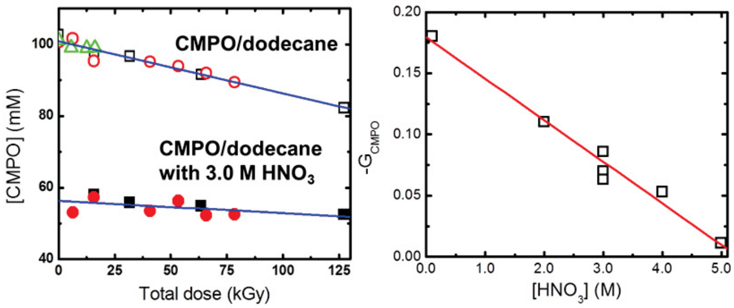

Figure 1. a) (left) ^{60}Co-induced loss of irradiated 0.10 M CMPO in dodecane with (filled symbols) and without (open symbols) contact with 3.0 M HNO_3. Dose rates of 0.175 (triangles), 3.14 (circles) and 15.9 (squares) kGy/hr. b) (right) shows dependence of the CMPO loss as a function of contact HNO_3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

However, no equivalent protection was observed for acid-contacted TODGA (tetraoctyldiglycolaminde) 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.[9,10] 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, $CH_3(CH_2)_nCH_3$, is generically represented by Eqn. 1:[11]

$$CH_3(CH_2)_nCH_3 \xrightarrow{radiation} CH_3(CH_2)_nCH_3^{\bullet+}, e_{solv}^{-}, CH_3(CH_2)_nCH_2^{\bullet}, {}^{\bullet}CH_3, H^{\bullet}, H_2, \text{etc.} \quad (1)$$

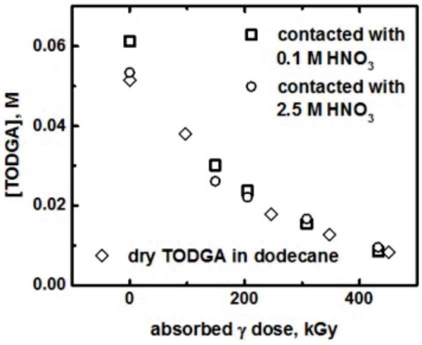

Figure 2: Effect of ^{60}Co γ radiation on dry and acid- equilibrated 0.05 M TODGA in dodecane.

Under anticipated large-scale processing conditions, the radicals e_{solv}^{-}, $CH_3(CH_2)_nCH_2^{\bullet}$, $^{\bullet}CH_3$ and $H^{\bullet}$ (collectively summarized as $R^{\bullet}$) will react with dissolved oxygen to ultimately produce peroxyl radicals ($RO_2^{\bullet}$):[11]

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \quad (2)$$

Therefore, reactions of the diluent radical cation, $CH_3(CH_2)_nCH_3{\bullet}^{+}$ will dominate ligand degradation, Equation 3.

$$CH_3(CH_2)_nCH_3{\bullet}^{+} + L \rightarrow CH_3(CH_2)_nCH_3 + L^{\bullet+} \quad (3)$$

The lifetime of radical cations will be dependent upon its organic structure, but can be relatively long (e.g. ~30 ns for cyclohexane).[12]

To begin to establish global structure-activity correlations between the radiation-induced degradation for ligands such as CMPO and TODGA in organic diluents, here we report on our kinetic measurements for the solvent radical cation reaction with these two ligands in dodecane and cyclohexane, under dry and nitric acid contacted conditions.

2. Experimental

Ligands (CMPO and TODGA) were provided by Idaho National Laboratory at the highest purity available. Dodecane and methylene chloride were >99 % purity from Sigma-Aldrich. Picosecond electron pulse radiolysis/transient absorption experiments were performed at the Brookhaven LEAF facility.[13] Samples were irradiated in 1.00 cm Suprasil semi-micro cuvettes. Time-resolved kinetics was obtained using an FND-100 silicon diode detector, digitized using a LeCroy WaveRunner 640Zi oscilloscope (8 bit, 4 GHz). Acid contacted measurements were performed on organic solutions after equal volumes of diluent/0.10-0.50 M CH_2Cl_2/ligand and acidic water were hand-shaken vigorously for 5 min followed by gravity phase separation for 10–20 min.

3. Results and Discussion

3.1 Experimental measurements.

In the presence of large (0.10 – 0.50 M) concentrations of methylene chloride, the initially-formed solvated electrons would quickly and quantitatively be removed by the reaction:

$$e^-_{solv} + CH_2Cl_2 \rightarrow Cl^- + \bullet CH_2Cl \qquad (4)$$

This isolates the organic solvent radical cation, allowing it to react with added solutes. Using this solvent mixture we recently determined[8] an absolute rate constant for the dodecane radical cation reaction with TODGA of $k = (9.7 \pm 1.1) \times 10^9\ M^{-1}\ s^{-1}$ (see data in Figure 3). The ligand was chosen for initial investigation as there was a previous investigation[14] showing that dodecane radical cations did react with TODGA, however, while transient spectra were identified, no reaction kinetics were obtained.

