

Lecture 14. Phenomenology of low temperature soot formation

The purpose of the lecture: consideration of the phenomenology of the soot formation process, differences in the mechanisms of the processes of low and high temperature soot formation.

Expected results: students mastering the knowledge of phenomenology, the differences in the mechanisms of the processes of low and high temperature soot formation.

The region of cold flames, as you know, covers the temperature regime from 500-800 K for long-chain hydrocarbons and 800-1000 K for methane. At the upper temperature limit of cold flames, soot formation is often observed, but due to the difficulty of studying such flames, changing experimental conditions, one can always exit the soot formation mode. At the same time, soot formation was never considered as a transitional phenomenon between cold and hot flames, and low-temperature soot formation itself was not studied in detail. A method has been developed for the production of olefins during cold-flame oxidation of butane, and it is noted that the process is complicated by the formation of soot at the upper temperature boundary of cold flames.

When studying the cold-flame oxidation of a propane-oxygen mixture in a 1:1 ratio, starting from 720 to 800 K, an oscillation mode of oxidation is observed, accompanied by soot emission. With an increase in the proportion of propane in the mixture at a propane: oxygen ratio of 2:1 in the temperature range 723-768, carbon black significantly increases. Analysis of gaseous products shows that in the soot formation mode, the concentration of ethylene in carbon monoxide increases by 3-4 times compared with the regime where soot formation is not observed and this is only 27° when the temperature of the reactor is increased. Although the reason for soot formation was not specifically considered, however, from comparison oxidation products, we can assume a certain relationship between carbon black emission and an increase in the concentration of ethylene and carbon monoxide with a possible change in the conversion mechanism with a slight increase in the temperature actor.

The given example is, apparently, one of the few cases when soot formation is observed at such low temperatures.

To date, there is no complete understanding in matters of nucleation, the growth of soot particles. An analysis of the literature shows that many researchers consider polycyclic aromatic hydrocarbons (PAH) as precursors to soot nuclei.

So, Homan and Wagner observed in the diffusion flame of acetylene with oxygen of type 2 polyaromatic molecules:

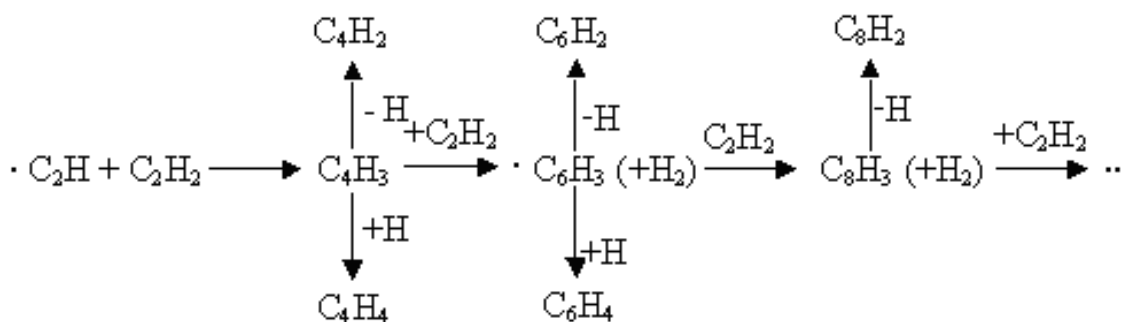
1) polycyclic aromatic compounds without side chains: naphthalene, acenaphthalene, coronene, phenanthrene;

2) polycyclic aromatic compounds with side chains (molecular weight from 150 to 500 atomic units).

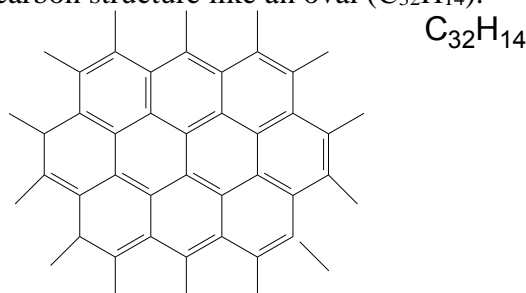
The concentration of polyaromatic compounds of the first group practically did not change in the soot formation zone, while the concentration of PAH of the second group increased sharply.

In the same work, the authors found that PAH without side chains, taken directly from the flame, are identical to those extracted from carbon black samples taken at a certain distance from the oxidation zone.

