## High-Temperature Pyrolysis |Hot Paper|

# Dimerization of the Benzyl Radical in a High-Temperature Pyrolysis Reactor Investigated by IR/UV Ion Dip Spectroscopy

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**Abstract:** We investigate the self-reaction of benzyl,  $C_7H_7$ , in a high-temperature pyrolysis reactor. The work is motivated by the observation that resonance-stabilized benzyl radicals can accumulate in reactive environments and contribute to the formation of polycyclic aromatic hydrocarbons (PAHs) and soot. Reaction products are detected by IR/UV ion dip spectroscopy, using infrared radiation from the free electron laser FELIX, and are identified by comparison with computed spectra. Among the reaction products identified by their IR absorption are several PAHs linked to toluene combustion such as bibenzyl, phenanthrene, diphenylmethane, and fluorene. The identification of 9,10-dihydrophenanthrene provides evidence for a mechanism of phenanthrene formation from bibenzyl that proceeds by initial cyclization rather than an initial hydrogen loss to stilbene.

## Introduction

Benzyl,  $C_7H_7$ , is the prototype of a resonance-stabilized radical with a  $\pi$ -electron system.<sup>[1]</sup> Owing to its low reactivity, a comparatively long lifetime in a reactive environment can be expected and knowledge about the high-temperature reactions of benzyl is considered relevant for understanding its role in combustion chemistry. In combustion, the benzyl radical is seen as the primary unimolecular reaction product of toluene, a common fuel additive. Indeed, recent flame experiments suggested benzyl to be a major precursor of various aromatic hydrocarbons.<sup>[2]</sup>

High-temperature (pyrolysis) flow microreactors are an efficient tool to generate hydrocarbon radicals and study them under collision-free conditions in a free jet by laser spectroscopy.<sup>[3]</sup> Pyrolytically generated benzyl radicals **2** (Figure 1) have been studied by time-resolved spectroscopy,<sup>[4]</sup> threshold photoelectron spectroscopy,<sup>[5]</sup> and photofragment spectroscopy.<sup>[6]</sup> Ellison and co-workers demonstrated that pyrolysis reactors are also a suitable tool to study the high-temperature chemistry of radicals and analyzed the flow dynamics in such a reactor in detail.<sup>[7]</sup> They focused on the decomposition of organic molecules, like furan<sup>[8]</sup> and anisole<sup>[9]</sup> at high temperature inside the reactor and recently extended their work to the decompo-

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Figure 1. Thermal decomposition of the precursor 1 by pyrolysis is employed to generate  $\mathbf{2}$ .

sition of **2**.<sup>[10]</sup> They observed  $C_7H_6$ ,  $C_7H_5$ ,  $C_5H_5$ , and acetylene as unimolecular decomposition products.

When operated under suitable conditions (i.e., backing gas pressure, temperature, precursor concentration), a pyrolysis reactor also provides an environment to study bimolecular reactions of radicals at high temperature and to detect polycyclic aromatic hydrocarbons (PAHs) that are efficiently formed. Such reactions have initially been observed in photoionization mass spectrometry (PIMS) experiments with tunable synchrotron radiation, where PAH molecules are identified through their ionization energy (IE). For example, mixtures of phenyl<sup>[11]</sup> and naphthyl<sup>[12]</sup> radicals with acetylene were studied with the aim to check the validity of the HACA (hydrogen abstraction C<sub>2</sub> addition) mechanism for PAH and soot formation. A better identification of products isomers is achieved, when ions and photoelectrons are detected in coincidence.<sup>[13]</sup> Alternatively, we recently showed that IR/UV ion dip spectroscopy<sup>[14]</sup> in a supersonically cooled free jet is also a successful tool to study hightemperature reactions in a flow reactor, because it combines the structural sensitivity of infrared spectroscopy with mass information. Although not applicable to small molecules without a UV chromophore and thus less general than photoionization, isomer-selective identification of aromatic molecules and PAH is straightforward. The ground-state IR spectra are obtained by monitoring the depletion in the resonance-enhance ionization signal (REMPI) that occurs upon vibronic excitation, so the technique results in mass-selected IR spectra. However, to

