

Modeling of Soot Precursors in Several Rich Hydrocarbon/Oxygen/Argon Flames

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Abstract

A detailed chemical mechanism, including 400 elementary reactions and 77 species, has been developed previously to simulate the formation of aromatic compounds in rich premixed laminar ethylene flames. In this work, this model is tested for less rich ethylene flames ($\phi = 1.0$ to 1.75) and for rich methane (CH_4), for rich acetylene (C_2H_2) and for rich ethane (C_2H_6) flames, at an equivalence ratio of 2.0. Among the kinetic analysis of main species occurring in those flames, the formation paths of the first aromatic ring is described in detail, in these different types of flames. Definitely, the model shows the predominance of the $\text{C}_3 + \text{C}_3$ pathways in CH_4 , C_2H_4 and C_2H_6 flames and of the $\text{C}_2 + \text{C}_4$ type reactions in C_2H_2 flames.

Introduction

Polycyclic Aromatic Hydrocarbons (PAH) are formed in most practical combustion systems and are important precursors of soot. It is now widely accepted that benzene and phenyl formations constitute the first step in this growth process that lead to PAH and ultimately soot particles. However, despite the extensive work on the elementary reactions leading to the first aromatic ring, the dominant benzene formation pathway does not seem to be identified. Two different sets of reactions had been proposed according the authors [1-18]: the C_4 hydrocarbons pathways with the reaction of $n\text{-C}_4\text{H}_5$ and $n\text{-C}_4\text{H}_3$ with C_2H_2 ; and the C_3 hydrocarbons channel with the recombinaison of propargyl radical (C_3H_3) and the reaction of C_3H_3 with propyne ($p\text{-C}_3\text{H}_4$).

Recently, a new reaction mechanism simulating rich ethylene/oxygen/argon flames ($\phi = 2.25$ and 2.50), and explaining the main pathways leading to the benzene formation and therefore that of soot precursors [8 and 9] has been built. In this article, we report the simulation performed by this same mechanism in less rich ethylene flames ($\phi = 1.0$ to

1.75) and in rich methane (CH_4), acetylene (C_2H_2) and ethane (C_2H_6) flames whose measurements were performed previously [10, 11, 12 and 13 respectively], at equivalence ratio of 2.0. In such way, we could confirm the degree of confidence of the model for several hydrocarbons and various equivalence ratios. Moreover, an examination of the major pathways involved in the benzene formation in these flames is performed.

Experimental

The structure of laminar premixed rich ethylene-, methane-, acetylene- and ethane/oxygen/argon flames was analyzed in our laboratory, by Musick et al. [10 and 11] for C_2H_4 and CH_4 , and Ancia et al. [12 and 13] for C_2H_2 and C_2H_6 . All these premixed flames were stabilized on a Spalding-Botha-type burner at low pressure and sampling was performed at different heights in the flame. Identification and signal intensity of species were monitored by molecular beam mass spectrometry (MBMS). A summary of the conditions of these flames simulated in the present study is given in Tables 1 and 2.

Flame	ϕ	$X_{\text{C}_2\text{H}_4}$	X_{O_2}	X_{Ar}	P_{tot}	D_{tot}	V_0
I	1,00	0,0675	0,2025	0,7300	20	3,939	78,36
II	1,25	0,0845	0,2025	0,7130	35	3,377	67,18
III	1,50	0,1012	0,2025	0,6963	40	2,955	58,79
IV	1,75	0,1180	0,2025	0,6795	50	2,364	47,03

Table 1: Initial compositions and experimental conditions in $\text{C}_2\text{H}_4/\text{O}_2/\text{Ar}$ flames, with ϕ : equivalence ratio, X_i : mole fraction of species i , P_{tot} : working pressure (Torr), D_{tot} : total flow rate at the working pressure (l/s), V_0 : initial flow velocity (cm/s).

