Fuel dependence of benzene pathways

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Abstract

The relative importance of formation pathways for benzene, an important precursor to soot formation, was determined from the simulation of 22 premixed flames for a wide range of equivalence ratios (1.0–3.06), fuels (C1–C12), and pressures (20–760 torr). The maximum benzene concentrations in 15 out of these flames were well reproduced within 30% of the experimental data. Fuel structural properties were found to be critical for benzene production. Cyclohexanes and C3 and C4 fuels were found to be among the most productive in benzene formation; and long-chain normal paraffins produce the least amount of benzene. Other properties, such as equivalence ratio and combustion temperatures, were also found to be important in determining the amount of benzene produced in flames. Reaction pathways for benzene formation were examined critically in four premixed flames of structurally different fuels of acetylene, n-decane, butadiene, and cyclohexane. Reactions involving precursors, such as C3 and C4 species, were examined. Combination reactions of C3 species were identified to be the major benzene formation routes with the exception of the cyclohexane flame, in which benzene is formed exclusively from cascading fuel dehydrogenation via cyclohexene and cyclohexadiene intermediates. Acetylene addition makes a minor contribution to benzene formation, except in the butadiene flame where C4H5 radicals are produced directly from the fuel, and in the n-decane flame where C4H5 radicals are produced from large alkyl radical decomposition and H atom abstraction from the resulting large olefins.

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1. Introduction

The present study is motivated by the need to develop kinetic mechanisms for hydrocarbons that can simulate the formation of soot in combustion from practical fuels. Practical distillate fuels (aviation and diesel) consist predominantly of n-paraffins, iso-paraffins, cyclo-paraffins (naphthenes), and aromatics; gasolines consist also of minor fractions of olefins; and natural gas consists primarily of methane with small amounts of other small paraffins. All of these practical fuels make soot by producing benzene or other small aromatic species, which are the major precursors to soot. Different fuels, with different molecular structures, make benzene in different ways, but once the first small aromatic species are produced, subsequent reaction pathways to soot are...
expected to be relatively independent of the original fuel.

Consequently, the focus of the present paper is on defining a composite mechanism to include all of the reaction pathways that produce benzene in flames burning a wide range of different fuels. In addition to contributing to particulate pollution via soot generation, combustion-generated benzene has also raised public health concerns since benzene is a carcinogen itself and participates in the formation of higher aromatics, many of which are also known carcinogens.

Benzene formation pathways via addition of C4 species to acetylene or combination of C3 species have been studied extensively. Reactions adding C4 radicals to molecular acetylene were proposed by Westmoreland et al. [1] and Frenklach et al. [2] to be the principal formation pathways for the first aromatic rings via the first class of reactions in the list below.

\[
\begin{align*}
\text{Class 1:} & \quad R1: \ C_2H_2 + CH_2CHCHCH \rightarrow C_6H_6 + H \\
& \quad R2: \ C_2H_2 + HCCHCCH \rightarrow C_6H_5 \\
\text{Class 2:} & \quad R3: \ H_2CCCH + H_2CCCH \rightarrow C_6H_6 \\
& \quad R4: \ H_2CCCH + CH_2CCH \rightarrow C_6H_6 + H \\
& \quad R5: \ H_2CCCH + H_2CCCH \rightarrow C_6H_5 + H \\
& \quad R6: \ H_2CCCH + CH_2CHCH \rightarrow \text{FULVENE} + 2H \\
\text{Class 3:} & \quad R7: \ C_3H_5 + CH_3 \rightarrow C_3H_6CH_3 + \text{radical} \rightarrow C_6H_6 \\
\text{Class 4:} & \quad R8: \ \text{cycloC}_6 - R \rightarrow C - C_6H_{10} \rightarrow C - C_6H_8 \rightarrow C_6H_6 \\
\text{Class 5:} & \quad R9: \ C_6H_6 - R + H
\end{align*}
\]

