

The Gas Phase Oxide and Oxyhydroxide Chemistry of Trace Amounts of Rhenium

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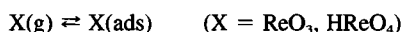
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(Received June 22, 1999; accepted in revised form October 19, 1999)

Rhenium / Thermochromatography / OLGA / Oxide / Oxyhydroxide / Adsorption

Summary

In preparation of experiments to investigate the chemical properties of bohrium (Bh, element 107) the behaviour of Re, its lighter homologue in group 7, was studied in different oxidizing chemical systems. The adsorption data of Re oxide and oxyhydroxide compounds on quartz surfaces were evaluated from results of thermochromatography experiments and confirmed in isothermal gas chromatography experiments applying 1 cm as standard state for the simple gas adsorption process:



$$\Delta H_{\text{ads}}(\text{ReO}_3) = -190 \pm 10 \text{ kJ/mol};$$

$$\Delta S_{\text{ads}}(\text{ReO}_3) = -179 \pm 30 \text{ J/mol K};$$

$$\Delta H_{\text{ads}}(\text{HReO}_4) = -77 \pm 5 \text{ kJ/mol};$$

$$\Delta S_{\text{ads}}(\text{HReO}_4) = -187 \pm 50 \text{ J/mol K}.$$

An on-line separation method for oxides and oxyhydroxides of short lived Re isotopes using isothermal high temperature gas-solid adsorption chromatography was developed. Separation yields and times of group 7 elements from lanthanides (model for actinides), polonium and bismuth were determined using the model isotopes ^{169,170,174,176}Re, ^{152–155}Er, ^{151–154}Ho, ²¹⁸Po, and ²¹⁴Bi. An updated correlation function between the microscopic adsorption enthalpy and the macroscopic sublimation enthalpy was calculated from the experimental adsorption data of this work and literature data.

1. Introduction

The growing use of the nuclides ^{186,188}Re in modern nuclear medicine requires the development of production methods and of fast and efficient separation techniques for radioactive Re nuclides [1]. Therefore, the knowledge of the inorganic and complex chemistry of this element is very essential. The behaviour of simple inorganic Re compounds is interesting too for a completely different field of chemistry – the chemical characterization of the heaviest elements. Of the currently 10 known transactinide elements ($Z > 103$) only the first three, namely rutherfordium (Rf, element 104), dubnium (Db, element 105) and seaborgium (element 106) have been chemically characterized. The main goal of a chemical characterization of

transactinide elements is their placement in the Periodic Table. Due to the high nuclear charge (Z), relativistic effects are strongly influencing the electronic structure of these elements [2, 3]. Relativistic effects affect also the binding energies of the valence electrons and thus the symmetry of the atomic orbitals, which determine the chemical behaviour of the transactinides. Thus, these effects may disturb the periodicity of properties in the transition metal groups of the Periodic Table. In extreme cases they might even change chemical properties to such an extent that the heavy elements behave no longer similar to their lighter homologues. In recent experiments the gas chemical behaviour of the first transactinide elements rutherfordium Rf [4, 5], Db [6, 7] and Sg [8, 9] was determined at an “one-atom-at-a-time” level using the on-line separation and detection technique OLGA [14]. Evidence for relativistic effects was observed in the behaviour of Rf-chlorides [4]. Most recently, experiments on the chemistry of seaborgium showed that SgO_2Cl_2 behaved similar to WO_2Cl_2 [8].

Experiments to determine for the first time the chemical behaviour of bohrium (Bh, element 107) are envisaged. All known Bh isotopes have been produced in so-called cold fusion reactions with Pb or Bi targets and are therefore neutron deficient and very short-lived ($t_{1/2} < 1\text{s}$), which is too short for a study of its chemical properties. More neutron-rich and hence, longer-lived isotopes of Bh could be produced in hot fusion reactions. The expected half-lives of e.g. ^{266/267}Bh are in the order of a few seconds [10, 11]. These isotopes can be produced in the reaction ²⁴⁹Bk(²²Ne;4,5n)^{266,267}Bh. The production cross sections are estimated to be in the order of 50 pb. Thus, the experimental determination of physico-chemical properties of Bh compounds requires the development of fast, efficient and at the same time selective separation techniques.

A first attempt of an experimental characterization of the chemical properties of Bh was carried out by Zvara *et al.* [12]. At the JINR, Dubna an attempt was made to produce Bh nuclides in the reaction ²⁴⁹Bk(²²Ne;4–6n)^{265–267}Bh. After a thermochromatography separation of volatile oxyhydroxides in the chemical system air/H₂O an off-line search for spontaneous fission (sf) tracks in the thermochromatography column was performed. No fission tracks related

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to Bh nuclides were detected. This negative result was interpreted that either the half-lives of the produced Bh nuclides were shorter than 2 s or that the production cross section was less than 100 pb. In another attempt at LBNL Berkeley, Schädel *et al.* [13] used the reaction $^{254}\text{Es}(^{16}\text{O};3-5\text{n})^{265-267}\text{Bh}$. The reaction products were transported by a He-KCl gas jet to an on-line gas chromatography apparatus (OLGA) [14]. A reactive gas mixture of $\text{O}_2/\text{H}_2\text{O}$ was added. The volatile Bh-oxyhydroxides were separated from heavy actinides and lighter transactinide elements and then condensed on Ni/Ta foils for on-line α -particle and sf spectroscopy. No genetically linked decay chains were detected. Either the half-lives of the produced Bh-nuclides were shorter than 2 s or the production cross section was less than 5 nb. In both experiments no chemical properties of Bh could be determined.

