Contribution to “Diamond Jubilee of RCA”

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On the volatility of protactinium in chlorinating and brominating gas media

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Abstract: A multi-target recoil chamber technique was applied to study online chemical properties of protactinium in chlorinating and brominating gas media using 226Pa (T1/2 = 1.8 min) decaying by alpha emission (74%) and β−EC decay (26%). A 58 MeV proton beam passing 15 × 50 μg/cm2 thick 232Th targets enabled production of 226Pa formed in the reaction 232Th(p,7n). Isothermal gas chromatography in quartz columns allowed for the determination of adsorption enthalpies of oxohalides and pure halides of Pa5+ compounds. On the basis of empirical correlations, these adsorption enthalpies (ΔH0 ads) could be converted to sublimation enthalpies (ΔH0 subl). Resulting values for the assumed compounds PaCl5, PaOCl3, PaBr5, and PaOBr3 were 113 ± 15, 329 ± 16, 165 ± 5 and 235 ± 17 kJ/mol, respectively. These values are rather similar to known ΔH0 subl data for group-5 elements Nb, Ta and Db in support of the assumption that Pa is a pseudo-group 5 element.

Keywords: gas phase chemistry; halides; oxohalides; protactinium; thin target production.

1 Introduction

In 1949 IUPAC credited the discovery of the element protactinium, the element with the atomic number 91 to O. Hahn und L. Meitner [1] who discovered 1918 the most long-lived isotope 231Pa simultaneously with F. Soddy and J.A. Cranston [2]. In nature, protactinium is found mainly as 233Pa, because the natural precursor of this isotope is 235U. Still, it is referred to as one of the rarest naturally occurring elements. Pa was isolated for the first time by Grosse [3] in mg amounts of the chemical form 231Pa2O5. 231Pa with a half-life (T1/2) of 3.3 × 104 years is the longest-lived isotope of this element, an α-emitter, that was identified as long-lived precursor of 227Ac (T1/2 = 21.8 y). Nevertheless, 28 other isotopes of protactinium are known – out of which only one more exists in nature, 230Pa (β−, T1/2 = 6.7 h), which is a decay product of 238U.

Early interest in this element came from nuclear energy research, particularly from R&D of 232Th-based fast reactors, which breed large amounts of 233Pa (β−, T1/2 = 27 d) as precursor of the fissioning 233U. As a consequence, three international conferences in the 1960s focused on protactinium [4–6]. With the declining interest in this nuclear technology, protactinium faded out of the research focus. In recent years the number of publications on this element is rather limited. Examples are the determination of excited atomic levels in protactinium by resonance ionization spectroscopy [7], an EXAFS study concluding a much less stable Pa-O bond in oxo-complex formation compared to U, which is likely the reason for the partitioning of U and Pa in nature [8], quantum molecular dynamics investigations of protactinium (V) fluoro and oxofluoro complexes in solution [9] or a publication pointing to the fact that protactinium is at the intersection between an actinide and transition metal [10]. Some recent work on separation and purification procedures of Pa can be found in Ref. [11, 12]. An interesting application of protactinium for targeted alpha therapy in nuclear medicine was discussed in Ref. [13] using 230Pa formed in the 232Th(p,3n) reaction. In a manuscript that is part of this volume the aqueous chemistry of protactinium is reviewed and declared to be “a nightmare” [14] – which is in contrast to its gas phase chemical behavior appearing to be very reproducible in this work.

The most widely used tracer of protactinium is 233Pa (T1/2 = 27 d), formed after neutron irradiation of 232Th and consecutive β−decay of formed 233Th [15]. The reason is its favorable half-life, its relative ease of preparation and its well detectable γ-spectrum.
Until Seaborg's suggestion of the actinides series as a group of elements being similar to those of the lanthanides [16], Pa was suggested to be a group 5 member, a heavy homolog of vanadium, niobium and tantalum. The reason is simply that its main oxidation state is +V similar to that of the group-5 members of the periodic table. In liquid phase, besides the +V state also the +IV-oxidation state has been observed. The oxidation state +III was stated to be unstable [17].

