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Gas-phase chemistry of technetium carbonyl complexes

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Gas-phase chemical behaviors of short-lived technetium carbonyls were studied by using low temperature isothermal chromatograph (IC) coupled with a ^{252}Cf spontaneous fission (SF) source. Fission products recoiled from the ^{252}Cf SF source were thermalized in a CO contained mixed gas, and then technetium carbonyls were formed in reactions of CO gas 10 and various technetium isotopes. A gas-jet system was employed to transport the volatile carbonyls from a recoil chamber to the IC. Short IC columns made of Fluorinated Ethylene Propylene (FEP) Teflon and quartz were used to obtain the chemical information of technetium carbonyls. The results of ^{104}Tc – ^{106}Tc carbonyls were found to be strongly influenced by their precursors, showing the chemical behaviors of ^{104}Mo – ^{106}Mo carbonyls, 15 respectively. However, ^{107}Tc and ^{108}Tc could represent the chemical information of element technetium, due to their high independent yields and very short half-lives of their precursors ^{107}Mo and ^{108}Mo. An adsorption enthalpy of about ΔH_{ads} = - 43 kJ/mol was determined for the Tc carbonyls on both the Teflon and quartz surfaces by fitting the breakthrough curves of the ^{107}Tc and ^{108}Tc carbonyls with a Monte Carlo simulation 20 program. Chemical yields of around 25% were given for the Tc carbonyls relative to the transport yields obtained with the gas-jet transport of KCl aerosols with Ar carrier gas. Furthermore, the influence of a small amount of O$_2$ gas on the yields of the Mo and Tc carbonyls were studied.

Introduction

25 The first synthesis of an organometallic compound of a superheavy element, seaborgium hexacarbonyl (Sg(CO)$_6$), has been successfully achieved, recently [1]. Hence, for the first time chemistry acquired a Sg compound in its zero oxidation state, and its adsorption properties on a SiO$_2$ surface were compared to 30 those of the group 6 element homologues Mo(CO)$_6$ and W(CO)$_6$. This opened the door for nuclear chemists to further study carbonyl complexes of the superheavy elements 107 (Bh), 108 (Hs), and even 109 (Mt).

For the further study of the Bh carbonyls, the lighter 35 homologues Tc and Re carbonyls should be investigated in advance to get the general gas-phase chemical information of the short-lived group7 carbonyls, and to optimize the experimental conditions for the future Bh carbonyl chemistry.

The well-known EAN rule (Effective Atomic Number rule), 40 which is also called as the 18-electron rule, describing the number of metal and ligand electrons that give the $s^2p^6d^{10}$ noble gas configuration, provides qualitative predictions for the coordination and structures of many transition metal complexes [2]. It is a powerful rule to deduce the complexes which exist as 45 mononuclear or multinuclear state. For the group 6 elements, Mo(CO)$_6$ and W(CO)$_6$ are well known in macro chemistry. The numbers of effective electrons in the Mo and W carbonyls are:

$$n = 6_{\text{ numbers of valence electrons for Mo and W}} + 6_{\text{numbers of ligand CO}} \times 2_{\text{numbers of electrons offered by CO}} = 18 \qquad (I)$$

50 According to the EAN rule, carbonyls of the group 6 elements are stable in the state of M(CO)$_6$, where M stands for central metal atom. And the species of their carbonyls formed with single atoms in CO and inert gas atmosphere were found with the trend of turning into carbonyls with 6 CO ligands, by using matrix 55 isolation technique [3].

For the group 7 elements, only stable multinuclear carbonyl complexes are observed in macro chemistry, and the most common ones are dimetal decacarbonyls like Tc$_2$(CO)$_{10}$ and Re$_2$(CO)$_{10}$, which are also known to be volatile. However, in gas- 60 phase chemistry experiments with the ^{252}Cf SF source, considering the extremely small numbers of Tc atoms from nuclear reactions and the relatively large volume in the recoil chamber, the chance of two Tc isotopes meeting each other can be ignored. Some reports [4, 5] gave the Tc(CO)$_5$ and Re(CO)$_5$ 65 states, which were very reactive and volatile, and also simulated the adsorption enthalpy of Re(CO)$_5$ on quartz surface and studied the thermal decomposition of Tc(CO)$_5$ in specific chemical conditions.

