Chemical characterization of short-lived selenium and their daughter isotopes from thermal neutron induced fission of ^{235}U at a gas-jet facility

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Selenium nuclides are available from thermal neutron induced nuclear fission of ^{235}U at the gas-jet facility at the Swiss spallation neutron source (SINQ) at Paul Scherrer Institute, Switzerland. The formation of stable selenium compounds, their transport yields using the gas-jet system and their relative thermal decomposition temperature were investigated under oxidizing and reducing conditions in the target chamber. Using O_2 , H_2 , CO , and propene as additional gases, the selenium isotopes are suggested to form H_2SeO_3 , H_2Se , COSe , and $\text{C}_3\text{H}_6\text{Se}$, respectively, with overall ^{84}Se yields of 1.5%, 4.7%, 6.3%, and 21.9%, respectively. Adsorption enthalpy, vapour pressure, solubility and acidity data for these species were collected from the literature or estimated from other known thermochemical properties. Carrier free bromine isotopes (^{84}Br , ^{86}Br) in the form of HOBr were obtained by thermally decomposing H_2SeO_3 and retaining elemental Se under oxygen rich conditions on quartz at 400 K.

Introduction

The use of short-lived nuclides opens a wide field of applications such as tracer studies^{1,2} to investigate reaction mechanisms³ or pathways of metabolites,⁴ radioimmunoassays for the determination of hormone concentration in blood plasma and many others.⁴ In laboratory experiments it is often necessary to establish a continuous and stable source of certain nuclides in liquid or gaseous form. In a previous work,⁵ a source of Br_2 , labeled with short-lived bromine isotopes, was established in view of applications in atmospheric chemistry. The bromine isotopes were obtained from thermal neutron induced fission of ^{235}U in the gas-jet facility mounted at the Swiss Spallation Neutron Source (SINQ). In contrast to the classical gas-jet approach, where the product nuclei are attached to aerosol particles and transported to the laboratory with carrier gas,⁶ in that study, a reactive gas has been added to the carrier gas to selectively catch bromine nuclides via formation of stable volatile compounds. It turned out that selenium nuclides, which are formed as ^{235}U fission products with high yield and which are through β^- -decay also the precursor of bromine nuclides, are playing a crucial role for the yield of the resulting bromine nuclides. Favored by the radical nature of the fission products after thermalization, Se is able to form stable, volatile and transportable molecules, which are not or only slightly retained on the tube walls. Further progress in establishing a source of bromine isotopes in the form of chemically well-defined molecules such as HOBr , BrONO_2 or BrO_2 can only be achieved by investigating thoroughly the chemical behavior of the Se nuclides in the gas-jet system. FENDEL et al.⁷ investigated the yield of Se nuclides in a comparable gas-jet system, using

ethene as reactive gas. However, the chemical environment in a target chamber is believed to facilitate radical initiated polymerization of ethene,⁸ so that it is difficult to reliably retrieve information on the chemical speciation of the fission products.⁹ Furthermore, data on the behavior of carrier-free Se isotopes in the gas-phase are very scarce. Therefore, our aim was to investigate the formation of stable Se compounds in the target chamber of the SINQ gas-jet facility under various oxidizing and reducing conditions, in which the transport was not influenced by polymerization reactions leading to particles. The resulting Se isotopes were characterized by the transport yield and their relative thermal decomposition temperature, which, together with known or estimated thermodynamic data, allow deriving conclusions on their chemical identity. Furthermore, the separation of daughter bromine nuclides as well as their chemical form is addressed.

Experimental

The design of the SINQ gas-jet facility containing the ^{235}U target follows the previous set-ups^{6,10} and includes three different cylindrical target chambers for various applications. For the present experiments, a chamber of 2.5 cm length was used, in which ^{235}U on Ni support was covered by a 6 μm nickel degrader foil. This ensured that the nuclide spectrum was governed by the light mass peak,¹¹ including Se nuclides. Within the chamber, the product nuclei are stopped to thermal velocity. Those nuclides, which form stable volatile chemical compounds, are transported by a gas capillary to the 80 m distant laboratory. The transport lines used in these experiments were flexible tubes with an inner diameter of 2 mm, made of polyethylene (PE).