Reactions of propargyl radicals (Class 2) present an alternative reaction pathway to benzene and phenyl radical [3]. Reactions 3 and 5 of the self-combination of propargyl radicals have been studied in detail [3–7] and is considered by many to provide the dominant route to the first aromatic rings. Other benzene formation pathways have also been proposed, including the combination of CH3 and C2H5 radicals via cyclo-dienes and advances in kinetics of small, unsaturated hydrocarbon species, have created a unique opportunity to investigate major benzene formation pathways in flames based on the chemical structure of the fuel. In the present study, benzene concentration predictions and benzene formation pathway analyses based on the chemical structure of the fuel, will be reported for 22 premixed flames with 14 different fuels, which include C1–C12 fuels with equivalence ratios.

### Table 1

<table>
<thead>
<tr>
<th>Benzene formation reactions used in the present calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactions</td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td>1. HACA reactions</td>
</tr>
<tr>
<td>1a. ( CH_2CHCHCH + C_2H_2 = C_4H_6 + H )</td>
</tr>
<tr>
<td>1b. ( HCCHCCH + C_2H_2 = C_4H_6 )</td>
</tr>
<tr>
<td>1c. ( CH_2CHCCH_2 + C_2H_5 = C_4H_6 + H )</td>
</tr>
<tr>
<td>1d. ( H_2CCCH + C_2H_5 = C_4H_6 )</td>
</tr>
<tr>
<td>2. C3 Combination reactions</td>
</tr>
<tr>
<td>2a. ( H_2CCCH + H_2CCCH = C_4H_6 )</td>
</tr>
<tr>
<td>2b. ( H_2CCCH + CH_2CCH = C_4H_6 + H )</td>
</tr>
<tr>
<td>2c. ( H_2CCCH + H_2CCCH = C_4H_6 + H )</td>
</tr>
<tr>
<td>2d. ( H_2CCCH + CH_2CHCH = \text{FULVENE} + 2H )</td>
</tr>
<tr>
<td>3. C-C_6H_5 + CH_3 = methyl cyclopentadiene</td>
</tr>
<tr>
<td>4. ( C_6H_6CH_3 + H = C_6H_5 + CH_3 )</td>
</tr>
</tbody>
</table>
between 1.0 and 3.06 and pressures between 20 and 760 torr [10,22–39].

2. Precursor chemistry of benzene formation

Benzene can be produced by a variety of kinetic pathways from a number of precursor species. Reliable kinetics for these precursors are required to achieve numerical accuracy in predicting levels of aromatic species in flames; in particular, kinetics for key species and reactions that are chemically related to allyl radical have been overlooked in many mechanisms.

Substantial improvements have been made for olefin chemistry during the development of the present mechanism, the Utah Surrogate Mechanisms, particularly for larger olefins that have significant impacts on predicted benzene concentrations in flames of large n-alkanes [40,41].

Reactions of species producing allyl and propargyl radicals, such as allene and propyne, are critical for the correct prediction of benzene concentrations. Reactions involving propyne, however, have been largely overlooked in early mechanism development, and C3H4 concentrations measured in experiments using mass spectrometry have often been assigned to the allene isomer. In recent studies, however, the measured peak concentration of propyne was found to be 270 ppm versus 150 ppm for allene in a peak concentration of propyne was found to be 270 ppm versus 150 ppm for allene in a n-heptane flame [37], and more propargyl radicals are formed from propyne via hydrogen abstraction than those obtained from allene [41]. Reactions of propyne have a lower energy barrier than those involving allene since it is easier to abstract hydrogen from an sp3 carbon than from an sp2 carbon.

Recent flame measurements [36–38] have used gas chromatography to identify structural isomers and to provide added insight on how C3H4 isomers are formed and consumed. This experimental data have aided in the generation of the reactions involving propyne in the present mechanism and were essential in predicting the benzene concentrations in flames burning different fuels.

Rates of reactions involving acetylene and vinyl radical are also very important for benzene production because the combination of vinyl and methyl radicals is a major formation route for allyl radical. Both acetylene and vinyl radical are formed from dehydrogenation of ethylene, and the selection of the vinyl decomposition rates and reactions involving C4 species have also been critically examined [42].