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Flame	ϕ	X_{CH_4}	$X_{\text{C}_2\text{H}_2}$	$X_{\text{C}_2\text{H}_6}$	X_{O_2}	X_{Ar}	P_{tot}	D_{tot}	V_0
F.CH ₄ (V)	1,94	0,2536			0,2621	0,4843	60	3,230	31,10
F.C ₂ H ₂ (VI)	2,00		0,12		0,15	0,73	27	5,066	100,80
F.C ₂ H ₆ (VII)	2,00			0,16	0,28	0,56	67	3,546	34,15

Table 2: Initial compositions and experimental conditions in CH₄/O₂/Ar, C₂H₂/O₂/Ar and C₂H₆/O₂/Ar flames, with ϕ : equivalence ratio, X_i : mole fraction of species i , P_{tot} : working pressure (Torr), D_{tot} : total flow rate at the working pressure (l/s), V_0 : initial flow velocity (cm/s).

Modeling

Previously, a kinetic model containing 77 species and 400 elementary reactions[†] has been built in order to examine the key processes governing the formation of soot precursors (C₃, C₄, C₅, C₆ and PAH), in laminar premixed rich ethylene/oxygen/argon flames, $\phi = 2.25$ and 2.50 [8 and 9].

The kinetics for the H₂/O₂ related species are based on the Westbrook mechanism [19] and Baulch et al. evaluation [20], and the C₁-C₂ species mainly based on Miller and Melius mechanism [2]. Ania [14] and Musick et al. [11], who used also the kinetic data from the GRI-Mech [21] and Warnatz [22], have optimized the first part of the model. The C₃-C₄ submechanism was taken from Davis et al. [15] which describe the propene pyrolysis. For the C₅-C₆-C₇-C₈-C₉ and C₁₀ hydrocarbons, kinetics has been elaborated at starting from several models in the literature [3, 5, 6, 16, 23 and 24], and by optimizing the simulated mole fraction profiles by comparing with the experimental data.

The numerical simulation of the mechanism of the investigated one-dimensional flames has been performed by using the PREMIX code of the CHEMKIN package [25]. Molecular and thermal diffusion is considered in the code. Modeling has been performed by including as input parameters the experimental temperature profile measured in similar conditions as the concentration ones, the initial composition of the flame and the initial total mass flux.

In this article, this mechanism has been tested in less rich ethylene flames ($\phi = 1.00$ to 1.75) and rich methane ($\phi = 1.94$), ethane ($\phi = 2.00$) and acetylene ($\phi = 2.00$) flames. Mole fraction profiles of C₂H₂, C₃H₃, C₃H₄ and C₆H₆ species are presented in these different flames, due to length restrictions.

Results and Discussion

Ethylene

Figures 1 to 4 show the simulated and experimental mole fraction profiles of C₂H₂, C₃H₃, C₃H₄ and C₆H₆, respectively, in premixed ethylene/oxygen/argon

flames with equivalence ratios of 1.00, 1.25, 1.50 and 1.75.

Acetylene (C₂H₂) is more important with the increase of the equivalence ratio in ethylene flames (Figure 1). The model gives a good simulation of the formation and consumption of this species. The main formation of C₂H₂ is from two reactions of vinyl radicals (C₂H₃): C₂H₃ + M = C₂H₂ + H + M and C₂H₃ + OH = C₂H₂ + H₂O. This last reaction is more important with the decrease of the equivalence ratio. Acetylene is an important compound since it has been recognized as important precursors for soot formation. Indeed, C₂H₂ allows the formation of C₃ and C₄ hydrocarbons.

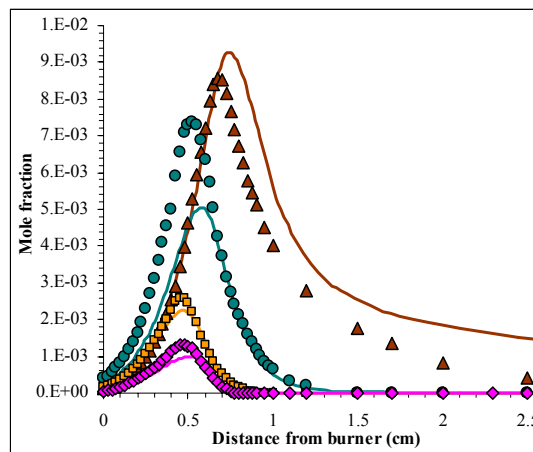


Figure 1: Experimental (symbols) and computed (lines) mole fraction profiles of C₂H₂ in the C₂H₄/O₂/Ar flames, $\phi = 1.00$ (pink), 1.25 (orange), 1.50 (green) and 1.75 (brown).