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Fig. 1. Setup for experiments to determine the decomposition temperature or to study the separation of bromine from precursor selenium. The gas from the SINQ facility, containing volatile fission products enters a quartz tube, heated by two tube furnaces in series. Nuclides leaving the tube were measured at a trap, filled with activated charcoal. For the decomposition experiments the first tube furnace was heated between 700 and 1050 °C and the second one was kept at about 200 °C (far below the boiling point of the decomposition products Se^0 and SeO_2)

Helium (99.9999%, Sauerstoffwerke Lenzburg, Switzerland) was applied as inert transport medium. In a typical run with a gas flow rate of $\sim 1 \text{ l} \cdot \text{min}^{-1}$ under standard temperature and pressure (STP), the transport time from the target chamber to the laboratory was about 10 seconds. The water vapour content in the gas-jet was about 3000 ppmv, presumably due to permeation of H_2O from the outside air through the PE and due to impurities in the transport gases. More details of the SINQ gas-jet facility were reported in Reference 5.

The reactive gases added to the inert He purge gas were: hydrogen (1% H_2/He , 99.9999% each, Sauerstoffwerk Lenzburg, Switzerland), oxygen (5% O_2/He , 99.998% and 99.9999% respectively, Sauerstoffwerk Lenzburg), carbon monoxide (99.997%) and propene (99.4%) each 1% in He (99.9990%, Carbagas). For security reasons, the latter two gases were diluted to not exceed 650 ppm. The transport yield for each type of transport gas mixture was determined by passing the whole gas flow through a trap filled with activated charcoal (Merck, 0.5–1 mm, 109246), and measuring the count-rate with a calibrated HPGe detector (total-deposition experiments). For experiments dealing with the speciation of different bromine isotopes resulting from the β^- -decay of selenium, the charcoal trap was replaced by a specially developed parallel glass plate denuder with 0.1 cm spacing and 2.6 cm width.¹²

The glass plates were coated with tetrabutylammonium hydroxide (TBAH, Fluka 86882, pract. $\sim 25\%$ in methanol) or carbon tetrabromide (CBr_4 , Fluka 86770, purum). These measurement configurations were calibrated using the lines of ^{152}Eu at 121.78 keV, 344.28 keV and 1408.01 keV. In order to monitor the beam stability in the SINQ during the experiments, the 121.82 keV and 1118.69 keV lines of noble gas ^{90}Kr were used for comparison. Depending on the specific experiment, the total gas flow in the system varied between $250\text{--}1300 \text{ ml} \cdot \text{min}^{-1}$ (STP). Downstream of the trap, the gas was pumped to waste by a diaphragm pump (KNF Neuberger AG, Baltherswil, Switzerland).

For the experiments, in which either the temperature for thermal decomposition of the gaseous species was determined or the separation of the descendant Br was studied, a quartz tube heated by two tube furnaces in series was installed in front of the charcoal filled trap (Fig. 1).

Results

The transport yield for the various gas compositions was determined by measuring the saturation count-rate at the activated charcoal trap (Table 1). ^{84}Se was used as tracer because its 408.2 keV γ -line has 100% abundance and is free from interferences by other nuclides.

Table 1. Measured selenium saturation activity, calculated transport efficiencies (based on a fission rate of $1.0 \cdot 10^6 \text{ s}^{-1}$ and a fractional cumulative yield for mass 84 of 1.005%, measured decomposition temperatures of assumed transported molecules, measured bromine saturation activity for $^{84,86}\text{Br}$ (without separation from precursor Se)

Gas composition	Saturation activities of ^{84}Se , Bq	Transport efficiencies of ^{84}Se , %	Decomposition temperature, °C	Assumed transported molecule	Saturation activities of ^{84}Br , Bq	Saturation activities of ^{86}Br , Bq
Helium	376	1.5	700	$\text{H}_2^{84}\text{SeO}_3$	926	~410
Oxygen (5% in He)	376	1.5	700	$\text{H}_2^{84}\text{SeO}_3/\text{H}_2^{84}\text{SeO}_4$	926	~410
Hydrogen (1% in He)	1170	4.7	900	H_2^{84}Se	1656	504
Carbon monoxide (650 ppm in He)	1557	6.3	800	OC^{84}Se	1307	352
Propene (650 ppm in He)	5420	21.9	1050	$\text{C}_3\text{H}_6^{84}\text{Se}$	10582	1076

