

Isothermal gas chromatography study of Zr and Hf tetrachlorides using radiotracers of ^{88}Zr and ^{175}Hf

– Towards investigation of gas-phase chemistry of Rf –

Kaori Shirai^a, Shin-ichi Goto^{a,*}, Kazuhiro Ooe^b, and Hisaaki Kudo^c

^aGraduate School of Science and Technology, Niigata University, Niigata, Niigata 950-2181, Japan

^bGraduate School of Medicine, Osaka University, Suita, Osaka 565-0871, Japan

^cFaculty of Science, Niigata University, Niigata, Niigata 950-2181, Japan

Received December 22, 2020; Accepted January 29, 2021; Published online March 24, 2021

Experiments on gas-phase chemistry for chlorides have been conducted to clarify chemical properties of the first superheavy element, rutherfordium (Rf), $Z = 104$. However, adsorption enthalpies obtained in each experiment are not the same, even for those of the homologues Zr and Hf. In the present study, off-line isothermal gas chromatography was done using long-lived radioactive tracers to obtain reliable adsorption enthalpies for ZrCl_4 and HfCl_4 when adsorbed on a quartz glass surface. To simulate a column surface modified by a chlorinating reagent in on-line experiments, chromatography was also performed using a chlorinated column. A newly developed analytical method which is independent of experimental parameters and uncertain physical quantities was applied to determine the adsorption enthalpies. The obtained enthalpies for ZrCl_4 and HfCl_4 were $-101.3 \pm 4.0 \text{ kJ mol}^{-1}$ and $-98.1 \pm 3.1 \text{ kJ mol}^{-1}$ for the non-treated column, respectively, and those for the chlorinated column were $-85.1 \pm 4.5 \text{ kJ mol}^{-1}$ and $-84.2 \pm 3.3 \text{ kJ mol}^{-1}$, respectively.

1. Introduction

Chemical properties of the superheavy elements ($Z \geq 104$) are not well known. Researchers have had a long-term interest in investigating whether the periodic law is applicable to the superheavy element region. According to theoretical calculations, relativistic effects of orbital electrons become more pronounced with increasing atomic number,¹ and hence it is possible that chemical properties of the superheavy elements are not reliably predicted from their homologues. Therefore, numerous efforts have been made to obtain their chemical properties experimentally, and they have been reviewed in the literature.²

Experimental gas-phase chemistry techniques are used to study the chemistry of superheavy elements. In gas-phase chemistry, elements of interest synthesized by nuclear reactions are converted to volatile species and a technique such as gas chromatography is used to obtain thermodynamic properties, for example adsorption enthalpy ($\Delta_{\text{ads}}H$) of the volatile species for the surface of the chromatography column. The gas-phase chemical study of rutherfordium (Rf), $Z = 104$, has been carried out for its tetrachloride together with the tetrachlorides of Zr and Hf, which are homologues of Rf in the periodic table.³ Zvara⁴ pointed out that the reported values of $\Delta_{\text{ads}}H$ were quite different between experiments and attributed it to the differences in the modification of the surface of the quartz glass column by different chlorinating reagents. On the other hand, Türler and Pershina³ argued that this variation was due to different physical constants such as the period of intrinsic oscillation in adsorption (τ_0) used in analysis of the experimental results. Then, they reanalyzed reported experimental results and concluded that the values of $\Delta_{\text{ads}}H$ of ZrCl_4 and RfCl_4 were about the same, while that of HfCl_4 was smaller than those of ZrCl_4 and RfCl_4 .³ However, this conclusion seems to be too crude since the order of magnitude of $\Delta_{\text{ads}}H$

for Zr and Hf differs among the experimental results. And the sequence of $\Delta_{\text{ads}}H$ s proposed by Pershina et al.⁵ could not be reproduced by the calculation with applying various adsorption mechanisms.

The present study was aimed at obtaining reliable $\Delta_{\text{ads}}H$ values of ZrCl_4 and HfCl_4 by using isothermal gas chromatography to overcome the above problem. In isothermal gas chromatography, the retention time can be determined either by continuously introducing a short-lived nuclide into the column as in an on-line experiment or by injecting a short pulse of chemical species into a carrier gas and measuring the time at which it emerges at the column exit. Off-line isothermal gas chromatography experiments were performed using long-lived radioactive tracers, ^{88}Zr and ^{175}Hf , to determine more reliable $\Delta_{\text{ads}}H$ of ZrCl_4 and HfCl_4 for adsorption onto a quartz glass surface. Migration behaviors of the chlorides were also investigated using a chlorinated column to clarify the effects of the chlorinated surface. The chlorination of the column surface was analyzed qualitatively with X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy with attenuated total reflection (ATR-IR).

2. Experimental

2.1. Experimental setup. A schematic diagram of an experimental apparatus for isothermal gas chromatography is shown in Figure 1. The apparatus consisted of four component parts as indicated in the figure: (i) a reaction part for formation of Zr and Hf oxides and chlorides; (ii) a chloride collection part for collection of the chlorides volatilized from the reaction part; (iii) an isothermal part for chromatography; and (iv) a measurement part for detection of the chlorides that passed through the isothermal column into a cold trap. The parts (i)–(iii) were heated individually using an electric tube furnace. A straight quartz glass tube 85 cm in length passed through the four parts. To make the temperature of the isothermal part as uniform as possible, copper jackets were installed around the

