Lecture No. 3 Thermal processes of oil refining in the gas phase. Fundamentals of the theory of gas-phase thermal reactions of hydrocarbons.

The chain mechanism is radical chain
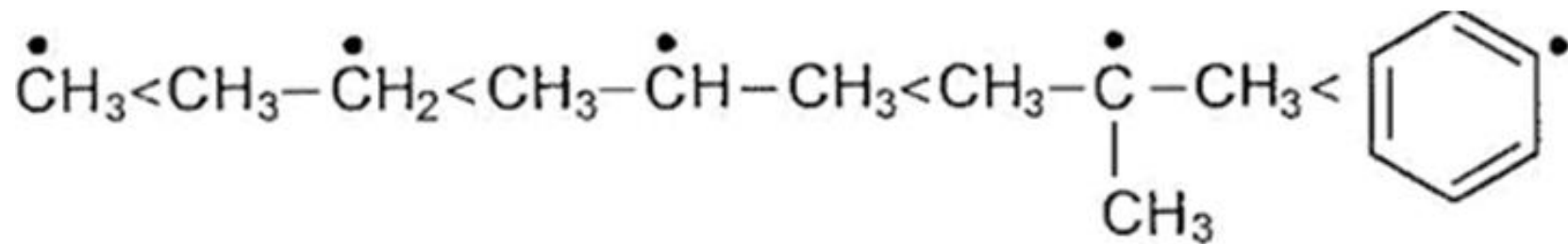
Stage 1 – Initiation

Stage 2 – Propagation

Stage 3 – Interruption

In thermal cracking processes, pyrolysis, coking, the energy required to break bonds in the molecule one of the reagents is supplied in the form of heat. Then:
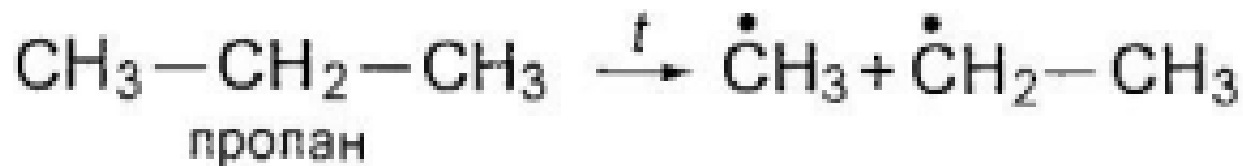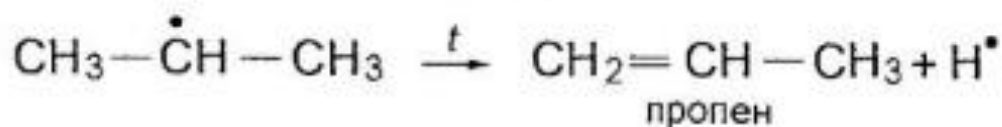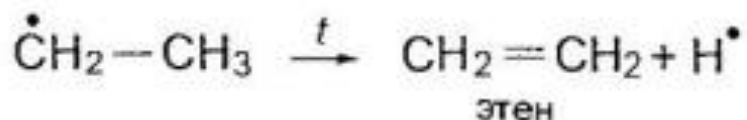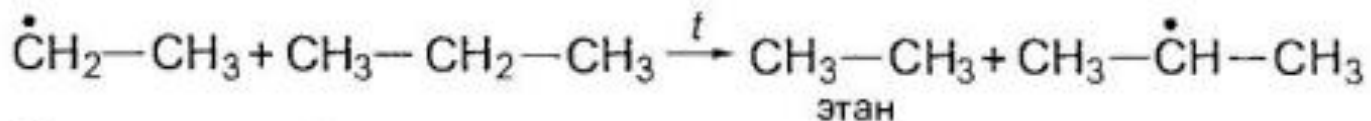
$$C_4H_{10} \rightarrow C_2H_5{}^{\bullet} + {}^{\bullet}C_2H_5.$$