In the zone of intense soot formation, one more large group of molecules can be distinguished - polyacetylenes, which act as intermediates in the formation of polyaromatic compounds. Homan proposed a model for the formation of polyacetylenes, represented by the following scheme:



However, this path alone cannot lead to the formation of soot, since - soot is not a large linear chain, but some polycyclic carbon structure like an oval ($\text{C}_{32}\text{H}_{14}$).

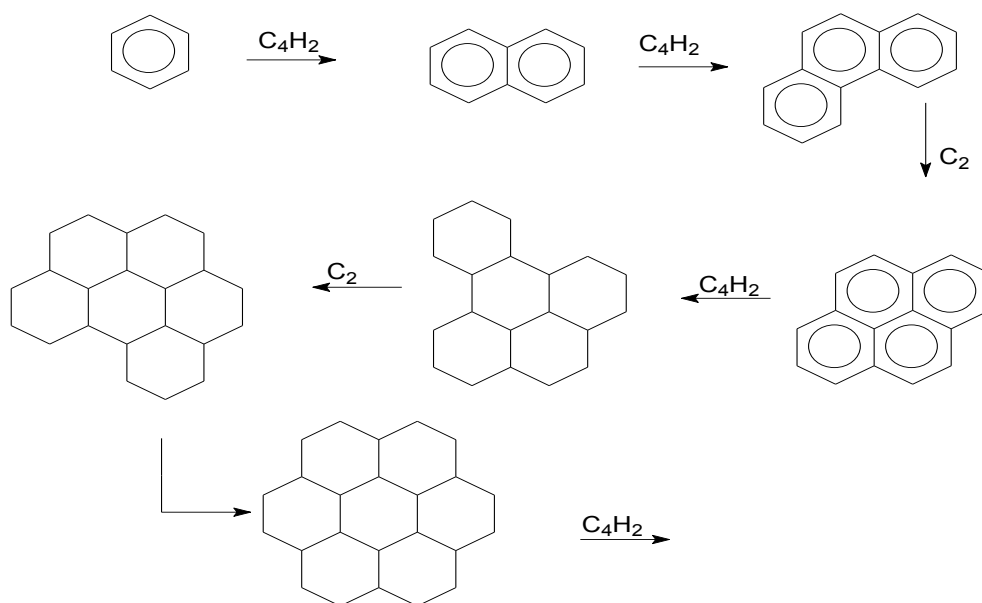


In addition, soot is formed almost instantly, and the transition of polyacetylene into an aromatic-graphite-like structure is a slow process.

Studying the pyrolysis of aromatic hydrocarbons in a shock tube, Graham and colleagues found a decrease in the rate of soot formation above 1800 K, while at a temperature of less than 1800 K this rate rapidly increased with increasing temperature.

The first way is quick, it leads to an increase in soot yield in the temperature range up to 1800 K. With a further increase in temperature, the destruction of aromatic rings leads to a decrease in the concentration of precursor molecules and, as a consequence, to a decrease in the network yield.

Using the thermochemical group method, the energetics of transformations of some PAH were estimated and, based on the data obtained, the equilibrium constants between PAH and H_2 and C_2H_2 were calculated. For the first six products of the most thermodynamically favorable polymerization reaction path, the following conversion scheme was given.



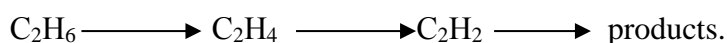
The designations C_2 and C_4H_2 should be understood as symbols denoting the number and type of atoms attached at each polymerization step, but not as chemical reagents. An important result of this work was the conclusion about the presence in the homogeneous equilibrium system at a temperature of more than 1700 K of some "critical" highly condensed PAH that have a minimum concentration over a wide range of varying external conditions. The consequence of this conclusion is the conclusion that there is a thermodynamic barrier to the processes of soot formation in a high-temperature homogeneous system.

According to the calculation results, polyacetylenes and PAH had the highest equilibrium concentrations, which is consistent with experimental data. The ratio between the hydrocarbon concentrations of these two classes depends on the ratio of the partial pressures of acetylene and hydrogen: at $P_{H_2}/P_{C_2H_2} > 1$, PAH are more stable, and at $P_{H_2}/P_{C_2H_2} < 1$ - polyacetylenes. Such an analysis of the stability of products allows you to get only a qualitative assessment of the situation.

The role of reactive macromolecules as intermediates has been confirmed by the study of pre-mixed benzene-oxygen-nitrogen flames. PAH in this case is formed in an amount 100 times larger than from aliphatic fuels. Their maximum concentration is found in the oxidation zone. The relative concentration of each of these substances is very close to the concentration in the acetylene flame.

