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The role of organic solvent radical cations in separations ligand degradation

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Abstract

The dodecane radical cation reaction rate constant with CMPO was measured using ps electron pulse radiolysis/absorption spectroscopy as $k = (1.30 \pm 0.11) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in dodecane/0.10 M CH_2Cl_2 solution. No reactivity increase occurred when these solutions were pre-contacted with nitric acid, similar to the behavior observed for TODGA. To corroborate these kinetic data with steady-state radiolysis measurements, where acid pre-contacted CMPO showed significantly less degradation, it is proposed that the dodecane radical cation always reacts directly with TODGA, but for CMPO the charge-transfer occurs with the $\text{CMPO} \bullet \text{HNO}_3$ complex formed in the acid contacted solvent.

Keywords

Dodecane radical cation, ps pulse radiolysis, CMPO, TODGA, acid contact

Introduction

The neutral, organophosphorous amide octylphenyl-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO) (Fig. 1) is an important ligand used to complex actinides and lanthanides both in analytical chemistry and in proposed nuclear fuel cycle applications. It was originally designed for use in the TRUEX (TRansUranium Extraction) process, where the highly basic phosphoryl group complexes trivalent actinides and lanthanides, while the carbamoyl group was reputed to complex nitric acid thus allowing for metal complexation even in highly acidic solution. [1] The TRUEX process was designed to remove trivalent actinides such as americium from high level waste, and has more recently been recommended for americium extraction from dissolved nuclear fuel. In either application the CMPO-containing solvent would see high radiation doses, and thus the stability of the ligand and the nature of its degradation products are of importance. The gamma-ray radiolysis of CMPO has been previously investigated with regard to its degradation products and G-values for decomposition, [2-6] however, there are only three reports concerning the alpha-radiolysis of CMPO, including one from this journal. [7-9]

Fig. 1. Chemical structures of CMPO (left) and TODGA (right).

Radiolysis of the biphasic solvent extraction system produces a complex suite of radical species which may have deleterious effects on the ligand. Among the species produced in the aqueous phase are the reactive products of water and nitric acid radiolysis: [10, 11]

The irradiation of the organic phase produces various neutral and ionic carbon-centered radicals: [12]

The effect of these produced reactive species on CMPO will depend on the kinetics of the reaction of each with the ligand, expressed as a bimolecular rate constant k , as those reactions occur in competition with other species in solution. In the acidic, aerated, aqueous phase, various scavenging reactions will remove the reducing e^-_{aq} and most $\cdot\text{H}$ atom from further consideration. [13] Thus, the oxidizing $\cdot\text{OH}$ and $\cdot\text{NO}_3$ radicals are most important in the aqueous phase.

In the organic phase comparatively less is understood about the impact of radiation. The organic phase diluent for TRUEX applications is dodecane, and thus an important product species on the organic side is the dodecane radical cation. Little is known of the reactions of this species. Sugo *et al.* postulated that it is a reactant that could undergo electron transfer reactions with the amidic fuel cycle ligand tetraoctyldiglycolamide (TODGA, Fig. 1), [14, 15] and Zarzana *et al.* reported the rate constant for the TODGA reaction with this species to be diffusion limited. [16] However, no corresponding work has been done for CMPO. Here we report the measurement of dodecane radical cation reactions with CMPO, both in the pure organic phase and when in contact with aqueous nitric acid. The results are compared to our previous reports of the rates of CMPO degradation in gamma-irradiations under similar solution conditions, where it was observed that pre-contact of nitric acid provided a protecting effect of CMPO degradation. [6] The decrease in the CMPO degradation rate ($-\text{G}_{\text{CMPO}}$) was attributed to the protective effect of the formation of a $\text{CMPO}\bullet\text{HNO}_3$ complex in dodecane [6]

which had been identified by mass spectrometry. [17, 18] This protection was not observed for TODGA, indicating that an equivalent nitric acid complex was not formed in the organic phase. [16]

The goal of this work was to further investigate the chemistry involved in ligand degradation occurring in the organic phase due to the dodecane radical cation. In particular, we wanted to determine whether the charge transfer kinetics of this cation were altered for CMPO when it had been pre-contacted with nitric acid.

Experimental

Ligands (CMPO and TODGA) were supplied from Idaho National Laboratory at the highest purity commercially available. Dodecane and methylene chloride (Sigma-Aldrich) were > 99% purity. Picosecond electron pulse radiolysis/transient absorption experiments were performed at the Brookhaven LEAF facility, as described previously. [19] Samples were irradiated in 1.00 cm Suprasil semimicro cuvettes sealed with Teflon stoppers. The doses per pulse for various experiments were in the range 20–40 Gy. Time-resolved kinetics were obtained using a FND-100 silicon diode detector and digitized using a LeCroy WaveRunner 640Zi oscilloscope (4GHz, 8 bit). Interference filters (~10 nm bandpass) were used for the wavelength selection of the analyzing light.

Acid contacted measurements were performed on dodecane solutions after equal volumes of dodecane/0.10 M CH₂Cl₂/ligand and acidic water were hand shaken vigorously for 5 minutes followed by gravity phase separation for 10-20 minutes.

