

Gas phase chemistry of bohrium (element 107)

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The transactinide element bohrium (Bh, element 107) was discovered in 1981 at GSI Darmstadt, Germany [1]. The systematic order of elements in the periodic table suggests Bh to be a member of group 7, together with manganese, technetium, and rhenium. Doubts about an unchanged periodicity of chemical properties along the rows of the periodic table rise especially for the heaviest elements. The fields of their highly charged nuclei may lead to strong relativistic effects deviating the order in the electron shell structure [2-4]. Relativistic effects force a stronger attraction of the relativistic electron orbitals with a spherical shape (s and $p_{1/2}$) to the nucleus. The resulting shielding of the nuclear charge causes an expansion of the other p-, d-, and f- electron orbitals - the indirect relativistic effect. Therefore, chemical properties as for example ionization potentials, binding energies and geometries of the electron orbitals of the heaviest elements and their compounds may be strongly influenced by relativistic effects. The chemical studies of rutherfordium (Rf, element 104), dubnium (Db, element 105) and seaborgium (Sg, element 106) revealed a typical behavior for members of the transition metal series in the groups 4 to 6 of the periodic table, respectively [5].

Prior to the studies described in the current presentation, two attempts to search for long-lived isotopes of bohrium and to study chemical properties of this element have been conducted in 1984 at JINR in Dubna, Russia in the reaction $^{249}\text{Bk}(^{22}\text{Ne},4-5n)^{266,267}\text{Bh}$ [6] and in 1992 at LBNL Berkeley, USA in the reaction $^{254}\text{Es}(^{16}\text{O},4-5n)^{265,266}\text{Bh}$ [7]. In both experiments Bh was assumed to form a volatile oxide or oxyhydroxide similar to its homologues in group 7 of the periodic table, Tc and Re. Gas phase chemical separations have been carried out. The cross section limits reached in these experiments were about 0.1 nb in Dubna and about 1 nb in the experiment in Berkeley. Both experiments were not sensitive enough to measure the decay of the Bh-isotopes $^{265-267}\text{Bh}$. Meanwhile, neutron-rich isotopes $^{266,267}\text{Bh}$ have been discovered at the LBNL Berkeley [8] in the heavy ion induced nuclear fusion reaction $^{249}\text{Bk}(^{22}\text{Ne},4-5n)$ revealing the enhanced nuclear shell stabilization against spontaneous fission (SF-) and α -decay, which is predicted and experimentally confirmed for deformed nuclei close to ^{270}Hs (Hassium, element 108) [9-13]. The half-life ($T_{1/2}$) of about 17 s and the predominant α -decay mode ($E_{\alpha} = 8.83 \pm 0.03$ MeV) made ^{267}Bh an ideal nuclide for fast gas chemical experiments. The production cross section of ^{267}Bh at a ^{22}Ne energy of 117 ± 1 MeV was about 60 pb, indicating the necessity of an exceptional sensitive experimental chemical approach. Hence, gas phase chemical model studies with Tc and Re were conducted in preparation of the experimental chemical characterization of the transactinide element [14, 15]. The gas phase separation of the volatile oxychloride species of these elements, presumably MO_3Cl (M=Tc, Re) in a low temperature isothermal gas chromatography, based on the OLGA technique [16], appeared to be most promising in terms of separation yield, quality, and velocity. The results of these model experiments were used for empirical predictions of the behavior of Bh in the reactive gas system HCl/O₂. The most stable gas phase compounds and their behavior in a gas-solid adsorption separation have been predicted. From thermochemical extrapolations the standard adsorption enthalpy of BhO_3Cl on a fused silica surface, $\Delta H_{\text{ads}} = -75 \pm 12$ kJ/mol, was predicted [17]. With a physisorption model adjusted to the experimental results with Tc and Re Pershina and Bastug [18] estimated $\Delta H_{\text{ads}} = -78 \pm 5$ kJ/mol.

The Bk-target preparation was conducted at LBNL. A HDEHP redox-extraction separation procedure for Pb, Bk, and Cf was carried out using ultra pure chemicals and carefully cleaned tools in an exceptionally clean glove box endeavouring to avoid accidental heavy metal contaminations.