Long and his colleagues studied the conditions for the formation of PAH directly in hydrocarbon flames. The amount of substances soluble in chloroform (SSC), the amount of PAH and the carbon residue (CR) were determined depending on the ratio of components in oxygen-nitrogen and oxygen-argon mixtures. An increase in the oxygen content in the mixture leads to an increase in temperature with a corresponding increase in soot formation to a certain value.

The number of PAH decreases, and the number of CR increases. The authors attribute this to the combustion of polyaromatics, which are in association with soot. The most optimal temperature for the formation of PAH should not exceed 978 K. From the results it can be seen that a decrease in the number of PAH is accompanied by an increase in CR and it can be assumed that the latter arises from the former. When studying the effect of the addition of hydrogen to the ethylene-air mixture, R. Long established that the composition of the carbon black obtained was close to that of the ethane flame (the composition of the PAH is the same in both carbon blacks). Most likely, in the pre-flame zone, pyrolysis gives the following sequence:



Thus, it was shown that acetylene plays a significant role in the formation of soot, and probably in the formation of PAH.

As follows from the foregoing, soot formation during the combustion of hydrocarbons occurs over a wide temperature range, and soot formation conditions can be conditionally divided into low-temperature and high-temperature. Accordingly, the formation mechanisms in these two modes will be somewhat different. The complexity of the soot formation process, the variety of elementary stages simultaneously proceeding, have also led to a significant number of soot formation mechanisms that can be grouped by the leading active intermediate: radical, ionic, and carbene mechanisms.

Of the radical mechanisms, the most developed and strict ones are polyacetylene and polyaromatization, but here, with a more thorough analysis, serious difficulties arise. Firstly, with regard to the polyacetylene theory, cyclic structures should be formed from linear particles and this should entail molecular rearrangements, including significant entropy changes. In addition, the reaction of the addition of free radicals will inevitably lead to a decrease in the degree of conjugation in a unsaturated molecule and, as a result, the lifetime of particles of high molecular weight is not enough for the ring to close into an aromatic structure. It should be noted the work of Kalls to study the reaction rate of the C_2H radical, where it was shown that the growth of polyacetylenes is not fast enough to explain the almost instantaneous formation in the flame. Most

PAH found in flames are condensed with very low reactivity, while PAH with side chains will disappear very quickly.

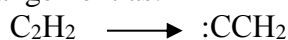
Thus, neither radical nor molecular mechanisms can fully explain the nucleation phase in the process of soot formation. Therefore, the attention of researchers was directed to other types of mechanisms. One of them is the ionic mechanism. Despite the fact that ions have long been discovered in gas flames, until recently they were considered nothing more than a scientific curiosity and products of insignificant side reactions. Calcote suggested and developed the ionic mechanism of the formation of soot nuclei, where the formation of the primary $C_3H_3^+$ ion occurs by the reaction:



Ions of larger sizes are obtained by attaching polyacetylenes to the primary $C_3H_3^+$ ion. It should be noted that the highly excited CH^* radical was not observed experimentally. In addition, the possibility of the formation of a large number of soot nuclei through one channel seemed difficult to explain.

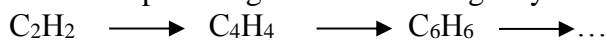
A common drawback of the radical and ionic mechanisms is the fact that the C/H ratio in molecules - the precursors of carbon black nuclei, has been steadily increasing from the very beginning of the process, while up to a certain point in time this ratio is close to 1. In addition, they explain how is the very fast transformation of the pyrolysis products into cyclic molecules carried out.

Of great interest is the mechanism based on carbene reactions. Introduction to the soot formation mechanism of particles such as carbenes, whose high reactivity due to two paired electrons can explain the rapid onset of cyclic molecules and the development of the process. Carbenes are formed as a result of rearrangement of hydrogen atoms in a hydrocarbon molecule. The activation energy of such a rearrangement as:



is 150-180 kJ/mol, which is close to the experimentally observed activation energy of C_2H_2 pyrolysis. Carbenes are non-activationally introduced into the π bond, forming unstable polycyclic structures with an activation energy of ~ 40 kJ/mol in the C-H bond.

The process goes the following ways:



or $C_2H_2 \longrightarrow C_4H_4 \longrightarrow C_4H_2 \longrightarrow C_6H_4$, where C_4H_4 , C_6H_6 , C_4H_2 , C_6H_4 - groups of isomer molecules. The formation of a large set of products characterized by the same molecular formula, but also differing in structure, is a characteristic feature of reactions involving carbenes.