*Corresponding author. E-mail: goto@chem.sc.niigata-u.ac.jp

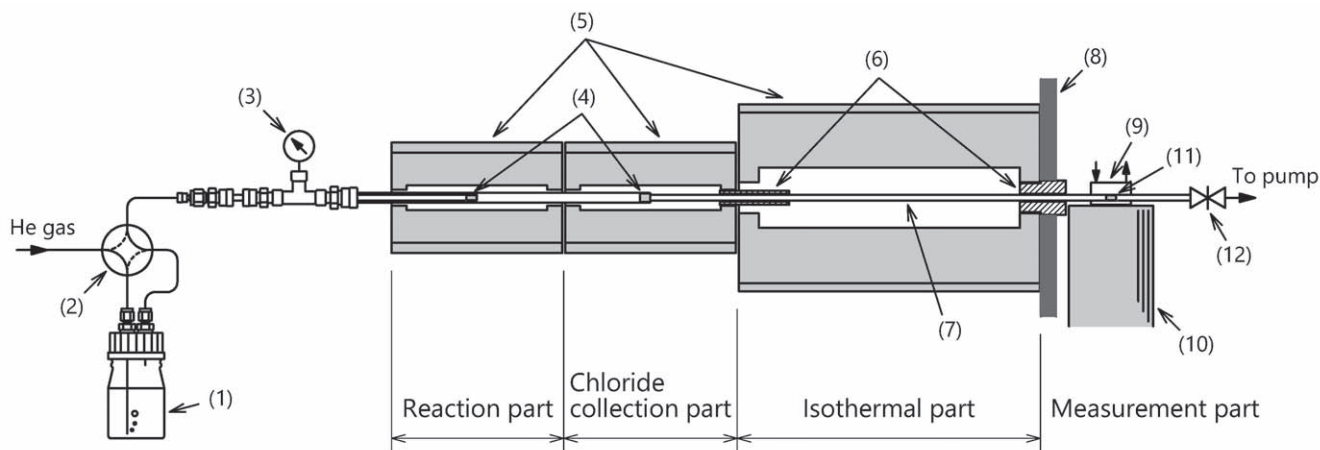


Figure 1. Schematic diagram of the off-line isothermal gas chromatography apparatus; (1) CCl_4 , (2) 4-way valve, (3) pressure sensor, (4) carbon filters, (5) electric tube furnaces, (6) Cu jackets, (7) quartz glass tube, (8) Pb shield, (9) water cooling jacket, (10) HPGe detector, (11) quartz wool, (12) needle valve.

quartz tube at both ends of the tubular furnace in the isothermal part. The inner diameter of the quartz tube at the reaction and chloride collection parts was 7 mm, and that at the isothermal and measurement parts was 4 mm. The length of the isothermal part was 30 cm.

An aliquot of tracer solution was dropped onto a carbon filter (Uni-Mitsubishi Pencil PFC, 80 ppi) inserted in a thin quartz tube (6 mm o.d., 4 mm i.d., 120 mm in length), and this tube was inserted into the reaction part. A carbon filter of the same type as that in the reaction part was placed in the chloride collection part to collect the volatilized chloride. The measurement part was plugged with quartz wool (TOHSO, grade FINE 10) and cooled with a water-cooled jacket at room temperature. An HPGe detector (CANBERRA, GC4018) was installed in front of the jacket to measure γ -rays. The detector was suitably shielded with Pb plates.

2.2. Isothermal gas chromatography. The radioactive tracers of ^{88}Zr ($t_{1/2} = 83.4$ d) and ^{175}Hf ($t_{1/2} = 70$ d) were produced via the $^{89}\text{Y}(d, 3n)$ and $^{141}\text{Lu}(d, xn)$ reactions, respectively, by a 24 MeV deuteron beam supplied by the RIKEN K70 AVF cyclotron. These tracers were chemically separated by anion exchange chromatography⁶ and prepared as 1 M HCl solution.

The no-carrier-added stock solution containing both ^{88}Zr and ^{175}Hf was suitably diluted with 1 M HCl, and 80 μL of the diluted solution was infiltrated into the carbon filter in the thin quartz tube. Then the tube was inserted into the reaction part. Chloride oxides of Zr and Hf may be formed when their HCl solution evaporates. Therefore, chloride oxides which may have been formed were completely converted to oxides by heating at 650 $^{\circ}\text{C}$ for 40 min with mixed air and helium gas flowing through the reaction part. After that, the formed oxides of Zr and Hf were converted to chlorides as follows. Carbon tetrachloride vapor was introduced instead of air in the He mixed gas flow by bubbling at room temperature. High-purity He dried with liquid nitrogen was used in the mixed gas. The flow rate of He was set to 0.5 L min^{-1} (0 $^{\circ}\text{C}$, 1 atm) using a mass flow controller (STEC, SEC-E40), and the pressure in the reaction part was kept to 111.3 kPa by adjusting the exhaust flow with a needle valve. Tetrachlorides of Zr and Hf were formed at 600 $^{\circ}\text{C}$ for 90 min. The chlorides immediately volatilized and migrated with the carrier gas flow, and were collected by the carbon filter in the chloride collection part. This part was kept at 75 $^{\circ}\text{C}$ to collect the Zr and Hf chlorides completely and also to prevent the deposition of hexachloroethane crystals which are the main pyrolysis product formed by heating carbon tetrachloride at 600 $^{\circ}\text{C}$.

When the conversion was completed, the supply of CCl_4

was stopped, and the flow rate of He gas was changed to 1.0 L min^{-1} (0 $^{\circ}\text{C}$, 1 atm). During the conversion, the isothermal part was kept at the temperature for isothermal chromatography.

As the sublimation temperatures of ZrCl_4 and HfCl_4 at 111.3 kPa are 337 $^{\circ}\text{C}$ and 321 $^{\circ}\text{C}$, respectively,⁷ the collected chlorides were volatilized at 400 $^{\circ}\text{C}$ for introduction into the isothermal column. The rising temperature of the tube furnace was sufficiently fast (about 95 $^{\circ}\text{C min}^{-1}$) and the time required for volatilization of ZrCl_4 and HfCl_4 was short enough, so that the difference in the start time of the ZrCl_4 and HfCl_4 chromatograms was negligible. From the time when the temperature of the chloride collection part reached 320 $^{\circ}\text{C}$, γ -ray spectra were measured every 30 s until the γ -ray counting rates from ^{88}Zr and ^{175}Hf were almost constant.

