

## MAIN REACTIONS OF FREE RADICALS IN THE PYROLYSIS OF HYDROCARBONS

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### **Abstract**

*The article discusses the thermal transformations of hydrocarbons during pyrolysis, the conditions for the formation of free radicals and the main reactions occurring in their environment.*

### **Key words**

*gas industry, olefins, pyrolysis, pyrogas, pyrocondensate, pyrodistillate, pyrolysis resin, conversion, selectivity.*

The raw material base of the organic synthesis industry is closely related to the structure of the fuel and energy balance of individual countries and regions. The appearance of coal in this balance formed the raw material base for the production of chemical products and the production of acetylene at coke plants.

With the transition of energy and transportation to the convenient use of oil and gas in most industrial processes, acetylene is being replaced by the petrochemical ethylene, and the source of aromatic hydrocarbons has changed from coke production to the oil refining industry.

Currently, the process of thermal pyrolysis of gasoline with water vapor in tube furnaces has become widespread in the global petrochemical industry. In this case, it is necessary to ensure standard production. Here, the development of the technological production system was a constant improvement of units. The technical development of the design of pyrolysis furnace blocks was focused on the maximum yield of target products and, above all, taking into account the possibility of carrying out the process under harsh conditions (in terms of temperature and time of separation of the starting material) when producing ethylene.

To produce lower olefins, it is necessary to increase the temperature of hydrocarbon pyrolysis to 600-700 °C, and to produce ethylene, a much higher

temperature is required than to produce propylene. The upper temperature limit of the process is determined by its ability to tolerate the formation of acetylene in small quantities.

The process of thermal decomposition of hydrocarbons is sequential and consists of simultaneous reactions of many elements.

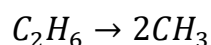
- In the first stage, the primary reactions of thermal decomposition of alkanes and cycloalkanes proceed with the formation of olefins, diolefins and alkanes with the same or less number of carbon atoms than the original hydrocarbons, and even hydrogen.

- Olefins and diolefins formed in the second stage undergo dehydrogenation reactions followed by decomposition and condensation to form unsaturated alkyls (cyclopolyenes) and aromatic hydrocarbons.

- At the next stage of the reaction, increasingly complex polynuclear aromatic hydrocarbons are obtained. As a result of the action of these compounds, hydrogen is released and partially adsorbed on the surface of the reactors, forming a solid carbon film called pyrolysis coke. After all, carbon and hydrogen can be produced in the correct order of hydrocarbons.

In industrial conditions, the pyrolysis process is carried out by combustion at atmospheric pressure or at pressures several times higher than atmospheric pressure, and at a temperature of 1000-1500 K. Under such conditions, the breakdown of hydrocarbons occurs in the form of free radicals in the gas phase of reactions.

Free radicals can be formed from the parent hydrocarbon molecule through thermal decomposition processes, often by cleavage of the C-C bond, such as in the pyrolysis of ethane.



As a major feature of pyrolysis, the practical breaking of the CH bond can be ignored. The energy for breaking C-C and C-H bonds in an alkane molecule is not the same for all bonds due to their gender and varies somewhat depending on the structure of the molecule and the position of the bonds in it. The C-C and C-H bonds in the molecules of olefins and aromatic hydrocarbons are stronger than such bonds in alkanes. Radicals can be formed not only in monomolecular reactions, but also in bimolecular reactions.



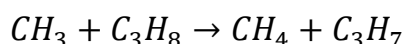
The lower the temperature and higher the pressure in the reaction system, the higher the ratio of the rates of formation of bi- and monomolecular radicals. Under

certain conditions (at low temperatures), the formation of radicals due to bimolecular reactions occurs faster than the monomolecular process.

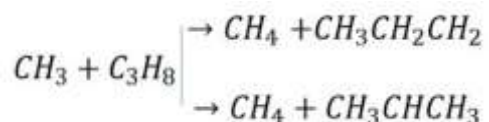
The ratio of the energies of cleavage of various C-C and C-H bonds in the affected hydrocarbon molecules determines the rate of the radical reaction in one direction or another and the amount of formation of various radicals in the overall composition of the reaction products.

The main reactions of radicals in pyrolysis reactors are discussed below.

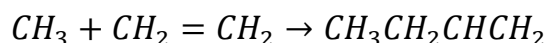
Substitution reaction (removal of a hydrogen atom), for example:



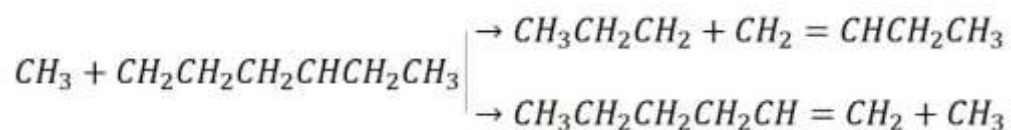
Depending on the position of the hydrogen atom in the molecule, the rate of rupture of these atoms is different due to the ratio of the activation energy of rupture, which determines the structure of the resulting radical, and the composition of the decomposition product of the molecules. Consequently, as a result of the interaction of a radical with propane, a  $C_3H_7$  radical can be formed, which is different from the free valency state:



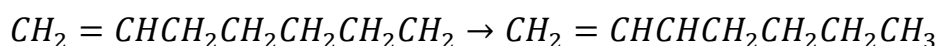
Clutch reaction. Radicals can attach to unsaturated hydrocarbon molecules with double bonds, for example:



Decomposition reaction. The direction of radical decay in b-state bonds is observed separately from the ratio of free valence to carbon atom. As a result of decomposition, an unsaturated hydrocarbon molecule and a low molecular weight radical, in particular H, are formed in front of it. For example:



Isomerization reaction. Isomerization of a radical is manifested by the intramolecular abstraction of a hydrogen atom from the active carbon atom in free valence:



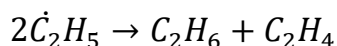
The isomerization reaction proceeds through cyclically activated complexes in an intermediate state.

Activated six-membered complexes are formed easily, while five- and seven-membered complexes are difficult to form. Activated complexes with cyclic content of other carbon atoms are difficult to form. Therefore, it is likely that the radicals of

the unbranched carbon chain will transfer to the  $n - th$  one and the carbon atoms  $(n + 4)$ ,  $(n + 5)$  and  $(n + 6)$  will become free valency.

Recombination reaction. This is a radical combination reaction, for example:  $C_2H_5 \rightarrow C_4H_{10}$ . The activation energy of the reaction is close to zero.

Disproportionation reaction. Disproportionation (redistribution of hydrogen) occurs as a result of the interaction of two olefin molecules or two radicals, for example:



The activation energy of such reactions is close to zero. However, the rate of recombination and disproportionation reactions and their role in the formation of final products are usually low, since the concentration of radicals during thermal pyrolysis is usually somewhat lower compared to the carbon molecule.

At the first stage, decomposition reactions of raw material components occur according to a radical chain mechanism. The result is products such as hydrogen, methane, ethylene and olefins, with relatively shorter carbon chains as in the feedstock components.

Secondary reactions of a relatively complex mechanism occur with the participation of products formed in the second stage. Products such as diolefins, benzene, acetylene, high molecular weight resins and coke are formed.

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