Stability of radicals increases $\longrightarrow$

$$\overset{\bullet}{C}H_3 < CH_3-\overset{\bullet}{C}H_2 < CH_3-\overset{\bullet}{C}H-CH_3 < CH_3-\underset{\underset{\textstyle CH_3}{|}}{\overset{\bullet}{C}}-CH_3 < C_6H_5^{\bullet}$$

Initiation

$$CH_3-CH_2-CH_3 \xrightarrow{t} \overset{\bullet}{C}H_3 + \overset{\bullet}{C}H_2-CH_3$$

пропан

Propagation

$$\overset{\bullet}{C}H_3 + CH_3-CH_2-CH_3 \xrightarrow{t} CH_4 + CH_3-\overset{\bullet}{C}H-CH_3$$

метан

$$\overset{\bullet}{C}H_2-CH_3 + CH_3-CH_2-CH_3 \xrightarrow{t} CH_3-CH_3 + CH_3-\overset{\bullet}{C}H-CH_3$$

этан

$$\overset{\bullet}{C}H_2-CH_3 \xrightarrow{t} CH_2=CH_2 + H^{\bullet}$$

этен

$$CH_3-\overset{\bullet}{C}H-CH_3 \xrightarrow{t} CH_2=CH-CH_3 + H^{\bullet}$$

пропен

$$CH_3-CH_2-CH_3 + H^{\bullet} \xrightarrow{t} CH_3-\overset{\bullet}{C}H-CH_3 + H_2$$

Interruption

$$\overset{\bullet}{C}H_3 + \overset{\bullet}{C}H_3 \longrightarrow CH_3-CH_3$$

$$\overset{\bullet}{C}H_3 + \overset{\bullet}{C}H_2-CH_3 \longrightarrow CH_3-CH_2-CH_3$$
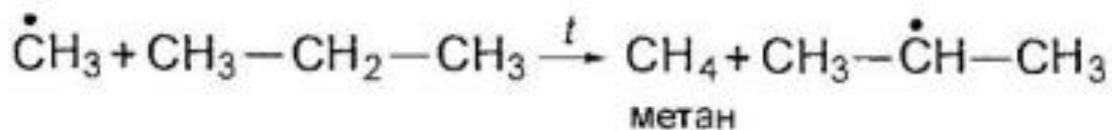
Cracking of alkanes

- **Methane cracking conditions can not be decomposed**

$$C_2H_5 \xrightarrow{700°C} C_2H_2 + 2H_2 \quad (1)$$
ацетилен

$$C_4H_{10} \xrightarrow{500°C} CH_4 + C_3H_6 \quad (0,6)$$
метан

$$C_2H_6 + C_2H_4 \quad (0,3)$$
этан

$$C_4H_8 + H_2 \quad (0,1)$$
бутен

$$C_3H_8 \xrightarrow{600°C} C_2H_4 + CH_4 \quad (0,5)$$
этен

$$C_3H_6 + H_2 \quad (0,5)$$
пропен

$$C_{10}H_{22} \xrightarrow{800°} C_5H_{10} + C_5H_{12} \quad (0,8)$$
пентен   пентан

