Mechanism and Kinetics of the Thermal Decomposition of Fe(C₅H₅)₂ in Inert and Reductive Atmosphere: A Synchrotron-Assisted Investigation in a Microreactor

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The decomposition and reduction of ferrocene, an important precursor for iron chemical vapor deposition and catalyst for nanotube synthesis, is investigated in the gas-phase. Reactive intermediates are detected to understand the underlying chemistry by using a microreactor coupled to a synchrotron light source. Utilizing soft photoionization coupled with photoelectron-photoion coincidence detection enables us to characterize exclusive intermediates isomer-selectively. A reaction mechanism for the ferrocene decomposition is proposed, which proceeds as a two-step process. Initially, the molecule decomposes in a homogeneous surface reaction at temperatures <900 K, leading to products such as cyclopentadiene and cyclopentadienyl radicals that are immediately released to the gas-phase. At higher temperatures, ferrocene rapidly decomposes in the gas-phase, losing two cyclopentadienyl radicals in conjunction with iron. The addition of hydrogen to the reaction mixture reduces the decomposition temperature, and changes the branching ratio of the products. This change is mainly attributed to the H-addition of cyclopentadienyl radicals on the surface, which leads to a release of cyclopentadiene into the gas-phase. On the surface, ligand fragments may also undergo a series of catalytic H-losses leading most probably to a high carbon content in the film. Finally, Arrhenius parameters for both global reactions are presented.

1. Introduction

Since its discovery in the 1950s,[1,2] the metallocene ferrocene (Fe(Cp)₂), is, due to its remarkable stability,[3] an extensively studied compound.[4] It is a classical sandwich complex, where two cyclopentadienyl ligands are attached to a central iron core. Ferrocene is characterized by a relatively high vapor pressure at moderate temperatures, it is nontoxic and stable in air and therefore an easy to handle precursor for the synthesis of functional materials.[5] In particular, the use of ferrocene has been successfully established in the preparation of iron-containing thin films for optoelectronic devices[6,7] or iron thin films in an oxidative atmosphere in metallurgical applications.[8] Upon thermal decomposition of Fe(Cp)₂, iron nanoparticles (Fe-NP) can be formed which may subsequently act as functional nanomaterials for energy conversion and storage systems.[9,10] Those Fe-NPs have additionally shown excellent performance and emission characteristics in biodiesel engines.[11,12] and as a burning catalyst in rocket propellants.[13] since hydrocarbon radicals, responsible for soot formation, are quenched.[11] Nowadays, ferrocene is among the most widely used precursors in the synthesis of carbon nanotubes (CNTs),[14] either as a feedstock to produce catalytic sites necessary for their growth,[15–22] or as both carbon and catalyst precursor.[23–26] Those functional nanomaterials are often manufactured by high yield, low-temperature methods,[14] as for instance by catalytic chemical vapor deposition (CCVD). The underlying synthesis routes and processes were extensively studied experimentally,[15–17,19,20,27–28] and numerically.[29–34] It can be concluded, that the hydrocarbon source has a major influence on the morphology, crystallinity, and growth kinetics of CNTs, mediated through its gas-phase decomposition products pertaining to its initial structure,[35] as well as the catalyst activity. The control of product quality requires understanding the gas-phase decomposition mechanism of ferrocene at various reaction conditions. The intermediates act either as a promoter of CNT growth by serving as carbon feedstock or as a detrimental impurity, lowering the growth rate by forming unwanted volatile and polyaromatic hydrocarbons,[36,37] deactivating the iron catalyst particles by forming Fe₃C (cementite), or by carbon incorporation or encapsulation.[38]
Consequently, vast research has been conducted on the decomposition products and kinetics experimentally and by molecular dynamic simulations. The latter suggests that the bonds in the ferrocene molecule break above 1073 K sequentially according to their bond strength: $\text{C} - \text{H} > \text{C} - \text{C} > \text{Fe} - \text{C}$. The formation of cyclopentadienyl radicals ($\text{C}_5\text{H}_5$) was observed experimentally by mass spectrometry and infrared laser pyrolysis at a pressure of $4 \times 10^3$ Pa. Dyagileva et al. conducted a kinetic study on the pyrolysis of ferrocene in closed glass vessels under vacuum by the manometric method at pressures of $1.3 - 2.4 \times 10^4$ Pa and concluded that the solid decomposition products, namely carbon and iron, catalyze the decomposition by a factor of almost 3000, lowering the decomposition onset temperature to 823 K. They proposed first-order reaction conditions with a rate constant of $1.6 \times 10^{-5}$ s$^{-1}$ at 823 K. Main products formed are $\text{H}_2$, $\text{CH}_4$, $\text{C}_2\text{H}_4$, and $\text{C}_2\text{H}_6$ in the static system, analyzed by electron ionization mass spectrometry, whereas no radicals or elusive species were observed in a continuous flow reactor. This may be due to the rather long residence times on the order of minutes. Gas-phase iron nanoparticles were also not observed in this study.

In a later study, also cyclopentadiene and ethylene ($\text{C}_2\text{H}_4$) were detected at temperatures starting from 873 K, which may also originate from reactions catalyzed by chemisorbed iron atoms on the surface, which explains the low decomposition temperature. These studies come to the conclusion that most of the species detected are either formed in the secondary decomposition of cyclopentadiene ($\text{C}_5\text{H}_5$) to methane and hydrogen, or in catalytic reactions on the wall. Ensuring homogenous conditions by infrared laser pyrolysis, Russel et al. studied the gas-phase pyrolysis of ferrocene and observed $\text{C}_2\text{H}_6$, $\text{C}_5\text{H}_5$, and naphthalene ($\text{C}_{10}\text{H}_8$) among the decomposition products and proposed reaction schemes for their formation. Nevertheless, those products are partially secondary products and owing to the detection method used, no short-lived iron species could be detected either, rendering the decomposition mechanism to be still elusive.

In earlier investigations, it was observed that adding hydrogen to the carrier gas stream has a beneficial outcome regarding catalyst lifetime because $\text{H}_2$ acts as a reductive agent and allows control of the amount of desired carbon product formed. $\text{H}_2$ is also reported to lead to a significantly lower decomposition temperature of ferrocene.

Recently, we demonstrated that vacuum ultraviolet (VUV) synchrotron radiation coupled with a vacuum flash pyrolysis microreactor and photoelectron photon coincidence ($\text{i}^2\text{PEPICO}$) detection can be used to unravel the gas-phase decomposition of CVD precursors. Thanks to the tunability of the photon energy together with velocity map imaging (VMI), we were able to distinguish fragmentation and direct ionization and thus identify important organometallic and organic reactive intermediates isomer-selectively to elucidate the underlying chemistry. Here, we report a detailed VUV-$\text{i}^2\text{PEPICO}$ study for the in-situ detection of gas-phase radicals and molecular iron during pyrolysis of $\text{Fe}(\text{C}_5\text{H}_5)_2$ at conditions relevant to CCVD and CNT growth. To investigate the influence of hydrogen on the reaction mechanism of $\text{Fe}(\text{C}_5\text{H}_5)_2$, 10% $\text{H}_2$ was added to the mixture before entering the reaction zone. Our results provide direct experimental evidence for the initial steps of the decomposition through a detailed analysis of the gas-phase composition. It can be used to improve simulation efforts of CNT as well as thin film growth and hence contribute to a more efficient material synthesis.