Subsequently, a target of ^{249}Bk ($670 \mu\text{g}/\text{cm}^2$) covered by a layer of ^{159}Tb ($100 \mu\text{g}/\text{cm}^2$) was prepared by a molecular plating procedure of $^{249}\text{Bk}(\text{NO}_3)_3$ and $^{159}\text{Tb}(\text{NO}_3)_3$ on a $2.77\text{mg}/\text{cm}^2$ Be foil. At the Philips cyclotron of the Paul Scherrer Institute, Switzerland this target was irradiated for about 4 weeks at a beam dose of $3 \cdot 10^{18} \text{ }^{22}\text{Ne}^{6+}$ at a beam energy of $119 \pm 3 \text{ MeV}$ in the middle of the target. ^{176}Re was simultaneously produced in the fusion reaction $^{159}\text{Tb}(^{22}\text{Ne}, 5n)$ and served as a yield monitor for the chemical separation of group 7 oxychlorides. The nuclear reaction products, recoiling from the target were thermalized in He gas loaded with carbon aerosol particles. Adsorbing on the particle surface, they are swept to the remotely controlled OLGA III device. HCl and O_2 are admixed. On a quartz wool plug in the reaction oven of the apparatus held at 1000°C the carbon particles are burned. At the same time the nuclear reaction products form compounds, which are evaporated and separated on-line in the isothermal chromatography quartz column. The retention times of the compounds in the column are mainly dependent on their adsorption interaction with the column surface at the isothermal temperature (Table 1, T_{iso}) and on the carrier gas velocity. The experiment ends for the individual molecule with the decay of the nuclide. Thus, only the species with a longer nuclear lifetime than the retention time pass the chromatography set-up and were subsequently attached to CsCl aerosol particles of a second gas-jet to be transported to the detection device - ROMA. There, the CsCl particles were impacted in vacuum on thin polyethylene foils ($\sim 30 \mu\text{g}/\text{cm}^2$) mounted on the circumference of a stepwise rotating wheel. Every 10 s the gathered samples are successively moved between a series of 12 pairs of PIPS detectors to measure α - and SF-decay in an event-by-event mode with about 70% detection efficiency. ^{176}Re was measured using a HPGE- γ -detector. About 180000 samples were measured during the entire experiment. The overall yield of the complete separation process, from the thermalization of the recoiling fusion products to the sample preparation in the detection device, was determined for ^{176}Re to be about 16%. During the irradiation three different temperatures were adjusted in the isothermal quartz column. Four correlated decay chains, attributed to the decay of ^{267}Bh , were detected at 180°C . At 150°C 2 decay chains were observed. Finally, at 75°C isothermal temperature, where $^{169}\text{ReO}_3\text{Cl}$ still passes the isothermal part of the column with about 80% relative yield, no ^{267}Bh was registered (see Table 1).

Table 1. Detected correlated decay chains related to the decay of ^{267}Bh .

| T_{iso} [$^\circ\text{C}$] | Beam dose: $^{22}\text{Ne}^{6+}$ | $E_{\alpha 1}$ [MeV] | t_1 [s] | E_2 [MeV] | Δt_2 [s] | $E_{\alpha 3}$ [MeV] | Δt_3 [s] | Decay assignment | N_R |
|--|-------------------------------------|-------------------------|--------------|----------------|---------------------|-------------------------|---------------------|---|-------|
| 180 | $1.02 \cdot 10^{18}$ | 8.84 | 26.7 | 8.35 | 73.4 | | | $^{267}\text{Bh} \rightarrow ^{263}\text{Db}$ or ^{259}Lr | 1.2 |
| | | 8.72 | 2.9 | 8.40 | 29.9 | | | $^{267}\text{Bh} \rightarrow ^{263}\text{Db}$ or ^{259}Lr | |
| | | 8.81 | 18.4 | 101/86 | 16.3 | | | $^{267}\text{Bh} \rightarrow ^{263}\text{Db}$ or ^{259}Lr | 0.1 |
| | | 8.91 | 10.5 | 8.37 | 0.8 | 8.41 | 14.6 | $^{267}\text{Bh} \rightarrow ^{263}\text{Db} \rightarrow ^{259}\text{Lr}$ | 0.001 |
| 150 | $1.00 \cdot 10^{18}$ | 8.81 | 24.5 | 82 | 21.1 | | | $^{267}\text{Bh} \rightarrow ^{263}\text{Db}$ or ^{259}Lr | 0.1 |
| | | 8.85 | 34.4 | 46 | 98.9 | | | $^{267}\text{Bh} \rightarrow ^{263}\text{Db}$ or ^{259}Lr | |
| 75 | $1.00 \cdot 10^{18}$ | | | | | | | | |

$E_{\alpha 1}$ and $E_{\alpha 3}$ represent the α decay energies of ^{267}Bh and ^{259}Lr , respectively.

E_2 indicates the α ($E_2 < 10 \text{ MeV}$) or SF ($E_2 > 30 \text{ MeV}$) decay energy of the indistinguishable in this experiment decay of ^{263}Db ($E_\alpha = 8.35, 8.41 \text{ MeV}$) and ^{259}Lr ($E_\alpha = 8.45 \text{ MeV}$).

t_1 is the life-time of ^{267}Bh from the beginning of the measurement.

Δt_2 shows the life-time of ^{263}Db or ^{259}Lr after the ^{267}Bh decay.

Δt_3 represents the life-time of ^{259}Lr after the ^{263}Db decay.

N_R is the number of random correlations.

