Supplementary Information: The Kinetic Model of Complex Formation

Mechanism:

Direct collision induced dissociation (CID)

$$V_4O_{11}^- \quad + \quad He \quad \rightarrow \quad V_4O_{10}^- \quad + \quad O \quad + \quad He \qquad (k_{CID}) \tag{1}$$

Pre-equilibrium of aggregation and irreversible hydrogen transfer:

$$V_4O_{11}^- \quad + \quad C_3H_6 \quad \rightleftharpoons \quad [V_4O_{11} \cdot C_3H_6]^- \qquad (k_{ad}/k_{de}) \tag{2}$$

$$[V_4O_{11} \cdot C_3H_6]^- \quad \rightarrow \quad [V_4O_{10}(OH) \cdot C_3H_5]^- \qquad (k_H) \tag{3}$$

Definitions:

A = $V_4O_{11}^-$; B = C_3H_6; C = $[V_4O_{11} \cdot C_3H_6]^-$; D = $[V_4O_{10}(OH)C_3H_5]^-$;
E = $V_4O_{10}^-$; F = He

Rate Equations:

$$\frac{d[A]}{dt} = -k_{ad}[A][B] + k_{de}[C] - k_{CID}[A][F] \tag{4}$$

$$\frac{d[B]}{dt} = 0 \tag{5}$$

$$\frac{d[C]}{dt} = +k_{ad}[A][B] - k_{de}[C] - k_H[C] \tag{6}$$

$$\frac{d[D]}{dt} = +k_H[C] \tag{7}$$

$$\frac{d[E]}{dt} = +k_{CID}[A][F] \tag{8}$$

$$\frac{d[F]}{dt} = 0 \tag{9}$$

Constant Gas Pressure:

$$k_{ad}[A][B] = k'_{ad}[A] \qquad define: \quad k'_{ad} = k_{ad}[B] \tag{10}$$

$$k_{ad}[A][F] = k'_{CID}[A] \qquad define: \quad k'_{CID} = k_{CID}[F] \tag{11}$$

Steady-State Appproximation:

$$\frac{d[C]}{dt} = 0 = +k_{ad}[A][B] - k_{ad}[C] - k_H[C]$$

$$with\ (10) \rightarrow \quad 0 = +k'_{ad}[A] - k_{de}[C] - k_H[C]$$

$$0 = k'_{ad}[A] - (k_{de} + k_H)[C]$$

$$[C] = \left(\frac{k'_{ad}}{k_{de} + k_H}\right)[A]$$

$$[C] = k_{Eq}[A] \qquad define: \quad k_{Eq} = \left(\frac{k'_{ad}}{k_{de} + k_H}\right) \tag{12}$$

Educt Behavior, $(V_4 O_{11}^-)$:

$$\begin{aligned}
\frac{d[A]}{dt} &= -\, k_{ad}[A][B] \;+\; k_{de}[C] \;-\; k_{CID}[A][F] \\
with\ (10),(11) \rightarrow \quad \frac{d[A]}{dt} &= -\, k'_{ad}[A] \;+\; k_{de}[C] \;-\; k'_{CID}[A] \\
with\ (15) \rightarrow \quad \frac{d[A]}{dt} &= -\, k'_{ad}[A] \;+\; k_{de}k_{Eq}[A] \;-\; k'_{CID}[A] \\
\frac{d[A]}{dt} &= \left(-\, k'_{ad} \;+\; k_{de}k_{Eq} \;-\; k'_{CID}\right)[A]
\end{aligned}$$

$$define: \; k_\Sigma = k'_{ad} - k_{de}k_{Eq} + k'_{CID} \tag{13}$$

$$\begin{aligned}
\frac{d[A]}{dt} &= -\, k_\Sigma[A] \\
\int_{[A_0]}^{[A(t)]} \frac{1}{[A]}\, d[A] &= -k_\Sigma \int_0^t dt \\
[A(t)] &= [A_0]e^{-k_\Sigma t}
\end{aligned} \tag{14}$$