2. Results and Discussion

A pyrolysis microreactor coupled to a molecular beam source, where reactive species are not quenched, is attached to a photoelectron-photosion coincidence spectrometer. Intermediates and products are detected by mass spectrometry and mass-selective threshold photoelectron spectra (ms-TPES). Furthermore, dissociative photoionization (DPI) is distinguished from direct ionization of reactive species, which allows to extract unimolecular decomposition pathways of ferrocene in an inert as well as in hydrogen atmosphere. Finally, we investigate the reaction kinetics in terms of activation energy and rate coefficients for the global reactions observed in the experiment, based on a numerical simulation of the flow field.

2.1. Dissociative Photoionization of Ferrocene: Does $\text{Fe}(\text{C}_5\text{H}_5)^+$ (m/z 121) form in the Gas-Phase?

As outlined in the introduction, many published reaction schemes propose the formation of $\text{Fe}(\text{C}_5\text{H}_5)$ as an initial product in the gas-phase, whereas none of these studies detected the molecule experimentally. A possible reason could be that, experimental limitations or fragmentation interfered with the results. Since our system is capable of detecting elusive species, as for instance $\text{Fe}(\text{C}_5\text{H}_5)$, its detection appears feasible.

When dealing with the detection of reactive radicals in ionization processes, fragment ions from DPI of the precursor need to be distinguished from direct ionization of the radical in the hot reactor. Considering the DPI mechanism, it is known that ferrocene (m/z 186) loses a cyclopentadienyl radical ($\text{C}_5\text{H}_5$) according to:

$$\text{Fe}(\text{C}_5\text{H}_5)_2 + h\nu \rightarrow \text{Fe}(\text{C}_5\text{H}_5)^+ + \text{C}_2\text{H}_6 + e^- \quad (1)$$

The literature offers a wide range of bond dissociation energies (BDE) of $\text{Fe}(\text{C}_5\text{H}_5)$, either experimentally, or by quantum chemistry that ranges from 2.6 to 6.7 eV. This wide range of reported BDEs is largely attributed to the deficiencies in the methods used to extract those energies. The calculated values range from 3.67 eV (B3LYP) to 4.86 eV (BP86), depending on the basis set used, whereas it has been stated that the first one systematically underestimates and the latter one overestimates experimental values and can therefore be considered as a numerical upper limit to the BDE. In terms of the experimental determination of the appearance energy of $\text{Fe}(\text{C}_5\text{H}_5)^+$ in this work, the BDE reported by Opitz and Härtnern of 4.61 ± 0.43 eV using electron-ionization mass spectrometry and the most recent value obtained by threshold collision-induced photodissociation mass spectrometry of 4.26 ± 0.15 eV which additionally considers the kinetic shift, that is usually observed in gas samples from hot sources, such...
as from our microreactor, are comparable to the method used in the approach here.

In order to understand the influence of dissociative ionization in our process using $i^2$PEPICO, we heated up the reactor to 1079 K and followed the m/z 121 signal as a function of the photon energy. The obtained threshold photoelectron spectrum (ms-TPES) and the photoion efficiency curve (PIE) of m/z 121 are depicted in Figure 1a. We clearly observe an increase in the relative intensity of the signal at 10.8 eV, but find some signal already at around 9.2 eV. Ionization energy calculations at different levels of theory for the Fe(C₅H₅)⁺ find values of 6.45 (B3LYP/6-311+G(2d,p)), 6.66 (ωB97Xv/d/6-311+G(2d,p)) and 6.13 eV M06L/6-311+G(2d,p)), respectively, which are much lower than the observed ionization onset. The signal increase at 9.2 eV in the PIE/ ms-TPES can thus not be rationalized with direct ionization, as we would expect to see a signal above zero already when the calculated ionization energy is reached.

Instead, the reason for the signal increase at lower photon energy is attributed to dissociative ionization.[54] The hot pyrolysis microreactor can shift the onset of the dissociative ionization to 2–3 eV below the 0 K onset, as the neutrals’ internal energy is transferred to the cations surface and leads to a fragmentation to Fe(C₅H₅)⁺, as observed in Figure 1a (green curve). This temperature-dependent red-shift was observed in the literature before, using similar reactors and was recently evaluated in detail.[34–36] While this fact leads to the appearance of the signal already at 9.2 eV, the majority of the ferrocene fragments appear only above 11.1 eV, which is shown by fitting a line to the linear increase of the signal. When adding the literature bond dissociation energy of the cation (Fe(C₅H₅)₂⁺ → Fe(C₅H₅)⁺ + C₅H₅) to the reported ionization threshold of ferrocene at 6.9 eV,[57] the appearance energy of the major fragment, Fe(C₅H₅)⁺ from ferrocene can be calculated to be 11.51 ± 0.43 eV (BDE: 4.61 ± 0.43 eV), using the values of Optiz and Härtner,[50] or from Rowland (11.16 ± 0.15 eV), which agrees slightly better.[51] We have strong evidence, that Fe(C₅H₅)⁺ is a DPI product, since first, we find an asymmetric peak shape of the TOF distribution in the mass spectra, caused by a slow unimolecular dissociation, which takes place upon acceleration of the ion in the mass spectrometer and was also observed for the peak at m/z 121.[52] Second, thanks to VMI, fragmentation can be clearly distinguished from direct ionization. While a directly ionized sample in a molecular beam shows a narrow velocity distribution along the molecular beam expansion direction (see Figure S1, Supporting Information), a fragment from dissociative ionization possesses a perpendicular contribution to the molecular beam direction, due to the release of kinetic energy as presented in Figure 1b.[38,39]

Due to the above mentioned analysis, we conclude that the signal of Fe(C₅H₅)⁺ is purely caused by dissociative rather than direct ionization. As a consequence, we cannot confirm the gas-phase formation of this species, which contradicts the literature mechanisms, which propose Fe(C₅H₅)⁺ to be the major initial decomposition product in the gas-phase.[25,33,39] However, we cannot exclude that Fe(C₅H₅)⁺ is formed and decomposes further or immediately adsorbs on the reactor wall, where it reacts at higher temperatures due to homogeneous or heterogeneous surface reactions. This possibility will be discussed later in this manuscript.

2.2. Photoionization Mass Spectra

After we successfully distinguished signals associated with dissociative from direct ionization of pyrolysis products, only product signals that emanate from pyrolysis are discussed in the following. Photoionization mass spectra were recorded and evaluated at fixed photon energies of 9.0, 10.5, and 11.5 eV over a temperature range of 333–1250 K. Figure 2 illustrates mass spectra of the pyrolysis products at fixed photon energies of 9.0, and 11.5 eV with and without (top trace) pyrolysis.
When the SiC-reactor is heated, we clearly see a depletion of the precursor’s ion signal at \( m/z \) 186. Product peaks at \( m/z \) 65, 66, 80, and 128 are observed in the mass spectra at temperatures above 781 K (Figure 2 (left)), which is a slightly lower temperature threshold than reported in the literature, where under catalytic conditions, the ferrocene decomposition already starts at 673 K,[40,42] but our value is way below the one reported for the low-pressure pyrolysis, where no decomposition was observed in the gas-phase up to 1178 K.[60] These peaks grow in intensity when the temperature is further increased up to 1087 K, together with a decline of the \( m/z \) 186 parent ion signal, which fits the latter temperature onset. The first iron-containing signal at \( m/z \) 56 is detected at temperatures >1087 K. Additionally, some new product peaks arise in the spectrum at \( m/z \) 39, 52, and 64, which are most likely secondary decomposition products of the initially observed hydrocarbons at lower temperatures. To assess the product species with lower masses or larger ionization energy onsets, mass spectra at higher photon energies were recorded (Figure 2b). At temperatures above 1200 K, several peaks appear at \( m/z \) ratio <70, while the primary decomposition product signal at \( m/z \) 65 decreases markedly. In addition to the previously noticed peaks in the literature,[39,40,60] our mass spectra show evidence of species with \( m/z \) 26, 39, 40, and 52 upon depletion of the primary decomposition product \( m/z \) 65, whose origin will be clarified in the next section.