Table 2. Overview of the physical constants of selenium, its oxides, hydroxides, hydride and two organic compounds under standard conditions

Compound	$\Delta H_{\text{f(s)}}$, kJ/mol	$\Delta H_{\text{f(v)}}$, kJ/mol	$\Delta H_{\text{subl.}}$, kJ/mol	$\Delta H_{\text{ads.}}$, kJ/mol	T_{m} , °C	T_{b} , °C	T_{d} , °C
H_2Se		29.7 ³⁵	22.4 ^a	−12.5 ^b	−65.7 ¹⁷	−41.4 ¹⁷	
Se^0	0	223.4 ⁴⁰	227.07 ⁴¹	−174.5 ^b	221 ³⁵	685 ³⁵	
SeO		54.585 ⁴²	49.8 ⁴³				
SeO_2	−225.35 ⁴¹	−127 ⁴⁰	98 ⁴⁰	−67.27 ^b	340 tp ³⁵	315 subl. ³⁵	
SeO_3	−166.9 ⁴¹	−92 ^c	81 ^d	−55.7 ^b	118 ³⁵	subl. ³⁵	
H_2SeO_2		−103.31 ⁴⁴					
H_2SeO_3	−524.46 ⁴¹	−482 ^d	43 ^e	−29.87 ^b	>70 ¹⁷		70 ³⁵
H_2SeO_4	−530.1 ⁴¹	−417.64 ⁴⁰	115 ^d	−78.8 ^b	−62.4 ¹⁷		260 ³⁵
OCSe			(21.9) ^f		−124.4 ¹⁸	−21.7 ¹⁸	
$\text{C}_3\text{H}_6\text{S}^*$					−91 ¹⁶	95.0 ¹⁶	

$\Delta H_{\text{f(s)}}$: enthalpy of formation in solid phase; $\Delta H_{\text{f(v)}}$: enthalpy of formation in gaseous phase; $\Delta H_{\text{subl.}}$: enthalpy of sublimation; $\Delta H_{\text{ads.}}$: enthalpy of adsorption on quartz; T_{m} : melting point; T_{b} : boiling point; T_{d} : temperature of decomposition; tp : triple point.

^a Calculated from the sum of the heat of fusion and vaporisation.³

^b Calculated using correlation functions of empirical data (see thermodynamic calculations below).

^c Calculated from the sum of the enthalpies of formation of the single oxidation stages.⁶

^d Calculated from $\Delta H_{\text{f(v)}} - \Delta H_{\text{f(s)}}$.

^e Calculated from the slope of the logarithmic vapour pressure function.

^f Heat of vaporization.

* No data for $\text{C}_3\text{H}_6\text{Se}$ available, but for the chemically analogue $\text{C}_3\text{H}_6\text{S}$, whose T_{m} and T_{b} are expected to be lower than the ones of $\text{C}_3\text{H}_6\text{Se}$ (compare COS and COSe).

The transport efficiencies, based on a fission rate of $1.0 \cdot 10^6 \text{ s}^{-1}$ and a fractional cumulative yield of mass 84 of 1.005%, were calculated for each reactive gas and are listed in Table 1. These data show clearly that the gas composition strongly affects the transport yield of Se isotopes. For the conditions of 650 ppm CO in He, the flow rate through the gas-jet was varied in the range of 250–1300 ml min^{−1}, which resulted in a decrease of the total selenium yield (Fig. 2). This decrease was due to both the increase in residence time and chromatographic retention on the 80 m long tube walls made of polyethylene. However, to separate the effect of decay due to the increased residence time of the bulk gas flow alone, the data in Fig. 2 were corrected for decays during

the time elapsed between the target chamber and the laboratory assuming plug flow conditions. The residual effect of the chromatographic retention can be related to the adsorption enthalpies ($\Delta H_{\text{ads.}}$) listed in Table 2 and further explained in the discussion section (see below). Obviously, the larger the adsorption enthalpy the stronger is the retention. In Fig. 2, ^{84}Se with a half-life of 3.1 minutes¹³ is compared to the short-lived inert gas isotopes ^{90}Kr ($T_{1/2} = 32.32 \text{ s}$) and ^{91}Kr ($T_{1/2} = 8.57 \text{ s}$), which are subject to considerably shorter chromatographic retention times. As, e.g., the data points for ^{91}Kr plot practically on top of those for ^{84}Se , the retention time for the Se isotopes must be a factor of 22 longer than the Kr isotopes.

