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Rapid Synthesis of Radioactive Transition-Metal Carbonyl Complexes at Ambient Conditions

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Ⓢ *Supporting Information*

ABSTRACT: Carbonyl complexes of radioactive transition metals can be easily synthesized with high yields by stopping nuclear fission or fusion products in a gas volume containing CO. Here, we focus on Mo, W, and Os complexes. The reaction takes place at pressures of around 1 bar at room temperature, i.e., at conditions that are easy to accommodate. The formed complexes are highly volatile. They can thus be transported within a gas stream without major losses to setups for their further investigation or direct use. The rapid synthesis holds promise for radiochemical purposes and will be useful for studying, e.g., chemical properties of superheavy elements.

More than 100 years after pioneering the synthesis of metal carbonyl complexes,[1] this compound class is still of high interest in various areas of fundamental and applied chemistry.[2] Classically, most highly coordinated metal carbonyl complexes (with more than three CO ligands) are synthesized under high CO pressure. These challenging technical aspects restrict their broad application. In radiopharmaceutical chemistry, e.g., higher coordinated carbonyl complexes are deemed powerful lung perfusion agents, but their potential could not yet be exploited, mainly because of limits in their synthesis.[3] Because these complexes are generally volatile, they would be ideal for gas-phase transport of short-lived isotopes of refractory metals for the production of radioactive-ion beams.[4] In the fundamental sciences, the study of carbonyl complexes of transactinide elements ($Z \geq 104$; superheavy elements, SHEs[5]) has raised interest in theoretical chemistry. A prominent example is the prediction that relativistic effects, which scale with Z^2 and are thus most pronounced and best studied in SHEs, would be expressed in a stronger π-back-bonding in $Sg(CO)_6$ compared to $Mo(CO)_6$ and $W(CO)_6$.[6] Baumgärtner and Reichold developed a discontinuous method to separate Mo as $Mo(CO)_6$ from fission products.[7] This, however, does not appear promising for studies of SHEs, mostly because of the short half-lives, $T_{1/2}$, of SHEs (generally at most a few seconds up to about 1 min). Furthermore, SHEs are produced in nuclear fusion reactions by irradiating thin targets with intense heavy-ion beams. Harsh conditions associated with these processes restricted the accessible SHE compound classes to those that are thermally stable.[8] To date, gas-phase chemical studies of SHEs include only inorganic compounds like (oxo)halides and oxides or focused on the elemental state.[5,8] Thanks to the recently established method[9] of spatial separation of SHEs from the intense heavy-ion beams in a magnetic separator prior to chemical synthesis, these limits can now be overcome. New SHE compound classes that were inaccessible before are now within reach.[10] Here, we report on the syntheses and gas chromatographic studies of single transition-metal carbonyl complexes with short-lived isotopes of Mo, W, and Os.

Short-lived Mo isotopes ($T_{1/2}$: a few seconds to several minutes) were produced in the neutron-induced fission of ^{249}Cf at the TRIGA Mainz reactor. Fission products (4d elements) recoiling from the ^{249}Cf target (e.g., on the order of 10^4 atoms per second of ^{104}Mo) were thermalized in a gas volume flushed with a N_2/CO mixture. Short-lived nuclides of the 5d elements W and Os were produced in the nuclear fusion reactions $^{144}Sm(^{24}Mg,4\text{–}5n)^{163,164}W$ ($T_{1/2} = 2.75$ and 6.0 s) and $^{152}Gd(^{24}Mg,5\text{–}6n)^{170,171}Os$ ($T_{1/2} = 7.3$ and 8.0 s) at the UNILAC accelerator at GSI Darmstadt. The nuclides of interest were isolated in the TransActinide Separator and Chemistry Apparatus (TASCA)[11,12] and guided into a gas-filled volume—the recoil transfer chamber (RTC)[13]—where they were thermalized in a 0.8 bar CO/He gas mixture. On the order of 10^3 ions per second of the isotopes of interest entered the RTC. During thermalization of nuclear reaction products, their

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charge states decrease. The thermalized ions or atoms of refractory metals interact with CO present in the gas phase during diffusion, yielding neutral carbonyl complexes. We found that these can be rapidly (within a few seconds, as follows from the observation of, e.g., short-lived ^{108}Mo and ^{163}W) transported with high yields (over 50%) with a gas stream over several meters through capillaries to, e.g., a collection station or gas chromatography setup. With this method, γ-ray emitting fission products of Se, Mo, Tc, Ru, and Rh (see Figure 1) as well as α- or γ-decaying nuclides of W, Re, Os, and Ir were identified. Here we present the results on Mo, W, and Os. A more detailed report involving also the other elements will be given elsewhere.[14]

