Characteristics of non-premixed oxygen-enhanced combustion: II. Flame structure effects on soot precursor kinetics resulting in soot-free flames

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A detailed computational study was performed to understand the effects of the flame structure on the formation and destruction of soot precursors during ethylene combustion. Using the USC Mech Version II mechanism the contributions of different pathways to the formation of benzene and phenyl were determined in a wide domain of $Z_{st}$ values via a reverse-pathway analysis. It was shown that for conventional ethylene–air flames two sequential reversible reactions play primary roles in the propargyl ($\text{C}_3\text{H}_3$) chemistry, namely

\begin{align}
  \text{C}_2\text{H}_2 + \text{CH}_3 & \rightleftharpoons \text{pC}_3\text{H}_4 + \text{H} \\
  \text{pC}_3\text{H}_4 & \rightleftharpoons \text{C}_3\text{H}_3 + \text{H}
\end{align}

with the corresponding overall endothermic reaction of propargyl formation

\begin{equation}
  \text{C}_2\text{H}_2 + \text{CH}_3 \rightleftharpoons \text{C}_3\text{H}_3 + 2\text{H}.
\end{equation}

The contributions of these reactions to propyne (pC$_3$H$_4$) and propargyl formation and propargyl self-combination leading to benzene and phenyl were studied as a function of physical position, temperature, $Z_{st}$, and H concentration. In particular, the role of H radicals on soot precursor destruction was studied in detail. At low $Z_{st}$, Reactions 1 and 2 contribute significantly to propyne and propargyl formation on the fuel side of the radical pool at temperatures greater than approx. 1600 K. At higher local temperatures near the radical pool where the concentration of H is significant, the reverse reactions begin to dominate resulting in soot precursor destruction. As $Z_{st}$ is increased, these regions merge and only net propargyl consumption is observed. Based on the equilibrium constant of Reaction 3, a $Z_{st}$ value was estimated above which the rate of propargyl formation as a soot precursor is greatly reduced ($Z_{st} \approx 0.3$). This condition compares well with the experimental results for permanently blue counterflow flames in the literature.

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1. Introduction

Soot particles can damage gas turbine blades used in power generation and jet propulsion [1], provide nucleation sites for aircraft contrails generating climate altering artificial cloudiness [2], make military aircraft susceptible to detection and/or tracking, and in general can be hazardous to the environment and human health [3–7]. Hansen and Nazarenko reported that the efficacy of soot climate forcing is twice that of CO$_2$ [3]. More specifically, given equivalent climate forcing by soot and CO$_2$, the change in equilibrium temperature induced by soot climate forcing will be twice that of CO$_2$. With respect to human health, epidemiological studies have linked soot inhalation to death from lung cancer and cardiopulmonary disease [5–12]. Moreover, the heightened health impact of particles formed via hydrocarbon combustion processes is due to their small size (<2.5 μm)—which allows them to travel deep into the lungs where they are quickly introduced into the blood stream—and their association with mutagenic and tumorigenic polycyclic aromatic hydrocarbons (PAH) [6,7,9–12]. Thus, for a variety of reasons understanding soot formation and developing technologies to inhibit soot formation is an area of important research.

One approach for inhibiting soot formation in non-premixed flames, which can be considered a form of oxygen-enhanced combustion (OEC), involves oxygen-enrichment of the oxidizer stream and fuel-dilution with an inert. Fuel dilution by an inert alone has
been shown to inhibit soot formation and temperature and dilution effects [13], with dilution having a more significant effect than temperature. Classman [14] argued that the inhibition of soot formation by fuel dilution was due to the altering of the thermal diffusivity in the fuel stream, which can impact the time available for soot growth within the critical temperature isomers. Conversely, oxygen-enrichment (without inert fuel dilution) can increase soot production rates in non-premixed flames due primarily to increased temperatures [15]. When combined, oxygen-enrichment and fuel-dilution alters the stoichiometric mixture fraction, $Z_{st}$, and can have a dramatic impact on the flame structure (i.e. the relationship between the local temperature and the local species profiles) and soot formation. The stoichiometric mixture fraction is given by

$$Z_{st} = (1 + \sigma Y_{F, L}/Y_{O_2, ox})^{-1}$$

where $\sigma = \nu_0 Y_{O_2}/Y_i W_i$ and $Y_i$, $\nu_0$, $W_i$ represent the mass fraction, stoichiometric coefficient, and molecular weight of species $i$, respectively, and $fu$ and $ox$ designate the fuel stream and oxidizer stream boundaries, respectively. Thus, pure fuel burning in air represents a stoichiometric coefficient, and molecular weight of species side of the flame conducive to soot precursor oxidation and the observed soot-free conditions [21,22,29].

