Experimental and Theoretical Investigation of Low Temperature PAH and Soot Formation on Hydrocarbon Flames

B.A.Urmashev, T.T.Mashan, B.Ya.Kolesnikov, Z.A. Mansurov
Al-Farabi Kazakh State National University
Almaty, Kazakhstan
Mansurov@lorton.com

Abstract

This paper presents the study of polycyclic aromatic hydrocarbons (PAH) and soot formation in cool sooting flames of methane and propane in a separately-heated two-sectional reactor under atmospheric pressure at the reactor temperatures of 670-1170 K. The temperature profiles of the flames were studied. The sampling was carried out with a quartz sampler and the samples were frozen with liquid nitrogen. A number of polyaromatic hydrocarbons such as pyrene, fluorantene, coronene, anthantrene, 1,12-benfherylene, were identified by spectroscopic methods in the extract of soot. Is offered numerical model of formation PAH at burning of methane. The accounts kinetics of burning of methane on a basis of kinetics scheme was executed. For accounts previously were designed a molar heat of formation of intermediate connections and are picked up kinetics of elementary constant reactions.

Introduction

The study of a structure of soot formation flames gives the valuable information on chemical and physical processes occurring up to and in time of soot formation. Kinetics investigation at hydrocarbon combustion is of great scientific and practical interest, in particular in connection with the problems of protection of the environment from the products of incomplete combustion in petrol and diesel engines.

In spite of the great number of investigations of hydrocarbon combustion now, there is no complete studying in the field of low-temperature soot formation (900-1200 K). The obtaining of soot, technical carbon (TC) can serve as a one of the ways of natural gas processing, degree of which utilization now insufficiently full. As is known [1] the field of cool flames covers a temperature region from 500 to 800 K for long-chain hydrocarbons and 800-1200 K for methane. On the upper temperature boundary of cool flames is frequently observed the soot formation, but in connection with difficulty of studying of such flames it is possible to leave the soot formation region by changing of experimental conditions. At the same time the soot formation process has never been considered as the transition phenomenon between cool and hot flames, and low temperature soot formation itself has not been investigated in details.

Wagner H. et al. for the first time have entered the term "cool sooting flames" at studying of influence of pressure and temperature on soot formation in previously stirred ethylene and benzene-air flames [2]. It was shown that the low temperature threshold of soot formation exists with a high-temperature threshold of soot formation.

In [2] is underlined, that "cool sooting flames" differ from properties of hot flames and have general features with pyrolysis of aromatic compounds. Is indicated on necessity of detail study of "cool flame soot particles" for understanding of a nature and mechanism of low temperature soot formation.

On department of chemical physics of al-Farabi University per the last years the researches low temperature soot formating flames are conducted, of which the formation of a plenty PAH - up to 50 % is characteristic. The large experimental material [3,4] is accumulated. The research of the indicated mode has large significance: first of all with the purpose of clearing up of the mechanism soot formation and in particular initial it of stages - of formation PAH. Secondly it is important to underline ecological aspect of the given problem, as PAH and among them such as benz(a)pyrene, fluorantene is products of partial combustion. They are contained in fair quantities in exhaust gases of drives of internal combustion especially working on diesel fuel. Therefore for directed work on prevention of formation PAH the knowledge of the mechanism of their formation is necessary. Thirdly, PAH, derivated for want of burning by rich fuel flames represent valuable chemical materials exhibiting liquid-crystal properties. The aim of this work are experimental and numerical simulation of PAH and soot formation.

Experimental

In the present work the results of investigations of low temperature, so-called "cool flame" soot formation being the transition phenomenon between cool and hot flames are given. The description of the reactor and the methodics of experiment and data on identification of polycyclic aromatic hydrocarbon (PAH) at low temperature soot formation in rich methane and propane flames, appropriate to the upper temperature border of cool flames are given in [5].

Discussion of results

The data on extraction of soot, formed from a flame of methane and propane are given in Table 2. From which it is visible, that if the greatest quantity PAH in methane soot is equal 22,31 %, in propane soot is equal 50,25 %. Besides from the table it is visible, that the reactor temperature when the maximum content of PAH is observed was lowered on 100 K at significant decreasing of T_1 at transition from a methane flame to a propane flame. The considered data allow to assume, that in a regime of low temperature methane and propane combustion the precursors of soot are PAH.

The temperature profiles in Fig. 1 are taken on length of the second section of the reactor at combustion of methane (T_1=773 K, T_2=973 K) and propane without benzene and with the benzene addition at T_1=423 K and T_2=923, 973 K. For methane-oxygen mixture, as it is visible, there is a brightly expressed maximum at 1273 K. It is established that at low temperature soot formation there is a threshold maximum flame temperature which is not depends on the temperature of the second section of the reactor, that is possible shows the existing of limiting stage in a combustion regime at soot formation.