Protactinium halides, which are particularly of interest for this work, are known in form of fluorides, chlorides and bromides as well as their oxo-complexes (for reviews see Ref. [18, 19]). Extensive experimental preparative work and quantitative analyses of Pa halide compounds were performed by D. Brown et al. and Bagnall et al., (see e.g. [20–22]). These studies demonstrated a general predominance of the oxidation states +V and, only at strongly reducing conditions with hydrogen gas, +IV. The formation of pure PaCl₅ was discussed and observed in the interaction of metallic Pa with elemental chlorine. Unstable oxohalides, PaOCl₃ and PaOBr₃ have been observed as side products as well. First thermodynamic data were obtained by calorimetry including also dissolution data for the halide complexes in aqueous phase (for review see Ref. [23]). More recently, some of these data were critically reviewed in [24–26]. Table 1 shows a selection of tabulated thermochemical formation data of the chloride and bromide systems. Some discrepancies reveal the problematic situation of those data (e.g. the available standard formation enthalpy data for the solid PaCl₅ differ by ~10%, which would induce an uncertainty of ~50% in the deduced sublimation enthalpy data).

From the preparative point of view, PaCl₅ was observed to be formed in the reaction of PaO₂ with CCl₄ and PaCl₃ and PaBr₅ in the reaction of Pa₂O₅ with CCl₄ or AlBr₃, respectively, at around 300–400 °C [22]. The corresponding oxochlorides (PaOCl₂) in the oxidation state +IV were formed upon interaction of the pure halides with the reducing and halide catching pure Sb₂O₃. The vapor pressure of PaCl₅ was measured in Ref. [30] where a production route over Pa₂O₅ heated in a Cl₂/CCl₄ mixture was used. A sublimation enthalpy of 93 kJ/mol and a sublimation entropy of 143.2 J/mol K respectively, were determined.

The pentahalides react with hydrogen at elevated temperatures to the corresponding tetrahalides, which are isostructural to UCl₄ and ThBr₄, respectively [31]. Furthermore, the same authors reported the chlorination of Pa₂O₅ with SOCl₂ at around 400 °C yielding PaCl₅ [32]. PaCl₅ reacted with oxygen to Pa₂O₅Cl₄, and subsequent heating to 500 °C which disproportionated upon heating at 500 °C to PaCl₃ and PaOCl₂. As by-product Pa₂OCl₈ was separated and identified by elemental analysis and spectroscopy. The preparation of protactinium pentabromide from the pentoxide using bromine vapor and carbon at 600–700 °C was described in Ref. [33]. A short overview on the crystal structures of some protactinium bromides is given in Ref. [34].

In this work we studied the gas adsorption chromatographic behavior of carrier-free protactinium compounds formed at elevated temperatures in chlorinating and brominating atmospheres. The carrier-free approach renders the formation of molecules containing more than one Pa atom impossible. For their synthesis stronger oxidizing and chlorinating atmospheres with elemental chlorine and bromine and on the other hand less oxidizing atmospheres with HCl, HBr were applied with various halogenating agents such as SOCl₂ or CCl₄ and BBr₃, respectively. We applied online gas chromatography using the OLGA II technique [35]. Short-lived isotopes of protactinium produced one-atom-at-a-time served as tracers, formed in fusion reactions of a ²²⁹Th target with 58 MeV protons, followed by emission of several neutrons. For a fast and continuous transport of formed products to the gas chromatographic column and the detector array, we applied a gas jet transportation system. Using empirical correlations of thermodynamic state functions, valid for group 5 compounds and other actinide compounds a tentative speciation was proposed. From measured adsorptionenthalpies information on the volatility of the formed compounds was deduced.

### 2 Experimental

To apply a gas jet transportation system for proton induced reactions very thin targets are required due to the low recoil energy of formed fusion products. To increase production rates it is therefore advisable to use multiple target arrays as outlined in Ref. [36]. This is indeed

