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Gas-phase chemistry of ruthenium and rhodium carbonyl complexes

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Short-lived ruthenium and rhodium isotopes were produced from the ^{252}Cf spontaneous fission (SF) source. Their volatile carbonyl complexes were formed in gas-phase reactions in situ with the carbon-monoxide contained gas. A gas-jet system was employed to transport the volatile carbonyls from the recoil chamber to the chemical separation apparatus. The gas-phase chemical behaviors of these carbonyl complexes were studied with an online low temperature isothermal chromatography (IC) technique. A long IC column made of FEP Teflon was used to obtained the chemical information of the high-volatility Rh carbonyls. By excluding the influence of precursor effects, short-lived isotopes of $^{109-110}$Ru and $^{111-112}$Rh were used to represent the chemical behavours of Ru and Rh carbonyls. Relative chemical yields of 75% and about 20% were measured for $Ru(CO)_5$ and $Rh(CO)_4$, respectively, relative to the yields of KCl aerosols transported in Ar gas. The adsorption enthalpies of ruthenium and rhodium carbonyl complexes on a Teflon surface were determined to be around $\Delta H_{ads} = -33^{+1}_{-2}$ kJ mol^{-1} and -36^{+1}_{-2} kJ mol^{-1}, respectively, by fitting the breakthrough curves of the corresponding carbonyl complexes with a Monte Carlo simulation program. Different from Mo and Tc carbonyls, a small amount of oxygen gas was found to be not effective for the chemical yields of ruthenium and rhodium carbonyl complexes. The general chemical behaviors of short-lived carbonyl complexes of group VI - IX elements were discussed, which can be used in the future study on the gas phase chemistry of superheavy elements – Bh, Hs, and Mt carbonyls.

Introduction

The synthesis of superheavy elements (SHEs; Z≥104) and their chemistry studies are attractive but challenging in the field of nuclear science. The superheavy elements can only be produced in heavy-ion reactions at the "one-atom-at-a-time" level with very short half-lives. These extreme conditions require the development of unique components and methods to achieve the ultimate goal of chemically isolating one single atom that lives for only a few seconds. Due to very strong relativistic effects on the valence electron shells, the SHEs should behave dissimilarly to their lighter homologs in the chemical groups.[1] Significant deviations of the chemical behaviors of SHEs require the studies of their lighter homologs, which can provide corresponding chemical information, and contribute to the further studies of SHEs.

Simple inorganic compounds like oxides, halides, hydroxides, and oxyhalides of SHEs and their homologs have been investigated in the past decades.[2-5] In recent years, transition metal – organic complexes are drawing much attention, and the new classes of carbonyl complexes opened the perspectives to the chemical studies of SHEs.[1] As these complexes were known to be volatile at ambient condition, gas-phase chromatography techniques were used to study their chemical properties.[6-11]

The EAN rule (Effective Atomic Number rule), as known as the 18-electron rule, primarily gives the qualitative predictions for the coordination and structures of many transition metal complexes.[12] In previous work, $Mo(CO)_6$ and $W(CO)_6$ were observed in the gas-phase experiments[7], and were confirmed in matrix isolation experiments.[13] For group VII-IX, $Tc(CO)_5$, $Ru(CO)_5$, $Rh(CO)_4$ were proposed according to the 18-electron rule.[14] In other studies, $Tc(CO)_5$ and $Re(CO)_5$ were considered to be the only possible structures, which should thermodynamically exist in specific conditions.[10-11] Short-lived Re and Ir carbonyls were studied at the TransActinide Separator and Chemistry Apparatus (TASCA),[10] and the coordination numbers of $^{170}Re(CO)_x$ and $^{178}Ir(CO)_x$ were proposed to be x = 5 and 4, respectively.[10]

The chemical behaviors of Mo and W carbonyl complexes were studied systematically in references.[8,10-11,14] Furthermore, the first synthesis of an organometallic compound of a superheavy element, seaborgium hexacarbonyl ($Sg(CO)_6$), was recently

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successfully achieved, and its adsorption enthalpy on quartz surface was deduced.[9] So far, the gas-phase chemistry of carbonyl complexes of group VI has been studied adequately. The chemical information on group VI-IX carbonyls were reported by Even *et. al.*[10] The adsorption enthalpy of Tc carbonyls and the thermal stablities of Mo, W, Tc, Ru, and Rh carbonyl complexes were also studied in other groups.[8,11,14] However, in reference 10, the authors didn't give final conclusions on the adsorption enthalpies or chemical yields of Tc, Ru or Rh carbonyls, since these observed isotopes were influenced by strong precursor effects in the experiment with a [249]Cf target irradiated at the nuclear reactor; no chemical yields of Ru and Rh carbonyls were reported. Therefore, the systematic studies on Ru and Rh carbonyl complexes are requisite and urgent for the future chemical investigation of carbonyl complexes of element 108, Hs and element 109, Mt, respectively.

