



Experimental study of fuel decomposition and hydrocarbon growth processes for cyclohexane and related compounds in nonpremixed flames

Charles S. McEnally* and Lisa D. Pfefferle

*Department of Chemical Engineering and Center for Combustion Studies, Yale University, P.O. Box 208286,
New Haven, CT 06520-8286, USA*

Received 6 May 2003; received in revised form 23 September 2003; accepted 24 September 2003

Abstract

C1 to C12 stable hydrocarbons, soot volume fraction, several major species, and gas temperature have been measured in a series of methane/air coflowing nonpremixed flames whose fuel was separately doped with 2000 ppm of cyclohexane, cyclohexene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, and benzene. The cyclohexadienes mostly dehydrogenated to benzene, while cyclohexane and cyclohexene mostly decomposed to C2, C3, and C4 hydrocarbons. Addition reactions were the main benzene source in the cyclohexane-doped flame, whereas both addition and dehydrogenation were important benzene sources in the cyclohexene-doped flame. Reaction pathways were identified in each flame from the hydrocarbon product distributions and from calculated rate constants of relevant reactions. Dehydrogenation was a minor pathway in the cyclohexane- and cyclohexene-doped flames because unimolecular dissociation, not H-atom abstraction, consumed the dopants and their conjugate radicals in these nonpremixed flames. The maximum soot volume fraction correlated poorly with the maximum benzene mole fraction in the cyclohexadiene-doped flames, which indicates that benzene formation was not a rate-determining step to soot production in those flames.

© 2003 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

Keywords: Burners; Diffusion; Inorganics; Soot

1. Introduction

This paper is the second of a series in which we report nonpremixed flame experiments that examine the fuel decomposition and hydrocarbon growth pathways of practical fuel components [1]. The first paper concerned a representative large linear alkane, heptane, while this paper mainly focuses on a representative cyclic alkane, cyclohexane. Cycloalkanes warrant separate study because they constitute a significant portion of most fuels (e.g., ~ 16 to 67% of

the aviation-grade kerosenes discussed in [2]) and because they can potentially form aromatic hydrocarbons through a pathway that does not exist for linear alkanes: dehydrogenation of six-membered alkyl rings to benzenoid rings.

The specific flames that we studied were CH₄/air coflowing nonpremixed flames whose fuel was separately doped with 2000 ppm of cyclohexane (CHXA), cyclohexene (CHXE), 1,3-cyclohexadiene (1,3-CHXD), 1,4-cyclohexadiene (1,4-CHXD), and benzene (BZ). (Figure 1, which is discussed below, shows the structures of these compounds. Our notation emphasizes whether each compound is a cyclic alkane, alkene, or alkadiene.) This set of dopants includes the stable reactants and products for each de-

* Corresponding author.

E-mail address: charles.mcenally@yale.edu (C.S. McEnally).

Table 1
Flame conditions

Flame	Q_{CH_4}	Q_{N_2} (all flow rates in cm^3/min at STP)	Q_{d}	Q_{Ar}	Q_{sa}	$[\text{Dopant}]_{\text{fuel}}$ (ppm)
Undoped	330	320	0	5.5	44,000	0
Doped	330	320	1.3	5.5	44,000	2000

Q_{CH_4} , Q_{N_2} , Q_{d} , Q_{Ar} , and Q_{sa} are the measured volumetric flow rates of CH_4 , N_2 , dopant, Ar, and secondary air ($\pm 5\%$); $[\text{dopant}]_{\text{fuel}}$ is the calculated dopant mole fraction in the fuel mixture ($\pm 10\%$).

hydrogenation step from CHXA to BZ. We measured stable C1 to C12 hydrocarbons, soot volume fraction, major species, and temperature on the centerline of each flame.

The objective of our experiments was to identify the primary decomposition and hydrocarbon growth pathways, particularly those that form BZ, for CHXA, CHXE, and CHXD in nonpremixed flames. Our results complement earlier oxidation studies of these compounds, which have considered jet-stirred reactors [3–5], rapid compression machines [6], and shock tubes [7]. Nonpremixed flames exemplify many practical combustors, especially soot-producing systems such as diesel engines and gas turbines. Furthermore, reaction pathways can differ between nonpremixed flames and these other systems; indeed, sooting tendency measurements in nonpremixed CHXA and CHXE flames indicate that dehydrogenation to BZ is much less important than it was in the studies cited above [8].

2. Experimental methods

We used the same equipment and procedures as in our heptane study [1]. Atmospheric-pressure coflowing laminar nonpremixed flames were generated with a burner in which the fuel mixture (CH_4 , N_2 , Ar, and, in most cases, a dopant) flows out of an 11.1-mm diameter tube and reacts with air that flows from the annular region outside this tube. (Figure 2, which is discussed below, depicts this geometry.) Table 1 lists the reactant flow rates. The reactants came from high-purity gas cylinders (CH_4 , N_2 , and Ar; 99.97 + % stated purities), reagent-grade bottles (dopants; 97 + % stated purities), and a compressor (air).

We measured gas temperature (T_g) with thermocouples, soot volume fraction (f_v) with laser-induced incandescence (LII), and species mole fractions (species) with a quartz gas sample probe and online mass spectrometry. A 118-nm photoionization/time-of-flight mass spectrometer (PTMS) quantified C3 to C12 hydrocarbons while an electron-impact/quadrupole mass spectrometer (EQMS) quantified CO_2 , O_2 , CH_4 , C_2H_2 , and C_2H_4 . The T_g measurements include radiation corrections, and a rapid

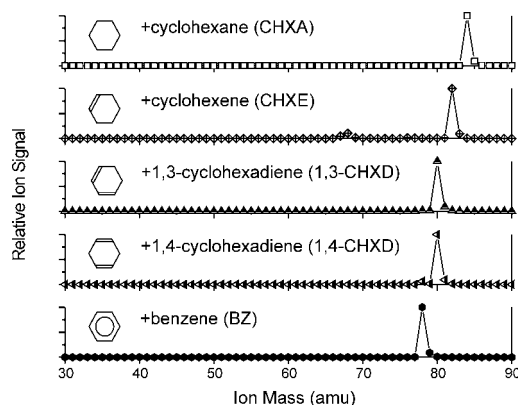


Fig. 1. PTMS mass spectra were measured for each doped-flame fuel mixture to determine the extent of $(\text{dopant})^+$ fragmentation. Each data point is the integrated ion signal corresponding to an integer mass.

insertion procedure minimized soot deposition onto the junction [9]. The LII was excited at 1064 nm and detected in the 400 to 450 nm range [10]; the volume fractions were calibrated with soot deposition rates onto the thermocouple [9]. The gas sample probe entered the flame from the side, such that it was cooled by the coflowing air, and the backing pressure was kept below 3 Torr [11]. The uncertainties depend on the property and the location, but conservative upper limits to the relative and absolute uncertainties are ± 10 and ± 65 K (T_g) and ± 10 and $+100/-50\%$ ([species] and f_v). The spatial resolutions were 0.3 mm (thermocouple) and 1 mm (gas sample probe and LII).

Single-photon photoionization at 118 nm is an ideal method for ionizing complex hydrocarbon mixtures: the photon energy (10.5 eV) barely exceeds the ionization energies of most hydrocarbons (e.g., 8.25 to 9.88 eV for the dopants [12]), so ion fragmentation is usually negligible [13]. Figure 1, which shows normalized PTMS mass spectra of each doped-flame fuel mixture, illustrates this attribute. The parent ion dominates each spectrum; the only significant fragment ions are 68 and 76 amu from CHXE (intensity ~ 10 and 2% of the parent ion) and 78 amu from 1,3-CHXD and 1,4-CHXD (~ 2 and 6%). The minor interferences from these fragments on the hydrocarbon

product profiles were removed by subtracting appropriately scaled versions of the parent ion profiles.

3. Results and discussion

3.1. Temperature and major species

The objective of this study was to identify the primary fuel decomposition and BZ formation processes that occur in nonpremixed CHXA-, CHXE-, and CHXD-fueled flames. Subsequent sections address this topic in terms of the dopant disappearance locations, the hydrocarbon product concentrations, and some simple kinetic calculations. This section discusses the measured gas temperatures and major species mole fractions; these results place the hydrocarbon product measurements in the context of the overall flame structure, demonstrate that the dopants did not significantly affect the overall flame structure, and provide consistency checks of the diagnostics.