In order to attempt a chemical characterization of Bh, the behaviour of Re, its closest lighter homologue, was studied in this work. The formation and gas chromatographic separation of ReO_3 and HReO_4 was investigated on-line using short-lived Re isotopes.

2. Thermochemistry of the Oxid/Oxyhydroxide compounds of Re

The formation of oxides and oxyhydroxides in $\text{O}_2/\text{H}_2\text{O}$ -containing gas chemical systems is typical for the group 7 elements and has extensively been studied [15–23]. Due to their high volatility the oxyhydroxides are especially interesting for gas chromatography studies, since a high volatility of the investigated compound allows high separation factors from less volatile by-products, such as heavy actinides, Po, Pb, and Bi, which usually hamper detection of final products by α -spectroscopy. Thermodynamic data (see Table 1) indicate, that for carrier-free amounts of rhenium in a $\text{O}_2/\text{H}_2\text{O}$ containing gas phase system, ReO_3 and HReO_4 are the only stable volatile species. The thermodynamically most stable molecule in this chemical system at standard conditions (298 K, 1 atm) is HReO_4 , the perrhenic acid.

3. Experimental

3.1 Investigations in the temperature gradient tube

Thermochromatography is a very suitable gas adsorption chromatographic separation method. It has been successfully applied to characterize the behaviour of various compounds in different chemical systems [18–24, 48, 49, 54].

3.1.1 Experiments with carrier free Re

The formation and the volatility of ReO_3 and HReO_4 in $\text{He}/\text{O}_2/\text{H}_2\text{O}$ atmosphere were investigated by thermochromatography using carrier free $^{183/184}\text{Re}$. The

Table 1. Thermodynamical formation data of carrier free Re compounds in the chemical system $\text{O}_2/\text{H}_2\text{O}/\text{Re}$ (* used in this work).

Formula	$\Delta_f H^\circ_{298}$ [kJ/mol]	S°_{298} [J/molK]	Lit.:	
Re(s)	0	36.53	[25]	
Re(g)	762.3	190.26	[25]	
	770.2	188.92	[26]	
	776.0	192.4	[27]	
ReO(s)	−604.6	44.37	[28]	
	−255.4		[29]	
ReO(g)	393.4	248	[28]	
	376.7		[27]	
	397.7		242.42	[29]
ReO ₂ (s)	−442.2	46.44	[25]	
	−422.8	41	[31]	
	−430.3±20.0	56.51±6.7	[32]	
	−423.6		[34]	
	−451.5	47.82	[37]	
	−433.9		[36]	
	−447.9	56.51	[29]	
−451.8	56.52	[41]		
ReO ₂ (g)	274.8	299	[25]	
	58.6±33.5		[30]	
	88.5		[31]	
	274.6		[36]	
	242.8		267.90	[29]
ReO ₃ (s)	−594.3*	80.75	[25]	
	−611.2		[35]	
	−611.6±3.4		[28]	
	−605.3		61.5	[31]
	−602.5±6.3		69.25	[37]
	−601.2±6.3			[37]
	−589.1±3.8			[36]
	−589.0±8.4		80.79±6.3	[32]
	−592.9±4.2			[39]
−593.2	80.79	[29]		
ReO ₃ (g)	−350.6*	339	[25]	
	−326.5±60		293 ±6	[30]
	−284.7±21.0		288.7 ±8.4*	[38]
	−280.5		284.65	[29]
HReO ₄ (s)	−762.7*	158.23	[26]	
	−762.7± 4.2		[40]	
	−762.7		[31]	
HReO ₄ (g)	−665.6	313.95*	[31]	
	−665.6*		[40]	

nuclides $^{183/184}\text{Re}$ were produced at the PSI Philips Cyclotron by proton irradiation of natural tungsten in the reaction $^{nat}\text{W}(p;xn)^{184,183}\text{Re}$ at a beam energy of 30 MeV [42]. The products were separated from macroamounts of tungsten by thermochromatography [43]. A carrier-free solution of $^{183/184}\text{Re}$ was obtained by leaching the thermochromatography column with concentrated ammonia solution. The preparation of a sample of carrier-free $^{183/184}\text{Re}$ suitable for a thermochromatography experiment involved the following steps. First, quartz filter stripes were drenched

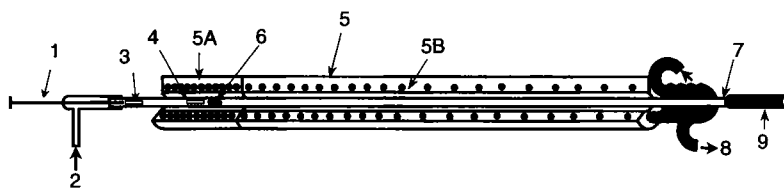


Fig. 1. Thermochromatography set-up: 1 – steel rod; 2 – carrier gas mixture $\text{He}/\text{O}_2/\text{H}_2\text{O}(\text{H}_2\text{O}_2)$; 3 – $^{183/184}\text{Re}$ on quartz filter stripe before starting experiment; 4 – $^{183/184}\text{Re}$ on quartz filter stripe in the reaction oven after starting experiment; 5 – thermochromatography oven with 5A-reaction oven 1430 K and 5B-temperature gradient; 6 – quartz wool plug; 7 – quartz column (i.d. 3 mm, $l = 1$ m); 8 – cooling spiral; 9 – char coal trap.

