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Decomposition studies of group 6 hexacarbonyl complexes. Part 2: Modelling of the decomposition process

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Abstract: The decomposition behavior of group 6 metal hexacarbonyl complexes ($M(CO)_6$) in a tubular flow reactor is simulated. A microscopic Monte-Carlo based model is presented for assessing the first bond dissociation enthalpy of $M(CO)_6$ complexes. The suggested approach superimposes a microscopic model of gas adsorption chromatography with a first-order heterogeneous decomposition model. The experimental data on the decomposition of $Mo(CO)_6$ and $W(CO)_6$ are successfully simulated by introducing available thermodynamic data. Thermodynamic data predicted by relativistic density functional theory is used in our model to deduce the most probable experimental behavior of the corresponding Sg carbonyl complex. Thus, the design of a chemical experiment with $Sg(CO)_6$ is suggested, which is sensitive to benchmark our theoretical understanding of the bond stability in carbonyl compounds of the heaviest elements.

Keywords: Transition metals, carbonyl complexes, transactinides, group 6, seaborgium, thermal stability.

1 Introduction

Recently, the synthesis of the seaborgium hexacarbonyl complex $Sg(CO)_6$ has been reported [1]. Thus, for the first time chemistry acquired a Sg compound in its zeroth oxidation state. The enthalpy of adsorption for $Sg(CO)_6$ on a quartz surface was found to be in a good agreement with the prediction from [2], which indirectly verified the presumed chemical state.

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Earlier, $Sg(CO)_6$ was predicted to be slightly more stable than the complex of its lighter homologue $W(CO)_6$ [3]. The first bond dissociation enthalpy (*FBDE*) was suggested as 204 ± 8 kJ/mol, which is about 12 kJ/mol higher compared to the FBDE of $W(CO)_6$ [4]. The performed calculations included relativistic effects [5], which play a significant role in case of the superheavy elements (SHE) [6–8] and have a profound influence on their chemical properties. In the relativistic scenario '*direct relativistic effects*' lead to contraction and stronger binding for the s and $p_{1/2}$ orbitals. This in turn leads to the increased shielding of the nucleus and to a subsequent expansion of the orbitals with higher angular momentum (d and $p_{3/2}$), a consequence known as the '*indirect relativistic effect*'. From the theoretical description of the binding conditions in carbonyl complexes [9], the indirect relativistic effects promote both the σ-donation form CO into the molecular e_g orbital and the contribution of the π-backbonding, involving the t_{2g} molecular orbitals. The latter effect strengthens the metal-carbon bond and accounts for the predicted trend of increasing stability of hexacarbonyls along the group 6. Despite controversial discussions in [10], a later analysis of the binding in $W(CO)_6$ confirmed that the π-backbonding accounts for about 60% of the orbital-driven binding, whereas the sum of sigma donation accounts for 40% of which again 80% are attributed to the sigma donation into the d_z orbital (e_g molecular orbital) [11, 12].

The influence of the principles of relativity on the chemical behavior of element Sg has recently observed a revival of interest [13, 14]. Particularly, in [13] a class of cage-compounds of group 6 elements with gold is discussed where the group 6 elements are in zeroth oxidation state leading to an 18 electron system similar to the hexacarbonyl complex. The calculated binding energies in the M-Au cluster revealed small differences along the group 6 following the order $Mo \leq W > Sg$. The effective atomic radii of the central transition metal atoms, connected to the electron density distributions of the s and d orbitals, are determining the binding in such compounds [13]. The radial expansion of the d-orbitals is predicted to slightly increase with the atomic number among these elements [14]. Remarkably, strong relativistic effects point to a Sg(*7s*) valence orbital level, energetically shifted below the Sg(*6d*) level [13] which is likely influencing the chemical binding in the hexacarbonyl complex $Sg(CO)_6$, too.

Our work focuses on the thermal decomposition of hexacarbonyl complexes of group 6 elements in the periodic table, Mo, W, and Sg. Particularly, we aim at the determination of the corresponding *FDBE*'s, which represent a measure for the bond stability within these complex molecules. Therefore, an adequate model for deducing the desired thermochemical property from the experimental decomposition data is developed here.