Figure 2 shows the centerline profiles of T_g and several major species. The data are plotted against the nondimensional flame height Z/H_T , where Z is the distance above the burner surface and H_T is the Z at which the centerline T_g peaks. $H_T = 62 \pm 1$ mm for the undoped flame and 64 ± 1 mm for the doped flames. We have demonstrated with experiments and computer simulations that H_T is an accurate surrogate for the height at which the stoichiometric surface intersects the centerline [14]; thus the local gas composition at the centerline is fuel rich for $Z/H_T < 1$ and fuel lean for $Z/H_T > 1$.

The profiles show the expected structure for a nonpremixed flame: T_g and $[CO_2]$ peak at the stoichiometric surface, while $[fuel]$ and $[oxidizer]$ peak at the

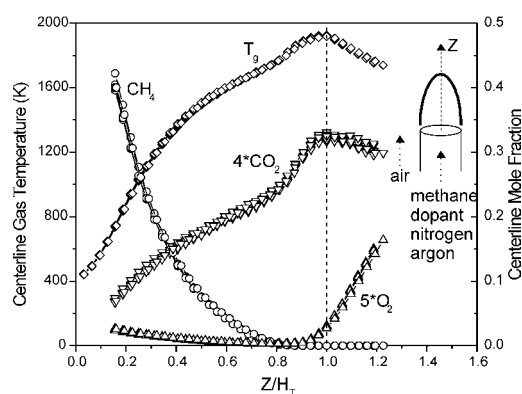


Fig. 2. Centerline profiles of T_g , $[CH_4]$, $[O_2]$, and $[CO_2]$ were measured with a thermocouple and the EQMS. Profiles from all six flames for each property are shown. The vertical dashed line marks $Z/H_T = 1$, which is the approximate position of the stoichiometric surface [14]. The diagram on the right shows the flame geometry.

fuel-rich and fuel-lean edges of the flame and decrease toward zero at the stoichiometric surface. In agreement with earlier nonpremixed flame measurements [15,16], O_2 penetrates through the stoichiometric surface to the fuel-rich side and some O_2 is entrained at the flame base and then consumed between $Z/H_T = 0.1$ and 0.7 as if it were premixed with the fuel. (We estimate that the effective ϕ is ~ 100 .)

The results in Fig. 2 demonstrate that the changes in the overall flame structure are too small to affect the hydrocarbon product concentrations. The profiles from all six flames are nearly identical for each property: the maximum variation in T_g is 24 K and the $[species]$ agree to within 20%. Furthermore, residence times in coflowing flames scale with $Z^{1/2}$ [17], so at a given Z/H_T they vary by less than $\{(64 - 62)/62\}^{1/2} = 2\%$ from flame to flame. These results are reasonable since the dopants constitute only 2% of the carbon flux and 0.003% of the total reactant flux. They indicate that the large differences in hydrocarbon product concentrations discussed below must be attributed to the chemical reactions of the dopants and their decomposition products.

3.2. Dopant decomposition rates; importance of unimolecular dissociation

We can characterize the decomposition rates of the dopants with the parameter $(Z/H_T)_{1\%}$, which is the Z/H_T at which $[dopant] = 20$ ppm, or 1% of the initial dopant mole fraction. This parameter is interesting because its dependence on dopant structure reveals that unimolecular dissociation is the main decomposition mechanism.

The top of Fig. 3 shows the measured centerline dopant profiles (i.e., $[CHXA]$ in the CHXA-doped flame, $[CHXE]$ in the CHXE-doped flame, etc.). Each

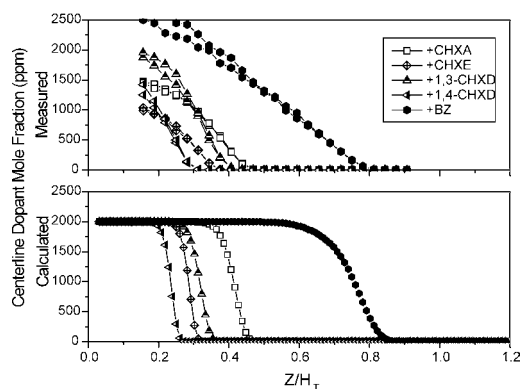


Fig. 3. (Top) Centerline dopant profiles were measured with the PTMS. (Bottom) Centerline dopant profiles were calculated in the limit at which unimolecular dissociation dominates H-atom abstraction.

profile was measured twice to indicate its reproducibility. The profiles behave as expected for a fuel component: in each flame the dopant concentration decreases monotonically with increasing Z/H_T until it reaches zero while still on the fuel-rich side of the stoichiometric surface. Each dopant decomposes at a significantly different rate and $(Z/H_T)_{1\%}$ increases in the order 1,4-CHXD < CHXE < 1,3-CHXD < CHXA < BZ.

(All of the PTMS measurements were calibrated with the sensitivity for propadiene; since the actual sensitivities vary, some of the profiles in Fig. 3 intersect at high concentrations (e.g., 1,4-CHXD and CHXE at about 850 ppm). However, $(Z/H_T)_{1\%}$ is not sensitive to the calibration since the dopant concentration decreases steeply. For example, if the sensitivity to CHXA is assumed to be half that of propadiene, i.e., all of the [CHXA] are doubled, then $(Z/H_T)_{1\%}$ changes only from 0.467 to 0.480.)

In general hydrocarbons in high-temperature systems can decompose by unimolecular dissociation or by bimolecular H-atom abstraction. The disappearance order of the dopants disagrees with the relative abstractability of each dopant's H atoms, which suggests that unimolecular dissociation is the main dopant decomposition pathway in our flames. For example, CHXE disappears before CHXA but has a more tightly bound set of H atoms (8 secondary and 2 vinylic versus 12 secondary), and the CHXD isomers disappear at different heights but have the same set of H atoms (4 vinylic and 4 allylic).

As a more quantitative test of this conclusion, we calculated dopant profiles in the limit at which dissociation dominates H-atom abstraction. The calculations ignored diffusion, assumed the dominant unimolecular dissociations for the dopants were reactions (R1) to (R5) in Table 2, adopted the high-pressure limit Arrhenius parameters listed in the table,

used the measured T_g profiles, and used residence times obtained by assuming a constant buoyant acceleration of 25 m/s^2 [17].

The bottom of Fig. 3 shows the calculated profiles. They agree reasonably with the measured profiles, particularly in terms of the decomposition order of the dopants. Thus we conclude that this order stems from the relative rates of (R1) to (R5). For example, 1,4-CHXD decomposes before 1,3-CHXD because H_2 elimination is symmetry-allowed for 1,4-CHXD but symmetry-forbidden for 1,3-CHXD [20].

The shapes of the calculated and measured profiles differ because the calculations neglect radial diffusion. In particular, the calculated profiles are flat in the first portion of the flame, whereas the measured profiles decrease steadily throughout the flame as the dopants diffuse away from the centerline. (Diffusion in the other direction, from the annular flame front toward the centerline, accounts for the increase in T_g and $[\text{CO}_2]$ until $Z/H_T \sim 0.8$, at which point CO_2 formation and heat release begin at the centerline.) The error in the calculated $(Z/H_T)_{1\%}$ caused by neglecting diffusion can be estimated by assuming that the primary effect of diffusion is to reduce the amount of dopant that has to be consumed when chemical consumption starts to occur. Such estimates show that the error is negligible; for example, if the effective [CHXA] is assumed to be 1000 ppm instead of 2000 ppm, then $(Z/H_T)_{1\%}$ decreases by about 1%, from 0.467 to 0.462.