2.3. Chlorination of the column surface with CCl_4 .

Surface-chlorinated quartz columns and non-treated quartz columns were examined to study the effect of the surface state of the isothermal column on the behaviors of Zr and Hf tetrachlorides in isothermal chromatography. McDaniel⁸ studied the chlorination of porous silica surfaces with various chlorinating reagents and reported that heating with carbon tetrachloride at 400–800 $^{\circ}\text{C}$ for 2 h resulted in the replacement of silanol and siloxane groups by chlorine atoms on the surface. Based on this result, the chlorination of the isothermal column was examined with carbon tetrachloride and the optimal conditions were identified. High-purity helium gas saturated with carbon tetrachloride was introduced into the apparatus with the flow rate of 0.5 L min^{-1} at room temperature, and the isothermal column was chlorinated while varying heating temperatures and durations. During chlorination, the reaction part and the chloride collection part were kept at room temperature. After the chlorination under each condition set, the ZrCl_4 and HfCl_4 chromatography was carried out and the changes in their chromatograms were investigated.

2.4. Re-hydroxylation of the chlorinated column surface.

Because the column is repeatedly heated and cleaned in a chromatography experiment, it is difficult to keep a uniform chlorinated surface. Therefore, chlorine atoms on the surface of the column were re-substituted once with hydroxyl groups (re-hydroxylation) and newly chlorinated. Re-hydroxylation of the isothermal column was performed at 300 $^{\circ}\text{C}$ for 24 h by flushing air saturated with water as described in previous reports.^{8–11} After this treatment, chromatography was carried out to confirm that the surface was reliably hydroxylated and the reproducibility was guaranteed.

2.5. Analysis of the quartz glass surface. Quartz glass was analyzed using X-ray photoelectron spectroscopy (XPS) to verify the presence of chlorine atoms on the surface as a result of the chlorination treatment. The hydroxyl groups on the surface, which were reduced by the chlorination, were measured using attenuated total reflection infrared (ATR-IR) spectroscopy. Small pieces of quartz glass plate of the same material as the chromatography column were used instead of the column itself for the convenience of observation. The chlorination was performed in the same way as in the case of the column.

The XPS measurements were performed by Quantum 2000 (ULVAC-PHI) using a monochromatic Al K α X-ray source (1486.6 eV) with a spot size of 100 μm and a take-off angle of 45°. Narrow scan spectra in the Cl 2p range were measured at a pass energy of 58.7 eV.

The instrument used for ATR-IR spectroscopy was the VIR-9500 (Jasco) with a diamond crystal ATR accessory (Specac). Spectra were stored in the 800–6000 cm^{-1} range with a resolution of 8 cm^{-1} by accumulating 1000 scans.

3. Results and Discussion

3.1. Derivation of average retention time. Example results of the isothermal chromatography experiments are shown in Figure 2, where cumulative yields of ZrCl $_4$ and HfCl $_4$ at the isothermal temperature (T_{iso}) of 140 °C using the non-treated column are plotted against elapsed time, and chromatogram values deduced from the cumulative yields are also shown. The characteristic parameter for the chromatogram is average retention time (\bar{t}_r), which is the weighted average time for volatile chemical species to pass through an isothermal column. The average retention time is defined as

$$\bar{t}_r = \sum_{i=1}^n \left\{ (2i-1) \frac{\Delta t}{2} y_i \right\} \quad (1)$$

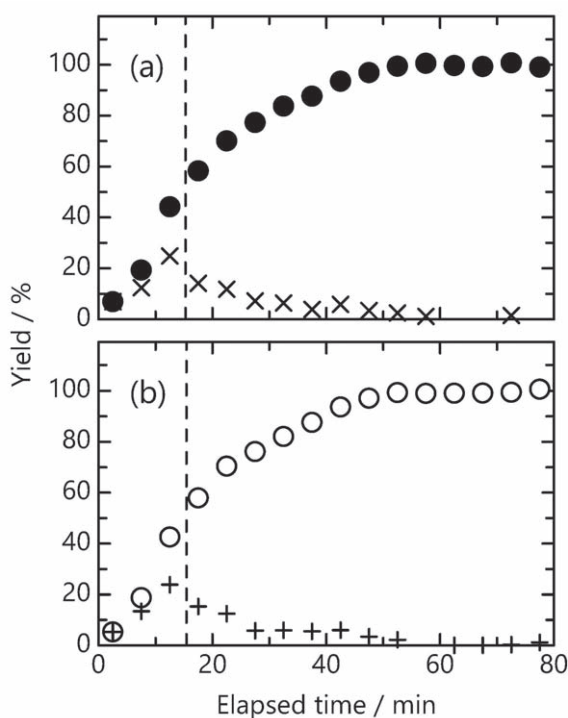


Figure 2. Cumulative yields of ZrCl $_4$ (a) and HfCl $_4$ (b) at an isothermal column temperature of 140 °C using a non-treated column (circles). The \times and $+$ symbols are chromatogram values obtained from the difference in cumulative yield. The dashed line indicates the average retention time.

where Δt the measurement time, n is the number of measurements, y_i is an independent yield defined as $c_i - c_{i-1}$, and c_i is the cumulative yield obtained in the i -th measurement. By rearranging eq (1), the following is obtained.

$$\begin{aligned} \bar{t}_r &= \frac{\Delta t}{2} \sum_{i=1}^n \{ (2i-1)(c_i - c_{i-1}) \} \\ &= \left(n\Delta t - \frac{\Delta t}{2} \right) c_n - \Delta t \sum_{i=1}^{n-1} c_{i-1} \end{aligned}$$

By setting $c_0 = 0$, $c_n = 1$, and $n\Delta t = t_n$, the following is obtained.

$$\bar{t}_r = \left(t_n - \frac{\Delta t}{2} \right) - \Delta t \sum_{i=1}^{n-1} c_i$$

In actuality, however, the cumulative yield c_i here is smaller than the true yield because the time at which the volatile species are measured depends on the time at which they reach the collection part during the measurement time. Correcting for this, the average retention time can be approximated as Equation (2).

$$\bar{t}_r \approx t_n - \Delta t \sum_{i=1}^{n-1} c_i \quad (2)$$

In the case of Figure 2, the average retention times of ZrCl $_4$ and HfCl $_4$ were 15.2 ± 0.2 min and 15.4 ± 0.2 min, respectively. Errors were derived from statistical errors in cumulative yield measurements. Hereafter, the weighted average retention time is simply denoted by the retention time.