In the present work, short-lived ruthenium and rhodium isotopes were generated from a [252]Cf spontaneous fission (SF) source, and their volatile carbonyl complexes were formed in gas phase reactions. [109-110]Ru and [111-112]Rh carbonyls, which could exclude the precursor effects, were studied using low-temperature IC technique. The adsorption enthalpies were obtained from the breakthrough curves of the corresponding carbonyl complexes. The relative chemical yields and the influence of a small amount of oxygen gas were also studied.

Experimental

The same experimental setup was used as the previous work[11], see Fig. 1. The system consists of (a) the gas-jet transport system, (b) the [252]Cf source chamber, (c) the low-temperature isothermal chromatography apparatus, and (d) the collecting, detection, and data acquisition system. The components were connected via Fluorinated Ethylene Propylene (FEP) Teflon tubes. For more details, please see reference 11.

According to the Monte Carlo simulation, a 5-m-long FEP IC column (i.d. = 4 mm) was used to obtain the complete breakthrough curves of high-volatile ruthenium carbonyls in the limited temperature range. And a 3-m-long (i.d. = 2 mm) FEP IC column was used in rhodium carbonyl experiment.
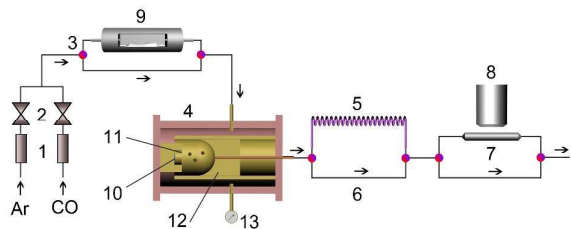

Fig. 1 Schematic of the experimental setup (1: mass flow controllers; 2: two-way valves; 3: three-way valves; 4: [252]Cf source chamber; 5: isothermal chromatography column at low temperature; 6: bypass; 7: charcoal filter; 8: HP Ge-γ detector; 9: KCl aerosol generator; 10: [252]Cf fission source; 11: 0.5 μm-thick polyester film covering; 12: Teflon cylinder collector; 13: pressure gauge)

All experiments were performed at 19 °C and at 1.05 bar with a total gas flow rate of 1000 mL min^{-1}, except for these with oxygen contained gas with a gas flow rate of 1500 mL min^{-1}. The online collecting time for each experiment was 30 min.

Results and discussion

Formation of Ru and Rh carbonyl complexes

Fig. 2 shows the typical γ-ray spectra of [252]Cf fission fragments transported with KCl aerosols in Ar gas. All fission fragments with suitable half-lives and γ-ray energies can be found without chemical selectivity. Fig. 3 shows only the volatile species among the fission products, e.g. [137-139]Xe, transported in pure Ar gas without any aerosol.
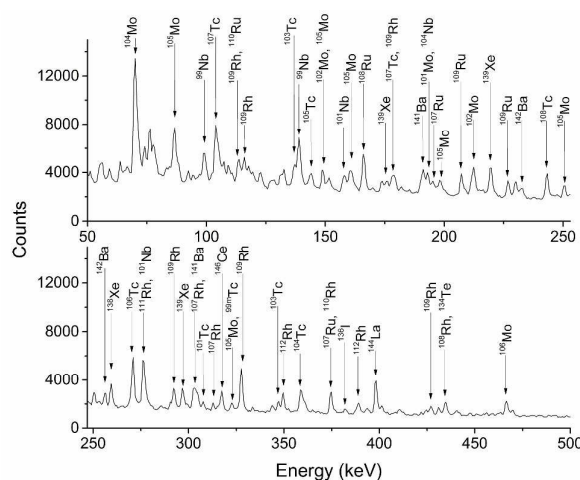

Fig. 2 γ-ray spectra of fission products transported in Ar gas with KCl aerosol particles. The total gas flow rate was 1 L min^{-1}. The sample was collected and detected on-line for 30 min.
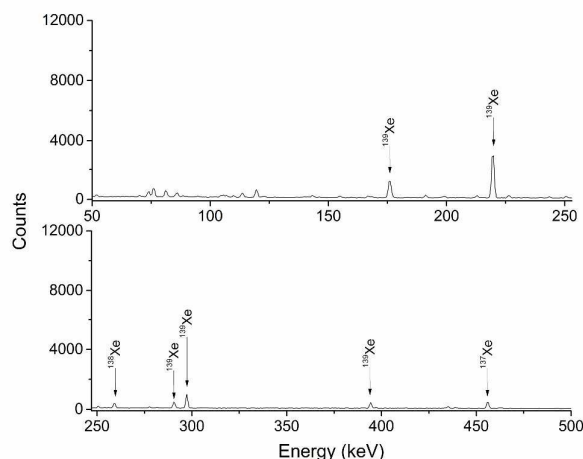