Figure 4 compares the measured and calculated $(Z/H_T)_{1\%}$. It includes additional data points that correspond to a 1-hexene-doped flame investigated as a supplement to this study and the *n*-heptane-doped flame in our previous study [1]; the dissociation reactions for these cases were assumed to be (R26) and (R27) in Table 2. All of the data points lie within 17% of the dashed line that corresponds to exact agree-

Table 2
Thermal dissociation Arrhenius parameters ($k = Ae^{-E_a/RT}$)

Number	Reaction	A (1/s)	E_a (kcal/mol)	Source
(R1)	CHXA $\rightarrow$ 1-hexene	$10^{16.7}$	88	[18]
(R2)	CHXE $\rightarrow$ 1,3-butadiene + C_2H_4	$10^{15.6}$	66	[19]
(R3)	1,3-CHXD $\rightarrow$ BZ + H_2	$10^{13.4}$	59	[20]
(R4)	1,4-CHXD $\rightarrow$ BZ + H_2	$10^{12.4}$	44	[21]
(R5)	BZ $\rightarrow$ BZ• + H	$10^{17.3}$	118	[22]
(R6)	1,3-CHXD $\rightarrow$ CHXD• + H	$10^{15.7}$	73	[23]
(R13)	CHXE $\rightarrow$ CHXE• + H	$10^{15.7}$	82	[23]
(R14)	CHXE $\rightarrow$ 1,3-CHXD + H_2	$10^{13.7}$	62	[7]
(R20)	CHXA $\rightarrow$ $3\text{C}_2\text{H}_4$	$10^{17.9}$	87	[4]
(R21)	CHXA $\rightarrow$ CHXA• + H	$10^{16.5}$	95	[23]
(R26)	<i>n</i> -Heptane	$10^{13.4}$	63	[24]
(R27)	1-Hexene $\rightarrow$ C_3H_5 + C_3H_7	$10^{15.9}$	71	[18]

BZ•, CHXD•, CHXE•, and CHXA• are phenyl, cyclohexadienyl, cyclohexenyl, and cyclohexyl radicals.

ment, which is good agreement considering the uncertainties in $(Z/H_T)_{1\%}$, T_g , and the estimates of the residence times. This agreement quantitatively confirms that unimolecular dissociation is the main decomposition process for most of the dopants.

BZ appears to be an exception: the calculations underpredict the decomposition rate for BZ but overpredict it for the other dopants. In fact, fall-off reduces the rate of (R5) by at least a factor of 2 [22], so the underprediction is worse than the high-pressure limit calculations imply. (Fall-off is insignificant for (R1) to (R4) at atmospheric pressure [18,19]; (R5) suffers more fall-off because it occurs at higher temperature—see the T_g scale on the right of Fig. 4—and the high-pressure limit requires higher pressures as temperature increases [23].) Furthermore, while the kinetic calculations presented below show that dissociation is the fastest decomposition pathway for CHXD, CHXE, and CHXA, similar calculations indicate that H-atom abstraction by OH radicals and H atoms is faster than unimolecular dissociation for BZ.

The agreement in Fig. 4 shows that the Arrhenius parameters in Table 2 for (R1) to (R4) are accurate for nonpremixed flame conditions. The “error bars” for the CHXA data point illustrate the effect of increasing or decreasing the A factors by a factor of 3, and they indicate an approximate upper bound to the errors in the Arrhenius parameters based on our results. This conclusion is significant because some of the Arrhenius parameters were obtained under conditions that are quite different from those in a flame. For example, (R3) was measured at $\sim 10^{-3}$ Torr [20] and (R4) at 600 to 660 K [21]. Lindstedt and Maurice obtained the Arrhenius parameters for (R26) by altering

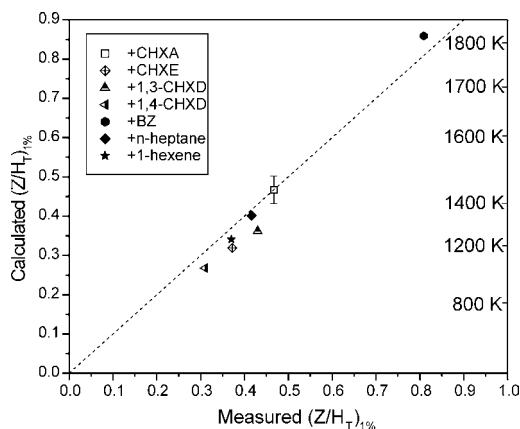


Fig. 4. The disappearance locations of the dopants were determined from their measured and calculated centerline mole fraction profiles. $(Z/H_T)_{1\%}$ is defined as the Z/H_T at which $[\text{dopant}] = 20$ ppm, which is 1% of $[\text{dopant}]_{\text{fuel}}$. The numbers on the right are the measured centerline T_g from the undoped flame plotted against the vertical Z/H_T scale.

an earlier set so that the rate was ~ 10 times slower at high temperatures [24]; our results support this alteration.

The importance of unimolecular dissociation in our nonpremixed flames differs from earlier studies of CHXA and CHXE oxidation in jet-stirred reactors [3–5], rapid compression machines [6], and shock tubes [7], in which H-atom abstraction was the dominant decomposition pathway. As discussed below, this difference significantly alters the BZ formation pathways. Our specific methodology particularly favors unimolecular dissociation because the dopants are mixed with a very stable fuel (CH_4); however, numerical simulations of neat propane and n -heptane nonpremixed flames have also concluded that dissociation is a key fuel decomposition pathway [24,25].

((R1) is an isomerization reaction, so our mass spectrometric diagnostic cannot directly detect its occurrence. However, Fig. 4 shows that CHXA consumption is much slower than 1-hexene consumption, so (R1) is the rate-determining step from CHXA to smaller molecular weight products.)

3.3. Hydrocarbon product concentrations

The hydrocarbon product concentrations provide further evidence regarding the decomposition and BZ formation processes for the dopants. About 30 products were detectable in these flames, and centerline mole fraction profiles of each one were measured in all six flames. We do not have enough space to show all of these data, but Fig. 5 shows the BZ profiles and Figs. 6–8 show the maximum centerline mole fractions of selected additional products. (We can provide an electronic version of the complete data set upon request.) The BZ profiles in the non-BZ-doped flames

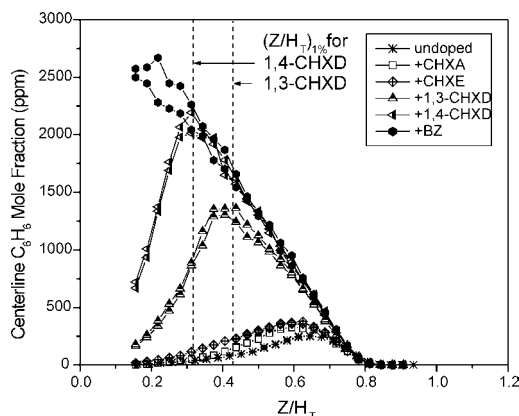


Fig. 5. Centerline [BZ] profiles were measured with the PTMS. The vertical dashed lines mark the heights at which 1,4-CHXD and 1,3-CHXD finish decomposing on the centerline.

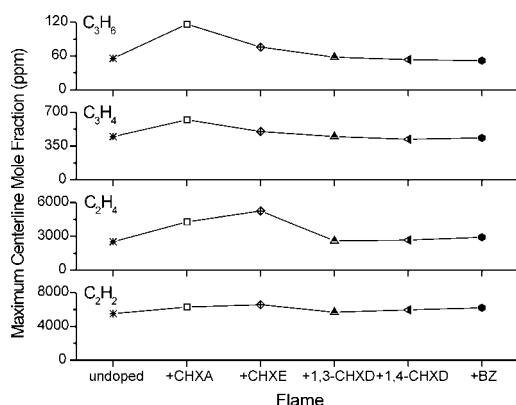


Fig. 6. Maximum centerline concentrations of important C2 and C3 hydrocarbons were determined from the EQMS and PTMS centerline profiles. C_2H_2 , acetylene; C_2H_4 , ethylene; C_3H_4 , propadiene/propyne; and C_3H_6 , propene.

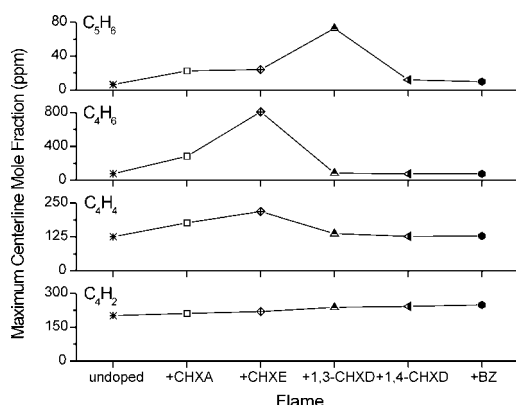


Fig. 7. Maximum centerline concentrations of important C4 and C5 hydrocarbons were determined from the PTMS centerline profiles. C_4H_2 , diacetylene; C_4H_4 , butenyne (vinylacetylene); C_4H_6 , butadiene; and C_5H_6 , cyclopentadiene.

