

Insights into the decomposition of zirconium acetylacetonate using synchrotron radiation: Routes to the formation of volatile Zr-intermediates

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Abstract

The thermal decomposition of $\text{Zr}(\text{acac})_4$ is studied in a SiC-microreactor on the micro-second time scale. By utilizing synchrotron radiation and photoelectron photoion coincidence spectroscopy, six important zirconium-intermediates, as for instance $\text{Zr}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{C}_5\text{H}_6\text{O}_2)$, and $\text{Zr}(\text{C}_5\text{H}_6\text{O}_2)_2$, are identified in the gas phase for the first time. The adiabatic ionization thresholds of intermediately formed zirconium species are estimated and the main products of their thermal decomposition, actylacetone, acetylallene and acetone are characterized unambiguously and isomer-selectively. Based on all detected intermediates, we deduce the predominant pyrolysis pathways of the precursor in the temperature range from 400 to 900 K. Our findings are complemented by numerical simulations of the flow field in the microreactor,

which show that the choice of seed gas significantly influences the temperature profile and residence times in the microreactor, such that helium provides a more uniform flow field than argon and should preferentially be used.

Keywords: photoelectron photoion coincidence spectroscopy, pyrolysis, zirconium acetylacetonate, chemical vapor deposition (CVD) (chemical reaction), in situ, mass spectroscopy/spectrometry

1. Introduction

Solid zirconia layers have interesting thermo-physical properties, are inert, have a wide bandgap and a high dielectric constant. Consequently, these ceramic layers are used i.e. as thermal barrier coatings [1,2], anti-corrosion layers [3], high- k dielectric layers [4,5], anti-reflective coatings [6], dielectric capacitors [7], or for energy storage applications [8]. High growth rates and uniform film thicknesses, allow film preparation by chemical vapor deposition (CVD). In CVD processes, a metal-containing precursor is evaporated and forms a thin film in a surface reaction, but often the precise formation mechanisms are not fully uncovered.

Until now, many studies have been published on the CVD of ZrO_2 layers, where various types of zirconium based derivatives, such as organo-zirconium complexes, zirconium aminoalkoxide-substituted precursors [9], alkoxides [10,11] and β -diketonates [12–14] were used as precursor for thin film formation.

Metal β -diketonates, as for instance zirconium acetylacetonate ($\text{Zr}(\text{acac})_4$), are frequently used as precursors due to their high volatility, stability in air and commercial availability. The homogeneous decomposition of the gaseous precursor is considered as the rate-limiting step for film growth, because of the intrinsically high bond dissociation energies of these complexes. At higher temperatures, competing processes like particle formation and nucleation may also occur in the gas phase, and reduce the growth rate significantly. The reactivity of metal containing intermediates determines, if the desired film structure and morphology is obtained or undesired side reactions occur. Clearly, gas phase reactions play an important role in the a-priori determination of film composition, purity and the total yield of CVD processes [15].

Consequently, attempts to characterize the reaction products and pathways were undertaken by thermogravimetric analysis [16,17] coupled to infrared spectroscopy [18–20] and mass spectrometry [21–23], respectively. The main conclusion drawn in previous work on $\text{Zr}(\text{acac})_4$ was, that the precursor undergoes a series of decomposition steps rationalized by the detection of various organic by-products in the gas phase. While acetylacetone (m/z 100; $\text{C}_5\text{H}_8\text{O}_2$), acetic

acid (m/z 60; $C_2H_3O_2$) and propyne (m/z 40, C_3H_4) were found at temperatures up to 523 K, carbon dioxide (m/z 44; CO_2), water (m/z 18; H_2O) and methane (m/z 16; CH_4) are the main products at temperatures higher than 623 K [18,22,23]. Those by-products are formed from the initial precursor and lead to the formation of metal acetates ($Zr(acac)_2(CH_3COO)_2$; $ZrOH(CH_3COO)_3$; $ZrO(CH_3COO)_2$), metal carbonates ($ZrOCO_3$), as well as other intermediate species, which were detected on the surface [18]. Finally, at high temperatures a ZrO_2 film, with a substantial amount of carbon contamination from unreleased ligand fragments, is formed [23]. Concerning the gas phase chemistry, so far experimental limitations precluded the detection of most of the postulated intermediate zirconium species [23], and thus reaction mechanisms are incomplete [18,22]. However, an analysis of these early stages of growth initiated in the gas phase, requires fast and sensitive analytical techniques with sufficiently low detection limits for short-living gaseous species, which are usually difficult to detect and characterize with conventional thermogravimetric and spectroscopic methods [24].

Here, we present a combined numerical and experimental study to elucidate the gas phase chemistry of zirconium acetylacetonate using a microreactor, which is characterized by short residence times of $< 50 \mu s$, coupled to an double imaging photoelectron photoion coincidence spectrometer (i^2 -PEPICO) combined with vacuum ultraviolet (VUV) radiation provided from the Swiss Light Source (SLS) synchrotron. The wide tunability of the photon energy emitted from a synchrotron facility combined with velocity map imaging (VMI), enables us to distinguish fragmentation from direct ionization, commonly observed in standard electron ionization mass spectrometry. This feature allows us to characterize and identify important organometallic and organic reactive intermediates isomer-selectively. This experimental strategy was demonstrated previously, to be an effective way to detect and characterize metal-containing intermediates and radicals with short lifetime in comparable systems [25–27]. By computational fluid dynamic (CFD) methods, the temperature and flow field in the microreactor is characterized, because the reaction area is hard to access experimentally, due to the small size (1 mm I.D.) of the reactor. In this context, the influence of two different inert gases with strongly differing thermal conductivities is investigated.

We report the results of our successful approach to use VUV and i^2 PEPICO for the *in-situ* detection of gas phase radicals and zirconium containing intermediates in the vacuum pyrolysis of $Zr(acac)_4$ at temperatures between 400-900 K under conditions relevant to thin film growth by CVD. Our results provide direct experimental evidence for the initial steps of the gas phase chemistry and can be used to improve the modelling of thin film synthesis pathways. Ultimately, as the work contributes to a more efficient materials synthesis.

2. Results and discussion

In the upcoming section we will first present and discuss the findings of the CFD simulations to interpret the decomposition mechanism, especially the temperature onsets, more accurately. Since it has been reported that $\text{Zr}(\text{acac})_4$ may be unstable in the evaporator [14,28], prior to its desired thermal decomposition in the microreactor, in the following paragraph influence of this effect on the products sampled at the outlet of the reactor is discussed. These insights are considered for the correct interpretation of mass spectra upon pyrolysis of $\text{Zr}(\text{acac})_4$. The identification of the corresponding pyrolysis products proceeds mainly via mass-selective threshold photoelectron spectra (ms-TPES) and an analysis of the photoionization efficiency curves (PIE). However, in the case of the identification of important zirconium intermediates that were formed by thermal excitation, their isotopic patterns are taken into account and their respective chemical structure is suggested. With aid of the flow field information provided by CFD, temperature-dependent species profiles and possible formation pathways for the zirconium-intermediates are discussed.

2.1 Flow field of the microreactor

In this section, we report on the pressure, temperature, and velocity fields, as well as residence time in the microreactor, modelled by CFD, using both argon and helium as dilution gas. In the left part of **Figure 1**, an axial temperature profile of the microreactor is shown. It can be stated, that a relatively small temperature difference in axial, as well as radial direction is observed, indicated by exemplary sampled streamlines at $y = 0, 0.25$ and 0.4 mm (dashed grey lines **Figure 1** right). The helium gas temperature reaches its target value of 671 K with a deviation

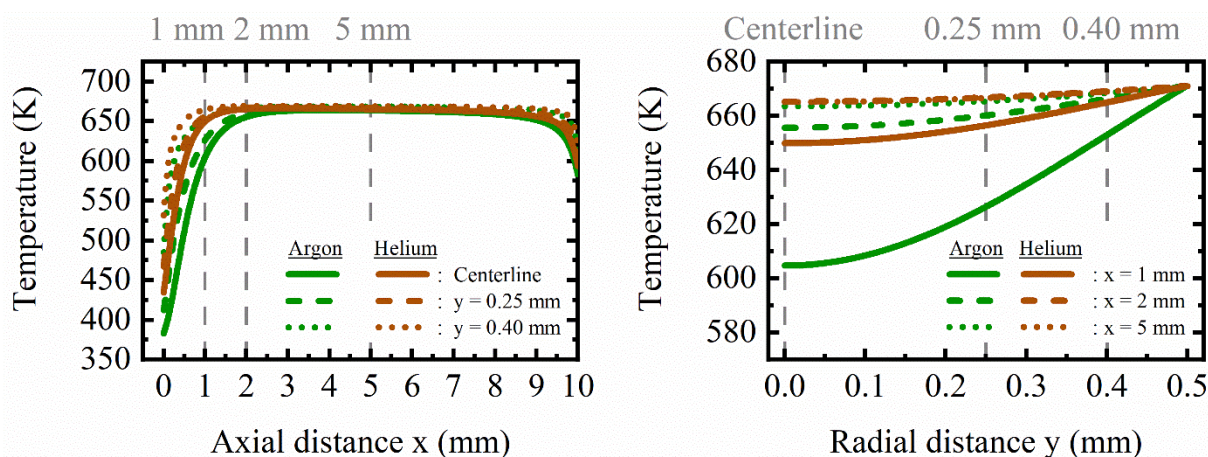


Figure 1 Temperature profiles calculated by CFD for an initial pressure of 2.15×10^5 Pa and a wall temperature of 671 K, a value, where most of the reactions occur. **Left:** Axial temperature profile extracted at $y = 0$ mm (straight), 0.25 mm (dashed), and 0.4 mm (dotted) from the reactor centerline inside the heated zone; **Right:** Radial temperature profile along a vertical line at $x = 1.0$ mm (straight), 2.0 mm (dashed), and 5.0 mm (dotted) measured from the inlet of the heated zone. The vertical dashed grey lines in each plot represent the exemplary sampled lines in the respective other graph marked with at their position.