3.2. Effect of the chlorination of the column surface. In order to determine the optimal conditions for chlorination of the column, the surface was chlorinated with CCl $_4$ at 400, 600, and 700 °C for 2 h, and at 600 °C for 1, 2, and 5 h. Here ‘optimal conditions’ mean the minimum temperature and time that would yield sufficient chlorination. As preliminary experiments showed that the retention time for chlorinated columns was shorter than that for non-treated columns, the conditions which gave the shortest retention time were regarded as the optimal conditions. The dependences of the retention time on chlorination temperature and on chlorination time for ZrCl $_4$ and HfCl $_4$ at $T_{\text{iso}} = 125$ °C are shown in Figures 3 and 4, respectively. From these results, the optimal conditions for the column surface chlorination was determined to be 600 °C and 2 h.

Figure 5 summarizes the retention times of ZrCl $_4$ and HfCl $_4$

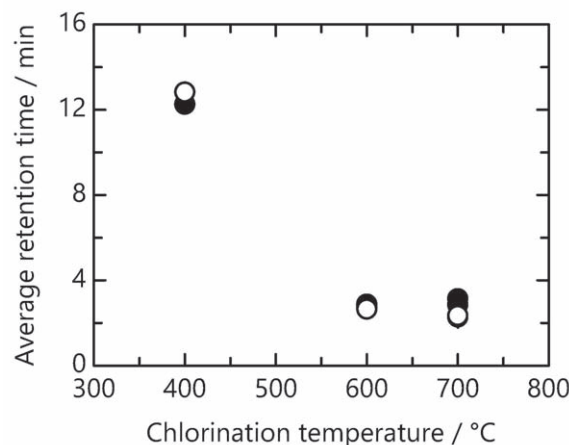


Figure 3. Average retention time of ZrCl $_4$ (black circles) and HfCl $_4$ (white circles) at the isothermal temperature of 125 °C using a column chlorinated at various temperatures for 2 h.

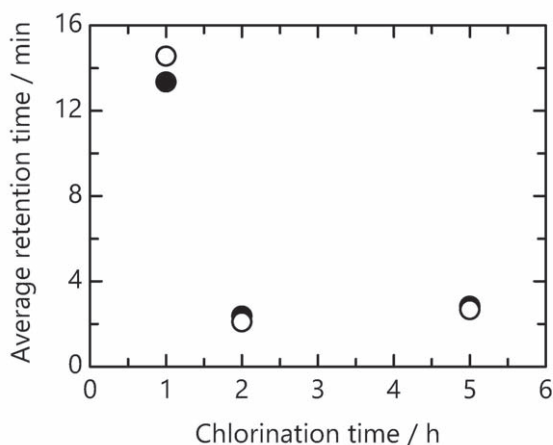


Figure 4. Average retention time of ZrCl₄ (black circles) and HfCl₄ (white circles) at 125 °C in the isothermal part by using a column chlorinated at 650 °C for various time.

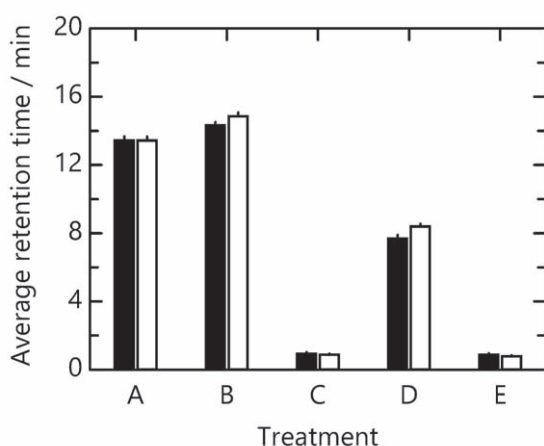


Figure 5. Retention times of ZrCl₄ (black bars) and HfCl₄ (white bars) at the isothermal temperature of 125 °C for non-treated (A), heat treated (B), chlorinated (C), re-hydroxylated (D), and re-chlorinated (E) columns.

obtained for non-treatment (A), simply heated (B), chlorinated (C), re-hydroxylated (D) and re-chlorinated (E) columns. It has been reported that some OH groups were desorbed from a quartz glass surface heated to 600 °C.¹² When the isothermal column was simply heated at 600 °C for 2 h, the retention time was almost the same as in the case without treatment. This finding implied that the OH groups desorbed by simple heating had little effect on the adsorption of the chlorides. When CCl₄ was introduced into the column under the same heating conditions, the retention time became very short. Re-hydroxylation of the chlorinated column resulted in a longer retention time, but that time was shorter than the retention time of the non-treated column, which meant that there might be an irreversible substitution of OH and Cl. When the re-hydroxylated column was newly chlorinated, the retention time was almost the same as that in the first chlorination. Therefore, chlorination after rehydroxylation could reproduce a uniform surface chlorination.

3.3. Surface analysis of the quartz glass surface. Narrow scan XPS spectra around Cl 2p for the chlorinated and non-treated quartz glass plates are shown in Figure 6. A peak around 200 eV was observed for the chlorinated plate, while no peak was observed for the non-treated plate. It is difficult to obtain definite information about the Cl chemical state because the peak positions are not clear due to poor statistical precision of counting rates. However, it was likely to be present as Si-Cl, since the peak position was very close to that

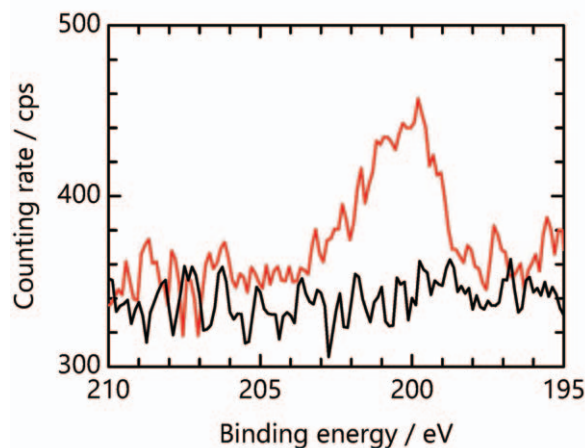


Figure 6. XPS spectra of the Cl 2p region taken using a narrow scan mode for the non-treated quartz glass plate (black) and the chlorinated plate (red).