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excite molecules in a free jet in the mid-IR fingerprint region, the high photon flux of a free electron laser (FEL) is required. In previous experiments, we investigated bimolecular reactions of propargyl,<sup>[15]</sup> phenyl,<sup>[16]</sup> and phenylpropargyl radicals<sup>[17]</sup> and observed formation of PAHs with up to three aromatic rings. Here, we extend our work to the benzyl radical, employing phenylethyl nitrite **1** as the precursor, see Figure 1. Note that an IR/UV ion dip spectrum of benzyl itself has already been observed.<sup>[18]</sup>

## **Results and Discussion**

#### Mass spectra

The photoionization mass spectra of the pyrolysis products of 1 (m/z=151) are depicted in Figure 2. The upper trace shows a one-photon ionization mass spectrum at 118 nm. Although



Figure 2. Photoionization mass spectra of 1 with pyrolysis at 118 nm (upper trace) and 265 nm (lower trace).

ionization cross-sections vary for the different molecules observed in the experiment, the spectrum gives an approximate measure of the relative concentration of molecules in the jet. The spectrum shows a complete conversion of the precursor (m/z=151) and the generation of **2** as the predominant mass peak at m/z = 91. Furthermore, dimerization products of **2** are observed at m/z = 182. The lower masses are side products of the pyrolysis such as NO or, less likely owing to its high IE, formaldehyde (m/z=30) and unimolecular decomposition products such as benzene (m/z=78) and cyclopentadienyl (m/z=65). The observation of benzene is expected as it is one of the main decomposition products in the combustion of toluene, whereas cyclopentadienyl has been observed before by Buckingham et al.<sup>[10]</sup> Mass 122 corresponds to phenyl ethanol, one of the reactants used in the precursor synthesis. Therefore, masses 122 and 106, which correspond to benzaldehyde or ethylbenzene (possible pyrolysis products of phenyl ethanol), will not be further considered in the discussion of the benzyl reaction products. The lower trace of Figure 2 shows the [1+1] mass spectrum at 265 nm, which is the basis of the IR/UV ion dip experiment. Because of the high sensitivity for aromatic molecules with a UV chromophore, additional mass signals are visible, in particular strong signals at m/z=166 and 168. The peak at m/z=168 corresponds to the addition of a phenyl unit to benzyl; additional H<sub>2</sub> loss leads to m/z=166. A similar reaction path can be observed for the benzyl dimer. Close to the mass of the dimerization product (m/z=182), additional peaks are visible two mass units apart at 178 and 180, suggesting consecutive H<sub>2</sub> loss. Interestingly, m/z=106 cannot be observed in the REMPI spectrum. This further supports the assignment to benzaldehyde with IE=9.47 eV, which is too high to be ionized with two photons at 265 nm (IE=9.36 eV).<sup>[19]</sup>

#### IR spectra of benzyl self-reaction products

In the following section, the IR/UV ion dip spectra will be discussed and compared with calculated IR spectra. The IR/UV spectrum of the benzyl radical itself has already been measured by Satink et al.<sup>[18]</sup> with the same methodology at 305 nm, utilizing the  $D_3 \leftarrow D_0$  transition. In our study, the UV wavelength (265 nm) excites the red edge of an intense UV band, which is dominated by excitation into several short-lived electronic states.<sup>[4b]</sup> The excitation wavelength was selected to efficiently ionize the most important reaction products. In all spectra presented below, the solid line corresponds to the experimental spectrum. In addition to the molecules discussed here, m/z = 104 has been identified as styrene. As it is possibly also a decomposition product of the alcohol contamination (m/z = 122), it will also not be further discussed.

#### The peaks at m/z = 182-178

The IR action spectra recorded for the peaks at m/z = 182, 180, and 178 are depicted in Figure 3. The largest detectable molecule in our pyrolysis experiment is the dimerization product at m/z = 182. It is the only condensation product with a sufficient concentration to be detected in the 118 nm mass spectrum. The corresponding IR spectrum is depicted in the top trace of Figure 3. Owing to mesomeric stabilization of the radical center in the benzyl, a large number of product isomers are possible; however, a comparison with computations (dotted line) shows that bibenzyl (3, diphenylethane) is the dominant reaction product and dimerization proceeds preferentially in the benzylic position. For comparison IR spectra of several other isomers of m/z = 182 were computed that would be formed by ortho- or para-attack, see the Supporting Information. Most of them can be ruled out immediately. Only 2-benzyltoluene shows peaks at the measured energies, but the computed intensities do not agree with the experimental ones.

