

GAS-PHASE THERMOCHEMICAL STUDIES OF ACTINIDE OXIDES

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INTRODUCTION

With the objective of contributing to a better thermodynamic characterization of species containing actinides (An) with relevance to the nuclear fuel cycle, as well as to the understanding of actinide chemistry at a fundamental level, we have recently made the first Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) studies of the gas-phase ion chemistry of the transuranium actinides Np, Pu, and Am [1-2].

As can be assessed in a recent review paper [3], prior to these studies, gas-phase ion chemistry experiments with the highly radioactive members of the actinide series Pa, Np, Pu, Am, Cm, Bk, Cf, and Es had been based on the use of the Laser Ablation with Prompt Reaction and Detection (LAPRD) technique, while FTICR-MS studies of An ions had been limited to Th and U.

EXPERIMENTAL

FTICR-MS is a technique that is specially suited to study the chemistry of ion-molecule systems in the gas phase. As a result of the applied magnetic and electrical fields, it is possible to trap ions for long periods of time and complex sequences of operations can be performed. To different event sequences correspond different types of experiments in which the structure of the ions can be probed, reagent/product sequences can be determined and kinetic and thermochemical studies can be made.

All the experiments were performed in a Finnigan FT/MS 2001-DT mass spectrometer equipped with a 3 Tesla superconducting magnet and with a Nd:YAG laser, which was used to produce the actinide ions from An-Pt alloys.

RESULTS AND DISCUSSION

The study of oxidation reactions can provide actinide-oxygen bond energies. We studied the reactions of An^+ , and AnO^+ ($An = Th, U, Np, Pu, Am$) with several oxidants ($N_2O, C_2H_4O, H_2O, O_2, CO_2, NO, CH_2O$), which allowed us to estimate unknown An^+-O and OAn^+-O bond dissociation energies (BDE) and to verify literature values obtained by other methods.

We were able to determine that $BDE[An^+-O] \geq 751.5$ kJ/mol for $An = Th, U, Np$, in agreement with literature values, while $BDE[Pu^+-O] \geq 631.6$ kJ/mol, in accord with one of two reported values [1]. In the case of Am, we found that $BDE[Am^+-O] \geq 532.2$ kJ/mol, and an estimate of $BDE[Am^+-O] = 560 \pm 30$ kJ/mol could be made [2].

In the case of the dioxide ions AnO_2^+ , we determined that $BDE[OAn^+-O] \geq 354.3$ kJ/mol for $An = Th, Am$, $BDE[OAn^+-O] \geq 498.4$ kJ/mol for $An = Np, Pu$, and $BDE[OU^+-O] \geq 631.6$ kJ/mol. While the values for Th and U were in agreement with the literature, the value for Pu was significantly higher than the reported ones. The values for Np and Am were previously unknown. The following estimates were made: $BDE[ONp^+-O] = 580 \pm 70$ kJ/mol,

$BDE[OPu^+-O] = 520 \pm 20$ kJ/mol, and $BDE[OAm^+-O] = 390 \pm 40$ kJ/mol [1,2].

The study of electron transfer reactions can provide ionization energies (IE) by means of “bracketing” experiments, in which the ions in question are reacted with compounds with well-known IE. From the reactions of AnO_2^+ ions with several amines it was possible to determine $IE(PuO_2) = 7.03 \pm 0.12$ eV [1], significantly lower than the literature values but in agreement with the results of the oxidation reactions, and $IE(AmO_2) = 7.23 \pm 0.15$ eV [2], the first experimental determination of this quantity.

From the study of reactions of AnO^+ with dienes (1,3-butadiene and isoprene), and using a model developed by H. Schwarz and co-workers for the lanthanides [4], it was possible to determine $IE(PuO) = 5.8 \pm 0.2$ eV and therefore recommend one of two discrepant literature values, and $IE(AmO) = 5.9 \pm 0.2$ eV, that was in this way experimentally obtained for the first time [2]. These values have now been revised to $IE(PuO) = 6.1 \pm 0.2$ eV and $IE(AmO) = 6.2 \pm 0.2$ eV as a consequence of a recent accurate determination of $IE(UO) = 6.0313 \pm 0.0006$ eV by M. C. Heaven and co-workers [5], which was ca. 0.3 eV higher than the literature value that we used to “anchor” the IE values for PuO and AmO. According to our experiments and to Heaven’s result, literature values for $IE(ThO)$ and $IE(NpO)$ should also be revised to $IE(ThO) = 6.4 \pm 0.2$ eV and $IE(NpO) = 6.0 \pm 0.2$ eV. A value of 6.4 eV for $IE(ThO)$ makes this quantity amenable to scrutiny by electron-transfer “bracketing” experiments with amines and these experiments are currently under way.

Bond energies for the neutral species $AnO(g)$ and $AnO_2(g)$ can be derived from the estimated BDEs and determined IEs through the following equations:

$$BDE(An-O) = BDE(An^+-O) + IE(AnO) - IE(An)$$

$$BDE(OAn-O) = BDE(OAn^+-O) + IE(AnO_2) - IE(AnO)$$

In the sequence of these experiments with the singly-charged An ions and of a previous study with uranium [6], work in progress is focused in the oxidation reactions of doubly-charged An ions. Future studies will extend the work to other actinides, including Pa and Cm, as well as to other types of actinide species.

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