Group VI Metal Hexacarbonyl Complexes: production, decomposition, modeling

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(*on behalf of the Carbonyl collaboration*)

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Carbonyl collaboration

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Introduction

Motivation

- The hexacarbonyl complex of Sg was synthesized.*
- It was predicted to be slightly more stable then the complex of its lighter homologue – $W(CO)_6$.**
- In our work we aimed at designing an experimental setup for testing this prediction.

*J. Even, et al., Science 2014, 345, 1491.

**C.S. Nash, B.E. Bursten, J. Am. Chem. Soc. 1999, 121, 10830.

Introduction

Stability...

... of transition metal carbonyl complexes can be expressed in terms of M-CO first bond dissociation energies (FBDE)*.

$M(CO)_6$	Calculated, kJ/mol	Experiment, kJ/mol
$Mo(CO)_6$	171	169
$W(CO)_6$	198	192
$Sg(CO)_6$	205/212	not available

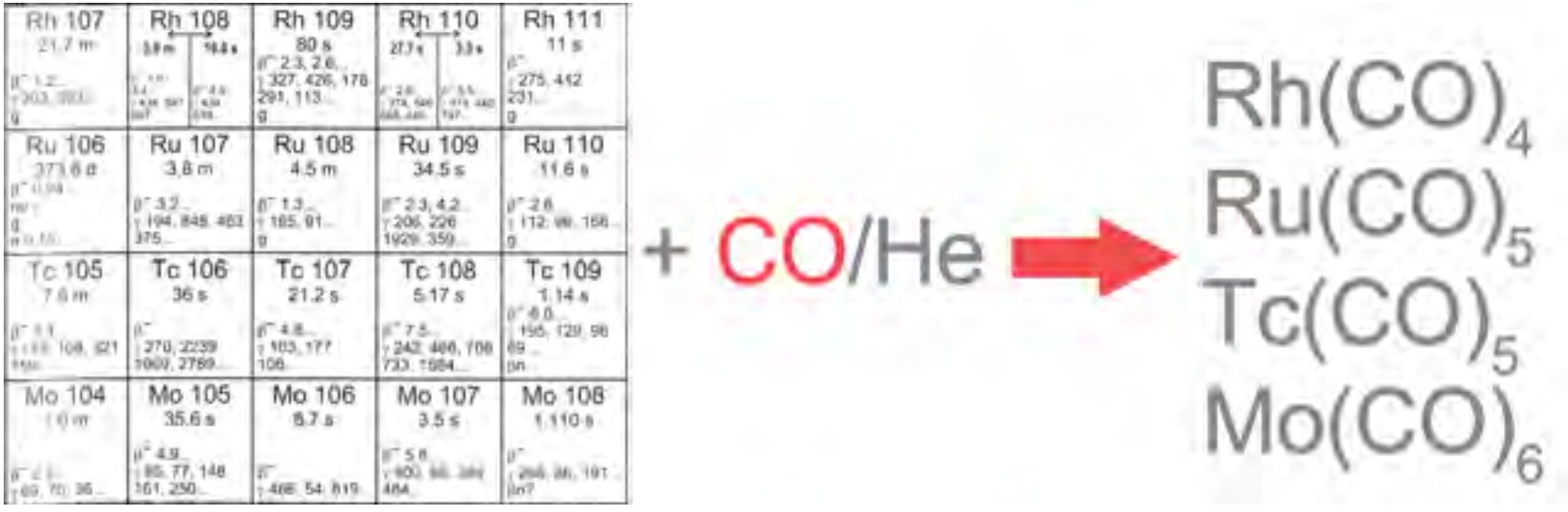
FBDE in turn determines the decomposition behavior of the given complex. **Thus by investigating its decomposition, stability of $Sg(CO)_6$ can be addressed.**

*C.S. Nash, B.E. Bursten, J. Am. Chem. Soc. 1999, 121, 10830.

Experimental

'Ms.Piggy'...