The peak at \( m/z \) 80 is assigned to cyclopentadienone (see Figure 2), which may result from traces of oxygen in the reaction mixtures. Because no oxygen flow was intentionally added in our experiments, it is considered an impurity, as will be discussed briefly in the ESI Figure S2, Supporting Information.

### 2.3. Identification of Elusive Species

Photoion mass-selected threshold photoelectron spectroscopy (ms-TPES) is an indispensable tool for the isomer-selective detection of reactive species in pyrolysis, combustion, and catalysis, if experimental data is compared to literature or Franck–Condon simulated spectra.[58,61] To understand the underlying chemistry of Fe\((C_5H_5)_2\) pyrolysis we plotted a threshold photoionization matrix (TPM) at a reactor temperature of 1117 K, as partially shown in Figure 3a.[62] In this presentation, our multidimensional data set is reduced to a photon energy and mass spectrometric axis, while the threshold photoelectron signal intensities correspond to a change in color from light blue to red. By analyzing this illustration, the mass channels, where the main pyrolysis products reside, can be identified. If we extract the data along a vertical line for a given mass, ms-TPE spectra can be derived, and it is possible to characterize the major pyrolysis species for each \( m/z \) ratio. The ms-TPE spectra of the most abundant species are shown in subfigures (b), (c), and in Figure 4.

We can clearly identify strong signals at \( m/z \) 26, 39, 56, 65, 66. Up till now, the coexistence of Fe and \( C_5H_5 \) as the most abundant products upon pyrolysis was hypothesized.[60] Clear onsets at 798 and 8.88 eV in the TPES of \( m/z \) 56, which corresponds to the published \( ^6D \leftarrow ^3D \) and \( ^4D \leftarrow ^3D \) transition of Fe.
iron (7.90 and 8.89 eV,[63] see Figure 3b), confirm the formation of Fe atoms during the pyrolysis of ferrocene. The analysis of the spectrum in Figure 3c additionally shows, that the cyclopentadienyl radical is the most abundant pyrolysis product, which contributes to the m/z 65 signal (IE = 8.42 eV).[64] The onset of the TPE spectrum of m/z 26 at 11.39 eV in Figure 4a fits the literature spectrum of acetylene (C2H2) (IE = 11.4 eV)[65] well. At 8.7 eV a peak in the TPE spectrum of m/z 39 emerges and can clearly be assigned to the propargyl radical (C3H3) with a vertical IE = 8.71 eV[66] (see Figure 4b). The majority of the TPE signal at m/z 66 in Figure 4c matches a strong transition of cyclopentadiene (c-C5H6) with an ionization energy of 8.57 eV.[67] Small contributions of the acyclic isomer 1,2,4-pentatriene at 8.70 eV[68] may also be present but are hidden below the band of c-C5H6. The small peak at around 8.4 eV can be explained by the 13C isomer contribution (5.7%) of the of C5H5 radical (m/z 65), but does not influence our conclusions drawn from Figure 4c, since the literature spectrum of cyclopentadiene matches our observed spectrum well. Due to the vibrational progression of the ground state band of cyclopentadiene and the limited signal-to-noise ratio (SNR), traces of other isomers with m/z 66 with higher ionization energies are, if present, difficult to characterize. In Figure 4d we have also plotted the excited state spectrum of ferrocene between 8 and 10 eV. Note that the ionization energy is 6.9eV.[69] The steady signal increase is associated with hot bands, while the difference in the He(I)[57] and He(II).[70] especially for the band at 9.3 eV in literature spectra, stem from the difference in cross-section of ferrocene used to record them. Nevertheless, the features in Figure 4d can be attributed to ferrocene.

In Figure 5, a collection of the most important minor product species are shown. The TPE-spectrum with m/z 50 in Figure 5a fits the literature photoelectron spectrum of 1,3-butadiyne at IE = 10.17 eV[71] well and is solely assigned to this isomer of C4H2. The majority of the signal at m/z 52 in panel (Figure 5b) is ascribed to vinylacetylene (1-butene-3-yne) by a strong band at its IE = 9.58 eV.[72] Besides these assignments, 4 other products were identified by comparison between the ms-TPES and literature data, whenever accessible and are shown in the ESI and summarized in Table 1. Noting that 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, as discussed later in the text.

2.4. Pyrolysis Pathways of Ferrocene

The pyrolysis reaction pathways are temperature-dependent so that a measurement of all decomposition products and intermediates at different temperatures is needed to deduce the overall reaction scheme. The temperature-dependent ion signals of the most important intermediates are shown in Figure 6. Based on the unambiguous species assignments in Figures 3, 4, and 5 and mechanistic considerations from the species profiles in Figure 6, we describe the predominant pathways for the pyrolysis of ferrocene in the temperature range of 333–1200 K (see Scheme 1). The reactions are assigned to Roman numbers, which will be used throughout the text to refer to the respective reaction. The colors of intermediates correspond to the data in Figure 6. Gray species are hypothetic intermediates, which were not detected by the i2PEPICO.
experiment. The asteriks denotes products, which are probably adsorbed on the surface. Ferrocene already starts to decompose at 600 K but only above 900 K iron and hydrocarbon intermediates appear in significant amounts in the gas-phase. Consequently, three regimes can be distinguished in this experiment, for \( T < 600 \) K no reaction is observed, for \( T = 600-900 \) K ferrocene decomposition is initiated, while above 900 K gas-phase intermediates and atomic iron are

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**Figure 4.** Representative examples of species identification and assignment of major species using experimental obtained TPE (black dots and lines) at 1117 K; species are either characterized by literature reference spectra (red), or by computed spectra (blue) in (a)-(d). References are as follows: a) \( m/z \) 26 acetylene (\( \text{C}_2\text{H}_2 \))\(^{[65]} \), b) \( m/z \) 39 propargyl radical (\( \text{C}_3\text{H}_3 \))\(^{[66]} \), c) \( m/z \) 66 c-C\(_5\)H\(_6\)\(^{[67]} \) and 1,2,4-pentatriene,\(^{[68]} \) d) \( m/z \) 186 ferrocene (Fe(C\(_5\)H\(_5\)))\(^{[69]} \). dotted line: He(I)\(^{[70]} \), straight line: He(II).\(^{[70]} \)