In summary, a group of precursors has been included in the present mechanism, and the species include propylene, 1-butene, 2-butene, isobutylene, propyne, 1-butyne, allene, 1,3-butadiene, vinyl acetylene, and di-acetylene, reactions of which have been critically examined and modified. These reactions are important for the formation of the intermediates for the first aromatic rings.

3. Numerical results

With the above-mentioned improvements in reactions of olefins and allyl-related species, simulation results when burning fuels using the Utah Surrogate Mechanisms have been compared favorably in earlier studies with experimental data of a few atmospheric premixed flames of n-heptane (φ = 1.0 and 1.9) [41–44], isooctane (φ = 1.9), n-decane (φ = 1.7) [43], gasoline (φ = 1.0) and kerosene (φ = 1.7) [9], and a 30 Torr premixed flame of cyclohexane (φ = 1.0) [45].

In the present study, the mechanism has been used to simulate 22 premixed flames using CHEMKIN IV, with fuels ranging from C1 to C12 species, including paraffins, olefins, acetylenes, aromatics, and liquid fuels. Experimental conditions such as fuel, inert and oxidizer levels, maximum temperatures and other quantities are summarized for these flames in Table 2, together with measured and predicted maximum benzene concentrations and the benzene peak locations for each flame. The simulated and experimental benzene profiles in most of these flames are compared in Fig. 1. The maximum benzene concentrations in 15 out of the 22 flames were predicted within 30% of the experimental data, and the overall agreement between computed and experimental results is very good.

4. Benzene level and fuel structure

The approach of using data from multiple flames for many structurally different fuels, using a single kinetic reaction mechanism, provides an opportunity to cross-examine these benzene formation mechanisms and relate how the benzene reaction pathways depend on the initial fuel structure and experimental conditions.

The flames that produce most benzene include Flame 12 (C3H6 φ = 2.3, 1220 ppm), Flame 13 (1.3-C4H6 φ = 2.4, 1300 ppm) and Flame 21 (kerosene φ = 1.7, 1090 ppm). The propylene flame produces a factor of two more benzene than that obtained in Flame 11 (C3H4 φ = 3.06, 575 ppm) and a factor of five more than that in Flame 10 (C2H4 φ = 2.76, 250 ppm), although both ethylene flames have higher equivalence ratios. The propylene flame produces large amounts of C3 benzene precursors directly from fuel consumption, while the ethylene flame chemistry must follow a much more complex and slower path to produce benzene.

Another example of the importance of the C3 reaction pathways is the substantially higher benzene concentrations in Flame 3 (C3H8 φ = 2.78,
Table 2
Experimental conditions and measured and predicted maximum benzene concentrations in 22 premixed flames