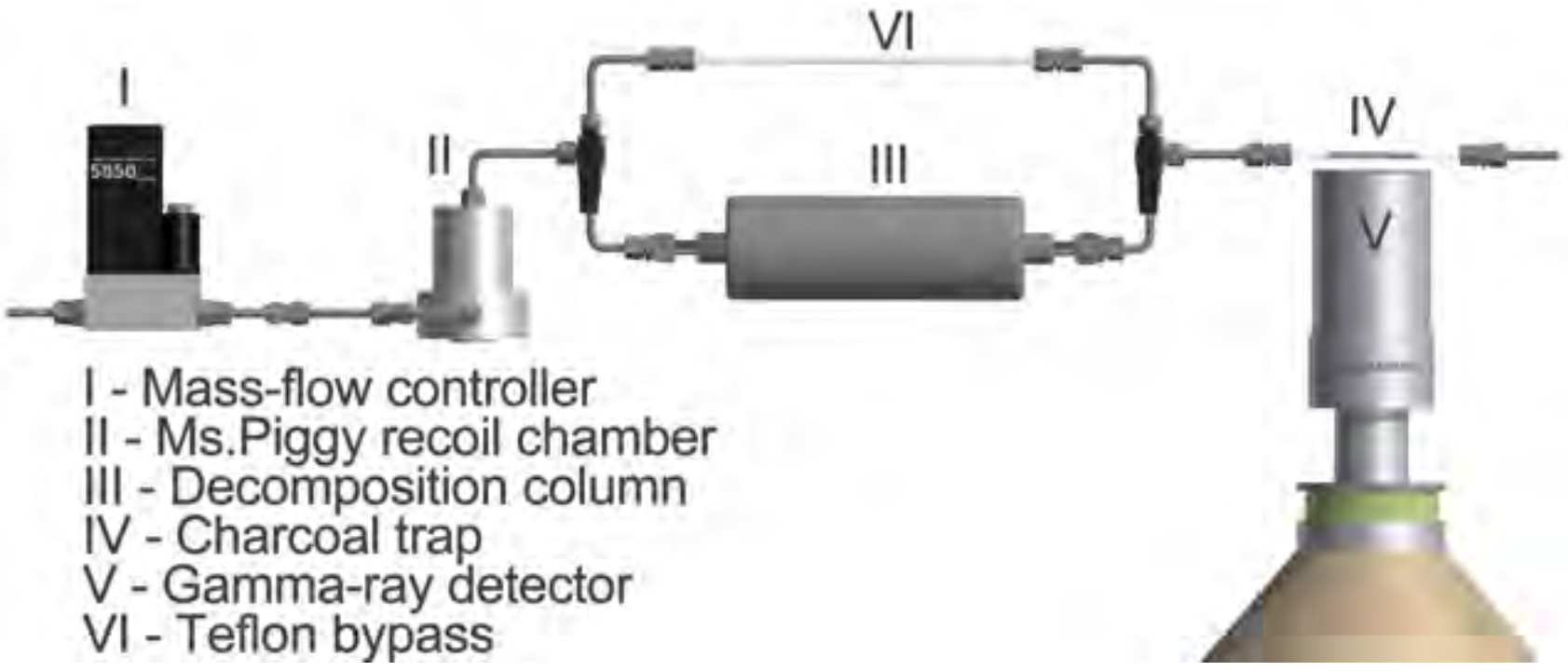
... ^{252}Cf spontaneous fission fragment source, located at University of Bern, allows for production:



Experimental

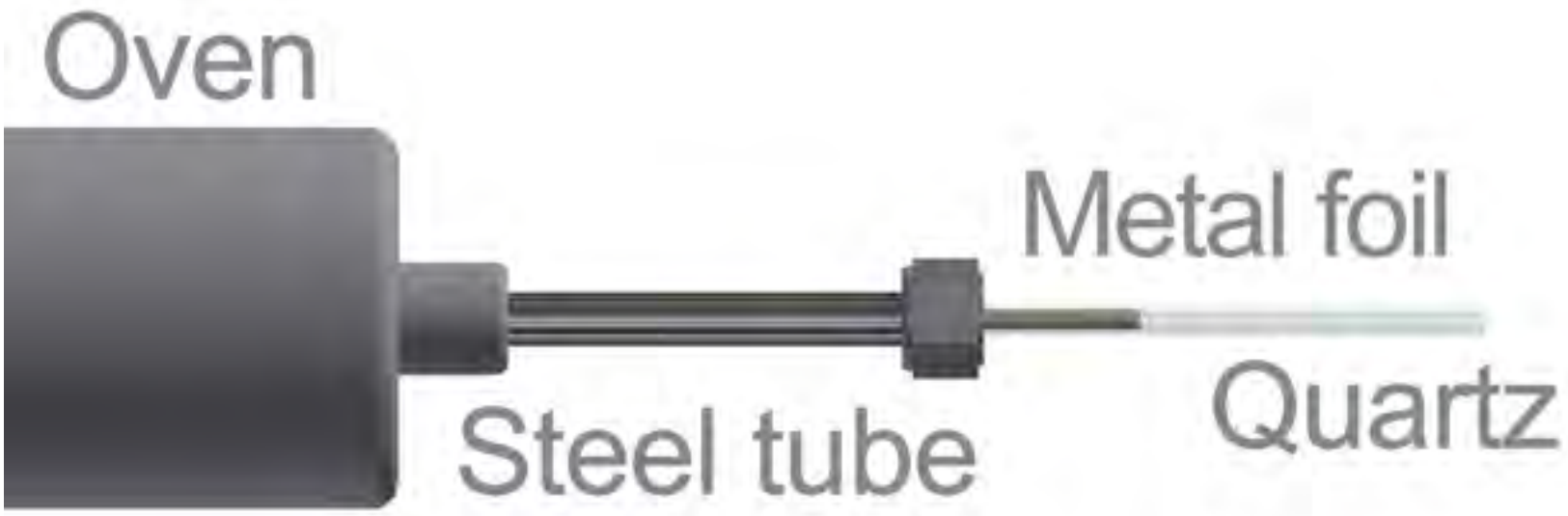
Setup

The following equipment was implemented at 'Ms.Piggy':