Results and discussion

The electron pulse radiolysis of an organic solvent such as dodecane results in a mixture of radical (H[•], C_xH_y[•]) and ionic (e⁻_{solv}, R⁺) species formed by the alkane bond breakage and ionization as shown in Equation 3. Under the aerated solution conditions, it is

expected that the solvated electrons would quickly react with the added 0.10 M dichloromethane;

thus eliminating any absorbance interference from this transient. All the carbon-centered radicals (generically listed as $\text{R}^\bullet$) would react with dissolved oxygen to form relatively inert peroxy radicals;

Therefore, the most important species remaining that could react with added extractant ligands such as CMPO is expected to be the solvent radical cation, $\text{R}^{+\bullet}$. The dodecane radical cation has been previously identified [16] using UV-visible absorption spectroscopy, and its reaction with TODGA quantitatively established. The rate constant for this reaction

was measured as $k_7 = (9.72 \pm 1.10) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. [16] However, no equivalent kinetics for CMPO have been reported, nor for any acid contacted ligand-containing solvents. Therefore in this study, the importance of the dodecane radical cation reaction with CMPO, and the impact of nitric acid contact with both CMPO and TODGA was elucidated by measurement of absolute second-order rate constants. Initially, transient absorption spectra were obtained over the visible/near IR wavelength region, as shown in Fig. 2. These spectra show that the same radical cation is initially generated under all conditions, and that the cation is apparently not immediately quenched by nitric acid contact. However, the kinetics of the dodecane radical cation at 800 nm are seen to decay faster in the presence of increasing amounts of CMPO (Fig. 3). These individual decays were fitted to an exponential decay function, which also included a small baseline adjustment. The pseudo-first-order rate constants obtained were plotted against the CMPO concentration, see Fig. 4, whose slope gave a second-order rate constant for the reaction

Fig. 2. Dose normalized initial ($t = 0$, extrapolated) transient intensities for aerated dodecane (■), CMPO in dodecane (●) and CMPO in dodecane pre-contacted with 5M HNO_3 (▲).

Fig. 3. Transient kinetics observed at 800 nm for dodecane radical cation reaction with 5-20 mM CMPO. Data offset in both time and absorbance intensity to aid clarity. Solid lines are exponential decay fits, with corresponding first-order rate constants of $(5.05 \pm 0.27) \times 10^8$ ($\square$, 5mM CMPO), $(5.48 \pm 0.34) \times 10^8$ ($\circ$, 10 mM CMPO), $(6.01 \pm 0.66) \times 10^8$ (Δ , 15 mM CMPO), and $(6.85 \pm 0.52) \times 10^8$ (∇ , 20 mM CMPO) s^{-1} , respectively.

Fig. 4. Top: Second-order rate constant plot for reaction of dodecane radical cation ($\text{R}^{\bullet+}$) with CMPO in dodecane/0.10 M CH_2Cl_2 at 295K. Individual data points and corresponding error bars are the average of 3 individual measurements for each CMPO concentration. Solid line is weighted linear fit, corresponding to a slope of $k_8 = (1.30 \pm 0.11) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, ($R^2 = 0.96$). Bottom: Measured rate constants for 20 mM CMPO in aerated dodecane/0.10 M CH_2Cl_2 contacted with different nitric acid concentrations showing no significant increase in reactivity.

of $k_8 = (1.30 \pm 0.11) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. This rate constant is slightly faster than the value obtained previously for TODGA.

Equivalent kinetic measurements were made for the highest concentration of 20 mM CMPO with two acid pre-contacts, 2.5 M and 5.0 M HNO_3 . These kinetic data are shown in Fig. 4. No significant change in the chemical reaction reactivity was observed. This

Fig. 5. Top: Second-order rate constant determination for dodecane radical cation reaction with TODGA in dodecane/0.10 M CH₂Cl₂ at 295K. Individual data points and 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 $k_7 = (9.72 \pm 1.10) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, ($R^2 = 0.974$). Bottom: Rate constants measured for 50 mM TODGA in aerated dodecane/0.10 M CH₂Cl₂ which had been contacted with different concentrations of nitric acid showing no significant increase in reactivity.

constant behavior at various acid concentration contacts is consistent with the interpretation that the charge transfer still occurs at effectively a diffusion controlled rate with the formed nitric acid complex:

However, for the $-\text{G}_{\text{CMPO}}$ data previously reported [6] to be consistent with the measured kinetics, the charge transfer reaction that occurs with the complex would have to have to

regenerate free unchanged CMPO (Reaction 9) whereas the charge transfer with the free CMPO would directly result in ligand degradation (Reaction 8).

To further investigate this phenomenon, we also performed equivalent experiments for acid-contacted TODGA, these data are shown in Fig. 5. The non-acid (zero concentration) contact data point was taken from Zarzana et al., [16], the acid-contacted measurements were performed in this study. Again the acid-contact data show minimal reactivity change, as observed for CMPO. This similarity implies that it is not only the presence of acid that is important for ligand protection from dodecane radical cation reaction, but rather the formation of a ligand-nitric acid complex. At this time we are pursuing additional experiments to further verify this.

Conclusions

The dodecane radical cation reaction rate constant with CMPO was directly measured using ps electron pulse radiolysis to be $k_8 = (1.30 \pm 0.11) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in dodecane/0.10 M CH_2Cl_2 . This value is slightly faster than determined for TODGA previously, $k_7 = (9.72 \pm 1.10) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. No change in reactivity was observed when these solvents were pre-contacted with nitric acid. These results suggest that the dodecane radical cation charge transfer always occurs directly with free TODGA, but in the case of the CMPO the formation of a $\text{CMPO} \bullet \text{HNO}_3$ complex in acid contacted solvent minimizes the charge-transfer induced degradation of this ligand.

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