<table>
<thead>
<tr>
<th>#</th>
<th>Fuel</th>
<th>Inert Ar, %</th>
<th>C/O</th>
<th>Eq. ratio</th>
<th>P torr</th>
<th>T (Max) K at cm</th>
<th>Flow rate(^a)</th>
<th>Exp. Max. [C(_6)H(_6)](^b) at cm</th>
<th>Cal. Max. [C(_6)H(_6)](^b) at cm</th>
<th>Deviation%</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>CH(_4)</td>
<td>0.453</td>
<td>0.626</td>
<td>2.50</td>
<td>760</td>
<td>1605 at 0.4</td>
<td>7.19 × 10(^{-2})</td>
<td>280 at 0.8</td>
<td>141 at 0.8</td>
<td>−49.6</td>
<td>[22]</td>
</tr>
<tr>
<td>F2</td>
<td>C(_2)H(_6)</td>
<td>0.578</td>
<td>0.306</td>
<td>2.06</td>
<td>760</td>
<td>1420 at 0.3</td>
<td>7.21 × 10(^{-2})</td>
<td>575 at 1.0</td>
<td>553 at 1.0</td>
<td>−3.8</td>
<td>[31]</td>
</tr>
<tr>
<td>F3</td>
<td>C(_3)H(_8)</td>
<td>0.03</td>
<td>0.874</td>
<td>2.40</td>
<td>20</td>
<td>2310 at 1.65</td>
<td>2.08 × 10(^{-2})</td>
<td>1300 at 0.8</td>
<td>1490 at 0.8</td>
<td>+14.6</td>
<td>[33]</td>
</tr>
<tr>
<td>F4</td>
<td>C(_3)H(_8)</td>
<td>0.3</td>
<td>0.717</td>
<td>1.79</td>
<td>20</td>
<td>1905 at 0.2</td>
<td>2.19 × 10(^{-2})</td>
<td>N/A</td>
<td>N/A</td>
<td>Good</td>
<td>[34]</td>
</tr>
<tr>
<td>F5</td>
<td>C(_3)H(_8)</td>
<td>0.164</td>
<td>0.72</td>
<td>1.80</td>
<td>760</td>
<td>1850 at 0.45</td>
<td>5.07 × 10(^{-2})</td>
<td>N/A</td>
<td>N/A</td>
<td>Good</td>
<td>[35]</td>
</tr>
<tr>
<td>F6</td>
<td>C(_3)H(_8)</td>
<td>0.03</td>
<td>0.874</td>
<td>2.40</td>
<td>20</td>
<td>2310 at 1.65</td>
<td>2.08 × 10(^{-2})</td>
<td>1300 at 0.8</td>
<td>1490 at 0.8</td>
<td>+14.6</td>
<td>[33]</td>
</tr>
<tr>
<td>F7</td>
<td>C(_3)H(_8)</td>
<td>0.3</td>
<td>0.717</td>
<td>1.79</td>
<td>20</td>
<td>1905 at 0.2</td>
<td>2.19 × 10(^{-2})</td>
<td>N/A</td>
<td>N/A</td>
<td>Good</td>
<td>[34]</td>
</tr>
<tr>
<td>F8</td>
<td>C(_3)H(_8)</td>
<td>0.3</td>
<td>0.517</td>
<td>1.79</td>
<td>20</td>
<td>1905 at 0.2</td>
<td>2.19 × 10(^{-2})</td>
<td>N/A</td>
<td>N/A</td>
<td>Good</td>
<td>[34]</td>
</tr>
<tr>
<td>F9</td>
<td>C(_3)H(_8)</td>
<td>0.3</td>
<td>0.517</td>
<td>1.79</td>
<td>20</td>
<td>1905 at 0.2</td>
<td>2.19 × 10(^{-2})</td>
<td>N/A</td>
<td>N/A</td>
<td>Good</td>
<td>[34]</td>
</tr>
<tr>
<td>F10</td>
<td>C(_3)H(_8)</td>
<td>0.3</td>
<td>0.517</td>
<td>1.79</td>
<td>20</td>
<td>1905 at 0.2</td>
<td>2.19 × 10(^{-2})</td>