Complex Product Behavior, $[V_4O_{10}(OH)C_3H_5]^-$:

$$\begin{aligned}
\frac{d[D]}{dt} &= +\, k_H[C] \\
with\ (12) \rightarrow \quad \frac{d[D]}{dt} &= +\, k_H k_{Eq}[A] \\
with\ (14) \rightarrow \quad \frac{d[D]}{dt} &= +\, k_H k_{Eq}([A_0]e^{-k_\Sigma t})
\end{aligned}$$

$$define: \; k_{CF} = k_H k_{Eq} \tag{15}$$

$$\begin{aligned}
\int_{[D_0]=0}^{[D(t)]} d[D] &= k_{CF}[A_0] \int_0^t e^{-k_\Sigma t}\, dt \\
[D(t)] &= \frac{k_{CF}}{k_\Sigma}[A_0](1 - e^{-k_\Sigma t})
\end{aligned} \tag{16}$$

CID-Product Behavior $(V_4 O_{10}^-)$:

$$\begin{aligned}
\frac{d[E]}{dt} &= +\, k_{CID}[A][F] \\
with\ (11) \rightarrow \quad \frac{d[E]}{dt} &= +\, k'_{CID}[A] \\
with\ (14) \rightarrow \quad \frac{d[E]}{dt} &= +\, k'_{CID}([A_0]e^{-k_\Sigma t}) \\
\int_{[E_0]=0}^{[E(t)]} d[E] &= k'_{CID}[A_0] \int_0^t e^{-k_\Sigma t}\, dt \\
[E(t)] &= \frac{k'_{CID}}{k_\Sigma}[A_0](1 - e^{-k_\Sigma t})
\end{aligned} \tag{17}$$

Fit Procedure:

The experimental data for the educt ($V_4O_{11}^-$), the final complex product ($[V_4O_{10}(OH)C_3H_5]^-$) and CID-product ($V_4O_{10}^-$) is normalized to the sum of all ion signals to account for the 5-7 % losses due to leakage from the ion trap over the substantial storage time of up to 12 s (as shown in Fig. 1). After normalization to the sum signal, the experimental data of the educt signal is fit with equation (14) for 200, 250 and 300 K. The values for k_Σ that are obtained form the fit give the behavior of $\frac{1}{k_\Sigma}(1 - e^{-k_\Sigma t})$ for the respective temperature. The values of this expression are used to extract k_{CF} and k_{CID} from the experimental data in the formation of the complex and CID-product over the full storage time with equations (16) and (17), respectively. The pressure normalized rate constants are given in Tables 1-3 below.

Rate Constants from the Model:

Tabelle 1: Rate Constants for the Educt Depletion: $k_\Sigma = k'_{ad} - k_{de}k_{Eq} + k'_{CID}$

Temperature / K	k_Σ* / s^{-1}
200	$2.38 \times 10^{-1} \pm 0.35 \times 10^{-1}$
250	$6.63 \times 10^{-1} \pm 0.22 \times 10^{-1}$
300	$8.40 \times 10^{-1} \pm 0.17 \times 10^{-1}$

Tabelle 2: Rate Constants for the Complex Formation: $k_{CF} = k_{Eq}k_H$

Temperature / K	k_{CF}* / s^{-1}
200	$1.98 \times 10^{-1} \pm 0.17 \times 10^{-1}$
250	$5.82 \times 10^{-1} \pm 0.26 \times 10^{-1}$
300	$7.39 \times 10^{-1} \pm 0.27 \times 10^{-1}$

Tabelle 3: Rate Constants for the CID-Product Formation: k'_{CID}

Temperature / K	k'_{CID}* / s^{-1}
200	$4.01 \times 10^{-2} \pm 1.32 \times 10^{-2}$
250	$8.01 \times 10^{-2} \pm 1.53 \times 10^{-2}$
300	$10.1 \times 10^{-2} \pm 2.12 \times 10^{-2}$

*Precision of the rate constants is given by the standard deviation of the experimental data form the kinetic model