$$C_2H_6 + C_8H_{16} \quad (0,2)$$
октен

$$C_{10}H_{20} + H_2 \quad (0)$$
декен
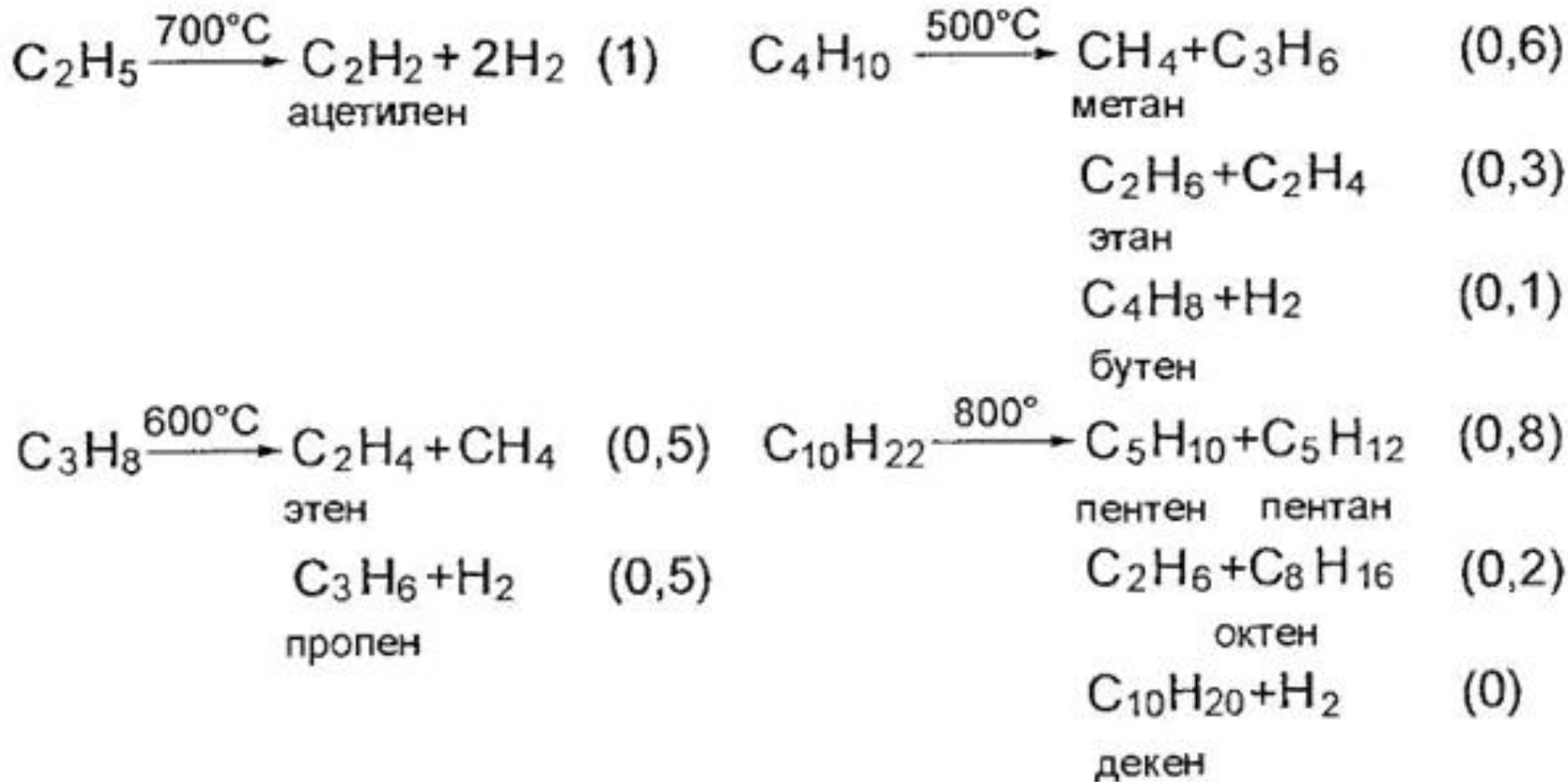
- **In parentheses is given the share of the product in this direction**

Cracking olefins

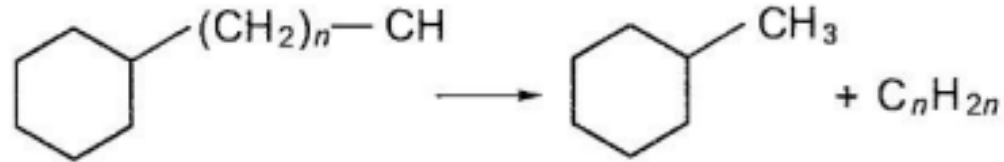Alkenes will preferably give allyl radicals of the formula:

$$H_2C{=}CH{-}CH_2{-}CH_2{-}\overset{\bullet}{C}H_2 \rightarrow C_2H_4 + \overset{\bullet}{C}_3H_5$$

or, give dienes:

$$H_3C{-}CH{=}CH{-}CH_2{-}\overset{\bullet}{C}H_2 \rightarrow H_3C{-}CH{=}CH{-}CH{=}CH_2 + \overset{\bullet}{H}$$

$$H_2C{=}CH{-}CH_2{-}\overset{\bullet}{C}H{-}CH_2{-}CH_3 \rightarrow H_2C{=}CH{-}CH_2{-}CH{=}CH_2 + \overset{\bullet}{C}H_3$$