The numbers of effective electrons in Tc and Re mononuclear

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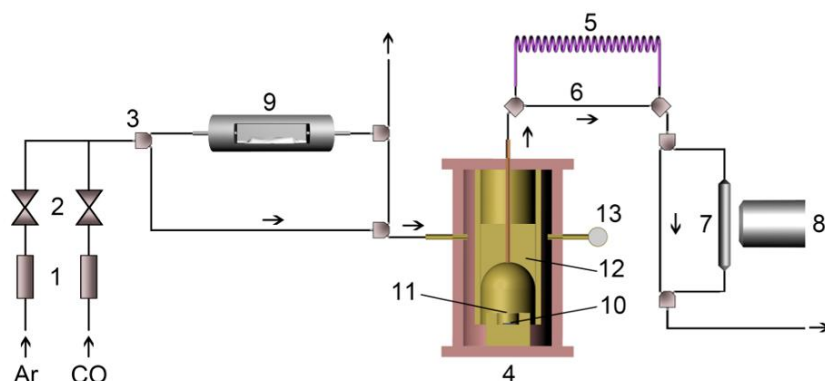
Fig. 1 Schematics of the experimental setup. The whole system consists of (1) mass flow controllers; (2) two-way valves; (3) three-way ball valves; (4) the cylindrical recoil chamber shielded with paraffin and lead blocks ; (5) the IC column (a 1.2 m long FEP Teflon column with i.d. = 2 mm or a 1.4 m long quartz column with i.d. = 2 mm) kept in a low temperature zone; (6) the FEP Teflon capillary with the same size of the IC column, kept at a room temperature through all the experiments; (7) the charcoal trap; (8) the HPGe γ-ray detector; (9) the KCl aerosol generator, a tube furnace with KCl in it and kept at 660 ℃; (10) the ^{252}Cf fission source; (11) the 0.5 μm thick PET film on the surface of ^{252}Cf source; (12) the movable Teflon hemispherical shape collector facing the fission source; (13) the pressure gauge. All equipment are connected with a FEP Teflon capillary (i.d. = 2 mm).

carbonyls are:

$$n = 7 \text{ numbers of valence electrons for Tc and Re} + 5 \text{ numbers of ligand CO} \times 2 \text{ numbers of electrons offered by CO} = 17 \qquad \text{(II)}$$

According to the EAN rule, carbonyls of the group 7 elements are unstable in the state of $M(CO)_5$. But they should still thermodynamically exist [4]. And this unstable molecules appeared in matrix isolation experiments as well [6].

However, from the measured breakthrough curves of the IC experiments with the ^{249}Cf source, no adsorption enthalpy of the Tc carbonyls could be extracted due to the influence of precursor effects, which could not be quantified [4]. The chemical yields of around 40% for both ^{106}Tc and ^{107}Tc carbonyls were reported. And in these experiments, N_2 gas was used as the carrier gas, so the species of the volatile Tc complexes could not be identified as pure carbonyls absolutely, since N_2 was also a well-known ligand for transition metals. Therefore, the adsorption enthalpy of pure Tc carbonyls is extremely necessary and important for the future investigation of the Bh carbonyls.

In this work, we used a ^{252}Cf fission source as the isotope generator, and in CO contained atmosphere, the Tc carbonyls were synthesized and studied with a short IC column. The adsorption enthalpy was obtained from the breakthrough curves of the ^{107}Tc and ^{108}Tc carbonyls. The relative chemical yields of all observed Tc isotopes were obtained using mixed gases of Ar with different CO concentrations. Furthermore, a strongly negative influence of a small amount of O_2 gas on the yields of the Mo and Tc carbonyls were observed.

Experimental

Figure 1 shows the schematics of the experimental setup. A gas-jet system was employed. High purity CO gas (99.997%) and

