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A PAH growth mechanism and synergistic effect on PAH formation in counterflow diffusion flames

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ABSTRACT

A reaction mechanism having molecular growth up to benzene for hydrocarbon fuels with up to four carbon-atoms was extended to include the formation and growth of polycyclic aromatic hydrocarbons (PAHs) up to coronene ($C_{24}H_{12}$). The new mechanism was tested for ethylene premixed flames at low (20 torr) and atmospheric pressures by comparing experimentally observed species concentrations with those of the computed ones for small chemical species and PAHs. As compared to several existing mechanisms in the literature, the newly developed mechanism showed an appreciable improvement in the predicted profiles of PAHs. The new mechanism was also used to simulate PAH formation in counterflow diffusion flames of ethylene to study the effects of mixing propane and benzene in the fuel stream. In the ethylene–propane flames, existing experimental results showed a synergistic effect in PAH concentrations, i.e. PAH concentrations first increased and then decreased with increasing propane mixing. This PAH behavior was successfully captured by the new mechanism. The synergistic effect was predicted to be more pronounced for larger PAH molecules as compared to the smaller ones, which is in agreement with experimental observations. In the experimental study in which the fuel stream of ethylene–propane flames was doped with benzene, a synergistic effect was mitigated for benzene, but was observed for large PAHs. This effect was also predicted in the computed PAH profiles for these flames. To explain these responses of PAHs in the flames of mixture fuels, a pathway analysis has been conducted, which show that several resonantly stabilized species as well as C_4H_4 and H atom contribute to the enhanced synergistic behaviors of larger PAHs as compared to the small ones in the flames of mixture fuels.

1. Introduction

Combustion generated polycyclic aromatic hydrocarbons (PAHs) and soot have been studied extensively because of their adverse health and environmental effects [1,2]. Especially, gaseous hydrocarbon fuels with up to four carbon-atoms (hereafter referred to as C_1–C_4 fuels) such as ethylene and propane have been studied in various flame configurations to understand the physical and chemical processes involved in PAHs and soot formation [3–7]. Detailed profiles for both major and minor species have been reported.

Appreciable effort has been devoted to developing and testing reaction mechanisms that can reliably predict the concentration of PAH molecules (which are used as soot precursors in soot models [1]). Frenklach and coworkers have proposed hydrogen-abstraction-acetylene-addition (HACA) mechanism for PAH growth [8–12]. Apart from acetylene, other species such as propargyl, allyl, cyclopentadienyl and indenyl have also been considered as contributors to PAH growth [13–23], mostly focusing on the role of resonantly stabilized radicals. The roles of phenyl addition/cyclization [24] and methyl addition/cyclization [25] have also been identified. The growth of large PAHs through coagulation has been modeled [26] where a detailed mechanism is used to describe the formation of aromatic species up to three rings [27] and coagulation takes place to form larger PAHs.

The PAH chemistry has also been developed and validated in [28–34]. In particular, PAH reactions channels present in the literature has been reviewed and further refined for C1 and C2 fuels for PAH growth up to five-ring aromatic species [32].

Such chemical mechanisms in predicting PAH formation has been tested for various flame configurations such as premixed flames [32,35–37], co-flow non-premixed [38–42] and counterflow non-premixed flames [33,43–47]. These mechanisms are typically limited to relatively small PAHs with up to four or five rings and were tested mainly for single component fuels.

Considering that larger PAHs are more likely to incept soot particles, a detailed description of their formation is important. Given that practical fuels typically include large number of hydrocarbons,

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it is important that a kinetic mechanism could be applicable to fuel mixtures. In this regard, a number of experiments have been conducted in counterflow diffusion flames (CDFs) of ethylene mixed with various hydrocarbons (binary component fuels), oxygen partial premixing, and oxygenated fuels [48–55] to study fuel structure effect on the formation and growth pathways of PAHs and soot.

Chemical cross-linking effects between binary component fuels observed in some of these flames have helped us achieve a clearer understanding about the underlying reaction channels. For instance, in the CDF with ethylene/propane mixtures, laser-induced fluorescence (LIF) and laser-induced incandescence (LII) techniques were used to measure relative PAHs and soot concentrations [48]. An enhancement in the productions of PAHs and soot as compared to the cases with individual fuel components was observed, revealing a synergistic effect. The synergistic effect was found to be more pronounced for larger PAHs as compared to small ones. This behavior has been explained based on the roles of: (a) C_2 species in PAH and soot growth through hydrogen-abstraction-C_2H_2-addition (HACA) mechanism, (b) methylene from methyl radicals in forming propargyl through reactions with C_2 species, and (c) propargyls producing incipient rings that can grow to form large PAHs.

Chemical reaction mechanisms developed for multi-component or surrogate fuels should be able to predict the above mentioned synergistic effects. However, computational simulations on such synergism were frequently limited to small aromatic species such as benzene because of the limitations in reliable reaction channels to large PAHs in many existing kinetic mechanisms. To the authors' knowledge, such synergistic effect, being more pronounced for larger PAHs as observed in [48], has never been tested through simulations.