of less than 1 % at an axial distance from the reactor inlet of $x = 1$ mm, which results in an almost isothermal zone of 9 mm. This length is considerably longer in comparison to the results with argon, where at almost 2.1 mm a maximum deviation of 1 % is reached, with respect to the target temperature. This difference becomes more evident in radial direction, where the centerline temperature of helium shows a deviation of 21 K (3.1 %) from the measured surface temperature (see **Figure 1 right**), whereas for argon the deviations in the inlet region are considerably higher with 66 K (9.8 %) at $x = 1$ mm. The deviations are much smaller inside the isothermal zone, for instance at $x = 2.5$ mm the temperature deviation is 15 K (2.2 %) using argon and 6 K (0.9 %) for helium, respectively. Therefore, we conclude that under the given experimental conditions, the experimental data obtained is suitable to develop a mechanistic understanding of chemical reactions that occur in the microreactor, since in both cases, the temperature profile is known with small uncertainties. Additionally, it is important to note, that the temperature profile is more uniform for helium than for argon using the same boundary conditions (see **Figure S 2** in the **ESI**). Besides the temperature profiles, we also investigated other important flow parameters and found an average pressure in the heated zone between 350 and 600 Pa and residence times of 5 - 30 μ s for wall temperatures ranging from 400 to 900 K (see **Figure S 3** in the **ESI**). These results are in accordance to previous findings with different boundary conditions [29–31] and allow to probe mainly the initial unimolecular decomposition products, provided they occur on a timescale of the order of a few microseconds. Further details on the flow field under the given experimental conditions are presented in section **S1** of the **ESI**.

2.2 Precursor stability: On the degradation products in the evaporator

As outlined in the introduction, our main goal was to determine the pyrolysis products of $\text{Zr}(\text{acac})_4$. Recent studies, however, propose that the precursor may already be unstable in the evaporator at temperatures of 423 K or higher, as typically used in CVD applications, but possible decomposition products have not been detected yet [14]. To distinguish between products that are due to pyrolysis in the reactor and those that are already formed in the evaporator, we kept the reactor temperature at the level of the evaporator and gradually increased both temperatures from 393 to 443 K. Because the residence time is increased by the time that the precursor spends in the reactor, giving it additional time for possible decomposition reactions, it can be safely assumed that if no decomposition products can be detected, the precursor will also stably evaporate at this temperature in the evaporator alone. By recording mass spectra at 8.0, 9.0, 10.0, 11.0 and 11.5 eV, relevant decomposition products

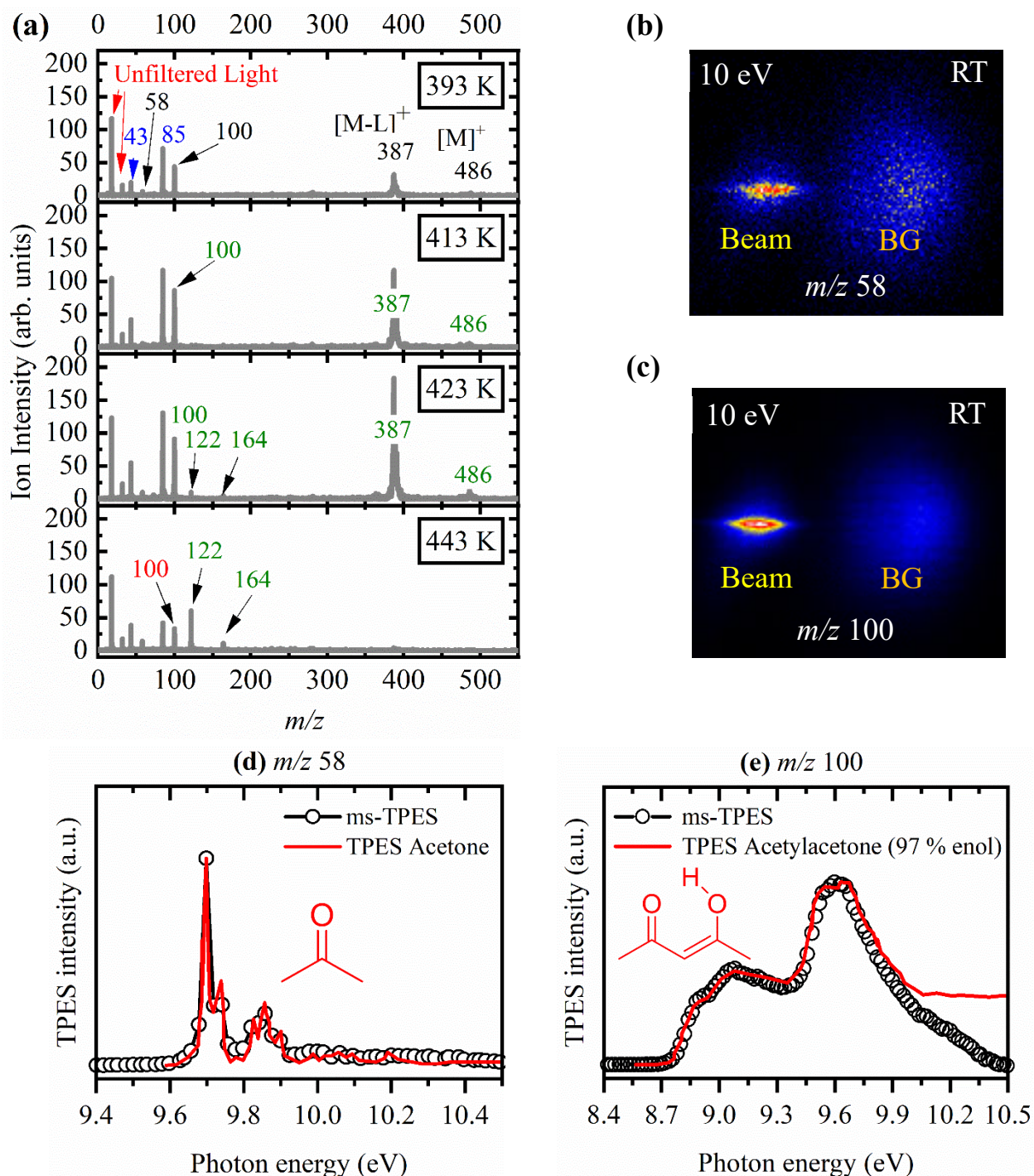


Figure 2 (a) Temperature-dependent mass spectra at 8.0 eV for various evaporation temperatures, which show a decrease in Zr(acac)₄ signal at temperatures higher than 423 K together with a simultaneous increase of the peaks denoted in green, whereas the red signals decrease in comparison to their intensity in the spectra above. Blue indicates signals that rise from small amounts of unfiltered light (i.e. light > 8.0 eV); (b) and (c) show VMI images of the most abundant degradation products at a photon energy of 10 eV, which is slightly higher than their respective ionization thresholds. The VMI images prove that the species with m/z of 58 and 100 are indeed attributed to decomposition in the sample container and do not come from dissociative ionization of Zr(acac)₄. The threshold photoelectron spectra (black dots) in (d) and (e) rationalize our assignment by comparison to literature reference spectra (red curves) as acetone (IE = 9.71 eV) [33] and acetylacetone (IE = 8.9 eV) [34].

were identified, based on their unique ionization onsets. It is evident from the mass spectra in **Figure 2 (a)**, that m/z 486 Zr(acac)₄ ionizes dissociatively by losing one ligand (m/z 99) to yield m/z 387 Zr(acac)₃⁺, as pointed out in the literature [32]. A comparison of the ms-TPE spectra

of the parent ion m/z 486 and its major fragment at m/z 387 proves this behavior of $\text{Zr}(\text{acac})_4$ (see **Figure S 4 (a)** in the **ESI**). Additionally, the analysis of the ion kinetic energy available from the VMI ion image shows a considerable momentum distribution (see **Figure S 5** in the **ESI**) perpendicular to the molecular beam propagation direction. This fact let us conclude, that at photon energies higher than 8.0 eV, we almost exclusively detect the major fragment of $\text{Zr}(\text{acac})_4$. In the following, when showing data recorded at higher photon energies, we ascribe the signal at m/z 387 to the precursor.

As can be seen in the recorded mass spectra of **Figure 2 (a)**, the signal of the main precursor fragment at 8.0 eV with m/z 387 increases up to an evaporation temperature of 423 K. This occurs at lower temperature than expected, since others determined a first weight loss of the precursor at around 453-463 K by coupled thermogravimetric and spectroscopic measurements [18,22]. However, such an onset is mainly a question of experimental detection limits and reaction times. They found volatile hydrocarbons such as C_3H_4 (m/z 40) and acetic acid (m/z 60) that are released to the gas phase upon precursor degradation. In agreement with these studies, we found traces of acetic acid formed in the evaporator, in a slow, but continuous decomposition process, which takes place prior to pyrolysis in the sample container. This interpretation of the mass spectra is substantiated by room temperature VMI ion images as well as characteristic features for acetic acid in the ms-TPES profile (see **Figure S 6** in the **ESI**). Since the signal intensities at m/z 60 are relatively low and remain almost constant upon pyrolysis, we attribute them to a degradation product in the evaporator. Slow degradation may be a possible explanation, why others observed acetic acid by spectroscopic methods, but ascribed this species to a major gaseous decomposition product [18,22]. In contrast to the observations in the literature, neither the room temperature mass spectra, nor the ion image or the experimental ms-TPES provides evidence that C_3H_4 forms in considerable amounts in the evaporator under the conditions used in this study.

