First Measurement of a Thermochemical Property of a Seaborgium Compound**

Andreas Türler,* Willy Brüchle, Rugard Dressler, Bernd Eichler, Robert Eichler, Heinz W. Gäggeler, Markus Gärtner, Jean-P. Glatz, Kenneth E. Gregorich,* Siegfried Hübener,* Dieter T. Jost, Vyacheslav Ya. Lebedev, Valeria G. Pershina, Matthias Schädel,* Steffen Taut, Sergeij N. Timokhin, Norbert Trautmann, Annett Vahle, and Alexander B. Yakushev*

The periodic table currently contains 112 elements. Until now, element 106, recently named seaborgium (Sg),[1] is the heaviest element whose chemical properties have been studied experimentally.[2] Seaborgium behaved like a typical member of Group 6 of the periodic table—that is, similar to Mo and W–-in group-specific separation procedures developed for the gas and the aqueous phase. This result is not trivial, since earlier studies of the first two transactinide elements rutherfordium[1] (Rf, element 104) and dubnium[1] (Db, element 105) revealed some unexpected chemical properties, which were attributed to the influence of relativistic effects.[3a,b] Owing to the increasingly large nuclear charge of very heavy elements, the binding energies of both the inner and the valence s and $p_{1/2}$ electrons increase and their orbital radii contract. The increased screening of the nuclear charge causes an energetic destabilization and a radial expansion of the outer d and f orbitals. Clearly, not only will the atomic properties of the heaviest elements be affected, but so will the chemistry of these elements in general.[4]

The difficulties in studying the chemistry of the heaviest elements lie in their short half-lives and their extremely low production rates. Chemical studies can only be performed on a "one atom at a time" scale. The nuclide ^{265}Sg with a half-life of $7.4^{+3.3}_{-2.7}$ s was synthesized in the reaction ^{248}Cm(^{22}Ne,5n)^{265}Sg at a rate of about three atoms per hour at the UNILAC accelerator of the Gesellschaft für Schwerionenforschung (GSI).[5] Despite these constraints, it was possible to isolate Sg, most probably in the form of volatile SgO_2Cl_2, using on-line gas chromatography and to determine the first thermochemical property of this Sg compound, namely, its adsorption enthalpy (ΔH_a) on the stationary phase (fused silica, dynamically modified by the reactive components of the carrier gas).

Nuclear reaction products, recoiling from the thin ^{248}Cm target because of the momentum transferred from the ^{22}Ne projectile, were stopped in He gas loaded with carbon aerosols. After a short diffusion time the reaction products adsorbed onto the suface of the aerosols, and were thus continuously transported through a thin capillary to the on-line gas chromatography apparatus (OLGA).[3a] The aerosols carrying the reaction products were collected on quartz wool inside the reaction oven kept at 1000 °C. Reactive gases—Cl_2 saturated with $SOCl_2$ and traces of O_2—were introduced in order to form volatile oxychlorides. Simultaneously, the carbon aerosols were converted into CO_2. The chromatographic separation took place downstream in the adjoining isothermal section of the column. At temperatures of 300 °C and above Group 6 oxychloride molecules travel through the column essentially without delay, while less volatile compounds are retained much longer. Thus, most of the nuclides interfering with the detection of ^{265}Sg decay in the column. The fraction of molecules that is detected at the exit depends thus on the retention time of the molecule in the column and the half-life of the nuclide. By measurement of the yields at different isothermal temperatures, the retention times and thus ΔH_a can be determined. Sophisticated counting equipment was used to unambiguously detect the α-particle decay of ^{265}Sg and its daughter nuclides ^{261}Rf and ^{257}No. A detailed description of the experiment parameters is given elsewhere.[3a, 5]

Two series of experiments were carried out at GSI. In the first series, the nuclide ^{265}Sg was unambiguously identified after chemical separation by the observation of its α-decay chains at isothermal temperatures of 300 and 400 °C in the OLGA setup.[2] These temperatures allowed a rapid passage of the Sg compound. In a second experiment at 350 °C isothermal temperature, the results of the first experiment were confirmed by observing further ^{265}Sg α-decay chains.[5] Without changing any of the other experimental parameters, the isothermal temperature was then lowered to 250 °C and the yield of ^{265}Sg was measured with a comparable sensitivity