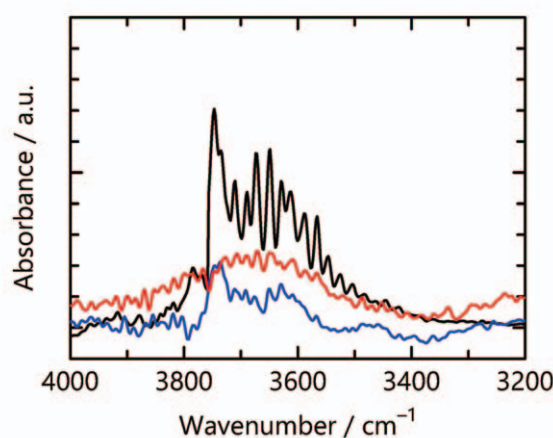


Figure 7. Infrared spectra of non-treated (black), chlorinated (red), and re-hydroxylated (blue) quartz glass plates. Normalized with the intensity of the Si-O-Si band around 1000 cm⁻¹.

observed in the implantation of chlorine ions into silicon crystals.^{13,14}

Figure 7 shows the IR spectra of variously treated quartz glass plates. For the non-treated plate, the sharp band at 3750 cm⁻¹ and the close-lying band to it originating from OH groups^{11,15-17} could be clearly recognized. In contrast, the signal in this range was much smaller for the chlorinated plates. This indicated a decrease in the amount of OH groups on the surface. Re-hydroxylation after chlorination regenerated the bands, but their intensities were weaker than those for the non-treated plate. This result was consistent with the change in the retention time of ZrCl₄ and HfCl₄, that is, chlorination led to an irreversible change in a part of the OH groups on the surface of the quartz glass.

The results obtained by XPS and IR qualitatively confirmed the substitution of OH for Cl on the surface of the quartz glass by chlorination.

3.4. Effect of column-surface modification on $\Delta_{\text{ads}}H$. In order to investigate the effect of by modification of the column surface on the $\Delta_{\text{ads}}H$ s of ZrCl₄ and HfCl₄, isothermal chromatography experiments were performed using the non-treated and chlorinated columns at various isothermal temperatures. Examples of cumulative yield curves obtained for the two types of columns are shown in Figures 8 and 9. In studying the gas-phase chemistry of superheavy elements, adsorption enthalpy ($\Delta_{\text{ads}}H$) of volatile species for a column surface is usually deduced by using a Monte Carlo simulation (MCS)

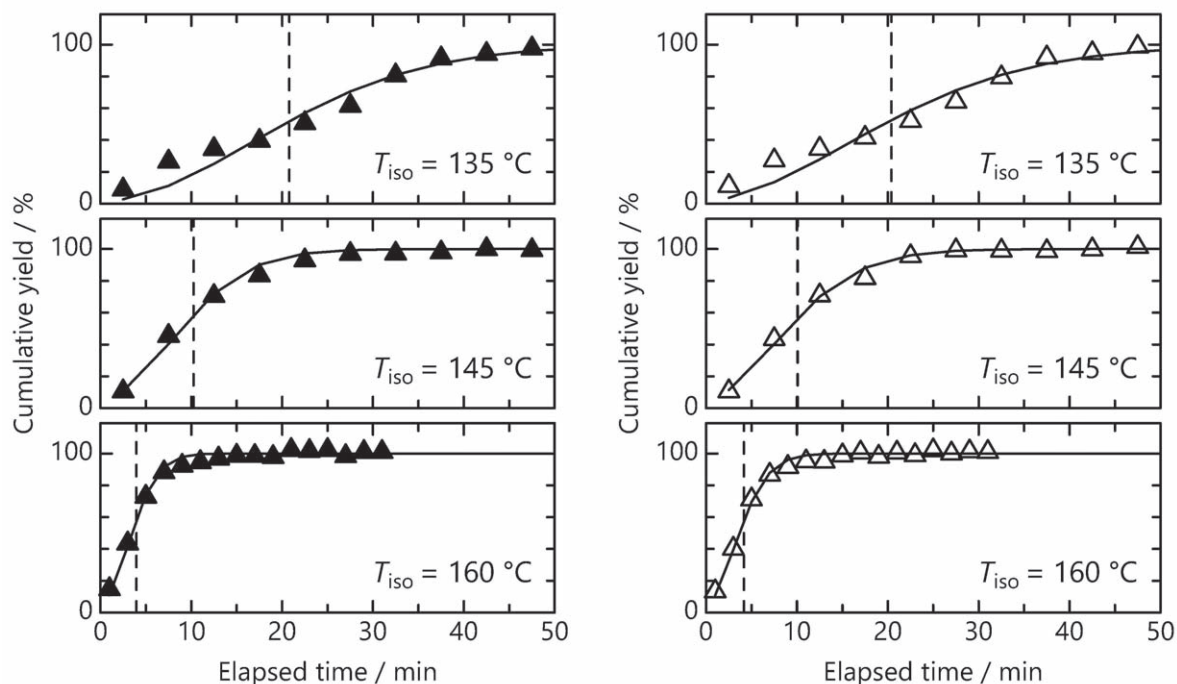


Figure 8. Examples of cumulative yields for the non-treated column. The black and white triangles represent ZrCl_4 and HfCl_4 , respectively. Solid lines show the results of MCS. Dashed lines indicate the position of the average retention time.