To more fully understand the influence of flame structure, as characterized by $Z_{st}$, on soot formation we perform a computational study using a counterflow flame code with detailed chemistry. The effect of the flame structure on soot precursor kinetics is evaluated by determining the primary reactions responsible for the formation of benzene and phenyl at low and high $Z_{st}$ using a reverse-pathway analysis, which is described in detail below. Observed changes in the benzene/phenyl formation pathway at high $Z_{st}$ involving the formation and destruction of propargyl are investigated in detail. Finally, the behavior of a key propargyl pathway is compared with an equilibrium relationship for the overall reaction (Reaction 3).

1.1. Numerical

The counterflow flame code employed here was originally developed by Kee et al. [30] for premixed opposed-flow flames and was later modified for adiabatic non-premixed combustion by Lutz et al. [31]. Chemical reaction rates, transport properties, and thermodynamic properties were evaluated by the Chemkin software package. Mixture averaged diffusion coefficients were utilized in the work presented here after verifying that using multi-component diffusion did not significantly affect the phenomena in question at low and high $Z_{st}$. In the mixture averaged formulation of Lutz et al. [31], thermal diffusion is taken into account for individual species. Thus, the potential impact of thermal diffusion on soot precursor formation is included [32].

The mechanism used in this study combines USC Mech Version II [33] with chemistry up to pyrene from Wang and Frenklach [34] and Appel et al. [35] resulting in 143 species and 938 reactions. While an evaluation of the uncertainties associated with each of the 938 reactions is beyond the scope of this work, we note that uncertainties in experimentally determined rate coefficients, $k$, can be as large as an order of magnitude [36,37]. The flame code and mechanism were validated by comparing numerical results with the experimental results of Sun et al. [38] and Otten and Senkan [39] as shown in Fig. 1a and b. Sun et al. [38] obtained major species and temperature profiles via spontaneous Raman scattering, while Otten and Senkan [39] measured temperatures with a thermocouple and measured major and several minor species using a quartz microprobe and gas chromatography mass spectrometry (GC–MS). The results in Fig. 1a show excellent agreement between the flame code used here and the experimental temperature and species profiles of ethylene, O₂, CO₂, H₂O, and acetylene from Sun et al. [38]. In Fig. 1b good agreement is observed between the flame code and the experimental species profiles of ethylene and CO from Otten and Senkan [39], with the exception of the three ethylene data points closest to the fuel boundary. Both acetylene and benzene are predicted by the flame code to within a factor of two (~1.6) when compared to the measurements; however, the modeled and experimental benzene profiles are not aligned. Finally, the numerical and experimental temperature profiles are also out of alignment; although the peak temperatures (after correcting the data of Ref. [39] for radiation losses) are within 50 K. Radiation corrections were made using an emissivity of 0.95 provided by Ref. [39], assuming a Nusselt number of two, and using the thermal conductivity of nitrogen at the bead temperature to compute the convection coefficient.

For the flames specific to this study, the fuel and oxidizer stream inlet boundaries were spaced 2 cm apart and adaptive grid refinement parameters were adjusted to ensure the attainment of converged solutions. The fuel and oxidizer inlet velocities were held constant at 15 cm/s for all flames resulting in similar strain rates, which were determined as described in Law [40]. The total amount of inert in the system was maintained at 11.28 mol per
mole of fuel resulting in an adiabatic flame temperature of 2370 K for all flames. Flame parameters are provided in Table 1.