---

[*] Dr. A. Türler, Dr. R. Dressler, Prof. B. Eichler, R. Eichler, Prof. H. W. Gäggeler, M. Gärtner, Dr. D. T. Jost
Labor für Radio- und Umweltchemie, Paul-Scherrer-Institut
CH-5232 Villigen PSI (Switzerland)
and
Departement für Chemie- und Biochemie der Universität
Freiestrasse 3, CH-3012 Bern (Switzerland)
Fax: (+41) 56-310-44-35
E-mail: Andreas.Tuerler@psi.ch

Dr. K. E. Gregorich
Lawrence Berkeley National Laboratory
Berkeley, CA94720 (USA)

Dr. S. Hübener, Dr. S. Taut, Dr. A. Vahle
Institut für Radiochemie, Forschungszentrum Rossendorf
D-01314 Dresden (Germany)

Dr. M. Schädel, Dr. W. Brüchle, Dr. V. G. Pershina
Gesellschaft für Schwerionenforschung mbH
Planckstrasse 1, D-64291 Darmstadt (Germany)

Dr. A. B. Yakushev, Dr. V. Ya. Lebedev, Dr. S. N. Timokhin
Flerov Laboratory of Nuclear Reactions
Joint Institute for Nuclear Research, Dubna (Russia)

Dr. J.-P. Glatz
European Commission, Directorate General JRC
Institute for Transuranium Elements
D-76125 Karlsruhe (Germany)

Dr. N. Trautmann
Institut für Kernchemie der Universität
D-55099 Mainz (Germany)

[**] We are indebted to the Division of Chemical Sciences, Office of Basic Energy Research, US Department of Energy, for making the ^{248}Cm target material available through the transplutonium element production program at the Oak Ridge National Laboratory. The support from the European Commission Institute for Transuranium Elements, Karlsruhe, for long-term storage of ^{252}Cf and the chemical separation of ^{248}Cm is highly appreciated. We thank the staff of the Kernchemie at Universität Mainz for preparing one of the targets. We also thank the staff and crew of the GSI UNILAC for providing intense beams of ^{22}Ne and for providing their help. This work was supported in part by the Swiss National Science Foundation, the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie (BMBF), and the Chemical Sciences Division of the Office of Basic Energy Sciences, US Department of Energy.

1433-7851/99/3815-2212 $ 17.50+.50/0

as at higher isothermal temperatures. To assure that the experimental setup performed as expected, the nuclide ^{168}W was simultaneously produced from a small ^{152}Gd admixture to the ^{248}Cm target material, and its yield was monitored.

In Figure 1, the relative yields measured for oxychlorides of short-lived Mo, W, and Sg nuclides are shown as a function of isothermal temperature. The yield curve for ^{168}W was measured with the same chromatography column and under the same experimental conditions as for the isolation of Sg, whereas the yield curve for ^{104}Mo was determined in an earlier measurement.[6] The solid lines show the results of a Monte Carlo simulation where the migration of a molecule through the chromatography column has been modeled, the only free parameter being ΔH_a.[7] As discussed in previous publications, thermodynamic calculations indicate that Mo and W were separated most probably in the form of the dioxydichloride.[6, 8]

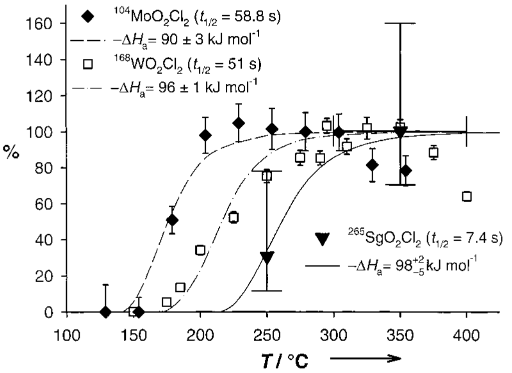

Figure 1. Relative yield y_{rel} of MO_2Cl_2 (M = Mo, W, Sg) as a function of isothermal temperature in the chromatography column.

