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Investigating repetitive reaction pathways for the formation of polycyclic aromatic hydrocarbons in combustion processes

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ABSTRACT

Repetitive hydrogen-abstraction and methyl- and acetylene-addition reaction sequences that contribute to the formation and growth of polycyclic aromatic hydrocarbons (PAHs) during incomplete combustion processes have been analyzed in flame-sampled electron ionization mass spectra. Specifically, we analyzed the range from C_6H_6 to $C_{16}H_{10}$ in the mass spectra obtained from atmospheric-pressure opposed-flow flames fueled by *n*-butane, *i*-butane, and *i*-butene, with conditions identical to those chosen by Schenk et al. [PAH formation and soot morphology in flames of C_4 fuels, Proc. Combust. Inst. 35 (2015)1761-1769]. To assist the interpretation of the complex flame-sampled mass spectral data, this work elucidates the possibility for providing mechanistic insights from a simple analysis approach that does not convert the mass spectral data into isomer-resolved mole fraction profiles but solely is based on signal strength and ratios. While such an approach has not been exploited before, it is shown in this work that the repetitive nature of the observed quantitative signal ratios in the methyl- and acetylene-addition reaction sequences provides interesting insights into the overall features of flame-sampled mass spectra and the growth chemistry of PAHs. For the flames studied here, the similarity between the spectra obtained from the three different flames suggests that the signal ratios in the covered range are not fuel-structure dependent and that it is possible to draw mechanistic conclusions without knowing the isomer-specific chemistry. For example, the chemical growth pathways supported by this work suggest that other isomers besides pyrene contribute to the measured signal at $m/z = 202$ u ($C_{16}H_{10}$), a result that adds concern regarding the general validity of the assumption of pyrene dimerization as the particle inception step.

1. Introduction

The molecular growth of small precursor molecules to large polycyclic aromatic hydrocarbons (PAHs) in combustion environments receives continuing attention in combustion chemistry research [1–6]. The motivation behind this interest stems from the facts that PAHs, which are generally considered precursors for soot particles, are byproducts of incomplete combustion processes and are known to be harmful to humans and the environment [7–11]. Because anthropogenic activities, including combustion processes, cause major PAH emissions into the atmosphere [12], understanding the formation pathways that lead to PAHs will eventually help to reduce the emission of these substances and to develop a model for soot particle inception.

A chemical understanding of and a predictive combustion chemistry model for PAH formation are based on two pillars, *i.e.*, an accurate description of the formation of the so-called *"first aromatic ring"* and the subsequent characterization of the molecular growth reactions towards PAHs. It is evident that the predictive capabilities of the PAH sub-model rely on the accuracy of the description of the formation of the *first aromatic ring*. Already this first step in the overall soot formation process can be very complex: Normally, benzene is considered to be this *first aromatic ring* and its formation is generally described by reactions of resonantly stabilized radicals like propargyl (C_3H_3), allyl (C_3H_5), *i*-C_4H_5, and cyclopentadienyl (C_5H_5) [5,13–19]. However, precursors and reactions have been identified that can form aromatic species without passing through benzene, and it is therefore important to note that benzene is not necessarily the *first aromatic ring* [5,6]. Noteworthy examples are the proposed formation routes of naphthalene via the reaction of two cyclopentadienyl (C_5H_5) radicals or the formation of benzyl and toluene via the ring-enlargement $C_5H_5+C_2H_2$

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reaction [20,21]. Toluene, phenylacetylene, and styrene can also be formed directly through various other reactions of C_4H_5 and C_5H_3 radicals [22–24]. Further complexity is added by the fact that the importance of these various formation pathways is likely to depend on the fuel structure [13,25].

In contrast, many combustion chemistry models describing the PAH growth chemistry from the first aromatic ring consider a repetitive sequence of hydrogen-abstraction and C_2H_2 (acetylene)-addition reactions, the so-called HACA mechanism [26]. This description is based on the original work of Frenklach and Wang [27] and was later updated by Appel et al. [28]. However, compelling evidence is now accumulating in the literature that the HACA mechanism alone cannot provide an accurate description of the molecular-growth chemistry. For example, it was shown that this HACA mechanism is too slow to account for the very fast process of PAH formation [29,30], that HACA is not needed to promote growth of large PAHs [31], and that PAHs can be formed in non-sequential order [32–35]. In addition, Kislov et al. showed that the HACA mechanism produces mostly cyclopenta-fused PAHs instead of PAHs with six-member rings only [36].

To overcome these limitations, many other reactions have been considered to contribute to PAH formation. For example, Panariello et al. identified not only the above discussed HACA steps in flame-sampled mass spectra but also C- and/or CH_2-addition reactions [37]. Similarly, Shukla and Koshi suggested methyl addition/cyclization reactions to be important [38,39] and Yoon et al. also emphasized the role of methyl radicals for the formation of PAHs [40,41]. Other radical species discussed in the literature that might contribute to PAHs include vinyl [42], propargyl [30,43–45], cyclopentadienyl [30,43,45,46], and aromatic ring radicals [38,47,48]. Reactions of vinylacetylene with aromatic radicals contributing to ring-formation chemistry were discussed, for example, in Refs. [28,43,45]. It is conceivable that the importance of these various reactions depends on the fuel structure, as it was shown to be the case for the formation of the *first aromatic ring*.