Fig. 3 γ-ray spectra of fission products transported in pure Ar gas. The total gas flow rate was 1 L min^{-1}. The sample was collected and detected on-line for 30 min.
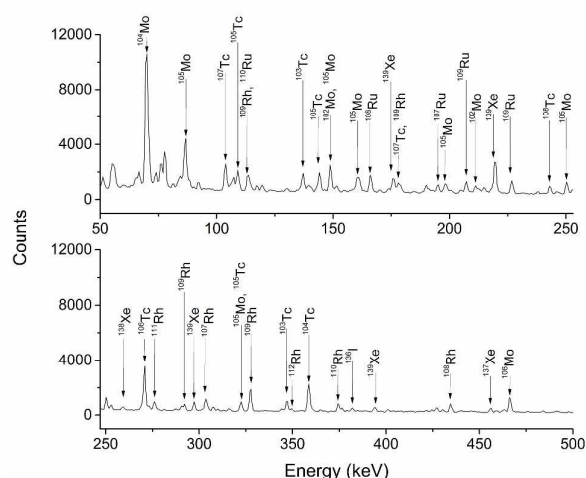
Fig. 4 γ-ray spectra of fission products transported in a mixed gas of 50% Ar and 50% CO. The gas flow rate was 1 L min⁻¹. The total sample was collected and detected on-line for 30 min.

When CO gas was added in Ar gas, several Mo, Tc, Ru, and Rh isotopes appeared in the spectra, see Fig. 4. This proved that volatile carbonyl complexes of these 4d elements were synthesized and transported from the [252]Cf source chamber to the charcoal trap.

Since there is no direct experimental evidence to provide any information on the configuration of Ru or Rh complexes at such conditions, the structures of these complexes can only be inferred theoretically.

As the production rates of metal atoms from the [252]Cf fission source are very low (not higher than few thousands per second), the probability of atoms meeting each other in gas-phase, and forming polynuclear complexes, e.g. $M_x(CO)_y$ ($x \geq 2$) can be excluded. It is convinced that these short-lived isotopes would form mononuclear complexes rather than polynuclear complexes.[10,11]
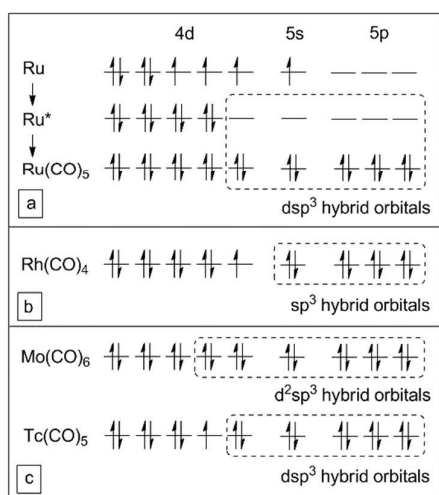

Fig. 5 The valence electron configurations of central atoms in $Ru(CO)_5$, $Rh(CO)_4$, $Mo(CO)_6$, and $Tc(CO)_5$

Fig. 5 shows the valence electrons (VEs) configurations of central atoms in Ru, Rh, Mo, and Tc carbonyls according to the Valence Bond (VB) theory. A free ruthenium atom has 8 VEs. The bonding arrangement results in four paired electrons in two of the 4d orbitals and four unpaired electrons in the other three 4d orbitals and 5s orbital. When ruthenium forms a carbonyl complex, one of the 4d orbitals, one 5s and three 5p orbitals are made available to form a set of empty dsp^3 hybrid orbitals by means of electron pairing.[12] Five empty orbitals can accept at most five pairs of electrons which are donated by CO ligands, and reach the number of electrons in the next noble gas atom. As a result, $Ru(CO)_5$ are the final saturated structure, which are known to be stable in macrochemistry, see Fig. 5a.

In the formation of rhodium carbonyls, 9 VEs from the Rh atom require all the five 4d orbitals, and one electron remains unpaired. Only one 5s and three 5p orbitals are used in the hybrids. The resulting sp^3 hybrid orbitals can accommodate at most four pairs of electrons, and for CO ligands the maximum coordination number is 4. In this case, $Rh(CO)_4$ gives a total of 17 electrons in the valence shell of Rh, see Fig. 5b. Since the formation of polynuclear carbonyls are excluded, this may be the only possibility which is closest to the stable structure according to the EAN rule.

In the same way, the maximum coordination number of Mo and Tc mononuclear carbonyls, which were mentioned in previous works,[7-11] can also be inferred to be 6 and 5, respectively, see Fig. 5c.

In a laser-ablation matrix-isolation infrared spectroscopy experiment,[13] the free Mo/W atoms form carbonyl complexes directly in CO and inert gas mixture. The low-coordinate complexes were found to be spontaneously transformed into high-coordinate complexes in such conditions, and saturated $Mo(CO)_6/W(CO)_6$ were the final stable products. It can be deduced that the low-coordinate carbonyl complexes of Ru/Rh have the same trend to transform into saturated complexes in the same conditions. Therefore, $Ru(CO)_5$ and $Rh(CO)_4$ should be the final products in reactions with free atoms and CO contained inert gas.

