Electronic Supplementary Material (ESI)

“Gas-phase aluminium acetylacetonate decomposition: Revision of the current mechanism by VUV synchrotron radiation”

Sebastian Grimm*\textsuperscript{a,e}, Seung-Jin Baik\textsuperscript{b,e}, Patrick Hemberger\textsuperscript{c}, Andras Bodi\textsuperscript{c}, Andreas Kempf\textsuperscript{b,e}, Tina Kasper\textsuperscript{d,e} and Burak Atakan\textsuperscript{a,e}

\textsuperscript{a} University of Duisburg-Essen, Institute of Combustion and Gas Dynamics, Chair of Thermodynamics, Duisburg 47057, Germany.

\textsuperscript{b} University of Duisburg-Essen, Institute of Combustion and Gas Dynamics, Chair of Fluid dynamics, Duisburg 47057, Germany.

\textsuperscript{c} Laboratory for Synchrotron Radiation and Femtochemistry, Paul Scherrer Institute, CH-5232 Villigen-PSI, Switzerland.

\textsuperscript{d} University of Duisburg-Essen, Institute of Combustion and Gas Dynamics, Chair of Mass spectrometry of reactive fluids, Duisburg 47057, Germany.

\textsuperscript{e} Center for Nanointegration Duisburg-Essen (CENIDE), Duisburg 47057, Germany.
S1  Numerical simulation of the microreactor

S 1.1 General equations and assumptions

The Navier-Stokes equations contain mass continuity and momentum conservation written as

\[
\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i} (\rho u_i) = 0 \tag{E1}
\]

\[
\frac{\partial (\rho u_i)}{\partial t} + \frac{\partial}{\partial x_j} (\rho u_i u_j) = -\frac{\partial p}{\partial x_j} + \frac{\partial}{\partial x_j} \left[ \mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \frac{u_l}{\partial x_l} \right) \right] + \frac{\partial}{\partial x_k} (-\rho u_i u_j) \tag{E2}
\]

where \( \mu \) is the dynamic viscosity. In the present work, the Knudsen number \( (Kn) \) is used as a key parameter to determine the rarefaction level of the investigation region. The Reynolds and Mach number define the local \( Kn \) as follows,

\[
Kn \equiv \frac{\lambda}{L} = \sqrt{\frac{\gamma \pi M}{2 \operatorname{Re}}} \tag{E3}
\]

\[
Re = \frac{\rho Ud}{\mu} \tag{E4}
\]

Generally, depending on the value of \( Kn \), the flow region can be divided into a continuous flow region \( (Kn < 0.01) \), a slip flow region \( (0.01 < Kn < 0.1) \), a transition flow region \( (0.1 < Kn < 10) \), and a free-molecular flow region \( (Kn > 10) \). Detailed transition of flow regimes based on the Knudsen number can be found elsewhere.\(^1\)

By applying slip boundary condition, a simple approximation for slip fluid velocity at the wall is

\[
V_{\text{slip}} = l_s \frac{\partial V}{\partial n} \text{ at wall} \tag{E5}
\]

, where \( n \) denotes the normal vector to the wall, and \( l_s \) is the slip length. The main difficulty to define the slip velocity comes from the treatment of the slip length. In the present work, the slip length \( l_s \) is calculated according to Morris et al.\(^2\):

\[
l_s = \alpha L \cdot Kn \tag{E6}
\]

The model constant \( \alpha \) is suggested as 1.15 in their work. The heated length (10 mm) in the reactor is consequently used as the characteristic length \( L \).
S 1.2. Computational domain and numerical setup

The computational domain is set up as axisymmetric two-dimensional geometry as shown in Fig. S 1 with detailed boundary conditions as shown in Tab. S 1.

![Fig. S 1 Two-dimensional axisymmetric geometry for the present simulation.](image)

### Tab. S 1 Boundary conditions for the domain in Fig. S 2

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Boundary type</th>
<th>Pressure mbar</th>
<th>Temperature K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Inlet</td>
<td>550, 1600</td>
<td>293.15</td>
</tr>
<tr>
<td>2</td>
<td>No-slip wall</td>
<td>-</td>
<td>405.15</td>
</tr>
<tr>
<td>3</td>
<td>Slip wall</td>
<td>-</td>
<td>423.15 - 1273.15</td>
</tr>
<tr>
<td>4</td>
<td>Outlet</td>
<td>$6 \times 10^{-5}$</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Symmetric</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

In the present work, a cell size of 10 μm is used for the complete computational domain, in order to assure accurate results, while keeping the computational costs at a minimum. Applying this grid size gives us more than 10 nodes in radial direction to resolve the flow field of a tiny pinhole (100 μm) of the connection between evaporator (see Fig. S1 Nr.2) and reactor (see Fig. S1 Nr.3). To test the influence of a further refinement of the mesh size on the simulation results, we halved the cell size. There is no significant difference of the calculated flow field properties, as demonstrated in Fig. S 2. Thus, we conclude, that the cell size of 10 μm is sufficient to resolve the present computational domain at the conditions evaluated in this study.