In contrast, we detected significant amounts of other decomposition products, which are partially shown in **Figure 2 (b-e)**. The mass spectra **(a)** and the velocity map images **(b)** and **(c)**, as well as ms-TPE spectra in **(d)** and **(e)** provide strong evidence, that the precursor partially decomposes in the evaporator even at temperatures below 443 K. Still a significant amount of $\text{Zr}(\text{acac})_4$ reaches the analytical chamber at the outlet of the microreactor, which is represented by a steep increase of the major fragment signal at m/z 387 ($\text{M}^+\text{-L}$). Its signal reaches a maximum at a temperature of 423 K. Major degradation products are identified at m/z 58, 100, 122 and 164, leaving a zirconium containing residue in the evaporator, which we did not characterize further. We assigned

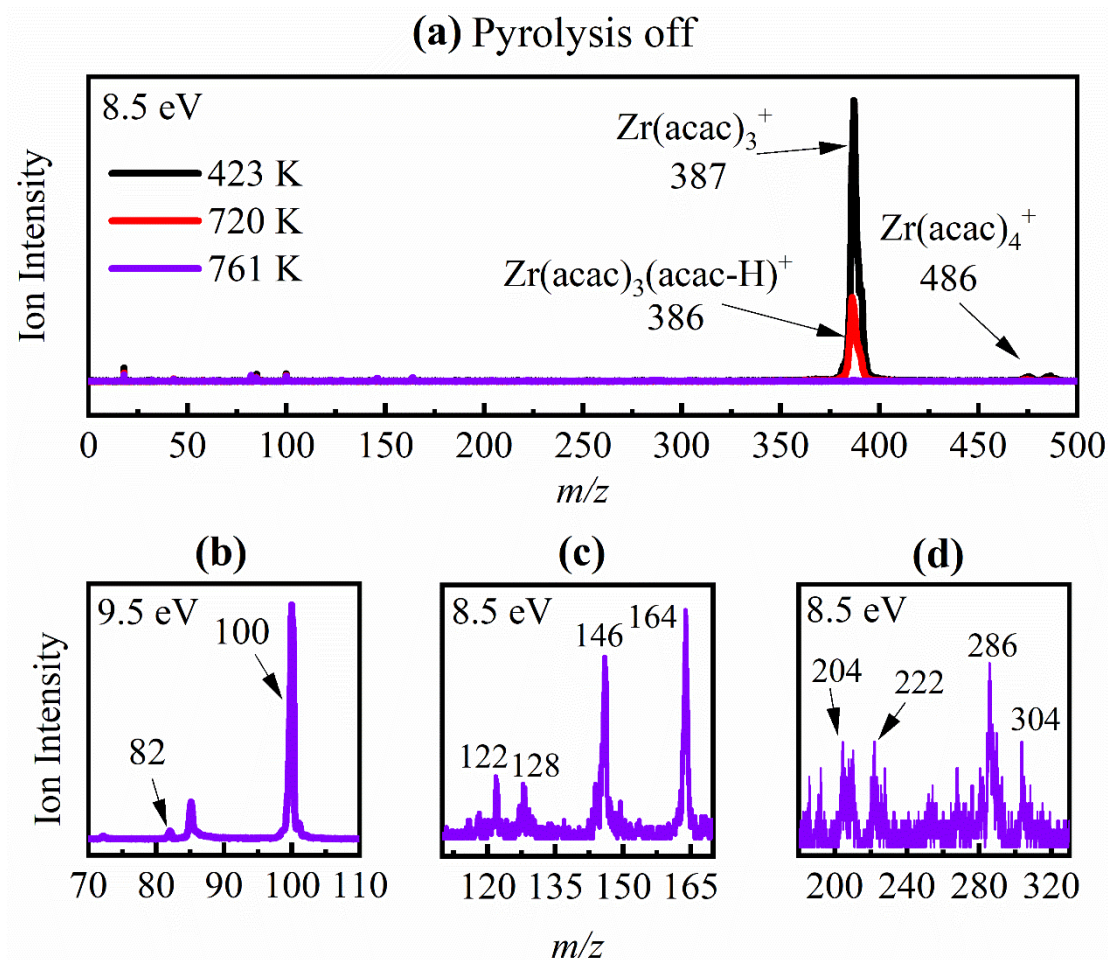


Figure 3 (a): Mass spectra obtained upon the pyrolysis of $\text{Zr}(\text{acac})_4$ recorded at 423 K (black), 720 K (red) and 761 K (purple) at a photon energy of 8.5 eV; Selected parts of the mass spectrum at 761 K are enlarged in **(b)** at a photon energy of 9.5 eV and in, **(c)** and **(d)** at a photon energy of 8.5 eV. The respective peaks are labelled by their assigned ions **(a)** and/ or mass-to-charge ratio **(a-d)**.

the oxygenated and hydrocarbon products in the gas phase based on their spectroscopic fingerprint and ion VMI image, exemplarily shown in **Figure 2 (b,d)** and **(c,e)**, to acetone ($\text{C}_3\text{H}_6\text{O}$) (IE = 9.71 eV) [33] and acetylacetone ($\text{C}_5\text{H}_8\text{O}_2$) (IE=8.9 eV) [34], as the most abundant species. Considerable amounts of 2-6 dimethylphenol ($\text{C}_8\text{H}_{10}\text{O}$) and two isomers of $\text{C}_{10}\text{H}_{12}\text{O}_2$, namely dimethyl-dihydroxo-dihydropentalene and dimethyl-hydroxo-keto-tetrahydropentalene were also found and characterized in the same manner (see **Section 2.3**, below). Our findings let us conclude, that an evaporation temperature of < 413 K is sufficient to minimize thermal degradation in the evaporator and allows probing the pyrolysis products in the flow reactor on a reasonable timescale. The subsequent pyrolysis experiments were carried out at a sufficiently low evaporation temperature of 403 K minimizing precursor decomposition before the reactor is reached.

2.3 Photoionization mass spectra upon pyrolysis

To investigate the pyrolysis of $\text{Zr}(\text{acac})_4$, photoionization mass spectra were evaluated at fixed photon energies of 8.0 to 11.5 eV in 0.5 eV increments over a temperature range of 400 - 900 K. The top trace of **Figure 3** illustrates an exemplary mass spectrum of $\text{Zr}(\text{acac})_4$ without pyrolysis. As discussed in the previous paragraph, small contributions from the degradation in the evaporator can already be identified on the left hand side in the m/z range 0 to 175. With pyrolysis turned on, that is at higher reactor temperature, some species emerge in the mass spectra, which are shown on the bottom graphs in **Figure 3 (b), (c), (d)**. At the highest temperature of 761 K the precursors ion signal at m/z 387 is absent (purple spectrum) **(a)** and product peaks at m/z 82, 100 **(b)**, 122, 128, 146 164 **(c)**, as well as 204, 222, 286 and 304 **(d)** are observed in the mass spectra.

2.4 Identification of elusive species

The species assignment by conventional mass-spectrometric methods is influenced, by fragmentation and is therefore often insufficient for the unambiguous assignment of reactive open-shell species, such as radicals in reactive mixtures. To identify zirconium-containing molecules, we utilize the distinct isotope distribution of zirconium, with its four stable isotopes at ^{90}Zr , ^{91}Zr , ^{92}Zr and ^{94}Zr and compare the natural distribution with our mass spectra. Additionally, we do not solely rely on the mass dimension alone, but also rely on further analytical features by scanning the photon energy. Given that each molecule has characteristic bands in its threshold photoelectron spectrum (ms-TPES), we assign the most abundant species by comparing them to literature reference spectra or Franck-Condon simulations obtained from quantum chemical calculations. This procedure has been proven to be an efficient analytical tool, to monitor chemical reactions in complex environments, such as the one investigated here [24,35].

2.4.1 Characterization of hydrocarbons and oxygenated species

Spectra of the most abundant species obtained at 776 K are shown in **Figure 4**. Because of the large internal energy of the neutrals obtained in the heated reactor, hot bands are responsible for non-zero signal levels below the adiabatic ionization onset in all the spectra observed here. We can clearly identify strong signals of hydrocarbons and oxygenated species at m/z 42, 58, 64, 82. In **Figure 4 (a)** we observe strong bands at m/z 42 between 9.6 and 10.2 eV. The spectrum shows clear vibrational features of ketene (9.62 eV) [36], but we cannot exclude minor contributions of propene (9.73 eV) [37], which both have the same nominal mass. We observe a clear band at 9.74 eV in the TPES of m/z 58, which aligns well with the published spectrum

