

Gas-Phase Plutonium Oxide Cluster Ions; and Initial Actinide Ion Trapping Experiments *

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A thorough understanding of the chemistry of plutonium is needed to predict and manipulate environmental migration, degradation of stockpile and disposition forms, physiological effects, MOX fuel behavior, etc. The complex chemistry of Pu is largely attributed to the accessibility of several common oxidation states, particularly Pu^{III}, Pu^{IV}, Pu^V and Pu^{VI}. Additionally, the quasi-valence 5f electrons can participate directly in bonding under suitable conditions, such as high atomic density or proximity to harmonious bonding partners. Although a plethora of solid compounds of Pu are known, the overall understanding of the nature of Pu bonding and reaction pathways is limited. Gas-phase reactions provide insights into fundamental chemistry; aspects of organoplutonium chemistry have been probed *via* studies of reactions between Pu⁺ and organic molecules¹. Lanthanide (Ln) studies² demonstrated that the compositions and abundance distributions of Ln_xO_y⁺ cluster ions were sensitive to the redox chemistry of the particular Ln—for example, divalent Eu and tetravalent Tb. In contrast to the predominantly trivalent Ln, the rich redox chemistry of Pu should be revealed in the formation of a variety of Pu_xO_y⁺ with diverse Pu oxidation states. Variations in chemistry among Pu_xO_y⁺ (and Pu_xO_y(OH)_z⁺) should illuminate interfacial and condensed phase processes. In the work described here, new plutonium oxide and oxyhydroxide cluster ions were synthesized by a technique previously applied to Ln_xO_y⁺. In conjunction with this project, quadrupole ion trap (QIT) techniques are being developed to probe actinide atomic, molecular and cluster ion chemistries and preliminary QIT results will be presented for uranium.

Experiment

The actinide laser ablation mass spectrometry facility and *in situ* synthetic techniques employed to prepare Ln_xO_y⁺ have been described in detail,^{1,2} and only a summary is included here. Cluster ions were produced by pulsed laser ablation of a Pu or Ce oxalate target, and analyzed by a time-of-flight mass spectrometer. Based upon results for Ln_xO_y⁺, f-element oxalates were selected as targets for the production of oxide cluster ions upon ablation into vacuum. The following hydrated oxalates were prepared by precipitation from chloride solutions: Pu^{III}₂(C₂O₄)₃-xH₂O; Pu^{IV}(C₂O₄)₂-xH₂O; Ce^{III}₂(C₂O₄)₃-xH₂O; and Ce^{IV}(C₂O₄)₂-xH₂O; the values of “x” were indeterminate, but x > 10 for most Ln^{III}₂(C₂O₄)₃-xH₂O. Cerium oxalates were studied because both Ce(III) and Ce(IV) are common oxidation states and Ce is often employed as a surrogate for Pu. Whereas both the Pu(III) [yellow] and Pu(IV) [black] oxidation states were retained in air, Ce(IV) oxalate was rapidly reduced to Ce(III) oxalate. Greater cluster yields were obtained for Pu^{III}₂(C₂O₄)₃-xH₂O compared with Pu^{IV}(C₂O₄)₂-xH₂O, and most reported results are for the former. Targets were fabricated by compressing oxalate powders into small pellets^{1,2}. A modified QIT with a glow discharge ion source was employed for the initial trapped uranium ion studies.

Results and Discussion

Significant yields of Pu_xO_y⁺ and Pu_xO_y(OH)_z⁺ were produced for values of x up to 6. The predominant ablated cerium oxide clusters were (average Ce valence in parentheses): Ce₂O₂⁺ (2.5); Ce₂O₃⁺ (3.5); Ce₃O₄⁺ (3.0); and Ce₃O₅⁺ (3.7). In contrast to the Ce results, a much wider variety of Pu clusters was produced in appreciable abundance, including several polyhydroxides and oxyhydroxides. A few of the more abundant Pu clusters were (average Pu valence in parentheses): Pu₂O₃⁺ (3.5); Pu₂O₂(OH)⁺ (3.0); Pu₂O₄⁺ (4.5); Pu₂O₃(OH)⁺ (4.0); Pu₂O₄(OH)⁺ (5.0); Pu₃O₄⁺ (3.0); Pu₃O₅⁺ (3.7); and Pu₃O₆⁺ (4.3). As these representative small clusters illustrate, significantly higher valence states were obtained for Pu compared with Ce. The highest valence state definitively identified for Ce was +3.8 in Ce₄O₇⁺, and that for Pu was +6.5 in Pu₂O₆⁺. The highest common valence state of Ce is +4 and that of Pu is +6; Pu^{VII} can be produced under extreme conditions and it is noteworthy that a the mixed valence species, Pu^{VI}Pu^{VII}O₆⁺ was identified here. Three primary differences between Pu and Ce cluster compositions and abundances were: 1) Pu produced clusters of a greater variety of

compositions; 2) Pu clusters exhibited a tendency to incorporate hydroxide ligands; and 3) Pu clusters exhibited a wider range of average valences, notably valence states up to +6 and even +7. It is expected that future studies of actinide cluster synthesis and reactivity will provide new insights into fundamental chemistry and reaction pathways of central importance to understanding processes such as oxidation, hydrolysis and polymerization of Pu, and Pu-induced degradation of organics.

In distinct contrast to Ln_xO_y^+ , where cluster ion intensities decreased monotonically with increasing values of x , small amounts of two “magic number” plutonium oxide clusters, $\text{Pu}_{16}\text{O}_{22}\text{H}_z^+$ and $\text{Pu}_{18}\text{O}_{23}\text{H}_z^+$ ($z = 2$) were identified, well-isolated from the preceding largest cluster, $\text{Pu}_6\text{O}_7(\text{OH})_2^+$. Structures are proposed for these large clusters which might account for their special stabilities. Their formation suggests a link between the molecular and solid states, and provides a unique opportunity for examining the nature of bonding in plutonium molecules and solids.

A primary intent of this research program is to investigate the chemistries, stabilities and structures of actinide clusters. The laser ablation / time-of-flight approach is not particularly well-suited to this goal, and QIT techniques are being pursued to study mass-selected trapped actinide ions in a more controlled fashion. Preliminary results will be presented for reactions of atomic uranium and uranium oxide molecular ions with organic molecules such as pentamethylcyclopentadiene. Ultimately, the ability to produce, isolate and study Pu clusters of specific oxidation states and structures in the QIT should provide a powerful avenue to understanding valence and structural effects in Pu chemistry.

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1. J. K. Gibson, *J. Am. Chem. Soc.*, **120**, 2633 (1998).
 2. J. K. Gibson, *J. Phys. Chem.*, **98**, 11321 (1994).