Additionally, Bogdan et al. reported that the ruthenium carbonyls like $Ru(CO)_5$ could be observed with the transient infrared spectroscopy.[15,16] Ozin et al. reported that $Rh(CO)_{1-4}$ were observed in solid argon in earlier thermal atom experiment.[17] Even et al. also proposed that the ruthenium and rhodium were most likely to form pentacarbonyl ruthenium and tetracarbonyl rhodium in similar conditions.[10] Though $Ru(CO)_5$ and $Rh(CO)_4$ could be reactive and unstable in macrochemistry, they are the only possible binary, mononuclear, neutral and saturated chemical forms in current study.

Relative chemical yields

In this work, the first step is to decide which isotopes can be used to represent the corresponding elements.

In the Even's work,[10] short-lived isotopes of [106-107]Tc, [107-108]Ru and [107-110,110m]Rh produced with the [249]Cf source were identified in the spectra. The transport yields of [106-107]Tc, [108]Ru, and [109]Rh as a function of CO concentrations were illustrated.

But these isotopes were all influenced by precursor effects, and cannot represent the behaviors of the corresponding elements. As a result, no quantified chemical information of ruthenium and rhodium could be deduced in that study.

In our recent study,[11] for a certain isotope the precursor effects can be excluded only if (1) the fraction (F_r) of the independent yields (Y_i) to the cumulative yields (Y_c) is large enough, and (2) the precursor's half-life is short enough to decay in the recoil chamber.

The Y_i and Y_c values of short-lived Tc, Ru, and Rh isotopes observed in the γ-ray spectra are shown in Table 1. For ruthenium, most of the ^{107}Ru ($t_{1/2}$ = 3.8 min) atoms are formed from the β-decay of ^{107}Tc ($t_{1/2}$ = 21.2 s), and only 13% are formed directly. This means the ^{107}Tc atoms form carbonyl complexes and pass through the IC column, but give the signals of ^{107}Tc and ^{107}Ru in the charcoal trap during the measurement, giving strong precursor effects on the daughter ^{107}Ru. ^{108}Tc and ^{108}Ru are in the same situation. These two isotopes should show almost the same behaviors of ^{108}Tc.

For ^{109}Ru ($t_{1/2}$ = 34.5 s; $E_γ$ = 206 keV, $I_γ$ = 22%; $E_γ$ = 226 keV, $I_γ$ = 20%), the Y_i is large enough (59%), and the half-life of its mother ^{109}Tc ($t_{1/2}$ = 0.86 s) is too short to be transported from the recoil chamber to the charcoal trap. This means the precursor effect of ^{109}Tc on ^{109}Ru can be completely excluded. Similarly, ^{110}Ru ($t_{1/2}$ = 11.6 s; $E_γ$ = 112.2 keV, $I_γ$ = 23%) will not be influenced by precursor effects, since its mother ^{110}Tc ($t_{1/2}$ = 0.83 s) has a very short half-life.

For rhodium, the isotopes of $^{109-112}$Rh can be observed. In view of above-mentioned reasons, $^{109-110}$Rh are strongly affected by the precursor effects and showed the same behavior of $^{109-110}$Ru. Only ^{111}Rh ($t_{1/2}$ = 11 s; $E_γ$ = 275 keV; $I_γ$ = 100%) and ^{112}Rh ($t_{1/2}$ = 6.8 s; $E_γ$ = 348.7 keV; $I_γ$ = 89%) can represent the behavior of element Rh.

Fig. 6 Relative chemical yields of $^{109-110}$Ru as a function of CO concentration in Ar carrier gas, normalized to the yields obtained with the KCl aerosol transport in Ar gas, and corrected by the yields of the volatile fission product of ^{139}Xe. The total gas flow rate was 1 L min^{-1}. The sample was collected and detected on-line for 30 min.
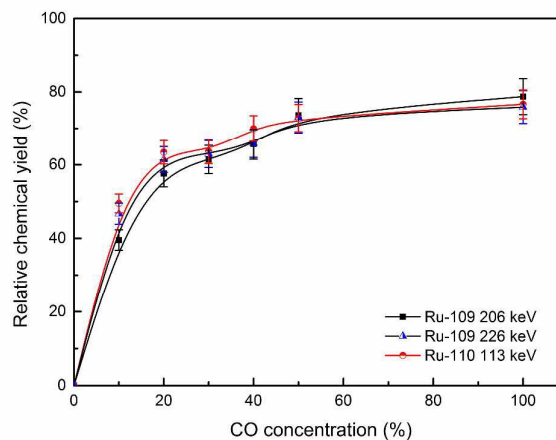

