Chemical Characterization of a Volatile Dubnium Compound, DbOCl₃

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Abstract: The formation and the chemical characterization of single atoms of dubnium (Db, element 105), in the form of its volatile oxychloride, was investigated using the on-line gas phase chromatography technique, in the temperature range 350–600°C. Under the exactly same chemical conditions, comparative studies with the lighter homologues of Group 5 in the Periodic Table clearly indicate the volatility sequence being $NbOCl_3 > TaOCl_3 \geq DbOCl_3$. From the obtained experimental results, thermochemical data for $DbOCl_3$ were derived. The present study delivers reliable experimental information for theoretical calculations on chemical properties of transactinides.

Despite over 150 years of research since D.I. Mendeleev proposed it in 1869, the Periodic Table still represents a challenge for chemists and physicists. Whereas strong focus is currently on the expansion towards the eighth row, an equally demanding effort is put into the discovery of the chemical properties of the existing heaviest elements.[1] In the last decades, fifteen new elements with atomic number Z above 103 have been synthesized and placed in the seventh row of the Periodic Table. This series of elements is usually called the transactinide series or, simply put, superheavy elements. Theoretical calculations predict that the greater is the nuclear charge of an atom, the stronger is the influence of relativistic effects on its valence orbitals.[2–4] These effects comprise a contraction of the s and $p_{1/2}$ shells, with a consequent expansion and energetic destabilization of the $p_{3/2}$, d, and f orbitals. Approximately, relativistic effects increase as Z^2, but it was also suggested that they depend even on higher powers of Z.[5] Since the chemical behavior of an element is governed by the distribution of the electrons in the atomic orbitals, relativistic effects can render the transactinides chemically different from their lighter homologues in the Periodic Table. An estimation of the chemical properties of superheavy elements can be performed by applying advanced quantum chemical methods, and by extrapolations from trends based on the Periodic Law.[6] However, to confirm (or disprove) such predictions, the direct investigation of the chemical properties of the transactinides and their compounds is highly desirable. Chemical experiments with superheavy elements are very demanding. Major challenges arise from the short half-lives of their accessible isotopes, and from their artificial production at extremely low rates in heavy-ion induced nuclear fusion reactions. Even with state-of-the-art technologies, it is currently possible to study the transactinides only at the "one atom at a time" scale.[6,7] As the quantities of the investigated radionuclides are at the sub-trace level (that is, at amounts ranging from 10^{-17} moles down to 10^{-23} moles, that is, just few atoms per experiment), a fast and highly sensitive technique is required. In such ultra-diluted conditions, the activities in the law of mass action are replaced by probabilities of finding the studied species in a given state and in a given phase. It follows that for single atom chemistry, the studied species must be subjected to a repetitive partition experiment to ensure a statistically significant behavior.[8] Thus, gas chromatography is the preferred experimental method, since it is essentially

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a dynamic partition experiment in which the column surface plays the role of one of the two phases, and it is the fastest available technique for studying nuclides with half-lives in the range of few seconds.[9,10] Difficulties in performing such chemical experiments are substantial. In fact, for example, after more than 50 years since the discovery of dubnium (Db, $Z = 105$), an unambiguous statement on the volatility of this transactinide and its compounds is (in comparison to its homologues) still missing. With an expected $[Rn]5f^{14}6d^37s^2$ ground state configuration, Db is placed among Group 5 elements, together with vanadium (V, $Z = 23$), niobium (Nb, $Z = 41$), and tantalum (Ta, $Z = 73$). The predicted electronic configuration suggests for Db a maximum oxidation state $+5$,[11] and, as its lighter homologues, it should form stable (penta)halides and oxyhalides.[2,6] The higher volatility of these species, when compared to, for example, Group 5 oxides, is instrumental for the required ultrafast experiments in the gas-phase. Due to the technical difficulties in handling fluorinated gaseous environments, former gas chromatography studies were mainly focused on the synthesis and on the chemical characterization of chlorides and bromides of Db: both species are more volatile than the corresponding oxychlorides and oxybromides.[6,10,12] However, with this approach discordant results were obtained, mostly due to: 1) the simultaneous (and unintentional) formation of halides and oxyhalides (for example, $DbBr_5/DbOBr_3$, $DbCl_5/DbOCl_3$) with unavoidable traces of oxygen and water in the carrier gas; and 2) the alteration of the chromatographic surface by material introduced from aerosol particles used to transport the radionuclides of interest from the production site to the chemical apparatus. In this work, the strong tendency of Group 5 elements to form oxyhalide compounds was exploited, and an on-line isothermal gas-chromatographic (IGC) setup (see Figure 1), exclusively devoted to synthesize and to study the chemical interaction of oxychloride species with quartz surfaces, was developed at the Japan Atomic Energy Agency (JAEA).[13] As in former