<td>N/A</td>
<td>N/A</td>
<td>Good</td>
<td>[34]</td>
</tr>
<tr>
<td>F11</td>
<td>C(_3)H(_8)</td>
<td>0.3</td>
<td>0.517</td>
<td>1.79</td>
<td>20</td>
<td>1905 at 0.2</td>
<td>2.19 × 10(^{-2})</td>
<td>N/A</td>
<td>N/A</td>
<td>Good</td>
<td>[34]</td>
</tr>
<tr>
<td>F12</td>
<td>C(_3)H(_8)</td>
<td>0.3</td>
<td>0.517</td>
<td>1.79</td>
<td>20</td>
<td>1905 at 0.2</td>
<td>2.19 × 10(^{-2})</td>
<td>N/A</td>
<td>N/A</td>
<td>Good</td>
<td>[34]</td>
</tr>
<tr>
<td>F13</td>
<td>C(_3)H(_8)</td>
<td>0.3</td>
<td>0.517</td>
<td>1.79</td>
<td>20</td>
<td>1905 at 0.2</td>
<td>2.19 × 10(^{-2})</td>
<td>N/A</td>
<td>N/A</td>
<td>Good</td>
<td>[34]</td>
</tr>
<tr>
<td>F14</td>
<td>C(_3)H(_8)</td>
<td>0.3</td>
<td>0.517</td>
<td>1.79</td>
<td>20</td>
<td>1905 at 0.2</td>
<td>2.19 × 10(^{-2})</td>
<td>N/A</td>
<td>N/A</td>
<td>Good</td>
<td>[34]</td>
</tr>
<tr>
<td>F15</td>
<td>C(_3)H(_8)</td>
<td>0.3</td>
<td>0.517</td>
<td>1.79</td>
<td>20</td>
<td>1905 at 0.2</td>
<td>2.19 × 10(^{-2})</td>
<td>N/A</td>
<td>N/A</td>
<td>Good</td>
<td>[34]</td>
</tr>
<tr>
<td>F16</td>
<td>C(_3)H(_8)</td>
<td>0.3</td>
<td>0.517</td>
<td>1.79</td>
<td>20</td>
<td>1905 at 0.2</td>
<td>2.19 × 10(^{-2})</td>
<td>N/A</td>
<td>N/A</td>
<td>Good</td>
<td>[34]</td>
</tr>
<tr>
<td>F17</td>
<td>C(_3)H(_8)</td>
<td>0.3</td>
<td>0.517</td>
<td>1.79</td>
<td>20</td>
<td>1905 at 0.2</td>
<td>2.19 × 10(^{-2})</td>
<td>N/A</td>
<td>N/A</td>
<td>Good</td>
<td>[34]</td>
</tr>
<tr>
<td>F18</td>
<td>C(_3)H(_8)</td>
<td>0.3</td>
<td>0.517</td>
<td>1.79</td>
<td>20</td>
<td>1905 at 0.2</td>
<td>2.19 × 10(^{-2})</td>
<td>N/A</td>
<td>N/A</td>
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</tr>
<tr>
<td>F19</td>
<td>C(_3)H(_8)</td>
<td>0.3</td>
<td>0.517</td>
<td>1.79</td>
<td>20</td>
<td>1905 at 0.2</td>
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</tr>
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<td>1.79</td>
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<td>1905 at 0.2</td>
<td>2.19 × 10(^{-2})</td>
<td>N/A</td>
<td>N/A</td>
<td>Good</td>
<td>[34]</td>
</tr>
<tr>
<td>F22</td>
<td>C(_3)H(_8)</td>
<td>0.3</td>
<td>0.517</td>
<td>1.79</td>
<td>20</td>
<td>1905 at 0.2</td>
<td>2.19 × 10(^{-2})</td>
<td>N/A</td>
<td>N/A</td>
<td>Good</td>
<td>[34]</td>
</tr>
</tbody>
</table>