**Figure 5.** Representative examples of species identification and assignment of minor decomposition products using experimental obtained TPE spectra (black dots and lines) at 1117 K; species are characterized by literature reference spectra (red) in a and b), References are as follows: (a) \( m/z \) 50 1,3-butadiyne (\( \text{C}_4\text{H}_2 \))\(^{[71]} \), (b) \( m/z \) 52 1-butene-3-yne (\( \text{C}_4\text{H}_4 \)) 1-butene-3-yne\(^{[72]} \).
formed. This behavior was not expected from the literature data, which reports ferrocene to decompose in very low-pressure pyrolysis in the gas-phase at around 1100–1200 K.\cite{38,60} However, the temperature onset of ferrocene decomposition in this study agrees with the onset reported by Dyagileva et al.\cite{40} at around 673 K, initiated by surface-catalysis. Since their reactor is operated in batch mode (residence time on the order of minutes), they reported that a considerable number of catalytic Fe-particles are produced, which reduced the decomposition temperature in their study. In contrast, in our study the high dilution in argon leads to a low number density of catalytic Fe-particles, which reduces the probability of catalytic surface reactions. Nevertheless, surface reactions cannot be fully ruled out, since we observe a small fraction of ferrocene to be decomposed at a temperature below 900 K. The species profiles in Figure 6 reveal that for temperatures up to 900 K, Fe(C_5H_5)_2 decomposes primarily via the loss of a cyclopentadienyl radical (m/z 65) leaving Fe(C_5H_5) (m/z 121) (Scheme 1: reaction (i)). The absence of any Fe(C_5H_5)_2 radicals may be rationalized by the lower bond energy of the second cyclopentadienyl radicals as compared to the first one.\cite{83,84} Often such fleeting intermediates are difficult to be observed in microreactors, due to very efficient rethermalization and comparable long residence times.\cite{64,85,86}

We postulate a second pathway of ferrocene decomposition, which may yield Fe(C_5H_4) (m/z 120) and C_5H_6 based on the observation of cyclopentadiene in minor amounts below 900 K, whereas major amounts can be observed at temperatures above 900 K (reaction (ii)). Neither atomic iron, nor other iron-containing intermediates were detected in the gas-phase at temperatures below 900 K. If these species were formed in gas-phase reactions, we expect to be able to detect them based on previous experimental experience.\cite{47} Additionally, previous studies of other investigators by quadrupole mass spectrometry also did not observe their formation at temperatures below 1173 K.\cite{25} It is evident from the findings by Dyagileva et al.\cite{42} that the activation energy for the thermolysis of the Fe–Cp bond on a surface is much lower than in the gas-phase. A similar behavior is observed in our study, because a significant amount of Fe is only detected in the gas-phase after heating the reactor

Table 1. List of identified species upon pyrolysis of Fe(C_5H_5)_2 and the reduction with H_2 (marked with an asterisk) by VUV-i^2PEPICO using their adiabatic and vertical ionization energies. 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.

| m/z | Formula | Name | IE [eV] |
|-----|---------|------|--------|
| 15  | CH_3    | Methyl radical | 9.84\cite{73} |
| 26  | C_2H_2  | Acetylene | 11.4\cite{83} |
| 39  | C_3H_3  | Propargyl radical | 8.71\cite{64} |
| 40  | C_4H_4  | Allen | 9.59\cite{61} |
|     |         | Propyne | 10.38\cite{62} |
| 42a | C_6H_6  | Propene | 9.72\cite{76} |
| 43a | C_7H_6  | i-Propyl radical | n.a. |
| 44a | C_6H_6  | n-Propyl radical | n.a. |
| 50  | C_6H_6  | 1,3-Butadiyne | 10.17\cite{90} |
| 51  | C_7H_4  | 1-Buten-3-yne | 9.58\cite{83} |
| 54a | C_8H_8  | 1,3-Butadiene | 9.07\cite{71} |
|     |         | 2-Butyne | 9.59\cite{71} |
|     |         | 1-Butyne | 10.18\cite{71} |
| 56  | Fe      | Atomic iron (^{5D}_{7/2}-^{3D}); (^{5D}_{5/2}-^{3D}) | 7.90; 8.89\cite{63} |
| 64  | C_8H_4  | Ethynylallene | 9.22\cite{70} |
|     |         | 1,3-Pentadiyne | 9.50\cite{83} |
| 65  | C_9H_4  | Cyclopentadienyl radical | 8.47\cite{83} |
| 66  | C_9H_5  | 1,3-Cyclopentadiene | 8.58\cite{83} |
|     |         | 1,2,4-Pentatriene | 8.70\cite{83} |
| 80  | C_{10}H_{10}O | 2,4-Cyclopentadiene-1-one (impurity) (see Figure S2, Supporting Information) | 9.42\cite{83} |
| 128 | C_{10}H_{12} | 1-Butene-3-ynylbenzene | 8.53\cite{83} |
|     |         | 3-Butene-1-ynylbenzene | 8.74\cite{83} |
| 186 | Fe(C_5H_5)_2 | Ferrocene (excited state band) | 6.9, [8.4–8.7]\cite{57} |

Figure 6. Temperature-dependent species profiles of products of thermal decomposition of Fe(C_5H_5)_2 at T_{vap} = 353 K (820 ppm), probed by i^2PEPICO vacuum ultraviolet (VUV)-mass spectrometry in our micro-reactor. The respective species that were characterized according to Section 2.3 are labelled by their formula and all signals are normalized to the initial ferrocene signal.
above 900 K, although ferrocene already decomposes at lower temperatures.

We suggest that at temperatures < 900 K, ferrocene undergoes decomposition on the surface, forming cyclopentadienyl $m/z$ 65 and cyclopentadiene $m/z$ 66, followed by a very fast desorption of these products and the iron-containing species $m/z$ 121 Fe(C$_5$H$_5$) and $m/z$ 120 Fe(C$_5$H$_4$) remain on the surface of the reactor (see Scheme 1 (i) and (ii)). Alternatively, ferrocene molecules react, e.g., with other ferrocene molecules or iron-containing reaction products from ferrocene on the surface under the liberation of cyclopentadiene, which could explain the minor amounts of cyclopentadiene observed at temperatures below 900 K. Previous studies presented evidence that this is a possible pathway for similar $\pi$-complexes of transition metals$^{[39,87]}$ under CVD conditions and that the unstable Fe(C$_5$H$_5$)(C$_5$H$_4$)* radical or Fe(C$_5$H$_4$)* decomposes on the surface to form the C$_5$H$_4$ species, which are also detected in our study (see Figure S3, Supporting Information).

Compared to the low-temperature decomposition pathways of ferrocene, the mechanism changes significantly at higher temperatures $>$ 900 K (see Figure 6). Following the species profiles in Figure 6, it is evident and commonly accepted in the literature$^{[60]}$ that at T $>$ 900 K ferrocene decomposes in the gas-phase leading to the formation of two cyclopentadienyl radicals $m/z$ 65 and atomic iron $m/z$ 56 (Scheme 1 (iii)).$^{[17]}$ In addition, the formation of cyclopentadiene is enhanced since the amount of C$_5$H$_6$ that we found in the gas-phase significantly increases at temperatures $>$ 900 K (see Figure 6). A possible explanation for this is that at higher temperatures, either a hydrogenation of the C$_5$H$_5$ ligands occurs, leading to the formation of cyclopentadiene, or Fe(C$_5$H$_4$) is formed in the gas-phase and immediately adsorbs on the surface, which is facilitated by the high temperatures, where we observe high amounts of cyclopentadiene.