with the ammonia leaching solution ($\text{NH}_4^{183/184}\text{ReO}_4$) and then dried in a desiccator. Each of the dry quartz filter stripes was placed into a thermochromatography column (i.d. 3 mm). The entire column was heated to 1273 K for 15 min with a mixture of argon and hydrogen (Vol.-% ratio 94:6, flow rate 100 ml/min) in order to reduce the $\text{NH}_4^{183/184}\text{ReO}_4$ to elemental Re. The column with the reduced rhenium sample was placed into a thermochromatography set-up at a position outside the reaction oven (Fig. 1). The He/O_2 mixture was dried with concentrated sulfuric acid followed by a molecular sieve and a cold trap kept at 198 K. A well defined partial pressure of H_2O was established by saturating the dry gas with water or ice kept at selected temperatures T_{sat} . A stable temperature gradient along the column was then established in the flowing carrier gas. The gas flow rates were varied between 25 and 1210 ml/min. Every experiment was started by pushing the quartz filter stripe into the hot reaction zone of the thermochromatography oven with a steel rod. After a given time the carrier gas flow was stopped and the quartz column was immediately removed from the oven through the cold end. The distribution of the Re-activity along the quartz column was measured with a HPGe- γ -detector using a lead collimator with a window size of 1.0×0.6 cm. The experiments were usually repeated several times.

3.1.2 Experiments with macroscopic amounts

The behaviour of macroscopic amounts of Re was studied by adding about 1 mg of Re_2O_7 carrier to the $\text{NH}_4^{183/184}\text{ReO}_4$ solution. The Re containing samples were again reduced to elemental Re using an Ar/H_2 - (Vol.-% 98:2) mixture at 1273 K. For these thermochromatography experiments the same set-up (Fig. 1) as for the thermochromatography experiments was used.

3.2 Isothermal gas chromatography

Based on the thermochromatography studies an on-line method for the investigation of the adsorption behaviour of oxide compounds of short-lived nuclides on quartz surfaces was developed.

So far, the OLGA-technique has been successfully applied to investigate the oxychloride and chloride chemistry of Rf, Db, and Sg [4–8]. Using an aerosol

gas-jet transport system, this technique allows an efficient on-line coupling to a production system (the target chamber at an accelerator). It provides a rapid separation of volatile compounds and can be connected directly to a high efficiency α -(sf)-detection system like ROMA (ROTating wheel Multidetector Analyser) or the PSI Tape Detection System – using a reclustered gas-jet technique [45].

The nuclide $^{169\text{m}}\text{Re}$ with a half-life of 16 s and its α -decay branch ($E_\alpha = 5.0$ MeV) is ideally suited to model the behaviour of the heavier group 7 element Bh. At the PSI Philips Cyclotron $^{169\text{m}}\text{Re}$ was produced in the heavy ion fusion reaction $^{156}\text{Dy}(^{19}\text{F};6n)^{169\text{m}}\text{Re}$ at a ^{19}F -beam energy of 128 MeV. The target material, enriched in ^{156}Dy (20%), also contained the other stable Dy isotopes ^{158}Dy (0.51%), ^{160}Dy (3.46), ^{161}Dy (19.82%), ^{162}Dy (22.19%), ^{163}Dy (16.92%), and ^{164}Dy (16.25%) from which the γ -emitting isotopes ^{170}Re ($t_{1/2} = 9.2$ s), ^{172}Re ($t_{1/2} = 16$ s), $^{172\text{m}}\text{Re}$ ($t_{1/2} = 55$ s), ^{174}Re ($t_{1/2} = 2.4$ min), and ^{176}Re ($t_{1/2} = 5.6$ min) were produced. Different lanthanide nuclides, produced in transfer reactions of the ^{19}F -beam with the Dy target, such as $^{152-155}\text{Er}$ and $^{151-154}\text{Ho}$, served as model elements for the behaviour of actinides.

In the target chamber, the fusion products were attached to carbon aerosol particles (5×10^6 particles/ cm^3), which were generated by spark discharge in a mixture of 1 l/min He and 10 ml/min N_2 and then transported through a steel capillary (50 m, i.d. 2 mm) to the OLGA set-up. In order to obtain HReO_4 100 ml/min O_2 (containing 500 ppm O_3) saturated with H_2O_2 at room temperature were added as reagents to the gas-jet gas shortly before the reaction oven. The carbon aerosols were stopped on a quartz wool plug at 1373 K in the reaction oven, where they were burned to CO_2 and the nuclear reaction products were oxidized. Volatile compounds were evaporated and chromatographically separated in a 1.5–2 m long (i.d. 1.3 mm) quartz column kept at variable isothermal temperatures. The time required for compounds to pass through the column at defined isothermal temperatures depends mainly on the adsorption behaviour on the quartz surface and on the gas flow rate. Thus, highly volatile Re-compounds pass through the column much faster compared to less volatile compounds of other nuclides which – depending on the isothermal temperature – are retained and decay inside the column. Volatile compounds leaving the exit of the column were reat-