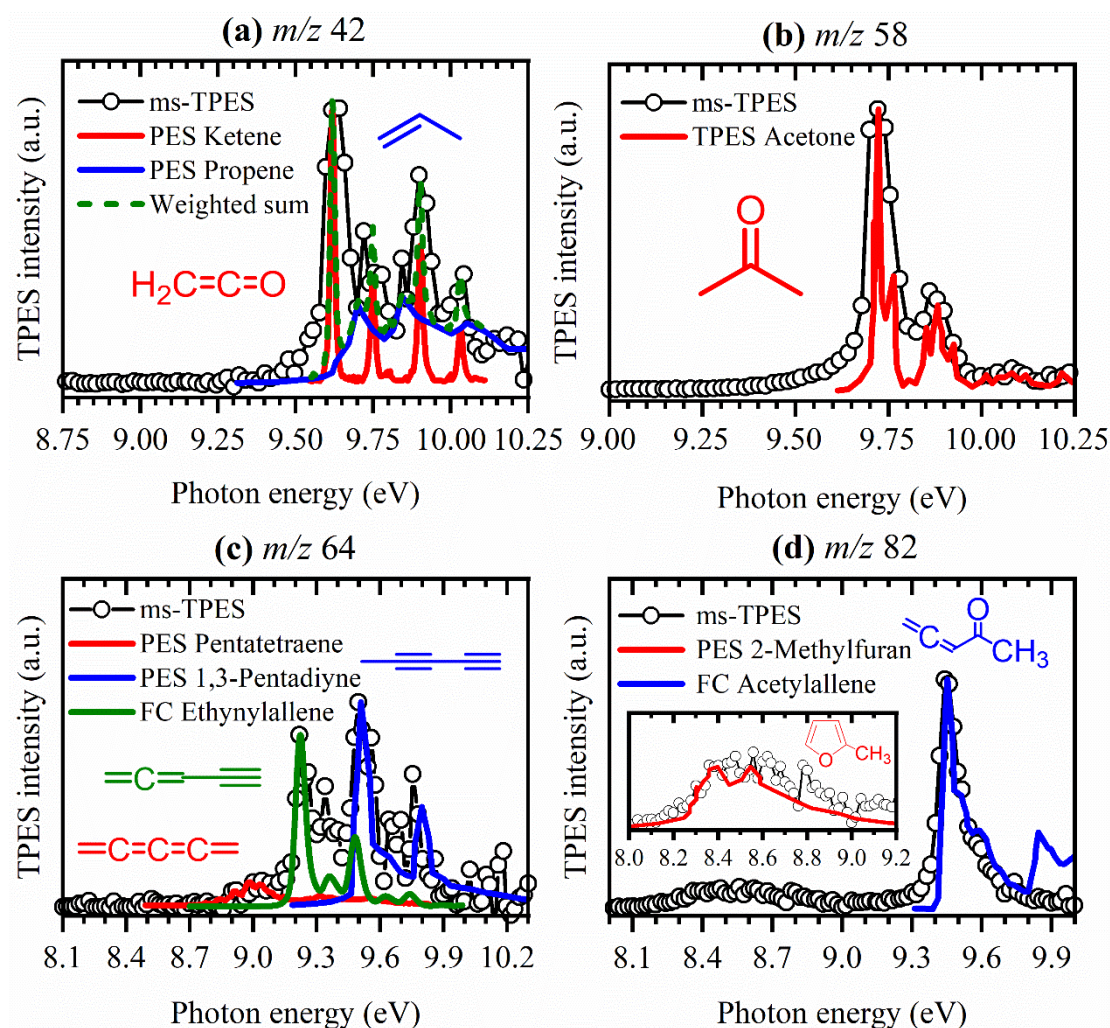


Figure 4 Representative examples for species identification and assignment of the major decomposition by-products using experimentally obtained TPE spectra (black dots and lines) recorded at 776 K; species are either characterized by literature reference spectra in (a)-(d), by specific ionization onsets in (c) or Franck-Condon simulations (FC) in (d). References are as follows: (a) m/z 42 red: ketene (C_2H_2O) [36], blue: propene (C_3H_6) [37]; (b) m/z 58 red: acetone (C_3H_6O) [33]; (c) m/z 64 C_5H_4 red: pentatetraene [37], blue: 1,3-pentadiyne [38] and green: ethynylallene [this work]; (d) m/z 82 C_5H_6O : red: 2-methylfuran, blue: acetyllallene.

of acetone (9.70 eV [33]) in **Figure 4 (b)**. The analysis of the spectrum in **Figure 4 (c)** shows, that we can distinguish between three isomers at m/z 64, whereas 1,3-pentadiyne (9.50 eV [38]) and ethynylallene (FC-simulation: 9.22 eV) are the spectral carriers. Traces of pentatetraene (8.99 eV [37]) could also be identified by a weak signal increase at around 8.9 eV. Because of the vibrational progression of the ground state band of 1,3-pentadiyne and the limited signal-to-noise ratio (SNR), traces of other isomers with m/z 64 with higher ionization energies are, if present, difficult to characterize. The majority of the ms-TPE signal at m/z 82 with a strong band at 9.50 eV fits to the published Franck-Condon simulated spectrum of acetyllallene (9.44 eV [34]). Minor contributions below 9.0 eV are assigned to its cyclic isomer 2-methylfuran (8.38 eV [39]). As already indicated in **Figure 3**, a few larger hydrocarbons with masses > 100 could also be identified in the mass spectra and we characterize these by using both, their PIE and ms-TPE signals and compare these to literature references (see **Figure 5**). The low energy

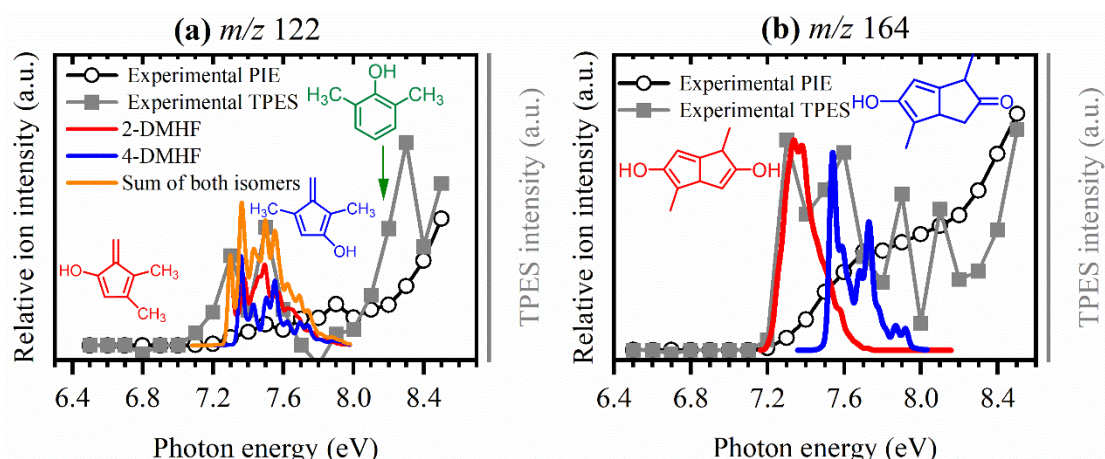


Figure 5 Representative examples of species identification and assignment of major species at a temperature of 676 K at masses > 100 using experimental obtained TPE spectra (grey squares and lines) and PIE curves (black dots and lines); species are either characterized by literature reference values (red label) in (a) or spectra obtained from FC-simulations (red and blue lines) in (b). References are as follows: (a) m/z 122 $C_8H_{10}O$: 2- and 4-dimethylhydroxyfulvene (red) [this work] and (blue) [this work]; 2,6-dimethylphenol (green) [42], (b) m/z 164 $C_{10}H_{12}O_2$ [27].

part of the ms-TPES at m/z 122 can be assigned to dimethyl-substituted hydroxyfulvenes. We have calculated four isomers, which possess *AIEs* of 7.57, 7.34, 7.26 and 7.35 eV (G4), respectively. A linear combination of the two isomers in the 7.34-7.35 eV energy range reproduce the ms-TPE spectrum well, but we cannot exclude contributions from the other isomers. Despite the matching *AIEs* and FC simulations, such species make also chemically sense as fulvene ($c\text{-}C_5H_5=CH_2$) is a well-known precursors for benzene [40,41]. In analogy to our substitution pattern, we expect the fulvene moiety, probably produced as intermediate after a ketene ($H_2C=C=O$) loss from m/z 166 to rearrange to dimethylphenol (also m/z 122). Based on the sharp increase of the PIE curve at energies > 8.0 eV on the m/z 122 channel in **Figure 5 (a)**, contributions of 2,6-dimethylphenol with an adiabatic IE of 8.05 eV [42] were detected. The comparison with Franck-Condon simulations of the spectrum at m/z 164 revealed, two isomers of a cyclic hydrocarbons with the formula $C_{10}H_{12}O_2$, which are the main contributors to the overall signal in our TPE-spectrum of m/z 164 in **Figure 5 (b)**. Dimethyl-dihydroxodihydropentalene [27] is identified by a sharp signal increase at its IE of 7.29 eV [27], whereas its isomer dimethyl-hydroxo-keto-tetrahydropentalene (IE 7.55 eV [27]) is the spectral carrier at energies > 7.55 eV.

Besides the assignments that were discussed so far, other minor products and intermediates were identified and characterized in the same manner. Their assignments are shown in **Table 1** and some of the spectra are included in **Figure S 7 the ESI**. Since the sample is highly diluted and only small amounts of the minor products were identified, they are not considered in the major thermal decomposition pathways discussed later in the text.

2.4.2 Identification and assignment of volatile zirconium species

Experimental data of the ionization onset, ionization cross sections and photoelectron spectra of metal-containing intermediates are, due to their high reactivity, scarce in the literature. For this reason, we utilized the isotopic pattern to identify which intermediates contain zirconium. Additionally, we measured the ionization onsets of the most abundant zirconium-containing intermediates in the gas phase, which will be useful in future studies.

Figure 6 shows a compendium of the most abundant species detected upon pyrolysis. The distribution of the zirconium isotopes is indicated by blue sticks in the respective spectra, with a focus on the four most intense isotopes at ^{90}Zr , ^{91}Zr , ^{92}Zr and ^{94}Zr . Here, by comparing the isotopic pattern to our mass spectra, it can be easily recognized, that zirconium species are present, hinting that these species have the general formula (m/z 286, $\text{Zr}(\text{C}_5\text{H}_6\text{O}_2)_2$; m/z 304, $\text{Zr}(\text{OH})(\text{C}_5\text{H}_7\text{O}_2)(\text{C}_5\text{H}_6\text{O}_2)$; m/z 344, $\text{Zr}(\text{C}_5\text{H}_7\text{O}_2)(\text{C}_5\text{H}_6\text{O}_2)(\text{C}_3\text{H}_5\text{O})$ and m/z 386, $\text{Zr}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{C}_5\text{H}_6\text{O}_2)$), respectively. The respective ion VMI images of these species confirm that they originate from pyrolysis and are no dissociative ionization products (see **Figure 6**