### 2. Results and discussion

As it is well accepted that the formation of the first aromatic ring is an important step in the path to soot formation for aliphatic fuels [41–43], this investigation evaluates the effects of flame structure on the detailed chemistry leading to the formation of benzene and phenyl. The dominant pathways to benzene and phenyl in both the fuel/air (low $Z_{st}$) and diluted-fuel/oxygen (high $Z_{st}$) flames were determined based on a reverse-pathway analysis, which can be explained by the following illustration.

Based on the flame conditions and kinetic model used in this study eight elementary reversible reactions contribute to the net production of phenyl. To determine the contribution from each reaction to the total phenyl produced, the net reaction rate profiles were integrated for each reaction over the entire domain. Because any of these reversible reactions may produce phenyl in one region of the flame and consume phenyl in another region of the flame, only the net positive contribution was considered in this analysis. In this way, our analysis could account for spatial variations in the net direction of each reaction that may result in some reactions being neglected or considered of less importance. For example, while the reaction $C_2H_4 + OH = C_2H_5 + H_2O$ produces phenyl in the high temperature region where OH is available, in the pyrolysis zone the reverse reaction rate is larger than the forward rate resulting in phenyl consumption. If both the net production and net destruction were integrated in this analysis, the relative contribution from this reaction to the total phenyl production would be reduced. Once the rates have been integrated, the sum of these quantities represents the total rate of phenyl produced via all contributing reactions in the flame. The relative contribution from each reaction was then determined based on the ratio of the integrated individual quantities to the sum.

In Fig. 2, the relative contributions from phenyl-producing reactions for the low $Z_{st}$ fuel/air flame are shown in a pie chart. For this analysis, and for other species evaluated, reactions producing less than 2.5% of the total have been neglected. The results in Fig. 2 indicate that 78% of the total phenyl produced in the flame is via propargyl self-combination, with 11.5% produced from the net conversion of benzene to phenyl (where multiple transformations are represented by $C_6H_6 + R = C_6H_5 + P$, with $R$ representing reactants and $P$ representing products), 6% from 2-phenylvinyl ($n$-A1C2H2), and 3% from phenylacetylene ($C_6H_5C_2H$). Additional analysis reveals that both 2-phenylvinyl and phenylacetylene are primarily produced through phenyl, and thus cannot be considered primary phenyl production reactions. Furthermore, benzene was determined to be primarily produced via propargyl self-combination, with a small contribution (~7%) from acetylene addition to $C_6H_5$ (but-2-yn-1-yl), and negligible contributions (<2.5%) from several other reactions including those involving $C_5H_6$ (cyclopentadiene). Thus, consistent with recent literature we conclude that under the fuel/air operating conditions of this study propargyl ($C_3H_3$) self-combination is the dominant reaction leading to phenyl [43].

Continuing in reverse order and performing this same analysis for propargyl yields the dominant propargyl producing reactions. In the fuel/air flame it is observed that two dominant pathways to propargyl exist. The first involves acetylene reacting with the methyl radical ($CH_3$) to form propyne ($pC_3H_4$)

![Fig. 1. Comparison of temperature and select species profiles from code used in this work with experimental results from: (a) Sun et al. [38] and (b) Olten and Senkan [39].](image)

![Fig. 2. Relative contribution of individual phenyl-producing reactions to total phenyl production rate.](image)

### Table 1
Flame Parameters.

<table>
<thead>
<tr>
<th>Flame</th>
<th>$Z_{st}$</th>
<th>$X_{Bu}$</th>
<th>$X_{O2,mix}$</th>
<th>$a$ (s$^{-1}$)</th>
<th>$(dZ/dx)^2$ at $Z_{st}$ (cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.06</td>
<td>1.00</td>
<td>0.21</td>
<td>8.7</td>
<td>0.08</td>
</tr>
<tr>
<td>B</td>
<td>0.10</td>
<td>0.64</td>
<td>0.22</td>
<td>8.9</td>
<td>0.17</td>
</tr>
<tr>
<td>C</td>
<td>0.20</td>
<td>0.32</td>
<td>0.25</td>
<td>8.9</td>
<td>0.45</td>
</tr>
<tr>
<td>D</td>
<td>0.30</td>
<td>0.21</td>
<td>0.28</td>
<td>9.2</td>
<td>0.78</td>
</tr>
<tr>
<td>E</td>
<td>0.40</td>
<td>0.16</td>
<td>0.33</td>
<td>9.4</td>
<td>0.98</td>
</tr>
<tr>
<td>F</td>
<td>0.50</td>
<td>0.13</td>
<td>0.40</td>
<td>9.5</td>
<td>1.12</td>
</tr>
<tr>
<td>G</td>
<td>0.60</td>
<td>0.11</td>
<td>0.51</td>
<td>9.8</td>
<td>1.08</td>
</tr>
<tr>
<td>H</td>
<td>0.70</td>
<td>0.10</td>
<td>0.70</td>
<td>9.7</td>
<td>0.98</td>
</tr>
<tr>
<td>I</td>
<td>0.78</td>
<td>0.08</td>
<td>1.00</td>
<td>9.8</td>
<td>0.75</td>
</tr>
</tbody>
</table>
C₂H₂ + CH₃ = pC₃H₄ + H \quad \text{(1)}