Table 2

Soot extraction results of the low temperature methane and propane combustion

The extracted soot mass - 1g

Feed rate of CH_4 - 2000 cm^3/min, C_3H_8 - 1600 cm^3/min

Sample number	Feed rate of O_2, cm^3/min	T_1, K	T_2, K	Dry residue mass (CO), mg	Dry extract yield, %
Methane 1	1150	823	873	223,1	22,31
Methane 2	1150	823	973	214,0	21,40
Methane 3	1150	823	1023	177,4	17,74
Methane 4	1400	298	298	301,5	30,15
Propane 5	2450	423	773	502,5	50,25

Propane 6	2450	423	873	410,2	41,02
Propane 7	2450	423	973	220,0	22,00

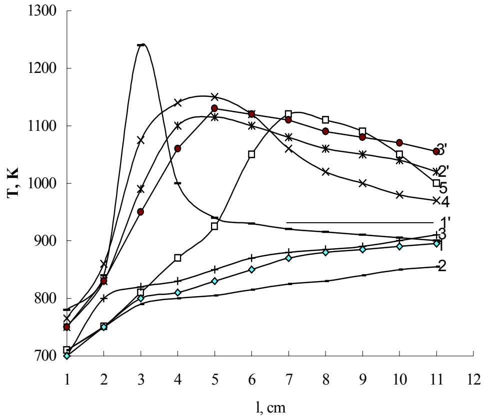


Fig. 1. Temperature profiles of methane flame T_2=973 K: 1 - in the inert medium; 1' - in the flame; of propane flames: in the inert medium 2 - T_2=923 K, 3 - T_2=973 K; in the flame 2' - T_2=923 K, 3' - T_2=973 K; of propane flames with the 5 % of benzene additions 4 - T_2= 923 K, 5 - T_2= 973 K.

Low temperature formation of PAH

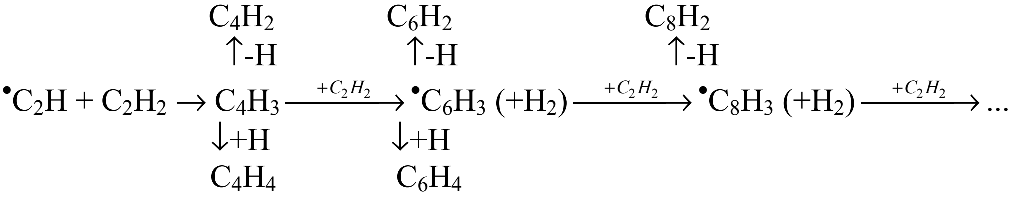
Soot formation is characteristic for rich hydrocarbon flames . Many contributors consider as the precursors of soot of particles being polycyclic aromatic hydrocarbons (PAH) [6].

Homan and Wagner observed in a diffusion flame of acetylene with oxygen two such as polyaromatic molecules:

1) polycyclic aromatic junctions without side circuits: naphtalyne, acetnaphtalyne, coronene, phenantrene;

2) Polycyclic aromatic junctions with side circuits (molecular mass from 150 up to 500 a.u.).

In a zone intensive soot formation it is possible to select one more large group of molecules -polyacetylenes, which act as intermediate substances in formation of polyaromatic junctions. Homan has offered a model of polyacetylene formation represented by the scheme:



$$\begin{array}{ccccccc}
 & C_4H_2 & & C_6H_2 & & C_8H_2 & \\
 & \uparrow\text{-H} & & \uparrow\text{-H} & & \uparrow\text{-H} & \\
{}^\bullet C_2H + C_2H_2 \rightarrow & C_4H_3 & \xrightarrow{+C_2H_2} & {}^\bullet C_6H_3\ (+H_2) & \xrightarrow{+C_2H_2} & {}^\bullet C_8H_3\ (+H_2) & \xrightarrow{+C_2H_2} \ldots \\
 & \downarrow\text{+H} & & \downarrow\text{+H} & & & \\
 & C_4H_4 & & C_6H_4 & & &
\end{array}$$

With the help of thermochemical group method the power of transformations some PAH was appreciated and because of obtained datas the constants of an equilibrium between PAH and H_2 and C_2H_2 are designed. For first six products following scheme of transformations was given to path of responsepolymerisation of PAH [4,7].

Earlier for want of study low temperature combustion the rich fuel flames observed soot formation with the high contents PAH [4,7]. Owing to complexity of process soot formation PAH large role the method of mathematical simulation of chemical processes in soot formation flames can play. Besides the important problem is the in-depth research thermochemistry and kinetics of all reacting substances in zone soot formation and evaluation of thermodynamic stability of these substances in researched conditions of combustion[8].

Method of mathematical simulation in the description of chemical processes

The simulation can be presented as a procedure of construction of the mathematical description of process, i.e. model, because of experimental outcomes. The mathematical description of a model has a kind [9,10]:

$$\vec{\eta} = \vec{f}(\vec{\varepsilon}, \vec{\theta}), \tag{1}$$

where $\vec{\varepsilon}$ - vector composed from m of controlled variables $\varepsilon_1, \varepsilon_2, ..., \varepsilon_m$; $\vec{\theta}$ -vector from *p* of parameters (or expected magnitudes); $\vec{f}$ – vector from *l* functions.

