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Chemical Kinetic Modeling of Soot Precursors Formation Characteristics in Ethylene Oxidation

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The chemical kinetics modeling study of soot precursor characteristics in laminar premixed ethylene flame at different pressure and broad ranged of equivalence ratio (stoichiometric and rich flames) was conducted using CHEMKIN-PRO and advanced functions. In the kinetic modeling work, the formation of soot precursors for ethylene flame is investigated by using Marinov and Dagaut gas mechanisms, respectively. The prediction focused on temperature, small molecules, single-ring aromatics benzene and polycyclic aromatic hydrocarbons macromolecules intermediates using one-dimensional laminar premix flame (PREMIX) model. By comparison with the experimental data, the results show that the distributions of flame temperature and the mole fractions for small molecules (following C₆H₆) are in good agreement experimental data for Marinov mechanism. However, the prediction for C₆H₆ and macromolecule polycyclic aromatic hydrocarbon intermediates, there have no obvious merits between two mechanisms.

Keywords: Chemical kinetics, Modeling, Flame temperature, Soot precursors, Reaction mechanism.

INTRODUCTION

Soot is an important particulate pollutant from the burning of fossil-fuel emissions and soot formation in large-scale boiler also reduces the combustion efficiency. The development of chemical kinetics makes it easier to calculate formation and emission of pollutants for combustion process. Particularly, increasing attention has been made in recent years on the combustion efficiency of devices, pollutant emissions and environmental issue, which has prompted people do a large number of research on soot formation and controlling mechanism¹⁻³. The C_xH_y combustion of development is relatively mature and some applied to soot and precursors formation simulation. However, there are still many controversies on simulation for formation pathway of soot and precursors. Then understanding of the detailed chemical and physical processes has important significance in suppressing soot emissions and developing clean, economical combustion equipment.

The main consideration of dynamics simulation is the chemical reaction mechanism and kinetics. Chemical kinetics can provide technical parameters to select the reaction conditions and control the conversion step of the final product through study of various factors (such as concentration, temperature, pressure, catalyzer, *etc.*) on reaction rate⁴⁻⁷. In addition,

researches of reaction mechanism can identify where key decision of reaction rate, thus control main reaction and suppress side one. Understanding of the basic chemical processes has great significance to study the combustion process. In many combustion processes, the chemical reaction rate controls burning velocity and determines the rate of pollutant formation in almost all of combustion. In addition to lots of harmful materials, such as SO_x, NO_x, carbon dioxide, dust and soot *etc.*, the polycyclic aromatic hydrocarbons is also one of the emissions to the environment. Benzene and its homologues (such as toluene, xylene and trimethylbenzene) are present in exhaust-gas from hydrocarbon fuel combustion. Pyrene, anthracene and other polycyclic aromatic hydrocarbons included in combustion products are carcinogens. Otherwise, polycyclic aromatic hydrocarbon are thought to be key intermediates and precursors in soot formation. The mass growth of aromatic species from benzene to polycyclic aromatic hydrocarbons has received considerable attention. Because polycyclic aromatic hydrocarbons are known products of fuel-rich combustion and are the most likely precursors to soot, a basic understanding of polycyclic aromatic hydrocarbon growth kinetics is of significant interest from both fundamental and practical standpoints.

At the current stage⁴⁻⁹, the picture of polycyclic aromatic hydrocarbon and soot formation, consisting in the following, partially parallel processes, is widely accepted for model prediction: (1) A monocyclic aromatic hydrocarbon formation in gas-phase, the process consists of fuel pyrolysis and oxidation at high temperature and formation for the first aromatic ring. (2) Growth and homogeneous nucleation of small molecule polycyclic aromatic hydrocarbon. polycyclic aromatic hydrocarbon of increasing size are mainly formed by sequences of chemical reactions of radicals of smaller polycyclic aromatic hydrocarbon with acetylene, polycyclic aromatic hydrocarbon or polycyclic aromatic hydrocarbon radicals. At some size, polycyclic aromatic hydrocarbon species react with each other while individual polycyclic aromatic hydrocarbon keep on growing, particle inception (nucleation) occurs. (3) Formation of spherical particles formation, growth and oxidation of particles, a process described through particle coagulation, surface reaction (growth and oxidation) and particle aggregation¹⁰⁻¹⁴.