![Fig. S 2 Axial profiles of the temperature and axial velocity for an outer surface temperature of 623 K at two grid sizes, 5μm and 10 μm.](image)
S 1.3 Flow regime characteristics in the heated zone

Fig. S 3 shows the axial profiles of Kn in the heated zone of the reactor at wall temperatures of 553.15, 673.15 and 833.15 K. If the outer surface temperature is increased, the flow in the heating zone has a higher Kn. Since the range of Kn at the experimental outer surface temperatures of 348-1273 K is 0.005 ≤ Kn ≤ 0.02, we can assume that the flow in microreactor is located in the slip flow region.

![Graph showing Knudsen number profiles](image)

Fig. S 3 Axial profile of the local Knudsen number for various experimental surface temperatures.

S 1.4 Validation of the simulation

To validate the feasibility of the present simulation method, additional simulations were performed with the same conditions that were used for the simulation of a microreactor by Weddle et al.3 A detailed description of the geometry and operating parameters can be found elsewhere.3 Our simulation reproduced Weddle’s conditions fairly well and shows a good agreement for important flow properties, as temperature and axial velocity, as shown in Fig S4. The deviations at the outlet section of the reactor ( >30 mm) can be explained by the simulation domain used in both studies. Our domain does include the downstream vacuum chamber (see 4 in Fig. S1), in which the flow is expanded, whereas the reference test case does only consider the microreactor as simulation domain.

![Graph showing axial profiles of temperature and velocity](image)

Fig. S 4 Axial centerline profiles of temperature (red) and axial velocity (blue) for a wall temperature of 1500 K and 1700 K. Data from Weddle et al.: dotted; our simulation: lines.3
S 1.5 Effect of wall reactions

Even though the residence time in the reaction (heating) zone is significantly smaller than in typical flow reactors, it is necessary to check whether surface reactions may dominate the mechanism under the experimental conditions. Guan et al.\textsuperscript{4} tried to explain the influence of wall reactions by a comparison between the residence time and the characteristic time for radial diffusion expressed as $t_{\text{diff}} = r^2 / D$. We also used this approach for our conditions, where $r$ as the radius of the SiC microreactor and $D$ is denoted as the diffusion coefficient of aluminium acetylacetonate in argon. Since, to our knowledge, there is no available data in the literature for the diffusion coefficient (aluminium acetylacetonate in argon), we approximate the diffusion coefficient with a correlation equation.\textsuperscript{5} This correlation equation estimates the binary diffusion coefficient with empirical constants (so-called atomic diffusion volumes) found from experimental data. However, since the original equation does not contain the metal component, we adjusted the equation constants by the previous observation from Siddiqui et al.\textsuperscript{6} (aluminium acetylacetonate in nitrogen).

**Figure S 5** displays the residence time in the reaction zone is much smaller than the diffusion time scales except at wall temperatures higher than 1200 K. Therefore, we can assume that the surface reaction at the wall is rather small in the present temperature range.
S2 Temperature-dependent gas expansion factor

Fig. S 6: Gas expansion factor as a function of calculated centreline temperature according to the numerical simulation.
Fig. S 7 Assignment of the ms-TPES at m/z 224 (dotted black curve) to Al(C₅H₇O₂)C₅H₆O₂ based on computed IEs from Franck-Condon simulations of Al(C₅H₇O₂)C₅H₆O₂ (red curve). Blue, green and yellow notations belong to calculated excited states of the molecule.

**S3 Assignment of m/z 224, Al(C₅H₇O₂)C₅H₆O₂**
S4 Species assignments of further decomposition products

At 9.82 eV, a clear peak in the TPES of m/z 15 emerges, which corresponds to the published ionization potential of the methyl radical (IE = 9.84 eV) (see Fig. S8 (a)). The spectrum in Fig. S8 (b) is consistent with the reported spectrum of acetylene (C<sub>2</sub>H<sub>2</sub>) and the experimental data in (c) is in line with the spectrum obtained by others for the photoionization of formaldehyde (CH<sub>2</sub>O) at IE = 8.71 eV. Strong evidence of a mixture of vinyl alcohol and acetaldehyde was found at the m/z 44 channel by comparing the TPE-spectrum to reference spectra in Fig. S8 (d).