Product **3** has two different conformational isomers, *anti* and *gauche*. Identification of the lowest energy isomer turned out to be inconclusive previously because the energy difference between both structures seems to be negligibly small.<sup>[20]</sup> Owing to the different symmetries of these rotamers ( $C_{2h}$  for

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**Figure 3.** IR/UV ion dip spectra (solid lines) of m/z = 182, 180, and 178 in comparison with computed IR spectra (dotted lines). Upper trace: IR/UV of mass 182 in comparison with bibenzyl. Middle trace: IR/UV of mass 180 in comparison with 9,10-dihydrophenanthrene. Lower trace: IR/UV of mass 178 in comparison with phenanthrene.

anti and  $C_2$  for gauche), they can be identified by their respective gas-phase IR spectra. Our data indicates that both isomers are present in the jet, in agreement with previous findings.<sup>[20c]</sup> The peak at 1334 cm<sup>-1</sup> has been shown to be a unique feature of the IR spectrum of the *gauche* isomer, whereas the relative intensity of the signal at 1488 cm<sup>-1</sup> compared with the enclosing vibrations at 1445 cm<sup>-1</sup> and 1593 cm<sup>-1</sup> suggest a contribution of the *anti* isomer. The relative composition at room temperature was predicted to be 70% gauche and 30% anti, a distribution that would qualitatively explain the intensities in our spectrum.

The experimental IR/UV spectrum of m/z = 180 is presented in the center trace of Figure 3. Based on the computation, it is assigned to 9,10-dihydrophenanthrene **4**, showing the major out-of-plane vibrational mode at 734 cm<sup>-1</sup> as well as two further bands between 1400 cm<sup>-1</sup> and 1500 cm<sup>-1</sup>. Finally, the IR spectrum of m/z = 178 is depicted in the bottom trace of Figure 3. Although the signal/noise ratio is low, the carrier can be identified as phenanthrene **5** by the two distinctive out-ofplane vibrations at 724 cm<sup>-1</sup> and 797 cm<sup>-1</sup>, as well as two smaller enclosing signals at 628 cm<sup>-1</sup> and 867 cm<sup>-1</sup>.

The dimerization of benzyl itself is well investigated. Sinha and  $Raj^{[21]}$  calculated the reaction to be barrierless and exothermic [Eq. (1)].

$$2 C_7 H_7 \to C_{14} H_{14} \quad \Delta H^0_R = -283.2 \frac{kJ}{mol}$$
 (1)

The rate constants of this reaction show a low pressure but high temperature dependence.<sup>[22]</sup> Whereas at lower temperature the dimerization of benzyl dominates, the back reaction to benzyl gains importance with increasing temperature.<sup>[19,23]</sup>

Our spectra indicate sequential  $H_2$  loss as a reaction pathway that leads from bibenzyl to phenanthrene formation, according to Figure 4. The reaction is endothermic by 66.6 kJmol<sup>-1</sup> and thus entropy-driven.<sup>[30]</sup> This is in agreement with recent work in toluene flames that suggested **3** to be a phenanthrene precursor simply based on the ratio of mole fractions of **3** and **5** under varying conditions.<sup>[2,19]</sup> Shukla et al.<sup>[24]</sup> also concluded in their toluene pyrolysis study that the formation of **5** is predominantly due to consecutive  $H_2$  elimination of the bibenzyl dimer product. It can alternatively be formed in HACA-like pathways, but suitable precursors such as acetylene and biphenyl<sup>[19,25]</sup> have not been added in the experiments.

The reaction from **3** to **5** can proceed via two pathways: (I) cyclization to **4**, associated with H<sub>2</sub> loss in a first step, followed by a subsequent second H<sub>2</sub> loss (see Figure 4) or (II) initial loss of H<sub>2</sub> to form stilbene and then cyclization concomitant with another H<sub>2</sub> loss in a second step. Interestingly, m/z = 180 has been observed in several studies and was usually identified as stilbene, based mainly on chemical intuition and simple calculations.<sup>[23a,24,26]</sup> However, recent CBS-QB3 calculations<sup>[21]</sup> questioned the involvement of stilbene in phenanthrene formation from **3** and rather suggested the pathway via **4** to be the more efficient above 1200 K reaction temperature.



Figure 4. Identified condensation products in the benzyl radical self-reaction. Top: Dimer formation and consecutive H<sub>2</sub> loss to 9,10-dihydrophenanthrene and phenanthrene. Bottom: Addition of phenyl in the formation of diphenylmethane and cyclization to fluorene.