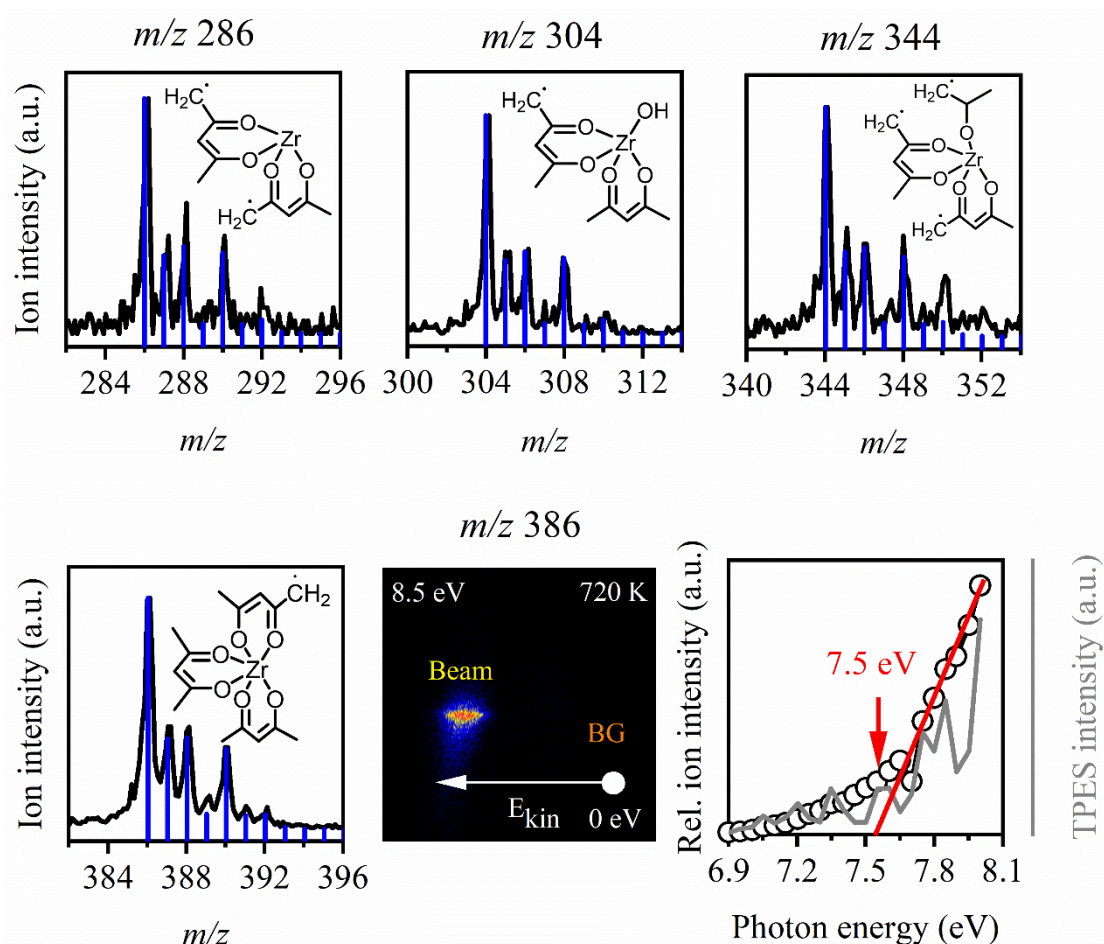


Figure 6 Identification of the most abundant gaseous zirconium-containing intermediates detected in the pyrolysis of $\text{Zr}(\text{acac})_4$ at a surface temperature of 775 K in helium (**Top**) and at a temperature of 720 K (**Bottom (left)**). Blue sticks indicate the isotopic pattern of the zirconium-containing species. **Bottom (Middle)**: Ion velocity map image (VMI) for the m/z 386 channel; narrow kinetic energy distributions approves that the species is formed in the reactor rather than a product of dissociative ionization (fragmentation). **Bottom (Right)**: Photoion intensity curve (PIE) (black) and threshold photoelectron spectrum (ms-TPES) (red) of m/z 386, where a clear ionization onset at 7.5 ± 0.2 eV was identified.

bottom (middle) and **Figure S 8** in the ESI). We also determined the ionization onsets of these species and recorded spectroscopic fingerprints (ms-TPES and PI spectra) of those volatile intermediates of zirconium for the first time (see **Figure 7**). The ionization onsets of the zirconium intermediates have been determined by a Wannier-type linear fit [43–45] to be 7.4 ± 0.2 ; 7.6 ± 0.2 ; 7.6 ± 0.2 , 7.5 ± 0.2 , 7.7 ± 0.2 and 7.5 ± 0.2 eV for m/z 204, 222, 286, 304, 344 and 386, respectively (see **Figure 6, bottom (left)**, **Figure 7**). It is evident from **Figure 7** that the ionization onsets of the zirconium intermediates are close to the *AIE* of the precursor, however only a tentative isomeric structure can be given here, as open-shell heavy atom

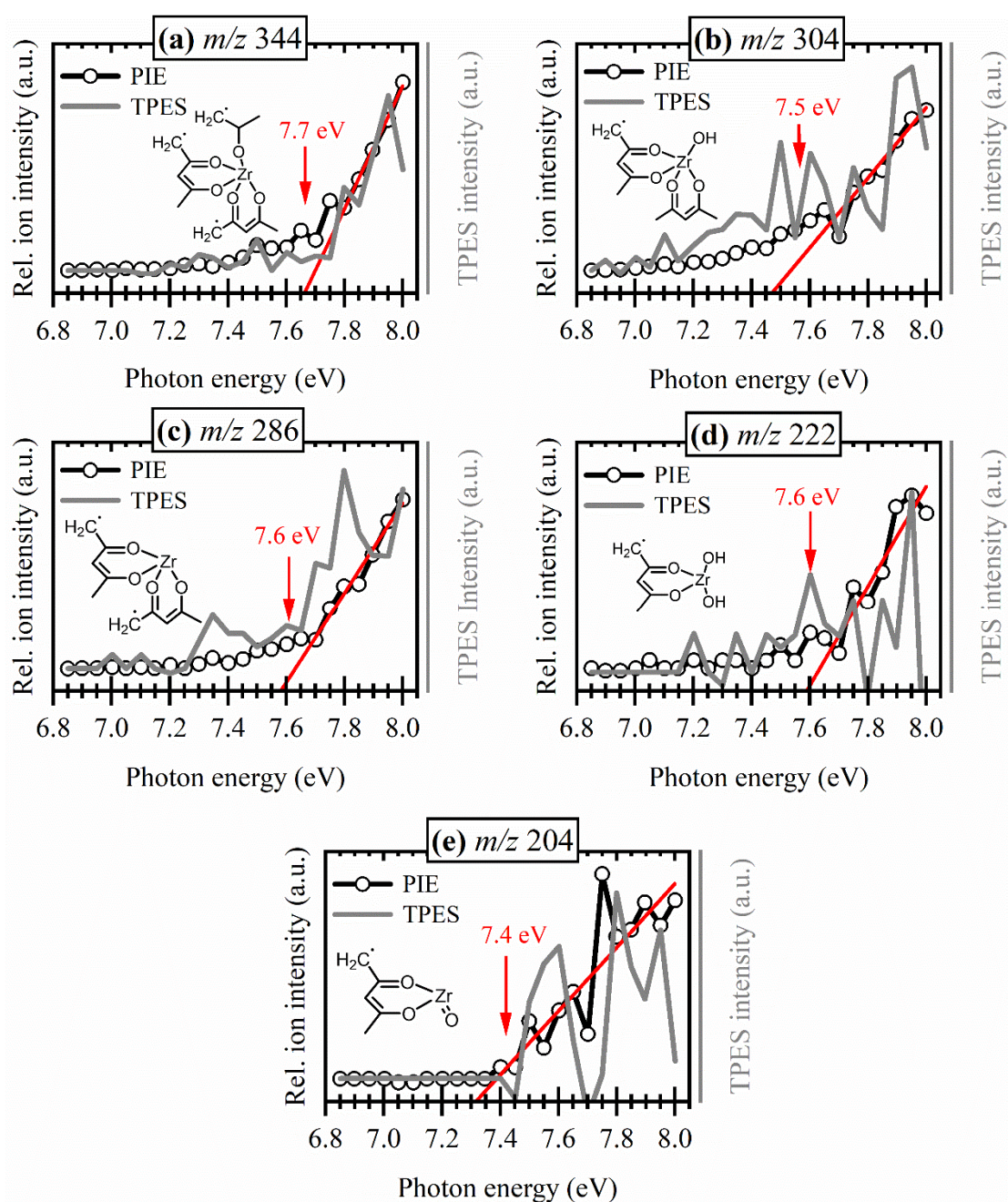


Figure 7 Recorded PIE-curves (black lines, symbols) and ms-TPE spectra (grey lines) of secondary zirconium species detected upon pyrolysis of $\text{Zr}(\text{acac})_4$ at 776 K. The adiabatic ionization onsets were determined by evaluating the intersection between the slope of the red line with the x-axis according to a Wannier-type linear fit. The isomeric structures are tentative ones.

calculations are outside the scope of the current study. All ionization potentials determined in this study are summarized in **Table 1** and indicated by a dagger symbol. Possible mechanisms to the formation of these intermediates are discussed in the following paragraph. All these characterized species may lead to the formation of ZrO₂ thin films, whereas additional oxygen is needed for its formation [23].

Table 1: List of identified species upon pyrolysis of Zr(C₅H₇O₂) by VUV-i²PEPICO using their adiabatic and vertical ionization energies, and, where necessary, their distinct isotopic pattern. Reference spectra and energies have been taken from the literature and are denoted at the respective value. The identification of the compounds in bold are discussed further in the paper. Species marked with an asterisk are tentatively assigned, based on mechanistic evidence.

