

THERMAL DECOMPOSITION OF ISO-BUTANE. II EFFECT OF SOME PRODUCTS AND OTHER PARAMETERS ON THE REACTION

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(Received 22th May, 1969)

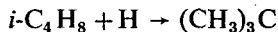
The effect of olefinic products formed in the decomposition has been studied in detail. It was found that propylene and ethylene inhibit the decomposition by capturing the chain carrier hydrogen atoms



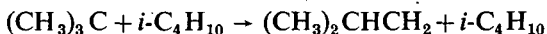
similarly as was observed in the case of iso-butene [3]. The alkyl radicals produced give rise to saturated products through hydrogen atom abstraction. Taking into consideration all the experimental results, a mechanism has been proposed which is able to interpret the formation of ethane and that of excess propane.

Introduction

The self-inhibiting effect of the products on the thermal decomposition of iso-butane [1] was first observed by DINCES and FROST. STEPUKHOVICH and his co-workers [2] pointed out that iso-butane and propylene exert an inhibiting influence on the reaction, and that the effect of the former is more pronounced. According to KONAR, PURNELL and QUINN [3], the strong inhibiting effect in the very early stages of the reaction is brought about by iso-butane. The explanation offered by the above authors implies the addition of hydrogen atom to iso-butene

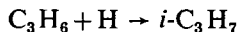


followed by the isomerization



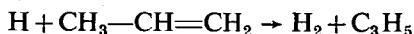
and thus gives a reasonable interpretation both of the inhibiting effect and the diminishing value of the P_{H_2}/P_{CH_4} ratio.

Since in the early stages of the reaction KONAR, PURNELL and QUINN did not observe any effect of the added small amounts of propylene in comparison to iso-butene, they did not take into consideration the addition of hydrogen atom to propylene



It has generally been observed that in the decomposition of organic compounds propylene is a well-known inhibitor of these processes. Since STEPUKHOVICH observed the inhibiting effect of propylene on this reaction, the question arises whether the

propylene exerts its inhibiting effect by the hydrogen atom abstraction alone



or by the hydrogen atom addition as well.

In order to have a better understanding of the nature of the inhibition taking place in this reaction, experiments were carried out in the presence of different amounts of added propylene and ethylene.

Experimental

The system and method applied were the same as previously described [4]. Iso-butane (200 torr) and ethylene or propylene (100 torr) were mixed and admitted into the reaction vessel at 520°C. Samples were taken and analyzed by a gas chromatograph. Propylene and ethylene were of commercial origin. They were purified as iso-butane [4].

Results and Discussion

Effect of Ethylene

It was found that added ethylene exerted only a slight inhibiting influence on the reaction. The product composition, however, was strongly altered. The effect of added ethylene on the distribution of products may be summarized as follows:

- (a) a great amount of added ethylene disappears (Fig. 1)
- (b) the amount of ethane sharply increases and no induction period can be observed (Fig. 2).

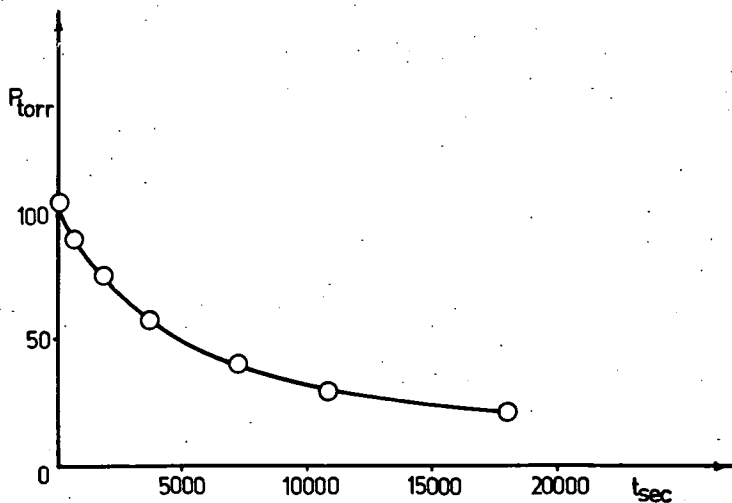


Fig. 1. Partial pressure of the ethylene against time in the ethylene-influenced decomposition of iso-butane ($T=520^{\circ}\text{C}$)

(c) the pressure of ethane plotted against the conversion shows a linear increase (Fig. 3)

(d) the yields of methane, propylene and propane also increase to some extent.