Both acetylene (C$_2$H$_2$) and the propargyl radicals (C$_3$H$_3$) are clearly observed in the ms-TPE spectra at temperatures
above 1117 K (Figure 4a,b). The decrease in the \( m/z \) 65 signal intensity and a simultaneous increase of \( m/z \) 26 and 39, explains that these organic products are formed in secondary reactions in the gas-phase (Scheme 1 (iv)). Likewise, it has been reported, that cyclopentadiene with \( m/z \) 66 decomposes to form propyne (\( m/z \) 40) and acetylene (\( m/z \) 26) (Scheme 1 (v)),[89] which were identified by their characteristic fingerprints utilizing ms-TPE spectra. Other experiments[8,39] revealed, that the pyrolysis of ferrocene at high temperatures, yields cementite (Fe\(_3\)C) and iron surrounded by graphite layers (FeC). Given these observations, the formation of FeC or Fe\(_3\)C is expected in the microreactor by further decomposition of ligand fragments on the surface, which is supported by the existence of a black residuum in our reactor after the experiments. Additionally, the presence of acetylene in the gas-phase accelerates the formation of carbon-coated iron nanoparticles or carbon nanotubes,[17,24] at particle forming conditions.[33] However, the characterization of this residuum and the adsorbed ligand fragments as Fe(C\(_5\)H\(_4\))\(_n\) requires advanced surface characterization techniques, as well as an optically accessible microreactor and is therefore beyond the scope of this study.

2.5. Influence of \( \text{H}_2 \) Addition

In comparison to the pyrolysis of pure ferrocene, higher signals for the masses \( m/z \) 26, 42, 43, and 44 were detected at temperatures below 1000 K if hydrogen is added to the reaction mixture (see Figure 7a). We were able to identify the latter three signals as C\(_3\) hydrocarbons according to their ionization onsets in the literature in comparison to our recorded threshold photoelectron spectra or PIE curves. The shape of the ms-TPES in Figure 7a is in agreement with the photoelectron spectrum of propene (C\(_3\)H\(_6\)) with a vertical ionization energy of 9.73 eV.[76] Based on the ionization onset at 10.9 eV, we assign the signal at \( m/z \) 44 to propane,[76] and also VMI images at low temperatures show that this species is detected by direct ionization. Unfortunately, we did not record spectra at photon energies higher than 11 eV, which would give a much clearer identification of this species, being the most abundant one at temperatures of 600–900 K (see Figure 8 (left)). The identity of \( m/z \) 43 is not determined here, because we did not record ms-TPE spectra at such low temperatures, where the formation of \( m/z \) 43 can be observed and at a higher temperature, dehydrogenation to propene dominates. Yet, we tentatively assign this species to

Figure 7. Representative examples of species identification and assignment of important decomposition products after adding 10% \( \text{H}_2 \) to the carrier gas flow, using experimentally obtained TPE spectra (black dots and lines) recorded at 1079 K (a)–(c). The species are characterized by literature reference spectra (colored). References are as follows: a) \( m/z \) 42 C\(_3\)H\(_6\) (propene),[76] b) \( m/z \) 64 red: contribution from c-C\(_5\)H\(_5\) (see main text for further explanation), blue: 1,3 pentadiyne;[79] c) \( m/z \) 66 c-C\(_5\)H\(_5\) (cyclopentadiene).[67]
C\textsubscript{5}H\textsubscript{5} according to a possible H-abstraction reaction of m/z 44 at temperatures higher than 600 K\textsuperscript{[90]} which is rationalized in the species profile on the lower part of Figure 8. Given the ionization energies of 8.42 and 8.67 eV for c-C\textsubscript{5}H\textsubscript{4}\textsuperscript{[79]} it is tempting to assign the signal to the cyclopentadienylidene carbenes, however, the peaks coincide with transitions of the cyclopentadienyl radical. Due to the large abundance of the cyclopentadienyl radical (C\textsubscript{5}H\textsubscript{5}, m/z 65) a small neighboring signal interference cannot fully be avoided, and is also a result of mass separation observed in the ms-TPES. We can however also find small contributions of the acyclic isomer 1,3-pentadiyne represented by its onset at 9.50 eV\textsuperscript{[80]} The abundances in the ms-TPES of the channel m/z 64 do change as compared to pure pyrolysis, but the signal is still assigned to the same product, 1,3-pentadiyne (see Figure S 3 in the ESI). We observe a change in the mechanism here, since the signal of m/z 66 significantly increases in the presence of hydrogen. We checked this mass for additional isomers, but found exclusively cyclopentadiene, as can be seen in Figure 7c.

It is evident from the data in Figure 8 (left) and (right) that the addition of H\textsubscript{2} leads to a decomposition of ferrocene at lower temperatures as compared to our measurements in argon (see Figure 6) and more hydrocarbon intermediates are observed. The decomposition temperature is shifted under these experimental conditions to a lower value of around 550 K in agreement with trends reported in the literature\textsuperscript{[6]} The exact temperature of the onset depends on the different reactor geometries and experimental conditions applied in both studies, but the general trend remains the same. Numerical simulations of the deployed microreactor in a previous study\textsuperscript{[47]} revealed, that the average temperature is at least 6% higher at the wall than on the centerline of the reactor, which may explain the temperature difference between our study and the literature values.

Figure 8 (left) shows the temperature-dependent profiles of the intermediates formed during the decomposition of ferrocene in the presence of hydrogen. Below 1000 K the main hydrocarbon intermediates are 1,3-cyclopentadiene (c-C\textsubscript{5}H\textsubscript{4}), propene (C\textsubscript{3}H\textsubscript{6}), and propane (C\textsubscript{3}H\textsubscript{8}), as well as acetylene (C\textsubscript{2}H\textsubscript{2}), indicating that the underlying decomposition mechanism changes. In contrast to the measurement without H\textsubscript{2} addition, the amount of C\textsubscript{5}H\textsubscript{4} is reduced in the high-temperature window. This observation is further rationalized by the steep signal increase of m/z 42, 44, and 65 in Figure 8 (right) starting at around 550 K. Here, direct reactions with hydrogen explain this behavior of ferrocene and its decomposition products.

The reaction sequence of ferrocene reduction in the temperature window from 550 to 650 K is likely initiated by a subsequent reaction starting from reaction (i) in the absence of H\textsubscript{2}, which may take place in the gas-phase or on the surface by the following pathway:

\[
\text{Fe(C}_5\text{H}_5\text{)}_2 \rightarrow \text{Fe(C}_5\text{H}_4\text{)}^+ + \text{C}_2\text{H}_6 \quad (\text{Ia})
\]

\[
\text{Fe(C}_5\text{H}_4\text{)}^+ \rightarrow \text{Fe(C}_5\text{H}_4\text{)}^0(\text{ads}) \quad (\text{Ib})
\]

\[
\text{C}_5\text{H}_5 + \text{H}_2 \rightarrow \text{C}_3\text{H}_6 + \text{H} \quad (\text{Ic})
\]
The C₂H₃ ligands are hydrogenated to form C₂H₄, which remains or subsequently desorbs into the gas-phase (lc). This interpretation is supported by the increase of the C₂H₄ signal in Figure 8 (right) relative to C₂H₂, as compared to the pyrolysis without H₂ (see Figure 6). In addition to the H-radicals formed by reaction (lc), hydrogen molecules are expected to dissociatively adsorb over iron on the surface of the reactor, which leads to a lower dissociation barrier of ferrocene upon hydrogen addition compared to the pure pyrolysis.[65]

