Exploring Old and New Benzene Formation Pathways
in Low-Pressure Premixed Flames of Aliphatic Fuels

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ABSTRACT

A modeling study of benzene and phenyl radical formation is performed for three low-pressure premixed laminar flat flames having an unsaturated C_2 or C_3 hydrocarbon fuel (acetylene, ethylene, and propene). Predictions using three published detailed elementary-step chemical kinetics mechanisms are tested against MBMS species profile data for all three flames. The differences between the three mechanisms predictive capabilities are explored, with an emphasis on benzene formation pathways. A new chemical kinetics mechanism is created combining features of all three published mechanisms. Included in the mechanism are several novel benzene formation reactions involving combinations of radicals such as $C_2H+C_4H_5$, $C_2H_3+C_4H_3$, and $C_5H_3+CH_3$. Reactions forming fulvene (a benzene isomer) are included, such as $C_3H_3+C_3H_5$, as well as fulvene-to-benzene reactions.

Predictions using the new mechanism show virtually all of the benzene and phenyl radical to be formed by reactions of either $C_3H_3+C_3H_3$ or $C_3H_3+C_3H_5$, with the relative importance being strongly dependent upon the fuel. $C_5H_3+CH_3$ plays a minor role in fulvene formation in the acetylene flame. The $C_2H_x+C_4H_x$ reactions do not contribute noticeably to benzene or phenyl radical formation in these flames, sometimes being a major decomposition channel for either fulvene or phenyl radical. The formation pathways for C_3H_3 and C_3H_5 are delineated for the three flames; while the key reactions differ from flame to flame, $^1CH_2+C_2H_2 \rightleftharpoons C_3H_3+H$ is important for all three flames.

INTRODUCTION

A molecular-level understanding of combustion chemistry is essential for controlling the products of molecular-weight growth, which can lead to the formation of polycyclic aromatic hydrocarbons (PAH), many of which are known mutagens and/or carcinogens. The PAH themselves are likely precursors of soot particles in flames. For flames of aliphatic fuels, all of the aromatic rings, including the first, need to be formed by combination of smaller hydrocarbon fragments, thus providing motivation for understanding benzene formation in combustion.

Considering the level of interest in benzene formation, the lack of consensus on what the major reaction pathways are might be surprising to the casual observer. Thorough reviews of all but the most recent work are provided by Westmoreland, *et al.* [1] and Melius *et al.* [2]. Two broad types of ring-forming reactions appear: (1) acetylene (C_2H_2) addition to a C_4 vinyl radical, with subsequent cyclization, i.e., reactions #296 [3] and #297 [4] in Table 1; (2) combination of resonantly stabilized free radicals (RSFRs), with subsequent rearrangement and ring formation, e.g., reaction #412, propargyl (H_2CCCH) radical recombination, $2C_3H_3(H_2CCCH) \rightleftharpoons C_6H_5(\text{phenyl}) + H$ [2,5].

In the acetylene-addition reactions, one reactant (C_2H_2) is a major product of fuel-rich combustion, present in high concentrations, and the adduct does not require intramolecular rearrangements prior to cyclization. However, both $n\text{-}C_4H_3$ ($HCCHCCH$) and $n\text{-}C_4H_5$ ($CH_2CHCHCH$) have more stable isomers -- $i\text{-}C_4H_3$ (H_2CCCCH) and $i\text{-}C_4H_5$ (CH_2CHCCH_2) [5] -- into which they can readily be converted, greatly diminishing the amount of the $n\text{-}C_4H_3$ and $n\text{-}C_4H_5$ available. While #296 and #297 are strongly

exothermic, they also have large decreases in entropy, becoming less favored at higher temperatures. Furthermore, #297 has a net decrease in number of moles, causing it to be less favored at lower pressures.

Relatively high concentrations of C_3H_3 are also seen in flames, due to the resonance-enhanced stability of propargyl. In low-pressure acetylene [1], 1,3-butadiene (C_4H_6) [4], and benzene [18] flames, peak mole fractions of C_3H_3 near 10^{-3} were observed. Recombination of propargyl radical also has no barrier to forming a ring-containing C6 species, whether it be fulvene, benzene, or phenyl+H [2,5,19]; R3 can therefore become a direct aromatic ring formation route, especially at low pressures. However, reaction #412 has a crossover temperature (above which $\Delta G > 0$) of 1729 K, and is much less thermodynamically favored than #297, with a crossover temperature of 2218 K.

Other pathways to benzene have been proposed. Lindstedt and Skevis [20] consider $C_2H_3 + C_4H_4(CH_2CHCCH) \rightleftharpoons C_6H_6(\text{benzene}) + H$ and $C_2H_3 + C_4H_6(CH_2CHCHCH_2) \rightleftharpoons C_6H_8(1,4\text{-cyclohexadiene}) + H$, with the C_6H_8 decomposing to benzene and H_2 . Marinov et al. [14] propose a combination of two C_3 RSFRs, propargyl and allyl (#416). Moskaleva et al. [21] consider methyl+cyclopentadienyl (also a RSFR), forming methylcyclopentadiene, which forms fulvene, then benzene. Mebel et al. [17] calculate the potential energy surface of $C_6H_6(\text{benzene}) \rightleftharpoons C_5H_3 + CH_3$ reactions. The reverse reactions can also be possible benzene formation pathways (#522-527) from either of the two most stable forms of C_5H_3 , $H_2CCCCCH$ (here called i- C_5H_3) and $HCCCHCCH$ (n- C_5H_3). Walch [22]

calculates the potential energy surface of both #297 and the reaction of $i\text{-C}_4\text{H}_3$ with acetylene.