\(^a\) g/(cm\(^2\) s).

\(^b\) Measured and predicted benzene concentrations in ppm.

\(^c\) Diluted by inert N\(_2\).

\(^d\) Also using krypton as internal standard.

\(^e\) ×4.2 means a factor of 4.2.
ponent n zene concentration of 65 ppm in the be 1090 ppm, as compared to the maximum ben- 
conzentration. The benzene level was reported to 
hexane produces a significant increase in benzene 
the kerosene mixture contains 10% methyl 
ene flame is a consequence of the direct formation 
from C 3 species combination.

Another structure-dependent example is ben-
ene formation in the kerosene-fueled Flame 21.
The high benzene formation in the 1,3-butadi-
ene flame is a consequence of the direct formation 
of C 4 precursors from the fuel. Higher C 4 species 
in the butadiene flame enhance benzene formation via acetylene addition reactions R1 and R2, with the benzene production rates comparable to those from C 3 species combination.

Another structure-dependent example is benz-
ene formation in the kerosene-fueled Flame 21. The kerosene mixture contains 10% methyl 
cyclohexane [9] in addition to the major fuel com-
ponent n-C 12 H 26 (73.5%), and the methyl cyclo-
hexane produces a significant increase in benzene 
concentration. The benzene level was reported to 
be 1090 ppm, as compared to the maximum ben-
ene concentration of 65 ppm in the n-C 10 H 22 
Flame 19, although both flames had very similar 
equivalence ratio, inert fraction, cold gas flow 
rate, and other physical conditions. A similarly 
very high level of benzene formation was also 
observed in the cyclohexane Flame 22. The 
473 ppm maximum benzene mole fraction mea-
sured in this 30 torr stoichiometric flame is 40 
times that obtained in the atmospheric pressure, 
stoichiometric n-heptane Flame 16 (n-C 7 H 16 , 1.0, 12 ppm). Benzene formation from the 
cyclohexane fraction (8.6% by volume) and the 
de-alkylation of aromatics in the gasoline Flame 
20 offsets the consumption rate of the benzene 
fraction in the fuel, leading to an interesting pla-
teau in the benzene profile (Fig. 1).

Benzene formation also depends strongly on 
other fuel structural features. For example, Flame 
18 (i-C 8 H 18 , 1.90, 292 ppm) produces much 
higher benzene levels than Flame 17 (n-C 7 H 16 , 1.0, 75 ppm). Both flames were operated under 
the almost identical experimental conditions. The 
much higher benzene concentrations in the isooc-
tane flame reflect the preferred formation of C 3 
and C 4 precursors, while the n-heptane flame pro-
duces primarily ethylene precursors that yield C 3 
species in subsequent steps. For example, the mea-
sured mole fractions of propylene in n-heptane 
and isoctane flames at the benzene peak 
positions of each flame are 2080:4500 ppm (n-
C 7 ; i-C 8 ); those of allene 150:1200 ppm; those of
Fig. 2. Major benzene formation pathways in the (a) F19 $n$-decane [38], (b) F6 acetylene [26], (c) F22 cyclohexane [10], (d) F13 1,3-butadiene flames [33]. The shaded areas represent benzene precursors.
ethylene 22,000:9500 ppm. Those values were also well predicted using the mechanism [41–43]. The predicted mole fractions of allyl radical, which was not measured, are 42.103 ppm; those of propargyl radical 129:209 ppm; those of isobutylene 21:4400 ppm; those of isobutylstyrene radical 0.7:61 ppm. Studies of these two flames and those that include cyclo-paraffins (Flames 20, 21, and 22) reveal a pattern of benzene formation potential that is related to how the carbon atoms are connected in the fuel molecule. More benzene is formed in flames of cyclo-paraffins than in those of other paraffins. Normal paraffin flames produce the least amount of benzene under similar flame conditions.

In addition to fuel structure, benzene formation depends strongly on the equivalence ratio of the fuel/oxidizer mixture, since oxidation is favored in leaner flames. For example, the measured maximum benzene concentration in Flame 4 (C2H4 φ = 1.8, 17.5 ppm) is only 2% of that obtained in the richer Flame 3 (C2H8 φ = 2.78, 840 ppm). Of the four ethylene flames, the richest Flame 11 (C2H4 φ = 3.06, 575 ppm) produces about 20 times more benzene than the leanest Flame 8 (C2H4 φ = 1.9, 33.1 ppm), and the same trend is seen between the stoichiometric and rich n-heptane Flames 16 and 17.

5. Detailed benzene production analysis

Four flames will be critically examined in this section, flames which represent different fuel classes of large n-paraffins, acetylenes, C4 dienes, and cyclohexanes. Because of the structural differences in these fuels, the dominant benzene formation pathways are unique in each flame. Benzene formation pathways have been presented in Fig. 2. The rates of important pathways at the location of peak benzene concentration in each flame are shown along the arrow indicating the reaction direction; the thickness of the arrow, representing the relative magnitude of the reaction rate in log scale, is normalized to the highest rate of formation routes in each flame. The shaded areas represent major benzene precursors that include C3H2, C3H3, C3H4, C3H5, C3H6, C4H5, C5H5, C–C6H7 and C–C6H8.