The observed production rate of one to three $Sg(CO)_6$ molecules per day [1] is considered to be sufficient for setting up a corresponding thermal stability experiment with Sg. Such a challenging endeavor, however, requires a careful design of the experimental setup and an appropriate strategy for carrying out the decomposition tests. The predictive power of the model is used to suggest possible strategies for a one-molecule-at-a-day experiment with Sg.

2 Implementation of the decomposition model

The metal-CO bond breakup in a carbonyl complex might occur both, homogeneously in the gas phase and heterogeneously at a phase boundary, see e. g. [4, 15]. The decomposition of a carbonyl complex, adsorbed on a surface, which is not covered by adsorbed CO, leads to the subsequent interaction between the central atom and the phase boundary material [16, 17]. The enthalpy of adsorption (ΔH_{ads}) of the metal on the surface quantifies the strength of this interaction. According to the Eichler–Miedema model [18], strong interaction is expected for elemental Mo and W on every transition metal surface with $-\Delta H_{ads} \geq 630$ kJ/mol. Therefore, we consider the heterogeneous decomposition process on a clean metallic surface to be irreversible as suggested in [17]. In contrast, the back reaction is assumed to be feasible if the M–CO bond breaks up in the gas phase, since there are no other reactions interfering with the dissociation/association equilibrium (Equation 1).

$$Mo(CO)_6 \leftrightarrow Mo(CO)_5 + CO \quad (1)$$

By lowering the CO content in the carrier gas, the equilibrium (Equation 1) shifts to the right, favoring the products. Since the maximization of the production yield is critical for experiments with superheavy elements, the CO content in the carrier gas must be kept high [20, 21], which shifts the equilibrium in the gas phase towards the reactants. The amount of homogeneous decomposition was shown experimentally to be negligible at high CO concentrations [19, 22]. Therefore, our idealized decomposition model includes only the heterogeneous reaction, simulated as a two-step process: reversible adsorption (Equation 2) is eventually followed by irreversible decomposition (Equation 3).

$$Mo(CO)_{6(g)} \leftrightarrow Mo(CO)_{6(ads)} \quad (2)$$

$$Mo(CO)_{6(ads)} \rightarrow Mo_{(ads)} + 6CO_{(g)} \quad (3)$$

The activation energy of the M–CO bond breakup on a nickel surface is found in [16] as 3–4 times lower compared to the dissociation in the gas phase, where it equals the *FBDE* [4]. The reduced activation barrier is attributed to the strong adsorption of CO and of the central atom on the Ni surface [16]. Such effects can be minimized by choosing silver as a surface for the decomposition studies [22]. Silver is fairly inert towards CO: $\Delta H_{ads}(CO) = -27$ kJ/mol [23, 24]. Furthermore, Mo and W have the weakest affinity to Ag compared to other transition metal surfaces [17].

Monte-Carlo modelling is successfully used in the data evaluation of gas phase adsorption experiments with SHE and their homologues, i. e., for assessing the adsorption behavior of the investigated compounds on a given stationary surface [1, 20, 25, 26]. This adsorption model was suggested in [27] and is described in detail in [8, 28].

The decomposition column, used for the stability studies, is described in [22], and represents a tubular flow reactor. The walls of the reactor can be viewed as a stationary phase for a gas-solid adsorption chromatography. This consideration enabled an estimation of the adsorption time (t_a) for the investigated carbonyl complex, taking into account its ΔH_{ads} on a specific stationary surface. In order to simulate the decomposition behavior in the laminar flow reactor, the gas-phase chromatography model was complemented by an idealized kinetic model, under the following assumptions:

1. The first order decomposition reaction happens only on the phase boundary and is irreversible.
2. The activation energy determining the decomposition reaction is directly connected to the corresponding *FBDE* (Figure 1).