The cyclization reaction and subsequent condensation
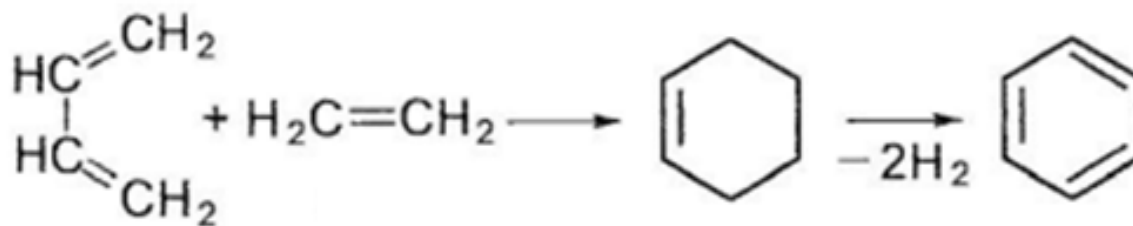
Cracking of naphthenes

- Dealkylation or shortening of the side chain paraffin:

- The dehydrogenation of naphthenic rings to form cycloolefins and aromatics;
- Partial or complete decyclization of polycyclic naphthenes after dealkylation:

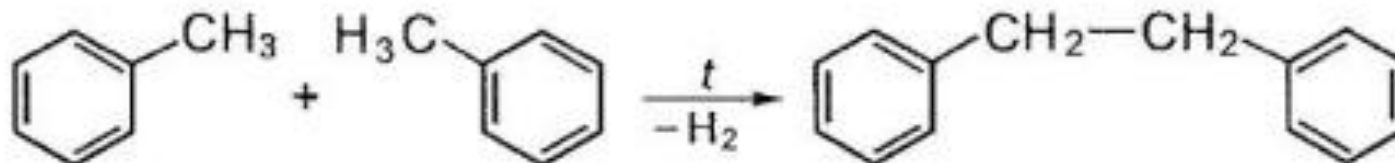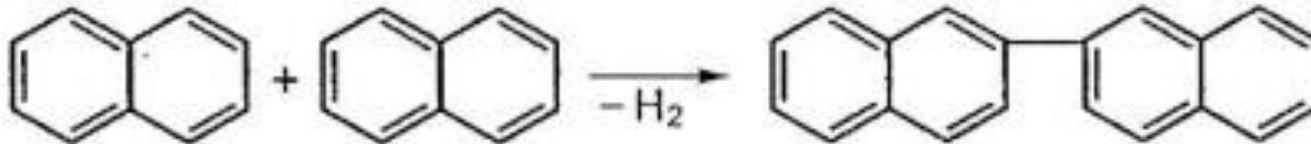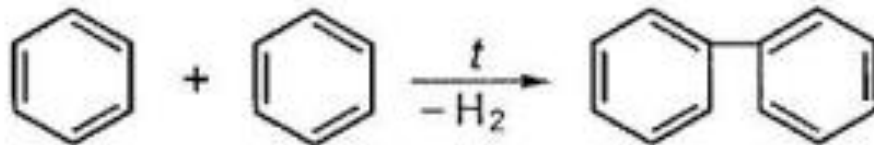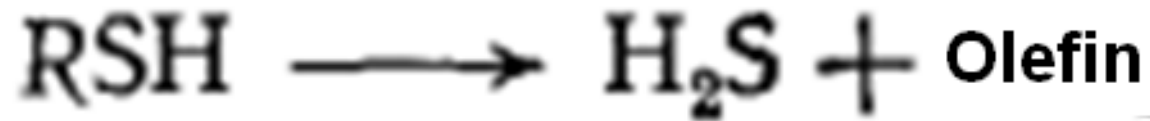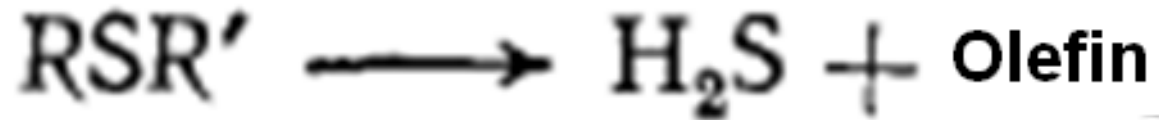- The decomposition of the monocyclic naphthenes to olefins:
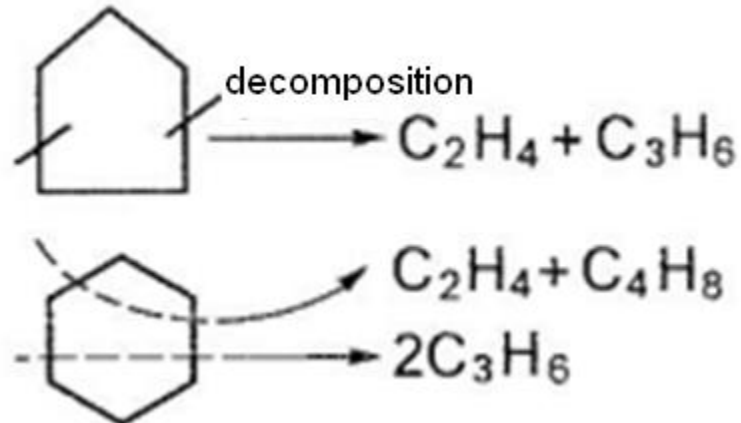
Cracking aromatics