There are not infinitely many benzene formation reactions. Considering only bimolecular reactions, the two reactants should collectively contain precisely six carbon atoms and roughly six hydrogen atoms (for the above examples, five to nine hydrogen atoms). An ultimate goal would be to determine which of the conceivable benzene formation pathways are important. The answer would be complex, probably depending on the fuel and on the reactor conditions, even for the rather restricted case of low-pressure premixed flames of aliphatic fuels.

APPROACH

To assess the possible importance of various benzene formation pathways, we performed a modeling study on three sets of flame data. The flames selected are all fuel-rich low-pressure premixed laminar flat flames with an unsaturated C_2 or C_3 hydrocarbon as a fuel (C_2H_2 -- flame F1 [23], C_2H_4 -- F2 [24], C_3H_6 propene -- F3 [25]), with measured temperature profiles and species concentration profiles (including benzene) measured by molecular beam mass spectrometry (MBMS). See Table 2 for flame properties. Modeling calculations employed the CHEMKIN programs [26-30]. Full multicomponent diffusion, including thermal diffusion, was calculated. The catalytic boundary condition for H-atom recombination at the burner surface was also included. Experimental temperature profiles were used as input, in lieu of solving the energy equation.

Three different chemical kinetics mechanisms were tested. The first (M1) is the mechanism of Pauwels et al. [6], derived from Miller and Melius [5], plus 47 reactions describing the chemistry of propene and of the three C₃H₅ isomers, from Marinov et al. [11,12], which allows modeling of the propene flame (F3). The second mechanism (M2) is from Richter et al. [16], based on Zhang and McKinnon [31], with extensive PAH formation chemistry at low-pressure (20 Torr). To afford a more complete comparison, the reaction ${}^1\text{CH}_2 + \text{C}_2\text{H}_2 \rightleftharpoons \text{H}_2\text{CCCH} + \text{H}$ was added to M2. The third mechanism (M3) is from Marinov et al. [11,12,14]. M3 builds on the Miller and Melius [5] chemistry by including additional reactions of RSFRs and PAH formation reactions at atmospheric-pressure. While many other chemical kinetics mechanisms are available in the literature, the three chosen here provide a reasonable basis for comparison, showing areas in which M1 can be improved.

MODELING RESULTS

All three mechanisms do well at predicting the decay of fuel and O₂ in the three flames. Table 3 lists the experimental and the predicted peak mole fractions for the three flames. The predictions also include those from an extensively modified and expanded version of M1, called M1a. The key changes made in forming M1a, and the modeling results using M1a, are discussed below.

All three mechanisms predict both the peak concentration and the shape of the C₂H₂ profiles quite well in all three flames. M3 over-predicts peak C₆H₆ mole fractions for all three flames. Many of the pressure-dependent reactions in M3 have rate coefficients that are fit for atmospheric pressure, so M3 over-predicts molecular-weight

growth in such reactions as $C_2H_3 + CH_3 \rightleftharpoons C_3H_6$, hence the over-prediction of C_3H_6 in F2, C_4H_8 in F2 and F3, and C_4H_3 and C_4H_5 in all three flames. However, C_6H_5 concentrations are under-predicted.

Peak C_6H_6 mole fraction predictions from M2 are within 25% for F1, a factor of 10 low for F2, and roughly 100 times too low for F3. M2 does not include the propargyl recombination reaction (R3), which most likely explains the C_6H_6 shortfall and C_3H_3 over-prediction for the three flames. In F1, formation of C_6H_6 is by $C_3H_3 + C_3H_4(\text{allene}) \rightleftharpoons C_6H_6 + H$, yet C_3H_4 is also over-predicted.

The predicted peak C_6H_6 mole fractions using M1 range from 30% to 50% of the data. Peak C_3H_3 is roughly 2.5 times the data for F1, 1.6 times for F2, and 1.3 times for F3, although for F1 and F2 the M1 predictions come closest to the data. Peak C_4H_3 mole fractions are higher than the data for all 3 flames. Predicted C_4H_5 peaks are 30 times low for F1, 8 times high for F2, and 15% low for F3. C_6H_5 predictions are roughly 8 times low for F2, and 40% high for F3, following the same trend as the M2 predictions.

EXPANDED BENZENE FORMATION CHEMISTRY

Building on the mechanism M1 [5,6], a significantly expanded mechanism (M1a) was created, containing 91 species and 527 reactions.* Beyond the C_3H_5 and C_3H_6 species and reactions, two other large additions were made using reactions from either M2 [16] or M3 [11,12]. The chemistry of the five new C_5 species (C_5H_5O , C_5H_6 , linear C_5H_5 , C_5H_4O , and C_5H_4OH) was added, making the benzene oxidation chemistry more complete. The chemistry of seventeen species from C_6H_7 (cyclohexadienyl) to $C_{10}H_8$

* The mechanism is available by contacting the authors at cjpope@sandia.gov or jamille@ca.sandia.gov.

(naphthalene) was added from M2, since M2 was developed to model a 20-Torr flame, although many of the reactions were contained in both M2 and M3.

In addition to the sweeping changes mentioned above, several individual reactions were added, and several of the rate coefficients for reactions already included were modified. Rate coefficients for reactions #296 and #297 are from Wang and Frenklach [10]. As an upper bound for these rates, the 20 Torr fits for #297 of all four product channels [10] were summed and used as the rate for $C_2H_2+n-C_4H_3(HCCHCCH) \rightleftharpoons C_6H_5(\text{phenyl})$. Similarly, the sum of the four product channels for #296 for 0-90 Torr [10] is for the product channel $C_6H_6(\text{benzene})+H$. The resulting sums for #296 and #297 were fit into the 3-parameter Arrhenius form. The barrier height used [10] for #297 was 3.1 kcal/mol; the barrier calculated by Walch [22] is 8.3 kcal/mol, close to the AM1 barrier height [10]. Accordingly, the activation energy for #297 fitted above was increased by 5.2 kcal/mol. The newly fitted activation energy for #296 was increased by the same amount. The rate for $C_6H_5+C_2H_2 \rightleftharpoons C_6H_5C_2H+H$ is taken from Yu *et al.* [15], by fitting the sum of the rates for all product channels.