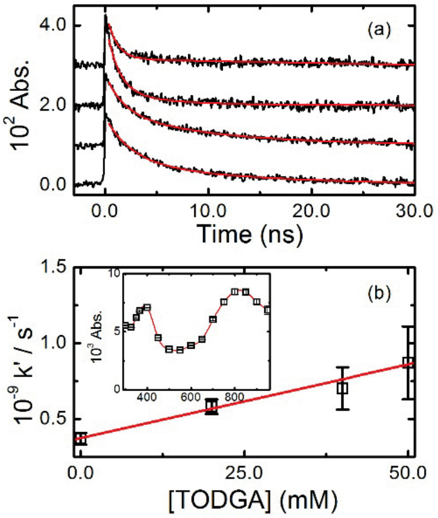

Figure 3: a) Kinetic traces obtained for 10 ps electron pulse radiolysis of dodecane/0.10 M CH_2Cl_2 aerated solutions containing zero (bottom), 20 mM (second bottom), 40 mM (second top) and 50 mM (top) TODGA at 650 nm. Data offset for clarity. b) Inset: Zero-time extrapolated transient absorption spectra obtained for pulse-irradiated, aerated 0.10 M TODGA/ 0.10 M CH_2Cl_2/dodecane. X-axis is wavelength in nm. Main: Second-order rate constant determination from kinetic data of part a). Individual data points and corresponding error bars are the average of 2-3 individual measurements for each TODGA concentration. Solid line is weighted linear fit, corresponding to a slope of $k_3 = (9.7 \pm 1.1) \times 10^9\ M^{-1}\ s^{-1}$.

Our transient spectra obtained (Figure 2 b, Inset) was in good agreement with the previous measurements.[14] Our calculated reaction rate constant of $k = (9.7 \pm 1.1) \times 10^9\ M^{-1}\ s^{-1}$ implies that the solvent radical cation reactions could be a major degradation pathway for extraction ligands.

In addition, kinetic measurements for acid-contacted TODGA/dodecane/CH_2Cl_2 were also performed. These kinetic data are shown in Figure 4 for 50 mM TODGA. Over the acidity range 0 – 5 M, no significant difference in rate constant value was observed.

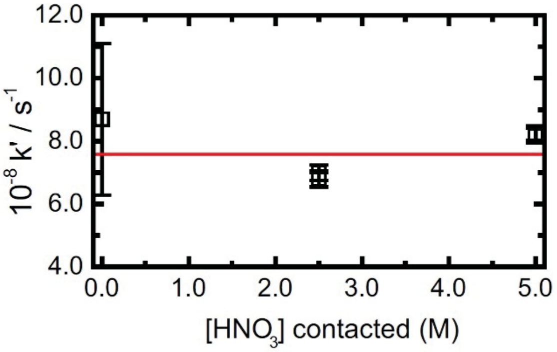

Figure 4. Rate constants measured for 50 mM TODGA in aerated dodecane/0.10 M CH_2Cl_2 that had been pre-contacted with different concentrations of nitric acid.

A similar kinetic investigation was conducted for CMPO in dodecane.[15] Similar findings to TODGA were obtained: the reaction rate constant for the dodecane radical cation with CMPO was slightly faster at $k = (1.30 \pm 0.11) \times 10^{10}$ M^{-1} s^{-1}, and no difference in rate constant was observed for 0 – 5 M nitric acid pre-contact. These data are also summarized in Table 1. As the organic radical cation kinetics for TODGA and CMPO were similar, no insight was gained into why CMPO was "protected" from radiolytic damage when pre-contacted with acidic water. In addition, the question still remained as to the actual mechanism of this reaction; whether electron transfer or proton donation (hole transfer) was occurring? For TODGA in dodecane this would, respectively, correspond to the following reactions:

$$C_{12}H_{26}^{+\bullet} + \text{TODGA} \rightarrow C_{12}H_{26} + [\text{TODGA}]^{+\bullet} \quad (5)$$

$$C_{12}H_{26}^{+\bullet} + \text{TODGA} \rightarrow C_{12}H_{25}^{\bullet} + [\text{H-TODGA}]^{+} \quad (6)$$

Table 1. Summary of kinetic parameters obtained for solvent radical cation reaction with extraction ligands.