Previous experimental studies agree that the decomposition of C₅H₅ is initiated by C-H bond fission, leading to the formation of the cyclopentadienyl radical.[99] As already discussed in the light of reaction (v), cyclopentadiene can additionally isomerize by hydrogen shifts and ring-opening and later breakdown to form C₂H₂ and C₅H₄ at higher temperatures.[68,89] This is in agreement with the development of the C₂H₂ and C₅H₆ signal at temperatures above 1000 K in the bottom trace of Figure 8 (right). However, these reaction channels do not explain the small acetylene signal below 1000 K, observed in the species profiles upon H₂ addition, in Figure 8 (right), which must have a different origin, though. It has been pointed out that the reduction of similar metalloccenes, undergoes a competitive reaction mechanism between the hydrogenation of the ligands followed by metal bond cleavage and the decomposition of the ligands on the surface leading to carbon incorporation in the solid films and the formation of particles.[90] It is likely, that a similar mechanism takes place here, while hydrogen is present, as proposed by Russel et al. for the pure pyrolysis of ferrocene.[10]

A surface hydrogenation followed by desorption of the hydrogenated ligands should be dominant. But, we found no evidence for C₅H₅ₙ (n = 8, 10) species in the gas-phase, which were proposed and observed by others for the hydrogenation of ligand radicals in ferrocene decomposition.[6,35] Possible reaction products from surface reactions of the postulated hydrogenated species may come from a rapid decomposition of C₅H₈ and C₅H₁₀ on the surface or in the gas-phase followed by the formation of the products m/z 26 acetylene (C₂H₃), m/z 42 propene (C₃H₆) and m/z 44 propane (C₄H₈), for n = 1,2 respectively:

\[
\begin{align*}
\text{C}_2\text{H}_4 + n\text{H}_2 & \rightarrow \text{C}_2\text{H}_4+2n \quad \text{(Ia)} \\
\text{C}_2\text{H}_4+2n & \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_2^* \quad \text{(Ib)} \\
\text{C}_5\text{H}_{10-2n} & \rightarrow \text{C}_5\text{H}_{10-2n} \quad \text{(Ic)} \\
\text{C}_5\text{H}_5^* & \rightarrow \text{C}_5\text{H}_3 \quad \text{(Id)} 
\end{align*}
\]

This explains, why we already observed acetylene in the sample in the initial stages of ferrocene decomposition.

Since we only observe traces of ligand fragments and significant amounts of hydrogenated ligands, we conclude, that with the addition of 10% H₂, the hydrogenation reaction of C₅H₅ on the surface is dominant due to active H radicals, in comparison to the destruction of the C₅H₅ ligand radicals to smaller hydrocarbons. This should promote the formation of iron films with less carbon content, since the destruction of the ligands is necessary for the formation of pure carbon on the surface.[39] Instead, H₂ purges the surface, leading to less carbon coverage, and suppressing the formation of Fe₃C and Fe₂C. This will lead to more active catalytic iron sites, which in turn enhances the decomposition of ferrocene by generating H-radicals from the decomposition of ferrocene and a possible contribution of hydrogen to the radical pool, as proposed by Luo and coworkers.[40]

If compared to the thermal decomposition in argon, significant amounts of C₂ hydrocarbons were also detected. Since the characterization of m/z 52 C₂H₄, as 1-buten-3-yne remains the same as in pyrolysis and is formed at higher temperatures, we concluded that this species is considered as a secondary decomposition product of ferrocene fragments. The detection of C₂H₂ can be attributed to either a methyl loss from cyclopentadiene to form C₂H₂ at higher temperatures and also a hydrogen loss of vinylacetylene, since we only observe 1,3-butadiene at temperatures higher than 1000 K (see Figure S4, Supporting Information).

2.6. Kinetics of the Thermal Decomposition of Ferrocene

Although the reaction conditions inside a microreactor are difficult to characterize and the pressure and temperature fields are rather complex, various studies, both experimentally[93,94] and by computational fluid dynamics (CFD)[47,95,96] were conducted and demonstrated, that kinetic interpretations, to a certain extent, are reasonable. Since the flow field of our microreactor has been investigated numerically by CFD simulations in a previous study,[47] we are able to determine the residence time, temperature, and pressure fields more precisely than it could be done using an analytical approach for various experimental boundary conditions. In the temperature window that applies to this study, an average pressure in the reactor of 1500 Pa and residence times between 26 and 44 µs were determined. Considering the extraction of kinetic rate data for microreactor experiments, main takeaway from previous CFD calculations was that most of the precursor conversion occurs within a specific area at x = 5–8.5 mm.[47,95]

Here we observe a small variation in both, pressure and temperature, which makes kinetic interpretations of simple unimolecular dissociation reactions, to some extent, possible, as demonstrated before for another organometallic precursors.[47]

Although the kinetic parameters such as activation energy and frequency factor can be pressure-dependent, it should be noted, that the pressure drop of about 2200 Pa along the microreactors flow axis mainly influences the frequency factor A that we derive in our kinetic analysis. This is because, assuming the validity of the ideal gas law and considering the reaction order of one, the difference in activation energy is on the order of the experimental uncertainties. Additionally, the influence of the total pressure on A is relatively small, due to the small pressure variation within the sweet spot of the reactor for a first approximation of the kinetic constants.

Also we compared our simple approach to use the average centerline temperature at 8.5 mm with the more sophisticated approach of a volume-weighted temperature in the whole reactor. Simulations show here a deviation of < 7% of the centerline temperature at the sweet spot to a volume-weighted temperature for the highest surface temperature of 1273 K, which, thanks to CFD, is a more precise approximation of the uncertainty than the one usually claimed in mechanistic
studies using microreactors of >10%. We obtained average residence times in our reactor in the same manner, although this approach seems rather simplistic. However, to check its feasibility, we determined the residence time distribution in the microreactor using the flow profile obtained by CFD calculations. We obtained the residence time distribution by seeding 1000 particles in our simulation domain and tracking their residence time while traveling through the microreactor. The results show, that the maximum deviation of the first moment of this distribution (average residence time) differs by 2.6 µs, which shows, that our simple approach has an uncertainty in the residence time of <10%. In sum, given the uncertainties in temperature, pressure, and residence time, we consider our simple approach to be feasible for extracting kinetic rate data with the stated uncertainty of each parameter. Since especially for the system ferrocene + H2, limited data is available in the literature, albeit contingent on a few assumptions, our approach is reasonable. Using these insights, we can relate the mole fraction profiles (see Figure 9 left) of m/z 186, Fe(C5H5)2 to the average centerline temperature of the reactor.

Taking a closer look at Figure 9 (left) and considering the discussion about the reaction mechanism in the previous sections (2.4) and (2.5), we think that the ferrocene decomposition can be divided into two main channels. First, at low temperatures, we observe the surface reaction of ferrocene or its initial decomposition product, probably after adsorption, with first-order kinetics according to:

\[ \text{Fe(C}_5\text{H}_5\text{)}_2(g) \rightarrow \text{Fe(C}_5\text{H}_5\text{)}^*(\text{ads}) + \text{Products} \]  

(2)

This is responsible for the decrease of the ferrocene mole fraction from ca. 300–950 K in Figure 9 (left). Following the course of the mole fraction profiles, one recognizes a steep decrease in mole fraction between 900 and 1000 K hinting at a change in the dominant decomposition process in this temperature regime. Since we observe the formation of cyclopentadienyl radicals, as well as atomic iron in the gas-phase at these temperatures (see Figure 6), they are formed in the gas-phase according to the following reaction initially proposed by Lewis and Smith:

\[ \text{Fe(C}_5\text{H}_5\text{)}_2(g) \rightarrow \text{Fe} + 2 \cdot \text{C}_5\text{H}_5 \]  

(3)

Reasonable Arrhenius plots were derived for the pyrolysis of Fe(C5H5)2, with and without 10% H2, as shown in Figure 9 (right) and Figure 10, respectively. The process of data evaluation is described in paragraph (4.1) in detail. Briefly, the measured mole fractions at different temperatures and reaction times were used to fit the parameters of Equation (9) by the linear least squares method, in order to derive both activation energy for the three reaction regimes are given next to the best fit plot (red: gas-phase, blue: surface, orange: reaction with H2 on the surface). The influence of H2 addition does play a large role at lower temperatures shown by the orange plot, where a reaction leads to the formation of C3 -species in the gas-phase (see Section 2.5).
energies and pre-exponential factors. All single fitting results combined with their validities, due to uncertainties of the fit, are summarized in Table 2. To quantify the goodness of the fit of the activation energy, uncertainties are given next to the respective energies. Additionally, the sum of squared residuals (SSR) of the fits are registered in the last column. It has become apparent, that the goodness of the fit is sensitive to the initial ferrocene concentration, since the signal intensities that underlie the mole fraction profiles are more concise.

