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Possible Stabilization of the Tetravalent Oxidation State of Berkelium and Californium in Acetonitrile with Triphenylarsine Oxide*

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Both non-aqueous solvents [1] and strongly complexing ligands [2, 3] have been used to stabilize the tetravalent (IV) state of certain lanthanides and actinides (Ln and An) [4, 5]. We have chemically oxidized selected Ln(III) and An(III) nitrates and chlorides to the IV state in acetonitrile (CH_3CN) in the presence of triphenylarsine oxide (TPAsO) [6, 7]. Once a M(IV) nitrate·*n*TPAsO complex is formed, the bulky ligands, which apparently surround the metal ion [8], seem to prevent its further reaction with reducing agents both in solution and in the solid state. The chloride complexes, on the other hand, are only stable in the CH_3CN solution. In the solid state these complexes are probably facial, and thus the TPAsO ligands do not provide the steric crowding necessary for stabilization of the M(IV) species [8]. These techniques were proven successful [6, 7] in stabilizing Ce(IV), Pr(IV), Tb(IV) and Am(IV) before they were applied to Bk, whose (IV)/(III) potential is very close to that of Ce. From the beta decay of Bk-249 ($t_{1/2}$ = 320 d; $E_{\max}$ = 0.126 MeV) it was anticipated that the corresponding Cf(IV) species might be obtained, as has been the case in the solid state halides of Bk-249 [9]. We summarize briefly our previous lanthanide results and report the present status of the decay studies to produce a Cf(IV)·*n*TPAsO complex from a Bk(IV)·*n*TPAsO complex.

Experimental

Reagent grade acetonitrile was dried over K_2CO_3 and stored over molecular sieves. Lanthanide(III) salts and TPAsO were obtained from commercial sources and used without further purification. Am-243 and Bk-249 were obtained from the transplutonium element production facility at the Oak Ridge National Laboratory and were purified by standard ion-exchange techniques [10]. Details of the preparations of the tetravalent lanthanide and Am complexes with TPAsO are given elsewhere [6, 7]. 250 μg of purified Bk(III) in 2 M HNO_3 were taken to dryness and then redissolved in conc. $HClO_4$. This latter operation was repeated, and once again the whole was dried and then dissolved in CH_3CN (2 ml). Another 250 μg of Bk(III) in 2 M HNO_3 were taken to dryness and dissolved in CH_3CN (2 ml). The effects of heating the solutions to 70–80 °C with and without concurrent ozonolysis, along with the influence of the TPAsO (usually 2–3 moles per mole of metal), were investigated. Solids were recovered from the solutions by evaporation of the solvent, dissolution of the residue in acetone and precipitation of solid upon addition of pentane. The solids were loaded into glass capillary tubes for study via X-ray powder diffraction and microscale absorption spectrophotometry [11]. Absorption spectra of the complexes in CH_3CN solution in 1-cm cuvettes fitted with quartz spacers ($\sim 10^{-4}$ M Bk) were obtained with a Cary Model 14-14-M spectrophotometer.

Results and Discussion

Ce(III), Pr(III) and Tb(III) nitrates in CH_3CN at 70 °C were subjected to ozonolysis ($\leqslant$24 h) in the presence of TPAsO to stabilize the IV state of these metal ions [6]. Separate CH_3CN solutions of the nitrates and chlorides of Ce(III) and Am(III) in the presence of TPAsO were bubbled with air/oxygen at 70 °C to achieve at least partial oxidation of the metal ions [7]. In both studies absorption spectrophotometry and cyclic voltammetry were used to determine that metal ion oxidation (to the IV state) had indeed occurred. Solids of most of these M(IV) complexes were obtained. The nitrates were stable to both air and moisture, in contrast to the Ce(IV) chloride complex which reduced to Ce(III) over a period of days.

In the case of Bk(III), the oxidation of both nitrate and perchlorate complexes was investigated. Heating the respective CH_3CN solutions at 80 °C or subjecting them to ozonolysis for 15 min at room temperature, both in the absence of TPAsO, produced no apparent oxidation based on visual and spectrophotometric analysis. However, upon addition of TPAsO to the ozonized Bk(III) nitrate in CH_3CN solution at room temperature, and to the ozonized Bk(III) perchlorate in CH_3CN solution at 70 °C, the solutions became pale yellow. Over a short time the nitrate solution became intensely yellow colored, whereas the perchlorate solution became first light brown and then brown. Both solutions were evaporated to dryness, taken up in acetone, and yielded

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recoverable precipitates upon addition of pentane. Unfortunately, neither solid produced an X-ray diffraction powder pattern or gave an absorption spectrum significantly different from the standard quartz capillary blank established for our single-beam microscope spectrophotometer [11].

In another set of Bk(III) oxidation experiments, a pale yellow solution resulted from heating the Bk(III) nitrate in CH_3CN solution to 80 °C but only after TPAsO was added to the solution. Following ozonolysis of this solution for 15 min at 70 °C, the solution was orange–yellow. Starting with the Bk(III) perchlorate in CH_3CN solution, no changes were observed visually or spectrophotometrically following heating to 80 °C, cooling and adding TPAsO, and subsequent reheating. During the course of a 15 min ozonolysis at ~70 °C, this same solution became pale yellow, then light brown, and finally brown. After standing for several days, this solution became intensely yellow–orange colored. The solution absorption spectra obtained from the ozonized Bk(III) nitrate and perchlorate complexes exhibited a UV cut-off of transmitted light around 300 nm when the complexes were ~98% Bk. Over time, as Cf grew into the solution, this UV cut-off moved more into the visible wavelength range, e.g., around 425 nm when the complexes were ~67% Bk. We associate this intense (allowed) absorption with the ligand-to-metal charge transfer (LMCT) bands of both Bk(IV) and Cf(IV), with that of the ingrowing Cf(IV) occurring at longer wavelength (lower energy) in accord with its lesser stability relative to that of $5f^7$-stabilized Bk(IV). It should be noted that our solution absorption spectra did not exhibit any of the characteristic, although weak (Laporte forbidden), $f \rightarrow f$ transitions in Bk(III), Cf(III), Bk(IV) and Cf(IV). This latter fact is not surprising when one considers that the molar extinction coefficients of the $f \rightarrow f$ transitions are probably $\leqslant 20$ and the total actinide ion concentration is about 10^{-4} M. The limited availability of Bk-249 in this work precluded an intense search for these $f \rightarrow f$ absorption bands.

Very recently, about a year following the initial preparation of these Bk(IV) complexes (43% Bk; 57% Cf), solution absorption spectra of the nitrate and perchlorate complexes were again recorded. The UV cut-off of transmitted light, which we have attributed to Cf(IV), is still the only spectral feature present. No $f \rightarrow f$ absorption bands were observed.

In conclusion, it appears that we may have prepared Bk(IV) nitrate·*n*TPAsO and Bk(IV) perchlorate·*n*TPAsO complexes which formed the corresponding Cf(IV) complexes through the beta decay of Bk-249. Definitive proof should come from similar experiments with quantities of Bk-249 large enough to allow spectrophotometric detection of the characteristic $f \rightarrow f$ transitions in these berkelium and californium species. It is clear, however, that TPAsO and acetonitrile can play a pivotal role in the stabilization of Ln(IV) and An(IV) species.

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