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Evidence for relativistic effects in the chemistry of element 104

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Abstract

On the basis of thermodynamic extrapolations, the first transactinide element 104 (Rf=rutherfordium[1]) is expected to form volatile tetrachlorides of lower volatility than those of the homologous element Hf. In contrast, relativistic calculations predict a higher volatility of $RfCl_4$ compared to $HfCl_4$. The nuclides ^{261}Rf and ^{165}Hf, with identical half-lives of 78 s, were simultaneously produced at the U-400 cyclotron of the Flerov Laboratory of Nuclear Reactions (FLNR), Dubna, Russia, by bombarding a mixed $^{248}Cm/^{152}Gd$ target with ^{18}O ions. With the on-line gas chemistry apparatus (OLGA), the retention behavior of volatile Rf- and Hf-chloride in a quartz chromatography column was investigated. The results showed that Rf forms chlorides of higher volatility than those of Hf, in agreement with relativistic calculations. In addition, the behavior of element 104 was investigated in chlorinating, oxygen containing carrier gas, in order to answer the question whether a volatile compound of the form $RfOCl_2$ exists. The results of our experiments give strong evidence for a transport reaction mechanism where $RfOCl_2$ exists only in the condensed phase and not in the gas phase. © 1998 Elsevier Science S.A.

Keywords: Relativistic effects; On-line gas chromatography; Rutherfordium; Halides; Oxyhalides

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1. Introduction

A central question concerning the chemistry of the heaviest elements is the influence of relativistic effects. Calculations of the electronic structure of heavy atoms showed, that relativistic effects, which increase proportionally with Z^2, are the reason for a strong energetic stabilization of s and p orbitals and their spatial contraction [see, e.g., Ref. [1] and references cited therein]. In contrast, the outer d and f orbitals are destabilized and spatially expanded. From relativistic molecular calculations, information about the bonding character, the stability of oxidation states and even thermodynamic properties such as the dissociation energy of a molecule were obtained [1]. These calculations showed, that the first transactinide elements Rf, Db and Sg are homologs of groups 4, 5 and 6. But, contrary to expectations on the basis of observed trends within the groups of the Periodic Table, unusual chemical properties have to be expected [1]. The experimental verification of the predicted relativistic effects is extremely difficult, since the transactinide elements can only be synthesized on an ‘‘atom-at-a-time’’ basis. In addition, even the longest lived known isotopes have half-lives of 1 min or shorter. Nevertheless, chemical studies of the first three transactinide elements Rf, Db and Sg have been performed in the gas phase as well as in the aqueous phase (see, e.g., Refs. [2,3] for review articles, [4,5]).

From relativistic calculations $RfCl_4$ is predicted to be more volatile than $HfCl_4$ [6–9], whereas from extrapolations of trends within the groups of the Periodic Table, exactly the opposite is expected [10,11]. In this special case, the predictions about the relative behavior of Rf and Hf can be directly verified experimentally. In a number of experiments, the volatility of Rf- and Hf-chlorides has already been studied. In the pioneering thermochromatography experiments of Zvara et al. [12], it was not possible to determine the relative volatility of Rf- and Hf-chlorides, since nuclides with grossly different half-lives were studied. Later, Türler et al. [13] and Kadkhodayan et al. [14] both established a higher volatility of Rf-chlorides compared to Hf-chlorides. However, Rf- and Hf-chlorides were studied in separate experiments where chemical conditions, especially the concentration of residual O_2, may have been different. As will be discussed in the

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[1] The element names recently approved by IUPAC are used.

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following, the concentration of O_2 plays an important role in the volatility behavior of group 4 halides.

We have therefore devised an experiment, in which ^{261}Rf and ^{165}Hf with nearly identical half-lives [14,15] were produced simultaneously on an ‘‘atom-at-a-time’’ basis. The corresponding halides were synthesized and their volatility with and without the presence of O_2 investigated.