Fig. 2. Saturation count-rates of ^{84}Se (● $T_{1/2} = 3.1$ m), and ^{90}Kr (■ $T_{1/2} = 32.32$ s) and ^{91}Kr (▲ $T_{1/2} = 8.57$ s), for reference, as function of the gas flow rate in total deposition experiments. The count-rates are normalized and corrected for the half-life to point out the relative changes. The transport time from the target chamber to the 80 m distant laboratory is plotted on the upper x-axis. The decrease of the short-lived Kr isotopes is caused by molecular adsorption with an adsorption enthalpy of around -40 kJ/mol. The decrease of the ^{84}Se count rates indicates significant retention due to either molecular adsorption or another surface process (see text). Values are estimated using a Monte-Carlo model calculation (see Section “thermodynamic considerations”)

In order to get a first idea about the speciation, the temperatures of thermal decomposition were measured (Table 1, 3rd column) by varying the temperature of the two tubular furnaces in series (Fig. 1). While keeping all other conditions constant, for each reactive gas a temperature of the first oven could be determined at which the ^{84}Se activity in the activated charcoal trap was below the detection limit.

This temperature was interpreted as decomposition temperature of the transported selenium compounds into elemental selenium or probably SeO_2 . These measurements were only used for an internal comparison of the five gas systems investigated and can not be set equal to the absolute decomposition temperatures of the assumed compounds, because they have been influenced by the high gas flow rate and its composition, the heat conductivity, the water and oxygen content etc. Expecting elemental selenium as decomposition product under all conditions investigated, the second tube furnace was held at a temperature far below the boiling point of Se, to avoid elemental selenium being transported to the trap. In these experiments, it was observed that those species with high transport efficiency also had a high decomposition temperature.

Discussion

The transport yield of the selenium compounds depends mainly on two effects: first, on the formation of the corresponding compound in the target chamber

(including the yield of formation and stability of the selenium species) and second, on the retention properties along the transport line of 80m length. For a better quantification of the latter effect, physical quantities as for example the adsorption enthalpy, the vapour pressure and others are discussed in the following section “thermodynamical considerations”. The formation and possible speciation of the selenium compounds formed in dependence of the added reactive gas is treated in the section “comparison of different gas transport systems”.

Thermodynamical considerations

Using a Monte-Carlo model calculation¹⁴ related to a microscopic model of gas solid adsorption chromatography,¹⁵ it could be shown that with a length of 80 m of our transport line and an isotope with 3.1-minute half-life, an adsorption enthalpy of around -50 kJ·mol⁻¹ represents a limit, above which chromatographic retention due to molecular adsorption would significantly reduce the yield. As no data for selenium compounds possibly present in our system are available, adsorption enthalpies for several compounds have been calculated using the following correlation functions, derived from empirical data for the elemental Se, its oxides and hydroxides:¹⁶

$$\begin{aligned} \text{Elemental Se: } -\Delta H_{\text{ads}} &= \\ &= (-5.61 \pm 8.8) + (0.806 \pm 0.042) \cdot \Delta H_{298}^0(\text{element}) (\text{g}) \\ \text{Oxides and hydroxides: } -\Delta H_{\text{ads}} &= \\ &= (0.63 \pm 7.8) + (0.68 \pm 0.028) \cdot \Delta H_{\text{subl}} \end{aligned}$$

Fig. 3. Vapour pressures of Se^0 ($\blacktriangle$), SeO_2 ($\blacklozenge$), H_2SeO_3 ($\blacksquare$), H_2SeO_4 (+), $\text{C}_3\text{H}_6\text{S}$ (*), OCSe ($\blacktriangledown$) and H_2Se ($\bullet$), which are assumed to be formed in the target chamber during the interaction of the fission products from the light mass peak and the reactive gas added to the carrier gas helium.