<i>m/z</i>	Formula	Name	IE (eV)
			Reference
15	CH ₃	Methyl radical	9.84 [46]
39	C ₃ H ₃	Propargyl radical	8.71 [47]
42	C₂H₂O	Ketene	9.62 [36]
	C₃H₆	Propene	9.73 [37]
43	C ₂ H ₃ O	DPI Acetone	AE: 9.5 eV [†]
		DPI Acetylacetone	AE: 10.2 eV [†]
58	C ₃ H ₆ O	Acetone	9.70 eV [33]
60	C ₂ H ₄ O ₂	Acetic Acid	10.69[48]
64	C₅H₄	Pentatetraene	8.99 [37]
		Ethynylallene	9.22 [†]
		1,3-Pentadiyne	9.50 [38]
82	C₅H₆O	2-Methylfuran	8.38 [39]
		Acetylallene	9.44 [34]
100	C₅H₈O₂	Acetylacetone (enol)	8.90 [34]
		Acetylacetone (diketo)	9.50 [34]
122	C₈H₁₀O	2,6-Dimethylphenol	8.05 [42]
		2-Dimethylhydroxofulvene	7.34 [†]
		4-Dimethylhydroxofulvene	7.35 [†]
146	C ₁₁ H ₁₄	2,4,6-Trimethylstyrene	7.72 [49]
164	C₁₀H₁₂O₂	Dimethyl-dihydroxo-dihdropentalene	7.29 [27]

		Dimethyl-hydroxo-keto-tetrahydropentalene	7.55 [27]
204	ZrO(C₅H₆O₂)	Zr-intermediate	$7.4 \pm 0.2^{\dagger}$
222	Zr(OH)₂(C₅H₆O₂)	Zr-intermediate	$7.6 \pm 0.2^{\dagger}$
286	Zr(C₅H₆O₂)₂	Zr-intermediate	$7.6 \pm 0.2^{\dagger}$
304	Zr(OH)(C₅H₇O₂)(C₅H₆O₂)	Zr-intermediate	$7.5 \pm 0.2^{\dagger}$
322*	Zr(OH) ₂ (C ₅ H ₇ O ₂) ₂	Possible surface product	Not detected
344	Zr(C₅H₇O₂)(C₅H₆O₂)(C₃H₅O)	Zr-intermediate	$7.7 \pm 0.1^{\dagger}$
386	Zr(C₅H₇O₂)₂(C₅H₆O₂)	Zr-intermediate	$7.5 \pm 0.2^{\dagger]$
387	Zr(C₅H₇O₂)₃	DPI from <i>m/z</i> 486	AE: 7.95 eV [†]
486	Zr(C₅H₇O₂)₄	Zirconium acetylacetonate	7.95 eV [50]

[†] Values from this work

2.5 Pyrolysis pathways of zirconium acetylacetonate

After successful identification of the relevant hydrocarbons and zirconium intermediates formed in the pyrolysis of Zr(acac)₄, their temperature-dependence is investigated. The centerline temperatures given are deduced from the CFD simulations (see **Section 3.1**). The precursor signal, as well as its first decomposition products in two inert bath gases argon (left graph) and helium (right graph) are shown in **Figure 8**, while the temperature dependencies of the most important intermediate species from a possible surface-mediated decomposition step, as well as from secondary zirconium intermediates that are formed from the primary decomposition products are displayed on the middle and lower trace of **Figure 8**. We note, that the type of bath gas changes the branching ratios of the products, for example, the amount of acetylacetone, represented by its major fragment *m/z* 85 increases considerably by a factor of three when argon is used as carrier gas. This phenomenon can be explained, by shorter residence times and a more uniform temperature distribution in the microreactor with a larger high-temperature zone, when helium is used as bath gas. The same observation is made for other zirconium species as well, whose signal intensity is five-times higher in the helium case, pointing to rapid formation and decomposition reactions of these intermediates. These fast reactions explain, why these intermediates were not observed in previous experiments using reactors with longer residence times. However, the difference in the decomposition mechanism

between the two dilution gases is gradual and mainly due to different time-temperature history. Consequently, the mechanistic findings that are described in the following are valid for both seed gases.

Combining the species assignments from the previous paragraphs, together with the species profiles in **Figure 8**, enables us to describe the dominant decomposition pathways in the temperature range from 400-900 K (see **Scheme 1**). Although, the temperature onset of decomposition at around 450 K found in this study is in accordance to the observation of others, who determined the onset of thermal decomposition to be around 450-550 K [18,19,51], the thermal decomposition pathways of $\text{Zr}(\text{acac})_4$ suggested here differs from previously published ones. It was stated in the literature, that zirconium acetylacetonate either decomposes by a coordination polymerization step of its, yet unknown, initial decomposition product [51], or, $\text{Zr}(\text{OH})(\text{CH}_3\text{COO})_3$ forms. The latter one was rationalized by the corresponding weight loss and the detection of C_3H_4 and $\text{C}_2\text{H}_3\text{O}_2$ at temperatures from 438 to 563 K by thermogravimetric and spectroscopic measurements [17–19], which mainly observe condensed phase chemistry. Another possible reaction path was observed, in which cyclic diketones are formed by an intramolecular interaction of two neighboring ligands [51].

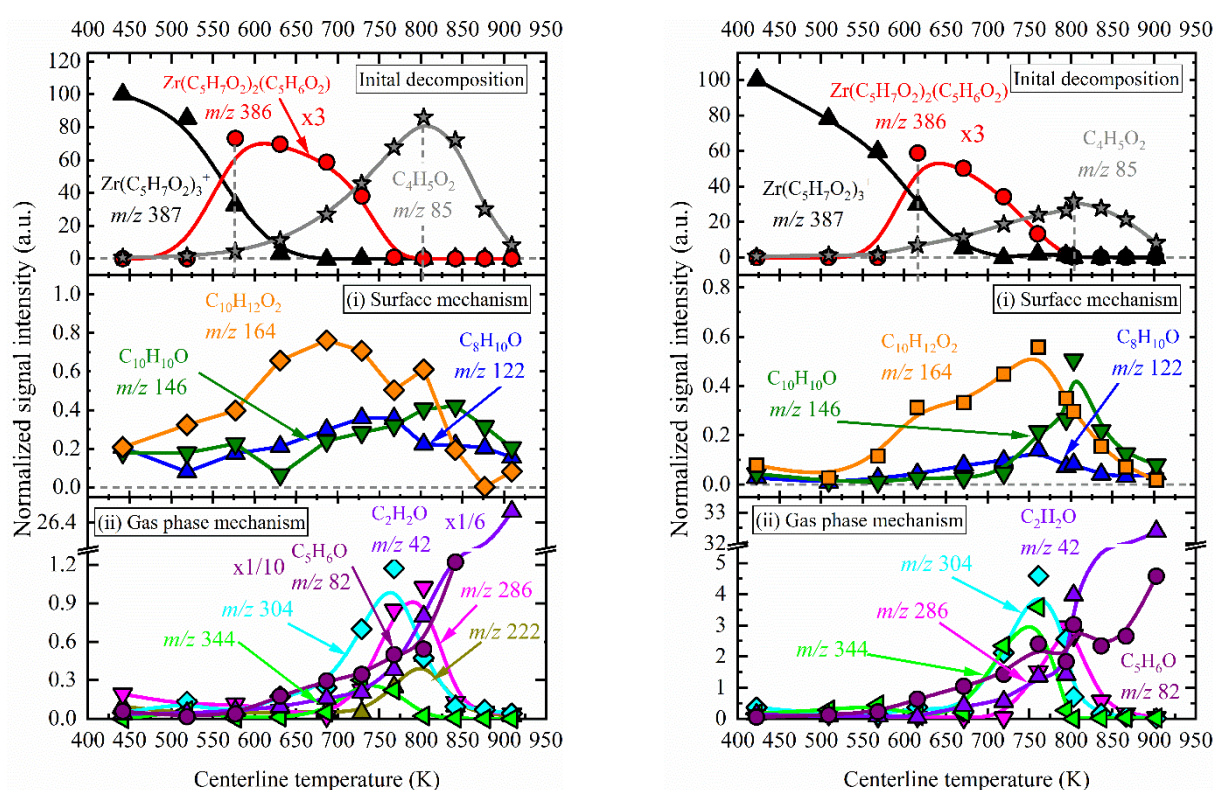
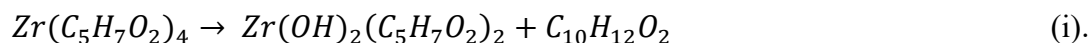


Figure 8 Temperature-dependent species profiles of intermediates and products upon the thermal decomposition of $\text{Zr}(\text{acac})_4$ at $T_{\text{vap}} = 403$ K (0.0048 %) in argon (left) and helium (right), probed by $i^2\text{PEPICO}$ VUV-mass spectrometry in the microreactor. The respective species that were characterized according to **Section 2.4** are labelled by their formula and all signals are normalized to the initial zirconium main fragment signal at m/z 387 at a photon energy of 8.5 eV. Note that the axis in the bottom trace of both graphs contain a break in order to display all signals that belong to the secondary decomposition of the zirconium intermediates.

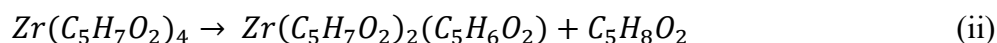
However, the results obtained in this study only partially agree with previous findings. We found a single heavier species than $\text{Zr}(\text{acac})_4$ at m/z 691 in our mass spectra, but verified by the VMI ion images, the detected species at m/z 691 is rather a cluster ion or a fragmentation product and can therefore not be ascribed as thermal decomposition product. This observation disagrees with the literature, where a dimerization product was found [51]. Its absence in the present study may be owed to the much higher dilution and an order of magnitude shorter residence times in the microreactor.

Furthermore, different temperature windows are recognized in the species profiles of **Figure 8**, which indicate three separate mechanisms. A surface-mediated mechanism that forms oxygenated cyclic hydrocarbons by a cyclic dimerization reaction of two neighboring ligands starting at temperatures > 500 K, leading to zirconium species, which may be attached to the surface and thus were not detected in the gas phase:

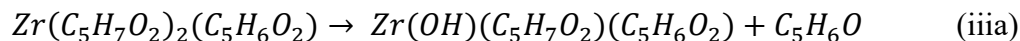


This pathway has been verified for similar group III and IV metal- β -diketonates and the formation of the three isomers detected at m/z 122 can be explained by a loss of ketene ($\text{C}_2\text{H}_2\text{O}$), which we found in our mass spectra starting from temperatures 575 K (see **Figure 8**, bottom trace) [27,51].