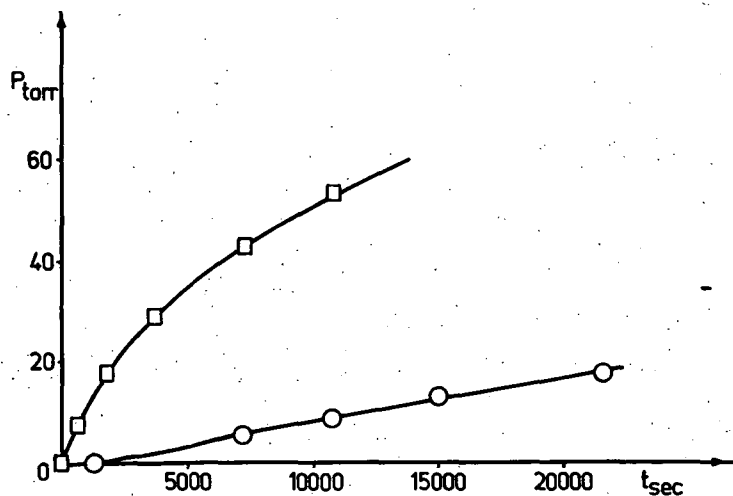


Fig. 2. Partial pressure of ethane against time in the ethylene-influenced (□), and in the non-influenced reaction (○).

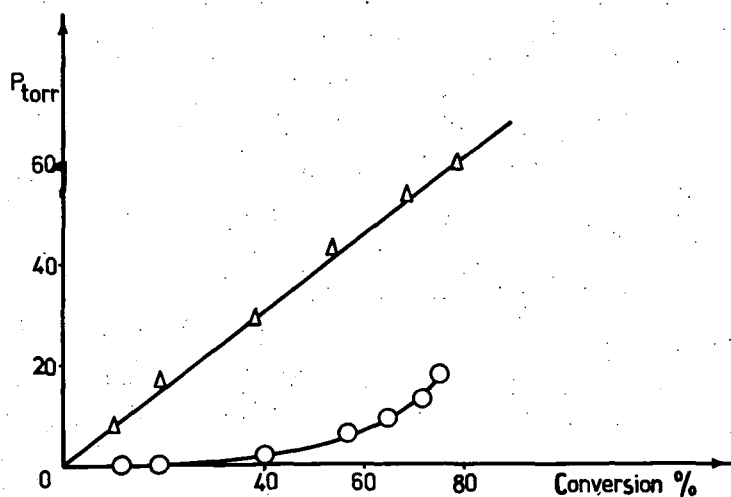


Fig. 3. Partial pressure of ethane against conversion in the uninhibited (○), and ethylene-inhibited (Δ) decomposition of iso-butane

Effect of propylene

There is a strong inhibiting effect to be observed in the presence of added propylene. The product distribution changes considerably in this case, too. The main changes in the pressure of the products are as follows:

- the partial pressure of propylene decreases (Fig. 4).
- the amounts of propane (Fig. 5), ethylene (Fig. 6) and ethane (Fig. 7) increase.

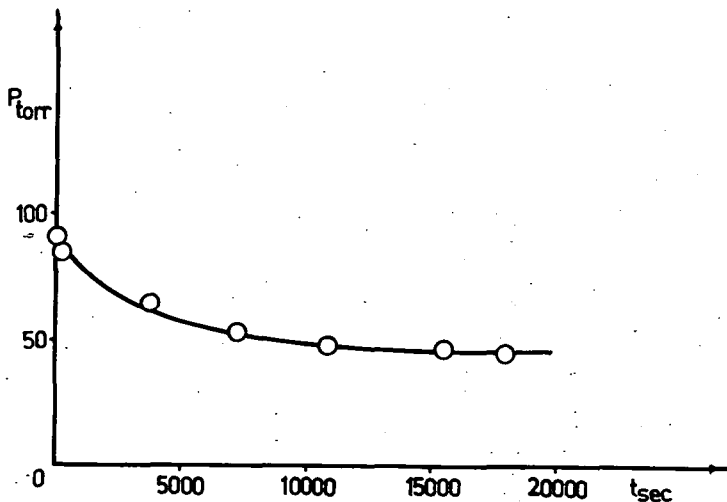


Fig. 4. Partial pressure of propylene against time in the propylene-influenced decomposition