- Dealkylation:
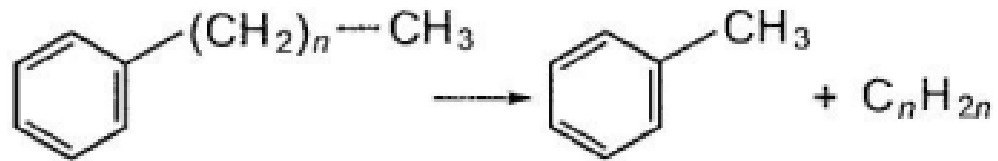
- Condensation:

Cracking of sulfur compounds

$$RSR' \longrightarrow H_2S + \text{Olefin}$$

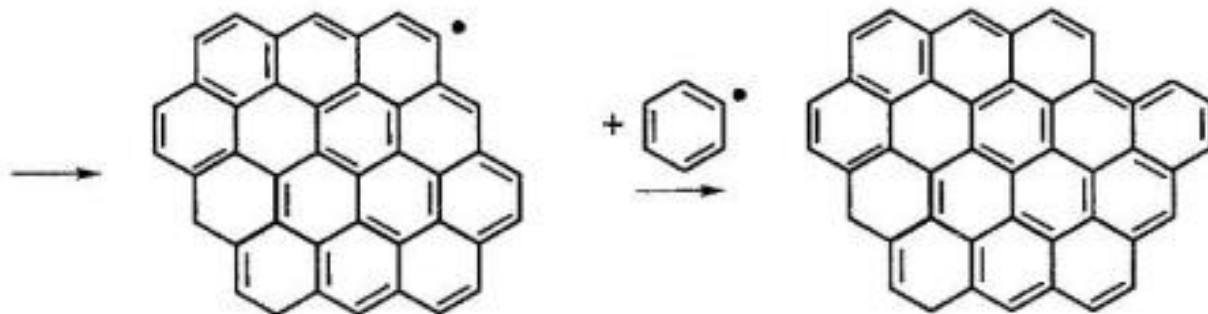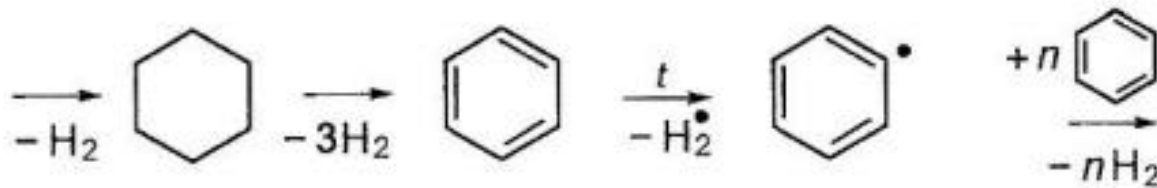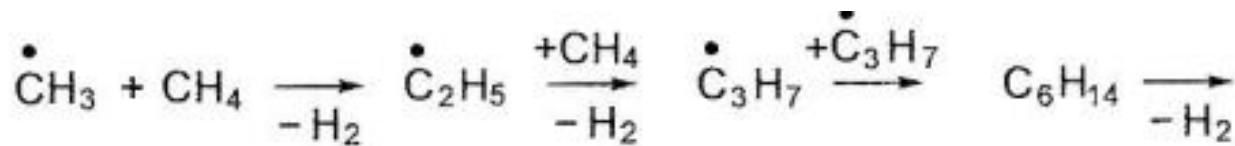$$RSH \longrightarrow H_2S + \text{Olefin}$$

