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TOWARD VOLATILE METAL COMPLEXES OF RUTHERFORDIUM - RESULTS OF TEST EXERIMENTS WITH Zr AND Hf

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Introduction

The chemical investigation of the transactinide elements (TAN, $Z \geq 104$) is a topic of great interest in recent nuclear chemistry research. The highly charged nucleus accelerates the innermost electrons to relativistic velocities thus causing contraction of spherical (s, $p_{1/2}$) orbitals and expansion of the others ($p_{3/2}$, d, and f), which directly affects the chemical behavior of these elements. Deviations from trends established in the periodic table may therefore occur due to these so-called relativistic effects [1,2]. In gas phase experiments, mostly volatile inorganic compounds (e.g., halides or oxides) of TAN were investigated. We refer to [3] for a recent review. For reasons such as low production cross-sections or short half-lives, but also technical challenges, more sophisticated chemical studies have not yet been possible. One restriction in present TAN research is the plasma behind the target caused by the intense heavy ion beam. "Weak" molecules (e.g., organic ligands) are immediately destroyed, thus limiting the possibilities of synthesizing chemical compounds directly behind the target to "simple" and robust inorganic compounds. It is highly desirable to expand the knowledge on the chemical behavior of the TAN to other compound classes, e.g., volatile metal complexes. The use of the Berkeley Gas-filled Separator (BGS) [4] as a physical pre-separator makes such studies possible by separating the beam from the desired TAN isotopes.

Volatile β-diketonate metal complexes

A compound class that appears suitable for such studies are the β-diketonates, i.e., coordination compounds of a metal with ligands of the structural type shown in Figure 1. The β-diketone anions are well known to act as bidentate ligands forming neutral complexes, some of which can be transferred to the gas phase without decomposition. It has been observed that the introduction of fluorine atoms leads to more volatile species [5]. In studies of Hf β-diketonates using long-lived ($T_{1/2} \sim$ h) carrier-free isotopes, Fedoseev et al. demonstrated that single molecules of Hf-hfa complexes deposited at temperatures below 100°C in a temperature gradient tube [6]. Therefore, we used the hfa system for first studies of a volatile metal complex. As a first system, rutherfordium (Rf, Z=104) was chosen since ^{257}Rf ($T_{½}$=4.7 s) can be produced at a relatively high rate of 1-2 atoms/min at the BGS. Here, we report on experiments with the lighter homologs of Rf, zirconium (Zr) and hafnium (Hf).

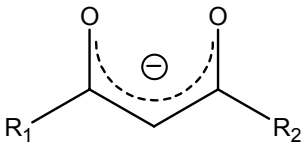

Figure 1: General structure of β-diketones

Experimental and Results

Production of short-lived Zr and Hf isotopes using a heavy ion cocktail

To rule out the role of differing experimental conditions in the measurement of chemical properties, it is desirable to investigate isotopes of all homologs simultaneously. Due to their different magnetic rigidities, BGS can not forward them to the chemistry setup simultaneously. The next best approach is to switch quickly between short-lived isotopes of these elements without having to open the chemistry setup. Short-lived Zr and Hf isotopes have therefore been produced in the nuclear reactions ^{nat}Ge(^{18}O,*x*n)^{85}Zr, ^{74}Se(^{18}O, α3n)^{85}Zr and ^{112,116,120,124}Sn(^{50}Ti,*x*n)^{158,161,165,169}Hf. Using a heavy-ion cocktail [7] of $^{18}O^{4+}$ and $^{50}Ti^{11+}$ and a target ladder holding up to 5 targets, which can be remotely introduced into the path of the beam, allowed for a quick switching between Zr and Hf. Magnetic rigidities for all produced isotopes were measured as well as the residual range of ^{169}Hf and ^{85}Zr in Mylar, which is used as the BGS exit window.

Formation of volatile hfa compounds of Hf

A schematic of the experimental setup is shown in Figure 2.