The overall rate for $C_2H_3+C_2H_3$ was changed to $9.0 \times 10^{13} \text{ cm}^3/\text{mol-s}$ [7,8]. Consistent with the observation of a $C_3H_3+CH_3$ product channel [9], the branching ratio was set to 10% $i-C_4H_5+H$, 20% $C_3H_3+CH_3$, 70% $C_2H_2+C_2H_4$. Rates for $C_2H_3+CH_3 \rightleftharpoons C_3H_6$ or C_3H_5+H are from Tsang and Hampson's [13] 20 Torr results. C_3H chemistry (#406-408) was added, with thermochemical properties from Guadagnini *et al.* [32]. Allyl-propargyl recombination (#416) in M3 forms much of the benzene in F2 and F3, so this reaction is added, although the authors [14] give the rate coefficient as an

upper bound at 1 atm. Also added are two reactions for converting fulvene into benzene (#415,#418). (See Table 1 for reactions and rate coefficients.)

RADICAL-RADICAL RECOMBINATION REACTIONS FOR C₆H₆ FORMATION

Several chemically activated radical-radical combinations are proposed as possible benzene-forming reactions in M1a (#506-527). For propargyl-propargyl recombination, not only the initial adduct but also several of the rearrangement products/intermediates are aliphatic C₆H₆ species [2,5,19]; many other radical-radical combinations can lead to the same aliphatic C₆H₆ species. Both n-C₄H₃+C₂H₃ and n-C₄H₅+C₂H can combine to form CH₂CHCHCHCCH. CH₃CHCCHCCH, formed by n-C₅H₃+CH₃, which can undergo a hydrogen shift to form CH₂CHCHCHCCH. Combination of i-C₄H₃+C₂H₃ or i-C₄H₅+C₂H can form CH₂C(CCH)CHCH₂. i-C₄H₅+C₂H also forms CH₂CCHCH₂CCH, which also directly forms from C₃H₃+C₃H₃. CH₃CHCCCCCH₂ from i-C₅H₃+CH₃ can undergo a hydrogen shift to form CH₂CCCHCHCH₂. CH₂CCCHCHCH₂ is also a product of i-C₄H₃+C₂H₃, converting via a hydrogen shift to CH₂CCHCHCCH₂, another direct propargyl-propargyl recombination product. Once any of these aliphatic C₆H₆ adducts is formed, the chemistry leading to either fulvene, benzene, or phenyl+H is described by Miller and co-workers [2,5,19]. The overall rate for adduct formation and subsequent reaction for each of these new reactions is estimated to be 2×10^{13} cm³/mol-s. H-abstraction reactions from these pairs of radicals are also included in the new mechanism, as are reactions interrelating C₅H₂, i-C₅H₃, and n-C₅H₃ (#409-411).

All of these new reactions are written in the exothermic direction. Standard heats of formation for the above C_6H_6 species and combinations of molecules with combined empirical formula of C_6H_6 are given in Table 4. The heat of formation used for propargyl radical is 86.0 kcal/mol [33,34], and the standard entropy is 59.9 cal/mol-K [34]; the earlier values used were 83.0 kcal/mol and 61.4 cal/mol-K. The less stable propargyl radical results in slightly lower predicted C_3H_3 mole fractions, and therefore a slightly diminished role of $C_3H_3+C_3H_3$ in benzene formation. Predicted peak mole fractions of C_4H_3 and C_4H_5 also increase by at least a factor of 3 in all three flames. The total rate for the propargyl+propargyl reaction is kept at 1×10^{13} cm³/mol-s; measured values are 2.4-7.2 $\times 10^{13}$ cm³/mol-s [35-38]. Master equation calculations [39] show that at conditions of the flames considered here benzene is not formed directly. Accordingly, the branching ratio used has the products being split nearly evenly between fulvene and phenyl+H, with $i-C_5H_3+CH_3$ being a minor pathway since it is slightly exothermic (#412-414). (Not enough confidence was placed in the 2.1 kcal/mol exothermicity of the $n-C_5H_3+CH_3$ product channel to believe that it would be significant.)

DISCUSSION OF RESULTS FROM IMPROVED MECHANISM

Predictions using M1 and M1a are compared against data in Figure 1 for C_6H_6 . Benzene is the only C_6H_6 species in M1, while M1a also includes fulvene. For F1 (Fig. 1a), M1a greatly improves C_6H_6 predictions. Little fulvene is predicted. An improvement is also seen for F2 (Fig. 1b), with an appreciable amount of fulvene predicted early in the flame. M1a overpredicts C_6H_6 concentrations in F3 (Fig. 1c), with fulvene being dominant early in the flame.

The major reaction pathways leading to phenyl, fulvene, and benzene are shown in Figure 2. For all three flames, the propargyl-propargyl reaction (#412-414) plays a major role. The propargyl-allyl reaction (#416) contributes a moderate amount in F2, and forms most of the benzene in F3; in F1, this reaction actually is a major fulvene decomposition pathway. Use of the 1-atm rate coefficient for this reaction is most likely responsible for the over-prediction of C_6H_6 in F3. The $C_2H_2+n-C_4H_3$ reaction (#297) is almost entirely a phenyl decomposition pathway in F2 and F3; in F1 there is a slight amount of phenyl production followed by phenyl decomposition, but the reaction is of negligible importance. The $C_2H_2+n-C_4H_5$ reaction (#296) has no discernible effect for any of the flames studied.