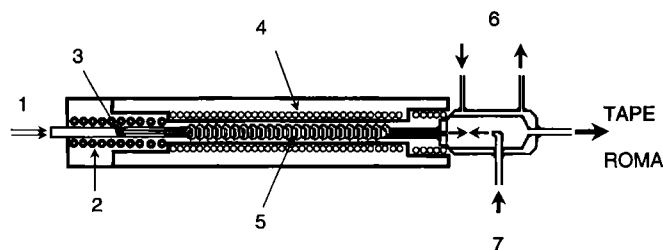


Fig. 2. Modified OLGA III – a high temperature isothermal gas chromatography set-up: 1 – $O_2(O_3)/H_2O(H_2O_2)$, aerosol gas-jet He/C; 2 – reaction oven 1400 K; 3 – quartz wool; 4 – isothermal oven 550–1200 K; 5 – quartz column with recluster unit; 6 – water cooling/heating 260–370 K; 7 – recluster aerosol gas-jet Ar/ MoO_3 .

tached to MoO_3 -aerosols in 1 l/min Ar in the recluster unit and transported to the PSI tape detection system. Here, the MoO_3 -aerosols were deposited by impaction on the surface of a tape which periodically moved the collected samples in front of a series of PIPS detectors to measure the α -decay of ^{169m}Re , $^{152-155}Er$ and $^{151-154}Ho$. In position 1 a HPGe-detector registered γ -rays of $^{170,172,172m,174,176}Re$.

A modified high temperature OLGA III system with an isothermal temperature range between 500 and 1200 K (Fig. 2) was developed and applied in another experiment to study the formation and the behaviour of less volatile ReO_3 . As carrier gas mixture 1 l/min He, 10 ml/min N_2 (gas jet mixture) and 100 ml/min O_2 (reactive gas) was used. With this set-up and the same carrier gas conditions, the behaviour of Po and Bi was also investigated using the nuclides ^{218}Po ($t_{1/2} = 3.05$ min) and ^{214}Bi ($t_{1/2} = 19.9$ min) from a ^{226}Ra source.

4. Results and discussion

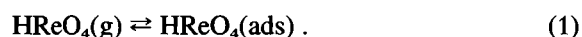
4.1 Investigation of the formation and the volatility of rhenium compounds

4.1.1 Thermochromatography with carrier-free $^{183/184}Re$

Using 25 ml/min He containing 0.001 volume-% O_2 and a water partial pressure $p_{H_2O} < 600$ Pa as carrier

gas (Table 2, exp. 4, 9, 12, 15, 16), a single volatile Re compound was observed that deposited at about 570 K (Fig. 3, deposition peak C) and was attributed to ReO_3 . About 5% of the activity remained in the starting zone at about 1430 K (Fig. 3, deposition peak A) as less volatile species, presumably ReO or ReO_2 . Adding more than 5 volume-% O_2 to the carrier gas led to a more volatile compound which deposited at about 340 K (Fig. 3, deposition peak D), and which was assumed to be $HReO_4$, the most volatile Re compound in this chemical system. In most cases (Table 2) the formation of both compounds (Fig. 3, deposition peaks C and D) was observed. To confirm the dependence of the formation of the more volatile $HReO_4$ on the oxidation potential of the carrier gas, H_2O_2 (30%) was used instead of water in the saturation unit which indeed led to a single peak from $HReO_4$ (Table 2, exp. 13).

The deposition peak at about 340 K (Fig. 3, deposition peak D), assigned to $HReO_4$, can be explained by a mobile adsorption process:



Applying higher gas flow rates (Table 2, exp. 20) a less volatile Re compound at about 820 K (Fig. 3, deposition peak B) was observed. With about 50% O_2 in the carrier gas two deposition peaks, C and D, at lower temperatures (Table 2) were found.

In further experiments (Table 2, exp. 39, 41) the chromatography columns were pretreated with oxygen

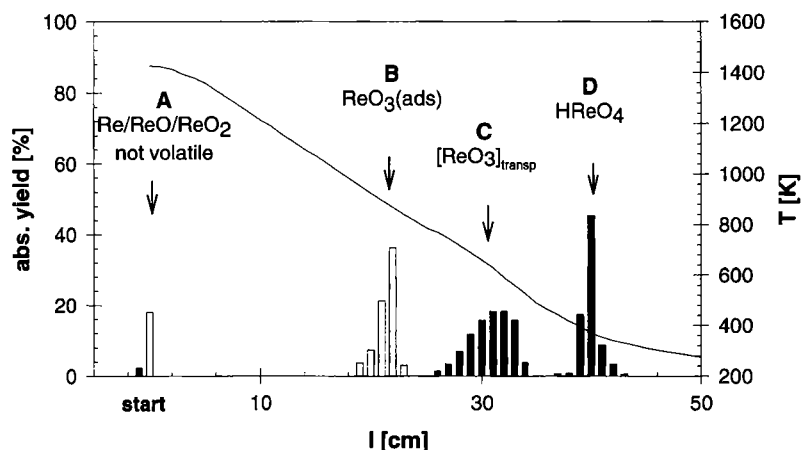


Fig. 3. Merged thermochromatograms of three different experiments (for details see text).

Table 2. Thermochromatography experiments assigned to mobile adsorption of HReO_4 (D) and ReO_3 (B) and to a transport reaction of ReO_3 (C) according to: $\text{HReO}_4(\text{g}) \rightleftharpoons \text{ReO}_3(\text{ads}) + 1/4 \text{O}_2 + 1/2 \text{H}_2\text{O}$.

