Putting Transactinides in the Periodic Table: Aqueous Chemistry of the New d Elements

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First investigations of chemical properties of transactinide elements in the aqueous phase concentrated on the most basic properties.

The principle oxidation state of rutherfordium (Rf, Z=104) was found to be 4+ by Silva et al [1] in elutions from cation exchange columns with α-hydroxyisobutyrate. In these experiments, Rf was sorbed onto a cation exchange column in dilute HCl, and was removed from the column as an anionic complex at higher HCl concentrations. This behavior is similar to that observed for Hf^{4+} and Zr^{4+}, and quite different from that for the 3+ actinides such as Lr^{3+}. The formation of anionic complexes of Rf was confirmed in later experiments by Hulet et al. in elutions from extraction chromatography columns loaded with the anion exchanger trimethylammonium chloride [2]. These experiments demonstrated that the actinide elements, with their stable 3+ oxidation state, end at Lr and that the transactinide elements begin with Rf behaving as a member group 4 of the periodic table.

The first aqueous-phase separations of hahnium (Ha, Z=105) were performed by Gregorich et al. [3] where Ha was found to sorb to glass surfaces from strong HNO_3 solutions. This sorption is a chemical property characteristic of elements in the fifth group of the periodic table, so these experiments showed Ha to be a member of this periodic table group. A second set of experiments showed that Ha was not extracted from HNO_3/HF solutions into methyl isobutyl ketone, under conditions where Ta was extracted. These experiments gave the first indication that while the main chemical properties of the transactinide elements follow those of their respective periodic table d-element homologs, smooth extrapolations down a given group of the periodic table can not reliably predict the detailed chemical properties of the transactinides.

More recently, aqueous phase chemical properties of seaborgium (Sg, Z=106) were measured [4]. These challenging experiments involved elutions of neutral or anionic Sg complexes from cation exchange columns with HNO_3/HF solutions. The results of these experiments were interpreted as being due to the formation of oxo- or oxo-fluoride Sg complexes similar to those for W and Mo, and quite different from those of other ions with the 6+ principle oxidation state, such as U.

During the last 12 years, the chemical properties of Rf and Ha have been studied in considerably greater detail. Direct comparisons between the chemical properties of Rf, Ha, and their lighter periodic table homologs have been made, showing interesting anomalous trends when moving down a particular group of the periodic table. Many of these results have been interpreted as being due to relativistic effects on the transactinide electronic orbitals [5].

78-s ^{261}Rf can be produced by the ^{248}Cm(^{18}O,5n) reaction at rates sufficient for detection of several atoms per hour [6]. The extraction of ^{261}Rf halides into triisooctyl amine (an anion extractor) [7,8] confirmed the earlier results of Silva et al. and Hulet et al. with better statistics. Extraction of neutral Rf-chloride complexes from HCl solutions into tributyl phosphate (a neutral complex extractor) [9,10] were also performed. While the extraction behavior was generally as expected for eka-hafnium, at the highest chloride concentrations, the extraction yield for Rf decreased, indicating formation of anionic chloride complexes. This is a property more similar to Pu^{4+} than the closest homologs Hf^{4+} and Zr^{4+}. Another set of experiments with thenoyltrifluoroacetone (a cation extractor) [11] was also performed. Because the electron donor groups in thenoyltrifluoroacetone are oxygen atoms, the tendencies for different metals to be extracted are a measure of their affinity for oxygen atoms, and should have a strong correlation with the hydrolysis of these metals. From these experiments, it can be deduced that the first hydrolysis constant for Rf^{4+} ions lies between those for Th ($\log K_H = -3.2$) and Pu ($\log K_H = -0.5$). Prelimininary studies of complex formation with the fluoride (a stronger ligand) [12] and bromide (a weaker ligand) [13] were also completed.

34-s ^{262}Ha is produced by the $^{249}Bk(^{18}O,5n)$ reaction at rates sufficient for detection of a few atoms per hour [14]. The formation and stability of anionic halide complexes of 34-s ^{262}Ha have been studied with column chromatography techniques from mixed chloride/fluoride solutions [15,16]. At higher acid concentrations, Ha was found to form oxygen-containing compounds such as $HaOX_4^-$, similar to the behavior of Pa and Nb (with formation of $PaOX_4^-$ and $NbOX_4^-$), and unlike its closest homolog Ta, where the tendency is to form pure halide complexes, such as TaX_6^-. At lower acid concentrations, the Ha properties were more similar to those of Pa than Nb, which was explained as being due to the formation of non-extractable hydrolyzed forms. In recent experiments, the formation of anionic hahnium complexes from pure HCl solutions was studied [17]. It was found that in earlier experiments, the anionic complex formation was dominated by the minor fluoride component of the aqueous solutions. In these more recent experiments, with the pure chloride system, the relative extractabilities of Ha and its homologs were found to follow theoretically predicted trends. [18]

7-s ^{265}Sg and 20-s ^{266}Sg can be produced in the $^{248}Cm(^{22}Ne,xn)$ reaction at rates sufficient for the detection of a few atoms per day. Automated column separations were performed where Sg was rapidly eluted from cation exchange columns from HNO_3 solutions with a small admixture of HF. [18] These experiments represented a dramatic increase in the experimental sensitivity for the study of transactinide element chemical properties, as detection rates were on the order of only one atom per day. These results have been interpreted as the formation of SgO_4^{2-}, according to theoretical calculations. [19]

A review of these transactinide production, chemical separation, and detection techniques will be presented. The measured transactinide chemical properties will be discussed in the context of the periodic table positions of these 6d elements.

It is now generally believed that deformed nuclear shells near N=162 and Z=108 stabilize the neutron-rich isotopes of elements 107 (bohrium, Bh) and 108 (hassium Hs) resulting in half-lives [20] long enough to allow the study of their chemical properties, and that they can be produced at rates on the order of one atom per day. There is currently much interest in performing the first chemical studies with these elements. Gas-phase chemical experiments are scheduled to measure the volatility of oxychlorides of element 107, based on a successful separation of rhenium. [21] Plans are also being made for the first chemical separations of element 108, based on the expected high volatility of the tetroxide. [22]

Experimental confirmation of this enhanced nuclear stabilty has lent renewed credibility to the theoretical prediction of relatively stable superheavy elements near N=184 and Z=114. [23] Half-lives for several isotopes of these superheavy elements are expected to be long enough for chemical studies, and future chemical studies with these elements are being considered.

Expected production rates for the Bh, Hs, and the superheavy elements are expected to be much less than those for the lighter transactinides; only atoms per week or less. Therefore, the sensitivity of the radiochemical techniques for the determination of their chemical properties must be increased accordingly. New techniques and planned experiments to extend aqueous-phase chemical studies to Ns (element 107) and Hs (element 108) and beyond will be discussed.

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