Thermal stability of the group 6 hexacarbonyl complexes

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Recently, the on-line production of $Sg(CO)_6$ was achieved.[1] The Sg-CO bond in the $Sg(CO)_6$ complex was predicted to be slightly more stable than the corresponding bond in the complex of its lighter homolog $W(CO)_6$.[2] In this work, we aim to design the experimental setup to verify this prediction. Alpha-decaying isotopes ^{163}W and ^{164}W were produced in fusion-evaporation reactions $^{144}Sm(^{24}Mg,xn)^{163\text{-}164}W$ at RIKEN Linear Accelerator (RILAC). Therefore, a ^{144}Sm target was bombarded with a 0.66 μA_{part} ^{24}Mg beam, at a center-of-target energy of 136 MeV. The Gas-filled Recoil Ion Separator (GARIS) allowed for efficient separation of the desired evaporation residues from the beam and from multinucleon transfer products. The separated isotopes were thermalized in a gas mixture of CO and He 1:1 by volume. The formed $^{163\text{-}164}W(CO)_6$ complexes were transported to the decomposition setup through PFA Teflon capillaries. The decomposition setup consisted of a *decomposition column*[3], covered inside by silver foil, and a bypass column of the same size made of PFA Teflon. Because of the high inertness toward carbonyl complexes the Teflon bypass was implemented to quantify the actual production yield of the carbonyl complexes. The yields of the carbonyl complex able to pass this decomposition setup were determined by means of total trapping of the volatile complexes in the cryo online thermochromatography detector array COMPACT.[1] The primary result of a complete decomposition experiment is given in a form of a decomposition curve, which pictures the survival probability for a complex as a function of decomposition temperature. The results of the model experiments with ^{104}Mo obtained from the ^{252}Cf spontaneous fission source "Miss Piggy" at the University of Bern [3] are presented together with the current results obtained for $^{163,164}W$ in Fig. 1. The difference of 23 kJ/mol in (FBDEs) of Mo-CO (169 kJ/mol) and W-CO (192 kJ/mol) leads to a decomposition temperature shift of about 100°C. The figure suggests that the experiment can be sensitive to a small difference in FBDE i.e., 10 kJ/mol.

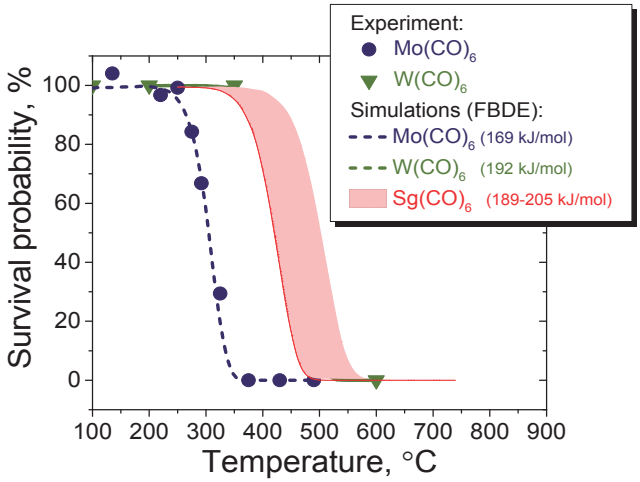

Fig. 1: $^{104}Mo(CO)_6$ and $^{163\text{-}164}W(CO)_6$ experimental decomposition curves (symbols) and simulated curves considering the relevant FBDE's (dashed lines). The predicted interval[2] for $^{265}Sg(CO)_6$ is indicated (red area).

We developed a Monte-Carlo based two-step reversible adsorption-irreversible decomposition model[3] for describing the heterogeneous decomposition process. This model successfully reproduced the experimental results for $Mo(CO)_6$ and $W(CO)_6$ (Fig. 1, dashed lines) and could be used for designing and evaluating data of the future decomposition experiments with $Sg(CO)_6$ (Fig. 1, red interval of FBDE= 197±8 kJ/mol). Thus, a complete method for the experimental verification of the prediction [2] was elaborated.

To conclude, we successfully tested a fast and efficient approach for assessing the thermal stability of group 6 carbonyl complexes. The dissociation energy of the Sg-CO bond can be therefore experimentally investigated and directly compared with the related properties of lighter homologs.

References

1) J. Even et al.: Science 345, 6203 (2014).
2) C. S. Nash: J. Am. Chem. Soc. 121, 10830 (1999).
3) I. Usoltsev: PHD Thesis Univ. Bern (2014).

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