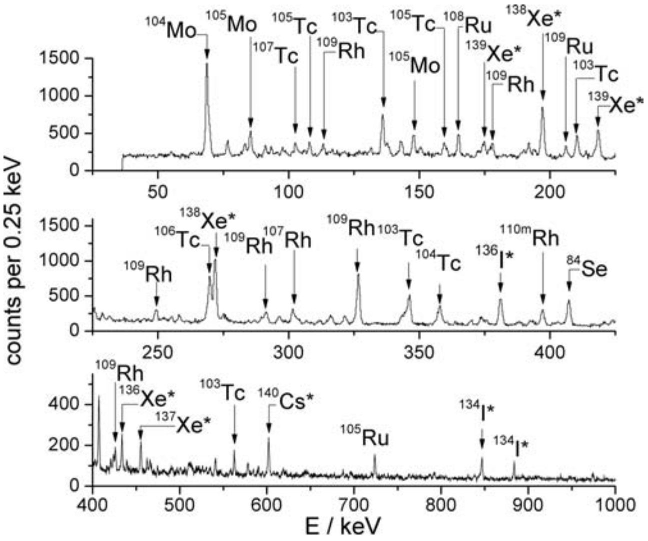

Figure 1. γ-ray spectrum of the transported fission products (gas mixture of 375 mL/min of CO and 125 mL/min of N_2) collected for 2 min in a charcoal trap. The sample was measured subsequently for 2 min. Isotopes, which were also visible in spectra of pure N_2 experiments (volatile elements and their radioactive decay products), are marked with asterisks. We focused on optimizing the speed and yield of our method to make short-lived nuclides of the refractory d elements easily and almost quantitatively available for further studies. We compared the yield of our method to that of a classical aerosol gas jet.[15] In this approach, nuclear reaction products are attached to KCl aerosol particles and are nonselectively transported with typical yields of 60−70%.[16] The relative yield of a N_2/CO pure gas jet (normalized to a N_2/KCl gas jet) was studied as a function of the CO fraction among the total gas flow rate of 500 mL/min (Figure 2). The yield increases with an increase in the CO fraction. Relative transport yields of >80% were achieved.

While direct speciation of the formed species is not possible with current analytical techniques because of the small number of molecules present, indirect arguments given below lead us to assign the transported species to $Mo(CO)_6$, $W(CO)_6$, and $Os(CO)_5$. They were found to be volatile at 22 °C, which we exploited for studies by two gas chromatography techniques: isothermal chromatography (IC)[17] and thermochromatography (TC).[18] These allow determination of the adsorption enthalpy, $-\Delta H_{ads}$, of the species on the column material. IC experiments with $Mo(CO)_6$ were conducted on a SiO_2 surface. The relative yield versus the column temperature is shown in Figure 3, along with the results of Monte Carlo simulations[19] (MCS) of the migration of the complexes through the IC column. The only free parameter in these simulations was $-\Delta H_{ads}$. The best fit to the experimental data set was obtained with $-\Delta H_{ads}$ = 42.5 ± 2.5 kJ/mol (Figure 3).

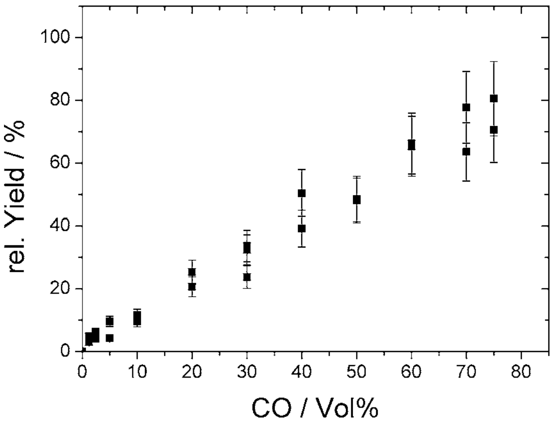

Figure 2. Relative yield of ^{104}Mo transported in a N_2/CO gas mixture normalized to the yield of a N_2/KCl cluster jet as a function of the fraction of CO in the gas stream (flow rate was 500 mL/min). The volatile compounds were collected for 120 s and then measured by γ-ray spectroscopy.

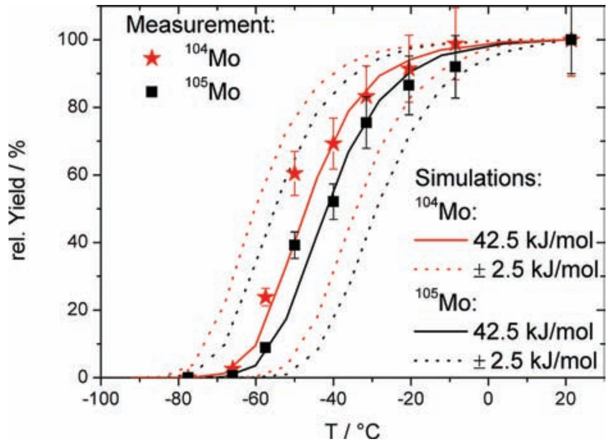

Figure 3. Isothermal chromatograms of ^{104}Mo and ^{105}Mo. The gas flow rate was 600 mL/min (40% N_2 and 60% CO). Symbols: experimental values. Solid lines: result of MCS with $-\Delta H_{ads}$ = 42.5 kJ/mol. Dotted lines: uncertainties of ±2.5 kJ/mol.