It is assumed that the decomposition reaction is taking place only if the residence time (t_a) between two jumps (Equation 4) is longer than the reaction time (t_r) needed for metal-carbon bond to break (Equation 5). The total time in the adsorbed state is distributed logarithmically and is

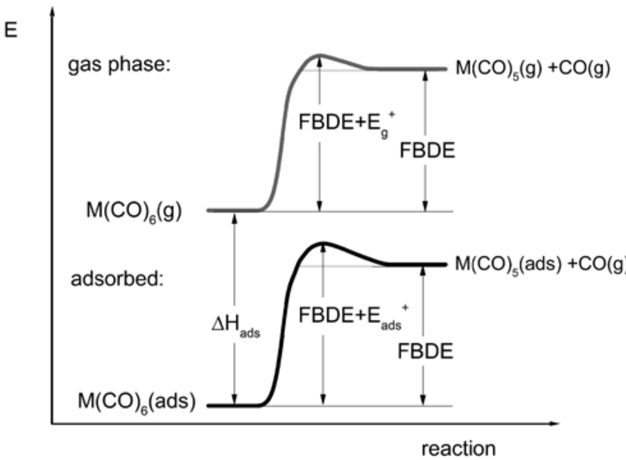

Figure 1: Energy diagram for the first bond dissociation of group 6 hexa carbonyl $M(CO)_6$ in the gas phase (grey line) and in the adsorbed state (black line). Our assumptions in the kinetic model are that the decomposition happens irreversibly in the adsorbed state and that ΔE^+_{ads} is equal for all hexacarbonyls of group 6. Therefore, the decomposition kinetics is assumed mainly being driven by the *FBDE* in both, gas phase [4] and adsorbed state.

computed as follows from [8]:

$$t_a = -N_m \cdot \frac{1}{\nu_b} \cdot e^{-\frac{\Delta H_{ads}}{R \cdot T}} \cdot \ln(1 - random) \qquad (4)$$

Where N_m is the mean number of wall collisions between two jumps; ν_b is the surface phonon vibrational frequency of Ag (4.65×10^{12}) [1/s]; R is the ideal gas constant [J/mol/K]; ΔH_{ads} is the standard adsorption enthalpy of a hexacarbonyl complex on a specific surface [J/mol]; T is the temperature [K]; and *random* is a randomly selected value between 0 and 0.999999.

The decomposition reaction is assumed to follow first-order kinetics. The reaction time (t_r) is logarithmically distributed (Equation 5), similarly to the lifetime of the central atom [8, 19]. The decomposition reaction time (t_r) was derived through the Eyring equation [29, 30] and was implemented in the model as follows:

$$t_r = -\frac{1}{k} \cdot \ln(1 - random), \qquad (5)$$

with

$$k = \frac{k_B \cdot T}{h} \cdot x_p \cdot \exp\left(\frac{\Delta S^+}{R}\right) \cdot \exp\left(-\frac{\Delta E^+_{ads}}{R \cdot T}\right) \cdot \exp\left(-\frac{FBDE}{R \cdot T}\right) \qquad (6)$$

Where k is the decomposition rate constant [1/s]; k_B is the Boltzmann constant [J/K]; h is the Plank constant [J · s]; ΔS^+ is the activation entropy [J/K/mol], x_p is an experimental setup parameter comprising, e. g., the ratio of the phases, depending on the surface roughness of the stationary phase and the open volume of the column [31]; ΔE^+_{ads} is an unknown part of the activation energy of the heterogeneous decomposition process [J/mol] (Figure 1) and *FBDE* is the first carbonyl bond dissociation enthalpy of the corresponding carbonyl species, taken from [4] [J/mol].