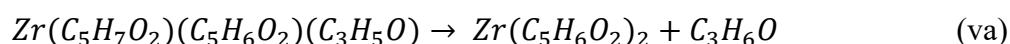
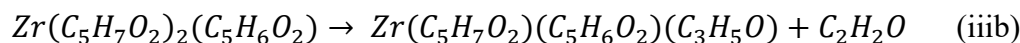
In contrast to other work, we neither found evidence for the formation of C_3H_4 , nor considerable amounts of acetic acid upon pyrolysis at low temperatures, which would lead to metal acetate species as primary decomposition products on the surface [18]. Instead, we detected zirconium tris(diketo)acetylacetonate-H, $\text{Zr}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{C}_5\text{H}_6\text{O}_2)$ and acetylacetone ($\text{C}_5\text{H}_8\text{O}_2$), as primary decomposition products which are formed in a unimolecular decomposition step according to:



We interpret these findings similar as in our previous study on the decomposition of $\text{Al}(\text{acac})_3$ [27], where an H-transfer from the CH_3 group of a neighboring acetylacetonate ligand to the second equatorial ligand initiates this reaction sequence, in which at first, one of the metal-oxygen bonds is cleaved. This step produces a weakly bound intermediate from which the second Zr-O bond breaks readily, yielding m/z 386 $\text{Zr}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{C}_5\text{H}_6\text{O}_2)$ and acetylacetone. This pathway is in line with the temperature-dependent species profiles, where the trace of m/z 387 (major fragment of $\text{Zr}(\text{acac})_4$) exhibits a steep decrease, while m/z 386 and 100 are increasing simultaneously. Given the absolute intensities, we can plausibly state that this H-transfer mechanism is the dominant primary decomposition step in pyrolysis of $\text{Zr}(\text{acac})_4$. All preceding steps that were observed can be traced back to a thermal fragmentation of the primary decomposition product m/z 386 $\text{Zr}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{C}_5\text{H}_6\text{O}_2)$, resulting in further zirconium intermediates, whose existences were suspected by others [23], but until now, has not been experimentally validated. The following gas phase decomposition mechanism at temperatures above 575 K follows two branches, where m/z 386 first undergoes a series of $\text{C}_5\text{H}_6\text{O}$ loss reactions leading to the stepwise formation of m/z 304, $\text{Zr}(\text{OH})(\text{C}_5\text{H}_7\text{O}_2)(\text{C}_5\text{H}_6\text{O}_2)$, and m/z 222 $\text{Zr}(\text{OH})_2(\text{C}_5\text{H}_6\text{O}_2)$, respectively:

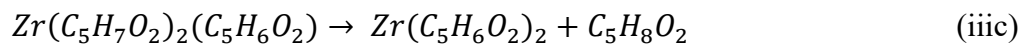


These steps are corroborated by identifying m/z 82 as acetyllallene at temperatures above 575 K and a simultaneous formation and decomposition of m/z 304 (see **Figure 8, bottom trace**). Another decomposition pathway of m/z 386 was identified in the same temperature window. After a loss of ketene ($\text{C}_2\text{H}_2\text{O}$), followed by a subsequent acetone ($\text{C}_3\text{H}_6\text{O}$) loss at temperatures higher than 750 K, m/z 286 ($\text{Zr}(\text{C}_5\text{H}_6\text{O}_2)_2$) is formed in the gas phase according to:

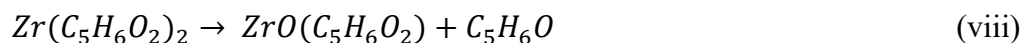
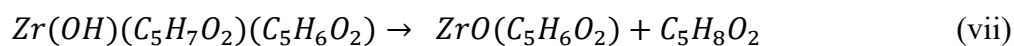
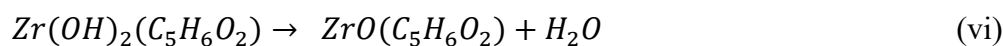
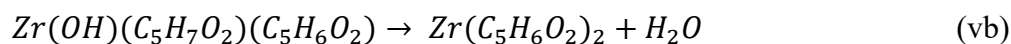


Similarly, ketene, acetone, as well as m/z 286, $\text{Zr}(\text{C}_5\text{H}_6\text{O}_2)_2$ were unambiguously identified in this temperature regime by their spectroscopic fingerprints, ion images and species profiles. The primary decomposition products m/z 386 may also lose another ligand at temperatures

above 725 K leading to the direct formation of m/z 286 following a similar mechanism as proposed for the initial cleavage of one ligand from $Zr(acac)_4$ in reaction (ii):

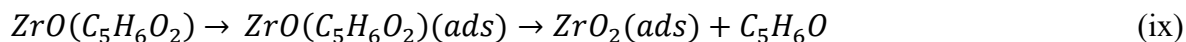


Further decomposition of zirconium intermediates in the gas phase was observed, starting at temperatures above 750 K. Here, the secondary zirconium intermediates, m/z 304, m/z 286 and m/z 222 decompose in probably unimolecular reactions yielding m/z 204, which is evidenced by the Zr-isotopic pattern in our mass spectra (see **Figure 3, bottom**). We propose four possible pathways that are in line with our findings:



The species with m/z 286 and 204 are probably formed in reaction (vb) and (vi) after water abstraction. Note that the latter is not observed in the mass spectra in **Figure 3**, due to its high ionization energy. Both reaction sequences, (vb) and (vi), are attributed to gas phase reactions, because the detected zirconium intermediates are expected to have very small vapor pressures and condense on the surface of the reactor. While acetylacetone can be formed from m/z 304 in reaction (vii), acetylallene may be formed in reaction (viii) from m/z 286. The occurrence of these reactions is substantiated by the steep increase of the ion signal intensity of m/z 100, acetylacetone between 750 and 800 K and the increase of m/z 82 at temperatures above 800 K, respectively. Given the absolute intensities of each of the oxygenated hydrocarbon products formed in these reactions, it appears, that the loss of acetylallene from m/z 286 is the dominant pathway.

The reason for the small quantities of m/z 204 found in the gas phase in our study may be due to an immediate subsequent decomposition of this intermediate forming acetylallene resulting in the formation of the final product m/z 122, ZrO_2 , on the surface of the microreactor:



Since we found a steep increase in m/z 82 at high temperatures > 800 K in the mass spectra, we think that such processes starting from reaction (ix) are dominant. However, other zirconium intermediates may also adsorb on the surface and may reside there, until oxidation to ZrO_2 occurs at temperatures above 1073 K in oxygen rich atmosphere [18], or an incomplete oxidation to ZrO_xC_y might occur, leaving a considerable carbon deposit on the reactor walls [23].

As expected from previous studies on the high temperature pyrolysis of acetylacetone [34,52], the observation of large amounts of ketene and acetone most likely stem from an unimolecular decomposition of acetylacetone through a C-C bond cleavage followed by a subsequent H-atom transfer. As indicated by the decrease in acetylacetone signal at temperatures above 800 K, we attribute the main fraction of these products to the decomposition of the liberated ligands, rather than to additional surface or gas phase decomposition products in the high temperature region.

3. Conclusion

We have investigated the pyrolysis of $\text{Zr}(\text{acac})_4$, a common precursor used in the synthesis of ZrO_2 thin films, by VUV soft ionization from a synchrotron light source coupled to double imaging photoelectron photoion coincidence spectroscopy ($i^2\text{PEPICO}$).

The accompanying numerical simulation of the microreactor's flow field by CFD confirmed that helium is the preferable inert gas ensuring low average residence times of < 15 μs and uniform temperature fields as compared to argon. For helium dilution, the experimental flow field approaches a plug-flow and the temperature of intermediate formation is close to the experimentally accessible wall temperatures. Additionally, the low residence times and much higher signal levels are advantageous for the detection of elusive zirconium intermediates.

We have identified the main gas phase degradation products formed in the evaporator prior to decomposition of the precursor in the microreactor. Interestingly, we cannot confirm previous observations that acetic acid and C_3H_4 are the major products formed, instead acetylacetone and acetone are the major gas phase species evolving from degradation in the evaporator. At our conditions, we could ensure stable evaporation conditions for several hours using an evaporation temperature of 403 K.

We showed, that the pyrolysis of $\text{Zr}(\text{acac})_4$ can be divided into three major steps, which take place in distinct temperature regimes starting from 525, 750 and 850 K. For the first time important zirconium intermediates formed in the gas phase were identified by analyzing the

isotopic pattern of zirconium, the momentum distribution of the ions (VMI), as well as the PI and ms-TPE spectra. In addition, we determined adiabatic ionization energies of these species for the first time, which may be of interest for subsequent kinetic investigations and theoretical studies. Besides minor amounts of possible surface reactions, which form aromatic hydrocarbons with masses > 100 , in particular 2,6-dimethylphenol ($C_8H_{10}O$), two dimethylhydroxo-fulvene isomers, as well as two isomers of $C_{10}H_{12}O_2$, we found strong evidence that the majority of the thermal decomposition of $Zr(acac)_4$ occurs in the gas phase. Here, $Zr(C_5H_7O_2)_2(C_5H_6O_2)$ (m/z 386) together with acetylacetone was identified as primary decomposition product at temperature above 525 K. In a further sequential decomposition of this intermediate at temperatures 550-750 K, mainly zirconium complexes like $Zr(OH)(C_5H_7O_2)(C_5H_6O_2)$ (m/z 304), and $Zr(C_5H_6O_2)_2$ (m/z 286), are formed in the gas phase and their reaction pathways are discussed. Several hydrocarbons are formed as by-products, such as acetyllallene, acetone and ketene, which were all identified unambiguously by their spectroscopic fingerprint in the gas phase. Probably these species are then adsorbed on the surface of the reactor. By surface reactions they may produce ZrO_xC_y films, which, under excess oxygen, may be oxidized to form ZrO_2 layers at temperatures higher than 1000 K. The present findings help to solve open questions in the mechanism of similar CVD precursors to model the growth of thin films, as well as the particle formation and growth processes and thus contribute to an increase in the yield of the desired product.