high purity Ar (99.999%) as carrier gas were regulated by mass flow controllers. Those gases were mixed before entering the ^{252}Cf SF source recoil chamber, whose inner surfaces were all made of Teflon. The ^{252}Cf source was prepared by electrodepositing about 0.1 mCi ^{252}Cf on a 0.127 mm thick palladium film. The fission source was covered with a 0.5 μm thick polyethylene terephthalate (PET) film. Fission fragments, recoiling from the ^{252}Cf source, were thermalized in the CO contained mixed gas, formed volatile carbonyls in situ in the recoil chamber and then were transported through the outlet in the Teflon collector to an IC device. FEP Teflon columns (i.d. = 2 mm) of 1.2 and 3 m long were kept at variable temperatures. The length of the column depends on the half-life of the expected isotope. The chromatography column was positioned in a low temperature cooling circulating unit (Model No.: DFY-5/80 ℃, Zhengzhou Yarong Instrument Company Limited, China). The isothermal temperature of this unit could be varied in 10 degree steps from 20 ℃ to - 80 ℃. The IC column could be by-passed through a FEP Teflon column held at a room temperature (20 ℃). After passing through the column, the survival carbonyls were transported to a charcoal trap (glass tube, i.d. = 4 mm, length = 5 cm, including 0.8 g of activated charcoal powders blocked with adsorbent cotton on both sides) facing an HPGe γ-ray detector (EG&G Ortec GEM-30200-P with a relative efficiency of 30%). The DSPEC-502TM Digital Gamma-Ray Spectrometer was used for data acquisition, and the energy resolution (FWHM) was 1.70 keV for the 1332.5 keV γ-ray.

The total gas flow rates of 1 and 1.5 L/min were used. The CO concentrations were varied from 0% to 100%. The recoil chamber depth was fixed at 5.5 cm between the outlet and the ^{252}Cf source, according to the SRIM calculations [7] for the particle with a mass number of around 107 and the incident energy of around 105 MeV [8] in about 1 bar pressure of Ar and CO gas. The

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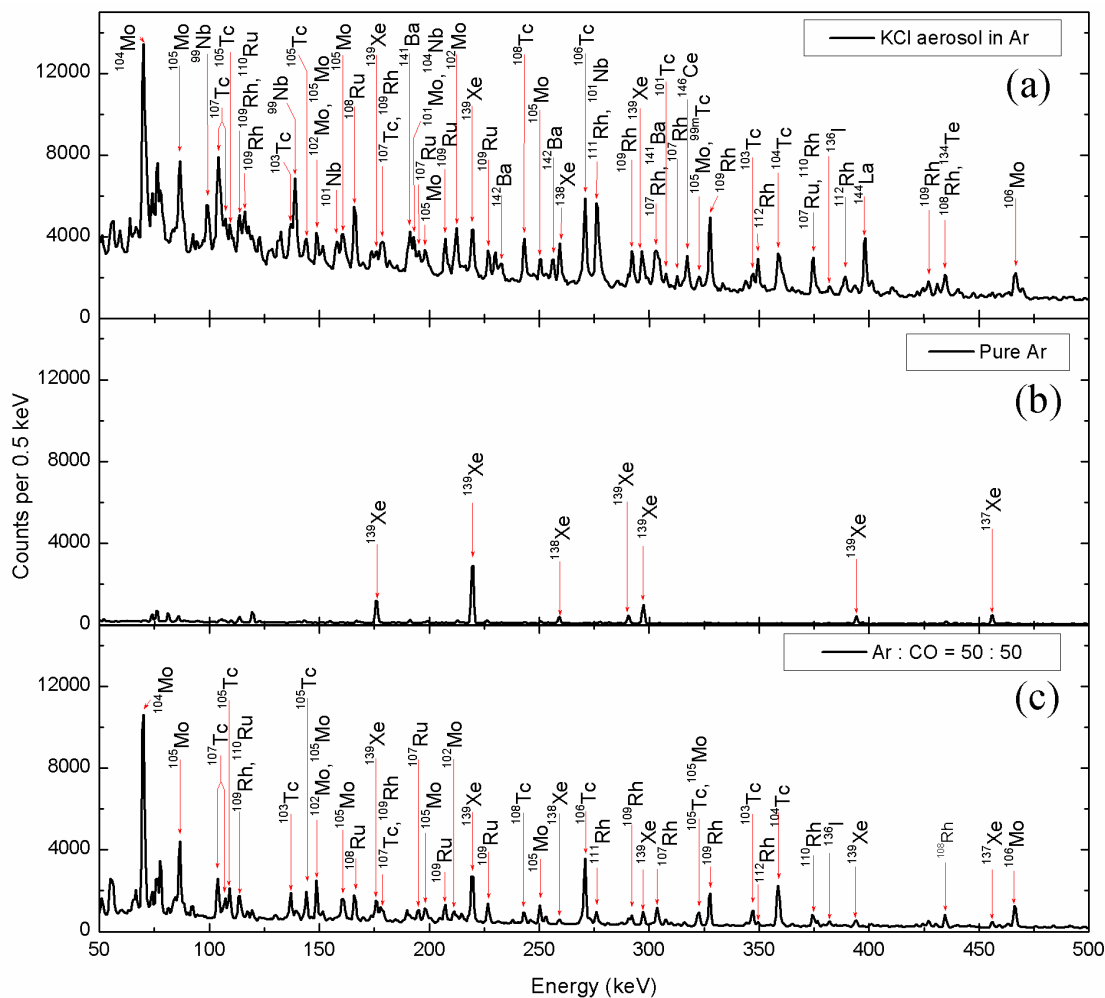
Fig. 2 γ-ray spectra of fission products transported (a) in Ar gas with KCl aerosol particles (top panel), (b) in pure Ar gas (middle panel), (c) in a mixed gas of Ar and CO (bottom panel), and collected on the charcoal trap. The total gas flow rates for each experiment were the same as 1 L/min. All the samples were collected and detected on-line for 30 min.