Consider only usual differential equations of a kind:

$$\frac{dS}{dt} = \vec{h}(t, \vec{S}, \vec{\varepsilon}, \vec{\theta}). \tag{2}$$

With the entry conditions $\vec{S}(t=0) = \vec{S}(\varepsilon)$, where t - Time, past from a beginning of a response; $\vec{S}$ – vector of variables (for example, concentration, pressure, temperature), analog, circumscribing a condition; $\vec{h}$ – vector of function.

The heat of formation $\Delta H^0_{f\,T}$ is determined, as a modification of an enthalpy for want of by constant to temperature in a response of formation of substance from elements in their standard condition. In such scheme of a response is accepted, that the elements originally are at the temperature of responses, pressure 1 a. Usually there is no necessity to know heats of formation of elements, since for want of account of a standard heat of a response, owing to preservation of atoms, the heats of formation of all elements compensate one another.

Accounts of thermochemical performances of individual hydrocarbon

The accounts were conducted as follows: in the beginning on a Bensons method the significance's of molar thermal capacities for junctions were designed which participate in chemical responses of burning of methane, for want of various temperatures (298, 300, 400, 600, 800, 1000 K).

Then the molar thermal capacities are approximated by a polynomial of the sixth degree from temperature:

$$C_{pj} = a_0 + a_1 T + a_2 T^2 + ... a_6 T^6. \tag{3}$$

The integration of the equation (3) results in expression for a molar heat of formation

$$\Delta H_j = A_I^j + \Sigma A_K^j Z_K, \tag{4}$$

where Zк = Tк/1000.

Main purpose of kinetic simulation of processes of burning of hydrocarbon is the creation of trial mechanisms with a minimum quantity of responses, which allow more precisely to explain flowing past processes. Those responses in most cases are resulted only, which velocities can be important for simulation of processes.

For analysis the recent direct measurements of constants of a velocity of elementary responses were considered. The outcomes obtained for want of mathematical simulation of complicated systems, are considered then, when is indicated, that the sensitivity to a selected elementary response is rather high, or when there is no direct measurements.

For low temperatures (400-420K) practically is not observed of modifications of concentration of methane and oxygen, that testifies to absence of process of burning. For want of temperatures the modification of concentration of fuel and oxygen is higher 500 To is observed, the accumulation of intermediate products - ethane, acetylene, water, oxide of carbon, dioxide of carbon etc happens. It is necessary to mark, that for want of significance's of a preexponential factor, smaller, than is indicated above, and high temperatures the elementary responses of PAH formation in the kinetic scheme do not result in some their noticeable accumulation.

The outcomes of simulation are confirmed by experimental data [11]. The experiments with a propane-oxygen mixture were conducted for want of atmospheric pressure for want of modification of temperature from 500 K to 800 K a for want of ratio fuel - oxidizer from 1:1 up to 2:1.

On the basis of the analysis of the literature and experimental data the possible scheme of cool flame soot formation is considered:

The diffusion from a zone of combustion in preflame field of atoms H and e-
↓
The formation of radicals, ions of ethane and ethylene
↓
The growth of radicals, ions, the formation of acetylene, propylene, hexane, benzene, substitute benzene, carbens on the basis of olefines.
↓
The formation of PAH
↓
The coagulation of PAH including of ions in soot

References

1. Shtern V.Ja. The mechanism of oxidation of hydrocarbons in a gas phase. AS USSR, 1960. 493 p.
2. Bohm H., Hesse D., Jander H., Luers B., Pietscher J., Wagner H.Gg., Weiss M. *22-nd Symp. (Int). on Combustion*, 1988. P. 403-411.
3. Z.A. Mansurov, G.O. Turesheva, V.I. Pesterev etc. A research of formation of polycyclic aromatic hydrocarbon for want of low temperature combustion of propane. // Petrochemistry, 1990, V. 31, N 1, P.P. 98-101.
4. Z.A. Mansurov, B.K. Tuleutaev, V.I. Pesterev etc. Use of polyaromatic hydrocarbon - products of low temperature combustion of methane. // Petrochemistry, 1989, V. 28, N 2, P. 188.
5. Mansurov Z.A. Combustion. Detonation. Shock Waves. *Proceeding of the Zeldovich Memorial*, M., 1994. V. 2. P. 51-54.
6. P.A. Tesner, Formation of carbon from hydrocarbon of a gas phase. M.: chemistry 1973, P. 135.
7. Z.A. Mansurov, B.K. Tuleutaev, V.T. Popov // Physics of burning and explosion, 1991, N1, P. 42.
8. Gardiner, Chemistry of burning, M.: Ed. “Mir” 1988, P. 72.
9. M. Frenklach, Simulation of kinetic processes. // Chemistry of burning, M.: Ed. “Mir” 1988, P.374.
10. J.Warnatz, U.Mass, R.W.Dibble, Combustion // Springer-Verlag, Heidelberg, 1996 and 1999, 209 p.
11. H. Bockhorn, Soot Formation in Combustion // Springer-Verlag, Berlin, 1994, p. 74.