studies with halides and oxyhalides of Group 5 elements, quartz was chosen as chromatographic surface due to its thermal and chemical stability. The synthesis of oxychloride compounds was preferred over the oxybromide ones due to their expected higher volatility.[14]

Two different series of gas-phase experiments with the IGC setup were carried out at the JAEA Tandem Accelerator. The first series concerned model experiments with single atoms of Nb and Ta in the chemical state of oxychlorides.[15] The thermodynamic quantities obtained in those model studies were in good agreement with tabulated thermochemical values, bolstering the suggested speciation (that is, the oxy(tri)chlorides $NbOCl_3$ and $TaOCl_3$) at the given experimental conditions. The second series of experiments, described in this study, regarded the gas-phase investigation of Db oxychloride under the exactly same chemical conditions as its lighter homologues. For this purpose, the isotope ^{262}Db with a half-life ($t_{1/2}$) of 34 s was synthesized in the nuclear fusion-evaporation reaction $^{248}Cm(^{19}F, 5n)^{262}Db$. The produced ^{262}Db atoms, recoiling from the target owing to the momentum transferred from the projectile, were thermalized by an inert carrier gas (He:N₂ mixture) and directly injected into the reaction region of a quartz column, which was held at 1000°C. Oxychloride compounds were formed in situ by addition of thionylchloride vapors ($SOCl_2$) containing a fixed amount of O₂.[13] The synthesized oxychlorides were subsequently transported downstream by the gas flow to the isothermal chromatographic section of the column. Here, the molecules interacted with the chromatographic surface in numerous adsorption–desorption steps, with retention times indicative of the strength of their interaction with the surface. Systematic isothermal gas chromatography experiments were performed, in the temperature range 350–600°C. In significant contrast to previous works, in none of the above-mentioned stages aerosol materials were introduced. Only after the oxychloride compounds exited the chromatographic column, they were attached to KCl aerosol particles and transported to the measurement system. For the detection of ^{262}Db and its daughter ^{258}Lr,[16] the IGC setup was connected to the MANON (measurement system for alpha particle and spontaneous fission events on-line) apparatus.[17] By determining the yields of $DbOCl_3$ at the applied isothermal temperatures, the external chromatogram was obtained. Established statistical analysis methods together with a Monte-Carlo approach for gas phase chromatography,[18,19] were used. Further details are given in the Supporting Information. Throughout the entire experiment, 24 timely correlated α-decay chains attributed to the decay $^{262}Db \rightarrow$ $^{258}Lr \rightarrow ^{254}Md$ were detected. The observed event chains represent true correlations of consecutive α-decays of ^{262}Db and ^{258}Lr, since the expected number of random correlations at each isothermal temperature was calculated being lower than 0.4 (see the Supporting Information for details). The chromatographic results for $DbOCl_3$ are presented in Figure 2. The external chromatograms of $NbOCl_3$ and $TaOCl_3$ obtained with the IGC setup are depicted as well. From the similarity of the shapes of the yield curves in Figure 2, it can be deduced that, as in the case of $NbOCl_3$ and $TaOCl_3$, only one chemical species of Db was formed and
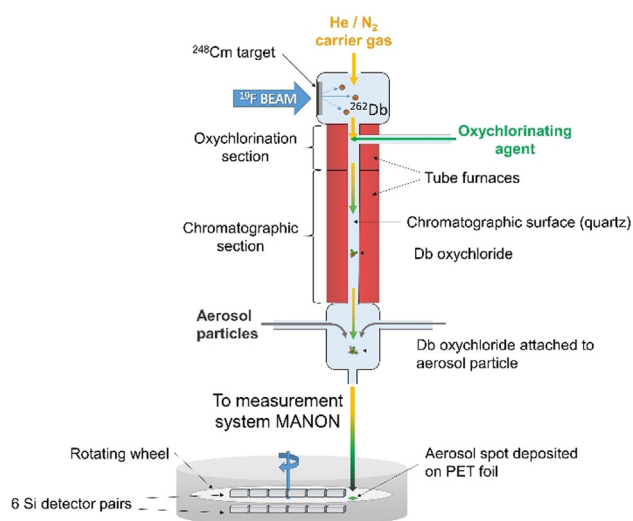
Figure 1. Representation of the isothermal gas-chromatographic (IGC) setup coupled to the α-detection system MANON used for the chemical investigation of the Db oxychloride.
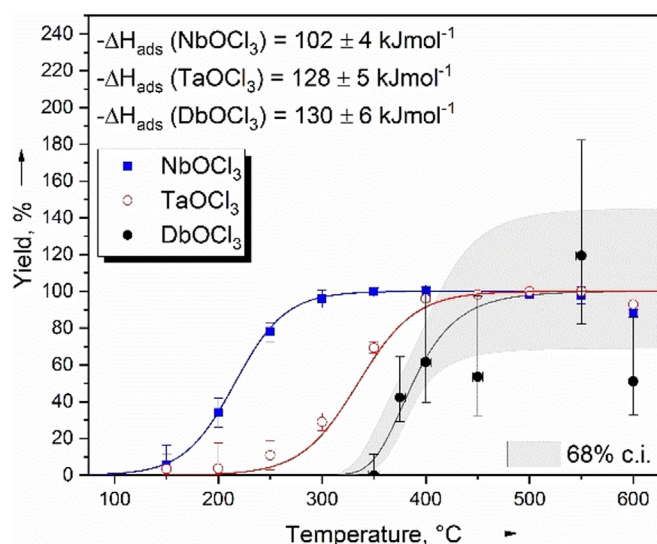
Figure 2. Comparative external chromatograms for $NbOCl_3$, $TaOCl_3$, and $DbOCl_3$. The gray area represents the 68% confidence interval (c.i.) of the $DbOCl_3$ yield.