### Table 1: Tabulated thermochemical data for gaseous and solid protactinium compounds with chlorine and bromine.

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔH°, kJ/mol</th>
<th>ΔS°, J/molK</th>
<th>ΔG°, kJ/mol</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pa(g)</td>
<td>607</td>
<td>198.1</td>
<td>563</td>
<td>[27]</td>
</tr>
<tr>
<td>PaCl(g)</td>
<td>−963</td>
<td>−774</td>
<td>−1043</td>
<td>[27]</td>
</tr>
<tr>
<td>PaCl₂(s)</td>
<td>−1184</td>
<td>−824</td>
<td>−963</td>
<td>[27]</td>
</tr>
<tr>
<td>PaCl₃(s)</td>
<td>−1256</td>
<td>−1145</td>
<td>−1050</td>
<td>[27]</td>
</tr>
<tr>
<td>PaCl₄(g)</td>
<td>−862</td>
<td>−753</td>
<td>−1159</td>
<td>[27]</td>
</tr>
<tr>
<td>PaCl₅(s)</td>
<td>−728</td>
<td>−666</td>
<td>−586</td>
<td>[27]</td>
</tr>
<tr>
<td>PaBr(g)</td>
<td>−975</td>
<td>−954</td>
<td>−788</td>
<td>[27]</td>
</tr>
<tr>
<td>PaBr₂(s)</td>
<td>−1092</td>
<td>−824</td>
<td>−963</td>
<td>[27]</td>
</tr>
<tr>
<td>PaBr₃(s)</td>
<td>−1088</td>
<td>−1145</td>
<td>−1256</td>
<td>[27]</td>
</tr>
<tr>
<td>PaBr₄(g)</td>
<td>−988</td>
<td>−1034</td>
<td>−1100</td>
<td>[27]</td>
</tr>
</tbody>
</table>
possible given the low energy loss of protons in matter [37]. We used $50 \mu g \text{ cm}^{-2}$ $^{232}$Th (metal) targets on $20 \mu m$ Al foils that were welded on 0.1 mm Al plates. These targets were prepared by the target laboratory of GSI Darmstadt. A stack of 15 targets were mounted in an irradiation chamber at a distance of 5 mm between successive targets (Figure 1, adapted from Ref. [36]). A 58 MeV proton beam, delivered by the PSI-PHILIPS cyclotron of $2 \mu A$ intensity bombarded the target stack. The calculated energy loss within the target stack was 5 MeV. At this beam energy $^{226}\text{Pa}$ and $^{227}\text{Pa}$ are predominantly formed in the $(p,6n)$ and $(p,7n)$ reactions, respectively. The carrier gas He (flow rate 1 L min$^{-1}$) was swept over each target in a zig-zag trajectory to collect the products which had a recoil range in helium of about 0.7 mm. The carrier gas contained aerosol particles to transport attached products through a $90 \text{ m}$ long PE (i.d. = 2 mm) capillary to a radiochemistry laboratory. Two types of particles were used, KCl and MoO$_3$, respectively. KCl particles were added to the He carrier by passing the gas over a ceramic boat filled with this salt and kept at 680 °C. MoO$_3$ particles were formed accordingly at a temperature of the ceramic boat of 630 °C [38].

The gas jet was fed to the chromatographic device OLGA II [35] that was operated with a quartz column of 55 cm length and 6 mm inner diameter. At the entrance to the column chlorinating or brominating reactive gases were added to the carrier gas inlet from a reservoir with a 100 ml/min N$_2$ stream. At this position a quartz wool plug was placed and kept at 900 °C to collect aerosol particles and to form the investigated halide molecules from the transported Pa atoms. The adjacent chromatography column could be kept at a variable but isothermal temperature between room temperature and 1100 °C. Figure 2 shows the real temperature profiles along the column at various $T_{iso}$. These temperature profiles were also used for the Monte-Carlo simulations.

After passing the chromatography column, the species were re-attached to new KCl particles suspended in a $2 \text{l/min}$ N$_2$ carrier gas and then transported through a new capillary of identical geometrical dimensions to a counting system [39]. These new aerosol particles were deposited onto the surface of a magnetic tape by Mach speed impaction in vacuum. The tape was stepped once a minute to transport the deposited activity in front of 450 mm$^2$ PIPS (passivated ion implanted planar silicon) detectors to analyze $\alpha$-events ($\alpha$-resolution about 50 keV) and fission fragment energies (single fragment kinetic energies only). Hence, the entire set-up from production via transportation, chromatography, re-attachment and deposition on a tape was optimized for nuclides with half-lives of minutes or longer.