which forms propargyl by dissociation

pC₃H₄ = C₃H₃ + H. \quad \text{(2)}

The overall reaction resulting from Reactions 1 and 2 is represented by

C₂H₂ + CH₃ = C₃H₃ + 2H. \quad \text{(3)}

The second dominant propargyl formation pathway involves acetylene reacting with methylene (CH₂ triplet, CH₂ singlet).

C₂H₂ + CH₂ = C₃H₃ + H. \quad \text{(4)}

C₂H₂ + CH₂ = C₃H₃ + H. \quad \text{(5)}

Other propargyl formation reactions that contribute ~5% individually include:

aC₃H₄ + OH = C₃H₃ + H₂O \quad \text{(6)}
aC₃H₄ = C₃H₃ + H \quad \text{(7)}

1.2-C₄H₆(+M) = C₃H₃ + CH₃(+M). \quad \text{(8)}

The reverse-pathway analysis presented above was utilized to evaluate the dominant pathways to benzene and phenyl at both low and high \( Z_{st} \), and a graphical representation of the results is provided in Fig. 3. Peak net rates for the reactions shown in Fig. 3 are also provided in Table 2. Before discussing Fig. 3 in detail, we point out that in non-premixed flames spatially distinct zones are observed within the reaction region that can be characterized by local sub-processes (e.g. pyrolysis and oxidation zones) [38]. For example, in Fig. 1b the acetylene and benzene mole fraction profiles characterizing the pyrolysis zone are clearly displaced from the location of peak temperature, while in Fig. 1a the H₂O and CO₂ species profiles characterizing the oxidation zone are centered near the location of peak temperature. When considering the pathways to benzene, it was observed that a distinction could be made in the pyrolysis zone between reactions responsible for benzene formation below and above a temperature of approx. 1600 K. On the right side of Fig. 3 we illustrate that at temperatures below approx. 1600 K benzene formation occurs via the even carbon