The present work is intended to shed further light on repetitive growth sequences in PAH formation chemistry and builds upon the studies of Panariello et al. [37], Shukla and coworkers [38,39], and Schenk et al. [49] in which repetitive sequences of acetylene and methyl additions were *qualitatively* identified as molecular-weight growth reactions via signal patterns in mass spectrometric experiments. This study elucidates the possibility of gaining information about the PAH growth process not just from the signal patterns but additionally from *quantitative* signal intensities. This approach is related to the earlier work [25], in which experimentally determined peak mole fractions of C_3H_3, C_4H_5, and C_5H_5 were correlated to C_6H_6 mole fractions to unravel benzene formation pathways in premixed flames.

It is outlined here, that a simplistic analysis of the signal intensities in the flame-sampled gas-phase mass spectra taken from atmospheric-pressure opposed-flow flames fueled by *n*-butane, *i*-butane, and *i*-butene might allow for gaining some insights into the PAH growth chemistry up to the $C_{16}H_{10}$ intermediates without the full knowledge of the detailed chemistry of isomer-resolved chemical structures. Such a simplified approach, in which the mass spectral signal is intentionally not converted into isomer-resolved mole fraction profiles, might become important because both the exponential growth of the number of isomers with the size of the molecular structure and the scarcity of calibration or cross section information preclude such comprehensive isomer-resolved analysis for the growth of larger PAHs. The presented concept is supported by the recent observation that the ratios of the maximum toluene and benzene mole fractions are constant in many flames of a variety of different fuels [50].

The new insights are intended to assist in connecting species measurements in non-premixed flames with the ongoing efforts in the soot community to develop flame chemistry models, that are often also relying on lumping, *i.e.* not isomer-specific, approaches, for PAH formation.

2. Experimental procedures

For the purpose of this paper, *i.e.,* to elucidate the possibilities to gain chemical information about PAH formation from signal intensities in flame-sampled mass spectra without resolving the details of isomeric contributions, we recorded mass spectra from opposed-flow diffusion flames of *n*-butane, *i*-butane, and *i*-butene. The flame conditions were identical to the ones reported in Ref. [49] and are provided here only as Supplementary Material. The fuels were chosen because their respective combustion chemistry are interesting research topics as outlined in Refs. [51–53] and further details are therefore not provided here. From the chemical point-of-view the selected fuels represent different chemical structures including isomeric long-chain (normal) and branched (iso) alkanes, and a branched (iso) alkene.

The experimental approach used to record the flame-sampled mass spectra has been detailed in Ref. [49]. In short, opposed-flow fuel-Ar/O_2-Ar diffusion flames were established at atmospheric pressure between the two outlets of a home-built burner system [54] while regulating the respective gas flows with an absolute precision of $\pm 0.5\%$ using calibrated mass flow controllers. The conditions were optimized to establish flames that provide sufficient signal for the investigated mass range up to $m/z = 202$ u while simultaneously avoid clogging of the sampling probe. The conditions result in slightly sooting flames as indicated by the observed orange incandescence. The adiabatic peak temperatures are calculated to be 2100 ($\pm$100) K using three different models [44,55,56]. The results of these calculations are summarized in the Supplementary Material. The *i*-butene flame is calculated to be the coldest with temperatures in the range of 2020 K ($\pm$15 K), while the *n*-butane flame is the hottest with temperatures calculated to be between 2196 K ($\pm$11 K). It is discussed later that the small differences in the peak flame temperature do not alter the conclusions.

In order to probe the chemical details of the opposed-flow flames and to eventually guide the model development, gases were sampled from the center-line of the flame configurations as function of the distance from the fuel outlet via a microprobe with a ~20 µm orifice into a differentially pumped molecular-beam mass spectrometer, as described previously [49,57]. Keeping the sampling probe fixed, flame-sampling from any axial position of the flame was achieved with an accuracy of 0.5 mm by vertically moving the entire burner assembly using a computer-controlled high-precision (0.05 mm) stepper motor. The given accuracy, which mainly results from the uncertainty in the determination of the zero-point, *i.e.,* "Distance from the Fuel Outlet" = 0 mm, implies that the provided experimental data might be shifted by this amount; a technique widely accepted in premixed flame experiments in order to achieve spatial agreement with modeling results [58,59]. In contrast, the spatial resolution of the measurements is mainly determined by the diameter of the microprobe's orifice.

The mass spectrometer was equipped with electron ionization (EI) and the ions were pulse-extracted into the time-of-flight region, separated by their mass-to-charge (m/z) ratio, and subsequently detected using a multi-channel plate detector with a multi-channel scaler for data recording. The sensitivity limit of ~1 ppm, a dynamic range of 10^6, and the mass resolution of $m/\Delta m$ ~2500 of the custom-built reflectron time-of-flight mass spectrometer enabled the detection of many PAH species [49] and their separation from oxygenated intermediates. The width of the electron's energy distribution (~2 eV full width at half maximum) precluded isomer-resolved EI measurements; however, a limited

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