Chemical Characterization of a Volatile Dubnium Compound, $DbOCl_3$

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Difficulties such as short half-lives and low production rates of superheavy elements have hindered performing chemical experiments of superheavy elements whose atomic number is larger than 103 in spite of importance of a better understanding of the Periodic Law and relativistic effects [1]. Even after more than 50 years since the discovery of dubnium (Db, Z = 105), an unambiguous statement on the chemical property of this superheavy element and its compounds is still missing. In order to elucidate an influence of the relativistic effects on the chemical properties of Db, we conducted a volatility study of oxychlorides of Db by using an on-line isothermal gas chromatographic technique [2]. It is known that volatility would reflect features of a molecule, such as symmetry, bond length, charge distribution, and so on.

The experimental setup is shown in Figure 1. The isothermal gas chromatographic apparatus consists of 3 parts, a reaction room, an isothermal column, and a clustering chamber. This apparatus is directly connected to a nuclear reaction chamber which is installed into a beam-line of the JAEA tandem accelerator facility. A ^{248}Cm target placed on the nuclear reaction chamber, was irradiated a ^{19}F ion beam provided from the accelerator to produce a short-lived Db isotope, ^{262}Db (half-life ($T_{1/2}$) = 34 s). The nuclear reaction products were transported to the reaction room by a continuously-provided carrier gas flow. A reactive gas, N_2 gas saturated a vapor of $SOCl_2$, was provided to the reaction room kept at 1000℃. A small amount of O_2 was added to the reactive gas. The synthesized oxychlorides were subsequently transported downstream by the gas flow to the isothermal column. The column was made by quartz and kept at a given temperature in the range between 150℃ and 600℃. Here, the molecules interacted with the chromatographic surface in numerous adsorption-desorption steps, with retention times (the time that a molecule spends in the column) indicative of the strength of their interaction with the surface. After the oxychloride compounds exited through the column, they were attached to KCl aerosol particles and transported to a measurement system.

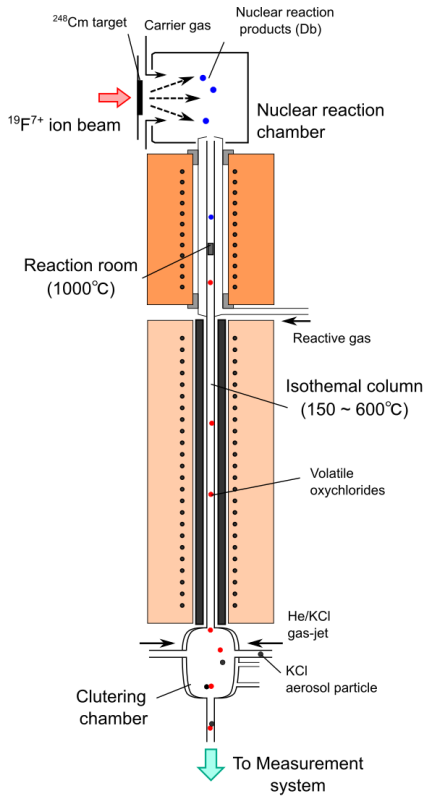

Fig.1. Schematic diagram of experimental setup

The chromatographic results for Db oxychloride are presented in Figure 2. The chromatograms of $NbOCl_3$ and $TaOCl_3$ taken in the identical condition are shown as well. As a result of analysis by using Monte-Carlo simulations, based on a microscopic adsorption-desorption kinetic model, values of adsorption enthalpies ($-\Delta H_{ads}$) were obtained to be 130 ± 6, 128 ± 5 and 102 ± 4 kJ mol^{-1} for Db, Ta, and Nb, respectively. The simulated curves are also shown in Figure 2. Measured $-\Delta H_{ads}$ values clearly indicate volatility of Db was almost similar to that of Ta while that of Db was expected to be lower than Ta from the Periodic Table (PT). The reason for this trend can be the increasing importance of relativistic effects on the molecular structure of $DbOCl_3$.

References

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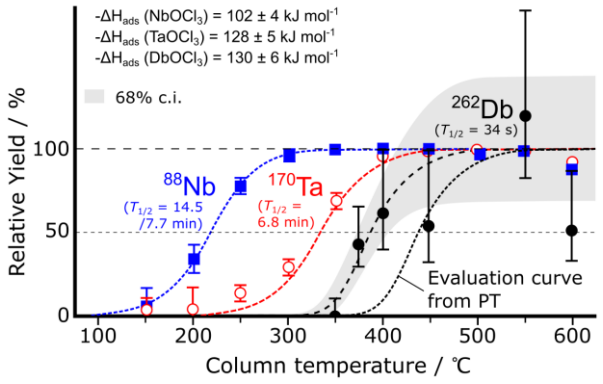

Fig.2 Comparative chromatograms for $NbOCl_3$, $TaOCl_3$, and $DbOCl_3$. A curve for $DbOCl_3$ evaluated from the Periodic Table is also shown. The gray area represents the 68% confidence interval (c.i.) of the $DbOCl_3$ yield.