transported to the measurement system. The clear speciation of the lighter homologues in the identical chemical system[15] supports the assignment of the observed Db species to $DbOCl_3$. The suggested speciation is also endorsed by 4c-DFT (relativistic density functional theory) and DS DVM (Dirac-Slater discrete variational method) calculations, that indicate (among the oxyhalides with Db in the $+5$ oxidation state) the stoichiometry $DbOX_3$ ($X = Cl$ or Br) as the most stable one.[20,21] Monte-Carlo simulations, based on a microscopic adsorption-desorption kinetic model,[18,19] allow for the reproduction of the experimental chromatograms. For each simulation, all the experimental conditions, the half-live of the studied radionuclides, as well the physical data of the gas and solid phase are used as an input, leaving the standard adsorption enthalpy ΔH_{ads} as the only free parameter. This quantity, independent of physical and experimental conditions, expresses the interaction energy between the investigated chemical species and the stationary chromatographic surface at zero surface coverage. The simulated chromatogram that best fits the experimental one (see solid lines in Figure 2) gives the ΔH_{ads} of the species of interest on the chromatographic surface. A thorough analysis of the external chromatogram of single molecules of $DbOCl_3$ (details in the Supporting Information) revealed an adsorption enthalpy of $-\Delta H_{ads}(DbOCl_3) = 130 \pm 6$ kJmol^{-1} (68% c.i.). This value differs significantly from the literature value $-\Delta H_{ads}$-$(DbOCl_3) = 117 \pm 3$ kJmol^{-1}.[22] However, the latter was deduced from a double-stepped yield curve due to the simultaneous presence of $DbCl_5$ and $DbOCl_3$ in the system, which complicated the data evaluation. Furthermore, in that work, an experimental temperature limitation to maximum 350°C did not allow for obtaining any information about the chemical behavior of $DbOCl_3$ at higher temperatures.

