

Gas-phase chemistry of Re carbonyl complexes with short-lived isotopes

Y. Wang,^{*1} Z. Qin,^{*1} F. Fan,^{*1} H. Haba,^{*2} Y. Komori,^{*2} S. Yano,^{*2} D. Kaji,^{*2} K. Morimoto,^{*2} and S. Cao^{*1}

Since the first organometallic compound of a superheavy element, Sg(CO)₆, was successfully synthesized in 2014,¹⁾ the door was opened for nuclear chemists to further study the carbonyl complexes of heavier elements such as bohrium, hassium, and even meitnerium. The next achievement was suggested to be the chemical investigation of mononuclear Bh carbonyl complexes Bh(CO)₅. First, however, the chemical properties of its lighter homologs Tc(CO)₅ and Re(CO)₅ required study. We previously investigated the chemical behaviours of Tc(CO)₅,²⁾ Ru(CO)₅, and Rh(CO)₄.³⁾ In this study, we performed a gas-phase chemical experiment on Re carbonyls with short-lived isotopes. The volatile Re carbonyls were synthesized and their adsorption enthalpies on a perfluorinated ethylene-propylene (FEP) Teflon surface were determined using low temperature isothermal chromatography (IC). Furthermore, the relative chemical yields of these Re carbonyls were obtained for the first time, which is very important for the future chemical investigation of Bh carbonyl complexes.

A ^{nat}Gd₂O₃ target with a thickness of 340 μg/cm² was prepared by electrodeposition onto a 2-μm Ti foil. The ²³Na⁷⁺ ion beam was extracted from RILAC. The beam energy was 130.6 MeV at the middle of the target, and the typical beam intensity was 2.5 particle μA. The short-lived Re isotopes were produced in the heavy-ion reactions ^{nat}Gd(²³Na,*xn*)¹⁷²⁻¹⁷⁷Re.⁴⁾ GARIS was employed to pre-separate the evaporation residues (ERs). For GARIS, the magnetic rigidity was 1.74 Tm and the He pressure was 33 Pa. The ERs were then guided into a recoil transfer chamber (RTC) with an inert internal surface through a 0.7-μm Mylar window that was supported by a honeycomb-hole grid with 84% transparency. In RTC, the ERs were thermalized in the mixed gas containing CO (high-purity CO/ He or high-purity CO/Ar), formed volatile carbonyl complexes *in situ*, and then were transported through a 10 m long Teflon (FEP) capillary (i.d. = 2 mm) to an IC device. The ERs could also be transported with KCl aerosols by a He gas-jet to the chemistry laboratory to evaluate relative chemical yields. The total gas flow rate was maintained at 1 L/min, and the pressure in the RTC chamber was around 80 kPa. The depths of the RTC were 7 and 100 mm for the Ar and He gas, respectively.

The gas-phase chemical behaviors of Re carbonyl complexes were systematically studied using an online low temperature IC with the Ar and CO mixture. A 5.28-m long IC column made of Teflon (i.d. = 2 mm) was used to obtain the chemical information of the high-volatile Re carbonyls.

After passing through the IC column, the surviving volatile carbonyls were collected with 800 mg of activated

charcoal powders in a glass tube (4-mm i.d. × 5 cm length) facing a high-purity Ge-γ-ray detector with a relative efficiency of 20% (EG&G Ortec). By fitting the breakthrough curves of the corresponding carbonyl complexes using a Monte Carlo simulation program,²⁾ it was found that three short-lived ^{172m,174,176}Re isotopes yield the same adsorption enthalpy on the Teflon surface $\Delta H_{\text{ads}} = -43_{-1}^{+2}$ kJ mol⁻¹, which is consistent with the literature.⁵⁾

Figure 1 shows the chemical yields of ^{172m}Re, ¹⁷⁴Re, and ¹⁷⁶Re carbonyls as a function of the CO concentration in the He gas relative to the yields obtained with the KCl aerosols in the He gas. The CO concentration was varied from 0% to 100% and all the data were normalized by the irradiation dose. The highest relative chemical yields for ¹⁷⁴Re and ¹⁷⁶Re carbonyls appeared at a 50% CO concentration with a value of around 25%. This value is the same as its lighter homolog Tc carbonyl (about 25%).²⁾ However, for the ^{172m}Re carbonyl complex, the highest relative chemical yield decreased to 10%, because of the shorter half-life and long transport time from the RTC to the charcoal trap. This study could help us to optimize the experimental conditions for future chemical behavior study of the Bh carbonyl complexes.

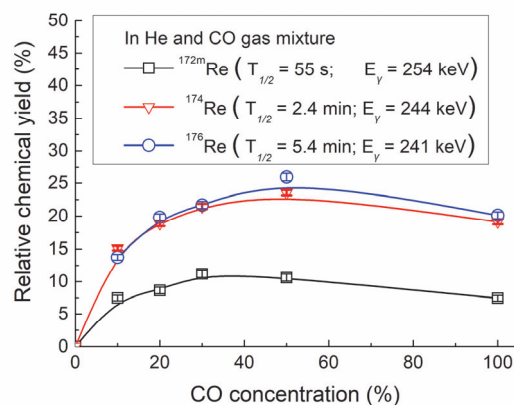


Fig. 1. Chemical yields of ^{172m,174,176}Re carbonyls transported with a CO and He mixed gas. The 100% value is the yield obtained with KCl aerosols in the He carrier gas.

References

- 1) J. Even et al., *Science* **345**, 1491 (2014).
- 2) Y. Wang et al., *Phys. Chem. Chem. Phys.* **17**, 13228 (2015).
- 3) S. Cao et al., *Phys. Chem. Chem. Phys.* **18**, 119 (2016).
- 4) H. Haba et al., *RIKEN Accel. Prog. Rep.* **45**, 293 (2015).
- 5) J. Even et al., *Radiochim. Acta* **102** (12), 1093 (2014).

^{*1} Institute of Modern Physics, Chinese Academy of Sciences

^{*2} RIKEN Nishina Center