A mechanism for gasoline surrogate fuels (referred to as KAUST PAH Mech 1 or KM1) [56] was developed from the base mechanism [57] to account for the growth of PAHs up to coronene ($C_{24}H_{12}$). KM1 has markedly improved the prediction of PAH concentrations as compared to the base mechanism. The base mechanism, however, was developed mainly for large hydrocarbon fuels. As such, sub-mechanisms for fuels with small hydrocarbons were simplified. This could lead to unsatisfactory predictions of the concentrations of small hydrocarbon species, some of which have been previously shown to be important for their synergistic effects [48,51]. Thus, KM1 may not be suitable in simulating flames of small hydrocarbon fuels to predict the behaviors of PAHs. It is therefore, useful to develop a kinetic mechanism for small hydrocarbon fuels that includes extended PAH chemistry containing PAHs with a wide mass range.

The objective of the present study was to develop a kinetic mechanism for C_1–C_4 fuels by including detailed reaction pathways for the formation and growth of PAH molecules up to coronene to enable the computation of the profiles of large PAHs. We validated this mechanism quantitatively with existing experimental data on premixed flames. And then, the mechanism has been applied to CDFs of ethylene/propane mixtures to test the prediction capability on PAH behaviors, such as the synergistic effect and the degree of synergism for different size PAHs together with the effect of benzene addition on PAH behaviors. Finally, the chemical cross-linking effect leading to the synergistic effects was analyzed.

2. Mechanism development

A recently updated and extensively validated mechanism for C_1–C_4 fuels [58] (hereafter called USC Mech) including molecular growth up to benzene was used as the base mechanism. This mechanism, containing 111 chemical species and 784 reactions, was extended by including reactions for PAH growth up to the formation of coronene based on KM1. The extended mechanism (called KM2) includes 202 species and 1351 reactions.

A brief description of notable features of KM2 is as follows. The role of cyclopentadienyl radicals (C_5H_5) in forming larger aromatics was described in [56,59–63]. Therefore, 17 reactions were included in USC Mech from [56] to improve the C_5H_5 sub-mechanism. These reactions mainly involve a pathway proposed in [59] for benzene formation from C_5H_5, formation of naphthalene through its recombination, and the abstraction of H atom from cyclopentadiene by H atom, methyl radical (CH_3) and propargyl radical (C_3H_3) along with the reverse reactions. H-abstraction reactions are particularly important because they activate chemical species for further reactions. In [61], the role of odd-carbon number species such as CH_3 and C_3H_3 in H-abstraction from PAHs and soot was discussed for diffusion flames. Thus, H-abstraction reactions for important species, such as benzene, PAHs and indene (C_9H_8) by H, CH_3 and C_3H_3 were also included. For all species smaller than C_5, the reactions and their rates were not altered from the base mechanism. In propane combustion, a noticeable amount of CH_3 is formed. Therefore, reactions involving the formation of benzene from C_5H_5 and CH_3, as proposed in [59], were included.

The reactions for the growth of PAHs larger than benzene are taken from [56]. The details are briefly reviewed here. Along with the HACA mechanism for PAH growth, several reactions involving species with odd-carbon number species such as indenyl (C_9H_7), benzyl ($C_6H_5CH_2$), C_5H_5 and C_3H_3 are included. The rate constant for the self-addition of C_5H_5 to form naphthalene were taken from an experimental study in [64]. For the prediction of the concentrations of cyclic C_5 species such as C_5H_5 and C_5H_6, reactions involving these species were added from [56] to the base mechanism. Some reactions involving the addition of C_4H_4 to large PAH radicals are also considered.

The rate constants for PAH reactions not present in the literature were determined through quantum calculations using the density functional theory (B3LYP hybrid functional and 6-311++G(d,p) basis set) along with the transition state theory. Note that none of the rate constants were arbitrarily changed or intuitively estimated to match the computed and the experimental results. Both forward as well as reverse rate constants were calculated for those reactions [56]. The thermodynamic data and the transport properties of all the chemical species present in KM2 were taken from [56,58], The rate constants for PAH reactions were obtained in the high pressure limit, as PAH molecules are large in size and their reactions do not exhibit substantial pressure dependence. The CHEMKIN format mechanism along with thermodynamic and transport data of species is included in the supplements. The chemical notation is the same as in [56] and aromatic species with 1–7 rings are named A1–A7, whose chemical structures are shown in Fig. 8 of this paper.

3. Results and discussion

3.1. Premixed flame simulations

Two premixed flames at different pressure conditions were simulated for the validation of KM2. First, the ethylene flame at 20 torr with $C_2H_4/O_2/Ar = 19.4/30.6/50.0$ was simulated (Flame 1). This flame was particularly chosen since experimental profiles for many intermediate C_1–C_6 hydrocarbons were available [65]. The simulation was conducted through the premixed flat flame model in Chemkin Pro software [66] using USC Mech [58], ABF Mech [11], KM1 [56] and KM2. Experimental temperature profiles were corrected for cooling effect of the probe (lower by 100 K and moved 0.5 mm away from burner surface as suggested in Ref. [65]) and