The single contributions of the activation entropy S^+, the exact ratio of the phases x_p, and ΔE^+_{ads} are either inaccessible experimentally or just the same if using the same experimental setup. Therefore, we combine this unknown part into a temperature independent and dimensionless preexponential factor A (Equation 6), keeping only the important temperature dependent term, since our decomposition experiments are performed under non-ideal isothermal conditions:

$$A = x_p \cdot \exp\left(\frac{\Delta S^+}{R}\right) \cdot \exp\left(-\frac{\Delta E^+_{ads}}{R \cdot T}\right) \qquad (7)$$

Equations (6) and (7) lead to the following Arrhenius-like decomposition rate equation used for the calculations:

$$k = \frac{1}{t_r} = \frac{k_B \cdot T}{h} \cdot A \cdot \exp\left(-\frac{FBDE}{R \cdot T}\right) \qquad (8)$$

Thus, the model describes an adsorption chromatographic transport of volatile molecules along the tubular stationary surface. Upon each adsorption of a carbonyl complex a decision is being made:

- if $t_a \le t_r$, then the hexacarbonyl complex desorbs form the surface without decomposition (Equation 2);
- if $t_a > t_r$, then an irreversible decomposition reaction is assumed (Equation 3).

The experimental approach, suggested in the part I of this work [22] and modeled here, is not applicable to macro amounts of the carbonyl complex in question. Only carrier free quantities ensure a clean silver surface. Decomposition curves, simulated here, were obtained with ultra-trace amounts of radioactive isotopes of Mo and W. Therefore, the radioactive decay of the central atom was included in the Monte-Carlo model [8, 19].

The presented model requires the adsorption data for carbonyl complexes on a silver surface in order to estimate the adsorption retention (Equation 4). No significant difference was observed in the adsorption behavior of OsO_4 on quartz and gold surfaces [32], concluding a van der Waals interaction. The similar adsorption enthalpy values for $Os(CO)_5$ and OsO_4 indicate a physisorption interaction between the carbonyl complexes and

Table 1: Adsorption enthalpies on a SiO_2 surface (ΔH_{ads}) and the first bond dissociation enthalpy (*FBDE*) of group 6 carbonyl complexes.

	$-\Delta H_{ads}$, kJ/mol	FBDE, kJ/mol
$Mo(CO)_6$	48.1 ± 2.5 [20]	169 [4]
	50 ± 2 [1]	169 [11]
$W(CO)_6$	46.5 ± 2.5 [20]	192 [4]
	49 ± 2 [1]	182 [9]
		200 [11]
$Sg(CO)_6$	50 ± 4 [1]	204 ± 8 [3]

a SiO_2 surface [21]. Furthermore, very similar adsorption enthalpies have been observed for the carbonyl species $W(CO)_6$ and $Os(CO)_5$ on fused silica and gold [21]. Finally, $^{104}Mo(CO)_6$ was observed to be inert towards silver, similarly to quartz and Teflon® [22]. Therefore, the adsorption enthalpy values for group 6 hexacarbonyl complexes on SiO_2 surface were assumed to be equal to the adsorption enthalpies on silver in the presented simulation model. The corresponding data are compiled in the Table 1.

The dimensionless preexponential factor A remains the only unknown parameter. It is determined through a least-square fitting procedure of the experimental results with $Mo(CO)_6$, using the introduced Monte-Carlo model. Therefore, the *FBDE* for $Mo(CO)_6$ from [4] and the adsorption enthalpies of $Mo(CO)_6$ on quartz ([1, 20], Table 1) were used. The resulting preexponential factor is assumed to be identical for all group 6 carbonyls decomposing under similar experimental conditions on silver in our laminar flow reactor.

3 Results and discussion

The experimental data on the stability is given in the form of decomposition curves [22]. These reflect the survival probability of a complex in the decomposition column at a given temperature. The real temperature profile inside the furnace is not ideally isothermal. It deviates at the edges of the furnace from the temperatures in the middle. Therefore, the real temperature profiles along the decomposition column were taken into account while modelling the decomposition behavior, representing a clear advantage of the microscopic Monte-Carlo approach. The temperature given on the abscissa in the Figures 2–5 refers to the plateau temperature in the middle of the furnace [22]. At the applied experimental conditions, i. e. 1.2 l/min gas flow rate, 1 m long silver column with 4 mm inner diameter, the carbonyl complexes can be effectively decomposed (Figure 2). The decomposition curve for $Mo(CO)_6$ at 0.3 l/min is shifted by 50 °C to lower temperatures due to the overall higher number of surface encounters (Equation 4). But the decomposition starts at the same temperature (275 °C), supporting the assumption of a predominantly heterogeneous process.