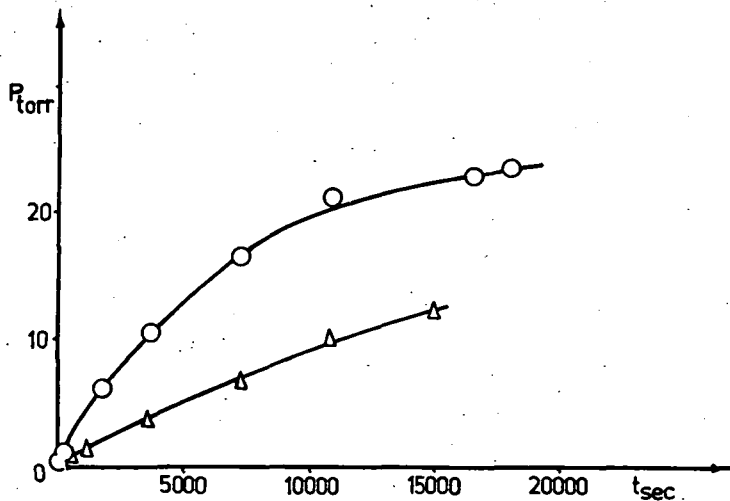


Fig. 5. Partial pressure of propane against time in the uninfluenced (Δ) and in the propylene-influenced (\circ) reaction

Effect of iso-butene

The effect of iso-butene was found to be the same as described by other authors [1, 2]. The sharp increase in the yield of propylene strongly supports the mechanism proposed by KONAR, PURNELL and QUINN. The formation of an excess amount of propylene takes place via the addition of hydrogen atom to iso-butene, followed by a tertiary-primary isomerization and by the decomposition of the iso-butyl radical produced.

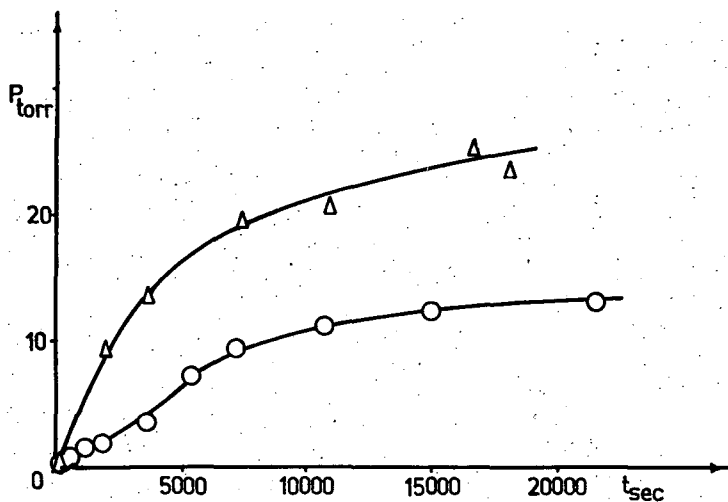


Fig. 6. Partial pressure of ethylene against time in the uninfluenced (\circ) and propylene-influenced (Δ) reaction

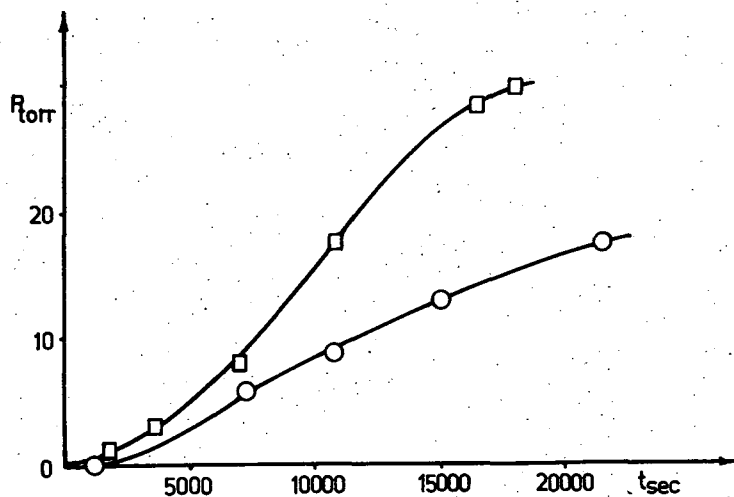


Fig. 7. Partial pressure of ethane against time in the uninfluenced (\circ) and propylene influenced (\square) decomposition