Table 2

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Peak rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Z_{st} = 0.064 )</td>
<td></td>
</tr>
<tr>
<td>( Z_{st} = 0.78 )</td>
<td></td>
</tr>
<tr>
<td>Fuel pyrolysis pathway</td>
<td></td>
</tr>
<tr>
<td>C₃H₃ + H = C₂H₂ + H₂</td>
<td>1.9E-4</td>
</tr>
<tr>
<td>C₂H₄(+M) = C₂H₂ + H₂</td>
<td>2.6E-4</td>
</tr>
<tr>
<td>C₃H₃ + CH₄ = C₃H₄ + H</td>
<td>6.7E-6</td>
</tr>
<tr>
<td>C₃H₃ + H = C₃H₂ + H₂</td>
<td>1.5E-6</td>
</tr>
<tr>
<td>pC₃H₄ = C₃H₂-2</td>
<td>1.3E-6</td>
</tr>
<tr>
<td>C₃H₂-2 + C₂H₂ = C₃H₆ + H</td>
<td>7.4E-7</td>
</tr>
<tr>
<td>Fuel oxidation pathway</td>
<td></td>
</tr>
<tr>
<td>C₂H₂ + CH₃ = C₃H₃ + H</td>
<td>1.0E-5</td>
</tr>
<tr>
<td>C₃H₂ + CH₂ = C₃H₃ + H</td>
<td>4.7E-6</td>
</tr>
<tr>
<td>C₂H₂ + CH₂ = pC₃H₄ + H</td>
<td>2.4E-5</td>
</tr>
<tr>
<td>pC₃H₄ = C₃H₂-2</td>
<td>2.0E-5</td>
</tr>
<tr>
<td>C₃H₂-2 + C₂H₂ = C₆H₆ + H</td>
<td>1.3E-5</td>
</tr>
<tr>
<td>C₃H₂ + C₂H₂ = C₆H₆</td>
<td>5.0E-6</td>
</tr>
<tr>
<td>Oxidation zone</td>
<td></td>
</tr>
<tr>
<td>C₂H₂ + H = C₂H + H₂</td>
<td>6.4E-5</td>
</tr>
<tr>
<td>C₂H₂ + OH = C₂H + H₂O</td>
<td>1.3E-5</td>
</tr>
<tr>
<td>C₂H₂ + OH = CH₂CO + H</td>
<td>3.6E-5</td>
</tr>
<tr>
<td>C₂H₂ + O = CH₂ + CO</td>
<td>5.2E-5</td>
</tr>
<tr>
<td>C₂H₂ + O = HCO + C₂H₂</td>
<td>2.1E-4</td>
</tr>
<tr>
<td>C₂H₂ + C = C₂H₂ + H</td>
<td>7.2E-5</td>
</tr>
<tr>
<td>C₂H₂ + OH = H₂C₃O + H</td>
<td>8.3E-5</td>
</tr>
<tr>
<td>H₂C₃O + C₂H₂ = HCO + CH₂CO</td>
<td>2.4E-5</td>
</tr>
<tr>
<td>HCO + H = CH₂CO + H</td>
<td>2.1E-5</td>
</tr>
<tr>
<td>CH₂CO + H = CH₂ + CO</td>
<td>7.6E-5</td>
</tr>
<tr>
<td>HCO + H = CH₂ + CO</td>
<td>1.5E-4</td>
</tr>
<tr>
<td>CH₂(+M) + CH₂(+M)</td>
<td>9.0E-5</td>
</tr>
<tr>
<td>CH₂CO(+M) = CH₂ + CO(+M)</td>
<td>1.6E-5</td>
</tr>
</tbody>
</table>

CH₂ and CH₃ are triplet and singlet methylene, respectively.

Rates in parenthesis indicate net destruction for rates that have reversed at high \( Z_{st} \).

Fig. 3. Dominant benzene and phenyl formation pathways.
pathway by acetylene addition to \( \text{C}_4\text{H}_5-2 \). Because the species required in this pathway are generated by fuel decomposition, we consider this to be a “fuel pyrolysis pathway”. In laminar co-flow flames of aliphatic fuels it is likely that this pathway primarily contributes to benzene formation leading to soot observed along the flame centerline. It is also interesting to note that benzene formation via acetylene addition to \( \text{C}_4\text{H}_5-2 \) is a reversible exothermic reaction in which the reverse reaction dominates at higher temperatures leading to significant benzene consumption near the flame. Thus, benzene formation via this pathway is restricted to lower temperature fuel-rich regions.

At temperatures greater than 1600 K in the pyrolysis zone of the fuel/air flame, benzene and phenyl formation is dominated by propargyl self-combination requiring methylene and the methyl radical as depicted in the top central illustration of Fig. 3 [41]. Both methylene and the methyl radical are predominantly produced in and near the radical pool during the oxidation of acetylene as indicated on the left side of Fig. 3. For this reason, we consider this benzene and phenyl production pathway to be a “fuel oxidation” pathway and it is hypothesized that this pathway is primarily responsible for benzene and phenyl formation leading to soot observed in laminar co-flow flames of aliphatic fuels near the flame sheet and in flames at their sooting limit [22,29].