Experimental

Decomposition column



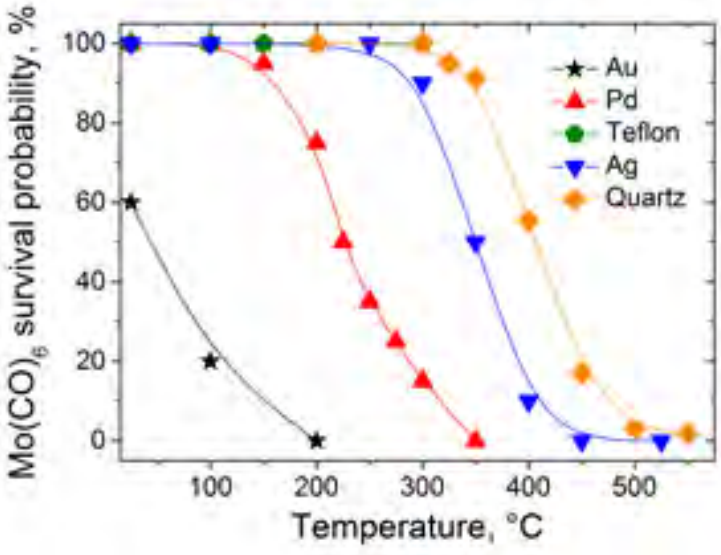
Decomposition process

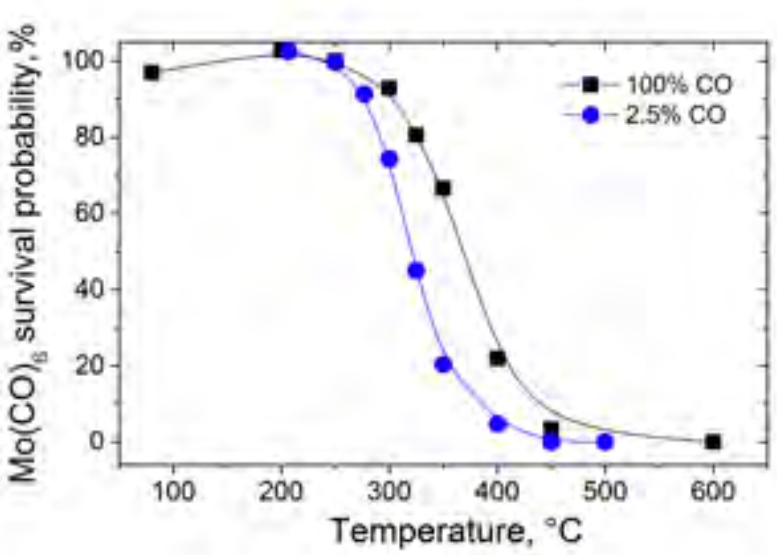
$$Mo(CO)_6 \longrightarrow Mo + 6\,CO$$

Results

Decomposition curves...

...are strongly influenced by **the CO content**, **decomposition surface** and the gas flow rate.

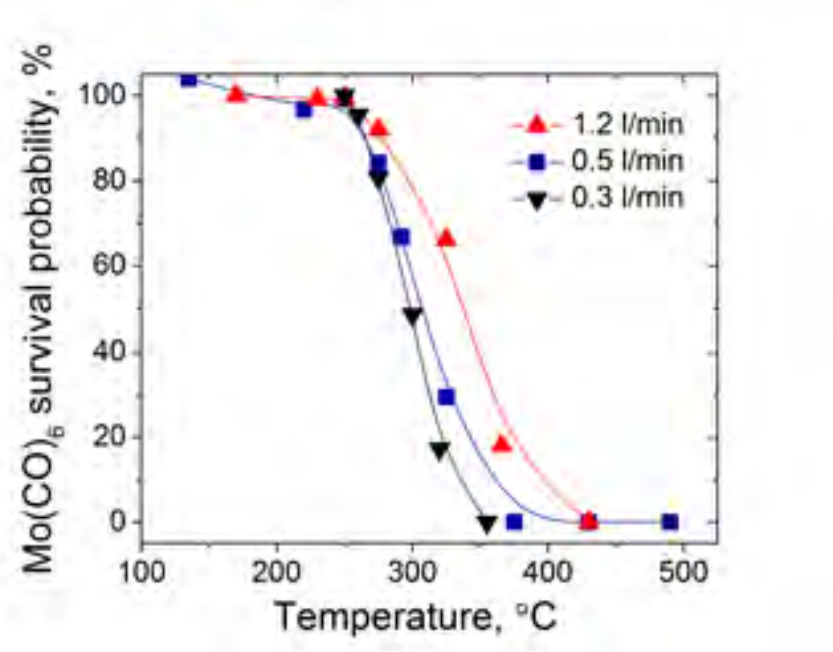




Results

Decomposition curves...

...are strongly influenced by the CO content, decomposition surface and **the gas flow rate**.



Results

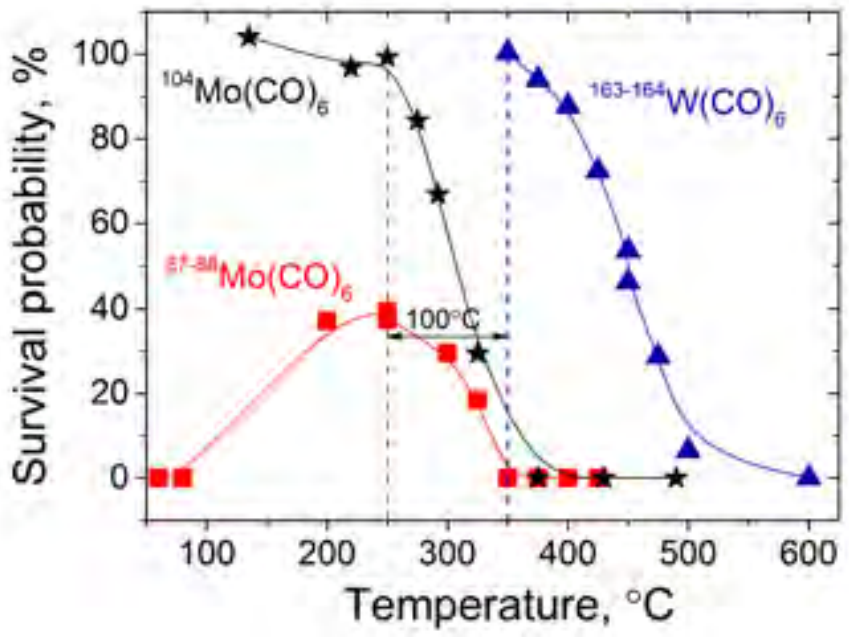
$Mo(CO)_6$ and $W(CO)_6$

Hexacarbonyl complexes were produced in the following fusion-evaporation reactions at GARIS (RIKEN, Japan) and detected with COMPACT:

$^{nat}Zn(^{24}Mg,xn)^{87-88}Mo$

$^{144}Sm(^{24}Mg,xn)^{163-164}W$

Significant difference in decomposition behavior was observed:



Analysis

Simulation approach

Implementation of the I.Zvara's Monte-Carlo model of gas adsorption chromatography, coupled to Monte-Carlo simulation of a single-step decomposition reaction, with the following assumptions:

Decomposition...

- ...happens only on the surface.
- ...is irreversible.
- ...is a first order kinetics process.
- ...activation enthalpy (ΔH^{+}) = FBDE.

Analysis

$$Mo(CO)_6 \rightleftharpoons Mo(CO)_{6(ads)} \longrightarrow Mo(CO)_{6\text{-}x} + xCO$$

Simulation

- If the reaction time (t_r) is shorter than the adsorption time (t_{ads}), decomposition happens.
- t_{ads} is given by I.Zvara's model:

$$t_{ads} = \frac{1}{\nu_\beta} \exp \frac{-\Delta H_{ads}}{RT}$$

- t_r is calculated from Eyring equation:

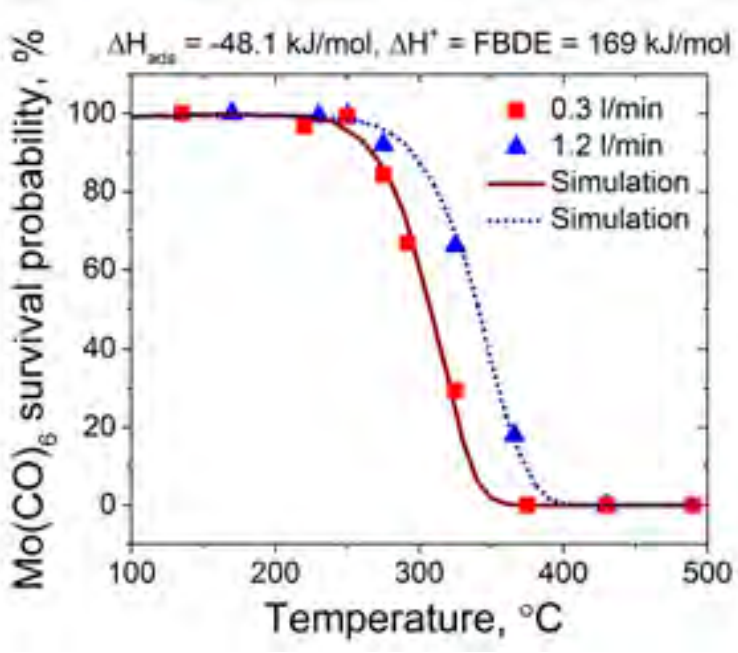
$$k = \frac{k_b T}{h} \exp \frac{\Delta S^+}{R} \exp \frac{-\Delta H^+}{RT}$$

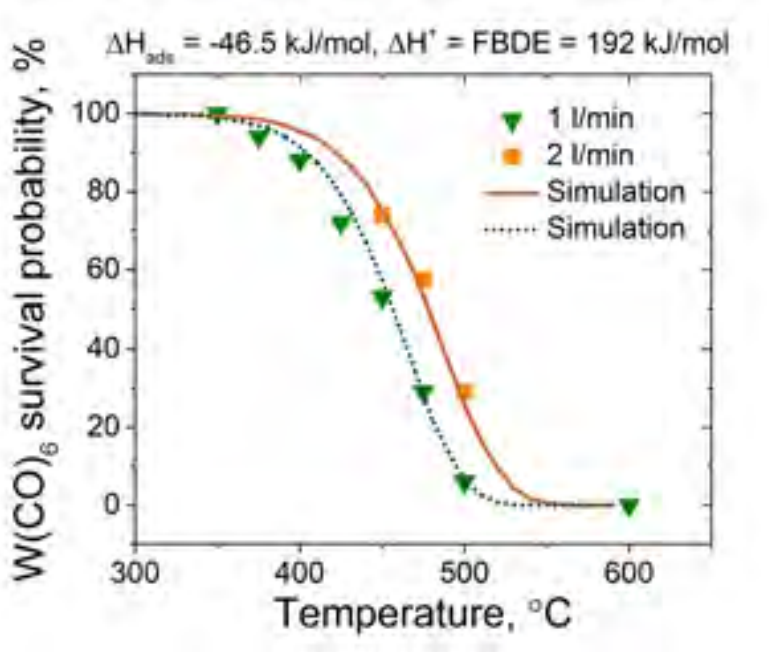
$$t_r = \frac{1}{k}$$

Results

By using the least squares fitting of the experimental results with the simulated curves,
ΔS^{+} was found to be 105 J/K/mol.