pressure in the recoil chamber was about 1.05 atm. All measurements were performed with the same counting time of 30 min. Three different ways to transport fission products were studied: (i) the transport of all fission fragments in Ar gas with KCl aerosol particles; (ii) the transport of volatile fission products in pure Ar gas; (iii) the transport of volatile carbonyl complexes in Ar and CO mixed gas. For (i) transport, the pure Ar gas passed a tube furnace, which contained a KCl powder kept at 660℃, and then entered the recoil chamber.

Results and discussion

Adsorption enthalpies of Tc carbonyl complexes on Teflon and quartz surfaces

Typicalγ-ray spectra obtained in this work are shown in Figure 2: (a) all fission fragments transported with KCl aerosols in Ar gas,

and no chemical selectivity, (b) only volatile fission products transported in pure Ar gas, and (c) both volatile fission products and volatile complexes containing carbonyls of 4d elements Mo, Tc, Ru, and Rh transported in the mixed gas (Ar : CO = 1 : 1). This shows the same information in our previous work [8], which proved that volatile carbonyls of 4d elements were synthesized and transported from the recoil chamber to the charcoal trap. Moreover, the γ-rays of ^{107}Tc ($T_{1/2}$ = 21.2 s, E_γ= 102.7 keV, I_γ =21.0%; E_γ= 106.3 keV, I_γ =7.6%) and ^{108}Tc ($T_{1/2}$ = 5.17 s, E_γ = 242.2 keV, I_γ =82%) can be clearly observed, but none of their precursors ^{107}Mo ($T_{1/2}$ = 3.5 s,E_γ = 400.3 keV, I_γ =100%) or ^{108}Mo ($T_{1/2}$ = 1.09 s,E_γ= 268.3 keV, I_γ =22%) appears in all spectra.

The key point to study the Tc carbonyls with the ^{252}Cf SF source is to determine which isotopes can be used to represent the chemical behaviors of the element Tc. As we know, the precursor

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Table 1 The half-lives, independent yields and cumulative yields of Mo and Tc isotopes formed in the ^{252}Cf SF source [9].

| Mo isotope	Half-life	Independent yield (%)	Cumulative yield (%)	Fr[a]	Tc isotope	Half-life	Independent yield (%)	Cumulative yield (%)	Fr[a]
^{104}Mo	60s	2.83E+00	5.22	54.21%	^{104}Tc	18.2min	4.31E-01	5.65	7.63%
^{105}Mo	36s	3.02E+00	4.04	74.75%	^{105}Tc	7.6min	2.10E+00	6.14	34.20%
^{106}Mo	8.4s	3.47E+00	3.91	88.75%	^{106}Tc	36s	2.19E+00	6.1	35.90%
^{107}Mo	3.5s	2.01E+00	2.1	95.71%	^{107}Tc	21.2s	3.63E+00	5.73	63.35%
^{108}Mo	1.5s	6.67E-01	6.77E-01	98.52%	^{108}Tc	5.1s	3.33E+00	4.01E+00	83.04%
^{109}Mo	1.41s	1.48E-01	1.49E-01	99.33%	^{109}Tc	1.4s	1.89E+00	2.04E+00	92.65%
^{110}Mo	2.77s	2.31E-02	2.31E-02	100.00%	^{110}Tc	0.83s	8.55E-01	8.78E-01	97.38%