4. Materials and Methods

4.1 Experimental Setup

The experiments were conducted at the vacuum ultraviolet (VUV, x04db) beamline of the Swiss Light Source (SLS) synchrotron facility located at the Paul Scherrer Institute (PSI) in Switzerland. The working principle of the Chen-type pyrolysis microreactor [27,53] coupled to the imaging i^2 -PEPICO spectrometer [54,55], as well as the VUV-beamline characteristics [56] have been described in detail before [27]. Only a brief explanation of the most important parts is given here. A schematic sketch of the setup can be found in the ESI (see **Figure S1**).

The $Zr(acac)_4$ powder was purchased from TCI Chemicals and was used without further purification. Approximately 2 g of the precursor was placed inside a stainless-steel tube with a 100 μm pinhole at the tip. In order to sublime the solid precursor, the sample was heated by two temperature-controlled cartridge heaters placed centrally inside two drillings of an isothermal copper block. The sublimation temperature was continuously monitored by two type-K thermocouples with an accuracy of ± 0.75 % and the pressure was held at approximately 2.0-

2.5×10^5 Pa. To entrain the gaseous precursor molecules and carry them into the reactor, either argon (99.999 %) or helium (99.999 %) was passed by calibrated mass flow controllers (MKS Instruments Inc.) to the evaporator with a constant flow rate of 22 sccm. Assuming thermal equilibrium in the evaporator and with the measured vapor pressure data from Morozova et al. [57], precursor concentrations of 17-1925 ppm entering the reactor were determined. In a first set of experiments, the temperature T_{vap} of the evaporator was varied from 393 to 443 K, to investigate the possible degradation of the precursor, prior to entering the microreactor. Based on these findings, the precursor concentration is kept constant at 48 ppm ($T_{\text{vap}} = 403$ K) in the seed (argon or helium) for the pyrolysis experiments. This low concentration largely suppresses bimolecular reactions [27,29,30] and ensures stable evaporation conditions in our reactor.

The saturated gas phase was then expanded to a SiC microtubular reactor ($L = 15$ mm; I.D. = 1 mm; O.D. = 2 mm), which was resistively heated and its outer surface temperature was measured by a centrally fixed type-C thermocouple with a maximum deviation of reading of ± 1 %. As pointed out by others, residence times of < 100 μs and pressures of a few tens of mbar can be expected in these Chen-type reactors [30]. A detailed examination of the flow field characteristics in the microreactor under the experimental conditions applied in this study is discussed in the course of the numerical simulation in the following section, which we conducted in a similar way as in our recent publication [27].

After passing the reaction zone, the products are expanded to high vacuum of 5×10^{-5} mbar to form a molecular beam, which suppresses further chemical reactions. The central part of the beam is cut out by a 2 mm conical nickel-skimmer and the remaining gas sample flows towards the ionization region at a background pressure $< 6 \times 10^{-6}$ mbar.

For VUV soft ionization, synchrotron radiation is collimated, dispersed by a grazing incidence monochromator with a 150 lines/mm laminar grating, and focused at the exit slit in a differentially pumped gas filter at a photon energy resolution of 5 meV (characterized at an incident photon energy of 8 eV). To suppress potential artificial signals due to higher-order radiation, diffracted by the grating, a differentially pumped gas filter was filled with a mixture of argon, neon and krypton or a MgF_2 mirror was used. The incoming photon energy was calibrated before the experiments, using the auto ionization lines (s' Rydberg series) in both the first and second order [58].

In the ionization volume, the molecular beam intersects with the VUV-light at a given energy, leading to photoions and photoelectrons, respectively. Both are separated in a constant electrical field of 213 V cm^{-1} and velocity map imaged (VMI) and detected, using position sensitive delay-line anode detectors (Roentdek, DLD40) in a multi-start, multi-stop approach [59]. In contrast

to conventional mass spectrometry, VMI allows to evaluate the kinetic energy distribution of the molecules as additional analytical dimension (see **Figure S 1**, “Ion Image”). By reducing the region of interest (ROI) to only the molecular beam component and choosing ionization energies close to the threshold of the specific molecules of interest, background free mass spectra can be recorded and dissociative ionization can be minimized suppressed. Plotting the threshold photoelectron signal in coincidence with the cation mass-to-charge ratio as a function of the photon energy yields the photoion mass-selected threshold photoelectron spectrum (ms-TPES), which enables isomer-selective assignment of intermediates and stable products by comparing to reference data or to Franck-Condon simulations [60]. During post-processing, these spectra are corrected for artificial hot-electron contributions as outlined by Sztaray and Baer [58] and normalized by the corresponding photon energy specific photon flux. Franck-Condon simulations were performed with the program ezSpectrum [61], while geometries and Hessian matrixes were calculated at the B3LYP/GTbas3 level of theory with Gaussian16 [62]. Adiabatic ionization energies (*AIE*) were determined using the G4 composite method.

The i²PEPICO experimental apparatus can register the molecular mass, as well as the photoionization and threshold photoelectron spectrum of the species of interest. These data can be compared to literature data, i.e. photoelectron spectra and used in this way for an unambiguous and isomer-selective characterization of most of the primary decomposition products [55]. In all experiments, we either kept the photon energy constant at near-threshold photoionization energies of the decomposition species of interest, or scanned the energy incrementally at constant temperatures of 676, 776 and 803 K. With the aim to detect most of the expected hydrocarbon and oxygenated decomposition products, we scanned with a step size of 0.025 eV in the 8.0–11.5 eV range and used a neon/argon/krypton gas mixture in the gas filter. Volatile zirconium species are expected to ionize at relatively low energies of < 8.0 eV. To detect these species the MgF₂ window was used. Photon losses at the window lead to much longer averaging times, but also better filtering of the higher harmonic radiation. To economize on beam time, the larger averaging times were in part compensated by a larger step width of 0.1 eV. Unfortunately, the signal-to-noise ratios of the ms-TPES were not sufficient to determine accurate ionization thresholds for intermediate species from these data, because these species are only present in small quantities. Additionally, Franck-Condon factors are hard to determine numerically. To overcome this issue, we estimated the values of the adiabatic ionization energies (*AIE*) of the unknown intermediate species, by a Wannier-type linear to the photoionization spectra [43–45]:

$$PIE(h\nu) = m * (h\nu)^1 + b \quad (1)$$

, where m is the slope of the fit and b represents the intersection with the y -axis. By finding the intersection between the fit and the photon energy-axis, adiabatic ionization energies can be determined with an estimated accuracy of ± 0.2 eV [44,45].

We were able to record a series of temperature-dependent mass spectra at 8.0-11.5 eV with an 0.5 eV increment in the temperature range from 400 K to 900 K, where most reactions should occur. The recorded spectra enable us to derive temperature-dependent species profiles and evaluate the reaction mechanism.

4.2 Numerical setup

The characterization of the flow field in the microreactor is important in order to accurately determine reaction conditions and extract reliable mechanistic and kinetic data. As demonstrated in previous work, given that the inlet and outlet pressure, as well as the exterior wall temperature are measured and the mass flow rate is constant, numerical simulations of these kind of microreactors are possible [27,29,30]. It has been shown both experimentally and numerically, that such resistively heated flow tubes have a non-uniform temperature and pressure distribution, which strongly depends on the seed gas used [30,31,63]. Recent studies with similar microreactors state, that using helium as carrier gas instead of argon not only yields better signal intensities and therefore smaller averaging times, but also a more plug-flow like flow field in the microreactor, which is beneficial for the interpretation of chemical kinetics. These benefits will most likely maximize the detection of short-living intermediates upon thermal decomposition of $Zr(acac)_4$ in the microreactor [30,31]. Since the geometries and the experimental conditions such as pressure and temperature examined by previous studies differ from ours, we decided to conduct a computational fluid dynamics (CFD) study using ANSYS Fluent 19.1 [64] with both, helium and argon, as dilution gas. Since the precursor is highly diluted, its contribution is negligible for the flow field calculations, such that the simulations were performed with pure argon and helium, respectively.

Previous studies on flow fields in microreactors [27,29–31] have also demonstrated that the gas velocity strongly accelerates up to the sonic condition near the outlet of the reactor. Therefore, the flow in the microreactor should be modelled with the slip regime corresponding to the range of Knudsen number ($0.01 \leq Kn \leq 0.1$). In the present study, we solved the Navier-Stokes equations combined with a slip (boundary) condition at the wall, in order to account for these

effects and accurately model the flow in the slip region. Because the microreactor was directly connected to a high vacuum chamber, the compressibility of the flow was taken into account in the simulation. Further details on the numerical domain and all relevant equations and boundary conditions used in this study are summarized in **section S 1** of the **ESI**.

Supporting Information

Electronic supplementary information (ESI) available. See DOI: xxx.

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Declarations

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Conflicts of interest

The authors have no competing interests to declare that are relevant to the content of this article.

Availability of data and material

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Code availability

Not applicable.

CRedit authorship contribution statement

S. Grimm: investigation, formal analysis, visualization, writing – original draft; S.-J. Baik: methodology, investigation, software, writing – review & editing; P. Hemberger: investigation, resources, writing – review & editing; T. Kasper: conceptualization, methodology, supervision, project administration, funding acquisition; A. Kempf: methodology, supervision, writing – review & editing, project administration, funding acquisition; B. Atakan: conceptualization, methodology, supervision, writing – review & editing, project administration, funding acquisition.

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