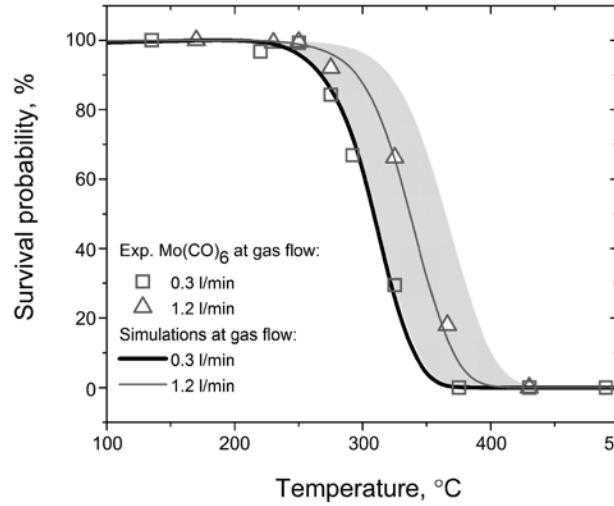

Figure 2: Experimental decomposition curves of $Mo(CO)_6$ at different gas flow rates (symbols) together with simulated decomposition curves (lines) using average $-\Delta H_{ads} = 48.8$ kJ/mol, *FBDE* = 169 kJ/mol and $A = 8.6 \cdot 10^5$. The shaded area shows the response of the model to a A within its 68% c. i. and $-\Delta H_{ads}$ within ± 4 kJ/mol at a gas flow of 1.2 l/min.

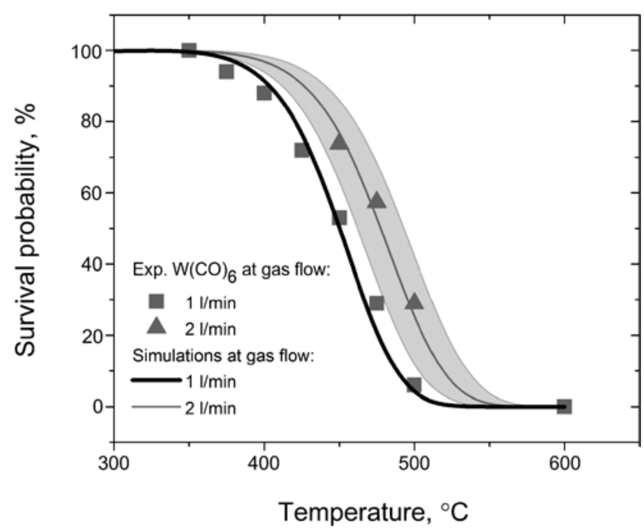

Figure 3: Experimental decomposition curves of the $W(CO)_6$ at different gas flow rates (symbols) together with simulated decomposition curves (lines) using $-\Delta H_{ads} = 47.5$ kJ/mol, *FBDE* = 192 kJ/mol and $A = 8.6 \cdot 10^5$. The shaded area shows the response of the model to a variation of $-\Delta H_{ads}$ within ± 4 kJ/mol at a gas flow of 2 l/min.