Diluent	**Ligand**	**10^{-9} k M^{-1} s^{-1}**	**Acid-contact change**	**Calc. Δ I.P. eV**	**Calc. Hole transfer eV**
Dodecane	TODGA	9.7 ± 1.1	No	-1.41	-1.76
Dodecane	CMPO	13.0 ± 1.1	No	---	---
Cyclohexane	TODGA	3.4 ± 0.2	---	-1.03	-1.44

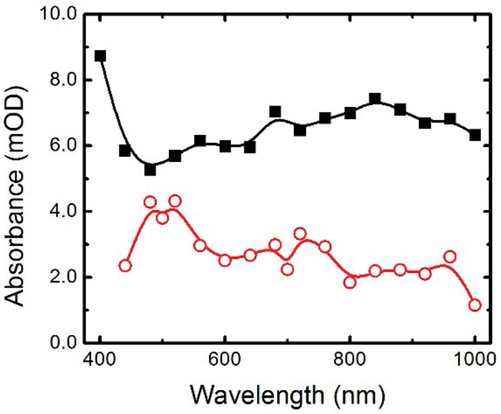

Figure 5. Initial transient absorption spectra for 10 ps pulse-electron irradiated aerated cyclohexane without (■) and with 0.50 M CH_2Cl_2 (O).

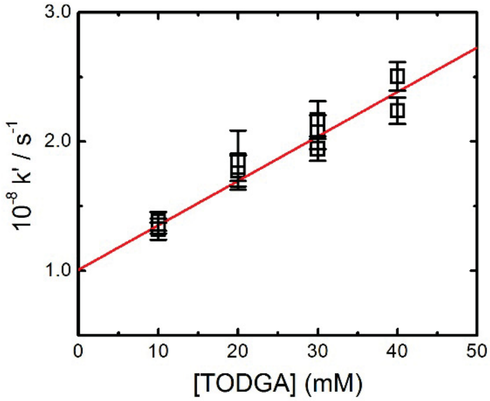

Figure 6. Second-order rate constant determination for the radical cation reaction with TODGA in c-C_6H_{12}/0.50 M CH_2Cl_2. The solid line is a weighted linear fit corresponding to $k = (3.4 \pm 0.2) \times 10^9$ M^{-1} s^{-1}.

To gain further insight into these reactions, experiments were recently conducted using cyclohexane (c-C_6H_{12}) as the diluent. Transient optical spectra were first obtained for pulse-irradiated, aerated, c-C_6H_{12} (see Figure 5) with and without 0.50 M CH_2Cl_2. The major loss of absorbance in the visible region 600-800 nm suggested that a radical cation was formed, similar to that of dodecane. Upon addition of 10-40 mM TODGA the decay at 800 nm became faster. By the same double-exponential analysis performed previously for dodecane, a second-order reaction rate constant for the cyclohexane radical cation reaction with TODGA of $k = (3.4 \pm 0.2) \times 10^9\ M^{-1}\ s^{-1}$, was obtained (see Figure 6, and Table 1).

3.2 DFT calculations.

Additional insight into the mechanism of radical cation reaction was attempted using DFT calculations of the ionization potential difference (corresponding to electron transfer, Reaction 5) between the solvent (dodecane, cyclohexane) and the solute (TODGA). The preliminary data were obtained using Gaussian 09 with a B3LYP/6-31g* basis set and a continuum solvent model. To simplify the calculations, ethyl (-C_2H_5) rather than octyl substituent chains were modeled. The ionization potential difference (Δ I.E.) is also summarized in Table 1. The difference in ionization potential between cyclohexane to TODGA is calculated to be greater than that for dodecane. However, the radical cation reactivity is opposite; the measured rate constant for the dodecane radical cation is about a factor of three greater than that for cyclohexane. A similar opposite trend was found for the hole transfer (Reaction 6) energy difference. At this time we cannot correlate these few measured and calculated parameters. Presently, we are performing additional measurements for both CMPO and TODGA in other organic solvents.

4. Conclusions

The kinetics for dodecane radical cation reaction with two important extraction ligands, CMPO and TODGA, have been directly measured using ps electron pulse radiolysis and transient UV/vis. absorption spectroscopy as $k = (1.30 \pm 0.11) \times 10^{10}\ M^{-1}\ s^{-1}$ and $k = (9.7 \pm 1.1) \times 10^9\ M^{-1}\ s^{-1}$, respectively. These near-diffusion controlled rate constants are significantly faster than determined for cyclohexane with TODGA, $k = (3.4 \pm 0.2) \times 10^9\ M^{-1}\ s^{-1}$. No difference in rate constant was found for acidic water pre-contact. Preliminary DFT calculations of energy differences between solvent and solute molecules did not give any useful correlation to help elucidate whether the electron or hole transfer mechanisms were occurring.

5. Acknowledgments

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