No data for $\text{C}_3\text{H}_6\text{Se}$ is available, but for the chemical analogue $\text{C}_3\text{H}_6\text{S}$. Comparing the vapour pressure of COSe and COS , $\text{C}_3\text{H}_6\text{Se}$ is expected to be little less volatile than $\text{C}_3\text{H}_6\text{S}$.

In Table 2, the values for the enthalpy of formation and enthalpy of sublimation needed for these estimates are listed, together with the resulting adsorption enthalpies. The adsorption properties can also be related to the vapour pressure. A comparison of vapour pressures of H_2SeO_3 ,^{17,18} H_2Se ,¹⁸ Se^0 ,¹⁹ OCSe ,^{18,20} SeO_2 ,¹⁷ H_2SeO_4 ¹⁸ and of the sulphur analogue $\text{C}_3\text{H}_6\text{S}$ ¹⁶ are shown in Fig. 3.

If retention is observed even though the enthalpy of adsorption is estimated to be too low to allow significant retention via molecular adsorption, it is likely that hydrolysis in water adsorbed on the tube walls is thought to play a more important role. This seems to be the case for the expected chemical form of the Se isotopes: even though the half-life of ^{84}Se is 3.1 minutes and the residence time in the gas-jet varies from 10–70 seconds, the yield is strongly affected by the flow rate although a relatively low adsorption enthalpy for selenous acid (H_2SeO_3) is estimated. It seems that in this case solvation of the molecules in surface adsorbed water and dissociation of dissolved molecules is causing retention. Rather apolar molecules as for example propane-selenal are expected to respond less sensitive to an increased content of water vapour than polar ones (e.g., H_2SeO_3). PE, the material that our transport lines are made of, is known to have a relatively high affinity to water, and losses of hydrophilic compounds are possible. This effect can be assessed by comparing the Henry's Law coefficients and the acid constants for the relevant compounds.

Summing up, the observed trends of transport yield as a function of carrier gas composition can be related to a species to species trend for each of the quantities,

adsorption enthalpy, vapour pressure, solubility, and acid constant, respectively. This leads to the following series for the expected transport yield:

Vapour pressure:	$\text{H}_2\text{Se} > \text{OCSe} > \text{C}_3\text{H}_6\text{S} > \text{H}_2\text{SeO}_3 \approx \text{H}_2\text{SeO}_4$
Adsorption enthalpy:	$\text{H}_2\text{Se} > \text{H}_2\text{SeO}_3 > \text{H}_2\text{SeO}_4$
Solubility in water:	$\text{H}_2\text{Se} > \text{H}_2\text{SeO}_3$
Acidity (pK_a):	$\text{H}_2\text{Se} > \text{H}_2\text{SeO}_3 > \text{H}_2\text{SeO}_4$

Implications for the speciation of the Se isotopes

In the case of helium transport without addition of any reactive gases (Table 1, 1st line) the Se atom resulting from the nuclear fission of ^{235}U is likely to be oxidised to SeO_2 (R1) in presence of trace amounts of oxygen. SeO_2 , however, has poor transport properties due to the expected high adsorption enthalpy (Table 2) and low volatility. Therefore, we suggest those Se isotopes reaching the laboratory have reacted to selenous acid²¹ (H_2SeO_3) (R2) in view of the humidity present at about 3000 ppm. The reaction enthalpies given are based on the enthalpies of formation from the elements in the gaseous state. They might help to draw conclusions about the stability of the product. We note that entropy data are not available to calculate the free energy changes. These, however, might be of limited help as the initial state of the Se atom in the target chamber is an excited atom or ion:

The low overall Se yield under these conditions, even for high flow rates, might be due to the fact that (R2) is not rapidly enough converting all SeO_2 into H_2SeO_3 .