Propargyl radicals are mainly produced from the reaction of acetylene with singlet methylene radicals: C₂H₂ + ¹CH₂ = C₃H₃ + H. Moreover, C₃H₃ can be produced from propyne (*p*-C₃H₄) and allene (*a*-C₃H₄) by hydrogen abstraction. Simulated profiles of C₃H₃ agree well with experimental ones (Figure 2). This species has been only detected in the richest ethylene flames ($\phi = 1.50$ and 1.75).

[†] The mechanism is available by contacting the authors at dias@chim.ucl.ac.be or vandooren@chim.ucl.ac.be.

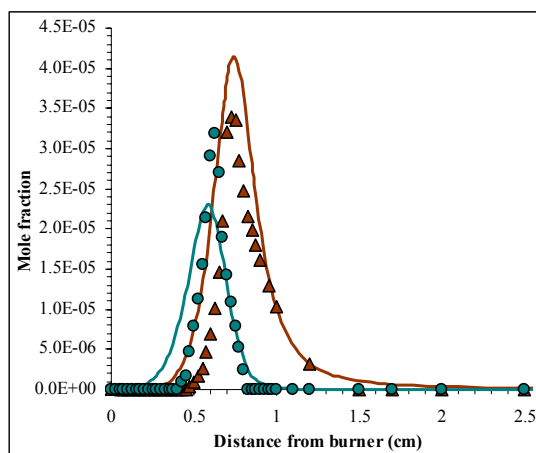


Figure 2: Experimental (symbols) and computed (lines) mole fraction profiles of C_3H_3 in the $C_2H_4/O_2/Ar$ flames, $\phi = 1.50$ (green) and 1.75 (brown).

Similarly, C_3H_4 molecule is well simulated by the mechanism in the four ethylene flames (Figure 3). The C_3H_4 modelled data represent the addition of *p*- C_3H_4 and *a*- C_3H_4 mole fractions, to be compared with the MBMS results which cannot separate both isomers.

The principal formation of C_3H_4 is from the reaction of vinyl radicals with triplet methylene: $C_2H_3 + {}^3CH_2 = p\text{-}C_3H_4 + H$ and $C_2H_3 + {}^3CH_2 = a\text{-}C_3H_4 + H$. For the allene, another process is non-negligible in less rich ethylene flames: $C_3H_5 + H = a\text{-}C_3H_4 + H_2$.

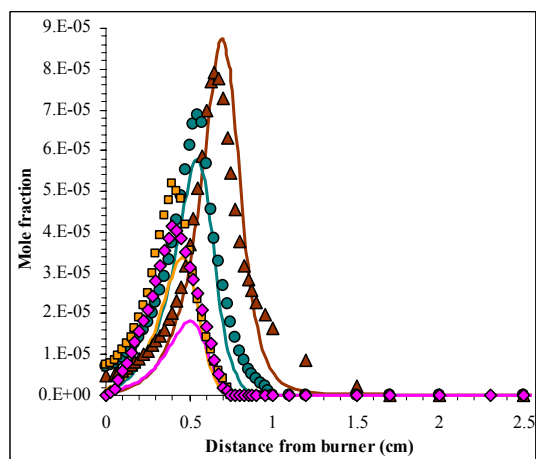
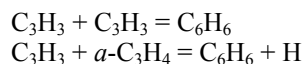
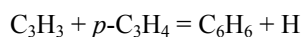


Figure 3: Experimental (symbols) and computed (lines) mole fraction profiles of C_3H_4 in the $C_2H_4/O_2/Ar$ flames, $\phi = 1.00$ (pink), 1.25 (orange), 1.50 (green) and 1.75 (brown).