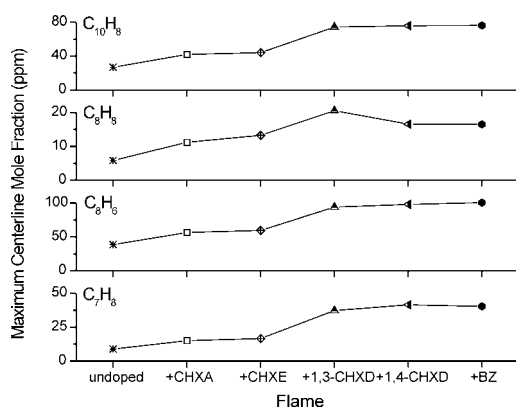


Fig. 8. Maximum centerline concentrations of important aromatic hydrocarbons were determined from the PTMS centerline profiles. C_7H_8 , toluene; C_8H_6 , phenylacetylene; C_8H_8 , styrene; and $C_{10}H_8$, naphthalene.

illustrate the behavior observed for all of the hydrocarbon products: the concentrations are near zero at the burner surface, increase to a peak in the fuel-rich part of the flame, and decrease back to zero by $Z/H_T = 0.9$, which is where O_2 begins to appear on the centerline.

In the CHXD-doped flames [BZ] increases very rapidly until the BZ profiles merge with the BZ profile in the BZ-doped flame. Furthermore, the heights at which [BZ] peaks (0.31 and 0.41) are very close to the heights at which the dopant disappears ($(Z/H_T)_{1\%} = 0.31$ and 0.43; see the dashed lines in Fig. 5). Thus dehydrogenation to BZ is the dominant decomposition pathway—and BZ formation pathway—for both CHXDs. This conclusion agrees with sooting tendencies measured in CHXD/ N_2 nonpremixed flames [8], so it is a general feature of nonpremixed flames and is not specific to the conditions in our doped flames.

Detailed inspection of our results reveals that 1,4-CHXD decomposes exclusively to BZ, whereas additional minor decomposition pathways exist for 1,3-CHXD. In particular, for $Z/H_T > 0.4$ [BZ] agrees to within 10% among the 1,4-CHXD- and BZ-doped flames, but it is systematically 10–20% lower in the 1,3-CHXD-doped flame. Furthermore, Figs. 6–8 show that the maximum mole fractions of all other hydrocarbon products are the same in the 1,4-CHXD- and BZ-doped flames, while $[C_4H_6]_{\max}$, $[C_5H_6]_{\max}$, and $[C_8H_8]_{\max}$ are higher in the 1,3-CHXD-doped flame. (The C_4H_6 results are difficult to make out in the figure; $[C_4H_6]_{\max} = 85, 75$, and 76 ppm in the 1,3-CHXD-, 1,4-CHXD-, and BZ-doped flames.)

In the CHXE- and CHXA-doped flames [BZ] increases slowly, and large increases (hundreds or thousands of ppm) occur in the mole fractions of C2, C3, and C4 hydrocarbons. The C_2H_4 and C4 concentrations are larger in the CHXE-doped flame, while the C3 concentrations are larger in the CHXA-doped flame. Thus fragmentation to lower carbon number products is the main decomposition process for both CHXE and CHXA, but it produces C4 + C2 products from CHXE and C3 + C3 products from CHXA.

Nonetheless, CHXE and CHXA produce some BZ, so the question arises of whether this BZ comes from addition reactions between the fragments or from dehydrogenation. (Although dehydrogenation is not the main decomposition pathway for these dopants, it could still be an important BZ formation pathway since BZ is a minor product.) Figure 9 shows the CHXD profiles measured in the CHXE- and CHXA-doped flames at the top and the “extra” BZ measured in these flames at the bottom (i.e., the BZ profiles from these flames minus the profile from the undoped flame). $[CHXD]_{\max}$ in the CHXE-doped flame is about one-third of the maximum extra [BZ]. The results from the CHXD-doped flames

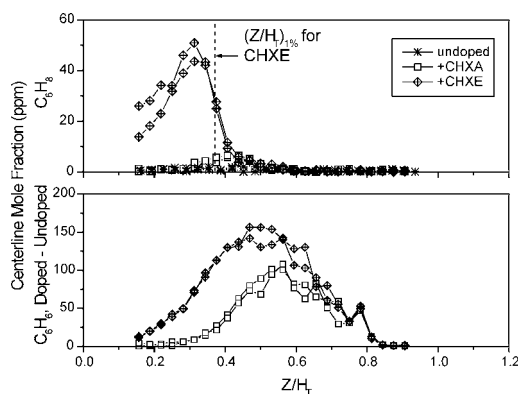


Fig. 9. (Top) Centerline [CHXD] profiles were measured with the PTMS. (Bottom) Approximate profiles of the BZ formed from CHXE and CHXA were obtained by subtracting the [BZ] profiles in the undoped flame from the [BZ] profiles in the CHXE- and CHXA-doped flames. The vertical dashed line in the top graph marks the height at which CHXE finishes decomposing on the centerline.

imply that this CHXD converts to BZ, so dehydrogenation roughly accounts for at least one-third of the extra BZ in the CHXE-doped flame. In fact, since $CHXD \rightarrow BZ$ probably overlaps $CHXE \rightarrow CHXD$ to some extent, the actual fraction of the extra BZ formed by dehydrogenation could be much larger than one-third. (Some of the measured C_6H_8 could be hexatriene, but, as discussed below, hexatriene also converts to BZ.)

The profile shapes support this conclusion. The extra [BZ] finishes increasing at roughly the height at which [CHXD] decreases to zero, which agrees with CHXD being the main source of BZ. Moreover, [CHXD]_{max} occurs at $Z/H_T = 0.31$, which is well before CHXE disappears ($(Z/H_T)_{1\%} = 0.37$; see the dashed line in Fig. 9), so CHXD consumption does indeed overlap CHXE consumption.

In the CHXA flame very little CHXD was detected ($[CHXD]_{\max} \sim 6$ ppm) and CHXE was undetectable (detection limit ~ 5 ppm, limited by interferences from fragment ions of CHXA). These observations suggest that very little CHXA dehydrogenated to BZ, but they are not conclusive: CHXE and CHXD both start to decompose before CHXA (see Fig. 3), so their concentrations could be small even if dehydrogenation was important.

Therefore, to obtain further evidence we examined the dependence of $[BZ]_{\max}$ on $[C_3H_4]_{\max}$. In our study of heptane-doped flames, in which BZ probably formed from self-reaction of propargyl radical (C_3H_3)—and definitely not by dehydrogenation of alkyl rings—we obtained a linear relationship between these two parameters [1]. Figure 10 shows the data point from the undoped flame, the five data points from the heptane-doped flames, the best-fit straight

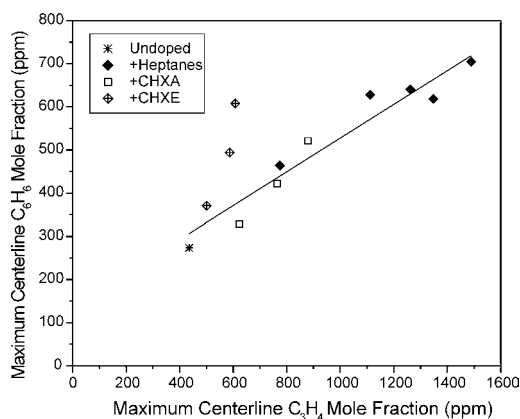


Fig. 10. $[BZ]_{\max}$ and $[C_3H_4]_{\max}$ were determined from PTMS centerline profiles measured in CHXA- and CHXE-doped flames with $[dopant]_{\text{fuel}} = 2000, 3500$, and 5000 ppm. The undoped and heptane-doped flame data points come from Ref. [1], and the line is the least-squares linear fit to them. $[Dopant]_{\text{fuel}} = 5000$ ppm in all of the heptane-doped flames, but the specific isomer varied.

line to those six points, and six new data points from CHXE- and CHXA-doped flames with $[dopant]_{\text{fuel}} = 2000, 3500$, and 5000 ppm. The data points from the CHXE-doped flames lie at systematically higher $[C_6H_6]$ for a given $[C_3H_4]$ than the best-fit line, which suggests that a large portion of the BZ is being formed by a new pathway, presumably dehydrogenation. The data points from the CHXA-doped flames follow the best-fit line much more closely, which suggests that most of the BZ is being formed by the same pathways as in the heptane-doped flames and therefore that very little BZ is formed by dehydrogenation.