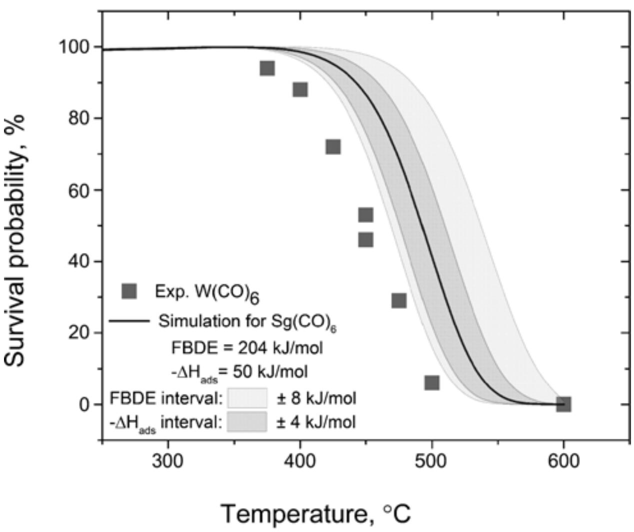

Figure 4: Simulated decomposition curve of the $Sg(CO)_6$ at *FBDE* = 204 kJ/mol, using $-\Delta H_{ads} = 50$ kJ/mol and $A = 8.6 \cdot 10^5$ at identical experimental conditions as used for $W(CO)_6$ with a gas flow of 1 l/min. Experimental decomposition curve for $W(CO)_6$ (grey squares) is given for orientation. The shaded areas covers the respective uncertainty of the *FBDE* [3] and ΔH_{ads} [1] of $Sg(CO)_6$.

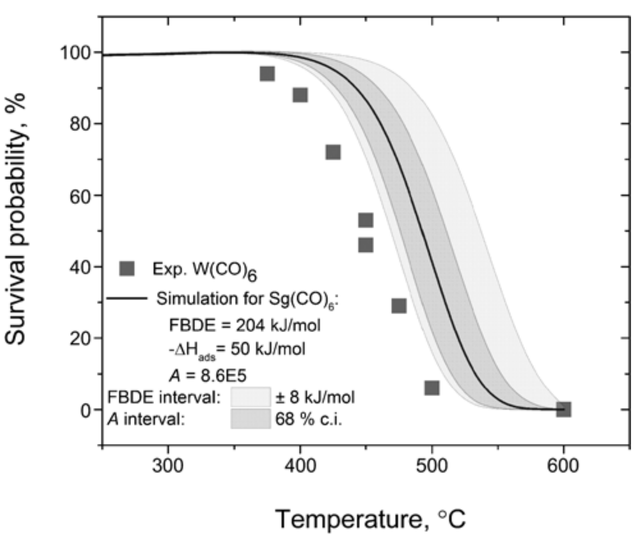

Figure 5: Simulated decomposition curve of the $Sg(CO)_6$ at *FBDE* = 204 kJ/mol, using $-\Delta H_{ads} = 50$ kJ/mol and $A = 8.6 \cdot 10^5$ at identical experimental conditions as used for $W(CO)_6$ with a gas flow of 1 l/min. Experimental decomposition curve for $W(CO)_6$ (grey squares) is given for orientation. The shaded areas covers the respective uncertainty of the *FBDE* [3] and the response of the model to a A within its 68% c. i.

The preexponential factor A was deduced as $(8.6^{+7}_{-4}) \cdot 10^5$ at 68% c. i. for the decomposition of $Mo(CO)_6$. The given uncertainty in A includes the spread in adsorption enthalpies reported for $Mo(CO)_6$ on quartz (Table 1), $-\Delta H_{ads} = 48.8 \pm 3.2$ kJ/mol. From the reported pre-exponential factor for the homogeneous decomposition of Mo and W carbonyls [4], A is deduced as $\sim 2 \cdot 10^2$. We conclude, that heterogeneous decomposition from an adsorbed state (with lower entropy) has quite likely a larger entropic contribution (Equation 6) compared to the homogeneous decomposition, thus lowering the Gibbs free energy of activation for the heterogeneous decomposition. Otherwise, the activation energy effects (ΔE^{+}_{ads}) introduced by the heterogeneous reactions [16] and the influence of the selected experimental setup (ratio of the phases) seem to be substantial.

