

## GAS-PHASE ACTINIDE ION CHEMISTRY\*

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A powerful approach to elucidating fundamental aspects of transition metal chemistry is the study of reactions of bare and ligated metal ions. In contrast to condensed phase chemistry, gas-phase ion - molecule reactions are simple two-body encounters that occur in the absence of secondary influences, such as competing reactions, solvation, and crystal fields. Accordingly, gas-phase reaction pathways and efficiencies can directly reveal intrinsic ion - molecule interactions. Techniques are available to probe reaction mechanisms, and the bonding and structures of product complexes. Also, elementary product complexes are amenable to theoretical modeling. For actinides, other advantages of this investigative approach are that only sub-milligram amounts of material are needed and self-radiation is not detrimental.

We employ a laser ablation time-of-flight mass spectrometry technique to study gas-phase chemistry of actinide ions,  $An^+$ . To date, we have examined reactions of ten actinide ions,  $Th^+$  through  $Es^+$ , and the emphasis has been on reactions with hydrocarbons, where a primary reaction channel is dehydrogenation via C-H activation. The results indicate that dehydrogenation efficiencies are inversely related to the energies required to promote an actinide ion 5f electron to a 6d orbital. Evidently, two non-5f valence electrons are required at the metal center to form a C- $An^+$ -H activated intermediate, as the quasi-valence 5f electrons are ineffective at sigma-type organometallic bonding. The 5f-to-6d promotion energies range from zero for  $Np^+$  ( $5f^4 6d^1 7s^1$  ground state) to  $400 \text{ kJ mol}^{-1}$  for  $Es^+$ , and reaction cross sections vary by several orders of magnitude across the series. Tremendous fluctuations in gas-phase ion chemistry emerge within the actinide series that are not apparent in the condensed phase. The gas-phase chemistry of oxo-ligated actinide ions was also investigated, and anomalous results for  $UO^+$  suggest that the 5f electrons of uranium may be chemically active. Other types of reactant molecules have been employed, and demonstrated novel actinide reactions and complexes.

Our second major thrust in this area is the synthesis and characterization of gas-phase actinide oxide clusters. As clusters contain multiple metal atoms, they represent a nanoscale form of matter intermediate between the molecular and solid states and can be studied to probe the nature of solids and gas-solid interactions. We have synthesized a variety of binary and mixed oxide clusters where the initial emphasis was on exploring variations in oxidation state stabilities among the actinides. One example is mixed  $UPuO_x^+$  cluster ions. Both  $UPuO_2^+$  and  $Pu_2O_2^+$  (average actinide valence = +2.5) formed (without  $U_2O_2^+$ ). Simultaneously,  $UPuO_4^+$  and  $U_2O_4^+$  (average valence = +4.5) formed (without  $Pu_2O_4^+$ ). Results such as these demonstrate clearly the lower propensity for the heavier actinides to exist in high oxidation states. We are pursuing a novel approach to synthesize larger actinide oxide clusters with the intent of studying their structures and chemistries to illuminate the behavior of solid materials. We have synthesized plutonium oxide clusters as large as  $Pu_{18}O_{23}^+$ , have proposed potential nanocrystalline structures, and demonstrated that chemical reactions of actinide oxide clusters can be studied. These preliminary cluster studies open the possibility for preparing nanoscale actinide materials with new properties, and elucidating important processes (e.g., the water-catalyzed oxidation of plutonium).

We are now extending our gas-phase actinide ion - molecule reaction and cluster studies into new directions. Development of a quadrupole ion trap mass spectrometer for transuranics will allow further characterization of actinide atomic, molecular and cluster ion chemistry, as well as the structures and bonding of complexes. Experiments may also be performed in a Fourier transform ion cyclotron resonance mass spectrometer. Ultimately it would be desirable to explore transeinsteinium ion chemistry, to pursue whether relativistic effects modify electronic structures and energetics. These encompassing experimental results will ultimately enable accurate modeling and predictions of actinide and transactinide electronic structures and

bonding.

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