Results for Mo and W carbonyls

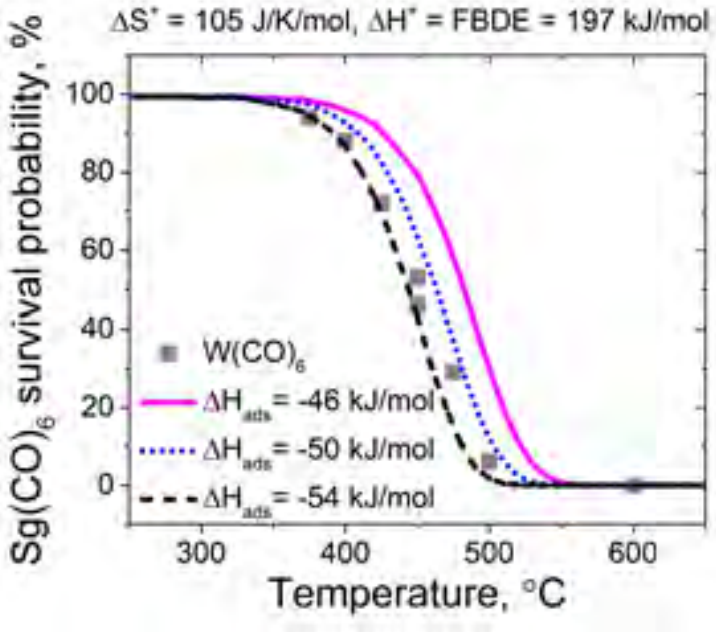


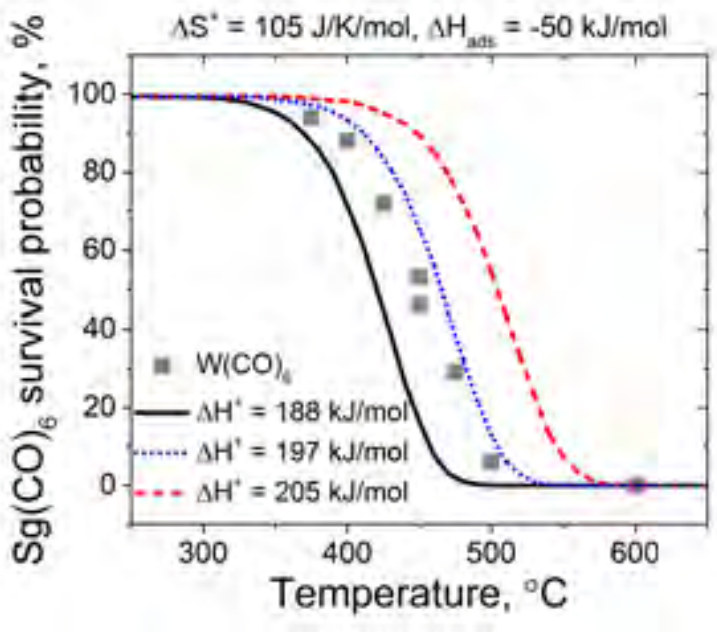


Prediction

Available theoretical and experimental data were used for simulating the decomposition behavior of Sg carbonyl.

