

LA-UR-03-0707

Approved for public release;
distribution is unlimited.

Title: Transuranic Actinide Reactions with Simple Gas-Phase Molecules

Author(s): Stephen P. Willson
Joseph P. Baiardo
D. Kirk Veirs

Submitted to: Plutonium Futures Conference 2003



Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

Form 836 (8/00)



Transuranic Actinide Reactions with Simple Gas-Phase Molecules

Stephen P. Willson and D. Kirk Veirs, LANL, NMT-11

Joseph P. Baiardo, LANL, NMT-16

Introduction

The intent of this research is to conduct an experimental study of f-element chemistry for the purpose of identifying reaction trends and mechanisms of the early actinide metals with simple gas phase molecules. Previous research has elucidated some of the fundamental chemistry of the 4f elements,¹⁻⁵ however, more complex chemistry is expected for the 5f series due to the inclusion of the 5f electrons in the valence shell. The matrix isolation approach, which is well-suited to the experimental study of transient species, will be used for sample collection, and IR/NIR/VIS spectroscopy will be employed to interrogate deposited matrices. The strength of this method lies in the use of isotopes of reactants, which permits the identification of guest molecules in a noble gas matrix by observation of vibrational frequency shifts and patterns upon isotopic substitution. Using this technique at the University of Virginia, the first noble gas-actinide bond has recently been identified, a weak U-Ar bond on the CUO molecule.⁶ Uranium has similarly been observed to bond to krypton and xenon, whereas thorium and the lanthanides have not exhibited this activity. It is expected that plutonium will be even more reactive in this respect. We will extend the body of actinide experimental evidence to include the transuranic elements neptunium, plutonium, and americium reacted with isotopes of oxygen, nitrogen, hydrogen, carbon monoxide, and carbon dioxide.

Results

As of February 2003, the experimental apparatus has been tested, and final authorizations are forthcoming. Installation is expected to be completed in March 2003, and analysis of the

plutonium and oxygen reaction system will be completed by May 2003. The presentation will include background on the experimental setup and presentation of data and conclusions from the initial plutonium and oxygen study.

Discussion

Much of the fundamental reaction chemistry of actinides remains unexplored. Greater knowledge of reaction pathways of actinides with common atmospheric constituents, and characterization of the products of such reactions, will have broad applicability ranging from elucidation of corrosion mechanisms to enhanced weapon surveillance. The spectroscopic data of these fundamental reaction intermediates and products is needed to identify corrosion products of actinide metals by providing an infrared fingerprint of particular actinide-containing chromophores and compounds. The reactivity data is needed for the development of models applicable to the corrosion process, as well as those applicable to the fundamental reactions at the solid-gas interface where radiolysis reactions are important.

The matrix isolation technique can be used to study the formation of actinide-containing molecules, including the direct study of short-lived reaction intermediates, in well-defined and reproducible reaction systems. In past studies, the most commonly used gaseous reactants have been atmospheric constituents such as O₂, N₂, H₂, H₂O and CO₂, and common pollutants NO, and CO.¹⁻⁷ Reaction trends of the lanthanides with several of these reactants were identified from results of experiments across the lanthanide series.⁵ Attempts to study the actinides at the University of Virginia have been limited to thorium and uranium due to safety concerns. This study seeks to identify similar trends in the early actinides. In this study, the matrix isolation

technique will be applied to reactions of the actinides Np, Pu, and Am with O₂, N₂, H₂, CO, and CO₂.

In concord with its relevance to the exploration of actinide reactivity, this direct experimental study of fundamental f-element chemistry will also be of importance to the theoretical community, providing experimental benchmarks for computation and, in conjunction with calculations, identification of the ground states of actinide-containing species, which is often complicated by the abundance of low-lying electronic states. Many novel ionic and neutral actinide compounds will be identified spectroscopically and substantiated by theoretical calculations.

References

- (1) Willson, S. P.; Andrews, L. *J. Phys. Chem. A* **1999**, *103*, 3171. (Ln + O₂)
- (2) Willson, S. P.; Andrews, L. *J. Phys. Chem. A* **1998**, *102*, 10238. (Ln + N₂)
- (3) Willson, S. P.; Andrews, L. *J. Phys. Chem. A* **2000**, *104*, 1640. (Ln + H₂)
- (4) Willson, S. P.; Andrews, L.; Neurock, M. *J. Phys. Chem. A* **2000**, *104*, 3446. (Ln + NO)
- (5) Willson, S. P. Ph.D. Thesis, University of Virginia, Charlottesville, VA, 1999.
- (6) Li, J.; Bursten, B. E.; Liang, B.; Andrews, L. *Science* **2002**, *295*, 2242. (U + CO)
- (7) Andrews, L.; Zhou, M.; Liang, B.; Li, J.; Bursten, B. E. *J. Am. Chem. Soc.* **2000**, *122*, 11440. (U, Th + CO₂)