However, under specific operation conditions, modeling of polycyclic aromatic hydrocarbon and soot particles formation still cannot provide satisfactory prediction. The main reasons are the uncertainty of kinetic data, the lack of important component of the reaction system and constrains of parameters application ranges or model dimensions. Therefore, continuous researches involved in detailed reaction pathways from reactants to products and combustion prediction involving in complex flow-field structures and chemical properties are needed.

The objectives of this study are to elucidate the chemistry of potential soot precursors (benzene, polycyclic aromatic hydrocarbons *etc.*) and to identify the important pathways for the formation of soot precursors. For this purpose, two kinetic models, which has been the basis for the Marinov *et al.*^{15,16}, Dagaut and Nicolle¹⁷ mechanisms are conducted using CHEMKIN-PRO and API function in this paper. The kinetic modeling results are compared against molecular-beam mass spectrometry (MBMS) data by Musick and Vandooern¹⁸⁻²⁰ in 0.03-0.05 atm pressure laminar premixed C₂H₄/O₂/Ar flames. This work will contribute to study on the formation single-ring aromatic species and molecular weight growth processes in flames fueled by C₃, C₅ and C₆ species.

Kinetics modeling approach

Chemical kinetics mechanism: The kinetic models used in the analysis of the flames considered here, were developed by Marinov *et al.*^{15,16} and Dagaut and Nicolle¹⁷, which named Dagaut and Marinov mechanism, respectively. The former reaction mechanism consists of 97 species and 732 elementary reactions to simulate NO_x reburning in hydrocarbon from C₁ to C₄ and chemistry kinetics mechanism for various fuel from methane to kerosene and the latter contains 150 species and 661 elementary reaction to simulate combustion of methane, ethene, ethyne, ethyl alcohol. The calculations were performed with PREMIX using CHEMKIN-PRO²¹. Thermodynamics data and transport data using in the mechanism are obtained from CHEMKIN own database and Sandia National Laboratories database.

Simulation methods and boundary conditions: In this paper, one-dimensional laminar premix flame (PREMIX)

model was applied to model study. The simulation engineering diagram is shown in Fig. 1. The project includes an entrance, a reaction model and product.



Fig. 1. Diagram of the system used to simulate the premix steady flame

The geometry model is a cylinder with 10 cm length and 8 cm diameter and computational domains and boundary conditions are as shown in Fig. 2. The boundary conditions is set: M is a constant known, temperature and mass flow fraction is given in inlet of cold boundary and zero-gradient ($\epsilon = Y_k + \rho Y_k V_k A / M$) is given in hot boundary outlet.

The model applied in this paper is PREMIX whose computational domains and boundary conditions are as shown in Fig. 2. The boundary conditions is set: M is a constant known, temperature and mass flow fraction ($\epsilon = Y_k + \rho Y_k V_k A / M$) are given in inlet of cold boundary and zero-gradient is given in hot boundary outlet.

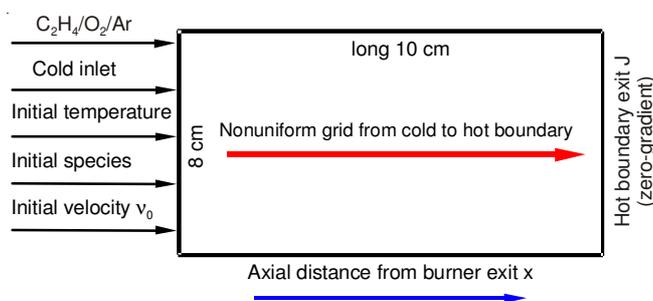


Fig. 2. Calculation geometry and boundary conditions

In cold boundary inlet, mass flow fraction and temperature is defined through eqns. 1-2:

$$e_{k,1} - Y_{k,1} - \left(\frac{\rho Y_k V_k A}{M} \right)_{j=1} = 0 \quad (1)$$

$$T_1 - T_b = 0 \quad (2)$$

In above two equations, $\epsilon_{k,1}$ is the reactant fraction of species k, T_b is the temperature of specify burner.