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Although the reaction from **3** to **4** was computed to be nearly isoenergetic with an activation barrier of 70.1 kJ mol<sup>-1</sup>, the formation of *E*-stilbene requires an activation energy of 168.8 kJ mol<sup>-1</sup> and the reaction is endergonic with 90.2 kJ mol<sup>-1</sup>.<sup>[21]</sup>

The IR spectrum (see Figure 3) shows no features resulting from *E*-stilbene (see the Supporting Information), which should be dominated by two vibrational bands in the 600–800 cm<sup>-1</sup> region with similar intensity. Hence, the data confirm this recent theoretical prediction that the reaction to **5** proceeds via pathway (I) with initial cyclization to dihydrophenanthrene.

#### The peaks at m/z = 168 and 166

At m/z = 166 and 168, two strong peaks appear in the mass spectrum recorded at 265 nm. From a comparison of the experimental and the computed IR spectrum given in Figure 5 mass 168 is unambiguously identified as diphenylmethane **6**. All major features present in the experimental spectrum are well represented by the calculated IR spectrum of diphenylmethane.



**Figure 5.** Comparison of the IR spectra of m/z = 168 and 166 (solid line) with the calculated IR spectrum of diphenylmethane and fluorene (dotted line).

A product at m/z = 168 has been observed in previous studies on toluene pyrolysis that used mass spectrometric detection.<sup>[24,27]</sup> It was explained by a reaction of benzyl with benzene, the second important pyrolysis product of toluene. The 118 nm mass spectrum (see Figure 2) shows indeed a signal at m/z = 78, so benzene and phenyl radicals are also formed in the pyrolysis reactor and become available for secondary reactions. Note that the concentration of phenyl is probably too small to be observed in the mass spectra owing to its high reactivity. Hence, **6** is likely formed by the strongly exothermic reaction of phenyl formed from activated benzene with benzyl [Eq. (2)].

 $C_{6}H_{5}+C_{7}H_{7}\rightarrow C_{13}H_{12}~~\Delta H^{0}_{R}=-382.3~\frac{kJ}{mol} \eqno(2)$ 

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The heat of reaction was calculated from Ref. [28]. In contrast, the reaction of benzyl and benzene to diphenylmethane + H would be endothermic by 93 kJ mol<sup>-1</sup>. The final observed product of benzyl condensation appears at m/z = 166 and can be identified as fluorene **7**. The IR spectrum, depicted in Figure 5, is dominated by the intense B<sub>1</sub> out-of-plane vibration at 732 cm<sup>-1</sup>.<sup>[29]</sup> We accredit the formation of **7** to the H<sub>2</sub> elimination and ring-closing reaction of **6**, see Figure 4, as suggested previously [Eq. (3)].<sup>[24,27]</sup>

$$C_{13}H_{12} \rightarrow 7 + H_2 \quad \Delta H_R^0 = +13 \frac{kJ}{mol}$$
 (3)

The heat of reaction was calculated based on literature data.<sup>[28, 30]</sup> The reaction is slightly endothermic, so at high temperatures the entropy increase will be the driving force. The increase of the fluorene signal with pyrolysis temperature observed in the mass spectra confirms this picture. Flame experiments also claimed 7 to appear as a product in premixed toluene laminar flames.<sup>[19]</sup> The formation of **7** was attributed to a HACA reaction growth chain starting from benzyl ( $C_7H_7 \rightarrow$  $C_9H_8 \rightarrow C_{11}H_8 \rightarrow C_{13}H_{10}$ ) owing to the high concentration of acetylene in their experiments and the observation of the intermediate PAHs. In contrast, we do not observe these intermediate molecules. Note that an IR spectrum of the most stable C<sub>9</sub>H<sub>8</sub> isomer indene has been recorded in previous experiments on phenyl condensation.<sup>[16]</sup> Thus, it is in principle identifiable, when present. Therefore, we conclude that 7 is formed by  $H_2$ loss from 6 rather than in a HACA process via indene, as shown in Figure 4.