2. Halides and oxyhalides of the group 4 elements

Vapor pressure curves give a good measure of the relative volatility of compounds. In Fig. 1, the vapor pressure curves of the monomeric gas over the respective solids for Zr and Hf tetrachlorides and -bromides are shown. The curves were calculated using tabulated standard sublimation enthalpies ($\Delta H_s^{0(298)}$) and standard sublimation entropies ($\Delta S_s^{0(298)}$) [16]. $HfCl_4$ and $HfBr_4$ are slightly more volatile than the Zr homologs. In isothermal adsorption chromatography experiments with transactinide elements, $\Delta H_s^{0(298)}$ of, e.g., $RfCl_4$ cannot be determined directly. Only the retention times of single molecules on the chromatographic surface (usually quartz) can be measured, using the half-life of the radioactive nuclide as a clock. By measuring the yield of a transactinide species at different isothermal column temperatures an integral chromatogram is obtained. From such measurements, the adsorption enthalpy ($\Delta H_a^{0(T)}$) of a molecule on the chromatographic surface can be determined. An estimate of $\Delta H_s^{0(298)}$ is obtained from an empirical linear correlation which exists between $\Delta H_a^{0(T)}$ and $\Delta H_s^{0(298)}$ for a number of chlorides [17].

The prediction of the volatility of transactinide halides from relativistic molecular orbital calculations is difficult. It appears from a large series of calculations [1,6–9], that the calculated effective charges on the central metal atom and the total overlap populations ($OP_{(tot)}$), which describe the ionizity and covalency of the metal–ligand bond, can be qualitatively correlated with the macroscopic volatility of a compound. For group 4 halides the higher calculated $OP_{(tot)}$ values of the 5d halides compared to the 4d ones correspond to their higher volatility. Therefore, $RfCl_4$ is a more covalent molecule than $HfCl_4$ and thus more volatile.

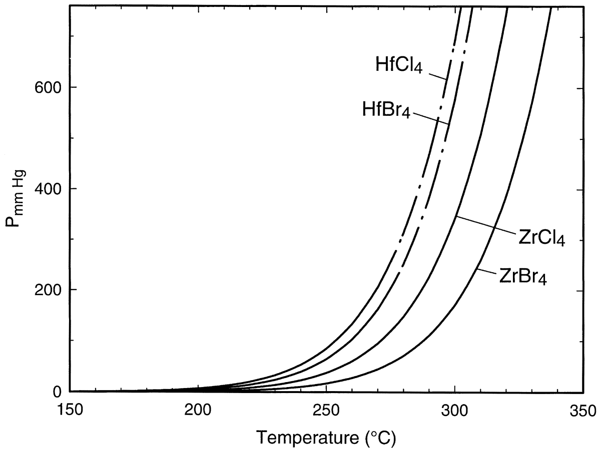

Fig. 1. Vapor pressure curves of the monomeric gas over the respective solids for $ZrCl_4$, $ZrBr_4$, $HfCl_4$ and $HfBr_4$.

Alternatively, the chemical properties of an unknown element and its compounds can be predicted by exploiting the fundamental relationships of the physico–chemical data of the elements and their compounds within the groups and the periods of the Periodic Table. In employing these trends, Eichler et al. [10,11] extrapolated $\Delta H_s^{0(298)}(RfCl_4)$ in two different ways. In a first approach, the ionic radius of the metal was correlated with the standard sublimation enthalpy of the tetrachlorides of Ti, Zr, Hf, Th and U. With a calculated orbital radius for 104^{4+} of 0.0706 nm [18] $\Delta H_s^{0(298)}(RfCl_4)=138$ kJ mol^{-1} resulted [10], considerably higher than the literature values of $\Delta H_s^{0(298)}(HfCl_4)=104.7$ kJ mol^{-1} [16] or $\Delta H_s^{0(298)}(ZrCl_4)=110.5$ kJ mol^{-1} [16]. In a second approach $\Delta H_s^{0(298)}(RfCl_4)$ was extrapolated as the difference of the standard formation enthalpies ($\Delta H_f^{0(298)}$) of the pure compounds in the gas- and solid phase. Generally, $\Delta H_f^{0(298)}$ of compounds of the same type within the same group correlate with the standard enthalpy of gaseous, monoatomic elements ($\Delta H^{0(298)} M_{(g)}$) of their respective elements. From these extrapolations $\Delta H_s^{0(298)}(RfCl_4)=122$ kJ mol^{-1} was estimated [11]. Again, a lower volatility resulted for $RfCl_4$ compared to $HfCl_4$ and $ZrCl_4$.