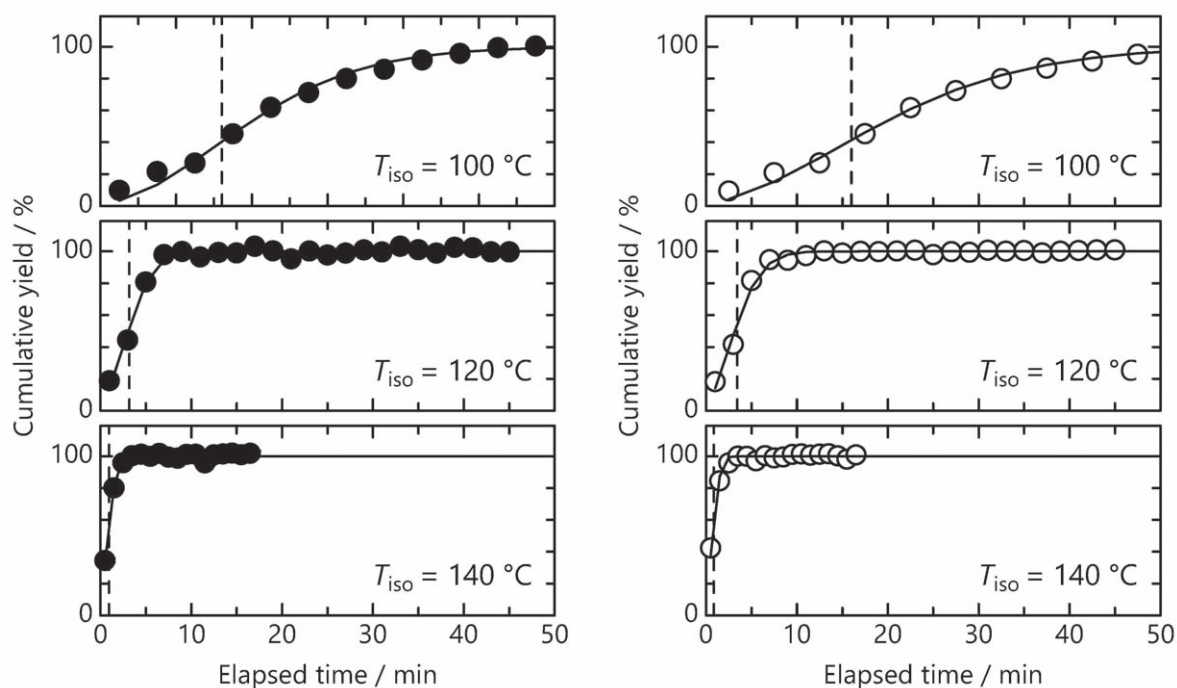


Figure 9. Examples of cumulative yields for the chlorinated column. The black and white circles represent ZrCl_4 and HfCl_4 , respectively. Solid lines show the results of MCS. Dashed lines indicate the position of the average retention time.

based on the column-migration model.¹⁸ In this method, usually the value of the oscillation period τ_0 is assumed and all values of experimental parameters are used as they are, and $\Delta_{\text{ads}}H$ is treated as a free parameter and determined from the value which yields the best fit of an experimental result. The time dependence for cumulative yield was very well reproduced by MCS. This indicated the validity of the column-migration model that MCS is based on for the present study.

Türler and Pershina³ reanalyzed the results of reported gas-phase chemistry experiments for the halides of group-4 elements by MCS with $\tau_0 = 2 \times 10^{-13}$ s. Their analysis allowed the $\Delta_{\text{ads}}H$ values of different experiments to be compared with each other. In the present work, the $\Delta_{\text{ads}}H$ values were obtained by using $\tau_0 = 2 \times 10^{-13}$ s and they are summarized in Tables 1 and 2 along with all the obtained retention times. The

obtained $\Delta_{\text{ads}}H$ values were almost the same at all column temperatures for each column type and there seemed to be no difference between ZrCl_4 and HfCl_4 . For the non-treated column, the average $\Delta_{\text{ads}}H$ values of ZrCl_4 and HfCl_4 were -92.6 ± 0.1 kJ mol⁻¹ and -93.2 ± 0.1 kJ mol⁻¹, respectively. On the other hand, those for the chlorinated column were -83.7 ± 0.2 kJ mol⁻¹ and -84.2 ± 0.2 kJ mol⁻¹ for ZrCl_4 and HfCl_4 , respectively. These values are plotted in Figure 10 together with those reported by Türler and Pershina.³ The reported results were somewhat scattered in each experiment, and this might come from fluctuation among different column-surface conditions.

3.5. Parameter-free evaluation of $\Delta_{\text{ads}}H$. The experimental cumulative yields were well reproduced by MCS as shown

TABLE 1: Retention times at various isothermal temperatures and adsorption enthalpies derived by MCS for the non-treated column.

$T_{\text{iso}} / ^\circ\text{C}$	\bar{t}_r / min		$\Delta_{\text{ads}}H (\text{MCS}) / \text{kJ mol}^{-1}$	
	ZrCl ₄	HfCl ₄	ZrCl ₄	HfCl ₄
135	20.8 ± 0.2	20.4 ± 0.2	-93.0	-93.4
	23.9 ± 0.3	22.6 ± 0.2	-93.1	-93.5
140	16.6 ± 0.1	16.0 ± 0.2	-93.1	-93.6
	15.3 ± 0.2	15.5 ± 0.2	-92.7	-93.3
145	15.5 ± 0.3	15.7 ± 0.3	-93.0	-93.6
	10.2 ± 0.2	10.4 ± 0.3	-92.6	-93.2
150	9.0 ± 0.2	8.9 ± 0.2	-92.1	-92.6
	10.2 ± 0.1	10.1 ± 0.2	-92.4	-93.0
155	7.5 ± 0.2	7.4 ± 0.2	-92.7	-93.3
	6.9 ± 0.2	7.1 ± 0.2	-92.2	-92.8
160	7.8 ± 0.1	7.9 ± 0.1	-92.6	-93.3
	5.6 ± 0.3	6.5 ± 0.3	-92.6	-93.6
155	5.6 ± 0.2	5.8 ± 0.3	-92.5	-92.8
	5.7 ± 0.2	5.4 ± 0.2	-92.3	-92.8
160	4.0 ± 0.1	4.2 ± 0.1	-92.3	-93.1
	4.1 ± 0.2	4.6 ± 0.2	-92.6	-93.6
	3.7 ± 0.1	3.8 ± 0.2	-92.3	-93.0

in the previous section. However, the evaluation of $\Delta_{\text{ads}}H$ by MCS depends on experimental parameters and the oscillation period τ_0 . A new analytical method was proposed here to evaluate the $\Delta_{\text{ads}}H$ value free from uncertain parameters such as τ_0 .