Considering these results, it is interesting to note that a recent modeling study by Slavinskaya and Frank [44] indicated that for premixed flame and shock tube conditions the reaction pathways leading to aromatics for methane and ethylene could be “conditionally divided into ‘low temperature steps’, which dominate at \( T < 1550 \text{ K} \) and ‘high temperature steps’, which give main contributions in PAH formation at \( T > 1550 \text{ K} \).” However, although two temperature dependent pathways to benzene have been distinguished spatially in our results, we emphasize that based on the mechanism and fuel/air flame conditions of this study the integrated contribution of acetylene addition to \( \text{C}_4\text{H}_5-2 \) to the total amount of benzene formed in the fuel/air flame is nearly seven times less than that produced via propargyl self-combination. Moreover, it was observed that the total amount of benzene produced via acetylene addition to \( \text{C}_4\text{H}_5-2 \) scales with the initial fuel concentration, thus reductions in soot through this pathway are a result of dilution and not changes in flame structure at high \( Z_{st} \). In contrast, the total amount of benzene produced via propargyl self-combination does not scale with the initial fuel concentration when increasing \( Z_{st} \) beyond \( Z_{st} = 0.3 \), but is reduced by a factor considerably larger than that associated with fuel dilution. In Table 2 it can be seen that the peak net rate of benzene production via acetylene addition to \( \text{C}_4\text{H}_5-2 \) decreases by a factor of \( \sim 6 \) at \( Z_{st} = 0.78 \) relative to the fuel/air flame, while both benzene and phenyl production via propargyl self-combination are reduced by two orders of magnitude at high \( Z_{st} \). Thus, the discussion below will focus only on reactions involving propargyl.

The most important result in Fig. 3, shown in the bottom center, involves the reversal of one of the key propargyl formation pathways at high \( Z_{st} \), which in fact, becomes the dominant route for propargyl destruction. The details of this phenomenon are further illustrated in Figs. 4 and 5, and as will be discussed below, this is a key point in understanding how the flame structure in high \( Z_{st} \) flames leads to soot-free (i.e. permanently blue) conditions in high temperature non-premixed flames. The relative contributions from selected propargyl formation reactions are shown in Fig. 4. Here it is observed that in the fuel/air flame \( (Z_{st} = 0.064) \) Reaction 2 is the dominant propargyl formation reaction contributing more than 30% of the total propargyl produced. As \( Z_{st} \) increases the contribution from this reaction drops sharply and propargyl production is dominated by reactions between acetylene and methylene. Moreover, it is apparent that when \( Z_{st} = 0.3 \) Reaction 2 no longer contributes to propargyl formation. We point out also that when considering the behavior of Reaction 1, which leads to propyne formation, the same reversing phenomenon was observed. In Fig. 5 the relative contributions from selected propargyl destruction reactions are shown. In the fuel/air flame \( (Z_{st} = 0.064) \) we observe that nearly 60% of the propargyl destroyed forms phenyl and benzene. As \( Z_{st} \) is increased the percentage of propargyl forming benzene and phenyl is reduced significantly. More importantly, for \( Z_{st} > 0.3 \) most of the propargyl returns to propyne via the reverse of Reaction 2. It is also interesting to note that increasing \( Z_{st} \), which results in more oxygen in the region of high temperature and appreciable oxygen at the location of maximum temperature [16,45], does not result in a greater percentage of the propargyl being directly oxidized. When considering the direct oxidation of other soot precursor species, only acetylene destruction by direct oxidation increased relative to other destruction pathways at high \( Z_{st} \). In spite of this, the peak mole fraction, peak production rate, and total amount of acetylene in the flame behaved less than first order in fuel when increasing \( Z_{st} \). That is, the reduction in these quantities when increasing \( Z_{st} \) was less significant than the reduction in the free-stream fuel concentration. Thus, enhanced destruction of acetylene by direct oxidation at high \( Z_{st} \) is not considered to be a primary factor resulting in permanently blue flames.

Returning to our discussion of Reactions 1 and 2, two important factors influence the net direction of these reactions in low and high \( Z_{st} \) flames. The first factor to consider is that \( H \) is produced in both reactions, and if sufficient \( H \) is available locally the reverse of these reactions will be preferred, even at high temperature.
Evidence of such a phenomenon was demonstrated by Marinov and coworkers [46], who performed a sensitivity analysis and showed that the consumption of propargyl by H atoms could limit propargyl, benzene, and naphthalene formation in a laminar premixed n-butane flame. The second factor to consider is that Reactions 1 and 2 are endothermic reactions. Thus, if the flame structure is altered such that the temperature in the reaction region of Reactions 1 and 2 is lowered, the reverse reaction will be preferred. As shown in Fig. 6a, there are two regions associated with the net rate profiles of R1 and R2 in the fuel/air flame. The first region is characterized by net propyne and propargyl production via R1 and R2 at temperatures near 1600 K. The second region is observed where the local temperature is high (ca. 2000 K) but sufficient H is available to drive Reactions 1 and 2 from net propyne and propargyl production to net destruction.