[a] "Fr" shows the fraction of the independent yield in the corresponding cumulative yield.
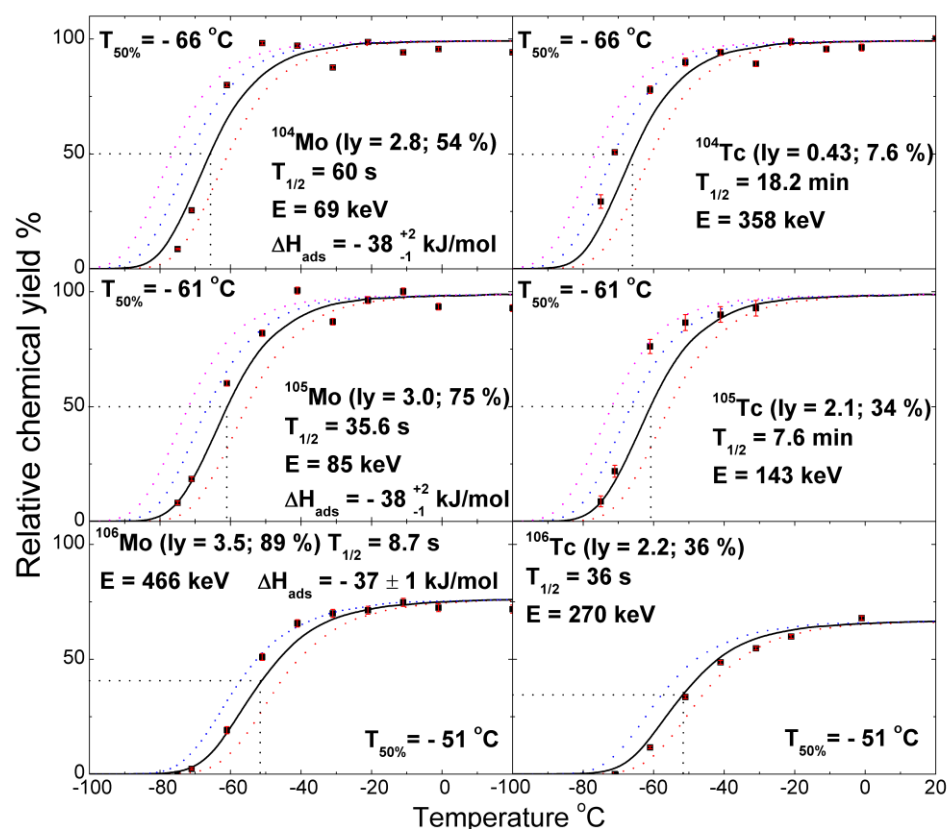
5 **Fig. 3** Breakthrough curves of $^{104-106}$Mo and $^{104-106}$Tc with a 3 m long FEP Teflon IC column (i.d. = 2 mm). The symbols are the experimental data. The solid curves are the results of the Monte Carlo simulations with the corresponding adsorption enthalpies. The dotted curves depict the error limits of + 2 and - 1 kJ/mol, or ±1 kJ/mol. For the Mo isotopes, the curves represent the simulated adsorption enthalpies of themselves. For the Tc isotopes, the curves are consistent with the simulation results of their precursors (Mo isotopes); the simulation can fit the breakthrough curves of the Mo isotopes very well, but can't give their own chemical behaviors. The mixed gas (Ar : CO = 1 : 1) was used with a total gas flow rate of 1 L/min.