In the column-migration model applied to isothermal chromatography,¹⁸ the average retention time (\bar{t}_r) is expressed as the product of the average number of collisions with the wall per unit length of the column ($\bar{\nu}$), the column length (L), and the average time spent at the surface for a single adsorption ($\bar{\tau}_a$). This is given as Equation (3):

$$\bar{t}_r = L \bar{\nu} \bar{\tau}_a = \frac{LrT_0P}{Q_0P_0} \sqrt{\frac{2\pi R}{MT_{\text{iso}}}} \tau_0 \exp\left(-\frac{\Delta_{\text{ads}}H}{RT_{\text{iso}}}\right) \quad (3)$$

where r is the inner radius of the column, T_{iso} and P are the isothermal temperature and pressure at which chromatography is performed, respectively, Q_0 is the flow rate at the reference temperature T_0 and pressure P_0 , M is the molar mass of the molecule of interest, and R is the gas constant.

Equation (3) can be rearranged as

$$\ln(\bar{t}_r \sqrt{T_{\text{iso}}}) = -\frac{\Delta_{\text{ads}}H}{R} \frac{1}{T_{\text{iso}}} + \ln\left(\frac{LrT_0P}{Q_0P_0} \sqrt{\frac{2\pi R}{M}} \tau_0\right). \quad (4)$$

Therefore, a plot of $\ln(\bar{t}_r \sqrt{T_{\text{iso}}})$ against $1/T_{\text{iso}}$ is expected to yield a straight line, and from its slope $\Delta_{\text{ads}}H$ can be obtained independent of parameters such as τ_0 .

Figure 11 plots the results of $\ln(\bar{t}_r \sqrt{T_{\text{iso}}})$ against $1/T_{\text{iso}}$, where the values of \bar{t}_r and T_{iso} tabulated in Tables 1 and 2 were used. As seen in the figure, the plotted values showed good linearity as expected. The straight lines were fitted using a weighted least squares method. From the slopes of the fitted lines, the values of $\Delta_{\text{ads}}H$ free from parameters were obtained for the first time and those of ZrCl₄ and HfCl₄ for the non-treated column were $-101.3 \pm 4.0 \text{ kJ mol}^{-1}$ and $-98.1 \pm 3.1 \text{ kJ mol}^{-1}$, respectively. For the chlorinated column, $\Delta_{\text{ads}}H$ of ZrCl₄ was $-85.1 \pm 4.5 \text{ kJ mol}^{-1}$ and that of HfCl₄ was $-84.2 \pm 3.3 \text{ kJ mol}^{-1}$. No significant difference was found between the adsorption enthalpies of ZrCl₄ and HfCl₄ for either type of col-

TABLE 2: Retention times at various isothermal temperatures and adsorption enthalpies derived by MCS for the chlorinated column.

$T_{\text{iso}} / ^\circ\text{C}$	\bar{t}_r / min		$\Delta_{\text{ads}}H (\text{MCS}) / \text{kJ mol}^{-1}$	
	ZrCl ₄	HfCl ₄	ZrCl ₄	HfCl ₄
100	16.0 ± 0.3	14.9 ± 1.0	-84.3	-84.8
	16.0 ± 0.3	16.0 ± 0.1	-84.7	-85.2
105	12.7 ± 0.2	12.4 ± 0.3	-84.4	-84.8
	10.1 ± 0.2	9.9 ± 0.2	-83.4	-84.0
110	9.4 ± 0.3	8.9 ± 0.4	-84.3	-84.6
	9.6 ± 0.4	9.9 ± 0.5	-84.5	-85.2
115	6.4 ± 0.1	6.4 ± 0.1	-83.8	-84.3
	5.4 ± 0.1	5.6 ± 0.1	-84.3	-84.8
120	4.0 ± 0.1	4.0 ± 0.1	-83.8	-84.4
	3.2 ± 0.2	3.4 ± 0.1	-83.2	-83.9
125	2.9 ± 0.3	2.6 ± 0.2	-83.2	-83.6
	2.8 ± 0.2	2.8 ± 0.2	-83.2	-83.6
140	0.9 ± 0.1	0.8 ± 0.1	-83.0	-83.0
	0.8 ± 0.1	0.9 ± 0.1	-81.9	-82.8

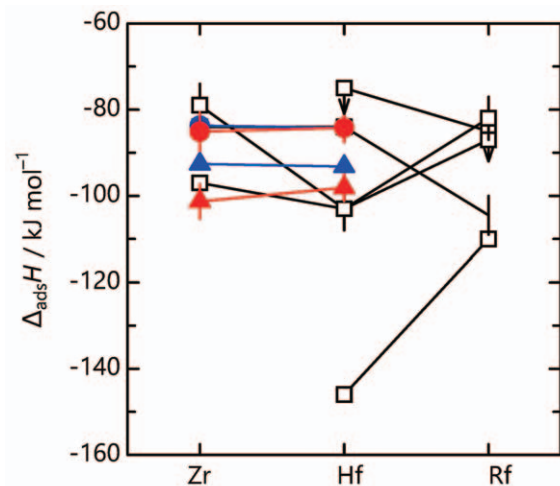


Figure 10. Comparison of the obtained adsorption enthalpies. Squares plot the enthalpies given by Türlér and Pershina³ in their Table 2. Blue marks indicate the results obtained in the present study by a MCS method with $\tau_0 = 2 \times 10^{-13}$ s. Red marks indicate the results obtained by the new method of the present study. Triangles are for non-treated column and circles are for chlorinated column. Lines connect values for the same series of experiments.

umn and the absolute value of $\Delta_{\text{ads}}H$ for the non-treated column was larger than that for the chlorinated column. These obtained values of $\Delta_{\text{ads}}H$ were compared with literature values³ in Figure 10. It was found that the values of $\Delta_{\text{ads}}H$ for the chlorinated column were about the same with those obtained by MCS, whereas the MCS method yielded a sizably smaller absolute value of $\Delta_{\text{ads}}H$ for the non-treated column compared to that obtained in the new method. The values of τ_0 could be estimated from the ordinate intercept of the fitted line of eq (4), although the evaluated values contained large uncertainties arising from the error propagation in the fitting process. For the chlorinated column, the evaluated values of τ_0 were 1.4×10^{-13} s and 2.1×10^{-13} s for ZrCl₄ and HfCl₄, respectively. These values were similar to the value used in the MCS method, 2×10^{-13} s. On the other hand, for the non-treated column the evaluated τ_0 values were smaller than those for the chlorinated column, that is, 1.7×10^{-14} s and 5.2×10^{-14} s for ZrCl₄ and HfCl₄, respectively. These trends in τ_0 might be the reason for the difference of $\Delta_{\text{ads}}H$ between the MCS method and the new method. However, discussion of the reason