The high H concentration at this location is due to rapid H production during the oxidation of H2 and CO by OH. Note that a significant concentration of H is not observed in the first region (region of pyrolysis), given that the pyrolysis reactions produce and consume H at comparable rates. In Fig. 6b it is observed that in the Zst = 0.3 flame, which is approaching the permanently blue flame conditions observed by Du and Axelbaum [16] and Lin and Faeth [17], that the two regions of net propyne and propargyl destruction by Reactions 1 and 2 can still be distinguished by the apparent extrema; however a region of net propyne and propargyl production through these reactions no longer exists. In the high Zst flame shown in Fig. 6c, which is well beyond the conditions required to achieve a permanently blue flame, the two regions of propyne and propargyl destruction by Reactions 1 and 2 are indistinguishable and the rates are amplified as the region of low temperature (characterized by T < 1600 K) has merged with the region in which the edge of the H radical concentration profile (characterized by the fall-off) is located. Thus, at high Zst, the two factors that influence the preferred direction of Reactions 1 and 2 (i.e. low temperature and ample H concentration) combine to drive propargyl, that was formed through other propargyl formation pathways, back to propyne and subsequently back to acetylene thereby significantly reducing the opportunity for benzene and phenyl formation by propargyl self-combination.

To better understand the conditions where net propargyl production via Reactions 1 and 2 ends, the reaction quotient of Reaction 3 (i.e. the overall reaction for Reactions 1 and 2) defined as

\[ Q_r = \frac{P_{C_3H_3}P_H}{P_{C_3H_4}} \]

where \( P_i \) is the partial pressure of species \( i \), is plotted for all nine flames as a function of temperature along with the equilibrium constant, \( K_p \) in Fig. 7. It is observed that the reaction quotient is less than \( K_p \) when \( Z_{st} < 0.3 \), which indicates that local thermodynamics prefer the formation of the products \( C_3H_3 \) and H for these flames. When \( Z_{st} = 0.3 \), the reaction quotient is nearly equivalent to \( K_p \) indicating that the local concentrations are near equilibrium conditions. And finally, when \( Z_{st} > 0.3 \) the reaction quotient is larger than \( K_p \) indicating that local thermodynamic conditions prefer the reverse of the overall reaction (Reaction 3) leading to the destruction of \( C_3H_4 \) and H and the formation of \( C_2H_2 \) and \( CH_2 \). Thus, for \( Z_{st} > 0.3 \) net propargyl destruction via this pathway prevails leading eventually to permanently blue flame conditions. We note also that the results of this analysis compare favorably with the experiments of Du and Axelbaum [16] and Lin and Faeth [17] who showed that soot formation would not occur in counterflow ethylene flames having an adiabatic flame temperature of 2370 K at strain rates approaching zero when \( Z_{st} > 0.35 \).

Recognizing that these computational results are mechanism dependent, we investigated the effect of replacing the rate parameters for Reactions 1 and 2 with rate parameters from Pauwels et al. [47] and Miller and Klippenstein [48]. When using the parameters from [47] the contribution of Reaction 2 to propargyl formation at low \( Z_{st} \) and destruction at high \( Z_{st} \) was observed to be slightly more significant. When using the parameters from [48] the contribution to propargyl production and destruction by Reaction 2 was somewhat reduced, nevertheless the observed trends shown in Fig. 6 remained the same. Moreover, our results can be applied when the condensation of soot precursor species via reversible reactions is accompanied by the generation of additional H radicals, i.e. \( C_{x1}H_{y1} + C_{x2}H_{y2} = C_{x1+x2}H_{y1+y2-1} + H \). That is, the net