As we have detailed previously [9], the benzene (C_6H_6) formation is mainly achieved from $C_3 + C_3$ type reactions, in rich ethylene flames ($\phi = 2.25$ and 2.50):



In less rich ethylene flames, these reactions are predominant but another involving phenyl radicals contributes also to the benzene formation: $C_6H_5 + H = C_6H_6$. At equivalence ratios of $\phi = 1.50$ and 1.75 , the simulated and experimental mole fraction profiles of benzene agree very well (Figure 4).

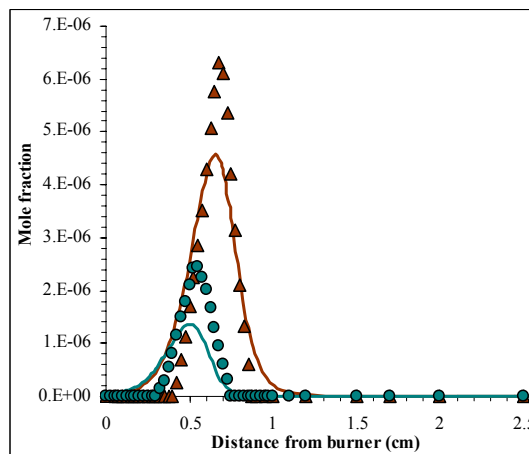


Figure 4: Experimental (symbols) and computed (lines) mole fraction profiles of C_6H_6 in the $C_2H_4/O_2/Ar$ flames, $\phi = 1.50$ (green) and 1.75 (brown).

Thanks to the comparison and the agreement between the simulated and experimental mole fraction profiles of species detected in these four less rich ethylene flames, we can validate the mechanism for all these ethylene flames: $\phi = 1.0$ to 2.5 .

Methane, Acetylene and Ethane

This kinetic model has been also tested for flames involving hydrocarbons like methane (CH_4), acetylene (C_2H_2) and ethane (C_2H_6).

Figures 5 to 8 show the simulated and experimental mole fraction profiles of C_2H_2 , C_3H_3 , C_3H_4 and C_6H_6 , respectively, in these four premixed flames, at equivalence ratio of 2.0 .

Acetylene is an initial reactant in the $C_2H_2/O_2/Ar$ flame, so its concentration decreases from the fresh gases to the burned ones (Figure 5). We should underline that acetylene is not completely consumed, 7 % of the initial concentration remains at 2.5 cm from the burner surface. The mechanism verifies very well this observation.

The agreement between simulated and experimental mole fraction profiles in CH_4 and C_2H_6 flames is quite good, although the shape in the burnt gases regime is not well reproduced. Like in ethylene flames, acetylene is mainly produced by the decomposition of vinyl radicals: $C_2H_3 + M = C_2H_2 + H + M$. At equivalence ratio of 2.0 , the most important consumption of C_2H_2 is the same for the

four flames (CH_4 , C_2H_2 , C_2H_4 and C_2H_6), with the atomic oxygen:

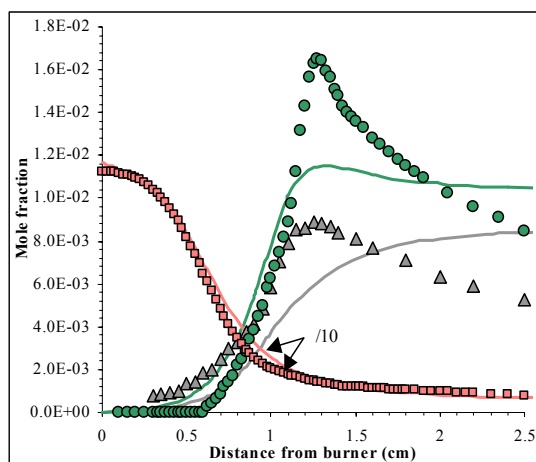
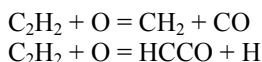


Figure 5: Experimental (symbols) and computed (lines) mole fraction profiles of C_2H_2 in the $\text{CH}_4/\text{O}_2/\text{Ar}$ (grey), $\text{C}_2\text{H}_2/\text{O}_2/\text{Ar}$ (pink) and $\text{C}_2\text{H}_6/\text{O}_2/\text{Ar}$ (green) flames, $\phi = 2.0$.