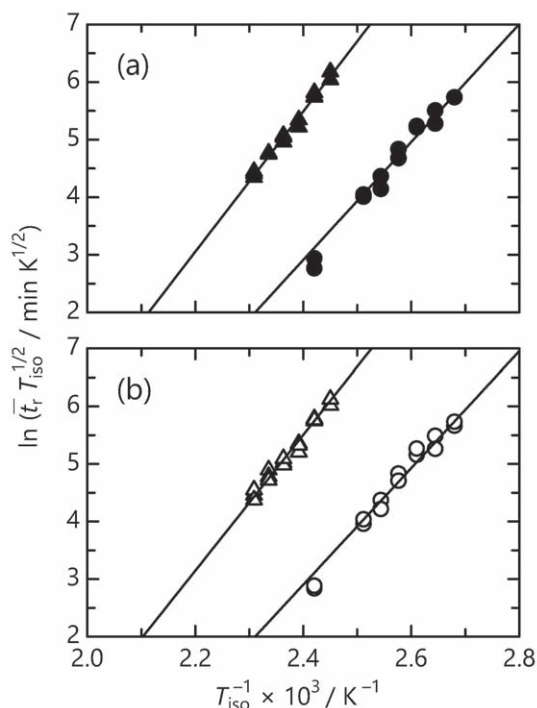


Figure 11. Plot of $\ln(\bar{t}_r \sqrt{T_{\text{iso}}})$ versus $1/T_{\text{iso}}$ for ZrCl_4 (a) and HfCl_4 (b). Triangles and circles indicate the type of the column, non-treated and chlorinated, respectively. Solid lines are the results of a weighted least-square fitting.

should be postponed until future experiments are made because of the large uncertainty of τ_0 .

The obtained trend in $\Delta_{\text{ads}}H$ was consistent with the trend in the sublimation enthalpy of macro amounts of ZrCl_4 and HfCl_4 .¹⁹ The theoretical calculation in the framework of the relativistic density functional theory by Pershina et al.⁵ predicted that the adsorption enthalpies of ZrCl_4 and HfCl_4 were almost the same with the adsorption mechanism being a physisorption provided by the van der Waals force. In the case of the chlorinated column, a mechanism for adsorption of not only the tetrachloride MCl_4 but also the hexachloride complex MCl_6^{2-} , which is formed by complexing with chlorine atoms on the surface, is also possible. However, the magnitude of the obtained adsorption enthalpy is smaller than that for the non-treated column and too small for chemisorption to form a complex. In the case of the chlorinated column, it is more likely to be a physisorption of MCl_4 as well. If this adsorption mechanism is adopted, RfCl_4 is expected to have an enthalpy close to those of homologues according to the theoretical prediction by Pershina et al.⁵ Therefore, it is very important to obtain the adsorption enthalpy of RfCl_4 experimentally with a reliable accuracy.

4. Conclusions

In previous studies on the gas-phase chemistry of Rf chlorides, the chemical properties of Rf could not be fully discussed because the values of the adsorption enthalpies of the homologues Zr and Hf for quartz glass and the relationship between them are different in each experiment. In this study, off-line isothermal gas chromatography was done using long-lived radioactive tracers to obtain reliable adsorption enthalpies of ZrCl_4 and HfCl_4 . In addition, chromatography by using a deliberately chlorinated column was also performed to simulate the case of a column surface modification by a chlorinating reagent in an online experiment. The chlorination of the isothermal column was achieved by heating with helium gas saturated with carbon tetrachloride and XPS and IR analyses

confirmed this chlorination for the same type of quartz glass plate as the column. The retention time for the chlorinated column was shorter than that for the non-treated column, which indicated the adsorption interaction for the chlorinated column was weaker than that for the non-treated column.

Detailed isothermal chromatography experiments were performed by using the non-treated and the chlorinated columns at various isothermal temperatures. The time dependence in cumulative yield was very well reproduced by MCS indicating the validity of the column-migration model. A conventional analysis using the MCS method found that there was no significant difference between the adsorption enthalpies of ZrCl_4 and HfCl_4 for either type of column and the absolute value of $\Delta_{\text{ads}}H$ for the non-treated column was larger than that for the chlorinated column.

In the present study, an analytical method was developed to obtain the adsorption enthalpy without depending on the parameters of the experimental apparatus or uncertain physical quantities. According to this method, the adsorption enthalpies of ZrCl_4 and HfCl_4 were $-101.3 \pm 4.0 \text{ kJ mol}^{-1}$ and $-98.1 \pm 3.1 \text{ kJ mol}^{-1}$ for the untreated column, respectively. For the chlorinated column, $-85.1 \pm 4.5 \text{ kJ mol}^{-1}$ for ZrCl_4 and $-84.2 \pm 3.3 \text{ kJ mol}^{-1}$ for HfCl_4 were obtained. There was no significant difference between the adsorption enthalpies of Zr and Hf for the two types of columns. These results were consistent with the trend in the sublimation enthalpy of macro amounts of ZrCl_4 and HfCl_4 and the theoretical calculation by Pershina et al.⁵, in which the adsorption mechanism was assumed to be a physisorption provided by the van der Waals force.

Acknowledgments

The ^{88}Zr and ^{175}Hf were supplied through the Supply Platform of Short-lived Radioisotopes, supported by JSPS Grant-in-Aid for Scientific Research on Innovative Areas, Grant Number 16H06278. This work was partly supported by the Sasakawa Scientific Research Grant from the Japan Science Society and JSPS KAKENHI Grant Number 18K11917.

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