### 3 Results and discussion

Figure 3 depicts a $\alpha$-spectrum of the first detector accumulated during a direct catch experiment bypassing OLGA II. The $\alpha$-lines belong to the $^{232}\text{Th}(p,6n)^{227}\text{Pa}$ and $^{232}\text{Th}(p,7n)^{226}\text{Pa}$ products and their progenies. Identification of the $\alpha$-lines was corroborated by list mode data taking, which enabled analysis of time correlated decay chains such as $^{226}\text{Pa} \rightarrow ^{222}\text{Ac} \rightarrow ^{218}\text{Fr} \rightarrow ^{214}\text{At}$ [39].
For chemical analysis, we exclusively used the alpha decay data of $^{226}$Pa and not those of $^{227}$Pa. The reason is the much shorter half-life of $^{226}$Pa of 1.8 min compared to that of $^{227}$Pa (38.2 min) which allowed achieving saturation activity within about 10 min.

It is important to note that in particle-induced reactions formed products are usually in their maximum oxidation state and ionized even higher [40]. The reason for high remaining charge is likely also the plasma condition caused by the high-intensity particle beam in the collecting gas chamber. Pa is therefore assumed to be present initially in form of its highest oxidation state $\text{Pa}^{5+}$.

In a first series of experiments HCl and HBr gases were used to study formation of the corresponding halides. The measured yield curves (in relative yield units) are depicted in Figures 4 and 5 respectively. The uncertainties given represent the statistical counting errors only. The maximum absolute yields were rather low, about 20 and 5% for HCl and HBr, respectively. The 100% relative yield corresponds to the results of measurements of the initial aerosol gas-jet directly injected into the measurement system. The obtained external chromatograms were fitted with a Monte Carlo model based on Zvara’s model of mobile adsorption to determine the adsorption enthalpies [41]. The real temperature conditions along the column have been taken into account (see Figure 2). Furthermore, the experimental gas flow rates were considered as well as the pressure in the column assumed to be 0.9 bar.

The halogenating strength was then increased by adding Cl$_2$/SOCl$_2$ or Cl$_2$/CCl$_4$ and HBr/BBr$_3$ as reactive gases. Indeed observed yields significantly increased to about 80 and 30% for the chlorinating and brominating agents, respectively. These reactive gas mixtures have also been successfully used for gas chemical studies of the group-5 elements, Nb, Ta and Db, respectively, all pseudo-homologs of Pa (for review see Ref. [42]). In those group-5 studies, the higher volatile species were always assigned to the pure halides, while the less volatile to the oxohalides, respectively. We therefore base our tentative species assignment on the same assumption.

Figure 6 depicts the behavior of $^{226}$Pa in a chlorinating gas, which contained SOCl$_2$ using KCl aerosol particles. The break-through temperature at which Pa is transported is similar to that with pure HCl (see Figure 3). We assign the observed volatile species to the oxochloride PaOCl$_3$. The use of KCl aerosols as gas-jet is known to be problematic because of the possible coating of the chromatographic surfaces with salt material. Therefore, we cannot exclude that the observations represent an interaction of the oxo-halides with KCl surfaces rather than SiO$_2$.

In the next experiment the aerosol particle were changed to MoO$_3$ and the reactive gas Cl$_2$ saturated with CCl$_4$. The advantage of using MoO$_3$ aerosol particles is the high volatility of formed Mo halides (e.g. MoO$_2$Cl$_2$) preventing the formation of depositions on the chromatographic surfaces [38]. Indeed, as depicted in Figure 7, the breakthrough temperature of $^{226}$Pa shifted to much lower...
temperatures, indicating formation of a highly volatile compound, presumably the pentachloride.

Furthermore, bromination of $^{226}\text{Pa}$ was investigated in a KCl gas jet system (see Figure 8) using the strongly brominating reactive gas HBr saturated with BBr$_3$. Similar to the chloride case, a significantly lower temperature compared to the pure HBr case (see Figure 5) was observed, at which the volatile bromide species is transported through the column. We therefore propose that PaBr$_5$ is the volatile species formed and transported under such conditions. This interpretation is also corroborated by the literature data mentioned in the introduction.