Fig. 7 Relative chemical yields of $^{109-112}$Rh as a function of CO concentration in Ar carrier gas, normalized to the yields obtained with the KCl aerosol transport in Ar gas, and corrected by the yields of the volatile fission product of ^{139}Xe. The total gas flow rate was 1 L min^{-1}. The sample was collected and detected on-line for 30 min.
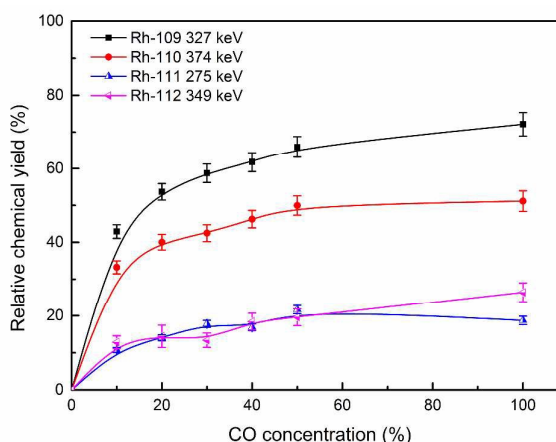
The relative chemical yields of the investigated carbonyl complexes as a function of CO concentration are shown in Fig. 6 and Fig. 7. The data were fixed by the constant yields of the volatile fission product ^{139}Xe, to eliminate the influence of the gas flow rate. The yields are given relative to that of KCl aerosol transport. The relative chemical yields of $^{109-110}$Ru carbonyl complexes reach the maximum of about 75% (Fig. 6). Meanwhile, the maximum yields of $^{111-112}$Rh approach about 20% (Fig. 7). As mentioned, the maximum yields of $^{109-110}$Rh isotopes are far higher than those of $^{111-112}$Rh, and similar to their precursors $^{109-110}$Ru. For all these carbonyl complexes, the relative chemical yields reach the maximum basically when CO concentration is higher than 40%.

The results show the difference in chemical yields of the carbonyl complexes of group VIII and group IX. According to the EAN rule, the numbers of effective electrons in Ru(CO)$_5$ are 18, and it suggests that Ru(CO)$_5$ has a stable structure, and

Table 1 The half-lives ($t_{1/2}$), independent yields (Y_i), cumulative yields (Y_c) of Tc, Ru, and Rh isotopes formed with the ^{252}Cf SF source.[19] F_r shows the fraction of Y_i in the corresponding Y_c as a percentage.

Isobar	Nuclide	Half-life	Independent Yield (Y_i)	Cumulative Yield (Y_c)	Fraction (F_r)
107	^{107}Tc	21.2 s	3.630	5.730	63%
	^{107}Ru	3.8 min	0.872	6.600	13%
108	^{108}Tc	5.17 s	3.330	4.010	83%
	^{108}Ru	4.5 min	1.980	5.990	33%
109	^{109}Tc	0.86 s	1.890	2.040	93%
	^{109}Ru	34.5 s	2.990	5.030	59%
	^{109m}Rh	50 s	0.254	2.770	9%
	^{109}Rh	1.34 min	0.652	5.930	11%
110	^{110}Tc	0.83 s	0.855	0.878	97%
	^{110}Ru	11.6 s	3.620	4.500	80%
	^{110m}Rh	29 s	0.675	0.675	100%
	^{110}Rh	3.1 s	0.672	5.170	13%
111	^{111}Ru	2.12 s	2.260	2.440	93%
	^{111}Rh	11 s	2.460	4.890	50%
112	^{112}Ru	1.75 s	0.939	0.962	98%
	^{112}Rh	6.73 s	2.390	3.350	71%

may have a relatively high chemical yield. However, Rh(CO)$_4$ has an unstable structure, because of its 17 effective electrons. This could make its chemical yields much lower than Ru(CO)$_5$.

Adsorption enthalpies

Fig. 8 shows the breakthrough curves of $^{109-110}$Ru with a 5-m-long FEP IC column (i.d. = 4 mm) using 1 L min^{-1} mixed gas (Ar:CO = 1:1; 1.05 bar; 19 °C). Since the Ru carbonyls are very volatile[8], a Monte Carlo simulation program[17] was used to select the length and the radius of the IC column according to an estimated adsorption enthalpy values and simulated breakthrough curves. At each experimental temperature, the products were collected and measured on-line for 30 minutes. In Fig. 8, the simulation results show a near-perfect match with the breakthrough curves. By fitting the experimental data with the Monte Carlo simulation, the adsorption enthalpy of Ru carbonyls was determined to be $\Delta H_{ads} = -33^{+1}_{-2}$ kJ mol^{-1} on the FEP surface. The $T_{50\%}$, where 50% of the molecules pass the IC column, is around −67 °C.

Since most of the ^{109}Rh atoms are formed from the β^--decay of ^{109}Ru in the charcoal trap, the precursor effects strongly affect ^{109}Rh. The breakthrough curve of ^{109}Rh is similar to ^{109}Ru and shows an equal $T_{50\%}$ value (Figs. 8a and 8b). ^{110}Rh is in the same situation and shows the behaviors of ^{110}Ru (Figs. 8c and 8d).