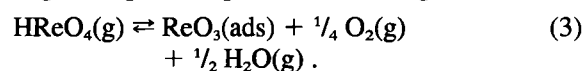
Exp.	Starting temperature T_s [K]	Gas flow rate v [ml/min]	Experiment duration t [min]	Temperature in the saturation unit with H_2O or with $^*\text{H}_2\text{O}_2$ T_{sat} [K]	O_2 content in the carrier gas [vol-%]	Temperature gradient g [K/cm]	Deposition temperature T_d [K]		
							B	C	D
1	1428	25	5	293	60	27.3	—	580	325
2	1428	25	5	253	60	27.3	—	603	329
3	1428	25	5	253	60	27.3	—	580	—
4	1428	25	5	273	0.001	27.3	—	628	—
5	1428	25	5	253	60	27.3	—	451	329
6	1428	25	5	253	60	27.3	—	—	368
7	1428	25	5	253	60	27.3	—	454	—
8	1428	25	5	253	100	27.3	—	—	347
9	1428	25	5	253	0.001	27.3	—	509	—
10	1428	25	5	253	4	27.3	—	505	325
11	1428	25	5	253	4	27.3	—	580	321
12	1428	25	5	273	0.001	27.3	—	562	—
13	1428	25	5	*273	0.001	27.3	—	—	349
14	1428	500	30	273	50	26.6	—	—	293
15	1428	500	30	253	0.001	26.6	—	380	—
16	1428	500	30	253	0.001	26.6	—	367	—
17	1329	25	60	303	40	11.6	—	—	339
18	1329	25	60	303	40	11.6	—	—	335
19	1408	1010	60	253	80	21.8	—	473	—
20	1408	1010	60	303	80	21.8	777	—	—
21	1408	1010	60	303	80	21.8	800	—	—
22	1408	1010	60	303	80	21.8	777	—	—
23	1408	830	60	323	20	21.8	—	549	—
24	1408	1000	60	313	100	21.8	—	—	298
25	1408	1610	20	313	50	21.8	800	—	298
26	1408	1610	20	313	50	21.8	824	—	298
27	1408	1610	60	293	60	21.8	753	—	—
28	1408	1610	60	293	60	21.8	—	408	298
29	1408	1610	20	303	50	21.8	800	—	—
30	1408	1010	10	313	50	21.8	824	—	298
31	1408	1210	10	293	80	21.8	847	—	—
32	1408	1210	10	293	80	21.8	—	524	—
33	1408	1210	5	203	80	21.8	823	—	—
34	1408	1000	5	293	100	21.8	—	—	338
35	1408	500	5	293	100	21.8	—	—	333
36	1408	500	5	293	100	21.8	—	—	344
37	1408	500	5	293	100	21.8	—	—	315
38	1273	25	150	77	0.007	17.6	—	506	—
39	1273	25	60	77	0.007	17.6	855	—	—
40	1273	25	60	77	0.007	17.6	—	608	—
41	1273	25	60	77	0.007	17.6	874	—	—

at 1273 K for 15 min. The Re samples were reduced in a separate quartz tube and then introduced into the pre-treated thermochromatography columns. Surprisingly, the same high temperature Re deposition peak **B** was observed. This deposition was also attributed to ReO_3 , since the formation of another oxide or oxyhydroxide species of rhenium (ReO_xH_y) is not probable. This is corroborated by mass spectrometric analyses of rhenium compounds in the $\text{O}_2/\text{H}_2\text{O}$ -gas phase [32, 38] and by thermochemical data (see Table 1). In the same set-up experiments (Table 2, exp. 38, 40) with columns heated in Ar/H_2 mixture at 1273 K led again to a ReO_3 deposition at 500–600 K (Fig. 3, deposition peak C). The formation of two deposition peaks of ReO_3 could be explained by two different adsorption mechanisms:

– mobile adsorption leading to a ReO_3 deposition at 770–870 K (Fig. 3, deposition peak **B**) which can be described by:



– a transport reaction where [15, 40, 43] ReO_3 can be transported to lower temperatures (410–610 K) (Fig. 3, deposition peak **C**) according to:



It is not possible to describe the real reaction path of the transport process, but the quartz surface has obviously a strong influence on it.

Two independent methods, the model of mobile adsorption [46] and the microscopic model of Zvara

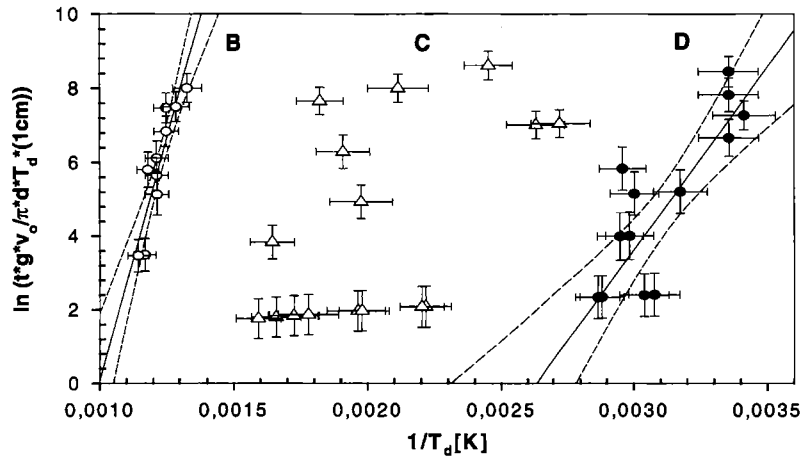


Fig. 4. Experimental adsorption data from Table 2 with either direct formation of (B) ReO_3 (open circles) and (D) HReO_4 (dots) or with superimposed chemical reaction (C) $[\text{ReO}_3]_{\text{transp}}$ (triangles).