Of the new radical-radical reactions added (#506-527), only the $i-C_5H_3+CH_3$ reaction appears as a substantial formation reaction (with a minor contribution from $n-C_5H_3+CH_3$), and then only in F1. The relation of the C_5H_2 and C_5H_3 species with the polyacetylene pool (reactions #267, 309-311, 409-411) leads to more of these species being formed in F1 (q.v. Table 3). Unfortunately, there are no data for testing these predicted concentrations. For F2 and F3, the major role of the $i-C_5H_3+CH_3$ reactions appears to be as another pathway for converting fulvene to benzene. Whether this indeed happens in reality is questionable; however, further investigation of the possible role of these C_5H_3 species is indicated. The only other new reactions appearing in Fig. 2 involve $i-C_4H_3+C_2H_3$ (#513,#514) as decomposition products of either fulvene or phenyl+H.

No C_2+C_4 reaction in the mechanism is predicted to lead to benzene formation in any of these flames -- only reactions involving C_3 radicals are important. Figure 3 shows the major predicted pathways for C_3 radical formation from the fuel for the three flames.

For F3, the main source of C_3H_3 and C_3H_5 radicals is by successive H-abstractions from the fuel. While ${}^1CH_2 + C_2H_2 \rightleftharpoons H_2CCCH + H$ and the reactions leading to it are the dominant source of C_3 radicals in F1 and F2, it appears as a secondary pathway in F3, with the fuel decomposing to ethylene or vinyl radical, forming acetylene by H-abstraction. In F2, C_2H_4 and C_2H_3 combine with C_1 radicals to form allyl radical. In F1, the fuel combines with methyl radical to give propyne+H, with the propyne then forming propargyl.

Therefore, for the low-pressure flames studied here, only combinations of C_3 radicals lead to production of benzene or phenyl. However, it is conceivable that there would be fuels or flame conditions that would favor the $C_2 + C_4$ pathways. For example, $C_2H_2 + n-C_4H_3 \rightleftharpoons C_6H_5$ (#297) is the only one of the important molecular-weight growth reactions involving phenyl (#297, 412, 417, 483, 487, 501, 507, 514, 523, 526) to have a net mole change. The rates of bimolecular reactions, expressed as mol C_6H_5 /g gas/sec (the molar rate divided by the gas density), would increase linearly with pressure, while those of unimolecular rates would remain constant, all else being equal. The relative importance of #297 to the other molecular-weight growth reactions at higher pressures can then be approximated by looking only at the forward rate of #297. However, the peak forward rate of #297 is 2.4% of the peak of the sum of the net rates of all the other molecular-weight growth reactions for F1, and less than 1% for F2 and F3. Therefore, increased pressure alone would decrease the importance of #297 as a phenyl decomposition channel, but would not make #297 an important phenyl production route. This is more noteworthy since C_4H_3 is overpredicted in all three flames, and since the $n-C_4H_3/i-C_4H_3$ and $n-C_4H_5/i-C_4H_5$ ratios are at least an order of magnitude above

partial equilibrium for all positions in all three flames. Secondary effects of pressure, such as increasing the rates of C_4 -radical forming reactions, cannot be ruled out.

In summary, for the three flames considered, the only major formation pathways for benzene or phenyl are the result of combination of C_3 radicals. The $C_2H_2+C_4$ radical pathways were tested thoroughly and found to be at best unimportant in single-ring aromatic formation. The relative importance of different benzene/phenyl/fulvene reaction pathways is fuel-dependent, as are the major pathways for formation of the C_3 radicals. No claims to generality can be made for other fuels, flow systems, or pressures. However, in modeling of low-pressure C_2H_2 flames [40] and atmospheric-pressure C_2H_4 flames [40-42], recombination of propargyl radical was found to be an important contributor to benzene formation.

The new pathways proposed to C_6H_6 are pertinent to the overall role of RSFRs in benzene formation, since the aliphatic C_6H_6 adducts formed are the same as for the $C_3H_3+C_3H_3$ reaction. The $C_5H_3+CH_3$ reactions played a role in the predicted benzene/phenyl formation chemistry, perhaps due to their only being ~32-38 kcal/mol higher in energy than phenyl+H. However, due to concentration effects and net increase in number of moles, even the $C_2H_2+i-C_4H_3$ channel, being 50.8 kcal/mol higher in energy than phenyl+H, is a phenyl decomposition channel in F1. There is a need for clarity as to the actual rates and branching ratios of these unsaturated radical-radical combinations which can undergo multiple rearrangements, especially considering some of the possible new pathways presented here.

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Table 1. Rate coefficients for reactions which are discussed in the text and in subsequent figures, and which are used in the expanded mechanism called M1a later in the text. Units are cm^3 , mol, s, kcal. pw=present work.