In the case of group 4 tetrachlorides, a clear experimental distinction between the relativistic predictions and the classical extrapolations of the chemical properties should be possible. If the relativistic calculations are correct, then $RfCl_4$ is more volatile than $HfCl_4$, whereas if the relativistic effects are much weaker than predicted, then $RfCl_4$ is less volatile than $HfCl_4$.

An experimental difficulty may be the presence of O_2. Domanov et al. [19] observed that in thermochromatography experiments the deposition temperature of Zr and Hf increased with higher partial pressures of O_2 in the reactive gas mixture. Not much is known about the ability of the group 4 elements to form oxyhalides. Morozov et al. [20] found that $ZrOCl_2$ and $HfOCl_2$ decompose to the tetrachloride and the oxide when heated and determined the vapor pressure curves of the tetrachlorides over their oxychlorides. In contrast to the group 5 oxychlorides, the oxychlorides of group 4 elements are expected to be less stable than the pure tetrachlorides and it is uncertain whether compounds such as $ZrOCl_2$ or $HfOCl_2$ exist in the gas phase. Therefore, not only the simple reversible adsorption of a stable molecule on the chromatographic surface, but also the possibility of a transport reaction mechanism should be considered in the interpretation of gas chromatography experiments [21]. The two possible processes can be written as:

$$MCl_{4(g)} \Leftrightarrow MCl_{4(ads)} \quad (1)$$

$$MCl_{4(g)} + \tfrac{1}{2}O_{2(g)} \Leftrightarrow MOCl_{2(ads)} + Cl_{2(g)}. \quad (2)$$

For reactions of type 2 the transit time of a molecule through a chromatographic column depends not only on the volatility of the pure chloride, but also on the oxygen concentration in the chlorinating carrier gas. Such a dependence has been experimentally observed by Gärtner et al. [22] in isothermal chromatography experiments with ^{165}Hf using chlorinating carrier gases and varying concentrations of O_2.

3. Experimental

The nuclides ^{261}Rf and ^{165}Hf were synthesized in the reactions ^{248}Cm/^{152}Gd(^{18}O, 5n)^{261}Rf/^{165}Hf by irradiating a 1.01 mg cm^{-2} ^{248}Cm target containing approximately 0.2 mg cm^{-2} Gd (about 30% enriched in ^{152}Gd) with a 99 MeV ^{18}O beam (typically 0.5–0.7 particle μA) at the vertical beam line of the U400 cyclotron at FLNR in Dubna, Russia. The PSI gas-jet target chamber was used for all irradiations [23]. The target was prepared by electrodeposition of the Cm material on 10 μm thick Be foil. The OLGA setup (Fig. 2) was installed at the so-called KHIPTI site in close vicinity of the vertical beam line. In the target chamber, the recoiling reaction products were thermalized in helium loaded with carbon aerosols and, attached to the surface of the aerosols, continuously transported through a capillary (5 m long, 2 mm I.D.) to the OLGA setup. In the first section of the chromatography column, the reaction products were stopped on a quartz wool plug heated to 900–1000°C where the reactive gases were added. In experiments to study the volatility of the tetrachlorides 200–300 ml min^{-1} HCl was added. Traces of O_2 were removed by means of an activated charcoal getter system operated at 1000°C. In addition, graphite strips dipped in $SOCl_2$, were introduced into the hot zone. In experiments to study the influence of O_2, a mixture of 150 ml min^{-1} Cl_2 saturated with $SOCl_2$ and 20 ml min^{-1} O_2 was used. The second part of the column (1.9 m long, 1 mm I.D.) served as the isothermal chromatography section. Volatile species were transported along the cooler section of the column by the carrier gas flow. Volatile products leaving the column through the tip were reattached to CsCl aerosol particles in the so-called recluster chamber for transport to the detection system. Here, the activity was deposited at the collection site on a magnetic tape and subsequently stepped in front of several PIPS detectors, where α-particles and SF decays were registered in an event-by-event mode. A HPGe-detector positioned at detector chamber 2 was used to measure the characteristic γ-rays following the ^{165}Hf EC decay.