Fig. 9 shows the breakthrough curves of $^{111-112}$Rh with a 3-m-long FEP IC column (i.d. = 2 mm), fitting with the Monte Carlo simulation. The gas flow rate was 1 L min^{-1} (Ar:CO = 1:1; 1.05 bar; 19 °C). An adsorption enthalpy of $\Delta H_{ads} = -36^{+1}_{-2}$ kJ mol^{-1} was deduced for Rh carbonyls on the FEP Teflon surface. The $T_{50\%}$ appears at −58 °C for both ^{111}Rh and ^{112}Rh. In contrast to Ru carbonyls, Rh carbonyl complexes are less volatile and have lower relative chemical yields.
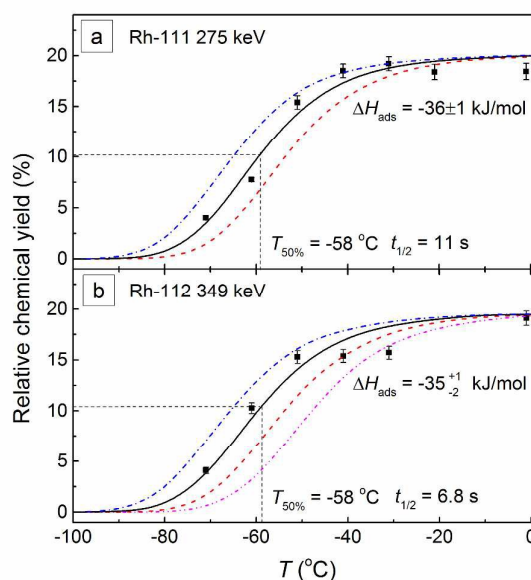

Fig. 9 Breakthrough curves of Rh carbonyls on FEP Teflon surface, fitting with Monte Carlo simulation. The symbols are the experimental data. The solid curves are the results of Monte Carlo simulations[17] with the corresponding adsorption enthalpies.

Influence of oxygen on the chemical yields of ruthenium and rhodium carbonyl complexes

In previous works, a trace amount of O$_2$ was found to have a strong negative influence on chemical yields of Mo, Tc, and W carbonyl complexes.[10,11] Wang *et al*. reported that 2% of oxygen gas already makes the relative yields drop from 100% to 70% for Mo, and from 25% to 15% for Tc. With 6% of O$_2$ gas,
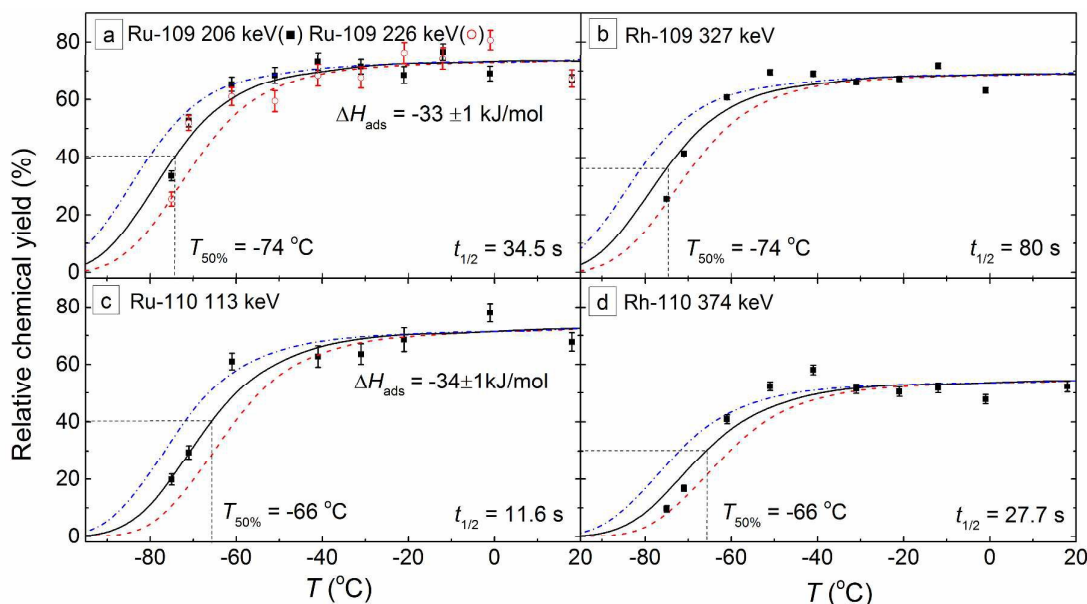

Fig. 8 Breakthrough curves of $^{109-110}$Ru and $^{109-110}$Rh carbonyls with a 5-m-long FEP Teflon IC column (i.d. = 4 mm). The symbols (black boxes and circles) are the experimental data. The solid curves are the results of the Monte Carlo simulations[17] with the corresponding adsorption enthalpies. For Rh isotopes, the curves are consistent with the simulation results of their precursors.

