THE STUDY OF RHENIUM PENTACARBONYL COMPLEXES USING SINGLE-ATOM CHEMISTRY IN GAS PHASE

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The single-atom synthesis of the first organometallic compound of superheavy elements, a seaborgium hexacarbonyl, has been a milestone in chemical investigations of superheavy elements and associated relativistic effects.[1] Towards chemical characterization of the superheavy element bohrium (Bh), a gas-phase chemical study of mononuclear rhenium carbonyls was carried out. Short-lived Re isotopes were produced in heavy-ion-induced nuclear fusion reactions of $^{nat}Gd(^{23}Na,xn)^{172-177}Re$. Their volatile carbonyl was synthesized in-*situ* in gas-phase reactions with the reactive gas mixture and transported through perfluorinated ethylene-propylene (FEP) Teflon capillaries held at various temperatures. From these isothermal chromatography experiments, their adsorption enthalpies were determined to be $\Delta H_{ads} = -42\pm2$ kJ mol^{-1} on the Teflon surface by fitting the external chromatograms with a Monte Carlo simulation program.[2,3] The chemical yield of 25% relative to that of the transport yield for Re by a He/KCl gas-jet was achieved for the first time. The similar experimental technique is envisaged for Bh in future experiments.

To identify the species of Re carbonyls produced in the gas-phase single-atom reaction, an improved laser-ablation time-of-flight mass-spectrometric (LA-ToF-MS) technique was employed. The most stable product for W and Re carbonyl cations were derived to be $[W(CO)_6]^+$ and $[Re(CO)_6]^+$, respectively. By detecting the isoelectronic carbonyl cations $[Os(CO)_5]^+$ based on the mass-spectrometric analysis, the neutral carbonyl $Re(CO)_5$ with 17 valence electrons was deduced to be the most stable species in the single-atom reaction in an inert atmosphere. The density functional theory (DFT) was also carried out, and shows that the kinetically fast formation of single-atom quantities of $Re(CO)_5$ in the gas phase which occurs thermodynamically spontaneous, i.e. exothermic.

References
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