Based on the general scheme of the mechanism of C_2H_2 pyrolysis, the following main types of reactions constituting it can be distinguished:

1. rearrangement reaction;
2. reaction of carbenes incorporation into π and δ bonds;
3. cyclization reactions;
4. hydrogen cleavage reaction.

These reactions are considered on the example of various groups (C_4H_4 and others).

In the framework of this mechanism, the time and temperature conversions of acetylene and the yields of some cyclic products were calculated. The calculated kinetics obtained is in good agreement with experimental data on acetylene pyrolysis.

Thus, the introduction of carbenes into the mechanism makes it possible to ensure a multi-channel process of the formation of carbon black nuclei and to obtain a set of isomer molecules with a C/H ratio close to 1.

The formation mechanism of PAH, the precursors of soot particles, can be divided into two stages.

In the first stage, methane oxidation reactions proceed with the formation of olefins and acetylene, which are the main intermediate products on the way to the formation of polycyclic aromatic hydrocarbons. The second stage covers the reaction of nucleation of soot - the reaction of the formation of PAH with subsequent coagulation to soot aggregates.

In the initial stage of methane oxidation, the CH₃ radical is formed. In addition, methane also reacts with the formed H, O atoms. The resulting CH₃ radical reacts with the O atom, which leads to the formation of formaldehyde, which reacts with the active centers of H, O, OH with the formation of CH₂O and CO. In methane-rich flames, the proportion of CH₃ radical recombination reactions increases, resulting in the formation of C₂ hydrocarbons. The interaction of ethane with H, O, and OH radicals leads to the formation of C₂H₄ and C₂H₂. The formation of benzene and naphthalene, the simplest aromatic compounds, is possible through the following channels:



The complete reaction mechanism of methane combustion leading to the formation of PAH consists of 68 reactions.

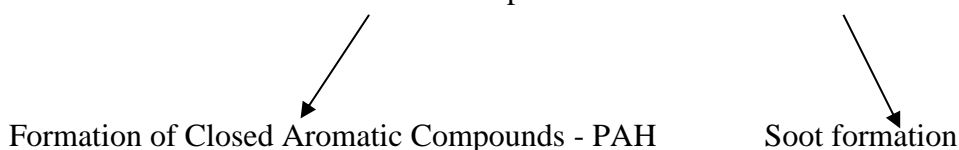
The time and temperature profiles of the components were obtained with the formation of benzene and naphthalene close to times of the order of (10⁻⁴–10⁻⁵ s), which is consistent with the characteristic time of initiation of nucleation during gas-phase pyrolysis of hydrocarbons. It is shown that the process of formation of PAH occurs in two stages:

- 1) the formation of radicals and precursor molecules of PAH;
- 2) the addition of vinyl and butadiene radicals to acetylene with the formation of the first aromatic ring.

It was established that, in contrast to the high-temperature regime, in which reactions with high activation energies predominate, in the low-temperature combustion zone, reactions with activation energy rate constants which do not exceed 10-15 kcal/mol play a decisive role. Low-temperature soot formation is characterized by the formation of a large amount of PAH in the form of final products, while at high temperatures, their concentration decreases sharply due to both their attack by H and O atoms and the reactions leading to their coagulation and conversion to soot aggregates.

Based on an analysis of the literature data on the composition of the products of combustion of hydrocarbon flames and the experimental data obtained on the formation of PAH and soot temperature profiles in methane and propane flames and the results of methane combustion in an electric field, the following qualitative model for the formation of PAH and soot in rich hydrocarbon flames is proposed:

1. hydrocarbon conversion in oxidation reactions with the formation of hydrocarbon radicals, hydrogen atoms. Diffusion from the combustion zone to the pre-flame region of H atoms and electrons.
2. formation of radicals, ions, ethane and ethylene, and acetylene.
3. the growth of radicals, ions, the formation of carbenes based on acetylene and olefins, resulting from the addition reactions to the extension of the carbon chain and subsequent cyclization with the formation of benzene and its derivatives.
4. the formation of aromatic compounds with side chains.



Literature

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2. Bockhorn H. Soot Formation in Combustion: Round Table Discussion / Ed. Heidelberg Springer Verlag, 1994.
3. Mansurov Z.A. Combustion, Expulsion and Shock Waves. Vol.48, №5, P. 561-569, 2012.