number	reaction	A	b	E	reference
132	$\text{C}_2\text{H}_4 + \text{H} = \text{C}_2\text{H}_3 + \text{H}_2$	$5.42\text{E}+14$	0.0	14902.0	[5,6]
154	$\text{C}_2\text{H}_2 + \text{O} = \text{HCCO} + \text{H}$	$1.43\text{E}+07$	2.0	1900.0	[5,6]
156	$\text{H} + \text{C}_2\text{H}_2(+\text{M}) = \text{C}_2\text{H}_3(+\text{M})$	$3.114\text{E}+11$	0.58	2589.0	[5,6]
	Low pressure limit:	$2.254\text{E}+40$	-7.269	6577.0	
	TROE centering:	$a = 0.5, T^{***} = 675.0, T^* = 675.$			
	Enhanced third body efficiencies:				
	$\text{H}_2 = 2.0, \text{CO} = 2.0, \text{CO}_2 = 3.0, \text{H}_2\text{O} = 5.0$				
157	$\text{C}_2\text{H}_3 + \text{H} = \text{C}_2\text{H}_2 + \text{H}_2$	$4.00\text{E}+13$	0.0	0.0	[5,6]
169	$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 = \text{CH}_2\text{CHCCCH}_2 + \text{H}$	$9.00\text{E}+12$	0.0	0.0	[7,8]
170	$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 = \text{H}_2\text{CCCH} + \text{CH}_3$	$1.80\text{E}+13$	0.0	0.0	[7-9]
171	$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 = \text{C}_2\text{H}_4 + \text{C}_2\text{H}_2$	$6.30\text{E}+13$	0.0	0.0	[7,8]
225	$\text{H} + \text{HCCO} = \text{CH}_2(\text{S}) + \text{CO}$	$1.00\text{E}+14$	0.0	0.0	[5,6]
240	$\text{CH}_2(\text{S}) + \text{H}_2 = \text{CH}_3 + \text{H}$	$7.00\text{E}+13$	0.0	0.0	[5,6]
243	$\text{CH}_2(\text{S}) + \text{C}_2\text{H}_2 = \text{H}_2\text{CCCH} + \text{H}$	$1.80\text{E}+14$	0.0	0.0	[5,6]
267	$\text{C}_3\text{H}_2 + \text{C}_2\text{H}_2 = \text{HCCCHCCH} + \text{H}$	$5.00\text{E}+12$	0.0	5000.0	[5,6]
274	$\text{H}_2\text{CCCH} + \text{H} = \text{C}_3\text{H}_2 + \text{H}_2$	$5.00\text{E}+13$	0.0	1000.0	[5,6]
275	$\text{H}_2\text{CCCH} + \text{OH} = \text{C}_3\text{H}_2 + \text{H}_2\text{O}$	$2.00\text{E}+13$	0.0	0.0	[5,6]
292	$\text{C}_6\text{H}_6 + \text{H} = \text{C}_6\text{H}_5 + \text{H}_2$	$3.00\text{E}+07$	2.0	8000.0	[5,6]
296	$\text{C}_2\text{H}_2 + \text{CH}_2\text{CHCHCH} = \text{C}_6\text{H}_6 + \text{H}$	$8.209\text{E}+08$	0.801	6348.0	[10],pw
297	$\text{HCCHCCH} + \text{C}_2\text{H}_2 = \text{C}_6\text{H}_5$	$1.667\text{E}+10$	0.446	7719.3	[10],pw
299	$\text{C}_3\text{H}_4 + \text{H} = \text{H}_2\text{CCCH} + \text{H}_2$	$3.00\text{E}+07$	2.0	5000.0	[5,6]
300	$\text{C}_3\text{H}_4 + \text{OH} = \text{H}_2\text{CCCH} + \text{H}_2\text{O}$	$2.00\text{E}+07$	2.0	1000.0	[5,6]
302	$\text{C}_3\text{H}_4\text{P} + \text{H} = \text{CH}_3 + \text{C}_2\text{H}_2$	$1.00\text{E}+14$	0.0	4000.0	[5,6]
306	$\text{C}_6\text{H}_5 + \text{O}_2 = \text{C}_6\text{H}_5\text{O} + \text{O}$	$2.60\text{E}+13$	0.0	6120.0	[5,6]
	Duplicate of 307				
307	$\text{C}_6\text{H}_5 + \text{O}_2 = \text{C}_6\text{H}_5\text{O} + \text{O}$	$3.00\text{E}+13$	0.0	8981.0	[5,6]
	Duplicate of 306				
308	$\text{C}_6\text{H}_5\text{O} = \text{C}_5\text{H}_5 + \text{CO}$	$7.40\text{E}+11$	0.0	43853.0	[5,6]
309	$\text{CH}_2 + \text{C}_4\text{H}_2 = \text{H}_2\text{CCCCCH} + \text{H}$	$1.30\text{E}+13$	0.0	4326.0	[5,6]
310	$\text{CH} + \text{C}_4\text{H}_2 = \text{C}_5\text{H}_2 + \text{H}$	$1.00\text{E}+14$	0.0	0.0	[5,6]
311	$\text{CH}_2(\text{S}) + \text{C}_4\text{H}_2 = \text{H}_2\text{CCCCCH} + \text{H}$	$3.00\text{E}+13$	0.0	0.0	[5,6]
315	$\text{C}_4\text{H} + \text{O}_2 = \text{CO} + \text{CO} + \text{C}_2\text{H}$	$1.20\text{E}+12$	0.0	0.0	pw