10 effects of the fission products play an important role in detailed data analysis. We found that these effects can be negligible in the case of (1) the fraction of the independent yield of certain isotope to the cumulative yield is large enough, (2) and the precursor's 15 half-life is short enough to decay in the recoil chamber. In our previous work [8], the results from ^{104}Tc, ^{105}Tc and ^{106}Tc were found to be influenced strongly by their precursors, showing the chemical behaviors of the Mo carbonyls of ^{104}Mo, ^{105}Mo and ^{106}Mo, respectively. According to Table 1, which shows the 20 Independent yields (Iy) and Cumulative yields of the Mo and Tc isotopes formed with the ^{252}Cf SF source, most of $^{104-106}$Tc are formed by β-decays of $^{104-106}$Mo, and less than 50% of them are
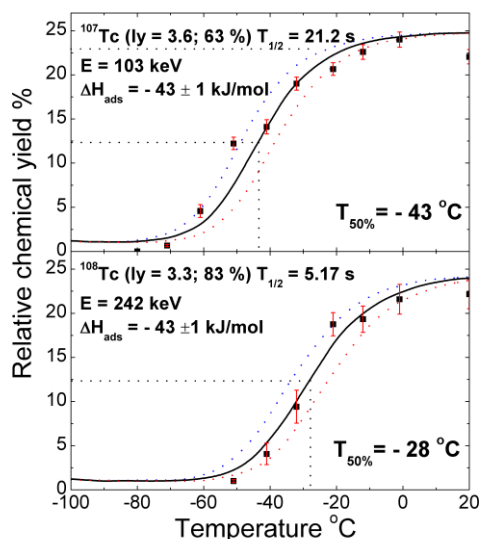
Fig. 4 Breakthrough curves of ^{107,108}Tc with a 1.2 m long FEP Teflon IC column (i.d. = 2 mm). The symbols are the experimental data. The solid curves are the results of the Monte Carlo simulations with $\Delta H_{ads} = -43$ kJ/mol. The dotted curves depict the error limits of ± 1 kJ/mol. High purity CO gas with a flow rate of 1.5 L/min was used.
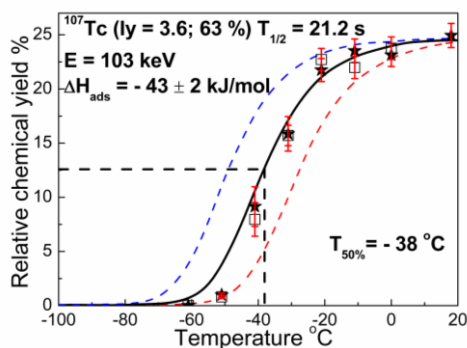
Fig. 5 Breakthrough curves and adetermination of the adsorption enthalpy of the ^{107}Tc carbonyls with a 1.4 m long quartz IC column (i.d. = 2 mm) in 1 L/min mixed gas (CO : Ar = 1 : 1). The two different symbols are from two of the repeated experiments.

formed directly in the fission reactions. This confirms to our conclusion [8] that the measured $^{104-106}$Tc were mostly formed in the charcoal trap and transported in the form of their precursors $^{104-106}$Mo from the recoil chamber.

Figure 3 shows the breakthrough curves of $^{104-106}$Mo and $^{104-106}$Tc with a 3 m long FEP Teflon IC column (i.d. = 2 mm) using the 1 L/min mixed gas (Ar : CO = 1 : 1). With Monte Carlo simulation program, the same adsorption enthalpies around $\Delta H_{ads} = -38$ kJ/mol were given for the short-lived $^{104-106}$Mo(CO)$_6$ [8]. The relative chemical yields of the Mo and Tc isotopes are given by using the yields obtained with the KCl aerosol transport in Ar gas as 100%. The absolute value of the maximum chemical yield is dependent on the half-life of the isotope [10]. The chemical yields for ^{104,105}Mo are 100%, but that for ^{106}Mo drops down to 80% since the half-life of ^{106}Mo is as short as 8.7 s. Because of the large precursor effects, the yield curves of $^{104-106}$Tc are the same as those of $^{104-106}$Mo, respectively. This confirms to our previous work again. The other information shown in Figure 3 is the independent yield (Iy), the fraction of the Iy in the cumulative

yield, the half-life of each nuclide, and the characteristic γ-ray energy we used.

From Table 1, we know that most of ^{107}Tc ($T_{1/2} = 21.2$ s) and ^{108}Tc ($T_{1/2} = 5.1$ s) are formed directly in the fission reactions with the yields of 63% and 83%, respectively. And the half-lives of their precursors ^{107}Mo ($T_{1/2} = 3.5$ s) and ^{108}Mo ($T_{1/2} = 1.5$ s) are too short to be transported from the recoil chamber to the charcoal trap. So, they shall represent the chemical behaviors of the element Tc, excluding the influence of precursor effect. Figure 4 shows the breakthrough curves of ^{107,108}Tc with a 1.2 m long FEP Teflon IC column (i.d. = 2 mm) using the 1.5 L/min pure CO gas. Since the half-life of ^{108}Tc is only $T_{1/2} = 5.1$ s, short IC columns and large gas flow rates were used to obtain more counts. The adsorption enthalpies around $\Delta H_{ads} = -43$ kJ/mol were given for both ^{107}Tc(CO)$_5$ and ^{108}Tc(CO)$_5$ using the Monte Carlo simulation program.