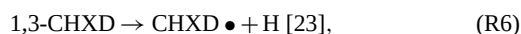
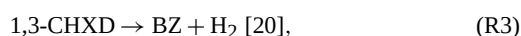
3.4. Reaction pathways

In this section we present calculations of effective rate constants (k_{eff}) for possible consumption reactions of the dopants and their conjugate radicals. These calculations further validate the conclusions of the previous sections, explain several of the key experimental observations, such as the importance of fragmentation for CHXA and CHXE in nonpremixed flames versus premixed systems, and demonstrate the reasonableness of the measured product concentrations. We define $k_{\text{eff}} \equiv k$ for unimolecular reactions ($R \rightarrow \text{products}$) and $k_{\text{eff}} \equiv k[X]$ for bimolecular reactions with species X ($R + X \rightarrow \text{products}$). Thus in both cases $k_{\text{eff}} = \text{rate}/[R]$ and the values can be directly compared.

These calculations require concentrations of radicals (H, CH_3 , OH, etc.) that were not measured in this study. Therefore we based the calculations on centerline species and T_g profiles that we obtained by numerically simulating a CH_4/air flame that was

identical to the experimental undoped flame except that its fuel was not diluted by N_2 [14]. The model used a detailed chemical kinetic mechanism, species-dependent transport coefficients, an optically thin radiation submodel, fully elliptic governing equations, etc., and the numerical results agreed with experimental measurements. The difference in N_2 dilution is not expected to significantly alter the relative importance of reactions.

CHXD-doped flames. Possible 1,3-CHXD reactions include H_2 elimination, C–H fission, H-atom abstraction (by $X = H, CH_3, O, OH, O_2$, etc.), and H-atom addition:



where $\text{CHXD} \bullet$ is the cyclohexadienyl radical and $\text{CHXE} \bullet$ is the cyclohexenyl radical.

Figure 11 shows centerline profiles of k_{eff} for these reactions based on the rate expressions in the cited references. All of the reactions that produce $\text{CHXD} \bullet$ are shown with open symbols, the reaction that produces $\text{CHXE} \bullet$ is shown with partially filled symbols, and the reaction that produces BZ with filled symbols. The numerical results indicate that the residence times in the pyrolysis zone of the flames are ~ 10 ms. This corresponds to $k_{\text{eff}} \sim 100 \text{ s}^{-1}$, which is marked with a dashed horizontal line. When the reactions first achieve this level (at $Z/H_T \approx 0.26$), H_2 elimination is the fastest reaction, followed by C–H fission (50% as fast), and H-atom addition (4%). The fastest H-atom abstraction reaction, abstraction by CH_3 , is only 0.7% as fast, so these calculations

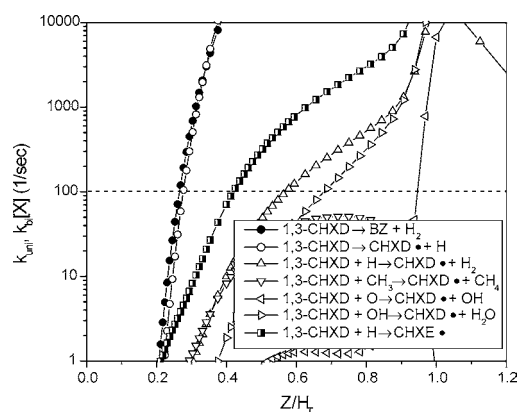
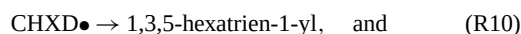
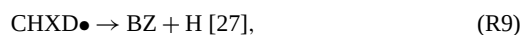


Fig. 11. Effective rate constants for various reactions of 1,3-CHXD were calculated from the computed centerline profiles in Ref. [14].

provide further evidence that unimolecular dissociation dominates H-atom abstraction for 1,3-CHXD.

Possible $\text{CHXD} \bullet$ reactions include C–H fission, C–C fission, and H-atom abstraction:



(H-atom addition is also possible, but unimportant in terms of CHXD decomposition products.) The barrier heights for (R9) and (R10) are 25.7 and 60.1 kcal/mol [28], so C–H fission is strongly favored. For illustrative purposes we have assumed a rate expression for (R10) with $A_{10} = A_9 = 2 \times 10^{13} \text{ s}^{-1}$ [27] and $E_{10} = 60.1 \text{ kcal/mol}$. ($E_9 = 26.0 \text{ kcal/mol}$ [27], which is close to the computed barrier height.)

Figure 12 shows k_{eff} for these reactions. The vertical dashed line marks the height at which k_{eff} of the 1,3-CHXD reactions first reaches 100 s^{-1} , which is where most $\text{CHXD} \bullet$ forms. At this location the dominant $\text{CHXD} \bullet$ reaction, by a factor of 2300, is C–H fission. The second and third most important reactions are H-atom abstraction by O_2 and CH_3 , which also form BZ. (The maximum in k_{eff} for H-atom abstraction by O_2 at $Z/H_T \approx 0.1$ results from the entrainment of $[O_2]$ at the base of the flame (see Fig. 2), which is accurately reproduced by the numerical simulations [14].) C–C fission is 6 orders of magnitude slower than C–H fission, which is much larger than the uncertainty in our estimate of A_{10} , so hexatrienyl formation is negligible.

Figure 13 shows a reaction scheme for fuel decomposition and BZ formation in nonpremixed 1,3-CHXD flames based on Figs. 11 and 12 and the ob-

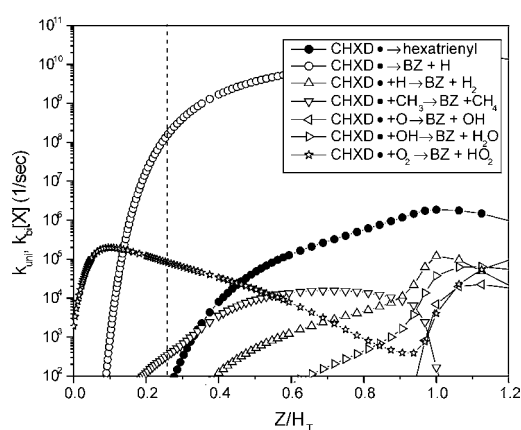


Fig. 12. Effective rate constants for various reactions of $\text{CHXD} \bullet$ were calculated from the computed centerline profiles in Ref. [14]. The vertical dashed line marks the height at which k_{eff} for the 1,3-CHXD reactions first reaches 100 s^{-1} .

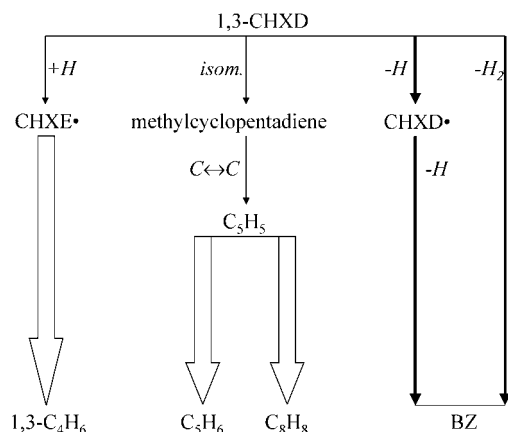


Fig. 13. A reaction scheme for 1,3-CHXD was developed based on the observed hydrocarbon products, Figs. 11 and 12. Thick arrows represent major elementary reactions, thin arrows represent minor elementary reactions, open arrows represent multistep pathways, and $C \leftrightarrow C$ represents C–C bond fission.

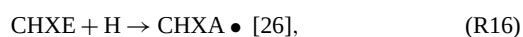
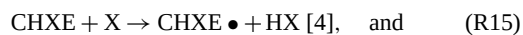
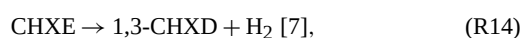
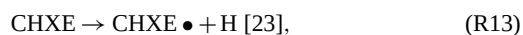
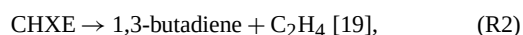
served hydrocarbon products. The major 1,3-CHXD consumption pathways, indicated by thick arrows, produce BZ by (R3) and $\text{CHXD}\bullet$ by (R6), and the main consumption pathway for $\text{CHXD}\bullet$ produces BZ by (R9). Thus this scheme readily explains why BZ is the dominant product in the experiments.