Table 3. Deposition temperatures (T_d) and evaluated adsorption enthalpies (ΔH_{ads}) assuming mobile adsorption of HReO_4 , ReO_3 , and of a hypothetical compound ReO_xH_y . The calculated adsorption enthalpy of ReO_3 assuming a transport reaction.

Compound	T_d [K]	$\Delta H_{\text{ads}}(298)$ [kJ/mol]
HReO_4	346 ± 20	-77 ± 5
ReO_3	823 ± 50	-190 ± 10
ReO_xH_y	523 ± 100	~ 120
$[\text{ReO}_3]_{\text{transp}}$	523 ± 100	-220 ± 30

[47], were used for the evaluation of the adsorption enthalpies of the compounds from the thermochromatograms (Table 3). By modifying the experimental conditions in thermochromatography over a wide range, the adsorption enthalpy and the adsorption entropy (ΔH_{ads} , ΔS_{ads}) can be evaluated simultaneously from an Arrhenius plot (Fig. 4). This so-called second law method (4) is the result of a simplified mobile adsorption model proposed in [46, 54], which is the only way for an experimental determination of the mobile adsorption entropy of HReO_4 and ReO_3 .

$$\ln \frac{t \cdot g \cdot v_0}{\pi \cdot d \cdot T_d \cdot (1 \text{ cm})} = a \cdot \frac{1}{T_d} + b; \quad (4)$$

$$a = \frac{-\Delta H_{\text{ads}}}{R}; b = \ln \frac{R \cdot T_0}{-\Delta H_{\text{ads}}} + \frac{\Delta S_{\text{ads}}}{R};$$

t : retention time, experiment time [min]; g : temperature gradient ($g > 0$) [K/m]; v_0 : gas flow (STP) [cm^3/min]; d : inner diameter of the column [mm]; T_d : deposition temperature [K]; T_0 : standard temperature (298.15 K); R : ideal gas constant (8.314 J/mol K); a, b : linear regression parameters.

From the regression parameters of the plot in Fig. 4 the following adsorption properties were evaluated for the reversible adsorption processes (1 and 2):

$$a(1) = 9900 \pm 1900 \\ \Rightarrow \Delta H_{\text{ads}}(\text{HReO}_4) = -82 \pm 16 \text{ kJ/mol};$$

$$b(1) = -26.1 \pm 5.8 \\ \Rightarrow \Delta S_{\text{ads}}(\text{HReO}_4) = -187 \pm 50 \text{ J/mol K};$$

$$a(2) = 26000 \pm 3600 \\ \Rightarrow \Delta H_{\text{ads}}(\text{ReO}_3) = -216 \pm 30 \text{ kJ/mol};$$

$$b(2) = -26.0 \pm 4.4 \\ \Rightarrow \Delta S_{\text{ads}}(\text{ReO}_3) = -179 \pm 30 \text{ J/mol K}.$$

Using the mobile adsorption model with a superimposed chemical reaction [48] the dissociative adsorption enthalpy and entropy of the transport reaction (3) have been determined:

$$\Delta H_{\text{diss.ads}}(\text{ReO}_3) = -23 \pm 30 \text{ kJ/mol}$$

and

$$\Delta S_{\text{diss.ads}}(\text{ReO}_3) = -58 \pm 50 \text{ J/mol K}.$$

This thermochemical calculation requires a complete set of thermodynamic data of $\text{ReO}_3(\text{g})$, $\text{ReO}_3(\text{g})$, $\text{ReO}_3(\text{ads})$ and $\text{HReO}_4(\text{g})$ (Table 1). Since no literature value for the gas phase entropy of HReO_4 existed, an approximated value from [40] was used. The standard formation data of $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ were taken from [25].

4.1.2 Thermosublimatography using macroscopic amounts of rhenium

With macroscopic amounts the gas adsorption chromatography changes to a sublimation chromatography reaching a multilayer coverage of the column surface. Thus, the sublimation enthalpy (ΔH_{subl}) and sublimation entropy (ΔS_{subl}) become the describing thermochemical values. The formation of polynuclear compounds is possible. From the thermosublimatograms one can determine the macroscopic property ΔH_{subl} (5) [49].

$$\ln \frac{m \cdot R \cdot T_0}{v_0 \cdot t \cdot M \cdot p_0} = \frac{-\Delta H_{\text{subl}}}{R \cdot T_d} + \frac{\Delta S_{\text{subl}}}{R} \quad (5)$$

m : mass of the compound [g]; p_0 : standard pressure [atm]; M : molar mass of the compound [g mol^{-1}].

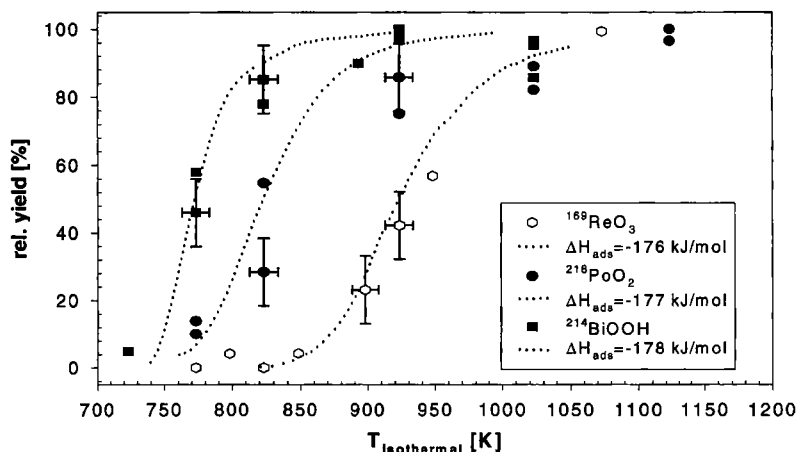


Fig. 5. Temperature vs. yield curves of ^{169}Re ($t_{1/2} = 16$ s, presumably ReO_3), ^{218}Po ($t_{1/2} = 3.05$ min, presumably PoO_2), ^{214}Bi ($t_{1/2} = 19.9$ min, presumably BiOOH) experimental data (symbols) with calculated Monte Carlo simulations (dotted curves) and evaluated adsorption enthalpies.