The adsorption enthalpies of ^{107}Tc carbonyls on quartz surface were also determined. Since the half-life of ^{107}Tc is much longer than ^{108}Tc, mixed Ar and CO gas with a 1 L/min flow rate, and a 1.4 m long quartz column (i.d. = 2 mm) were used. The adsorption enthalpy of about $\Delta H_{ads} = -43$ kJ/mol was given according to the $T_{50\%}$ value of the breakthrough curve as shown in Figure 5. This adsorption enthalpy is consistent with the literature data of Re carbonyls on the quartz surface, which is $\Delta H_{ads} = -43$ kJ/mol with uncertainty limits of ± 3 kJ/mol [4]. The same adsorption enthalpy of $\Delta H_{ads} = -43$ kJ/mol for the Tc carbonyls on both Teflon and quartz surface, was determined fromthe different breakthrough curves in the different experimental conditions, which can point to a physical sorption process in their surface interactions.

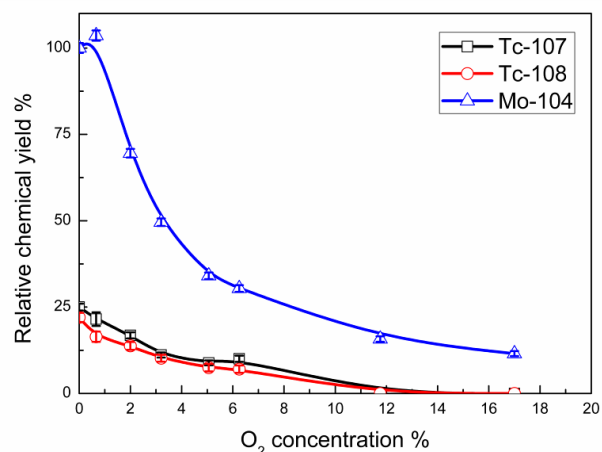**Relative chemical yields of Tc carbonyl complexes**

Figure 6 shows the chemical yields of the Mo and Tc isotopes as a function of the CO concentration in the Ar carrier gas, relative to the yields obtained with the KCl aerosol transport in Ar gas. The top one shows quite high chemical yields for the Mo carbonyls (which are stable mono-nuclear complexes in the form of M(CO)$_6$), almost 100% for ^{104,105}Mo, whose half-lives are longer than 30 s. The bottom one shows different chemical yields of the Tc isotopes. For $^{104-106}$Tc, as mentioned above, they were transported in the form of their precursor Mo isotopes and formed in the charcoal trap, so their yields are almost the same as those of $^{104-106}$Mo, respectively. ^{107,108}Tc, which were mainly formed in the recoil chamber, show relatively low chemical yields of about 25%, and they represent the real chemical yields of the Tc carbonyls, which would be unstable mono-nuclear complexes in the form of M(CO)$_5$.

For all these carbonyls, in Ar carrier gas at about 1 bar, they all reach the highest yields when the CO concentration is higher than 20%. Thus we may be able to get the highest yields of the group 6 and 7 carbonyls with> 50% CO concentrations in the mixed gas, including the carbonyls of superheavy elements Sg and Bh.

Influence of O$_2$ gas on the relative chemical yields of Tc carbonyl complexes
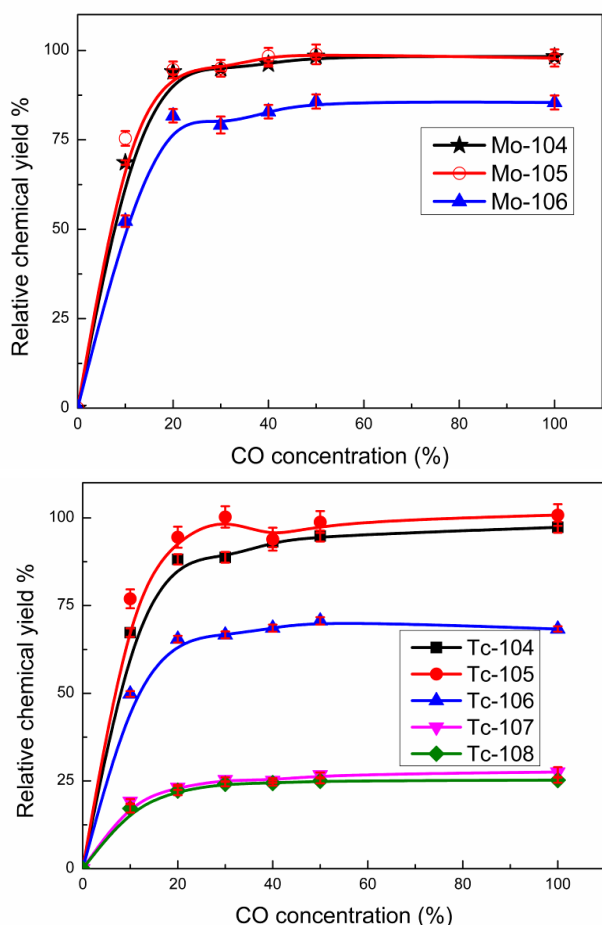
Fig. 6 Relative chemical yields of Mo (the top one) and Tc (the bottom one) isotopes as a function of the CO concentration in the Ar carrier gas, normalized to the yieldsobtained with the KCl aerosol transport in Ar gasand corrected by the yields of the volatile fission product of ^{139}Xe in each γ-spectrogram. All experiments were performed with a 1 L/min gas flow rate.