In hot boundary exit, zero-gradient definition is obtained by

$$\frac{Y_{k,J} - Y_{k,J-1}}{x_J - x_{J-1}} = 0 \quad (3)$$

$$\frac{T_J - T_{J-1}}{x_J - x_{J-1}} = 0 \quad (4)$$

where, M is the mass flow rate, T is the temperature, Y_k is the mass fraction of the k_{th} species, ρ is the density, V_k is the diffusion velocity of species k and A is the cross-section area of flame transport.

In PREMIX model, there is an assumption that pressure is constant and heat loss is neglected, momentum conservation equation does not required to be solved. The continuity equation, energy equation and species equations are solved to get temperature and species concentrations in the burner-stabilized

flame. The governing conservation equations were discretized using finite difference scheme on a non-uniform grid with point numbered 1 at cold boundary to J (J refers to the mesh point) at the hot boundary, as shown in Fig. 2. The convective terms were discretized using central differences. The diffusive terms in the species conservation was approximate in a similar way. All non-differential terms in equations are calculated at point J , for example chemical productivity.

PREMIX has applicable grid quantities with the initial simulation conducted in a thick grid including about 9 or 10 grid points. After calculation, new grid points are added in the area where temperature and species concentration change faster. The results of thick grid calculation performed as the initial value for fine grid. The process is continuous until new point is not needed with precision controlled by users.

The computational domain of simulation is 10 cm long, the maximum number of grid points is allowed 100, number of adaptive grid points is 50, the adaptive grid control based on gradient and curvature is 0.9. More details can be found in the CHEMKIN-PRO manual.

EXPERIMENTAL

Prediction of polycyclic aromatic hydrocarbon and soot formation requires an accurate description of the main flame structure. Therefore, previous research^{18,19} is adopted to simulate in this paper.

This paper performed several modeling and validation for flame structure and some intermediate (soot precursors) of fuel-rich combustion, premixed $C_2H_4/O_2/Ar$ flame at different pressures (0.03-0.05 atm) and equivalence ratios (1-2.5). First of all, a simulation is conducted at pressures (0.03-0.05 atm) and equivalence ratios (1-2.5) using Marinov *et al.*^{15,16} mechanism and comparing representative species to experimental data^{18,19} to prove the reasonableness of the simulation. Then on this basis, under condition of $P = 0.05$ atm, $T_0 = 298$ K, equivalence ratio $\Phi = 2.5$, calculate ethylene flame structure and concentrations of main intermediate and compare simulation results to experimental data in the ref.²⁰ used two mechanisms (Marinov^{15,16} mechanism and Dagaut¹⁷ mechanism), respectively.

The simulation conditions, species of fuel and oxidizer, setting of cold boundary inlet applied are given in Table-1. In Table-1, $X(i)$ is the concentration of each species, P is the pressure, v_0 is the inlet velocity, Φ is the equivalence ratio, T_0 is the initial temperature.

Experimental data: The experimental data of $C_2H_4/O_2/Ar$ premixed flames are measured by Renard and Vandoorn¹⁸ using MBMS method at 0.03, 0.04 and 0.05 atm pressure, corresponding equivalence ratio are respectively 1, 1.50 and 2. The values of concentration for intermediate species include steady species and intensify molecules are also obtained by

this method. The objective of the work was to determine specific rate constants on the basis of a reaction mechanism and to provide experimental data over a large range of composition for further modeling. There are only comparison ethylene (C_2H_4 , on behalf of steady species) and hydrogen (H_2 , on behalf of intensified molecules) in order to certificate the kinetics model methods are rational in this paper.