The effect of change in surface/volume ratio

The increase in the S/V ratio brings about a decrease in the rate of the reaction, indicating that the initiation is less influenced by the surface of the reaction vessel than the termination. Similar effects were observed in the thermal decomposition of other paraffins, such as n-butane [5], the isomeric hexanes [6], and especially in that of ethane and propane [13], where hydrogen atoms are important chain carriers. The decrease in rate was found to diminish with increasing pressure, however, its value was still about 50 per cent of the rate in the unpacked vessel even at 300 torr (520°C) (Fig. 8)

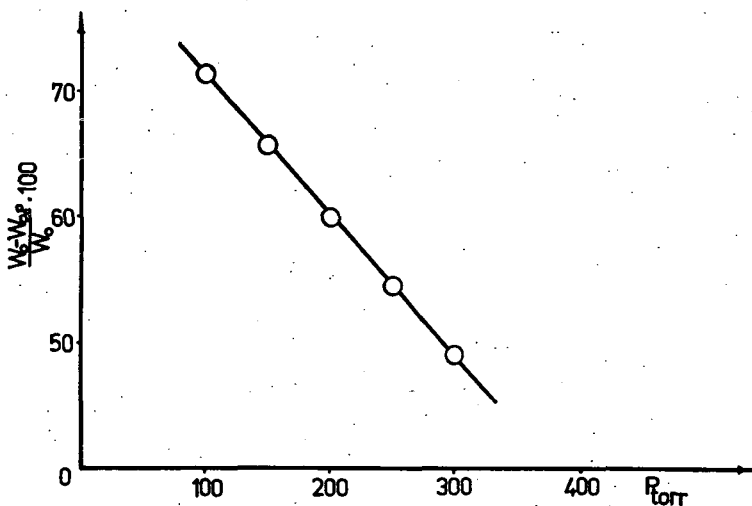
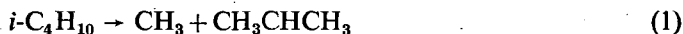


Fig. 8. Percentage reduction in the rate due to packing
 W_0 : initial rate in the unpacked vessel
 $W_{0,p}$: initial rate in the packed vessel

From the results shown in Fig. 8 it is to be concluded that all the kinetic parameters calculated for the decomposition of iso-butane on the basis of experiments carried out at low initial pressures and at relatively low temperatures are not free from the effect of the surface, even in the unpacked reaction vessels. On the other hand, the change in the surface/volume ratio has no effect on the product distribution within the limits of experimental errors.

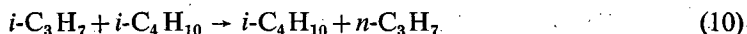
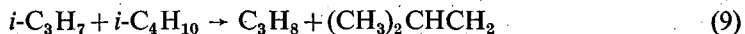
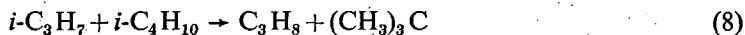
The mechanism of the reaction

Some important steps of the reaction can be understood on the basis of the RICE-mechanism:

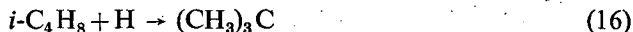




The iso-propyl radicals can react with iso-butane, as was shown by KONAR, MARSHALL and PURNELL [7].

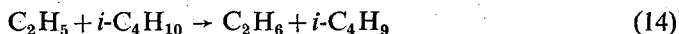
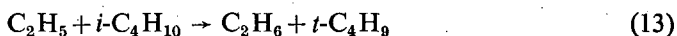


In order to interpret the strong inhibiting effect of isobutene, the addition and isomerization steps

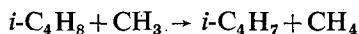
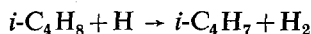


must be included [2, 3].