Coke formation

1. Hydrogen abstraction from the hydrocarbon molecules:

$$CH_4 \xrightarrow{t} \dot{C}H_3 + \dot{H}$$

2. Interaction of the hydrocarbon radical to form heavier and stable radicals:

$$\dot{C}H_3 + CH_4 \xrightarrow[-H_2]{} \dot{C}_2H_5 \xrightarrow[-H_2]{+CH_4} \dot{C}_3H_7 \xrightarrow{+\dot{C}_3H_7} C_6H_{14} \xrightarrow[-H_2]{}$$

Under the forces of intermolecular interaction coke layers are combined into associates similar molecules associate of asphaltenes and then associates are combined into coke particles.

coke layers → coke associate → coke particles → Structure coke
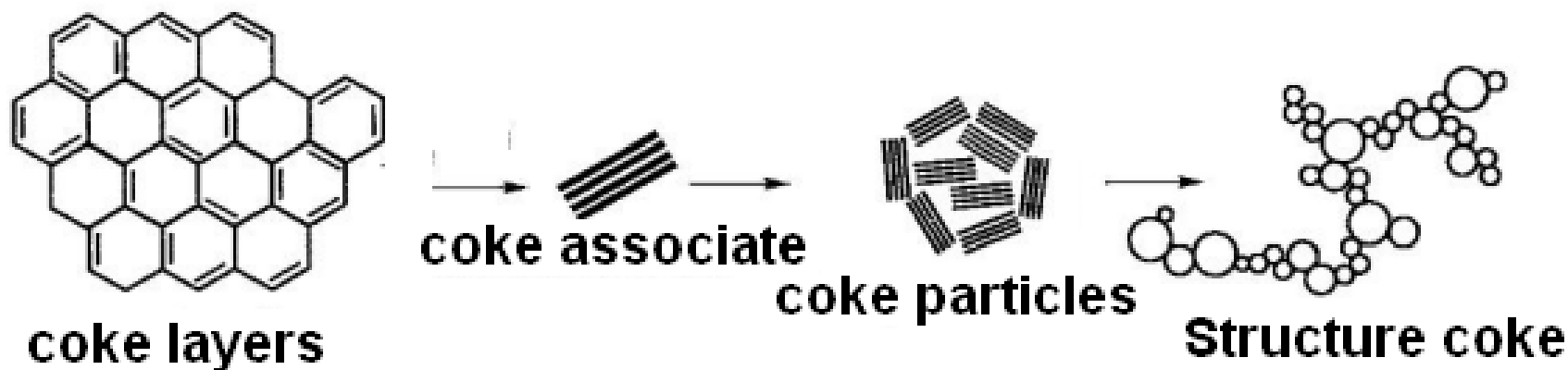
Structure coke - with small or large coke particles - it depends on pyrolysis temperature, the concentrations of hydrogen and residence time of feedstock in the reaction zone.