Fig. 7 Relative chemical yields of Mo and Tc 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-spectrogram. All experiments were performed in the fixed CO and Ar mixed gas (CO : Ar = 1 : 1) with the additional O$_2$ gas.

In the previous experiments [1], a trace amount of O$_2$ was found to have a strong negative influence on chemical yields of W carbonyl complexes. To verify such an influence on the group 7 carbonyls, a small amount of O$_2$ gas was added into the mixed Ar and CO gas (Ar : CO = 1 : 1) at a flow rate of 1.5 L/min, and then the yields of the Mo and Tc carbonyls were obtained as a function of the O$_2$ concentration (see Figure 7). The yields of the carbonyls were normalized to the yields of the volatile fission product of ^{139}Xe in each measurement to eliminate the influence of variations of the gas-jet transport yields. The yields of each isotopes obtained with the KCl aerosol transport in Ar gas were used as the 100% value.

In Figure 7, we can see that 2% of the O$_2$ gas already has a strong negative influence on both Mo and Tc carbonyls, and the relative chemical yields were reduced from 100% to 70% for Mo, and from 25% to 15% for Tc. With 6% of the O$_2$ gas, about 70% of both Mo and Tc carbonyls were lost. Especially for Tc, no carbonyl complexes could be observed above the O$_2$ concentrations of more than 12%. However, the Mo carbonyls could still be observed in higher O$_2$ concentrations with reduced yields, but they were totally disappeared in pure O$_2$ gas. Therefore, in the future experiments of the Bh carbonyls, the O$_2$ gas must be fully excluded from the reaction and carrier gases.

Conclusions

An on-line low temperature isothermal gas-phase chromatography apparatus coupled to a ^{252}Cf SF source at IMP was used to study technetium carbonyls synthesized in reactions with carbon monoxide. Almost the same adsorption enthalpies on both Teflon and quartz surfaces were observed for ^{107}Tc and ^{108}Tc carbonyls, which points to a physical sorption process of short-lived technetium carbonyls in their surface interactions. This work for the first time gave the adsorption enthalpies of the Tc carbonyls on specific chemical surfaces, which may offer some necessary chemical information of the group 7 carbonyls, especially for the experiments of Bh carbonyls in the future. The measured adsorption enthalpy of the Tc carbonyls on the quartz surface, around ΔH_{ads} = - 43 kJ/mol, agreed well with the literature data of Re carbonyls on the quartz. This may suggest that the Bh carbonyls shall also have an adsorption enthalpy around ΔH_{ads} = - 43 kJ/mol, if its chemical properties are not influenced strongly by the relativistic effects. Low chemical yields of about 25% were measured for the Tc carbonyls. This may suggest the chemical yield of the Bh carbonyls shall be four times lower than that of Sg, since our measured chemical yields of Mo carbonyls were around 100%. Furthermore, 20% of CO concentration in the mixed gas was found to be enough to give the highest chemical yields for both the Mo and Tc carbonyls, without regard to the influence of recoil ranges of these fission fragments.

Moreover, relative yields of the Mo and Tc isotopes as a function of the O$_2$ concentration in the Ar and CO mixed gas were obtained, which showed that a small amount of the O$_2$ gas drastically reduce the yields of the Mo and Tc carbonyls. Thus, in the future experiments with the Bh carbonyls, O$_2$impurity shall be removed completely from the reaction gas.

Notes and references

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