Based on above simulation method, other kinetics modeling will go on used Marinov^{15,16} mechanism and Dagaut¹⁷ mechanism to predict and analyze on intermediates in ethylene oxidation flames. Experimental data^{19,20} about $C_2H_4/O_2/Ar$ premix flame under condition of $P = 0.05$ atm, $\Phi = 2.5$ is from reference^{19,20} which focuses on the effects additions of CO_2 , NH_3 and H_2O on $C_2H_4/O_2/Ar$ flame structure and soot formation precursors. The measuring way is also MBMS.

RESULTS AND DISCUSSION

The simulations were performed for three premixed flames at equivalence ratios in the range of 1-2 (1, 1.5 and 2) to test the original model on a flame burner 8 cm in diameter at pressures varying from 0.03-0.05 atm (Table-1). The simulations of experimental data from Renard¹⁸, the molecular beam mass spectrometry (MBMS) measurements of species in a fuel-rich $C_2H_4/O_2/Ar$ flame, are presented in Fig. 3. The predicted and experimental mole fractions of C_2H_4 and H_2 concentrations are shown in Fig. 3. The simulated concentrations of small molecules and radicals H_2 and C_2H_4 are in good agreement with the experimental data. In general the maximum error of C_2H_4 and H_2 concentrations for three equivalence ratios are under-predicted by 13.3 %. In view of systematic errors in the measurement, this under-prediction can be accepted.

In addition, the maximal emissions of H_2 during ethylene oxidation increase with the increase of equivalence ratio, which is consistent previous results¹⁸. Therefore, it is reasonable that adopted in simulations for reaction models, gas-phase mechanism models and numerical methods.

In order to better simulate the properties of main intermediate and soot precursors in $C_2H_4/O_2/Ar$ premixed flames. The simulation is conducted for premixed flames $C_2H_4/O_2/Ar$ at $P = 0.05$ atm pressure and $\Phi = 2.5$ equivalence ratio using different gas-phase models (Marinov mechanism^{15,16} and Dagaut mechanism¹⁷) and the calculated results and the experimental data^{19,20} were compared and analyzed (Figs. 4-8).

Fig. 4 shows a comparison between the predicted temperature curves (used by Marinov mechanism^{15,16} and Dagaut mechanism¹⁷) and the experimental measurements. As can be seen from Fig. 4, different reaction mechanisms are consistent with the experimental results to prediction tendency. However, Marinov^{15,16} mechanism to predict the temperature distribution is relatively consistent with the experimental results better, but Dagaut¹⁷ mechanism over-predicted the temperature of the

TABLE-1
SPECIES AND SIMULATION CONDITIONS

Model	Flame	Φ	$X(C_2H_4)$	$X(O_2)$	$X(Ar)$	$T_0(K)$	$P(atm)$	$v_0(cm/s)$	Ref.
Laminar premix flame model	F1.0	1	0.0675	0.2025	0.7300	298	0.03	78.36	18
	F1.5	1.5	0.1012	0.2025	0.6963	298	0.04	58.79	18
	F2.0	2	0.1350	0.2025	0.6625	298	0.05	47.03	18
	F2.5	2.5	0.3300	0.4000	0.2700	298	0.05	40.3	19, 20