Two minor 1,3-CHXD consumption pathways produce the other observed products. The first is $\text{CHXE}\bullet$ formation by (R8). As discussed below, $\text{CHXE}\bullet$ decomposes to C4 hydrocarbons, so this pathway explains the observed C_4H_6 . The second minor pathway is isomerization to methylcyclopentadiene ($\text{CHXD} \rightarrow \text{C}_5\text{H}_5\text{--CH}_3$). This is a hypothetical reaction that we have included in the reaction scheme to provide a source of C_5H_6 and C_8H_8 . Specifically, methylcyclopentadiene readily dissociates via C–C fission to CH_3 and cyclopentadienyl radical ($\text{C}_5\text{H}_5\text{--CH}_3 \rightarrow \text{C}_5\text{H}_5 + \text{C}_3\text{H}_3$) [29], and the C_5H_5 can then form cyclopentadiene by H-atom addition and styrene by an addition reaction with C_3H_3 . This part of the reaction scheme is uncertain and is intended only to show the existence of plausible formation pathways for C_5H_6 and C_8H_8 , not to be the definitive explanation; detailed kinetic studies of 1,3-CHXD reactions under simpler conditions are clearly needed.

The reaction scheme for 1,4-CHXD resembles the one for 1,3-CHXD. However, as discussed above, H_2 elimination is much faster from 1,4-CHXD than from 1,3-CHXD (by a factor of 100 at 1100 K), so the $\text{CHXE}\bullet$ and methylcyclopentadiene pathways are much less important. For example, if we assume that the rate expression for H-atom addition is the same for 1,4-CHXD as for 1,3-CHXD, then when the rate of H_2 elimination first achieves 100 s^{-1} in the 1,4-

CHXD-doped flame (at $Z/H_T \approx 0.19$), H-atom addition is only 0.6% as fast, versus 4% as fast in the 1,3-CHXD-doped flame. Thus the reaction scheme readily explains why 1,4-CHXD produces BZ exclusively while 1,3-CHXD produces additional products.

CHXE-doped flame. Possible CHXE reactions include retro-Diels–Alder dissociation, C–H fission, H_2 elimination, H-atom abstraction, and H-atom addition,



where $\text{CHXA}\bullet$ is the cyclohexyl radical. Kiefer and Shah have shown definitively that (R2) is the dominant unimolecular reaction for CHXE [19]; however, (R14) is potentially still important since 1,3-CHXD is a more direct BZ precursor than is 1,3-butadiene. Smith and Gordon detected CHXD during static reactor pyrolysis of CHXE and concluded that it was formed by a unimolecular process based on experiments with deuterium-labeled compounds [30]. Dayma et al. have reanalyzed Smith and Gordon's data to obtain the Arrhenius parameters for (R14) that are listed in Table 2. More recently, Barnard and Parrott observed CHXD formation during shock tube pyrolysis of CHXE [31].

Figure 14 shows k_{eff} for these reactions. When k_{eff} first reaches 100 s^{-1} (at $Z/H_T \approx 0.24$) the retro-Diels–Alder dissociation is the fastest reaction, followed by H_2 elimination (9% as fast), H-atom addition (1.2%), and H-atom abstraction by CH_3 (0.7%).

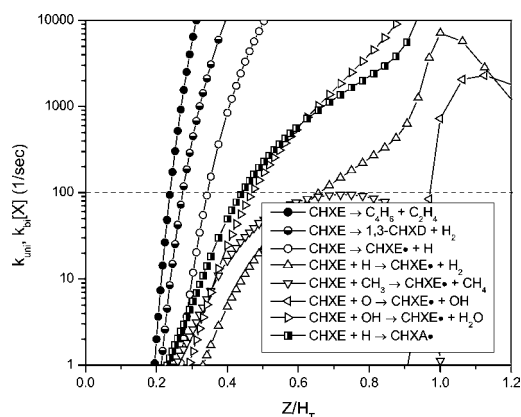


Fig. 14. Effective rate constants for various reactions of CHXE were calculated from the computed centerline profiles in Ref. [14].

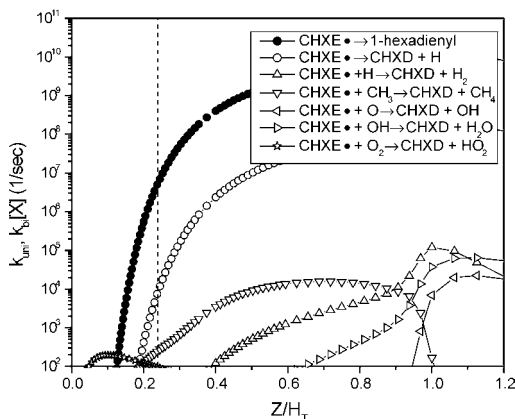


Fig. 15. Effective rate constants for various reactions of $\text{CHXE}^\bullet$ were calculated from the computed centerline profiles in Ref. [14]. The vertical dashed line marks the height at which k_{eff} for the CHXE reactions first reaches 100 s^{-1} .

Possible $\text{CHXE}^\bullet$ reactions include C–C fission, C–H fission, and H-atom abstraction:

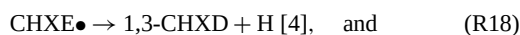
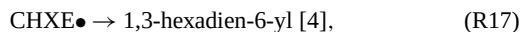


Figure 15 shows k_{eff} for these reactions. The dashed line marks the height at which most $\text{CHXE}^\bullet$ forms. At this location the dominant $\text{CHXE}^\bullet$ reaction, by a factor of 700, is C–C fission. Thus a negligible fraction of the CHXE dehydrogenates to CHXD via $\text{CHXE}^\bullet$ ($= \text{CHXE}^\bullet / \text{CHXE} \times \text{CHXD} / \text{CHXE}^\bullet \sim 0.7\% \times 1/700 = 10^{-5}$), so (R14) is necessary to explain the 50 ppm CHXD measured in the CHXE -doped flame.

Figure 16 shows a reaction scheme for fuel decomposition and BZ formation in nonpremixed CHXE flames based on Figs. 14 and 15 and the observed hydrocarbon products. The major CHXE consumption pathway produces C_4H_6 and C_2H_4 by (R2), and the most important minor pathway produces 1,3- CHXD by (R14). The dominance of (R2) explains why C_2H_4 and C_4H_6 are the main products in the CHXE -doped flame (see Figs. 6 and 7). Subsequent reactions of C_4H_6 produce the observed C_3H_4 and C_4H_4 [32,33]. BZ is formed by dehydrogenation of 1,3- CHXD and various $\text{C}_4 + \text{C}_2$ and $\text{C}_3 + \text{C}_3$ addition reactions.

Formation of $\text{CHXE}^\bullet$ and $\text{CHXA}^\bullet$ is also included in the reaction scheme for completeness, but Fig. 14 demonstrates that these are minor pathways. As discussed below, $\text{CHXA}^\bullet$ leads to C_4H_6 and C_2H_4 , which are the same products as from (R2). Figure 15 shows that $\text{CHXE}^\bullet$ overwhelmingly decomposes by C–C fission to the 1,3-hexadien-6-yl radical, which decomposes in turn by C–C fis-

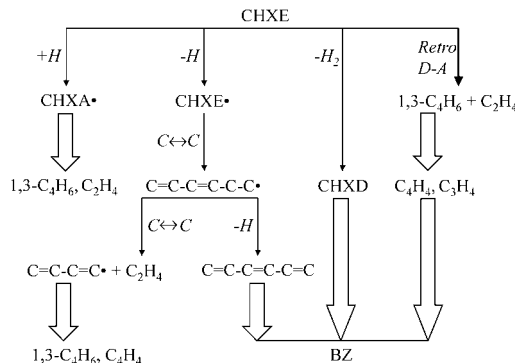


Fig. 16. A reaction scheme for CHXE was developed based on the observed hydrocarbon products, Figs. 14 and 15. Thick arrows represent major elementary reactions, thin arrows represent minor elementary reactions, open arrows represent multistep pathways, and $\text{C} \leftrightarrow \text{C}$ represents C–C bond fission.

sion to butadienyl + C_2H_4 and by C–H fission to 1,3,5-hexatriene. The sooting tendencies of hexatrienes are similar to those of BZ [8], which implies that they readily convert to BZ, so hexatrienes presumably do as well. However, only $\sim 0.7\%$ of the CHXE is converted to $\text{CHXE}^\bullet$, so the upper limit to $[\text{hexatriene}]_{\text{max}}$ is ~ 14 ppm, and BZ formation by this pathway is less important than from $\text{CHXE} \rightarrow \text{CHXD} \rightarrow \text{BZ}$.