Ten decay chains were attributed to the decay of ^{265}Sg in experiments at isothermal temperatures between 300 and 400 °C.[5] Since at all temperatures of 300, 350, and 400 °C decay chains of ^{265}Sg were observed, which, within the error limits, yielded about the same production rate (i.e., the Sg compound passed the column without significant losses by nuclear decay), the data from all three measurements are summarized in one data point at 350 °C in Figure 1. In the experiment at 250 °C, three decay chains were attributed to ^{265}Sg, corresponding to a relative chemical yield of 30^{+47}_{-18} %. For the simultaneously produced ^{168}W an average relative yield of 47 ± 3 % was observed at 250 °C as compared to the result at 350 °C, which is in agreement with previous measurements. The lower yield of Sg at 250 °C as compared to 350 ± 50 °C is therefore due to a considerably longer retention time at 250 °C. Owing to the relatively large error bars on both Sg data points, which are even slightly overlapping, a careful statistical analysis was performed, which resulted in a most probable value of $-\Delta H_a(SgO_2Cl_2) = 98^{+2}_{-5}$ kJ mol^{-1} (68 % error interval). For WO_2Cl_2 $-\Delta H_a(WO_2Cl_2) = 96 \pm 1$ kJ mol^{-1} was deduced, whereas for MoO_2Cl_2 $-\Delta H_a(MoO_2Cl_2) = 90 \pm 3$ kJ mol^{-1} resulted. The larger error limits for MoO_2Cl_2 include systematic uncertainties due to the fact that Mo was investigated in an earlier study under slightly different experimental conditions.[6] The sequence in volatility of MO_2Cl_2 (M = Mo, W, Sg) on the stationary phase is $MoO_2Cl_2 > WO_2Cl_2 \approx SgO_2Cl_2$. The probability that SgO_2Cl_2 is equally or even more volatile than MoO_2Cl_2 was estimated to be less than 15 %.

The experimentally determined ΔH_a values, measured with trace amounts (at zero surface coverage), can be directly correlated with their macroscopic sublimation enthalpies ΔH_s. With an empirically derived linear correlation between ΔH_a and ΔH_s (Figure 2), determined from the measurement of 30 chlorides and oxychlorides on fused silica surface, it is possible to directly estimate $\Delta H_s(SgO_2Cl_2) = 127^{+10}_{-21}$ kJ mol^{-1} from only a few investigated molecules. $\Delta H_s(SgO_2Cl_2)$ is a very important quantity in order to estimate, for example, ΔH_S(Sg). Seaborgium is expected to have an equal or even higher sublimation enthalpy than W, the least volatile element in the periodic table.[9]

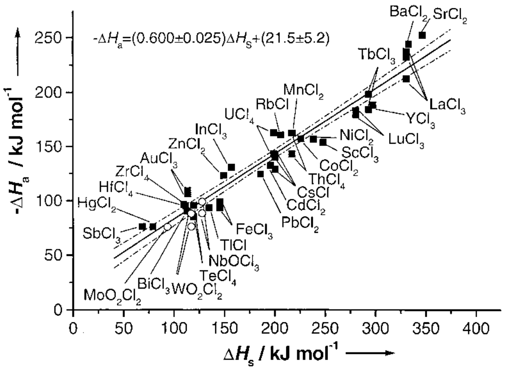

Figure 2. Empirical correlation between the macroscopic sublimation enthalpy ΔH_s and the corresponding adsorption enthalpy ΔH_a of single chloride (■) and oxychloride molecules (○) on fused silica surface.

Received: February 3, 1999 [Z12993IE]
German version: *Angew. Chem.* **1999**, *111*, 2349–2351

Keywords: gas chromatography · gas-phase chemistry · seaborgium · thermochemistry · transuranium elements

---

[1] International Union of Pure and Applied Chemistry, Inorganic Chemistry Division, Commission on Nomenclature of Inorganic Chemistry, *Pure Appl. Chem.* **1997**, *69*, 2471–2473.

[2] 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* **1997**, *388*, 55–57.

[3] a) A. Türler, *Radiochim. Acta* **1996**, *72*, 7–17; b) M. Schädel, *Radiochim. Acta* **1996**, *70/71*, 207–223.

[4] V. G. Pershina, *Chem. Rev.* **1996**, *96*, 1977–2010.

[5] A. Türler, R. Dressler, B. Eichler, H. W. Gäggeler, D. T. Jost, M. Schädel, W. Brüchle, K. E. Gregorich, N. Trautmann, S. Taut, *Phys. Rev. C* **1998**, *57*, 1648–1655.

[6] 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* **1997**, *78*, 59–68.

[7] I. Zvara, *Radiochim. Acta* **1985**, *38*, 95–101.

[8] V. Pershina, B. Fricke, *J. Phys. Chem.* **1996** *100*, 8748–8751.

[9] B. Eichler, *Kernenergie* **1976**, *10*, 307–311.

1433-7851/99/3815-2213 $ 17.50+.50/0