H_2SeO_3 is weakly acidic ($\text{pK}_{\text{a}1}$: 2.62, $\text{pK}_{\text{a}2}$: 8.32).²² As the conditions in a film of adsorbed water on the tube walls are assumed to be rather acidic, H_2SeO_3 is not expected to undergo dissociation in surface adsorbed water. Acids with a comparable pK_{a} as for example nitrous acid (pK_{a} : 3.25) are known to chemically behave in the same way, whereas strong acids, e.g., nitric acid (pK_{a} : -1.32)²³ are retained strongly on tube walls.²⁴ Therefore, adsorbed water on the PE tube causes some retention due to solvation of H_2SeO_3 as observed in Fig. 2, without a significant contribution from dissociation. In a more oxidative environment as for example after addition of 5% oxygen (Table 1, 2nd line), all Se atoms are oxidized to SeO_2 or even partially to SeO_3 . SeO_3 would be converted to selenic acid (H_2SeO_4), which would be lost on the walls due its higher adsorption enthalpy (quartz, Table 2), its higher acidity ($\text{pK}_{\text{a}2}$: 1.7) and its low vapour pressure (Fig. 3).

As a consequence, the transported compound for both, oxygen poor and oxygen rich, cases is mainly selenous acid, and selenic acid apparently plays a minor role, if it is formed at all.

The addition of 1% H_2 to the inert carrier gas He (Table 1, 3rd line) possibly results in the formation of hydrogen selenide (H_2Se):

In contrast to the two previous compounds, H_2Se has a lower stability in the gaseous state, but it is even less acidic than H_2SeO_3 ($\text{pK}_{\text{a}1}$: 3.89, $\text{pK}_{\text{a}2}$: 11.0). Additionally, its solubility is $8.4 \cdot 10^{-2} \text{ M atm}^{-1}$ ²⁵ and, therefore, lower than that of H_2SeO_3 .²⁶ Finally, H_2Se has only a very small adsorption enthalpy (quartz, Table 2) and is extremely volatile (Fig. 3). These considerations seem consistent with a more than three times higher yield. Whether because of traces of oxygen and humidity H_2SeO_3 is formed too, would be difficult to assess. However, the measurement of the decomposition temperature indicated only the presence of one species, H_2Se , as H_2SeO_3 would have been lost at lower temperatures already.

The volatile compound carbonyl selenide (OCSe , Table 1, 4th line) is formed from the interaction of carbon monoxide (CO) with selenium:

The vapour pressure of this compound is extremely high (100 kPa at -22°C)^{21,25} and the enthalpy of vaporisation at the boiling point ($\Delta H_{\text{vap}}(\text{Tb})$: $21.89 \text{ kJ} \cdot \text{mol}^{-1}$)²¹ is very small compared with other volatile compounds.²⁷ Unfortunately, no further data, with exception of the melting and boiling point, are available. We assume that the low adsorption enthalpy justifies the four times higher transport yield when adding CO, compared to when He is used alone.

The highest transport efficiency was observed using propene as reactive gas (Table 1, 5th line):

The most probable transport molecule is propane-selenal, where the double bonded selenium atom is placed at the terminal C-3-atom.²⁸ Unfortunately, no data are available about this molecule. As comparison, the volatility of the sulphur analogue thiopropionaldehyde is shown in Fig. 3. As propane-selenal is an unpolar molecule (electro negativity of 2.55 on the Pauling scale for C and Se),²⁹ we expect it to be insoluble in water and to rather weakly interact with the humid tube surface. These properties would be consistent with the observed high yield.

Implications for the speciation of the daughter bromine isotopes

Bromine, the β^- -decay product of Se, is of interest for experiments in which the Se gas-jet system is used as a bromine generator. The most prominent bromine activity observed under our conditions was ^{84}Br with a half-life of 31.8 minutes and an abundance of 42% of the γ -line at 881 keV.¹³ ^{83}Br and ^{85}Br could not be observed due to their small abundances ($I_{\gamma 529.6} = 1.2\%$, $I_{\gamma 802.4} = 2.5\%$, respectively) and due to the relatively high background of fission noble gases and their descendants. On the other hand some ^{86}Br activity ($T_{1/2} = 56 \text{ s}$, $I_{\gamma 1564} = 64\%$) was detectable. However, its precursor, ^{86}Se , has a half-life of 15.3 seconds only and is, therefore, prone to a low yield due to the various retention processes discussed above. Compared to the independent yield of ^{86}Br nuclides from fission of ^{235}U , only a fraction of 0.5–2% was observed as generated from the Se precursor, depending on the reactive gas added. The observed Br activities are also listed in Table 1 (5th and 6th column). The Br saturation activities shown were determined in an on-line total-deposition experiment without separation of Se.

