

2 - 41 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 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, 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 $\Delta H_{\text{ads}} = -43 \pm 2 \text{ kJ/mol}$ 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 program (Fig. 1). 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.

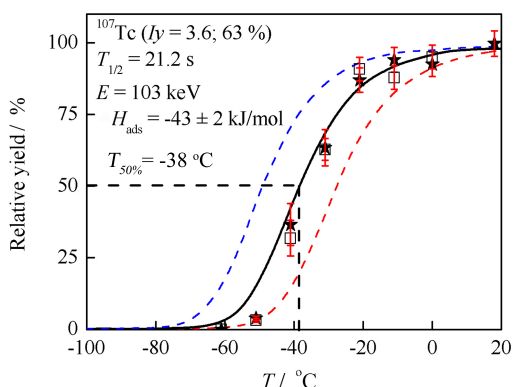


Fig. 1 (color online) Relative chemical yield and adsorption enthalpy on quartz and Teflon surfaces of short-lived Tc carbonyls were obtained.

2 - 42 Gas-phase Chemistry Study of Ruthenium and Rhodium Carbonyls

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In this work, gas-phase chemistry of ruthenium and rhodium was studied using online isothermal chromatography apparatus at low temperature coupled to the ^{252}Cf SF source^[1] at IMP (Fig.1). Apart from the interference of precursor effect^[2], $^{109-110}\text{Ru}$ and $^{111-112}\text{Rh}$ were chosen as the representative isotopes for the two elements respectively. An improved Monte Carlo molecular simulation program was compiled according to the gas-phase chemistry model^[3], and was used in the optimization of the experimental condition. The adsorption enthalpies of pentacarbonyl ruthenium and tetracarbonyl rhodium on the FEP surface were obtained.

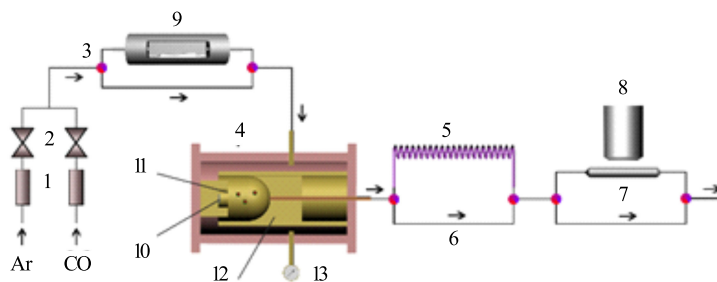


Fig. 1 (color online) Schematic of the experiment setup used in this work.

1: Mass flow controller; 2: Two-way valve; 3: Three-way valve; 4: The Chamber; 5: Isothermal chromatography column at low temperature; 6: Bypass; 7: Active charcoal filter; 8: HPGe- γ detector; 9: KCl aerosol generator; 10: The Fission source containing $0.2 \mu\text{g}$ ^{252}Cf ; 11: A $5 \mu\text{m}$ -thick polyester film covering; 12: The Cylinder Teflon collector; 13: the Pressure gauge.

According to the result of Monte Carlo simulation, carbonyl ruthenium requires greater length and radius of the IC column than carbonyl molybdenum to keep the molecules inside the tube within finite interval under the

limitation of the devices. Meanwhile, the breakthrough curves reveal that the chemical yields decrease below -60 °C, and reaches the limit of detection at -75 °C. $T_{50\%}$ appears around -67 °C. By fitting the experimental points with the simulation curve, we obtained that the adsorption enthalpy was -33^{+1}_{-2} kJ/mol on FEP surface (Fig. 2).

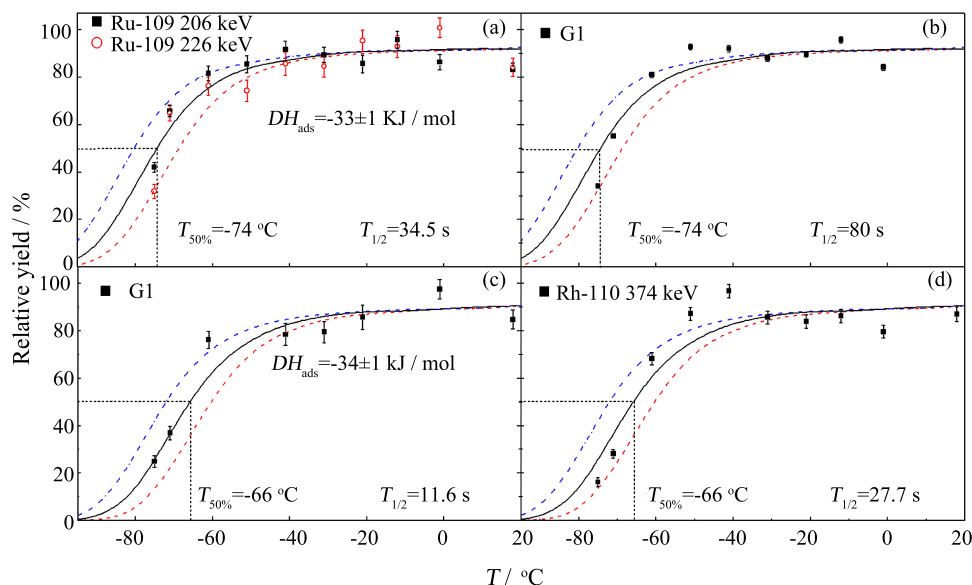


Fig. 2 (color online) Experimental data of ^{109}Ru , ^{109}Rh , ^{110}Ru , ^{110}Rh fitting with Monte Carlo simulation.

Monte Carlo simulation revealed that carbonyl rhodium has higher $T_{50\%}$ than carbonyl ruthenium at the specific breakthrough curve. The breakthrough curves fitting with the experimental data show that $T_{50\%}$ appears at -58 °C and $\Delta H_{\text{ads}} = -36^{+2}_{-1}$ kJ/mol on FEP surface (Fig. 3). As the representative isotopes, ^{111}Rh and ^{112}Rh are the key to studying gas-phase chemistry of rhodium in the experiment with ^{252}Cf .

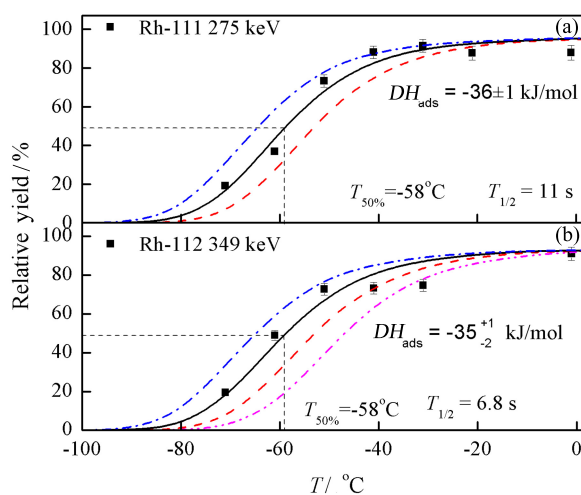


Fig. 3 (color online) Experimental data of ^{111}Rh , ^{112}Rh fitting with Monte Carlo simulation.

As an effective way of studying these metal-organic complexes, the gas-phase isothermal chromatography lays the foundation for further study on the gas-phase chemistry of superheavy elements.

References

- [1] C. E. Düllmann, B. Eichler, R. Eichler, et al., Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, 512(2003) 595.
- [2] J. Even, A. Yakushev, C. E. Düllmann, et al., Radiochimica Acta, 102(2014)1093.
- [3] I. Zvára, Methods for Studying Gaseous Compounds Springer, (2008).