Results for $Sg(CO)_6$





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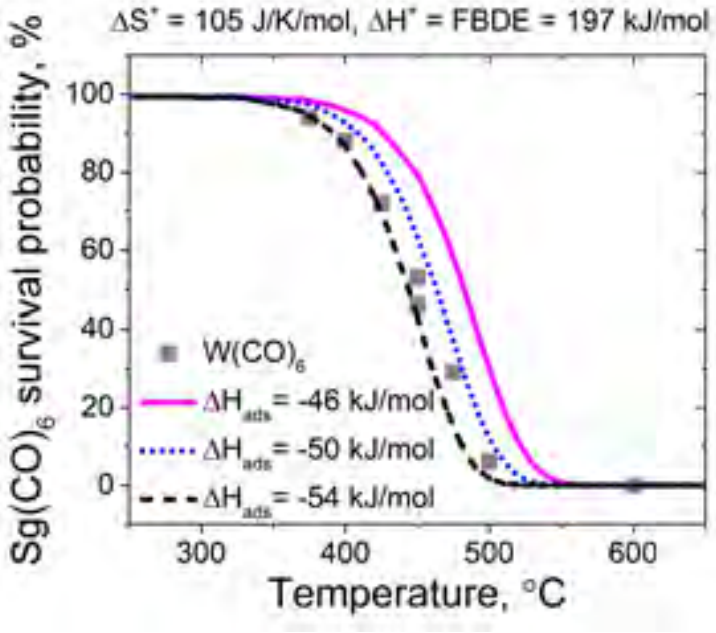
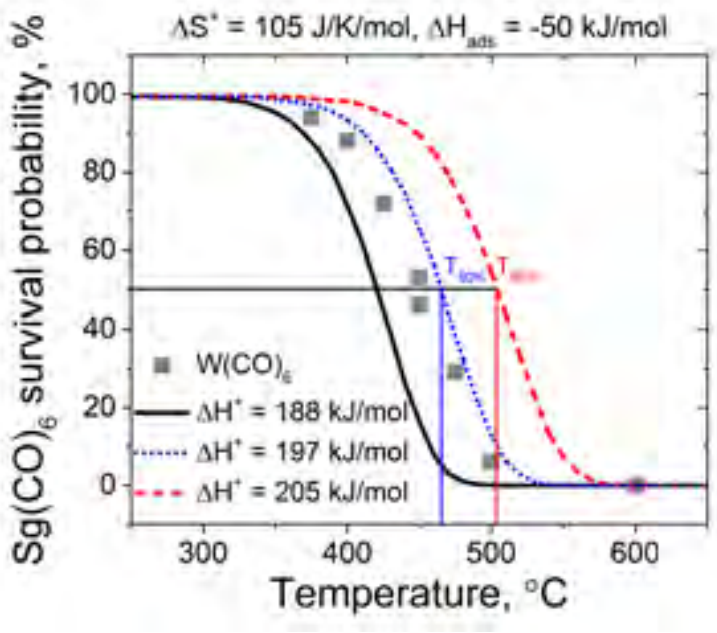
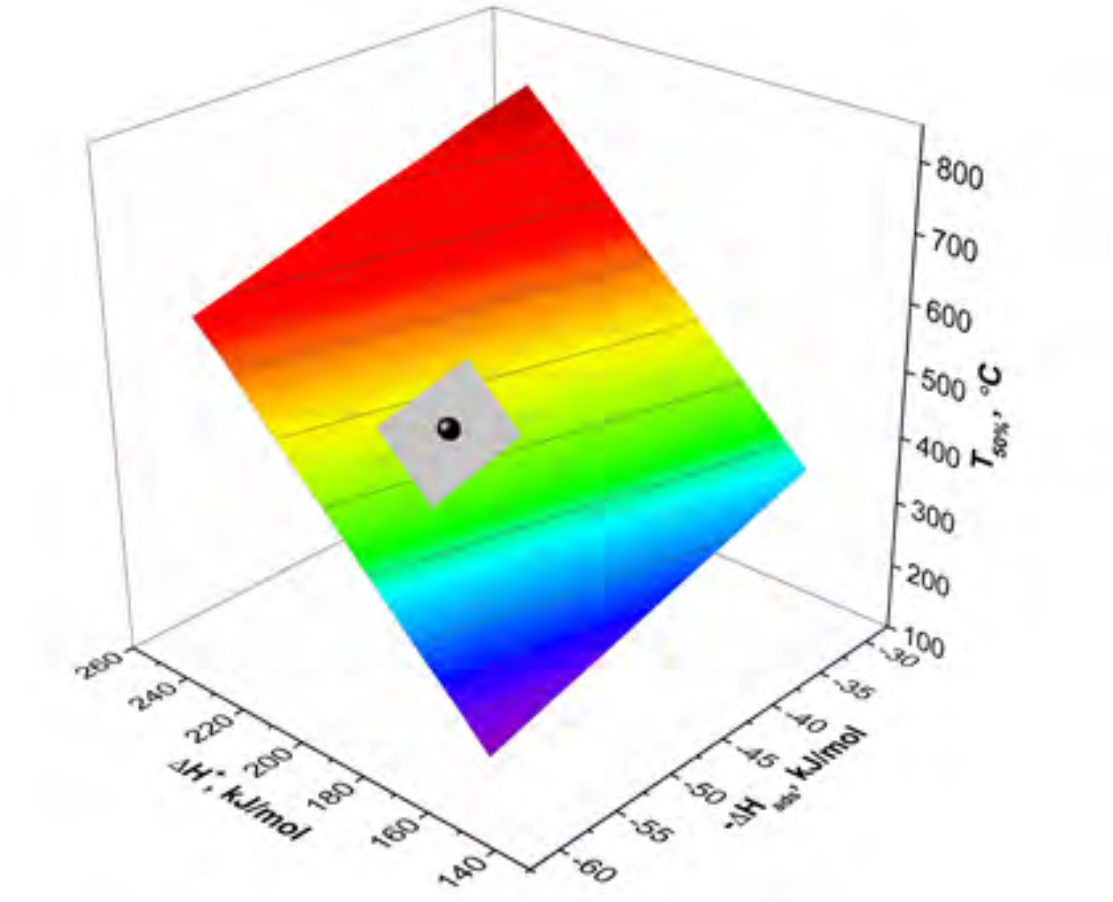




Prediction

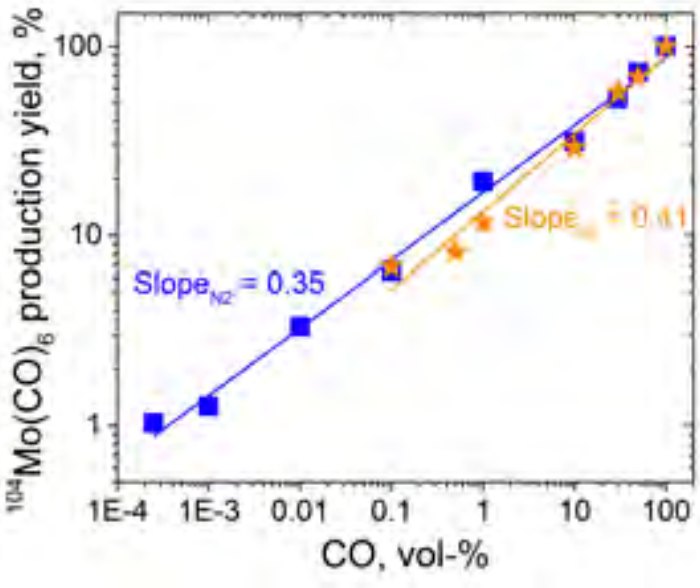
For a given ΔS^{+} of 105 J/K/mol.