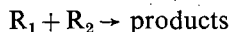
To interpret the effect of ethylene and propylene on the rate and the change in the distribution of products at greater conversions similar steps must be considered



The excess amount of propylene and methane produced in the ethylene-influenced decomposition can be interpreted in terms of the mechanism given by QUINN [14]. However, the existence of a hydrogen atom abstraction by the chain carriers from the olefins present cannot be excluded [15]. In the case of iso-butene, this reaction takes place according to the following steps:



As regards the termination, any of the radicals present in the system can take part in the step



where, $\text{R}_1, \text{R}_2 = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, n-, i\text{-C}_3\text{H}_7, i-, t\text{-C}_4\text{H}_9, \text{C}_2\text{H}_3, \text{C}_4\text{H}_5, i-, t\text{-C}_4\text{H}_7$

The reaction of two $(\text{CH}_3)_3\text{C}$ radicals



can be accepted as the most important termination step in the early stages of the uninfluenced reaction. The termination involving chain carriers seems most improbable even in the presence of a third body because of their relatively low concentrations.

A steady-state treatment of the sequence of steps (1)–(18) leads to the following expressions of the stationary radical concentrations

$$[H] = \frac{k_6 F_1}{[A]^{1/2}}$$

$$[CH_3] = \frac{1}{k_4} \left[k_1 + k_1 \frac{k_9 + k_{10}}{k_8 + k_9 + k_{10}} + \frac{k_6 F_1 F_2}{[A]^{1/2}} + k_{17} \left(\frac{2k_1}{k_{18}} [A] \right)^{1/2} \right]$$

$$[C_2H_5] = \frac{k_6 k_{12} F_1 [E]}{(k_{13} + k_{14}) [A]^{3/2}}$$

$$[i-C_3H_7] = \frac{1}{k_8 + k_9 + k_{10}} \left[k_1 + \frac{k_6 k_{15} F_1 [P]}{[A]^{3/2}} \right]$$

$$[n-C_3H_7] = \frac{k_{10}}{k_{11}(k_8 + k_9 + k_{10})} \left[k_1 + \frac{k_6 k_{15} F_1 [P]}{[A]^{3/2}} \right] [A]$$

$$[(CH_3)_3C] = \left(\frac{2k_1}{k_{18}} \right)^{1/2} [A]^{1/2};$$

$$[(CH_3)_2CHCH_2] = \frac{[A]}{k_7} \left\{ \frac{k_4 + k_5}{k_4} \left[k_1 + \frac{k_1(k_9 + k_{10})}{k_8 + k_9 + k_{10}} + \frac{k_6 F_1 F_2}{[A]^{1/2}} + k_{17} \left(\frac{2k_1}{k_{18}} [A] \right)^{1/2} \right] - k_1 - \frac{k_{10}}{k_8 + k_9 + k_{10}} \left(k_1 + \frac{k_6 k_{15} F_1 [P]}{[A]^{3/2}} \right) \right\}$$

In these equations, $[A]$, $[B]$, $[E]$, $[P]$ represent the concentrations of *i*-butane, *i*-butene, ethylene and propylene, respectively, and

$$F_1 = \left(\frac{2k_1}{k_{18}} \right)^{1/2} \frac{[A]}{(k_2 + k_3)[A] + k_{12}[E] + k_{15}[P] + k_{16}[B]}$$

$$F_2 = \frac{k_{12} k_{14}}{k_{13} + k_{14}} \frac{[E]}{[A]} + (k_9 + k_{10}) \left[\frac{k_{15}}{k_8 + k_9 + k_{10}} \frac{[P]}{[A]} \right] + k_3$$

The expressions for the constants k_1 – k_{18} were taken from the literature [7, 8, 9, 10, 11], and on the basis of these data their actual values were calculated for 520°C. The overall rate of the reaction deduced from the mechanism is described by the equation

$$-\frac{d[i-C_4H_{10}]}{dt} = K_1[A] + K_2[A]^{3/2} + K_3[A]^{1/2} \cdot F_1 + K_4[A]^{1/2} + K_5[A]^{-1/2}$$

Numerical calculations showed that for a reaction at a temperature of 520°C, and at an initial pressure of 200 torr the last two members of the right hand side are negligible and thus they were omitted. Accordingly, the former equation is reduced to

$$W \cong K_1 A + K_2 A^{3/2} + K_3 A^{1/2} F_1 \quad (I)$$

$D \qquad F \qquad G$

which is able to interpret the most important features of the reaction.