In order to allow for on-line gas chemistry experiments with labeled bromine compounds, precursor selenium has to be eliminated by separation, because it would persist as a continuous source for bromine nuclides. In a previous study, using CO as reactive gas, Br_2 had to be added in order to force the mobilisation of Br after decomposition of OCSe . Following the extremely fast isotope exchange, the resulting bromine compound was labeled Br_2 ($^{83-86}\text{Br}-\text{Br}$).⁵ In the present study, Br could be mobilised without addition of carrier Br_2 , but only under the condition of 5% oxygen. This is in contrast to the behavior of the precursor Se, the yield of which was not dependent on the O_2 concentration (Fig. 4).

Fig. 4. Measurements of ^{84}Se under 5% O_2 in He. The γ -spectrum of a total deposition experiment (thin line) and after passing the gas flow through two tube furnaces, heated to 750 and 130 $^{\circ}\text{C}$, respectively (thick solid line), is shown. Obviously, all selenium atoms are, most likely in the form of Se^0 , retained on the surface of the quartz tube in the region of the second furnace after thermal decomposition in the first one. After β^- -decay, the resulting Br^* is, in presence of 3% humidity, able to react to HOBr (see text). Note that the different γ -intensities in the two experiments are due to the varying fission rates caused by the variability of the neutron flux

Thermochromatography experiments using the set-up identical to that used by EICHLER et al.^{30,31} showed that all bromine activity produced under the conditions of 5% O_2 was deposited at one temperature only, approximately 210 K. This is a clear indication, that only one species was formed. The adsorption enthalpy derived from these experiments performed on quartz and ice surfaces using the procedures as described in the references given above was between 30 and 40 $\text{kJ}\cdot\text{mol}^{-1}$, as typically observed for molecules being able to form H-bonds to polar surfaces. In order to further specify this compound, the activated charcoal trap in total-deposition experiments (Fig. 1) was replaced by a trap in which a solid substrate was coated with tetrabutylammonium hydroxide (TBAH, weakly basic, good absorption properties for all inorganic bromine compounds) or with carbon tetrabromide (CBr_4 , non-polar, strong interaction with Br_2). While only a small fraction of the bromine activity was observed to be retained on the CBr_4 trap, all bromine activity was absorbed on the TBAH trap.

From these additional experiments we conclude that a single, relatively polar molecular species of bromine was formed. When Se decays, the probably highly excited Br atom or ion can undergo a variety of reactions. The decay process itself, i.e., the emission of a highly energetic electron, leads to the formation of radicals in the immediate vicinity of the decaying atom and may also have influenced the fate of the Br isotope.

A few established reactions in the system $\text{Br}-\text{H}_2\text{O}-\text{O}_2$ are:

The only product stable enough to escape the experimental set-up under our conditions would be HBr or HOBr. Carrier-free bromine activity in the form of HBr is very efficiently absorbed into quartz at room temperature, which was not observed in our experiments. In addition, it is expected to undergo strong retention in humid gases in tubes of all materials due to its strong acidity. In our experiments, the bromine activity obtained did not undergo significant retention along 1 m of polyethylene, quartz, Teflon, perfluoroalkoxy-copolymer (Teflon-PFA), and pyrex tubes. We, therefore, suggest that bromine obtained from decay of Se isotopes under 3000 ppm H_2O and 5% O_2 at 400 K turns up as hypobromous acid (HOBr), a weak acid with pK_a of 8.7.

Conclusions

The addition of reactive gases enables the formation of stable and volatile molecules as carrier for short-lived selenium nuclides (mainly ^{84}Se) received from thermal neutron induced fission of ^{235}U in the SINQ gas-jet

system. Using O_2 , H_2 , CO , and propene, the selenium isotopes are suggested to form H_2SeO_3 , H_2Se , $COSe$, and C_3H_6Se , respectively, with varying yield. Important factors determining the overall yield in the gas-jet system are chromatographic retention effects caused by molecular adsorption on the material of the transport lines and hydrolysis within adsorbed water.

When the Se molecules obtained under oxygen rich conditions were thermally decomposed to elemental Se and deposited on quartz, the daughter bromine isotopes formed $HOBr$ molecules. Therefore, in this set-up, the system also serves as a source of carrier-free $HO^{84,86}Br$ molecules.

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