Table 2 summarizes measured breakthrough temperatures from this work, together with one literature study of Pa under chlorinating conditions applying thermochromatography.

As breakthrough, we define the temperature ($T_{50\%}$) of an isothermal gas-phase chromatography experiment at which the yield is 50%, hence the retention time being one half-life of $^{226}\text{Pa}$ (1.8 min). This retention temperature corresponds approximately to the deposition temperature in a thermochromatography experiment.

Table 3 summarizes the measured adsorption enthalpies on quartz surfaces for the halides and oxohalides of group 5 elements and of Pa halides and its tentatively assigned oxohalides, as evaluated from the results of this work.

To compare measured micro-chemical adsorption enthalpies with macro-chemical sublimation enthalpies empirical correlations may be used [49].

$$\Delta H^0_{\text{subl}} = -(1.66 \pm 0.025) \Delta H^0_{\text{ads}} - (32.5 \pm 5.2), \text{kJ/mol}$$  \(1\)

with $\Delta H^0_{\text{ads}}$ and $\Delta H^0_{\text{subl}}$ representing the adsorption and the sublimation enthalpies, respectively.
Due to lack of data we assume the same correlation to be valid also for the bromides and oxobromides. A reasonable argument for this assumption is the similarity of both processes leading to such correlations, i.e. the adsorption process of the single molecules on a chlorinated and brominated silica surfaces and the process of de-sublimation of halide molecules from the macroscopic solid halide phase. For oxochlorides, the most recent correlation was established between $\Delta H_{\text{ads}}^{\text{SO2}}$ on quartz surfaces and $\Delta H_{\text{subl}}^{0}$ with new adsorption data for Nb and Ta [45].

This correlation is in good agreement with the more general correlation valid for available chlorides and oxochlorides (Eq. (1)). Therefore, Eq. (1) was applied to deduce the corresponding sublimation enthalpies related to the volatilities of the macroscopic compounds of the assumed Pa species. The data set is summarized in Table 4.

### 3.1 Thermochemical assessment and speciation of pentahalides

To corroborate some of the assumed speciation we add here a thermochemical assessment of the volatility of the pure Pa pentachloride and Pa pentabromide, respectively. A comparison of the results of this assessment with the experimentally deduced results shown in Table 4 allows bolstering the assumed chemical state of Pa observed in the experiments.

Figures 9 and 10 depict the correlations between the standard formation enthalpies of solid ($\Delta H_{\text{f}}^{298 \text{(s)}}$) and gaseous ($\Delta H_{\text{f}}^{298 \text{(g)}}$) group 5 chlorides and bromides, respectively, as tabulated in the referenced literature. The difference between $\Delta H_{\text{f}}^{298 \text{(g)}}$ and $\Delta H_{\text{f}}^{298 \text{(s)}}$ yields the sublimation enthalpy, $\Delta H_{\text{subl}}^{0}$.

The observed correlations depicted in Figures 9 and 10, respectively, are purely empirical and are valid only, since all the pentachlorides and pentabromides used in those correlations have similar monoclinic solid state structure [32, 34]. The correlations read as:

1. $\Delta H_{\text{f}}^{298 \text{(g)}} = (−43.055 ± 21.6) + (0.924 ± 0.03) \Delta H_{\text{f}}^{298 \text{(s)}}$ for the chlorides (2)
2. $\Delta H_{\text{f}}^{298 \text{(g)}} = (−23.26 ± 21.84) + (0.795 ± 0.038) \Delta H_{\text{f}}^{298 \text{(s)}}$ for the bromides (3)

### Table 2: Summary of gas phase chromatographic studies with Pa halides in quartz columns using halogenating carrier gas mixtures.