Propargyl radicals are an important intermediate for the formation of benzene, mainly through $\text{C}_3 + \text{C}_3$ type reactions. These radicals have been detected only in methane and acetylene flames (Figure 6). The model overestimates C_3H_3 mole fraction in the CH_4 flame and underpredicts these radicals in the C_2H_2 flame. However, the shape and the position of the simulated profiles agree well with experimental ones. According to the model, in C_2H_2 and C_2H_6 flames, the C_3H_3 production is from the reaction between acetylene with singlet methylene: $\text{C}_2\text{H}_2 + {}^1\text{CH}_2 = \text{C}_3\text{H}_3 + \text{H}$. This reaction contributes also in the CH_4 flame, but the most important reaction of C_3H_3 formation is from the propyne: $p\text{-C}_3\text{H}_4 + \text{H} = \text{C}_3\text{H}_3 + \text{H}_2$.

The C_3H_4 molecule has been detected only in methane and ethane flames. Like for ethylene flames, the C_3H_4 simulated data showed on figure 7, represents the sum of $p\text{-C}_3\text{H}_4$ and $a\text{-C}_3\text{H}_4$ mole fractions, to be compared with the experimental global C_3H_4 values. The calculated mole fractions are higher than experimental ones for both flames. Moreover, in the C_2H_6 flame, the simulated C_3H_4 is shifted toward the fresh gases due to an early formation of C_3H_4 .

According to the model, the formation of propyne in C_2H_6 flame (like in C_2H_4 flames) is mainly due to the reaction of vinyl radicals with triplet methylene: $\text{C}_2\text{H}_3 + {}^3\text{CH}_2 = p\text{-C}_3\text{H}_4 + \text{H}$. But in CH_4 and C_2H_2 flames, propargyl radicals are responsible for the production of $p\text{-C}_3\text{H}_4$ by the reaction with atomic hydrogen: $\text{C}_3\text{H}_3 + \text{H} + \text{M} = p\text{-C}_3\text{H}_4 + \text{M}$. For these two last flames, the allene is mainly formed from the

propyne: $p\text{-C}_3\text{H}_4 + \text{H} = a\text{-C}_3\text{H}_4 + \text{H}$. In ethane flame, the consumption of C_3H_5 radicals allows the allene production: $\text{C}_3\text{H}_5 + \text{H} = a\text{-C}_3\text{H}_4 + \text{H}_2$.

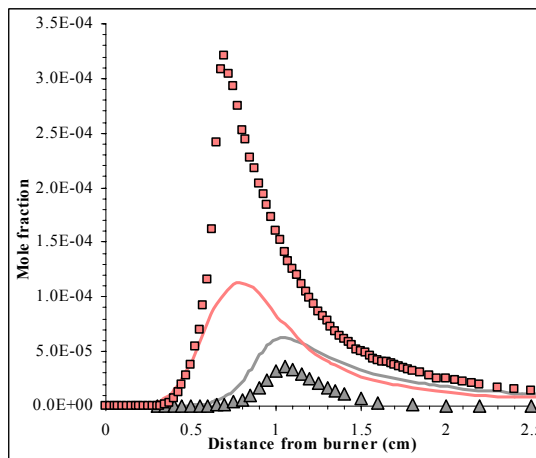


Figure 6: Experimental (symbols) and computed (lines) mole fraction profiles of C_3H_3 in the $\text{CH}_4/\text{O}_2/\text{Ar}$ (grey) and $\text{C}_2\text{H}_2/\text{O}_2/\text{Ar}$ (pink) flames, $\phi = 2.0$.