### Conclusions

The products of the self-reaction of benzyl radicals in a pyrolysis microreactor at high temperatures have been investigated by IR/UV ion dip spectroscopy. The approach combines the mass selectivity of REMPI-TOF spectroscopy with the isomer selectivity of IR spectroscopy. This novel method has allowed us to identify several PAH products originating from the benzyl radical 2, the primary decomposition product of toluene in combustion. We identified bibenzyl (diphenylethane), dihydrophenanthrene, phenanthrene, diphenylmethane, and fluorene as bimolecular reaction products. All condensation products are formed from the two main decomposition products of toluene combustion: benzyl and phenyl, and were identified by their IR spectra. Particularly, the identification of a species at m/z = 180 as 9,10-dihydrophenanthrene gives new insight into the formation of phenanthrene (see Figure 4) and shows that the reaction proceeds by initial cyclization to 4 followed by a second H<sub>2</sub> loss, in agreement with recent computations. An intermediate with m/z = 180 has been observed before, but was often assigned to stilbene owing to a lack of isomer sensitivity in the experiments, leading to the assumption of an initial H<sub>2</sub> loss to stilbene followed by cyclization in a second step. A further pathway in the bimolecular high-temperature chemistry of benzyl leads to diphenylmethane, probably through a reaction with phenyl radicals. Subsequent cyclization associated

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with  $H_2$  loss leads to **7**. The experiments thus suggest a new route to fluorene formation that will occur in the high-temperature chemistry of toluene.

## **Experimental Section**

Benzyl radicals **2** were generated by flash pyrolysis of **1** (see Figure 1), synthesized from 2-phenyl ethanol and used without further purification.<sup>[31]</sup> The precursor was heated to 85-95 °C and seeded in 1.4 bar argon. A pulsed jet was produced by using a solenoid valve (20 Hz, Parker General Valve) with a resistively heated SiC tube mounted at the exit to cleave the precursor molecules. The pyrolysis unit measures 38 mm in length with an inner diameter of 1 mm. It was heated to approximately 1100 °C and served as a chemical flow reactor. Note that the comparably large length of the SiC tube promotes bimolecular processes. The experimental conditions like sample temperature, pyrolysis power, gas pressure, UV wavelength, etc. have been optimized with respect to dimer formation when using 118 nm one-photon photoionization.

After expansion into the source chamber of a differentially pumped vacuum apparatus, the beam was skimmed and entered the ionization region of a time-of-flight mass spectrometer (TOF-MS).<sup>[32]</sup> Here, the free jet was crossed by the IR beam and UV laser radiation to perform the IR/UV ion dip experiment. This methodology has previously been successfully employed to study a variety of different system, for example, biomolecules,<sup>[33]</sup> hydrated aromatic molecules,<sup>[34]</sup> and radicals.<sup>[16,17]</sup> A frequency-doubled Nd:YAG pumped dye laser ionized molecules in the jet via [1+1] REMPI. The UV wavelength was fixed at 265 nm by using frequency-doubled Coumarin 153 with 0.65 mJ of power and a repetition rate of 20 Hz. The ions were subsequently detected by TOF-MS. The IR radiation was provided by the free electron laser for infrared experiments FELIX (FELIX Laboratory, Radboud University, The Netherlands). It was scanned over the fingerprint region from 550-1750 cm<sup>-1</sup> with a step width of 2.5 cm<sup>-1</sup>, delivering an output power of up to 100 mJ at a repetition rate of 10 Hz. The spectra above are only displayed from 600 cm<sup>-1</sup> upwards owing to experimental artifacts appearing below this value. The IR spectra depicted above were obtained by dividing the signal without and with IR excitation, taking the decadic logarithm, correcting for IR laser power and averaging. Finally, the spectra were smoothed by using digital Savitzky-Golay filtering.

Isomers were identified with the aid of frequency calculations, conducted at the DFT/B3LYP/6–311G(p,d) level of theory and carried out by using the Gaussian09 computational chemistry software.<sup>[35]</sup> The computed vibrational spectra were scaled by a factor of 0.975 and convolved with a Lorentzian (FWHM=8 cm<sup>-1</sup>).

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## **Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** gas-phase reactions • high-temperature chemistry • IR spectroscopy • pyrolysis • radical reactions

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# **FULL PAPER**

**Radical self-reaction**: The self-reaction of benzyl radicals at high temperature, studied with IR/UV ion dip spectroscopy, leads to phenanthrene and fluorene as polycyclic aromatic hydrocarbons.



## High-Temperature Pyrolysis

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Dimerization of the Benzyl Radical in a High-Temperature Pyrolysis Reactor Investigated by IR/UV Ion Dip Spectroscopy