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>T, °C</th>
<th>Reactive gas</th>
<th>Assigned species</th>
<th>$\Delta H_{\text{ads}}^{\text{SO2}}$, kJ/mol</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{231}\text{Pa}$</td>
<td>95 (TC)</td>
<td>CCl$_4$/Cl$_2$</td>
<td>PaCl$_5$</td>
<td>86</td>
<td>[43, 44]</td>
</tr>
<tr>
<td>$^{232}\text{Pa}$</td>
<td>90 (IC/MoO$_3$)</td>
<td>CCl$_4$/Cl$_2$</td>
<td>PaCl$_5$</td>
<td>88 ± 7</td>
<td>This work</td>
</tr>
<tr>
<td>$^{232}\text{Pa}$</td>
<td>740 (IC/KCl)</td>
<td>SOCl$_2$/Cl$_2$</td>
<td>PaOCl$_5$</td>
<td>218 ± 8</td>
<td>This work</td>
</tr>
<tr>
<td>$^{232}\text{Pa}$</td>
<td>≥ 700 (IC/KCl)</td>
<td>HCl</td>
<td>PaOCl$_5$</td>
<td>≥ 197</td>
<td>This work</td>
</tr>
<tr>
<td>$^{232}\text{Pa}$</td>
<td>260 (IC/KCl)</td>
<td>BBr$_3$/HBr</td>
<td>PaBr$_5$</td>
<td>119 ± 2</td>
<td>This work</td>
</tr>
<tr>
<td>$^{232}\text{Pa}$</td>
<td>480 (IC/KCl)</td>
<td>HBr</td>
<td>PaOBr$_5$</td>
<td>161 ± 9</td>
<td>This work</td>
</tr>
</tbody>
</table>

TC, deposition temperature in a thermochromatography experiment; IC, $T_{50\%}$ for isothermal chromatography experiment (this work); KCl resp. MoO$_3$, aerosol particles for transportation of products.

### Table 3: Adsorption enthalpies ($\Delta H_{\text{ads}}^{\text{SO2}}$) of group 5 elements and of Pa halides and oxohalides on silica surfaces assuming the adsorption of the species on halogenated silica.

<table>
<thead>
<tr>
<th>Element</th>
<th>MCl$_5$</th>
<th>MOCl$_5$</th>
<th>MBr$_5$</th>
<th>MOBr$_5$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>$−84 ± 5^{a,b}$</td>
<td>$−99 ± 10^{b}$</td>
<td>$−88 ± 5^{a,b}$</td>
<td>$−155 ± 10^{b}$</td>
<td>[42, 48]</td>
</tr>
<tr>
<td>Ta</td>
<td>$−102 ± 4$</td>
<td>$−128 ± 5$</td>
<td>$−102 ± 3^{a,b}$</td>
<td>$−121 ± 11^{b}$</td>
<td>[46, 48]</td>
</tr>
<tr>
<td>Db</td>
<td>$−94 ± 5^{a,b}$</td>
<td>$−117 ± 10^{b}$</td>
<td>$−87 ± 5^{a,b}$</td>
<td>$−119 ± 2^{b}$</td>
<td>[57]</td>
</tr>
<tr>
<td>Pa</td>
<td>$−88 ± 7$</td>
<td>$−218 ± 8^{b}$</td>
<td>$−119 ± 2^{b}$</td>
<td>$−161 ± 9^{b}$</td>
<td>This work</td>
</tr>
</tbody>
</table>

$^a$Average value from literature data summarized in [41]; $^b$data may be influenced by the use of KCl as aerosol gas-jet material.

### Table 4: Standard sublimation enthalpies of Pa halides and oxohalides deduced from the adsorption enthalpies listed in Table 1 for halogenated silica surfaces$^a$ using Eq. (1).

<table>
<thead>
<tr>
<th>Assumed Compound</th>
<th>PaCl$_5$</th>
<th>PaOCl$_5$</th>
<th>PaBr$_5$</th>
<th>PaOBr$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_{\text{ads}}^{\text{SO2}}$, kJ/mol</td>
<td>$−88 ± 7$</td>
<td>$−218 ± 8$</td>
<td>$−119 ± 2$</td>
<td>$−161 ± 9$</td>
</tr>
<tr>
<td>$\Delta H_{\text{subl}}^{0}$, kJ/mol</td>
<td>$113 ± 15$</td>
<td>$329 ± 16$</td>
<td>$165 ± 5$</td>
<td>$235 ± 17$</td>
</tr>
</tbody>
</table>