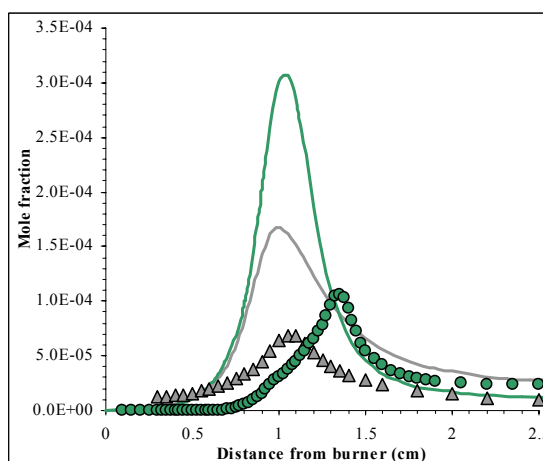
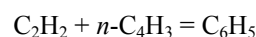


Figure 7: Experimental (symbols) and computed (lines) mole fraction profiles of C_3H_4 in the $\text{CH}_4/\text{O}_2/\text{Ar}$ (grey) and $\text{C}_2\text{H}_6/\text{O}_2/\text{Ar}$ (green) flames, $\phi = 2.0$.

Like in ethylene flames, in rich flames of CH_4 , C_2H_2 and C_2H_6 , C_2H_2 , C_3H_3 and C_3H_4 compounds are important intermediates for benzene formation. However, mole fractions of C_6H_6 has been measured only in the acetylene flame (Figure 8). The simulation agrees well with the experiment, even if the maximum of calculated concentration is lower of 50 % than experimental one. In C_2H_2 flame, the principal formation of C_6H_6 is from phenyl radicals (C_6H_5), which are produced from the reaction of acetylene with C_4H_3 radicals:





We can underline that in rich acetylene flames, the benzene formation is mainly achieved from $C_2 + C_4$ type reactions, even if the recombination of propargyl radicals is also non negligible: $C_3H_3 + C_3H_3 = C_6H_6$. On the contrary, in methane and ethane flames, C_6H_6 is mainly produced from the $C_3 + C_3$ reactions: $C_3H_3 + p\text{-}C_3H_4 = C_6H_6 + H$.

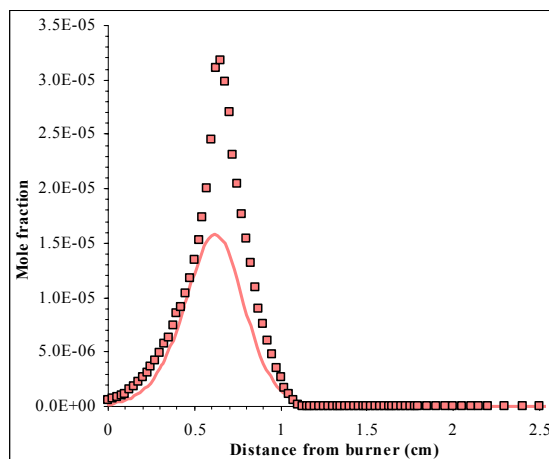


Figure 8: Experimental (symbols) and computed (lines) mole fraction profiles of C_6H_6 in the $C_2H_2/O_2/Ar$ (pink) flames, $\phi = 2.0$.

Benzene formation

The paths analysis in CH_4 , C_2H_2 , C_2H_4 and C_2H_6 flames allows to underline the specific kinetic according to the identity of initial hydrocarbon. Indeed, benzene formation is achieved by two sets of reaction depending on the nature of the flame: the $C_3 + C_3$ pathways in the rich CH_4 , C_2H_4 and C_2H_6 flames

and mainly the $C_2 + C_4$ type reactions in the rich C_2H_2 flames.

Figure 9 illustrates the main reaction paths starting from CH_4 , from C_2H_4 and from C_2H_6 to produce C_6H_6 . Each substantial reaction is represented by an arrow, whose thickness is representative of the relative importance of that particular reaction of formation.

Similarly, Fig. 10 indicates the reaction paths from acetylene to benzene, where $C_2 + C_4$ reaction is the main process and where the propargyl radicals recombination is non completely negligible in this flame.