Table 2 Chemical information on the Mo/W, Tc/Re, Ru/Os, and Rh/Ir carbonyls

Group	VEs numbers	Complexes	Relative chemical yield	$-\Delta H_{ads}$ on Teflon surface (kJ mol^{-1})	$-\Delta H_{ads}$ on SiO$_2$ surface (kJ mol^{-1})
VI	18	Mo(CO)$_6$	100% [a]	38 ± 2 [a]	39 ± 2 [a]
		W(CO)$_6$			46.5 ± 2.5 [b]
VII	17	Tc(CO)$_5$	25% [a]	43 ± 2 [a]	43 ± 2 [a]
		Re(CO)$_5$			43 ± 3 [b]
VIII	18	Ru(CO)$_5$	75%	33$^{+1}_{-2}$	35 ± 1 [c]
		Os(CO)$_5$			43.5$^{+3.5}_{-2.5}$ [b]
IX	17	Rh(CO)$_4$	20%	36$^{+1}_{-2}$	
		Ir(CO)$_4$			37 ± 3 [b]

[a] data from Ref. 11; [b] data from Ref. 10; [c] data from Ref. 8
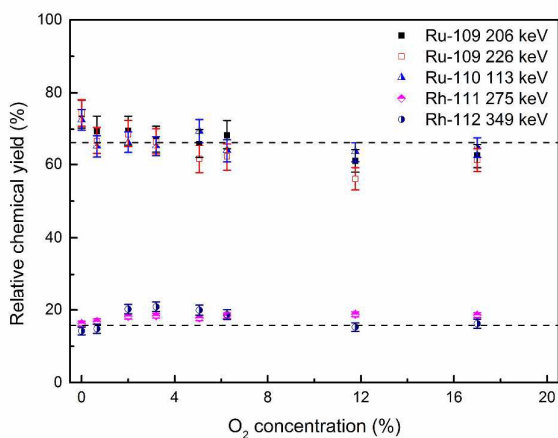

Fig. 10 Relative chemical yields of Ru and Rh isotopes as a function of the O$_2$ concentration in the mixed Ar and CO gas, normalized to the yields obtained with the KCl aerosol transport in Ar gas, and corrected by the yields of the volatile fission product of ^{139}Xe in each γ-spectrum. The dashed lines show the average values of relative chemical yields of Ru and Rh carbonyls.

about 70% of Mo and Tc carbonyls were lost.[11]

To verify such an influence on carbonyl complexes of group VIII and group IX elements, experiments with the same condition were performed. A small amount of O$_2$ was added into the gas mixture (Ar:CO = 1:1) with a total flow rate of near 1.5 L/min. The relative chemical yields of Ru and Rh were obtained in different O$_2$ concentrations. The relative chemical yields of corresponding carbonyls were obtained, relative to the transport yields with KCl aerosol in Ar gas.

In Fig. 10, we can see that with the O$_2$ concentrations varying from 0% to 17%, the relative chemical yields of Ru and Rh carbonyls remain basically constant, which stay around 70% and 20%, respectively. Thus, no significant influence of O$_2$ gas was observed on the chemical yields of Ru and Rh carbonyls in the present experimental condition.

Gas-phase behaviors of group VI-IX elements carbonyl complexes

The chemical information of group VI-IX elements carbonyl complexes is shown in Table 2. The VEs numbers of the corresponding carbonyls are listed. For group VI and group VIII elements, their carbonyls have 18 VEs, and should be stable according to the EAN rule. Not surprisingly, they were found to have high chemical yields in the experiments. For group VII and group IX elements carbonyls, they have 17 VEs. They would be unstable and low-yield according to the EAN rule. The low chemical yields were confirmed in the present experiments.

For group VI and group VIII elements, the $-\Delta H_{ads}$ of W/Os carbonyls on quartz surface are about 8 kJ mol^{-1} higher than those of Mo/Ru carbonyls. However, for group VI and group VIII elements, Re/Ir and Tc/Rh carbonyls have basically the same adsorption enthalpies, respectively.

This work gives important information for the future study on the carbonyls of SHEs – $_{108}$Hs and $_{109}$Mt. If their chemical properties are not strongly affected by the relativistic effects, it may suggest that Hs carbonyl complexes will have higher stability than Mt carbonyl complexes.

Additionally, the Hs carbonyls may be less volatile than Os carbonyls, while the ΔH_{ads} value of Mt carbonyl complexes may still be close to that of Ir carbonyls, which is around -37 kJ mol^{-1}.

Conclusions

Short-lived ruthenium and rhodium carbonyl complexes were synthesized and their gas-phase chemistry was studied using an online isothermal chromatography apparatus coupled to a ^{252}Cf SF source. In this work, the VB theory and the EAN rule were used to deduce the coordination and VEs configuration of the 4d elements carbonyls formed in gas-phase reactions of ^{252}Cf SF fission fragments and CO gas. As a result, Mo(CO)$_6$, Tc(CO)$_5$, Ru(CO)$_5$, and Rh(CO)$_4$ should be the final products in current study. Chemical yields of 75% and about 20% were measured for Ru(CO)$_5$ and Rh(CO)$_4$, respectively. The CO concentration of 40% was found to be enough to give the highest yield for Ru and Rh carbonyls in the Ar/CO gas mixture. By fitting the breakthrough curves with the Monte Carlo simulation, the adsorption enthalpies of Ru(CO)$_5$ and Rh(CO)$_4$ on FEP Teflon surface were deduced to be around $\Delta H_{ads} = -33$ kJ mol^{-1} and -36 kJ mol^{-1}, respectively. Furthermore, a small amount of oxygen gas was found to have no remarkable influence on the chemical yields of Ru and Rh carbonyls, which was totally different from Mo and Tc carbonyls.