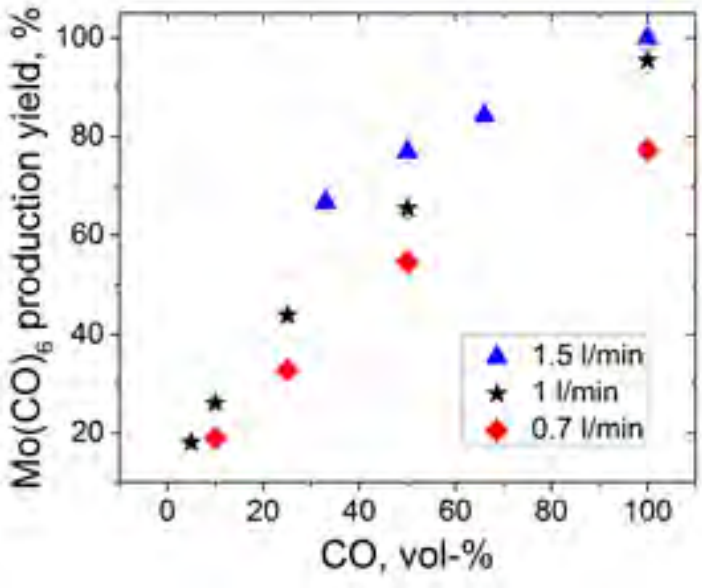


Results

$Mo(CO)_6$ production yield...

...is strongly influenced by the **CO concentration** and by the gas flow rate.





Results

$Mo(CO)_6$ production yield...

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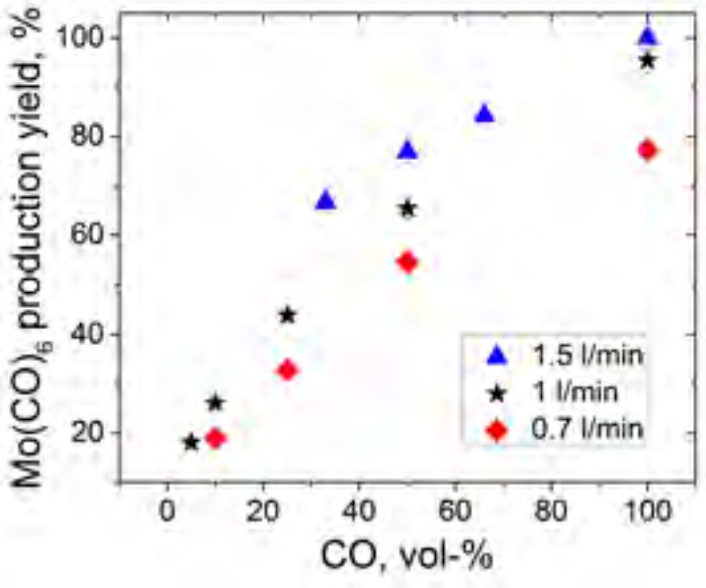
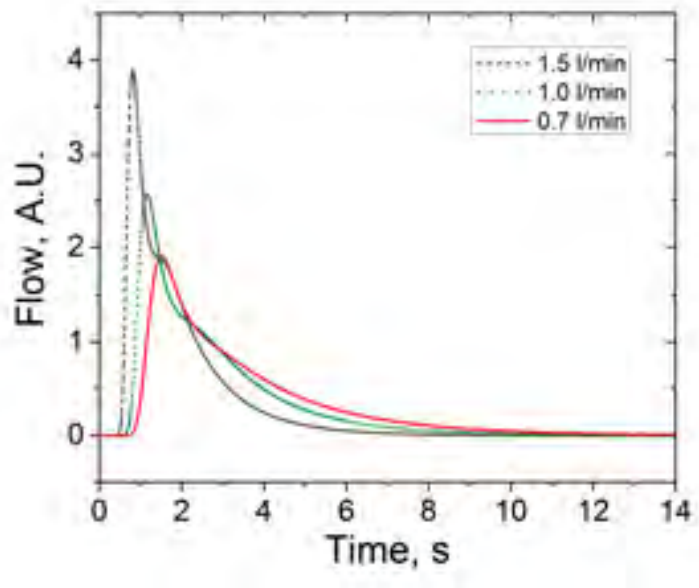




Results

Transport time

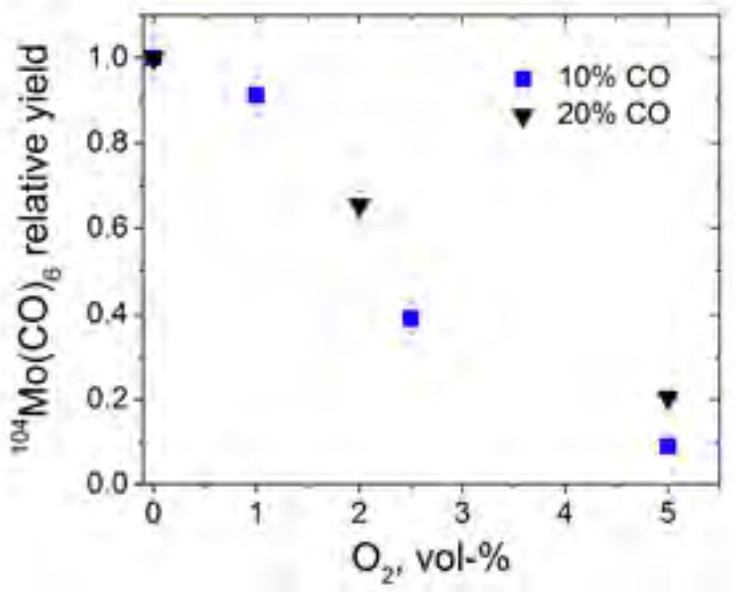
Retention time of $Sg(CO)_6$ in a 10 m Teflon capillary is strongly influenced by the temperature and by the gas flow rate.