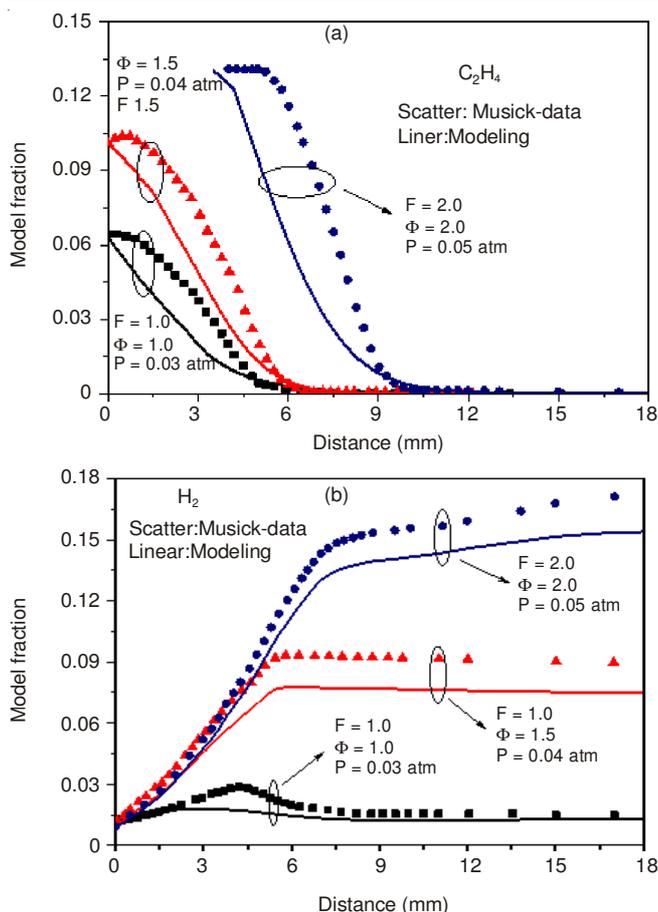


Fig. 3. Comparison of predicted mole fraction with the experimental data¹⁸ in the $C_2H_4/O_2/Ar$ premix flame at different pressure and equivalence ratio (F) (a) C_2H_4 (b) H_2

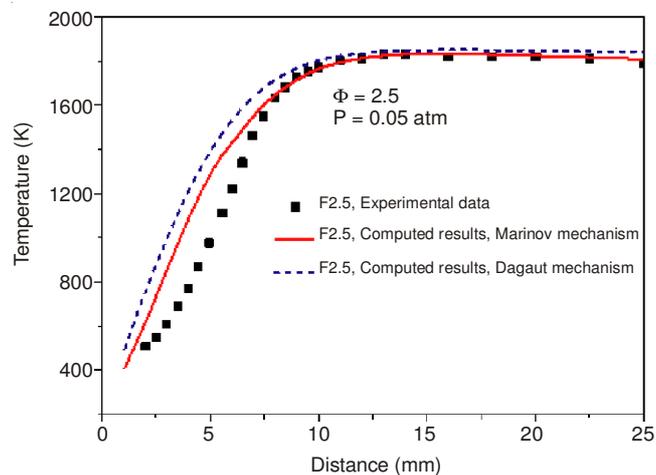


Fig. 4. Comparison of predicted temperature with the experimental data^{19,20} in the $C_2H_4/O_2/Ar$ premix flame at $P = 0.05$ atm, $\Phi = 2.5$

flame. Meanwhile, the maximum error of the temperature distribution from Dagaut¹⁷ prediction is higher than the former over 50 K. As errors for various factors mentioned above, it is concluded that prediction result is greatly affected by gas-phase model. So it is important to select suitable mechanism and model for premixed flame chemical kinetics simulation.

Fig. 5 compares prediction values of generation H_2O concentration curves and measurement values 19-20 in $C_2H_4/O_2/Ar$ flame. Fig. 5 showed the prediction value of Dagaut¹⁷

mechanism^{15,16} is more closer to experiment than Marinov mechanism^{15,16} in area distance away from burner exit is within 9 mm and in the region remote from 9 mm, the prediction value of Marinov mechanism^{15,16} is more closer to the experimental measurements. Therefore, there are no obvious advantages both mechanisms for H_2O prediction.