CHXA-doped flame. Possible CHXA reactions include isomerization to 1-hexene, dissociation to C_2H_4 , C–H fission, and H-atom abstraction:

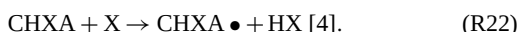
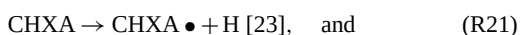


Figure 17 shows k_{eff} for these reactions. The dominant process is C_2H_4 formation via (R20), which implies that the CHXA -doped flame is effectively a C_2H_4 -doped flame. However, the measurements strongly contradict this notion; for example, $[\text{C}_2\text{H}_4]_{\text{max}}$ is higher in the CHXE -doped flame than in the CHXA -doped flame. Thus we conclude that the rate expression for (R20) given in [4] overpredicts the rates in our temperature regime. (Our conditions are much more sensitive to unimolecular dissociation rates than were the near-stoichiometric experiments in [4].) With (R20) excluded, isomerization to 1-hexene is the fastest CHXA consumption reaction when k_{eff} first reaches 100 s^{-1} (at $Z/H_T \approx 0.35$), followed by H-atom abstraction by H atom (33% as fast) and by CH_3 (7%).

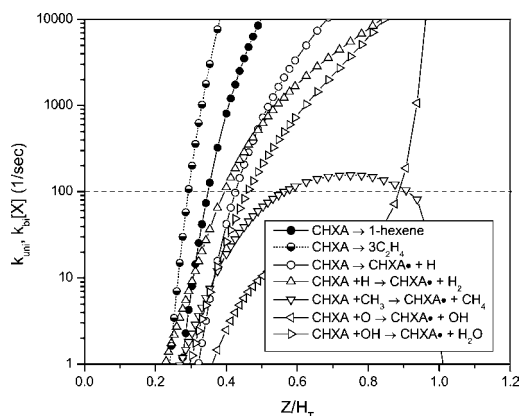


Fig. 17. Effective rate constants for various reactions of CHXA were calculated from the computed centerline profiles in Ref. [14].

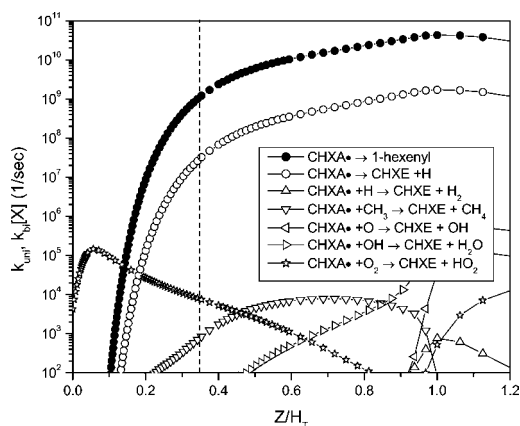


Fig. 18. Effective rate constants for various reactions of CHXA• were calculated from the computed centerline profiles in Ref. [14]. The vertical dashed line marks the height at which k_{eff} for the CHXA reactions (excluding (R20)) first reaches 100 s^{-1} .

Possible CHXA• reactions include C–C fission, C–H fission, and H-atom abstraction:

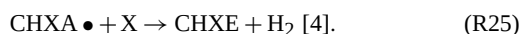
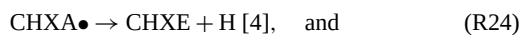
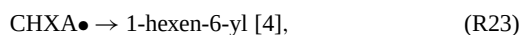


Figure 18 shows k_{eff} for these reactions. The dashed line marks the height at which most CHXA• forms. At this location the dominant CHXA• consumption reaction, by a factor of 40, is C–C fission. Thus only a small fraction of CHXA is converted to CHXE ($= \text{CHXA}\bullet / \text{CHXA} \times \text{CHXE} / \text{CHXA}\bullet \sim 40\% \times 1/40 = 1\%$), which explains why CHXE was undetectable in the CHXA-doped flame and dehydrogenation formed very little BZ.

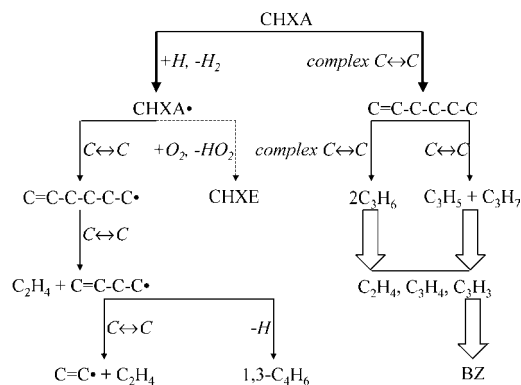


Fig. 19. A reaction scheme for CHXA was developed based on the observed hydrocarbon products, Figs. 17 and 18. Thick arrows represent major elementary reactions, thin arrows represent minor elementary reactions, open arrows represent multistep pathways, and $\text{C} \leftrightarrow \text{C}$ represents C–C bond fission.

Figure 19 shows a reaction scheme for fuel decomposition and BZ formation in nonpremixed CHXA flames based on Figs. 17 and 18 and the observed hydrocarbon products. The major CHXA consumption pathways produce 1-hexene by (R1) and CHXA• by (R22). The central C–C bond in 1-hexene is the weakest C–C bond (by about 12 kcal/mol [34]); thus the dominant dissociations of 1-hexene are fissions of this bond to produce allyl + *n*-propyl and $\text{C}_3\text{H}_6 + \text{C}_3\text{H}_6$ [18]. Subsequent reactions of these products lead to the observed C_3H_4 and C_2H_4 and to BZ via C_3H_3 recombination. Our measurements in a 1-hexene-doped flame confirm the production of C_2H_4 , C_3H_4 , and C_3H_6 from 1-hexene. CHXA• decomposes through a series of C–C fissions to produce the observed C_4H_6 and C_2H_4 .

This kinetic scheme, combined with the schemes for CHXD and CHXE, clearly explains why BZ is the dominant decomposition product of CHXD but not of CHXA and CHXE. First, unimolecular dissociation is a major consumption pathway for all of these dopants, and the fastest CHXD dissociation reactions, (R3) and (R4), produce BZ directly while the fastest CHXA and CHXE dissociation reactions, (R1) and (R2), produce linear hydrocarbons. Second, C–H fission dominates CHXD• dissociation due to the effects of resonance on the C–H and C–C bond strengths, whereas C–C fission dominates CHXE• and CHXA• dissociation since alkyl C–C bonds are weaker than alkyl C–H bonds [35].

The kinetic scheme for CHXA also explains why dehydrogenation is much more important in premixed systems [3–6]. The key is abstraction of an H atom from CHXA• by O_2 ; this pathway is shown with a dotted line in Fig. 19 since it is insignificant in our flames, but premixing greatly increases its impor-

tance. The main reason is that premixing increases $[O_2]$ (by a factor of ~ 50 at $\phi = 2$). Furthermore, premixing increases radical concentrations in the pyrolysis zone [14], which shifts CHXA consumption toward CHXA• instead of 1-hexene. Finally, the increased radical concentrations cause CHXA• to be produced at lower Z/H_T , which favors H-atom abstraction over dissociation due to the shape of the $[O_2]$ profile and the negative temperature dependence of the abstraction reaction.

3.5. Soot volume fractions; rate-limiting steps to soot formation

Soot volume fractions (f_v) connect fuel decomposition and hydrocarbon growth with the practical problem of particle emissions from combustors. The f_v profiles measured in the current flames resemble those we have presented earlier for heptane-doped flames [1]. $f_{v,max}$ equals ~ 0.0005 (undoped flame), 0.043 (+CHXA), 0.055 (+CHXE), 0.23 (+1,3-CHXD), 0.25 (+1,4-CHXD), and 0.26 ppm (+BZ).

In our heptane-doped flames $f_{v,max}$ depended linearly on $[BZ]_{max}$. The bottom of Fig. 20 shows the data from that study, a straight line fit to it, and the corresponding results from the current flames. The CHXA- and CHXE-doped flames fit the line reasonably well, but the CHXD and BZ-doped flames do not: their $f_{v,max}$ are much smaller than would be expected on the basis of their $[BZ]_{max}$. Undoubtedly the reason is that in these flames [BZ] peaks before hydrocarbon growth is possible and then is reduced by mixing before growth starts. Or, to put it another way, CHXD converts to BZ so easily that BZ formation is not a rate-determining soot formation step.