We interpret the data as follows: Adsorption and subsequent surface reactions as Equation (2) dominate the temperature regime up to 900 K, where the conversion is relatively low. The activation energy in this regime is 19.7 ± 1.4 kJ mol⁻¹. The kinetic parameters estimated by Hirasawa et al. (A₀ = 1 × 10⁷ s⁻¹ Eₐ = 12.54 kJ mol⁻¹) using thermochemistry and quantum chemistry is in the order of our low-temperature activation energy, which we attribute to the existence of radicals and loosely bound H-atoms on the surface. Also the pre-exponential factor for the surface reaction is on the order of 10⁷, which is in line with the physical understanding, that the probability of a molecule to be adsorbed on the surface and react is relatively low in comparison to gas-phase reactions in our microreactor. The Arrhenius plots for the decomposition according to Equation (3) in the temperature range from 330 to 1230 K are displayed in Figure 9 (right). It should be noted, that the temperature regime where atomic iron and cyclopentadienyl radicals were detected as major primary decomposition products is starting at around 900 K (see Section 2.3). Since at these high temperatures the depletion of Fe(C₅H₅)₂ is starting at around 900 K (see Section 2.3). The Arrhenius plots for the decomposition of ferrocene in the presence of hydrogen, since H₂ is present in excess and contributes significantly to the H-radical pool in our reactor. In contrast, earlier work by Lewis and Smith quotes an activation energy of 382 kJ mol⁻¹, which is significantly higher than the value obtained in our study. We attribute this discrepancy to the influence of surface reactions and H-radical formation on the surface as well as bimolecular reactions in the gas-phase of ferrocene with H₂ as in part already suggested by others for metallocenes under the presence of hydrogen. The uncertainty in the temperature determination is also a possible impact factor that let us underestimate the activation energy.

The influence of H₂ addition on the kinetics can be seen in the green curve of Figure 9 (left), where the mole fraction of ferrocene in the hydrogen-rich atmosphere exhibits an earlier decrease at around 500 K, compared to the pure pyrolysis. As already discussed in the previous paragraph, we attribute this observation to a hydrogenation of the ligands on the surface and a subsequent desorption of these hydrogenated species. From the Arrhenius plot in Figure 10, we can distinguish between two reaction regimes. First, we obtain a pre-exponential factor of 3.9 × 10¹⁴ s⁻¹ and an activation energy of 88.0 ± 14.6 kJ mol⁻¹, which is valid in the low-temperature regime from 500–625 K. Second, we observe an overlap between a dominant surface reaction according to the one discussed in the previous paragraph (Scheme 1: (j) and a gas-phase reaction (Scheme 1 (iii)) starting at temperatures >900 K. We derived an activation energy of 170 ± 1.8 kJ mol⁻¹, which is similar to the one obtained for pure pyrolysis, hinting that the same reaction is responsible for the consumption of ferrocene at temperatures from 625–900 K. However, one should note, that considering the pyrolysis data in the temperature range from 500–900 K, we must consider that there is an overlap between both surface reactions, leading to an additional error in the reaction rate constants obtained in this study. Additionally, it is clear from Figure 10 that our fit overestimates the gas-phase activation energy with a value of 260.0 kJ mol⁻¹ compared to the value proposed by Kuwana and Saito of 218 kJ mol⁻¹ for the global reaction:

\[
\text{Fe(C}_5\text{H}_5\text{)}_2 + \text{H}_2 \rightarrow \text{Fe} + 2\cdot\text{C}_5\text{H}_6
\]
3. Conclusion

Sensitive, selective, and multiplexed i²PEPICO spectroscopy was utilized with VUV synchrotron radiation to investigate the thermal decomposition of ferrocene in a hot microreactor with a residence time <50 µs in an inert or hydrogen atmosphere. It was demonstrated that the thermal decomposition under these conditions can be mainly divided in two temperature regimes. At temperatures up to 900 K, surface reactions dominate, while at higher temperatures gas-phase reactions are faster. The first one involves the surface-mediated decomposition and adsorption of ferrocene or fragments as Fe(C₅H₅) and Fe(C₅H₄) on the surface, which are corroborated by the findings of cyclopentadienyl radicals and cyclopentadiene. The latter one includes the direct formation of atomic iron and cyclopentadienyl radicals in the gas-phase.

We showed that other organic decomposition products could be identified, such as m/z 26, 39, 50, 52, 64, and 128. These were identified as acetylene, the propargyl radical, acyclic isomers of C₅H₄ as well as 1-butene-3-ynylbenzene, respectively. The roles of these species in the reaction mechanism have been discussed. In the case of H₂, the reaction mechanism changes significantly, such that the decomposition products of ferrocene are either hydrogenated on the surface or directly react with hydrogen to form cyclopentadiene at temperatures <900 K. At higher temperatures, the hydrogenation of ligand in the gas-phase to form cyclopentadiene becomes dominant. In sum, new dissociation channels could be identified from ferrocene, which were not fully uncovered in previous studies.

The kinetics of the two main decomposition channels were analyzed at an average pressure of 1500 Pa in the microreactor. Both reactions follow first-order kinetics with a low activation energy of 19.7 ± 1.4 kJ mol⁻¹ for the surface reaction, dominating the decomposition at low temperatures and 247.6 ± 20.7 kJ mol⁻¹ for the gas-phase decomposition, dominating the mechanism above 900 K. Upon addition of H₂, the kinetics, as well as the decomposition temperature change. At temperatures between 600 and 700 K, a probably bimolecular reaction of ferrocene with hydrogen is observed in parallel to the above stated ferrocene decomposition mechanism. The kinetics for the reaction with hydrogen were determined to have an activation energy of 88.0 ± 14.6 kJ mol⁻¹ at low temperatures. The latter should lead to reduced temperatures in iron CVD with hydrogen addition.

Nevertheless, although there are several deficiencies of the high-temperature microreactor that complicates the interpretation of experimental data, given the circumstances, that only limited data is available and that our kinetic parameters are on the order of the ones measured in other systems, we think that our approach marks a good starting point here to exploit microreactor data for kinetic rate measurements of simple unimolecular dissociation reactions. We have shown that our method is very versatile, due to its capability of detecting highly reactive and elusive radicals and can be utilized to investigate the kinetics of CVD precursors.