$-\Delta H_{ads}$, kJ/mol	T,°C	P, bar	Gas flow, l/min	Retention time, s
54	25	0.7	1.0	70
54	25	0.7	2.0	35
54	25	0.5	2.0	25
54	50	0.5	2.0	5
54	100	0.5	2.0	<1
50	25	0.5	2.0	5
50	15	0.5	2.0	10

Results

Detrimental effect of oxygen

Few percent of O_2 in the carrier gas bring the production yield of $Mo(CO)_6$ to zero. This effect is expected to be even more pronounced with Sg.



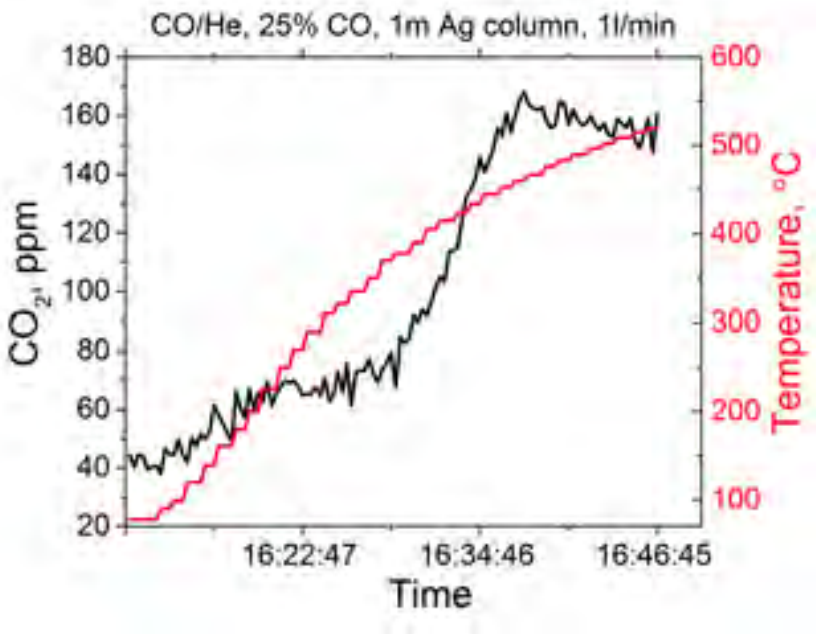
Compound	ΔH°, kJ/mol
MoO_2	-589
MoO_3	-745
WO_2	-590
WO_3	-843
*SgO_3	-874, -951

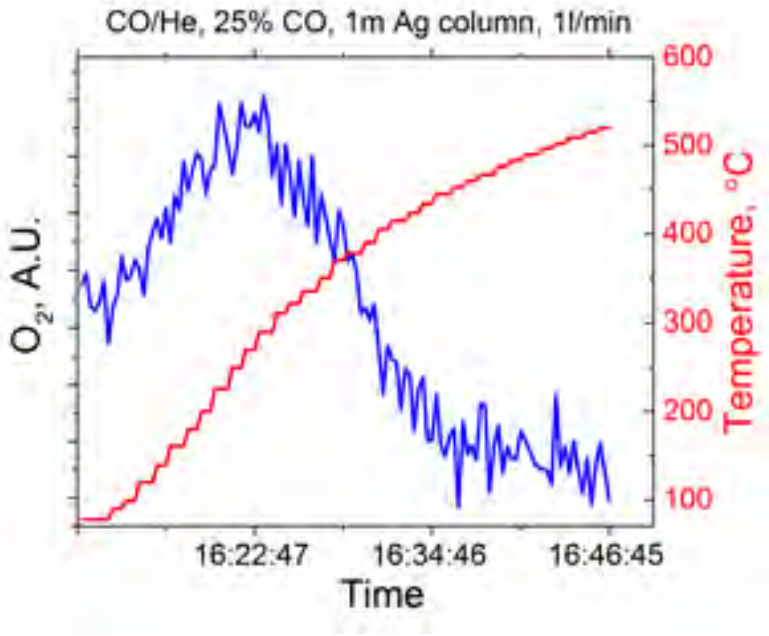
*B. Eichler, A. Türler, and H. Gäggeler, J. Phys. Chem. A, vol. 103, pp. 9296–9306, 1999.

Results

CO_2

Oxydation of CO to CO_2 in the *decomposition column* is inevitable if oxygen is present in the carrier gas.





Conclusions

- We suggested a fast and efficient approach for testing the stability of the group VI carbonyl complexes.
- Experimental results were successfully reproduced by the model both for $Mo(CO)_6$ and $W(CO)_6$.
- Suggested simulation can be used for designing and evaluating data of the future decomposition experiments with $Sg(CO)_6$.
- In order to maximize the yield of the Sg carbonyl complex CO concentration and the carrier gas flow rate must be kept as high as possible.
- Oxygen must be constantly monitored and removed from the system efficiently.
- The transport efficiency could be improved drastically by heating up a capillary between RTC and detection unit.

Acknowledgements

We thank the ion source and accelerator staff at the RIKEN Nishina Center for Accelerator-Based Science for providing intense and stable ion beams. The present work is partially supported by the Reimei Research Program (Japan Atomic Energy Agency), the German Federal Ministry for Education and Research contract No. 06MZ7164, the Helmholtz association contract-No.VH-NG-723, the Swiss National Science Foundation contract No. 200020-144511, and the Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, Heavy Element Chemistry Program of the U.S. Department of Energy at Lawrence Berkeley National Laboratory under Contract No. DE-AC02-05CH11231, and the National Natural Science Foundation of China (Grant No. 11079006).