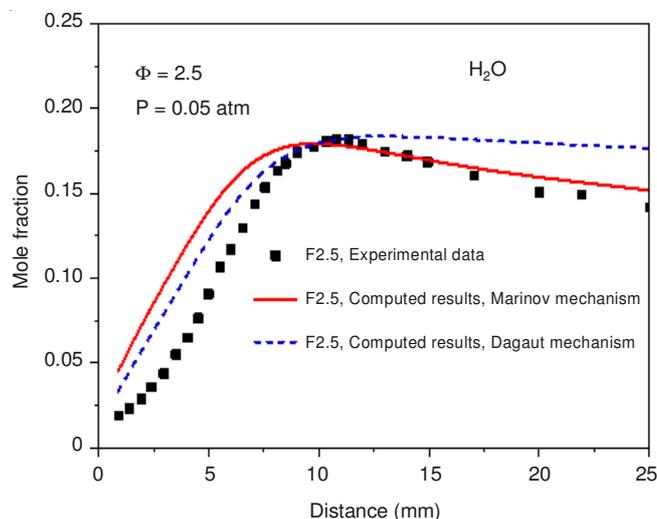


Fig. 5. Comparison of predicted H_2O concentration with the experimental data^{19,20} in the $C_2H_4/O_2/Ar$ premix flame at $P = 0.05$ atm, $\Phi = 2.5$

Figs. 6 and 7 show the comparison of concentration curves between the prediction values of CO , CO_2 , C_2H_4 , C_2H_2 and the measured values^{19,20} in $C_2H_4/O_2/Ar$ flame at $P = 0.05$ atm, $\Phi = 2.5$. As can be seen from Figs. 6 and 7, the prediction values are consistent well with experimental values. In comparison, the prediction value for Marinov mechanism^{15,16} is closer to experimental value than Dagaut¹⁷ mechanism. Of course, Marinov prediction^{15,16} is not totally matched with measured value especially prediction of CO_2 and C_2H_4 for the reason of uncertainty of experiment²⁰, the absence of some species in model and boundary conditions.

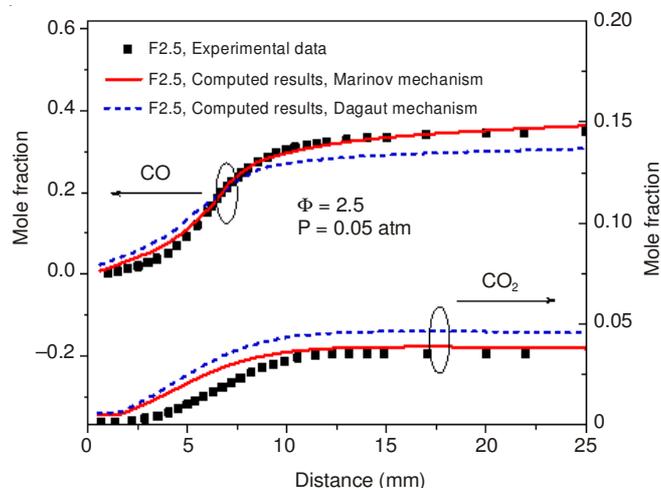


Fig. 6. Comparison of predicted H_2O , CO_2 concentration with the experimental data^{19,20} in the $C_2H_4/O_2/Ar$ premix flame at $P = 0.05$ atm, $\Phi = 2.5$

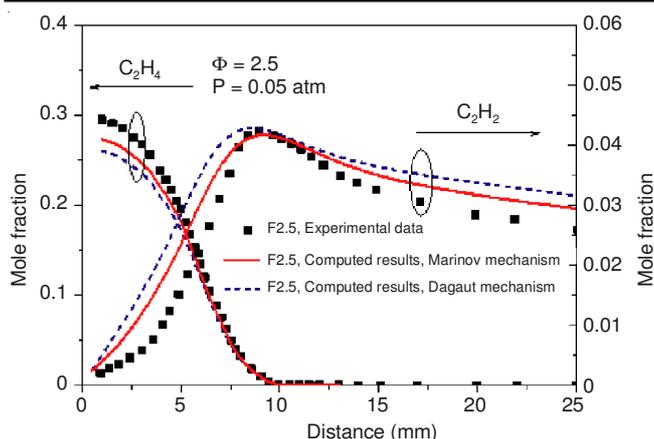


Fig. 7. Comparison of predicted C_2H_4 , C_2H_2 concentration with the experimental data^{19,20} in the $C_2H_4/O_2/Ar$ premix flame at $P = 0.05$ atm, $\Phi = 2.5$