In the n-decane flame, benzene formation is dominated by C3 species combination. The C3H3 radical combination (R3) accounts for 51% of the total benzene formation, followed by contributions of 13% from the combination of C3H3 and C3H5 radicals via the intermediate fulvene (R6), 13% from the combination of C3H4 and C2H3 radical (R4), 12% from acetylene addition (R1 and R2), and 11% from the de-alkylation of toluene (R9, –CH3). The contribution from the self-combination of C3H3 radicals via phenyl radical (R5) is more difficult to assess because the importance of phenyl hydrogenation (C6H5→C6H6) is displaced by that of the reverse hydrogen abstraction of benzene. It is noteworthy, however, that reaction R5 is 66% faster than the fastest direct formation (R3) producing benzene.

The detailed n-decane reaction mechanism shows that H atom abstraction from the fuel, followed by β-scission of resulting decyl radicals, produce large amounts of C3–C8 olefins [41–43]. These olefins then decompose to produce the high levels of C3 and C4 precursors to benzene formation. For example, CH2CHCHCH comes from hydrogen abstraction from 1,3-butadiene and C3H3 is formed mainly from CH2CHCCH2 radical decomposition (R10, the reverse reaction dominates) and hydrogen abstraction from C3H4 isomers (R11 and R12).

\[ R10: H2CCCH + CH3 = CH2CHCCH2 + H (43\%) \]
\[ R11: CH2CH + H = H2CCCH + H2 (29\%) \]
\[ R12: CH2CCH2 + H = H2CCCH + H2 (13\%) \]

In the acetylene flame, the combination of C3H3 radicals (R3) is the only significant pathway, which accounts for 94% of benzene formation. All other important routes identified in the n-decane flame are insignificant in the acetylene flame. The self-combination of C3H3 radicals forming phenyl radical (R5) is 26% faster than the fastest (R3) of the direct benzene formation routes. The crucial precursor C3H3 comes from the combination of C2H2 and CH2 (both singlet and triplet) in contrast to its formation from large species (R10–R12) in the n-decane flame.

\[ R13: ^1CH2 + C2H2 = H2CCCH + H (87\%) \]
\[ R14: ^3CH2 + C2H2 = H2CCCH + H (11\%) \]

The cyclohexane flame also includes a single benzene formation pathway that is significantly greater than all other routes. Benzene is produced via the sequential dehydrogenation of the fuel through cyclohexene and cyclohexadiene, and this dominant pathway is two orders of magnitude faster than C3 species combination and three orders faster than acetylene addition.

The 1,3-butadiene flame provides the most complicated benzene formation mechanism of these four flames, involving significant contributions from both C3 combination and acetylene addition. The combination of C3H3 radicals (R3) accounts for 48% of the total benzene formation, followed by 20% from acetylene addition (R1), 12% from the combination of C3H3 and C3H5 radicals via the intermediate fulvene (R6), 10% from the de-acylation of C3H2CHO, 5% from the de-methylation of C3H5CH3 (R9), and 5% from the combination of C3H3 and C3H5 radicals followed by dehydrogenation (R8). The C3H3 radical combination producing phenyl radical (R5) is 86% faster than the fastest (R3) of the
direct formation routes. The unique structure of the butadiene fuel leads to preferential formation of C4H5 isomers that produces the significant contribution of acetylene addition. The formation of C4H5 isomers also determines the dominance of the butadiene fuel leads to preferential formation of acetylene (R13).

6. Conclusions

The relative importance of pathways to benzene formation has been examined in 22 premixed flames, using a single kinetic reaction mechanism that includes all of the reaction pathways currently understood to lead to benzene formation. The predicted maximum benzene concentrations agree very well overall with the experimental data. Fuel structural properties were found to be critical in determining rates of benzene production via the multiple formation pathways among different fuels in premixed flames. Depending on the fuel structure, different reaction pathways are responsible for benzene production. The present mechanism represents an important step towards providing a unified kinetic description of soot formation in many different fuel mixtures and combustion environments.

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Appendix A. Supplementary data


References