In combination with the previous works, the general chemical behaviors of group VI - IX elements carbonyl complexes were discussed. And several important information was provided for the future study on the gas phase chemistry of SHEs – Bh, Hs and Mt.

Acknowledgements

Notes and references

1 A. Türler and V. Pershina, *Chem. Rev.*, 2013, **113**, 1237-1312.
2 A. Türler, *Radiochim. Acta*, 1996, **72**, 7-18.
3 S. Hübener, S. Taut, A. Vahle, R. Dressler, B. Eichler, H. Gäggeler, D. Jost, D. Piguet, A. Türler and W. Brüchle, *Radiochim. Acta*, 2001, **89**, 737.
4 B. Eichler, A. Türler and H. Gäggeler, *J. Phys. Chem. A*, 1999, **103**, 9296-9306.
5 R. Eichler, B. Eichler, H. Gäggeler, D. Jost, D. Piguet and A. Türler, *Radiochim. Acta*, 2000, **88**, 87.
6 M. S. Lin, Z. Qin, F. A. Lei, J. S. Guo, L. N. Zhang, H. J. Ding, F. L. Fan, J. Bai and X. L. Wu, *Radiochim. Acta*, 2010, **98**, 321-326.
7 J. Even, A. Yakushev, C. E. Düllmann, J. Dvorak, R. Eichler, O. Gothe, D. Hild, E. Jäger, J. Khuyagbaatar and J. V. Kratz, *Inorg. Chem.*, 2012, **51**, 6431-6433.
8 Y. Wang, Z. Qin, F. L. Fan, F. Y. Fan, S. W. Cao, X. L. Wu, X. Zhang, J. Bai, X. J. Yin and L. L. Tian, *Radiochim. Acta*, 2014, **102**, 69-76.
9 J. Even, A. Yakushev, C. E. Düllmann, H. Haba, M. Asai, T. Sato, H. Brand, A. Di Nitto, R. Eichler and F. Fan, *Science*, 2014, **345**, 1491-1493.
10 J. Even, A. Yakushev, C. E. Düllmann, J. Dvorak, R. Eichler, O. Gothe, W. Hartmann, D. Hild, E. Jäger and J. Khuyagbaatar, *Radiochim. Acta*, 2014, **102**, 1093-1110.
11 Y. Wang, Z. Qin, F. L. Fan, H. Haba, Y. Komori, S. W. Cao, X. L. Wu and C. M. Tan, *Phys. Chem. Chem. Phys.*, 2015, **17**, 13228-13234.
12 J. E. House, in *Inorganic Chemistry*, ed. J. E. House, Academic Press, America, Second Edition, 2013, Chapter 16, 553-590.
13 F. L. Fan, Y. Wang, Z. Qin, presented in Poster Contributions at 5th International Conference on the Chemistry and Physics of the TransActinide Elements, Japan, May, 2015.
14 I. Usoltsev, R. Eichler, Y. Wang, J. Even, A. Yakushev, H. Haba, M. Asai, H. Brand, A. Di Nitto, Ch.E. Düllmann, F. Fangli, W. Hartmann, M. Huang, E. Jäger, D. Kaji, J. Kanaya, Y. Kaneya, J. Khuyagbaatar, B. Kindler, J.V. Kratz, J.Krier, Y. Kudou, N. Kurz, B. Lommel, S. Miyashita, K. Morimoto, K. Morita, M. Murakami, Y. Nagame, H. Nitsche, K. Ooe, T.K. Sato, M. Schädel, J. Steiner, P. Steinegger, T. Sumita, M. Takeyama, K. Tanaka, A. Toyoshima, K. Tsukada, A. Türler, Y. Wakabayashi, N. Wiehl, S. Yamaki, Z. Qin, *J. Radioanal. Nucl. Chem.,* in press.
15 M. Zhou, L. Andrews and C. W. Bauschlicher, *Chem. Rev.*, 2001, **101**, 1931-1962.
16 P. L. Bogdan and E. Weitz, *J. Am. Chem. Soc.*, 1989, **111**, 3163-3167.
17 G. A. Ozin and A. L. Hanlan, *Inorg. Chem.*, 1979, **18**, 2091-2101.
18 I. Zvára, *The Inorganic Radiochemistry of Heavy Elements: Methods for Studying Gaseous Compounds*, Springer Science & Business Media, Germany, 2008.
19 Fission Product Yields, http://ie.lbl.gov/fission.html, (accessed 20 Dec, 2014).