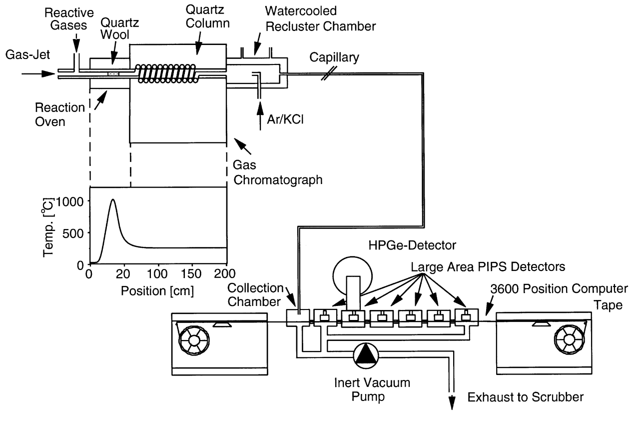

Fig. 2. Schematic diagram of OLGA III with the PSI tape detection system.

4. Results and discussion

The sum of all α-spectra from detectors 1–5 from all tetrachloride chromatography experiments is depicted in Fig. 3. The spectrum is dominated by α-lines from the contaminants ^{211}Bi, ^{211m,212m}Po and ^{214}Po (decay of ^{214}Bi), which also form volatile chlorides. The α-particle group in the range from 8.05–8.45 MeV was assigned to ^{261}Rf ($T_{\frac{1}{2}} = 78$ s) [14] and its daughter ^{257}No ($T_{\frac{1}{2}} = 26$ s) [24]. The assignment is corroborated by the decay of this event group (insert in Fig. 3). The measured decay data agrees well with the calculated growth and decay curve, using literature half-lives [14,24] and assuming that the initial activity of the ^{257}No daughter nuclide was due to ingrowth during the 45 s collection time.

In Fig. 4 the measured yields of the 8.05–8.45 MeV

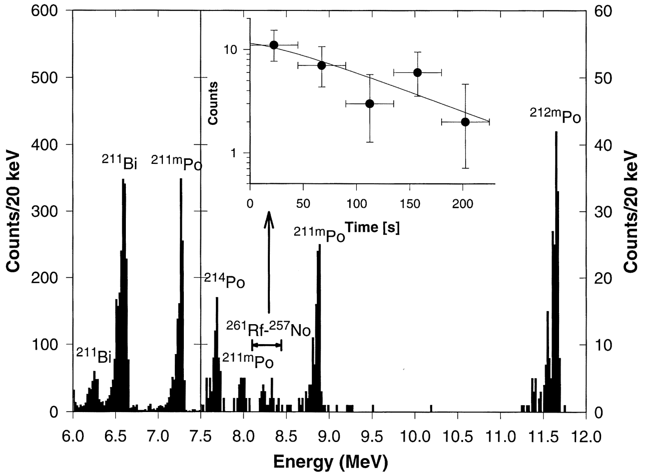

Fig. 3. Sum of α-spectra from detectors 1–5 from all tetrachloride chromatography experiments. The decay of the 8.05–8.45 MeV α-particle group, which is attributed to the decay of ^{261}Rf and its daughter ^{257}No, is shown in an insert of the figure. The line through the data points corresponds to a calculated decay curve (see text for details).