The overall order of the reaction depends upon the relative importance of the three terms of equation (I). For example at $T = 520^\circ\text{C}$, $P_0 = 200$ torr and 0 per cent conversion $D:F:G \cong 1:2:11$ and at 15 per cent conversion, $D:F:G = 1:2:6$. The kinetic behaviour of the reaction, especially as regards its order, is primarily determined by the term G . The numerical value of G decreases as the value of F_1 sharply diminishes with increasing conversion. This leads to an increase in the overall order of the reaction which is also indicated by the diminishing value of the first order rate constants with increasing conversion.

On the basis of equation (I), we consider that the observed increase in the overall order of the reaction with increasing temperature [4] reflects the fact that the initial rates determined on the basis of pressure-changes are rather misleading. The reason for this is that these processes are differently influenced by the products formed during the time of admission. This is a consequence of the fact that at higher temperatures neither the pressure measurements nor the analytical determinations can be carried out at the same conversion in the early stages of the reaction as they can be done at lower temperatures. On the other hand, the increase in the order with increasing S/V ratio can also be interpreted on the basis of a possible change in the term F_1 , which includes the concentrations of all those additives that bring about inhibition in specific terms of its denominator. From this it follows that, in agreement with the experimental evidence, the terminations taking place partly on the wall give rise to an increase in the denominator of F_1 , resulting in a decrease in the velocity of the reaction and in an increase in the order of the reaction.

Additives that can also take part in the initiation, may influence the order of the reaction by increasing the relative importance of the term D in equation (I).

The rate expressions for the change in the concentration of ethylene, propylene and i-butylene

$$\frac{d[\text{C}_2\text{H}_4]}{dt} = k_{11}[n\text{-C}_3\text{H}_7] - k_{12}[\text{H}][\text{C}_2\text{H}_4]$$

$$\frac{d[\text{C}_3\text{H}_6]}{dt} = k_7[(\text{CH}_3)_2\text{CHCH}_2] - k_{15}[\text{H}][\text{C}_3\text{H}_6]$$

$$\frac{d[i\text{-C}_4\text{H}_8]}{dt} = k_6[(\text{CH}_3)_3\text{C}] - k_{16}[\text{H}][i\text{-C}_4\text{H}_8]$$

depend on the relative importance of the two terms in the corresponding equation.

The values of the second terms in the right hand side increase with increasing conversion; the amount of olefins in the products of the uninfluenced reaction should change according to maximum curves. The second term is greater from the onset

of the reaction in the presence of added olefins, whose concentrations diminish with increasing conversion.

An increase in the rate of formation of ethane and propane occurs

$$\frac{d[C_2H_6]}{dt} = (k_{13} + k_{14})[C_2H_5][A] = \frac{k_6 k_{12} F_1 [E]}{[A]}$$

$$\frac{d[C_3H_8]}{dt} = [k_8 + k_9][i-C_3H_7][A] = \frac{k_8 + k_9}{k_8 + k_9 + k_{10}} \left[k_1 [A] + \frac{k_6 k_{15} F_1 [P]}{[A]} \right]$$

when the concentrations of olefins become higher with increasing conversion in the uninfluenced reaction. The rate of production of ethane in the presence of added ethylene is a definite value, while in the uninfluenced decomposition it shows an induction period.

In conclusion, the mechanism consisting of steps (1)—(18) gives a good interpretation of (a) the decomposition of iso-butane, (b) of the influence exerted by olefinic products and (c) of the increased production of some minor products in the later stages of the reaction.

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ТЕРМИЧЕСКОЕ РАЗЛОЖЕНИЕ ИЗО-БУТАНА. II

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Подробно изучалось влияние продуктов разложения. Нашли, что пропилен и этилен замедляют реакцию схватывая водородные атомы — носители цепей



таким же образом как наблюдалось в случае изо-бутилена. Срывая водородные атомы возникающие алкильные радикалы приведут к предельным продуктам. Учитывая все экспериментальные данные предлагается механизм при помощи которого формирование этана и избытка пропана можно объяснить.