Based on the detection of 6 atoms we conclude that Bh behaves like a typical member of group 7 in the periodic table. Bh, similarly to Tc and Re, forms a volatile oxychloride compound, presumably

BhO₃Cl. A careful statistical analysis of the experimental data was applied. The number of random correlations (Table 1, N_R) was evaluated. From the number of detected correlated decay chains, the initial number of ²⁶⁷Bh atoms in the measured samples was determined. Assuming the experimental result at 180°C to be 100 %, the relative yields at 150°C and 75°C were calculated (see Fig.1, filled squares). Assuming the same adsorption process as for TcO₃Cl and ReO₃Cl, using a microscopic model of mobile adsorption [19], first thermodynamic data of element Bh - the standard adsorption enthalpy of BhO₃Cl on a quartz surface - was evaluated: $\Delta H_{\text{ads}}(\text{BhO}_3\text{Cl}) = -75^{+9.6}$ kJ/mol [20]. This value is in a very good agreement with the predictions. Using empirical thermochemical methods different macroscopic properties related to Bh and its compounds have been evaluated. In different chemical systems it was shown that ΔH_{ads} is closely related to the macroscopic volatility of the species. Employing a linear correlation between the microscopic data ΔH_{ads} and the macroscopic data sublimation enthalpy (ΔH_{subl}), which was obtained for the adsorption of chlorides and oxychlorides on quartz surfaces in [21], we estimated from our experimental result $\Delta H_{\text{subl}}(\text{BhO}_3\text{Cl}) = 89 \pm 20$ kJ/mol. Consequently, in agreement with the predictions, BhO₃Cl is supposed to be less volatile than TcO₃Cl ($\Delta H_{\text{subl}} = 49 \pm 12$ kJ/mol) and ReO₃Cl ($\Delta H_{\text{subl}} = 67 \pm 12$ kJ/mol)

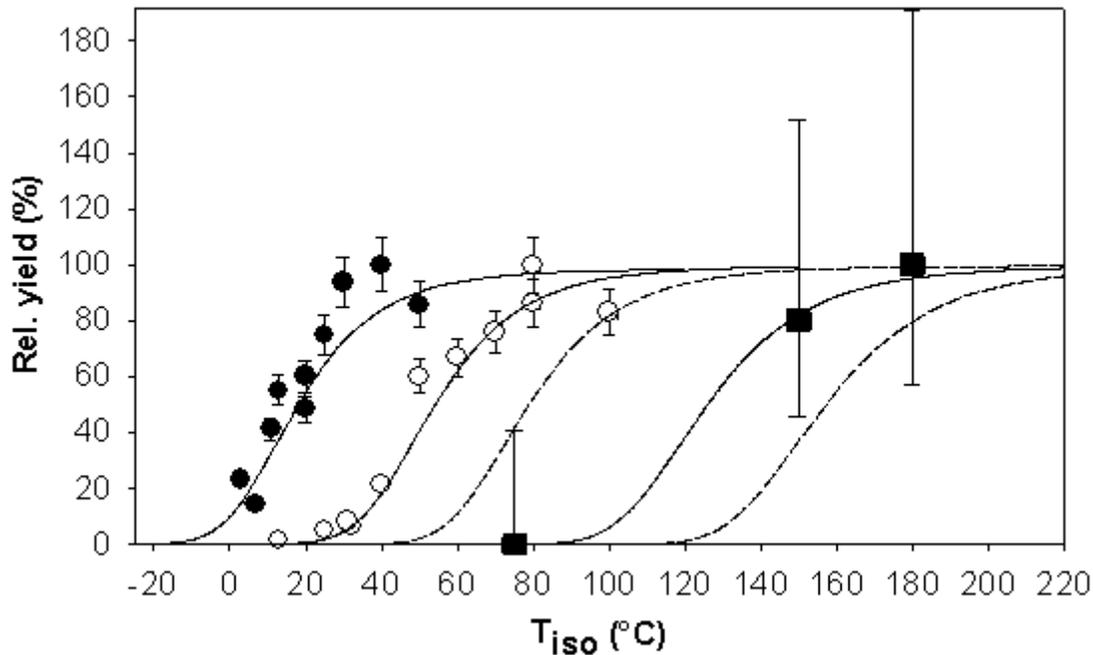


Figure 1. Experimental results of isothermal gas adsorption chromatographic separations in quartz columns. Presented are the relative yields of the compounds ¹⁰⁸TcO₃Cl (filled black circles), ¹⁶⁹ReO₃Cl (open circles) and ²⁶⁷BhO₃Cl (filled black squares, this work) after separation in a OLGA device as a function of isothermal temperature (T_{iso}). The error bars indicate a 68% confidence interval. The lines represent calculated relative yields applying a microscopic model of the adsorption process based on a Monte Carlo approach, with standard adsorption enthalpies of -51 kJ/mol (TcO₃Cl), -61 kJ/mol (ReO₃Cl), and $-75^{+9.6}$ kJ/mol (BhO₃Cl), respectively.

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