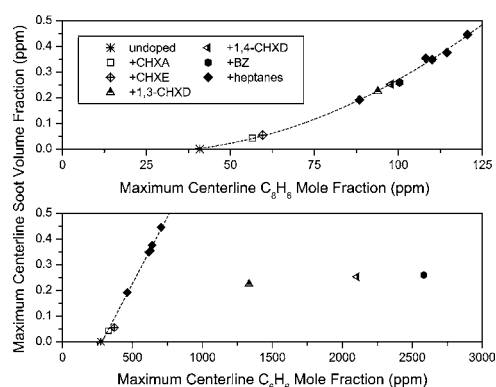


Fig. 20. $[Phenylacetylene]_{max}$ (top), $[BZ]_{max}$ (bottom), and $f_{v,max}$ were determined from the PTMS and LII centerline profiles. The undoped and heptane-doped flame data points come from Ref. [1]. The dashed line in the bottom graph is a linear least-squares fit to the undoped and heptane-doped flame data, and the dashed line in the top graph is a second-order polynomial least-squares fit to all of the data.

(The $f_{v,max}$ in the cyclic C6-doped flames is smaller than in the heptane-doped flames because [dopant] in the fuel mixture was 2000 ppm versus 5000 ppm.)

Based on several of our earlier studies we assume that naphthalene formation in these flames is dominated by C_2H_2 addition to phenylacetylene (i.e., the HACA mechanism [36]) [10,37]. Therefore phenylacetylene is the next critical growth product beyond BZ. The top of Fig. 20 shows $f_{v,max}$ as a function of $[phenylacetylene]_{max}$. In this case all of the data points fit on a single curve. Thus phenylacetylene formation is a rate-limiting step to soot formation in these flames.

4. Concluding remarks

Benzene formation is important in at least two contexts: as part of air toxics formation [38] and as a precursor to soot formation [39]. Air toxics tend to form when fuel partially oxidizes under low-temperature, near-stoichiometric conditions, e.g., when gasoline in an engine is trapped in crevices and then released during the expansion stroke [40,41]. Under these conditions cyclohexane readily produces benzene through dehydrogenation [3–6], and indeed substantial benzene formation via this pathway has been observed in cyclohexane-fueled spark-ignition engines [40,41]. In contrast, soot forms when fuel pyrolyzes under high-temperature, fuel-rich conditions, e.g., in a burning diesel fuel spray. The experiments reported in this paper show that under these conditions cyclohexane negligibly dehydrogenates to benzene. Thus soot production from cycloalkanes mirrors that from similar-sized linear alkanes.

Acknowledgments

We appreciate assistance from Isabelle Chumfong in conducting these experiments, useful discussions with William Green, and financial support from the National Science Foundation (CTS-0121765), Environmental Protection Agency (R-82816701-0) and Defense Advanced Research Projects Agency.

References

- [1] C.S. McEnally, D.M. Ciuparu, L.D. Pfefferle, *Combust. Flame* 134 (2003) 339–353.
- [2] W.G. Dukek, in: Kirk–Othmer Encyclopedia of Chemical Technology, Wiley, New York, 1991, p. 791.
- [3] S.K. Gulati, R.W. Walker, *J. Chem. Soc. Faraday Trans. II* 85 (1989) 1799–1812.

- [4] D. Voisin, A. Marchal, M. Reuillon, J.-C. Boettner, M. Cathonnet, *Combust. Sci. Technol.* 138 (1998) 137–158.
- [5] A. El Bakali, M. Braun-Unkhoff, P. Dagaut, P. Frank, M. Cathonnet, *Proc. Combust. Inst.* 28 (2000) 1631–1638.
- [6] O. Lemaire, M. Ribaucour, M. Carlier, R. Minetti, *Combust. Flame* 127 (2001) 1971–1980.
- [7] G. Dayma, P.A. Glaude, R. Fournet, F. Battin-Leclerc, *Int. J. Chem. Kinet.* 35 (2003) 273–285.
- [8] A. Gomez, G. Sidebotham, I. Glassman, *Combust. Flame* 58 (1984) 45–57.
- [9] C.S. McEnally, Ü.Ö. Köylü, L.D. Pfefferle, D.E. Rosner, *Combust. Flame* 109 (1997) 701–720.
- [10] C.S. McEnally, L.D. Pfefferle, *Combust. Flame* 129 (2002) 305–323.
- [11] C.S. McEnally, L.D. Pfefferle, R.K. Mohammed, M.D. Smooke, M.B. Colket, *Anal. Chem.* 71 (1999) 364–372.
- [12] NIST Standard Reference Database 69, <http://webbook.nist.gov/chemistry>.
- [13] J.H. Arps, C.H. Chen, M.P. McCann, I. Datskou, *Appl. Spectrosc.* 43 (1989) 1211–1214.
- [14] B.A.V. Bennett, C.S. McEnally, L.D. Pfefferle, M.D. Smooke, *Combust. Flame* 123 (2000) 522–546.
- [15] R.E. Mitchell, A.F. Sarofim, L.A. Clomburg, *Combust. Flame* 37 (1980) 227–244.
- [16] Y.R. Sivathanu, G.M. Faeth, *Combust. Flame* 82 (1990) 211–230.
- [17] F.G. Roper, *Combust. Sci. Technol.* 40 (1984) 323–329.
- [18] W. Tsang, *Int. J. Chem. Kinet.* 10 (1978) 1119–1138.
- [19] J.H. Kiefer, J.N. Shah, *J. Phys. Chem.* 91 (1987) 3024–3030.
- [20] Z.B. Alfassi, S.W. Benson, D.M. Golden, *J. Am. Chem. Soc.* 95 (1973) 4784–4788.
- [21] S.W. Benson, R. Shaw, *Trans. Faraday Soc.* 63 (1967) 985–992.
- [22] J.H. Kiefer, L.J. Mizerka, M.R. Patel, H.-C. Wei, *J. Phys. Chem.* 89 (1985) 2013–2019.
- [23] A.M. Dean, *J. Phys. Chem.* 89 (1985) 4600–4608.
- [24] R.P. Lindstedt, L.Q. Maurice, *Combust. Sci. Technol.* 107 (1995) 317–353.
- [25] K.M. Leung, R.P. Lindstedt, *Combust. Flame* 102 (1995) 129–160.
- [26] K. Hoyeremann, A.W. Preuss, H.G. Wagner, *Ber. Bunsenges. Phys. Chem.* 79 (1975) 156–165.
- [27] W. Tsang, *J. Phys. Chem.* 90 (1986) 1152–1155.
- [28] H. Wang, M. Frenklach, *J. Phys. Chem.* 98 (1994) 11465–11489.
- [29] E. Ikeda, R.S. Tranter, J.H. Kiefer, R.D. Kern, H.J. Singh, Q. Zhang, *Proc. Combust. Inst.* 28 (2000) 1725–1732.
- [30] S.R. Smith, A.S. Gordon, *J. Phys. Chem.* 65 (1961) 1124–1128.
- [31] J.A. Barnard, T.K. Parrott, *J. Chem. Soc. Faraday Trans. I* 72 (1976) 2404–2415.
- [32] J.A. Cole, J.D. Bittner, J.P. Longwell, J.B. Howard, *Combust. Flame* 56 (1984) 51–70.
- [33] C.S. McEnally, L.D. Pfefferle, A.G. Robinson, T.S. Zwier, *Combust. Flame* 123 (2000) 344–357.
- [34] D.F. McMillen, D.M. Golden, *Annu. Rev. Phys. Chem.* 33 (1982) 493–532.
- [35] H.J. Curran, P. Gaffuri, W.J. Pitz, C.K. Westbrook, *Combust. Flame* 114 (1998) 149–177.
- [36] H. Wang, M. Frenklach, *Combust. Flame* 110 (1997) 173–221.
- [37] C.S. McEnally, L.D. Pfefferle, *Proc. Combust. Inst.* 28 (2000) 2569–2576.
- [38] C.P. Koshland, *Proc. Combust. Inst.* 26 (1996) 2049.
- [39] I. Glassman, *Proc. Combust. Inst.* 23 (1988) 295.
- [40] E.W. Kaiser, W.O. Siegl, D.F. Cotton, R.W. Anderson, *Environ. Sci. Technol.* 26 (1992) 1581–1586.
- [41] P.J. Bennett, D. Gregory, R.A. Jackson, *Combust. Sci. Technol.* 115 (1996) 83–103.