333	H+C6H5=C6H6	5.00E+13	0.0	0.0	[5,6]
337	CH2(S)+C2H4=CH2CHCH2+H	1.30E+14	0.0	0.0	[11,12]
338	C2H3+CH3=CH2CHCH2+H	2.861E+21	-2.118	11841.8	[13]
339	C2H3+CH3=C3H6	3.688E+30	-5.034	7691.9	[13]
353	C3H6+H=C2H4+CH3	7.23E+12	0.0	1302.0	[11,12]
368	CH2CHCH2+H=C3H4+H2	5.00E+13	0.0	0.0	[11,12]
369	CH2CHCH2+H=C3H6	1.88E+26	-3.6	5468.0	[11,12]
406	C3H2+H=C3H+H2	1.00E+13	0.0	0.0	pw
407	C3H+O2=HCCO+CO	1.00E+13	0.0	0.0	pw
408	C3H+O=C2H+CO	1.00E+13	0.0	0.0	pw
409	H2CCCCCH+H=C5H2+H2	1.00E+13	0.0	0.0	pw
410	HCCCHCCH+H=C5H2+H2	1.00E+13	0.0	0.0	pw
411	HCCCHCCH+H=H2CCCCCH+H	1.00E+13	0.0	0.0	pw
412	H2CCCH+H2CCCH=C6H5+H	5.00E+12	0.0	0.0	pw
413	H2CCCH+H2CCCH=FUL VENE	4.50E+12	0.0	0.0	pw
414	H2CCCH+H2CCCH=HCCCHCCH+CH3	5.00E+11	0.0	0.0	pw
415	FUL VENE=C6H6	7.586E+13	0.0	73853.0	[2]
416	H2CCCH+CH2CHCH2=FUL VENE+H+H	5.562E+20	-2.535	1692.0	[14]
417	C6H5+C2H2=C6H5C2H+H	2.469E+06	1.77	2289.0	[15]
418	FUL VENE+H=C6H6+H	3.00E+12	0.5	2000.0	[14]
483	C6H5+C4H2=C6H5C2H+C2H	2.00E+13	0.0	0.0	[16]
487	C6H5+CH3=C7H8	2.00E22	-3.045	2304.0	[16]
501	C6H5+CH3=C7H7+H	5.00E+13	0.0	0.0	[16]
506	HCCHCCH+C2H3=FUL VENE	4.00E+12	0.0	0.0	pw
507	HCCHCCH+C2H3=C6H5+H	1.60E+13	0.0	0.0	pw
508	HCCHCCH+C2H3=C4H2+C2H4	1.00E+12	0.0	5000.0	pw
509	HCCHCCH+C2H3=CH2CHCCH+C2H2	2.00E+12	0.0	5000.0	pw
510	CH2CHCHCH+C2H=FUL VENE	4.00E+12	0.0	0.0	pw
511	CH2CHCHCH+C2H=C6H5+H	1.60E+13	0.0	0.0	pw
512	CH2CHCHCH+C2H=CH2CHCCH+C2H2	3.00E+12	0.0	5000.0	pw
513	H2CCCCH+C2H3=FUL VENE	1.00E+13	0.0	0.0	pw
514	H2CCCCH+C2H3=C6H5+H	6.00E+12	0.0	0.0	pw
515	H2CCCCH+C2H3=2H2CCCH	4.00E+12	0.0	0.0	pw
516	H2CCCCH+C2H3=C4H2+C2H4	1.00E+12	0.0	5000.0	pw
517	H2CCCCH+C2H3=CH2CHCCH+C2H2	2.00E+12	0.0	5000.0	pw
518	CH2CHCCH2+C2H=FUL VENE	1.00E+13	0.0	0.0	pw
519	CH2CHCCH2+C2H=C6H5+H	6.00E+12	0.0	0.0	pw

520	<chem>CH2CHCCH2+C2H=2H2CCCH</chem>	4.00E+12	0.0	0.0	pw
521	<chem>CH2CHCCH2+C2H=CH2CHCCH+C2H2</chem>	3.00E+12	0.0	5000.0	pw
522	<chem>H2CCCCCH+CH3=FULVENE</chem>	1.40E+13	0.0	0.0	[17],pw
523	<chem>H2CCCCCH+CH3=C6H5+H</chem>	6.00E+12	0.0	0.0	[17],pw
524	<chem>H2CCCCCH+CH3=C5H2+CH4</chem>	3.00E+12	0.0	5000.0	pw
525	<chem>HCCCHCCH+CH3=FULVENE</chem>	1.00E+13	0.0	0.0	[17],pw
526	<chem>HCCCHCCH+CH3=C6H5+H</chem>	1.00E+13	0.0	0.0	[17],pw
527	<chem>HCCCHCCH+CH3=C5H2+CH4</chem>	3.00E+12	0.0	5000.0	pw

Table 2. Key properties of flames used in the present study. For all flames, O₂ is the oxidant and Ar is the diluent.

#	fuel	inlet equivalence ratio, C/O ratio	inlet mol% Ar	pressure (Torr)	mass flow rate (g/cm ² -s)	maximum Temperature (K)	reference
F1	C ₂ H ₂	2.50,1.000	45%	20.0	3.55E-03	1866	[23]
F2	C ₂ H ₄	1.90,0.633	50%	20.0	2.37E-03	2208	[24]
F3	C ₃ H ₆	2.32,0.772	25%	37.5	3.12E-03	2300	[25]

Table 3. Predicted peak mole fractions, for mechanisms, M1, M1a, M2, M3: a) flame F1, b) flame F2, c) flame F3. Modeling results for many species are sums of predicted concentrations of more than one isomer. "xxx" means that no such species is present in that mechanism or that no data are available.

a) C₂H₂ flame -- F1

species	M1	M1a	M2	M3	data
H	8.36E-03	7.98E-03	6.26E-03	7.35E-03	1.79E-02
H2	1.15E-01	9.67E-02	6.58E-02	1.05E-01	1.59E-01
CH3	1.13E-03	1.31E-03	1.66E-03	2.08E-03	1.63E-03
CH4	7.58E-04	7.25E-04	1.20E-03	1.14E-03	1.40E-03
OH	9.98E-04	1.25E-03	1.94E-03	1.08E-03	4.94E-04
H2O	8.65E-02	9.98E-02	1.23E-01	9.14E-02	8.07E-02
C2H	7.51E-05	7.02E-05	3.96E-05	2.87E-05	6.36E-05
C2H3	4.78E-05	4.73E-05	1.74E-05	6.66E-05	3.77E-05
C2H4	1.14E-03	4.04E-04	5.34E-04	1.38E-03	2.99E-04
CO	3.36E-01	3.19E-01	2.85E-01	3.27E-01	3.61E-01
HO2	4.81E-04	5.49E-04	6.35E-05	3.76E-04	1.93E-04
C3H3	5.63E-04	5.30E-04	1.29E-02	1.89E-03	2.24E-04
C3H4	9.65E-05	5.21E-05	2.63E-03	2.35E-04	5.49E-04
CO2	3.28E-02	3.76E-02	5.03E-02	3.69E-02	3.29E-02
C4H2	1.99E-03	2.92E-03	1.21E-02	7.12E-03	4.57E-03
C4H3	9.45E-05	9.21E-05	3.51E-04	1.02E-04	8.76E-06
C4H4	1.24E-04	1.00E-04	8.57E-04	2.58E-04	2.49E-04
C4H5	1.04E-06	5.84E-06	1.60E-06	6.94E-05	3.13E-05
C5H2	4.37E-05	1.79E-05	5.58E-04	2.28E-04	xxx
C5H3	5.06E-04	2.36E-03	1.94E-03	1.11E-03	xxx
C6H5	2.24E-06	2.71E-06	5.23E-07	1.44E-05	xxx
C6H6	2.31E-05	4.93E-05	4.35E-05	7.27E-04	5.87E-05

