GAS PHASE CHROMATOGRAPHY OF HALIDES OF ELEMENTS 104 AND 105

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On-line isothermal gas phase chromatography was used to study halides of 261104 (T1/2 = 65 s) and
26226105 (T1/2 = 34 s and 27 s) produced atom-at-a time via the reactions 248Cm(14O, 5n) and 256Bk(14O,
5n, 4n), respectively. Using HBr and HCl gas as halogenating agents, we were able to produce volatile
bromides and chlorides of the above mentioned elements and study their behavior compared to their lighter
homologs in Groups 4 or 5 of the periodic table. Element 104 formed more volatile bromides than its
homolog Hf. In contrast, element 105 bromides were found to be less volatile than the bromides of the group
5 elements Nb and Ta. Both 104 and Hf chlorides were observed to be more volatile than their respective
bromides.

Introduction

Recently, considerable interest has been shown in the study of the chemistry of the transactinide
elements (atomic number > 103) by both experimental and theoretical chemists. At these very high
atomic numbers the inner electrons are subjected to such large nuclear charges that they attain
relativistic velocities. These relativistic effects are also felt by the valence electrons to such an
extent that the chemical properties may no longer be extrapolated from those of their lighter
homologs in the periodic table. Recent extensive theoretical calculations1-4 have provided chemists
with predictions on how the relativistic rearrangements of valence electrons may affect the
chemical properties of the heaviest elements and in which compounds these effects should become
important. The practical investigation of the chemical properties of the transactinide elements,
however, is extremely difficult. Currently, these elements can only be produced by heavy ion fusion
reactions at accelerators at a rate of a few atoms per hour of beam time. In addition, even the
longest-lived known isotopes of these elements have half-lives of only one minute or less, which
further complicates chemical studies. Due to the low production rates and short half-lives very fast

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chemical procedures, which work continuously or can be performed with a high repetition rate, must be devised to study the chemistry of these elements. Studies of chemical properties have only been performed on elements through 105 so far.

Based on relativistic calculations for element 103, KELLER proposed that in the case of element 104 the ground state configuration should be \([\text{Rn}]5f^{14}7s^27p^2\) rather than \(6d^27s^2\) analogous to the \([\text{Xe}]4f^{14}5d^26s^2\) configuration of its lighter homolog Hf. Therefore, he suggested that element 104 might behave like a heavy p-element similar to Pb. In recent accurate Multi-Configuration Dirac-Fock (MCDF) calculations using 468 jj-configurations, GLEBOV et al. determined that the ground state of 104 should be a \(J = 2\) level consisting primarily of the \(6d^7s^27p\) configuration (80%) with a level only 0.5 eV higher consisting of the \(6d^27s^2\) configuration (95%), while the \(7s^27p^2\) state is 2.9 eV above the ground state. They concluded that element 104 should show no distinctive p-character, but should behave like Hf, a typical d-element. Recent experimental evidence indicates that element 104 does not exhibit p-element properties.

As early as 1966 ZVARA et al. performed the first gas phase chemistry experiments with 104-halides. Their extensive studies have continued until today. By using thermochromatographic methods, they found that element 104 forms chloride and bromide compounds noticeably more volatile than the corresponding compounds of Hf and Zr. Until the current study no other groups have attempted volatility studies of 104-halides. The results of all chemical studies (gas phase and aqueous) indicate that element 104 behaves like a group 4 element, thus supporting its assignment as the first transactinide element.

Element 105 is anticipated to be the heaviest group 5 element and, as such, may be expected to have a ground state configuration of \([\text{Rn}]5f^{14}6d^37s^2\). By analogy to calculations for Lr, a probable ground state configuration could be \(6d7s^27p^2\). However, recent calculations by JOHNSON and FRICKE indicate that the ground state of element 105 is \(6d^36s^2\) with the \(6d^26s^27p\) configuration about 1 eV above the ground state. First experiments on the volatility of 105 halides have again been performed by ZVARA et al. They concluded that element 105 is a homolog of Nb and Ta. Its chloride appeared to be less volatile than NbCl₅ and more similar to HfCl₄. The bromide seemed to be less volatile than NbBr₅ and HfBr₄.

In 1988 on-line isothermal gas chemistry experiments were performed to study the volatility of 105 bromides in empty quartz columns, using ²⁶²,²⁶³¹⁰⁵. In agreement with the work done in Dubna, the 105 bromides seemed to be less volatile than those of its lighter homolog Nb. However, these experiments were hampered by contaminating Po-activities and poor statistics.

In the current work, the same technique is used to study the volatility of 104 and 105 bromides and chlorides and those of their homologs, Hf and Ta. Alpha particles and spontaneous fissions (SFs) from the decay of the isotopes ²⁶¹104 and ²⁶²,²⁶³105 produced by the ²⁴⁸Cm(¹⁸⁰, 5n) and ²⁴⁹Bk(¹⁸⁰, 5n, 4n) reactions, respectively, were detected directly at the exit of the chromatography system in order to identify those nuclides unambiguously.