\[ \text{Fig. 6. Rate profiles for R1 (} C_2H_2 + CH_3 = pC_3H_4 + H) \text{ and R2 (} pC_3H_4 = C_3H_3 + H) \text{, H mole fraction profile, and temperature profile in physical space for: (a) Flame A, (b) Flame D, and (c) Flame I.} \]

\[ \text{Fig. 7. Quotient of Reaction 3 (overall) vs. temperature.} \]
forward rate of reversible aromatic growth steps following benzene formation (i.e. naphthalene, phenanthrene, pyrene, etc.) that produce H can be significantly reduced, or even reversed completely when changes in flame structure at high $Z_{st}$ force these reactions to occur in the region of high H concentration near the flame.

A modeling study by Guo et al. [49] used a somewhat similar argument when explaining the chemical effect of H$_2$ addition on the inhibition of soot formation in methane and ethylene flames. However, Guo et al. concluded that the increased H$_2$ concentrations in H$_2$ diluted flames resulted in larger reverse rates of hydrogen abstraction acetylene addition (HACA) steps producing soot precursor species along with H$_2$, while an effect due to H was not observed given that the change in H in the region of interest was negligible even at 24 vol.% H$_2$ dilution. We investigated the H$_2$ diluted ethylene flame conditions of Guo et al. with the counterflow flame code used here and found that H$_2$ dilution does not alter the H profile relative to the temperature profile. That is, the structural changes observed at high $Z_{st}$ that result in lower temperatures in the region of high H and that drive the key propargyl formation in reverse, resulting in permanently blue flames, are not observed when merely diluting the fuel with H$_2$.

3. Concluding remarks

The phenomenon of high $Z_{st}$ soot-free non-premixed flames at strain rates approaching zero (a.k.a. permanently blue flames) has been attributed to the effects of hydrodynamics by Lin and Faeth [17,18,23] and flame structure by Du and Axelbaum [16]. Experiments performed with spherical flames in microgravity by Sunderland et al. [21,25,26], in which the effects of hydrodynamics and structure could be isolated, have confirmed that structure is primarily responsible for soot suppression at high $Z_{st}$, with hydrodynamics having a secondary effect. In this work a counterflow flame code with detailed chemistry was used to understand the effects of flame structure, as described by $Z_{st}$ on the chemistry of soot precursors leading to the permanently blue flame phenomenon. The dominant pathway leading to the formation of the first aromatic ring (i.e. benzene and phenyl) was evaluated at low and high $Z_{st}$ and significant changes were observed in the production and destruction characteristics of propargyl suggesting that in some domain the H concentration plays a significant role in the suppression of soot formation.

In the fuel/air flame two dominant propargyl formation routes are observed—one direct route via the reaction of acetylene with methylene and a second via the dissociation of propyne, which is predominantly formed from acetylene reacting with the methyl radical. As $Z_{st}$ is increased, propargyl formation through propyne dissociation is eliminated and the C$_2$H$_4$ + H reaction becomes the dominant propargyl destruction route. Because the C$_2$H$_4$ + H = pC$_2$H$_3$ + H and pC$_2$H$_3$ + H reactions are endothermic and produce H in the direction of soot precursor formation, the forward and reverse rates can be influenced by the local H concentration and the local temperature. At low $Z_{st}$ these reactions proceed in the direction of soot formation until a sufficiently high H concentration in the high temperature region promotes the reverse rates. At high $Z_{st}$ the flame structure changes resulting in lower temperatures and more H in the pyrolysis zone, which promotes the reverse reactions of the acetylene + propyne and propyne ↔ propargyl pathway. Moreover, the increased H in the pyrolysis zone observed at high $Z_{st}$ is a consequence of reduced spatial separation between the location of H production via CO and H$_2$ oxidation by OH and the temperature required for fuel pyrolysis on the fuel side of the flame. Thus, at high $Z_{st}$ the formation of the first aromatic ring via propargyl self-combination is severely limited because a key pathway that dominated propargyl production at low $Z_{st}$ has been reversed resulting in rapid propargyl destruction. Finally, this concept of H radical control of soot precursor elimination can be extended to subsequent reversible, endothermic soot precursor formation reactions.

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