Table 4. Experimental sublimation enthalpies ($\Delta H_{\text{subl}}(\text{exp.})$) of HReO_4 , ReO_7 and ReO_3 in comparison to literature data ($\Delta H_{\text{subl}}(\text{lit.})$) together with their deposition temperature ranges (T_d).

Compound	T_d [K]	$\Delta H_{\text{subl}}(\text{exp.})$ [kJ/mol]	$\Delta H_{\text{subl}}(\text{lit.})$ [kJ/mol]
(1) HReO_4	370–380	101 ± 10	97.1 [31]
			78.1 [26]
			115.3 [29]
(2) Re_2O_7	400–440	132 ± 10	139.8 [31]
			147.8 [25]
(3) ReO_3	730–740	212 ± 10	208.4 [34]
			243.7 [25]

Using 15 ml/min He and 10 ml/min O_2 as carrier gas three compounds were observed that deposited at different temperatures T_d , independently of the pre-treatment of the column: $T_d(1) = 370\text{--}380$ K, $T_d(2) = 400\text{--}440$ K and $T_d(3) = 730\text{--}740$ K.

The three compounds in the thermosublimograms were related to $\text{HReO}_4(1)$, $\text{Re}_2\text{O}_7(2)$, and $\text{ReO}_3(3)$ since the evaluated sublimation enthalpies of these compounds $\Delta H_{\text{subl}}(\text{exp.})$, are in good agreement with the literature data $\Delta H_{\text{subl}}(\text{lit.})$ (Table 4).

4.2 Isothermal gas chromatography

In the isothermal gas chromatographic process the quartz surface is heated in a $\text{He}/\text{O}_2/\text{H}_2\text{O}(\text{g})$ atmosphere. The separation is carried out applying high gas flow rates. Considering the results of the thermochromatography experiments with carrier-free Re isotopes, neither the transport reaction nor the direct formation reaction of HReO_4 can be expected.

Indeed, no Re isotopes were measured with OLGA III at isothermal temperatures up to 773 K. At the given experimental conditions HReO_4 is not

formed. A kinetic hindrance of the formation reaction of HReO_4 can be excluded, since there was also no longer-lived ^{176}Re observed after chemical separation.

In high temperature isothermal gas chromatography the adsorption behaviour of ReO_3 was determined on-line, using the short-lived $^{169,170}\text{Re}$ isotopes. In the temperature range between 720 and 1070 K the yield of ReO_3 as a function of isothermal temperature, has been measured (Fig. 5). The adsorption enthalpy of ReO_3 on the quartz surface was evaluated from these curves by a Monte Carlo model to $\Delta H_{\text{ads}}(\text{ReO}_3) = -176 \pm 10$ kJ/mol (Fig. 5). This result is in good agreement with the results of the thermochromatography experiments (Table 3) with high gas flow rates or with quartz columns pre-treated with oxygen at 1273 K, where only mobile adsorption of ReO_3 leading to a Re deposition at 750–870 K (Fig. 3, deposition peak B), was found. The overall yields of the gas phase separation were about 60% for $^{176}\text{Re}(t_{1/2} = 5.3$ min), 40% for $^{169}\text{Re}(t_{1/2} = 16.3$ s), and 25% for $^{170}\text{Re}(t_{1/2} = 9.2$ s). Employing the yield ratio of short-lived $^{169,170}\text{Re}$ and long-lived $^{174,176}\text{Re}$ in a so-called “direct catch” (DC) measurement (without chemical separation) and in a gas chemical experiment a separation time of 16 s was calculated [52]. The formation of ReO_3 seems to be kinetically hindered because the transit time of the carrier gas of about 5 s through the OLGA-system is short in comparison to the determined separation time of 16 s.

Since the isotopes $^{266,267}\text{Bh}$ were expected to have half-lives of about 10 s only, this gas phase separation system is probably not fast enough for a chemical characterization of Bh.