b) C₂H₄ flame -- F2

species	M1	M1a	M2	M3	data
H	6.67E-03	6.23E-03	9.82E-03	4.06E-03	1.10E-02
H2	1.48E-01	1.44E-01	1.47E-01	1.33E-01	1.41E-01
CH2	1.53E-04	1.78E-04	2.97E-04	2.12E-04	6.31E-05
CH3	1.46E-03	1.96E-03	3.01E-03	2.31E-03	3.36E-03
CH4	3.19E-03	4.76E-03	5.74E-03	5.38E-03	4.45E-03
OH	1.18E-03	1.19E-03	1.93E-03	8.87E-04	2.17E-03
H2O	1.71E-01	1.75E-01	1.79E-01	1.78E-01	1.64E-01
C2H	2.89E-05	3.12E-05	1.62E-05	1.03E-05	4.99E-05
C2H2	2.91E-02	3.01E-02	2.56E-02	3.68E-02	3.33E-02
C2H3	1.08E-03	9.05E-04	4.55E-04	3.85E-04	6.74E-05

CO	2.44E-01	2.42E-01	2.42E-01	2.31E-01	2.49E-01
C2H5	1.44E-04	1.25E-04	3.62E-04	9.87E-05	1.07E-03
CH2O	6.16E-03	5.88E-03	5.26E-03	1.64E-03	4.32E-03
C3H2	4.59E-04	2.82E-04	1.04E-04	7.44E-05	2.25E-04
C3H3	6.77E-04	4.96E-04	2.82E-03	1.01E-03	4.26E-04
C3H4	7.21E-04	5.51E-04	2.40E-04	6.32E-04	7.32E-04
C3H5	6.70E-04	4.84E-04	3.24E-04	1.31E-03	6.80E-05
C3H6	6.96E-04	5.96E-04	1.80E-03	5.00E-03	8.40E-04
CH2CHO	1.10E-04	1.01E-04	xxx	1.32E-05	3.49E-04
CH3CHO	4.83E-05	4.66E-05	xxx	8.18E-05	3.51E-04
CO2	4.56E-02	4.72E-02	4.63E-02	5.05E-02	5.18E-02
C4H2	4.92E-04	8.66E-04	1.70E-03	2.28E-03	2.52E-03
C4H3	1.23E-04	1.40E-04	6.84E-05	9.85E-05	6.70E-06
C4H4	2.92E-04	3.36E-04	1.71E-04	3.56E-04	1.69E-04
C4H5	2.42E-05	8.96E-05	2.79E-05	3.18E-04	2.90E-06
C4H6	9.83E-05	1.02E-04	1.70E-06	9.75E-05	4.63E-05
C4H7	xxx	xxx	xxx	1.27E-06	2.03E-06
C4H8	xxx	xxx	xxx	5.31E-04	7.99E-05
C5H2	6.01E-06	4.80E-06	6.08E-05	3.22E-05	xxx
C5H3	1.23E-04	2.78E-04	1.76E-04	2.34E-04	xxx
C5H6	xxx	3.27E-06	1.28E-06	8.58E-06	1.37E-05
C5H7	xxx	xxx	xxx	1.91E-08	5.45E-06
C5H8	xxx	xxx	xxx	1.90E-07	7.98E-06
C6H2	9.11E-06	1.62E-05	2.22E-05	6.77E-05	2.40E-04
C6H4	6.80E-05	8.11E-05	3.35E-07	xxx	1.78E-05
C6H5	2.08E-06	2.16E-06	3.92E-07	1.62E-06	1.70E-05
C6H6	9.84E-06	2.14E-05	3.54E-06	1.18E-04	3.33E-05

c) C₃H₆ flame -- F3

species	M1	M1a	M2	M3	data
H2	2.75E-01	2.94E-01	2.91E-01	2.76E-01	2.60E-01
CH2	1.92E-04	2.02E-04	8.61E-04	2.58E-04	8.90E-04
CH3	4.50E-03	4.64E-03	6.23E-03	7.89E-03	1.01E-02
CH4	1.80E-02	2.01E-02	3.05E-03	2.63E-02	3.10E-02
CO	3.65E-01	3.79E-01	3.78E-01	3.70E-01	4.00E-01
HCO	1.01E-04	9.44E-05	7.26E-05	9.06E-05	1.50E-04
CH2O	4.33E-03	4.00E-03	3.55E-04	1.45E-03	6.90E-04
OH	1.21E-03	9.69E-04	2.42E-03	7.48E-04	5.50E-03
H2O	1.93E-01	1.81E-01	2.41E-01	1.83E-01	1.64E-01
C2H2	3.29E-02	4.62E-02	5.22E-02	5.79E-02	3.69E-02
C2H3	6.70E-04	6.05E-04	2.45E-04	3.01E-04	2.48E-03
C2H4	1.17E-02	1.26E-02	6.30E-03	1.32E-02	3.42E-02
C2H5	4.66E-05	4.18E-05	1.29E-05	1.05E-05	3.30E-05
C2H6	8.80E-04	8.34E-04	2.11E-04	1.70E-03	1.80E-03