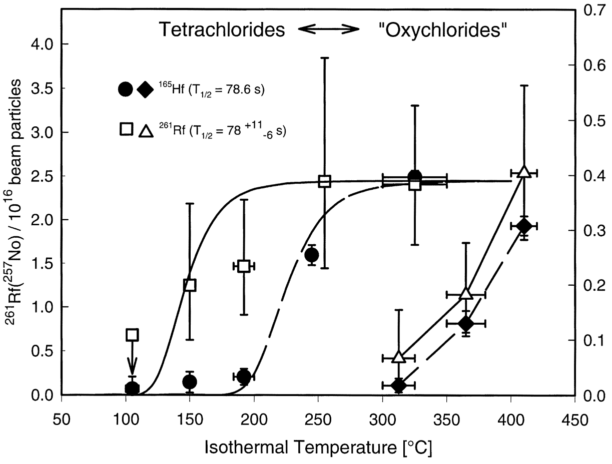

Fig. 4. Yields observed for ^{261}Rf (□) and ^{165}Hf (●) with 200–300 ml min^{-1} HCl, purified from traces of O_2, as reactive gas, and, yields of ^{261}Rf (Δ) and ^{165}Hf (♦) with 150 ml min^{-1} Cl_2, saturated with $SOCl_2$, and 20 ml min^{-1} O_2 as reactive gas, are shown as a function of the isothermal oven temperature. The lines through the data points (□,●) are calculated yield curves from a Monte Carlo simulation procedure.

α-particle group (□) and of the 180 keV γ-ray of ^{165}Hf (●) are shown as a function of the isothermal temperature of OLGA. Already at isothermal temperatures of 150°C, Rf forms volatile chlorides with HCl as reactive gas, whereas Hf becomes volatile only above 200°C. Since both nuclides have nearly identical half-lives, it can be stated without further analyses (e.g., evaluation of $\Delta H_a^{0(T)}$), that Rf forms more volatile chloride species than does Hf under exactly the same experimental conditions. Since great efforts were taken to eliminate O_2 from the system, the volatile species are attributed to $RfCl_4$ and $HfCl_4$, respectively. The lines through the data points are calculated yield curves from a Monte Carlo simulation procedure [2]. Our results are in very good agreement with the data of Kadkhodayan et al. [14], where Rf-chlorides were also volatile at 150°C, whereas Hf-chlorides were volatile only above 200°C.

In a second experiment oxygen was introduced into the system. The measured yields of the 8.05–8.45 MeV α-particle group (Δ) and of the simultaneously measured 180 keV γ-ray of ^{165}Hf (♦) are also shown in Fig. 4. Runs with similar isothermal temperatures were combined in one data point. The addition of O_2 induces a dramatic shift in volatility of Rf and Hf to about 200°C higher temperatures. The yields reached for ^{261}Rf and ^{165}Hf at 410 ± 10°C isothermal temperature are comparable with the yields with HCl as reactive gas. But clearly, the observed species cannot be the same as in the experiments with HCl. Since $HfOCl_2$ is not stable in the gas phase, we attribute the observed behavior to the proposed transport reaction mechanism (Eq. (2)), which appears to be also valid for $M=Rf$.

In conclusion, our experiments showed that under exactly the same experimental conditions, with HCl purified from O_2 as chlorinating gas, $RfCl_4$ is more volatile than the homolog $HfCl_4$. This result is positive evidence for the presence of relativistic effects in the chemistry of the transactinides, as they were predicted consistently and independently by various relativistic calculations [6–9]. Extrapolations of chemical properties from periodic trends can account only for relativistic effects as far as they are present in the lighter homologs. Clearly, the influence of relativistic effects was underestimated in this case.

In addition, the influence of O_2 on the volatility of Hf- and Rf-chlorides was investigated. The addition of O_2 led to a lower volatility of both, Hf and Rf. Nevertheless, Rf and Hf were still volatile above 400°C under the conditions of the experiment. The observed behavior was explained by a transport reaction mechanism, where the observed volatility is determined by the O_2 partial pressure.