Another crucial point is the separation efficiency from heavy actinides, which are produced in transfer reactions with high production cross sections, and from Po, Pb, and Bi nuclides which are produced in interactions of the heavy ion beam with traces of lead in the target material or the target assembly. These by-products interfere with an unambiguous identification of Bh due to their partly very similar α -decay energies

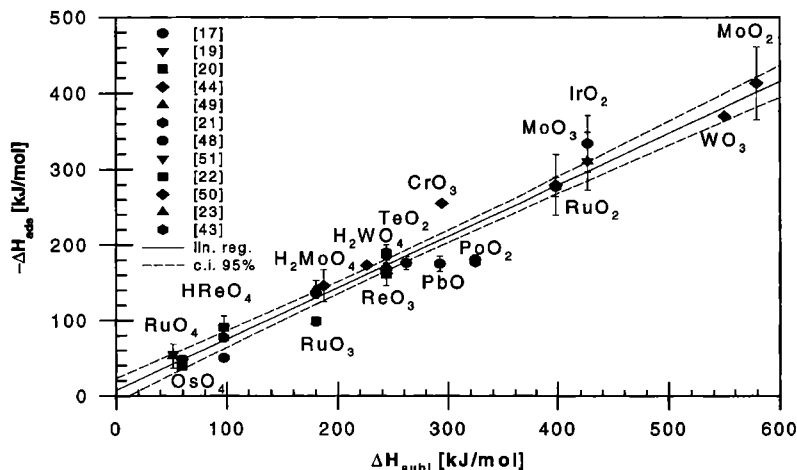


Fig. 6. Updated correlation plot between ΔH_{subl} [kJ/mol] and $-\Delta H_{\text{ads}}$ [kJ/mol] for the adsorption of oxides and oxyhydroxides on quartz surfaces.

and half-lives and due to spontaneous fissioning heavy actinide nuclei. In the developed high temperature gas chromatography it is not possible to separate Po- and Bi-compounds from the group 7 elements (Fig. 5). The separation of lanthanides as model elements for actinides was evaluated from the total of the α -decays of the nuclides $^{152-155}\text{Er}$ and $^{151-154}\text{Ho}$, which were produced in transfer reactions of the ^{19}F beam with the Dy target. Since no α -decays of these nuclides were observed in the α -spectra after chemical separation, a separation factor of $\geq 10^3$ was deduced.

4.3 Update of the correlation chart:

$$\Delta H_{\text{subl}} / -\Delta H_{\text{ads}}$$

With regard to our results a re-evaluation of previous thermochromatography experiments with Re in oxygen and water containing gas systems [17–22, 44] was carried out. At similar experimental conditions Re compounds were observed in these experiments at deposition temperatures near 820 K, 520 K, and in the charcoal trap behind the column. In the light of the present experiments these compounds should be assigned to ReO_3 , $[\text{ReO}_3]_{\text{transp}}$, and HReO_4 , respectively. Using the model of mobile adsorption with $\Delta S_{\text{a,mob}}$ instead of ΔS_{subl} [46] and assuming a transport reaction (3) for ReO_3 , the adsorption enthalpies ($\Delta H_{\text{ads}}(\text{lit.})$) in these experiments can be re-determined ($\Delta H_{\text{ads}}(\text{new})$ or $\Delta H_{\text{ads}}([\text{ReO}_3]_{\text{transp}})$). The results of this evaluations for the Re compounds are shown in Fig. 6.

For different gas adsorption systems (e.g. metals [56], oxides [17] and chlorides/oxychlorides [55] on quartz surfaces) empirical linear correlations exist between the microscopic property adsorption enthalpy and the macroscopic sublimation enthalpy. These correlations seem to suggest a similarity of the quartz surface modified by the reactive gas to the surface of the macroscopic solid of the compound which is adsorbed. Using thermodynamic sublimation data [25, 26, 41], recalculated experimental adsorption data for different

oxides and oxyhydroxides, and the determined adsorption data of this work an updated linear correlation (6) was calculated (Fig. 6), resulting in:

$$-\Delta H_{\text{ads}}[\text{kJ/mol}] = 6.271(\pm 7.780) + 0.680(\pm 0.028) * \Delta H_{\text{subl}}[\text{kJ/mol}]; r^2 = 0.953. \quad (6)$$

The determination of the adsorption enthalpies of the lighter group 7 species is essential to predict the behaviour of the homologue Bh compounds in the selected chemical system. For this prediction theoretical evaluation of the sublimation enthalpies of the bohrium compounds are important. Since no relativistic *ab initio* calculations of the electronic structure for the Bh compounds exist, this evaluation can be made only from a classical thermochemical approach, using trends in the thermodynamic data of homologue compounds within the 7 group. For these predictions in the chemical system of the oxides and oxyhydroxides, additional gaschromatography investigations of Tc are needed.

5. Conclusions

In thermochromatography experiments optimum formation conditions for HReO_4 and ReO_3 and their adsorption properties on quartz surfaces were determined. These conditions were applied in on-line studies with short-lived Re isotopes using isothermal gas adsorption chromatography. The formation of the less volatile ReO_3 was observed and its adsorption enthalpy on quartz surfaces was confirmed.

The low volatility of lanthanide (actinide) oxides allow a good separation of ReO_3 with good separation factors. However, this is not the case for Bi and Po, which form oxides or oxyhydroxides of similar volatility as ReO_3 .

Unfortunately, the more volatile HReO_4 which would allow a separation of Re from Po, Pb, and Bi, could not be synthesized on-line.

Due to the long separation time (including the time of the formation reaction) the high temperature iso-

thermal gas chromatography of oxides is applicable for nuclides with half-lives longer than about 10 s.

For the prediction of the behaviour of unknown oxide and oxyhydroxide compounds in the gas chemical system $O_2(g)/H_2O(g)/SiO_2(s)$ an updated linear correlation function between the microscopic adsorption behaviour of oxide/oxyhydroxide species on quartz surfaces and their macroscopic sublimation enthalpy has been established.

Acknowledgements

These studies were supported by the Swiss National Science Foundation. We thank Dr. P. A. Schmelzbach and his staff of the PSI Philips Cyclotron for providing intense beams of ^{19}F and E. Rössler for preparing the ^{156}Dy target.

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