C2H2O	1.20E-03	2.35E-03	3.27E-04	5.02E-03	7.50E-04
CO2	3.86E-02	3.44E-02	4.48E-02	3.92E-02	2.14E-02
C3H2	1.37E-03	8.36E-04	1.60E-04	2.66E-04	1.90E-04
C3H3	3.95E-03	2.46E-03	7.77E-03	2.88E-03	3.09E-03
C3H4	1.46E-02	1.64E-02	1.93E-03	1.03E-02	1.01E-02
C3H5	1.10E-02	1.22E-02	3.69E-03	1.08E-02	3.50E-03
C3H7	xxx	xxx	xxx	1.06E-05	3.90E-04
C3H4O	xxx	xxx	xxx	4.12E-03	3.50E-05
C4H2	1.19E-03	2.92E-03	4.75E-03	4.47E-03	5.92E-03
C4H3	6.54E-04	9.84E-04	2.78E-04	3.70E-04	1.55E-04
C4H4	1.30E-03	1.36E-03	3.51E-04	9.36E-04	1.43E-03
C4H5	1.01E-04	5.63E-04	1.04E-06	1.56E-03	1.20E-04
C4H6	1.84E-05	2.23E-04	6.74E-06	9.43E-04	1.00E-03
C4H7	xxx	xxx	xxx	1.98E-05	1.30E-04
C4H8	xxx	xxx	xxx	2.88E-03	1.13E-03
C4H10	xxx	xxx	xxx	2.03E-05	4.50E-04
C5H2	1.00E-05	6.33E-05	2.79E-04	2.83E-05	xxx
C5H3	3.00E-04	6.66E-04	6.09E-04	3.63E-04	xxx
C5H5	1.13E-02	1.42E-03	1.02E-06	1.63E-04	2.50E-04
C5H6	xxx	3.53E-04	2.08E-06	1.87E-04	6.60E-04
C5H7	xxx	xxx	xxx	1.12E-07	1.50E-04
C5H8	xxx	xxx	xxx	7.13E-07	2.10E-04
C6H2	2.47E-05	6.62E-05	7.90E-05	1.08E-04	1.50E-03
C6H4	1.70E-03	1.22E-03	1.90E-06	1.00E-88	2.12E-04
C6H5	1.06E-04	7.77E-05	1.31E-07	2.86E-05	7.43E-05
C6H6	6.23E-04	2.93E-03	1.08E-05	3.22E-03	1.22E-03
C6H7	xxx	3.35E-08	9.64E-09	8.34E-08	2.02E-04
C6H8	xxx	1.54E-08	1.97E-06	5.40E-05	1.82E-04
C6H5O	2.16E-04	7.54E-05	1.47E-07	7.50E-06	2.10E-05
C6H6O	xxx	5.90E-07	2.71E-06	3.89E-05	3.00E-05
C7H7	xxx	5.71E-05	2.56E-08	1.08E-05	5.20E-05
C7H8	xxx	1.09E-04	6.05E-08	4.18E-05	6.00E-05
C8H6	1.47E-05	1.35E-05	7.31E-07	1.33E-05	5.30E-05
C9H8	xxx	4.22E-05	8.78E-09	4.30E-07	2.00E-05
C10H8	xxx	4.92E-05	3.90E-09	4.28E-06	1.30E-05

Table 4. Standard heats of formation (in kcal/mol) of C_6H_6 species and selected combinations of molecules with combined empirical formula of C_6H_6 . Thermodynamic properties are from Miller and Melius [5] and Kee *et al.* [30] unless otherwise noted.

molecule(s)	ΔH_f° (298 K)
n- $C_4H_5 + C_2H$	218.7
i- $C_4H_5 + C_2H$	206.3
o-benzyne+2H	205.8
n- $C_4H_3 + C_2H_3$	201.0
i- $C_4H_3 + C_2H_3$	182.3
$C_3H_3 + C_3H_3$	172.0 [33,34]
n- $C_5H_3 + CH_3$	169.9
i- $C_5H_3 + CH_3$	163.1
$C_5H_2 + CH_4$	147.3
phenyl+H	131.5
$C_4H_2 + C_2H_4$	123.8
$CH_2CHCCH + C_2H_2$	123.3
$HCCCH_2CHCCH_2$	104.3
$CH_3CHCCHCCH$	99.7
$CH_2CCHCHCCH_2$	96.5
$CH_3CHCCCCH_2$	93.2 [17]
$CH_2CCCHCHCH_2$	85.6 [17]
$CH_2C(CCH)CHCH_2$	82.4
$CH_2CHCHCHCCH$	80.0
fulvene	52.5
benzene	19.8

Figure Captions

Figure 1. Predictions of C_6H_6 species from mechanisms M1 and M1a compared with data: a) C_2H_2 flame (F1), b) C_2H_4 flame (F2), c) C_3H_6 flame (F3). Circles, data; dashed line, benzene from M1; open squares, benzene from M1a; open triangles, fulvene from M1a; solid line, total C_6H_6 from M1a.

Figure 2. Predicted major reaction pathways involving phenyl, benzene, and fulvene for the three flames from mechanism M1a. Notations such as #297 mean that the arrow indicates the reaction so numbered in Table 3. See text for discussion.

Figure 3. Predicted primary and secondary formation pathways of C_3 radicals for the three flames from mechanism M1a. Notations such as #297 mean that the arrow indicates the reaction so numbered in Table 3. See text for discussion.

Fig. 1a

Fig. 1b

Fig. 1c

F.g. 3