Conclusions

The previous mechanism [8 and 9] established for rich ethylene flames ($\phi = 2.25$ and 2.50) has been tested for less rich ethylene flames ($\phi = 1.0$ to 1.75) as well as for rich methane (CH_4), acetylene (C_2H_2) and ethane (C_2H_6) flames, at equivalence ratio of 2.0 , whose measurements were performed previously [10, 11, 12 and 13 respectively]. We have compared the simulated mole fraction profiles with experimental ones. Although there are some discrepancies between some maximum of concentration, we can confirm the reliability of the model and its validity for several hydrocarbons and equivalence ratios.

Moreover, an examination of the major pathways involved in the benzene formation in these flames definitely shows the predominance of $C_3 + C_3$ pathways in CH_4 , C_2H_4 and C_2H_6 flames and of $C_2 + C_4$ reactions in C_2H_2 flames.

These results allow to highlight that main reactions leading to the formation of the first aromatic ring are strongly sensitive to the nature of the initial fuel.

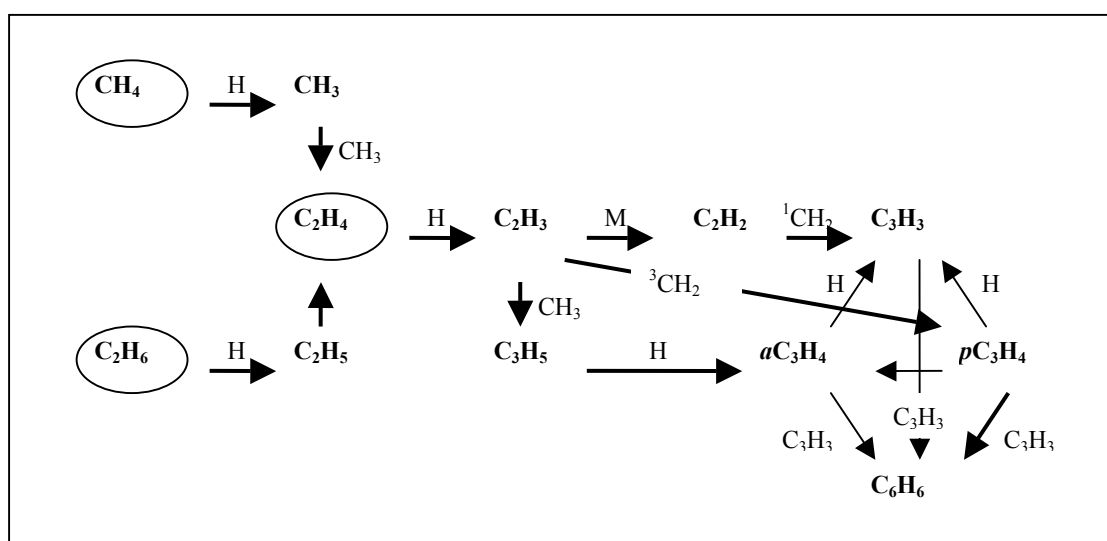


Figure 9: Reaction pathways of formation from methane, ethylene and ethane to benzene.

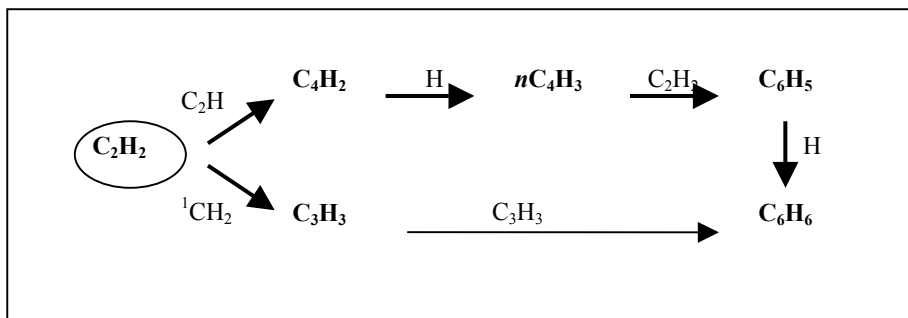


Figure 10: Reaction pathways of formation from acetylene to benzene.

Acknowledgements

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