Here, the thermochemical information for $NbOCl_3$, $TaOCl_3$, and $DbOCl_3$ was obtained under identical experimental conditions, and thus, no additional inferences influ-

encing the data evaluation are drawn. To deduce the relative volatility of each compound, it is necessary to relate the microscopic ΔH_{ads} to the macroscopic standard sublimation enthalpy, ΔH_{subl}. ΔH_{ads} can be expressed as the sum of two independent terms: the net adsorption enthalpy (that is, the difference in enthalpy between the pure solid compound and its adsorbed state at zero surface coverage) and the desublimation enthalpy (that is, the reverse of sublimation). Whereas the net adsorption enthalpy depends on the nature of adsorbate and adsorbent, the desublimation enthalpy is an exclusive property of the adsorbate. Hence, ΔH_{ads} is proportional to ΔH_{sub}. The magnitude of this proportion is established by empirical correlations.[23] For metal-oxychlorides interacting with a quartz surface, the revised empirical correlation between ΔH_{ads} and ΔH_{subl} gives:[15]

$$\Delta H_{subl} = -(1.590 \pm 0.010) \, \Delta H_{ads} - (34.7 \pm 2.1) \, [\text{kJmol}^{-1}] \qquad (1)$$

By using Equation (1), the sublimation enthalpy of the Db compound is estimated to be $\Delta H_{subl}(DbOCl_3) = 172 \pm 10$ kJmol^{-1}. From literature, it is known that ΔH_{subl}-$(NbOCl_3) = 128.5$ kJmol^{-1} and $\Delta H_{subl}(TaOCl_3) = 170$ kJmol^{-1}.[24] It follows that the sequence in volatility along the Group 5 oxychloride compounds is $NbOCl_3 > TaOCl_3 \geq DbOCl_3$. Theoretical calculations[2,20] predict for the oxyhalides of Group 4 to Group 7 an increase of the molecular dipole moment with increasing Z, and thus, a stronger molecule-surface interaction in the adsorption process of these molecules on a quartz surface. Therefore, a lower volatility for $DbOCl_3$ in comparison to its lighter homologues was estimated. Similar predictions, successively confirmed by experimental results, were made for the oxychlorides of the superheavy elements seaborgium[25] and bohrium.[26] However, in the present study, a comparable volatility of $DbOCl_3$ and $TaOCl_3$ was observed. This might indicate an enhanced covalency (accompanied by a decrease in the ionic character) of the transactinide compound, in a greater extent than expected from DS DVM calculations.[20] Reason for this trend can be the increasing importance of relativistic effects on the molecular structure of $DbOCl_3$, as discussed in ref. [27].

The standard formation enthalpy of atomic Db in the gas phase, which is equal to the standard sublimation enthalpy of metallic dubnium, $\Delta H_{subl}(Db)$, can be inferred from the experimental $\Delta H_{ads}(DbOCl_3)$ value by mutually correlating thermochemical state functions.[23] As discussed in the Supporting Information, the estimated $\Delta H_{subl}(Db) = 792 \pm 10$ kJmol^{-1} strikes precisely the extrapolated $\Delta H_{subl}(Db) = 795$ kJmol^{-1}.[28] This indicates Db as one of the least volatile transactinides, together with seaborgium and bohrium.[25,26]

The results of this work might be used in recently developed periodic models[2,29] for further theoretical predictions of interaction energies of transactinide molecules with inert surfaces. Once again, the strong synergy between experimental and theoretical approaches is fundamental to successfully assess and interpret the relativistic effects driving the chemical properties of the heaviest elements.

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