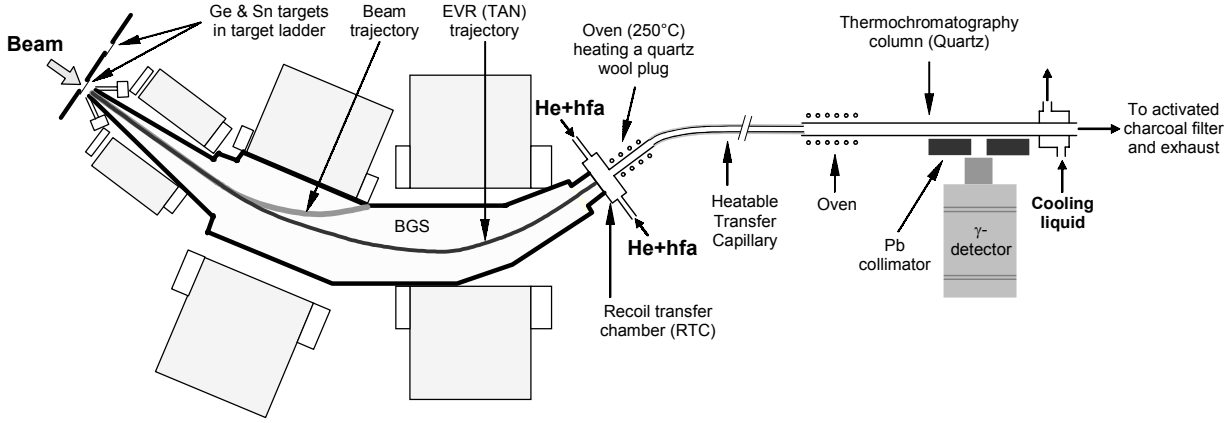

Figure 2: Setup used to chemically investigate volatile metal complexes at the BGS.

The beam, delivered by the 88-inch cyclotron, induced nuclear reactions in the target at the irradiation position. The beam was deflected using the BGS and did not reach the focal plane of the separator. The evaporation residues (EVR) entered the recoil transfer chamber (RTC) [8] through a 3.6-μm thick Mylar window. The RTC was flushed with 1.3 l/min He that was enriched in hfa by passing part of the gas through a bubbler containing hfa. Hfa is a liquid at room temperature. The thermalized recoils were transported to a nearby oven where the volatile complexes were formed. These were forwarded through a PFA Teflon transfer capillary to a thermochromatography (TC) setup located at a distance of 5 m. The gas-flow rate, temperature of the RTC-oven and hfa concentration in the He carrier gas were optimized to produce maximum yields. The following partial yields were measured for ^{169}Hf: Formation of volatile complexes: >95% of the Hf present in the RTC; transport to the chemistry setup: >95%; giving an overall yield of more than 90% for this 3.24-min isotope.

Thermochromatography experiments

The adsorption behavior of the formed compounds was investigated in on-line TC experiments by introducing them into an open quartz column with a negative longitudinal temperature gradient from +75 to -50°C. It is not possible to use a lower minimum

temperature because macroamounts of hfa present in the carrier gas deposit at about -65°C. Deposition of Hf and Zr isotopes along the temperature gradient was determined by scanning the column with a HPGe γ-detector using a lead collimator with a window of 2-cm width. Each section was counted for 2 min. A considerable fraction of the transported ^{169}Hf passed through the chromatography column and reached an activated charcoal (ACC) trap that was installed after the exit of the column. Such traps absorb 100% of the formed species. The reminder of the ^{169}Hf deposited at temperatures between 0 and -20°C. This is in contradiction to a deposition temperature of 40°C as reported in [9].

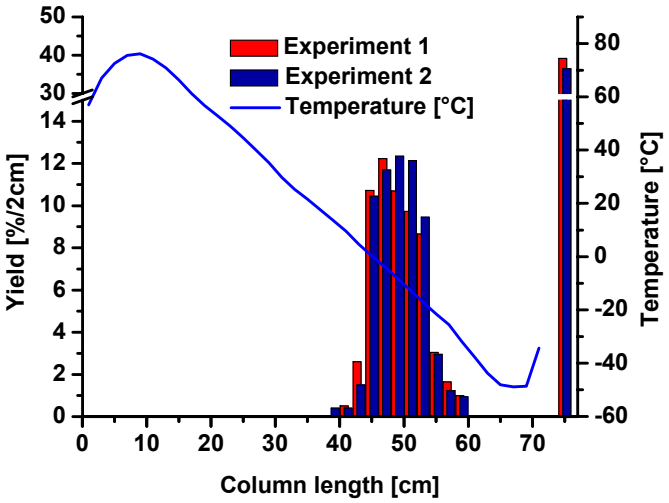

Figure 3. Thermochromatogram of ^{169}Hf. Two experiments conducted under identical conditions are shown. The temperature gradient is indicated (right-hand scale). An activated char coal trap (ACC) was mounted after the exit of the TC column to retain ^{169}Hf that was passing the column.

These first results are very encouraging and can be considered as a proof that it is indeed possible to form fragile compounds containing short-lived radionuclides produced in heavy-ion induced fusion reactions when the beam is separated. Further experiments are under way and the results will be presented at the conference.

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