At otherwise identical conditions, the decomposition curve of $W(CO)_6$ is shifted by 100 °C towards higher temperatures in comparison to $Mo(CO)_6$ (Figure 3). This experimental observation is a consequence of a 23 kJ/mol higher stability of the W–CO bond. The influence of the uncertainty of the corresponding adsorption enthalpies (Table 1) is rather weak (Figure 3, grey shaded area). The proposed Monte-Carlo based approach proves to reproduce the experimental data for $Mo(CO)_6$ and $W(CO)_6$ even at varied experimental conditions (Figures 2 and 3). Hence, a direct comparison between Mo, W, and eventually Sg seems feasible, if investigated in the same setup and under similar experimental conditions.

A hypothetical $Sg(CO)_6$ decomposition pattern was modeled, assuming the same experimental setup as used for $Mo(CO)_6$ and $W(CO)_6$. The predicted *FBDE* [3], the experimental value of ΔH_{ads} [1], and the preexponential factor A, obtained from the $Mo(CO)_6$ decomposition experiments and supported by the experimental results obtained with $W(CO)_6$, provided the necessary inputs. At *FBDE* = 204 ± 8 kJ/mol the decomposition behavior of $Sg(CO)_6$ seems to be distinct from the corresponding behavior of $W(CO)_6$ (Figures 4 and 5).

Despite there is no substantial difference between the predicted [2] and the experimental value [1] for the adsorption enthalpy of $Sg(CO)_6$ on SiO_2, we would like to illustrate the sensitivity of the prediction with respect to uncertainties in the adsorption enthalpy (Figure 4). There, the decomposition curve shifts by ± 25 °C as the value of the adsorption enthalpy is varied by ± 4 kJ/mol, corresponding to the experimental uncertainty of $\Delta H_{ads}(Sg(CO)_6)$ [1]. The model was also applied to investigate the influence of the uncertainty of the preexponential factor A on the expected behavior of $Sg(CO)_6$ (Figure 5). The uncertainty of the predicted FBDE is clearly dominating the uncertainty in the expected behavior of Sg during the envisaged experiment.

A reasonable strategy for investigating the stability of $Sg(CO)_6$ will be based on a first experiment at 375 °C, where 100% survival probability is expected. A direct comparison to the high yield of $W(CO)_6$ can be made. This experiment would also confirm the $Sg(CO)_6$ production and observation rate of about one molecule per day [1]. Thus, seven days of the beam time should provide the first point on the decomposition curve with the following uncertainty 100^{+86}_{-57} %, assuming a 95% confidence interval and Poisson statistics. Subsequently, a measurement at 550 °C is required for another seven days. If not a single $Sg(CO)_6$ molecule passes through the decomposition column within this time period, then the second point would be plotted on the decomposition curve as 0^{+43}_{-0} %, again assuming a 95% confidence interval and Poisson statistics. If the $Sg(CO)_6$ complex still survives, an indication for a higher stability can be deduced. Additional measurements would be needed to bolster this, e. g. at 600 °C. Thus, we conclude that at least two experiments, or at maximum three, are required to assess the *FBDE* of $Sg(CO)_6$.

4 Conclusions

A kinetic Monte-Carlo model of gas adsorption chromatography was complemented by a first order kinetic decomposition model. The combined model was applied for describing the heterogeneous thermal decomposition of group 6 hexacarbonyl complexes in a laminar flow reactor on silver surface, based on given thermochemical data. The model assumes laminar gas phase transport, reversible adsorption-desorption, and irreversible first order heterogeneous decomposition. Despite the significant simplification of the decomposition mechanism, the experimental results were successfully reproduced by the proposed approach, for both $Mo(CO)_6$ and $W(CO)_6$ at varied experimental conditions.

The suggested model can be used twofold: 1) for designing future decomposition experiments with $Sg(CO)_6$; and 2) for the evaluation of the *FBDE* of $Sg(CO)_6$ from experimentally measured decomposition data. The quality of the predictions and the data analysis are strongly dependent on the used theoretical data for the decomposition of $Sg(CO)_6$. Hence, relativistic DFT calculations using improved theoretical models are instrumental for a comparative study of the stability and bonding in this molecule.

Furthermore, the suggested model can be easily adapted to describe results of gas phase investigations of elemental and molecular states interacting with reactive and nonreactive substrates in tubular laminar flow reactors.

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