$^a$the influence of the KCl aerosol gas-jet material is neglected.
The slopes of the correlations (Eqs. (2) and (3)) are smaller than one which means in turn that the standard formation enthalpies in the solid phase increase stronger than the standard formation enthalpies in the gas phase. Therefore, a decreasing volatility, hence increasing value for the sublimation enthalpy with increasing radius is observed (Figure 11 (green symbols)). Generally, it is observed that the stability order of molecules is determined by the ionic radius of the metal in oxidation state +V (r) [49]. To visualize this, the formation enthalpies of gaseous and solid pentachlorides are plotted as a function of the ionic radius in Figure 11. An increasing ionic bond character was also predicted by relativistic density functional theory [54] for protactinium. Thus, increasingly strong lattice energies are expected for higher ionic radii thermochemically stabilizing the solid states (Figure 11, upper part).

From the literature data of Table 1 for PaCl₅ a sublimation enthalpy for PaCl₅ (blue triangle: 94 ± 1 kJ/mol [27, 30]) results that is contradicting significantly from the expected value deduced from the volatility trend (green line to guide the eye: 145 kJ/mol) [27, 50–53]. The value ΔH₀^subl Pa_extr (red open triangle), deduced from the correlation depicted in Figure 9 of 130 kJ/mol is closer to this expectation. The value deduced from the measured adsorption enthalpy from our work applying Eq. (1) (red point in Figure 3) is shown as Pa_exp (gray triangle: 113 ± 15 kJ/mol).

Within the given uncertainties, the results from these correlations support the assigned chemical state as Pa-pentachloride. For PaBr₅ the extrapolated value of ΔH₀^subl from our measured adsorption enthalpy is 165 kJ/mol (Table 4). This value has to be compared with the significantly lower value of 109 kJ/mol calculated from the literature data (Table 1, [27]). However, it agrees well with 160 kJ/mol deduced from the thermochemical extrapolations (Figure 10). In view of the general volatility...
sequence of the halides a higher sublimation enthalpy – and thus lower volatility – seems reasonable for the protactinium pentabromide compared to the pentachloride.

3.2 Thermochemical assessment and speciation of oxo-halides

Due to a lack of thermodynamic stability data for the protactinium oxohalides a reasonable thermochemical assessment is not possible. The sublimation enthalpies of the hypothetical oxohalides were deduced from our measured adsorption enthalpies on quartz surfaces (Table 2) as $329 \pm 5$ kJ/mol for the oxochloride and $235 \pm 17$ kJ/mol for the oxobromide using Eq. (1). These values deviate from the general trend for d-element halides with an expected higher volatility for the chloride form compared to the bromide form. However, the situation in group 5 is rather unclear. While this statement holds for Nb, it does not hold for Db (see Table 3). Unfortunately, for Ta no data exist for the oxobromide. Hence, a prediction concerning the pseudo group-5 element Pa is not possible. Several aspects could be of importance: given the low stability of the Pa-O chemical bond a general instability of the assumed oxohalides is expected. This is supported by the reported thermal instability of the oxochloride [32]. As alternative, a transport mechanism might be involved with an intermediate formation of oxides followed by a re-chlorination by the reactive carrier gas (see e.g. [56]). The analysis required for such transport processes, however, is beyond the scope of our work and requires a profound knowledge of missing thermochemical data as well as partial pressures of oxygen and chlorinating species in the carrier gas.

4 Conclusions

On-line gas phase chemical studies of protactinium produced in the $^{232}\text{Th}(p;7n)^{226}\text{Pa}$ reaction enabled to determine adsorption enthalpies of Pa-pentachloride and Pa-oxochloride as well as the corresponding pentabromide and oxotribromide complexes on quartz surfaces. From the measured adsorption enthalpies sublimation enthalpies were extrapolated based on empirical correlations. The resulting values clearly point to a high volatility of these compounds with the chlorides being more volatile than the bromides. This is expected for group-5 elements and points to the well known fact, that Pa behaves in many aspects more like a 5d-element rather than an actinide. Therefore, this study compares also to other studies of group 5 elements, including Db [57].

To our knowledge, this work describes the first online chemistry experiment of an element formed in a proton-induced fusion reaction using a multi-stack target arrangement. This technique might enable future thermochemical studies of Pa and other elements accessible by proton induced fusion reactions. Moreover, a possible application of this technique might be the online production of Pa isotopes for nuclear medical applications.

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