However, the kinetic studies should be complemented by investigations with traditional mass-spectrometric detection behind larger flow reactors, since the temperature profiles are easier to characterize, and the measurement times are less restricted. Since the decomposition of ferrocene is a homogeneous-heterogeneous process, studies to detect and characterize species that are formed on or attached to the surface are absolutely needed, in order to explore the fate of reaction products adsorbed on the surface and further develop the proposed decomposition mechanism given in Scheme 1. Hence, a combination of those methods should give an even deeper insight to the reactions of such organometallic precursors used for the synthesis of functional materials, which remain rare so far.

4. Experimental Section

The experiments were conducted at the vacuum ultraviolet (VUV) beamline[98] at the Swiss Light Source of the Paul Scherrer Institute in Switzerland. A detailed description of the experimental apparatus[99,100] as well as the microreactor setup,[101] can be found elsewhere[40] and only a brief explanation is given here (see Figure 11). Ferrocene (>98% pure, 98% pure,
Sigma Aldrich Inc.) is sublimed in a stainless-steel tube, jacketed by a copper block, to ensure isothermal sublimation conditions. Temperature and pressure of the sublimation source are continuously monitored and are constant during each measurement. Special attention was paid to reactor conditions that ensure primarily unimolecular dissociation. This is achieved by using a highly diluted sample stream, which minimizes the potential of bimolecular reactions. For this purpose, the precursor gas is diluted in a large excess of argon (99.9999% purity), which is delivered by mass flow controllers (MKS Instruments) at a constant flow rate of 22 sccm. Three separate experiments operating at an evaporator pressure of 1500 mbar and sublimation temperatures of 323/333/353 K were conducted. Assuming thermal equilibrium, the precursor mole fractions at the reactor inlet are calculated from the vapor pressure data to be between \( x_{Fe(C_5H_5)2} = 7.4 \times 10^{-5} \) – \( 8.2 \times 10^{-4} \). After sublimation, the mixture is expanded through a 100 µm pinhole into a resistively heated silicon-carbide (SiC)\(^{102}\) flow reactor with an inner diameter of 1.0 mm and a heated length of 10 mm. To measure the decomposition temperature, a C-Type thermocouple is attached to the reactor, with an estimated uncertainty in the examined temperature range between the centerline and surface temperature of \( \pm 0.00 \) K. Under the conditions used here, residence times of 26–44 µs and an average pressure of 1500 Pa in the microreactor were calculated.\(^{47}\) A CFD simulation of the temperature field provided more realistic centerline temperatures, which were used in this study for the derivation of temperature-dependent species profiles. Since it is expected, that after a while, a considerable amount of deposit may be formed on the reactor surface, the SiC-microreactor tube was replaced before conducting the experiments in reductive atmosphere. After the heated reaction zone, the decomposition products are rapidly expanded to a high vacuum at \( \approx 6 \times 10^{-5} \) mbar, leading to the formation of an effusive molecular beam that provides contact time, and preserves the actual gas composition including highly reactive species. The ejected gas is sampled by a nickel that minimizes contact time, and preserves the actual gas composition.

In brief, to determine the temperature dependence of the Fe(C_5H_5)\(_2\) mole fraction, the procedure proposed by Zhang et al.\(^{106}\) was followed, where the influence of temperature-dependent signal variations of argon (\( m/z 40 \)) due to a change in expansion behavior and therefore the sampling efficiency is characterized by the gas expansion coefficient \( \lambda(T) \). This expansion coefficient was determined by recording temperature-dependent mass spectra at a fixed photon energy of 15.8 eV in the 300–1300 K range (Figure S4, Supporting Information). The correlation between the mole fraction of ferrocene at temperature \( T \) and the mole fraction at \( T_0 \) at an incident photon energy of 9.0 eV and a fixed photon flux is given as follows:

\[
S(T) = \frac{S(T_0)}{S(T_0)}
\]

where \( S(T) \) represents the ion signal intensity measured at temperature \( T \) and \( S(T_0) \) is defined as the precursor concentration measured at temperature \( T_0 \). The gas expansion factor is unity at room temperature. As a starting point, the inlet mole fraction was calculated assuming saturated conditions inside the evaporator; for an evaporation temperature of 323/333 and 353 K, respectively. This results in \( x_{Fe(C_5H_5)2}(T_0) = 7.4 \times 10^{-5} \) to \( 8.2 \times 10^{-4} \) from previously measured vapor pressure data by the group.\(^{8} \) Given this, reasonable Arrhenius plots were derived using the integral method for the unimolecular dissociation reaction of ferrocene (see Section 2.6). Since unimolecular gas-phase dissociation reactions of metal-organic precursors often follow first-order kinetics, which was also determined here experimentally, the rate constant was approximated using the Arrhenius law shown in Equation (6):

\[
k_{uni} = A_0 \exp \left( \frac{E_a}{RT} \right)
\]

where \( A_0 \) represents the collision frequency and \( E_a \) is the molar activation energy in kJ mol\(^{-1}\). This holds for gas-phase and for surface reactions, but the pre-exponential factor and the activation energies differ. The time-dependent concentration change for a unimolecular reaction is given by:

\[
dc = -k_{uni}(T)\cdot c
\]

where \( \tau \) is the residence time obtained by CFD at temperature \( T \). Separation of variables, integration of Equation (7) and combination with Equation (6) yields:

\[
c(t) = c(t_0) \exp \left( -A_0 \cdot \exp \left( \frac{E_a}{RT} \right) \left( t - t_0 \right) \right)
\]

Taking the natural logarithm gives:

\[
\ln \left( \frac{c(t)}{c(t_0)} \right) = -k_{uni}(T - t_0)
\]

Since surface and gas-phase reactions take place concurrently in the microreactor, the total rate constant was the sum of both contributions. Since both rate constants follow the Arrhenius expression given in...
Equation (6) the authors derived them simultaneously according to Equation (10):

\[ k_{\text{eff}}(T) = k_{\text{eff}}^{\text{H}}(T) + k_{\text{eff}}^{\text{surf}}(T) \]  

(10)

The experimental data \( c_{\text{Fe}}(c, T, t) \) was then fitted by the linear least-squares method applied to Equation (9), with \( k_{\text{eff}} \) replaced by the sum of the two Arrhenius expressions according to Equation (6), which results in the unknown kinetic parameters \( A_0 \) and \( E_a \) for the homogeneous and the heterogeneous reaction, respectively. Earlier experiments using metallocenes by others conclude that this is also the case for surface reactions following the Langmuir–Hinshelwood mechanism, which is first order at low partial pressures of \( \text{Fe(C}_5\text{H}_5\text{)}_2 \).\(^{[40]} \) The uncertainties of the kinetic parameters given in Table 2 (Section 2.4) only relate to the linear least-squares fitting process.

In the case of ferrocene mixed with \( \text{H}_2 \), one might expect a bimolecular reaction, with its reaction being second-order. Since hydrogen is present in excess in the reaction mixture and the concentration of ferrocene does not exceed 820 ppm, the reaction of ferrocene with hydrogen can be approximated as pseudo-first-order leading to a similar Arrhenius expression as in Equation (6):

\[ k_{\text{eff}}(T) = A_{\text{ZH}} \exp \left( \frac{E_{\text{ZH}}}{RT} \right) \]  

(11)

Following the procedure, described above, also pseudo-first-order rate constants for ferrocene in 10% hydrogen have been determined, which is discussed in Section 2.6 in more detail.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

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

Data Availability Statement

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

Keywords

ferrocene, kinetics of thermal decomposition of ferrocene, metallocene, photoelectron-photoion coincidence spectroscopy, pyrolysis

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