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References

[1] V.G. Pershina, Chem. Rev. 96 (1996) 1977.
[2] A. Türler, Radiochim. Acta 72 (1996) 7.
[3] M. Schädel, Radiochim. Acta 70–71 (1996) 207.
[4] A.B. Yakushev, S.N. Timokhin, M.V. Vedeneev, X. Honggui, I. Zvara, J. Radioanal. Nucl. Chem. Articles 205 (1996) 63.
[5] M. Schädel, W. Brüchle, R. Dressler, B. Eichler, H.W. Gäggeler, R. Günther, K.E. Gregorich, D.C. Hoffman, S. Hübener, D.T. Jost, J.V. Kratz, W. Paulus, D. Schumann, S. Timokhin, N. Trautmann, A. Türler, G. Wirth, A. Yakushev, Nature 388 (1997) 55.
[6] B.L. Zhuikov, V.A. Glebov, V.S. Nefedov, I. Zvara, J. Radioanal. Nucl. Chem. 143 (1990) 103.
[7] M.V. Ryzhkov, V.A. Gubanov, I. Zvara, Radiochim. Acta 57 (1992) 11.
[8] V. Pershina, B. Fricke, J. Phys. Chem. 98 (1994) 6468.
[9] V.A. Glebov, V.S. Nefedov, B.L. Zhuikov, Extended Abstracts, in: J.C. Krupa (Ed.), 4th International Conference on Nuclear and Radiochemistry, Vol. I, 1996, A-P27.
[10] B. Eichler, A. Türler, H.W. Gäggeler, Paul Scherrer Institute Annual Report 1994, Annex 3A (1995) 76.
[11] B. Eichler, A. Türler, H.W. Gäggeler, Paul Scherrer Institute Annual Report 1994, Annex IIIA (1995) 77.
[12] I. Zvara, V.Z. Belov, L.P. Chelnokov, V.P. Domanov, M. Hussonois, Yu.S. Korotkin, V.A. Schegolev, M.R. Shalaevsky, Inorg. Nucl. Chem. Lett. 7 (1971) 1109.
[13] A. Türler, H.W. Gäggeler, K.E. Gregorich, H. Barth, W. Brüchle, K.R. Czerwinski, M.K. Gober, N.J. Hannink, R.A. Henderson, D.C. Hoffman, D. T Jost, C.D. Kacher, B. Kadkhodayan, J. Kovacs, J.V. Kratz, S.A. Kreek, D.M. Lee, J.D. Leyba, M.J. Nurmia, M. Schädel,

U.W. Scherer, E. Schimpf, D. Vermeulen, A. Weber, H.P. Zimmermann, I. Zvara, J. Radioanal. Nucl. Chem. 160 (1992) 327.

[14] B. Kadkhodayan, A. Türler, K.E. Gregorich, P.A. Baisden, K.R. Czerwinski, B. Eichler, H.W. Gäggeler, T.M. Hamilton, D.T. Jost, C.D. Kacher, A. Kovacs, S.A. Kreek, M.R. Lane, M.F. Mohar, M.P. Neu, N.J. Stoyer, E.R. Sylwester, D.M. Lee, M.J. Nurmia, G.T. Seaborg, D.C. Hoffman, Radiochim. Acta 72 (1996) 169.

[15] D. Schumann, R. Dressler, S. Fischer, S. Taut, R. Binder, Z. Szeglowski, B. Kubica, L.I. Guseva, G.S. Tikhomirova, O. Constantinescu, V.P. Domanov, M. Constantinescu, D.T. Lien, Y.T. Oganessian, V.B. Brudanin, H. Bruchertseifer, Radiochim. Acta 69 (1995) 35.

[16] O. Knacke, O. Kubaschewski, K. Hesselmann (Eds.), Thermochemical Properties of Inorganic Substances II, Springer Verlag, Berlin, 1991.

[17] B. Eichler, V.P. Domanov, I. Zvara, Report JINR, Dubna, P12-9454, 1976.

[18] E. Johnson, B. Fricke, O.L. Keller Jr., C.W. Nestor Jr., T.C. Tucker, J. Chem. Phys. 93 (1990) 8041.

[19] V.P. Domanov, K.U. Zin, Radiokhimiya 31 (1989) 19.

[20] A.I. Morozov, E.V. Karlova, Russ. J. Inorg. Chem. 16 (1971) 12.

[21] B. Eichler, Radiochim. Acta 72 (1996) 19.

[22] M. Gärtner, M. Boettger, B. Eichler, H.W. Gäggeler, M. Grantz, S. Hübener, D.T. Jost, D. Piguet, R. Dressler, A. Türler, A.B. Yakushev, Radiochim. Acta. 78 (1997) 59.

[23] D. Piguet, A. Türler, D.T. Jost, Paul Scherrer Institute Annual Report 1994, Annex IIIA (1995) 86.

[24] K. Eskola, M. Nurmia, A. Ghiorso, P. Eskola, Phys. Rev. C 2 (1970) 1058.