The adsorption of $Os(CO)_5$ and $W(CO)_6$ on quartz was studied with the TC detector channel COMPACT,[20] which is suitable to register α-decaying species deposited inside the TC column. To evaluate these experiments, the MCS procedure was adapted to take into account the rectangular cross section of the COMPACT column by using a modified Golay equation.[21] Typical thermochromatograms along with the results of MCS are shown in Figure 4. The peak of the deposition of $Os(CO)_5$ on the SiO_2 surfaces in COMPACT was found at −64 ± 10 °C. Similar experiments with $W(CO)_6$ yielded an adsorption temperature of −42 ± 10 °C. From the deposition patterns of W and Os, $-\Delta H_{ads}$ for $W(CO)_6$ of 46.5 ± 2.5 kJ/mol and $43.5^{+3.5}_{-2.5}$ kJ/mol for $Os(CO)_5$ were deduced. Such values for $-\Delta H_{ads}$ are comparable to those reported for OsO_4, 39.6 ± 1.3 kJ/mol,[22] and indicative of physisorption processes. This is in agreement with the results of IR spectroscopy studies,[23] where the physisorption of $M(CO)_6$ complexes on SiO_2 was investigated. The volatility trend expressed in the sublimation enthalpies ΔH_{sub} of $Mo(CO)_6$ and

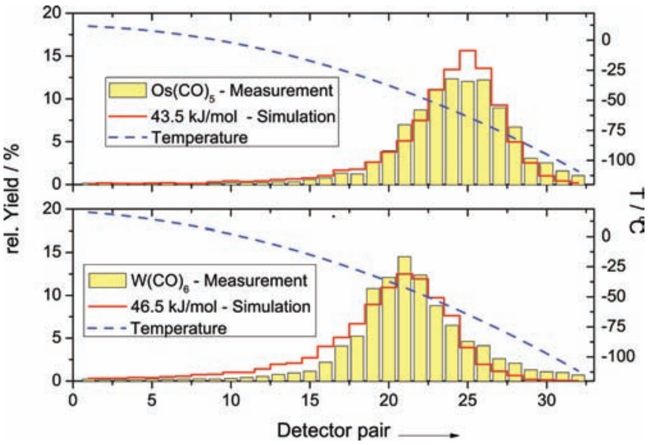

Figure 4. Upper graph: Combined thermochromatogram of ^{170}Os(CO)$_5$ and ^{171}Os(CO)$_5$. Lower graph: Combined thermochromatogram of ^{163}W(CO)$_6$ and ^{164}W(CO)$_6$. Dashed blue lines: temperature gradient (right-hand y axis). Yellow bars: relative yields per detector pair using $-\Delta H_{ads}$ values as given in the figure. Red solid lines: results of MCS. The gas mixture was 50% He and 50% CO. The total gas flow rates were 0.73 L/min [Os(CO)$_5$] and 0.85 L/min [W(CO)$_6$]. The pressure inside the RTC was 0.8 bar.

W(CO)$_6$ is in line with our measured $-\Delta H_{ads}$ values of these two species (Table 1).

Table 1. Overview of the Thermodynamic Properties of the Carbonyl Complexes

	ΔH_{sub},[a] kJ/mol	$-\Delta H_{ads}$,[b] kJ/mol	$-\Delta H_{ads}$,[c] kJ/mol
Mo(CO)$_6$	71.22	42.5 ± 2.5	48.5 ± 10
W(CO)$_6$	77.55	46.5 ± 2.5	52.6 ± 10
Os(CO)$_5$	not available	$43.5^{+3.5}_{-2.5}$	not available

[a] Reference 24. [b] This work. [c] Calculated according to the physisorption model as applied in ref 22.

On the basis of our results, fast chemical and nuclear spectroscopy studies of the transactinide elements seaborgium (Sg, $Z = 106$) and hassium (Hs, $Z = 108$) appear to be possible. The method developed in this work promises to find applications also in other fields, such as nuclear medicine, or the production of radioactive-ion beams, where fast and efficient synthesis of carbonyl complexes is of interest.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and the complete refs12, 13, and 20a. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The experiments were prepared by J.E. and A.Y. and were performed by all authors. J.E. analyzed the data. J.E. and Ch.E.D. prepared the manuscript. All authors commented on the manuscript at all stages and have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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