Fig. S 8 Representative examples of product species identification and assignment for C-C hydrocarbons and oxygenated species in the pyrolysis of Al(C<sub>3</sub>H<sub>12</sub>O<sub>3</sub>), using TPE-spectra (black lines, dot symbol); Literature reference spectra (red, blue) are as follows: (a) m/z 15 (CH<sub>3</sub>)<sup>+</sup> (b) m/z 26 (C<sub>2</sub>H<sub>5</sub>)<sup>+</sup> (c) m/z 30 (CH<sub>3</sub>OH) and (d) m/z 44 (C<sub>2</sub>H<sub>3</sub>CHO) and (C<sub>2</sub>H<sub>5</sub>OH).
Additional assignments have been made for C4-C5 hydrocarbons revealing that beneath the pyrolysis products vinylacetylene\(^{12}\) is present (see Fig. S 9 (a)). The TPE-spectrum for the \(m/z\) 54 channel reveals the contribution of at least four isomers of \(C_6H_6\), 1,3-butadiene (IE: 9.07 eV\(^{13}\)), 1,2-butadiene (IE: 9.33 eV\(^{14}\)), 2-butyne (IE: 9.59 eV\(^{12}\)) and 1-butyne (IE: 10.18 eV\(^{14}\)), which were assigned by their literature values and PES (see Fig. S 9 (b)). The cyclopentadienyl has been identified among the pyrolysis products with an ionization onset of 8.42 eV by a literature PIS.\(^{15}\) At least three species reside on the \(m/z\) 66 channel, where strong evidence has been found for 1,3-cyclopentadiene\(^{16}\) and 1,2,4-pentatriene\(^{17}\) by a comparison to literature TPES. Additionally, at 9.0 eV, evidence in the TPES for 1-penten-3-ynyl\(^{12}\) has been found.
As far as the C_5-C_10 hydrocarbons as secondary decomposition products of the pyrolysis of Al(C_5H_7O_2)_3 are concerned, we found evidence for 2-pentanone m/z 86 (C_5H_{10}O)\textsuperscript{14}, phenol m/z 94 (C_6H_6O)\textsuperscript{14}, anisole m/z 108 (C_7H_6O)\textsuperscript{18} and azulene m/z 128 (C_{20}H_{10})\textsuperscript{19} in the TPE-spectra (see Fig. S 10).

Fig. S 10 Representative examples of product species identification and assignment for C_5-C_10 hydrocarbons and oxygenated species in the pyrolysis of Al(C_5H_7O_2)_3 using TPE-spectra (black lines, dot symbol); Literature reference spectra (red) are as follows: (a) m/z 86 (C_5H_{10}O)\textsuperscript{14} (b) m/z 94 (C_6H_6O)\textsuperscript{14} (c) m/z 108 (C_7H_6O)\textsuperscript{18} and (d) m/z 128 (C_{20}H_{10})\textsuperscript{19}.
Possible product species identification and assignment for m/z 146 and 186 formed by pyrolysis of Al(C₆H₁₁O₂), with the aid of ms-TPE-spectra (black lines, dot symbol) as well as ms-TPE-spectra and their respective PIS for m/z 146, 186, and 210; literature reference spectra (red, blue and orange) are as follows: (top) m/z 146 (C₆H₄, red); m/z 186 (C₆H₄O₂, green); and m/z 210 (C₆H₄O₂, orange); (middle) m/z 186 (C₆H₄O₂, red); m/z 186 (C₆H₄O₂, blue); and m/z 210 (C₆H₄O₂, orange).
The shape of the TPE-spectra in Fig. S 12 are in good agreement with the reference spectrum of acetylacetone \((C_5H_8O_2)\) in its 97 % enol (IE = 8.9 eV)\(^{23}\) and 3% diketo (IE: 9.5 eV)\(^{23}\) tautomers at 300 K. The signal does not follow the reference photoelectron spectrum at photon energies > 10.06 eV, due to DPI, leading to the formation of the major fragments \(m/z\) 43, 58, 72 and 85.\(^{23}\) Because of keto-enol tautomerism, gaseous acetylacetone exists primarily in its enol form (first band 8.9 eV) at room temperature, whereas at higher temperatures, the equilibrium shifts to more gaseous diketo-acetylacetone (second band 10.2 eV).\(^{24,23}\) The central band at 9.5 eV represents a superposition of both tautomer signals. Antonov et al.\(^{23}\) stated that the \(m/z\) 43 peak is due to the DPI of diketone-acetylacetone. At temperatures higher than 600 K, the equilibrium constant is around unity,\(^{23}\) representing similar concentrations of enol- and keto-acetylacetone in the gas phase. This leads to enhanced formation in pyrolysis conditions due to DPI of \(m/z\) 100.
According to a review study by Igumenov et al.\textsuperscript{25} significant amounts of $m/z$ 164 ($C_{10}H_{12}O_2$) may also be formed by heterogeneous surface reactions. Since these reactions are controlled by the $\text{Al(C}_5\text{H}_7\text{O}_2)\text{}_3$ feed concentration, we carried out experiments with different evaporation temperatures. A significant difference in the decomposition behavior was observed, supporting the idea that, at low temperatures, surface reactions are dominant in the pyrolysis tube (see Fig S 13). The strong increase at 673 K implies that another gas-phase process is also responsible for the formation of $m/z$ 164.
References