Fig. 8 shows the maximum mole fractions of some C_3 - C_{10} (C_3H_3 , C_6H_6 , C_6H_6O , C_8H_8 , $C_{10}H_8$) species in $C_2H_4/O_2/Ar$ flame at $P = 0.05$ atm, $\Phi = 2.5$. The simulated maximum concentrations both are consistent with experimental data well^{19,20}. However, the regularity is not obvious for comparison the similarities and differences between the prediction values for two mechanisms and the experimental data. The maximum concentration of C_3H_3 , C_6H_6 and C_8H_8 by Marinov prediction^{15,16} is closer to experiment, while Dagaut mechanism¹⁷ predicted C_6H_6O and $C_{10}H_8$ are closer to the experimental measurements. Therefore, rules and conclusions are concluded: The advantages and disadvantages of intermediates prediction for C_6H_6 above between the two models will no longer evident. The main reasons are: System error for experimental measurements and macromolecular intermediates test uncertainty; Absence of some important species and reactions in mechanism; Impact of boundary conditions during the simulation. So, modeling study macromolecules intermediates and soot generated paths will be continuous.

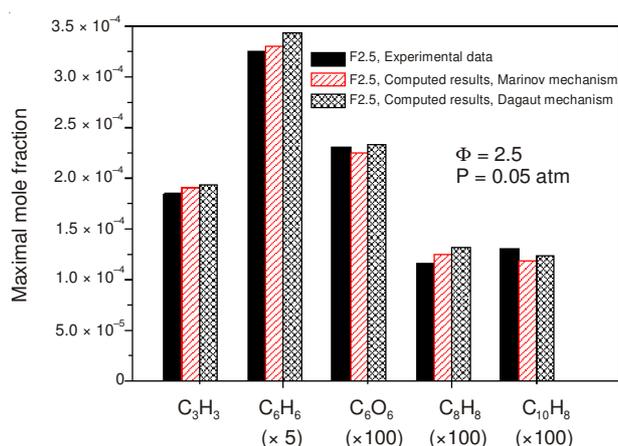


Fig. 8. Comparison of predicted maximal concentration of C_3 - C_{10} species (C_3H_3 , C_6H_6 , C_6H_6O , C_8H_8 , $C_{10}H_8$) with the experimental data^{19,20} in the $C_2H_4/O_2/Ar$ premix flame at $P = 0.05$ atm, $\Phi = 2.5$

Conclusions

A chemical kinetics modeling for formation of potential soot precursors (such as benzene, polycyclic aromatic hydrocarbons *etc.*) in laminar premixed ethylene is reported. The

kinetic modeling results are compared against molecular-beam mass spectrometry (MBMS) data by Musick and Vandooren¹⁸⁻²⁰. Through the above simulation study and validation, the following conclusions are concluded:

- The prediction value for temperature and experimental results are in good agreement in $C_2H_4/O_2/Ar$ premixed flames, indicating that the choice of kinetics simulation methods is reasonably practicable.

- The prediction values of some small molecular components (H_2 , C_1 - C_2) for Marinov mechanism¹⁵⁻¹⁶ are in good agreement with experimental data at simulated conditions of this paper. Prediction of soot precursors for C_6H_6 above macromolecular, the merits of prediction for Marinov mechanism^{15,16} and Dagaut¹⁷ mechanism are no longer apparent. Therefore, modeling study macromolecular intermediates and soot generated paths will be an ongoing process.

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